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CORRELATION AND PREDICTION OF VAPOR-LIQUID EQUILIBRIUM IN
ELECTROLYTIC SOLUTIONS

New Jersey Institute of Technology

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CORRELATION AND PREDICTION OF
VAPOR-LIQUID EQUILIBRIUM IN
ELECTROLYTIC SOLUTIONS

by

Anil Krishna Rastogi

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Dissertation submitted to the Faculty of the Graduate School
of the New Jersey Institute of Technology in partial fulfillment
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1981

APPROVAL SHEET

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Equilibrium in Electrolytic Solutions

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"Prediction of Binary Vapor-Liquid Equilibrium
from One Parameter Equations," A. Krumins, A.
Rastogi, M. Rusak, and D. Tassios, Presented at
27th Canadian Chemical Engineering Conference,
Alberta, Canada, (1977); Canadian Journal of
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"Estimation of Thermodynamic Properties of
Binary Aqueous Electrolytic Solutions in the
Range 25-100°C," Anil Rastogi and D. Tassios,
Ind. Eng. Chem. Process Design Develop., Vol
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ABSTRACT

Title of Thesis: Correlation and Prediction of Vapor-Liquid
Equilibrium in Electrolytic Solutions

Anil Krishna Rastogi, Doctor of Engineering Science, 1981

Thesis directed by: Dimitrios Tassios, Professor of Chemical
Engineering

Two expressions for the excess Gibbs free energy are presented which correlate and predict vapor-liquid equilibrium and the mean molal activity coefficient of an electrolyte in a ternary mixture containing water and either MeOH or EtOH. The proposed equations take into account coulombic forces between ions and the physical interaction forces between ion-solvent and solvent-solvent molecules in a solution.

Model #1 is a combination of an extended Debye and Hückel equation and the local composition of non-random two liquid (NRTL) model. A ternary mixture requires six adjustable binary parameters to predict activity coefficients. These six parameters are evaluated from three separate binary data reductions. Ternary data are predicted with an average error of $|\Delta Y|$ less than 0.03 up to $I = 2$. The parameters are considered temperature independent within a 30 to 40°C temperature range for aqueous electrolyte mixtures and within a 15 to 20°C temperature range for nonaqueous electrolyte mixtures. Both isothermal and isobaric ternary experimental data have been tested for ternary correlation. Iso-

thermal ternary data correlation for systems containing water-methanol solvents give results with an average error of $|\Delta Y|$ less than 0.01 up to $I = 6$. Whereas isobaric ternary data are correlated with an average error of $|\Delta Y|$ less than 0.02 up to $I = 4$. It is possible to extend this model to multi-component mixtures although this has not been investigated in this work.

Model #2 is a combination of the Bromley equation, the simplified NRTL equation and an additional ternary salting out expression. The behavior of each electrolyte-solvent binary is described by a one parameter form of the Bromley equation. The temperature dependency of the binary parameters has been established with a two constant equation. Prediction of aqueous electrolyte binary data (γ_{\pm} and vapor pressure depression) is obtained with an average percent error less than 10.0 at intermediate temperatures. Correlation of ternary VLE and γ_{\pm} data require four binary parameters and two additional ternary adjustable parameters. This model is limited to binary and ternary data correlation only. The maximum concentration range for the correlation of ternary systems containing water and methanol solvents is about $I = 3$. The correlation of vapor-liquid equilibrium data results in an average error of $|\Delta Y|$ less than 0.012, except for the LiCl-H₂O-MeOH system at 60°C where the average error in $|\Delta Y|$ is 0.02.

PREFACE

The thermodynamic study of electrolytic solutions can be categorized into three groups: one containing strong electrolytes in aqueous solvents; the second comprising volatile weak electrolytes in aqueous/nonaqueous solvents; and the third consisting of strong electrolytes in nonaqueous solvents or in mixed solvents.

The first type of system has been of interest in various chemical, metallurgical and geological problems. Debye and Hückel (1923) proposed the classic thermodynamic excess Gibbs free energy expression for strong electrolytes in a single solvent. Guggenheim (1935) extended the range of validity of the Debye-Hückel equation to 0.1 molal solutions. Recently, many workers have proposed semi-empirical correlations for concentrated electrolyte aqueous solutions viz, Bromley et al. (1972, 1973, 1974); Meissner et al. (1972); Pitzer et al. (1973, 1974, 1977, 1979); and Cruz and Renon (1978). Two important and different approaches among the above are by Bromley (1973) and Cruz and Renon. Bromley modified Guggenheim's equation to a one parameter form per binary whereas the Cruz and Renon expression is a combination of the Debye-Hückel equation, a salting out contribution given by the Born model, and the NRTL model.

The second type of systems recently became important due to the necessity of pollution control in the chemical and

petroleum industries. The recovery of weak volatile electrolytes such as ammonia, carbon dioxide, hydrogen sulfide, sulfur dioxide and hydrogen cyanide from effluent streams requires the thermodynamic representation of vapor-liquid equilibrium. The most interesting work reported in this area is by Van Krevelen (1949); Van Krevelen, Hofzer and Huntens (1949); Edwards et al. (1975, 1978); Beutier and Renon (1978); Chen et al. (1979); and Mason and Kao (1979).

Theoretical and correlation for the third type of system, electrolytes in nonaqueous solvents and in mixed solvents is sparse. A knowledge of the VLE and electrolyte activities in such solutions could be useful in different chemical and electrochemical applications. The correlation work in the literature for this category are by Rousseau et al. (1972, 1975, 1978); Bakerman and Tassios (1975); Hala (1969); Chen et al. (1979) and Tomasula and Tassios (1980). The most systematic approach is given by Hala and Chen et al. They have considered different ion-ion, ion-solvent and solvent-solvent interactions in an electrolytic solution. Both have used two types of terms for the Gibbs free energy. One of these terms is the Debye-Hückel equation to represent ion-ion interactions. For the other interactions, Hala used the two suffix Margules equation, whereas Chen et al. used an expression based on the two liquid nonrandom theory. Unfortunately, none of the above approaches presents a predictive scheme for a ternary electrolytic solution; also they are complex in nature.

It would be appropriate to categorize the present state of the art for such systems as in a developmental stage. Therefore we have taken an approach to develop thermodynamic analytical expressions to represent VLE of the third type of electrolytic solutions. Our models also combine the two types of terms, which are derived by the modification of Bromley (1973) and Cruz and Renon (1978) binary equations. These are different than the equations of Hala and Chen et al. The proposed models require a minimum amount of information. Model I has the possibility of extension to multicomponent mixtures containing more than two solvents and single or multi electrolytes.

DEDICATION

I dedicate this thesis to my parents whose encouragement and love made it possible.

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INTRODUCTION

Fundamental knowledge of the VLE behavior of electrolytic solutions and electrolytes in mixed solvents is limited at present. The characterization of equilibrium properties of such systems has become important in the process design and process simulation of different processes.

In this study, two semi-empirical models have been developed based on molecular and ionic interactions in the solutions. Both the models combine modified forms of the NRTL equation and some form of the extended Debye-Hückel equation for physical and coulombic forces in a solution, respectively.

In Chapter 1 thermodynamic relationships for the VLE of electrolytic solutions are presented. In Chapters 2 and 3 the two models are developed. Also, their performance in correlating and predicting binary and ternary data is investigated. In Chapter 4 a comparative study of the two models is discussed. The detailed development of the two models is given in Appendices A, B and C.

CHAPTER 1

DEVELOPMENT OF FUNDAMENTAL RELATIONSHIPS FOR VAPOR-LIQUID EQUILIBRIUM IN ELECTROLYTIC SOLUTIONS

ASBTRACT

In vapor liquid equilibrium calculations it might be necessary to find y - T data from known x - P data or to find y - P data from given x - T data or it may be required to interpolate or extrapolate the limited x - y - P - T data. Secondly, in chemical processes and electrochemical energy conversion, a knowledge of the activities of the solvents and the electrolyte may be useful to characterize the solution behavior. Therefore, in this chapter, some important thermodynamic relationships have been developed which are applied to a binary or a ternary electrolytic solution.

1.1 Criteria of Equilibria

Consider an electrolytic solution at equilibrium at a temperature 'T' and pressure 'P' as shown in (figure 1.1). In the liquid phase, the electrolyte will be in ionic equilibrium due to the dissociation of the electrolyte into ions. In a concentrated electrolytic solution, one expects the presence of ion-pairs and ions depending upon the degree of dissociation. However, in this work, the electrolyte is assumed to be completely dissociated into ions for the concentration range and solvents under consideration. Therefore the liquid-phase, specifically, will consist of solvent molecules and ions. The vapor phase will consist of solvent molecules and the electrolyte in molecular form (if the electrolyte is volatile), because, for the temperature range considered in this work, dissociation of the electrolyte in the vapor phase is negligible.

When two phases are in equilibrium, the chemical potential for component i in the two phases will be the same

$$\mu_i^L = \mu_i^V \quad (1-1)$$

The chemical potential in a single phase can be related to the fugacity of component i in a mixture by--

$$d\bar{G}_i = d\mu_i = RT \, d \ln \hat{f}_i \quad (1-2)$$

A combination of equations (1-1) and (1-2), results in--

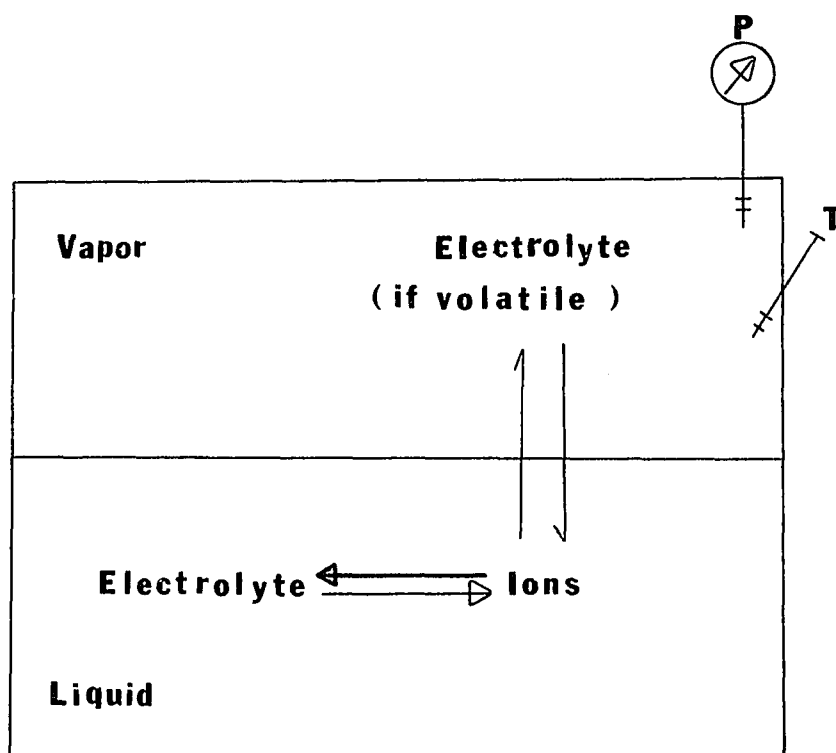


Figure 1.1 Representation of the Vapor-Liquid Equilibrium in Electrolytic Solutions

$$\hat{f}_i^L = \hat{f}_i^V \quad (1-3)$$

The fugacity of a component can be further expressed in terms of measurable quantities, viz., X, Y, P and T. A ternary mixture, in this study, is defined as a mixture of an electrolyte and two solvents and the ternary mixture, is considered a combination of three binary mixtures

- (1) binary 1-2: electrolyte (1) - solvent (2)
- (2) binary 1-3: electrolyte (1) - solvent (3)
- (3) binary 2-3: solvent (2) - solvent (3)

An expression of the fugacity in terms of X-Y-P-T data, for an individual binary mixture and a ternary mixture, is considered in the following sections.

1.2 Mixture of Solvent (2) - Solvent (3) (Binary 2-3)

The liquid-phase fugacity for solvent 2 or 3 is given by

$$\hat{f}_i^L = X_i \gamma_i (\text{P.E.})_i \phi_i^O P_i^O \quad (1-4)$$

where,

$$(\text{P.E.})_i = \text{EXP} \left[\int_0^{P_i^O} \left(\frac{v_i^{\circ L}}{RT} \right) dP \right] \quad (1-5)$$

$$\phi_i^O = \text{EXP} \left[- \frac{B_{ii} P_i^O}{RT} \right] \quad (1-6)$$

The vapor phase fugacity is given by

$$\hat{f}_i^V = y_i P \phi_i^V \quad (1-7)$$

where,

$$\phi_i^V = \text{EXP} \left[\frac{P}{RT} (B_{ii} + y_j^2 \delta_{ij}) \right] \quad (1-8)$$

Combining equations (1-4) to (1-8) gives

$$X_i \gamma_i P_i^O = y_i P F_i \quad (1-9)$$

and

$$F_i = \frac{\phi_i^V}{\phi_i^O (\text{P.E.})_i} \quad (1-10)$$

At low pressures, and $TR_i \ll 1.0$, $F_i \approx 1.0$ (Appendix I)

This simplifies equation (1-9) to

$$X_i \gamma_i P_i^O = y_i P \quad (1-11)$$

The total pressure is calculated by

$$P = X_2 \gamma_2 P_2^O + X_3 \gamma_3 P_3^O \quad (1-12)$$

Equations (1-11) and (1-12) are used to correlate or predict the VLE in a solvent-solvent binary.

1.3 Mixture of an Electrolyte and a Solvent (Binary 1-2 or 1-3)

Case I volatile electrolyte

The liquid-phase fugacity for the electrolyte is given by

$$\hat{f}_1^L = m\gamma_{\pm} H_1 \quad (1-13)$$

where,

$$H_1 = f(T) \text{ at low pressures} \quad (1-14)$$

And the liquid-phase fugacity for the solvent is given by an equation similar to equation (1-11) in section (1-2)

$$f_i^L = X_i \gamma_i P_i^O \quad (1-15)$$

The vapor-phase fugacity for both the electrolyte and the solvent is

$$\hat{f}_\ell^V = y_\ell P, \text{ assuming } \hat{\phi}_\ell^V \approx 1.0 \quad (1-16)$$

(ℓ = electrolyte or solvent)

Combining equations (1-13), (1-14) and (1-16)

$$m\gamma_{\pm} H_1 = y_1 P \quad (1-17)$$

$$X_i \gamma_i P_i^O = y_i P \quad (1-18)$$

Case II non-volatile electrolyte

The vapor phase will have only solvent molecules. Equation (1-18) will be the only equilibrium relationship for the solvent i

$$X_i \gamma_i P_i^O = P \quad (1-19)$$

Usually, binary electrolytic experimental data are expressed in terms of the osmotic coefficient ϕ , which is defined as

$$\phi = - \frac{1000}{\nu m M_w} \ln \hat{a}_i \quad (1-20)$$

for Case II, the activity and the activity coefficient of the solvent are interrelated by

$$\hat{a}_i = \frac{P}{P_i^0} = \gamma_i X_i \quad (1-21)$$

1.4 Mixture of an Electrolyte (1) - Solvent (2) - Solvent (3)
(Ternary 1-2-3)

Case I volatile electrolyte

The VLE relationship for the electrolyte and solvents (2) and (3) will be given by equations (1-17) and (1-18) respectively.

Case II non-volatile electrolyte

The vapor-phase will have only solvent (2) and (3) molecules. The VLE relationships will be the same as given in section (1.2), equations (1-11) and (1-12). In sections (1.2) to (1.4), the liquid mole-fraction of any component is defined, based on the complete dissociation of the electrolyte.

$$X_i = \frac{N_i}{v_m + N_2 + N_3} \quad (i = 2 \text{ or } 3) \quad (1-22)$$

and

$$X_1 = \frac{m}{v_m + N_2 + N_3} \quad (1-23)$$

Equations (1-1) to (1-23) developed in sections (1.1) to (1.4) are used for relating X-Y-P-T and mean molal activity coefficient data in a binary or a ternary mixture. However, in this work all the systems used are non-volatile, except for the HCl-H₂O system where pressure is given as partial pressure of water.

1.5 Criteria for the Excess Gibbs Free Energy

In practical applications, where the liquid-phase composition and the temperature of the system are known, it is necessary to calculate the total pressure of the system and the vapor-phase composition or the mean molal activity coefficient of the electrolyte. In order to obtain this information the equations presented in sections (1.1) to (1.4) are applied, depending upon the type of system. For the above problem, the additional information needed are P_i^O , H_1 (if electrolyte is volatile) and liquid-phase activity coefficients (γ_i and γ_{\pm}).

At a given temperature, the pure component vapor pressure can be estimated by equation (1-24) which expresses P_i^O as a function of temperature--

$$P_i^O = \text{Exp} \left(C_1 + \frac{C_2}{C_3 + T} + C_4 T + C_5 T^2 + C_6 \ln T \right) 760 \quad (1-24)$$

At low pressures, the Henry's constant for the electrolyte (volatile) is expressed as a quadratic function of temperature--

$$H_1 = a_1^1 + b_1^1 T + c_1^1 T^2 \quad (1-25)$$

For the activity coefficients, an expression is required in terms of the known variables i.e. liquid-phase composition and temperature of the system. In the liquid-phase the total excess Gibbs free energy can be developed as a function of known variables considering the different interaction forces in solution. The excess Gibbs free energy is then used to obtain expressions for the activity coefficients, as shown

below--

$$\frac{G^E}{RT} = f(T, N_1, N_2 \dots) \quad (1-26)$$

$$\ln \gamma_i = \left. \frac{\partial G^E/RT}{\partial N_i} \right]_{T, P, N_{\ell \neq i}} \quad (1-27)$$

$$\ln \gamma_{\pm}^* = \left. \frac{\partial G^E/RT}{\partial N_1} \right]_{T, P, N_{\ell \neq 1}} \quad (1-28)$$

$$\ln \gamma_{\pm} = \ln \gamma_{\pm}^* - \ln(0.001 v_m M_w + 1) \quad (1-29)$$

where

γ_{\pm} = mean molal activity coefficient

γ_{\pm}^* = mean molar activity coefficient

In an electrolytic liquid solution, the total excess Gibbs free energy can be attributed to, mainly two type of molecular interactions. One interaction is due to the long-range electrostatic forces or ion-ion interactions. The other interaction takes into account the physical forces due to interactions of ion-solvent and solvent-solvent molecules. In Chapters 2 and 3, two different models have been considered for the excess Gibbs free energy. These models propose different forms of expressions to represent the non ideal behavior of a solution.

The equations developed in sections (1.1) to (1.5) are used first to fit experimental binary data with the activity coefficient expressions presented in Chapters 2 and 3. These are then extended to predict and/or correlate the ternary vapor-liquid equilibrium and mean molal activity coefficient data.

CHAPTER 2

CORRELATION AND PREDICTION OF VAPOR-LIQUID EQUILIBRIUM AND THE MEAN MOLAL ACTIVITY COEFFICIENT BY MODEL I IN ELECTROLYTIC SOLUTIONS

ABSTRACT

Mean activity coefficient data and vapor pressure depression data of aqueous and nonaqueous electrolytic solutions are correlated successfully. The maximum molality applicable to model for aqueous-electrolytic and MeOH-electrolytic solutions can be approximated up to $I = 6$. The binary parameters are considered temperature independent within a 30 to 40°C temperature range, presetting the ion-solvent nonrandom parameters α_{Ai} and α_{Bi} to 0.2 and 0.0 respectively. The prediction of ternary VLE and γ_{\pm} is of acceptable quality with an average error of 0.028 in ΔY and a 15% average error in γ_{\pm} up to $I = 2$. Ternary data correlation of both isothermal and isobaric data are of good quality. In general, the prediction of binary data using the parameters obtained by ternary data regression is possible, with an average percent error in DP and γ_{\pm} of 15%.

Model I: Combination of the Extended Debye-Hückel
Equation and the NRTL Equation

2.1 Excess Gibbs Free Energy Function

A complete theoretical account of the thermodynamic properties of electrolyte solutions must deal with both long range interionic and short range interactions between ions and solvent molecules. In a dilute electrolytic solution, the magnitude of the long range electrostatic forces is dominant. Based on this fact, Debye and Huckel developed a limiting law to predict the properties of a dilute solution by considering the electrical potential at a point in the solution in terms of the concentrations and charges of the ions and the properties of the solvent. Gronwall, Lamer and Sandved (1928) modified the Debye-Huckel equation by extending the potential functions with additional higher order terms. However, in a solution of an electrolyte in mixed solvents, the solvent-solvent interactions are of as much importance as those of ion-ion and ion-solvent interactions. Therefore, in Model I, an empirically extended form of the Debye-Huckel equation is combined with the non-random two liquid model (NRTL). The NRTL part of the equations not only accounts for solvent-solvent interactions, but describes unaccounted ion-solvent interactions also.

The equations for the excess Gibbs free energy, G^E , are as below

$$\frac{G^E}{RT} \Big|_{\text{Total}} = \frac{G^E}{RT} \Big|_{\text{Ext.D.H.}} + \frac{G^E}{RT} \Big|_{\text{NRTL}} \quad (2-1)$$

$$\begin{aligned} \frac{G^E}{RT} \Big|_{\text{Extended D.H.}} &= 2.303v \frac{M_w N_T}{1000} \frac{m}{I} |z_+ z_-| \left[-A_\gamma \frac{2}{\rho} \right. \\ &\left. \{ (1 + \rho I^{1/2})^2 - 2(1 + \rho I^{1/2}) + \ln(1 + \rho I^{1/2}) + \frac{3}{2} \} \right. \\ &\left. + A_\gamma^2 \left\{ \frac{2(aI - 2)}{3a^2} (1 + aI)^{1/2} + \frac{4}{3} \frac{1}{a^2} \right\} \right] \\ &+ N_T [(0.001vmM_w + 1) \ln(0.001vmM_w + 1) \\ &\quad - 0.001vmM_w] \end{aligned} \quad (2-2)$$

where,

$$\rho = 1.0$$

$$a = 1.5/|z_+ z_-|$$

A_γ = Debye-Hückel constant (see Appendix D)

$$\begin{aligned} \frac{G^E}{RT} \Big|_{\text{NRTL}} &= \frac{1}{RT} \left[N_2 \frac{N_A z_{\pm 2} + N_3 z_{32}}{N_A G_{\pm 2} + N_3 G_{32} + N_2} \right. \\ &+ N_3 \frac{N_A z_{\pm 3} + N_2 z_{23}}{N_A G_{\pm 3} + N_2 G_{23} + N_3} \\ &- N_A \frac{N_2 z_{\pm 2}}{N_3 G_{32} + N_2} + \frac{N_3 z_{\pm 3}}{N_2 G_{23} + N_3} \\ &\left. + N_A N_2 N_3 \frac{z_{32} G_{\pm 2}}{(N_3 G_{32} + N_2)^2} + \frac{z_{23} G_{\pm 3}}{(N_2 G_{23} + N_3)^2} \right] \end{aligned} \quad (2-3)$$

where,

$$Z_{ij} = \Delta g_{ij} G_{ij}$$

$$G_{ij} = \text{EXP}\left[-\alpha_{ij} \frac{\Delta g_{ij}}{RT}\right] \quad (2-4)$$

$$\alpha_{ij} = \alpha_{ji}$$

$$\Delta g_{ij} \neq \Delta g_{ji}$$

$$Z_{\pm i} = Z_{Ai} + \frac{v_B}{v_A} Z_{Bi}$$

$$G_{\pm i} = G_{Ai} + \frac{v_B}{v_A} G_{Bi} \quad (2-5)$$

$$Z_{Ai} = \Delta g_{Ai} G_{Ai} \text{ and } Z_{Bi} = \Delta g_{Bi} G_{Bi}$$

$$G_{Ai} = \text{EXP}\left[-\alpha_{Ai} \frac{\Delta g_{Ai}}{RT}\right]$$

$$G_{Bi} = \text{EXP}\left[-\alpha_{Bi} \frac{\Delta g_{Bi}}{RT}\right] \quad (2-6)$$

A stepwise procedure for the development of these expressions is given in Appendix B, sections B.1 and B.2.

2.2 Procedure: Data Reduction and Prediction

In Model I, each of the three binaries have two adjustable parameters. In order to predict ternary behavior it is necessary to evaluate the binary parameters first. Also, the accuracy of the binary data correlation will justify the extension of Model I to ternary or multicomponent mixtures. A stepwise scheme for the data correlation and prediction is depicted in figure 2.1. A nonlinear subroutine LSQ2 is used in the binary or ternary data regression.

The detailed steps for binary and ternary correlation with different objective functions have been discussed separately, as below

A. Binary 2-3: Mixture of Solvent (2) - Solvent (3)

The activity coefficient expressions for these type of systems are obtained by substituting $m = 0.0$ and $N_A = 0.0$ in equations (2-2) and (2-3) and differentiating the resulting excess Gibbs free energy function. This results in the original NRTL equation of Renon and Prausnitz (1968)--

$$\ln \gamma_i \equiv \frac{x_j^2}{RT} \left[\frac{z_{ji} G_{ji}}{(X_j G_{ji} + X_i)^2} + \frac{z_{ij}}{(X_i G_{ij} + X_j)^2} \right] \quad (2-7)$$

G_{ij} and z_{ij} are given by equation (2-4).

The experimental X-y-P-T data for these binaries are correlated for the two temperature independent parameters-- Δg_{23} and Δg_{32} by presetting α_{23} to -1.0 as recommended by Marina

Desired : Correlation and Prediction of
 Y_i ; P and / or γ_{\pm}
 in a Ternary Electrolytic Solution

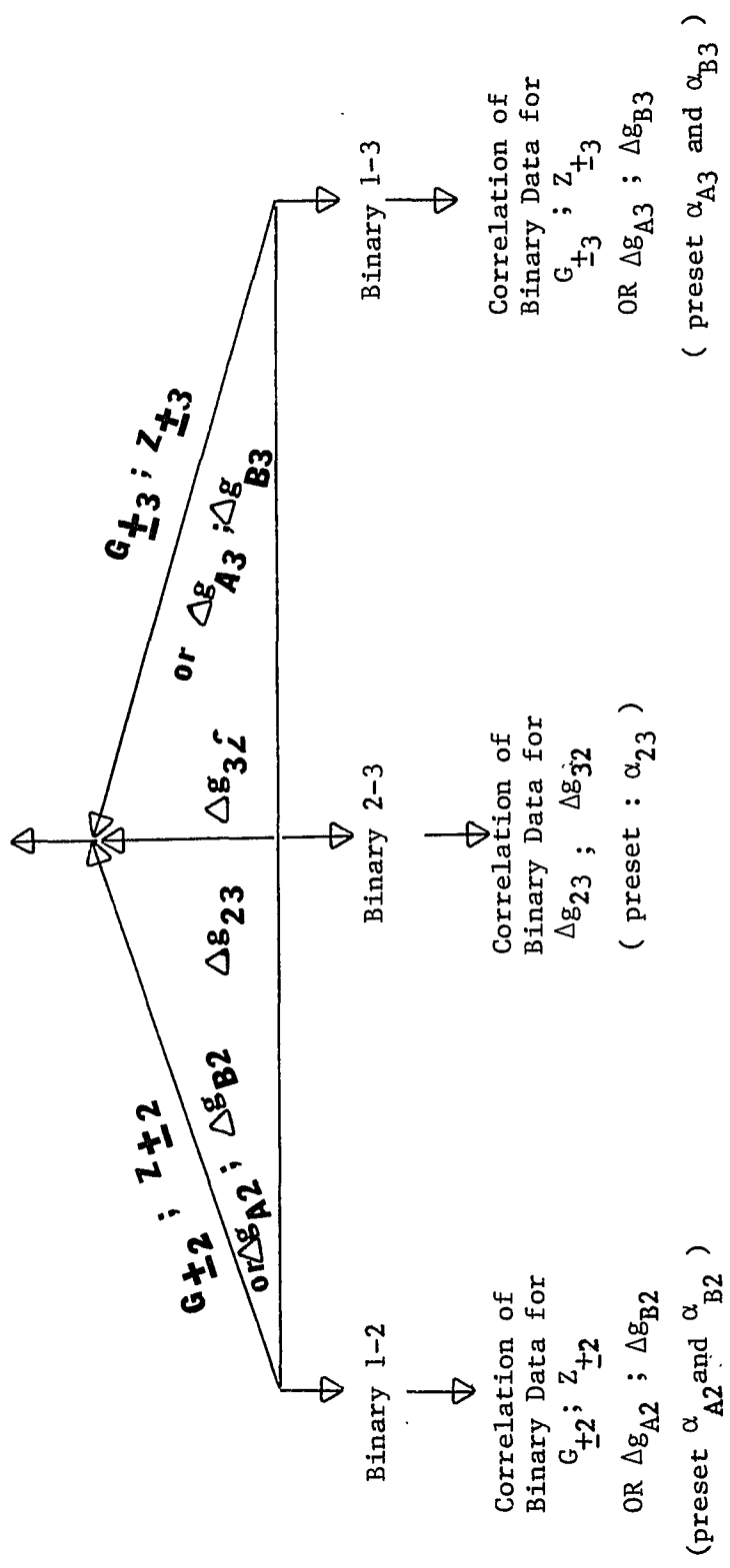


Figure 2.1 A Stepwise Scheme for Correlation and Prediction of the VLE and Mean Molal Activity Coefficients with Model I

and Tassios (1972) or to 0.2, 0.3, 0.47 as recommended by Renon and Prausnitz (1968). The objective function used in the regression for this type of binary system is

$$\text{o.f.} = \sum_{s=1}^{\text{NP}} \sum_{i=2}^3 \left[\frac{\gamma_{s_{ca}} - \gamma_{s_E}}{\gamma_{s_E}} \right]_i^2 \quad (2-8)$$

NP = # of points in a system

γ_{s_E} is calculated using experimental X-y-P-T data with equations (1-11) and (1-12).

B. Binary 1-2 or 1-3: Mixture of an Electrolyte and a Solvent

The activity coefficient expressions are given by equations (A-5), (A-10), (A-8), (A-12) and (A-9). Experimental binary data can be correlated either through regression for $G_{\pm i}$ and $Z_{\pm i}$ or Δg_{Ai} and Δg_{Bi} in equations (2-5) and (2-6). However, the temperature independent form (Δg_{Ai} and Δg_{Bi}) would require values of α_{Ai} and α_{Bi} . These two forms of the parameters make Model I applicable to both isothermal and isobaric data. Two objective functions are used to evaluate the binary parameters.

$$\text{o.f. \#1} = \sum_{s=1}^{\text{NP}} \left[\frac{\gamma_{s_{ca}} - \gamma_{s_E}}{\gamma_{s_E}} \right]_{i(=2 \text{ or } 3)}^2 + \sum_{s=1}^{\text{NP}} \left[\frac{\gamma_{\pm ca} - \gamma_{\pm E}}{\gamma_{\pm E}} \right]^2 \quad (2-9)$$

$$\text{o.f. \#2} = \sum_{s=1}^{\text{NP}} \left[\frac{DP_{ca} - DP_E}{DP_E} \right]_s^2 + \sum_{s=1}^{\text{NP}} \left[\frac{\gamma_{\pm ca} - \gamma_{\pm E}}{\gamma_{\pm E}} \right]_s^2 \quad (2-10)$$

where,

$$DP = P_i^O - P \quad (2-11)$$

$\gamma_{i,EXP}$ and DP are calculated using equations (1-17) to (1-21). If experimental binary data are available only as vapor pressure vs molality, the second term in equations (2-9) and (2-10) is zero. In the case where the data are γ_{\pm} vs molality only, the first term in equations (2-9) and (2-10) is zero.

C. Prediction of Ternary VLE (y_2 , y_3 , P and γ_{\pm})

The binary parameters obtained by individual binary data correlation with the best objective function [Equation (2-10)] are used to predict the activity coefficients γ_2 , γ_3 and γ_{\pm} in a ternary mixture with equations (2-12) to (2-18) and (1-29).

$$\ln\gamma_{\pm}^* = \ln\gamma_{\pm Ext.D.H.}^* + \ln\gamma_{\pm NRTL}^* \quad (2-12)$$

$$\ln\gamma_{\pm}^* = 2.303 \left[-A_{\gamma} \frac{I^{1/2}}{1 + \rho I^{1/2}} + A_{\gamma}^2 \frac{I}{(1 + aI)^2} \right] |z_+ z_-| + \ln(0.001 v m M_w + 1) \quad (2-13)$$

$$\begin{aligned} \ln\gamma_{\pm NRTL}^* = & \frac{v_A}{v} \frac{1}{RT} \left[\frac{X_2 \{ X_3 G_{32} z_{\pm 2} + X_2 z_{\pm 2} - X_3 z_{32} G_{\pm 2} \}}{(X_A G_{\pm 2} + X_3 G_{32} + X_2)^2} \right. \\ & + \frac{X_3 \{ X_2 G_{23} z_{\pm 3} + X_3 z_{\pm 3} - X_2 z_{23} G_{\pm 3} \}}{(X_A G_{\pm 3} + X_2 G_{23} + X_3)^2} \\ & - \frac{X_2 z_{\pm 2}}{(X_3 G_{32} + X_2)} - \frac{X_3 z_{\pm 3}}{(X_2 G_{23} + X_3)} + \frac{X_2 X_3 z_{32} G_{\pm 2}}{(X_3 G_{32} + X_2)^2} \\ & \left. + \frac{X_2 X_3 z_{23} G_{\pm 3}}{(X_2 G_{23} + X_3)^2} \right] \quad (2-14) \end{aligned}$$

$$\ln \gamma_{i(2 \text{ or } 3)} = \ln \gamma_{i, \text{Ext.D.H.}} + \ln \gamma_{i, \text{NRTL}} \quad (2-15)$$

$$\begin{aligned} \ln \gamma_{i, \text{Ext.D.H.}} = & 2.303 \frac{v_m}{1000} [M_{wi} \frac{A_\gamma}{3} I^{1/2} \sigma_1(\rho I^{1/2}) \\ & - N_T M_w I^{1/2} \sigma_1^1(\rho I^{1/2}) \frac{\partial A_\gamma}{\partial N_i} + M_{wi} A_\gamma^2 \frac{I}{2} \\ & \psi_1(aI) + N_T M_w A_\gamma \frac{\partial A_\gamma}{\partial N_i} I \psi_1^1(aI)] |z_+ z_-| \\ & + \ln(0.001 v_m M_w + 1) - 0.001 v_m M_w \end{aligned} \quad (2-16)$$

where,

$\sigma_1(\rho I^{1/2})$, $\psi_1(aI)$ are defined in equations (A-12) and (A-13)

$\sigma_1^1(\rho I^{1/2})$, $\psi_1^1(aI)$ are given by equations (B-35) and (B-36)

$$\begin{aligned} \ln \gamma_{i, \text{NRTL}} = & \frac{1}{RT} \left[\frac{X_A G_{\pm i} Z_{\pm i} + X_A X_j Z_{\pm i} G_{ji} + X_A X_j Z_{ji} G_{\pm i} + X_j^2 Z_{ji} G_{ji}}{(X_A G_{\pm i} + X_j G_{ji} + X_i)^2} \right. \\ & + \frac{X_A X_j Z_{ij} G_{\pm j} - X_A X_j Z_{\pm j} G_{ij} + X_j^2 Z_{ij}}{(X_A G_{\pm j} + X_i G_{ij} + X_j)^2} \\ & + X_A X_j \frac{Z_{ji} G_{\pm i} - Z_{\pm i} G_{ji}}{(X_j G_{ji} + X_i)^2} + \frac{Z_{ij} G_{\pm j} + Z_{\pm j} G_{ij}}{(X_i G_{ij} + X_j)^2} \\ & \left. - 2X_A X_i X_j \frac{Z_{ji} G_{\pm i}}{(X_j G_{ji} + X_i)^3} + \frac{Z_{ij} G_{\pm j} G_{ij}}{(X_i G_{ij} + X_j)^3} \right] \end{aligned} \quad (2-17)$$

where,

$$X_A = v_A X_1 \quad (2-18)$$

$$i = 2 \text{ and } j = 3$$

or

$$i = 3 \text{ and } j = 2$$

In equations (2-13) and (2-16) the Debye Hückel constant and the slope of the Debye Hückel constant are calculated by a procedure given in Appendix D. Once the solvent activity coefficients are estimated, they are then used to predict γ_i and p with equations (1-11) and (1-12).

D. Correlation of Ternary Data

The activity coefficient equations (2-12) to (2-18) with equations (1-29), (1-11) and (1-12) are used in ternary data correlation. Three objective functions are attempted

$$\text{o.f. \#1} = \sum_{s=1}^{\text{NP}} \sum_{j=2}^{\text{NP}} \left[\frac{\gamma_{j_{\text{ca}}} - \gamma_{j_{\text{E}}}}{\gamma_{j_{\text{E}}}} \right]^2 + \sum_{s=1}^{\text{NP}} \left[\frac{\gamma_{\pm_{\text{ca}}} - \gamma_{\pm_{\text{E}}}}{\gamma_{\pm_{\text{E}}}} \right]^2 \quad (2-19)$$

$$\begin{aligned} \text{o.f. \#2} = & \sum_{s=1}^{\text{NP}} \left[\frac{P_{\text{ca}} - P_{\text{E}}}{P_{\text{E}}} \right]^2 + \sum_{s=1}^{\text{NP}} \left[(Y_{3_{\text{ca}}} - Y_{3_{\text{E}}}) \times 10 \right]^2 \\ & + \sum_{s=1}^{\text{NP}} \left[\frac{\gamma_{\pm_{\text{ca}}} - \gamma_{\pm_{\text{E}}}}{\gamma_{\pm_{\text{E}}}} \right]^2 \end{aligned} \quad (2-20)$$

$$\begin{aligned} \text{o.f. \#3} = & \sum_{s=1}^{\text{NP}} \sum_{j=2}^{\text{NP}} \left[\frac{\gamma_{j_{\text{ca}}} - \gamma_{j_{\text{E}}}}{\gamma_{j_{\text{E}}}} \right]^2 + \sum_{s=1}^{\text{NP}} \left[(Y_{3_{\text{ca}}} - Y_{3_{\text{E}}}) \times 10 \right]^2 \\ & + \sum_{s=1}^{\text{NP}} \left[\frac{\gamma_{\pm_{\text{ca}}} - \gamma_{\pm_{\text{E}}}}{\gamma_{\pm_{\text{E}}}} \right]^2 \end{aligned} \quad (2-21)$$

In equations (2-20) and (2-21), a weighing factor of ten is used for the deviation in the vapor-phase composition in order to make the magnitude of this term equal to that of the relative percent error in ΔP and γ_{\pm} . In the case where the ternary data are in the form of m-X-y-P-T only, the second term in equation (2-19) is zero and the third term in equations (2-20) and (2-21) is zero. If the data are m-X vs γ_{\pm} only, the first term in equation (2-19), and the first and second terms in equations (2-20) and (2-21) are zero.

The activity coefficient expressions [(2-13) to (2-18)] have six adjustable parameters for a ternary mixture. However, in this work, data are regressed only for four parameters with preset values of Δg_{23} and Δg_{32} obtained by binary 2-3 data correlation, corresponding to $\alpha_{23} = -1.0$. If the experimental data are isothermal, the parameters evaluated are $G_{\pm 2}$, $Z_{\pm 2}$, $G_{\pm 3}$ and $Z_{\pm 3}$. For isobaric data, the temperature independent parameters Δg_{A2} , Δg_{B2} , Δg_{A3} and Δg_{B3} are evaluated.

A stepwise procedure was used for the rapid convergence of the regression program for the four parameters. In the case of isothermal data, first $G_{\pm 2}$ and $Z_{\pm 2}$ were set to the values obtained by binary aqueous electrolyte data correlation and the ternary data were regressed for $G_{\pm 3}$ and $Z_{\pm 3}$. The second time $G_{\pm 3}$ and $Z_{\pm 3}$ were fixed at the regressed values obtained in the first step and $G_{\pm 2}$ and $Z_{\pm 2}$ were evaluated by ternary data correlation. The third time, the values of $G_{\pm 2}$ and $Z_{\pm 3}$ obtained in the second trial were used and the step

one was repeated to obtain new values of $G_{\pm 3}$ and $Z_{\pm 3}$. This procedure is performed for four or five trials. Finally, the four parameters are evaluated together by ternary data reduction using the values of $G_{\pm 2}$, $Z_{\pm 2}$, $G_{\pm 3}$ and $Z_{\pm 3}$ obtained from the last step as starting values in the regression.

E. Binary Data Prediction Using the Parameters Evaluated by Ternary Data Reduction

The binary parameters [Section 2.2 D] obtained in ternary data correlation are used to predict the activity coefficients for binaries 1-2 and 1-3, with equations (A-5), (A-8), (A-10), (A-11) and (A-9). These are then used to calculate vapor pressure depressions.

2.3 Results

A list of binary and ternary systems used in this study is presented in Tables G.1 and G.2.

A. Binary Data Reduction

The solvent-solvent binary data correlation was obtained with two values of α_{23} . Both the values result in the same order of ΔY_{AVG} and ΔP_{AVG} , Table G.3. The quantities ΔY_{AVG} and ΔP_{AVG} are defined below

$$\Delta Y_{AVG} = \frac{\sum_{s=1}^{NP} |\Delta Y|_s}{NP} \quad (2-22)$$

$$\Delta P_{AVG} = \frac{\sum_{s=1}^{NP} |\Delta P|_s}{NP} \quad (2-23)$$

where

$$\Delta Y = Y_{3_{ca}} - Y_{3_E} \quad (2-24)$$

$$\Delta P = P_{ca} - P_3 \quad (2-25)$$

The aqueous or nonaqueous electrolytic binary results are presented in Tables G.4 to G.7. The quantities used to define the accuracy of the correlation are as below

$$\text{Avg \% error in } \gamma_{\pm} = \frac{\sum_{s=1}^{NP} \left| \frac{\gamma_{\pm ca} - \gamma_{\pm E}}{\gamma_{\pm E}} \right|_s \times 100}{NP} \quad (2-26)$$

$$\text{Avg \% error in DP} = \frac{\sum_{s=1}^{NP} \left| \frac{D_{P ca} - D_{P E}}{D_{P E}} \right|_s \times 100}{NP} \quad (2-27)$$

The objective function #2, given in equation (2-10) gives a better fit of the data, Tables G.4 and G.5, specifically for the nonaqueous electrolytic binaries. In further studies, only objective function #2 is used in the binary data correlation, except for the HCl-H₂O binary at 25°C. Since HCl is a volatile electrolyte, and the experimental data are in the form of partial pressure of water in the vapor phase, objective function #1 is used.

B. Temperature Dependency of the Binary Parameters

Next, the temperature dependency of the binary parameters was determined. The parameters Δg_{Ai} and Δg_{Bi} (equation 2-6) were evaluated by presetting α_{Ai} and α_{Bi} . The meaningful values of α_{Ai} and α_{Bi} will be those which can interrelate two forms of the parameters: $G_{\pm i}$; $Z_{\pm i}$ and Δg_{Ai} ; Δg_{Bi} . It was observed that one of the two α 's (α_{Ai} or α_{Bi}) should be set to zero in order to represent one form of the parameters in terms of the other form. In this work, α_{Bi} is set to zero and the value of α_{Ai} was selected arbitrarily and is set equal to 0.2. The results of data reduction obtained for aqueous/nonaqueous electrolytic binaries in the temperature independent form are given in Tables G.6 and G.7. The accuracy of binary data correlation with Δg_{Ai} and Δg_{Bi} is of the same order as that obtained with $G_{\pm i}$ and $Z_{\pm i}$ (Tables G.4 and G.5). Typical results are given for the system NaCl-H₂O at 25°C in Figure 2.2 and the system LiBr-MeOH at 15°C, Figure 2.3. However, to test the validity of 0.2 and 0.0 for α_{Ai} and α_{Bi} respectively, different values of α_{Ai} and α_{Bi} were also tried, Tables G.8 and G.9. The

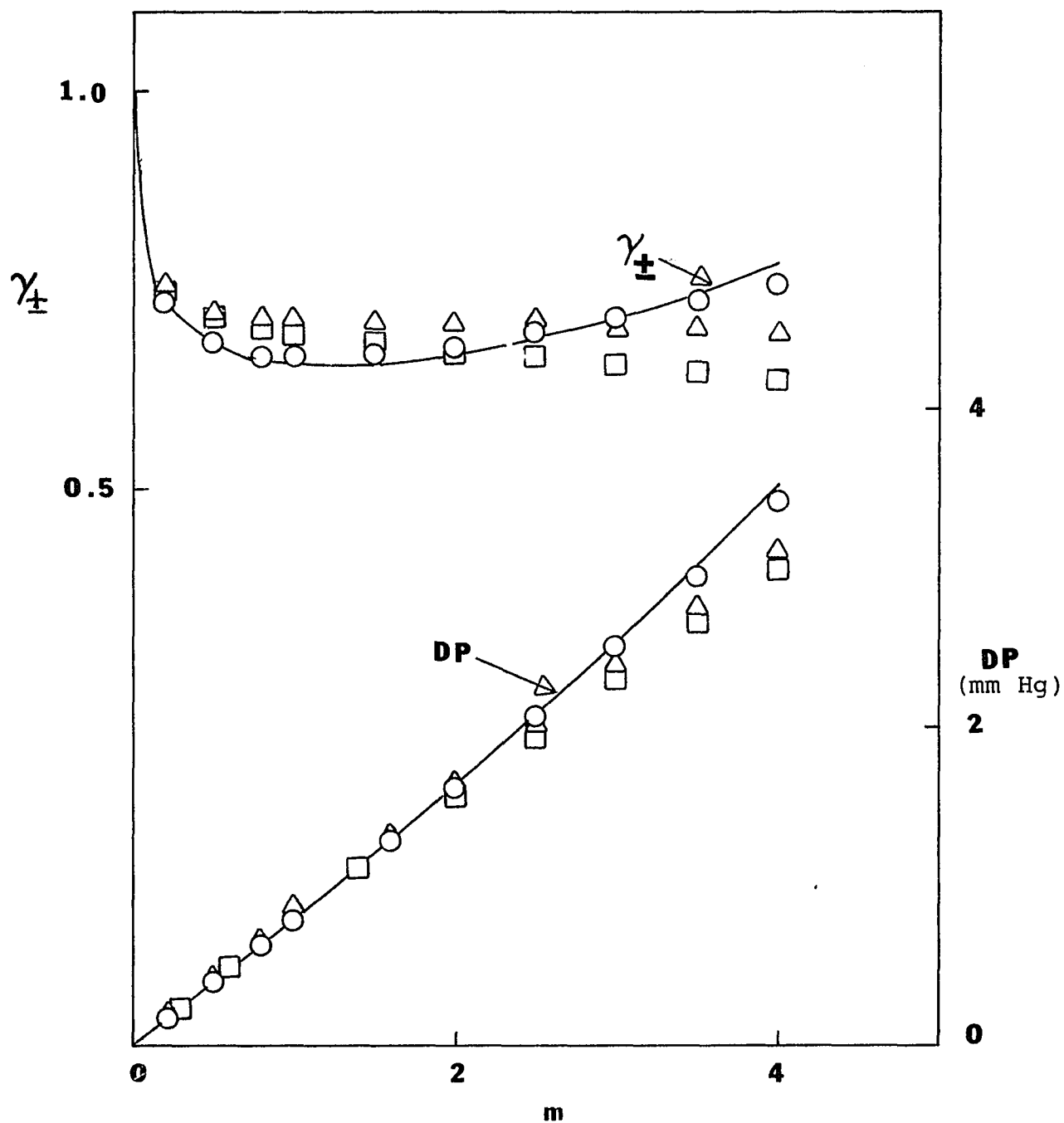


Figure 2.2 Comparison of Experimental Mean Molal Activity Coefficients and Vapor Pressure Depressions with those Predicted by Model I for the System NaCl-H₂O at 25°C . _____ Experimental , Robinson & Stokes (1955) ; O Correlation Pair of Roots #1 ($\alpha_{A2}=0.2$, $\alpha_{B2}=0.0$) ; Δ Correlation , Pair of Roots # 2 ($\alpha_{A2}=0.2$; $\alpha_{B2}=0.0$) ; \square Predicted Using Parameters of 60°C (see Table 2.1 for the roots).

Figure 2.3 Comparison of Experimental Vapor Pressure Depressions with Predicted and Correlated by Model I for the System LiBr-MeOH at 15°C

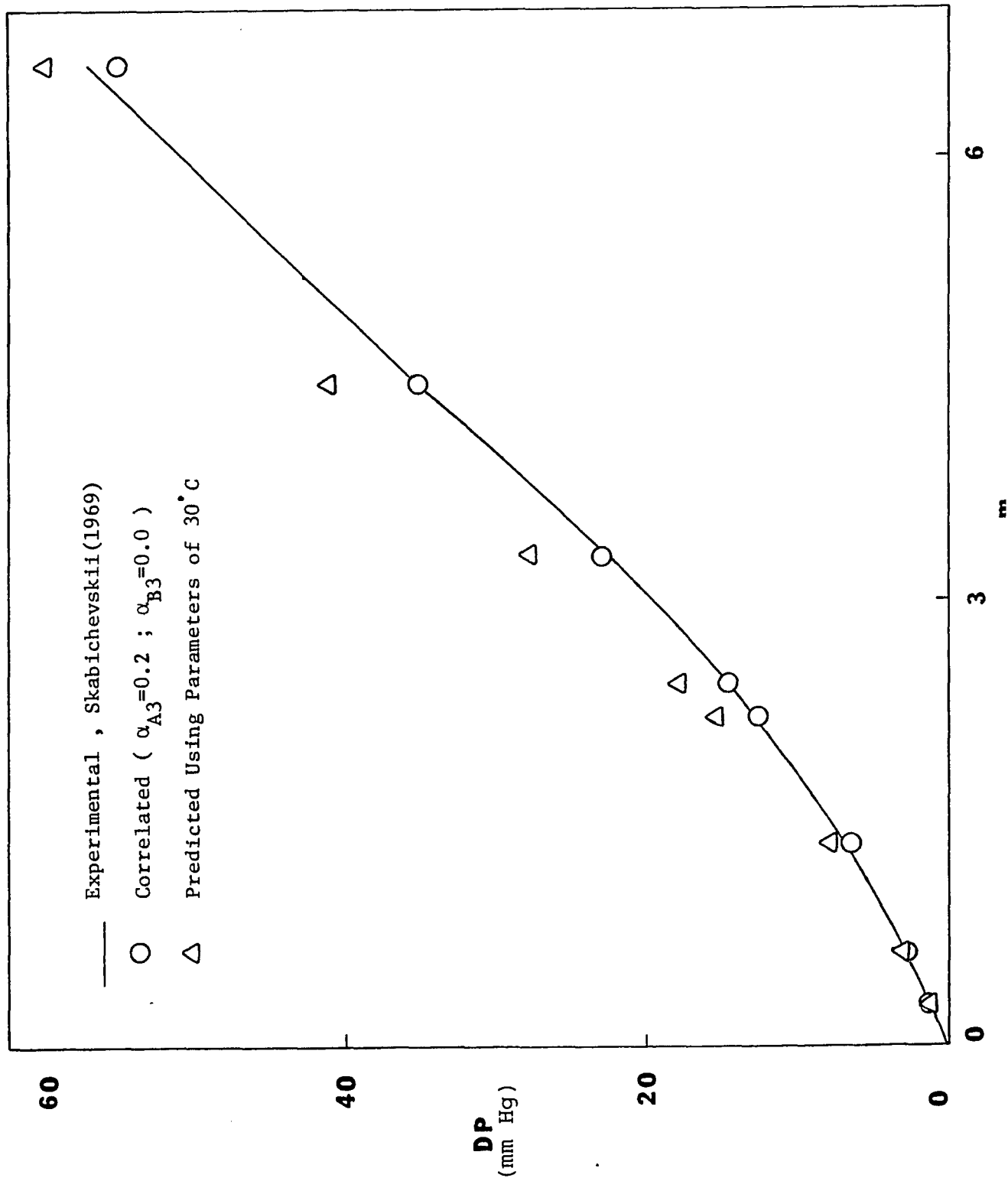


TABLE 2.1 Multiplicity of Roots in Model #1 for Aqueous
Electrolytic Solutions with Preset Values of

$$\alpha_{A2} = 0.2 \text{ and } \alpha_{B2} = 0.0$$

Maximum $m = 4.0$

System	T (°C)	Δg_{A2}	Δg_{A3}	% Error in γ_{\pm}		% Error in DP	
				Max	Avg	Max	Avg
NaCl-H ₂ O	25	-32.396	444.79	3.4	1.2	3.3	1.0
NaCl-H ₂ O	60	-34.009	399.74	2.6	1.4	2.2	0.9
NaCl-H ₂ O	70	-29.051	227.36	4.1	2.4	4.0	1.6
NaCl-H ₂ O	80	-34.000	349.27	2.2	1.2	2.0	0.9
NaCl-H ₂ O	90	-36.82	427.07	1.0	0.6	0.6	0.4
NaCl-H ₂ O	100	-30.668	228.68	3.9	2.2	5.0	2.2
NaBr-H ₂ O	25	-24.258	174.11	9.4	4.0	8.1	2.3
NaCl-H ₂ O	25	156.75	18.271	11.0	6.0	11.7	3.7
NaCl-H ₂ O	60	171.48	21.695	9.8	6.0	9.8	3.6
NaCl-H ₂ O	70	187.42	24.751	10.1	6.1	10.3	3.8
NaCl-H ₂ O	80	155.12	28.38	10.3	6.3	10.7	4.0
NaCl-H ₂ O	90	199.24	32.278	11.0	6.5	11.0	4.2
NaCl-H ₂ O	100	138.47	36.876	11.6	6.9	11.4	5.2
NaBr-H ₂ O	25	163.29	12.545	12.8	6.0	11.6	3.3

results are of poor quality. This again reinforces the use of $\alpha_{Ai} = 0.2$ and $\alpha_{Bi} = 0.0$.

The parameters obtained with $\alpha_{Ai}=0.2$ and $\alpha_{Bi}=0.0$ were used to predict binary data from one temperature to another temperature (Table G.10). In general, for an aqueous electrolyte binary, the data are predicted with a 15 percent average error in γ_{\pm} and a seven percent average error in DP within a 30-40°C temperature range. The prediction of binary data for the system NaCl-H₂O at 25°C using the parameters obtained by the data correlation of the system NaCl-H₂O at 60°C is depicted in Figure 2.2. The availability of nonaqueous electrolytic binary data is limited, therefore it is not possible to establish a temperature range for such binary systems. However, for the two systems LiBr-MeOH and LiCl-MeOH (Table G.10), the results show that the data prediction is less reliable than aqueous electrolytic binaries. The typical result for the system LiBr-MeOH at 15°C is shown in Figure 2.3.

Aqueous electrolytic binary data reduction also indicated a multiplicity of roots for binary parameters (Table 2.1). A binary has two pair of roots. It is interesting to note that the pair of roots with positive values of Δg_{A2} should be used to predict data from one temperature to the other temperature, though these sets of parameters are less accurate in correlating binary data than the other pair of roots (Tables 2.1 and 2.2).

TABLE 2.2 Prediction of Binary VLE Data by Model #1 at One
 Temperature Using Binary Parameters (2nd Pair of Roots)
 at Another Temperature with Preset Values of
 $\alpha_{A2} = 0.2$ and $\alpha_{B2} = 0.0$

System	# of Points	Max 'm'	T (°C)	T of T (°C)	Parameters Used		% Error in γ_{\pm}		% Error in DP	
					Δg_{A2}	Δg_{B2}	Max	Avg	Max	Avg
NaCl-H ₂ O	17	4.0	25	100	138.47	36.876	45.3	11.6	31.9	8.3
NaCl-H ₂ O	11	4.0	60	100	138.47	36.876	35.9	11.6	24.2	8.2
NaCl-H ₂ O	11	4.0	70	100	138.47	36.876	30.5	9.7	21.5	7.1
NaCl-H ₂ O	11	4.0	80	100	138.47	36.876	24.4	7.8	18.3	6.1
NaCl-H ₂ O	11	4.0	90	100	134.47	36.876	17.7	6.8	15.1	5.1
NaCl-H ₂ O	11	4.0	60	25	156.75	18.271	13.2	7.6	6.6	3.2
NaCl-H ₂ O	11	4.0	70	25	156.76	18.271	16.4	10.9	5.8	3.4
NaCl-H ₂ O	11	4.0	80	25	156.75	18.271	21.2	14.9	7.0	4.0
NaCl-H ₂ O	11	4.0	90	25	156.75	18.271	27.3	19.3	8.5	5.3
NaCl-H ₂ O	11	4.0	100	25	156.275	18.271	35.4	24.6	10.7	8.0
NaCl-H ₂ O	11	4.0	25	60	171.48	21.695	18.6	5.7	15.4	4.0
NaCl-H ₂ O	11	4.0	70	60	171.48	21.695	12.7	7.4	7.5	3.5
NaCl-H ₂ O	11	4.0	80	60	171.48	21.695	16.8	11.0	5.9	3.5
NaCl-H ₂ O	11	4.0	90	60	171.48	21.695	22.3	15.3	7.3	4.1
NaCl-H ₂ O	11	4.0	100	60	171.48	21.695	29.3	20.4	9.3	6.5

TABLE 2.3 Performance of Model I in Correlating Binary VLE Data for Different Molality Ranges

System	Max 'm'	# of Points	T (°C)	$G_{\pm i}$	$Z_{\pm i}$	% Error in γ_{\pm}		% Error in DP	
						Max	Avg	Max	Avg
CaCl ₂ -H ₂ O	2.0	15	25	24.1	17.026	3.4	1.3	2.2	1.3
	3.0	17	25	27.31	15.854	9.3	2.6	4.4	2.0
	4.0	19	25	31.499	14.72	16.8	4.8	6.3	3.0
	5.0	21	25	37.755	13.545	24.2	7.6	7.7	4.3
	6.0	23	25	41.19	13.041	32.3	10.3	9.2	5.0
LiCl-H ₂ O	4.0	6	60	0.0294	-77.911	-	-	4.6	2.4
	5.0	9	60	0.0316	-245.0	-	-	7.2	4.2
	6.0	11	60	0.0563	-180.44	-	-	8.3	4.7
	7.0	13	60	0.0213	-585.13	-	-	9.4	5.1
	8.0	14	60	0.029	-465.38	-	-	10.0	5.4
LiCl-MeOH	9.0	16	60	0.054	-286.8	-	-	10.8	5.7
	4.0	8	60	5.877	84.288	-	-	12.2	5.8
	5.0	10	60	5.3481	88.825	-	-	15.6	6.4
	6.0	11	60	5.086	91.269	-	-	17.5	7.3
	8.0	12	60	4.8525	93.557	-	-	21.7	8.6

No multiplicity of roots was observed for the nonaqueous electrolyte binaries.

C. Maximum Molality Applicability

Before this model was extended to ternary systems, its maximum molality applicability was investigated. Three typical systems were used for this: $\text{CaCl}_2\text{-H}_2\text{O}$ at 25°C , $\text{LiCl-H}_2\text{O}$ at 60°C and LiCl-MeOH at 60°C (Table 2.3). The data correlation for binaries $\text{CaCl}_2\text{-H}_2\text{O}$ and $\text{LiCl-H}_2\text{O}$ indicate that for aqueous electrolytic mixtures the correlation yields a good fit up to $I = 9$, whereas for the system LiCl-MeOH , the data are fitted within an average fifteen percent error only up to $I = 6$. This molality limit will be different for different electrolytes, solvents and temperatures of the system. Based on the above study in water and MeOH solvents, the maximum concentration range of an electrolyte is considered $I = 6$.

D. Ternary Data Prediction

The binary parameters obtained by the individual binary data reduction were used to predict isothermal γ_{\pm} , vapor phase compositions and the total pressures in ternary solutions. For the solvent-solvent binary, both sets of parameters were used corresponding to two different values of α_{23} . The best results are tabulated in Tables 2.4 and 2.5.

Out of four ternary systems with m vs γ_{\pm} data, only the two systems $\text{LiCl-H}_2\text{O-MeOH}$ at 25°C and $\text{HCl-H}_2\text{O-MeOH}$ at 25°C

TABLE 2.4 Prediction of γ_{\pm} in Ternary Mixtures Using Binary Parameters from Tables
 G.4 (Binary 1-2); G.5 (Binary 1-3); and G.3 (Binary 2-3)

System	# of Max Points 'm' (°C)	T	α_{23}	Δg_{23}	Δg_{32}	$G_{\pm 2}$	$Z_{\pm 2}$	$G_{\pm 3}$	$Z_{\pm 3}$	% Error in γ_{\pm}		
										Max	Avg	
HCl-H ₂ O-MeOH	48	2.0	25	-1.0	-150.9	336.47	0.1061	-33.295	10.9	39.70	50.7	13.5
LiCl-H ₂ O-MeOH	45	1.0	25	-1.0	-150.9	336.47	0.0557	-81.532	6.1745	56.382	52.0	15.3
HCl-H ₂ O-MeOH	48	2.0	25	0.3	806.1	-321.4	0.1061	-33.295	10.9	39.70	28.2	4.1
LiCl-H ₂ O-MeOH	45	1.0	25	0.3	806.1	-321.4	0.1061	-33.295	10.9	39.70	44.6	13.6
*LiCl-H ₂ O-EtOH	23	0.1	25	-1.0	105.7	383.87	0.094	-34.79	117.0	12.35	28.7	8.4

*Results are shown excluding two points because error for this two points is >60%.

TABLE 2.5 Prediction of Vapor-Phase Composition and Total Pressure by Model #1 Using Binary

Parameters from Tables G.4 (Binary 1-2); G.5 (Binary 1-3); and G.3 (Binary 2-3)

System	# of Max T Points 'm' (°C)	P or T	α_{23}	Δg_{23}	Δg_{32}	Δg_{A2} or G $_{\pm 2}$	Δg_{B2} or Z $_{\pm 2}$	Δg_{A3} or G $_{\pm 3}$	Δg_{B3} or Z $_{\pm 3}$	ΔY		ΔP (mmHg)		
										Max	Avg	Max	Avg	
LiCl-H ₂ O-EtOH	20	1.0	25	0.3	894.5	-62.0	0.0557	-81.532	4.1	144.2	0.091	0.028	5.2	1.4
LiCl-H ₂ O-EtOH	20	1.0	25	-1.0	105.8	383.8	0.0557	-81.532	4.1	144.2	0.078	0.028	5.9	1.4
LiCl-H ₂ O-MeOH	5	1.0	25	0.3	806.1	-321.4	0.0557	-81.532	6.1745	56.832	0.053	0.032	3.6	1.9
LiCl-H ₂ O-MeOH	5	1.0	25	-1.0	-150.9	336.47	0.0557	-81.532	6.1745	56.382	0.054	0.033	3.5	1.9
NaBr-H ₂ O-MeOH	6	1.9	25	0.3	806.1	-321.4	36.949	1.261	6.876	54.598	0.068	0.025	9.0	4.7
NaBr-H ₂ O-MeOH	6	1.9	25	-1.0	-150.9	336.47	36.949	1.261	6.876	54.598	0.034	0.019	8.8	4.9
LiCl-H ₂ O-MeOH	10	2.0	60	0.3	431.65	43.59	0.0353	-287.85	5.09	91.21	0.074	0.052	33.7	18.0
LiCl-H ₂ O-MeOH	10	2.0	60	-1.0	140.3	235.92	0.0353	-287.85	5.09	91.21	0.069	0.048	31.7	14.2
*LiCl-H ₂ O-MeOH	19	2.0	atm	-1.0	97.08	312.47	81.74	-11.59	19.5	170.9	0.075	0.023	52.5	17.4
**NaBr-H ₂ O-MeOH	19	2.0	atm	-1.0	97.08	312.50	163.3	12.55	-21.56	177.3	0.081	0.027	42.9	16.5

*Binary parameters are used corresponding to the values evaluated at 60°C, Tables 6.6 and 6.7

**Binary parameters are used corresponding to the values evaluated at 25°C, Tables 2.1 and 6.7

NOTE: 1. a) Parameters Δg_{A2} , Δg_{B2} , Δg_{A3} and Δg_{B3} are used for isobaric data with $\alpha_{A1} = 0.2$; $\alpha_{B1} = 0.0$

b) Parameters $G_{\pm 2}$, $Z_{\pm 2}$, $G_{\pm 3}$ and $Z_{\pm 3}$ are used for isothermal data

2. In general, prediction is better with parameters corresponding to $\alpha_{23} = -1.0$, therefore isobaric data are predicted using $\alpha_{23} = -1.0$ only.

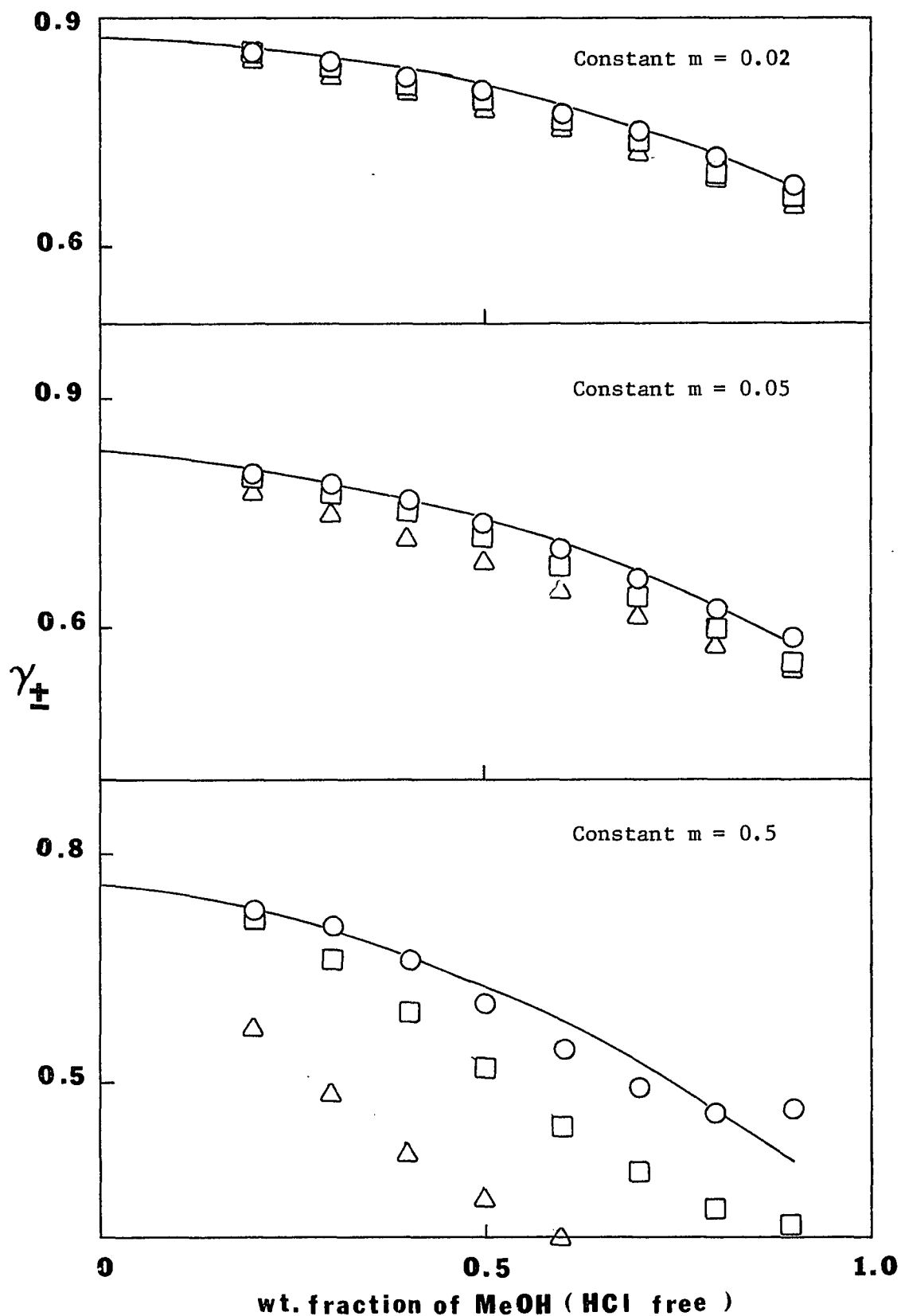


Figure 2.4 Comparison of Experimental Mean Molal Activity Coefficients with those Predicted and Correlated by Model I for the System HCl-H₂O-MeOH at 25°C. — Experimental, Akerlof(1930); ○ Correlated ($\alpha_{23}=-1.0$); △ Predicted ($\alpha_{23}=-1.0$); □ Predicted ($\alpha_{23}=0.3$)

and HCl-H₂O-MeOH at 25°C gave acceptable results. The average errors for the HCl-H₂O-MeOH system at 25°C are 13.5 and 4.1 for two values of α_{23} , -1.0 and 0.3, respectively [Figures 2.4, G.4 and G.5]. The maximum error with $\alpha_{23} = 0.3$ is 28%, which is of good quality. For the system LiCl-H₂O-MeOH at 25°C, again $\alpha_{23} = 0.3$ gives slightly better results with an average percent error of 14 and a maximum percent error a maximum of 45% (Figures G.6 and G.7). However, prediction of γ_{\pm} for the system HCl-H₂O-EtOH at 25°C is possible only at low molalities and water concentration (HCl free) $\geq 95\%$ [Figures G.1 to G.3]. The prediction of γ_{\pm} data for the system NaCl-H₂O-MeOH at 25°C was not of acceptable quality.

Prediction of the vapor-phase composition and the total pressure was attempted for four systems, depending upon the availability of binary data (Table 2.5 and Figures G.1 to G.12). The average error in ΔY , in general, is about 0.028. Also, it is interesting to note that as the concentration of MeOH or EtOH increases, the prediction improves, Figures 2.4 and 2.5. However, prediction of the VLE for the system LiCl-H₂O-MeOH at 60°C is not of presentable quality.

E. Ternary Data Correlation

All four isothermal ternary data for γ_{\pm} were correlated alone, Table G.11 and Figures G.1 to G.9. In general, the ternary γ_{\pm} data are correlated with an average percent error less than eight, except for the NaCl-H₂O-MeOH system at 25°C where the maximum percent error in γ_{\pm} is 27.0. Typical results are

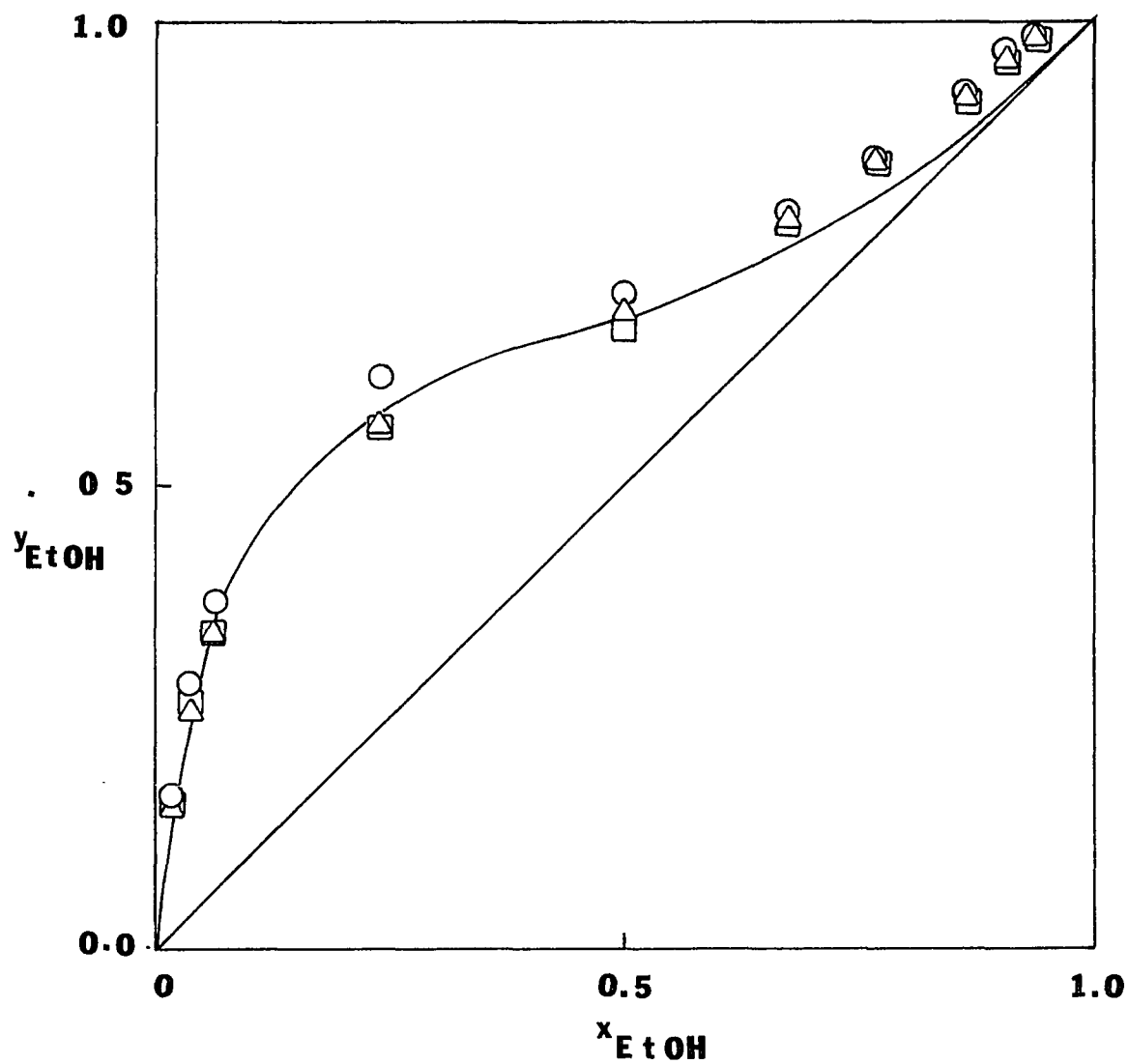


Figure 2.5 Comparison of Experimental VLE with that Predicted Using Model I for the System LiCl-H₂O-EtOH at 25°C . _____ Experimental (LiCl free) Ciparis (1966); ○ Experimental with LiCl, Ciparis(1966) ; △ Predicted with LiCl ($\alpha_{23}=0.3$) ; □ Predicted with LiCl ($\alpha_{23}=-1.0$)

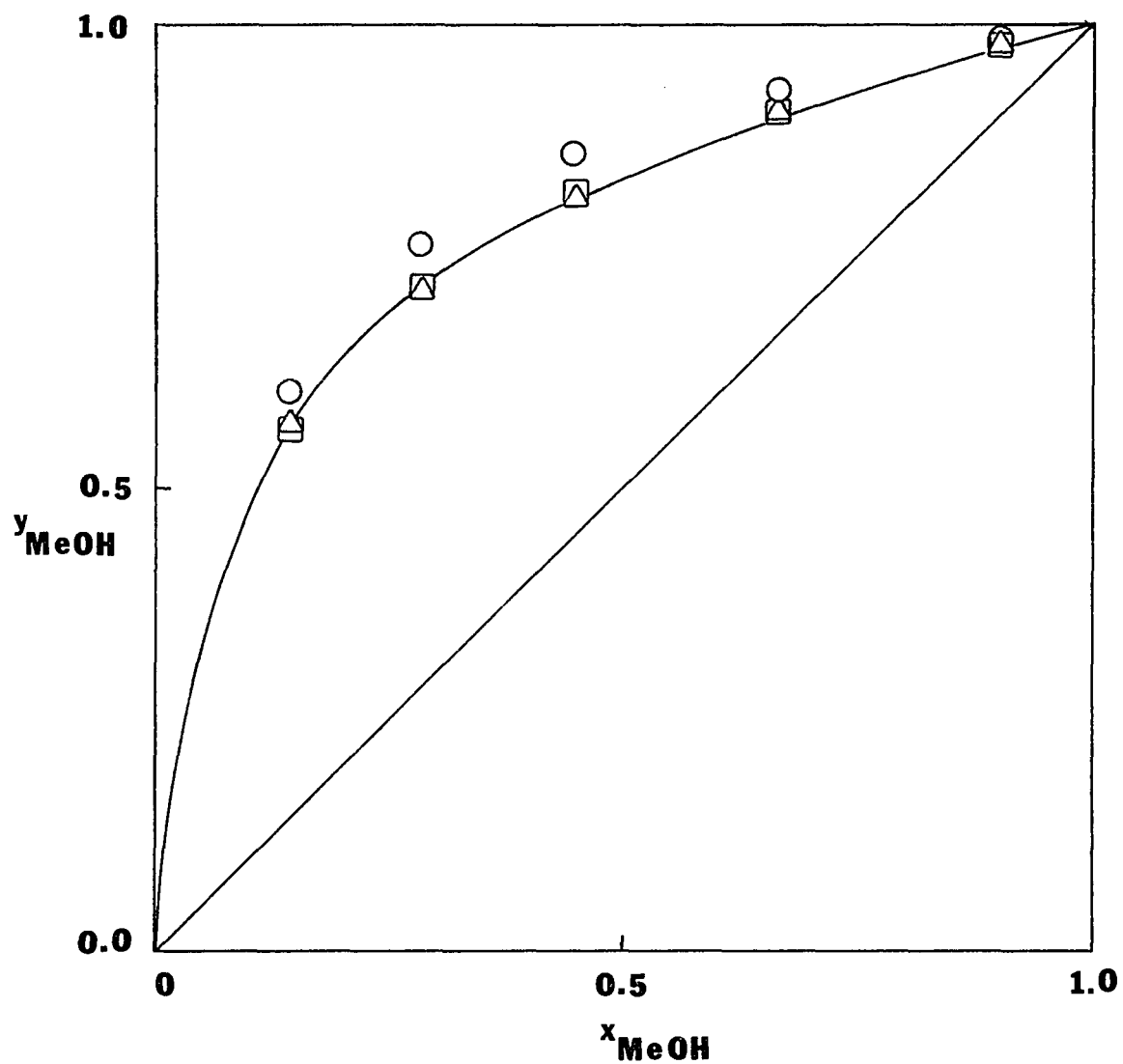


Figure 2.6 Comparison of Experimental VLE with that Predicted Using Model I for the System LiCl-H₂O-MeOH at 25°C . _____ Experimental (LiCl free), Ciparis(1966); ○ Experimental with LiCl, Ciparis(1966); △ Predicted ($\alpha_{23}=0.3$) ; □ Predicted ($\alpha_{23}=-1.0$)

given for the HCl-H₂O-MeOH system at 25°C in Figure 2.4.

Five isothermal and four isobaric ternary VLE data are correlated with three objective functions. Objective function #2, equation 2.20, yields the best results for both ΔY and ΔP (Tables G.13 and G.14 and Figures G.10 to G.19). In general, the average error in ΔY is about 0.015. The correlation of ternary data for the NaBr-H₂O-MeOH system at 25°C and 40°C (Figures G.13 and G.14) is good, even for molalities greater than six, although it was not possible to predict the data for $m > 2$. For the LiCl-H₂O-MeOH system at 60°C the prediction of ternary data was not possible, yet the data are correlated successfully up to $I = 6$ with an average error in ΔY of 0.015, Figure G.15. The data for the LiCl-H₂O-EtOH system at 25°C are fitted only up to $m = 1.0$, Figures G.11 and G.11. The data available at $m = 4.0$ for this system could not be fitted within acceptable quality, but this is expected since LiCl is incompletely dissociated in EtOH at this molality. The overall ternary data correlation is of good quality. The parameters obtained with three objective functions are listed in Tables G.13 and G.15.

F. Binary Data Prediction

Finally, aqueous/nonaqueous electrolyte binary data are predicted using the parameters obtained by ternary data reduction, Table 2.6. In general, aqueous electrolyte binary data are predicted with an average percent error of 15 in γ_{\pm}

TABLE 2.6 Prediction of Binary VLE and γ_{\pm} Data Using Parameters Obtained by Ternary Data Correlation, Tables G.11 and G.12

System	# of Points	Max 'm'	T (°C)	$G_{\pm i}$	$Z_{\pm i}$	% Error in γ_{\pm}		% Error in DP	
						Max	Avg	Max	Avg
LiCl-H ₂ O	19	4.0	25	12.666	0.1983	27.6	5.8	15.9	3.7
HCl-H ₂ O	15	2.0	25	19.677	1.7897	28.6	13.4	-	-
LiCl-H ₂ O	11	6.0	60	15.463	5.126	-	-	28.8	22.1
NaCl-H ₂ O	10	1.0	25	38.981	4.216	29.2	21.9	12.0	9.8
HCl-EtOH	8	0.1	25	9.4608	84.647	20.0	16.2	-	-
NaCl-MeOH	7	0.1	25	44.11	14.638	13.1	5.8	-	-
LiCl-MeOH	7	3.67	25	75.82	-11.24	-	-	19.01	149.9
NaBr-MeOH	9	1.56	25	0.1382	601.16	-	-	114.9	104.5

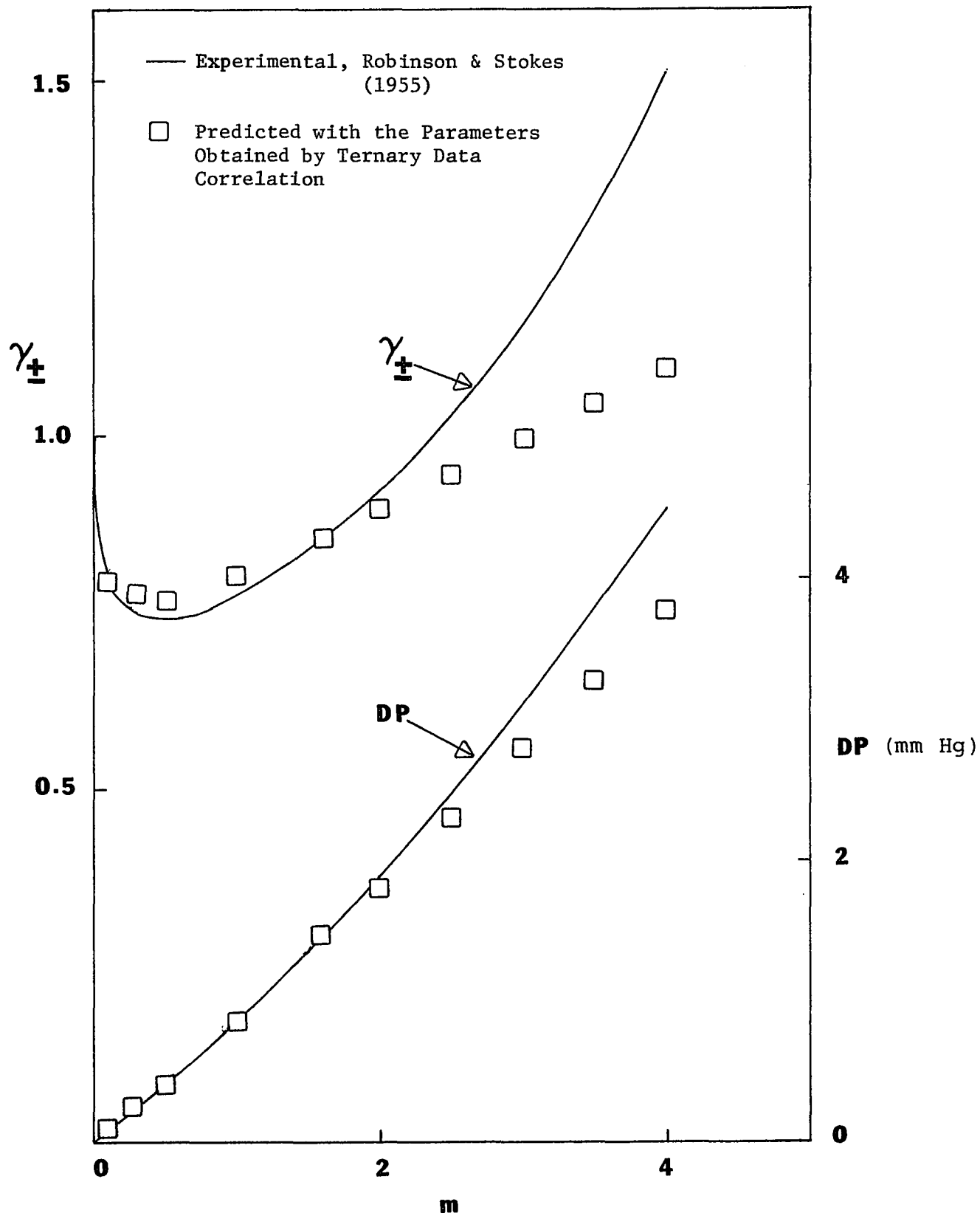


Figure 2.7 Prediction of γ_{\pm} and DP Data for the System LiCl-H₂O at 25°C Using the Parameters Obtained by Ternary Data Correlation with Model I

and DP. However, the prediction of DP for nonaqueous electrolyte is not possible. Typical results for the LiCl-H₂O system at 25°C are compared with the experimental data in Figure 2.7.

2.4 Discussion

The main objective of this work is to be able to predict or correlate γ_{\pm} and the salting out or salting in effect in ternary mixtures. The thermodynamic representation of ternary systems would serve as a guideline in the extension of this model to multicomponent mixtures. An additional term was required with the Debye-Hückel term to represent ternary mixture behavior. Therefore it would be important to analyze the contribution of different terms to understand the behavior of ternary mixtures physically.

In a ternary mixture the impact of the NRTL term, though shifted a little, follows the same trend as it does in a solvent-solvent binary, Figure G.20. However, the contribution of the Debye-Hückel term in a ternary mixture decreases as the dielectric constant of the solvent decreases, i.e.

$$\ln\gamma_{D.H.EtOH} < \ln\gamma_{D.H.MeOH} < \ln\gamma_{D.H.H_2O}$$

So, in a ternary mixture of LiCl-H₂O-EtOH, the Debye-Hückel term will always result in salting in for EtOH, Figure 2.8. This salting in effect is due to the Debye Hückel term and is not counterbalanced by the NRTL term. In reality, EtOH is salted-out, which is contrary to the effect of the Debye-Hückel term. Therefore it was necessary to include a higher order term ($\ln\gamma_{PHY}$) with the Debye-Hückel equation to cancel the salting-in effect, Figure 2.8. The extended term ($\ln\gamma_{PHY}$)

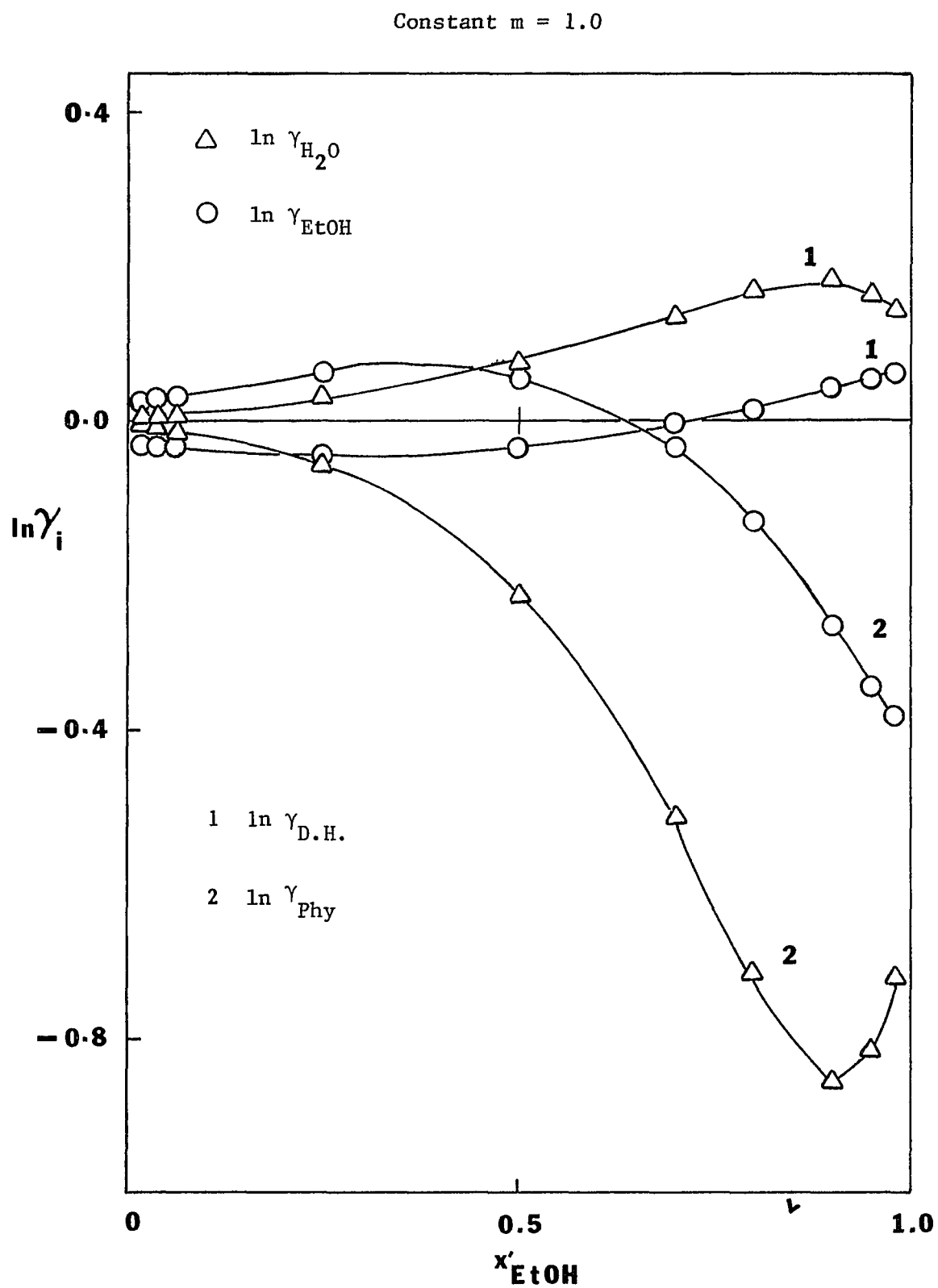


Figure 2.8 Contribution of Different Terms to $\ln \gamma_i$ for the System $\text{LiCl-H}_2\text{O-EtOH}$ at 25°C in Model I

gives an opposite contribution to that of the Debye-Hückel term, i.e.

$$\ln\gamma_{\text{PHY,EtOH}} > \ln\gamma_{\text{PHY,MeOH}} > \ln\gamma_{\text{PHY,H}_2\text{O}}$$

Next, it is important to justify the assumption of complete dissociation of the electrolyte for the applicability of this model. In general, dissociation of an electrolyte in a liquid solution depends upon the characteristics of the electrolyte, properties of the solvent and temperature of the system. As the dielectric constant of the solvent decreases, the ionization of electrolyte decreases also. If dissociation data are not available, it would be appropriate to accept Waddington's (1969) approximation as a guideline. According to Waddington, an electrolyte can be considered completely dissociated up to a moderate concentration range in a solvent with dielectric constant ≥ 30 . To determine the moderate range, the correlation of three typical binary data have been studied, Table 2.3. As mentioned in section 2.3, the maximum concentration range for water and MeOH solvents is accepted as $I = 6.0$. However, this is based on data at 25°C and 60°C, where the dielectric constant of MeOH is closed to 30. But, if the temperature of the system increases, the dielectric constant decreases and the molality range applicability should be expected to be less than $I = 6.0$. This is justified by the ternary VLE data correlation for the NaBr-H₂O-MeOH system at one atm (temperature range 65-100°C) and isothermal data

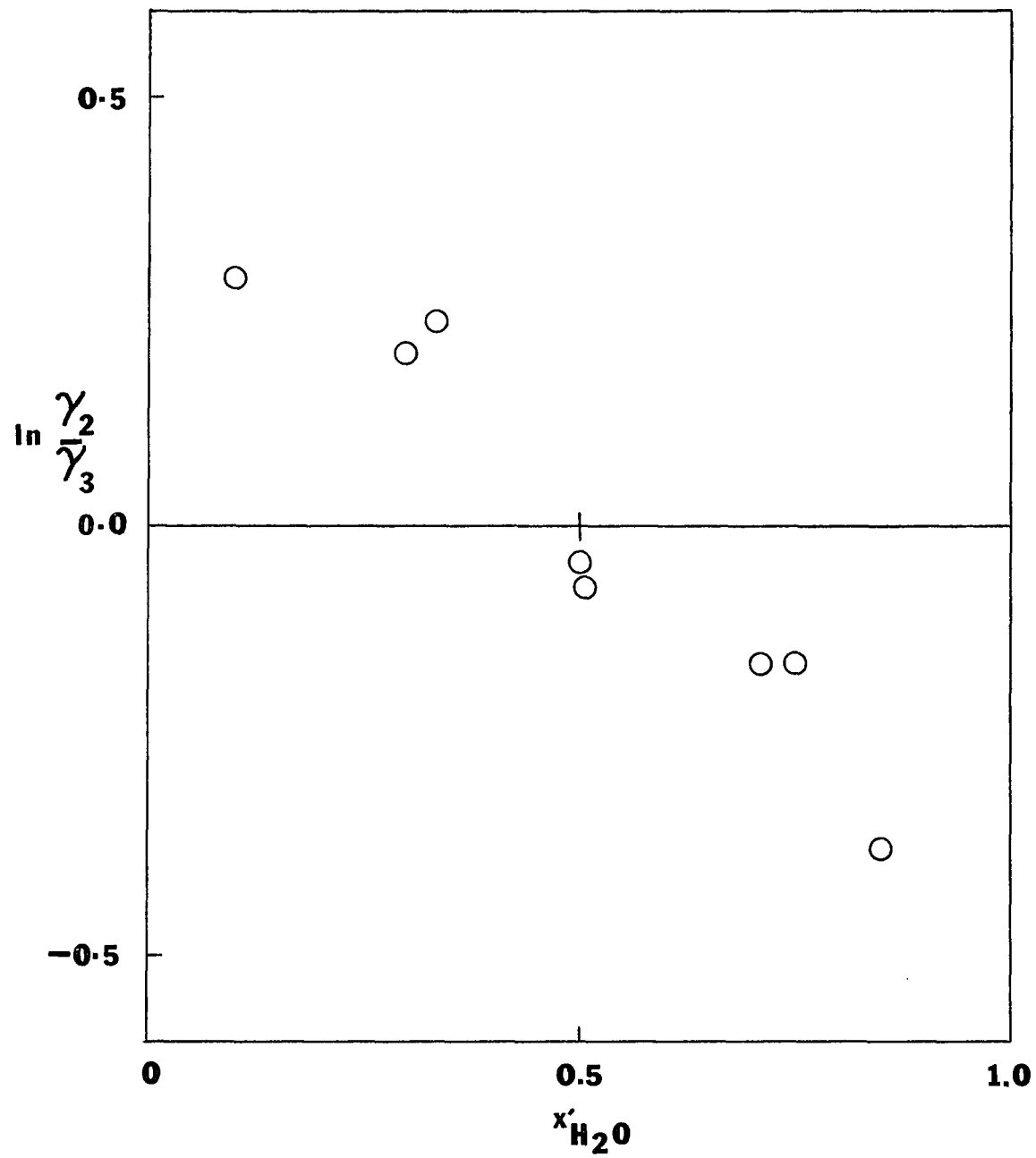


Figure 2.9 Thermodynamic Consistency Test for the System H_2O -MeOH at $25^\circ C$

at 25°C and 40°C. The average errors in ΔY are 0.017 and 0.012 at 25°C and 40°C, respectively where the data are correlated up to $I = 7.1$ and $I = 6.2$ for the two temperatures respectively, Table G.12. However, for isobaric data at one atm, the average error goes up to 0.021, although data up to $I = 4$ only are used.

In general, ternary γ_{\pm} and VLE data prediction, as shown in Tables 2.4 and 2.5, are of acceptable quality. These can be used as a guideline in preliminary design. Prediction of vapor phase composition and total pressure is better with $\alpha_{23} = -1.0$ than $\alpha_{23} = 0.3$. It is interesting to note that prediction of y and P data for two isobaric systems using the temperature independent parameters (LiCl-H₂O-MeOH and NaBr-H₂O-MeOH at $P = 1$ atm, Table 2.5) is obtained with an average error in ΔY of 0.023 and 0.027, respectively. VLE data for four systems out of six systems presented in Table 2.5, are predicted with a ΔY_{AVG} of less than 0.028. The average error in ΔY for the other two systems LiCl-H₂O-MeOH at 25°C and LiCl-H₂O-MeOH at 60°C is larger than 0.028. However, it was found that the maximum concentration limits for reasonable prediction is $I = 2$. The large errors are observed at higher molality which are due to incomplete dissociation of an electrolyte in the solution.

As shown in Tables 2.4 and 2.5, large errors are obtained for some systems, e.g. especially for the prediction of γ_{\pm} for the HCl-H₂O-EtOH system at 25°C and the NaCl-H₂O-MeOH system at 25°C and y and P data for the systems LiCl-H₂O-MeOH at 60°C and LiCl-H₂O-MeOH at 25°C. It is important as a first step to

question the accuracy of binary or ternary data, because the performance of the model in the correlation or prediction of the data is equally dependent upon the quality of the data itself. A plot of $\ln \gamma_2/\gamma_3$ vs X_2 (Figure 2.9) which enables the thermodynamic consistency of the data for the system H_2O - $MeOH$ at $25^\circ C$ shows a lot of scattering of the experimental data. This is the best set of data out of three sources which are definitely thermodynamically inconsistent. Hence, binary parameters evaluated for this binary will affect the prediction of γ_{\pm} for the systems HCl - H_2O - $MeOH$ at $25^\circ C$ and $NaCl$ - H_2O - $MeOH$ at $25^\circ C$ and y and P prediction for the systems $LiCl$ - H_2O - $MeOH$ at $25^\circ C$ and $NaBr$ - H_2O - $MeOH$ at $25^\circ C$.

The solvent-solvent binary data can be tested for thermodynamic consistency, but there is no thermodynamic consistency test to check electrolyte-solvent binary or ternary data. In the literature, a great deal of aqueous electrolyte binary data are available and their quality and accuracy can be considered valid. However, the nonaqueous electrolyte binary or ternary data are not frequently available and those found in the literature can not be checked for accuracy. However, a comparison of isothermal and isobaric data prediction with the same binary parameters evaluated at $60^\circ C$ indicate that isobaric data can be predicted with an average error in ΔY of less than 0.028 whereas the error is large for isothermal ternary data prediction. This shows a possible inconsistency in the VLE data of the $LiCl$ - H_2O - $MeOH$ system at $60^\circ C$, though this can not be verified.

Another point to be examined in ternary prediction is the difference in the available molality range for binary and ternary systems. As in the case of the HCl-H₂O-EtOH system at 25°C, ternary data are available up to $m = 2.5$ for $X'_{\text{EtOH}} = 0.5$, whereas the corresponding HCl-EtOH binary data are available only up to 0.1 m. The data for $m \geq 0.1$ for the HCl-EtOH binary can not be used with this model because of the incomplete dissociation of HCl. The binary parameters obtained in the regression of the HCl-EtOH data up to 0.1 m can not be expected to perform well for higher molalities in a ternary mixture, especially when the concentration of EtOH increases, (Figures G.1 to G.3). This is also observed with the system NaBr-H₂O-MeOH at 25°C. The prediction of this ternary is possible only up to $m = 1.9$, because the binary NaBr-MeOH data are available only up to $m = 1.6$, Table 2.5.

The performance of this model in correlating ternary data as tested with four isothermal systems for γ_{\pm} (Table G.11) and nine systems for VLE (5 isothermal, Table G.12 and 4 isobaric, Table G.14) is of good quality. The data correlated for the NaBr-H₂O-MeOH system at 25°C are compared with the results of Chen et al. (1979) (Figure G.14). The results obtained by this model are definitely superior to their model.

Finally, the prediction of the binary data with the parameters obtained by ternary data correlation is generally of acceptable quality for aqueous electrolyte binaries, Table 2.6 and Figure 2.7. The average error in DP and γ_{\pm} is about 15%.

But the prediction of DP data for nonaqueous electrolytes is not possible, as shown for the systems LiCl-MeOH at 25°C and NaBr-MeOH at 25°C (Table 2.6).

2.5 Conclusions

The main objective of this work, which was to represent the thermodynamic behavior of strong electrolytic solutions, is achieved. Aqueous/nonaqueous binary data (DP and γ_{\pm} vs m) are correlated up to $I = 6$ with an average percent error of 7.0. The prediction of γ_{\pm} for ternary systems up to $I = 2$ is possible with an average percent error of 15.0. The prediction of ternary VLE data as shown with six systems is possible with an average error in ΔY of 0.028 up to $I = 2$, except for the LiCl-H₂O-MeOH at 60°C, where error in ΔY is large even at $I = 2$. The prediction of VLE data above $I = 2$ results in large errors. This sets the limitation of the model for ternary prediction. The correlation of ternary γ_{\pm} and VLE data for systems containing water and MeOH is of good quality up to $I = 6$. Ternary system containing water and ethanol was correlated only up to $I = 1$.

CHAPTER 3

CORRELATION OF VAPOR-LIQUID EQUILIBRIUM AND MEAN MOLAL ACTIVITY COEFFICIENTS WITH MODEL II IN ELECTROLYTIC SOLUTIONS

ABSTRACT

Vapor pressure depression data (DP) of 53 aqueous electrolytes at 100°C were correlated with the one parameter (B_{12}) Bromley equation. These B_{12} constants can be used to calculate mean molal activity coefficients up to $I = 6$. However, maximum molality applicability for MeOH-electrolyte solutions is only up to $I = 3$. In addition, these B_{12} values, along with those at 25°C reported by Bromley, can lead to reliable estimates of DP and γ_{\pm} in the temperature range 25-100°C.

The extended form of the Bromley equation with the additional NRTL equation and the salting-out term give excellent correlation of the isothermal ternary VLE and γ_{\pm} data in electrolytic solutions. This model requires two ternary adjustable parameters, therefore prediction of ternary data with binary data only is not possible.

Model II: Combination of the Bromley Equation, the
Simplified NRTL Equation and the Salting Out Term

3.1 Gibbs Free Energy Expression

Bromley (1973) proposed a one parameter equation to correlate binary aqueous electrolytic mixtures. The same equation has been applied successfully to correlate nonaqueous binary data. This equation represents long-range electrostatic forces and ion-solvent interactions in a binary mixture. However, in a ternary mixture additional solvent-solvent molecular interactions must be considered. Therefore in Model II the Bromley equation has been extended to ternary mixtures and combined with a simplified form of the NRTL equation and an additional salting out term:

$$\frac{G^E}{RT}]_{\text{Total}} = \frac{G^E}{RT}]_{\text{Bromley}} + \frac{G^E}{RT}]_{\text{NRTL-S}} + \frac{G^E}{RT}]_{\text{Salting Out}} \quad (3-1)$$

A stepwise procedure to obtain the total Gibbs free energy expression is presented in Appendix-C (Sections C.1, C.2 and C.3). The final forms of the equations are given below

$$\begin{aligned} \frac{G^E}{RT}]_{\text{Bromley}} &= 2.303 v \frac{m}{I} \frac{N_T M_w}{1000} \left[-A_\gamma \frac{2}{\rho^3} \frac{1}{2} \left\{ (1 + \rho I^{1/2})^2 \right. \right. \\ &\quad \left. \left. - 2(1 + \rho I^{1/2}) + \ln(1 + \rho I^{1/2}) + \frac{3}{2} \right\} \right. \\ &\quad \left. + \frac{(0.06 + 0.6 B)}{a^2} \left\{ \ln(1 + aI) + \frac{1}{(1 + aI)} - 1 \right\} \right] \end{aligned}$$

$$+ \frac{B}{2} I^2] + N_T [(0.001 \nu M_w + 1)$$

$$\ln(0.001 \nu M_w + 1) - 0.001 \nu M_w] \quad (3-2)$$

where,

$$B = B_{12} X_2' + B_{13} X_3' + B_{123} \frac{(X_2' X_3')^{1/2} e^{-\alpha X_3'}}{(1 + n_1^{1/2})^3} \quad (3-3)$$

B_{123} is ternary adjustable parameter

$$\begin{aligned} \frac{G^E}{RT} \text{NRTL-S} &= \frac{N_T}{RT} \left[\left\{ \frac{X_2 X_3 Z_{32}}{(X_A \frac{\nu}{A} + X_2 + X_3 G_{32})} + \frac{X_2 X_3 Z_{23}}{(X_A \frac{\nu}{A} + X_3 + X_2 G_{23})} \right\} \right. \\ &\quad \left. + \frac{\nu}{v_A} X_A X_2 X_3 \left\{ \frac{Z_{32}}{(X_3 G_{32} + X_2)^2} + \frac{Z_{23}}{(X_2 G_{23} + X_3)^2} \right\} \right] \quad (3-4) \end{aligned}$$

where, G_{ij} and Z_{ij} are the binary solvent-solvent parameters, equation (2-4).

$$\frac{G^E}{RT} \text{Salting Out} = \frac{\delta_{123}}{e} \frac{\epsilon^2}{\alpha n_1^{1/2}} \sum_k \frac{v_k z_k^2}{b_k} \frac{n_1^2}{2} \delta' (N_2 N_3)^{1/2} \quad (3-5)$$

where,

$$\delta' = e^{\alpha X_2'} (X_2' B_{13} - X_3' B_{12}) \quad (3-6)$$

$$\alpha = 2.0$$

δ_{123} is a ternary adjustable salting out parameter. A combination of equations (3-2) to (3-5) with equations (1-27) to (1-29) is used to derive activity coefficient expressions for solvents and the electrolyte. The detailed procedure is given in Appendix-C.

Desired : Correlation of
 Y_i ; P and / or Y_{+}
 in a Ternary Electrolytic Solution

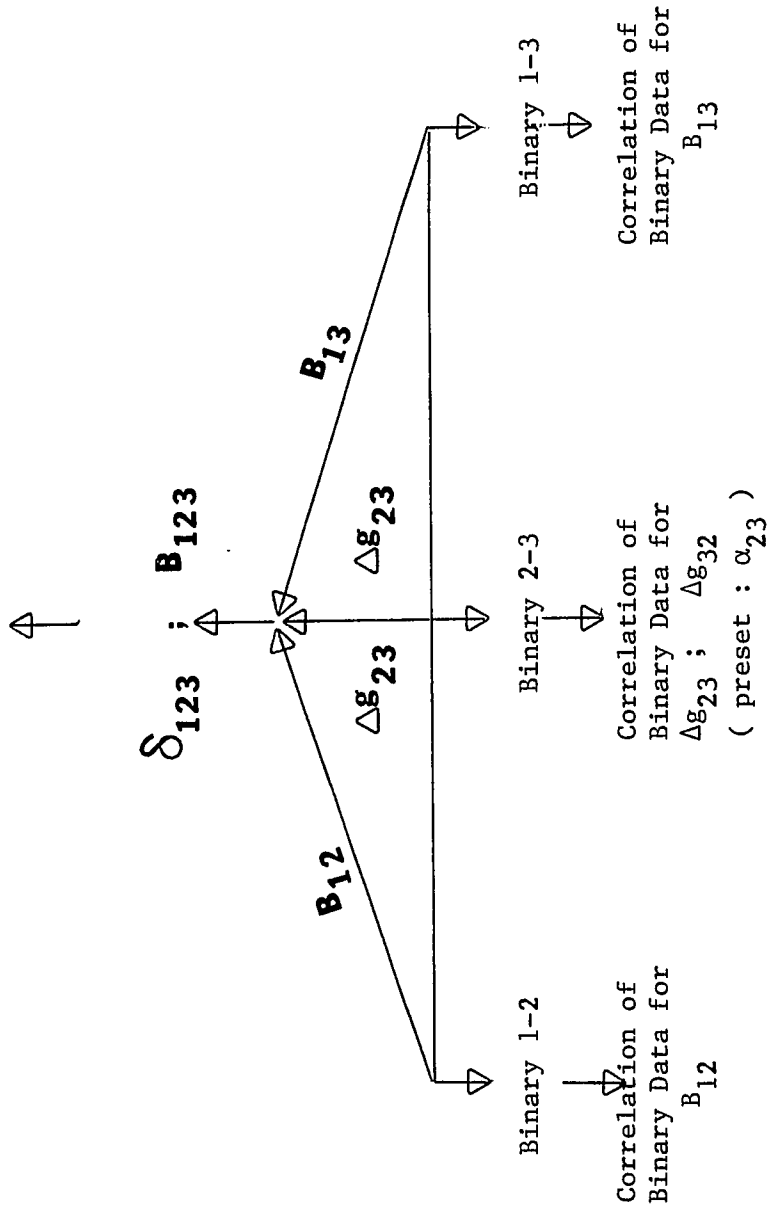


Figure 3.1 A Stepwise Scheme for Correlation for the VLE and Mean Molal Activity Coefficients with Model II

3.2 Procedure--Data Reduction

Each binary set is correlated with the appropriate equations for the activity coefficients and the VLE relationships developed in Chapter 1. Binary parameters are then used in the ternary expressions and the ternary isothermal data are correlated. A stepwise scheme for the data correlation is shown in Figure 3.1. A detailed description of the data reduction is given in the following sections.

A. Solvent-Solvent Binary

The activity coefficient equations for these types of systems are derived by setting $m = 0$ and $N_A = 0$ in equations (3-2) to (3-5). The expressions are the same as equation (2-7). The binary data correlation is the same as discussed in Section 2.2-A.

B. Electrolyte-Solvent Binary

An aqueous/non-aqueous electrolytic binary is correlated with the one parameter Bromley equation given by equations (C-1), (C-2) and (C-9). A Fibonacci single variable regression program is used to find the best value of the binary adjustable parameter ' B_{12} ' or ' B_{13} '. Two objective functions, equations (2-9) and (2-10) (Section 2.2-B), with equations (C-1), (C-2), (C-9), (1-19) to (1-21) are used to correlate the binary experimental data.

C. Electrolyte-Solvent-Solvent Ternary

A ternary mixture requires four binary parameters viz Δg_{23} , Δg_{32} (preset α_{23}), B_{12} and B_{13} and two additional ternary parameters.

$$\ln \gamma_{\pm}^* = \ln \gamma_{\pm, \text{Bromley}}^* + \ln \gamma_{\pm, \text{NRTL-S}}^* + \ln \gamma_{\pm \text{Salt Out}}^* \quad (3-7)$$

where,

$$\begin{aligned} \ln \gamma_{\pm, \text{Bromley}}^* = & 2.303 [-A_{\gamma} |z_+ z_-| \frac{I^{1/2}}{1 + \rho I^{1/2}} \\ & + \frac{(0.06 + 0.6B) |z_+ z_-| I}{(1 + aI)^2} + BI] \\ & + 2.303 v \frac{N_T M_w}{1000 I} \left[\frac{0.6}{a^2} |z_+ z_-| \right. \\ & \left. \{ \ln(1 + aI) + \frac{1}{(1 + aI)} - 1 \} + \frac{I^2}{2} \right] \frac{\partial B}{\partial N_1} \\ & + \ln(0.001 v m M_w + 1) \end{aligned} \quad (3-8)$$

where, $\frac{\partial B}{\partial N_1}$ is defined by equation (C-19)

$$\begin{aligned} \ln \gamma_{\pm, \text{NRTL-S}}^* = & \frac{X_2 X_3}{RT} \left[- \frac{z_{23}}{(X_{A \frac{v}{v_A}} + X_3 G_{32} + X_2)^2} \right. \\ & - \frac{z_{23}}{(X_{A \frac{v}{v_A}} + X_2 G_{23} + X_3)^2} + \frac{z_{32}}{(X_3 G_{32} + X_2)^2} \\ & \left. + \frac{z_{23}}{(X_2 G_{23} + X_3)^2} \right] \end{aligned} \quad (3-9)$$

$$\ln \gamma_{\pm, \text{Salt Out}}^* = \delta_{123} \frac{\epsilon^2}{KTD} \sum_k \frac{v_k z_k}{b_k} (N_2 N_3)^{1/2} \delta' \frac{N_1}{e^{\alpha N_1^{1/2}}} \left[1 - \frac{\alpha}{4} N_1^{1/2} \right] \quad (3-10)$$

For the solvents 2 and 3

$$\ln \gamma_i = \ln \gamma_{i, \text{Bromley}} + \ln \gamma_{i, \text{NRTL-S}} + \ln \gamma_{i, \text{Salt Out}} \quad (3-11)$$

where,

$$\begin{aligned} \ln \gamma_{i, \text{Bromley}} = & 2.303 \frac{v_m}{1000} M_{wi} \left[A_\gamma \frac{I^{1/2}}{3} \sigma_2(\rho I^{1/2}) |z_+ z_-| \right. \\ & - (0.06 + 0.6B) \frac{I}{2} \psi_2(aI) |z_+ z_-| + B \frac{I}{2} \left. \right] \\ & + 2.303 v_m \frac{N_T M_w}{1000} \left[-I^{1/2} \sigma_2^1(\rho I^{1/2}) |z_+ z_-| \frac{\partial A_\gamma}{\partial N_i} \right. \\ & + 0.6 \frac{I}{2} \psi_2^1(aI) |z_+ z_-| \frac{\partial B}{\partial N_i} + I \frac{\partial B}{\partial N_i} \left. \right] \\ & + \ln(0.001 v_m M_w + 1) - 0.001 v_m M_w \quad (3-12) \end{aligned}$$

$\sigma_2(\rho I^{1/2})$, $\psi_2(aI)$, $\sigma_2^1(\rho I^{1/2})$, $\psi_2^1(aI)$ and $\frac{\partial B}{\partial N_i}$ are defined in equations (C-24) to (C-29). B is given by equation (3-3).

$$\begin{aligned} \ln \gamma_{i, \text{NRTL-S}} = & \frac{1}{RT} \left[\frac{X_A X_j \frac{v}{v_A} z_{ji} + X_j^2 z_{ji} G_{ji}}{(X_A \frac{v}{v_A} + X_j G_{ji} + X_i)^2} \right. \\ & + \frac{X_A X_j \frac{v}{v_A} z_{ij} + X_j^2 z_{ij}}{X_A \frac{v}{v_A} + X_i G_{ij} + X_j} + X_A X_j \frac{v}{v_A} \left\{ \frac{z_{ji}}{(X_j G_{ji} + X_i)^2} \right. \\ & \left. \left. + \frac{z_{ij}}{(X_i G_{ij} + G_j)^2} \right\} - 2 X_A X_i X_j \frac{v}{v_A} \left\{ \frac{z_{ji}}{(X_j G_{ji} + X_i)^3} \right. \right. \end{aligned}$$

$$+ \frac{z_{ij}G_{ij}}{(X_i G_{ij} + X_j)^3}] \quad (3-13)$$

Where,

$$i = 2 \text{ and } j = 3$$

or

$$i = 3 \text{ and } j = 2$$

$$\ln \gamma_{i, \text{Salt Out}} = \frac{\delta_{123}}{e^{\alpha N_1^{1/2}}} \frac{\epsilon^2}{KTD} \sum_k \frac{v_k z_k^2 N_1^2}{b_k} \left[\frac{1}{2} \left(\frac{N_j}{N_i} \right)^{1/2} \delta' - (N_2 N_3)^{1/2} \frac{\delta'}{D} \frac{\partial D}{\partial N_i} + (N_2 N_3)^{1/2} \frac{\partial \delta'}{\partial N_i} \right] \quad (3-14)$$

Where, δ' is given by equation (3-6) and $\frac{\partial \delta'}{\partial N_i}$ is defined in equations (C-36) and (C-39).

Note: For the development of equations (3-7) to (3-14), see Appendix-C (Section C.4).

The four binary parameters are obtained by individual binary data correlation. A ternary mixture is correlated for the two ternary parameters, B_{123} and δ_{123} , using the LSQ2 non-linear regression subroutine. Again, as in Model I, three objective function equations, (2-19) to (2-21), have been tried to correlate the experimental data. In all the ternary data reductions, Δg_{23} and Δg_{32} are preset to their respective values obtained by binary data correlation with $\alpha_{23} = -1.0$.

Equations (3-7) to (3-14) with equations (1-11), (1-12), (1-22) and (1-24) are used to correlate the ternary VLE and γ_{\pm} data.

TABLE 3.1 Data Sources *

System	T (°C)	m	Reference
NaCl-H ₂ O	25,50,75,100	0.1 - 6.0	Gibbard et al. (1974)
	25,60,70,80,90,100	0.05 - 4.0	Robinson and Stokes (1955)
KCl-H ₂ O	25,40,50,60,70,80	0.1 - 4.0	Snipes et al. (1975)
KBr-H ₂ O	25,60,70,80,90,100	0.1 - 4.0	Robinson and Stokes (1955)
MgSO ₄ -H ₂ O	25,40,50,60,70,80	0.1 - 2.0	Snipes et al. (1975)
MgCl ₂ -H ₂ O	25,40,50,60,70,80	0.1 - 2.0	Snipes et al. (1975)
Na ₂ SO ₄ -H ₂ O	25,40,50,60,70,80	0.1 - 1.6	Snipes et al. (1975)

*In addition to the Weast compilation

3.3 Results

A list of aqueous electrolyte binary systems used with this model, in addition to the systems presented in Table G.1, are given in Table 3.1. The results of binary and ternary data correlation are discussed below.

A. Aqueous Electrolyte Binary

Maximum Molality Applicability--Bromley recommended the applicability of his equation [Equations (C-1), (C-2) and (C-9)] up to $I = 6$ for strong electrolytes in water, i.e. nearly completely ionized. This has been demonstrated by combining equations (C-9), (1-20) and (1-21) in the form

$$Y = B_{1i}X \quad (3-15)$$

where,

$$Y = (1 - \phi) - 2.303 A_{\gamma} |z_+ z_-| \sigma_2 (\rho I^{1/2}) I^{1/2} + 2.303 [0.06 \frac{\psi_2(aI)}{2}] |z_+ z_-| I \quad (3-16)$$

$$X = -2.303 [0.6I |z_+ z_-| \frac{\psi_2(aI)}{2} + \frac{I}{2}] \quad (3-17)$$

Figures H.1 and H.2 indicate that reasonably good results are obtained for strong electrolytes up to $I = 6$, i.e. $m = 6$ for 1-1 electrolytes (Figure H.1) and $m = 2$ for 2-1 electrolytes (Figure H.2). On the other hand, very poor results are observed for $MgSO_4$ (Figure H.3) which is incompletely ionized.

Results at 100°C--In the literature a good deal of data at 100°C are available as DP vs m , Weast (1969). Some typical systems are shown in Table H.1. Equation (C-9) with (1-21) was used to calculate the values of B_{12} at 100°C and γ_{\pm} values are obtained using equations (C-1) and (C-2). Values of m up to $I = 6$ were used as above, even though the range of applicability may be somewhat lower here because of the higher temperature. Hence, for 1-1 electrolyte data up to $m = 6$ (7 points) were used; for 1-2 and 2-1 electrolytes, up to $m = 2$ (3 points); for 2-2 electrolytes, up to $m = 1.5$, and since at $m = 1.5$ is not given, data to $m = 2$ ($I = 8$) were used. Finally, for higher electrolytes (3-1, 3-2, etc.) only two points ($m = 0.5$ and $m = 1.0$) could be used.

This was considered too limited a data base and these electrolytes were not included in this study. The obtained values of B_{12} , along with those at 25°C from Bromley, are presented in Table H.2.

In the case that data are correlated for the maximum m value (m_{\max}) reported by Weast, the resulting error in DP (DP'_{\max}) is also included in Table H.2. The larger values of DP'_{\max} as compared to those of DP_{\max} further support Bromley's suggestion that this equation is applicable only up to $I = 6$ for aqueous electrolytic mixtures.

The accuracy of the mean molal activity coefficients, calculated using these B_{12} values with equations (C-1) and

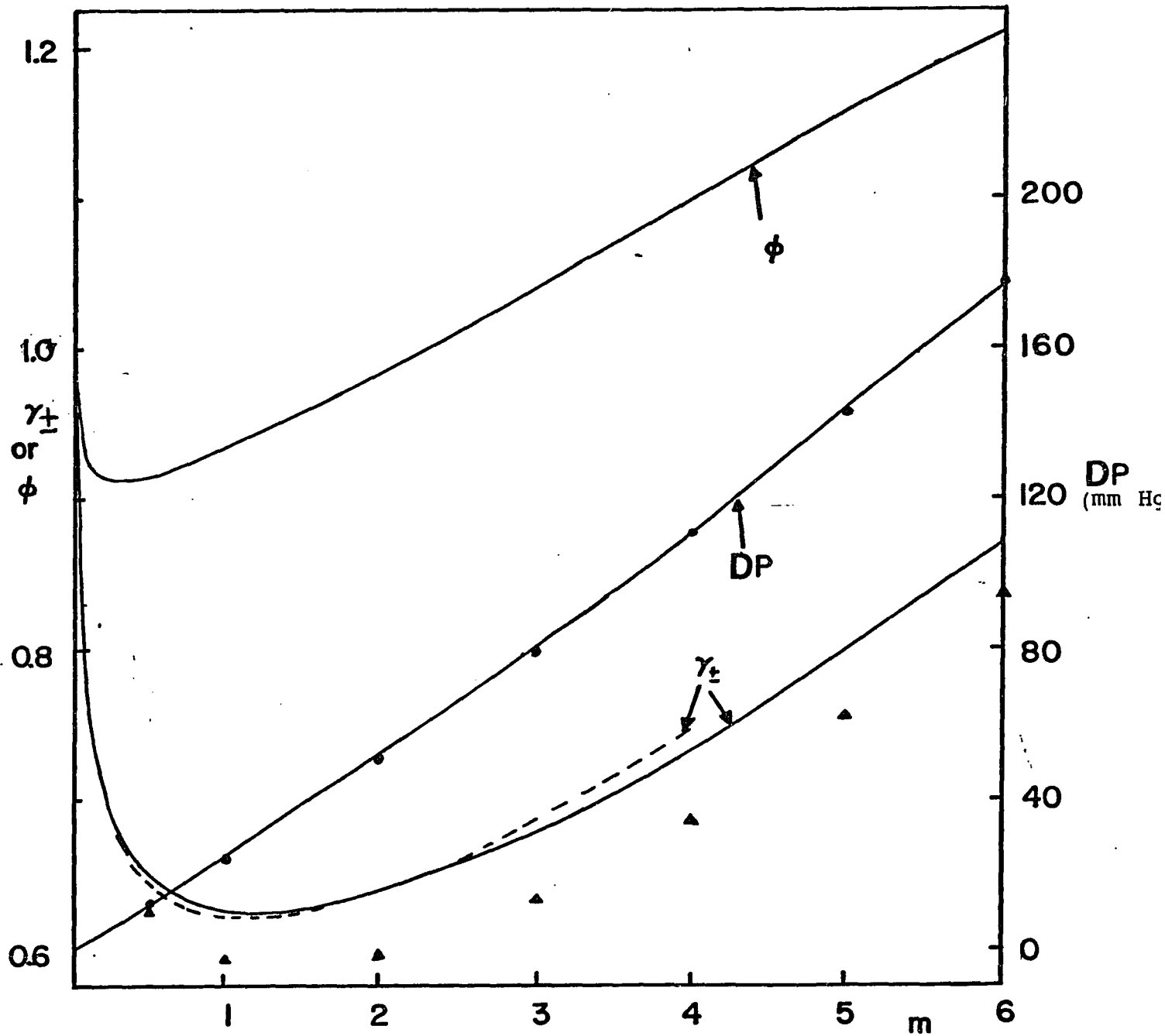


Figure 3.2 Activity and Osmotic Coefficients for the System Water-Sodium Chloride at 100°C

----- (Gibbard et al., 1974)

———— (Robinson and Stokes, 1955)

▲ From Weast's Data

● Calculated DP Values, eqn. (C-9), (1-21) and (1-22)

TABLE 3.2 Effect of the Number of Data Points Used in Evaluating B_{12}
on the Accuracy of the Calculated γ_{\pm} Values ($T = 100^{\circ}\text{C}$)

Max m Value	Number of Points	B_{12}	Error % in γ_{\pm}	
			Max	Avg
<u>NaCl-Water</u>				
2.0	3	0.0671	10.9	4.0
3.0	4	0.0595	5.3	3.5
4.0	5	0.0582	5.9	4.4
5.0	6	0.0572	6.4	5.1
6.0	7	0.0567	6.7	5.4
<u>KBr-Water</u>				
2.0	3	0.0533	6.7	2.7
3.0	4	0.0479	4.9	3.5
4.0	5	0.0442	6.6	4.3

(C-2), is examined next. Figure 3.2 presents γ_{\pm} values for aqueous NaCl calculated with this approach along with the data from Robinson and Stokes and those of Gibbard et al. (1974). The agreement can be considered reasonably good; maximum error is 6.7%; average error is 5.4%. The other system for which γ_{\pm} data at 100°C are available is aqueous KBr (Robinson and Stokes, 1955). Since this system is not included in the Weast compilation, the ϕ values of Robinson and Stokes at $m = 0.5, 1, 2, 3$ and 4 were used. The results are presented in Figure H.4 and they are of the same quality as those in the NaCl case; maximum error is 6.6%; average error is 4.3%. Since this is not the case for all electrolytes, especially for electrolytes other than 1-1, the effect of the number of data points used on the accuracy of the calculated γ_{\pm} values is examined in Table 3.2. The results obtained by using only three data points (m up to 2) are comparable to those obtained by using all points available, up to $m = 6$ for NaCl and up to $m = 4$ for KBr.

Estimation of DP and γ_{\pm} Values in the Range 25-100°C--In the typical case, values of DP and γ_{\pm} are needed at temperatures other than 25 or 100°C. Hence, it would be desirable if B_{12} values could be estimated within this temperature range. Bromley recommends two expressions for the temperature dependency of B_{12} .

$$B_{12} = B^* \ln\left(\frac{T - 243}{T}\right) + \frac{B_1^1}{T} + B_2^1 + B_3^1 \ln T \quad (3-18)$$

TABLE 3.3 Values of B^* and B'_1 in Equation (3-20) for
the Systems in Figures H.5 and H.6

Electrolyte	B^*	B'_1
NaCl	0.05127	42.97
KBr	0.06867	43.26
KCl	0.04361	29.164
Na_2SO_4	0.040945	14.763
MgCl_2	0.01305	41.895
MgSO_4	0.0007	6.346

and

$$B_{12} = \frac{C^*}{T - 230} + \frac{C_1^{11}}{T} + C_2^{11} + C_3^{11} \ln T \quad (3-19)$$

Since B_{12} values are available only at 25°C (Bromley) and 100°C (this study), equations (3-18) and (3-19) were tested in their two adjustable constants form by setting B_2^1 , B_3^1 , C_2^{11} and C_3^{11} equal to zero.

$$B_{12} T = B_1^1 + B^* T \ln \left(\frac{T - 243}{T} \right) \quad (3-20)$$

and

$$B_{12} T = \frac{C^* T}{T - 230} + C_1^{11} \quad (3-21)$$

The equations are written in this linear form so that they can be tested by plotting $B_{12} T$ vs $[T \ln ((T - 243)/T)]$ in equations (3-20) and vs $[T/(T - 230)]$ for equation (3-21). Both expressions give reasonably good results as demonstrated in Figures H.5 and H.6 for equation (3-20). The straight lines were obtained by regressing all the points, excluding those from the Weast data. The values of the constants B^* and B_1^1 are reported in Table 3.3.

Use of equation (3-20) for interpolation purposes is demonstrated in Table H.3. The B_{12} values at 70°C were obtained from equation (3-20) with B^* and B_1^1 calculated using only the B_{12} (25°C) and the B_{12} (100°C) values. The large error for MgSO_4 is due to incomplete dissociation figure H.3. Values of γ_{\pm} at 70°C for the electrolytes of Table 3.3 are given in the references presented in Table 3.1. It should be

noted that the γ_{\pm} data for KCl, MgCl₂, MgSO₄ and Na₂SO₄ (Snipes et al., 1975) were derived from heat of dilution data, and those for NaCl (Gibbard, 1974) are reported at rounded molalities and temperatures.

B. Nonaqueous Electrolyte Binary

Maximum Molality Applicability--As shown for the aqueous electrolyte binaries, the Bromley equation in the form of equation (3-15) is used to test the maximum molality range for MeOH electrolyte binaries. The results for the LiBr-MeOH system at 15°C and the LiCl-MeOH system at 60°C (Figures H.7 and H.8) show that the applicability of the Bromley equation is good only up to $I = 3$, for 1-1 electrolytes. For the higher order electrolytes (1-2, 2-1, 2-2, etc.) data are not available. The only data available for higher order electrolytes is for the CaCl₂-MeOH system at 25°C. Because of the scattering and unavailability of the experimental data at low molality (Figure H.9), it is not possible to conclude the maximum molality range for this system. Based on 1-1 electrolytes only the molality limit for MeOH system is set $I = 3$. Other nonaqueous binaries could not be tested since this type of data is not available in literature. It would be expected that the molality range would be even lower than $I = 3$ for solvents with dielectric constants less than that of MeOH.

Accuracy of the Binary Data Correlation--The results of some nonaqueous electrolyte binary data correlation are

given in Table H.4. The accuracy of data correlation of such systems is less than the accuracy of the corresponding aqueous electrolytic binaries (Table H.5). In a typical case of the system LiCl-H₂O at 60°C, the maximum percent error in DP is 2.0 and the average percent error is 1.0 (Table H.5) whereas for the system LiCl-MeOH at 60°C, the maximum percent error in DP is 15.6% and the average percent error is 7.3 (Table H.4). The correlation of the system CaCl₂-MeOH at 25°C, up to $m = 2.6$ is of poor quality (Table H.4). This is expected for 1-2, 2-1 or higher order electrolytes in MeOH because of the maximum molality limitation.

C. Isothermal Ternary Data Correlation

The mean molal activity coefficient data of three isothermal ternary systems are correlated with this model (Table H.6), Figure H.9 to H.17. The systems HCl-H₂O-MeOH at 25°C and NaCl-H₂O-MeOH at 25°C have average percent errors in γ_{\pm} of 1.4 and 7.4, respectively (Figures H.13 to H.17). The correlation of the system HCl-H₂O-EtOH at 25°C is good up to $m = 2.0$ and EtOH concentration (HCl free) <9% (Figures H.10 and H.11). The results are of poor quality for the same system at $X'_{\text{EtOH}} = 0.5$, especially when $m > 0.5$.

The vapor-liquid equilibrium data of five isothermal ternary systems are correlated (Table H.7) with this model. Again, three objective functions [Equations (2-19), (2-20) and (2-21)] are applied for the data reduction. In general, objective

function #2 gives the best results. In Table H.7 results are given for the correlation up to $m = 3$ and also for the higher molality range. The overall performance of the model in correlating the ternary VLE data is of good quality within the limited range of molality (Figures H.17 to H.22). The molality applicability decreases to even less than $I = 3$ with an increase in temperature, as in the case of the LiCl-H₂O-MeOH system at 60°C, the fit is good only up to $m = 2.0$.

The ternary parameters δ_{123} and B_{123} obtained by the ternary correlation, indicates that these cannot be considered temperature independent. Therefore this model is not applied to isobaric ternary systems.

3.4 Discussion

As already shown, only three DP-m points were used in evaluating B_{12} for 1-2, 2-1 and 2-2 electrolytes. In addition, no experimental γ_{\pm} data at 100°C are available for such electrolytes as in the case for 1-1 types, where good results are obtained from three points only (Table 3.2). Figures H.5 and H.6 and Table H.9 demonstrate, however, that the B_{12} values obtained from the Weast data are very close to those obtained by extrapolation of the data in the range from 25 to 80°C. The closeness of the γ_{\pm} values obtained from these two B_{12} (100°C) values is depicted in Table H.10 for MgCl_2 with a maximum difference of 5.8%. For the Na_2SO_4 system, where the fractional difference between the two B_{12} (100°C) values is the largest, the maximum difference in γ_{\pm} is 5.7%. Therefore it is suggested that, in addition to the 1-1 electrolytes, reasonably accurate γ_{\pm} values can be calculated for 1-2, 2-2, and 2-1 types from B_{12} values obtained using three data points from the Weast compilation.

Table H.3 demonstrates that use of the B_{12} values at 25 and 100°C, along with equation (3-20), can lead to reasonably accurate estimates of γ_{\pm} and DP values at intermediate temperatures. However, when the same approach was used to evaluate the derivative (dB_{12}/dT), needed to calculate apparent relative molal enthalpies (ϕL) and relative partial molal enthalpies (\bar{L}_2) for four individual salts, NaCl , KCl , Na_2SO_4 and MgCl_2

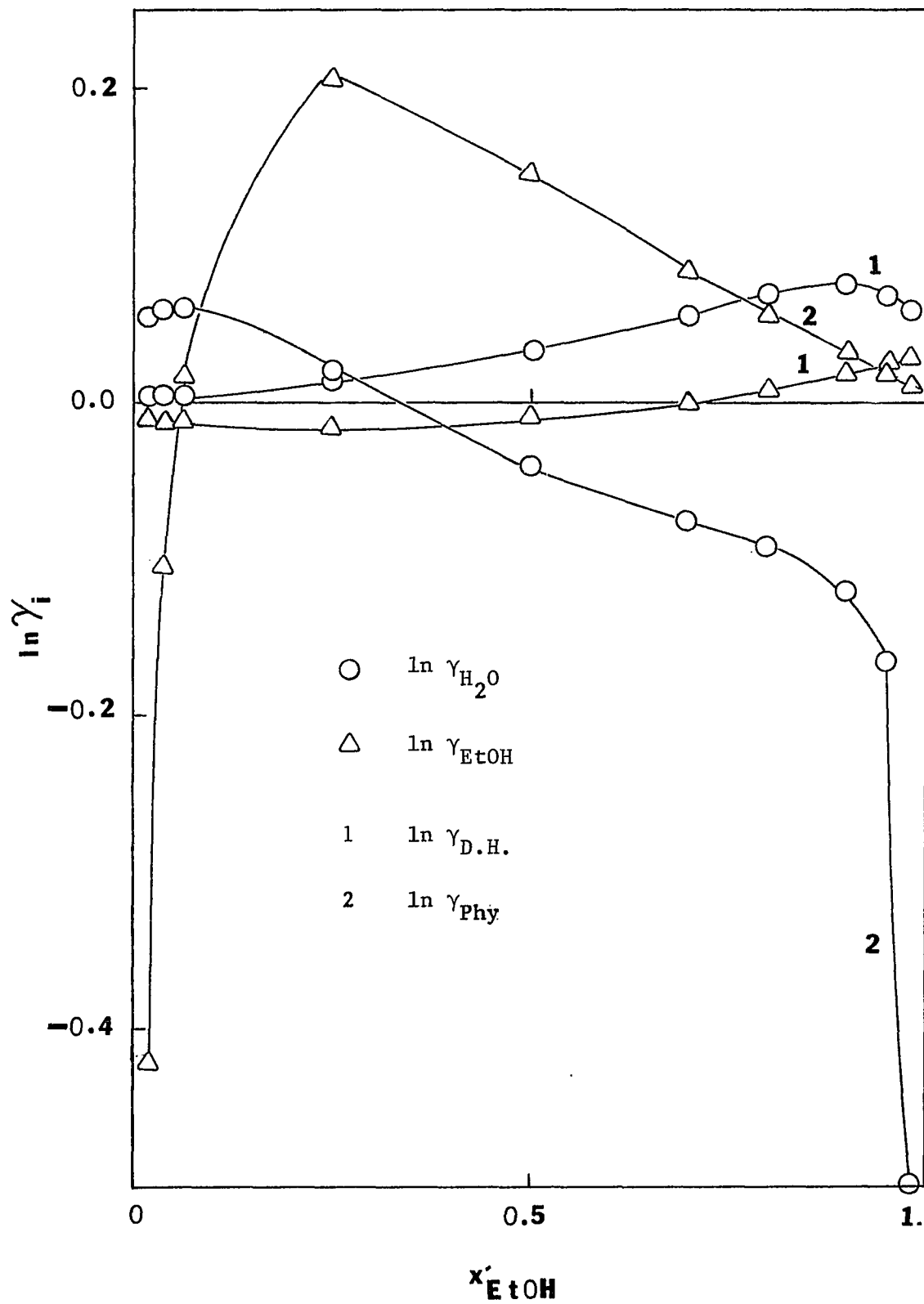


Figure 3.3 Contribution of Different Terms to $\ln \gamma_i$ for the System LiCl-H₂O-EtOH at 25°C in Model II

with water at 100°C the typical average error was about 50%. This failure becomes apparent from Figures H.5 and H.6 while equation (3-20) is valid for interpolation purposes, it does not provide reliable values for the slope dB_{12}/dT . The calculated values for (ϕL) and (\bar{L}_2) , however, were in the right direction, but lower than the experimental ones. The expressions used to calculate these quantities are given by Bromley (1973).

When the Bromley equation was applied to nonaqueous electrolytic binaries, the maximum molality range is ≤ 3 , also the binary data reduction is less accurate for such binaries. This is expected since the empirical constants in the original Bromley equation (C-1) were obtained by applying aqueous electrolytic binary data only. However, considering the simplicity of this equation, the results for nonaqueous mixtures are of acceptable quality. The temperature dependency of such systems can also be established by equation (3-20), as shown by Tomasula and Tassios (1980) for the electrolyte-MeOH binaries.

The isothermal ternary data correlation of the VLE and γ_{\pm} is of good quality for $m \leq 3.0$. An investigation of the contribution of different terms in a ternary system indicates that the salting in effect of the Debye-Hückel term in the Bromley equation (Figure 3.3) is compensated by the additional salting out term at low EtOH concentration (Figure 3.4) and

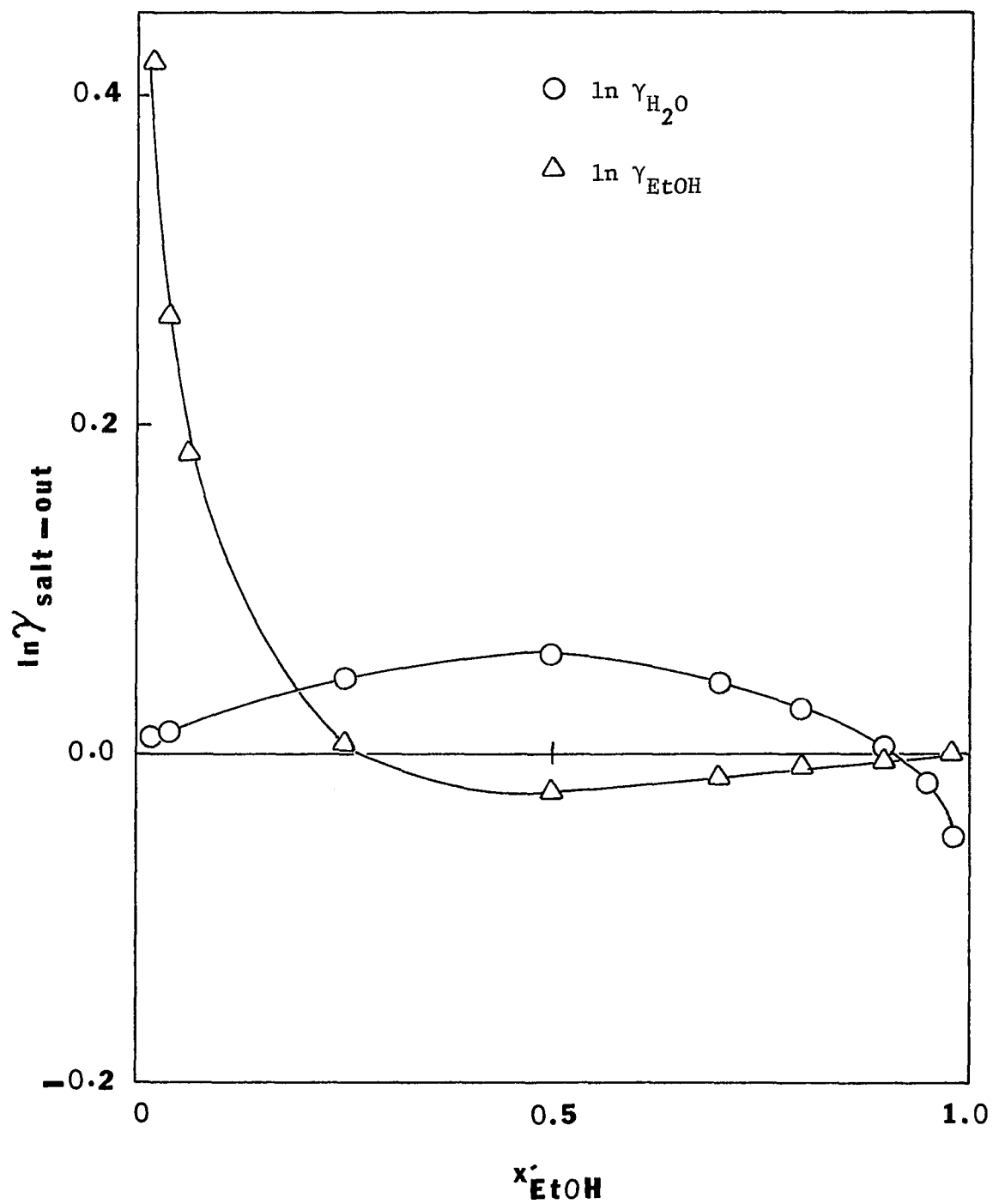


Figure 3.4 Contribution of the Salting-Out Term to $\ln \gamma_i$ for the System LiCl-H₂O-EtOH at 25°C in Model II

by the additional part of the Bromley equation at higher EtOH concentration (Figure 3.3). It is important to note that for ternary data correlation both binary and ternary experimental data are used.

3.5 Conclusions

A method for the correlation of the DP-m data for 53 aqueous electrolytes at 100°C (Weast, 1969), and the evaluation of γ_{\pm} values for these electrolytes, is presented. A procedure for the estimation of γ_{\pm} , ΔP , ϕL and \bar{L}_2 in the temperature range of 25-100°C for these electrolytes is also presented. While reasonably good results are obtained for γ_{\pm} and ΔP , ϕL and \bar{L}_2 values are smaller than the experimental ones by about 50%.

The binary Bromley equation is applied to nonaqueous electrolytic binaries and also has been extended to ternary systems of electrolyte in mixed solvents. The correlation of isothermal nonaqueous binary and ternary data is of good quality; however, the maximum concentration range for such systems is less than the range for aqueous electrolytic binaries.

CHAPTER 4

A COMPARATIVE STUDY OF TWO MODELS IN CORRELATING AND PREDICTING BINARY/TERNARY γ_{\pm} AND VLE DATA IN ELECTROLYTIC SOLUTIONS

ABSTRACT

Model I is superior to Model II in correlating binary nonaqueous electrolytic and ternary electrolytic mixtures. However, Model II can be used to predict γ_{\pm} using DP vs m data only in a binary mixture more accurately than Model I. Model II is limited only to isothermal ternary data correlation whereas Model I can be applied to predict and/or correlate isothermal or isobaric ternary data.

In principle, the two models presented in Chapters 2 and 3 are similar but consist of different forms of the expressions to represent various interactive forces in the liquid solution. Both the models have the Debye-Hückel equation and an intermediate term also called the transition term represents the change of magnitude of electrostatic forces from the dilute solution to the concentrated solution. The NRTL term has been included in both models, but it represents different molecular interactions in the two models. In Model I the NRTL term describes ion-solvent and solvent-solvent molecular interactions [Equation (2-3)], whereas in Model II ion-solvent interactions are represented by a term: $B \frac{I^2}{2}$ [Equation (3-2)] and the solvent-solvent molecular interactions are by the NRTL-S [Equation (3-4)]. Also, in Model II an additional salting out term is used [Equation (3-5)], which is not needed with Model I.

A. Binary Data Correlation

Both models simplify to the original NRTL expression [Equation (2-7)] for a solvent-solvent binary. Electrolyte-solvent binary data reduction require two parameters in Model I, i.e. $G_{\pm i}$; $Z_{\pm i}$ or Δg_{A_i} ; Δg_{B_i} and one parameter ' B_{1i} ' with Model II. In general, the fit of aqueous electrolyte binaries is better with Model II than Model I, Tables G.4 and H.5. But the correlation of nonaqueous electrolyte binaries shows the reverse trend, Tables G.5 and H.4. However, on the overall

analysis of binary data evaluation, it is concluded that both models can be applied successfully. Model I can be used up to $I = 6$ for electrolyte MeOH binaries and up to even higher molality ranges for aqueous electrolyte binaries, Table 2.3, whereas Model II is limited to $I = 3$ for MeOH-electrolyte binaries and $I = 6$ for aqueous electrolyte mixtures. The binary parameters in Model I are considered temperature independent within a 30 to 40°C temperature range, but in Model II, the temperature dependency of the binary parameter ' B_{1i} ' is represented by a two parameter expression, Equation (3-20). This indicates the applicability of Model I to isothermal and isobaric systems without any alterations in the Model itself. The biggest advantage of Model II is that it requires only three data points (DP vs m) to find the optimum value of a single parameter (B_{1i}) in a binary mixture which can lead to reliable prediction of γ_{\pm} data for the whole concentration range. The use of three typical data points (DP vs m) with Model I is too small for the evaluation of two parameters in a binary mixture and also the parameters obtained with three points only, cannot be expected to predict γ_{\pm} with reasonable accuracy.

B. Ternary Data Prediction and Correlation

Model I requires only binary parameters for the ternary VLE and γ_{\pm} data prediction. The binary parameters are obtained by three respective binary data correlation, Tables

2.4 and 2.5. Model II is good only for binary/ternary data correlation. Prediction of a ternary mixture is not possible, because of two ternary parameters ' B_{123} and δ_{123} ' which should be obtained by ternary data reduction. Also, in Model II binary and ternary parameters (B_{1i} , B_{123} , δ_{123}) are temperature dependent, hence its applicability is limited to only isothermal data. Model I can be used to correlate binary or ternary data individually whereas with Model II both binary and ternary data are used for ternary data correlation.

Finally, Model I has the possibility of extension to multicomponent systems containing more than two solvents and one electrolyte. In a multicomponent mixture, only binary parameters are required with Model I. The extension of Model II to multicomponent mixtures will be a tedious task.

APPENDIX A

EXPRESSIONS FOR THE ACTIVITY COEFFICIENT
OF THE SOLVENT AND THE MEAN ACTIVITY
COEFFICIENT OF AN ELECTROLYTE IN A
BINARY MIXTURE FOR MODEL I

In a binary mixture, the activity coefficients are a combination of an extended form of the Debye-Hückel equation and the modified NRTL equation proposed by Cruz and Renon (1978).

$$\ln\gamma_{\pm} = \ln\gamma_{\pm} \text{ , Ext. D.H. } + \ln\gamma_{\pm}^* \text{ , NRTL} \quad (\text{A-1})$$

$$\ln\gamma_i = \ln\gamma_i \text{ , Ext. D.H. } + \ln\gamma_i^* \text{ , NRTL} \quad (\text{A-2})$$

Gronwall, LaMer and Sandved (1928) extended the Debye-Hückel equation to higher order terms for symmetrical valence type electrolytes

$$\ln\gamma_{\pm}^* = -\frac{(\epsilon Z)^2}{2DkT} \frac{\kappa}{1 + \kappa a} + \sum_{m=1}^{\infty} \left(\frac{\epsilon^2 Z^2}{DkTa} \right)^{2m+1} \left[\frac{1}{2} X_{2m+1}(\kappa a) - 2m Y_{2m}(\kappa a) \right] \quad (\text{A-3})$$

where X and Y are functions of (κa) and

$$\kappa = \sqrt{\frac{8\pi N\epsilon^2 Z^2 C}{1000 DkT}} \quad (\text{A-4})$$

The additional higher order terms in equation (A-3) take into account long-range electrostatic forces in the concentrated solution. Further, Gronwall, LaMer and Grieff (1931) extended the above theory to unsymmetrical electrolytes. A semi-empirical extended form of the Debye-Hückel equation is proposed in this work which is analogous to those proposed by Gronwall et al. An additional term with the original D.H. term represents electrostatic forces in concentrated electrolytic solutions.

$$\ln\gamma_{\pm} \text{ Ext.D.H.} = 2.303 \left[-A_{\gamma} \frac{I^{1/2}}{1 + \rho I^{1/2}} + A_{\gamma}^2 \frac{I}{(1 + aI)^n} \right] |Z_+ Z_-| \quad (\text{A-5})$$

where ρ , a and n are adjustable parameters.

The expression for the activity coefficient of the solvent is obtained through the excess Gibbs free energy function, as shown below

$$\left. \frac{G^E}{RT} \right]_{\text{Ext. D.H.}} = \int_0^{N_1} \ln \gamma_{\pm}^* dN_1 \quad (\text{A-6})$$

$$\ln \gamma_{\pm}^* = \ln \gamma_{\pm} + \ln(0.001 \nu m M_w + 1) \quad (\text{A-7})$$

$$\ln \gamma_{i \text{ Ext. D.H.}} = \left. \frac{\partial G^E/RT}{\partial N_i} \right|_{T_1, P_1, N_{j \neq i}} \quad (\text{A-7A})$$

The NRTL part in equations (A-1) and (A-2) for the activity coefficients are the same as given by Cruz-Renon (1978)

$$\ln \gamma_{\pm \text{NRTL}}^* = \frac{1}{RT} \frac{\nu_A}{\nu} \left[\frac{X_i^2 Z_{\pm i}}{(X_A G_{\pm i} + X_i)^2} - Z_{\pm i} \right] \quad (\text{A-8})$$

and

$$\ln \gamma_{i \text{NRTL}} = \frac{1}{RT} X_A^2 \frac{G_{\pm i} Z_{\pm i}}{(X_A G_{\pm i} + X_i)^2} \quad (\text{A-9})$$

Equations (A-5) and (A-7A) have three known adjustable parameters, ρ , a and n . Equations (A-5) and (A-7A), when combined with the NRTL equations (A-8) and (A-9), have five parameters, ρ , a , n , $G_{\pm i}$ and $Z_{\pm i}$ for a binary mixture. Also, it should be noted that the final form of the $\ln \gamma_{i \text{ Ext. D.H.}}$ equation will depend upon the integration of the $\ln \gamma_{\pm}^*$ term. The integration is accomplished by fixing a value of n , which can be an integer or a noninteger. So the first five parameters were reduced to the two NRTL parameters, $G_{\pm i}$ and $Z_{\pm i}$, by presetting

the values of ρ , a and n . Secondly, the $\ln\gamma_i$, Ext. D.H. expression is derived by equations (A-6) to (A-7A). Equation (A-5) and the final form of equation (A-7A), when combined with equations (A-8) and (A-9), were used to correlate both binary aqueous electrolyte and nonaqueous electrolyte data. It was found that the best results are obtained (Tables G.4 and G.5) by setting the three adjustable parameters in the extended Debye-Hückel equation to

$$\begin{aligned}\rho &= 1.0 \\ a &= 1.5/|z_+z_-| \\ n &= 1/2\end{aligned}\tag{A-10}$$

When the parameters of equation (A-10) are substituted in equation (A-5) the following form of the expression for the solvent activity coefficient is obtained

$$\begin{aligned}\ln\gamma_i, \text{ Ext. D.H.} &= \frac{2.303 \text{ vmM}_w}{1000} \left[\frac{A_\gamma}{3} I^{1/2} \sigma_1(\rho I^{1/2}) + A_\gamma^2 \frac{I}{2} \psi_1(aI) \right] \\ &\quad + |z_+z_-| + \ln(0.001 \text{ vmM}_w + 1) - 0.001 \text{ vmM}_w\end{aligned}\tag{A-11}$$

where

$$\sigma_1(\rho I^{1/2}) = \frac{3}{(\rho I^{1/2})^3} \left[(1 + \rho I^{1/2}) - 2 \ln(1 + \rho I^{1/2}) - \frac{1}{(1 + \rho I^{1/2})} \right]\tag{A-12}$$

and

$$\psi_1(aI) = \frac{2}{3aI} \left[\frac{2(aI - 2)}{aI} (1 + aI)^{1/2} + \frac{4}{aI} - \frac{(aI - 2)}{(1 + aI)^{1/2}} - 2(1 + aI)^{1/2} \right]\tag{A-13}$$

APPENDIX B

A STEPWISE PROCEDURE FOR THE DEVELOPMENT OF
TERNARY ACTIVITY COEFFICIENTS
FOR MODEL I

MODEL I:

Combination of the Extended Debye-Hückel Equation
and the Modified NRTL Equation

B.1--Development of the $\frac{G^E(\text{ternary})}{RT}$ Ext. D.H. expression

The extended Debye-Hückel part of the mean molal activity coefficient developed in Appendix A for a binary mixture has been extended to a ternary mixture containing one electrolyte and two solvents. This is obtained by modifying the Debye-Hückel constant for the solvent mixture. For a ternary mixture, in equation (A-5), the Debye-Hückel constant is

$$A_{\gamma} = 1.8246 \times 10^6 d^{1/2} \left[\frac{1}{DT} \right]^{3/2} \quad (\text{B-1})$$

where

D and d = Dielectric constant and density of a solvent mixture (electrolyte-free) (Appendix D)

The excess Gibbs free energy function for a ternary mixture can be derived by integrating the expression for $\ln \gamma_{\pm}^*$ for a ternary system. Combination of equations (A-6), (A-7), (A-5) and (B-1) yields

$$\frac{G^E(\text{ternary})}{RT} \text{ Ext. D.H.} = \int_0^{N_1} \left[2.303 \left\{ -A_{\gamma} \frac{I^{1/2}}{(1 + \rho I^{1/2})} + A_{\gamma}^2 \frac{I}{(1 + aI)^{1/2}} \right\} \right. \\ \left. + |z_+ z_-| dN_1 + \int_0^{N_1} \ln(0.001 v_m M_w + 1) dN_1 \right] \quad (\text{B-2})$$

Equation (B-2) can be integrated, term by term, with the following additional equations

$$m = \frac{1000 N_1}{N_T M_w} \quad (\text{B-3})$$

$$N_T = N_2 + N_3 \quad (\text{B-4})$$

$$I = \frac{1}{2} m \sum_k v_k z_k^2 = \frac{1}{2} m \xi \quad (\text{B-5})$$

$\xi = \text{a constant}$

$$M_w = \frac{N_2}{N_T} M_{w2} + \frac{N_3}{N_T} M_{w3} \quad (\text{B-6})$$

$$\frac{\partial m}{\partial N_1} = \frac{1000}{N_T M_w} \quad (\text{B-7})$$

$$\frac{\partial I}{\partial m} = \frac{1}{2} \xi \quad (\text{B-8})$$

Integration of different terms is as below

$$\begin{aligned} \int_0^{N_1} \ln(0.001 v m M_w + 1) \partial N_1 &= \int_0^m \ln(0.001 v m M_w + 1) \frac{\partial N_1}{\partial m} \partial m \\ &= \frac{v N_T M_w}{1000} \left[\frac{1000}{v M_w} \{ (0.001 v m M_w + 1) \right. \\ &\quad \left. \ln(0.001 v m M_w + 1) - 0.001 v m M_w \} \right] \\ \int_0^{N_1} \ln(0.001 v m M_w + 1) \partial N_1 &\equiv N_T [(0.001 v m M_w + 1) \ln(0.001 v m M_w + 1) \\ &\quad - 0.001 v m M_w] \quad (\text{B-9}) \end{aligned}$$

$$\begin{aligned}
v \int_0^{N_1} A_\gamma \frac{|z_+ z_-| I^{1/2}}{1 + \rho I^{1/2}} \partial N_1 &= v A_\gamma |z_+ z_-| \int_0^I \frac{I^{1/2}}{1 + I^{1/2}} \frac{\partial N_1}{\partial m} \frac{\partial m}{\partial I} \cdot \partial I \\
&= v A_\gamma \frac{N_T M_w}{1000} |z_+ z_-| \frac{2}{\xi} \int_0^I \frac{I^{1/2}}{1 + \rho I^{1/2}} \partial I \\
v \int_0^{N_1} A_\gamma \frac{|z_+ z_-| I^{1/2}}{1 + \rho I^{1/2}} \partial N_1 &= v A_\gamma \frac{N_T M_w}{1000} |z_+ z_-| \frac{2}{\xi} \left[\frac{2}{\rho^3} \left\{ \frac{1}{2} (1 + \rho I^{1/2})^2 \right. \right. \\
&\quad \left. \left. - 2(1 + \rho I^{1/2}) + \ln(1 + \rho I^{1/2}) + \frac{3}{2} \right\} \right] \quad (B-10)
\end{aligned}$$

$$\begin{aligned}
v \int_0^{N_1} A_\gamma^2 |z_+ z_-| \frac{I}{(1 + aI)^{1/2}} \partial N_1 \\
&= v A_\gamma^2 |z_+ z_-| \int_0^I \frac{I}{(1 + aI)^{1/2}} \frac{\partial N_1}{\partial m} \frac{\partial m}{\partial I} \partial I \\
&= v A_\gamma^2 |z_+ z_-| \frac{N_T M_w}{1000} \frac{2}{\xi} \int_0^I \frac{I}{(1 + aI)^{1/2}} \partial I
\end{aligned}$$

$$\begin{aligned}
v \int_0^{N_1} A_\gamma^2 |z_+ z_-| \frac{I}{(1 + aI)^{1/2}} \partial N_1 &= v A_\gamma^2 |z_+ z_-| \frac{N_T M_w}{1000} \frac{2}{\xi} \left[\frac{2(aI - 2)}{3a^2} (1 + aI)^{1/2} \right. \\
&\quad \left. + \frac{4}{3a^2} \right] \quad (B-11)
\end{aligned}$$

Utilizing the change of variables $m/I = 2/\xi$, and combining equations (B-9 to (B-11), results in the excess Gibbs free energy expression, equation (2-2).

B.2--Development of the $\frac{G^E(\text{ternary})}{RT}$ NRTL expression

Note: Equations are derived taking into account that $\gamma_\pm^* \rightarrow 1.0$ as $x_1 \rightarrow 0.0$ (Asymmetric Convention).

Renon and Prausnitz (1968) proposed an expression for the excess Gibbs free energy in a multicomponent mixture based on the Non-Random Two Liquid Theory. Since the original NRTL equation applies to mixtures following the symmetric convention, it is converted for ternary mixtures utilizing the asymmetric convention as indicated below

$$g_{\text{NRTL}}^{\text{E}'} = \sum_{\ell} x_{\ell} \frac{\sum_m x_m Z_{m\ell}}{\sum_n x_n G_{n\ell}} \quad (\text{B-12})$$

where,

$$Z_{m\ell} = \Delta g_{m\ell} G_{m\ell}$$

$$G_{m\ell} = \text{Exp}\left[-\alpha_{m\ell} \frac{\Delta g_{m\ell}}{RT}\right] \quad (\text{B-12a})$$

$$\Delta g_{m\ell} = g_{m\ell} - g_{\ell\ell}$$

$$\alpha_{m\ell} = \alpha_{\ell m} \text{ and } \Delta g_{m\ell} \neq \Delta g_{\ell m}$$

Equation (B-12) can be expanded for a mixture containing electrolyte molecules - 1, cation - A, anion - B, and solvents 2 and 3

$$g_{\text{NRTL}}^{\text{E}'} = x_A \left[\frac{x_A Z_{AA} + x_B Z_{BA} + x_1 Z_{1A} + x_2 Z_{2A} + x_3 Z_{3A}}{x_A G_{AA} + x_B G_{BA} + x_1 G_{1A} + x_2 G_{2A} + x_3 G_{3A}} \right]$$

$$+ x_B \left[\frac{x_A Z_{AB} + x_B Z_{BB} + x_1 Z_{1B} + x_2 Z_{2B} + x_3 Z_{3B}}{x_A G_{AB} + x_B G_{BB} + x_1 G_{1B} + x_2 G_{2B} + x_3 G_{3B}} \right]$$

$$+ x_1 \left[\frac{x_A Z_{A1} + x_B Z_{B1} + x_1 Z_{11} + x_2 Z_{21} + x_3 Z_{31}}{x_A G_{A1} + x_B G_{B1} + x_1 G_{11} + x_2 G_{21} + x_3 G_{31}} \right]$$

$$\begin{aligned}
& + x_2 \left[\frac{x_A Z_{A2} + x_B Z_{B2} + x_1 Z_{12} + x_2 Z_{22} + x_3 Z_{32}}{x_A G_{Z2} + x_B G_{B2} + x_1 G_{12} + x_2 G_{22} + x_3 G_{32}} \right] \\
& + x_3 \left[\frac{x_A Z_{A3} + x_B Z_{B3} + x_1 Z_{13} + x_2 Z_{23} + x_3 Z_{33}}{x_A G_{A3} + x_B G_{B3} + x_1 G_{13} + x_2 G_{23} + x_3 G_{33}} \right] \tag{B-13}
\end{aligned}$$

Equation (B-13) is simplified by setting $Z_{\ell\ell} = 0.0$ and $G_{\ell\ell} = 1.0$ based on the original development of the equation (B-12). Cruz and Renon (1972) proposed the following additional assumptions for an electrolytic mixture considering that the energy parameter $g_{m\ell}$ increases from low to large numerical values in the following order:

(solvent - ion) < (solvent or electrolyte)-(solvent or electrolyte) << (electrolyte - ion) or (ion - ion of opposite signs) < (ion - ion of the same signs). On the right sign <<, very large values of $g_{m\ell}$ are found, and true local mole fractions are taken equal to zero. Thus

$$\begin{aligned}
Z_{1A} = Z_{1B} = Z_{A1} = Z_{B1} = Z_{AB} = Z_{BA} = 0.0 \\
G_{1A} = G_{1B} = G_{A1} = G_{B1} = G_{AB} = G_{BA} = 0.0 \tag{B-14}
\end{aligned}$$

For specific ion interaction limitation--

$$G_{AA} = G_{BB} = Z_{AA} = Z_{BB} = 0.0$$

And, also

$$\begin{aligned}
X_{2A} = X_{2B} = X_{3A} = X_{3B} = 1.0 \\
G_{2A} = G_{2B} = G_{2A} = G_{3B} = 1.0 \tag{B-15}
\end{aligned}$$

where

$$x_{\ell m} = \frac{x_{\ell} G_{\ell m}}{\sum_n x_n G_{nm}} \quad (\text{B-16})$$

$$Z_{\ell m} = \Delta g_{\ell m} G_{\ell m} \quad (\text{B-17})$$

Substitution of equations (B-15) to (B-17) into equation (B-13) yields

$$\begin{aligned} g_{\text{NRTL}}^{E'} &= x_A \left[\frac{x_2 \Delta g_{2A} + x_3 \Delta g_{3A}}{x_2 + x_3} \right] + x_B \left[\frac{x_2 \Delta g_{2B} + x_3 \Delta g_{3B}}{x_2 + x_3} \right] \\ &+ x_1 \left[\frac{x_2 Z_{21} + x_3 Z_{31}}{x_1 + x_2 G_{21} + x_3 G_{31}} \right] \\ &+ x_2 \left[\frac{x_A Z_{A2} + x_B Z_{B2} + x_1 Z_{12} + x_3 Z_{32}}{x_A G_{A2} + x_B G_{B2} + x_1 G_{12} + x_3 G_{32} + x_2} \right] \\ &+ x_3 \left[\frac{x_A Z_{A3} + x_B Z_{B3} + x_1 Z_{13} + x_2 Z_{23}}{x_A G_{A3} + x_B G_{B3} + x_1 G_{13} + x_2 G_{23} + x_3} \right] \end{aligned} \quad (\text{B-18})$$

$$\begin{aligned} G_{\text{NRTL}}^{E'} &= (N_T g_{\text{NRTL}}^{E'}) = N_A \left[\frac{N_2 \Delta g_{2A} + N_3 \Delta g_{3A}}{N_2 + N_3} \right] \\ &+ N_B \left[\frac{N_2 \Delta g_{2B} + N_3 \Delta g_{3B}}{N_2 + N_3} \right] \\ &+ N_1 \left[\frac{N_2 Z_{21} + N_3 Z_{31}}{N_1 + N_2 G_{21} + N_3 G_{31}} \right] \\ &+ N_2 \left[\frac{N_A Z_{A2} + N_B Z_{B2} + N_1 Z_{12} + N_3 Z_{32}}{N_A G_{A2} + N_B G_{B2} + N_1 G_{12} + N_3 G_{32} + N_2} \right] \\ &+ N_3 \left[\frac{N_A Z_{A3} + N_B Z_{B3} + N_1 Z_{13} + N_2 Z_{23}}{N_A G_{A3} + N_B G_{B3} + N_1 G_{13} + N_2 G_{23} + N_3} \right] \end{aligned} \quad (\text{B-19})$$

$$\begin{aligned}
RT \ln \gamma_A' &= \left. \frac{\partial G^E}{\partial N_A} \right|_{T,P,N_{\ell} \neq A} \\
&= \left[\frac{N_2 \Delta g_{2A} + N_3 \Delta g_{3A}}{N_2 + N_3} \right] \\
&\quad + N_2 \left[\frac{Z_{A2}}{N_A G_{A2} + N_B G_{B2} + N_1 G_{12} + N_3 G_{32} + N_2} \right. \\
&\quad \left. - \frac{(N_A Z_{A2} + N_B Z_{B2} + N_1 Z_{12} + N_3 Z_{32}) G_{A2}}{(N_A G_{A2} + N_B G_{B2} + N_1 G_{12} + N_3 G_{32} + N_2)^2} \right] \\
&\quad + N_3 \left[\frac{Z_{A13}}{N_A G_{A13} + N_B G_{B3} + N_1 G_{13} + N_2 G_{23} + N_3} \right. \\
&\quad \left. - \frac{(N_A Z_{A3} + N_B Z_{B3} + N_1 Z_{13} + N_2 Z_{23}) G_{A3}}{(N_A G_{A3} + N_B G_{B3} + N_1 G_{13} + N_2 G_{23} + N_3)^2} \right] \tag{B-20}
\end{aligned}$$

$$\begin{aligned}
\lim_{\substack{N_A \rightarrow 0 \\ N_B \rightarrow 0 \\ N_1 \rightarrow 0}} RT \ln \gamma_A' &= N_A \left[\frac{N_2 \Delta g_{2A} + N_3 \Delta g_{3A}}{N_2 + N_3} \right] + \frac{N_A N_2 Z_{A2}}{N_3 G_{32} + N_2} \\
&\quad - \frac{N_A N_2 N_3 Z_{32} G_{A2}}{(N_3 G_{32} + N_2)^2} + \frac{N_A N_3 Z_{A3}}{(N_2 G_{23} + N_3)} \\
&\quad - \frac{N_A N_2 N_3 G_{A3} Z_{23}}{(N_2 G_{23} + N_3)^2} \tag{B-21}
\end{aligned}$$

Similarly

$$\begin{aligned}
\lim_{\substack{N_B \rightarrow 0 \\ N_A \rightarrow 0 \\ N_1 \rightarrow 0}} RT \ln \gamma_B' &= N_B \left[\frac{N_2 \Delta g_{2B} + N_3 \Delta g_{3B}}{N_2 + N_3} \right] + \frac{N_B N_2 Z_{B2}}{N_3 G_{32} + N_2} \\
&\quad - \frac{N_B N_2 N_3 Z_{32} G_{B2}}{(N_3 G_{32} + N_2)^2} + \frac{N_B N_3 Z_{B3}}{N_2 G_{23} + N_3} \\
&\quad - \frac{N_B N_2 N_3 G_{B3} Z_{23}}{(N_2 G_{23} + N_3)^2} \tag{B-22}
\end{aligned}$$

$$G_{\text{NRTL}}^{\text{E(ternary)}} = G_{\text{NRTL}}^{\text{E}} - N_A \lim_{N_A \rightarrow 0} \text{RT} \ln \gamma_A' - N_B \lim_{N_B \rightarrow 0} \text{RT} \ln \gamma_B' \quad (\text{B-23})$$

Substituting equations (B-19), (B-21) and (B-22) in equation (B-23) results in the following expression for

$$\begin{aligned} G_{\text{NRTL}}^{\text{E(ternary)}} = & N_1 \left[\frac{N_2 Z_{21} + N_3 Z_{31}}{N_1 + N_2 G_{21} + N_3 G_{31}} \right] \\ & + N_2 \left[\frac{N_A Z_{A2} + N_B Z_{B2} + N_1 Z_{12} + N_3 Z_{32}}{N_A G_{A2} + N_B G_{B2} + N_1 G_{12} + N_3 G_{32} + N_2} \right] \\ & + N_3 \left[\frac{N_A Z_{A3} + N_B Z_{B3} + N_1 Z_{13} + N_2 Z_{23}}{N_A G_{A3} + N_B G_{B3} + N_1 G_{13} + N_2 G_{23} + N_3} \right] \\ & - N_2 \left[\frac{N_A Z_{A2} + N_B Z_{B2}}{N_3 G_{32} + N_2} \right] - N_3 \left[\frac{N_A Z_{A3} + N_B Z_{B3}}{N_2 G_{23} + N_3} \right] \\ & + N_2 N_3 Z_{32} \left[\frac{N_A G_{A2} + N_B G_{B2}}{(N_3 G_{32} + N_2)^2} \right] \\ & + N_2 N_3 Z_{23} \left[\frac{N_A G_{A3} + N_B G_{B3}}{(N_2 G_{23} + N_3)^2} \right] \end{aligned} \quad (\text{B-24})$$

Considering macroscopic electrical neutrality

$$N_A v_B = N_B v_A \quad (\text{B-25})$$

Substituting equation (B-25) into equation (B-24) gives

$$\begin{aligned} G_{\text{NRTL}}^{\text{E(ternary)}} = & N_1 \left[\frac{N_2 Z_{21} + N_3 Z_{31}}{N_1 + N_2 G_{21} + N_3 G_{31}} \right] \\ & + N_2 \left[\frac{N_A \left(Z_{A2} + \frac{v_B}{v_A} Z_{B2} \right) + N_1 Z_{12} + N_3 Z_{32}}{N_A \left(G_{A2} + \frac{v_B}{v_A} G_{B2} \right) + N_1 G_{12} + N_3 G_{32} + N_2} \right] \\ & + N_3 \left[\frac{N_A \left(Z_{A3} + \frac{v_B}{v_A} Z_{B3} \right) + N_1 Z_{13} + N_2 Z_{23}}{N_A \left(G_{A3} + \frac{v_B}{v_A} G_{B3} \right) + N_1 G_{13} + N_2 G_{23} + N_3} \right] \end{aligned}$$

$$\begin{aligned}
& - N_2 \left[\frac{N_A (Z_{A2} + \frac{v_B}{v_A} Z_{B2})}{N_3 G_{32} + N_2} \right] - N_3 \left[\frac{N_A (Z_{A3} + \frac{v_B}{v_A} Z_{B3})}{N_2 G_{23} + N_3} \right] \\
& + N_2 N_3 Z_{32} \left[\frac{N_A (G_{A2} + \frac{v_B}{v_A} G_{B2})}{(N_3 G_{32} + N_2)^2} \right] \\
& + N_2 N_3 Z_{23} \left[\frac{N_A (G_{A3} + \frac{v_B}{v_A} G_{B3})}{(N_2 G_{23} + N_3)^2} \right]
\end{aligned} \tag{B-26}$$

Let

$$\begin{aligned}
G_{\pm 2} &= G_{A2} + \frac{v_B}{v_A} G_{B2} \\
G_{\pm 3} &= G_{A3} + \frac{v_B}{v_A} G_{B3} \\
Z_{\pm 2} &= Z_{A2} + \frac{v_B}{v_A} Z_{B2} \\
Z_{\pm 3} &= Z_{A3} + \frac{v_B}{v_A} Z_{B3}
\end{aligned} \tag{B-27}$$

Combining equations (B-25) and (B-27) and setting $N_1 = 0.0$ for the case of complete dissociation, leads to equation (2-3) which is the final expression for $\frac{G^E(\text{ternary})}{RT} \Big|_{\text{NRTL}}$ used in this study.

B.3--Development of the ternary $\ln \gamma_{\pm}$, $\ln \gamma_2$ and $\ln \gamma_3$ expressions

The total excess Gibbs free energy function in this model

is obtained by combining equations (2-2) and (2-3). The activity coefficient expressions are obtained by the appropriate differentiation of the total excess Gibbs free energy expression, equations (1-27) to (1-29). The differentiation of the Debye-Hückel and NRTL terms of the expression have been performed separately as shown below

B.3-I--Debye-Hückel equation--

$$v \ln \gamma_{\pm \text{Ext.D.H.}}^* = \frac{\partial}{\partial N_1} \left[\frac{G^E}{RT} \Big|_{\text{Ext.D.H.}} \right]_{T,P,N_2,N_3} \quad (\text{B-28})$$

Since, $\frac{G^E}{RT} \Big|_{\text{Ext.D.H.}}$ was obtained by the integration of $\ln \gamma_{\pm \text{Ext.D.H.}}^*$, differentiation of this excess Gibbs free energy function gives the same expression for $\ln \gamma_{\pm \text{Ext.D.H.}}^*$, equation (2-13).

For solvents (2) and (3)

$$\ln \gamma_{2 \text{Ext.D.H.}} = \frac{\partial}{\partial N_2} \left[\frac{G^E}{RT} \Big|_{\text{Ext.D.H.}} \right]_{T,P,N_1,N_3}$$

Equation (2-2) is differentiated term by term by utilizing the change of variables, i.e. $\frac{m}{I} - \frac{2}{\xi}$

$$\begin{aligned} \text{I term} = \frac{\partial}{\partial N_2} \left[-2.303 v |z_+ z_-| \frac{2}{\xi} \frac{N_T M_w}{1000} A_\gamma \frac{2}{\rho_3} \left\{ \frac{1}{2} (1 + \rho I^{1/2})^2 \right. \right. \\ \left. \left. - 2(1 + \rho I^{1/2}) + \ln(1 + \rho I^{1/2}) + \frac{3}{2} \right\} \right] \end{aligned}$$

$$\begin{aligned} \text{I term} = -2303 \frac{v |z_+ z_-|}{1000} \frac{2}{\xi} \left[N_T M_w \frac{2}{\rho_3} \left\{ \frac{1}{2} (1 + \rho I^{1/2})^2 - 2(1 + \rho I^{1/2}) \right. \right. \\ \left. \left. + \ln(1 + \rho I^{1/2}) + \frac{3}{2} \right\} \frac{\partial A_\gamma}{\partial N_2} + A_\gamma \frac{2}{\rho} \left\{ \frac{1}{2} (1 + \rho I^{1/2})^2 \right. \right. \end{aligned}$$

$$\begin{aligned}
& - 2(1 + \rho I^{1/2}) + \ln(1 + \rho I^{1/2}) + \frac{3}{2} \left. \frac{\partial}{\partial N_2} (N_T M_w) \right. \\
& + N_T M_w A_\gamma \frac{2}{\rho^3} \frac{\partial}{\partial I} \left[\frac{1}{2} (1 + \rho I^{1/2})^2 - 2(1 + \rho I^{1/2}) \right. \\
& \left. + \ln(1 + \rho I^{1/2}) + \frac{3}{2} \right] \frac{\partial I}{\partial m} \frac{\partial m}{\partial N_2} \quad (B-29)
\end{aligned}$$

from equations (B-3) and (B-6)

$$\frac{\partial m}{\partial N_2} = \frac{m M_{w2}}{N_T M_w} \quad (B-30)$$

$$\frac{\partial (N_T M_w)}{\partial N_2} = M_{w2} \quad (B-31)$$

Simplifying equation (B-29) and substituting equations (B-30) and (B-31) results in the following expression for term I

$$\begin{aligned}
\text{I term} &= 2.303 \frac{v m}{1000} |z_+ z_-| [A_\gamma I^{1/2} \frac{1}{(\rho I^{1/2})^3} \{ (1 + \rho I^{1/2}) \\
& - 2 \ln(1 + \rho I^{1/2}) - \frac{1}{(1 + \rho I^{1/2})} \} - N_T M_w I^{1/2} \\
& \frac{1}{(\rho I^{1/2})^3} \{ \frac{1}{2} (1 + \rho I^{1/2})^2 - 2(1 + \rho I^{1/2}) + \ln(1 + \rho I^{1/2}) \\
& + \frac{3}{2} \} \frac{\partial A_\gamma}{\partial N_2}] \quad (B-32)
\end{aligned}$$

$$\begin{aligned}
\text{II term} &= \frac{\partial}{\partial N_2} \left[2.303 \frac{v |z_+ z_-|}{1000} \frac{2}{\xi} N_T M_w A_\gamma^2 \left\{ \frac{2(aI - 2)}{3a^2} + \right. \right. \\
& \left. \left. (1 + aI)^{1/2} + \frac{4}{3a^2} \right\} \right]
\end{aligned}$$

$$\begin{aligned}
&= 2.303 \frac{v|z_+z_-|}{1000} \frac{2}{\xi} \left[\left\{ \frac{2(aI-2)}{3a^2} + (1+aI)^{1/2} + \frac{4}{3a^2} N_{T^M W} \right. \right. \\
&\quad \left. \left. \frac{\partial A_Y^2}{\partial N_2} + A_Y^2 \left\{ \frac{2(aI-2)}{3a^2} + (1+aI)^{1/2} + \frac{4}{3a^2} \right\} \frac{\partial (N_{T^M W})}{\partial N_2} \right. \right. \\
&\quad \left. \left. + A_Y^2 N_{T^M W} \frac{\partial}{\partial I} \left\{ \frac{2(aI-2)}{3a^2} + (1+aI)^{1/2} + \frac{4}{3a^2} \right\} \frac{\partial I}{\partial m} \frac{\partial m}{\partial N_2} \right] \\
\text{II term} &= 2.303 \frac{vm}{1000} |z_+z_-| [M_{w2} A_Y^2 \frac{I}{2} \frac{2}{3aI} \left\{ \frac{2(aI-2)(1+aI)^{1/2}}{aI} \right. \\
&\quad \left. + \frac{4}{aI} - \frac{(aI-2)}{(1+aI)^{1/2}} - 2(1+aI)^{1/2} \right\} \\
&\quad \left. + N_{T^M W} \frac{2}{3aI} \left\{ \frac{2(aI-2)(1+aI)^{1/2}}{aI} + \frac{4}{aI} \right\} I A_Y \frac{\partial A_Y}{\partial N_2} \right] \quad (\text{B-33})
\end{aligned}$$

$$\begin{aligned}
\text{III term} &= \frac{\partial}{\partial N_2} [N_T \{ (0.001 \ v m M_w + 1) \ln(0.001 \ v m M_w + 1) \\
&\quad - 0.001 \ v m M_w \}]
\end{aligned}$$

$$\begin{aligned}
\text{III term} &= \{ (0.001 \ v m M_w + 1) \ln(0.001 \ v m M_w + 1) - 0.001 \ v m M_w \} \frac{\partial N_T}{\partial N_2} \\
&\quad + N_T \{ \ln(0.001 \ v m M_w + 1) \} \frac{\partial}{\partial N_2} (0.001 \ v m M_w + 1) \\
&\quad + (0.001 \ v m M_w + 1) \frac{\partial}{\partial N_2} \ln(0.001 \ v m M_w + 1) - 0.001 \ v \frac{\partial}{\partial N_2} (m M_w) \}
\end{aligned}$$

$$\text{III term} = \ln(0.001 \ v m M_w + 1) - 0.001 \ v m M_w \quad (\text{B-34})$$

The combination of equations (B-32), (B-33) and (B-34) yields equation (2-16). A similar approach leads to the expression for $\ln \gamma_{3\text{Ext.D.H.}}$.

In equation (2-16) $\sigma_1^1(\rho I^{1/2})$ and $\psi_1^1(aI)$ are given by

$$\sigma_1^1(\rho I^{1/2}) = \frac{2}{(\rho I^{1/2})^3} \left[\frac{1}{2}(1 + \rho I^{1/2})^2 - 2(1 + \rho I^{1/2}) + \ln(1 + \rho I^{1/2}) + \frac{3}{2} \right] \quad (\text{B-35})$$

$$\psi_1^1(aI) = \frac{2}{3aI} \left[\frac{2(aI - 2)}{aI} (1 + aI)^{1/2} + \frac{4}{aI} \right] \quad (\text{B-36})$$

B.3.II--NRTL equation

$$\begin{aligned} \nu \ln \gamma_{\pm}^* &= \frac{\partial}{\partial N_1} \left[\frac{G^E(\text{ternary})}{RT} \right]_{T,P,N_2,N_3} \\ \nu \ln \gamma_{\pm}^* &= \frac{\partial}{\partial N_A} \left[\frac{G^E(\text{ternary})}{RT} \right]_{T,P,N_2,N_3} \frac{\partial N_A}{\partial N_1} \end{aligned} \quad (\text{B-37})$$

Assuming complete dissociation of the electrolyte

$$N_A = \nu_A N_1 \quad (\text{B-38})$$

$$\frac{\partial N_A}{\partial N_1} = \nu_A \quad (\text{B-39})$$

Combining equations (B-37) and (B-39) yields

$$\nu \ln \gamma_{\pm}^* = \nu_A \ln \gamma_{A,NRTL} \quad (\text{B-40})$$

$\ln \gamma_{\pm}^*$ can be obtained by differentiating equation (B-28) with respect to N_A

$$\begin{aligned} \ln \gamma_A &= \frac{1}{RT} \left[\frac{N_2(N_A G_{\pm 2} Z_{\pm 2} + N_3 G_{32} Z_{\pm 2} + N_2 Z_{\pm 2} - N_A G_{\pm 2} Z_{\pm 2} - N_3 Z_{32} G_{\pm 2})}{(N_A G_{\pm 2} + N_3 G_{32} + N_2)^2} \right. \\ &+ \frac{N_3(N_A G_{\pm 3} Z_{\pm 3} + N_2 G_{23} Z_{\pm 3} + N_3 Z_{\pm 3} - N_A G_{\pm 3} Z_{\pm 3} - N_2 Z_{23} G_{\pm 3})}{N_A G_{\pm 3} + N_2 G_{23} + N_3)^2} \\ &- \left. \left\{ \frac{N_2 Z_{\pm 2}}{(N_3 G_{32} + N_2)} + \frac{N_3 Z_{\pm 3}}{(N_2 G_{23} + N_3)} \right\} \right] \end{aligned}$$

$$+ N_2 N_3 \left\{ \frac{Z_{32} G_{\pm 2}}{(N_3 G_{32} + N_2)^2} + \frac{Z_{23} G_{\pm 3}}{(N_2 G_{23} + N_3)^2} \right\} \quad] \quad (\text{B-41})$$

Combining equations (B-37) and (B-41) and converting moles to the mole fraction leads to equation (2-14).

The activity coefficient of the solvent is obtained by differentiating $\frac{G^E}{RT} \Big|_{\text{NRTL}}$ with respect to N_2

$$\begin{aligned} \ln \gamma_{2, \text{NRTL}} &= \frac{\partial}{\partial N_2} \left[\frac{G^E(\text{ternary})}{RT} \Big|_{\text{NRTL}} \right]_{T, P, N_A, N_B, N_3} \\ &= \frac{1}{RT} \left[\frac{N_A Z_{\pm 2} + N_3 Z_{32}}{(N_A G_{\pm 2} + N_3 G_{32} + N_2)} - \frac{N_2 (N_A Z_{\pm 2} + N_3 Z_{32})}{(N_A G_{\pm 2} + N_3 G_{32} + N_2)^2} \right. \\ &\quad + \frac{N_3 Z_{23}}{(N_A G_{\pm 3} + N_2 G_{23} + N_3)} - \frac{N_A (N_A Z_{\pm 3} + N_2 Z_{23}) G_{23}}{(N_A G_{\pm 3} + N_2 G_{23} + N_3)^2} \\ &\quad - N_A \left\{ \frac{Z_{\pm 2}}{N_3 G_{32} + N_2} - \frac{N_2 Z_{\pm 2}}{(N_3 G_{32} + N_2)^2} - \frac{N_3 Z_{\pm 3} G_{23}}{(N_2 G_{23} + N_3)^2} \right\} \\ &\quad + N_A N_3 \left\{ \frac{Z_{32} G_{\pm 2}}{(N_3 G_{32} + N_2)^2} + \frac{Z_{23} G_{\pm 3}}{(N_2 G_{23} + N_3)^2} \right\} \\ &\quad \left. - N_A N_2 N_3 \left\{ \frac{2Z_{32} G_{\pm 2}}{(N_3 G_{32} + N_2)^3} + \frac{2Z_{23} G_{\pm 3} G_{23}}{(N_2 G_{23} + N_3)^3} \right\} \right] \quad (\text{B-42}) \end{aligned}$$

Equation (B-42) can be simplified in the form of equation (2-17). Utilizing a similar approach an expression for $\ln \gamma_{3, \text{NRTL}}$ is obtained.

APPENDIX C

A STEPWISE PROCEDURE FOR THE DEVELOPMENT
OF TERNARY ACTIVITY COEFFICIENT
EXPRESSIONS FOR MODEL II

MODEL II: Combination of the Bromley Equation; The
Simplified NRTL Equation and the Salting Out Term

Bromley (1973) presented a generalized analytic correlation for mean activity coefficients of electrolytes in binary aqueous electrolytic solutions.

$$\ln \gamma_{\pm} = 2.303[-A_{\gamma} |z_+ z_-| \frac{I^{1/2}}{1 + \rho I^{1/2}} + \frac{(B_o - B_{1i})^I}{(1 + aI)^{\eta}} + B_{1i} I + cI^2] \quad (C-1)$$

where

$$A_{\gamma} = \text{Debye-Hückel constant} \quad (\text{Appendix-L})$$

$$I = \frac{1}{2} \sum m_k z_k^2 \quad (C-1-A)$$

η , ρ , a , B_o , B_{1i} and c : adjustable parameters

On the basis of a comprehensive study using data for γ_{\pm} , but also osmotic coefficients and other related thermodynamic properties at 25°C, as well as at other temperatures up to 200°C, Bromley concluded that reasonable agreement is obtained by using

$$\eta = 2$$

$$a = 1.5/|z_+ z_-|$$

$$c = 0.0$$

$$\rho = 1.0$$

$$(B_o - B_{1i}) = (0.06 + 0.6B_{1i}) |z_+ z_-| \quad (C-2)$$

in equation (C-1).

Substitution of (C-2) into (C-1) simplifies this equation in terms of only one adjustable parameter ' B_{1i} ' per binary. When the above equation was applied to correlate non-aqueous

electrolytic binary with the same constants, the fit was good. Considering the simplicity and success of the above equation in correlating binary systems and the success of the NRTL equation in correlating solvent-solvent binaries, Model II proposes to combine them with an additional ternary salting out term for the correlation of electrolyte (1) - solvent (2) - solvent (3) ternary systems. The following procedure is followed in developing Model II:

C.1: Development of the $\frac{G^E(\text{ternary})}{RT} \Big|_{\text{Bromley}}$ expression

Equation (C-1) with (C-2) is first integrated to derive

$\frac{G^E(\text{binary})}{RT} \Big|_{\text{Bromley}}$, which is then extended to ternary mixtures.

$$\begin{aligned} \frac{G^E(\text{binary})}{RT} \Big|_{\text{Bromley}} &= 2.303 \int_0^{N_1} \left\{ -A_\gamma \left| Z_+ Z_- \right| \frac{I^{1/2}}{1 + \rho I^{1/2}} \right\} dN_1 \\ &+ \int_0^{N_1} \left\{ \frac{(0.06 + 0.6B_{1i})^I}{(1 + aI)^2} \right\} dN_1 \\ &+ \int_0^{N_1} B_{1i} I dN_1 \\ &+ \int_0^{N_1} \ln(0.001 \nu m M_w + 1) dN_1 \end{aligned} \quad (\text{C-3})$$

Equation (C-3) can be integrated term by term with equations (B-3) to (B-8)

$$I \text{ term} = 2.303 \int_0^I -A_\gamma \left| Z_+ Z_- \right| \frac{I^{1/2}}{1 + \rho I^{1/2}} \frac{\partial N_1}{\partial m} \frac{\partial m}{\partial I} \partial I$$

$$\begin{aligned} \text{I term} = & -2.303vA_{\gamma} \frac{N_1 M_w}{1000} \frac{m}{I} \left[\frac{2}{\rho^3} \left\{ \frac{1}{2} (1 + \rho I^{1/2})^2 \right. \right. \\ & \left. \left. - 2(1 + \rho I^{1/2}) + \ln(1 + \rho I^{1/2}) + \frac{3}{2} \right\} \right] |z_+ z_-| \end{aligned} \quad (\text{C-4})$$

$$\text{II term} = 2.303v \int_0^I \frac{(0.06 + 0.06B_{1i})^I}{(1 + aI)^2} \frac{\partial N_1}{\partial m} \frac{\partial m}{\partial I} \partial I$$

$$\begin{aligned} \text{II term} = & 2.303v \frac{N_1 M_w}{1000} |z_+ z_-| \frac{(0.06 + 0.6B_{1i})}{a^2} \frac{m}{I} \left[\ln(1 + aI) + \frac{1}{(1 + aI)} - 1 \right] \end{aligned} \quad (\text{C-5})$$

$$\text{III term} = 2.303v \int_0^I B_{1i} I \frac{\partial N_1}{\partial m} \frac{\partial m}{\partial I} \partial I$$

$$\text{III term} = 2.303v \frac{N_1 M_w}{1000} \frac{m}{I} B_{1i} \frac{I^2}{2} \quad (\text{C-6})$$

$$\text{IV term} = v \int_0^1 \ln(0.001vmM_w + 1) \frac{dN_1}{\partial m} \partial m$$

$$= N_1 [(0.001vmM_w + 1) \ln(0.001vmM_w + 1)$$

$$- 0.001vmM_w] \quad (\text{C-7})$$

Combining equations (C-4) to (C-7) leads to the following expression for

$$\begin{aligned} \frac{G^E(\text{binary})}{RT} \Big|_{\text{Bromley}} = & 2.303v \frac{N_1 M_w}{1000} \frac{m}{I} \left[-A_{\gamma} |z_+ z_-| \frac{2}{\rho^3} \right. \\ & \left. \left\{ \frac{1}{2} (1 + \rho I^{1/2})^2 - 2(1 + \rho I^{1/2}) + \ln(1 + \rho I^{1/2}) \right. \right. \\ & \left. \left. + \frac{3}{2} \right\} + \frac{(0.06 + 0.6B_{1i})}{a^2} |z_+ z_-| \right. \\ & \left. \left[\ln(1 + aI) + \frac{1}{(1 + aI)} - 1 \right] + \frac{B_{1i} I^2}{2} \right] \end{aligned}$$

$$\begin{aligned}
& + N_i [(0.001 \nu m M_w + 1) \ln(0.001 \nu m M_w + 1) \\
& - 0.001 \nu m M_w] \quad (C-8)
\end{aligned}$$

In a binary aqueous/nonaqueous electrolyte solution, equation (C-8) can be used to derive the expression for the activity coefficient of the solvent, by equation (1-27)

$$\begin{aligned}
\ln \gamma_{i, \text{Bromley}}^{(\text{binary})} &= 2.303 \frac{\nu m}{1000} M_{w_i} [A_\gamma \frac{I^{1/2}}{3} \sigma(\rho I^{1/2}) |Z_+ Z_-| \\
&- (0.06 + 0.6 B_{1i}) \frac{I}{2} \psi(aI) |Z_+ Z_-| - B \frac{I}{2}] \\
&+ \ln(0.001 \nu m M_w + 1) - 0.001 \nu m M_w \quad (C-9)
\end{aligned}$$

Equation (C-8) is modified for a ternary system by the appropriate substitution of B for B_{1i} and the Debye-Hückel constant for mixture. The most important conditions to be satisfied are

$$\begin{aligned}
\lim_{\substack{N_2 \rightarrow 0 \\ \text{or} \\ N_3 \rightarrow 0}} \frac{G^E(\text{ternary})}{RT} \Big|_{\text{Bromley}} &= \frac{G^E(\text{binary})}{RT} \Big|_{\text{Bromley}} \quad (C-10)
\end{aligned}$$

This requires--

$$\lim_{N_2 \rightarrow 0} B = B_{12}$$

$$\lim_{N_2 \rightarrow 0} A_\gamma(N_2, N_3, d_2, d_3, D_2, D_3, T) = A_\gamma(d_2, D_2, T)$$

or

$$\lim_{N_3 \rightarrow 0} B = B_{13}$$

$$\lim_{N_3 \rightarrow 0} A_\gamma(N_2, N_3, d_2, d_3, D_2, D_3, T) = A_\gamma(d_3, D_3, T) \quad (C-11)$$

The above constraints lead equation (C-8) to

$$\frac{G^E(\text{ternary})}{RT} \Big|_{\text{Bromley}}, \text{ equation (3-2)}$$

Note: equation (3-2) involves no solvent-solvent interaction parameters.

C.2--Development of the $\frac{G^E(\text{ternary})}{RT} \Big|_{\text{NRTL-S}}$ Expression

The NRTL equation developed in model I, equation (2-3) is simplified further by considering that the NRTL equation in Model II accounts only for solvent-solvent interactions. Hence, assuming that

$$X_{A2} = X_{B2} = X_{A3} = X_{B3} = 1.0 \quad (\text{C-12})$$

in equation (2-3) then,

$$\Delta g_{A2} = \Delta g_{A3} = \Delta g_{B2} = \Delta g_{B3} = 0.0$$

$$G_{A2} = G_{B2} = G_{A3} = G_{B3} = 1.0$$

$$G_{\pm 2} = G_{\pm 3} = \frac{v}{v_A} \quad (\text{C-13})$$

$$Z_{A2} = Z_{B2} = Z_{A3} = Z_{B3} = 0.0$$

$$Z_{\pm 2} = Z_{\pm 3} = 0.0 \quad (\text{C-14})$$

$$\begin{aligned} \frac{G^E(\text{ternary})}{RT} \Big|_{\text{NRTL-S}} &= \frac{1}{RT} \left[\frac{N_2 N_3 Z_{32}}{(N_A \frac{v}{v_A} + N_2 + N_3 G_{32})} + \frac{N_2 N_3 Z_{23}}{(N_A \frac{v}{v_A} + N_3 + N_2 G_{23})} \right. \\ &\quad \left. + \frac{v}{v_A} N_A N_2 N_3 \left\{ \frac{Z_{32}}{(N_3 G_{32} + N_2)^2} + \frac{Z_{23}}{(N_2 G_{23} + N_3)^2} \right\} \right] \quad (\text{C-15}) \end{aligned}$$

Equation (C-15) can be converted in terms of mole fractions, equation (3-4).

C.3--Development of the Salting-Out Term for a Ternary Mixture

It is well known that the addition of an electrolyte in mixed solvents, causes salting-out of one of the solvents. Combination of the Bromley equation and the simplified NRTL equation alone is not enough to account for the salting-out effect, therefore an additional salting-out term was sought. Different theories have been proposed specifically by Debye-McAulay (1925), Butler (1929) and Born (1932), to account for salting-out. In this work, an expression based on the above theories, has been proposed, which requires one ternary salting-out parameter ' δ_{123} ' and is shown below

$$\frac{g^E(\text{ternary})}{RT} \Big|_{\text{salt-out}} = \frac{D' - D}{D^2} \frac{\epsilon^2}{\kappa T} \sum_k \frac{\nu_k z_k^2}{bk} \frac{1}{2} \quad (\text{C-16})$$

where,

$$D' = D \left[1 - \frac{\delta_{123}}{e^{\alpha N_1^{1/2}} (X_2' X_3')^{1/2} N_1 (X_2' B_{13} - X_3' B_{12}) e^{\alpha X_2'}} \right] \quad (\text{C-17})$$

$$\alpha = 2.0$$

Combining equations (C-16) and (C-17) leads to the form--

$$\frac{G^E(\text{ternary})}{RT} \Big|_{\text{salt-out}} = N_T \frac{g^E(\text{ternary})}{RT} \Big|_{\text{salt-out}}$$

equation (3-5).

C.4--Development of the Ternary $\ln \gamma_{\pm}$, $\ln \gamma_2$ and $\ln \gamma_3$ Expressions

The total excess Gibbs free energy function is obtained by combining equations (3-2) to (3-5). The activity coefficient expressions are obtained by the appropriate differentiation of the total Gibbs free energy function. Since the activity coefficients are a combination of three different terms, the differentiation of each term is performed separately, as below

C.4-I--The Bromley Equation

Combining equations (1-26) (3-2) and (3-3) results in--

$$\begin{aligned} v \ln \gamma_{\pm}^{*(\text{ternary})}, \text{Bromley} &= \frac{\partial}{\partial N_1} \left[2.303 v \frac{m}{I} \frac{N_T M_W}{1000} \left\{ \frac{1}{2} (1 + \rho I^{1/2})^2 \right. \right. \\ &\quad \left. \left. - 2(1 + \rho I^{1/2}) + \ln(1 + \rho I^{1/2}) + \frac{3}{2} \right\} + \frac{(0.06 + 0.06B)}{a^2} \right. \\ &\quad \left. \left\{ \ln(1 + aI) + \frac{1}{1 + aI} - 1 \right\} + \frac{B}{2} I^2 \right] + \\ &\quad \frac{\partial}{\partial N_1} \left[N_T \left\{ (0.001 v m M_W + 1) \ln(0.001 v m M_W + 1) \right. \right. \\ &\quad \left. \left. - 0.001 v m M_W \right\} \right] \end{aligned} \quad (\text{C-18})$$

Equation (C-18) simplifies to the original $\ln \gamma_{\pm}^{*}, \text{Bromley}$ equation with an additional term, equation (3-8), where

$$\frac{\partial B}{\partial N_1} = -\frac{3}{2} \alpha B_{123} \frac{1}{N_1^{1/2}} \frac{1}{(1 + \alpha N_1^{1/2})^4} e^{-\alpha X_3'} (X_2' X_3')^{1/4} \quad (\text{C-19})$$

For solvent 2, equation (3-2) with (3-3) is differentiated term by term

$$\begin{aligned}
 \text{I term} &= \frac{\partial}{\partial N_2} \left[-2.303 v \frac{m}{I} \frac{N_T M_w}{1000} A_\gamma \frac{2}{\rho^3} \left\{ \frac{1}{2} (1 + \rho I^{1/2})^2 \right. \right. \\
 &\quad \left. \left. - 2(1 + \rho I^{1/2}) + \ln(1 + \rho I^{1/2}) + \frac{3}{2} \right\} \right] \\
 \text{I term} &= 2.303 \frac{vm}{1000} [M_{w2} A_\gamma I^{1/2} \frac{1}{(\rho I^{1/2})^3} \{ (1 + \rho I^{1/2}) \\
 &\quad - 2 \ln(1 + \rho I^{1/2}) - \frac{1}{(1 + \rho I^{1/2})} \} - N_T M_w \\
 &\quad I^{1/2} \frac{2}{(\rho I^{1/2})^3} \{ \frac{1}{2} (1 + \rho I^{1/2})^2 - 2(1 + \rho I^{1/2}) \\
 &\quad + \ln(1 + \rho I^{1/2}) + \frac{3}{2} \} \frac{\partial A_\gamma}{\partial N_2}] \tag{C-20}
 \end{aligned}$$

$$\begin{aligned}
 \text{II term} &= \frac{\partial}{\partial N_2} \left[2.303 v \frac{m}{I} \frac{N_T M_w}{1000} \frac{(0.06 + 0.06B)}{a^2} \right. \\
 &\quad \left. \{ \ln(1 + aI) + \frac{1}{(1 + aI)} - 1 \} \right] \\
 \text{II term} &= + 2.303 \frac{vm}{1000} [-M_{w2} (0.06 + 0.6B) \frac{I}{2} \frac{2}{aI} \\
 &\quad \{ \frac{(1 + 2aI)}{(1 + aI)^2} - \frac{\ln(1 + aI)}{aI} \} + 0.6 N_T M_w \frac{I}{2} \frac{2}{aI} \\
 &\quad \{ \frac{\ln(1 + aI)}{aI} - \frac{1}{(1 + aI)} \} \frac{\partial B}{\partial N_2}] \tag{C-21}
 \end{aligned}$$

$$\begin{aligned}
 \text{III term} &= \frac{\partial}{\partial N_2} \left[2.303 v \frac{m}{I} \frac{N_T M_w}{1000} \frac{B}{2} I^2 \right] \\
 \text{III term} &= + 2.303 \frac{vm}{1000} [-M_{w2} B \frac{I}{2} + N_T M_w I \frac{\partial B}{\partial N_2}] \tag{C-22}
 \end{aligned}$$

$$\text{IV term} = \frac{\partial}{\partial N_2} [(0.001 vm M_w + 1) \ln(0.001 vm M_w + 1) - 0.001 vm M_w]$$

$$\text{IV term} = \ln(0.001 \nu m M_w + 1) - 0.001 \nu m M_w \quad (\text{C-23})$$

Combining equations (C-20) to (C-23) results in $\ln \gamma_{2, \text{Bromley}}^{(\text{ternary})}$ expression, equation (3-12). Similarly an expression for $\ln \gamma_{3, \text{Bromley}}^{(\text{ternary})}$ can be obtained.

The different terms of equation (3-12) are defined below

$$\sigma_2(\rho I^{1/2}) = \frac{3}{(\rho I^{1/2})^3} [(1 + \rho I^{1/2}) - 2 \ln(1 + \rho I^{1/2}) - \frac{1}{(1 + \rho I^{1/2})}] \quad (\text{C-24})$$

$$\sigma_2^1(\rho I^{1/2}) = \frac{2}{(\rho I^{1/2})^3} [\frac{1}{2}(1 + \rho I^{1/2}) - 2(1 + \rho I^{1/2}) + \ln(1 + \rho I^{1/2}) + \frac{3}{2}] \quad (\text{C-25})$$

$$\psi_2(aI) = \frac{2}{aI} [\frac{(1 + 2aI)}{(1 + aI)^2} - \frac{\ln(1 + aI)}{aI}] \quad (\text{C-26})$$

$$\psi_2^1(aI) = \frac{2}{aI} [\frac{\ln(1 + aI)}{aI} - \frac{1}{(1 + aI)}] \quad (\text{C-27})$$

$$\begin{aligned} \frac{\partial B}{\partial N_2} = & (B_{12} - B_{13}) \frac{X_2'}{N_T} + \frac{B_{123}}{(1 + \alpha N_1^{1/2})^3} \left[\left\{ \frac{1}{2} \left(\frac{X_3'}{X_2'} \right)^{1/2} \frac{1}{X_2'^{1/2}} - (X_2' X_3')^{1/4} \right\} \right. \\ & \left. \frac{1}{2} \frac{1}{N_T} e^{-\alpha X_3'} + \alpha \frac{X_3'}{N_T} e^{-\alpha X_3'} (X_2' X_3')^{1/4} \right] \end{aligned} \quad (\text{C-28})$$

$$\begin{aligned} \frac{\partial B}{\partial N_3} = & (B_{13} - B_{12}) \frac{X_3'}{N_T} + \frac{B_{123}}{(1 + \alpha N_1^{1/2})^3} \left[\left\{ \frac{1}{2} \left(\frac{X_2'}{X_3'} \right)^{1/2} \frac{1}{X_3'^{1/2}} - (X_2' X_3')^{1/4} \right\} \right. \\ & \left. \frac{1}{2} \frac{1}{N_T} e^{-\alpha X_3'} - \alpha \frac{X_2'}{N_T} e^{-\alpha X_3'} (X_2' X_3')^{1/4} \right] \end{aligned} \quad (\text{C-29})$$

C.4-II--The NRTL-S equation

Equation (C-15) can be differentiated appropriately to obtain the activity coefficient expression for electrolyte and solvents. Utilizing equations (B-35) to (B-38) with equation (C-15) leads to

$$\begin{aligned} \ln \gamma_{\pm}^{*}(\text{ternary})_{\text{NRTL-S}} &= \frac{N_2 N_3}{RT} \left[-\frac{Z_{32}}{\left(N_A \frac{v}{v_A} + N_2 + N_3 G_{32}\right)^2} \right. \\ &\quad - \frac{Z_{23}}{\left(N_A \frac{v}{v_A} + N_3 + N_2 G_{23}\right)^2} + \frac{Z_{32}}{\left(N_3 G_{32} + N_2\right)^2} \\ &\quad \left. + \frac{Z_{23}}{\left(N_2 G_{23} + N_3\right)^2} \right] \end{aligned} \quad (\text{C-30})$$

Equation (C-30) can be converted in terms of mole fraction, equation (3-8).

$$\begin{aligned} \ln \gamma_{2,\text{NRTL-S}}^{(\text{ternary})} &= \frac{\partial}{\partial N_2} \left[\frac{G^E(\text{ternary})}{RT} \right]_{\text{NRTL-S}} \\ \ln \gamma_{2,\text{NRTL-S}}^{(\text{ternary})} &= \frac{1}{RT} \left[\frac{N_3 Z_{32} \left(N_A \frac{v}{v_A} + N_2 + N_3 G_{32}\right) - N_2 N_3 Z_{32}}{\left(N_A \frac{v}{v_A} + N_2 + N_3 G_{32}\right)^2} \right. \\ &\quad + \frac{N_3 Z_{23} \left(N_A \frac{v}{v_A} + N_3 + N_2 G_{23}\right) - N_2 N_3 G_{23} Z_{23}}{\left(N_A \frac{v}{v_A} + N_3 + N_2 G_{23}\right)^2} \\ &\quad \left. + \frac{v}{v_A} N_A N_3 \left\{ \frac{Z_{32}}{\left(N_3 G_{32} + N_2\right)^2} + \frac{Z_{23}}{\left(N_2 G_{23} + N_3\right)^2} \right\} \right] \end{aligned}$$

$$\begin{aligned}
& + \frac{v}{v_A} N_A N_2 N_3 \left[-\frac{2Z_{32}}{(N_3 G_{32} + N_2)^3} - \frac{2Z_{23} G_{23}}{(N_2 G_{23} + N_3)^2} \right] \\
\ln \gamma_{2, \text{NRTL-S}}^{(\text{ternary})} = & \frac{1}{RT} \left[\frac{v}{v_A} N_A N_3 \left\{ \frac{Z_{32}}{(N_A \frac{v}{v_A} + N_2 N_3 G_{32})^2} \right. \right. \\
& + \frac{Z_{23}}{(N_A \frac{v}{v_A} + N_3 + N_2 G_{23})^2} + N_3^2 \left\{ \frac{G_{32} Z_{32}}{(N_A \frac{v}{v_A} + N_2 + N_3 G_{32})^2} \right. \\
& \left. \left. + \frac{Z_{23}}{(N_A \frac{v}{v_A} + N_3 + N_2 G_{23})^2} \right\} + \right. \\
& \left. \frac{v}{v_A} N_A N_3 \left\{ \frac{Z_{32}}{(N_3 G_{32} + N_2)^2} + \frac{Z_{23}}{(N_2 G_{23} + N_3)^2} \right\} \right. \\
& \left. - 2 \frac{v}{v_A} N_A N_2 N_3 \left\{ \frac{Z_{32}}{(N_3 G_{32} + N_2)^3} + \frac{Z_{23} G_{23}}{(N_2 G_{23} + N_3)^3} \right\} \right] \quad (\text{C-31})
\end{aligned}$$

Using the above approach, an expression for $\ln \gamma_{3, \text{NRTL-S}}^{(\text{ternary})}$ can be obtained. These expressions can be rearranged in terms of mole fractions, equation (3-13).

C.3-III--The Salting-Out Term

Equation (3-5) with equation (3-6) is differentiated to obtain the salting-out contribution for the activity coefficients.

$$\ln \gamma_{\pm, \text{salt-out}}^{* (\text{ternary})} = \delta_{123} \frac{\epsilon^2}{kTD} \sum_k \frac{v_k z_k^2}{b_k} (N_2 N_3)^{1/2} \delta' \frac{\partial}{\partial N_1} \left[\frac{N_1^2}{2} \frac{1}{e^{\alpha N_1^{1/2}}} \right] \quad (\text{C-32})$$

$$\frac{\partial}{\partial N_1} \left[\frac{1}{2} \frac{1}{e^{\alpha N_1^{1/2}}} \right] = \frac{1}{e^{\alpha N_1^{1/2}}} \left[N_1 - \frac{1}{2} \alpha \frac{1}{N_1^{1/2}} \frac{N_1^2}{2} \right] \quad (\text{C-33})$$

Combining equations (C-32) and (C-33) leads to equation (3-1). And

$$\begin{aligned} \ln \gamma_{2, \text{salt-out}}^{(\text{ternary})} &= \delta_{123} \frac{\epsilon^2}{kT} \sum_k \frac{v_k z_k^2}{b_k} \frac{N_1^2}{2} \frac{1}{e^{\alpha N_1^{1/2}}} \left[\frac{\delta'}{D} \frac{\partial}{\partial N_2} \{ (N_2 N_3)^{1/2} \} \right. \\ &\quad \left. + (N_2 N_3)^{1/2} \frac{\partial}{\partial N_2} \delta' + \delta' (N_2 N_3)^{1/2} \frac{\partial}{\partial N_2} \left(\frac{1}{D} \right) \right] \quad (\text{C-34}) \end{aligned}$$

where,

$$\frac{\partial}{\partial N_2} \{ (N_2 N_3)^{1/2} \} = \frac{1}{2} \left(\frac{N_3}{N_2} \right)^{1/2} \quad (\text{C-35})$$

$$\begin{aligned} \frac{\partial \delta'}{\partial N_2} &= \frac{\partial}{\partial N_2} \left[e^{\alpha X_2'} (X_2' B_{13} - X_3' B_{12}) \right] \\ &= e^{\alpha X_2'} (X_2' B_{13} - X_3' B_{12}) \frac{\partial X_2'}{\partial N_2} + e^{\alpha X_2'} \frac{\partial}{\partial N_2} (X_2' B_{13} - X_3' B_{12}) \\ \frac{\partial \delta'}{\partial N_2} &= \alpha e^{\alpha X_2'} (X_2' B_{13} - X_3' B_{12}) \frac{X_3'}{N_T} + (B_{12} + B_{13}) e^{\alpha X_2'} \frac{X_3'}{N_T} \quad (\text{C-36}) \end{aligned}$$

$$\frac{\partial}{\partial N_2} \left[\frac{1}{D} \right] = - \frac{1}{D^2} \frac{\partial D}{\partial N_2} \quad (\text{C-37})$$

A combination of equations (C-34) to (C-37) results in equation (3-14).

Similarly an expression for $\ln \gamma_{3, \text{salt-out}}^{(\text{ternary})}$ can be

obtained with the following additional relationships

$$\frac{\partial}{\partial N_3} [(N_2 N_3)^{1/2}] = \frac{1}{2} \left(\frac{N_2}{N_3}\right)^{1/2} \quad (\text{C-38})$$

$$\frac{\partial \delta'}{\partial N_3} = -e^{\alpha X_2'} \frac{X_2'}{N_T} [\alpha (X_2' B_{13} - X_3' B_{12}) + (B_{12} + B_{13})] \quad (\text{C-39})$$

$$\frac{\partial}{\partial N_3} \left[\frac{1}{D}\right] = -\frac{1}{D^2} \frac{\partial D}{\partial N_3} \quad (\text{C-40})$$

APPENDIX D

DEBYE-HÜCKEL CONSTANTS, DIELECTRIC CONSTANTS AND
DENSITIES OF PURE SOLVENTS AND MIXED SOLVENTS; VAPOR
PRESSURE CONSTANTS OF PURE SOLVENTS

The Debye-Hückel constant at the system temperature and pressure is given by

$$A_{\gamma} = \left[\frac{2\pi N d}{1000} \right]^{1/2} \left[\frac{\epsilon^2}{D k T} \right]^{3/2} \quad (D-1)$$

or

$$A_{\gamma} = 1.8246 \times 10^6 d^{1/2} \left[\frac{1}{D T} \right]^{3/2} \quad (D-2)$$

where,

d - density of the solvent

D - dielectric constant of the solvent

The values of the above two properties for the pure solvent or the mixed solvent mixture are presented below

A. Electrolyte-solvent binary (binary 1-2 or 1-3)

d = d_i - pure solvent (2 or 3) liquid density at the system temperature and pressure.

The density data are estimated if experimental data are not available by the following relationship

$$d = \frac{M_w}{V_T^L} \quad (D-3)$$

M_w = M_{w_i} - molecular weight of the solvent i

V_T^L = v_i^{oL} - pure solvent liquid molar volume.

A quadratic equation is used to calculate the pure solvent liquid molar volume, as given in the monograph by Prausnitz et al. (1967)

$$v_i^{oL} = a' + b'T + c'T^2 \quad (D-4)$$

The constants a' , b' and c' are obtained, using experimental liquid volume data at three temperatures, by a method used in the monograph. In Table D-1, liquid volume data are listed for the solvents used in this work.

$D - D_i$ - pure component dielectric constant at the system temperature and pressure.

B. Electrolyte (1) - solvent (2) - solvent (3) ternary

d - solvent mixture (electrolyte free) density at the system temperature and pressure.

I - if the experimental solvent mixture data are available, a six-constant polynomial is fitted to get the concentration dependency of the density. The polynomial expression is then used to calculate the density at different temperatures.

$$d = a_1 + a_2 X_3' + a_3 X_3'^2 + a_4 X_3'^3 + a_5 X_3'^4 + a_6 X_3'^5 \quad (D-5)$$

In tables D-2 and D-3, liquid density data for H_2O -MeOH at $25^\circ C$ and H_2O -EtOH at $25^\circ C$, used in this work are tabulated.

II - if the experimental mixture density data are not available, the solution density is approximated using a linear relationship for the volume equation (D-3). Where,

$$V_T^L = X_2' V_2^{oL} + X_3' V_3^{oL} \quad (D-6)$$

$$M_w = X_2' M_{w2} + X_3' M_{w3} \quad (D-7)$$

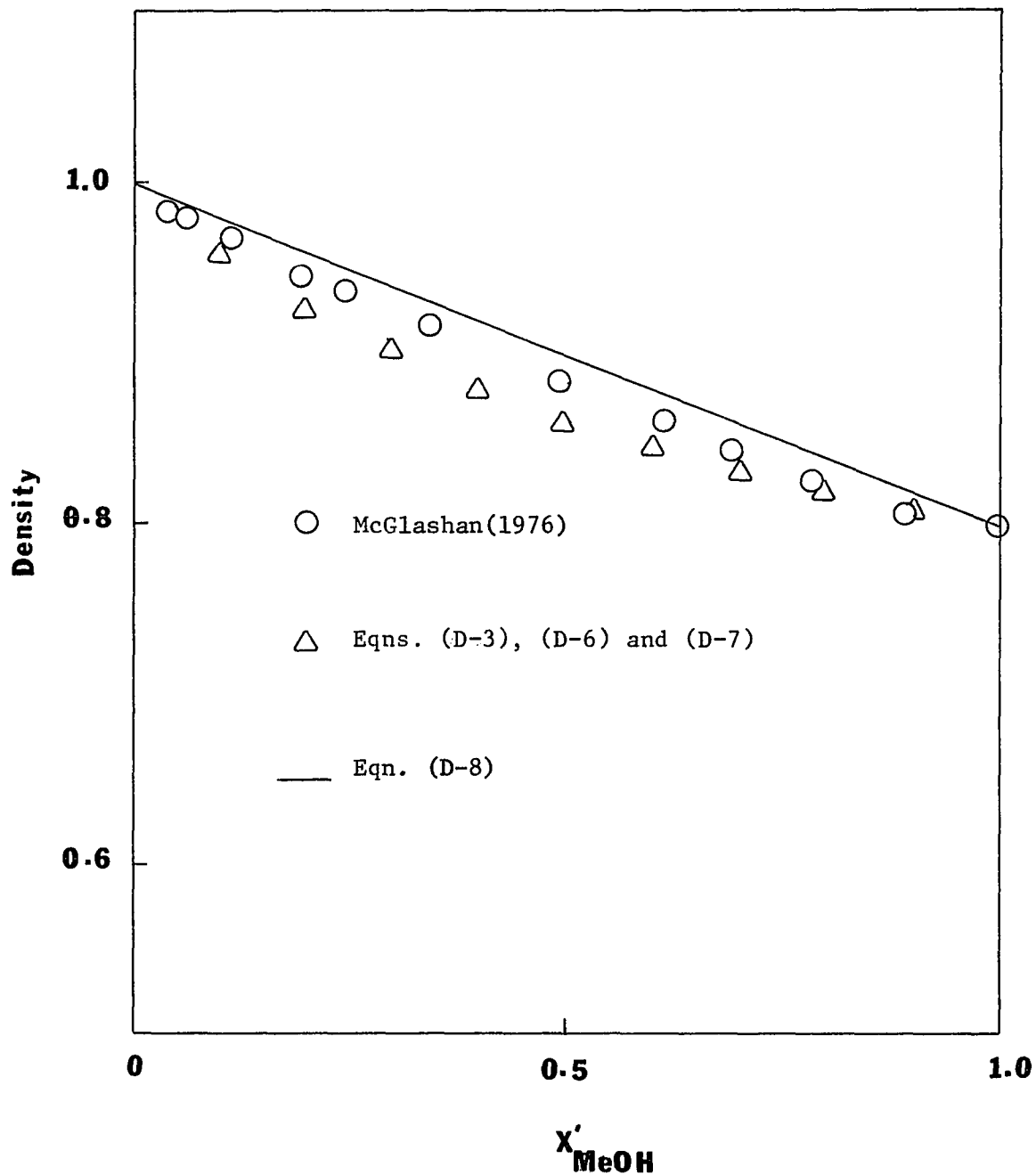


Figure D.1 Comparison of Experimental and Estimated Densities for the System $\text{H}_2\text{O}-\text{MeOH}$ at 25°C

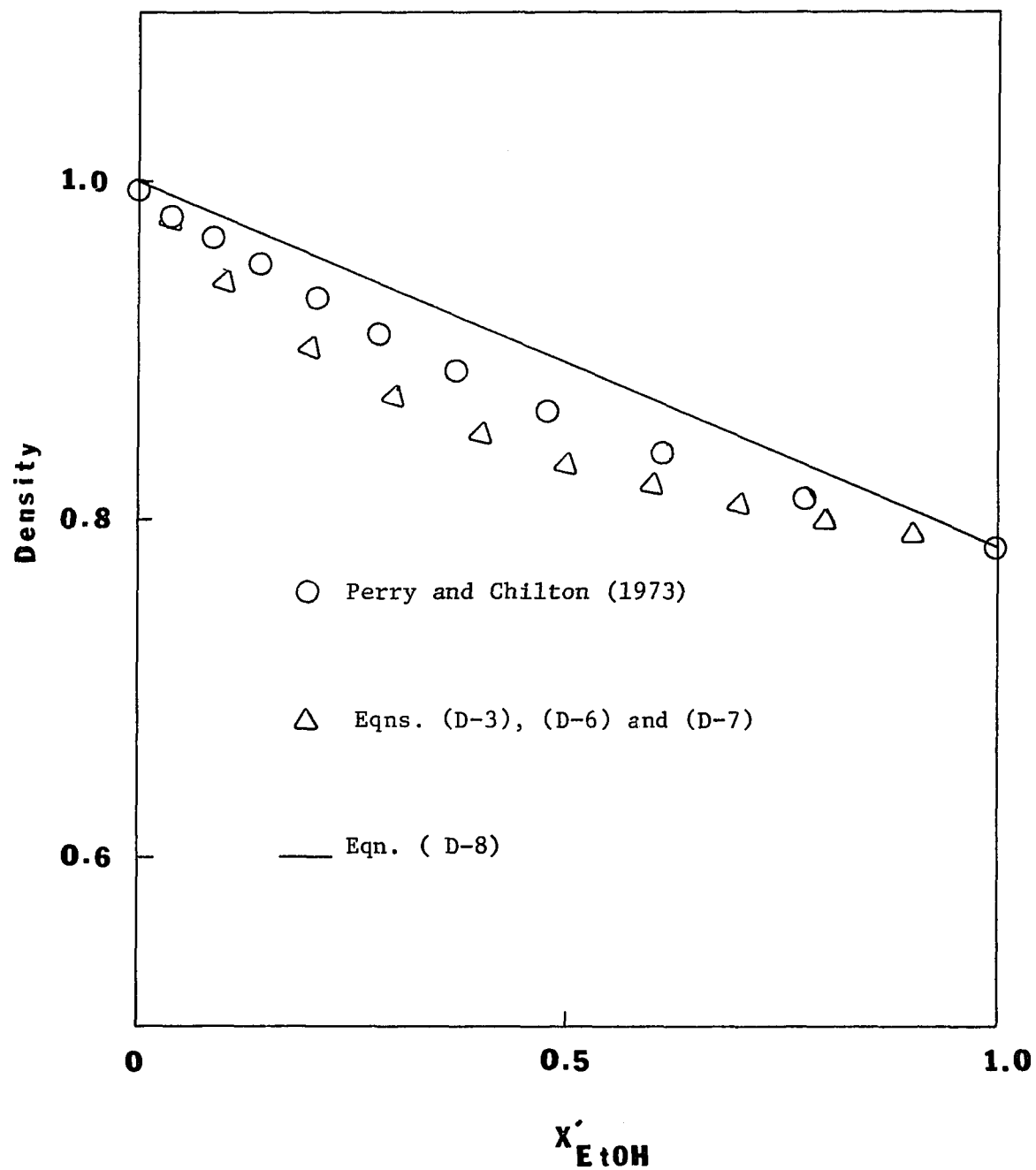


Figure D.2 Comparison of Experimental and Estimated Densities for the System $H_2O-EtOH$ at $25^\circ C$

$v_2^{\circ L}$ and $v_3^{\circ L}$ are calculated, using equation (D-4) for the pure solvents. Alternatively,

$$d = X_2' d_2^{\circ} + X_3' d_3^{\circ} \quad (D-8)$$

The validity of equations (D-3) and (D-8) for the mixture is shown in the figures D.1 and D.2 for the H₂O-MeOH system at 25°C and the H₂O-EtOH system at 25°C respectively.

D = Dielectric constant of the liquid solvent mixture
(electrolyte-free)

III - if the experimental solvent mixture dielectric constant data are available, a six-constant polynomial is fitted to get the concentration dependency of the dielectric constant. The polynomial expression is then used to calculate the dielectric constant at a different concentrations.

$$D = A_1 + A_2 X_3' + A_3 X_3'^2 + A_4 X_3'^3 + A_5 X_3'^4 + A_6 X_3'^5 \quad (D-9)$$

The data given by Akerlöf (1932) for the mixture dielectric constant have been used in this work. The data at a constant composition has been represented as a function of temperature by

$$\ln D = 2.303 AD_1 + AD_2 \ln(T - 293.15) \quad (D-10)$$

The constants AD_1 and AD_2 are listed in the Tables D.4 and D.5 for the mixtures considered in this study.

IV - if the experimental data are not available, the dielectric constant of the solution is approximated using either equation (D-11) or (D-12)

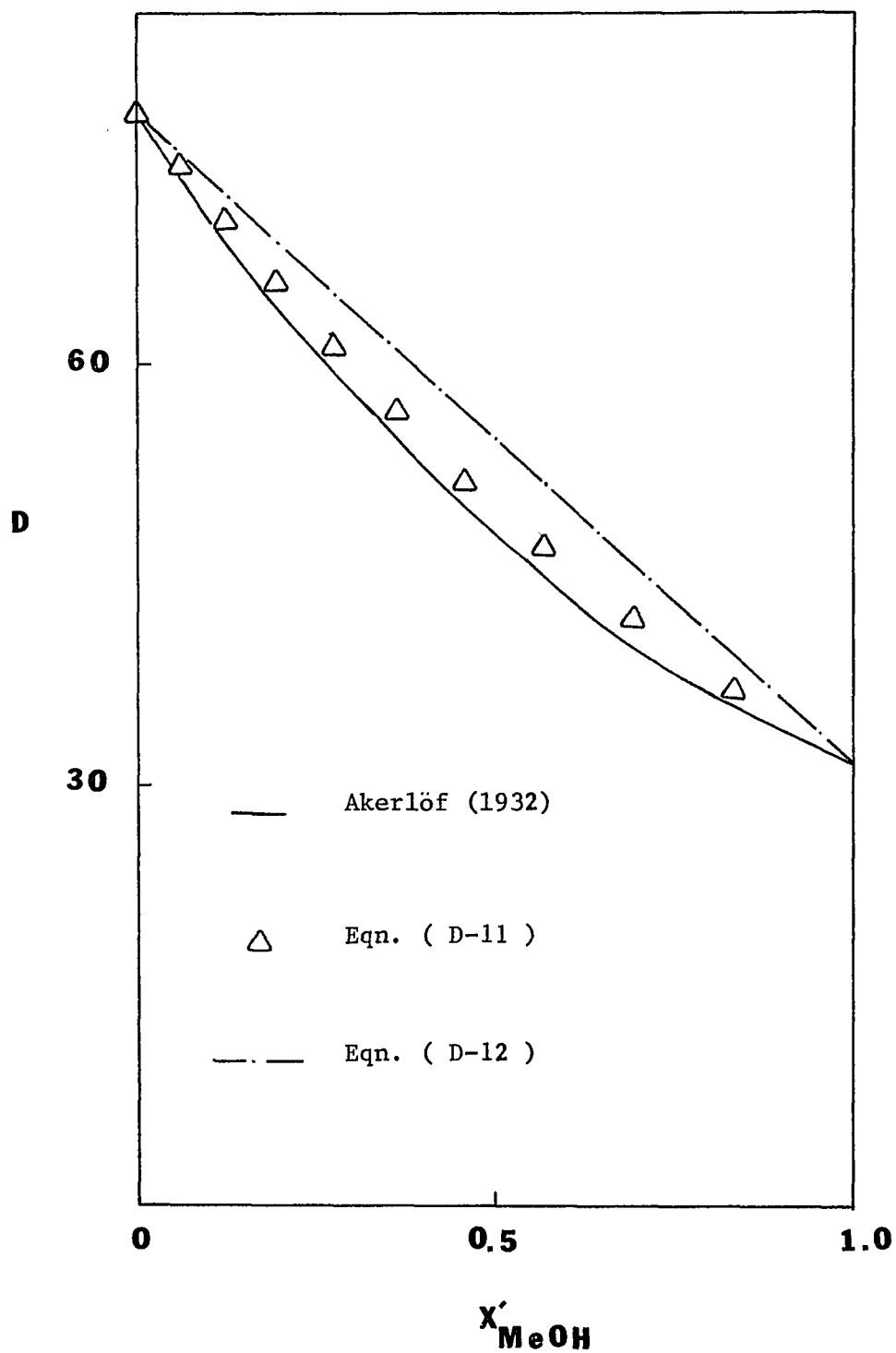


Figure D.3 Comparison of Experimental and Estimated Dielectric Constants of the Mixture H_2O -MeOH at $25^\circ C$

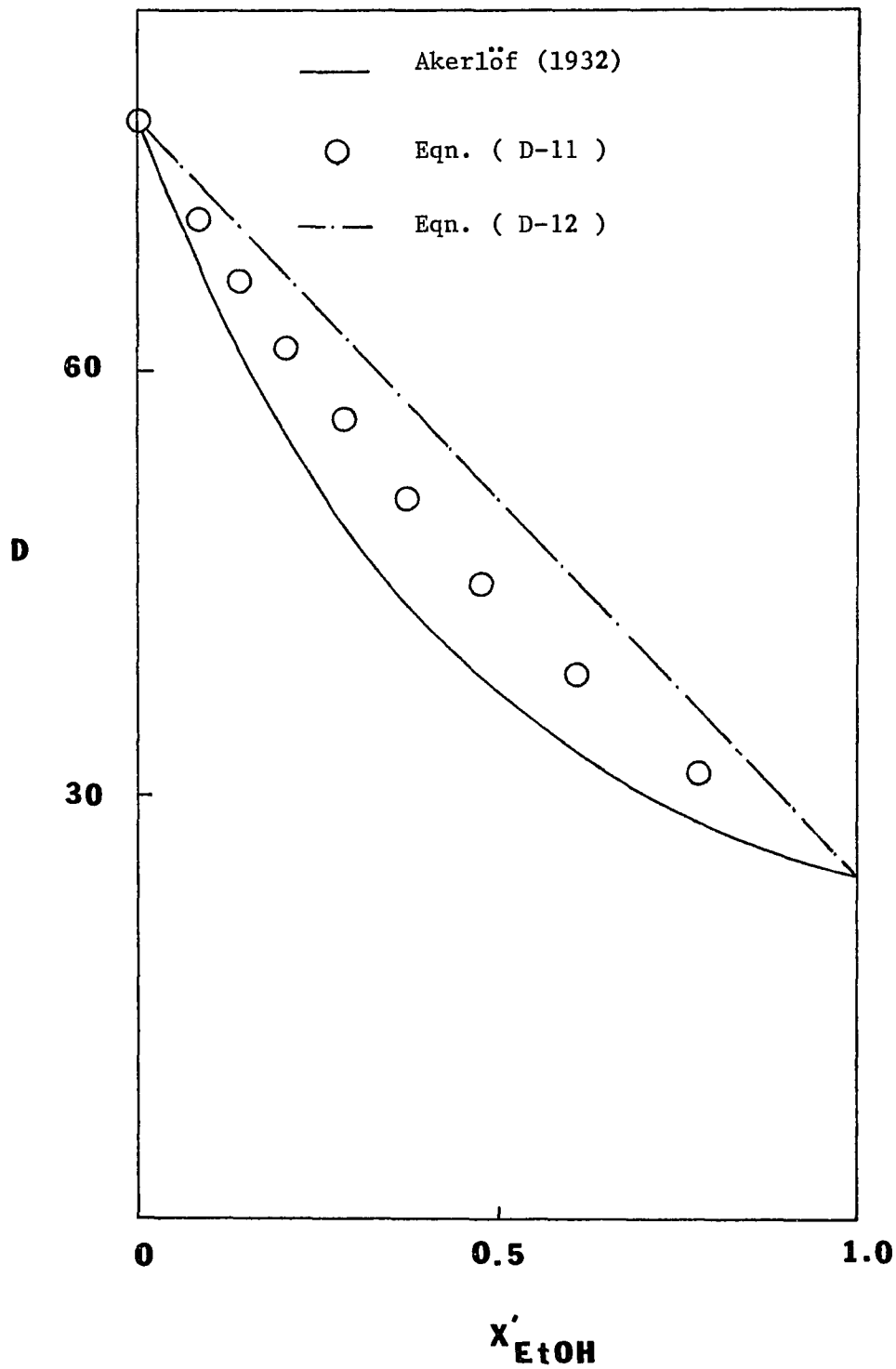


Figure D.4 Comparison of Experimental and Estimated Dielectric Constants of the Mixture $H_2O-EtOH$ at $25^\circ C$

$$D = D_2 \text{Exp}[AX_3'] \quad (\text{D-11})$$

where,

$$A = \ln\left[\frac{D_3}{D_2}\right] \quad [\text{Note: } D_3 < D_2]$$

or

$$D = D_2 X_2' + D_3 X_3' \quad (\text{D-12})$$

The experimental dielectric constant data are compared with the expressions (D-11) and (D-12) in figures (D.3) and (D.4) for the H₂O-MeOH system at 25°C and the H₂O-EtOH system at 25°C respectively.

Effect of Temperature on A_γ

The Debye-Hückel constant ' A_γ ' is $\propto \frac{1}{T^{3/2}}$ (equation D-2). Also, the dielectric constant and the density of the solvent are functions of temperature. Therefore A_γ is a strong function of temperature.

Effect of Pressure on A_γ

This work is limited only to low pressures. At low pressures, the liquid density and the dielectric constant can be considered to be pressure independent. Therefore A_γ has no effect of pressure.

Vapor-Pressure of the Pure Solvent

A six-parameter equation given in the monograph of Prausnitz et al. (1967) has been used to estimate the vapor pressures of the pure components, equation (1-24). Constants C_1 , C_2 , C_3 , C_4 , C_5 and C_6 are listed in Table D.6.

TABLE D.1
Liquid Molar Volume Data at Three Temperatures

Ref: Prausnitz et al. (1966)

<u>Solvent</u>	<u>T (°K)</u>	<u>v^{oL}, cc/gmole</u>
EtOH	273.15	57.141
	323.15	60.356
	373.15	64.361
MeOH	273.15	39.556
	373.15	44.874
	473.15	57.939
Water	277.15	18.06
	323.15	18.278
	373.15	18.844

TABLE D.2

Liquid Density Data for the H₂O-MeOH System @ 25°C

Ref: McGlashan (1976)

<u>X_{MeOH}</u>	<u>d, cc/gmole</u>
0.0	0.99707
0.04085	0.98472
0.06168	0.97919
0.11445	0.96649
0.19739	0.94796
0.24867	0.93658
0.34382	0.91534
0.49446	0.88242
0.61267	0.8579
0.69241	0.8421
0.78454	0.82458
0.89229	0.8051
1.0	0.78663

TABLE D.3

Liquid Density Data for the H₂O-EtOH System @ 25°C

Ref: Perry and Chilton (1973)

<u>X'_{EtOH}</u>	<u>d, cc/gmole</u>
0.0	0.99708
0.0417	0.98043
0.0891	0.96639
0.1436	0.95067
0.2069	0.93148
0.2813	0.90985
0.3699	0.88699
0.4773	0.86340
0.6102	0.83911
0.7788	0.81362
1.00	0.78506

TABLE D.4
 Constants for Calculating the Dielectric Constants of
 Water-EtOH Mixtures at Various Temperatures,
 Equation (D-10)

Ref: Akerlöf (1932)

<u>X_{EtOH}</u>	<u>A_{D1}</u>	<u>A_{D2}</u>
0.0	1.9051	-0.00205
0.0417	1.8727	-0.00209
0.0891	1.8367	-0.00214
0.1436	1.7968	-0.00221
0.2069	1.752	-0.0023
0.2813	1.7024	-0.0024
0.3699	1.6500	-0.0025
0.4773	1.5926	-0.00262
0.6102	1.530	-0.00272
0.7788	1.4625	-0.00268
1.00	1.3979	-0.00264

TABLE D.5
 Constants for Calculating the Dielectric Constants of
 Water-MeOH Mixtures at Various Temperatures,
 Equation (D-10)

Ref: Akerlöf (1932)

<u>x_{MeOH}</u>	<u>A_{D1}</u>	<u>A_{D2}</u>
0.0	0.19051	-0.00205
0.0588	1.8799	-0.00208
0.1233	1.8505	-0.00212
0.1942	1.8190	-0.00218
0.2727	1.7865	-0.00225
0.3600	1.7513	-0.00234
0.4576	1.7120	-0.00244
0.5676	1.6658	-0.00252
0.6923	1.616	-0.00248
0.8351	1.5648	-0.00242
1.00	1.5099	-0.00234

TABLE D.6

Constants for the Vapor Pressure, Equation (D-12)

<u>Solvent</u>	<u>C₁</u>	<u>C₂</u>	<u>C₃</u>	<u>C₄</u>	<u>C₅</u>	<u>C₆</u>	<u>Ref</u>
EtOH	123.9120350	-8754.0896	0.0	0.020198435	0.0	-18.1	Prausnitz et al. (1966)
MeOH	12.3858228	-3880.50203	0.0	-24.355	0.0	0.0	Hala (1969)
Water	70.4346943	-7362.6981	0.0	0.006952085	-	-9.0	Prausnitz et al. (1966)

APPENDIX E

CALCULATION OF FUGACITY COEFFICIENTS AND
POYNTING EFFECT

The following two data points are used for the calculation of ϕ_i^O , $\hat{\phi}_i^V$, P.E. and F_i --

[Ref: Hala (1968)]

Point #	System	T(°C)	X ₃ ¹	Y ₃	P (mmHg)
1	H ₂ O(2)-MeOH(3)	60	0.0343	0.2106	183.64
2	H ₂ O(2)-MeOH(3)	60	0.7582	0.901	538.64

Pure component second virial coefficients for H₂O and MeOH and the cross-virial coefficient for H₂O-MeOH mixture are estimated by Pitzer's correlations, [Smith and VanNess (1973)]

$$B^O = 0.083 - \frac{0.422}{T_r^{1.6}} \quad (E-1)$$

$$B^1 = 0.139 - \frac{0.172}{T_r^{4.2}} \quad (E-2)$$

$$B_{ij} = (B^O + \omega B^1) \frac{RT_c}{P_c} \quad (E-3)$$

Pure component liquid molar volumes and pure component vapor pressures are calculated as shown in Appendix D.

The mixture properties necessary to estimate the cross-virial coefficient of the mixtures are calculated by

$$T_{cij} = \sum_{i=2}^3 y_i T_{ci} \quad (E-4)$$

$$P_{cij} = \sum_{i=2}^3 y_i P_{ci} \quad (E-5)$$

$$\omega_{ij} = \sum_{l=2}^3 Y_l \omega_l \quad (\text{E-6})$$

$$\delta_{23} = 2B_{23} - B_{22} - B_{33} \quad (\text{E-7})$$

Applying equations (E-4) to (E-7) with equations (E-1) to (E-3) the cross-properties for the two data points are listed in Table E.2.

The pure component properties listed in Table E.1 and the mixture properties presented in Table E.2 are used in equations (1-5), (1-6), (1-8) and (1-10) to calculate ϕ_i^O , $(P.E.)_i$, $\hat{\phi}_i^V$ and F_i (see Tables E.3 and E.4 for the two data points).

The values of F_i in Tables E.3 and E.4 for H_2O and $MeOH$ justifies the assumption that, at low pressures, $F_i \approx 1.0$.

TABLE E.1

Pure Component Properties

Component	v_i^{OL} (cc/gmole)	P_1^O (mmHg)	B_i^O	B_i^1	ω_i	B_{ii} (cc/gmole)
H ₂ O	18.364	149.383	-1.13793	-2.6577	0.348	-503.4
MeOH	41.8187	634.315	-0.75793	-0.91993	0.556	-665.9

TABLE E.2

Mixture Properties

Point #1	ω_{23}	B_{23} (cc/gmole)	δ_{23} (cc/gmole)
1	0.3912	-513.0	143.3
2	0.5354	-622.3	-75.3

TABLE E.3

 ϕ_i^O , P.E., $\hat{\phi}_i^V$ and F_i for Data Point #1

Component	ϕ_i^O	(P.E.) _i	$\hat{\phi}_i^V$	F_i
H ₂ O	0.99556	1.00003	0.99562	1.0009
MeOH	0.99413	0.99909	0.99492	1.0075

TABLE E.4

 ϕ_i^O , P.E., $\hat{\phi}_i^V$ and F_i for Data Point #2

Component	ϕ_i^O	(P.E.) _i	$\hat{\phi}_i^V$	F_i
H ₂ O	0.98703	1.00034	0.98548	0.9981
MeOH	0.98288	0.9998	0.98288	1.0002

APPENDIX F

COMPUTER PROGRAMS

CORRELATION AND PREDICTION OF ACTIVITY COEFFICIENTS: TOTAL
PRESSURE AND VAPOR PHASE COMPOSITIONS

This appendix contains the following programs:

F.1 Main Program

Calls subroutines INPDAT, LSQ2, FIBN, TITLE. The main program reads the different indicating markers to perform correlation or prediction of binary or ternary VLE. The comment cards included in this section explain the different options used in this program.

F.2 INPDAT

Subroutine reads the input data.

F.3 FITIT [calls POLIFI]

Subroutine fits a polynomial of degree 5.

F.4 POLIFI

Subroutine makes a least-square fit for FITIT [calls subroutine DETERM].

F.5 DETERM

Subroutine performs the error analysis for POLIFI.

F.6 VAPPRE

Subroutine calculates the pure component vapor pressures at the system temperature [Equation (1-24)].

F.7 TEMPD

Subroutine calculates pure component liquid molar volumes at the system temperature. This also calculates the dielectric-constant of the mixtures. This calls subroutine FITIT to obtain the polynomial constants for the concentration dependence of the dielectric constants at the system temperature.

The following equations are used for the temperature dependence.

For the liquid molar volume

$$V = A + BT + CT **2$$

Where A, B, C - constants. T - temperature of the system.

For the dielectric constant

$$DS = EXP [2.303(ADT1 + ADT2 (T - 293.15))]$$

Where ADT1, ADT2 - Constants for the temperature dependency of a solvent mixture. T - temperature of the system. DS - dielectric constant of the mixture (see Appendix-D).

F.8 LSQ2

Subroutine applies a search technique to find the best unknown variables that will result in the minimum value of an objective function [number of variables should be greater or equal to 2]. Calls subroutine FN.

F.9 FN

Subroutine calls different subroutines to calculate the different contributions for the activity coefficients in two models. Finally it calls subroutine MINFUN to set up the objective function. Calls subroutines NRTL1, BROML, ADITON, NRTL2, DEBHUC, VAPPRE, MINFUN.

F.10 FIBN

Subroutine applies the Fibonacci method to find the one unknown variable that will minimize the non-linear objective function.

F.11 FUNCT

Subroutine calls different subroutines as in subroutine FN.

F.12 NRTL1

Subroutine calculates solvent-solvent interaction contributions of the activity coefficients in a ternary mixture using the simplified and the modified form of the NRTL equation in Model #2 [see Chapter 3; Equation (2-4)].

F.13 BROML

Subroutine calculates ion-ion and ion-solvent interaction contributions of the activity coefficients in a binary or ternary mixture using the Bromley equation in Model #2 [see Chapter 3; Equations (3-8), (3-12) and (C-9)].

F.14 ADITON

Subroutine calculates salting-out contribution for the activity coefficients in a ternary mixture in Model #2 [see Chapter 3; Equations (3-10) and (3-14)].

F.15 FUNCB

Subroutine for mixing rule for the Bromley parameter in a ternary mixture [see Chapter 3; Equation (3-3)].

F.16 FUNCT

Subroutine calculates the Debye-Huckel constant of mixtures and derivatives of the Debye-Huckel constant with respect to the number of moles of solvents [see Appendix-D].

F.17 NRTL2

Subroutine calculates ion-solvent and solvent-solvent interaction contributions of the activity coefficient in a binary or ternary mixture using the modified NRTL equation in Model #1 [see Chapter 2; Equations (2-7), (2-14) and (2-17)].

F.18 DEBHUC

Subroutine calculates ion-ion interaction contributions for the activity coefficients in a binary or ternary mixture in Model #1 [see Chapter 2; Equations (2-13) and (2-16)].

F.19 MINFUN

Subroutine sets up the objective function.

F.20 TITLE

Subroutine makes tables for output results.

The comment cards included in the programs are assumed to make this program self-explanatory.

MAIN PROGRAM -

THIS PROGRAM IS TO CORRELATE OR PREDICT EITHER BINARY
OR TERNARY VLE DATA OR BINARY & TERNARY VLE DATA
TOGETHER. THE PROGRAM CAN BE USED EITHER FOR ISOBARIC
OR ISOTHERMAL DATA.

A BINARY IN THIS WORK IS DEFINED AS A MIXTURE OF
EITHER TWO SOLVENTS OR ONE ELECTROLYTE AND ONE SOLVENT.
A TERNARY MIXTURE IS DEFINED AS A MIXTURE OF ONE
ELECTROLYTE AND TWO SOLVENTS.

THIS PROGRAM IS WRITTEN BY ANIL K. RASTOGI AT THE
NEW JERSEY INSTITUTE OF TECHNOLOGY AS A PART OF
DOCTORAL DISSERTATION, YEAR 1981.

NSET - # OF SYSTEM DATA TO BE USED
LL - TOTAL # OF TRIAL TO BE USED IN LSQ2
EE - TOLERANCE ERROR FOR THE LSQ2

NAME(J) - INFORMATION ABOUT THE SYSTEM ; J=10; 20 CARDS
XLIM - (MAXIMUM MOLALITY - 1) RANGE OF THE ELECTROLYTE
XLLIM - MINIMUM MOLALITY RANGE OF THE ELECTROLYTE
NAME1,ETC- NAME OF THE SYSTEM TO BE USED

INDF - # OF INCREMENTS TO BE GIVEN FOR THE MAXIMUM
MOLALITY RANGE

KP - = 1 EQUATIONS USED ARE BROOMLEY;SIMPLIFIED NRTL1;
AND SALTINGOUT.(MODEL # 2 IN THE THESIS)
= 2 EQUATIONS USED ARE EXTENDED DEBYE-HUCKEL &
NRTL2.(MODEL # 1 IN THE THESIS)

NBIN - (WHEN KP=1)
= 1 PARAMETER B012 REGRESSED

C = 2 PARAMETER B013 REGRESSED
 C = 3 PARAMETER B123 OR DELTA REGRESSED (WHEN M=1)
 C = 3 PARAMETERS B123 & DELTA REGRESSED (WHEN M=2)
 C - (WHEN KP=2)
 C = 1 GPN2 & ZPN2 REGRESSED (IF NNRTL=2)
 C = 1 DGA2 & DGB2 REGRESSED (IF NNRTL=1)
 C = 2 GPN3 & ZPN3 REGRESSED (IF NNRTL=2)
 C = 2 DGA3 & DGB3 REGRESSED (IF NNRTL=1)
 C = 4 DG23 & DG32 REGRESSED
 C = 5 GPN2,ZPN2,GPN3 & ZPN3 REGRESSED (IF NNRTL=2)
 C = 5 DGA2,DGB2,DGA3 & DGB3 REGRESSED (IF NNRTL=1)
 C
 C NPIÓN - TYPE OF POSITIVE ION FOR THE CRYSTALLOGRAPHIC RADII
 C = 1 H ION
 C = 2 LI ION
 C = 3 NA ION
 C = 4 CA ION
 C NNION - TYPE OF NEGATIVE ION FOR THE CRYSTALLOGRAPHIC RADII
 C = 1 BR ION
 C = 2 CL ION
 C NREG - = 1 VLE DATA ARE PREDICTED
 C = 2 VLE DATA ARE CORRELATED
 C NDEN - = 1 EXPERIMENTAL DATA ARE USED FOR THE DENSITY. A
 C SIX PARAMETER POLYNOMIAL IS USED FOR THE CONCENTRATI
 C DEPENDENCY OF THE DENSITY.
 C = 2 AN APPROXIMATE RELATIONSHIP FOR THE DENSITY IS
 C USED (= MW/VS)
 C NBRDM - = 1 DELTA IS FIXED AND B123 IS REGRESSED (M=1)
 C = 2 B123 IS FIXED AND DELTA IS REGRESSED (M=1)
 C NTYPE - = 1 DATA OF BINARY 1-2 ARE REGRESSED
 C = 2 DATA OF BINARY 1-3 ARE REGRESSED
 C = 3 DATA OF BINARY 2-3 ARE REGRESSED
 C = 4 DATA OF TERANARY 1-2-3 ARE REGRESSED
 C = 5 DATA OF TERNARY 1-2-3 & BINARY 1-3 REGRESSED
 C = 6 DATA OF TERNARY 1-2-3 & BINARY 1-2 REGRESSED
 C = 7 DATA OF TERNARY 1-2-3 & BINARY 2-3 REGRESSED
 C = 8 DATA OF TERNARY 1-2-3 & BINARY 1-2 & BINARY 1-3
 C REGRESSED
 C = 9 DATA OF TERNARY 1-2-3 & BINARY 1-2 & BINARY 1-3
 C & BINARY 2-3 REGRESSED
 C
 C NMIN - INTEGER FOR THE DIFFERENT OBJECTIVE FUNCTION
 C = 1 SUM OF ((GCAL-GEXP)/GEXP)**2. IS MINIMIZED
 C = 2 SUM OF (DP/PEXP)**2. + (DY*10.))**2. IS MINIMIZED
 C = 3 SUM OF ((GCAL-GEXP)/GEXP)**2. + (DY*10.))**2. IS
 C MINIMIZED
 C = 4 SUM OF ((DPCAL-DPEXP)/DPEXP)**2. IS MINIMIZED FOR
 C THE BINARY
 C
 C ALFA - ALFA FOR ~~THE~~ NON-ELECTROLYTE BINARY IN THE NRTL

```

C          EQUATION
C      DG23,DG32- NON-ELECTROLYTE BINARY PARAMETERS IN THE NRTL
C          EQUATION
C      ALFA2,ALFB2- IONIC ALFAS FOR 1-2 & 1-3 BINARIES (EQ. 2-6 )
C      ALFA3,ALFB3
C
C      DGA2,DGB2, - TEMPERAURE INDEPENT PARAMETERS IN THE MODIFIED
C      DGA3,DGB3   NRTL EQUATION FOR THE IONS (EQ. 2-6 )MODEL#1
C
C      GPN2,ZPN2, - IONIC PARAMETERS IN THE MODIFIED NRTL EQUATION
C      GPN3,ZPN3   MODEL # 1 ( EQ. 2-5 )
C
C      B012,B112, - BROMLEY BINARY TEMPERATURE INDEPENT PARAMETRES
C      B013,B113   MODEL # 2 (CHAPTER 3 )
C
C      B123       - TERNARY ADJUSTABLE PARAMETER FOR THE MIXING RULE IN
C                  THE BROMLEY EQUATION
C      DELTA      - TERNARY SALTING OUT PARAMETER FOR THE MODEL # 2
C
C      ALPHA1     - TOLERANCE LIMIT FOR THE FIBBNAUCHI SUBROUTINE
C      AXT1,BXT1  - PARAMETER LIMITS FOR THE FIBBNAUCHI SUBROUTINE
C
C      M          - INTEGER TO SPECIFY # OF PARAMETER TO BE REGRESSED
C                  = 1 ONE PARAMETER (B012 OR B013 OR B123 OR DELTA)
C                  = 2 MORE THAN 1 PARAMETER
C
C      XTX        - INITIAL VALUES OF THE PARAMETERS FOR THE LSQ2
C      DXX        - INCREMENT FOR THE PARAMETERS IN THE LSQ2

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C      *****

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```

C      COMMON XXMOL(99),XX(3,99),XXF(3,99),GG(3,99),FF(99),YY(3,99),
C      Z GNRT(3,99),GEL(3,99),GCAL(3,99),AMW(3),ERROR(3,99)
C      Z ,GDH(3,99),GPHY(3,99),TTT(99),BM(99),GADD(3,99)
C      Z ,YCAL(3,99),ADD(6),PTC(99)
C      COMMON NP,INDF,FNF,FNM,FZP,FZN,FK,ALFA,DG23,DG32,GPN2,
C      Z GPN3,ZPN2,ZPN3,KP,M,NBIN,NPION,NNION,DELTA
C      COMMON NDEN,NNRTL,ALFA2,ALFB2,ALFA3,ALFB3,DGA2,DGB2,
C      DG23,DG32,Z23,Z32 - CAL/SMOLE-K

```

```

C      *****

```

```

C      Z DGA3,DGB3,NBROM,NREG,NTYPE,NMIN
C      COMMON B012,B112,B013,B113,CP2(6),CP3(6),CV2(3),CV3(3),
C      Z B123,ADT(2,20),NXD,XD(20)

```

```

DIMENSION YU(3,99),XL(3,99),P(99),XMOL(99),XF(3,99),
% G(3,99),T(99),PSM(3),DY(99),DP(99)
REAL *8 NAME(10)
REAL *8 NAME1,NAME2,NAME3

C
C
C
DIMENSION XT(6),DX(6),Y(7),X(7,10),XTX(6),DXX(6)
READ(5,9001)NSET,LL,EE
9001  FORMAT(2I3,F10.1)
      WRITE(6,9002)NSET,LL,EE
9002  FORMAT('1',10X,' # OF DATA SET TO BE USED =',I3,' TRIAL
% I3,'E=',F10.8)
      DO 9110 JAN=1,NSET
      DO 4100 I=1,20
      READ(5,2100)(NAME(J),J=1,10)
      WRITE(6,2100)(NAME(J),J=1,10)
4100  CONTINUE
2100  FORMAT(10A8)
      READ(5,2200)XLIM,XLLIM
      WRITE(6,2200)XLIM,XLLIM
2200  FORMAT(2F10.5)
      READ(5,6080)NAME1,NAME2,NAME3
6080  FORMAT(3A8)
      READ(5,2300)INDF,KP,NBIN,NPION,NNION,NREG,NDEN,NNRTL,
1 ,NTYPE,NMIN
      WRITE(6,2300)INDF,KP,NBIN,NPION,NNION,NREG,NDEN,NNRTL
1 ,NTYPE,NMIN
2300  FORMAT(11I2)
      CALL INPDAT(XL,XF,XMOL,T,AMW,FK,FNP,FNM,FZP,FZN,
% G,NPT,YU,P,NCOMP,ADD,CV2,CV3,CP2,CP3,ADT,NXD,XD)
2400  FORMAT(8F10.5)
      READ(5,2400)ALFA,DG23,DG32,ALFA2,ALFB2,ALFA3,ALFB3
      WRITE(6,2400)ALFA,DG23,DG32,ALFA2,ALFB2,ALFA3,ALFB3
      READ(5,2400)GPN2,ZFN2,GPN3,ZFN3,DGA2,DGB2,DGA3,DGB3
      WRITE(6,2400)GPN2,ZFN2,GPN3,ZFN3,DGA2,DGB2,DGA3,DGB3
      READ(5,2400)BO12,B112,BO13,B113,B123,DELTA
      WRITE(6,2400)BO12,B112,BO13,B113,B123,DELTA
      READ(5,9141)ALPHA1,AXT1,BXT1
      WRITE(6,9141)ALPHA1,AXT1,BXT1
9141  FORMAT(F10.7,2F10.4)
      READ(5,2300)M,MM
      WRITE(6,2300)M,MM
      DO 4400 I=1,MM
      READ(5,2600)XTX(I),DXX(I)
      WRITE(6,2600)XTX(I),DXX(I)
4400  CONTINUE
2600  FORMAT(2F10.4)
C
C
INITIALIZATION  FOR THE LSQ2

```

C
C
C

DO 4300 KJ=1,INDF
DO 4200 JJ=1,7
DO 4200 JI=1,10
X(JJ,JI)=0.0
4200 CONTINUE

C
C
C

DO 4401 IK=1,MM
XT(IK)=XTX(IK)
DX(IK)=DXX(IK)
4401 CONTINUE
ALPHA=ALPHA1
AXT=AXT1
BXT=BXT1

C
C
C
C
C
C

THIS PART OF THE MAIN PROGRAM SPECIFIES THE TYPE OF
DATA TO BE USED. ALSO DATA ARE CONVERTED INTO DIFFERENT
SYMBOLS FOR MINIMUM AND MAXIMUM MOLALITY LIMITS.

XLIM=XLIM+1.0
J=0
WRITE(6,2410)XLIM
2410 FORMAT('1',5X,'*****MAXIMUM MOLALITY USED=',F10.5)
DO 4310 I=1,NPT
GO TO (9901,9902,9003,9004,9005,9006,9007,9008,9000),NTYPE
9901 IF(XL(3,I).EQ.0.0)GO TO 9000
GO TO 4310
9902 IF(XL(2,I).EQ.0.0)GO TO 9000
GO TO 4310
9003 IF(XMDL(I).EQ.0.0)GO TO 9000
GO TO 4310
9004 IF(XMDL(I).EQ.0.0)GO TO 4310
IF(XL(2,I).EQ.0.0)GO TO 4310
IF(XL(3,I).EQ.0.0)GO TO 4310
GO TO 9000
9005 IF(XMDL(I).EQ.0.0)GO TO 4310
IF(XL(3,I).EQ.0.0)GO TO 4310
GO TO 9000
9006 IF(XMDL(I).EQ.0.0)GO TO 4310
IF(XL(2,I).EQ.0.0)GO TO 4310
GO TO 9000
9007 IF(XL(2,I).EQ.0.0)GO TO 4310
IF(XL(3,I).EQ.0.0)GO TO 4310
GO TO 9000

```

9008 IF(XMDL(I).EQ.0.0)GO TO 4310
9000 IF(XMDL(I).LT.XLLIM)GO TO 4310
      IF(XMDL(I).LE.XLIM)GO TO 3100
      GO TO 4310
3100  J=J+1
      NP=J
      YY(2,J)=YV(2,I)
      YY(3,J)=YV(3,I)
      PP(J)=P(I)
      TTT(J)=T(I)
      XXMDL(J)=XMDL(I)
      XX(1,J)=XL(1,I)
      XX(2,J)=XL(2,I)
      XX(3,J)=XL(3,I)
      XXF(2,J)=XF(2,I)
      XXF(3,J)=XF(3,I)
      GG(1,J)=G(1,I)
      GG(2,J)=G(2,I)
      GG(3,J)=G(3,I)
4310  CONTINUE
      IF(KP.LE.1)MO=2
      IF(KP.GT.1)MO=1

```

```

C
C
C
C
C

```

PROGRAM FOR THE PREDICTION

```

IF(NREG.GT.1)GO TO 110
WRITE(6,160)MO
160  FORMAT(/,5X,' VLE DATA ARE PREDICTED USING MODEL #',I3)
      LIC=1
      CALL FN(YYD,XT,LIC)
      GO TO 3300

```

```

C
C
C
C
C

```

PROGRAM FOR THE CORRELATION

```

110  WRITE(6,170)KP
170  FORMAT(/,5X,' VLE DATA ARE CORRELATED USING MODEL #',I3)
      IF(M.GT.1)GO TO 3200
      CALL FIBN(ALPHA,AXT,EXT)
      GO TO(240,250,260),NBIN
240  WRITE(6,270)B012
270  FORMAT(/,10X,' B012 =',G12.5)
      GO TO 3300
250  WRITE(6,280)B013
280  FORMAT(/,10X,' B013 =',G12.5)
      GO TO 3300
260  GO TO(210,220),NBROM

```

```

210  WRITE(6,290)B123
290  FORMAT(/,10X,'B123 =',G12.5)
     GO TO 3300
220  WRITE(6,300)DELTA
300  FORMAT(/,10X,'DELTA =',G12.5)
     GO TO 3300
3200 L=LL
     E=EE
     M1=M+1
     M3=M+3
     CALL LSR2(XT,X,DX,Y,M,M1,M3,L,E)
     WRITE(6,2800)(I,XT(I),I=1,M)
2800  FORMAT(/,5X,' FINAL VALUES OF XT(',I2,')=',E15.8)
     WRITE(6,2900)(I,Y(I),I=1,M1)
2900  FORMAT(/,5X,' Y(',I2,')=',E15.8)
C
C
C   FROM HERE MAIN PROGRAM ARRANGES THE OUTPUT
C
C
C
C
C   GCAL(J,I)   - CALCULATED ACTIVITY COEFFICIENT
C   GG(J,I)    - EXPERIMENTAL ACTIVITY COEFFICIENT
C   ERROR(J,I) - % ERROR IN ACTIVITY COEFFICIENT
C
C   ALL THE SEPARATE PARTS LISTED BELOW ARE IN THE LN FORM.
C
C   GDH(J,I)   - DEBYE-HUCKEL PART OF THE ACTIVITY COEFFICIENT
C   GPHY(J,I)  - EXTENDED D.H. PART OF THE COULOMBIC TERMS
C               BESIDES D.H. PART IN THE ACTIVITY COEFFICIENT
C   GADD(J,I)  - SALTING OUT CONTRIBUTION TO THE ACTIVITY COEFFICI
C   GNRT(J,I)  - NRTL CONTRIBUTION TO THE ACTIVITY COEFFICIENT
C
C
C
3300  YSUM=0.0
     PSUM=0.0
     NV=0
     NVF=0
     DO 4530 I=1,NF
     IF(XXMOL(I).EQ.0.0)GO TO 3400
     IF(XX(3,I).EQ.0.0)GO TO 3401
     IF(XX(2,I).EQ.0.0)GO TO 3402
     IF(GG(1,I).EQ.1.0)GO TO 3400
     IF(GG(2,I).EQ.1.0)GO TO 3405
     GO TO 3416
3405  GG(2,I)=1.0 E 58
     GG(3,I)=1.0 E 58
     ERROR(2,I)=1.0 E 58
     ERROR(3,I)=1.0 E 58

```



```

      GO TO 3415
3401  GG(3,I)=1.0 E 58
      ERROR(3,I)=1.0 E 58
      IF(GG(2,I).EQ.1.0)GO TO 3403
      IF(GG(1,I).EQ.1.0)GO TO 3400
      GO TO 3415
3403  GG(2,I)=1.0 E 58
      ERROR(2,I)=1.0 E 58
      GO TO 3415
3402  GG(2,I)=1.0 E 58
      ERROR(2,I)=1.0 E 58
      IF(GG(3,I).EQ.1.0) GO TO 3404
      IF(GG(1,I).EQ.1.0) GO TO 3400
      GO TO 3415
3404  GG(3,I)=1.0 E 58
      ERROR(3,I)=1.0 E 58
      GO TO 3415
3400  GG(1,I)=1.0 E 58
      ERROR(1,I)=1.0 E 58
      IF(XX(2,I).EQ.0.0)GO TO 3415
      IF(XX(3,I).EQ.0.0)GO TO 3415
3416  DP(I)=PTC(I)-PP(I)
      PSUM=PSUM+ABS(DP(I))
      NVP=NVP+1
3410  NV=NV+1
      DY(I)=YCAL(3,I)-YY(3,I)
      YSUM=YSUM+ABS(DY(I))
      WRITE(6,2110)
2110  FORMAT(/,4X,'COMPONENT #',2X,'MOLE-FRACTION',8X,'YEXP ',8X,'
% YCAL ',10X,'YCAL-YEXP',7X,'PCAL-PEXP')
2115  FORMAT(8X,I2,5(5X,F12.5))
      DO 4520 J=2,NCOMP
      WRITE(6,2115)J,XX(J,I),YY(J,I),YCAL(J,I),DY(I),DP(I)
4520  CONTINUE
3415  WRITE(6,2120)
2120  FORMAT('- ',2X,' COMPONENT #',3X,' MOLALITY ',2X,' LOG NRTL ',
% 2X,' LOG COULOMBIC ',1X,' LOG PHYSICAL ',1X,' LOG ADDITION ',
% 3X,' GAM CAL ',2X,' GAM EXP ', 2X,' % ERROR IN GAMA ')
      DO 4530 J=1,NCOMP
      WRITE(6,2125)J,XXMOL(I),GNRT(J,I),GDH(J,I),GPHY(J,I),GADD(J,I),
% GCAL(J,I),GG(J,I),ERROR(J,I)
4530  CONTINUE
2125  FORMAT(8X,I2,8X,G10.3,3X,G10.3,5X,G10.3,4X,G10.3,5X,G10.3,4X,
% G10.3,3X,G10.3,4X,G10.3)
C
C
C   TABLE FOR THE MEAN MOLAL ACTIVITY COEFFICIENT
C
C   CALL TITLE(NAME1,NAME2,NAME3,ALFA,DG23,DG32,GPN2,GPN3,ZPN2,

```

```

% ZPN3,B012,B013,B112,B113,B123,DELTA,KP,NTYPE,XX(2,1),
% XXMOL(1),NNRTL,DGA2,DGA3,DGB2,DGB3,ALFA2,ALFB2,ALFA3,
% ALFB3)
WRITE(6,7165)
7165  FORMAT(/,4X,'MOLALITY',5X,'X2',10X,'X3',6X,'MEANMOLALGAM',1X,
% 'MEANMOLALGAM',2X,'%ERROR')
WRITE(6,7167)
7167  FORMAT(37X,'EXPERIMENTAL',2X,'CALCULATED')
      GSUM=0.0
      NS=0
      DO 8110 I=1,NP
      IF(ERROR(1,I).GE.1.0 E 58)GO TO 8110
      NS=NS+1
      GSUM=GSUM+ABS(ERROR(1,I))
      WRITE(6,7170)XXMOL(I),XX(2,I),XX(3,I),GG(1,I),GCAL(1,I),
% ERROR(1,I)
7170  FORMAT(2X,6G12.5)
8110  CONTINUE
      IF(NS.LE.0)NS=1
      GMEAN=GSUM/NS
7180  FORMAT(//,6X,'AVG ZERROR IN MEAN MOLAL ACTIVITY COEFFICIENTS
% ',6G12.5)
      WRITE(6,7181)NS
7181  FORMAT(7X,' BASED ON #OF POINTS FOR GAMA SALT=',I3)
C
C
C   TABLE FOR TERNARY Y & P
C
C
      CALL TITLE(NAME1,NAME2,NAME3,ALFA,DG23,DG32,GPN2,GPN3,ZPN2,
% ZPN3,B012,B013,B112,B113,B123,DELTA,KP,NTYPE,XX(2,1),
% XXMOL(1),NNRTL,DGA2,DGA3,DGB2,DGB3,ALFA2,ALFB2,ALFA3,
% ALFB3)
      WRITE(6,7190)
7190  FORMAT(//,2X,'MOLALITY',3X,'X2',10X,'X3',8X,'Y3EXP',8X,'Y3CAL'
% ,5X,'DY',9X,'DP')
      DO 8220 I =1,NP
      IF(XX(2,I).EQ.0.0) GO TO 8220
      IF(XX(3,I).EQ.0.0) GO TO 8220
      WRITE(6,7195)XXMOL(I),XX(2,I),XX(3,I),YY(3,I),YCAL(3,I)
% ,DY(I),DP(I)
7195  FORMAT(6G10.3,4G12.5,2G10.3)
8220  CONTINUE
      IF(NV.LE.0)NV=1
      IF(NVP.LE.0)NVP=1
      DYAVG=YSUM/NV
      DPAVG=PSUM/NVP
      WRITE(6,7200) DYAVG
7200  FORMAT(///,10X,'AVERAGE DY(YCAL-YEXP)=' ,6G12.5)
?
```

```

WRITE(6,7201)NV
7201  FORMAT(9X,' BASED ON # OF POINTS FOR Y =',I3)
WRITE(6,7210)DPAVG
7210  FORMAT(///,10X,'AVERAGE DP(PCAL-PEXP)=' ,G12.5)
WRITE(6,7221)NVP
7221  FORMAT(9X,'BASED ON # OF POINTS FOR DP =',I3)
C
C
C   TABLE FOR THE BINARY DELTA F
C
C
CALL TITLE(NAME1,NAME2,NAME3,ALFA,DG23,DG32,GPN2,GPN3,ZPN2,
% ZPN3,B012,B013,B112,B113,B123,DELTA,KP,NTYPE,XX(2,1),
% XXMOL(1),NNRTL,DGA2,DGA3,DGB2,DGB3,ALFA2,ALFB2,ALFA3,
% ALFB3)
NDP=0
XDPSUM=0.0
WRITE(6,8290)
8290  FORMAT(//,2X,'MOLALITY',3X,'XSOLVENT',6X,'DPEXP',6X,'DPCAL',
% 2X,'% ERROR IN DP')
DO 8230 I=1,NP
CALL VAPPRE(CP2,CP3,PSM,TTT(I))
IF(XX(2,I).EQ.0.0)GO TO 8235
IF(XX(3,I).EQ.0.0)GO TO 8240
GO TO 8245
8235  IF(GG(3,I).EQ.1.0)GO TO 8245
DPEXP=PSM(3)-XX(3,I)*GG(3,I)*PSM(3)
DPCAL=PSM(3)-XX(3,I)*GCAL(3,I)*PSM(3)
PDF=(DPCAL-DPEXP)/DPEXP*100.0
XDP=XX(3,I)
GO TO 8250
8240  IF(GG(2,I).EQ.1.0)GO TO 8245
DPEXP=PSM(2)-XX(2,I)*GG(2,I)*PSM(2)
DPCAL=PSM(2)-XX(2,I)*GCAL(2,I)*PSM(2)
PDF=(DPCAL-DPEXP)/DPEXP*100.0
XDP=XX(2,I)
8250  WRITE(6,8255)XXMOL(I),XDP,DPEXP,DPCAL,PDF
8255  FORMAT(2X,G10.3,2G12.5,G10.3,G12.5)
NDP=NDP+1
XDPSUM=XDPSUM+ABS(PDF)
GO TO 8230
8245  NDP=1
8230  CONTINUE
PDPAVG=XDPSUM/NDP
WRITE(6,8265)PDPAVG
8265  FORMAT(///,6X,'AVG % ERROR IN DP =',G12.5)
WRITE(6,8270)NDP
8270  FORMAT(7X,'BASED ON # OF POINTS =',I3)
IF(KP.GT.1)GO TO 4300
WRITE(6,9220)

```

```
9220  FORMAT('1',4X,'MOLALITY',5X,'X3',10X,'BMIXTURE')
      WRITE(6,9230)(XXMOL(I),XXF(3,I),BM(I),I=1,NP)
9230  FORMAT(//,4X,G10.3,2G12.5)
4300  CONTINUE
      WRITE(6,7202)
7202  FORMAT('1')
9110  CONTINUE
      STOP
      END
```

```

SUBROUTINE INPDAT(X,XF,XMOL,T,AMW,FK,FNF,FNM,FZP,
% FZN,G,NP,Y,P,NCOMP,ADD,CV2,CV3,CP2,CP3,ADT,NXD,XD)

```

```

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SUBROUTINE INPDAT

```

```

THIS SUBROUTINE READS ALL INPUT VLE DATA AND PURE
COMPONENT DATA

```

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*****

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```

NCOMP      - # OF COMPONENTS (= 3 FOR THIS PROGRAM )
NP         - # OF DATA POINTS IN A SYSTEM
NXD       - # OF SOLUTION DIELECTRIC CONSTANT DATA POINTS
NXDD      - # OF SOLUTION DENSITY DATA POINTS
CP2,CP3   - PURE COMPONENT VAPOR PRESSURE CONSTANTS FOR THE
            COMPONENTS 2 & 3 RESPECTIVELY.
AMW(I)    - MOLECULAR WEIGHT OF THE COMPONENT I
V21,V22,V23 - PURE COMPONENT LIQUID VOLUMES AT DIFFERENT
V31,V32,V33 TEMPERATURES
CV2(I),   - TEMPERATURE DEPENDENT LIQUID VOLUME CONSTANTS
CV3(I)    - FOR THE COMPONENT 2 & 3 RESPECTIVELY.
ADT(1,I)  - DIELECTRIC CONSTANTS FOR A TEMPERATURE OF THE
ADT(2,I)  - SOLUTION.
XD(I)     - MOLE-FRACTION OF THE SOLVENT(3) IN THE SOLUTION
            FOR THE DIELECTRIC CONSTANTS(ELECTROLYTE FREE)
FK        - TOTAL # OF IONS OF THE ELECTROLYTE
FNF       - # OF POSITIVE IONS IN THE ELECTROLYTE
FNM       - # OF NEGATIVE IONS IN THE ELECTROLYTE
FZP       - POSITIVE ION VALENCY(ABSOLUTE UNITS)
FZN       - NEGATIVE ION VALENCY(ABSOLUTE UNITS)
DENS(I)   - DENSITY OF THE SOLUTION(ELECTROLYTE FREE)
XDD(I)    - MOLE-FRACTION OF THE SOLVENT(3) IN A SOLUTION
            FOR THE DENSITY DENS(I).

XMOL(I)   - MOLALITY OF THE I TH POINT
X(J,I)    - LIQUID MOLE FRACTION ; J DENOTES COMPONENT
            I DENOTES I TH POINT
Y(J,I)    - VAPOR PHASE MOLE FRACTION
G(J,I)    - EXPERIMENTAL VALUES OF THE ACTIVITY COEFFICIENT
P(I)      - TOTAL PRESSURE OF THE SYSTEM
T(I)      - TEMPERATURE OF THE SYSTEM
XF(J,I)   - SOLVENT MOLE FRACTIONS(ELECTROLYTE FREE)
PSM(J)    - PURE COMPONENT VAPOR PRESSURE OF THE COMPONENT
            J AT THE SYSTEM TEMPRATURE.

```

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*****

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```

C
C
      DIMENSION X(3,99),XF(3,99),AMW(3),G(3,99),Y(3,99),P(99),
% ADD(6),T(99),PSM(3),XMOL(99),DENS(20),XDD(20)
      DIMENSION CV2(3),CV3(3),CP2(6),CP3(6),ADT(2,20),XD(20)

C
C
C
      WRITE(6,1000)
1000  FORMAT(' ',5X,' INPUT DATA ')
      READ(5,2000)NCOMP,NP,NXD,NXDD
2000  FORMAT(4I2)
      WRITE(6,2000)NCOMP,NP,NXD,NXDD
      READ(5,2100)(CP2(I),I=1,6)
      READ(5,2100)(CP3(I),I=1,6)
      WRITE(6,2100)(CP2(I),I=1,6)
      WRITE(6,2100)(CP3(I),I=1,6)
2100  FORMAT(F12.7,F11.5,F8.3,F13.9,F3.1,F10.5)
      READ(5,2200)(AMW(I),I=1,NCOMP)
2200  FORMAT(6F10.5)
      WRITE(6,2200)(AMW(I),I=1,NCOMP)
      READ(5,2200)V21,T21,V22,T22,V23,T23
      WRITE(6,2200)V21,T21,V22,T22,V23,T23
      READ(5,2200)V31,T31,V32,T32,V33,T33
      WRITE(6,2200)V31,T31,V32,T32,V33,T33

C
C
      CALCULATION OF LIQUID MOLAR VOLUME CONSTANTS USING
      THREE VALUES OF LIQUID MOLAR VOLUME AT THREE
      DIFFERENT TEMPERATURES.

C
C
      CV2(3)=((T23-T21)*(V22-V21)-(V23-V21)*(T22-T21))/((T22**2.-
% T21**2.)*(T23-T21)-(T23**2.-T21**2.)*(T22-T21))
      CV2(2)=((V22-V21)-CV2(3)*(T22**2.-T21**2.))/(T22-T21)
      CV2(1)=V21-CV2(2)*T21-CV2(3)*T21**2.0
      CV3(3)=((T33-T31)*(V32-V31)-(V33-V31)*(T32-T31))/((T32**2.-
% T31**2.)*(T33-T31)-(T33**2.-T31**2.)*(T32-T31))
      CV3(2)=((V32-V31)-CV3(3)*(T32**2.-T31**2.))/(T32-T31)
      CV3(1)=V31-CV3(2)*T31-CV3(3)*T31**2.0
      WRITE(6,5000)
5000  FORMAT(/,5X,' LIQUID MOLAR VOLUME CONSTANTS')
      WRITE(6,5010)CV2(1),CV2(2),CV2(3)
      WRITE(6,5010)CV3(1),CV3(2),CV3(3)
5010  FORMAT(5X,3(G12.5,3X))
5020  FORMAT(5X,6G12.5)
      DO 10 I=1,NXD
      READ(5,2800)ADT(1,I),ADT(2,I),XD(I)
      WRITE(6,2800)ADT(1,I),ADT(2,I),XD(I)
2800  FORMAT(3F10.5)
10    CONTINUE
?
```

```

2300  FORMAT(6F10.5)
      READ(5,2400)FK,FNP,FNM,FZP,FZN
      WRITE(6,2400)FK,FNP,FNM,FZP,FZN
2400  FORMAT(5F10.5)
      DO 50 I=1,NXDD
      READ(5,2300)DENS(I),XDD(I)
      WRITE(6,2300)DENS(I),XDD(I)
50    CONTINUE
      CALL FITIT(NXDD,XDD,DENS,ADD)
      WRITE(6,5020)(ADD(II),II=1,6)

C
C
C    EXPERIMENTAL M-P-T-X-Y-MEAN MOLAL ACTIVITY COEFFICIENT DATA
C
C    FOLLOWING INSTRUCTIONS ARE IMPORTANT
C
C    1. IF DATA ARE MOLALITY VS MEAN MOLALITY ACTIVITY
C       COEFFICIENT ONLY, READ P(I)=1.0
C
C    2. IF DATA ARE MOLALITY VS VAPOR PRESSURE ONLY, READ
C       G(1,I)=1.0
C
C    3. IF A BINARY DATA ARE USED ,READ X AND Y VALUES OF THE
C       OTHER SOLVENT(WHICH IS NOT PRESENT) =0.0
C
C
      DO 4100 I=1,NP
      READ(5,2500)XMOL(I),(X(J,I),Y(J,I),J=2,NCOMP),G(1,I),P(I),T(I)
      WRITE(6,2500)XMOL(I),(X(J,I),Y(J,I),J=2,NCOMP),G(1,I),P(I),T(I)
2500  FORMAT(8F10.6)
      CALL VAPPRE(CP2,CP3,PSM,T(I))
      WRITE(6,2501)PSM(2),PSM(3)
2501  FORMAT(1X,G10.3,3X,G10.3)

C
C
C    CALCULATION OF THE EXPERIMENTAL ACTIVITY COEFFICIENT
C    OF SOLVENTS. ASSUMING POYNTING EFFECT = 1.0 &
C    FUGACITY COEFFICIENT = 1.0.
C
C
      SUM=1.0
      DO 4200 K=2,NCOMP
      SUM=SUM-X(K,I)
4200  CONTINUE
      X(1,I)=SUM/FK
      XSUM=0.0
      DO 4300 K=2,NCOMP
      XSUM=XSUM+X(K,I)
      IF(P(I).EQ.1.0)GO TO 3100
      IF(X(K,I).EQ.0.0)GO TO 3100

```

?

```
G(K,I)=Y(K,I)*P(I)/X(K,I)/PSM(K)
GO TO 4300.
3100 G(K,I)=1.0
4300 CONTINUE
      DD 4400 K=2,NCOMP
      XF(K,I)=X(K,I)/XSUM
4400 CONTINUE
4100 CONTINUE
      WRITE(6,2601)
2601 FORMAT('- ',18X,' X1 ',10X,' X2 ',12X,' X3 ',9X,' GAMA1 ',8X,
% ' GAMA2 ',8X,' GAMA3 ')
      DD 4500 I=1,NF
      WRITE(6,2600)X(1,I),X(2,I),X(3,I),G(1,I),G(2,I),G(3,I)
2600 FORMAT(10X,6F15.6)
4500 CONTINUE
      RETURN
      END
```


SUBROUTINE FITIT(NPOINT,X1,AGAMA,A)

THIS PROGRAM FITS A POLYNOMIAL OF DEGREE 5

DIMENSION SIGMAY(20),X1(20),AGAMA(20),A(6),DELTAY(20),YCAL(20)
IF(NPOINT.LE.3) GO TO 99

DO 2 I=1,NPOINT
SIGMAY(I)=0.
CONTINUE
NCODE=0
MAXORD=5
IF(NPOINT.LE.4) MAXORD=2
IF(MAXORD.GT.6) MAXORD=6
NNK=1
DO 3 K=5,NNK
K1=K+1

CALL POLIFI(X1,AGAMA,SIGMAY,NPOINT,K1,0,A,CHISQR)

ERROR=0.0
DO 4 J=1,NPOINT
SUM=A(1)
DO 5 I=2,K1
SUM=SUM+A(I)*X1(J)**(I-1)
CONTINUE
YCAL(J)=SUM
DELTAY(J)=YCAL(J)-AGAMA(J)
ERROR=ERROR+DELTAY(J)**2
ERROR=ERROR/NPOINT

CONTINUE

RETURN
END

```

SUBROUTINE POLIFI(X,Y,SIGMAY,NPTS,NTERMS,MODE,A,CHISQR)
C
C   EXTRACTED FROM: BEVINGTON,P. R., "DATA REDUCTION AND
C   ERROR ANALYSIS FOR THE PHYSICAL SCIENCES", MCGRAW HILL,1969
C
C   SUBROUTINE POLIFIT PURPOSE
C
C   MAKE A LEAST-SQUARES FIT TO DATA WITH A POLYNOMIAL CURVE
C    $Y = A(1) + A(2)*X + A(3)*X**2 + A(4)*X**3 + \dots$ 
C
C   DESCRIPTION OF PARAMETERS
C   X   -ARRAY OF DATA POINTS FOR INDEPENDENT VARIABLE
C   Y   -ARRAY OF DATA POINTS FOR DEPENDENT VARIABLE
C   SIGMAY - ARRAY OF STANDARD DEVIATIONS FOR Y DATA POINTS
C   NPTS  -NUMBER OF PAIRS OF DATA POINTS
C   NTERMS -NUMBER OF COEFFICIENTS(DEGREE OF POLYNOMIAL + 1)
C   MODE  -DETERMINANTS METHOD OF WEIGHTING LEAST-SQUARES FIT
C           +1 (INSTRUMENTAL) WEIGHT(I)=1./SIGMAY(I)**2
C           0 (NO WEIGHTING) WEIGHT =1.
C           -1 (STATISTICAL) WEIGHT(I) = 1./Y(I)
C   A   - ARRAY OF COEFFICIENTS OF POLYNOMIAL
C   CHISQR - REDUCED CHI SQUARE FOR FIT
C
C   SUBROUTINES AND FUNCTION SUBPROGRAMS REQUIRED
C   DELTERM (ARRAY,NORDER)
C   EVALUATES THE DETERMINANTS OF A SYMMETRIC TWO-DIMENSIONAL
C   MATRIX OF NORDER
C
C   DOUBLE PRECISION SUMX,SUMY,XTERM,YTERM,ARRAY,CHISQ
C   DIMENSION X(20), Y(20), SIGMAY(20), A(6)
C   DIMENSION SUMX(20),SUMY(20),ARRAY(8,8)
C
C   ACCUMULATE WEIGHTING SUMS
C
11  NMAX = 2*NTERMS - 1
13  DO 13 N=1, NMAX
15  SUMX(N) = 0.
17  DO 15 J=1, NTERMS
19  SUMY(J)= 0.
21  CHISQ =0.
23  DO 21 I=1, NPTS
25  XI=X(I)
27  YI= Y(I)
31  IF (MODE) 32,37,39
32  IF(YI) 35,37,33
33  WEIGHT = 1./YI
35  GO TO 41
37  WEIGHT = 1./(-YI)
39  GO TO 41
41  WEIGHT = 1.

```

```

GO TO 41
39  WEIGHT = 1. / SIGMAY(I)**2
41  XTERM=WEIGHT
   DO 44 N=1,NMAX
      SUMX(N) = SUMX(N) + XTERM
44  XTERM = XTERM * XI
45  YTERM = WEIGHT*YI
   DO 48 N=1, NTERMS
      SUMY(N)=SUMY(N) + YTERM
48  YTERM = YTERM *XI
49  CHISQ = CHISQ + WEIGHT*YI**2
50  CONTINUE
C
C   CONSTRUCT MATRICES AND CALCULATE COEFFICIENTS
C
51  DO 54 J=1, NTERMS
   DO 54 K=1, NTERMS
      N = J + K - 1
54  ARRAY(J,K) = SUMX(N)
      DELTA = DETERM (ARRAY,NTERMS)
      IF(DELTA) 61,57,61
57  CHISQR = 0.
   DO 59 J=1, NTERMS
59  A(J) = 0.
      GO TO 80
61  DO 70 L=1, NTERMS
62  DO 66 J=1, NTERMS
   DO 65 K=1,NTERMS
      N = J+K-1
65  ARRAY(J,K)=SUMX(N)
66  ARRAY(J,L)=SUMY(J)
70  A(L)=DETERM(ARRAY,NTERMS)/DELTA
C
C   CALCULATES CHI SQUARE
C
71  DO 75 J=1, NTERMS
      CHISQ = CHISQ - 2.*A(J)*SUMY(J)
   DO 75 K=1, NTERMS
      N=J+K-1
75  CHISQ=CHISQ+A(J)*A(K)*SUMX(N)
76  FREE=NPTS-NTERMS
77  CHISQR=CHISQ/FREE
80  RETURN
END

```

```

FUNCTION DETERM (ARRAY, NORDER)
C
C   EXTRACTED FROM: BEVINGTON, P. R., "DATA REDUCTION AND
C   ERROR ANALYSIS FOR THE PHYSICAL SCIENCES", MCGRAW HILL, 1969
C
C   FUNCTION DETERM
C
C   PURPOSE
C   CALCULATES THE DETERMINANT OF A SQUARE MATRIX
C
C   USAGE
C   DET = DETERM (ARRAY, NORDER)
C
C   DESCRIPTION OF PARAMETERS
C   ARRAY  -MATRIX
C   NORDER -ORDER OF DETERMINANT (DEGREE OF MATRIX)
C
C   SUBROUTINE AND FUNCTION SUBPROGRAMS REQUIRED
C   NONE
C
C   COMMENTS
C   THIS SUBPROGRAM DESTROYS THE INPUT MATRIX ARRAY
C
C   DOUBLE PRECISION ARRAY, SAVE
C   DIMENSION ARRAY(8,8)
10  DETERM = 1.
11  DO 50 K=1, NORDER
C
C     INTERCHANGE COLUMNS IF DIAGNOL ELEMENT IS ZERO
C
C   IF (ARRAY(K,K)) 41,21,41
21  DO 23 J=K, NORDER
C   IF (ARRAY(K,J)) 31,23,31
23  CONTINUE
C   DETERM = 0.
C   GO TO 60
31  DO 34 I=K, NORDER
C   SAVE = ARRAY(I,J)
C   ARRAY(I,J)=ARRAY(I,K)
34  ARRAY(I,K)=SAVE
C   DETERM = -DETERM
C
C   SUBTRACT ROW K FROM LOWER ROWS TO GET DIAGONAL MATRIX
C
41  DETERM = DETERM*ARRAY(K,K)
C   IF (K - NORDER) 43,50,50
43  K1=K+1
C   DO 46 I=K1, NORDER
C   DO 46 J=K1, NORDER
46  ARRAY(I,J)=ARRAY(I,J)-ARRAY(I,K)*ARRAY(K,J)/ARRAY(K,K)
C
50  CONTINUE
60  RETURN
END

```

```
      SUBROUTINE VAPPRE(CP2,CP3,PSM,T)
```

```
C  
C  
C  
C  
C  
C  
C  
C  
C  
C  
C  
C  
C  
C  
C
```

```
*****
```

```
      SUBROUTINE VAPPRE
```

```
      THIS SUBROUTINE CALCULATES PURE COMPONENT VAPOR-PRESSURES
```

```
      OF THE SOLVENTS AT THE SYSTEM TEMPERATURE.
```

```
*****
```

```
      DIMENSION CP2(6),CP3(6),PSM(3)  
      PSM(2)=(EXP(CP2(1)+CP2(2)/(CP2(3)+T)+CP2(4)*T+  
% CP2(5)*T**2.+CP2(6)*ALOG(T)))*760.  
      PSM(3)=(EXP(CP3(1)+CP3(2)/(CP3(3)+T)+CP3(4)*T+  
% CP3(5)*T**2.+CP3(6)*ALOG(T)))*760.  
      RETURN  
      END
```

```
?
```

```

SUBROUTINE TEMPD(CV2,CV3,NXD,XD,ADT,AD,VO,T)

```

```

*****

```

```

SUBROUTINE TEMPD

```

```

THIS SUBROUTINE CALCULATES THE TEMPERATURE DEPENDENCY OF
THE LIQUID MOLAR VOLUME AND DIELECTRIC CONSTANT.

```

```

CALLS SUBROUTINE FITIT FOR CONCENTRATION DEPENDENCE
OF DIELECTRIC CONSTANT.

```

```

*****

```

```

DIMENSION CV2(3),CV3(3),XD(20),ADT(2,20),AD(6),VO(3),DSXD(20)
VO(2)=CV2(1)+CV2(2)*T+CV2(3)*T**2.0
VO(3)=CV3(1)+CV3(2)*T+CV3(3)*T**2.0
DO 10 I=1,NXD
DSXD(I)=EXP(2.303*(ADT(1,I)+ADT(2,I)*(T-293.15)))
CONTINUE
CALL FITIT(NXD,XD,DSXD,AD)
RETURN
END

```

```

10

```

```

?

```

```
SUBROUTINE LSQ2(XT,X,DX,Y,M,M1,M3,L,E)
```

```
*****
```

```
  SUBROUTINE LSQ2
```

```
  NON-LINEAR REGRESSION SUBROUTINE CALLS SUBROUTINE FN FOR  
  THE OBJECTIVE FUNCTION.
```

```
*****
```

```
  DIMENSION XT(6),DX(6),X(7,10),Y(7),JJ(3),A(3,3)
```

```
  IL=0
```

```
  IH=0
```

```
  LIC=0
```

```
  IF(L.LE.0) GO TO 50
```

```
  IHC=M1+1
```

```
  EN=M
```

```
  EN=EN*1.5
```

```
  L1=L
```

```
  L=-L
```

```
  L2=(3*M)/2+5
```

```
  K3=2
```

```
  IF(M.GE.3)K3=3
```

```
  K4=K3-1
```

```
  G=K3*2
```

```
  G=1.0/G
```

```
100 DO 100 I=1,M
```

```
  X(I,1)=XT(I)
```

```
  CALL FN(Y(1),XT,LIC)
```

```
  DO 106 J=2,M1
```

```
  XT(J-1)=XT(J-1)+DX(J-1)
```

```
104 DO 104 I=1,M
```

```
  X(I,J)=XT(I)
```

```
  CALL FN(Y(J),XT,LIC)
```

```
  XT(J-1)=X(J-1,1)
```

```
106 CONTINUE
```

```
  L2C=0
```

```
  FLG=1.0
```

```
  GO TO 50
```

```
108 LIC=LIC+1
```

```
  IF(LIC.GE.L1)GO TO 400
```

```
50 YL=1.0E38
```

```
  YH=-YL
```

```
  Y2=YH
```

```
?
```

```

      Y3=YL
      DO 110 J=1,M1
      IF(Y(J).LT.YH)GO TO 1091
      Y2=YH
      I2=IH
      YH=Y(J)
      IH=J
      GO TO 109
1091  IF(Y(J).LT.Y2)GO TO 109.
      Y2=Y(J)
      I2=J
109   IF(Y(J).GT.YL)GO TO 1101
      Y3=YL
      I3=IL
      IL=J
      YL=Y(J)
      GO TO 110
1101  IF(Y(J).GT.Y3)GO TO 110
      Y3=Y(J)
      I3=J
110   CONTINUE
      L2C=L2C+1
      IF(L2C.LT.L2)GO TO 111
      L2C=0
      JJ(1)=IL
      JJ(2)=I2
      JJ(3)=I3
      DO 60 K1=1,K3
      J1=JJ(K1)
      DO 60 K2=K1,K3
      J2=JJ(K2)
      S=0.0
      DO 55 I=1,M
55     S=S+(X(I,J1)-X(I,IH))*(X(I,J2)-X(I,IH))
60     A(K1,K2)=S
      D=A(1,1)*A(2,2)-A(1,2)**2
      GO TO (62,61),K4
61     D1=A(1,1)*A(2,3)-A(1,2)*A(1,3)
      IF(A(1,1).EQ.0.0)A(1,1)=1.0E-5
      D=((A(1,1)*A(3,3)-A(1,3)**2)*D-D1*D1)/(A(1,1)*9.0)
62     IF(D.EQ.0.0)GO TO 65
      IF(D.LE.0.0)D=ABS(D)
      D=(D/4.0)**G
      IF(D.LT.E)GO TO 65
      FLG=1.0
      GO TO 111
65     IF(FLG.LT.0.0)GO TO 400
      FLG=-1.0
111   DO 115 I=1,M
      XT(I)=0.0

```



```

DO 112 J=1,M1
IF(J.NE.IH)XT(I)=XT(I)+X(I,J)
112 CONTINUE
115 XT(I)=(3.0*XT(I)+X(I,I2)-X(I,IL))/EN-X(I,IH)
121 CALL FN(YT,XT,LIC)
IF(YT.GE.Y2)GO TO 167
IHC=M1+1
IF(YT.GE.YL)GO TO 140
YTT=YT
DO 135 I=1,M
135 XT(I)=1.5*XT(I)-0.5*X(I,IH)
CALL FN(YT,XT,LIC)
IF(YT.LE.YL)GO TO 140
DO 138 I=1,M
138 X(I,IH)=(2.0*XT(I)+X(I,IH))/3.0
Y(IH)=YTT
GO TO 108
140 DO 142 I=1,M
142 X(I,IH)=XT(I)
Y(IH)=YT
GO TO 108
167 IHC=IHC-1
IF(IHC.EQ.0)GO TO 300
IF(YT.GE.YH)GO TO 173
DO 168 I=1,M
XS=XT(I)
XT(I)=X(I,IH)
168 X(I,IH)=XS
173 DO 174 I=1,M
174 XT(I)=0.75*X(I,IH)+0.25*XT(I)
CALL FN(YT,XT,LIC)
IF(YT.GT.YH)GO TO 180
Y(IH)=YT
DO 175 I=1,M
175 X(I,IH)=XT(I)
GO TO 108
180 DO 185 J=1,M1
IF(J.EQ.IL)GO TO 185
DO 182 I=1,M
XT(I)=(X(I,J)+X(I,IL))/2.0
182 X(I,J)=XT(I)
CALL FN(Y(J),XT,LIC)
185 CONTINUE
GO TO 108
300 IHC=2*M1
IF(M.GE.3)GO TO 350
S=0.0
DO 302 I=1,M
X(I,M+2)=X(I,IH)-X(I,IL)
X(I,M+3)=X(I,IH)-X(I,I3)

```

```

302  S=S+X(I,M+2)**2
303  S=SQRT(S)
      IF(S.EQ.0.0)S=1.0E-5
304  U=-X(2,M+2)/S
      X(2,M+2)=X(1,M+2)/S
      X(1,M+2)=U
      S=X(1,M+2)*X(1,M+3)+X(2,M+2)*X(2,M+3)
      DO 305 I=1,M
305  X(I,M+2)=X(I,M+2)*S
306  DO 307 I=1,M
307  XT(I)=X(I,IH)+X(I,M+2)
      CALL FN(YT,XT,LIC)
      DO 309 I=1,M
309  XT(I)=X(I,IH)-X(I,M+2)
      CALL FN(YTT,XT,LIC)
      IF(YTT.LE.YT)GO TO 320
      DO 311 I=1,M
311  XT(I)=X(I,IH)+X(I,M+2)
      YTT=YT
320  Y(IH)=YTT
      DO 321 I=1,M
321  X(I,IH)=XT(I)
      GO TO 108
350  DO 352 I=1,M
      XT(I)=X(I,IH)-X(I,IL)
      X(I,M+2)=X(I,IH)-X(I,I2)
352  X(I,M+3)=X(I,IH)-X(I,I3)
      S=0.0
      S1=0.0
      DO 355 I=1,M
      S=S+XT(I)**2
355  S1=S1+X(I,M+3)**2
      S=SQRT(S)
      S1=SQRT(S1)
      S2=0.0
      DO 357 I=1,M
      IF(S.EQ.0.0)S=1.0E-5
      XT(I)=XT(I)/S
      S2=S2+XT(I)*X(I,M+2)
      IF(S1.EQ.0.0)S1=1.0E-5
357  X(I,M+3)=X(I,M+3)/S1
      DO 360 I=1,M
360  X(I,M+2)=X(I,M+2)-XT(I)*S2
      S1=0.0
      DO 362 I=1,M
362  S1=S1+X(I,M+2)**2
      S1=SQRT(S1)
      DO 365 I=1,M
      IF(S1.EQ.0.0)S1=1.0E-5
365  X(I,M+2)=X(I,M+2)/S1

```

```
S1=0.0
S2=0.0
DO 367 I=1,M
S1=S1+XT(I)*X(I,M+3)
367 S2=S2+X(I,M+2)*X(I,M+3)
DO 370 I=1,M
370 X(I,M+2)=S*(S1*XT(I)+S2*X(I,M+2)-X(I,M+3))
GO TO 306
400 S=Y(1)
Y(1)=Y(IL)
Y(IL)=S
DO 402 I=1,M
XT(I)=X(I,IL)
X(I,IL)=X(I,1)
402 X(I,1)=XT(I)
WRITE(6,772) LIC
772 FORMAT('-', 'LIC=', I5)
RETURN
END
```

SUBROUTINE FN(YY,XT,LIC)

SUBROUTINE FN

THIS SUBROUTINE IS CALLED BY SUBROUTINE LSQ2. THIS
SUBROUTINE ESTABLISHES THE OBJECTIVE FUNCTION BY CALLING
SUBROUTINE MINFUN.

GCAL(J,I) - CALCULATED ACTIVITY COEFFICIENT
GADD(J,I) - LN OF THE SALTING OUT CONTRIBUTION TO THE
ACTIVITY COEFFICIENT.
GEL(J,I) - LN OF DEBYE HUCKEL CONTRIBUTION AND THE
ADDITIONAL TERMS FOR THE COULOMBIC INTERACTION
TO THE ACTIVITY COEFFICIENT.
GNRT(J,I) - LN OF THE NRTL CONTRIBUTION TO THE ACTIVITY
COEFFICIENT.
PTC(I) - CALCULATED TOTAL PRESSURE OF THE SYSTEM
YCAL(J,I) - CALCULATED VAPOR PHASE COMPOSITION.

COMMON XMOL(99),X(3,99),XF(3,99),GG(3,99),P(99),YV(3,99),GNRT(
% 3,99),GEL(3,99),GCAL(3,99),AMW(3),ERROR(3,99),GDH(3,99)
% ,GFHY(3,99),T(99),BMM(99),GADD(3,99),YCAL(3,99),ADD(6)
% ,PTC(99)
COMMON NP,INDF,FNF,FNM,FZP,FZN,FK,ALFA,DG23,DG32,
% GPN2,GPN3,ZP2,ZP3,KP,M,NBIN,NPION,NNION,DELTA
COMMON NDEN,NNRTL,ALFA2,ALFB2,ALFA3,ALFB3,DGA2,DGB2,
% DGA3,DGB3,NBROM,NREG,NTYPE,NMIN
COMMON B012,B112,B013,B113,CP2(6),CP3(6),CV2(3),CV3(3),
% B123,ADT(2,20),NXD,XD(20)
DIMENSION XT(6),PSM(3)
IF(NREG.LE.1)GO TO 1070
GO TO (1040,1050,1060,1080,1085),NBIN
1040 GO TO(10,20),NNRTL
10 DGA2=XT(1)
DGB2=XT(2)
GO TO 1070
20 IF(XT(1).LT.0.0)XT(1)=0.0
?

```

      GPN2=XT(1)
      ZP2=XT(2)
      GO TO 1070
1050  GO TO(30,40),NNRTL
      30  DGA3=XT(1)
          DGB3=XT(2)
          GO TO 1070
      40  IF(XT(1).LT.0.0)XT(2)=0.0
          GPN3=XT(1)
          ZP3=XT(2)
          GO TO 1070
1060  DELTA=XT(2)
      B123=XT(1)
      GO TO 1070
1080  DG23=XT(1)
      DG32=XT(2)
      GO TO 1070
1085  GO TO (50,60),NNRTL
      50  DGA2=XT(1)
          DGB2=XT(2)
          DGA3=XT(3)
          DGB3=XT(4)
          GO TO 1070
      60  IF(XT(1).LT.0.0)XT(1)=0.0
          IF(XT(3).LT.0.0)XT(3)=0.0
          GPN2=XT(1)
          ZPN2=XT(2)
          GPN3=XT(3)
          ZPN3=XT(4)
1070  IF(KP.GT.1) GO TO 3100
      CALL NRTL1(X,T,GNRT,FK,FNP,NF,ALFA,DG23,DG32)
      CALL BROML(XMOL,XF,AMW,FNP,FNM,FK,FZP,FZN,T,GEL,
% NP,B123,GDH,GPHY,BMM,ADD,NDEN,CV2,CV3,NXD,XD,ADT,B012,B112
% ,B013,B113)
      CALL ADITON(XF,T,AMW,XMOL,FK,FZP,FZN,FNP,FNM,GADD,
% DELTA,NPION,NNION,NP,ADD,NDEN,CV2,CV3,NXD,XD,ADT,
% B012,B112,B013,B113)
      GO TO 3200
3100  CALL NRTL2(X,T,GNRT,FK,FNP,NF,GPN2,GPN3,ZP2,ZP3,ALFA,DG23,
% DG32,FNM,NNRTL,ALFA2,ALFB2,ALFA3,ALFB3,DGA2,DGB2,
% DGA3,DGB3)
      CALL DEBHUC(XMOL,XF,X,FK,FNP,FNM,FZP,FZN,GEL,AMW,
% T,NP,GDH,GPHY,ADD,NDEN,CV2,CV3,NXD,XD,ADT)
      DO 8010 IJ=1,NP
          GADD(1,IJ)=0.0
          GADD(2,IJ)=0.0
          GADD(3,IJ)=0.0
8010  CONTINUE
3200  YS=0.0
      DO 4000 I=1,NP

```

```

IF(XF(2,I).EQ.0.0)GO TO 1000
IF(XF(3,I).EQ.0.0)GO TO 1010
GO TO 1020
1000  GNRT(2,I)=0.0
      GEL(2,I)=0.0
      GADD(2,I)=0.0
      GADD(1,I)=0.0
      GO TO 1020
1010  GNRT(3,I)=0.0
      GEL(3,I)=0.0
      GADD(3,I)=0.0
      GADD(1,I)=0.0
1020  AMS = XF(2,I)*AMW(2)+XF(3,I)*AMW(3)
      CALL VAPPRE(CF2,CF3,PSM,T(I))
      GCAL(1,I)=EXP(GNRT(1,I)+GEL(1,I)+GADD(1,I)-ALOG(0.001*FK*AMS*
% XMOL(I)+1.0))
      GCAL(2,I)=EXP(GNRT(2,I)+GEL(2,I)+GADD(2,I))
      GCAL(3,I)=EXP(GNRT(3,I)+GEL(3,I)+GADD(3,I))
      PTC(I)=X(2,I)*GCAL(2,I)*PSM(2)+X(3,I)*GCAL(3,I)*PSM(3)
      YCAL(2,I)=X(2,I)*GCAL(2,I)*PSM(2)/PTC(I)
      YCAL(3,I)=X(3,I)*GCAL(3,I)*PSM(3)/PTC(I)
      ERROR(1,I)=(GG(1,I)-GCAL(1,I))/GG(1,I)*100.
      ERROR(2,I)=(GG(2,I)-GCAL(2,I))/GG(2,I)*100.
      ERROR(3,I)=(GG(3,I)-GCAL(3,I))/GG(3,I)*100.
      IF(XMOL(I).EQ.0.0)ERROR(1,I)=0.0
      IF(X(2,I).EQ.0.0)ERROR(2,I)=0.0
      IF(X(3,I).EQ.0.0)ERROR(3,I)=0.0
      IF(GG(1,I).EQ.1.0)ERROR(1,I)=0.0
      IF(GG(2,I).EQ.1.0)ERROR(2,I)=0.0
      IF(GG(3,I).EQ.1.0)ERROR(3,I)=0.0
      DIF1=ABS(ERROR(1,I)/100.)
      DIF2=ABS(ERROR(2,I)/100.)
      DIF3=ABS(ERROR(3,I)/100.)
      DIF4=ABS(YCAL(3,I)-YV(3,I))
      DIF5=ABS((PTC(I)-P(I))/P(I))
      IF(NMIN.GT.3)GO TO 2000
      GO TO 2010
2000  IF(X(2,I).EQ.0.0)GO TO 2020
      IF(X(3,I).EQ.0.0)GO TO 2030
2020  DIF3=ABS((P(I)-PTC(I))/(PSM(3)-P(I)))
      IF(P(I).EQ.1.0)DIF3=0.0
      GO TO 2010
2030  DIF2=ABS((P(I)-PTC(I))/(PSM(2)-P(I)))
      IF(P(I).EQ.1.0)DIF2=0.0
2010  CALL MINFUN(NTYPE,NMIN,DIF1,DIF2,DIF3,DIF4,DIF5,Y,X(2,I),
% X(3,I))
      YS=YS+Y
4000  CONTINUE
      YY=YS
      IF(LIC/20*20.NE.LIC)GO TO 301

```

```
WRITE(6,302)LIC
302  FORMAT(10X,' TRIAL # USED = ',I4)
    WRITE(6,303)YY,(XT(I),I=1,M)
303  FORMAT(///,5X,' YY= ',F15.7,5X,' XT VALUES ',6F15.6)
301  RETURN
    END
```

```

SUBROUTINE FIBN(ALPHA,A,B)
C
C *****
C
C SUBROUTINE FIBN
C
C THIS SUBROUTINE USES THE FIBONACCI METHOD TO FIND THE
C
C MINIMUM VALUE OF A NON LINEAR FUCTION.
C
C *****
C
C DIMENSION FIB(50)
C
C SUBROUTINE FOR FIBONACCI PROCEDURE
C
C DEL=B-A
C WRITE(6,001)
001 FORMAT(///,10X,35HFIBONACCI SINGLE-VARIABLE PROCEDURE )
C
C DEFINE THE FIRST THREE FIBONACCI NUMBERS
C
C FIB0=1.0
C FIB(1)=1.0
C FIB(2)=2.0
C
C CALCULATE THE REMAINING FIBONACCI NUMBERS
C
C 5 BB=1.0/ALPHA
C IF(BB-2.)10,10,11
C 10 GO TO 14
C 11 CONTINUE
C JJ=2
C 12 JJ=JJ+1
C FIB(JJ)=FIB(JJ-1)+FIB(JJ-2)
C CC=FIB(JJ)
C IF(CC-BB)13,15,15
C 13 GO TO 12
C 14 WRITE(6,002)
002 FORMAT(///,10X,' ACCURACY SPECIFIED IN FUNC NOT SUFFICIENT.',
% //,10X,' PROGRAM RESET ALPHA,ALPHA=0.01')
C ALPHA=0.01
C GO TO 5
C
C FIRST STEP IN THE TABLEAU
C 15 I=0
C KK=JJ-2
C IK=JJ-2
C BL=B-A
C
C ?

```



```

ALL=FIB(IK)*BL/FIB(JJ)
W=A+ALL
V=B-ALL
CALL FUNC(W,T)
CALL FUNC(V,U)
JK=1
WRITE(6,003)
003  FORMAT(/,1X,1HK,5X,2HLK,12X,2HAK,13X,2HBK,12X,3HLLK,9X,1HX,
% 8X,1HY)
WRITE(6,004)JK,BL,A,B,ALL,W,T
004  FORMAT(/,I3,6G11.4)
006  FORMAT(41X,E12.4,2X,E12.4)
C
C  SUCCEEDING STEPS IN THE TABLEAU
C
IK=IK-1
JJ=JJ-1
DO 70 I=1,KK
IF(U-T)20,20,22
20  A=A+ALL
BL=B-A
W=V
CALL FUNC(W,T)
ALL=FIB(IK)*BL/FIB(JJ)
V=B-ALL
CALL FUNC(V,U)
II=I+1
IK=IK-1
JJ=JJ-1
IF(IK-1)28,29,29
28  IK=1
29  CONTINUE
WRITE(6,004)II,BL,A,B,ALL,W,T
WRITE(6,006)V,U
GO TO 70
22  B=B-ALL
BL=B-A
V=W
CALL FUNC(V,U)
ALL=FIB(IK)*BL/FIB(JJ)
W=A+ALL
CALL FUNC(W,T)
II=I+1
IK=IK-1
JJ=JJ-1
IF(IK-1)30,31,31
30  IK=1
31  CONTINUE
WRITE(6,004)II,BL,A,B,ALL,V,U
WRITE(6,006)W,T

```

```
GO TO 70
70 CONTINUE
C
C CALCULATION OF THE FINAL RANGE OF THE DEPENDENT VARIABLE
C
EPS=0.001*W
DL=W+EPS
CALL FUNC(DL,YL)
IF(YL-T)80,80,81
80 CALL FUNC(B,BF)
WRITE(6,007)W,B
007 FORMAT(///,25HTHE FINAL FEASIBLE REGION ,2X,2HX=,E15.4,2X,2HX=,
% E15.4)
WRITE(6,008)T,BF
008 FORMAT(/ ,20HWITH FUNCTION VALUES,7X,2HY=,E10.4,2X,2HY=,E10.4)
GO TO 87
81 CALL FUNC(A,AF)
WRITE(6,009)W,A
009 FORMAT(/// ,25HTHE FINAL FEASIBLE REGION,2X,2HX=,E15.4,2X,2HX=,
% E15.4)
WRITE(6,017)T,AF
017 FORMAT(/ ,20HWITH FUNCTION VALUES,7X,2HY=,E10.4,2X,2HY=,E10.4)
87 ACC=(W-A)/(DEL)
WRITE(6,018)ACC
018 FORMAT(/ , 15HTHE ACCURACY IS,12X,E10.4)
WRITE(6,019)ALPHA
019 FORMAT(/ , 'THE REQUIRED ACCURACY WAS =',E10.4)
C
RETURN
END
```



```

% NP,B123,GDH,GPHY,BMM,ADD,NDEN,CV2,CV3,NXD,XD,ADT,B012,B112
% ,B013,B113)
  CALL ADITON(XF,T,AMW,XMOL,FK,FZP,FZN,FNF,FNM,GADD,
% DELTA,NPION,NNION,NF,ADD,NDEN,CV2,CV3,NXD,XD,ADT,
% B012,B112,B013,B113)
  GO TO 3200
3100  CALL NRTL2(X,T,GNRT,FK,FNF,NF,GN2,GN3,ZPN2,ZPN3,ALFA,DG23,
% DG32,FNM,NNRTL,ALFA2,ALFB2,ALFA3,ALFB3,DGA2,DGB2,DGA3,DGB3)
  CALL DEBHUC(XMOL,XF,X,FK,FNF,FNM,FZP,FZN,GEL,AMW,
% T,NF,GDH,GPHY,ADD,NDEN,CV2,CV3,NXD,XD,ADT)
  DO 8010 IJ=1,NF
    GADD(1,IJ)=0.0
    GADD(2,IJ)=0.0
    GADD(3,IJ)=0.0
8010  CONTINUE
3200  YS=0.0
      DO 4000 I=1,NF
        IF(XF(2,I).EQ.0.0)GO TO 1000
        IF(XF(3,I).EQ.0.0)GO TO 1010
        GO TO 1020
1000  GNRT(2,I)=0.0
      GEL(2,I)=0.0
      GNRT(1,I)=0.0
      GADD(2,I)=0.0
      GADD(1,I)=0.0
      GO TO 1020
1010  GNRT(3,I)=0.0
      GEL(3,I)=0.0
      GNRT(1,I)=0.0
      GADD(3,I)=0.0
      GADD(1,I)=0.0
1020  AMS = XF(2,I)*AMW(2)+XF(3,I)*AMW(3)
      GCAL(1,I)=EXP(GNRT(1,I)+GEL(1,I)+GADD(1,I)-ALOG(0.001*FK*AMS*
% XMOL(I)+1.0))
      GCAL(2,I)=EXP(GNRT(2,I)+GEL(2,I)+GADD(2,I))
      GCAL(3,I)=EXP(GNRT(3,I)+GEL(3,I)+GADD(3,I))
      CALL VAPPRE(CP2,CP3,PSM,T(I))
      PTC(I)=X(2,I)*PSM(2)*GCAL(2,I)+X(3,I)*PSM(3)*GCAL(3,I)
      YCAL(2,I)=X(2,I)*PSM(2)*GCAL(2,I)/PTC(I)
      YCAL(3,I)=X(3,I)*PSM(3)*GCAL(3,I)/PTC(I)
      ERROR(1,I)=(GG(1,I)-GCAL(1,I))/GG(1,I)*100.
      ERROR(2,I)=(GG(2,I)-GCAL(2,I))/GG(2,I)*100.
      ERROR(3,I)=(GG(3,I)-GCAL(3,I))/GG(3,I)*100.
      TF(XMOL(I).EQ.0.0)ERROR(1,I)=0.0
      IF(X(2,I).EQ.0.0)ERROR(2,I)=0.0
      IF(X(3,I).EQ.0.0)ERROR(3,I)=0.0
      IF(GG(1,I).EQ.1.0)ERROR(1,I)=0.0
      IF(GG(2,I).EQ.1.0)ERROR(2,I)=0.0
      IF(GG(3,I).EQ.1.0)ERROR(3,I)=0.0
      DT F1=ABS(ERROR(1,I)/100.)

```

```
DIF2=ABS(ERROR(2,I)/100.)
DIF3=ABS(ERROR(3,I)/100.)
DIF4=ABS(YCAL(3,I)-YV(3,I))
DIF5=ABS((PTC(I)-P(I))/P(I))
IF(NMIN.GT.3)GO TO 2000
GO TO 2010
2000 IF(X(2,I).EQ.0.0)GO TO 2000
IF(X(3,I).EQ.0.0)GO TO 2000
2020 DIF3=ABS((P(I)-PTC(I))/(PSM(2)-P(I)))
IF(P(I).EQ.1.0)DIF3=0.0
GO TO 2010
2030 DIF2=ABS((P(I)-PTC(I))/(PSM(2)-P(I)))
IF(P(I).EQ.1.0)DIF2=0.0
2010 CALL MINFUN(NTYPE,NMIN,DIF1,DIF2,DIF3,DIF4,DIF5,Y-Y(2,I)
% ,X(3,I))
YS=YS+Y
4000 CONTINUE
YY=YS
RETURN
END
```

C
C
C
C
C
C
C
C
C
C
C

SUBROUTINE NRTL1(X,T,GNRT,FK,FNP,NP,ALFA,DG23,DG32)

SUBROUTINE NRTL1

THIS SUBROUTINE CALCULATES SOLVENT-SOLVENT INTERACTION

FOR A TERNARY MIXTURE IN MODEL # 2.

DIMENSION XA(99),X(3,99),GNRT(3,99),T(99)

R=1.987

DO 4001 I=1,NP

G32=EXP(-ALFA*DG32/R/T(I))

Z32=DG32*G32

G23=EXP(-ALFA*DG23/R/T(I))

Z23=DG23*G23

XA(I)=FNP*X(1,I)

FNT1=(FK*XA(I)/FNP+X(2,I)+X(3,I)*G32)**2.

FNT2=(FK*XA(I)/FNP+X(3,I)+X(2,I)*G23)**2.

FNT3=X(2,I)+X(3,I)*G32

FNT4=X(3,I)+X(2,I)*G23

GNRT(1,I)=(-Z32/FNT1-Z23/FNT2+Z32/(FNT3**2.))+Z23/(FNT4**2.))*

Z X(2,I)*X(3,I)/R/T(I)

AT2=XA(I)*X(3,I)*FK*(Z32/FNT1+Z23/FNT2+Z32/(FNT3**2.))+

Z Z23/(FNT4**2.))/(FNP*R*T(I))

AT3=XA(I)*X(2,I)*FK*(Z32/FNT1+Z23/FNT2+Z32/(FNT3**2.))+Z23

Z /(FNT4**2.))/(FNP*R*T(I))

BT3=X(2,I)**2.*(Z32/FNT1+Z23*G23/FNT2)/(R*T(I))

BT2=X(3,I)**2.*(G32*Z32/FNT1+Z23/FNT2)/(R*T(I))

CT2=-2.*FK*X(2,I)*X(3,I)*XA(I)*(Z32/(FNT3**3.))+G23*Z23

Z /(FNT4**3.))/(FNP*R*T(I))

CT3=-2.*FK*X(2,I)*X(3,I)*XA(I)*(Z32*G32/(FNT3**3.))+

Z Z23/(FNT4**3.))/(FNP*R*T(I))

GNRT(2,I)=AT2+BT2+CT2

GNRT(3,I)=AT3+BT3+CT3

4001

CONTINUE

RETURN

END

?

```

SUBROUTINE BROML(XMOL, XF, AMW, FNP, FNM, FK, FZP, FZN, T, GBM,
% NP, B123, GDH, GPHY, BM, ADD, NDEN, CV2, CV3, NXD, XD, ADT, B012,
% B112, B013, B113)

```

```

*****

```

```

SUBROUTINE BROML

```

```

THIS SUBROUTINE CALCULATES ION-ION INTERACTION &
ION-SOLVENT INTERACTION ACCORDING TO THE BROMLEY
EQUATION, IN MODEL # 2.

```

```

*****

```

```

GDH(J,I) - CONTRIBUTION OF THE DEBYE-HUCKEL TERM
GPHY(J,I) - CONTRIBUTION OF THE B TERMS IN THE EQUATION
           (i.e. ION-SOLVENT INTERACTION )
GBM(J,I) - COMBINATION OF THE ABOVE TWO TERMS

```

```

THIS SUBROUTINE CALLS SUBROUTINES FUNCT & FUNCB.

```

```

*****

```

```

DIMENSION XMOL(99), XF(3,99), AMW(3), T(99)
DIMENSION SIG(99), SAI(99), SIG1(99), SAI1(99), GBM(3,99),
% AI(99), F2(99), F3(99), BM(99), VO(3), AD(6)
% ,GDH(3,99), GPHY(3,99)
DIMENSION ADD(6), CV2(3), CV3(3), XD(20), ADT(2,20)
ROW=1.0
DO 4001 I=1, NP
IF(XMOL(I).EQ.0.0)GO TO 2010
B12=B012*ALOG((T(I)-243.)/T(I))+B112/T(I)
B13=B013*ALOG((T(I)-243.)/T(I))+B113/T(I)
CALL TEMPD(CV2, CV3, NXD, XD, ADT, AD, VO, T(I))
AA=1.5/(FZP*FZN)
AI(I)=(FNP*FZP**2.+FNM*FZN**2.)*XMOL(I)/2.
XT1=1.+ROW*AI(I)**0.5
XT2=AA*AI(I)
XT3=1.+XT2
XT4=1.+2.*XT2
AMS=XF(2,I)*AMW(2)+XF(3,I)*AMW(3)
TNS=1000./AMS
XT5=(ROW*AI(I)**0.5)**3.
XT6=0.001*FK*XMOL(I)
XT7=XT6*AMS+1.

```

```

IF(XF(2,I).EQ.0.0)GO TO 1000
IF(XF(3,I).EQ.0.0)GO TO 1010
CALL FUNCT(XF(2,I),XF(3,I),T(I),TNS,F2(I),F3(I),
% ADB,FD2,FD3,AD,DS,ADD,UO,NDEN,AMW)
CALL FUNCB(XF(2,I),XF(3,I),B12,B13,BM(I)
% ,FB2,FB3,TNS,B123,AI(I),FNP,FNM,FZP,FZN,AMS,AMW(2),AMW(3)
% ,FB1,XMDL(I))
GO TO 1020
1000 BM(I)=B13
D30=AD(1)+AD(2)*XF(3,I)+AD(3)*XF(3,I)**2.+AD(4)*XF(3,I)**3.
% +AD(5)*XF(3,I)**4.+AD(6)*XF(3,I)**5.
D03=AMW(3)/UO(3)
ADB3=1.8246*10.**(6.0)*(D03**0.5)*((D30*T(I))**(-1.5))
FB1=0.0
FB2=0.0
FB3=0.0
F2(I)=0.0
F3(I)=0.0
FD2=0.0
FD3=0.0
ADB=ADB3
GO TO 1020
1010 BM(I)=B12
D20=AD(1)+AD(2)*XF(3,I)+AD(3)*XF(3,I)**2.0+AD(4)*XF(3,I)**3.
% +AD(5)*XF(3,I)**4.+AD(6)*XF(3,I)**5.
D02=AMW(2)/UO(2)
ADB2=1.8246*10.**(6.0)*(D02**0.5)*((D20*T(I))**(-1.5))
FB1=0.0
FB2=0.0
FB3=0.0
F2(I)=0.0
F3(I)=0.0
FD2=0.0
FD3=0.0
ADB=ADB2
1020 SIG(I)=3.*(XT1-1./XT1-2.*ALOG(XT1))/XT5
SAI(I)=2.*(-ALOG(XT3)/XT2+XT4/(XT3**2.))/XT2
SIG1(I)=2.*(XT1**2./2.-2.*XT1+ALOG(XT1)+1.5)/XT5
SAI1(I)=0.6*2.0*FZP*FZN*(ALOG(XT3)/XT2-1./XT3)/XT2+1.0
YBT1=XT6*2.303*ADB*SIG(I)*AI(I)**(0.5)/3.*(FZP*FZN)
YBT2=2.303*FZP*FZN*XT6*(0.06+0.6*BM(I))*SAI(I)*AI(I)/2.
YBT3=2.303*XT6*BM(I)*AI(I)/2.
YBT4=2.303*XT6*TNS*AMS*SIG1(I)*AI(I)**(0.5)*(FZP*FZN)
YBT5=FB3
YBT7=FB2
YBT6=2.303*XT6*AMS*TNS*AI(I)/2.0
FT1=-YBT2-YBT3
FT5=XT6*AMS
FT6=ALOG(XT7)
FT7=FT6-FT5

```



```
GDH(1,I)=-2.303*ADB*FZF*FZN*AI(I)*0.5/XT1
GDH(2,I)=YBT1*AMW(2)-YBT4*F2(I)
GDH(3,I)=YBT1*AMW(3)-YBT4*F3(I)
GPHY(1,I)=((0.06+ 0.6*BM(I))*AI(I)/(XT3**2.)
% *FZF*FZN+BM(I)*AI(I))*2.303+2.303*XMOL(I)*AI(I)*TNS*AMS*SAI1(I)
% *FB1/2.0/1000.0
GPHY(2,I)=FT1*AMW(2)+YBT7*YBT6*SAI1(I)
GPHY(3,I)=FT1*AMW(3)+YBT5*YBT6*SAI1(I)
GBM(1,I)=GDH(1,I)+GPHY(1,I)+ALOG(XT7)
GBM(2,I)=GDH(2,I)+GPHY(2,I)+FT7
GBM(3,I)=GDH(3,I)+GPHY(3,I)+FT7
GO TO 4001
2010 GBM(1,I)=0.0
      GBM(2,I)=0.0
      GBM(3,I)=0.0
      GDH(1,I)=0.0
      GDH(2,I)=0.0
      GDH(3,I)=0.0
      GPHY(1,I)=0.0
      GPHY(2,I)=0.0
      GPHY(3,I)=0.0
4001 CONTINUE
      RETURN
      END
```

```

SUBROUTINE ADITON(XF,T,AMW,XMOL,FK,FZP,FZN,FNP,FNM,

```

```

*****

```

```

SUBROUTINE ADITON

```

```

THIS SUBROUTINE CALCULATES THE SALTING OUT CONTRIBUTION IN A
A TERNARY MIXTURE IN MODEL # 2. DELTA IS THE SALTING OUT
PARAMETER.

```

```

*****

```

```

% GADD,DELTA,NPION,NNION,NP,ADD,NDEN,CV2,CV3,NXD,XD,ADT,B012
% ,B112,B013,B113)

```

```

DIMENSION XMOL(99),XF(3,99),T(99),AMW(3),AD(6),GADD(3,99)
DIMENSION RP(6),RN(6),VO(3),ADT(2,20),CV2(3),CV3(3),ADD(6)

```

```

DIMENSION XD(20)

```

```

RP(1) = H ION

```

```

RP(2) = LI ION

```

```

RP(3) = NA ION

```

```

RP(4) = CA ION

```

```

RN(1) = BR ION

```

```

RN(2) = CL ION

```

```

RP(1)=2.08*10.**(-8.0)

```

```

RP(2)=0.60*10.**(-8.0)

```

```

RP(3)=0.95*10.**(-8.0)

```

```

RP(4)=0.99*10.**(-8.0)

```

```

RN(1)=1.95*10.**(-8.0)

```

```

RN(2)=1.81*10.**(-8.0)

```

```

CONST=1.6710383*10.**(-3.0)

```

```

DO 10 I=1,NP

```

```

ALFA=2.0

```

```

AN1=XMOL(I)

```

```

IF(XF(2,I).EQ.0.0)GO TO 20

```

```

IF(XF(3,I).EQ.0.0)GO TO 20

```

```

AMS=XF(2,I)*AMW(2)+XF(3,I)*AMW(3)

```

```

TNS=1000./AMS

```

```

CALL TEMPD(CV2,CV3,NXD,XD,ADT,AD,VO,T(I))

```

```

B12=B012*ALOG((T(I)-243.)/T(I))+B112/T(I)

```

```

B13=B013*ALOG((T(I)-243.)/T(I))+B113/T(I)

```

```

CONST1=FNP*FZF**2./RP(NPION)+FNM*FZN**2./RN(NNION)

```

```

CALL FUNCT(XF(2,I),XF(3,I),T(I),TNS,F2,F3,

```

```

% ADB,FD2,FD3,AD,DS,ADD,VO,NDEN,AMW)

```

```

TN3=XF(3,I)*TNS

```

```

TN2=XF(2,I)*TNS

```

```

?
```

```
D=EXP(-ALFA*AN1**0.5)
A=(TN2*TN3)**0.5
B=XF(2,I)*B13-XF(3,I)*B12
C=EXP(2.0*XF(2,I))
AX=(1.0-ALFA*XMOL(I)/(4.0*AN1**0.5))
GADD(1,I)=DELTA*D*CONST*CONST1*A*B*C*XMOL(I)*AX/(FK*T(I)*DS)
GADD(2,I)=DELTA*D*CONST*CONST1*(XMOL(I)**2.0)*((TN3/TN2)**0.5
% *B*C/2.0-A*B*C*FD2/DS+(B12+B13)*XF(3,I)*A*C/TNS+A*B*C*2.0*
% XF(3,I)/TNS)/(DS*T(I)**2.0)
GADD(3,I)=DELTA*D*CONST*CONST1*(XMOL(I)**2.0)*((TN2/TN3)**0.5
% *B*C/2.0-A*B*C*FD3/DS-(B12+B13)*XF(2,I)*A*C/TNS-A*B*C*2.0*
% XF(2,I)/TNS)/(DS*T(I)**2.0)
GO TO 10
20 GADD(1,I)=0.0
   GADD(2,I)=0.0
   GADD(3,I)=0.0
10 CONTINUE
   RETURN
   END
```

```

SUBROUTINE FUNCB(X2,X3,B12,B13,BM,FB2,FB3,TNS,B123,
% AI,FNF,FNM,FZF,FZN,AMS,AMW2,AMW3,FB1,XMDL)

```

```

*****

```

```

SUBROUTINE FUNCB

```

```

THIS SUBROUTINE CALCULATES THE MIXTURE TERNARY BROMLEY

```

```

CONSTANT 'BM' . B123 IS THE TERNARY ADJUSTABLE PARAMETER.

```

```

*****

```

```

AN1=XMDL
D23=B123
A=(X2*X3)**0.25
ALFA=2.0
D=(1.0+ALFA*AN1**0.5)**3.0
D1=((1.0+ALFA*AN1**0.5)**4.0)*(AN1**0.5)
B=EXP(-ALFA*X3)
FDEN2=ALFA*X3*B/TNS
FDEN3=-ALFA*X2*B/TNS
FDAN2=((X3/X2)**0.25/(X2**0.5))/2.0-A)/TNS/2.0
FDAN3=((X2/X3)**0.25/(X3**0.5))/2.0-A)/TNS/2.0
BM=B12*X2+B13*X3+D23*A*B/D
FB2=(B12-B13)*X3/TNS+D23*(A*FDEN2+B*FDAN2)/D
FB3=(B13-B12)*X2/TNS+D23*(A*FDEN3+B*FDAN3)/D
FB1=-3.0*ALFA*D23*A*B/(2.0*D1)
RETURN
END

```



```

XA(I)=X(1,I)*FNP
DT1=(XA(I)*GPN3+X(2,I)*G23+X(3,I))**2.0
DT2=(XA(I)*GPN2+X(3,I)*G32+X(2,I))**2.0
DT3=X(3,I)*G32+X(2,I)
DT4=X(2,I)*G23+X(3,I)
TT1=ZPN2*GPN2*XA(I)**2.+XA(I)*X(3,I)*ZPN2*G32+XA(I)*X(3,I)
% *Z32*GPN2+Z32*G32*X(3,I)**2.
TT2=XA(I)*X(3,I)*Z23*GPN3+Z23*X(3,I)**2.
% -XA(I)*X(3,I)*ZPN3*G23
TT3=X(2,I)*(X(3,I)*G32*ZPN2+X(2,I)*ZPN2-X(3,I)*Z32*GPN2)
TT4=X(3,I)*(X(2,I)*G23*ZPN3+X(3,I)*ZPN3-X(2,I)*Z23*GPN3)
TT5=ZPN3*GPN3*XA(I)**2.+XA(I)*ZPN3*G23*X(2,I)+XA(I)
% *X(2,I)*Z23*GPN3+Z23*G23*X(2,I)**2.
TT6=XA(I)*X(2,I)*Z32*GPN2+Z32*X(2,I)**2.-XA(I)*
% X(2,I)*ZPN2*G32
GNRT(1,I)=(TT3/DT2+TT4/DT1-X(2,I)*ZPN2/DT3-X(3,I)*ZPN3/DT4
% +X(2,I)*X(3,I)*Z32*GPN2/(DT3**2.))+X(2,I)*X(3,I)*Z23*GPN3/
% (DT4**2.))*FNP/R/T(I)/FK
TT7=(Z32*GPN2-ZPN2*G32)/(DT3**2.)+(Z23*GPN3+ZPN3*G23)
% /(DT4**2.)
TT8=2.*XA(I)*X(2,I)*X(3,I)*(Z32*GPN2/(DT3**3.))+Z23*GPN3*G23/
% (DT4**3.)
TT9=2.*XA(I)*X(2,I)*X(3,I)*(G32*Z32*GPN2/(DT3**3.))+Z23*GPN3
% /(DT4**3.)
TT10=(Z32*GPN2+ZPN2*G32)/(DT3**2.)+(Z23*GPN3-G23
% *ZPN3)/(DT4**2.)
GNRT(2,I)=(TT1/DT2+TT2/DT1+XA(I)*X(3,I)*TT7-TT8)/R/T(I)
GNRT(3,I)=(TT5/DT1+TT6/DT2+XA(I)*X(2,I)*TT10-TT9)/R/T(I)
4001 CONTINUE
      RETURN
      END

```

```

SUBROUTINE DEBHUC(XMOL,XF,X,FK,FNP,FNM,FZP,FZN,GEL,
% AMW,T,NP,GDH,GPHY,ADD,NDEN,CV2,CV3,NXD,XD,ADT)

```

```

*****

```

```

SUBROUTINE DEBHUC

```

```

THIS SUBROUTINE CALCULATES ION-ION INTERACTION USING
THE EXTENDED DEBYE-HUCKEL EQUATION, IN MODEL # 1.

```

```

GDH(J,I) - D.H CONTRIBUTION IN EQUATION
GPHY(J,I) - EXTENDED PART OF THE D.H EQUATION
GEL(J,I) - COMBINATION OF ABOVE TWO TERMS

```

```

*****

```

```

DIMENSION VO(3),XF(3,99),X(3,99),XMOL(99),GEL(3,99),GDH(3,99),
% GPHY(3,99),AI(99),AMW(3),T(99),AD(6)
DIMENSION F2(99),F3(99)
DIMENSION SIG(99),SIG1(99),SAI(99),SAI1(99)
DIMENSION ADD(6),CV2(3),CV3(3),XD(20),ADT(2,20)
AA=1.5/(FZP*FZN)
DO 4001 I=1,NP
IF(XMOL(I).EQ.0.0)GO TO 2010
AMS=XF(2,I)*AMW(2)+XF(3,I)*AMW(3)
TNS=1000./AMS
CALL TEMPD(CV2,CV3,NXD,XD,ADT,AD,VO,T(I))
IF(XF(2,I).EQ.0.0)GO TO 1000
IF(XF(3,I).EQ.0.0)GO TO 1010
CALL FUNCT(XF(2,I),XF(3,I),T(I),TNS,F2(I),F3(I),
% ADB,FD2,FD3,AD,DS,ADD,VO,NDEN,AMW)
GO TO 1020
1000 F2(I)=0.0
F3(I)=0.0
D30=AD(1)+AD(2)*XF(3,I)+AD(3)*XF(3,I)**2.+AD(4)*XF(3,I)
% **3.+AD(5)*XF(3,I)**4.+AD(6)*XF(3,I)**5.
GO TO (10,20),NDEN
10 D03=ADD(1)+ADD(2)+ADD(3)+ADD(4)+ADD(5)+ADD(6)
GO TO 30
20 D03=AMW(3)/VO(3)
30 FD2=0.0
FD3=0.0
ADB=1.8246*10.**((6.0)*(D03**0.5))*((D30*T(I))**(-1.5))
GO TO 1020
1010 F2(I)=0.0
?
```



```

      F3(I)=0.0
      D20=AD(1)+AD(2)*XF(3,I)+AD(3)*XF(3,I)**2.+AD(4)*XF(3,I)
1    **3.+AD(5)*XF(3,I)**4.+AD(6)*XF(3,I)**5.
      GO TO (40,50),NDEN
40   DO2=ADD(1)
      GO TO 60
50   DO2=AMW(2)/VO(2)
60   FD2=0.0
      FD3=0.0
      ADB=1.8246*10.**(6.0)*(DO2**0.5)*((D20*T(I))**(-1.5))
1020 AI(I)=XMOL(I)*(FNF*FZF**2.+FNM*FZN**2.)/2.
      XT1=0.001*FK*XMOL(I)*AMS
      XT2=ALOG(XT1+1.)
      ROW=1.0
      FT1=ROW*AI(I)**0.5
      FT2=1.+FT1
      FT3=AA*AI(I)
      FT4=1.+FT3
      SIG(I)=3.*(FT2-2.*ALOG(FT2)-1./FT2)/(FT1**3.)
      SIG1(I)=2.*(FT2**2./2.-2.*FT2+ALOG(FT2)+1.5)/(FT1**3.)
      SAI(I)=2.*(2.*(FT3-2.)*((1.+FT3)**0.5)/FT3+4./FT3-(FT3-2.)/
% ((1.+FT3)**0.5)-2.*((1.+FT3)**0.5))/3./FT3
      SAI1(I)=2.*(2.*(FT3-2.)*((1.+FT3)**0.5)/FT3+4./FT3)/3./FT3
      GEL(1,I)=-2.303*ADB*FZF*FZN*AI(I)**0.5/FT2+2.303*AI(I)
% *FZF*FZN*ADB**2.0/(FT4**0.5)+XT2
      TT1=2.303*FK*XMOL(I)*ADB*SIG(I)*AI(I)**0.5/3./1000.
      TT2=2.303*FK*XMOL(I)*TNS*AMS*AI(I)**0.5*SIG1(I)/1000.
      TT3=2.303*FK*XMOL(I)*AI(I)*SAI(I)*ADB**2./2./1000.
      TT4=2.303*FK*XMOL(I)*TNS*AMS*AI(I)*ADB*SAI1(I)/1000.
      GEL(2,I)=((TT1+TT3)*AMW(2)+(TT4-TT2)*F2(I))*FZF*FZN+
% XT2-XT1
      GEL(3,I)=((TT1+TT3)*AMW(3)+(TT4-TT2)*F3(I))*FZF*FZN+
% XT2-XT1
      GDH(1,I)=-2.303*ADB*FZF*FZN*AI(I)**0.5/FT2
      GDH(2,I)=(TT1*AMW(2)-TT2*F2(I))*FZF*FZN
      GDH(3,I)=(TT1*AMW(3)-TT2*F3(I))*FZF*FZN
      GPHY(1,I)=2.303*AI(I)*FZF*FZN*ADB**2./(FT4**0.5)
      GPHY(2,I)=(TT3*AMW(2)+TT4*F2(I))*FZF*FZN
      GPHY(3,I)=(TT3*AMW(3)+TT4*F3(I))*FZF*FZN
      GO TO 4001
2010 GEL(1,I)=0.0
      GEL(2,I)=0.0
      GEL(3,I)=0.0
      GDH(1,I)=0.0
      GDH(2,I)=0.0
      GDH(3,I)=0.0
      GPHY(1,I)=0.0
      GPHY(2,I)=0.0
      GPHY(3,I)=0.0
4001 CONTINUE

```

RETURN
END


```
150   FORMAT(/,3X,'ALFA3=',G12.5,'ALFB3=',G12.5,'DGA3=',  
      % G12.5,'DGB3=',G12.5)  
      GO TO 9052  
40    WRITE(6,9086)GPN3,ZPN3  
9086  FORMAT(/,10X,'GPN3=',G12.5,3X,'ZPN3=',G12.5)  
      GO TO 9052  
9061  WRITE(6,7140)ALFA,DG23,DG32  
7140  FORMAT(/,3X,' NONELECTROLYTE BINARY : ALFA=',G12.5,  
      % 'DG23=',G12.5,'DG32=',G12.5)  
      IF(XMOL.EQ.0.0)GO TO 9052  
      IF(KP.GT.1)GO TO 9051  
      WRITE(6,130)  
      WRITE(6,7150)B012,B112,B013,B113  
7150  FORMAT(/,5X,'B012=',G10.3,'B112=',G10.3,'B013=',G10.3  
      % , 'B113=',G10.3)  
      WRITE(6,200)B123,DELTA  
200   FORMAT(/,15X,' B123=',G12.5,'DELTA =',G12.5)  
      GO TO 9052  
9051  WRITE(6,110)  
      GO TO(70,80),NNRTL  
70    WRITE(6,100)ALFA2,ALFB2,DGA2,DGB2  
      WRITE(6,150)ALFA3,ALFB3,DGA3,DGB3  
      GO TO 9052  
80    WRITE(6,7160)GPN2,ZPN2,GPN3,ZPN3  
7160  FORMAT(/,6X,'GPN2=',G12.5,'ZPN2=',G12.5,'GPN3=',  
      % G12.5,'ZPN3=',G12.5)  
9052  RETURN  
      END
```

INPUT DATA SEQUENCE

Card #	<u>Variables</u>	<u>Format</u>
1	NSET,LL,EE	2I3,F10.1
2-21	INFORMATION	8A10
22	XLIM,XLLIM	2F10.5
23	NAME1,NAME2,NAME3 (name of the system)	3A8
24	INDF,KP,NBIN,NPION,NNION,NREG,NDEN,NNRTL,NBROM,NTYPE,NMIN	11I2
25	NCOMP,NP,NXD,NXDD	4I2
26	CP2(I), I=1,6	
27	CP3(I), I=1,6 (pure component vapor pressure constants)	F12.7,F11.5,F8.3, F3.1,F10.5
28	AMW(I), I=1,3	6F10.5
29	V21,T21,V22,T22,V23,T23	
30	V31,T31,V32,T32,V33,T33	6F10.6
31-(30+NXD)	ADT(1,I),ADT(2,I),XD(I) (total # of data are nxd) (if NXD = 11, card #31-41)	3F10.5
42	FK,FNP,FNM,FZP,FZN	5F10.5
43-(42+NXDD)	DENS(I),XDD(I) (only two data on a card,total # NXDD) (if NXDD=13, card #43-55)	6F10.5
56-(55+NP)	XMOL(I), XG(I), Y(J,I), J=2,3), G(1,I), P(I),T(I) (8 data on a card, total card = NP) (IF NP=34, card #56-89)	8F10.6
90	ALFA,DG23,DG32,ALFA2,ALFB2,ALFA3,ALFB3	8F10.5
91	GPN2,ZPN2,GPN3,ZPN3,DGA2,DGB2,DGA3,DGB3	8F10.5
92	BO12,B112,BO13,B113,B123,DELTA	8F10.5
93	ALPHA1,AXT1,BXT1	F10.7,2F10.4

94 M,MM 2I2
95-(94+MM) XTX(I),BXX(I) (two data on a card, 2F10.4
total cards = MM) (if MM=4 cards 95-98)

SAMPLE INPUT

```

1. 0014000.0000010
2. *****
3. * FILE NAME - LICLH2O.MEOHAT25.COMBINED
4. *
5. *
6. *
7. *
8. * BINARY 1-3: SKABICHVESKKI
9. *
10. * TERNARY 1-2-3: CIPARIS
11. *
12. *
13. *
14. *
15. *
16. *
17. *
18. *
19. *****
20.
21.
22. 3.000000000.0
23. LICL - H2O - MEOH
24. 1 2 5 2 2 1 1 2 1 4 2
25. 3341113
26. 0070.4346943-7362.698100000.000000.0069520850.0 -9.0
27. 0012.3858228-3880.50203 -24.355000.0000000000.0 00.000
28. 42.4 18.0 32.0
29. 18.06 277.13 18.278 323.15 18.844 373.15
30. 39.556 273.15 44.874 373.15 57.939 473.15
31. 1.9051 -0.00205 0.0
32. 1.8799 -0.00208 0.0588
33. 1.8505 -0.00212 0.1233
34. 1.8190 -0.00218 0.1942
35. 1.7865 -0.00225 0.2727
36. 1.7513 -0.00234 0.3600
37. 1.7120 -0.00244 0.4576
38. 1.6658 -0.00252 0.5676
39. 1.6160 -0.00248 0.6923
40. 1.5648 -0.00242 0.8351
41. 1.5099 -0.00234 1.0
42. 2.000 1.000 1.000 1.00 1.0
43. 0.99707 00.0
44. 0.98472 00.04085
45. 0.97919 00.06168
46. 0.96649 00.11445

```


47.	0.94796	00.19739							
48.	0.93658	00.24867							
49.	0.91534	00.34382							
50.	0.88242	00.49446							
51.	0.85790	00.61267							
52.	0.84210	00.69241							
53.	0.82458	00.78454							
54.	0.80510	00.89229							
55.	0.78663	01.0							
56.	1.0	0.815184	0.395	0.146118	0.605	1.0	47.3	298.15	
57.	1.0	0.672192	0.235	0.285347	0.765	1.0	65.3	298.15	
58.	1.0	0.505166	0.14	0.447977	0.86	1.0	80.0	298.15	
59.	1.0	0.284199	0.07	0.66313	0.93	1.0	96.3	298.15	
60.	1.0	0.039517	0.007	0.901372	0.993	1.0	115.3	298.15	
61.	0.328	0.0	0.0	0.979440	1.0	1.0	125.0818	298.15	
62.	1.340	0.0	0.0	0.921014	1.0	1.0	116.4291	298.15	
63.	1.933	0.0	0.0	0.889908	1.0	1.0	109.5579	298.15	
64.	2.560	0.0	0.0	0.859225	1.0	1.0	101.9232	298.15	
65.	2.971	0.0	0.0	0.840234	1.0	1.0	96.1972	298.15	
66.	3.667	0.0	0.0	0.809921	1.0	1.0	85.3814	298.15	
67.	0.100000	0.996413	1.000000	0.000000	0.000000	0.790000	23.675820298.149900		
68.	0.200000	0.992852	1.000000	0.000000	0.000000	0.757000	23.595910298.149900		
69.	0.300000	0.989316	1.000000	0.000000	0.000000	0.744000	23.514770298.149900		
70.	0.400000	0.985805	1.000000	0.000000	0.000000	0.740000	23.431860298.149900		
71.	0.500000	0.982318	1.000000	0.000000	0.000000	0.739000	23.347740298.149900		
72.	0.600000	0.978857	1.000000	0.000000	0.000000	0.743000	23.261910298.149900		
73.	0.700000	0.975420	1.000000	0.000000	0.000000	0.748000	23.174160298.149900		
74.	0.800000	0.972006	1.000000	0.000000	0.000000	0.755000	23.084890298.149900		
75.	0.900000	0.968617	1.000000	0.000000	0.000000	0.764000	22.994150298.149900		
76.	1.000000	0.965251	1.000000	0.000000	0.000000	0.774000	22.901130298.149900		
77.	1.2	0.958589	1.0	0.0	0.0	0.796	22.711330298.15		
78.	1.4	0.952018	1.0	0.0	0.0	0.823	22.513356298.15		
79.	1.6	0.945537	1.0	0.0	0.0	0.853	22.309082298.15		
80.	1.8	0.939144	1.0	0.0	0.0	0.885	22.098690298.15		
81.	2.0	0.932836	1.0	0.0	0.0	0.921	21.880828298.15		
82.	2.5	0.917431	1.0	0.0	0.0	1.026	21.301025298.15		
83.	3.0	0.902527	1.0	0.0	0.0	1.156	20.675445298.15		
84.	3.5	0.888099	1.0	0.0	0.0	1.317	19.999737298.15		
85.	4.0	0.874126	1.0	0.0	0.0	1.510	19.282137298.15		
86.	4.5	0.860585	1.0	0.0	0.0	1.741	18.531818298.15		
87.	5.0	0.847457	1.0	0.0	0.0	2.02	17.750526298.15		
88.	5.5	0.834724	1.0	0.0	0.0	2.34	16.949615298.15		
89.	6.0	0.822368	1.0	0.0	0.0	2.72	16.134811298.15		
90.	-1.00000	-150.900000	336.470000000	0.20000	00.000000000	0.20000	00.0		
91.	12.66600	068.1660	075.8180	-11.239000	135.11000	-4.12000	-17.800000	134.9	
92.	-0.07341	0.00000	-0.170760000	0.00000	-18.800000000	0.016			

9

93. 00.0000005 -1.0000001.0
94. 4 4
95. 0012.666000000.01
96. 68.166000000.10
97. 00075.818000000.1
98. -11.239000000.1

SAMPLE OUTPUT

OF DATA SET TO BE USED = 1 TRIAL #400E=0.00000100

* FILE NAME - LICLH20.MEOHAT25.COMBINED

*
*
*
*
*
*
*
*
*
*
*
*
*
*
*

BINARY 1-3: SKABICHVESKKI

TERNARY 1-2-3: CIPARIS

3.00000 0.0
 1 2 5 2 2 1 1 2 1 4 2
 INPUT DATA

3341113

70.4346924	-7362.69531	0.0	0.0069520850.0	-9.00000
12.3858223	-3880.50195	-24.355	0.0	0.0 0.0
42.39999	18.00000	32.00000		
18.06000	277.12988	18.27800	323.14990	18.84399 373.14990
39.55600	273.14990	44.87399	373.14990	57.93900 473.14990

LIQUID MOLAR VOLUME CONSTANTS

22.887	-0.36416E-01	0.68557E-04
64.510	-0.19716	0.38735E-03
1.90510	-0.00205	0.0
1.87990	-0.00208	0.05880
1.85050	-0.00212	0.12330
1.81900	-0.00218	0.19420
1.78650	-0.00225	0.27270
1.75130	-0.00234	0.36000
1.71200	-0.00244	0.45760
1.66580	-0.00252	0.56760
1.61600	-0.00248	0.69230
1.56480	-0.00242	0.83510
1.50990	-0.00234	1.00000

0.070387	0.0	0.859225	1.000000	1.000000	1.000000	0.932243
0.079883	0.0	0.840234	1.000000	1.000000	1.000000	0.899757
0.095039	0.0	0.809921	1.000000	1.000000	1.000000	0.828483
0.001794	0.996413	0.0	0.790000	1.000259	1.000000	1.000000
0.003574	0.992852	0.0	0.757000	1.000459	1.000000	1.000000
0.005342	0.989316	0.0	0.744000	1.000582	1.000000	1.000000
0.007098	0.985805	0.0	0.740000	1.000606	1.000000	1.000000
0.008841	0.982318	0.0	0.739000	1.000552	1.000000	1.000000
0.010572	0.978857	0.0	0.743000	1.000399	1.000000	1.000000
0.012290	0.975420	0.0	0.748000	1.000136	1.000000	1.000000
0.013997	0.972006	0.0	0.755000	0.999784	1.000000	1.000000
0.015692	0.968617	0.0	0.764000	0.999338	1.000000	1.000000
0.017375	0.965251	0.0	0.774000	0.998766	1.000000	1.000000
0.020706	0.958589	0.0	0.796000	0.997357	1.000000	1.000000
0.023991	0.952018	0.0	0.823000	0.995487	1.000000	1.000000
0.027232	0.945537	0.0	0.853000	0.993216	1.000000	1.000000
0.030428	0.939144	0.0	0.885000	0.990546	1.000000	1.000000
0.033582	0.932836	0.0	0.921000	0.987413	1.000000	1.000000
0.041285	0.917431	0.0	1.025999	0.977389	1.000000	1.000000
0.048737	0.902527	0.0	1.155999	0.964350	1.000000	1.000000
0.055951	0.888099	0.0	1.316999	0.947989	1.000000	1.000000
0.062937	0.874126	0.0	1.509999	0.928585	1.000000	1.000000
0.069708	0.860585	0.0	1.740999	0.906494	1.000000	1.000000
0.076271	0.847457	0.0	2.020000	0.881726	1.000000	1.000000
0.082638	0.834724	0.0	2.339999	0.854786	1.000000	1.000000
0.088816	0.822368	0.0	2.719999	0.825920	1.000000	1.000000
-1.000000	-150.89999	336.46997	0.20000	0.20000	0.0	
12.66600	68.16599	75.81799	-4.12000	-17.79999	134.89999	
-0.07341	0.0	-0.17076	0.0	0.0	0.0	
0.0000005	-1.0000	1.0000	-18.79999	0.01600		

4 4
 12.6660 0.0100
 68.1660 0.1000
 75.8180 0.1000
 -11.2390 0.1000
 *****MAXIMUM MOLALITY USED= 4.00000

VLE DATA ARE PREDICTED USING MODEL # 1

COMPONENT #	MOLE-FRACTION	YEXP	YCAL	YCAL-YEXP	PCAL-PEXP	GAM EXP	% ERROR IN GAM
2	0.81518	0.39500	0.39209	0.00291	6.00903	0.100E 59	0.100E 59
3	0.14612	0.60500	0.60791	0.00291	6.00903		
1	1.00	-4.22	-0.724	0.0	0.127E-01		

2	1.00	0.810E-01	0.107E-01	-0.145E-01	0.0	1.08	0.965	-11.9	
3	1.00	0.557	-0.158E-01	0.148E-01	0.0	1.74	1.54	-13.2	
COMPOONENT # MOLE-FRACTION									
2	0.67219	0.23500	0.24449	YCAL	YCAL-YEXP	PCAL-PEXP			
3	0.28535	0.76500	0.75551	0.24449	-0.00949	5.62950			
COMPOONENT # MOLALITY									
1	1.00	LOG NRTL	LOG COULOMBIC	LOG PHYSICAL	LOG ADDITION	GAM CAL	GAM EXP	% ERROR IN GAMMA	
2	1.00	-3.60	-0.883	0.856	0.0	0.265E-01	0.100E 59	0.100E 59	
3	1.00	0.947E-01	0.193E-01	-0.305E-01	0.0	1.09	0.961	-13.0	
		0.389	-0.155E-01	0.165E-01	0.0	1.48	1.38	-7.27	
COMPOONENT # MOLE-FRACTION									
2	0.50517	0.14000	0.14603	YCAL	YCAL-YEXP	PCAL-PEXP			
3	0.44798	0.86000	0.85397	0.14603	-0.00603	7.16751			
COMPOONENT # MOLALITY									
1	1.00	LOG NRTL	LOG COULOMBIC	LOG PHYSICAL	LOG ADDITION	GAM CAL	GAM EXP	% ERROR IN GAMMA	
2	1.00	-2.59	-1.11	1.35	0.0	0.951E-01	0.100E 59	0.100E 59	
3	1.00	0.922E-01	0.347E-01	-0.668E-01	0.0	1.06	-0.933	-13.7	
		0.267	-0.128E-01	0.143E-01	0.0	1.31	1.21	-8.20	
COMPOONENT # MOLE-FRACTION									
2	0.28420	0.07000	0.06173	YCAL	YCAL-YEXP	PCAL-PEXP			
3	0.66313	0.93000	0.93827	0.06173	0.00827	6.08536			
COMPOONENT # MOLALITY									
1	1.00	LOG NRTL	LOG COULOMBIC	LOG PHYSICAL	LOG ADDITION	GAM CAL	GAM EXP	% ERROR IN GAMMA	
2	1.00	-0.814	-1.48	2.41	0.0	1.12	0.100E 59	0.100E 59	
3	1.00	0.354E-01	0.659E-01	-0.166	0.0	0.936	0.998	6.24	
		0.144	-0.150E-02	-0.118E-01	0.0	1.14	1.06	-7.26	
COMPOONENT # MOLE-FRACTION									
2	0.03952	0.00700	0.00622	YCAL	YCAL-YEXP	PCAL-PEXP			
3	0.90137	0.99300	0.99378	0.00622	0.00078	-9.29149			
COMPOONENT # MOLALITY									
1	1.00	LOG NRTL	LOG COULOMBIC	LOG PHYSICAL	LOG ADDITION	GAM CAL	GAM EXP	% ERROR IN GAMMA	
2	1.00	1.64	-1.97	4.24	0.0	50.1	0.100E 59	0.100E 59	
3	1.00	-0.109	0.105	-0.347	0.0	0.703	0.860	18.3	
		-0.246E-02	0.247E-01	-0.105	0.0	0.919	0.998	7.99	

TABLE#

SYSTEM: LICL - H2O - MEOH

** VALUES OF THE PARAMETERS **

NONELECTROLYTE BINARY : ALFA= -1.0000 DG23= -150.90 DG32= 336.4

EXTENDED DEBYE-HUCKEL + MODIFIED NRTL

GPN2= 12.666 ZPN2= 68.166 GPN3= 75.818 ZPN3= -11.239

MOLALITY	X2	X3	Y3EXP	Y3CAL	DY	DP
1.00	0.81518	0.14612	0.60500	0.60791	0.291E-02	6.01
1.00	0.67219	0.28535	0.76500	0.75551	-0.949E-02	5.63
1.00	0.50517	0.44798	0.86000	0.85397	-0.603E-02	7.17
1.00	0.28420	0.66313	0.93000	0.93827	0.827E-02	6.09
1.00	0.39517E-01	0.90137	0.99300	0.99378	0.779E-03	-9.29

AVERAGE DY(YCAL-YEXP)= 0.54953E-02
 BASED ON # OF POINTS FOR Y = 5

AVERAGE DP(PCAL-PEXP)= 6.8366
 BASED ON # OF POINTS FOR DP = 5

?

APPENDIX G

TABLES AND FIGURES FOR MODEL I

TABLE G.1 Binary Data Sources

#	System	T(°C) or P(atm)	'm' Range	Type of Data	# of Data Points	Reference
1	CaCl ₂ -H ₂ O	25	0.1-6.0	m vs γ_{\pm} and P	23	Robinson & Stokes (1955)
2	HCl-H ₂ O	25	0.1-2.0	m vs γ_{\pm} & γ_{solvent}	15	Robinson & Stokes (1955)
3	LiCl-H ₂ O	25	0.1-6.0	m vs γ_{\pm} and P	27	Robinson & Stokes (1955)
4	LiCl-H ₂ O	60	0.88-9.0	m vs P	17	Hala (1969)
5	NaBr-H ₂ O	25	0.1-4.0	m vs γ_{\pm} and P	19	Robinson & Stokes (1955)
6	NaBr-H ₂ O	40	4.0	m vs P	4	Ciparis (1966)
7	NaCl-H ₂ O	25, 60, 70 80, 90, 100	0.1-4.0	m vs γ_{\pm} and P	11	Robinson & Stokes (1955)
8	CaCl ₂ -MeOH	25	0.3-2.6	m vs P	7	Eric (1979)
9	HCl-MeOH	25	0.002-0.56	m vs γ_{\pm}	22	Harned & Owen (1958)
10	HCl-EtOH	25	0.005-0.1	m vs γ_{\pm}	8	Janz & Taniguichi (1957)
11	LiBr-MeOH	15, 25	0.3-6.6	m vs P		Skabichevskii (1969)
12	LiCl-MeOH	25	0.33-3.67	m vs P	6	Skabichevskii (1969)
13	LiCl-MeOH	60	0.33-7.4	m vs P	12	Hala (1969)
14	NaBr-MeOH	25	0.56-1.56	m vs P	9	Eric (1979)
15	NaCl-MeOH	25	0.0001-0.1	m vs γ_{\pm}	7	Convington (1973)

TABLE G.1 Binary Data Sources (Cont'd.)

#	System	T (°C) or P (atm)	'm' Range	Type of Data	# of Data Points	Reference
16	H ₂ O-MeOH	25	0.0	X-y-P-T	8	Ciparis (1966)
17	H ₂ O-MeOH	40	0.0	X-y-P-T	6	Ciparis (1966)
18	H ₂ O-EtOH	25	0.0	X-y-P-T	10	Ciparis (1966)
19	H ₂ O-MeOH	1 atm	0.0	X-y-P-T	34	Rebollada (1958)

TABLE G.2 Ternary Data Sources

#	System	T or P	'm' Range	Type of Data	# of Data Points	Reference
1	HCl-H ₂ O-EtOH	25°C	0.006-2.5	m-X-γ _±	44	Harned & Owen (1958)
2	HCl-H ₂ O-MeOH	25°C	0.02-0.5	m-X-γ _±	24	Akerlof (1930)
3	HCl-H ₂ O-MeOH	25°C	0.001-2.0	m-X-γ _±	24	Harned & Owen (1958)
4	LiCl-H ₂ O-EtOH	25°C	0.5-4.0	m-X-y-P-T	31	Ciparis (1966)
5	LiCl-H ₂ O-MeOH	25°C	0.02-1.0	m-X-γ _±	45	Akerlof (1930)
6	LiCl-H ₂ O-MeOH	25°C	1.0	m-X-y-P-T	5	Ciparis (1966)
7	LiCl-H ₂ O-MeOH	60°C	0.58-14.1	m-X-y-P-T	25	Hala (1969)
8	NaBr-H ₂ O-MeOH	25°C	1.0-7.1	m-X-y-P-T	16	Ciparis (1966)
9	NaBr-H ₂ O-MeOH	40°C	1.0-6.2	m-X-y-P-T	10	Ciparis (1966)
10	NaCl-H ₂ O-MeOH	25°C	0.02-0.5	m-X-γ _±	35	Akerlof (1930)
11	KCl-H ₂ O-MeOH	1 atm	0.012-2.0	m-X-y-P-T	33	Rousseau et al. (1975)
12	LiCl-H ₂ O-MeOH	1 atm	0.085-3.8	m-X-y-P-T	24	Rousseau et al. (1975)
13	NaBr-H ₂ O-MeOH	1 atm	0.076-3.8	m-X-y-P-T	23	Rousseau et al. (1975)
14	NaF-H ₂ O-MeOH	1 atm	0.012-0.95	m-X-y-P-T	24	Rousseau et al. (1975)

TABLE G.3 Solvent-Solvent Binary Data Correlation

System	# of Points	T or P	α_{23}	Δg_{23}	Δg_{32}	ΔY			ΔP (mmHg)	
						Max	Avg	Max	Max	Avg
H ₂ O-MeOH	8	25°C	0.3	806.03	-321.46	0.013	0.004	2.0	1.4	
H ₂ O-MeOH	8	25°C	-1.0	-150.9	836.76	0.012	0.0038	2.1	1.4	
H ₂ O-MeOH	6	40°C	0.3	1453.1	-498.7	0.0146	0.0066	7.8	3.4	
H ₂ O-MeOH	6	40°C	-1.0	-364.7	493.7	0.0226	0.0086	3.5	2.2	
H ₂ O-MeOH	12	60°C	0.3	431.65	43.59	0.01	0.0057	-	4.1	
H ₂ O-MeOH	12	60°C	-1.0	140.3	235.9	0.011	0.0057	-	4.2	
H ₂ O-EtOH	10	25°C	0.3	894.5	-62.9	0.049	0.012	2.2	0.7	
H ₂ O-EtOH	10	25°C	-1.0	105.7	383.87	0.054	0.013	2.6	0.8	
H ₂ O-MeOH	34	1 atm	0.3	627.6	-54.5	0.0086	0.003	13.1	5.6	
H ₂ O-MeOH	34	1 atm	-1.0	97.077	312.5	0.007	0.0026	13.0	5.4	

TABLE G.4 Aqueous Electrolytic Binary Data Correlation with Two Objective Functions, Equations (2-9) & (2-10)

System	# of Points	Max 'm'	T (°C)	Objective Function #1				Objective Function #2							
				$G_{\pm 2}$	$Z_{\pm 2}$	% Error in γ_{\pm} Max Avg	% Error in DP Max Avg	$G_{\pm 2}$	$Z_{\pm 2}$	% Error in γ_{\pm} Max Avg	% Error in DP Max Avg				
CaCl ₂ -H ₂ O	21	5.0	25	37.755	13.545	24.2	7.6	7.7	4.3	36.411	13.766	25.9	7.5	7.8	4.1
HCl-H ₂ O	15	2.0	25	0.094	-32.79	5.4	2.4	-	-	-	-	-	-	-	-
LiCl-H ₂ O	22	4.0	25	0.209	-19.1	16.6	6.4	11.7	3.3	0.056	-81.532	15.1	6.5	11.1	3.3
LiCl-H ₂ O	11	6.0	60	0.0515	-279.7	-	-	10.4	5.1	0.0353	-287.85	-	-	8.4	4.7
NaBr-H ₂ O	19	4.0	25	37.37	1.2447	4.1	1.1	3.2	1.0	36.949	1.261	4.3	1.1	3.3	1.0
NaBr-H ₂ O	4	10.3	40	0.05	-109.4	-	-	9.4	4.6	0.0266	-108.23	-	-	7.7	4.7
NaCl-H ₂ O	10	1.0	25	12.63	3.136	0.3	0.14	1.0	0.4	12.638	3.173	0.37	0.17	0.9	0.3

TABLE G.6 Aqueous Electrolytic Binary Data Correlation with Temperature Independent Parameters Using Objective Function #2, Equation (2-10) and Presetting

System	# of Points	Max 'm'	T (°C)	Δg_{A2}	Δg_{B2}	% Error in γ_{\pm}		% Error in DP	
						Max	Avg	Max	Avg
CaCl ₂ -H ₂ O	17	3.0	25	-42.589	668.8	7.1	4.2	5.0	2.8
HCl-H ₂ O*	15	2.0	25	77.553	-3.3056	5.5	2.4	-	-
LiCl-H ₂ O	19	4.0	25	61.958	-5.0817	15.8	6.6	11.6	3.3
LiCl-H ₂ O	11	6.0	60	81.743	-11.592	-	-	8.6	5.0
NaBr-H ₂ O	4	10.3	40	98.318	-3.2249	-	-	7.8	4.9
NaBr-H ₂ O	19	4.0	25	-24.258	174.11	9.4	4.0	8.1	2.3
NaCl-H ₂ O	17	4.0	25	-32.396	444.79	3.4	1.2	3.3	1.0

$$\alpha_{A2} = 0.2; \alpha_{B2} = 0.0$$

*For the system HCl-H₂O binary objective function #1 [Equation (2-9)] is used.

TABLE G.7 Nonaqueous Electrolytic Binary Data Correlation with Temperature Independent Parameters Using Objective Function #2, Equation (2-10) and Presetting $\alpha_{A3} = 0.2$; $\alpha_{B3} = 0.0$

System	# of Points	Max 'm'	T (°C)	ΔG_{A3}	ΔG_{B3}	% Error in γ_{\pm}		% Error in DP	
						Max	Avg	Max	Avg
CaCl ₂ -MeOH	7	3.0	25	-16.156	289.16	-	-	16.3	9.3
HCl-EtOH	8	0.1	25	-58.994	6897.7	8.7	6.0	-	-
HCl-MeOH	22	0.56	25	-28.306	317.33	0.66	0.4	-	-
LiCl-EtOH	3	4.0	25	-14.056	187.82	-	-	15.3	12.3
LiCl-MeOH	6	4.0	25	-20.384	161.93	-	-	7.0	3.4
LiCl-MeOH	11	6.0	60	-19.497	170.92	-	-	17.5	7.3
NaBr-MeOH	9	1.6	25	-21.556	177.28	-	-	4.1	1.9
NaCl-MeOH	7	0.1	25	-10.262	210.86	11.3	6.6	-	-
LiBr-MeOH	8	6.64	15	-20.198	158.28	-	-	2.9	1.5
LiBr-MeOH	8	6.64	30	-23.999	216.56	-	-	14.0	5.7

TABLE G.8 Binary Data Correlation with Temperature Independent Parameters Using Objective Function #2, Equation (2-10) and Presetting $\alpha_{Ai} = 0.2$; $\alpha_{Bi} = -1.0$

System	# of Points	Max γ_m	T (°C)	Δg_{Ai}	Δg_{Bi}	% Error in γ_{\pm}		% Error in DP	
						Max	Avg	Max	Avg
LiCl-H ₂ O	19	4.0	25	-2.8668	-12.27	16.1	6.6	11.6	3.4
NaBr-H ₂ O	4	10.3	40	-2.1801	-13.616	-	-	7.7	5.0
LiCl-EtOH	2	1.0	25	20.872	6.102	-	-	26.6	22.5
LiCl-MeOH	6	3.7	25	20.285	5.32	-	-	16.6	9.7
NaBr-MeOH	9	1.6	25	19.938	5.2467	-	-	6.9	5.7
LiCl-MeOH	11	6.0	60	23.133	6.3664	-	-	42.7	27.4

TABLE G.9 Binary Data Correlation with Temperature Independent Parameters Using Objective Function #2, Equation (2-10) and Presetting $\alpha_{Ai} = -1.0$; $\alpha_{Bi} = -1.0$

System	# of Points	Max 'm'	T (°C)	Δg_{Ai}	Δg_{Bi}	% Error in DP	
						Max	Avg
LiCl-EtOH	2	1.0	25	6.1822	-27.801	27.5	25.3
LiCl-MeOH	6	3.7	25	5.4454	-32.375	17.7	10.5
NaBr-MeOH	9	1.6	25	5.3709	-32.753	7.3	3.9
LiCl-MeOH	11	6.0	60	6.479	-51.103	43.6	28.3
CaCl ₂ -MeOH	7	2.6	25	-50.83	7.1956	275.7	205.0

TABLE G.10 Prediction of Binary Data at One Temperature Using the Parameters of Another Temperature, Presetting $\alpha_{Ai} = 0.2$ and $\alpha_{Bi} = 0.0$

System	# of Points	Max 'm'	T (°C)	T of T (°C)	Parameters Used		% Error in γ_{\pm}		% Error in DP	
					Δg_{Ai}	Δg_{Bi}	Max	Avg	Max	Avg
LiCl-H ₂ O	19	6.0	25	60	81.743	-11.592	24.3	11.2	14.3	5.2
LiCl-H ₂ O	11	6.0	60	25	61.958	-5.0817	-	-	13.0	5.8
NaBr-H ₂ O	19	4.0	25	40	98.318	-3.2249	33.5	20.5	9.4	6.8
NaBr-H ₂ O	4	10.3	40	25	163.29	12.545	-	-	25.1	11.6
LiBr-MeOH	8	6.6	15	30	-23.999	216.56	-	-	23.4	13.8
LiBr-MeOH	8	6.6	30	15	-20.198	158.28	-	-	30.4	9.4
LiCl-MeOH	9	6.0	25	60	-19.497	170.9	-	-	62.0	42.0
LiCl-MeOH	11	6.0	60	25	-20.384	161.8	-	-	39.6	35.1

TABLE G.11 Isothermal Ternary γ_{\pm} Data Correlation for the Four Parameters: $G_{\pm 2}$, $Z_{\pm 2}$, $G_{\pm 3}$ and $Z_{\pm 3}$,
 Presetting the Solvent-Solvent Binary Parameters Corresponding to $\alpha_{23} = -1.0$

System	# of Points	Max 'm'	T (°C)	α_{23}	Δg_{23}	Δg_{32}	$G_{\pm 2}$	$Z_{\pm 2}$	$G_{\pm 3}$	$Z_{\pm 3}$	% Error in γ_{\pm}	
											Max	Avg
HCl-H ₂ O-EtOH	44	2.5	25	-1.0	105.8	383.8	19.677	1.789	9.460	84.647	10.0	2.0
HCl-H ₂ O-MeOH	48	2.0	25	-1.0	-150.9	336.5	19.677	1.789	7.63	40.14	18.4	2.2
LiCl-H ₂ O-MeOH	45	1.0	25	-1.0	-150.9	336.5	28.32	3.141	21.875	24.882	22.8	7.7
NaCl-H ₂ O-MeOH	35	1.0	25	-1.0	-150.9	336.5	38.981	4.216	44.11	14.638	27.0	6.1

TABLE G.12 A Comparative Study of the Three Objective Functions [Equations (2-19), (2-20), (2-21)] in Correlating Ternary Isothermal VLE Data with the Four Parameters $[G_{\pm 2}, Z_{\pm 2}, G_{\pm 3}, Z_{\pm 3}]$, Presetting Δg_{23} and Δg_{32} from Table G.3 Corresponding to $\alpha_{23} = -1.0$

System	Max 'm'	T (°C)	ΔY		ΔP (mmHg)	
			Max	Avg	Max	Avg
<u>Objective Function #1</u>						
LiCl-H ₂ O-EtOH	1.0	25	0.035	0.011	5.6	2.2
LiCl-H ₂ O-MeOH	1.0	25	0.022	0.012	8.0	4.8
NaBr-H ₂ O-MeOH	6.2	40	0.023	0.012	11.5	5.1
NaBr-H ₂ O-MeOH	7.1	25	0.047	0.017	15.0	8.8
LiCl-H ₂ O-MeOH	6.0	60	0.04	0.015	33.2	13.8
<u>Objective Function #2</u>						
LiCl-H ₂ O-EtOH	1.0	25	0.034	0.009	3.1	1.2
LiCl-H ₂ O-MeOH	1.0	25	0.009	0.0055	9.3	6.8
NaBr-H ₂ O-MeOH	6.2	40	0.022	0.01	17.7	5.6
NaBr-H ₂ O-MeOH	7.1	25	0.02	0.0088	11.4	4.8
LiCl-H ₂ O-MeOH	6.0	60	0.023	0.009	54.3	11.7
<u>Objective Function #3</u>						
LiCl-H ₂ O-EtOH	1.0	25	0.035	0.01	6.1	2.3
LiCl-H ₂ O-MeOH	1.0	25	0.011	0.0066	10.2	5.6
NaBr-H ₂ O-MeOH	6.2	40	0.022	0.011	15.2	5.4
NaBr-H ₂ O-MeOH	7.1	25	0.021	0.0092	11.3	5.0
LiCl-H ₂ O-MeOH	6.0	60	0.025	0.0097	50.3	11.6

TABLE G.13 Values of the Parameters Obtained with the Three Objective Functions for Isothermal Ternary VLE Data

System	T (°C)	$G_{\pm 2}$	$Z_{\pm 2}$	$G_{\pm 3}$	$Z_{\pm 3}$
<u>Objective Function #1</u>					
LiCl-H ₂ O-EtOH	25	6.3977	76.681	0.1946	1346.3
LiCl-H ₂ O-MeOH	25	5.4754	124.08	0.0	930.92
NaBr-H ₂ O-MeOH	40	23.21	20.24	3.653	52.82
NaBr-H ₂ O-MeOH	25	22.76	1.56	0.2243	316.1
LiCl-H ₂ O-MeOH	60	22.32	0.025	1.5917	131.0
<u>Objective Function #2</u>					
LiCl-H ₂ O-EtOH	25	12.666	68.166	0.1983	2076.1
LiCl-H ₂ O-MeOH	25	12.666	68.166	75.818	-11.239
NaBr-H ₂ O-MeOH	40	20.762	21.419	3.4156	55.672
NaBr-H ₂ O-MeOH	25	13.657	13.023	0.1382	601.16
LiCl-H ₂ O-MeOH	60	15.463	5.1261	0.2639	531.88
<u>Objective Function #3</u>					
LiCl-H ₂ O-EtOH	25	13.644	53.324	0.1282	2122.4
LiCl-H ₂ O-MeOH	25	13.644	53.324	59.022	-11.455
NaBr-H ₂ O-MeOH	40	21.205	20.357	3.364	53.684
NaBr-H ₂ O-MeOH	25	14.979	11.67	0.1367	604.9
LiCl-H ₂ O-MeOH	60	17.929	4.017	0.2525	634.78

TABLE G.14 A Comparative Study of the Three Objective Functions [Equations (2-19), (2-20), (2-21)] in Correlating Ternary Isobaric VLE Data with the Four Parameters [Δg_{A2} , Δg_{B2} , Δg_{A3} & Δg_{B3}] Presetting Δg_{23} and Δg_{32} Corresponding to $\alpha_{23} = -1.0$ [Table G.3] and $\alpha_{A2} = 0.2$; $\alpha_{B2} = 0.0$; $\alpha_{A3} = 0.2$; $\alpha_{B3} = 0.0$

System	Max 'm'	P (mmHg)	ΔY		ΔP (mmHg)	
			Max	Avg	Max	Avg
<u>Objective Function #1</u>						
LiCl-H ₂ O-MeOH	3.8	760.0	0.04	0.0135	39.0	15.7
NaBr-H ₂ O-MeOH	3.8	760.0	0.053	0.021	35.1	14.9
KCl-H ₂ O-MeOH	2.0	760.0	0.055	0.016	34.3	14.4
NaF-H ₂ O-MeOH	1.0	760.0	0.051	0.01	35.6	13.9
<u>Objective Function #2</u>						
LiCl-H ₂ O-MeOH	3.8	760.0	0.036	0.0136	39.7	16.2
NaBr-H ₂ O-MeOH	3.8	760.0	0.052	0.02	35.1	13.1
KCl-H ₂ O-MeOH	2.0	760.0	0.056	0.0155	38.9	15.7
NaF-H ₂ O-MeOH	1.0	760.0	0.051	0.01	35.5	15.6
<u>Objective Function #3</u>						
LiCl-H ₂ O-MeOH	3.8	760.0	0.036	0.0136	40.0	16.1
NaBr-H ₂ O-MeOH	3.8	760.0	0.051	0.02	53.3	19.1
KCl-H ₂ O-MeOH	2.0	760.0	0.056	0.0155	35.3	14.9
NaF-H ₂ O-MeOH	1.0	760.0	0.051	0.01	34.4	15.0

TABLE G.15 Values of the Parameters Obtained with the Three Objective Functions for Isobaric VLE Data

System	P (mmHg)	Δg_{A2}	Δg_{B2}	Δg_{A3}	Δg_{B3}
<u>Objective Function #1</u>					
LiCl-H ₂ O-MeOH	760	142.84	-19.8	-35.0	319.10
NaBr-H ₂ O-MeOH	760	0.0506	12.009	99.65	-303.26
KCl-H ₂ O-MeOH	760	105.8	-44.06	-40.16	340.5
NaF-H ₂ O-MeOH	760	-11.81	40.08	4916.8	-2559.8
<u>Objective Function #2</u>					
LiCl-H ₂ O-MeOH	760	125.35	-26.6	-33.52	334.05
NaBr-H ₂ O-MeOH	760	-5.695	23.0	111.3	-320.36
KCl-H ₂ O-MeOH	760	124.21	-79.67	-41.151	446.55
NaF-H ₂ O-MeOH	760	104.95	-176.71	12394.0	-2932.0
<u>Objective Function #3</u>					
LiCl-H ₂ O-MeOH	760	153.03	-24.3	-35.571	336.4
NaBr-H ₂ O-MeOH	760	65.9	-21.77	89.295	-454.8
KCl-H ₂ O-MeOH	760	50.72	-50.618	-40.88	432.38
NaF-H ₂ O-MeOH	760	21.952	-79.58	3674.4	-2767.1

Constant $X'_{\text{EtOH}} = 0.0417$

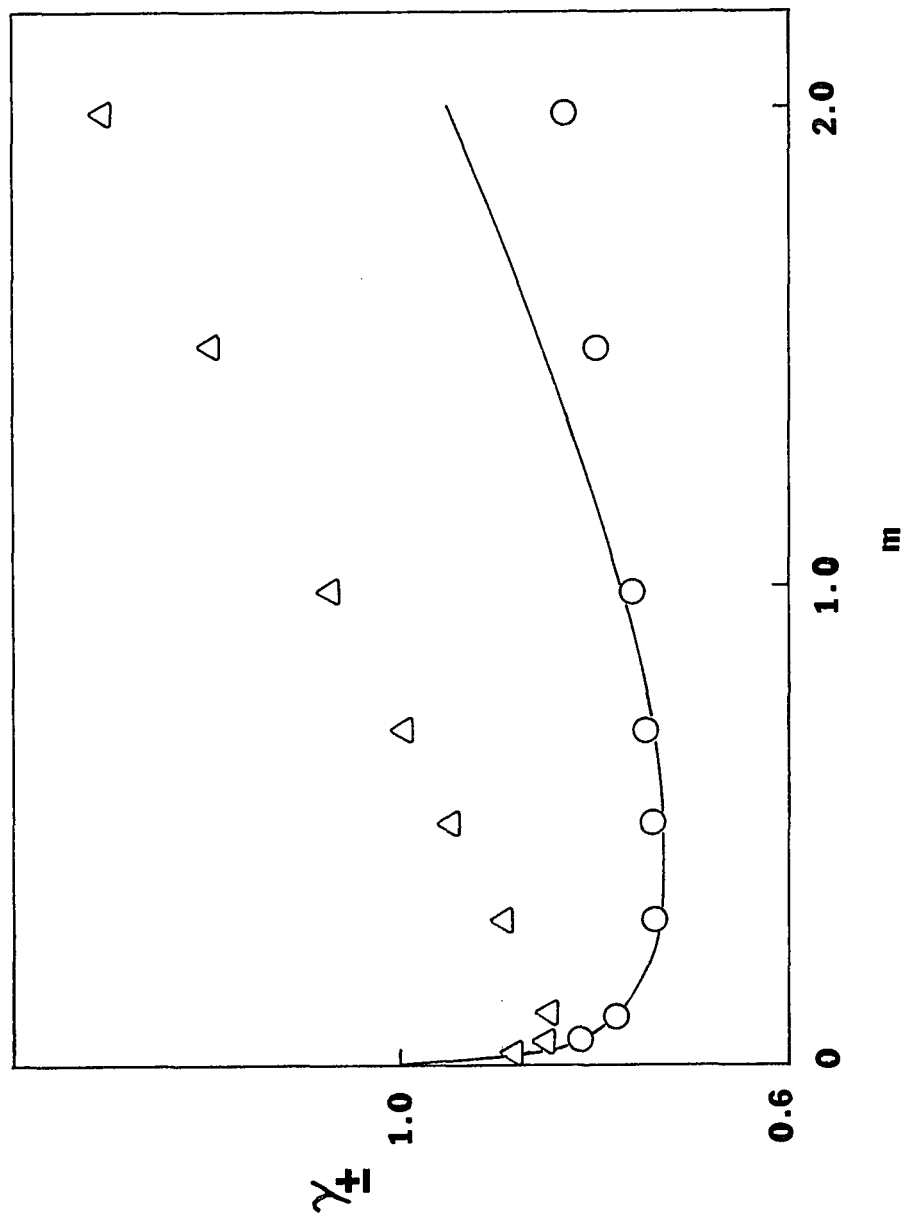


Figure G.1 Comparison of Experimental Mean Molal Activity Coefficients with those Predicted and Correlated by Model I for the System HCl-H₂O-EtOH at 25°C and Constant $X'_{\text{EtOH}} = 0.0417$.
 Experimental, Harned and Owen(1958) ; \circ Correlated ($\alpha_{23} = -1.0$) ; \triangle Predicted ($\alpha_{23} = -1.0$)

— Experimental, Harned & Owen (1958) ; ○ Correlated
 ($\alpha_{23} = -1.0$) ; △ Predicted ($\alpha_{23} = -1.0$)

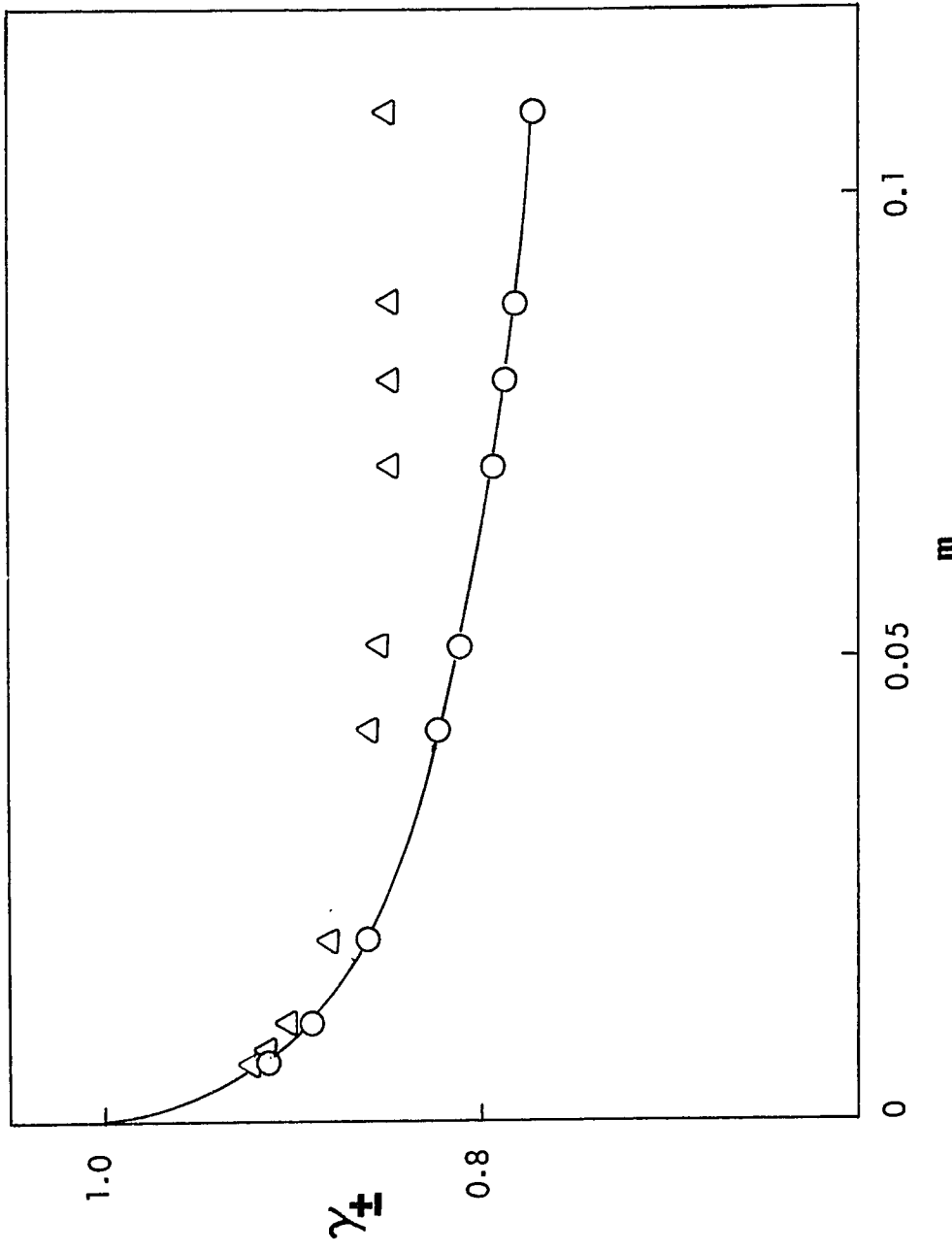


Figure G.1A Comparison of Experimental Mean Molal Activity Coefficients with those Predicted and Correlated by Model I up to $m = 0.2$ for the System HCl-H₂O-EtOH at 25°C and Constant $X'_{EtOH} = 0.0417$

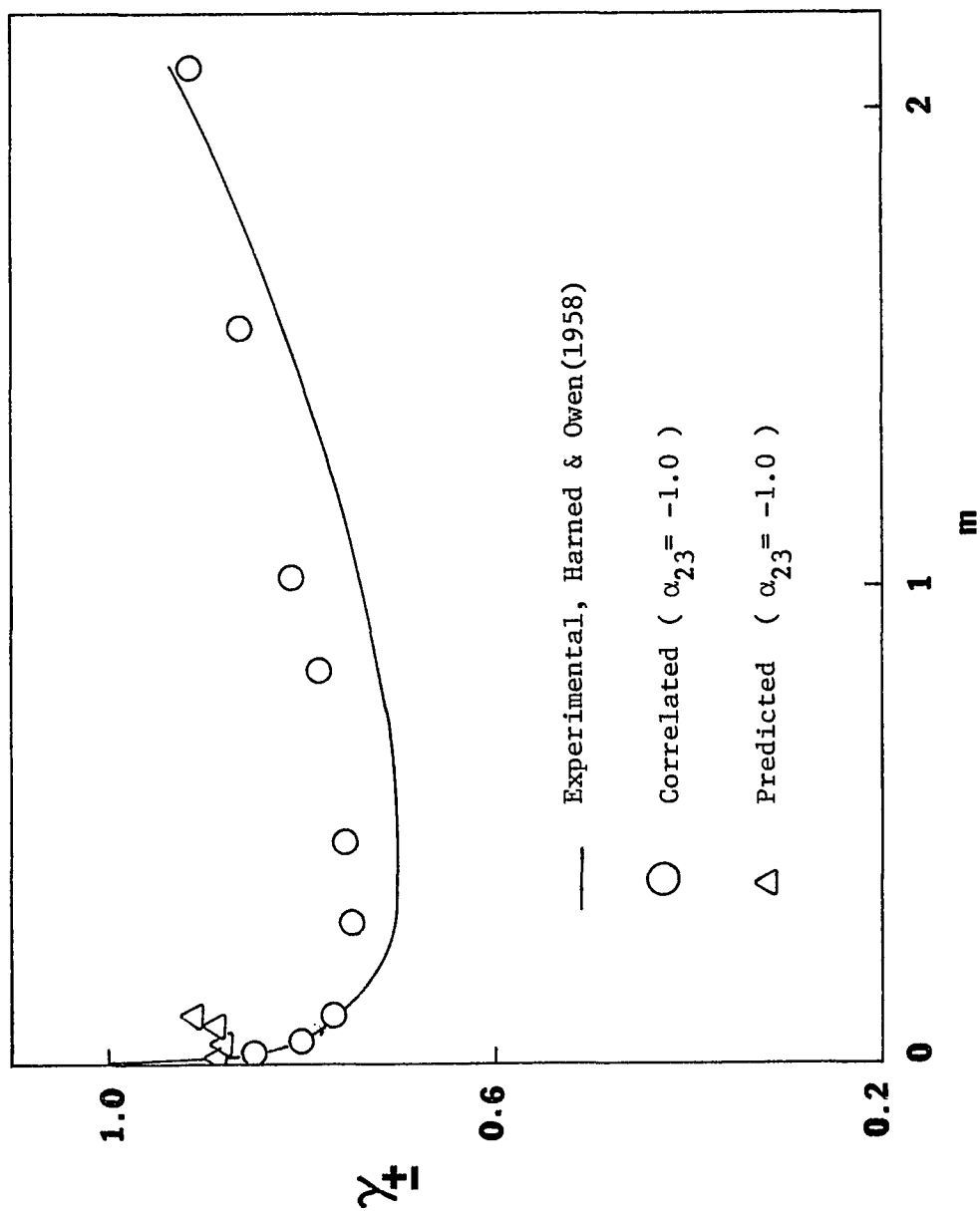


Figure G.2 Comparison of Experimental Mean Molal Activity Coefficients with those Predicted and Correlated by Model I for the System HCl-H₂O-EtOH at 25°C and Constant $X'_{\text{EtOH}} = 0.0891$

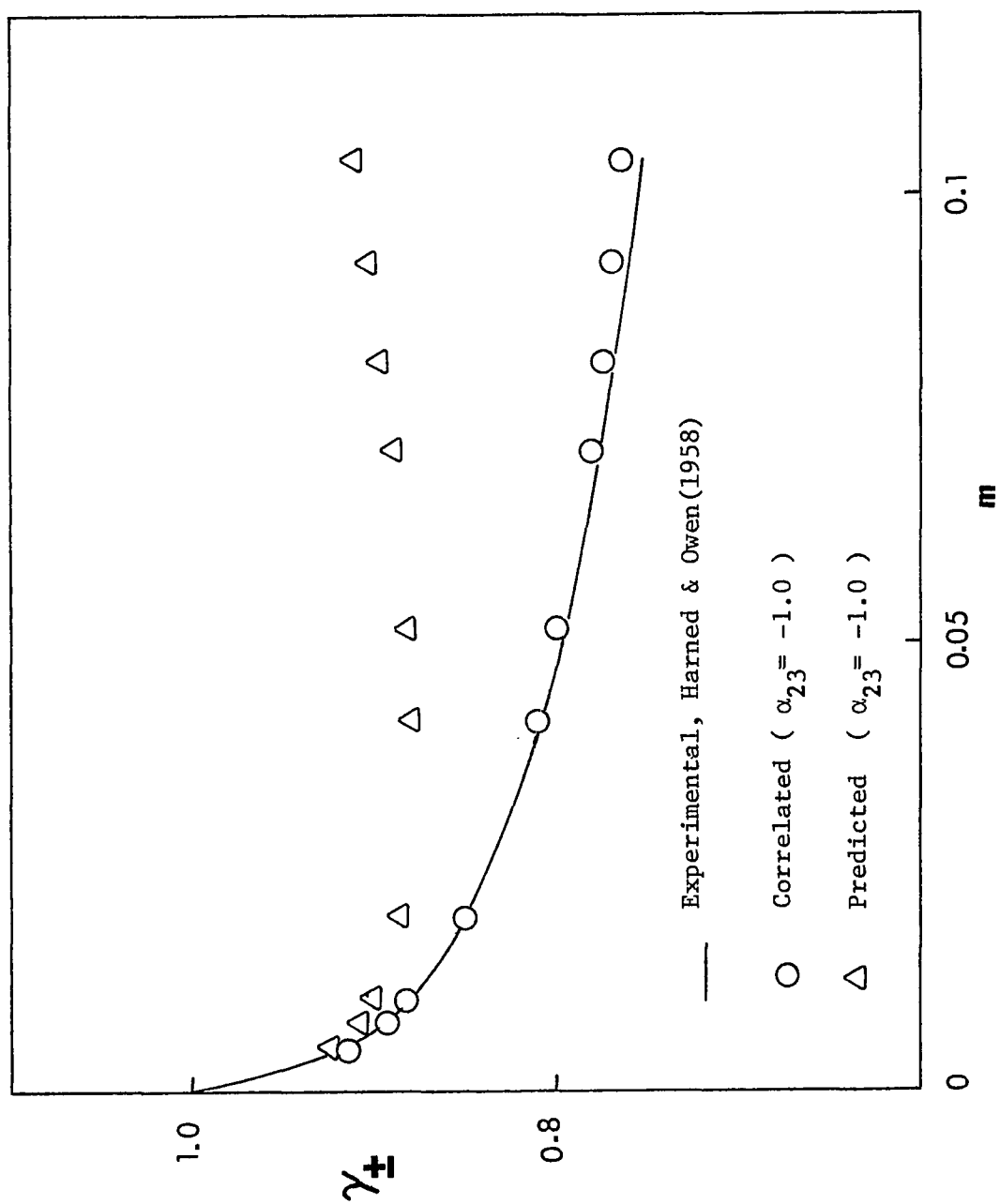


Figure G.2A Comparison of Experimental Mean Molal Activity Coefficients with those Predicted and Correlated by Model I up to $m = 0.2$ for the System HCl-H₂O-EtOH at 25°C and Constant $X_{\text{EtOH}} = 0.0891$

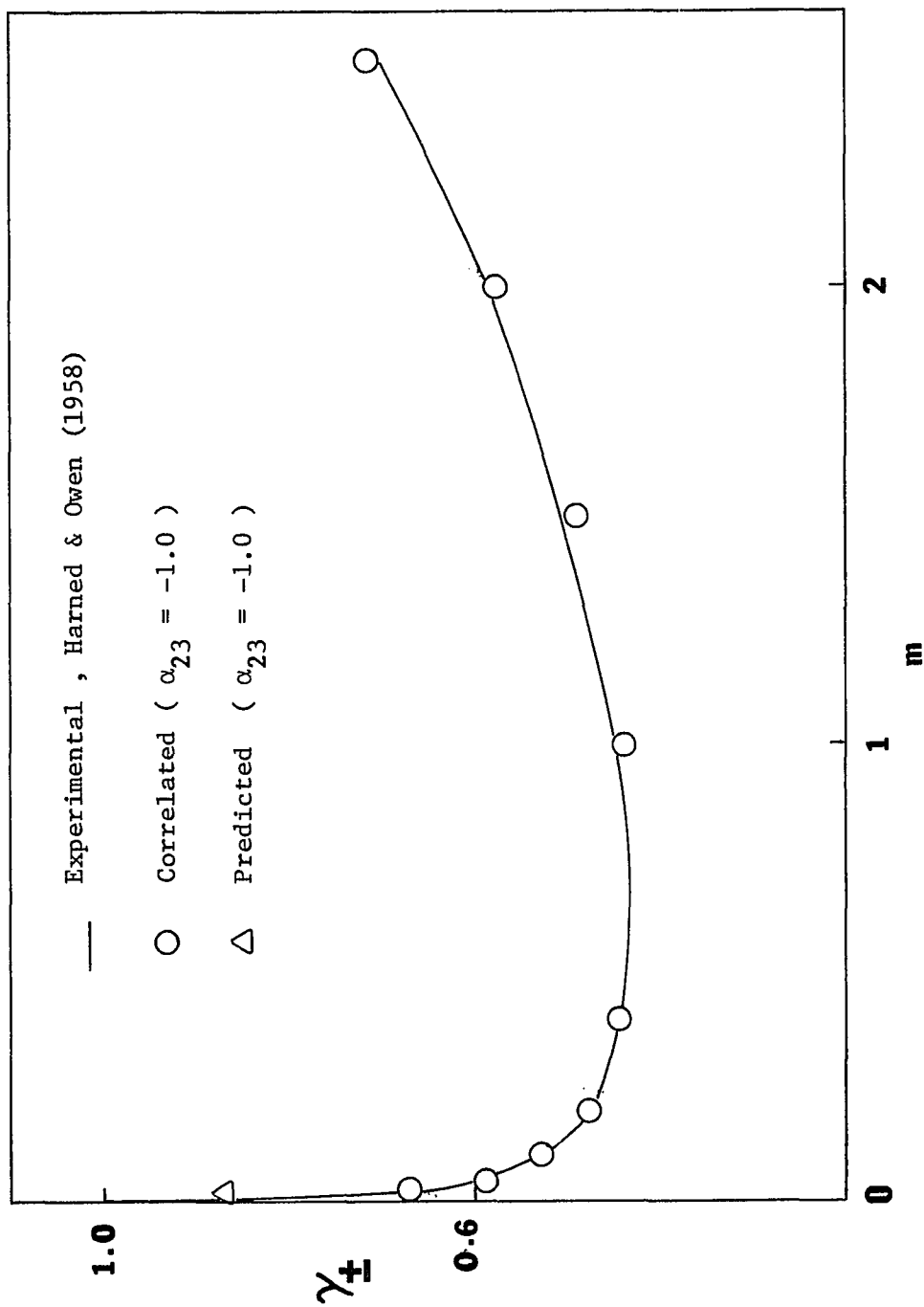


Figure G.3 Comparison of Experimental Mean Molal Activity Coefficients with those Predicted and Correlated by Model I for the System HCl-H₂O-EtOH at 25°C and Constant $X_{\text{EtOH}}^{\text{I}} = 0.5$

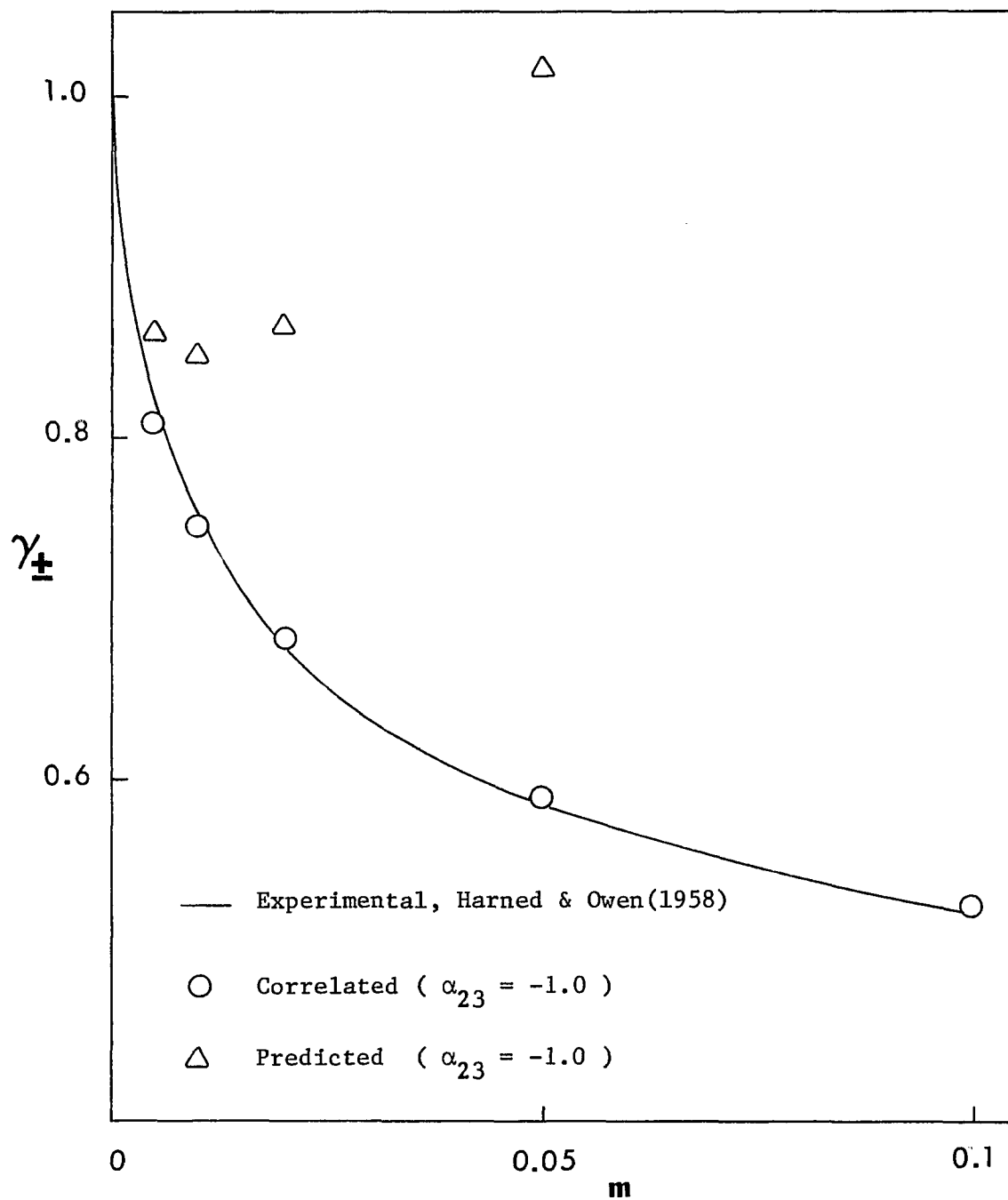


Figure G.3A Comparison of Experimental Mean Molal Activity Coefficients with those Predicted and Correlated by Model I up to $m = 0.2$ for the System HCl-H₂O-EtOH at 25°C and Constant $X'_{\text{EtOH}} = 0.5$

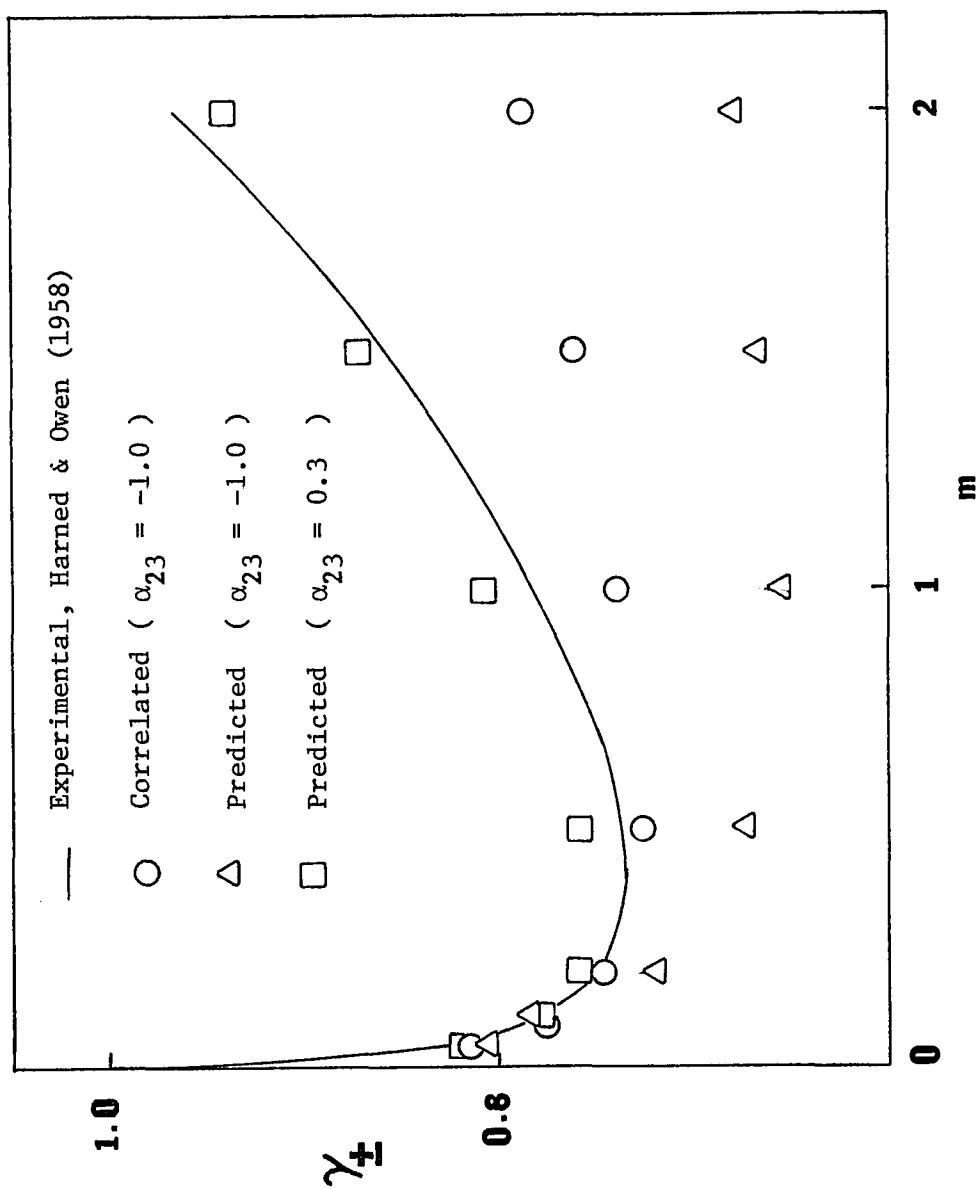


Figure G.4 Comparison of Experimental Mean Molal Activity Coefficients with those Predicted and Correlated by Model I for the System HCl-H₂O-MeOH at 25°C and Constant $X_{\text{MeOH}} = 0.0584$

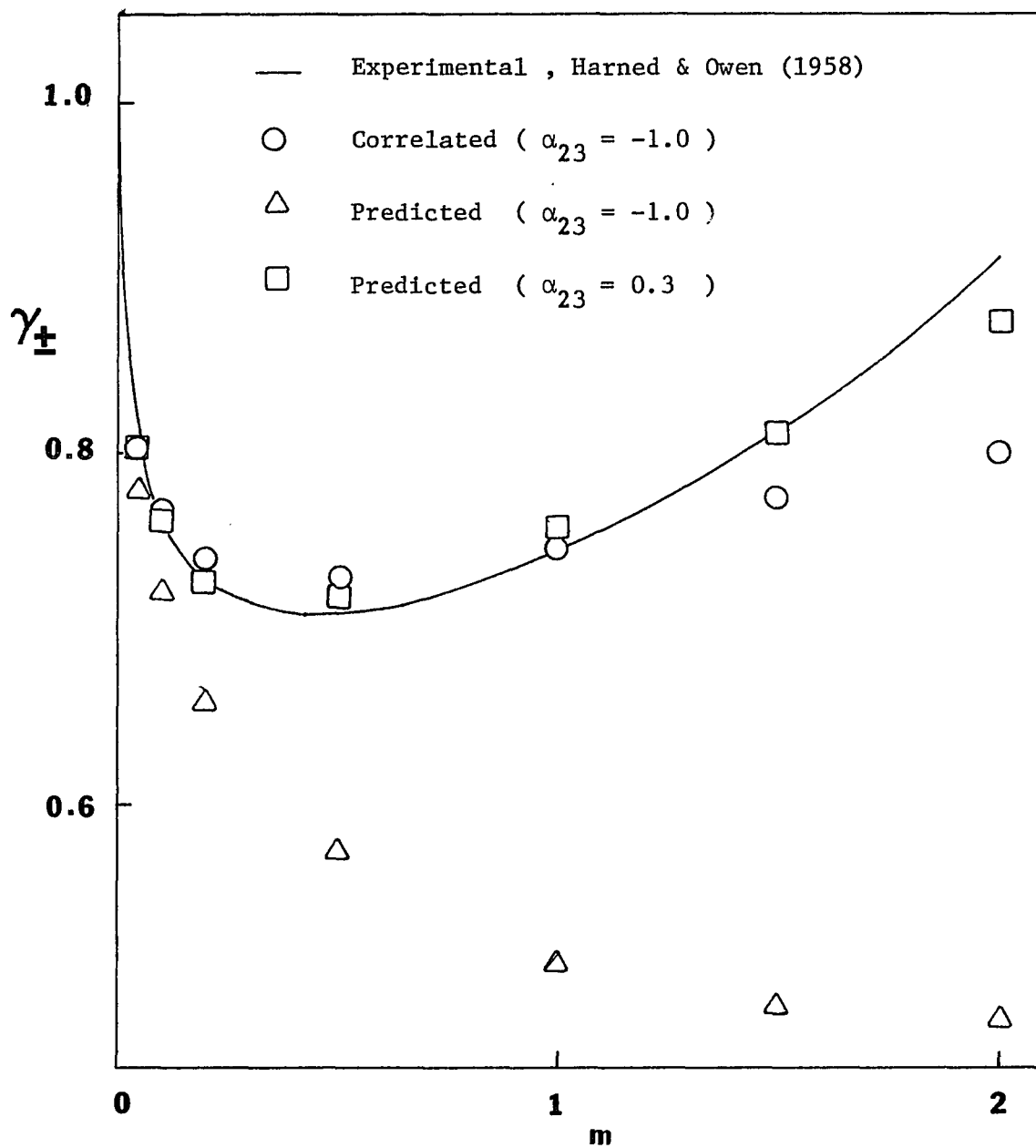


Figure G.5 Comparison of Experimental Mean Molal Activity Coefficients with those Predicted and Correlated by Model I for the System HCl-H₂O-MeOH at 25°C and Constant $X_{\text{MeOH}} = 0.1233$

— Experimental, Akerlof (1930) ; ○ Correlated ($\alpha_{23}=-1.0$); 228
 △ Predicted ($\alpha_{23}=-1.0$) ; □ Predicted ($\alpha_{23}=0.3$)

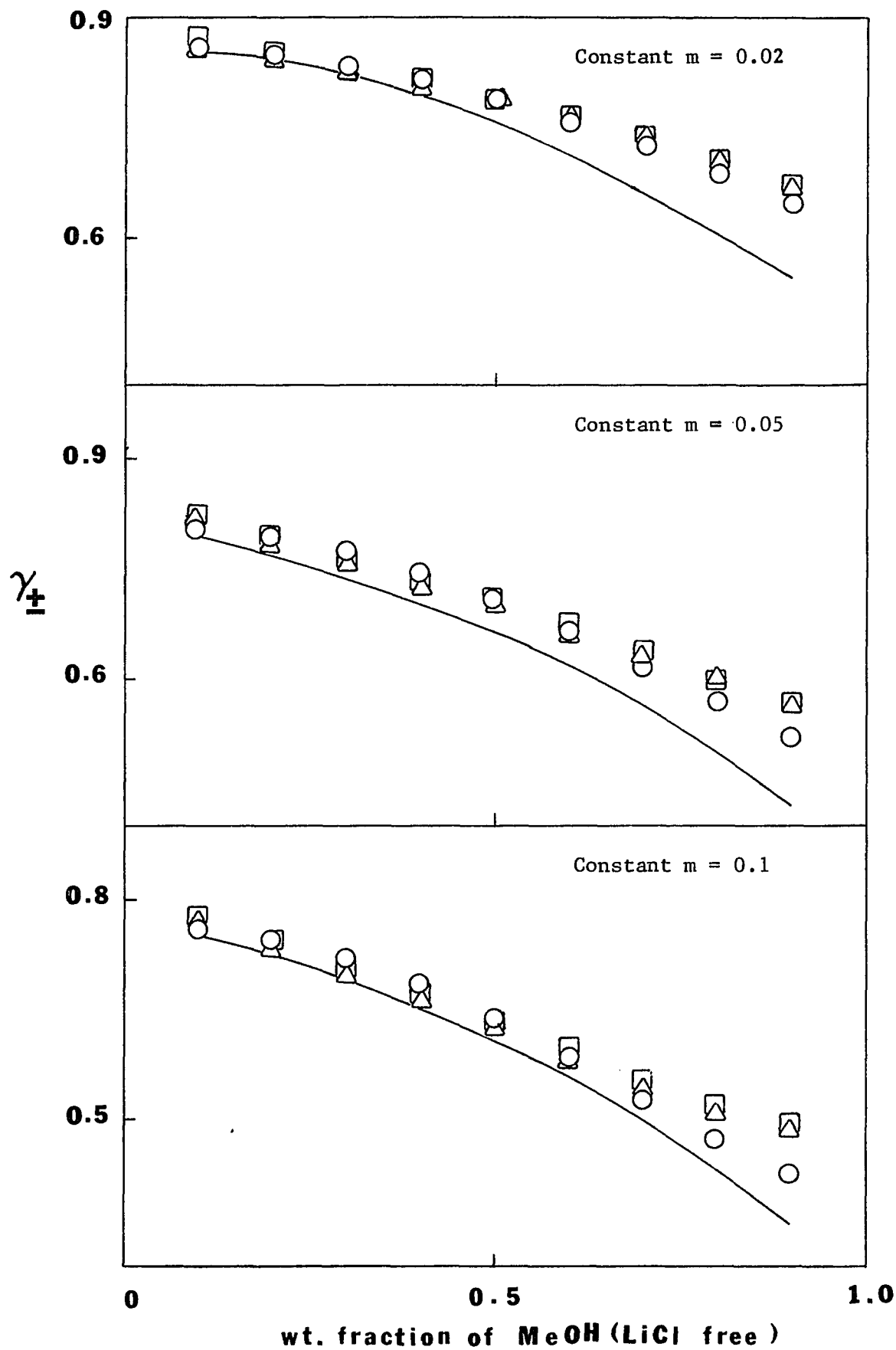


Figure G.6 Comparison of Experimental Mean Molal Activity Coefficients with those Predicted and Correlated by Model I for the System LiCl-H₂O-MeOH at 25°C

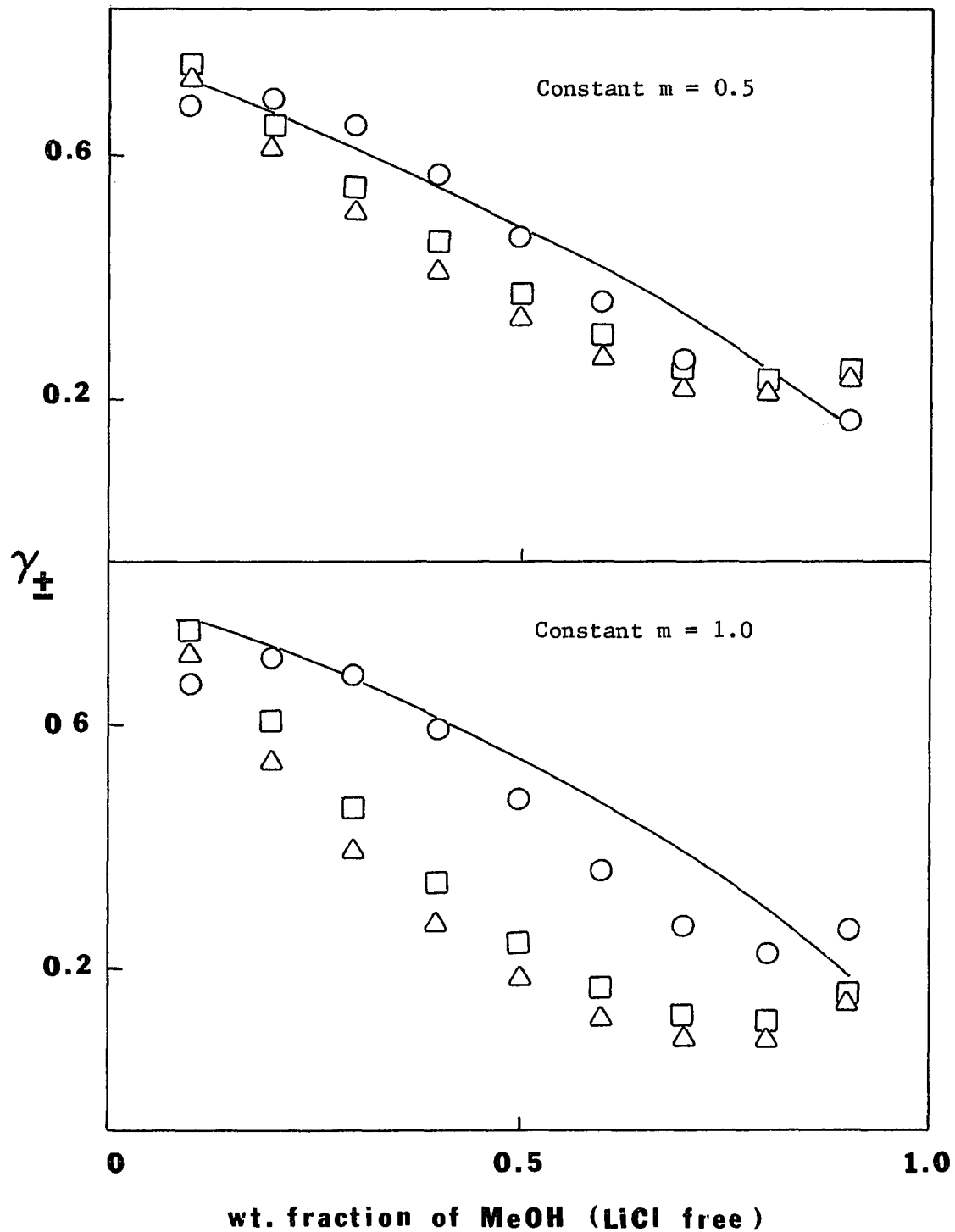


Figure G.7 Comparison of Experimental Mean Molal Activity Coefficients with those Predicted and Correlated by Model I for the System LiCl-H₂O-MeOH at 25°C and Constant $m = 0.5, 1.0$. — Experimental, Akerlof(1930); ○ Correlated ($\alpha_{23} = -1.0$); Δ Predicted ($\alpha_{23} = -1.0$); □ Predicted ($\alpha_{23} = 0.3$)

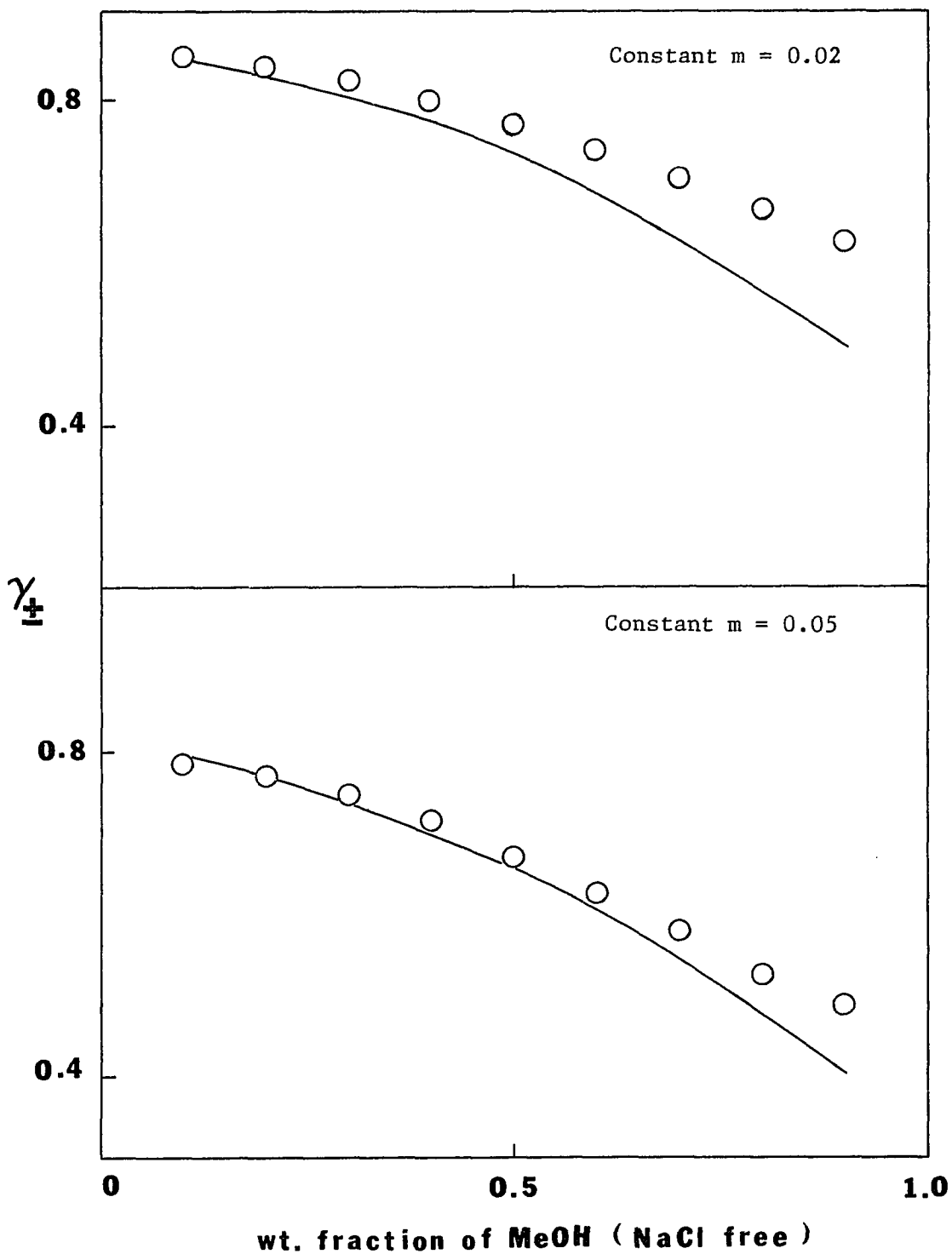


Figure G.8 Comparison of Experimental Mean Molal Activity Coefficients with those Correlated for the System NaCl - H₂O - MeOH at 25°C and Constant $m = 0.02, 0.05$

— Experimental, Akerlof (1930) ; ○ Correlated ($\alpha_{23} = -1.0$)

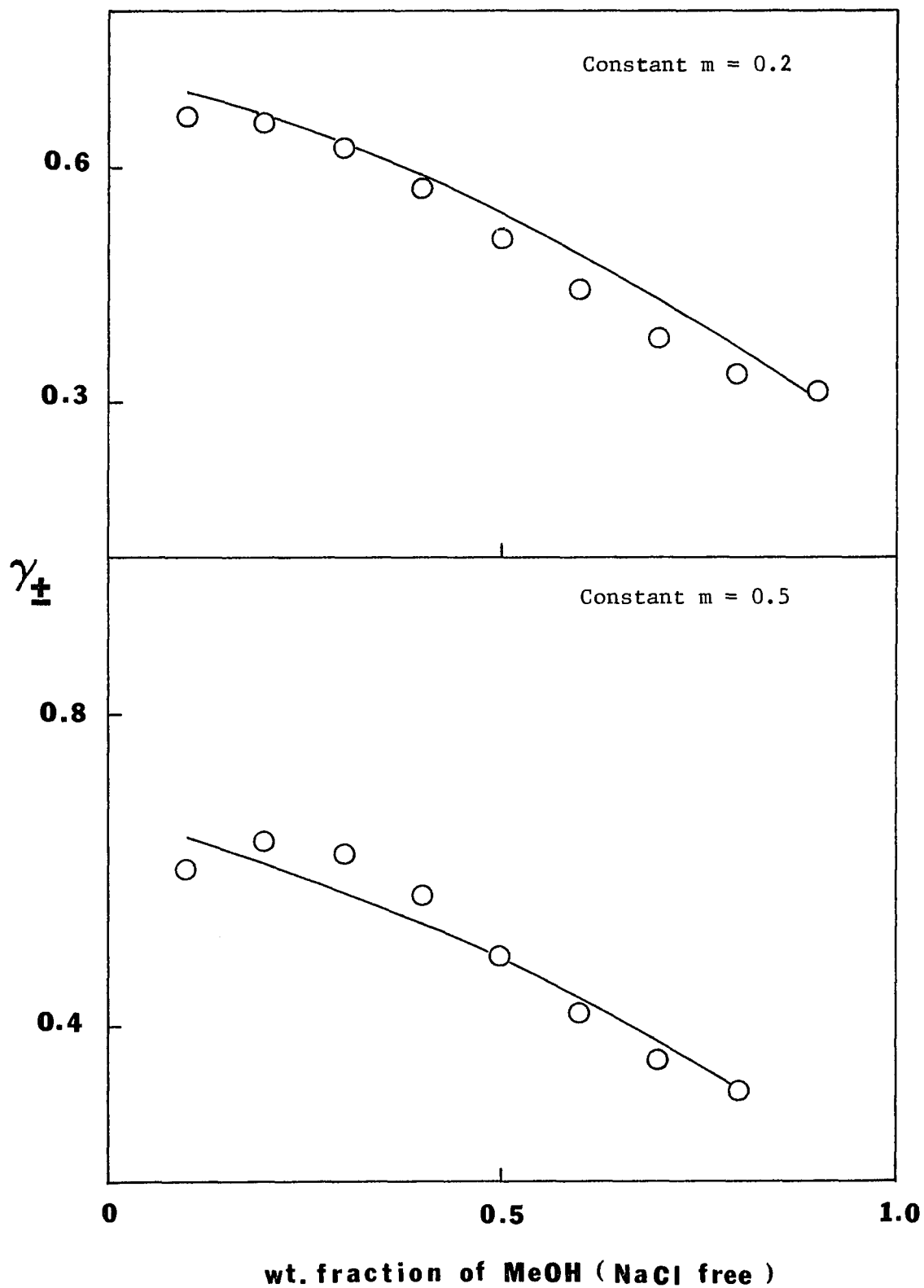


Figure G.9 Comparison of Experimental Mean Molal Activity Coefficients with those Correlated for the System NaCl-H₂O-MeOH at 25°C and Constant $m = 0.2, 0.5$.

— Experimental, Akerlof (1930); ○ Correlated ($\alpha_{23} = -1.0$)

Figure G.10 Comparison of Experimental Vapor Phase Compositions with those Predicted and Correlated by Model I for the System LiCl-H₂O-EtOH at 25°C and Constant $m = 0.5$

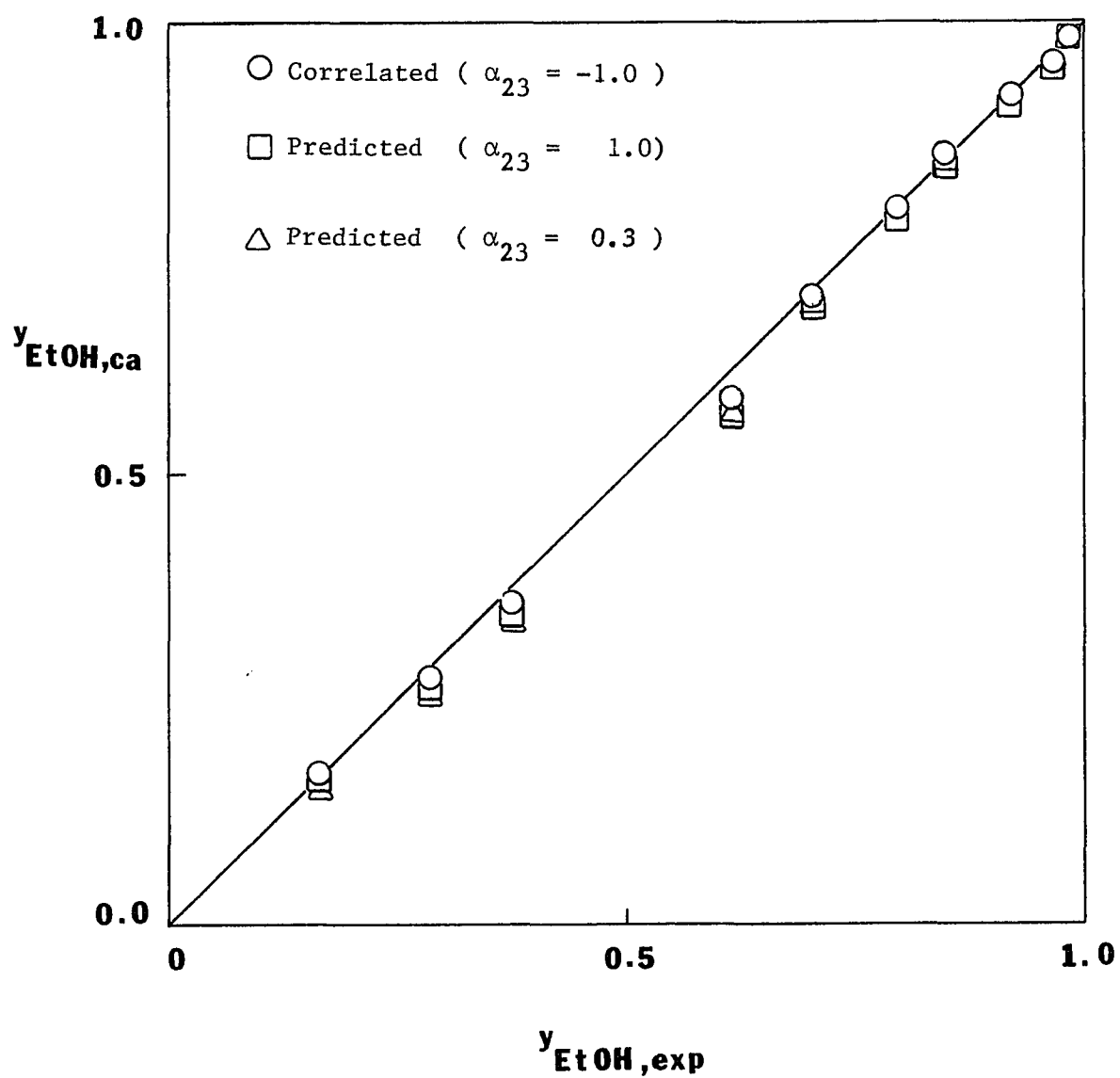


Figure G.11 Comparison of Experimental with Predicted and Correlated Vapor-Phase Compositions Using Model I for the System LiCl-H₂O-EtOH at 25°C and Constant $m = 1.0$

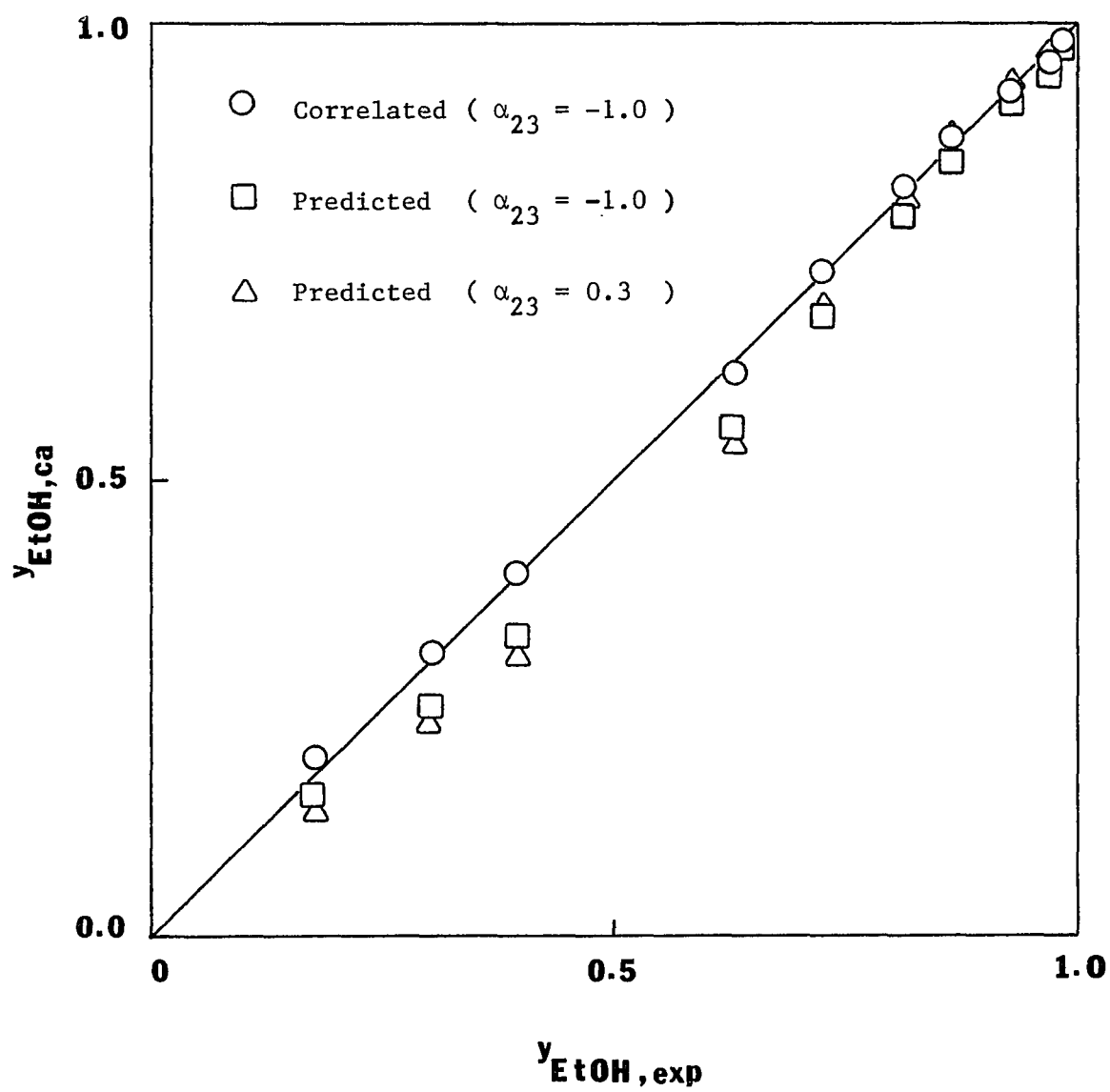
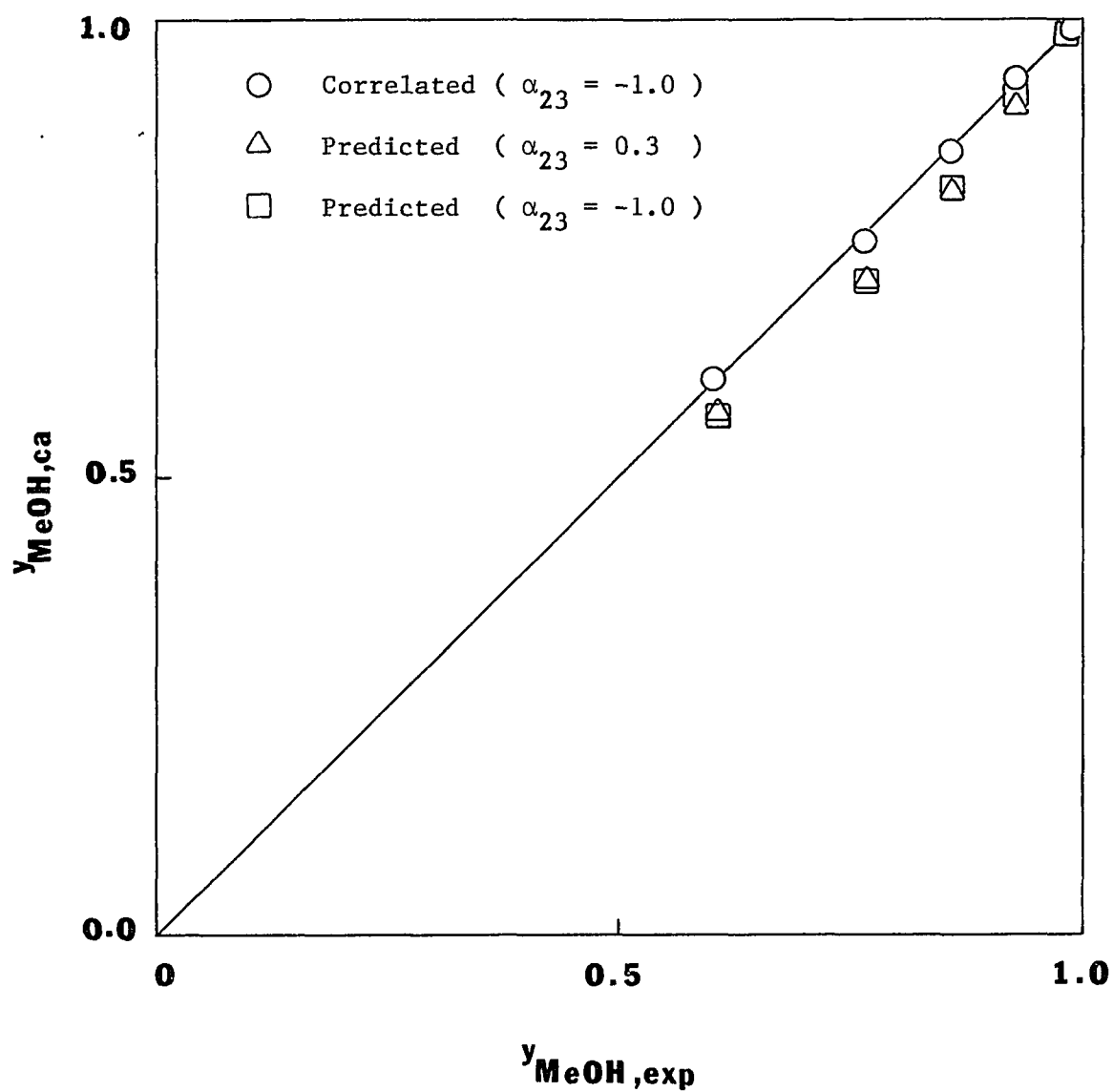


Figure G.12 Comparison of Experimental with Predicted and Correlated Vapor-Phase Compositions Using Model I for the System LiCl-H₂O-MeOH at 25°C and Constant $m = 1.0$



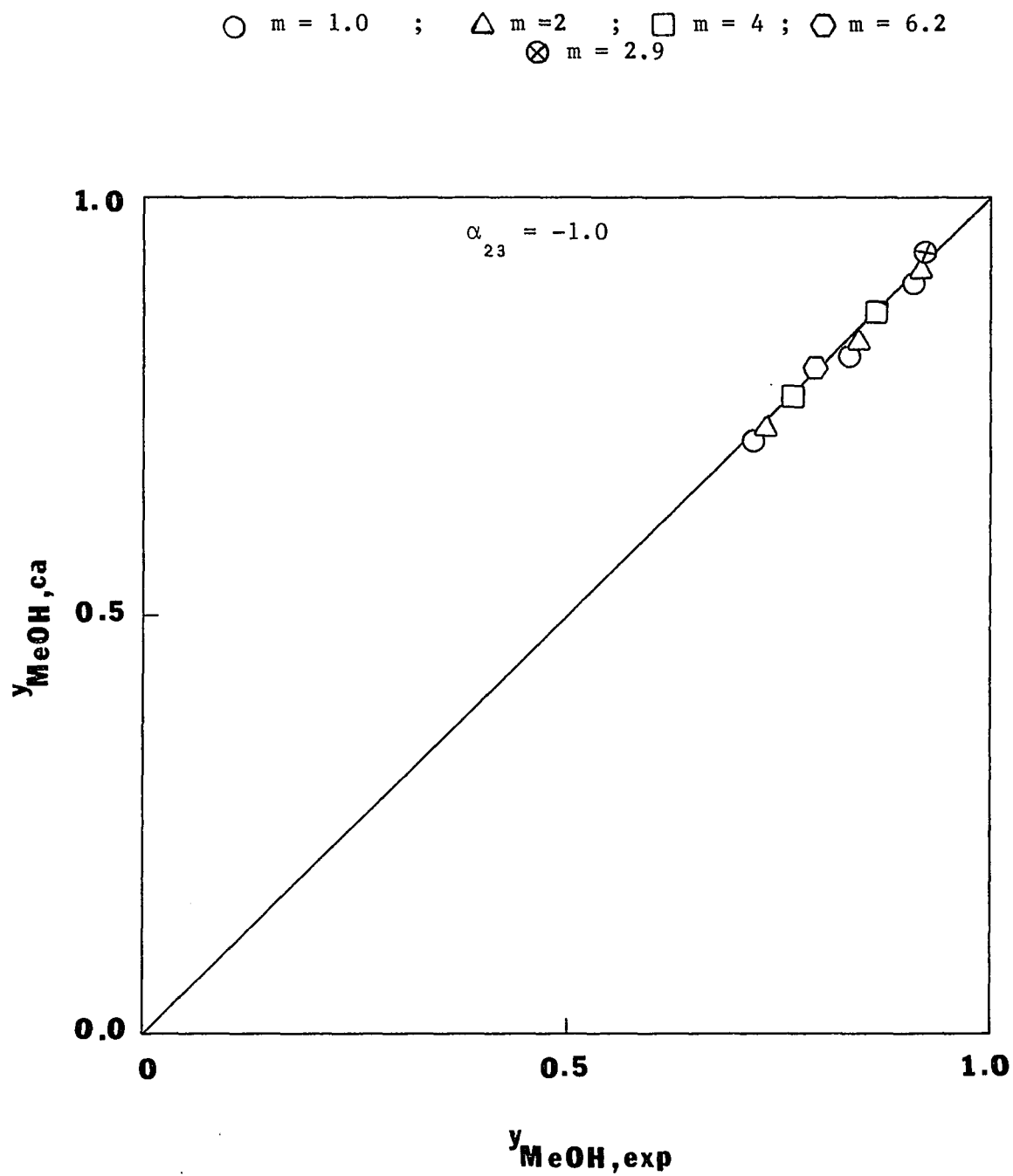
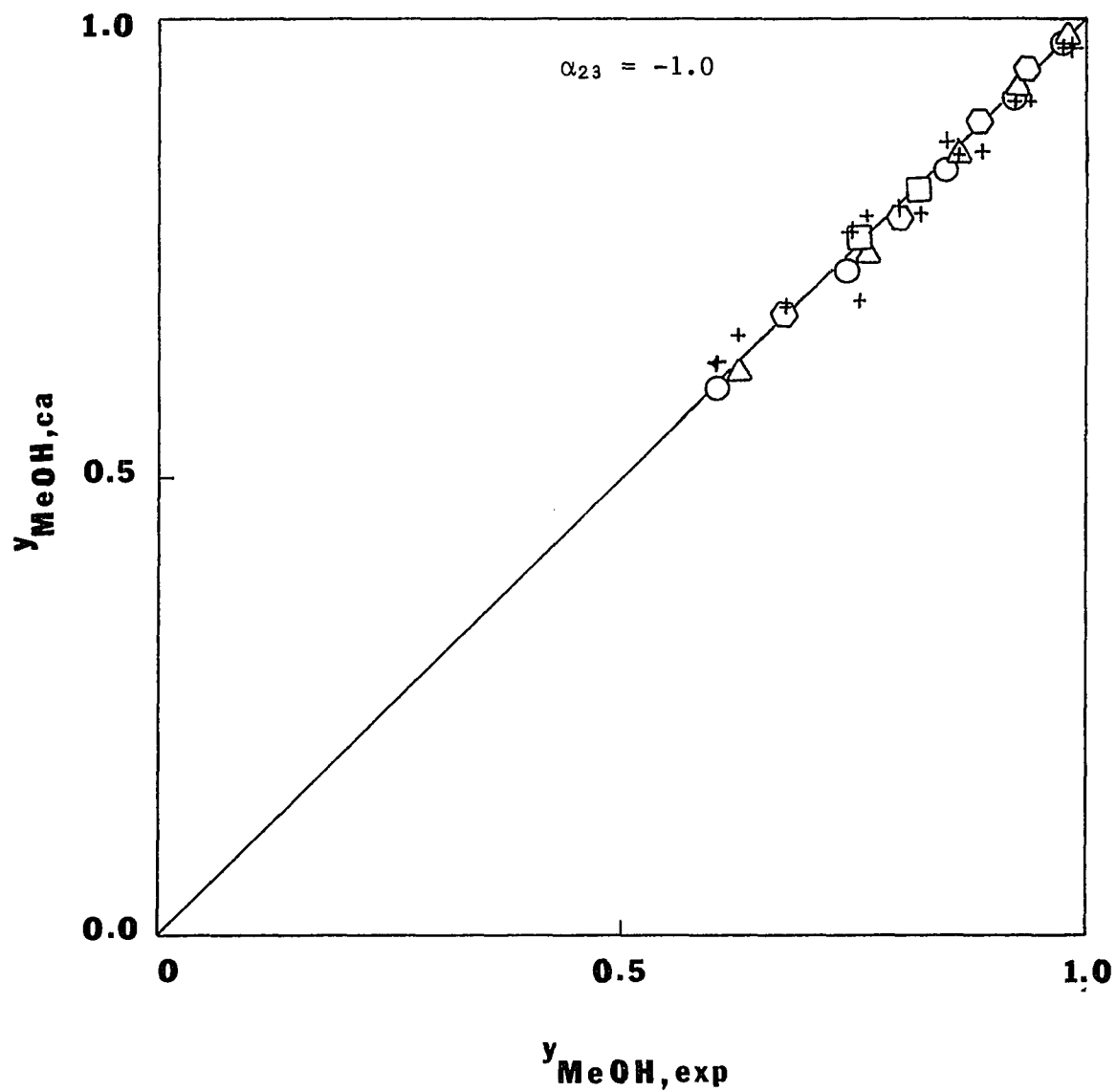


Figure G.13 Comparison of Experimental with Correlated Vapor-Phase Compositions Using Model I for the System NaBr-H₂O-MeOH at 40°C

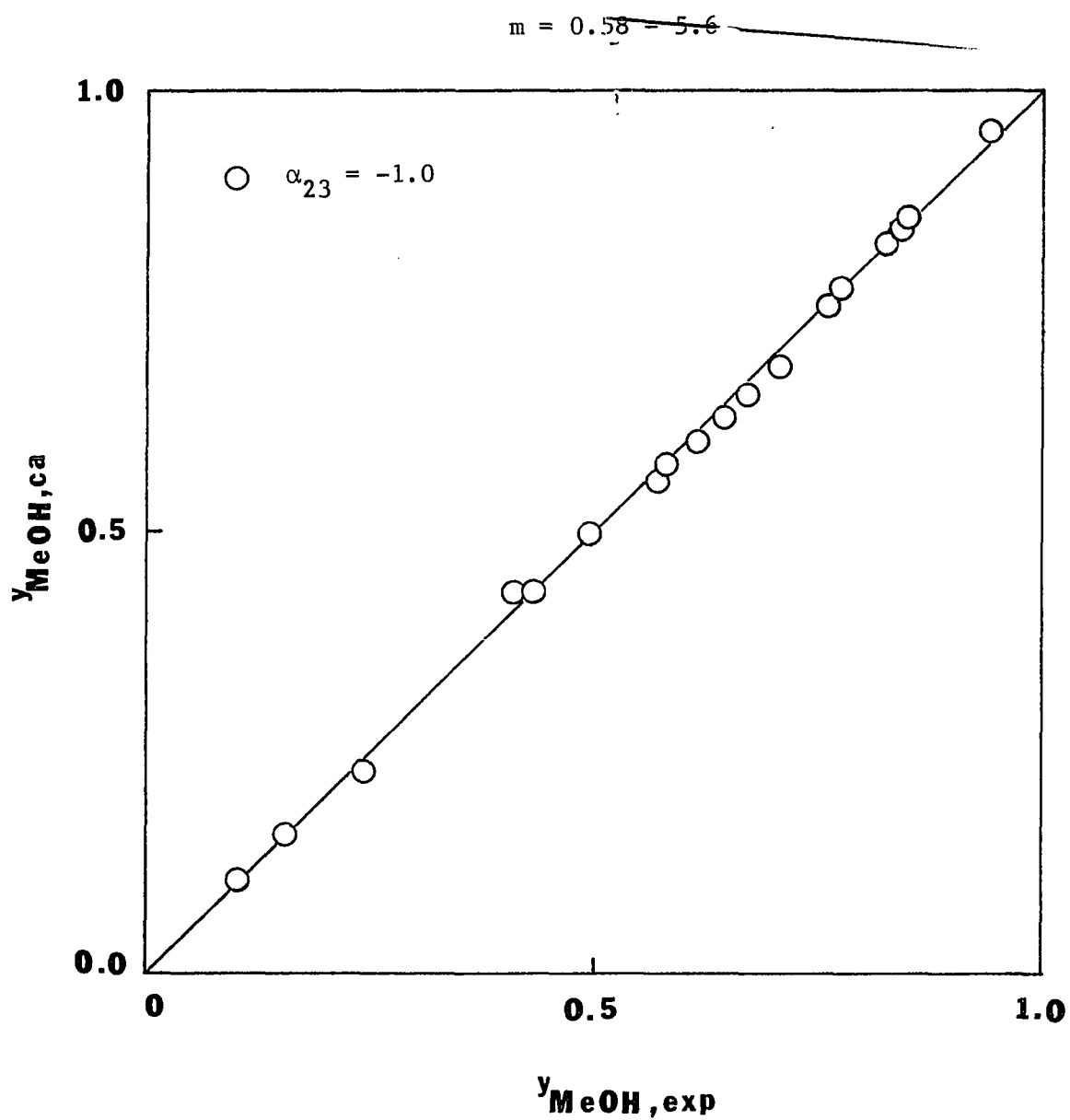


○ $m = 1$; △ $1 < m \leq 2$; ◡ $2 < m \leq 4$; ◻ $m > 4$

+ Evans et.al. (1979)

Figure G.14 Comparison of Experimental with Correlated Vapor-Phase Compositions Using Model I for the System NaBr-H₂O-MeOH at 25°C

Figure G.15 Comparison of Experimental with Correlated Vapor-Phase Compositions Using Model I for the System LiCl-H₂O at 60°C



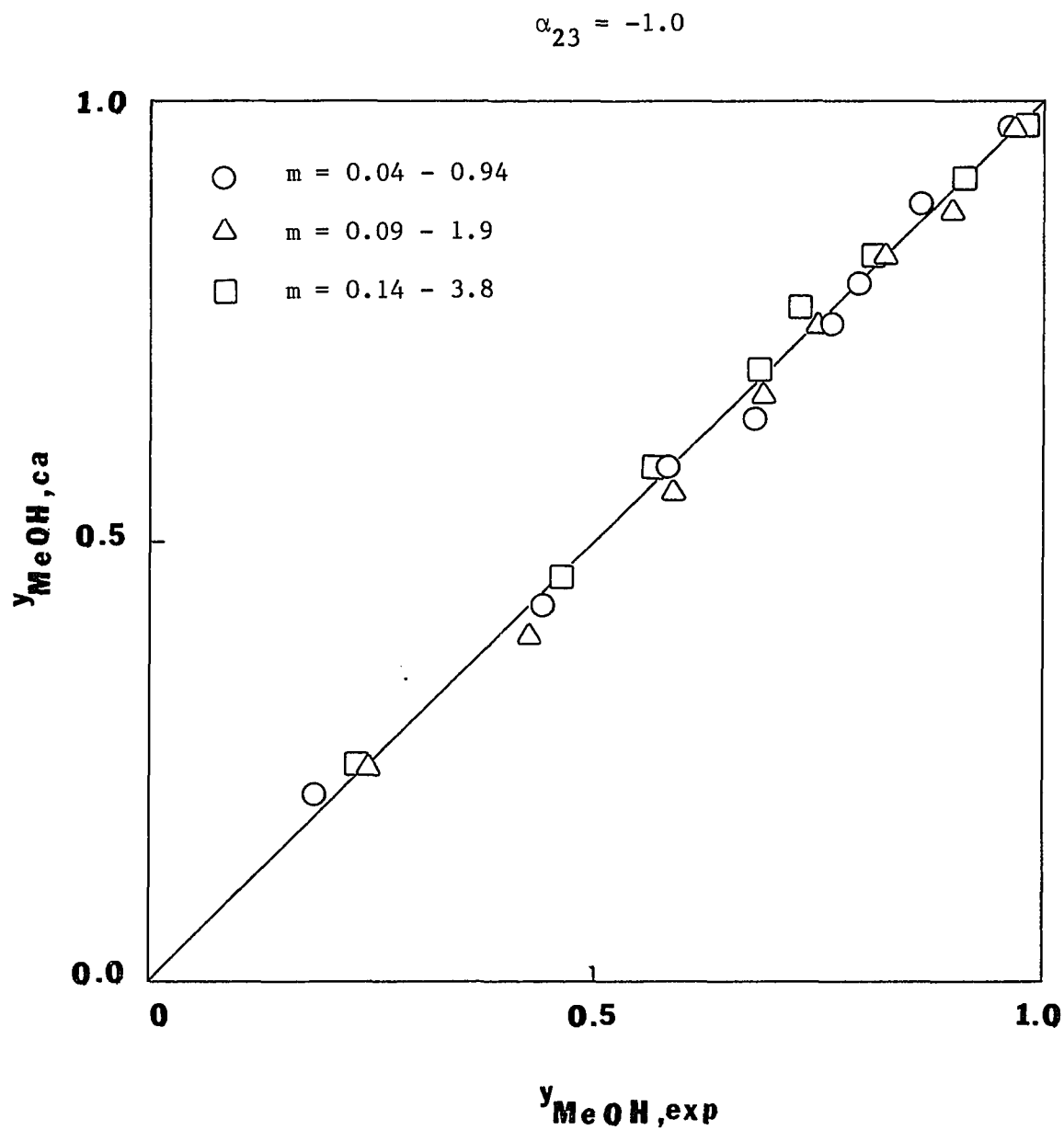


Figure G.16 Comparison of Experimental with Correlated Vapor-Phase Compositions Using Model I for the System LiCl-H₂O-MeOH at P = 1 atm

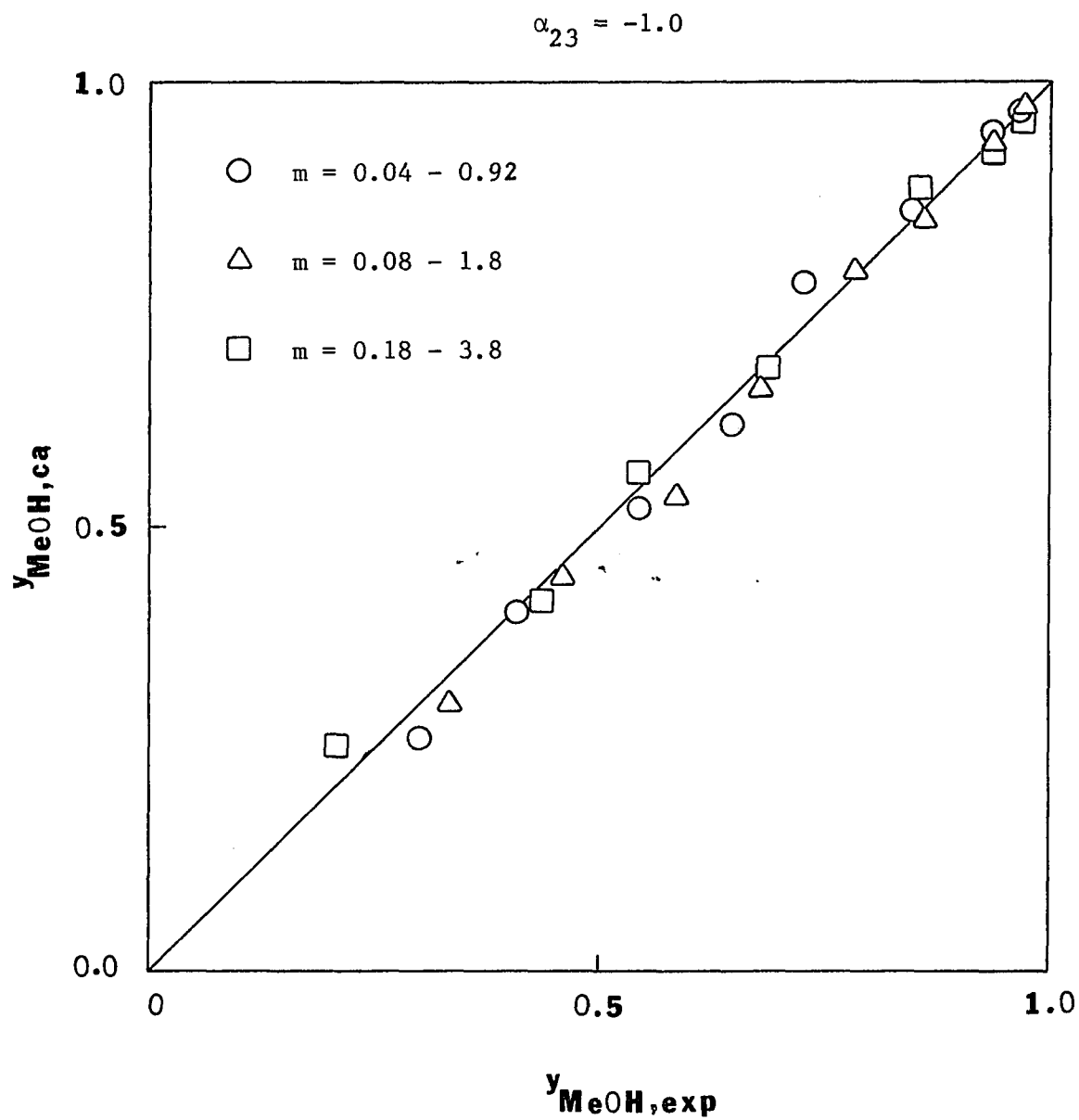


Figure G.17 Comparison of Experimental with Correlated Vapor-Phase Compositions Using Model I for the System NaBr-H₂O-MeOH at P = 1 atm

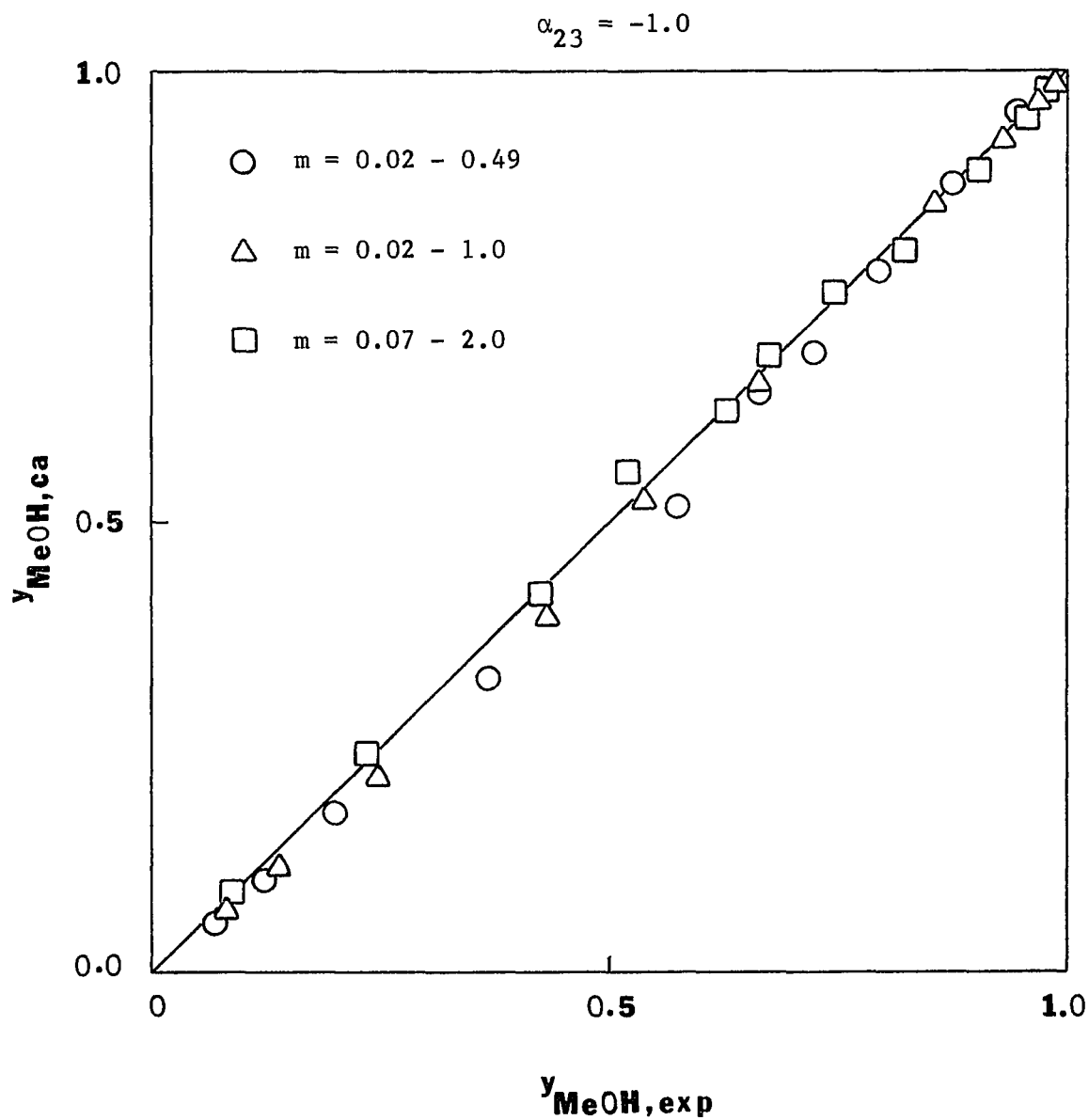


Figure G.18 Comparison of Experimental with Correlated Vapor-Phase Compositions Using Model I for the System KCl-H₂O-MeOH at P = 1 atm

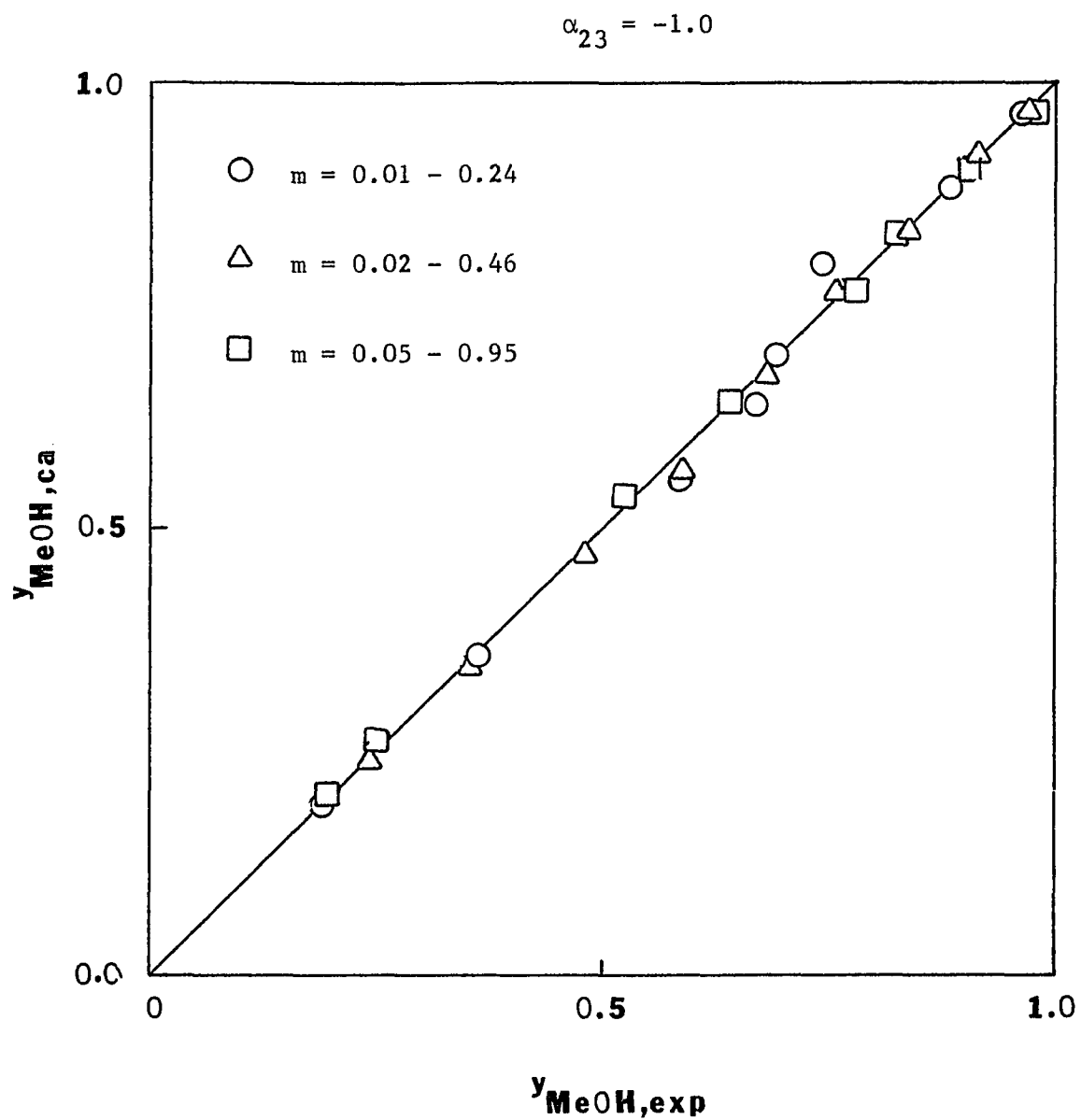
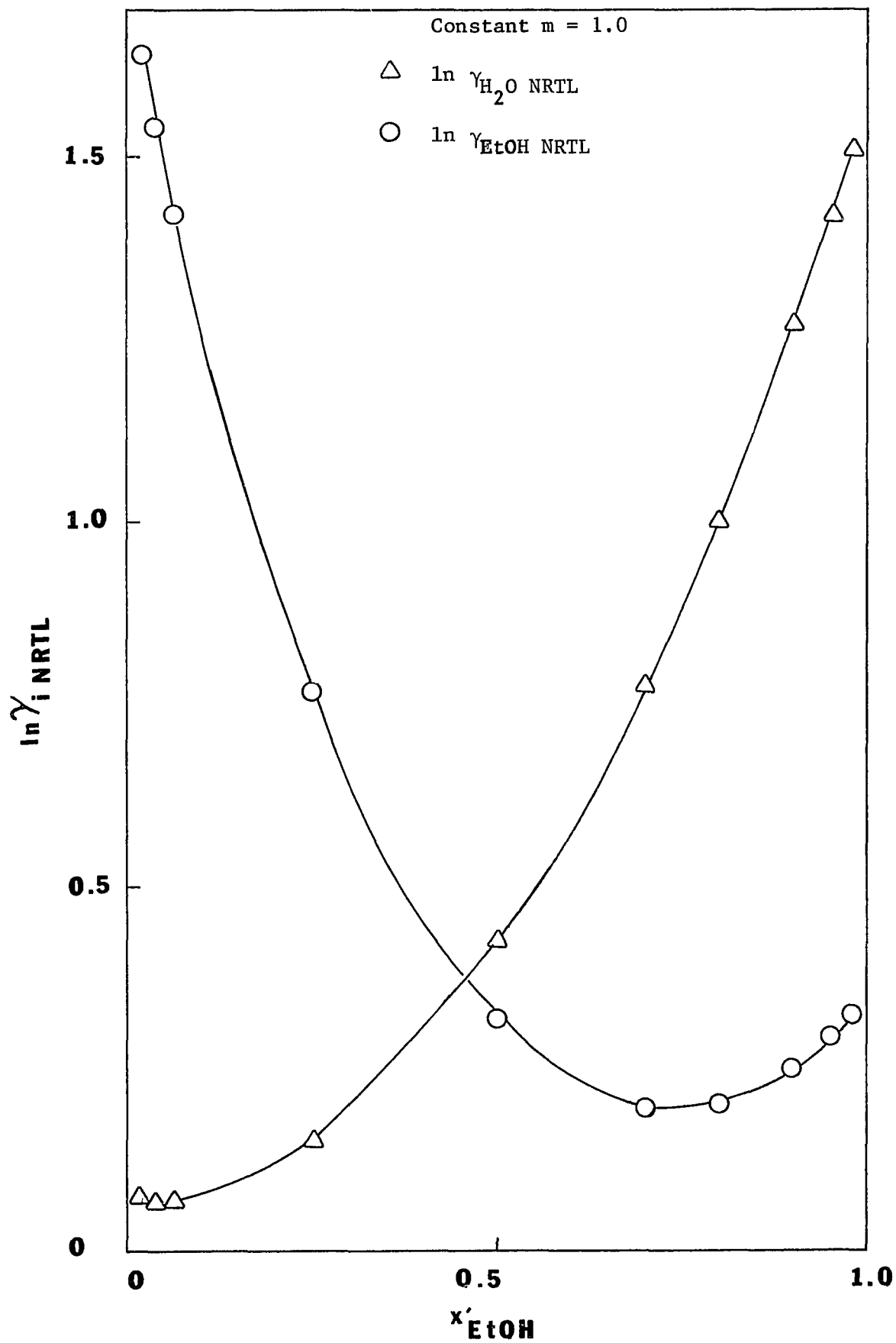


Figure G.19 Comparison of Experimental with Correlated Vapor-Phase Compositions Using Model I for the System NaF-H₂O-MeOH at P = 1 atm

Figure G.20 Contribution of the NRTL Term to $\ln \gamma_i$ for the System LiCl-H₂O-EtOH at 25 C in Model I



APPENDIX H

TABLES AND FIGURES FOR MODEL II

TABLE H.1 Typical m- $\bar{\Delta}P$ Data from the Weast Compilation

Electrolyte	DP (mm Hg)						
	0.5	1.0	2.0	3.0	4.0	5.0	6.0
KCl	12.2	24.4	48.8	74.1	100.9	128.5	152.2
MgCl ₂	16.8	39.0	100.5				
Na ₂ SO ₄	12.6	25.0	48.9				
MgSO ₄	6.5	12.0	24.5				

TABLE H.2 Values of B_{12} and Quality of Correlation of the Weast Data

Electrolyte	max m	\overline{DP}	DP_{\max}	DP'_{\max}	$B_{12}(100^{\circ}\text{C})$	$B_{12}(25^{\circ}\text{C})$
KBr*	4.0	0.6	1.0	1.0	0.0442	0.0296
KCl	6.0	1.1	2.1	2.1	0.0311	0.0240
KI	10.0	1.7	3.6	9.3	0.0537	0.0428
KNO ₃	10.0	0.8	1.2	2.7	-0.0256	-0.0862
KOH	10.0	3.6	6.0	9.8	0.1176	0.1131
LiBr	10.0	1.6	2.9	3.8	0.1325	0.1527
LiCl	10.0	0.7	2.3	3.6	0.1089	0.1283
LiI	10.0	1.0	1.3	15.4	0.1645	0.1815
LiNO ₃	10.0	2.5	4.8	11.2	0.0742	0.0938
LiOH	2.0	2.6	5.1	5.1	0.3064	-0.0097
NaBr	8.0	1.5	3.0	5.2	0.0832	0.0749
NaCl	6.0	0.4	1.1	1.1	0.0567	0.0574
NaI	10.0	2.2	5.8	12.5	0.1129	0.0994
NaNO ₃	10.0	0.9	1.2	6.2	0.0074	-0.0128
NaOH	10.0	1.0	2.1	2.5	0.0508	0.0747
NH ₄ Br	10.0	1.4	3.1	6.7	0.0235	-0.0066
NH ₄ Cl	10.0	1.0	2.1	6.8	0.0154	0.0200

TABLE H.2 (Cont'd.)

Electrolyte	max m	\bar{DP}	DP_{max}	DP'_{max}	$B_{12}(100^\circ C)$	$B_{12}(25^\circ C)$
NH_4I	10.0	1.8	2.8	10.9	0.0361	0.0210
NH_4NO_3	10.0	1.0	1.6	2.9	-0.0051	-0.0358
$BaBr_2$	4.0	0.6	1.2	8.3	0.0773	0.0852
$BaCl_2$	2.0	1.3	2.8	2.8	0.0501	0.0638
$Ba(NO_3)_2$	1.0	0.4	0.6	0.6	-0.0021	-0.0545
$Ba(OH)_2$	2.0	0.6	0.9	0.9	-0.0275	-0.024
$CaBr_2$	5.0	2.2	3.4	4.4	0.1083	0.1179
$CaCl_2$	5.0	0.6	1.1	4.9	0.0853	0.0948
$Ca(NO_3)_2$	5.0	0.9	1.8	26.3	0.0436	0.0461
$CdBr_2$	4.0	3.4	4.7	8.3	-0.0341	-0.1701
$CdCl_2$	5.0	2.7	3.7	9.7	-0.0336	-0.1448
CdI_2	3.0	4.5	6.7	8.7	-0.0411	-0.2497
$Cd(NO_3)_2$	2.0	0.9	2.1	2.1	0.0505	0.0719
$CoCl_2$	4.0	0.7	1.4	5.9	0.0593	0.1016
$Co(NO_3)_2$	6.0	1.0	2.2	13.7	0.0730	0.0912
$MgBr_2$	4.0	0.4	1.1	3.8	0.1260	0.1419
$MgCl_2$	5.0	0.8	1.0	5.0	0.0951	0.1129

TABLE H.2 (Cont'd.)

Electrolyte	max m	\overline{DP}	DP_{max}	DP'_{max}	$B_{12}(100^\circ C)$	$B_{12}(25^\circ C)$
$Mg(NO_3)_2$	3.0	0.8	1.7	2.4	0.0975	0.1014
$MnCl_2$	5.0	0.6	0.9	9.0	0.0457	0.0869
$NiCl_2$	4.0	0.5	0.7	2.5	0.0674	0.1039
$Pb(NO_3)_2$	3.0	1.0	1.4	1.6	-0.0163	-0.0606
$SrBr_2$	4.0	0.7	1.7	1.8	0.0977	0.1038
$SrCl_2$	5.0	0.6	1.2	10.5	0.0773	0.0847
$Sr(NO_3)_2$	4.0	0.7	0.9	3.4	0.0221	0.0138
$ZnCl_2$	6.0	4.1	6.2	12.9	-0.0167	0.0364
$Zn(NO_3)_2$	4.0	0.6	0.9	5.3	0.0814	0.1002
K_2CO_3	8.0	0.4	0.9	5.3	0.0298	0.0372
K_2CrO_4	2.0	0.7	1.5	1.5	0.0141	-0.0003
Li_2SO_4	3.0	0.4	1.1	1.2	0.0072	0.0207
Na_2CO_3	4.0	0.8	1.2	5.1	-0.0086	0.0089
Na_2HPO_4	6.0	0.8	1.3	8.0	-0.0200	-0.0265
Na_2SO_4	3.0	0.8	1.2	1.5	-0.0086	-0.0204
$(NH_4)_2SO_4$	6.0	1.5	2.6	4.7	-0.0135	-0.0287
$CdSO_4$	2.0	0.8	2.0	2.0	-0.0029	-0.0371

TABLE H.2 (Cont'd.)

Electrolyte	max m	\overline{DP}	DP_{\max}	DP'_{\max}	$B_{12}(100^{\circ}\text{C})$	$B_{12}(25^{\circ}\text{C})$
MgSO ₄	3.0	0.2	0.3	2.8	0.0107	-0.0153
NiSO ₄	2.0	1.5	2.3	2.3	0.0029	-0.0298
ZnSO ₄	4.0	0.9	1.4	4.4	0.0037	-0.0240

*Data for KBr are from Robinson and Stokes (1955) because they are not reported by Weast.

TABLE H.3 Quality of Results with the B_{12} Value at 70°C Obtained by Interpolation of the B_{12} (25°C) and B_{12} (100°C) Values in Equation (3-20)

Electrolyte	B_{12} (70°C)	Abs. % Error in γ_{\pm}		DP	
		Max	Avg	Max	Avg
KBr	0.0421	4.7	3.3	0.3	0.1
KCl	0.0303	3.8	2.9	0.3	0.1
NaCl	0.0619	4.3	3.2	0.2	0.1
Na ₂ SO ₄	-0.0090	2.9	1.6	0.2	0.1
MgCl ₂	0.1119	8.8	6.3	0.7	0.4
MgSO ₄	0.0182	34.0	29.3	0.5	0.3

TABLE H.4 Nonaqueous Electrolytic Binary Data Correlation with the Bromley Equation

System	# of Points	Max 'm'	T (°C)	B ₁₃	% Error in γ_{\pm}		% Error in DP	
					Max	Avg	Max	Avg
CaCl ₂ -MeOH	7	2.6	25	0.15541	-	--	75.2	27.4
HCl-EtOH	8	0.1	25	-0.44655	16.0	10.8	-	-
HCl-MeOH	22	0.56	25	0.40686	1.7	0.6	-	-
LiCl-EtOH	3	4.0	25	0.41205	-	-	13.5	7.8
LiCl-MeOH	6	4.0	25	0.28811	-	-	8.8	3.6
LiCl-MeOH	11	6.0	60	0.25195	-	-	15.6	7.3
NaBr-MeOH	9	1.6	25	0.30629	-	-	9.9	4.1
NaCl-MeOH	7	0.1	25	-0.3223	10.7	6.2	-	-

TABLE H.5 Aqueous Electrolytic Binary Data Correlation
with the Bromley Equation

System	# of Points	Max 'm'	T (°C)	B_{12}	% Error in γ_{\pm}		% Error in DP	
					Max	Avg	Max	Avg
CaCl ₂ -H ₂ O	21	5.0	25	0.1000	11.0	5.5	3.6	2.10
HCl-H ₂ O	15	2.0	25	0.13963	0.9	0.6	-	-
LiCl-H ₂ O	19	4.0	25	0.12366	2.5	0.9	2.0	0.5
LiCl-H ₂ O	11	6.0	60	0.12049	-	-	1.9	0.9
NaBr-H ₂ O	4	10.3	40	0.06607	-	-	13.0	5.5
NaBr-H ₂ O	19	4.0	25	0.07376	0.5	0.1	1.1	0.2
NaCl-H ₂ O	10	1.0	25	0.05586	0.1	0.04	1.0	0.3

TABLE H.6 Isothermal Ternary γ_{\pm} Data Correlation with Model II

System	# of Points	Max 'm'	T (°C)	Ternary Parameters		% Error in γ_{\pm}	
				B_{123}	δ_{123}	Max	Avg
HCl-H ₂ O-EtOH	25	0.1	25	-4.283	-0.0245	13.8	2.4
	44	2.5	25	-4.283	-0.0245	92.1	13.1
HCl-H ₂ O-MeOH	48	2.0	25	0.57215	-0.0498	11.6	1.4
NaCl-H ₂ O-MeOH	35	0.5	25	-11.967	-0.0286	28.0	7.4

TABLE H.7 A Comparative Study of the Three Objective Functions
 [Equations (2-19), (2-20), (2-21)] in Correlating Ternary
 Isothermal VLE Data with Model II

System	Max 'm'	T (°C)	ΔY		ΔP (mmHg)	
			Max	Avg	Max	Avg
<u>Objective Function #1</u>						
LiCl-H ₂ O-EtOH	1.0	25	0.034	0.0145	4.7	2.0
LiCl-H ₂ O-MeOH	1.0	25	0.015	0.0087	11.7	9.0
NaBr-H ₂ O-MeOH	3.0	40	0.035	0.0165	9.0	3.6
	6.2	40	0.026	0.014	8.0	4.4
NaBr-H ₂ O-MeOH	3.0	25	0.028	0.01	4.9	1.9
	7.1	25	0.066	0.015	3.9	1.5
LiCl-H ₂ O-MeOH	2.0	60	0.054	0.026	16.8	7.4
	3.0	60	0.05	0.028	12.6	6.6
<u>Objective Function #2</u>						
LiCl-H ₂ O-EtOH	1.0	25	0.023	0.009	8.9	3.3
LiCl-H ₂ O-MeOH	1.0	25	0.011	0.007	4.4	3.1
NaBr-H ₂ O-MeOH	3.0	40	0.021	0.012	11.4	3.9
	6.2	40	0.021	0.011	11.4	4.6
NaBr-H ₂ O-MeOH	3.0	25	0.013	0.0064	5.0	2.0
	7.1	25	0.042	0.0096	12.7	4.5
LiCl-H ₂ O-MeOH	2.0	60	0.038	0.018	40.0	27.7
	3.0	60	0.036	0.02	46.4	30.2
<u>Objective Function #3</u>						
LiCl-H ₂ O-EtOH	1.0	25	0.025	0.01	8.0	3.0
LiCl-H ₂ O-MeOH	1.0	25	0.011	0.008	10.2	8.0
NaBr-H ₂ O-MeOH	3.0	40	0.02	0.012	13.2	3.8
	6.2	40	0.02	0.011	12.1	4.8
NaBr-H ₂ O-MeOH	3.0	25	0.014	0.007	5.1	2.0
	7.1	25	0.048	0.011	10.5	3.4
LiCl-H ₂ O-MeOH	2.0	60	0.042	0.019	31.0	19.6
	3.0	60	0.036	0.02	46.4	30.2

TABLE H.8 Values of the Parameters Obtained with Three Objective Functions for Model II

System	Max 'm'	T (°C)	Ternary Parameters	
			B_{123}	δ_{123}
<u>Objective Function #1</u>				
LiCl-H ₂ O-EtOH	1.0	25	-117.68	0.0604
LiCl-H ₂ O-MeOH	1.0	25	-145.85	-0.0612
NaBr-H ₂ O-MeOH	3.0	40	-60.53	-0.182
	6.2	40	-68.105	-0.1582
NaBr-H ₂ O-MeOH	3.0	25	-93.462	-0.1135
	7.1	25	-81.45	-0.11248
LiCl-H ₂ O-MeOH	2.0	60	-21.409	0.0282
	3.0	60	-32.164	0.03745
<u>Objective Function #2</u>				
LiCl-H ₂ O-EtOH	1.0	25	-152.94	0.0899
LiCl-H ₂ O-MeOH	1.0	25	-64.026	-0.1587
NaBr-H ₂ O-MeOH	3.0	40	-59.76	-0.1246
	6.2	40	-64.96	-0.113
NaBr-H ₂ O-MeOH	3.0	25	-93.2	-0.0235
	7.1	25	-99.38	-0.0102
LiCl-H ₂ O-MeOH	2.0	60	-72.477	0.0759
	3.0	60	-80.63	0.0847
<u>Objective Function #3</u>				
LiCl-H ₂ O-EtOH	1.0	25	-145.91	0.08379
LiCl-H ₂ O-MeOH	1.0	25	-133.37	-0.0573
NaBr-H ₂ O-MeOH	3.0	40	-51.02	-0.1674
	6.2	40	-62.74	-0.1292
NaBr-H ₂ O-MeOH	3.0	25	-93.997	-0.0507
	7.1	25	-95.00	-0.0483
LiCl-H ₂ O-MeOH	2.0	60	-59.4	0.0639
	3.0	60	-68.70	0.0724

TABLE H.9 B_{12} Values Obtained from Weast's Data and Equation (3-20)
with B^* and B_1' Values from Table 3.3

Electrolyte	B_{12} from Weast Data	B_{12} from Eqn (3-20)
NaCl	0.0567	0.0612
KBr	0.0462	0.0436
KCl	0.0311	0.0322
Na_2SO_4	-0.0086	-0.0036
MgCl_2	0.0951	0.1017
MgSO_4	0.0107	0.0163

TABLE E.10 γ_{\pm} Values for MgCl_2 Using B Values from
 $_{12}$
 Weast's Data and Equation (3-20)

molality	γ_{\pm} from Weast Data	γ_{\pm} from Eqn (3-20)
0.2	0.4034	0.4071
0.4	0.3737	0.3796
0.6	0.3713	0.3792
0.8	0.3820	0.3924
1.0	0.4018	0.4150
1.2	0.4292	0.4458
1.4	0.4636	0.4842
1.6	0.5050	0.5304
1.8	0.5537	0.5848
2.0	0.6103	0.6482

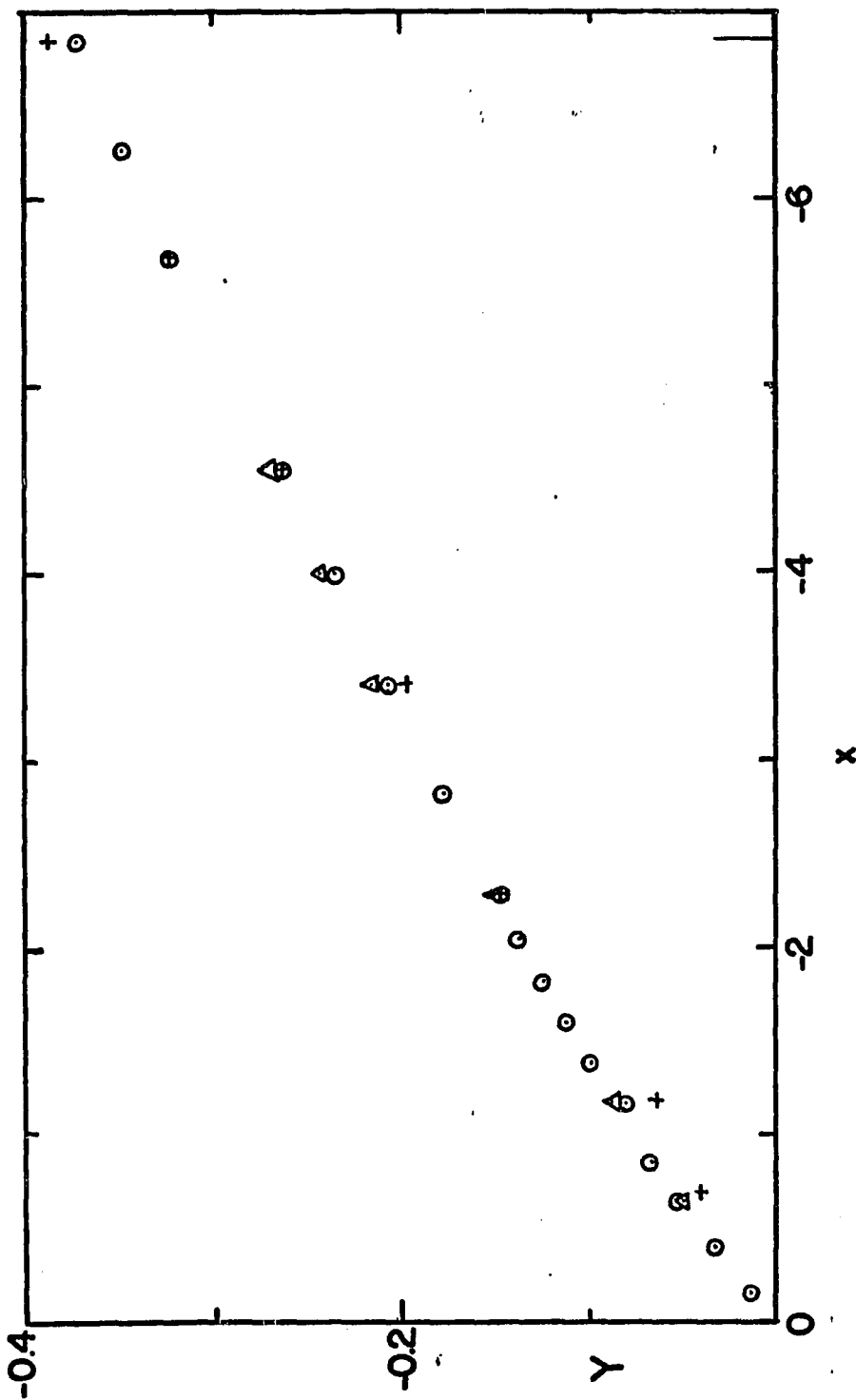


Figure H.1 Test of the Bromley Equation

System: NaCl-Water at 100°C

+ Weast (1969)

Δ Robinson and Stokes (1955)

⊙ Gibbard et al., (1974)

Y, X are defined in equation (3-15)

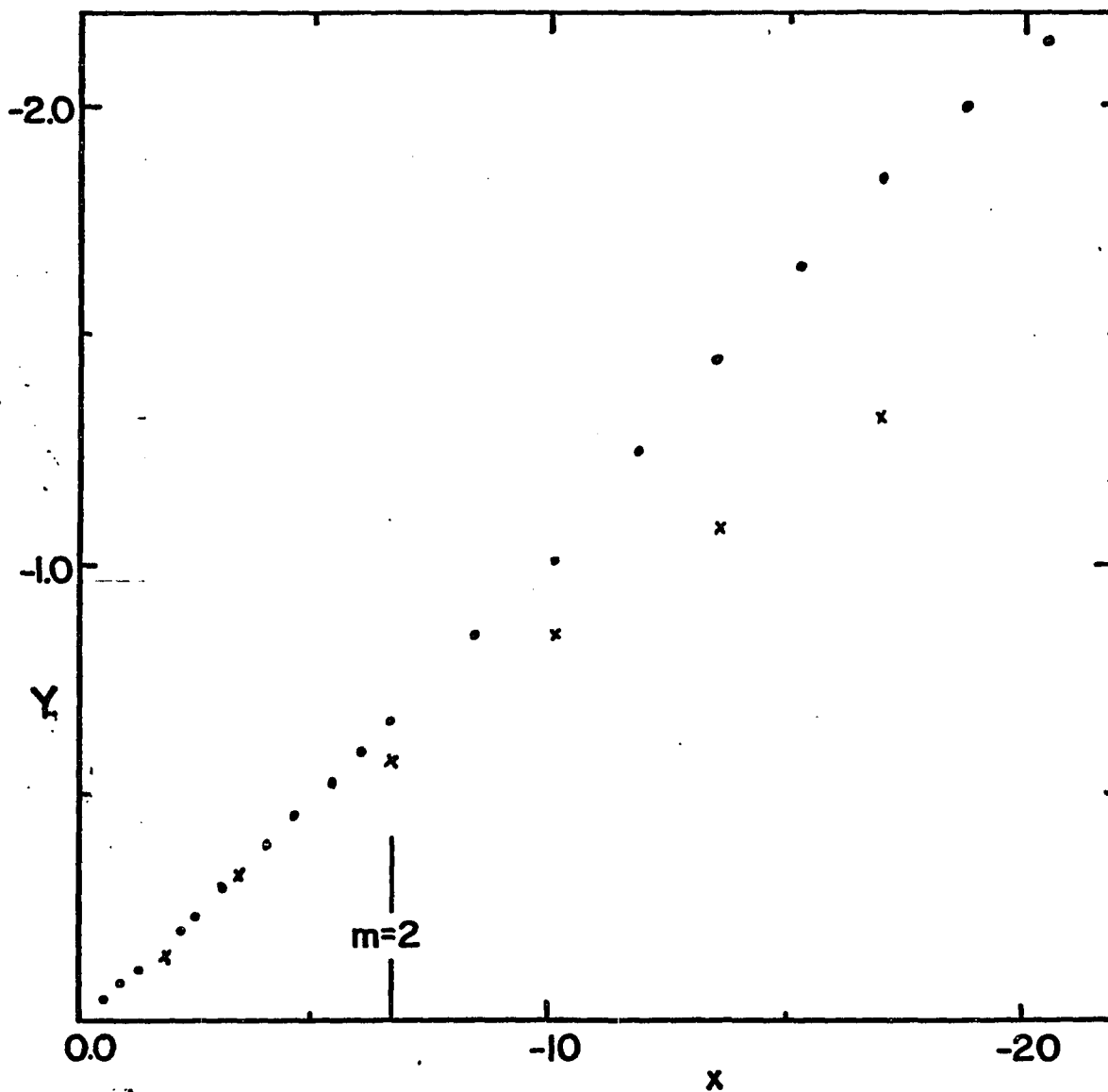


Figure H.2 Test of the Bromley Equation

System: $\text{CaCl}_2\text{-H}_2\text{O}$

● Robinson and Stokes (25°C)

x Weast (100°C)

Y,x are defined in equation (3.15)

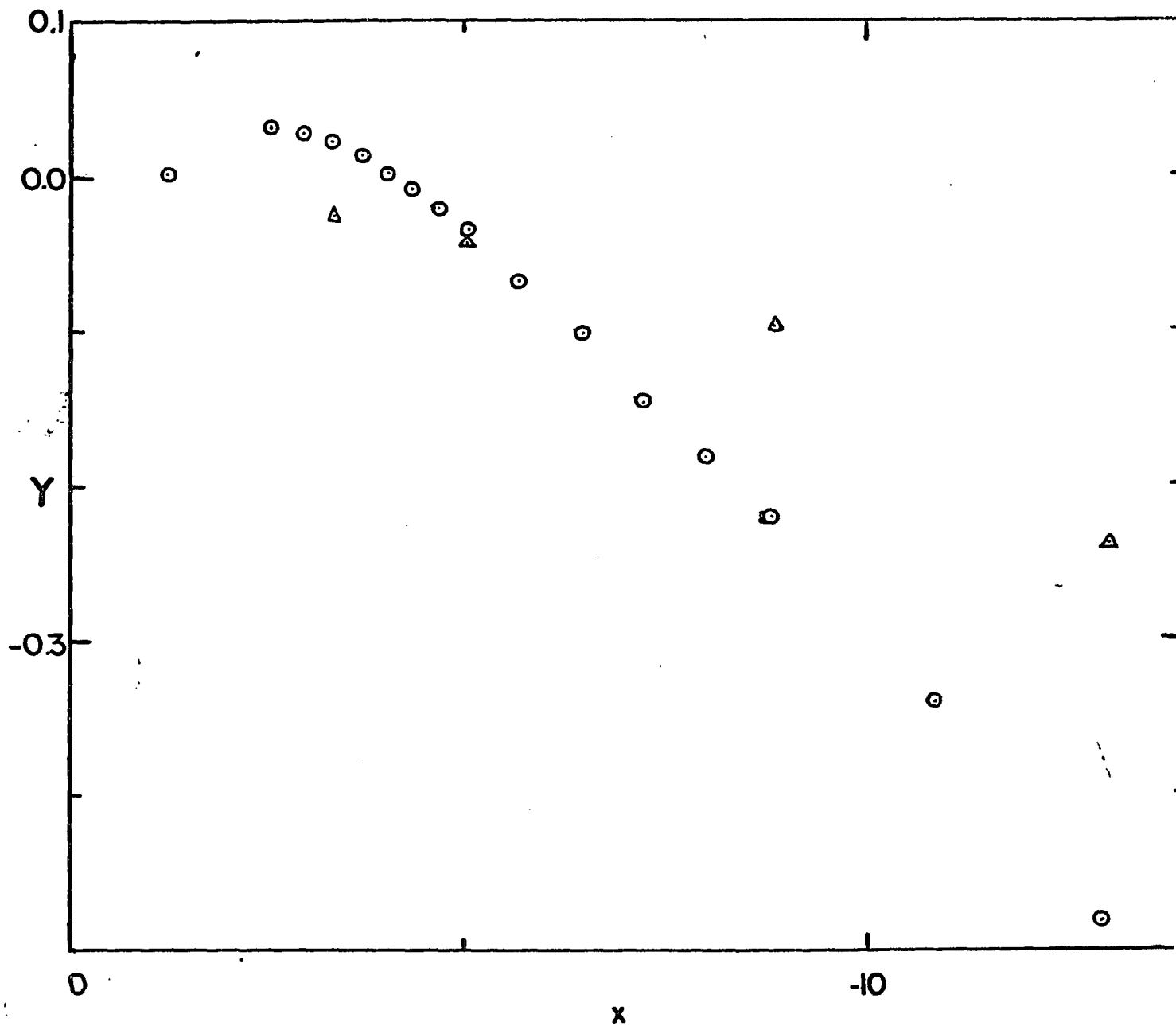


Figure H.3 Test of the Bromley Equation

System: MgSO_4

○ Robinson and Stokes (25°C)

△ Weast (100°C)

Y, x are defined in equation (3-15)

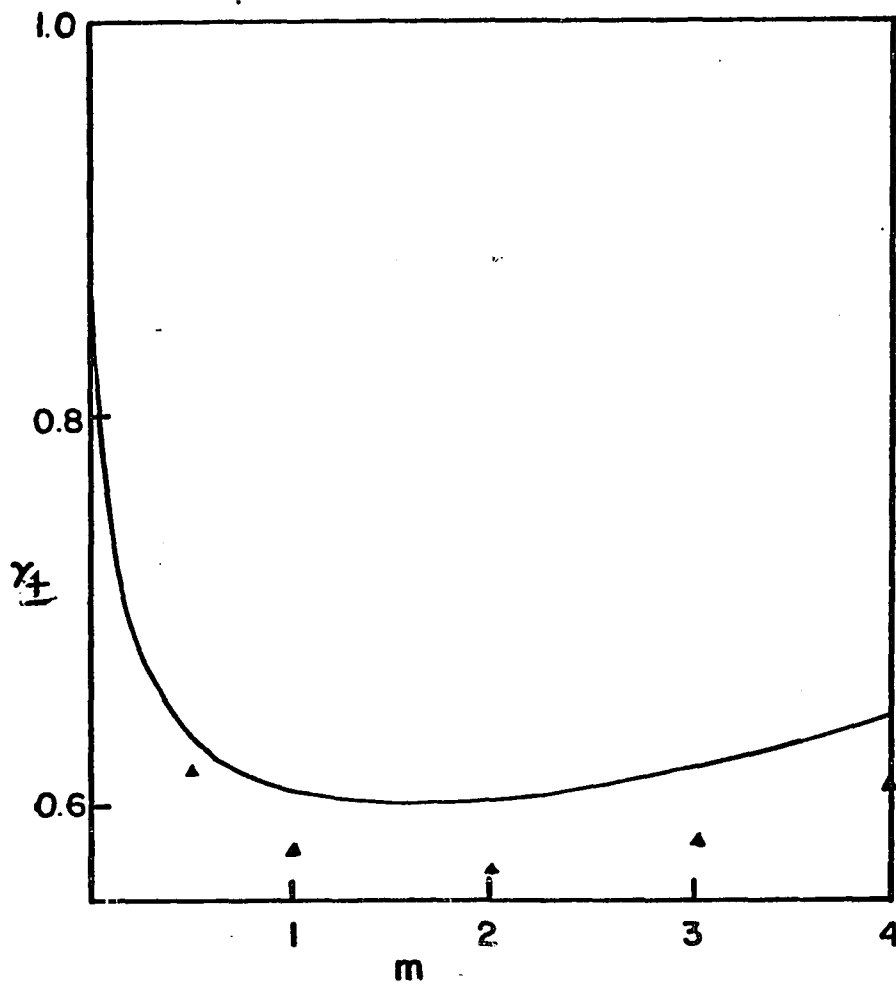


Figure H.4 Activity Coefficients as a function of concentration for the System KBr-Water at 100°C

— Robinson and Stokes

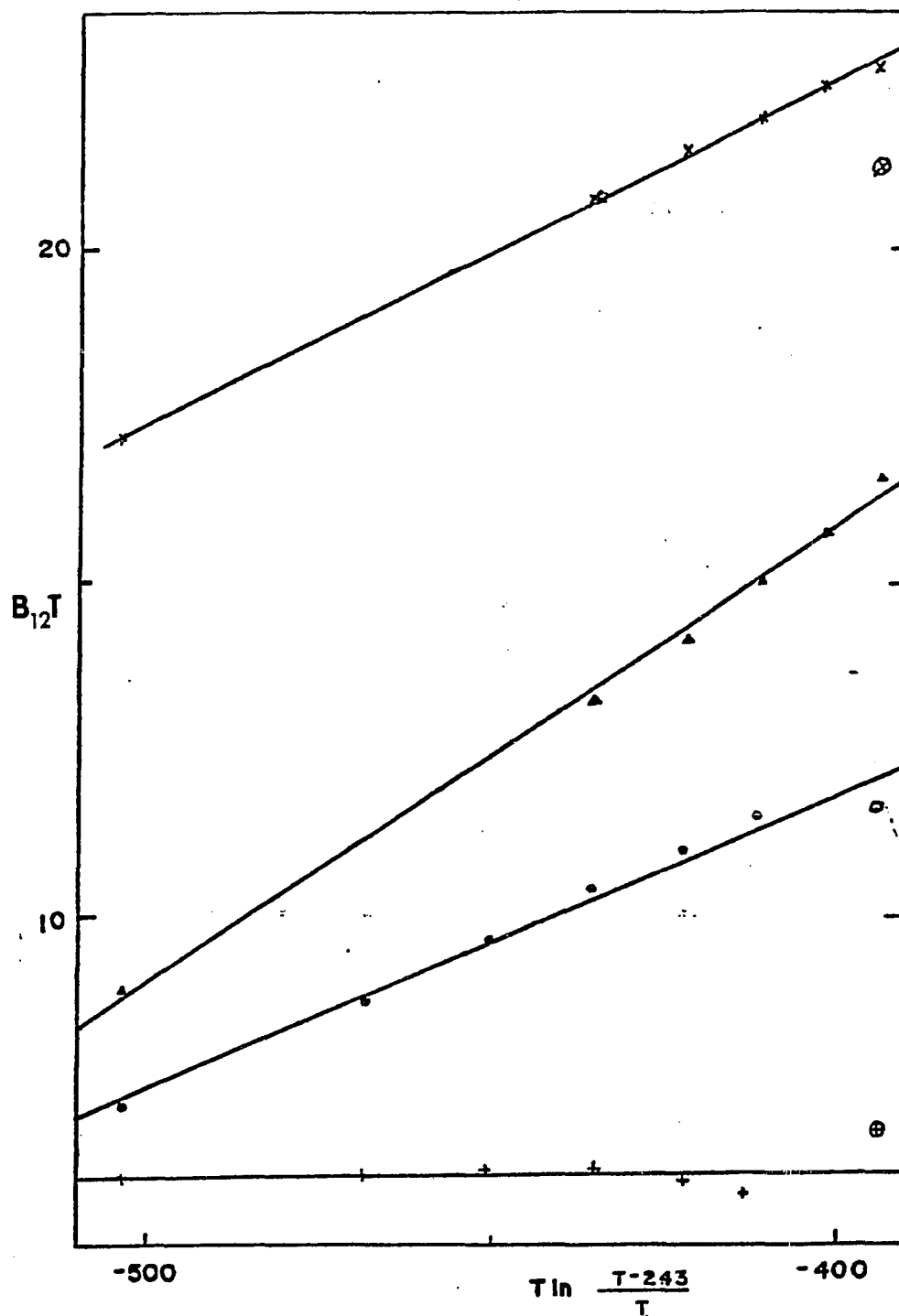


Figure H.5 Test of Temperature Dependency of B_{12} Equation (3-20)

- KCl (Snipes et al., 1975)
- ⊕ KCl (Weast, 1969)
- ▲ KBr (Robinson and Stokes, 1955)
- + $MgSO_4$ (Snipes, et al., 1975)
- ⊕ $MgSO_4$ (Weast, 1969)
- × NaCl (Robinson and Stokes, 1955)
- ⊗ Weast (1969)

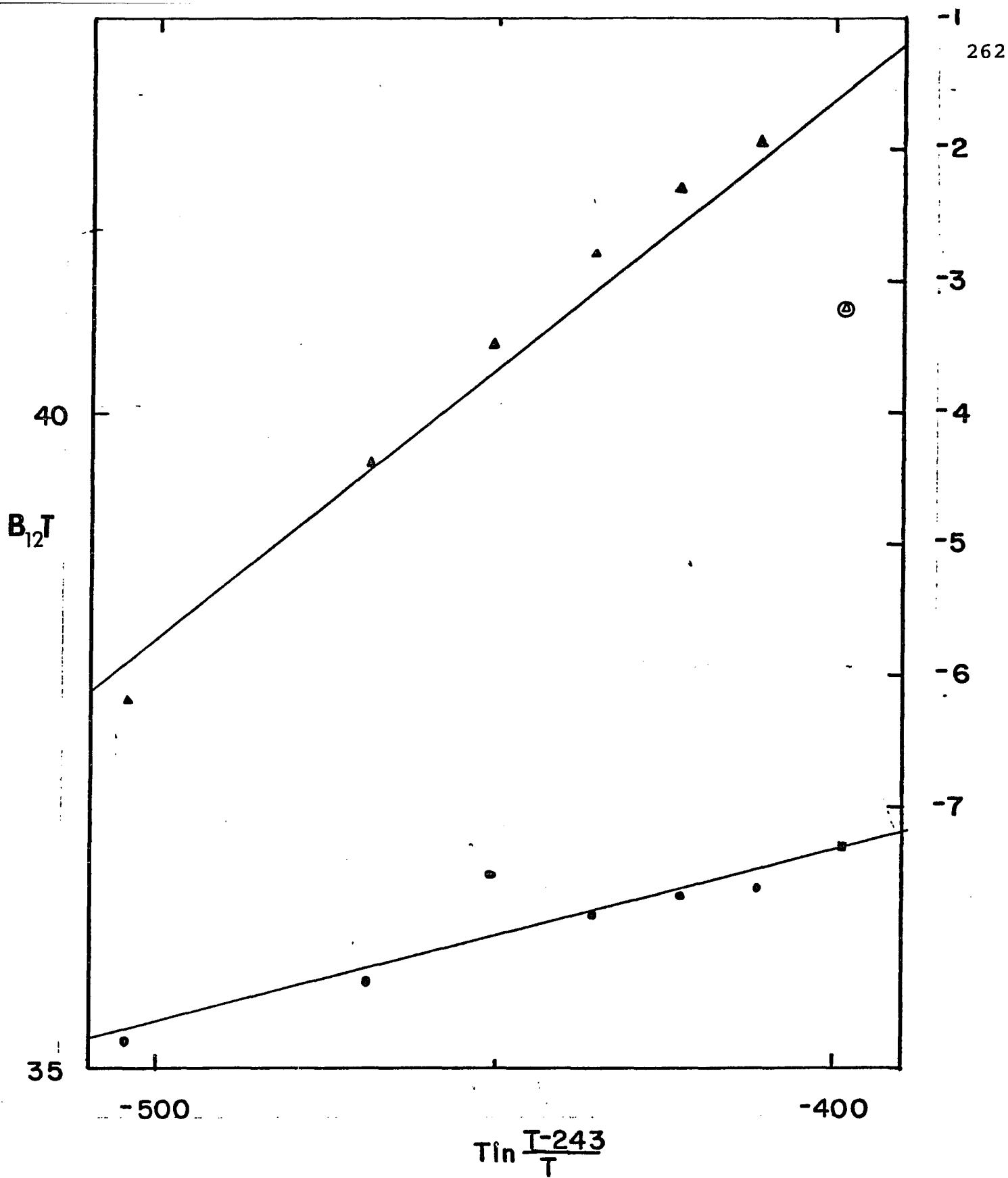
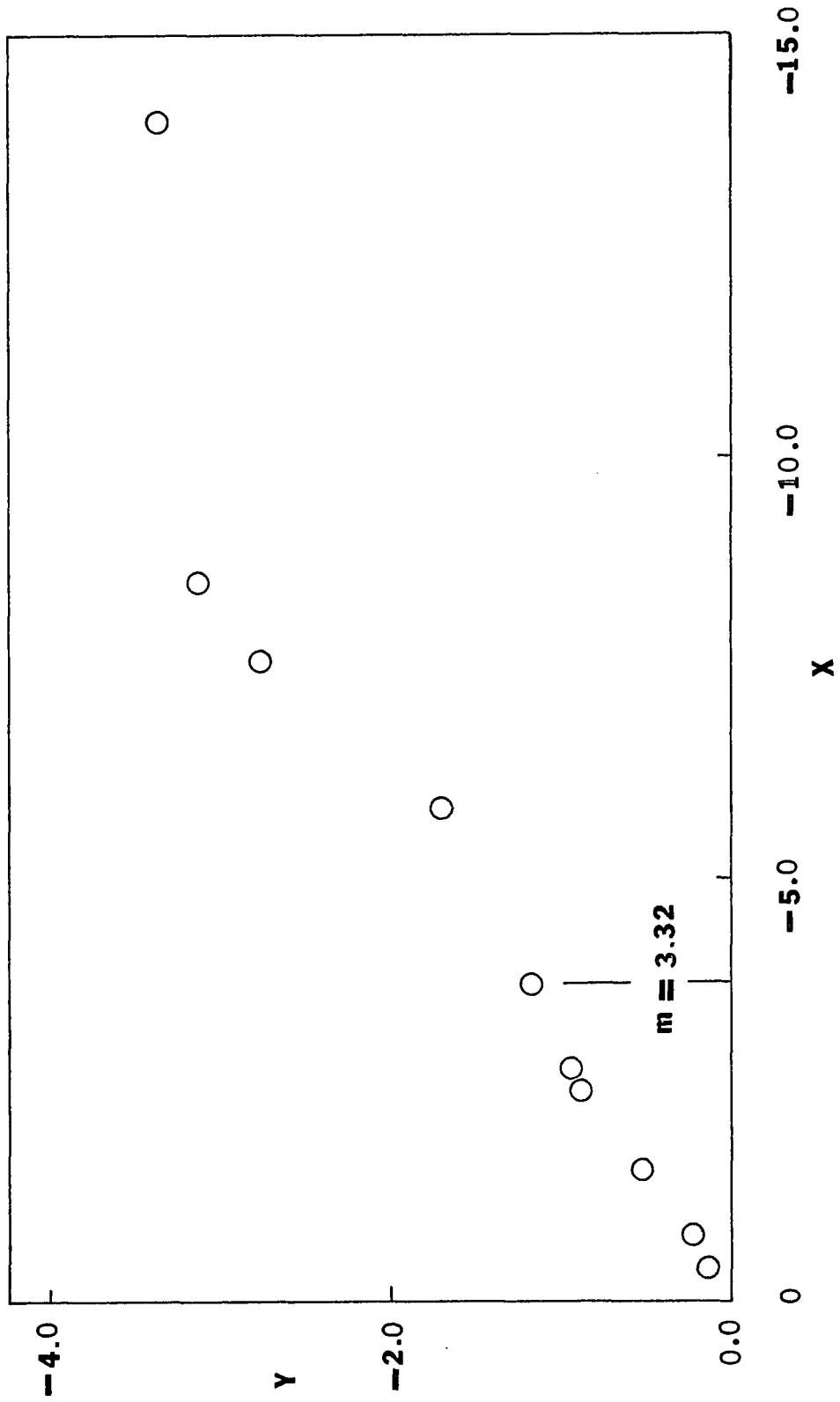


Figure H.6 Test of Temperature Dependency of B_{12} Equation (3-20)

- MgCl_2 (Snipes et al., 1975)
- MgCl_2 (Weast, 1969)
- ▲ Na_2SO_4 (Snipes et al., 1975)
- ⊙ Na_2SO_4 (Weast, 1969)

Figure H.7 Test of the Bromley Equation , System : LiBr-MeOH at 25°C

Y,x are defined in equation (3-15)



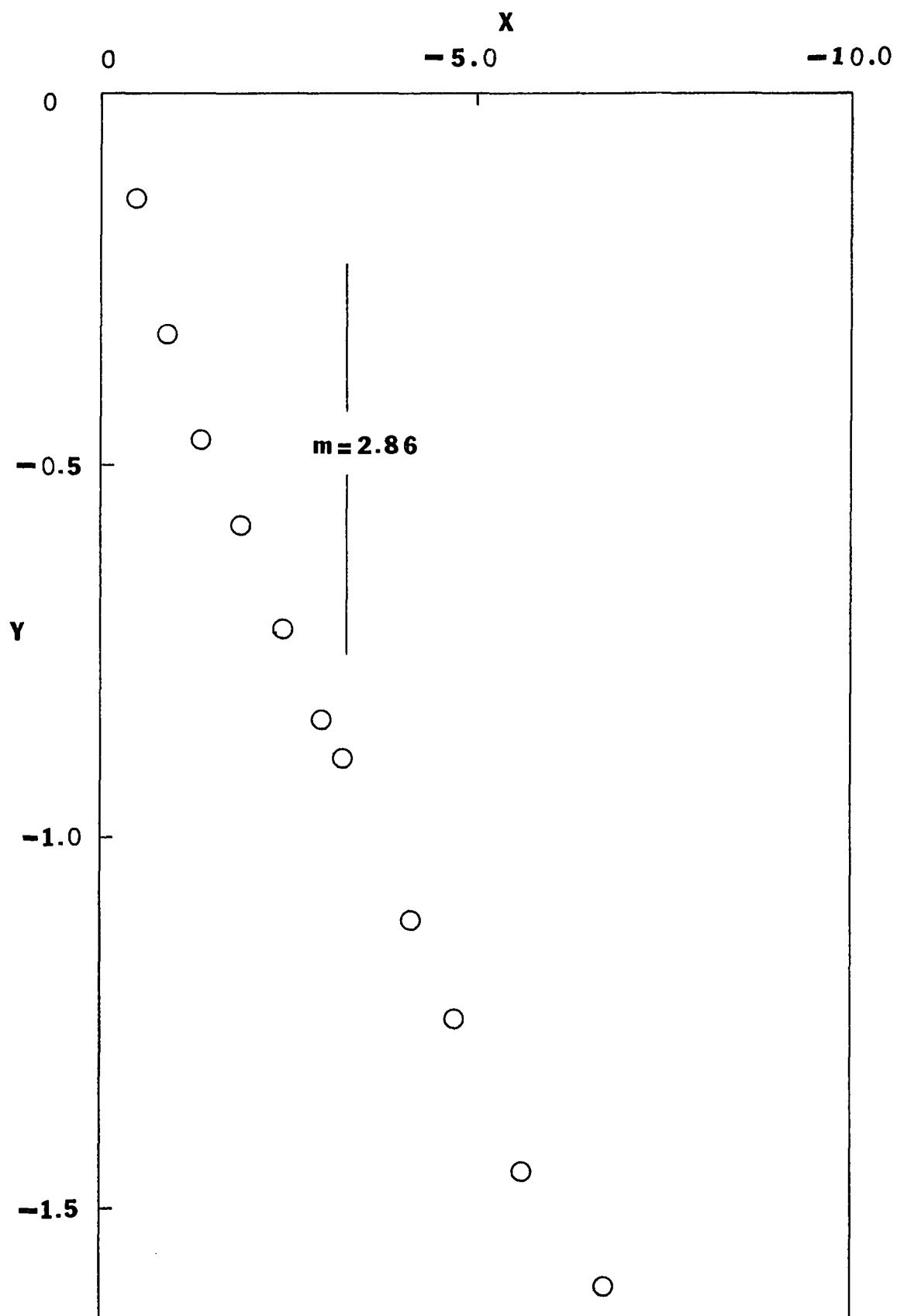


Figure H.8 Test of the Bromley Equation, System : LiCl-MeOH at 60°C

Y,x are defined in equation (3-15)

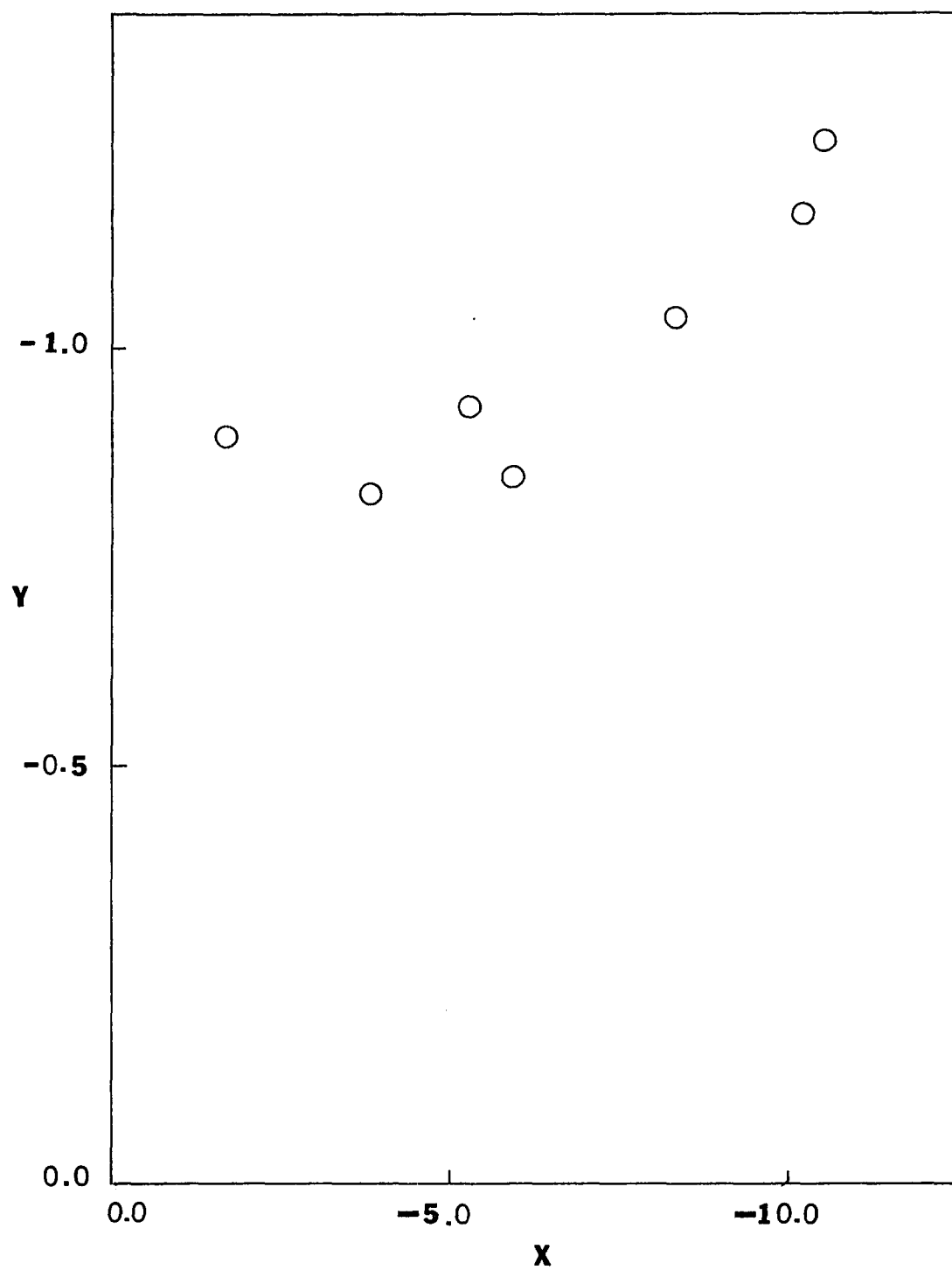


Figure H.9 Test of the Bromley Equation, System : CaCl_2 -
MeOH at 25°C

Y,x are defined in equation (3-15)

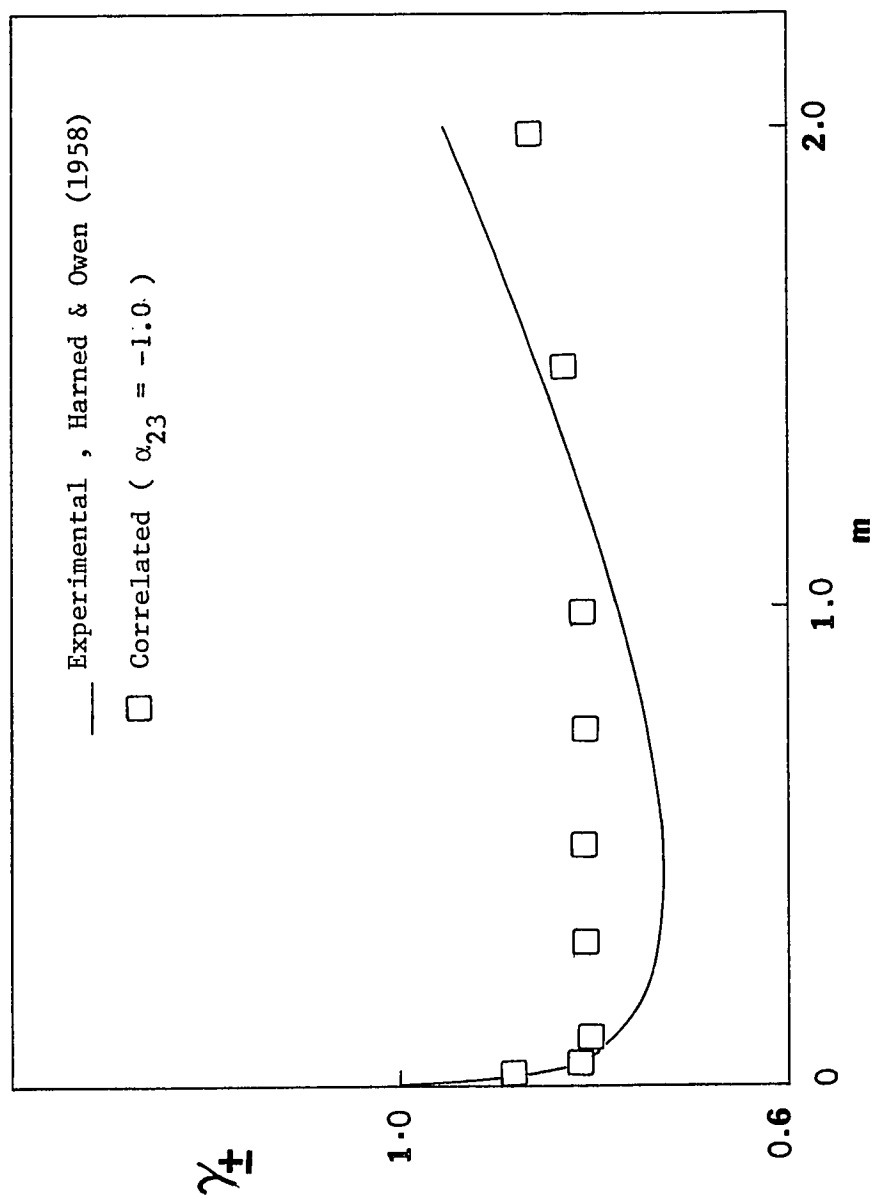


Figure H.10 Comparison of Experimental Mean Molal Activity Coefficients with those Correlated by Model II for the System HCl-H₂O-EtOH at 25 C and Constant $X_{\text{EtOH}} = 0.0417$

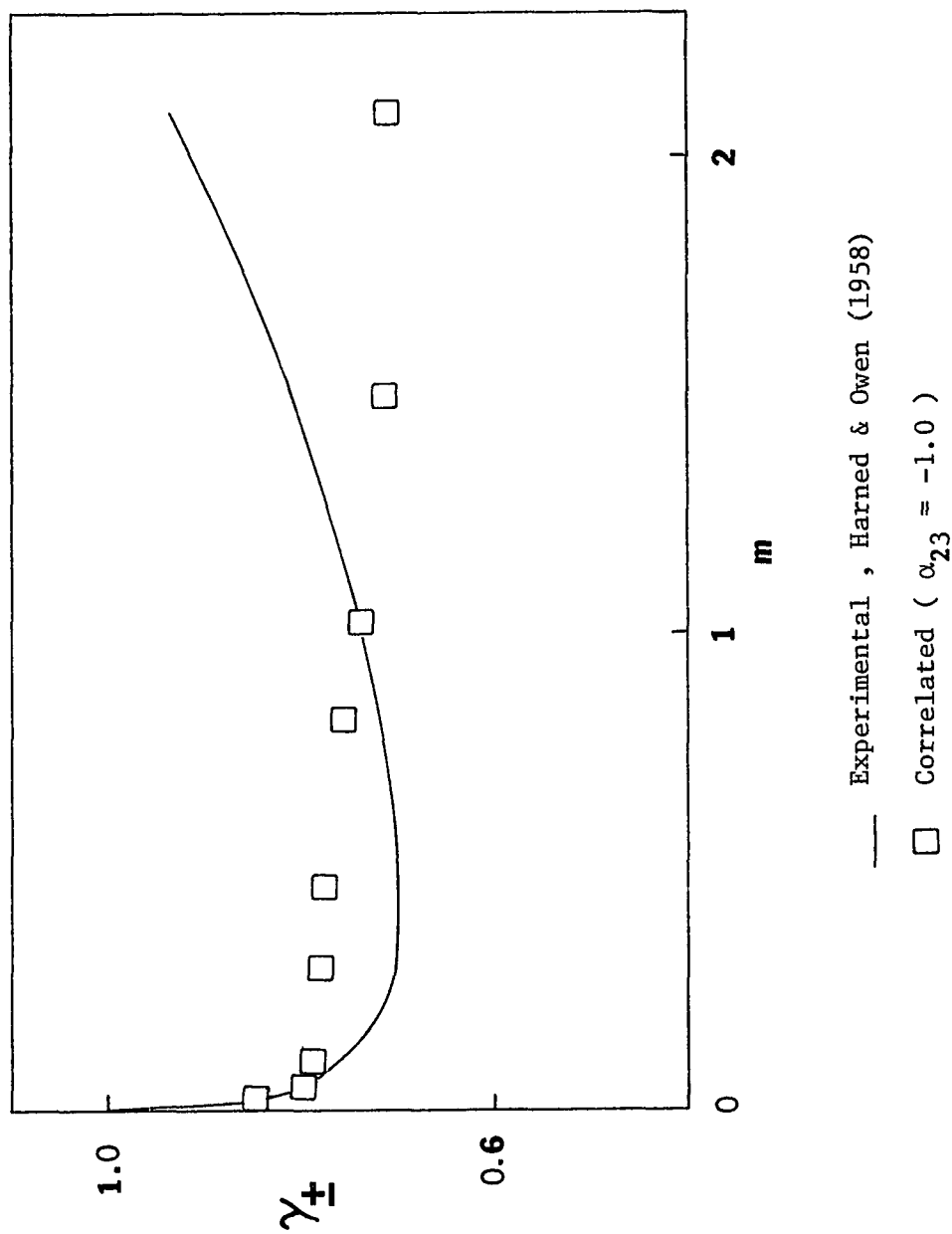


Figure H.11 Comparison of Experimental Mean Molal Activity Coefficients with those Correlated by Model II for the System HCl-H₂O-EtOH at 25 °C and Constant $X_{\text{EtOH}} = 0.0891$

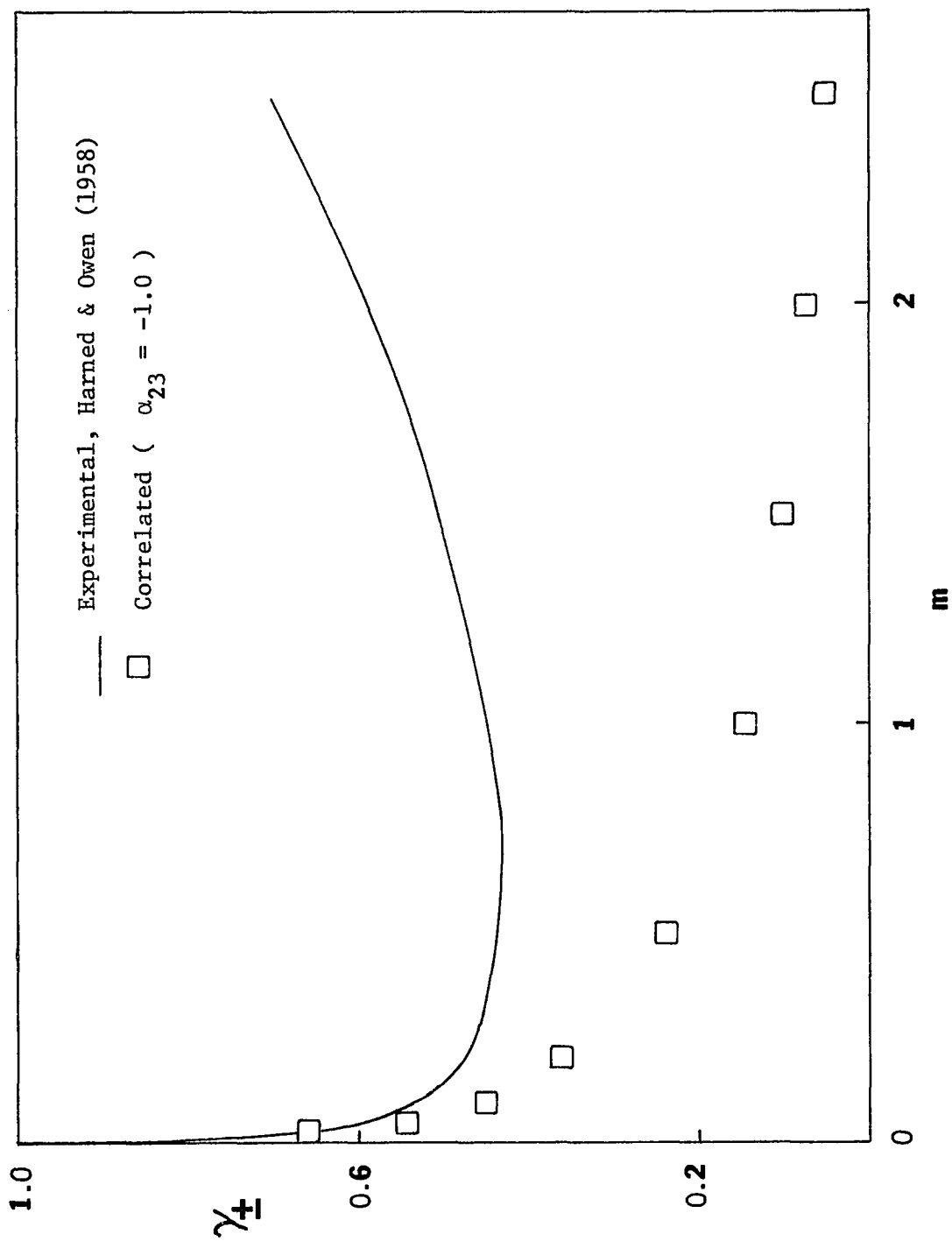


Figure H.12 Comparison of Experimental Mean Molal Activity Coefficients with those Correlated by Model II for the System HCl-H₂O-EtOH at 25°C and Constant $X'_{\text{EtOH}} = 0.5$

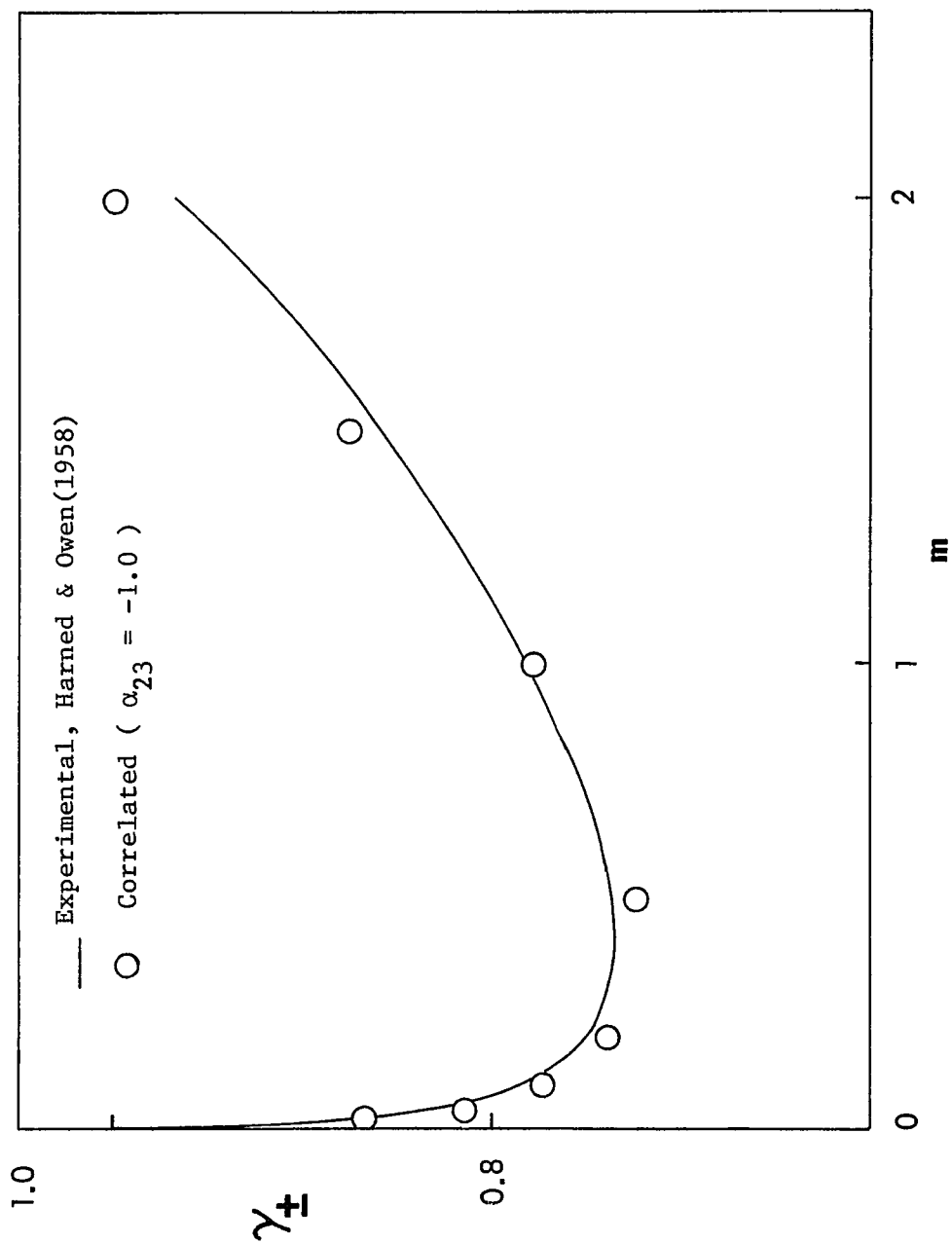


Figure H.13 Comparison of Experimental Mean Molal Activity Coefficients with those Correlated by Model II for the System HCl-H₂O-MeOH at 25 °C and Constant $X_{\text{MeOH}} = 0.0584$

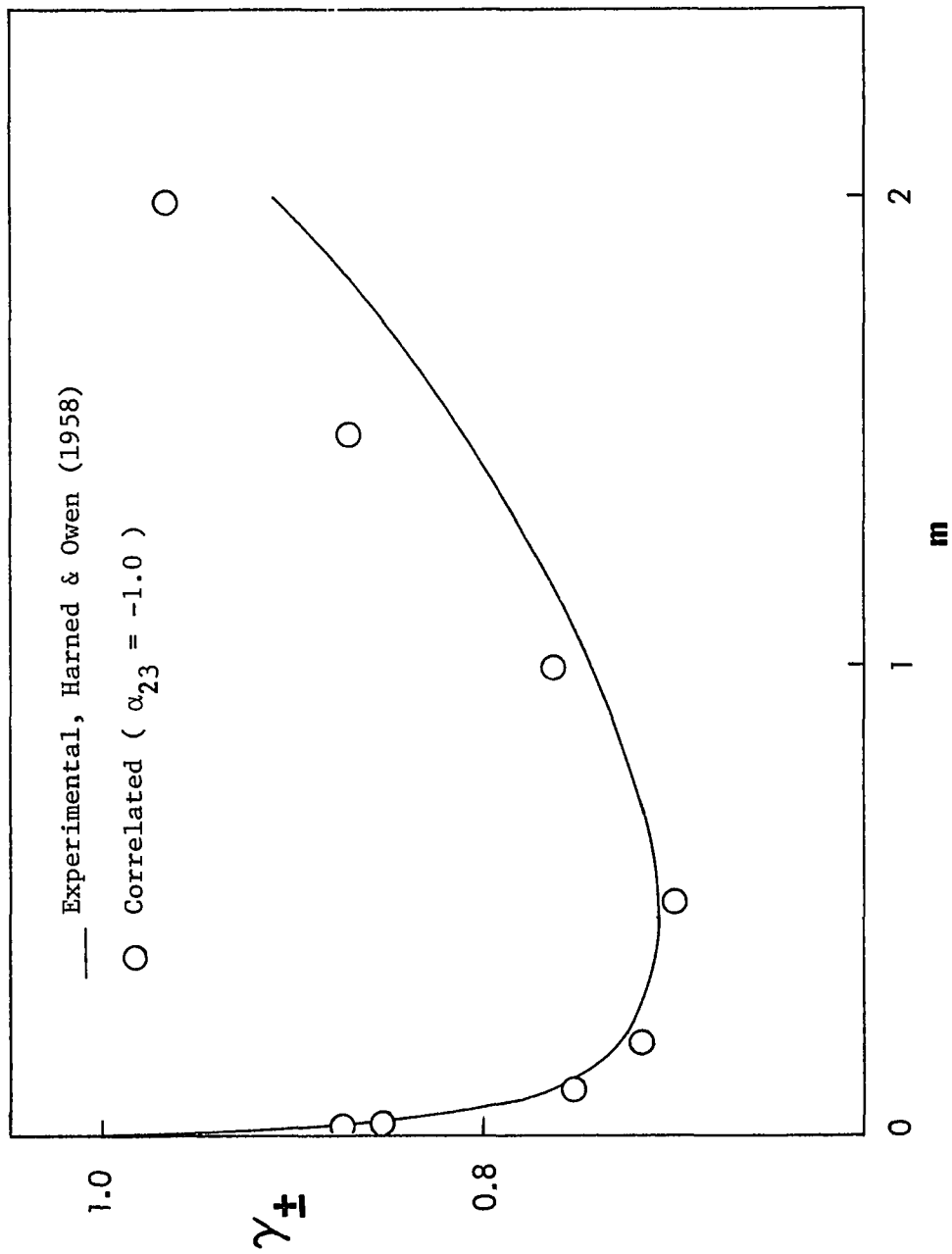


Figure H.14 Comparison of Experimental Mean Molal Activity Coefficients with those Correlated by Model II for the System HCl-H₂O-MeOH at 25 °C and Constant $X_{\text{MeOH}} = 0.1233$

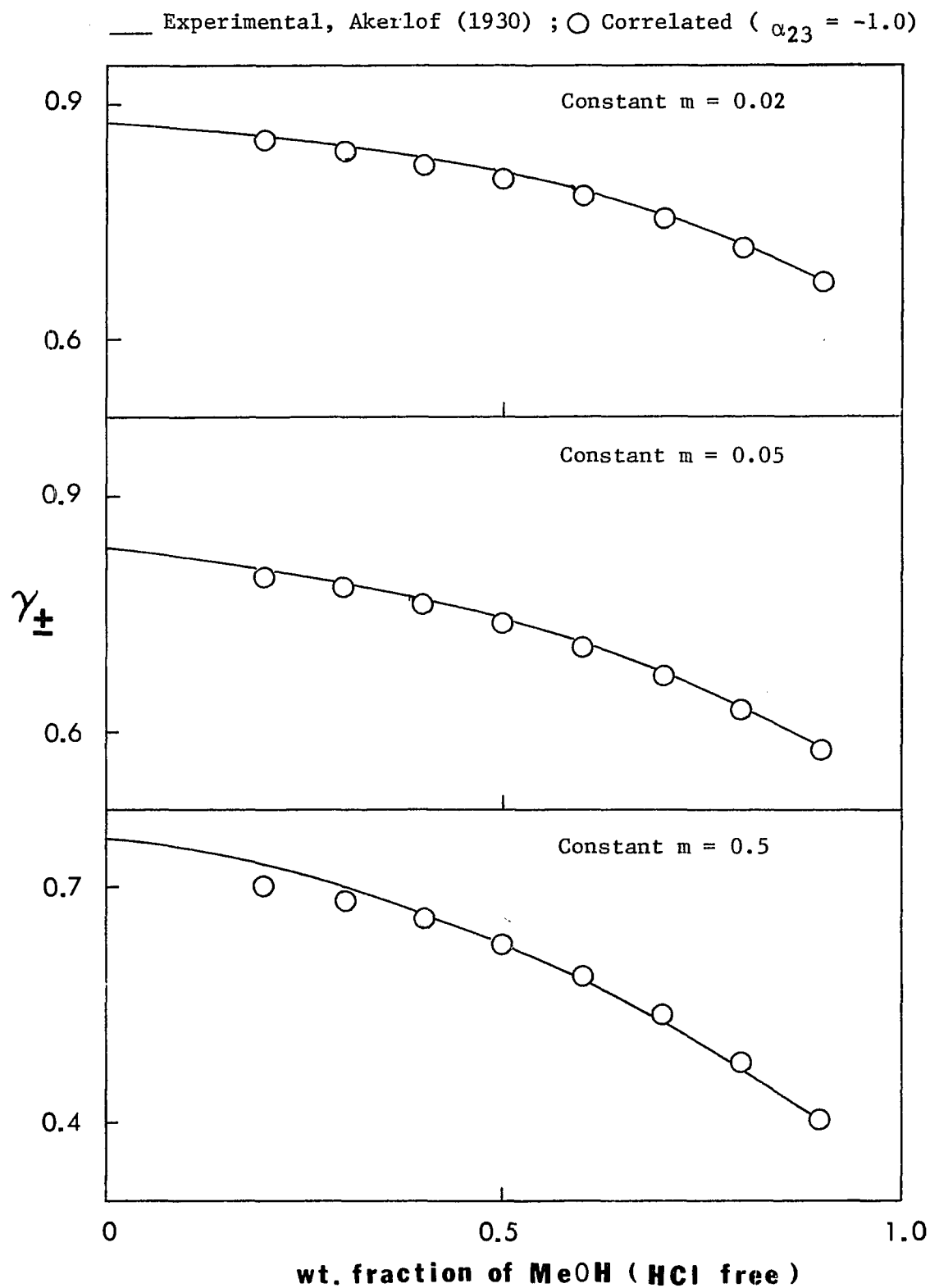


Figure H.15 Comparison of Experimental Mean Molal Activity Coefficients with Those Correlated by Model II for the System HCl-H₂O-MeOH at 25°C and Constant $m = 0.02, 0.05, 0.5$

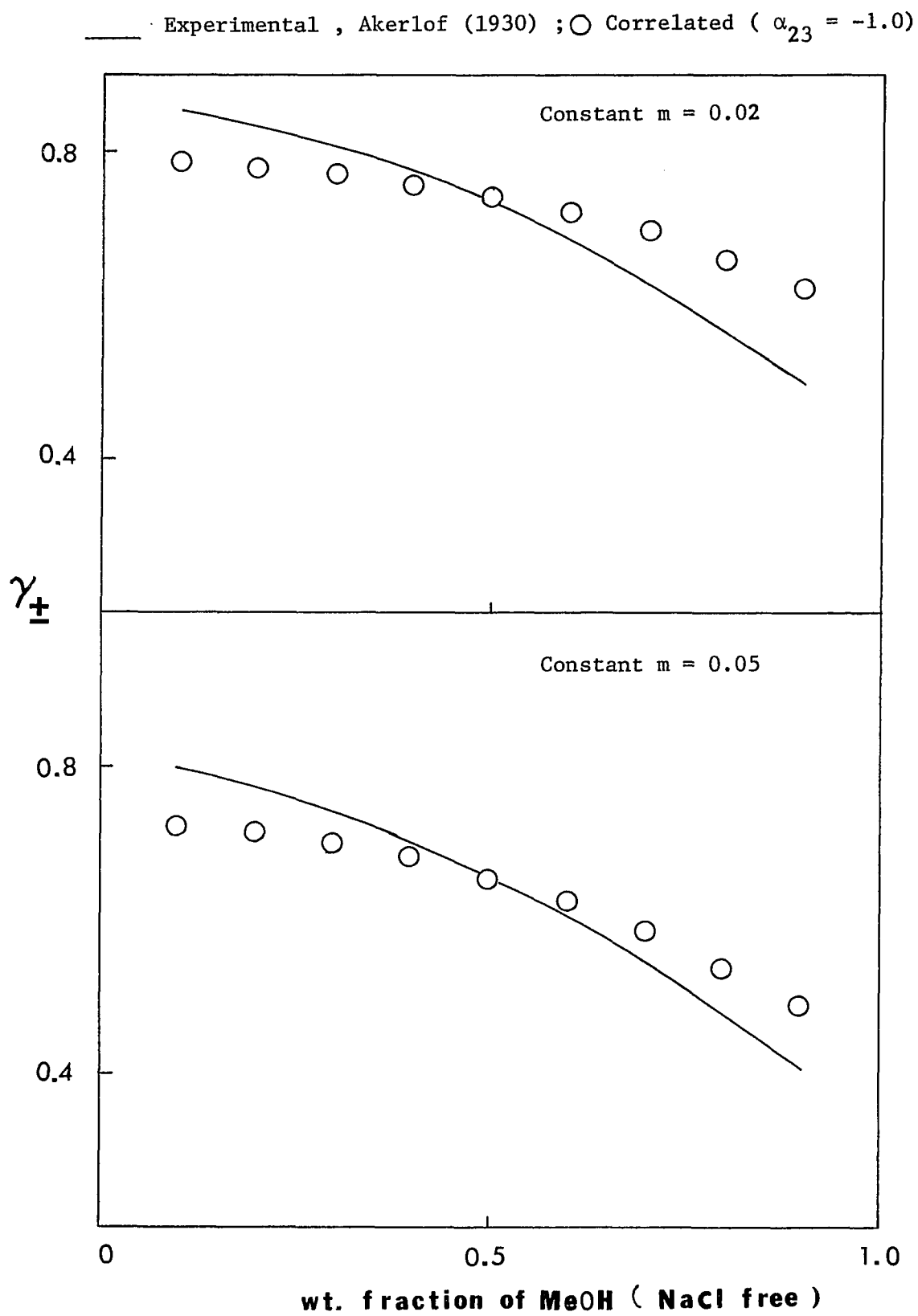


Figure H.16 Comparison of Experimental Mean Molal Activity Coefficients with those Correlated by Model II for the System NaCl-H₂O-MeOH at 25°C and Constant $m = 0.02$ and 0.05

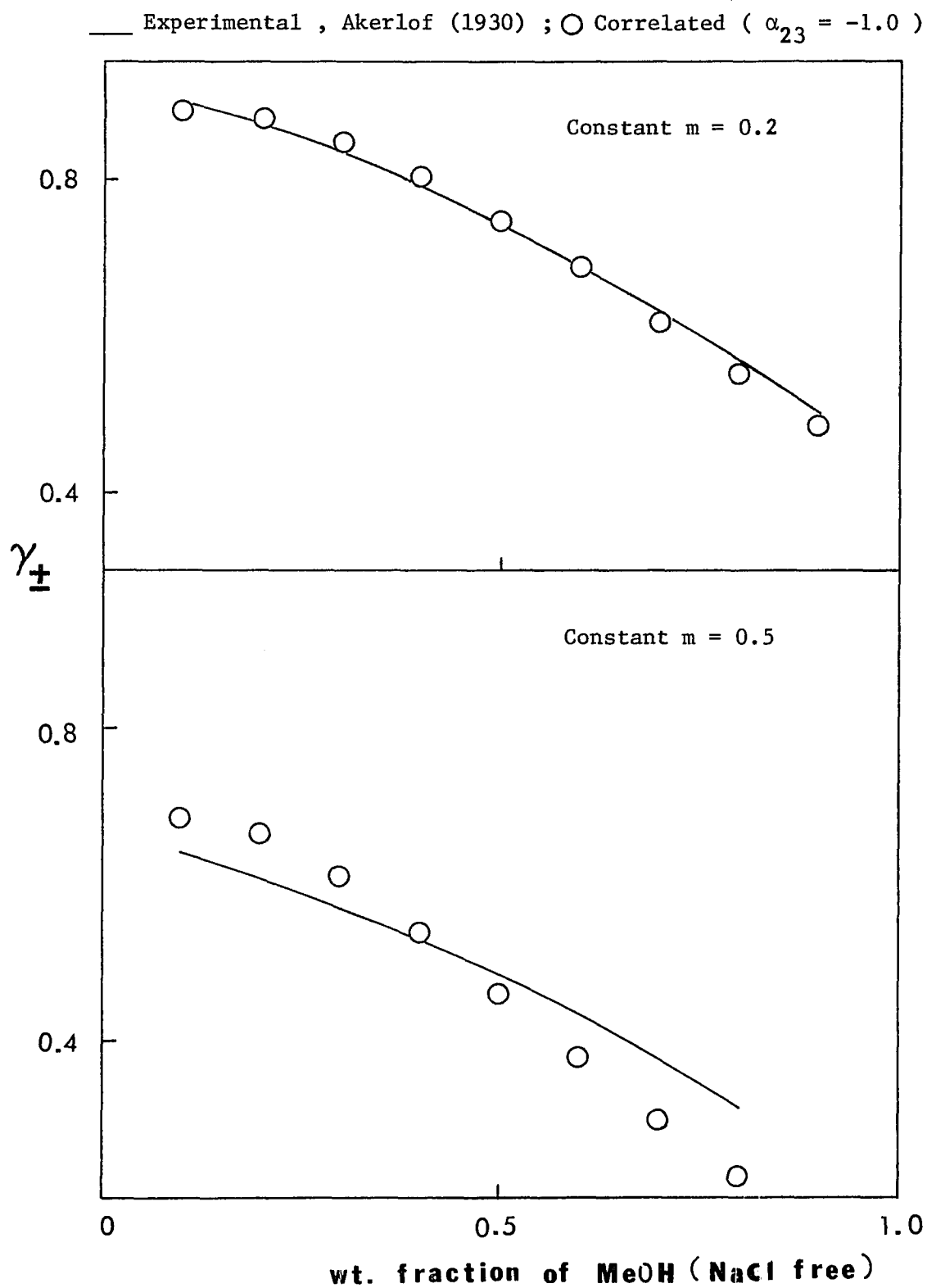


Figure H.17 Comparison of Experimental Mean Molal Activity Coefficients with those Correlated by Model II for the System NaCl-H₂O-MeOH at 25°C and Constant $m = 0.2, 0.5$

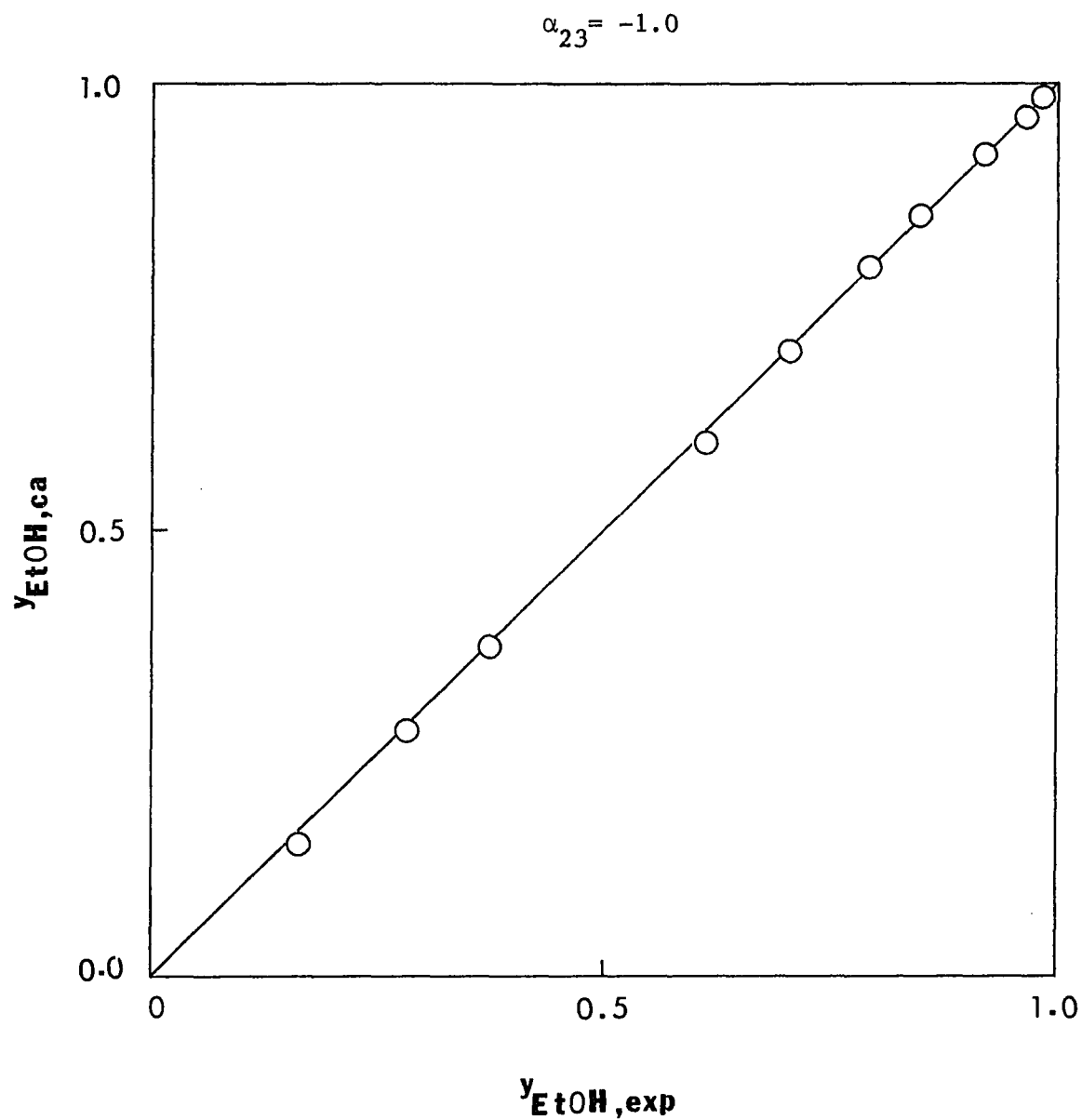


Figure H.18 Comparison of Experimental and Correlated Vapor-Phase Compositions Using Model II for the System LiCl-H₂O-EtOH at 25 °C and Constant $m = 0.5$

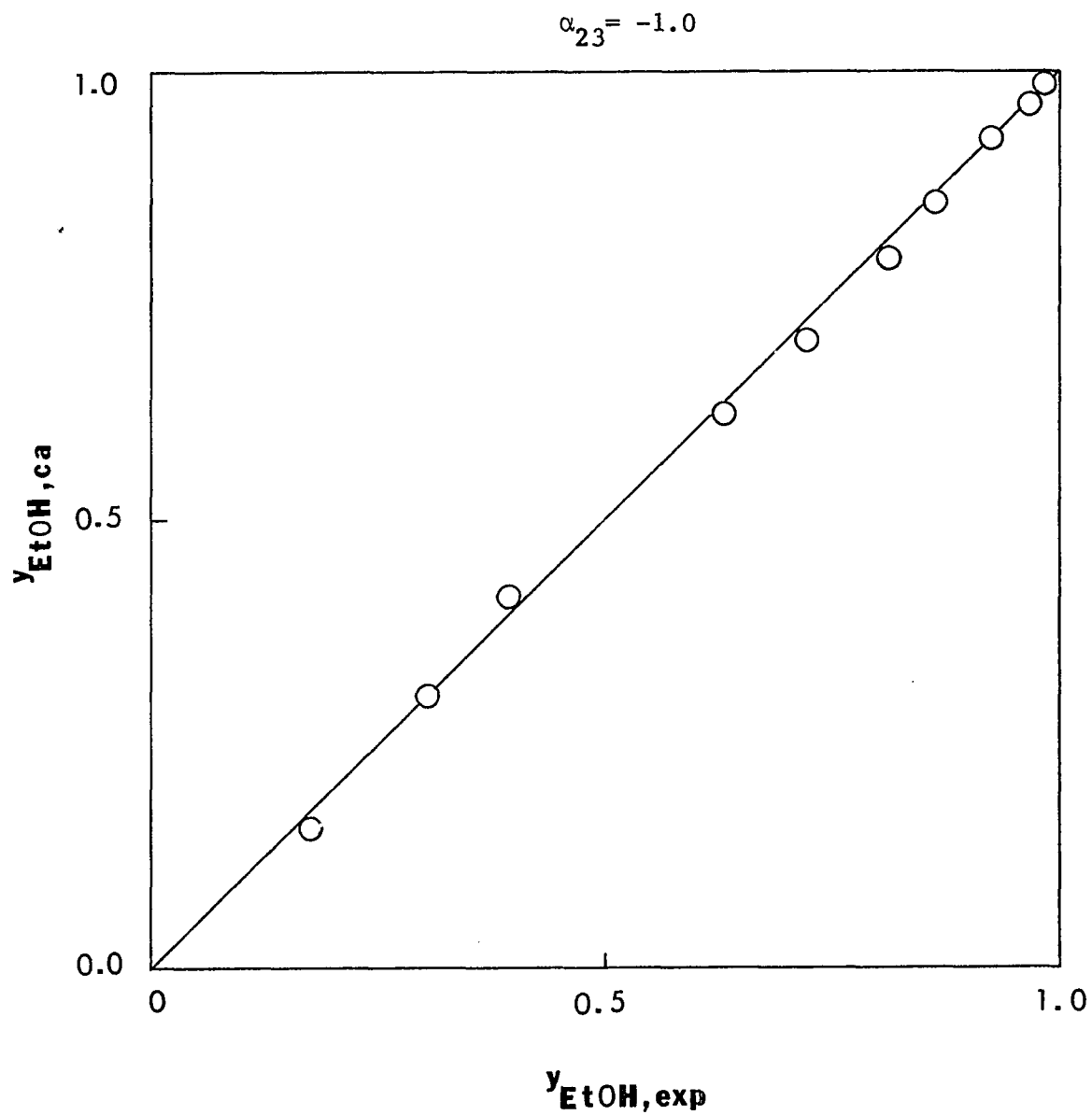


Figure H.19 Comparison of Experimental and Correlated Vapor-Phase Compositions Using Model II for the System $\text{LiCl-H}_2\text{O-EtOH}$ at 25°C and Constant $m = 1.0$

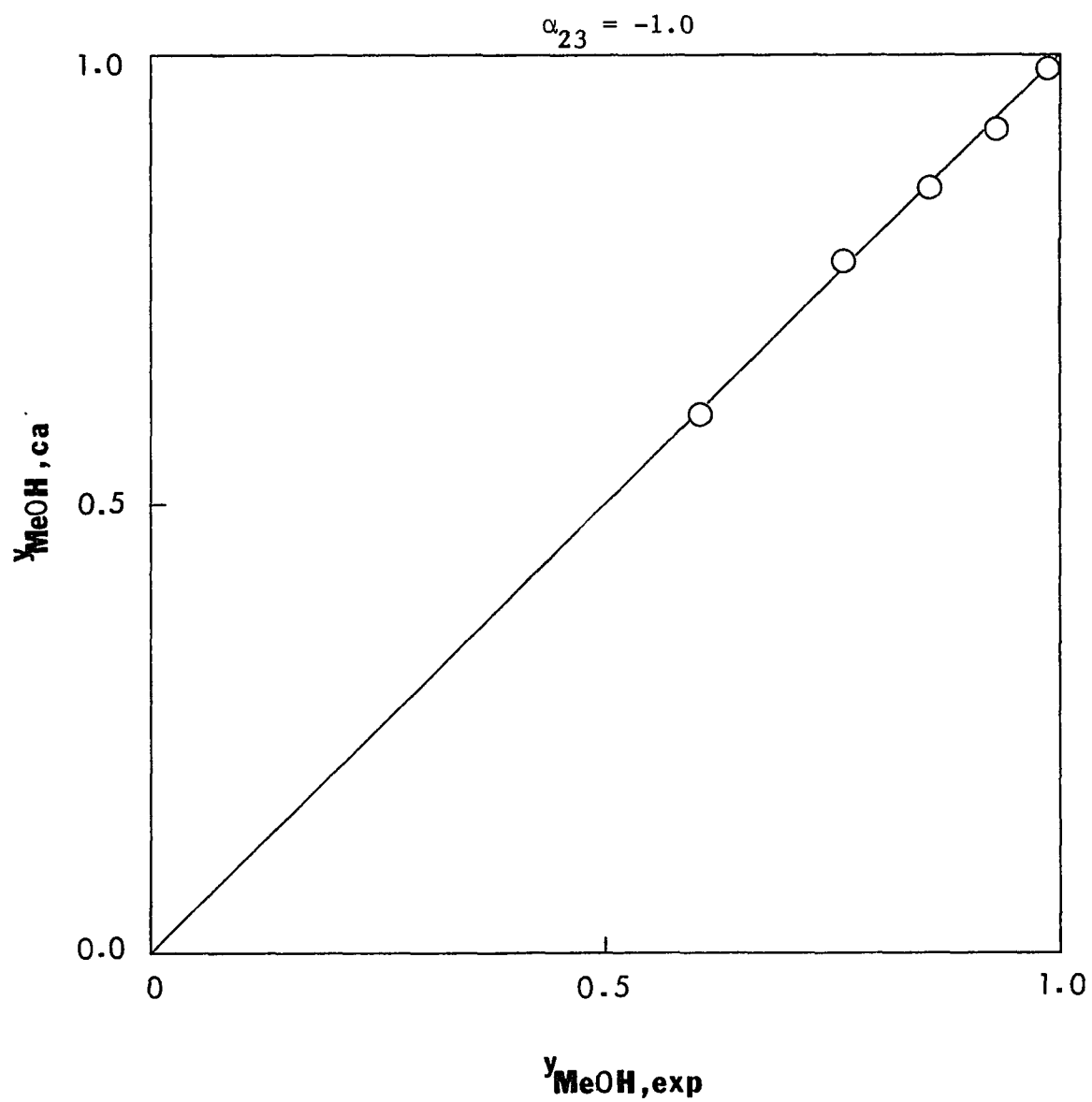


Figure H.20 Comparison of Experimental with Correlated Vapor-Phase Compositions Using Model II for the System $\text{LiCl-H}_2\text{O-MeOH}$ at 25°C and Constant $m = 1.0$

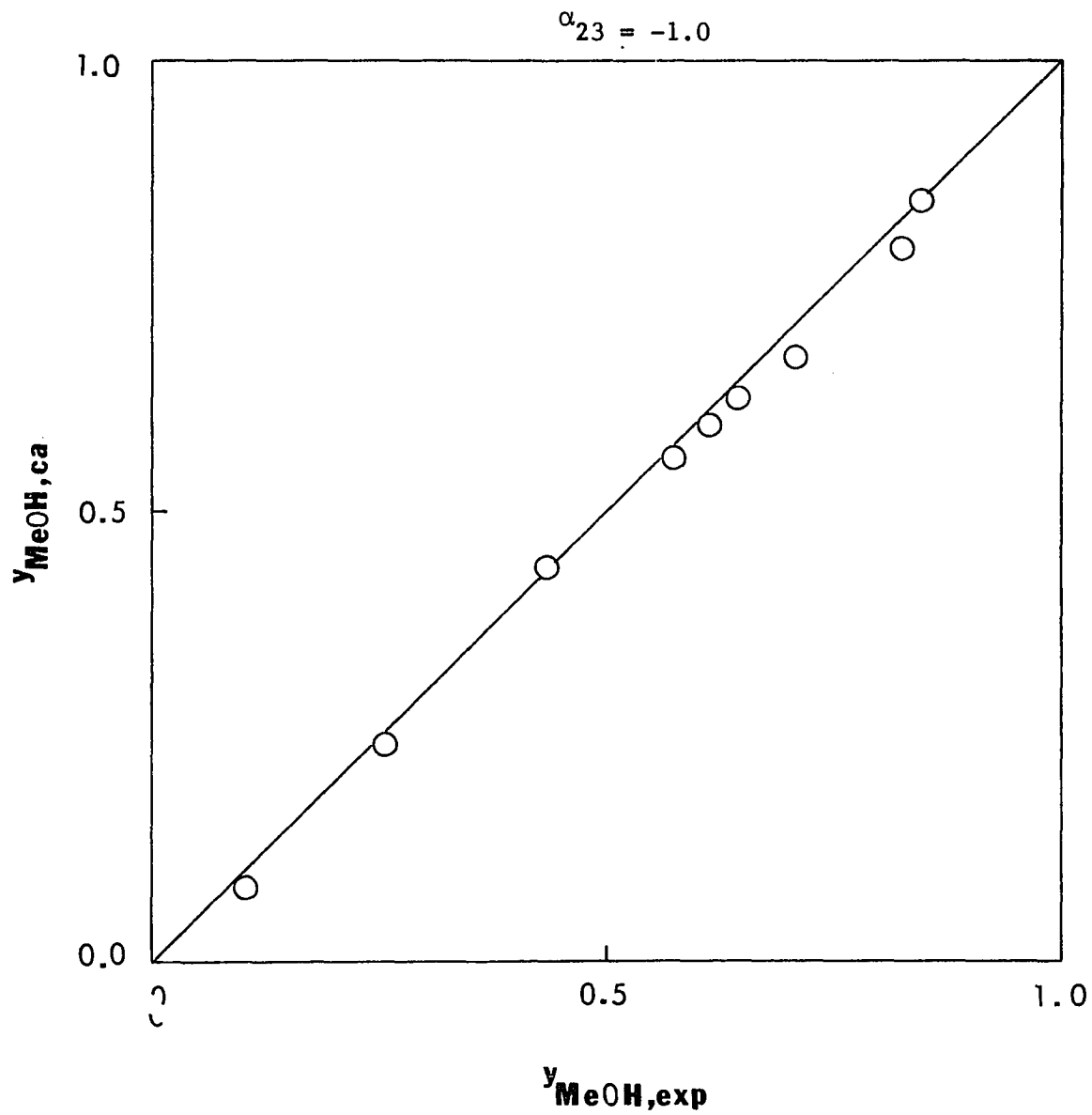


Figure H.21 Comparison of Experimental with Correlated Vapor-Phase Compositions Using Model II for the System $\text{LiCl-H}_2\text{O-MeOH}$ at 60°C

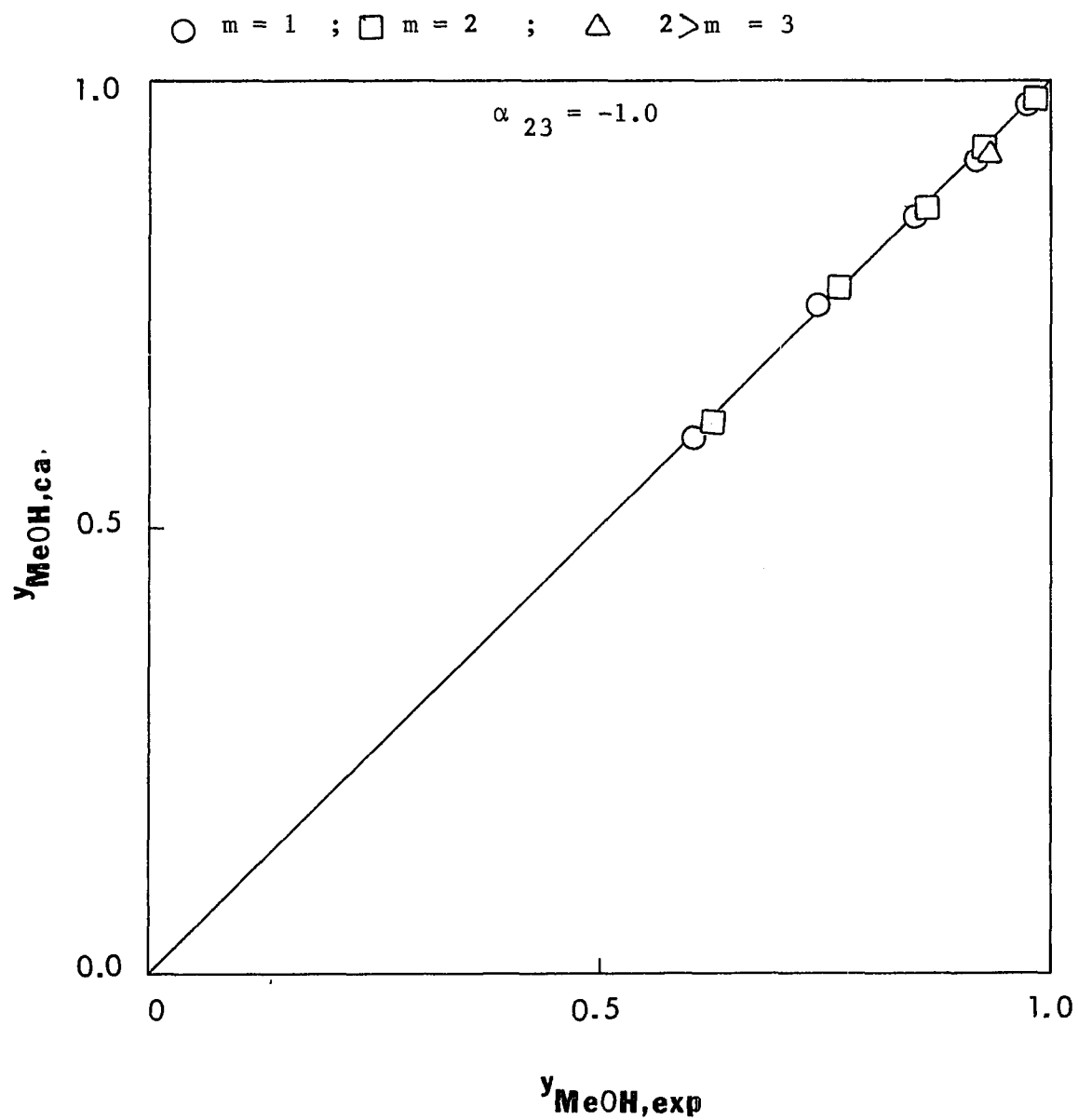


Figure H.22 Comparison of Experimental with Correlated Vapor-Phase Compositions Using Model II for the System NaBr-H₂O-MeOH at 25°C

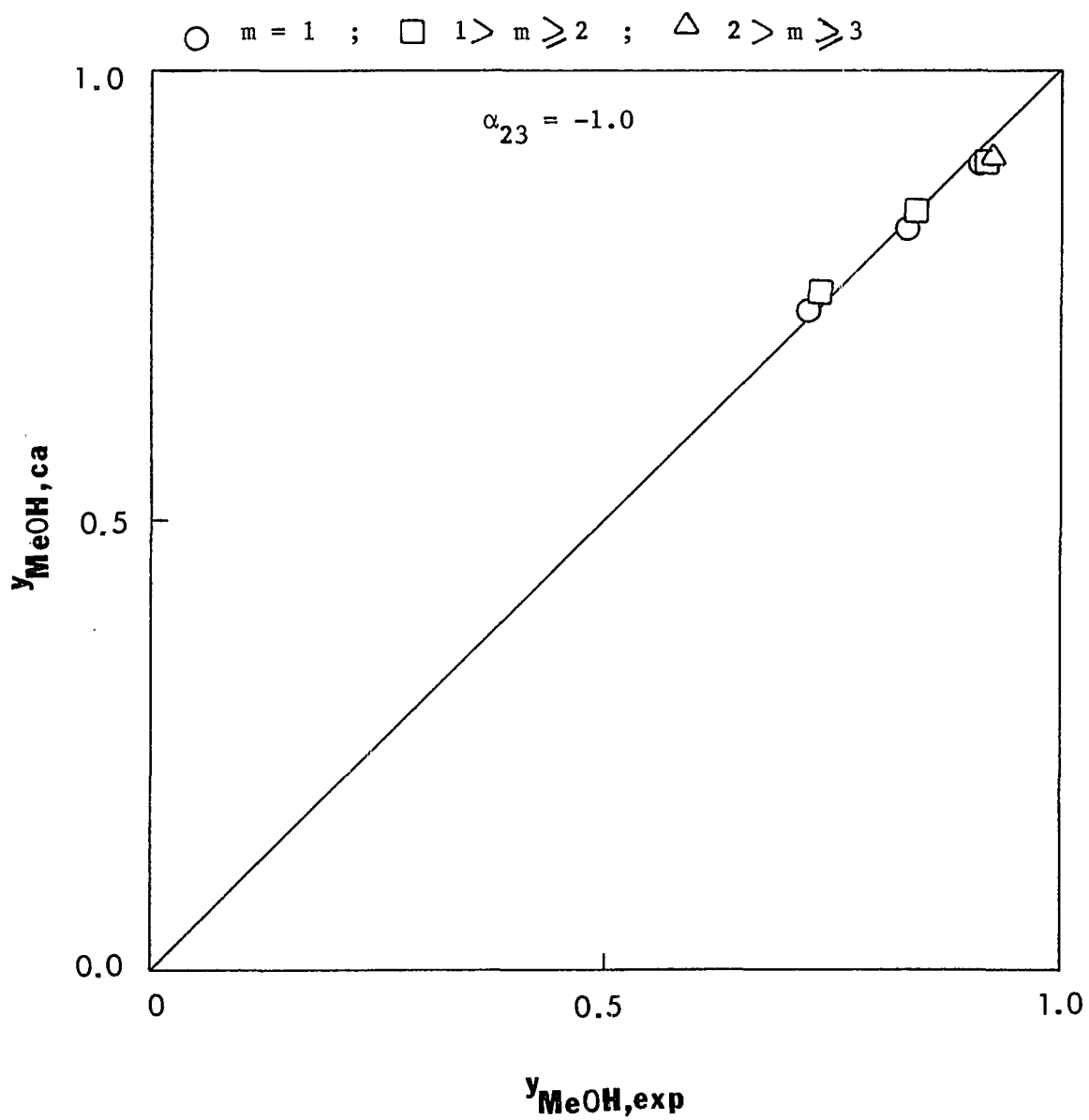


Figure H.23 Comparison of Experimental with Correlated Vapor-Phase Compositions Using Model II for the System NaBr-H₂O-MeOH at 40°C

NOMENCLATURE

\hat{a}_i	- activity of solvent i
A_γ	- Debye-Hückel constant, (Kg/g mole) ^{1/2} , Appendix-D
A	- a constant used in equation (D-11)
$A_1, A_2, A_3, A_4, A_5, A_6$	- constants defined in equation (D-5)
$a_1, a_2, a_3, a_4, a_5, a_6$	- constants defined in equation (D-9)
AD_1 and AD_2	- constants defined in equation (D-10)
a', b' and c'	- pure component liquid molar volume constants, equation (D-4)
a_1^1, b_1^1 and c_1^1	- constants used in equation (1-25)
B_{li}	- binary 1-2 or 1-3 parameter in the Bromley Equation
B_{ii}	- second virial coefficient of component i, cm ³ /g mole
B_{ij}	- cross second virial coefficient, cm ³ /g mole
B^*, B_1^1, B_2^1, B_3^1	- constants defined in equation (3-18)
B_{123}	- ternary adjustable parameter in the Bromley Equation
c	- molar concentration of the electrolyte, g mole/cm ³ equation (A-4)
$c_1, c_2, c_3, c_4, c_5, c_6$	- pure component vapor pressure constants, equation (1-24)
$c^*, c_1^{11}, c_2^{11}, c_3^{11}$	- constants defined in equation (3-19)
d	- density of the solvent/solvent mixture (electrolyte free), gm/cc
D	- dielectric constant of the solvent/solvent mixture (electrolyte free)
\hat{f}_i	- fugacity of the component i, in the mixture
F_i	- a factor used in equation (1-10)

- g^E - molar excess Gibbs free energy, cal/g mole
- G^E - total excess Gibbs free energy, cal
- G_{ij} - binary 2-3 adjustable parameter, in equation (2-4)
- Δg_{ij} - temperature independent parameter in equation (2-4), cal/g mole
- G_{Ai} and G_{Bi} - binary adjustable parameter, defined in equation (2-6)
- Δg_{Ai} and Δg_{Bi} - binary adjustable temperature independent parameters, defined in equation (2-6), K joules/g mole
- $G_{\pm i}$ - adjustable parameters for binary 1-2 or 1-3, in equation (2-5)
- H_1 - Henry's constant, mmHg-Kg solvent/g mole
- I - ionic strength = $\frac{1}{2} \sum_k m_k z_k^2$, g mole/kg of solvent
- k - Boltzman constant, 1.38054×10^{-23} J/K (molecules)
- NP - total # of points in a system
- N_T - total # of moles of the solvent or solvent mixture (electrolyte free)
- m - molality of an electrolyte, g mole/Kg of solvent
- M_w - molecular weight of the solvent/solvent mixture, gm/g mole
- P - total pressure of the system, mmHg
- P_i^O - vapor pressure of the pure component i , mmHg
- P.E. - poynting effect defined in equation (1-15)
- R - gas constant, 1.987 cal/g mole-°K
- R^1 - gas constant, 8.314×10^{-3} KJ/K-g mole
- T - temperature, °K

V	- molar volume, cc/g mole
X_m	- liquid-phase mole fraction of component m, defined in equations (1-22) and (1-23)
X_i'	- liquid-phase mole fraction of solvent i, electrolyte free
Y_m	- vapor-phase mole fraction of component m
X, Y	- defined in equation (3-15)
$Z_+ Z_-$	- valency of cation and anion, respectively
Z_{ij}	- binary 2-3 constant, defined in equation (2-4)
$Z_{\pm i}, Z_{Ai}$ and Z_{Bi}	- binary parameters defined in equations (2-5) and (2-6), K Joules/g mole

GREEK LETTERS

α_{23}	- a constant used in equation (2-4) (= -1.0 or 0.2, 0.3, 0.47)
α_{Ai}, α_{Bi}	- constants defined in equation (2-6)
γ_i	- activity coefficient of solvent i
γ_{\pm}	- mean molal activity coefficient
γ_{\pm}^*	- mean molar activity coefficient
$\hat{\phi}_i$	- fugacity coefficient of the solvent i, in the mixture
ϕ_i°	- fugacity coefficient of the pure component i
ϕ	- osmotic coefficient in a binary (1-2 or 1-3) mixture, as defined in equation (1-20)
$\sigma_1(\rho I^{1/2})$	- defined in equation (A-12)
$\psi_1(aI)$	- defined in equation (A-13)
$\sigma_1^1(\rho I^{1/2})$	- defined in equation (B-35)
$\psi_1^1(aI)$	- defined in equation (B-36)
$\sigma_2(\rho I^{1/2}), \psi_2(aI),$ $\sigma_2^1(\rho I^{1/2}) \text{ \& } \psi_2^1(aI)$	- defined in equations (C-24) to (C-27), respectively
ν_A, ν_B	- number of cations and anions, respectively
ν	- total number of ions (= $\nu_A + \nu_B$)
ϵ	- charge of an electron
δ_{123}	- salting out ternary parameter, in equation (3-5)
δ_{23}	- a constant in equation (E-7)
δ'	- defined in equation (3-6)
ω	- acentric factor

SUPERSCRIPTS

- o - pure component
- L - liquid-phase
- v - vapor-phase

SUBSCRIPTS

- 1,2,3 - electrolyte, solvent 2 and solvent 3, respectively
- A,B - cation and anion, respectively
- C - critical property
- Ca - calculated property
- E - experimental
- i,j - solvent 2 or 3
- k - cation or anion
- li - binary 1-2 or 1-3
- ij - solvent-solvent binary
- 123 - ternary 1-2-3
- l,m,n - ions or electrolyte or solvent 2 or 3

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