ABSTRACT

Vapor pressure depression data for $CaCl_2$, NaI, LiBr, and LiCl were measured at a molality ranging between 0.2-7.5 depending on the solubility of the salt in ethanol. Data were also measured at 35° C for the LiCl. The apparatus used was a recirculation still of the Othmer type.

Osmotic coefficients were calculated from the total pressure of the system. The one parameter Bromley equation and the three parameter Pitzer equation were used to correlate the data. For all the systems, the Pitzer equation correlated the data better as one would expect. Mean activity coefficients were calculated graphically and from the equation parameters obtained from the nonlinear regression of the experimental osmotic coefficient data. Since experimental data were only taken to a molality of about 0.2, extrapolation to infinite dilution was necessary. This graphical technique can lead to errors of about 25% in the mean activity coefficient.

In order to determine if there was a temperature dependency in the parameters of the two equations, the literature was searched for data at other temperatures. Some data was found for the $CaCl_2$ and NaI systems. Analysis of these data in conjunction with the data measured here indicate that: 1) the Bromley "B" parameter could be represented by a simple first order polynomial in temperature and 2) no functionallity could be found between the three parameters in the Pitzer equation and temperature. This is in agreement with the findings of another study for strong electrolytes in methanol.

OSMOTIC AND MEAN ACTIVITY COEFFICIENTS OF
$CaCl_2$, NaI, LiBr, AND LiCl IN ETHANOL AT 50° C

by
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APPENDIX E

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2) Zudkevitch, D., G.J. Czerwienski, and Y.Z. Wang, Thermodynamic Aspects of Enhanced Oil Revovery with Supercritical CO_2, 64th Annual GPA Convention, Houston, Texas, March 1985.

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CHAPTER I

INTRODUCTION

The influence of electrolytes on phase and chemical equilibria must be accounted for in order to properly design and operate many of the processes related to the chemical industry. Examples of some of the more familiar processes include; absorption and distillation, solvent extraction, ion-exchange, crystallization, and osmosis. Other applications arise in water treatment (boiler feed and waste water), electrochemical processes (electrolysis, electroplating, and corrosion), and metallurgy.

Historically, the solvent medium for most of these processes has been water. It is no small wonder then, that over the years, a preponderance of thermodynamic data for aqueous electrolyte systems has evolved. Extensive compilations of mean activity coefficients, osmotic coefficients, and vapor pressure depression data are readily available in todays literature (19,20,32,33,34,35,36). The National Bureau of Standards (NBS) has even made available a computerized data base capable of calculating the mean activity coefficients and osmotic coefficients of 350 binary aqueous electrolyte systems at 25° C (37).

Conversely, a comprehensive literature in nonaqueous electrolyte systems is virtually nonexistent (38,39), and data for electrolytes in mixed solvent systems is even more limited (40,41). This lack of information has often led to making simplifying assumptions about the interactions between the electrolyte and the nonaqueous solvent. The net result of these assumptions is usually the overdesign or underdesign of a particular piece of

process equipment.

In order to apply the principles of thermodynamics to multicomponent systems, some rational approach is necessary to overcome the need to measure the vast amount of data required in the design of complex chemical processes. Advances made over the past two decades in understanding the nature of the liquid phase of nonelectrolyte systems has significantly reduced the amount of experimental data needed to model multicomponent phase equilibria.

Several semi-empirical models (42,43,44) are available to determine activity coefficients in nonelectrolyte mixtures. The underlying principle behind these models, is that the interactions between all the molecules comprising the mixture need only be obtained from the constituent binary pairs. No higher order terms are needed. Two other models, which are based on the concept of "group contributions", are also available (45,46).

In principle, these methods can also be applied to electrolyte-nonaqueous solvent systems, provided there is sufficient binary data available to fit the necessary parameters. In practice, however, very little is known about the application of these methods to nonaqueous media (47,48,49, 50,51). These five references represent perhaps only a dozen or so binary systems, compared to the thousands tested for nonelectrolyte systems.

In the early 70's, Pitzer (24) and Bromley (26) presented semi-empirical equations which were capable of representing the behavior of elec-

trolytes in aqueous solutions to fairly high concentrations, about 6m. Both models have been used to generate specific parameters for an electrolyte in aqueous solution. Also, the models contain additional parameters which appear to be specific for the type of solvent. The present values of these parameters were obtained by fitting many aqueous electrolyte systems.

The purpose of this study, is to expand the data base of electrolytes in nonaqueous solvents and to test the capabilities of these two equations to model systems of this nature. Osmotic and mean activity coefficients were measured for $CaCl_2$, LiCl, LiBr, and NaI in ethanol at 50° C using a recirculation still of the Othmer type. These systems present a logical extension of the work of Bixon et al. (52) and Tomasula (53) who studied similar systems in methanol.

CHAPTER II

Theory

A. Chemical Potential

The chemical potential is a quantity which was first introduced by

Gibbs (1). The advantage of using the Gibbs chemical potential is that

it gives one a concise way of stating the condition for chemical equilib-

rium in PVT systems of uniform temperature (T) and pressure (P) :

$$\mu_i^{I} = \mu_i^{II} = \,,\, = \mu_i^{M} \qquad (i = 1,2,\,,\,N) \qquad (1)$$

Equation 1 provides a general criterion for equilibrium with respect to

mass transfer and requires that the chemical potential of each of the N

components be uniform throughout the M phases.

B. Ideal Systems

Consider the simple case in which the chemical potentials of the N

components could all be written in the following form:

$$\mu_i = \mu_i^{\varnothing} + RT\ln x_i \qquad (2)$$

where $\mu_i^{\varnothing}$ is a function of only T and P (2). In other words, the chemical

potential of i, in its standard state. Systems for which μ_i has the above

form, posses very simple properties. Examples of such systems are: mix-

tures of perfect gases and very dilute solutions. As a group, such sys-

tems are known as **ideal** systems.

It can be seen from the above definition, that a system is ideal if

4

the chemical potential of component i varies linearly with the logarithm
of the mole fraction of i, with slope RT. In most cases, this linearity
does not exist over the entire concentration range, so that $\mu_i^\emptyset$ is, in
general, the value of μ_i extended to $x_i = 1$.

A mixture may be considered ideal when all but one of the components
is present in very small amounts. Systems such as these are called **ideal
dilute** systems. Hence, if the component present in excess (solvent) is
denoted by 1, then

$$\mu_i^\emptyset = \mu_i^o \tag{3a}$$

for all other components

$$\mu_i^\emptyset \neq \mu_i^o \tag{3b}$$

where μ_i^o is the chemical potential of component i in the standard state.

C. Mean Activity Coefficient

The reason for bringing up the concept of an ideal dilute solution as
defined above, is because in the early days, the existence of ions in
solution and interactions between these ions was not as self evident as
it is today. Early workers tended to treat electrolytic solutions as
though they were ideal dilute solutions of non-electrolytes. No inter-
actions were considered between solute particles or between the solute
and solvent.

If one were to consider that the solute (electrolyte) is actually
made up of ν_i particles, equation 2 could be rewritten in the following

form:

$$v_i \mu_i = v_i \mu_i^o + v_i RT \ln m_i \qquad (4)$$

where v_i is the number of particles (ions) comprising the electrolyte

and m_i the molality (moles solute/kg solvent) of i in the solution. Also,

μ_i^o is the chemical potential of i in the standard state defined by

$$\mu_i = \mu_i^o \qquad \text{when } m_i = 0 \qquad (5)$$

The application of equations 4 and 5 to electrolyte systems does not

predict the effect of what are known as long range ion-ion interactions

on the chemical potential. These Coulombic effects are present in most

dilute solutions and arise from the interactions between the positively

and negatively charged ions.

In order to more effectively utilize equation 4, Lewis (3) intro-

duced the concept of "effective concentration" :

$$\mu_i = \mu_i^o + RT \ln \gamma_i x_i \qquad (6)$$

or

$$\mu_i = \mu_i^o + RT \ln a_i \qquad (7)$$

This effective concentration is called the **activity**, a_i, of species i and

is defined as:

$$a_i = \gamma_i x_i \qquad (8)$$

where γ_i is known as the **activity coefficient**.

In applying equations 6, 7, and 8 to an electrolyte solution, one can

write:

$$a_i = \gamma_i m_i \tag{9}$$

$$\upsilon_i \mu_i(\text{real}) - \upsilon_i \overset{o}{\mu}_i = \upsilon_i RT \ln a_i \tag{10}$$

and

$$\upsilon_i \mu_i(\text{real}) - \upsilon_i \overset{o}{\mu}_i = \upsilon_i RT \ln \gamma_i m_i \tag{11}$$

where γ_i is now a single ion activity coefficient which accounts for the chemical potential change when a charged species i is added to a solvent.

To illustrate that the single ion activity coefficient is a measure of the deviation in the chemical potential of an ideal noninteracting solute due to the presence of an ionic species, one may subtract equation 4 from 11 to obtain

$$\upsilon_i \mu_i(\text{real}) - \upsilon_i \mu_i(\text{ideal}) = \upsilon_i RT \ln \gamma_i m_i \tag{12}$$

Since individual ions cannot be added to a solution separately, it is impossible to experimentally determine the contribution each positively and negatively charged particle makes to the chemical potential. It is, however, possible to measure the overall change in chemical potential of the electrolyte due to the effect of both ions. This link between the activity coefficient of the electrolyte in solution and the individual ions is known as the mean activity coefficient of the electrolyte.

In order to better understand the concept of mean activity coefficient, equation 10 can be written for individual ions:

$$v_+\mu_+(\text{real}) - v_+\mu_+^o = v_+\ln RT\ln a_+ \tag{13}$$

and

$$v_-\mu_-(\text{real}) - v_-\mu_-^o = v_-\ln RT\ln a_- \tag{14}$$

The equations for the individual activities can be written:

$$a_+ = \gamma_+ m_+ \tag{15}$$

and

$$a_- = \gamma_- m_- \tag{16}$$

Equations for the chemical potentials of the positive and negative ions can now be written by substitution of equations 15 and 16 into 13 and 14 respectively.

$$v_+\mu_+(\text{real}) - v_+\mu_+^o = v_+ RT\ln\gamma_+ m_+ \tag{17}$$

and

$$v_-\mu_-(\text{real}) - v_-\mu_-^o = v_- RT\ln\gamma_- m_- \tag{18}$$

Addition of equations 17 and 18 and division by $v = v_+ v_-$ where v is the total number of ions per mole of salt yields the following:

$$\mu_2(\text{real}) - \mu_2^o = RT\ln(\gamma_+\gamma_-)^{1/v} + RT\ln(m_+ m_-)^{1/v} \tag{19}$$

or

$$\mu_2(\text{real}) - \mu_2^O = RT\ln(\gamma_\pm) + RT\ln(m_\pm) \tag{20}$$

where

$$\mu_2(\text{real}) = \frac{\upsilon_+\mu_+ + \upsilon_-\mu_-}{\upsilon} \tag{21}$$

$$\mu_2^O = \frac{\upsilon_+\mu_+^O + \upsilon_-\mu_-^O}{\upsilon} \tag{22}$$

$$m_\pm = (\, m_+^{\upsilon_+} \; m_-^{\upsilon_-})^{1/\upsilon} \tag{23}$$

$$\gamma_\pm = (\, \gamma_+^{\upsilon_+} \; \gamma_-^{\upsilon_-})^{1/\upsilon} \tag{24}$$

where μ_2, μ_2^O, $m_\pm$, and $\gamma_\pm$ are the chemical potential of, the electrolyte, the standard state, the mean molality, and the mean activity coefficient.

To further illustrate that the mean activity coefficient is a direct measure of ion-ion interactions in solution, equation 4 is written for each species

$$\upsilon_+\mu_+(\text{ideal}) - \upsilon_+\mu_+^O = \upsilon_+RT\ln m_+ \tag{25}$$

$$\upsilon_-\mu_-(\text{ideal}) - \upsilon_-\mu_-^O = \upsilon_-RT\ln m_- \tag{26}$$

Addition of equations 25 and 26 and division by υ followed by application of equations 23 and 24 yields:

$$\mu_2(\text{ideal}) - \mu_2^o = RT\ln m_{\pm} \tag{27}$$

where

$$\mu_2(\text{ideal}) = \frac{\upsilon_+\mu_+ + \upsilon_-\mu_-}{\upsilon} \ (\text{ideal}) \tag{28}$$

Subtracting equation 28 from 20 gives

$$\mu_2(\text{real}) - \mu_2(\text{ideal}) = RT\ln\gamma_{\pm} \tag{29}$$

D. Gibbs-Duhem Equation

Once the mean activity coefficient of the electrolyte has been deter-
mined, one would like to be able to obtain the activity or osmotic coeffi-
cient of the solvent. Classical solution thermodynamics provides us with
an appropriate technique, namely, the **Gibbs-Duhem** equation.

Thermodynamics tells us that for an open heterogeneous system, the
internal energy change for a binary mixture may be written as follows:

$$dU = TdS - PdV + \mu_1 dn_1 + \mu_2 dn_2 \tag{30}$$

Equation 30 is the fundemental property equation relating the primary
thermodynamic variables in a single-phase PVT system, either open or
closed. The convention here being 1 refers to the solvent and 2 the
solute or in this case the electrolyte. Integration of the above equa-
tion from a state of zero mass to some final state at constant concentra-
tion yields:

$$U = TS - VP + \mu_1 n_1 + \mu_2 n_2 \tag{31}$$

Differentiation of this expression gives

$$dU = SdT + T\,dS - VdP - PdV + \mu_1 dn_1 + n_1 d\mu_1 + \mu_2 dn_2 + n_2 d\mu_2 \tag{32}$$

Subtraction of equation 30 from 32 yields

$$0 = SdT - VdP + n_1 d\mu_1 + n_2 d\mu_2 \tag{33}$$

This expression is one of the more common forms of the Gibbs-Duhem equation. At constant temperature and pressure equation 33 becomes

$$n_1 d\mu_1 + n_2 d\mu_2 = 0 \tag{34}$$

solving for $d\mu_1$

$$d\mu_1 = - \frac{n_2 d\mu_2}{n_1} \tag{35}$$

If one were now to differentiate equation 20 for μ_2

$$d\mu_2 = RT(d\ln\gamma_\pm + d\ln m_\pm)^{1/\upsilon} \tag{36}$$

Substituting back into equation 35 produces the following:

$$d\mu_1 = -\frac{n_2}{n_1} RT(d\ln\gamma_\pm + d\ln m_\pm)^{1/\upsilon} \tag{37}$$

Rearranging the terms yields

$$d\mu_1 = -\frac{n_2}{n_1} RT(d\ln\gamma_{\pm}m_{\pm})^{1/\upsilon} \qquad (38)$$

The ratio of the moles of the electrolyte to moles of solvent may also be written as

$$\frac{n_2}{n_1} = \frac{mM1}{1000} \qquad (39)$$

where M_1 is the molecular weight of the solvent. Substituting into equation 38 yields

$$d\mu_1 = \frac{mM_1 RT}{1000} d\ln(\gamma_{\pm}m_{\pm})^{1/\upsilon} \qquad (40)$$

This equation, derived from the Gibbs-Duhem equation, relates the chemical potential of the solvent to the mean activity coefficient and mean molality of the electrolyte. To complete the derivation, one would like to have the chemical potential of the solvent, μ_1, in more manageable quantities. Writing equation 10 in terms of the activity of the solvent we have

$$\mu_1(\text{real}) - \mu_1^o = RT\ln a \qquad (41)$$

By differentiating the above expression and substituting into equation 40 one gets

$$d\ln a_1 = \frac{\upsilon m M_1}{1000} d\ln\gamma_{\pm}m_{\pm} \qquad (42)$$

and since

$$m_{\pm} = (v_+^{v_+} + v_-^{v_-})\ ^{1/v}m$$

(43)

Equation 42 becomes after differentiation of equation 43

$$d\ln a_1 = \frac{vmM_1}{1000}\ d\ln \gamma_{\pm} m_{\pm}$$

(44)

Normally, the activity of the solvent will not deviate very much from unity. In order to better illustrate the deviation of the solvent from ideality, Bjerrum (4) introduced the function, ϕ_p, the practical osmotic coefficient. He defined ϕ_p in the following manner

$$\bar{G} - \bar{G}^O = -\phi_p RT\Sigma\ m_i/1000 = RT\ln a_1$$

(45)

or

$$\bar{G} - \bar{G}^O = -\phi_m RT vmM_1/1000 = RT\ln a_1$$

(46)

where $\bar{G}_1$ and $\bar{G}^O$ are the partial molal Gibbs energy of the solvent in solution and the standard molal Gibbs energy of the solvent, respectively. For single electrolytes dissociating into v ions per molecule

$$\Sigma m_i = vm$$

(47)

and ϕ_p becomes ϕ_m and from equation 46, it follows that

$$\phi_m = \frac{-1000}{vmM_1}\ \ln a_1$$

(48)

where ϕ_m is the molal osmotic coefficient. Hereafter, the subscript m

will be dropped. Differentiating equation 48 and substituting into 44 yields

$$-mdln(\gamma_{\pm}m) = -d(\phi m) \tag{49}$$

Carrying out the above differentiation gives an expression for the mean activity coefficient in terms of the osmotic coefficient.

$$ln\gamma_{\pm} = \phi-1 + (\phi-1)dlnm \tag{50}$$

This expression allows one to determine $\gamma_{\pm}$ values from experimentally determined values of the osmotic coefficient.

E. Debye-Huckel Theory

Central to the description of electrolytic solutions is the Debye-Huckel Limiting Law (5). Their formulation is both a simple yet powerful model in the description for the time-average distribution of ions in very dilute solutions of electrolytes. From this distribution, they were able to get the electrostatic potential contributed by the surrounding ions to the total electrostatic potential at the reference ion and, therefore, the chemical potential change arising from ion-ion inter-actions.

The assumptions which make up this model will be stated briefly. First, is the selection of an arbitrary ion out of the entire assembly and it is called a reference or central ion. Only this central ion is given the distinction of having a descrete charge. The remaining ions in

solution are laped into a continuous spatial distribution of charge. Thus, the electrolytic solution is considered to consist of a central ion standing alone in a continuum. Second, the electrolyte is completely dissociated and the ions interact only through Coulombic forces. Next, the solvent medium is assumed to be of constant dielectric. Finally, they decided that the average electrostatic potential, ψ_r, would be so small that a linearized form of the Boltzmann equation could be used.

The results of these assumptions give the following expression for the mean activity coefficient of an electrolyte

$$\log\gamma_{\pm} = -A_{\gamma}Z_{+}Z_{-}I^{\frac{1}{2}} \tag{51}$$

here Z_{+} and Z_{-} are the charges of the positive and negative ions respectively. The ionic strength, I, is defined by the following expression

$$I = 0.5\Sigma m_{i}Z_{i}^{2} \tag{52}$$

and is a measure of the total number of charges in solution. A_{γ} is a proportionality constant and is a function of temperature only.

$$A_{\gamma} = \frac{1.824829238\times10^{6}d^{\frac{1}{2}}}{(T\epsilon)^{1.5}} \tag{53}$$

where ϵ is the dielctric constant of the solvent and d the pure solvent density.

The Debye-Huckel limiting law agrees well with experimental results only at an ionic strength up to almost 0.002 molar (6). Examination of experimental plots of mean activity coefficients vs. molality indicate

that the activity coefficient goes through a minimum and then increases

with increasing electrolyte concentration. Experiments also show that $\gamma_{\pm}$

is also a function of the type of electrolyte as well a temperature.

At higher concentrations of electrolyte, the ions can no longer

be considered point charges, since the relative sizes of the ionic cloud

and ion shrinks with increasing concentration.

When the size, a_i, of ions is taken into account, the Debye-Huckel

equation becomes

$$\log \gamma_{\pm} = \frac{-A_{\gamma} Z_+ Z_- I^{1/2}}{1 + B_{\gamma} a_i I^{1/2}} \tag{54}$$

where

$$B_{\gamma} = \frac{50.29158649 \times 10^6 d^{1/2}}{(T\epsilon)^{1.5}} \tag{55}$$

Here, the symbols have the same meaning as in A_{γ}.

The introduction of the ion size parameter increases the range of

validity of the Debye-Huckel equation up to an ionic strength of about

0.1m for 1-1 electrolytes. This also makes the activity coeficient

specific for each electrolyte as "a" is different for each salt.

The values of a are determined experimentally. Upper and lower

bounds may be imposed on a in the following manner. As a minimum, the

sum of the crystallographic radii of the cation and anion comprising

the electrolyte may be taken. An upper boundary that can be assumed,

is the sum of the hydrated radii of the cation and anion of the electro-

lyte in aqueous solution. In aqueous solution, it is assumed that the

solvation shells about the ions are crushed when ions collide (7).

Since this is a distance which would be difficult to measure, the para-

meter a is best regarded as a mean distance of closest approach having

an upper and lower bound as previously described.

F. Modifications of the Debye-Huckel Model

In a publication for the NBS, Hamer (8) describes several different

equations based on the theory of interionic attraction which have been

used to calculate the activity coefficients of electrolytes in water from

the freezing point to the boiling point of water. The ionic stengths

ranged from zero to 0.1 molal for various different types of electrolytes.

The following is a brief description of some of these models.

Guntelberg (9) suggested a simpler form for equation 54

$$\log\gamma_{\pm} = \frac{-A_{\gamma} Z_{+} Z_{-} I^{\frac{1}{2}}}{1+I^{\frac{1}{2}}} \tag{56}$$

This is equivalent to assigning a value of approximately 3Å as calculated

by equation 56 to the ion size at all temperatures. A modified or extended

Guntelberg equation would be

$$\log\gamma_{\pm} = \frac{-A_\gamma Z_+ Z_- I^{\frac{1}{2}}}{1+3B_\gamma I^{\frac{1}{2}}} \qquad (57)$$

where the denominator is now temperature dependent since B_γ is a function of temperature. A better representation is obtained if a linear term in ionic strength is added to the right hand side of equations 56 and 57. Guggenheim (10) proposed the following

$$\log\gamma_{\pm} = \frac{-A_\gamma Z_+ Z_- I^{\frac{1}{2}}}{1+I^{\frac{1}{2}}} + bI \qquad (58)$$

where b is an adjustable parameter.

Scatchard (11) suggested that a better average fit is obtained if $(1+1.5I^{\frac{1}{2}})$ is used in the denominator of the first term on the right hand side for expressions for $\log\gamma_{\pm}$.

$$\log\gamma_{\pm} = \frac{-A_\gamma Z_+ Z_- I^{\frac{1}{2}}}{1+1.5I^{\frac{1}{2}}} + \text{terms} \qquad (59)$$

A modified or extended Scatchard equation results if the denominator in the above equation is made temperature dependent.

$$\log\gamma_{\pm} = \frac{-A_\gamma Z_+ Z_- I^{\frac{1}{2}}}{1+4.5B\gamma I^{\frac{1}{2}}} \qquad (60)$$

Bjerrum (12) has shown that ion pairs (associated ions with charges of unlike sign) occur if the diameter of the ion is less than

$$a_B = \frac{Z_+ Z_- e^2}{2\epsilon kT} \qquad (61)$$

The Bjerrum equation is thus

$$\log\gamma_{\pm} = \frac{-A_\gamma Z_+ Z_- I^{\frac{1}{2}}}{1+B_\gamma a_B I^{\frac{1}{2}}} \qquad (62)$$

Several review articles on how to extend the range of the Debye-Huckel model beyond 0.1 molal have appeared in the literature over the past fifteen years (6,13,14). Some of the more theoretical approaches to the extention of the Debye-Huckel model come from the application of modern statistical thermodynamics (15,16,17,18).

Traditional Debye-Huckel theory of electrolyte solutions (19,20) recognizes the distance of closest approach *a* in the calculation of the electrostatic energy of the distribution of ions but ignores the kinetic effect of the hard core on the osmotic pressure and other properties.

Rasaiah and Friedman (15) and Hill (18) have shown that there are several equations which relate the intermolecular potential and the radial distribution function to thermodynamic properties. Provided each distribution function is exact, each equation will give the same results. However, difficulties arise from approximation to the distribution function. A convinient equation for the hard-core potential is the "pressure" equation which yields the pressure of a pure fluid or the osmotic pressure of a solution.

$$\Pi - ckT = -\frac{1}{6}\sum_{ij} c_i c_j \int_0^\infty (\partial u_{ij}/\partial r)g_{ij}4\pi r^3 dr \tag{63}$$

Where Π is the osmotic pressure, c_i and c_j are concentrations of i and j c is the total solute concentration Σc_i, u_{ij} is the intermolecular potential, and g_{ij} is the radial distribution function.

When the following potential is introduced

$$u_{ij} = \infty \ , \ r<a \tag{64}$$

$$u_{ij} = z_i z_j e^2/Dr, \ r\geq a \tag{65}$$

and inserted into equation 63 one obtains

$$\Pi - ckT = (e^2/6D)\sum_{ij}\sum c_i c_j z_i z_j \int_0^\infty g_{ij}(r)4\pi r dr +$$

$$\tag{66}$$

$$\frac{2}{3}(\pi a^3 kT)\sum_{ij}\sum c_i c_j g_{ij}(a)$$

In this expression, the term involving $g(a)$ constitutes the kinetic effect of the hard core and the integral represents the second virial coefficient accounting for the deviations form the ideal solution due to short and long range interactions among the ions and the ions and the solvent. It should be noted here that the same hard core size a has been assumed for all species of ions, however different charges z_i and z_j have been assumed in accordance with Debye Huckel theory.

Values of the osmotic coefficient at different concentrations for

1-1 electrolytes may be calculated if expressions for the radial distribution function, $g_{ij}(r)$, and interionic potential, $u_{ij}(r)$, are available.

An expression for the interionic potential is

$$u_{ij}(r) = u^*_{ij}(r) + \frac{z_+ z_- e^2}{\epsilon r} \tag{67}$$

According to the "primitive" model, (when forces between the particles are described using a "hard core" and an "electrostatic" contribution, in electrolyte theory such a model is usually called primitive) the direct potential u_{ij} between ions i and j of charges $z_i e$ and $z_j e$ separated by a distance r_{ij} is given by

$$u_{ij} = z_i z_j e^2 / \epsilon r_{ij} \qquad (r_{ij} \geq a),$$
$$u_{ij} = \infty \qquad (r_{ij} < a) \tag{68}$$

and by using Monte Carlo techniques, Card and Valleau (17) obtained values of the osmotic coefficient for several electrolytes in aqueous solution at 25° C that agreed with experimental results up to 2m.

A promising "non-primitive" model is that of Planche and Renon (22). Their model takes into account interactions between all kinds of species present in the liquid mixture, i.e. both ionic and molecular ones. Besides a hard core and an electrostatic contribution to the potential energy, short-range interactions are included. The dielctric constant of the solvent is corrected for the presence of ions. With a statistical thermodynamic approximation, the radial distribution function is derived and the internal energy as well as the Helmholtz free energy are calculated. The

model requires seven parameters to describe the properties of the pure solvent, one size parameter for each ionic compound and one energy parameter. Results have been published for the osomotic pressure of nine halide solutions and the agreement with experiment is good up to an ionic strength of 6m.

G. Semiempirical Models

Pitzer, in a series of articles (23,24,25) proposed the following model for the osmotic coefficient of an electrolyte in aqueous solution

$$\phi - 1 = |z_+ z_-| f^\phi + m(\frac{2\upsilon_+ \upsilon_-}{\upsilon}) B^\phi + m^2 2(\frac{\upsilon_+ \upsilon_-}{\upsilon})^{1.5} C^\phi \tag{69}$$

where

$$f^\phi = \frac{-A_\phi I^{\frac{1}{2}}}{1 + b I^{\frac{1}{2}}} \qquad \text{and} \qquad B^\phi = \beta^0 + \beta^1 e^{-\alpha I^{\frac{1}{2}}}$$

Using equation 69, he was able to obtain values for the parameters β^0, β^1, and C^ϕ for 1-1 and 1-2, and electrolytes with one or both ions univalent. The data are fit within experimental error up to an ionic strenght of 6m.

Using appropriate thermodynamic transformations, equation 69 may be converted into an expression for the mean activity coefficient.

$$\ln\gamma_\pm = |z_+ z_-| f^\gamma + m(\frac{2\upsilon_+ \upsilon_-}{\upsilon}) B^\gamma + m^2 2(\frac{\upsilon_+ \upsilon_-}{\upsilon})^{1.5} C^\phi \tag{70}$$

where

$$f^\gamma = -A_\phi \left[\frac{I^{\frac{1}{2}}}{1+bI^{\frac{1}{2}}} + \frac{2}{b}\ln(1+bI^{\frac{1}{2}}) \right]$$

$$B^\gamma = 2\beta^0 + \frac{2\beta^1}{\alpha^2 I}\left[1 - e^{-\alpha I^{\frac{1}{2}}}(1+\alpha I^{\frac{1}{2}} - 0.5\alpha^2 I) \right]$$

$$C^\gamma = \frac{3}{2}C^\phi$$

The parameters b and α were fixed at values of 1.2 and 2 respectively.

Another expression which came out around the same time as that of Pitzer, is due to Bromley (26). This expression is an extension of the Guggenheim model, equation 58, for the mean activity coefficient. The interesting point of this expression is that it contains only one adjustable parameter and is capable of correlating experimental data up quite a high molality. The form of this extension is as follows

$$\log\gamma_\pm = \frac{-A_\gamma |z_+ z_-| I^{\frac{1}{2}}}{1+\rho I^{\frac{1}{2}}} + \frac{(B_0 - B)}{(1+aI)^n} + BI + CI^2 \tag{71}$$

where n=2 and $\rho=1$. He found that a, which is not the ion size parameter described earlier, is close to one but tends to decrease with increasing valency. The value of a may be represented as follows

$$a = \frac{1.5}{|z_+ z_-|} \tag{72}$$

From the regression of many sets of osmotic coefficient and mean activity

coefficient data, Bromley found that the values of B_0 and B scatter badly. However, at 25° C, a relationship between B_0, B and $|z_+z_-|$ was found which fit the data well. This relationship takes on the following form

$$\frac{B_0 - B}{|z_+z_-|} = 0.06 + 0.6B \tag{73}$$

Except for extremely high concentrations, the value of C may be taken to be zero. The final expression for the mean activity coefficient may be found by substituting equations 72 and 73 into equation 71.

$$\log\gamma_\pm = \frac{-A_\gamma z_+z_- I^{\frac{1}{2}}}{1+\rho I^{\frac{1}{2}}} + \frac{(0.06 + 0.6B)z_+z_- I}{1+(1.5/z_+z_-)I^2} + BI \tag{74}$$

In the above equation, the first term on the right hand side is the Debye-Huckel term which accounts for long range forces between ions. The second term represents a transition between the Debye-Huckel region and the linear portion of a plot of $\gamma_\pm$ vs. ionic strength at the higher concentrations.

Again using appropriate thermodynamic transformations, an expression for the osmotic coefficient may be obtained

$$1-\phi = 2.303Ag|z+z-|\frac{I^{\frac{1}{2}}}{3}\sigma(\rho I^{\frac{1}{2}})-2.303(0.06+0.6B)z_+z_- - \frac{I}{2}\psi(aI) -$$

$$2.303B\frac{I}{2} \tag{75}$$

where

$$\sigma(\rho I^{\frac{1}{2}}) = \frac{3}{(\rho I^{\frac{1}{2}})^3} \ [1+\rho I^{\frac{1}{2}} - \frac{1}{1+\rho I^{\frac{1}{2}}} - 2\ln(1+\rho I^{\frac{1}{2}})] \tag{76}$$

and

$$\psi(aI) = \frac{2}{aI} \ [\ \frac{1+2aI}{(1+aI)^2} - \frac{\ln(1+aI)}{aI} \ ] \tag{77}$$

Using equations 71 and 77, Bromley obtained values for the adjustable

parameter B for numerous sets of aqueous electrolyte systems at 25° C.

There are several other models (27,28,29,30) based on the "local

composition" concept which have been developed recently, and like the

models of Pitzer and Bromley can be extended up to a concentration of

6M. However, as shown by Ball et al. (29), these models show no real im-

provement in predictive power over the Pitzer equation. In fact, they

are just slightly worse. One last model should be mentioned, and that

is due to Ball et al. (31), and it is obtained from the solution of the

mean spherical approximation given by Planche and Renon (22) for a non-

primitive model of interactions. It has been tested for 80 aqueous sys-

tems at 25° C up to a molality of 6 and contains 3 parametrs. Its strong

background in statistical mechanics may make this model worth looking

into in the future.

CHAPTER III

EXPERIMENTAL

A. Materials

1)   The sodium iodide used was Matheson reagent grade and had a minimum assay of 99%.

2)   The calcium chloride used was 'Baker Analyzed' reagent grade and was assayed at 98.4%.

3)   The lithium chloride and lithium bromide were Matheson reagent grade and had a minimum assay of 99%.

4)   The silver nitrate was Matheson reagent A.C.S.. The label stated that the maximum impurities and specifications conform to the A.C.S. listing.

5)   The indicator used in the Mohr titrations was a standard one molar potassium chromate solution.

6)   The ethanol used was anhydrous, denatured, GOLD LABEL and was purchased from SGA, Bloomfield, NJ.

The reagents in items 1-3 were used without further purification and each was dried in an oven at 120° C for at least two days before use.

B. Vapor-Liquid Equilibrium Measurement Techniques

Before the details of the apparatus used in this study are presented, a brief description of the techniques available for measuring vapor pressures will be given.

Vapor-liquid equilibrium measurement techniques fall into two basic categories; static methods and dynamic methods. Each type has many variations and the details of these are thoroughly discussed in Hala (54). Each method has certain advantages and disadvantages, and some of these will be discussed below.

In the static method, one of the main advantages is rapid equilibration of the vapor and liquid phases. The still itself is simply a container into which a charge is placed and allowed to come to equilibrium, at the desired temperature and pressure. The liquid is continuously stirred to ensure intimate contact between the two phases. Generally, in order to maintain its simplicity, no provision is made for sampling the vapor phase. Herein, lies one of the main disadvantages of the static method. Since the vapor phase is not measured, very precise determinations of the liquid composition must be made. Another, is the thorough degassing needed for the liquid charge. If dissolved gasses are not removed, significant deviations in the pressure measurement may occur, particularly if the total pressure is low.

In the dynamic method, the stills fall into two groups: 1) stills with circulation of the vapor phase and 2) stills with circulation of the

vapor and liquid phase.

In stills which circulate only the vapor phase, such as the Othmer still used in this study, the pressure is maintained such that the solution boils at the desired temperature. As the vapor is evolved, it is initially richer in the more volatile component. The vapor is condensed and collected in a reservoir whose volume is between five and ten cm^3. As the condensate overflows the reservoir, it is returned to the boiling liquid. It should be noted, that the time it takes the reservoir to fill is usually measured. After three or four residence times, the condensate and the boiling liquid are normally in equilibrium. This step is quite time consuming. However, if one of the components in a binary mixture is nonvolatile, as is the case with strong electrolytes, the evolved vapor is always pure solvent, and the problem now becomes one of stabilizing the system temperature and pressure. Another problem which can arise is the correct measurement of the temperature at a given pressure. If only one thermometer is used, accurate determination of the temperature becomes very difficult, as the temperature in the two phases can be different. This matter will be discussed in more detail in a later section.

In stills in which both the vapor and liquid are circulated, a Cottrell pump is introduced into the lower portion of the still in order to "shoot" a mixture of vapor and liquid onto the thermometer. This method tends to alleviate the problem of where to place the thermometer so that accurate temperature and pressure readings can be made. However, the improved accuracy has a price. Stills of this nature are usually hand blown

pieces of glassware which are quite delicate and also expensive. The
operations of these stills is also very complicated.

Overall, each method has its advantages and disadvantages. The static
method is easy to use and rapid measurements can be made. Auxiliary equip-
ment, such as volumetric pumps and balances for measuring the liquid
charge and refrigeration for degassing carry a high cost. The dynamic
method in which only the vapor is circulated is inexpensive, but the mea-
surements can be inaccurate. Finally, when both the vapor and liquid are
circulated, accurate measurements can be made, but the equipment is both
fragile and expensive.

C. Apparatus

The equipment setup used in this study is very similar to the one
used by Bixon (55), and can be seen in Figure 1. Before the equipment was
used however, it was completely disassembled and rebuilt.

All the gaskets and seals on the vacuum pumps were replaced and addi-
tional traps were placed between the two sides of the manometer. The
traps served as additional protection against the pump oil being contam-
inated by mercury or any solvent vapors.

The condenser consists of two eighteen inch glass condensers connect-
ed in series. The coolant is a mixture of acetone and ethylene glycol and
the temperature is maintained at about -35° C. Dry ice is used to main-
tain the coolant temperature. It is important to keep the integrity of
the seal between the two condensers as it is a potential source of vacuum

leak.

The heat exchanger consists of a coil of copper tubing immersed in the dry ice bath. The original coil was replaced by one of a slightly larger inside diameter to better maintain the flow of coolant to the condenser. An Oberdorfer Gear Pump is used to pump coolant from a separate reservoir through the tubing, the condenser, and back to the reservoir. This is done to prevent any pumping difficulties which may arise from the evolution of carbon dioxide gas in the bath itself.

A Precision Micro-Set Manostat is the heart of the pressure control system. Under ideal conditions, it is capable of maintaining a vacuum of 3.0 ± 0.1 mmHg. The Manostat operates on the principle of bleeding air into the system to control vacuum. The system is allowed to attain a vacuum slightly higher than desired. This causes a solenoid valve to open intermittently bleeding a small amount of air into the system. Needle valves allow the amount of air to be regulated until the desired pressure is achieved. A twenty-five liter surge tank provides a buffer for pressure fluctuations inherent in the Manostat operation.

A cathetometer is used to measure the pressure difference read on a standard mercury manometer and a McLeod gage is used to measure vacuum.

D. Procedure

The charge to the still was prepared by adding a predetermined amount of salt to approximately 300 ml of ethanol. It was not necessary to know

the exact amount of electrolyte at this time since the solution would be analyzed at the completion of a run.

The solution was then poured into the boiling chamber of the still. Once the charge was in the place, the heat exchanger was loaded with dry ice, the coolant pump turned on, and one side of the manometer was evacuated. When the temperature of the coolant reached about -35° C, the system vacuum pump was started, and the system slowly evacuated. The rate of evacuation was controlled by a separate bleed valve in the system. This rate was extremely important. If the system was evacuated to rapidly, the solution would flash and cause unwanted mixing of the electrolyte with the pure solvent in the condensate reservoir. This was not a serious problem, but one which was time consuming, since the reservoir would have to taken off, cleaned, and replaced. However, if the evacuation was done slowly enough the system would eventually come under the influence of the Manostat. Patience, at this stage of the procedure, was definitely a virtue that paid off in time saved.

Once the system was under the control of the Manostat, the heaters, used to control the temperature of the mixture, were turned on and the system allowed to reflux for about and hour. This was usually enough time for the temperature and pressure of the system to stabilize. At this time, pressure readings were taken at ten minute intervals until four or more readings agreed to within ±0.2 mmHg. The system pressure was then taken as the average of these readings.

At this point, air was let into the system and all the pumps and mo-

tors were shut off. A sample was immediately taken so that the density could be measured. The concentration of the salt was then determined using a Mohr titration. This is an extremely sensitive technique for the detection of halides in solution. This concentration, used in conjunction with the density, allows one to convert from molarity to the molality of the solution.

E. Vapor Pressure Measurements

As was mentioned earlier, when using a still which only recirculates the vapor, a problem could arise as to where to place the thermometer so that the pressure which is measured actually corresponds to the temperature being measured. According to the Gibbs phase rule, a pure liquid in equilibrium with its vapor, has but one degree of freedom. In other words, at a given temperature, the liquid will only boil at "one" pressure. It will be shown, that the simple task of boiling a pure liquid is not as simple as it appears.

A glance at Figure 2 will show that a single thermometer could actually be placed anywhere in the vapor space or in the liquid itself. The question which had to be answered was "where"? To answer this question, the still was modified so that another thermometer could be used. The liquid charging port was fit with taperd joints so that it could be used to measure the temperature of the vapor, and the other thermometer was then used to measure the temperature in or around the boiling liquid.

To start with, the two thermometers were calibrated against NBS

standards at several different temperatures and certified to be ±0.01° C.
The technique followed was the same as mentioned in the procedure sec-
tion, but only pure solvent was used. Once the system had reached equilib-
rium, the following steps were taken: First, the liquid phase thermo-
meter was located such that it was entirely in the vapor space. After a
time, the temperature was read to be 50.65° C and the pressure 228.95
mmHg. The Manostat was then adjusted so the temperature would read
50.0° C exactly. Upon equilibration, the pressure was 223.23 mmHg. The
next step was to immerse the thermometer completely in the liquid. Again,
after a time, the temperature leveled out and was read to be 50.25° C.
Readjustment of the Manostat to obtain a temperature of 50.0° C, pro-
duced a pressure reading of 216.68 mmHg. This procedure of moving the
thermometer around and readjusting the Manostat was repeated several
more times. The optimum location for the liquid phase thermometer was
found to be in a space where the bulb was about 0.125 inches above the
the liquid surface, when the surface was calm. When the solution was
boiling, the liquid would gently splash on the thermometer's bulb, the
temperature would read 50.0° C and the pressure would read 220.8±0.06
mmHg (this action of the liquid gently splashing on the thermometer
bulb is known as "incipient boiling", and if one were to note, the vapor
would be condensing at a rate of about ten to twelve drops per minute).
This value compares favorably with the literature of 220.97 mmHg
as reported by Kretschmer and Wiebe (57).

When the thermometer is properly placed, the difference between the

readings on the two should never be more than 0.1° C. Thermodynamically speaking, the two temperatures should be equal. Realistically speaking, the two will never be equal, no matter how well you try to insulate the still or control temperature or pressure. The best that one can hope for is to minimize the difference between the two.

F. Treatment of Experimental Results

The quantity measured for each data point is the vapor pressure depression (ΔP), the difference between the pure solvent vapor pressure and the total pressure over the solution.

$$\Delta P = P^S - \pi \tag{78}$$

where P^S is the vapor pressure of the pure solvent and π is the total pressure over the solvent-salt solution. The activity, a_1, and hence the activity coefficient, γ_1, of the solvent can be calculated in the following manner:

$$a_1 = \Delta P / P^S \tag{79}$$

and

$$\gamma_1 = a_1 / x_1 \tag{80}$$

where x_1 is the mole fraction of the solvent.

The osmotic coefficient, ϕ is then calculated by combination of equations 79 and 48

$$\phi = \frac{-1000 \ln a_1}{\upsilon m M_1} \tag{81}$$

Once the osmotic coefficient is know over a range of molalities, the mean activity coefficient of the salt may be obtained by utilizing the method described by Randall and White (56). The following equation is obtained by rearrangement of the logarithmic term in equation (50).

$$\ln \gamma_{\pm} = \phi - 1 - 2 \int_0^m (1-\phi)/m^{\frac{1}{2}} \, dm^{\frac{1}{2}} \tag{82}$$

Then by plotting $1-\phi/m^{\frac{1}{2}}$ vs $m^{\frac{1}{2}}$ and evaluating the area under the resulting curve, a value of $\gamma_{\pm}$ may be obtained at any point. This is the classical technique for obtaining mean activity coefficients for experimental osmocoefficient data. The major drawback to this method is that the molality must be extrapolated back to zero in order to obtain the area. If data is not available at sufficiently low molalities (eg. less than 0.1m), the exact shape of the curve in this region is very difficult to determine. Both Tomasula (53) and Bixon (55) have discussed these problems. It was therefore decided to calculate the mean activity coefficients following the approach used by Goldberg et al. (37) and Rard et al. (58). In this technique, the osmotic coefficient data is fit to an equation of the following form

$$\phi = 1 - (1/3) A_{\gamma} |z_+ z_-| I^{\frac{1}{2}} + \Sigma \, A_i m^{r_i} \tag{83}$$

In this equation, the powers r_i start at 1 and increase in increments of

0.25 and the A_i are constants which are found by fitting the experimental data. The above equation is equivalent to the Debye-Huckel limiting law with a power series added. In order to obtain the mean activity coefficients, the Gibbs-Duhem equation is applied to equation (83) above with the following result

$$\ln\gamma_{\pm} = -A_{\gamma}m^2 + \Sigma A_i \left(\frac{r_i+1}{r_i}\right) m^{r_i} \tag{84}$$

To check an the validity of this approach, the osmotic coefficient data for $CaCl_2$ in ethanol at 50° C were graphically integrated to obtain $\gamma_{\pm}$. These values were than compared to the values calculated by equation 84. The comparison is shown in Appendix A.

FIGURE 1

37

EXPERIMENTAL SET-UP

HEAT EXCHANGER

CONDENSER

BLEED VALVE

MCLEOD GAGE

OTHMER STILL

FIGURE 2   OTHMER STILL

to condenser

CHARGING PORT

CONDENSATE
RESERVOIR

CONDENSATE
RETURN LINE

LIQUID SAMPLING
PORT
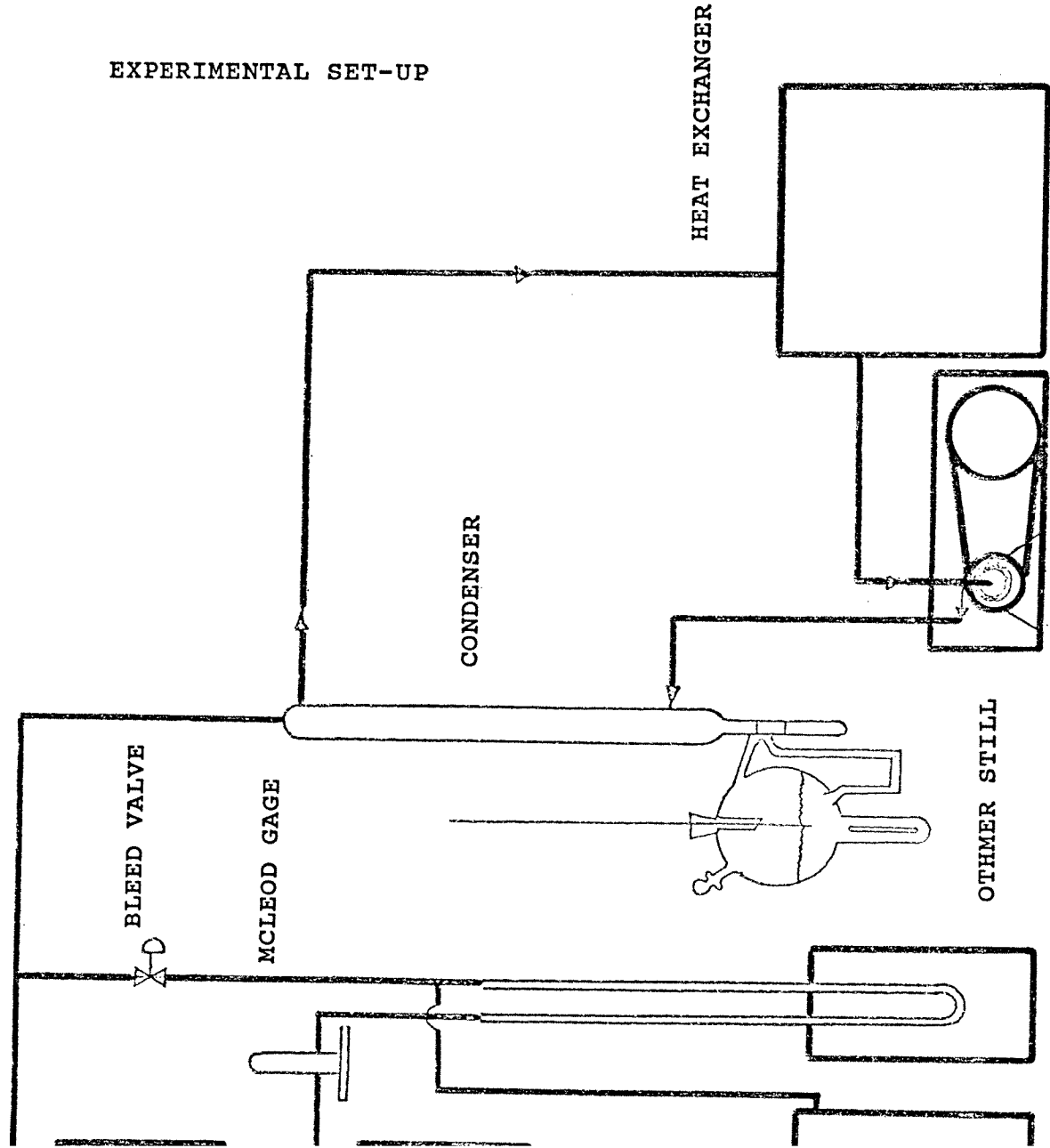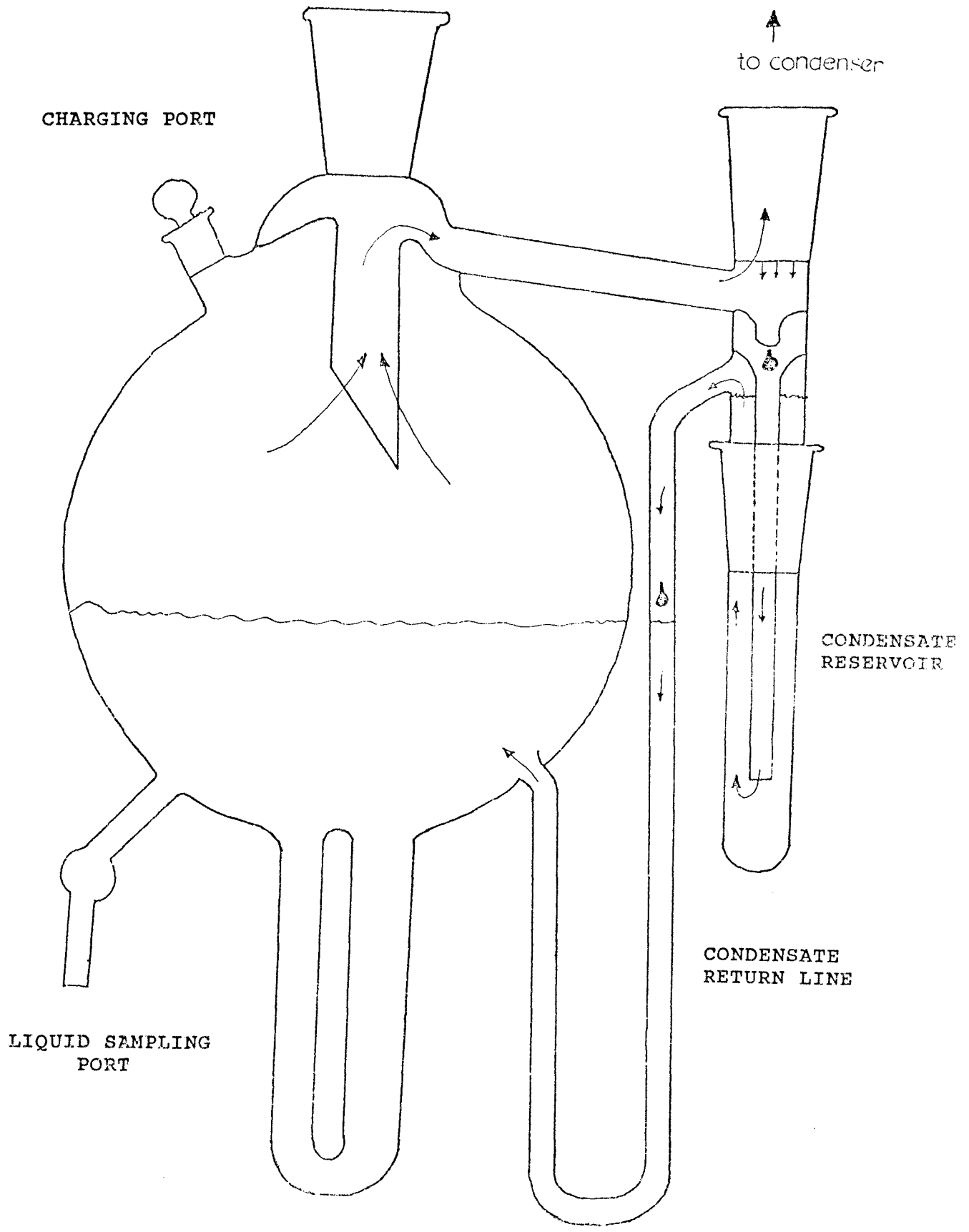
CHAPTER IV

RESULTS

A. Experimental Results

It has already been established that the experimental apparatus is capable of reproducing the vapor pressures of a pure solvent, and Table I shows the results of these measurements at two temperatures for the various batches of ethanol used. In order to determine if the equipment would operate properly for the electrolyte solutions, the literature was searched to find a system comparable to the ones which would be measured. Hayward and Perman (59) report vapor pressure data for $CaCl_2$ in ethanol at several different temperatures including the temperature of interest in this study, 50° C. Figure 3 shows a comparison of the vapor pressure depression data (ΔP) if Hayward and Perman and this study. Agreement be-tween the two is very good.

The vapor pressure depressions of NaI, LiCl, and LiBr in ethanol were then measured at 50° C. The LiCl system was also measured at 35° C. The concentration of the salt ranged form about 0.3 to 7.5 m depending on the solubility of the particular salt. The results of these measurements are presented in Figures 4-7 as plots of ΔP vs molality. It can be seen, that in general, the vapor pressure depression increases with increasing electrolyte concentration and that lowering the temperature decreased ΔP at the same molality.

The activity coefficient of the solvent, γ_1, was calculated for the

TABLE I   Vapor Pressure Data (mmHg) of Pure Ethanol
Experimental and Literature Values

	Experimental		Literature	
t, C	P,mmHg			
35.0	103.0		103.06	(57)
50.0	220.3		220.97	(57)
50.0	220.9			
50.0	221.4			
50.0	220.9			

Average
at 50.0   220.8

Figure 3
Vapor Pressure Depression vs Molality:
CaCl2 — EtOH at 50 deg C
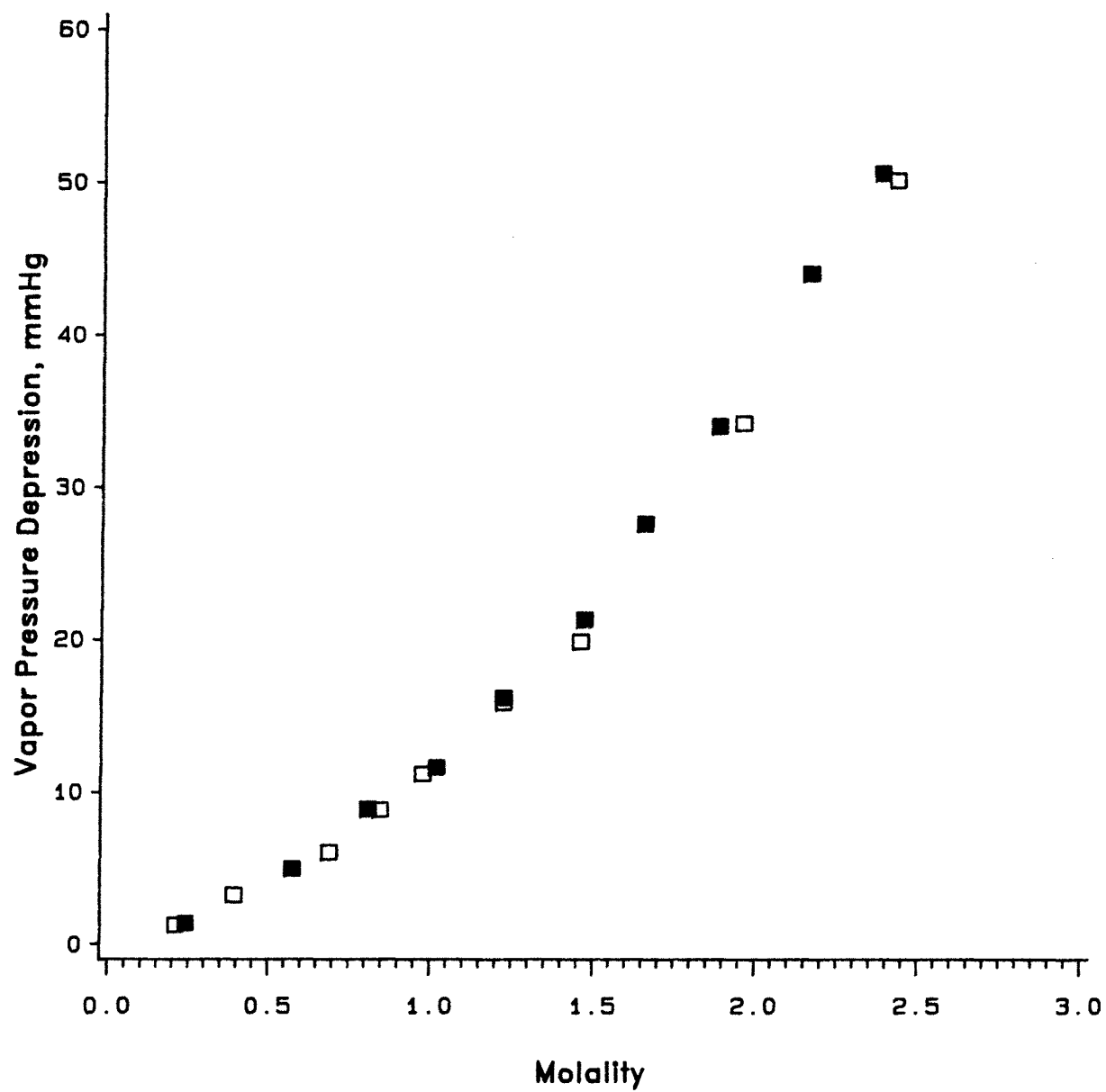
Figure 4
Vapor Pressure Depression vs Molality:
NaI — EtOH at 50 deg C
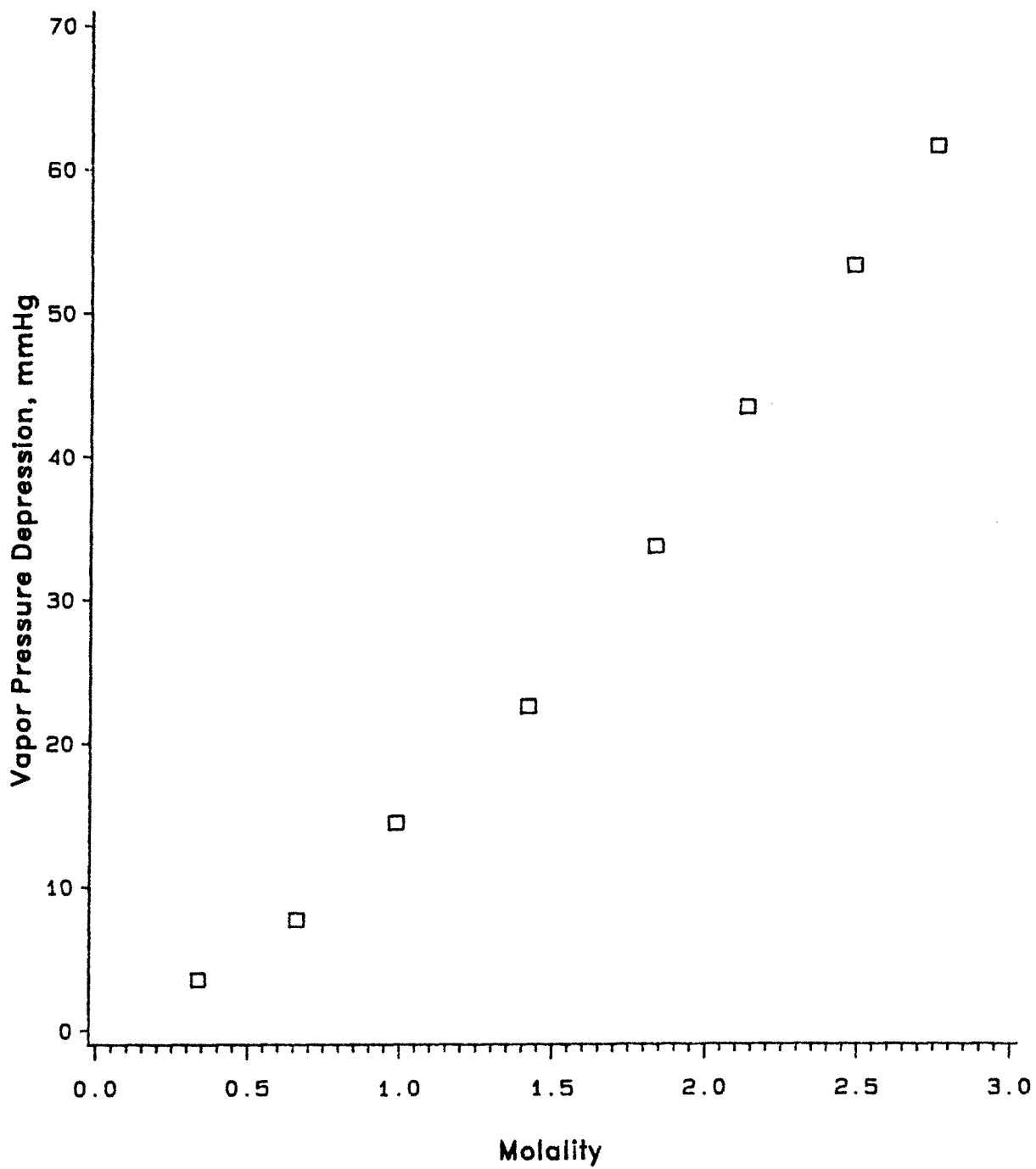
Figure 5
Vapor Pressure Depression vs Molality:
LiCl — EtOH at 50 deg C
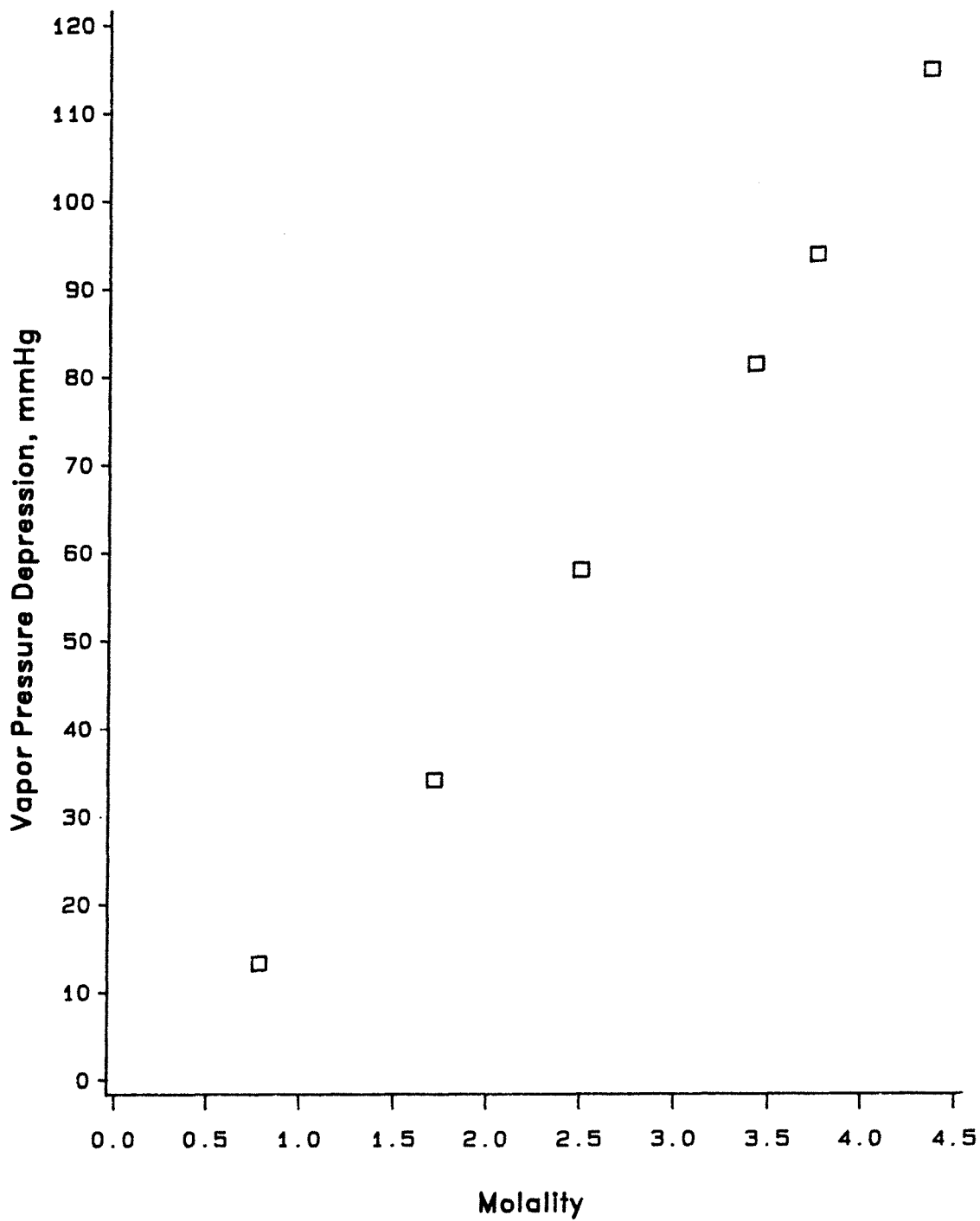
Figure 6
Vapor Pressure Depression vs Molality:
LiCl — EtOH at 35 deg C
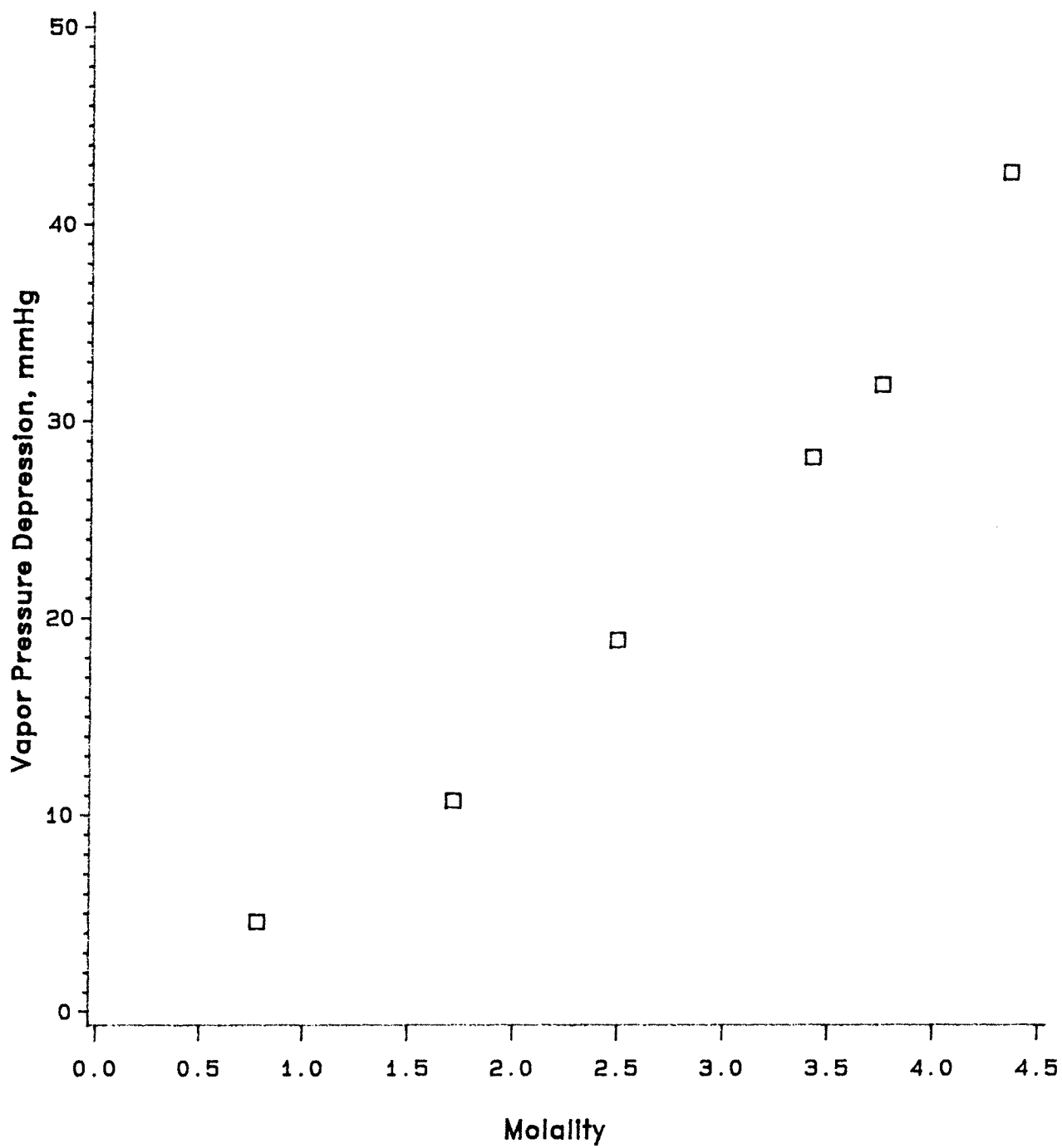
Figure 7
Vapor Pressure Depression vs Molality:
LiBr — EtOH at 50 deg C
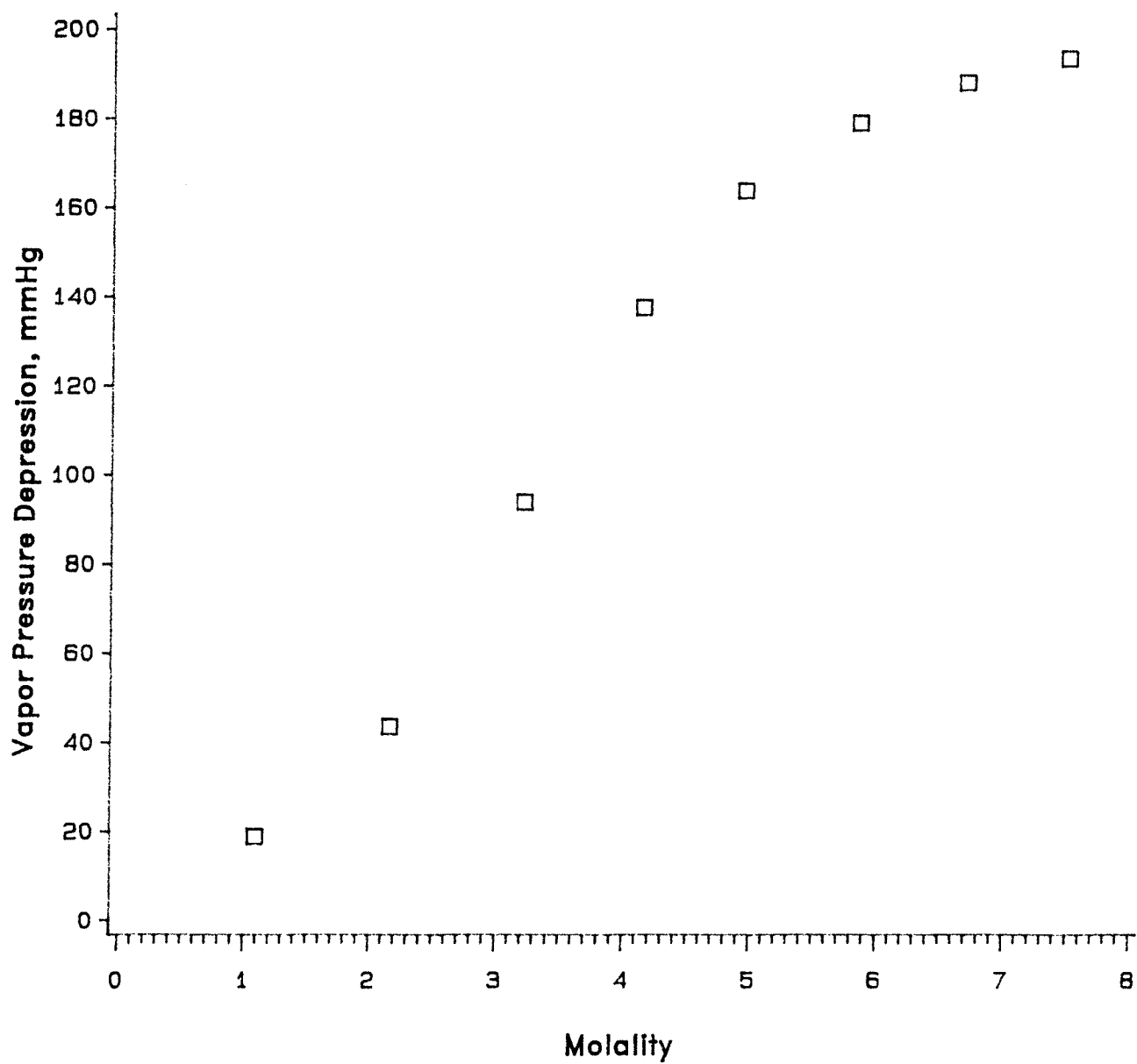
various systems through the use of equations 79 and 80. These results are presented in Tables II-VII. In general, as the molality or mole fraction of the salt increases, the activity coefficient of the solvent increases, goes through a maximum, and then decreases. For the LiCl system, decreas- the temperature, had the effect of increasing the activity coefficient at the same concentration.

The osmotic coefficient was then calculated using equation 48. These results are again shown in Tables II-VII. The general trend is for the osmotic coefficient to increase as the salt concentration increases. The effect of temperature is to lower the osmotic coefficient at the same concentration.

As mentioned earlier, rather then using equation 82 to determine the mean activity coefficient of the electrolyte, a different approach would be tried. In this technique (37,58), the osmotic coefficient vs concen- tration data were fit to an expression of the form shown by equation 83. In order to test this method, the experimental $CaCl_2$ data was fit using this equation and mean activity coefficients were determined using equa- tion 84. The same data were also used to calculate the mean activity coefficients using equation 82. A comparison of the two methods is shown in Figure 21 in Appendix A. The parameters used in equations 83 and 84 are also given in this Appendix. It can be seen that the agreement be- tween the two methods is excellent. The use of equations 83 and 84 also alleviate one of the major problems associated with the graphical inte- gration and that is, how to extrapolate data which is not close to zero

TABLE II   Experimental Values of Vapor Pressure, Solvent
Activity Coefficient, and Osmotic Coefficient
for CaCl2 - EtOH at 50° C

molality moles per kg solvent ±0.0001	P^S mmHg ±0.1	γ_{solv}	ϕ	ΔP mmHg ±0.1
0.0000	220.33	0.0000	1.0000	0.000
0.2097	219.05	1.0230	0.2010	1.280
0.3937	217.08	1.0389	0.2731	3.250
0.6901	214.27	1.0653	0.2924	6.060
0.8468	211.48	1.0722	0.3502	8.848
1.0183	208.71	1.0806	0.3850	11.620
1.2248	204.46	1.0851	0.4416	15.870
1.4583	200.46	1.0932	0.4689	19.870
1.9569	186.13	1.0733	0.6237	34.200
2.4270	170.19	1.0315	0.7698	50.141

TABLE III Literature Values of Vapor Pressure, Solvent
Activity Coefficient, and Osmotic Coefficient
for CaCl2 - EtOH at 50° C

molality moles per kg solvent ±0.0001	P^S mmHg ±0.1	γ_{solv}	ϕ	ΔP mmHg ±0.1
0.0000	221.60	0.0000	1.0000	0.000
0.2415	220.20	1.0268	0.1899	1.400
0.5759	216.60	1.0552	0.2867	5.000
0.8104	212.70	1.0673	0.3660	8.900
0.9776	210.40	1.0777	0.3838	11.200
1.2235	205.40	1.0836	0.4489	16.200
1.4704	200.30	1.0876	0.4973	21.300
1.6551	194.00	1.0757	0.5815	27.599
1.8831	187.60	1.0669	0.6400	34.000
2.1615	177.60	1.0409	0.7409	44.000
2.3795	171.00	1.0254	0.7882	50.599

TABLE IV   Experimental Values of Vapor Pressure, Solvent
Activity Coefficient, and Osmotic Coefficient
for NaI - EtOH at 50° C

molality moles per kg solvent ±0.0001	P^S mmHg ±0.1	γ_{solv}	ϕ	ΔP mmHg ±0.1
0.0000	221.48	0.0000	1.0000	0.000
0.3367	217.93	1.0145	0.5208	3.550
0.6603	213.77	1.0239	0.5824	7.710
0.9881	207.01	1.0198	0.7421	14.470
1.4196	198.91	1.0156	0.8217	22.570
1.8329	187.77	0.9910	0.9777	33.710
2.1313	178.08	0.9619	1.1106	43.400
2.4837	168.24	0.9335	1.2014	53.240
2.7552	159.93	0.9054	1.2826	61.549

TABLE V Experimental Values of Vapor Pressure, Solvent
Activity Coefficient, and Osmotic Coefficient
for LiCl - EtOH at 50° C

molality moles per kg solvent ±0.0001	P^S mmHg ±0.1	γ_{solv}	ϕ	ΔP mmHg ±0.1
0.0000	220.92	0.0000	1.0000	0.000
0.7840	207.63	1.0077	0.8589	13.290
1.7156	186.78	0.9791	1.0620	34.141
2.4965	162.90	0.9070	1.3245	58.021
3.4194	139.46	0.8302	1.4601	81.461
3.7506	126.98	0.7734	1.6024	93.941
4.3572	105.96	0.6722	1.8301	114.962

TABLE VI   Experimental Values of Vapor Pressure, Solvent
            Activity Coefficient, and Osmotic Coefficient
            for LiCl - EtOH at 35° C

molality moles per kg solvent ±0.0001	P^S mmHg ±0.1	γ_{solv}	ϕ	ΔP mmHg ±0.1
0.0000	102.98	0.0000	1.0000	0.000
0.7840	98.41	1.0247	0.6284	4.570
1.7156	92.26	1.0376	0.6952	10.717
2.4965	84.12	1.0048	0.8793	18.858
3.4194	74.84	0.9557	1.0131	28.140
3.7506	71.17	0.9299	1.0692	31.812
4.3572	60.40	0.8220	1.3289	42.577

TABLE VII   Experimental Values of Vapor Pressure, Solvent
Activity Coefficient, and Osmotic Coefficient
for LiBr - EtOH at 50° C

molality moles per kg solvent ±0.0001	P^S mmHg ±0.1	γ_{solv}	ϕ	ΔP mmHg ±0.1
0.0000	220.92	0.0000	1.0000	0.000
1.0950	202.06	1.0069	0.8845	18.860
2.1652	177.37	0.9630	1.1006	43.550
3.2221	127.04	0.7458	1.8637	93.881
4.1475	83.42	0.5219	2.5485	137.502
4.9489	57.19	0.3769	2.9637	163.732
5.8547	41.96	0.2924	3.0792	178.962
6.6974	32.99	0.2415	3.0815	187.933
7.4944	27.56	0.2109	3.0142	193.363

molality. One other advantage of using equation 83 is that it helps smooth the experimental osmotic coefficient data in a logical manner since the Debye-Huckel limiting las is built into the equation. Plots of smoothed osmotic coefficient data are shown in Figures VIII-XII.

Tables VIII-XII show the experimental mean activity coefficients cal-culated by equation 84 for the systems studied. Unfortunately, there does not appear to be any mean activity coefficient data reported for these systems in the literature. However, Tables VIIIa and VIIIb show the mean activity coefficients as determined by equation 84, for the data of Hayward and Perman and the $CaCl_2$ data from this study. It can be seen that the values are indeed fairly close. The general trend for the mean activity coefficients is to decrease and the begin to increase with in-creasing concentration. These trends are similar to those observed in aqueous electrolyte systems.

Figure 8a
Literature and Smoothed Osmotic Coefficients:
CaCl2 — EtOH at 50 deg C
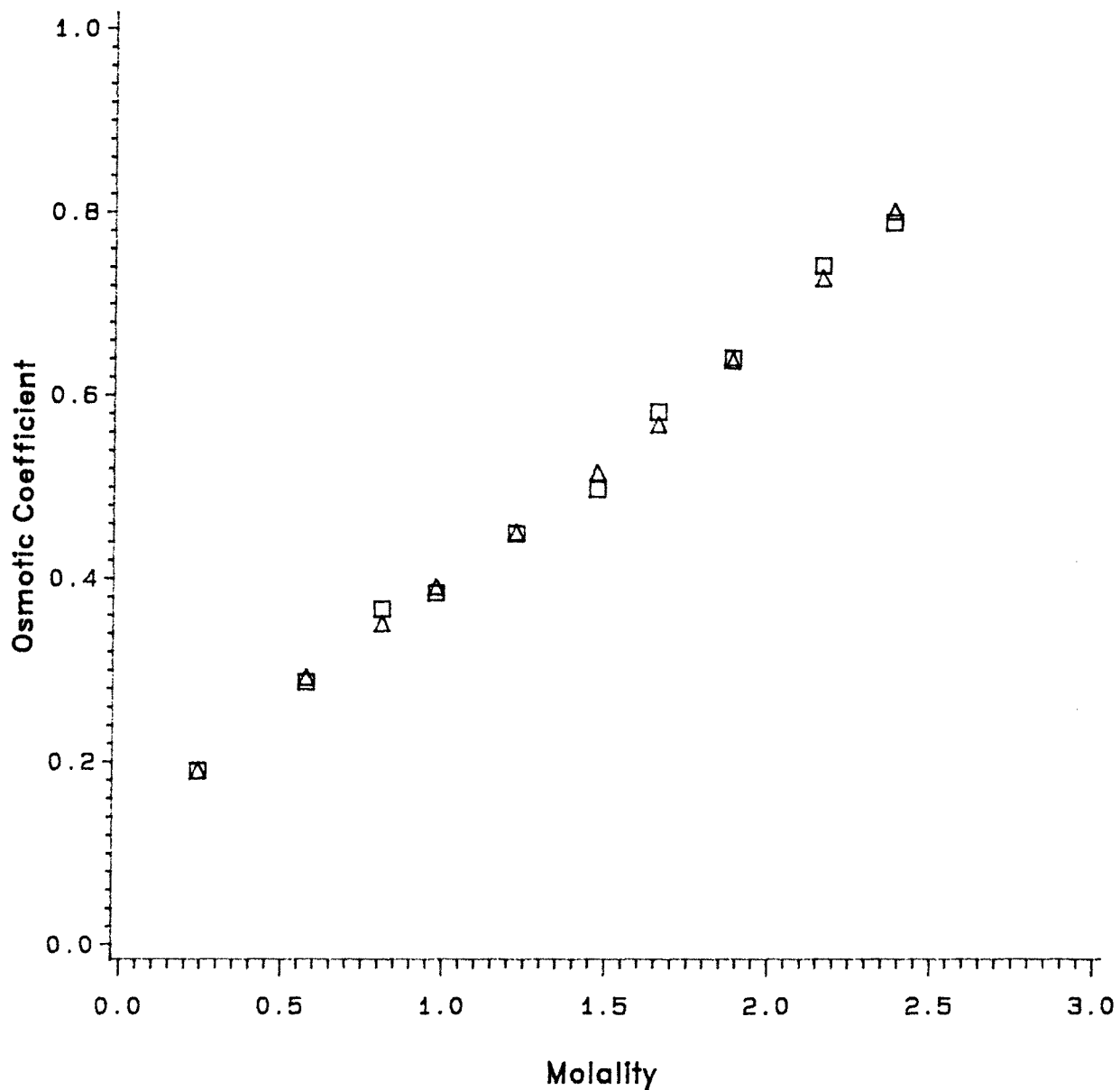
Literature ■

Smoothed ▲

Figure 8b
Experimental and Smoothed Osmotic Coefficients:
CaCl2 — EtOH at 50 deg C
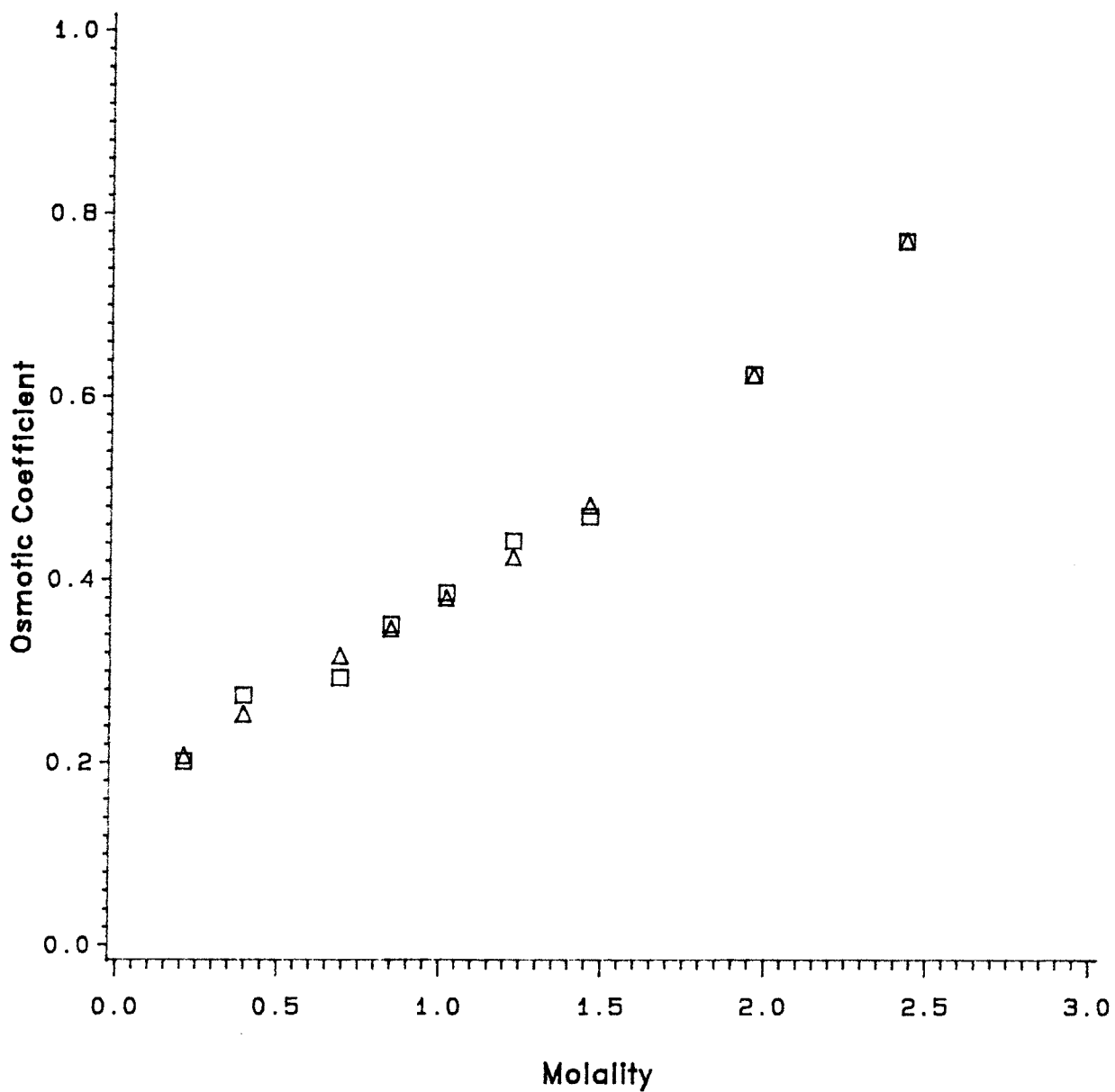
Experimental □
Smoothed △

Figure 9
Experimental and Smoothed Osmotic Coefficients:
NaI — EtOH at 50 deg C
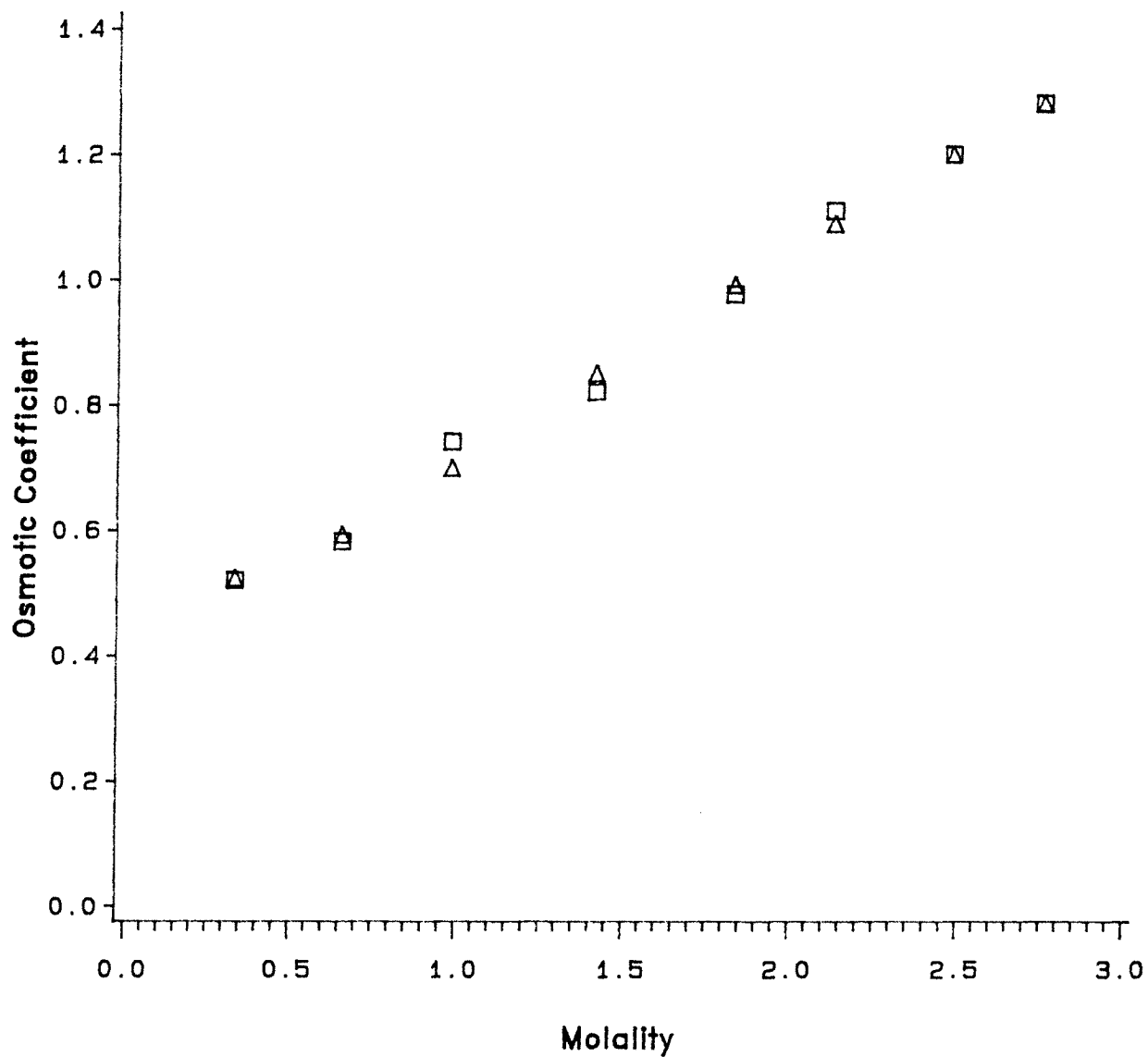
Experimental □
Smoothed △

Figure 10
Experimental and Smoothed Osmotic Coefficients:
LiCl – EtOH at 50 deg C
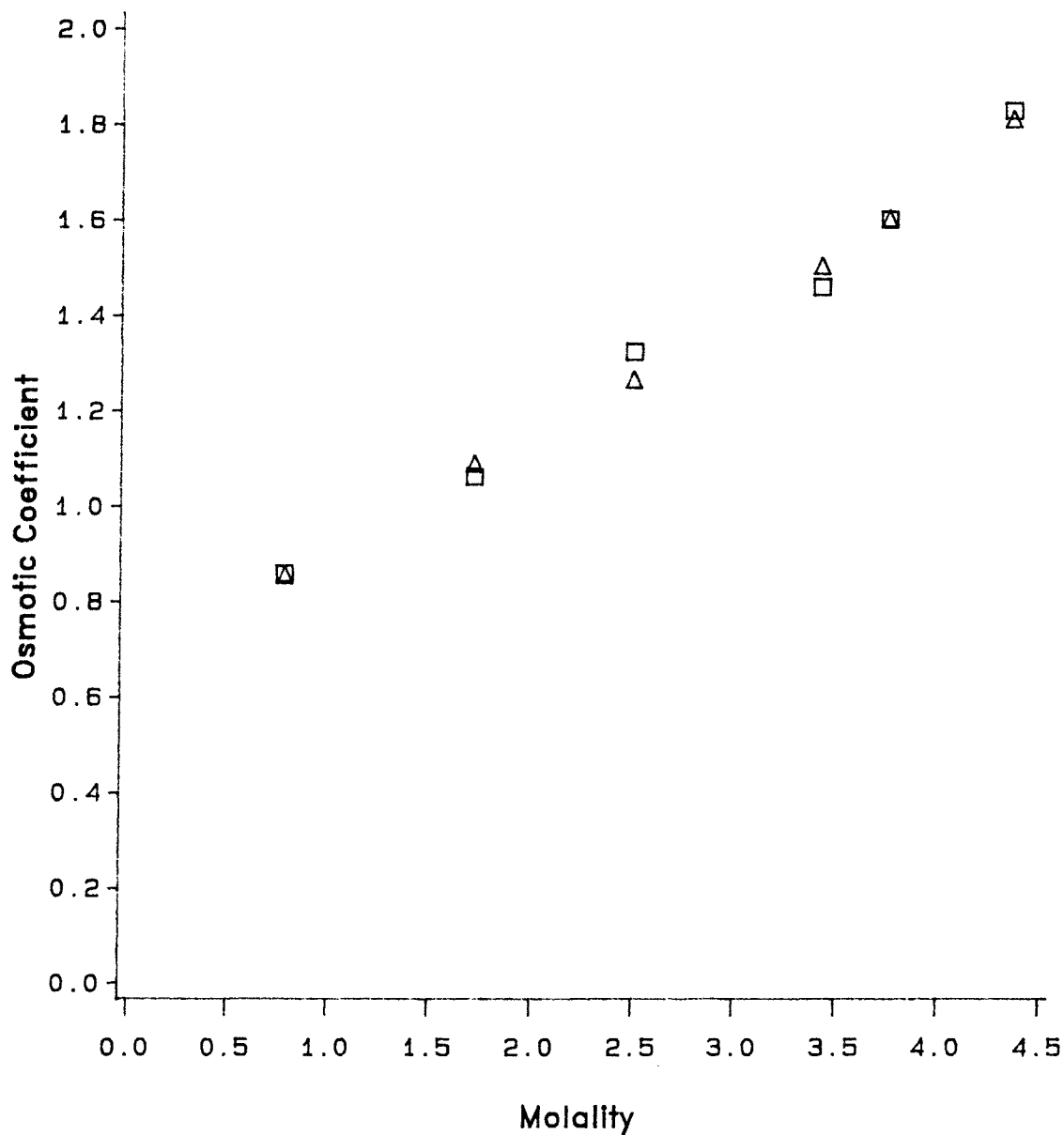
Experimental □
Smoothed △

Figure 11
Experimental and Smoothed Osmotic Coefficients:
LiCl — EtOH at 35 deg C
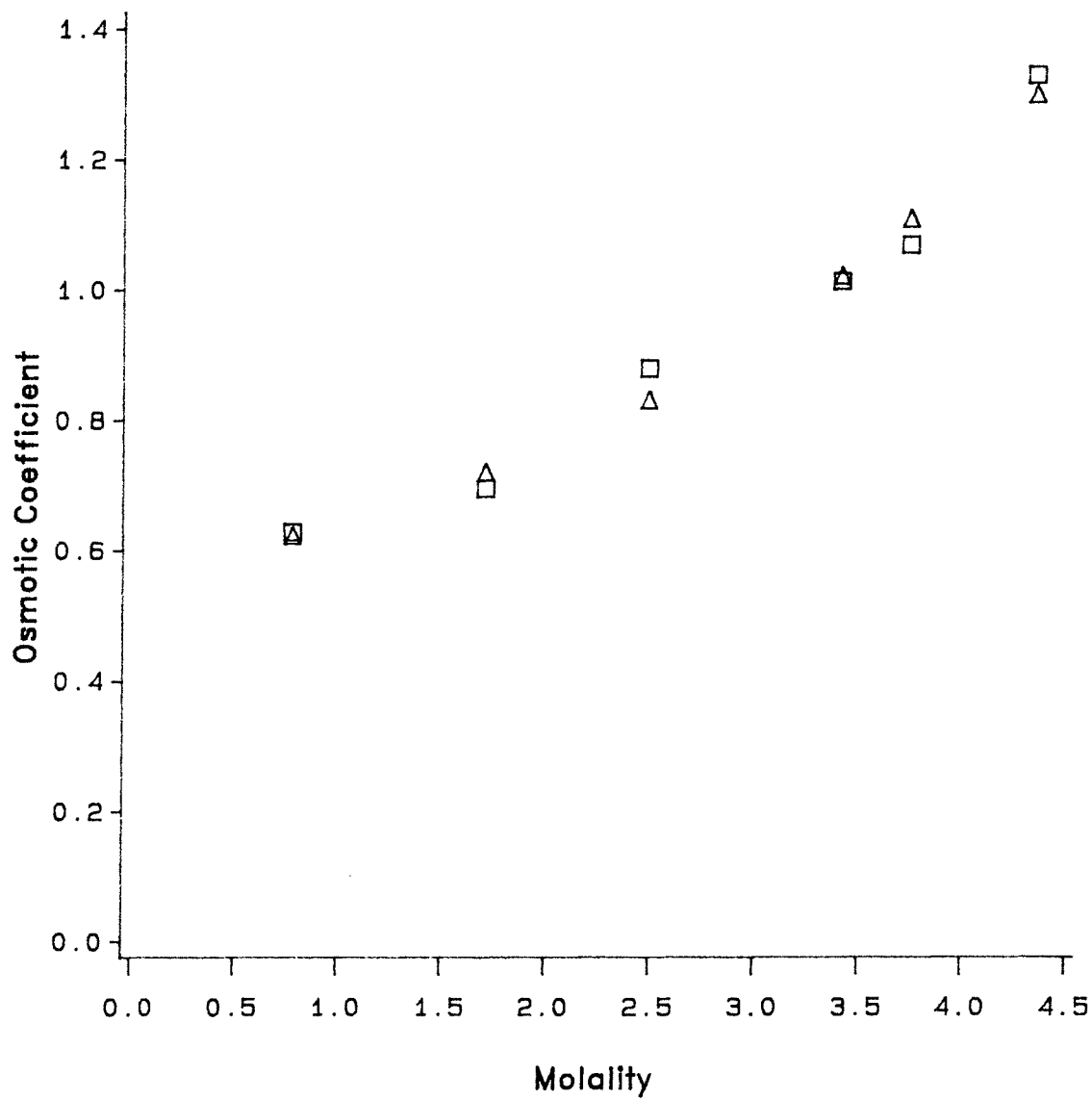
Experimental □
Smoothed △

Figure 12
Experimental and Smoothed Osmotic Coefficients:
LiBr — EtOH at 50 deg C
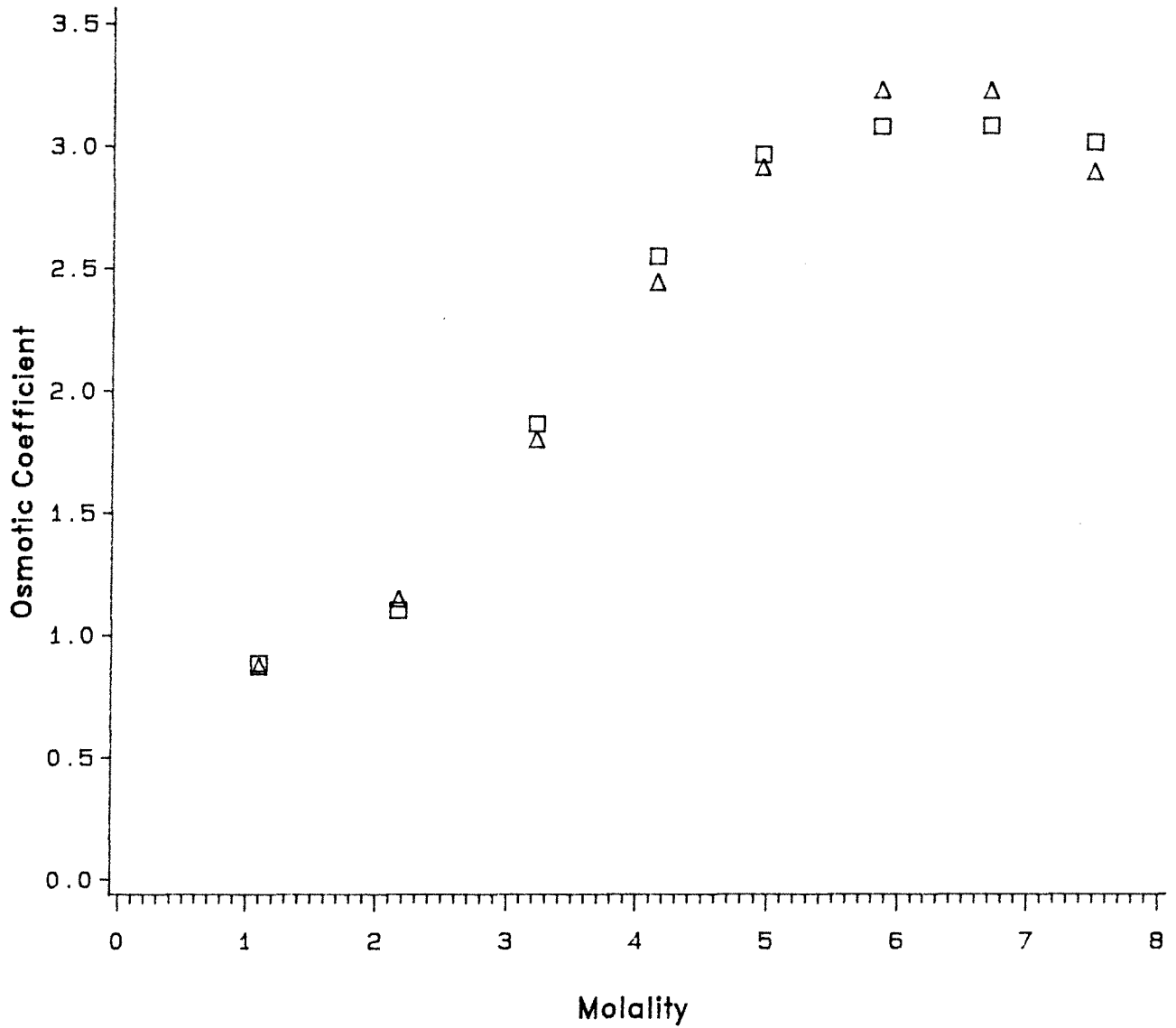
Experimental □
Smoothed △

Table VIIIa Literature Values of the Mean
Activity Coefficient for $CaCl_2$
at 50° C

molality	$\gamma_{\pm}$
0.2415	0.0126
0.5759	0.0072
0.8104	0.0060
0.9776	0.0056
1.2235	0.0052
1.4704	0.0050
1.6551	0.0050
1.8831	0.0051
2.1615	0.0053
2.3795	0.0056

Table VIIIb Experimental Values of the Mean
Activity Coefficient for $CaCl_2$
at 50° C

molality	$\gamma_{\pm}$
0.2097	0.0154
0.3937	0.0099
0.6901	0.0070
0.8468	0.0063
1.0183	0.0058
1.2248	0.0054
1.4583	0.0052
1.9569	0.0053
2.4270	0.0057

Table IX   Experimental Values of the Mean
             Activity Coefficient for NaI at
             50° C

molality	$\gamma_\pm$
0.3367	0.1199
0.6603	0.0949
0.9881	0.0914
1.4196	0.0978
1.8329	0.1104
2.1313	0.1225
2.4837	0.1399
2.7552	0.1556

Table X   Experimental Values of the Mean
           Activity Coefficient for LiCl
           at 50° C

molality	$\gamma_{\pm}$
0.7840	0.2218
1.7156	0.3276
2.4965	0.4873
3.4194	0.8367
3.7506	1.0398
4.3572	1.6069

Table XI Experimental Values of the Mean
Activity Coefficient for LiCl
at 35° C

molality	$\gamma_{\pm}$
0.7840	0.1184
1.7156	0.1002
2.4965	0.1026
3.4194	0.1208
3.7506	0.1327
4.3572	0.1653

Table XII   Experimental Values of the Mean
            Activity Coefficient for LiBr
            at 50° C

molality	$\gamma_{\pm}$
1.0950	0.5180
2.1652	0.6585
3.2221	1.5027
4.1475	3.7778
4.9489	8.1332
5.8547	15.8501
6.6974	21.4158
7.4944	19.4214

B. Correlation of the Results Using the Pitzer and Bromley Equations

In order to test the applicability of these two equations to fit non-aqueous electrolyte systems, all the experimental data were correlated using the three parameter Pitzer equation and a one and two parameter Bromley equation. Values of β^0, β^1, and C^ϕ in the Pitzer equation and B and ρ in the Bromley equation were obtained through the nonlinear regression of the experimental ΔP vs molality data.

So that the experimental results be most effectively utilized, the ΔP data were converted to osmotic coefficient data through the use of equations 78-80 and 48. This data then served as input for the regression program shown in Appendix B. This program uses Powell's Method to find the unknown parameters in either of the two equations by minimizing the relative sum of the squares between the experimental and calculated osmotic coefficients. Details on Powell's method may be found in Himmelblau (61).

Once the parameters for the two equations were found, they were substituted into equations 70 and 74 to obtain the calculated values of the mean activity coefficients for the various electrolytes. These results are presented in Tables XIII-XVII and Figures XIII-XVII. The parameters are shown in Tables XVIII and XIX.

When correlating the data with any of the equations, it was decided to retain all of the experimental data. This may not be an appropriate assumption since the dielectric constant of ethanol is approximately a

TABLE XIIIa Values of the Mean Activity Coefficient for $CaCl_2$ (Literature) in Ethanol at 50° C as Calculated by the Pitzer, Bromley (avg. ρ), and Bromley (optimum ρ)

molality	$\gamma_{\pm P}$	relative percent error	$\gamma_{\pm B}$	relative percent error
0.2415	0.0346	174.60	0.0139	10.32
0.5759	0.0317	340.28	0.0077	6.94
0.8104	0.0347	478.33	0.0065	8.33
0.9776	0.0384	585.71	0.0060	7.14
1.2235	0.0461	786.54	0.0057	9.62
1.4704	0.0561	1022.00	0.0055	10.00
1.6551	0.0651	1202.00	0.0055	10.00
1.8831	0.0775	1419.61	0.0056	9.80
2.1615	0.0935	1664.15	0.0058	9.43
2.3795	0.1056	1785.71	0.0060	7.14

molality	$\gamma_{\pm B}$	relative percent error
0.2415	0.0137	8.73
0.5759	0.0076	5.56
0.8104	0.0064	6.67
0.9776	0.0059	5.36
1.2235	0.0056	7.69
1.4704	0.0055	10.00
1.6551	0.0055	10.00
1.8831	0.0055	7.84
2.1615	0.0057	7.55
2.3795	0.0059	5.36

TABLE XIIIb   Values of the Mean Activity Coefficient for
$CaCl_2$ (Experimental) in Ethanol at 50° C as
Calculated by the Pitzer, Bromley (avg. ρ),
and Bromley (optimum ρ)

molality	$\gamma_{\pm P}$	relative percent error	$\gamma_{\pm B}$	relative percent error
0.2097	0.0394	155.84	0.0154	0.00
0.3937	0.0349	252.53	0.0097	-2.02
0.6901	0.0357	410.00	0.0069	-1.43
0.8468	0.0381	504.76	0.0062	-1.59
1.0183	0.0420	624.14	0.0058	0.00
1.2248	0.0483	794.44	0.0055	1.85
1.4583	0.0574	1003.85	0.0053	1.92
1.9569	0.0827	1460.38	0.0054	1.89
2.4270	0.1091	1814.04	0.0057	0.00

molality	$\gamma_{\pm B}$	relative percent error
0.2097	0.0162	5.19
0.3937	0.0102	3.03
0.6901	0.0073	4.29
0.8468	0.0066	4.76
1.0183	0.0061	5.17
1.2248	0.0058	7.41
1.4583	0.0056	7.69
1.9569	0.0055	3.77
2.4270	0.0057	0.00

TABLE XIV Values of the Mean Activity Coefficient for NaI in Ethanol at 50° C as Calculated by the Pitzer, Bromley (avg. ρ), and Bromley (optimum ρ)

molality	$\gamma_{\pm P}$	relative percent error	$\gamma_{\pm B}$	relative percent error
0.3367	0.1213	1.17	0.1797	49.87
0.6603	0.0966	1.79	0.1514	59.54
0.9881	0.0944	3.28	0.1448	58.42
1.4196	0.1046	6.95	0.1482	51.53
1.8329	0.1236	11.96	0.1585	43.57
2.1313	0.1425	16.33	0.1691	38.04
2.4837	0.1709	22.16	0.1849	32.17
2.7552	0.1978	27.12	0.1994	28.15

molality	$\gamma_{\pm B}$	relative percent error
0.3367	0.1306	8.92
0.6603	0.1019	7.38
0.9881	0.0959	4.92
1.4196	0.1007	2.97
1.8329	0.1137	2.99
2.1313	0.1277	4.24
2.4837	0.1497	7.01
2.7552	0.1713	10.09

TABLE XV   Values of the Mean Activity Coefficient for LiCl
in Ethanol at 50° C as Calculated by the Pitzer,
Bromley (avg. ρ), and Bromley (optimum ρ)

molality	$\gamma_{\pm P}$	relative percent error	$\gamma_{\pm B}$	relative percent error
0.7840	0.2100	-0.52	0.1698	-23.44
1.7156	0.2529	-22.80	0.2050	-38.19
2.4965	0.3314	-32.00	0.2691	-44.78
3.4194	0.4931	-41.07	0.4010	-52.07
3.7506	0.5772	-44.49	0.4672	-55.07
4.3572	0.7821	-51.33	0.6234	-61.20

molality	$\gamma_{\pm B}$	relative percent error
0.7840	0.2150	-3.07
1.7156	0.2614	-20.21
2.4965	0.3420	-29.82
3.4194	0.4923	-41.16
3.7506	0.5652	-45.63
4.3572	0.7325	-54.42

TABLE XVI   Values of the Mean Activity Coefficient for LiCl
             in Ethanol at 35° C as Calculated by the Pitzer,
             Bromley (avg. ρ), and Bromley (optimum ρ)

molality	$\gamma_{\pm P}$	relative percent error	$\gamma_{\pm B}$	relative percent error
0.7840	0.1260	6.42	0.1441	21.71
1.7156	0.1030	2.79	0.1300	29.74
2.4965	0.1043	1.66	0.1356	32.16
3.4194	0.1198	-0.83	0.1510	25.00
3.7506	0.1290	-2.79	0.1584	19.37
4.3572	0.1521	-7.99	0.1742	5.38

molality	$\gamma_{\pm B}$	relative percent error
0.7840	0.1083	-8.53
1.7156	0.0947	-5.49
2.4965	0.1009	-1.66
3.4194	0.1180	-2.32
3.7506	0.1264	-4.75
4.3572	0.1452	-12.16

TABLE XVII   Values of the Mean Activity Coefficient for LiBr
in Ethanol at 50° C as Calculated by the Pitzer,
Bromley (avg. ρ), and Bromley (optimum ρ)

molality	$\gamma_{\pm P}$	relative percent error	$\gamma_{\pm B}$	relative percent error
1.0950	0.0970	-82.49	0.2133	-58.82
2.1652	0.1821	-72.35	0.3474	-47.24
3.2221	0.4292	-71.44	0.6444	-57.12
4.1475	0.9585	-74.63	1.1588	-69.33
4.9489	1.9304	-76.27	1.9639	-75.85
5.8547	4.1989	-73.01	3.6157	-77.19
6.6974	8.4451	-60.56	6.4396	-69.93
7.4944	15.9072	-18.09	11.1832	-42.42

molality	$\gamma_{\pm B}$	relative percent error
1.0950	0.1451	-71.99
2.1652	0.2281	-65.36
3.2221	0.4319	-71.26
4.1475	0.8072	-78.63
4.9489	1.4273	-82.45
5.8547	2.7758	-82.49
6.6974	5.2264	-75.60
7.4944	9.5965	-50.59

Figure 13a
Values of the Mean Activity Coefficient
System: CaCl2 — EtOH at 50 deg C
Literature Data
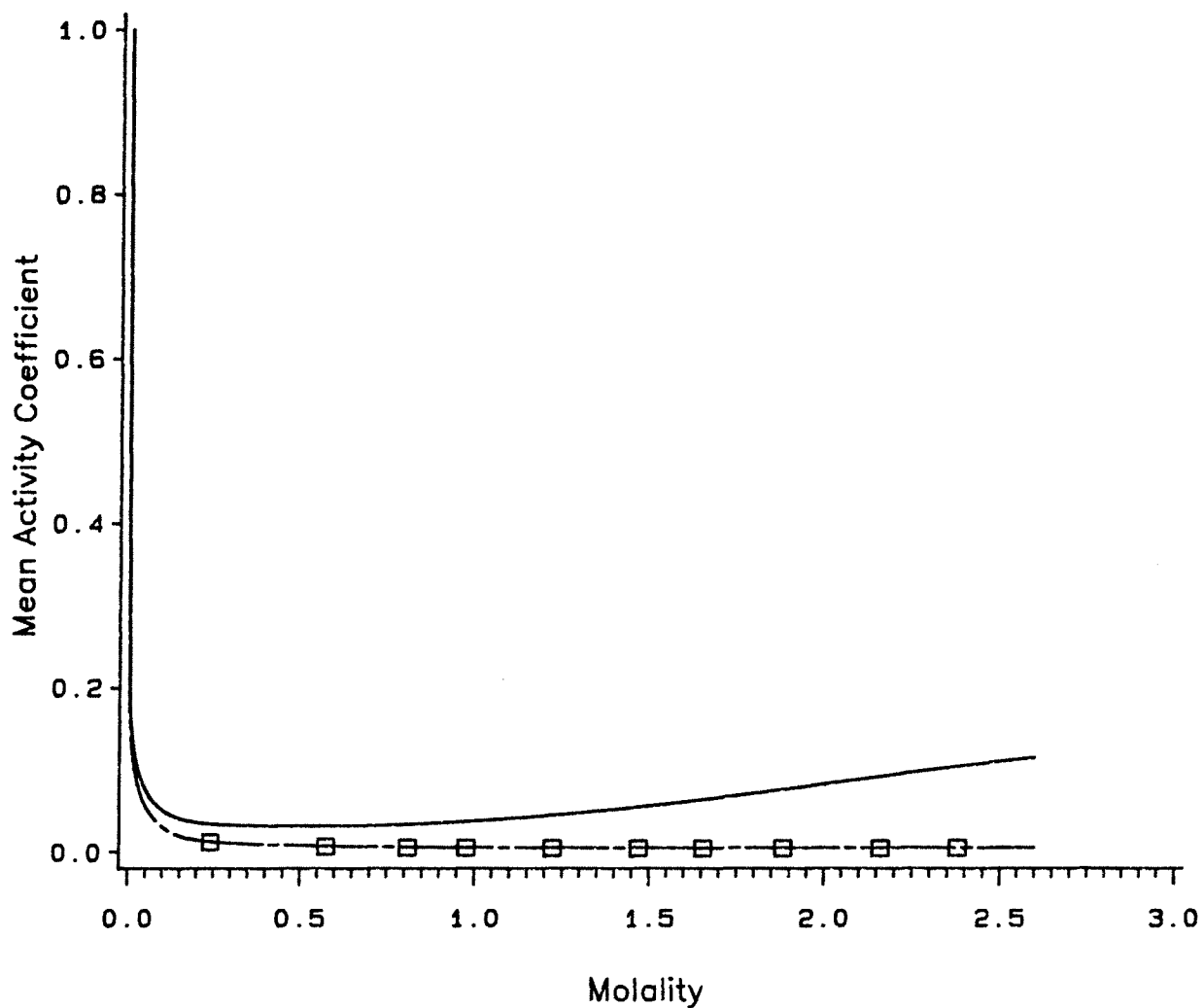
Pitzer
Bromley(avg rho)
Bromley(opt rho)
Experimental

Figure 13b
Values of the Mean Activity Coefficient
System: CaCl2 — EtOH at 50 deg C
Experimental Data
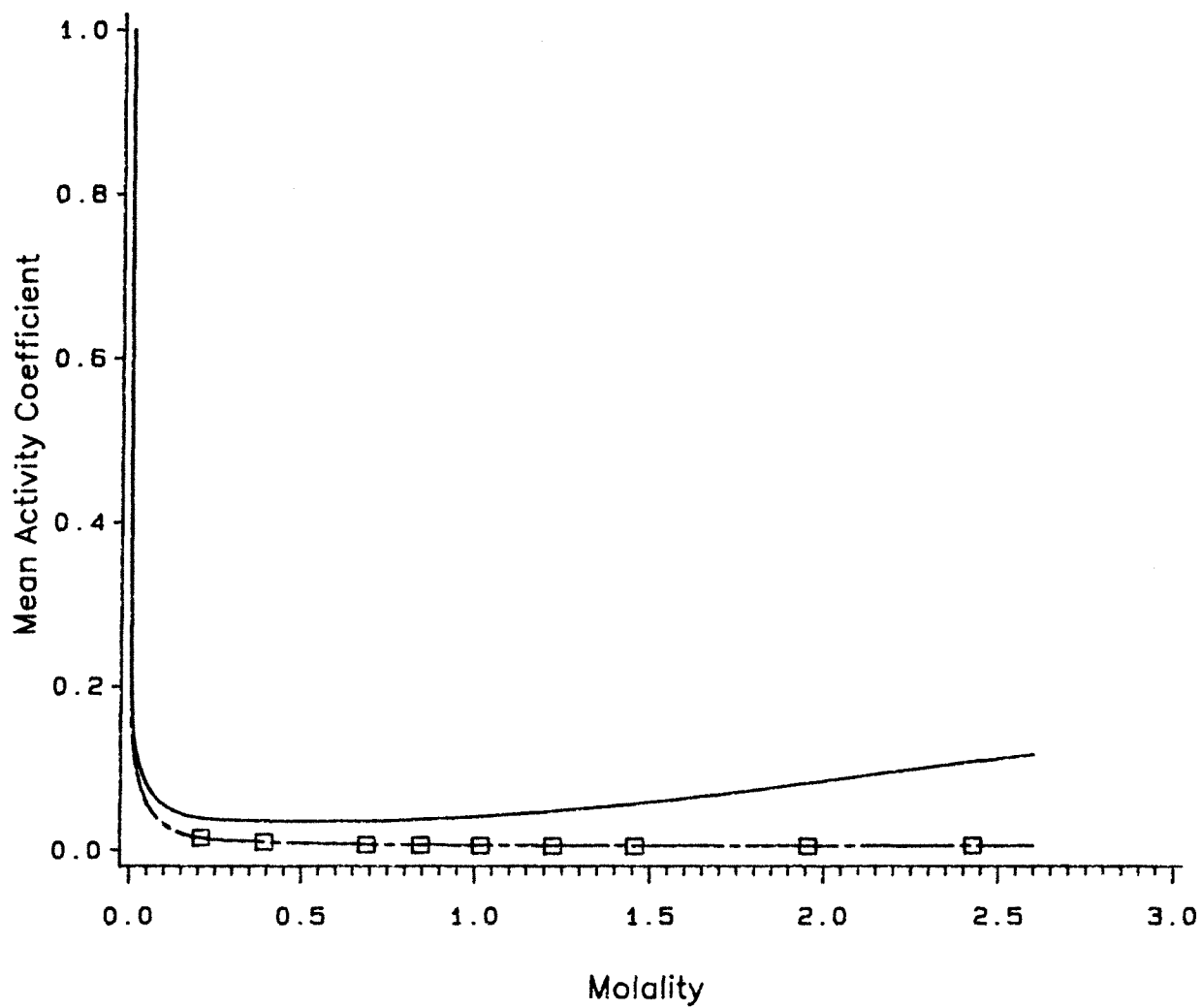
Pitzer ——————
Bromley(avg rho) ——————
Bromley(opt rho) —— —— · —
Experimental ☐

Figure 14
Values of the Mean Activity Coefficient
System: NaI — EtOH at 50 deg C
Experimental Data
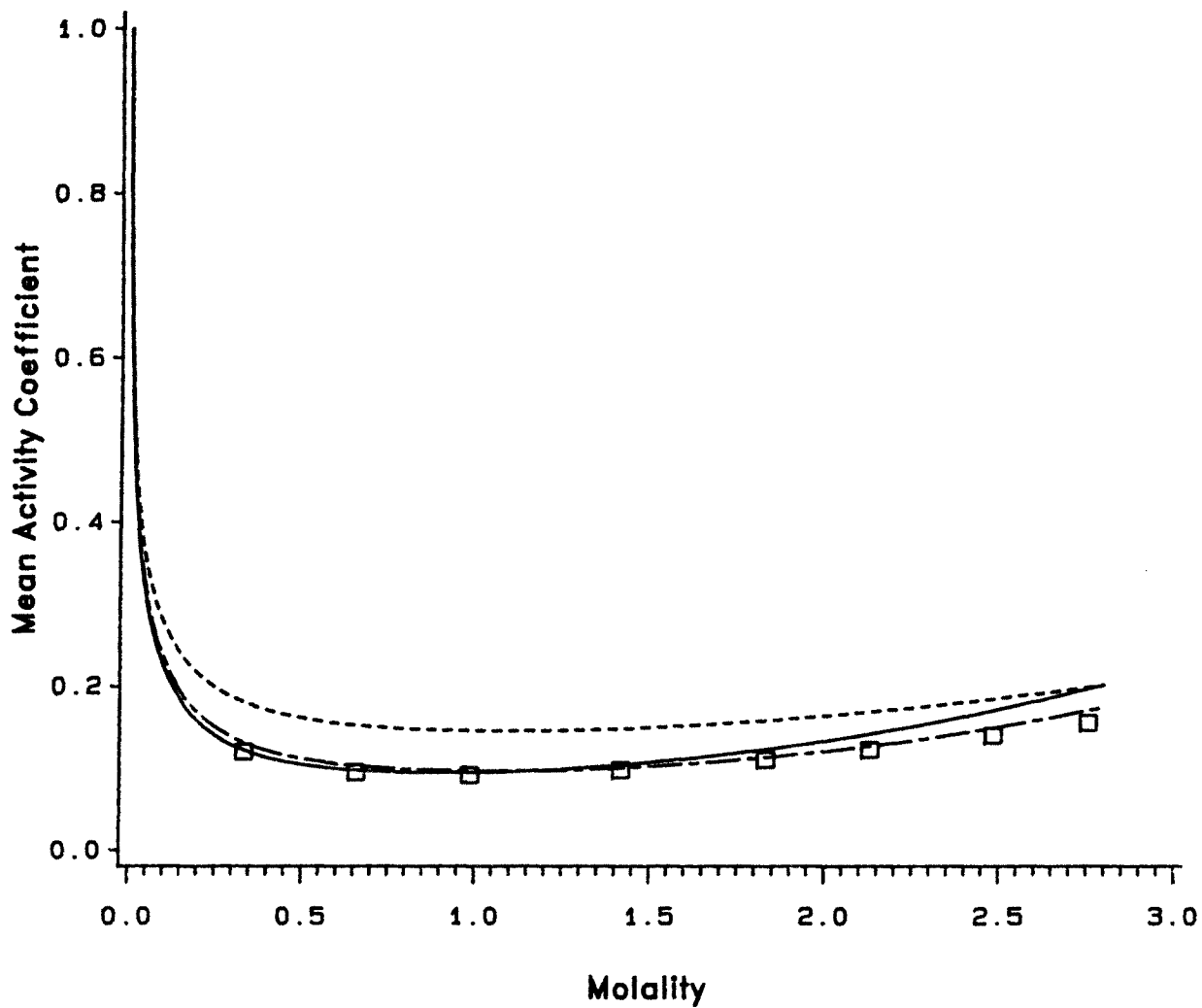
Pitzer ——————
Bromley(avg rho) - - - - - - -
Bromley(opt rho) — - —— - —.
Experimental □

Figure 15
Values of the Mean Activity Coefficient
System: LiCl — EtOH at 50 deg C
Experimental Data
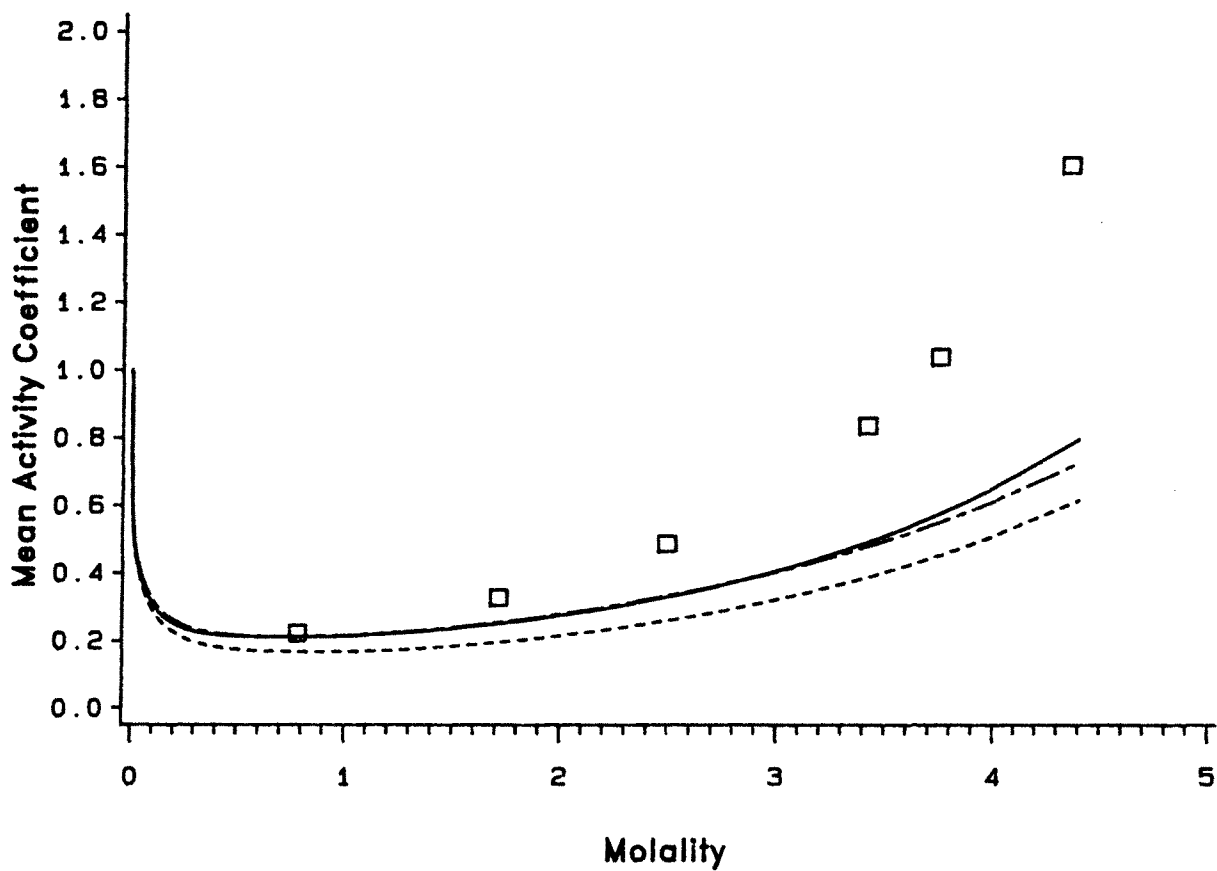
Pitzer	———————
Bromley(avg rho)	- - - - - - -
Bromley(opt rho)	— — — · —
Experimental	□

Figure 16
Values of the Mean Activity Coefficient
System: LiCl – EtOH at 35 deg C
Experimental Data
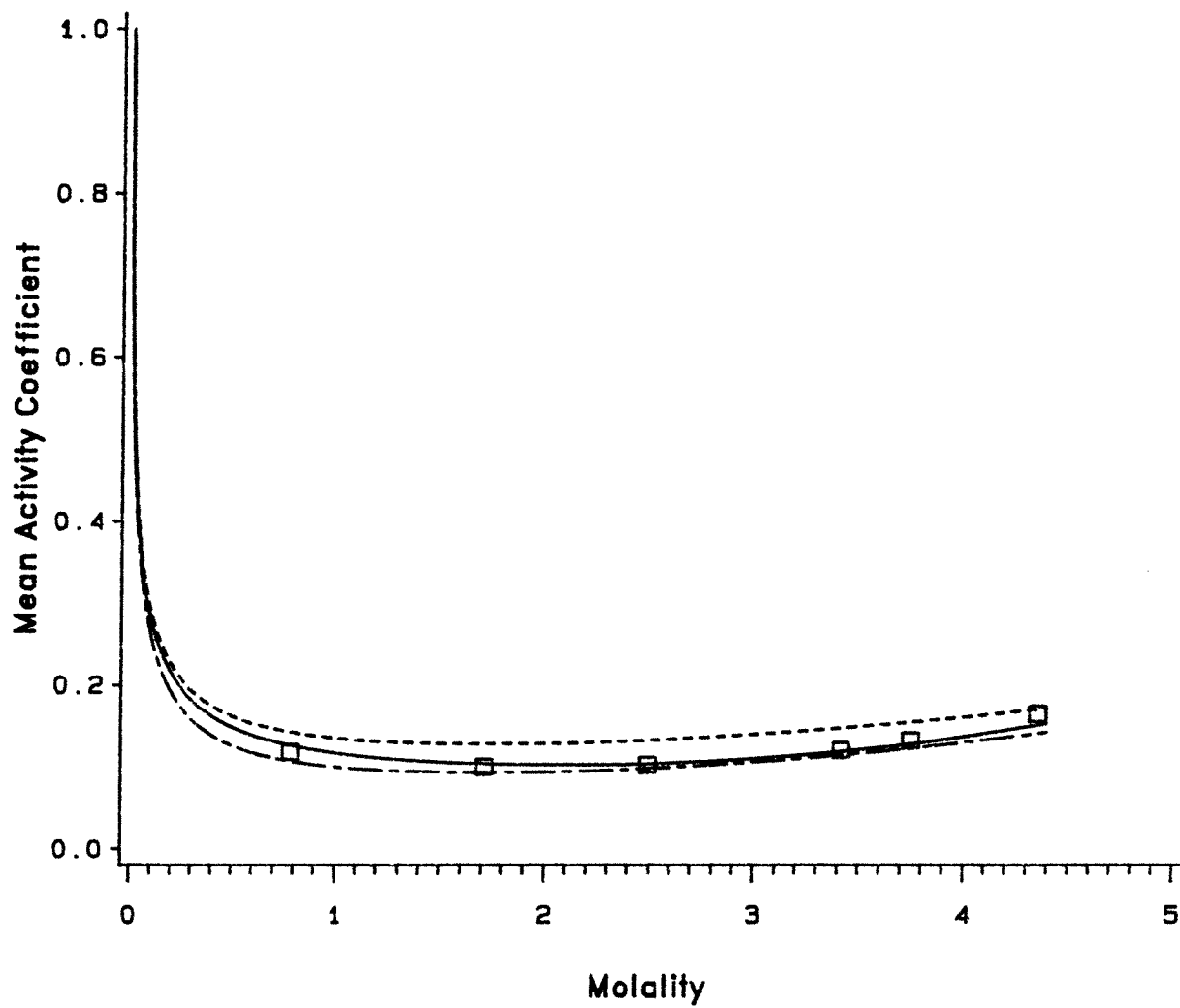
Pitzer ——————
Bromley(avg rho) — — — — — —
Bromley(opt rho) — — · — · —
Experimental □

Figure 17
Values of the Mean Activity Coefficient
System: LiBr — EtOH at 50 deg C
Experimental Data
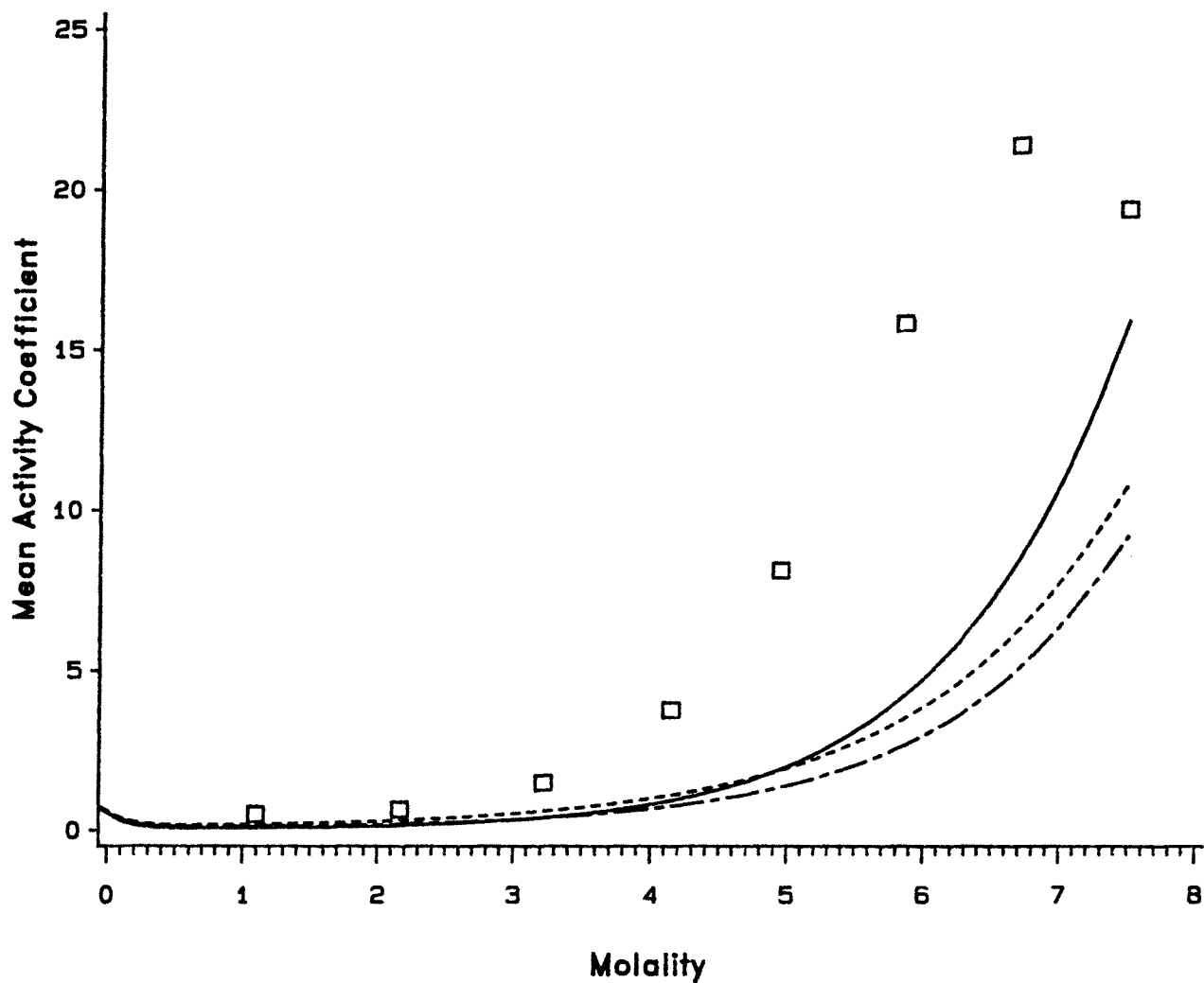
Pitzer ——————
Bromley(avg rho) - - - - - - -
Bromley(opt rho) — - — - — - —
Experimental □

Table XVIII Values β^0, β^1, and C^ϕ in the Pitzer Equation
Obtained form the Regression of the Experimental
Data at 50° C

System	β^0	β^1	C^ϕ
$CaCl_2$ - EtOH[1]	1.27398	11.6257	-0.155677
$CaCl_2$ - EtOH	1.23241	12.1854	-0.146673
NaI - EtOH	0.703157	0.525618	-0.631198E-1
LiCl - EtOH	0.472231	3.36594	-0.889164E-2
LiCl - EtOH[2]	0.256885	2.37794	0.133038E-1
LiBr - EtOH	0.774619	0.130755	-0.374688E-1

1 - Literature
2 - 35° C

Table XVIXa   Values B in the Bromley Equation Obtained from
              the Regression of the Experimental Data Using
              an Average Value of $\rho = 1.75$ at 50° C

System	B
$CaCl_2$ - EtOH[1]	0.619215E-01
$CaCl_2$ - EtOH	0.585617E-01
NaI - EtOH	0.185932
LiCl - EtOH	0.244468
LiCl - EtOH[2]	0.102968
LiBr - EtOH	0.319062

1 - Literature
2 - 35° C

Table XVIXb   Values B and the Optimum Values of ρ in the Bromley
              Equation Obtained from the Regression of the
              Experimental Data at 50° C

System	B	ρ
$CaCl_2$ - EtOH[1]	0.635499E-01	1.73869
$CaCl_2$ - EtOH	0.512412E-01	1.79705
NaI - EtOH	0.342786	1.06260
LiCl - EtOH	0.212810	2.18336
LiCl - EtOH[2]	0.151803	1.31584
LiBr - EtOH	0.360093	1.29141

1 - Literature
2 - 35° C

third of that of water at the temperature of the study. Since the equations correlate aqueous electrolyte solutions up to an ionic strength of 6m, this would mean that for ethanol, the maximum molality should have been 2m. The effect of neglecting data above 2m would be to eliminate most of the experimentally determined data points. However, since the purpose of this study was to gain insight into the limitations of the Pitzer and Bromley equations in correlating nonaqueous systems, all of the data was retained.

Correlation of the data using Pitzer's equation was a straight forward determination of the three parameters involved, and nothing more needs to be added except that deleting concentrations above 2m had no effect on the mean activity coefficients for $CaCl_2$ and NaI where this procedure was feasible. For the LiCl and LiBr systems, this would have meant deleting too many points to make the parameter estimation meaningful.

When correlating the data with Bromley's equation, its initially assumed that all other parameters, except B, could remain the same as he reported for aqueous electrolyte systems. That is $\rho=1$, n=2, and the value of a as is given by equation 72. It became apparent very quickly that this approach would not work. It was decided to see if changing the value of ρ would have any effect on the correlation results. This change was accomplished in two different ways. The first was to see if there was a single value of ρ which could be used for all of the system. This is similar to the approach used by Bromley when he determined that the value should be one for aqueous systems. The second approach was to find the optimum value

of ρ for each salt, this would then give the Bromley equation two adjustable parameters instead of just one.

Both methods were tried. Figure 18 is a plot of the total error (taken over all of the experimental systems plus the literature data of Hayward and Perman) vs. ρ. It can be seen that a minimum occurs at a value of $\rho=1.75$. This was taken to be the value of ρ which "best fit" all of the systems involved. When the second approach was used, ρ in the Bromley equation became another adjustable parameter just as B. Table XIX shows that for the most part, when this approach was used, the value of B did not change appreciably except for the NaI system. However, except for the $CaCl_2$ systems, the value of ρ did change significantly from the average of 1.75.

The results of the correlation procedure are mixed with some surprises. The most surprising result was the complete inability of the Pitzer equation to predict mean activity coefficients for the $CaCl_2$ system. Whereas, both Bromley methods did very well here. However, the average value of ρ used just happened to be in the vicinity of the optimum value in this case. It should also be noted that the Pitzer equation predicts a much more rapid increase in $\gamma_\pm$ that is actually observed.

In the NaI system, the Bromley equation with an optimum ρ performed very well (average error in $\gamma_\pm$, about 6.1%). The Pitzer equation did well up to a molality of about 1.4, at this point, the predicted $\gamma_\pm$ values began to increase more rapidly than the experimental values. The average er-

Figure 18
Total Error vs Rho in Bromley Equation
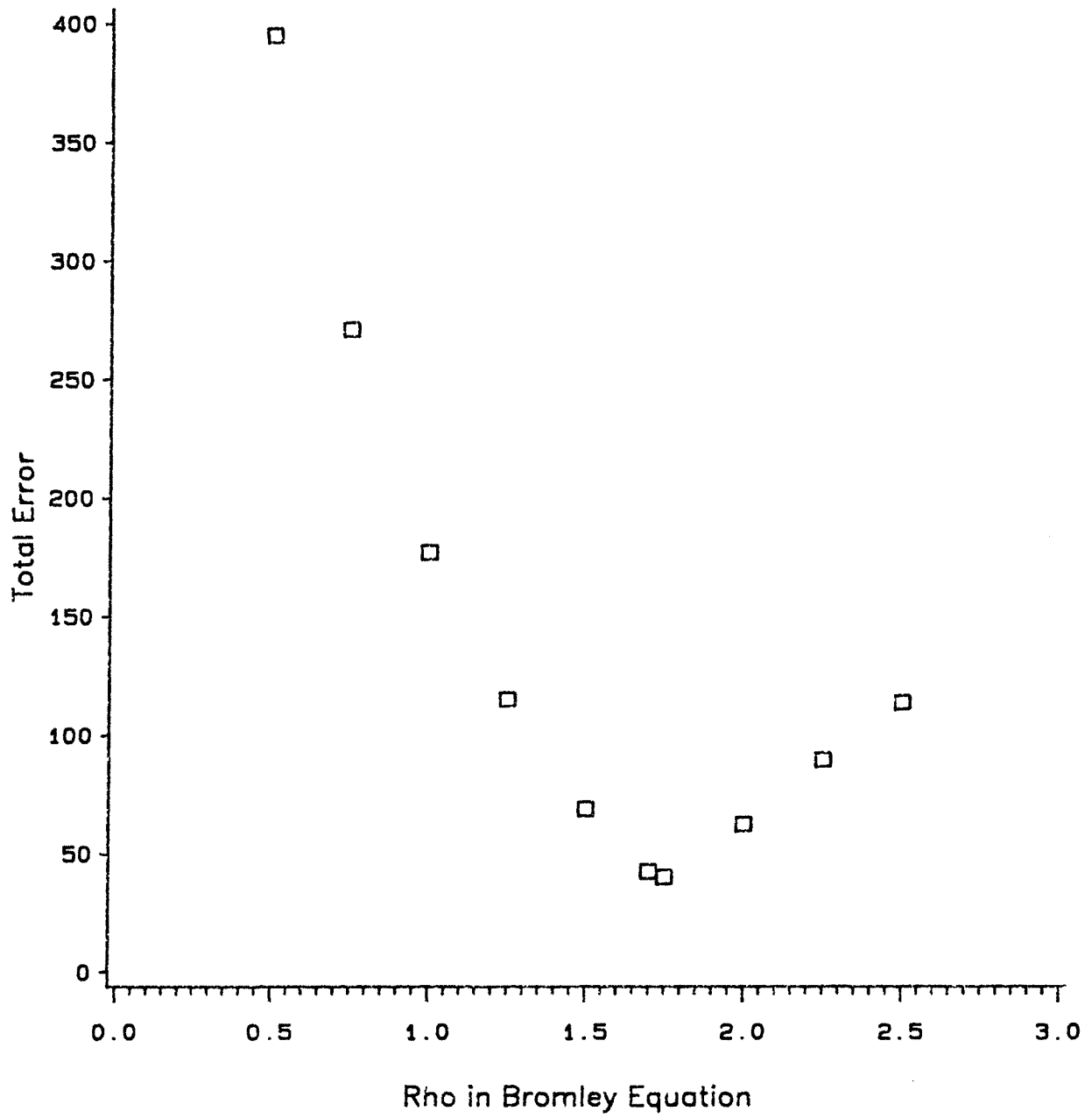
ror here was about 11.3%. The Bromley model using an average value for ρ

gave an average error of about 45%, consistently over predicting the

values of $\gamma_{\pm}$.

For the LiCl systems, none of the models were capable of predicting the

data at 50° C. The Pitzer and Bromley (with an optimum ρ) gave approx-

imately the same results up to a molality of 3.2 and the Bromley with the

average ρ consistently under predicts at all concentrations.

At 35° C, both the Pitzer and Bromley (optimum ρ) predict the mean

activity coefficients very well with the Pitzer doing slightly better (

average error of 3.75 vs 5.82). Again, the Bromley (average ρ) gave the

poorest performance, this time consistently over predicting $\gamma_{\pm}$.

For the last system, LiBr in ethanol, none of the models predicted $\gamma_{\pm}$

very well. This might be expected as LiBr is the most soluble of the salts

used and would provide the most severe test for the two equations. The

results show that all the models consistently under predict the mean acti-

vity coefficients and had an overall error of about 65%.

In the last part of the correlation procedure, an attempt was made to

determine if there is a temperature dependency in any of the parameters

in the models. Using the other $CaCl_2$ data found in Hayward and Perman and

some solvent activity data found for NaI (60), values of B in the Bromley

equation were found at the various temperatures reported. The average ρ

found previously was used. The B values were than fit to a simple poly-

nomial of the form y=mx+b. The results are shown in Figures 19 and 20

along with the 95% confidence intervals. It can be seen that in both cases, a simple linear relationship exists. An even more interesting study would have been to utilize these expressions and find the optimum ρ value. This would have added a third parameter to the equation and would begin to detract from one of the most attractive aspects of the Bromley model, namely, fewer adjustable parameters.

This approach was not tried with the Pitzer correlation as it would have added three adjustable parameter for a total of six. There are far too few data points to warrant this many adjustable parameters.

Figure 19
Impact of Temperature on Bromley B
NaI − EtOH
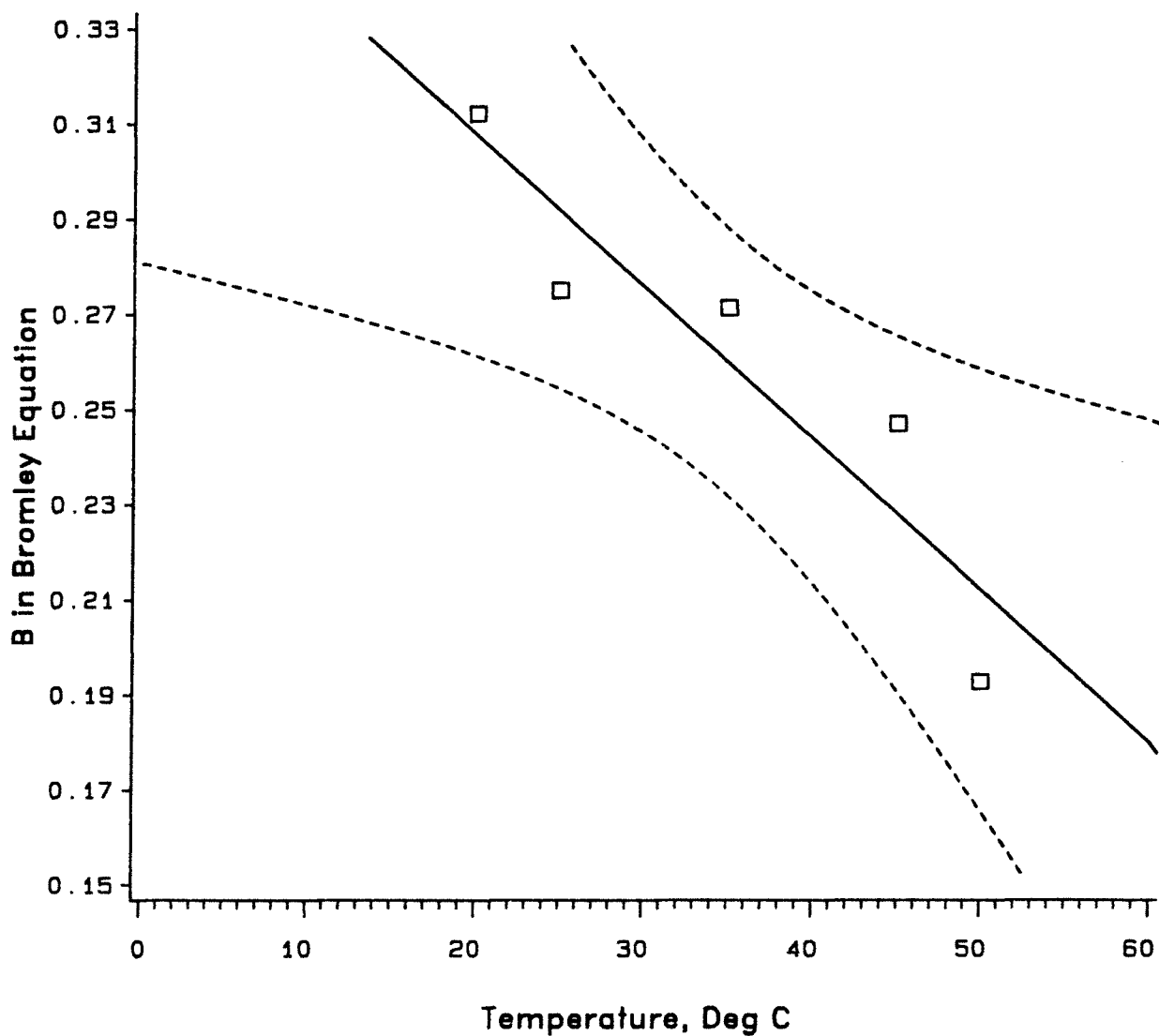
Figure 20
Impact of Temperature on Bromley B
CaCl2 – EtOH
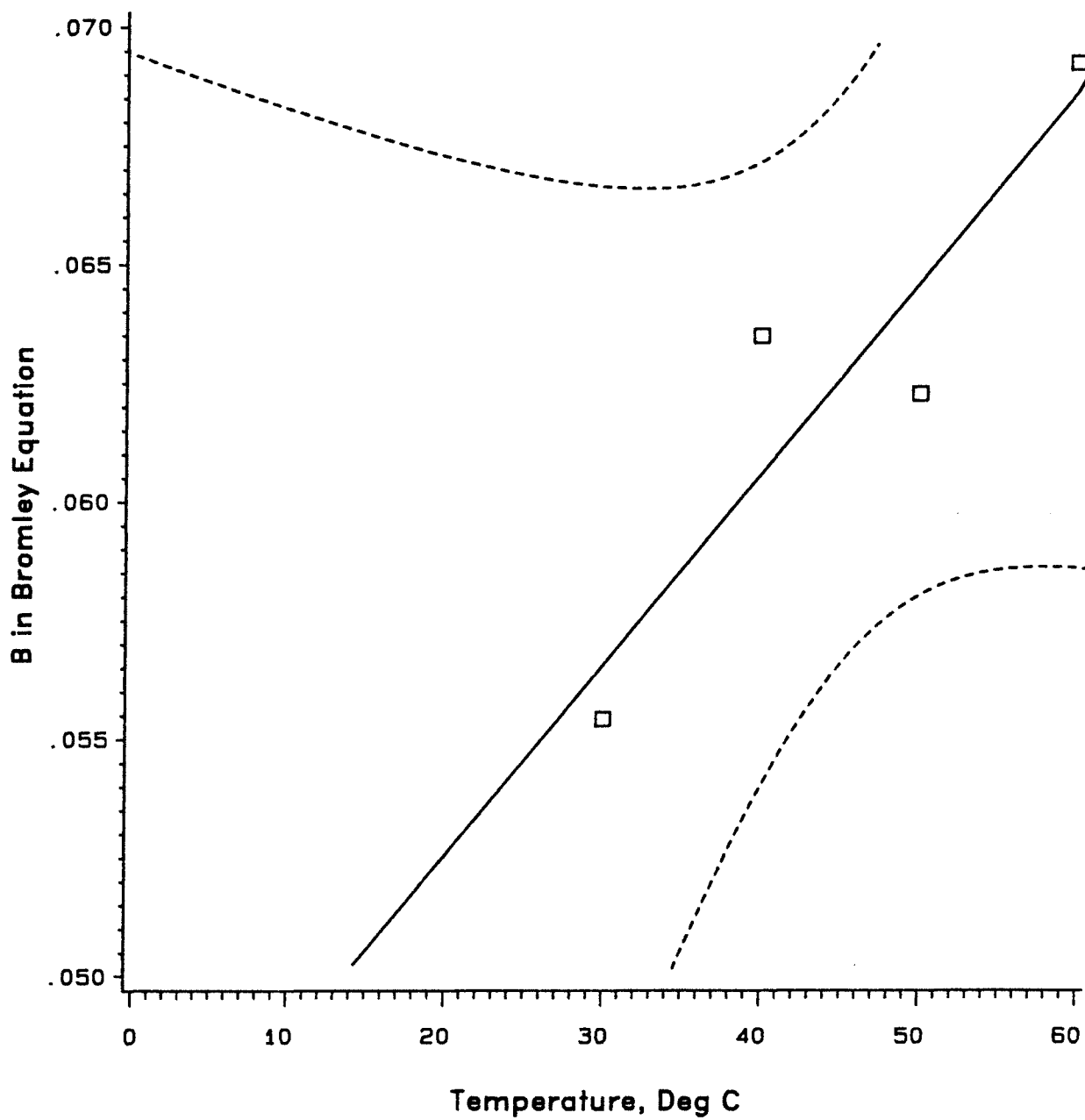
CHAPTER V

DISCUSSION OF RESULTS

As mentioned previously, the primary objectives of this study were to 1) experimentally determine the mean activity and osmotic coefficients of $CaCl_2$, NaI, LiCl, and LiBr at 50° C, 2) test the applicability of the Pitzer and Bromley formalisms to this data, and 3) investigate the temperature dependency of the parameters in both models. A discussion of these points follows.

The mean activity coefficients as a function of molality for $CaCl_2$, NaI, LiCl (50° C and 35° C) and LiBr at 50° C are shown in Figures 13-17 and their values are given in Tables VIII-XII. They were obtained through the use of experimental osmotic coefficient data and the use of equations 83 and 84. Although this approach differs somewhat from the classical approach, which involves the graphical integration of equation 82, it has been shown that the results of the two methods are the same. Prior to even attempting its use, the mean activity coefficients for the $CaCl_2$-H_2O system as calculated by Rard (58) were compared to the data for this system as reported by Lewis and Randall (32). The agreement between the two is excellent (see Appendix C). Good agreement can also be seen between the mean activity coefficient data obtained from this study and the values obtained form the data of Hayward and Perman. The value of this technique is that it does away with many of the difficulties encountered in the graphical approach. Particularly, how to extrapolate data which is not close to zero to the infinitely dilute solution.

That is not to say that this method is correct and the other wrong, but only that this method allows for the much more rapid determination of $\gamma_\pm$ values, since it does away with the arduous task of essentially "guessing" the proper section of a french curve to use to meet the limiting slope and then counting boxes. It should be mentioned here, that the application of equation 83 is actually very similar to the approach which was tried by Bixon (55). Both his equations 55 and 56 are of the same form.

One of the cautions which must be applied to the use of equations 83 and 84 is the extrapolation to regions beyond the maximum molality fit. These equations should be used strictly for correlation purposes, not as a predictive tool. But then again, the same caution is applied whenever a polynomial is used to correlate data.

The ability of either the Pitzer or Bromley equation to generate mean activity coefficients can not be determined solely by comparing the calculated values to the experimental values since the reliability of the experimental values is unknown, there simply are no values to compare to.

Be that as it may, some other device must then be used in order to determine the ability of these equations to model nonaqueous systems. The most likely candidate would be the system pressure since it was not directly involved in the parameter estimation.

The parameters obtained from each of the fitting techniques were then substituted back into each model and the total pressure calculated.

Tables XX-XXXIV show the results of this effort. These tables also show the fit between the experimental and calculated osmotic coefficients.

The results indicate that for the $CaCl_2$ systems, both Bromley procedures fit the experimental vapor pressures better than the Pitzer equation. However, for all the 1-1 electrolytes, the Pitzer model gave better predictions of the experimental pressures. Also, the Bromley (optimum ρ) fit better than the Bromley (average ρ).

For the osmotic coefficients, again the two Bromley procedures fit the data better than the Pitzer model for CaCl2 and likewise, the Pitzer model fit the 1-1 electrolyte systems better. Again the Bromley (optimum ρ) fit better than the Bromley (average ρ).

To truly minimize the relative sum of the squares between the experimental and calculated osmotic coefficients, the parameters which were initially assumed to be the same as in aqueous systems must be looked at.

For the Bromley equation, this has already be done in a manner of speaking, by searching for different values of ρ in equation 75. A glance back at Figure 18 will indicate the impact of ρ on the overall fit of the data, and it has been demonstrated, that an even better fit can be achieved if individual values of ρ are used for each electrolyte. A correlation between the values of ρ and the individual salts was tried, but insufficient data caused this method to fail. Varying the values of a and n in equation 74 had no significant effect on the overall fit of the data.

Table XXa   Calculated and Literature Osmotic Coefficients and Vapor
Pressures of $CaCl_2$ at 50° C Using the Pitzer Equation

molality moles per kg solvent	ϕ_{Pit}	ϕ_{exp}	relative % error	P_{Pit} mmHg	P_{exp} mmHg	relative % error
0.2415	0.2042	0.1899	7.532	220.09	220.20	-0.05
0.5759	0.2584	0.2867	-9.874	217.09	216.60	0.23
0.8104	0.3254	0.3660	-11.089	213.67	212.70	0.46
0.9776	0.3814	0.3838	-0.629	210.47	210.40	0.03
1.2235	0.4682	0.4489	4.282	204.73	205.40	-0.32
1.4704	0.5520	0.4973	11.008	198.08	200.30	-1.11
1.6551	0.6082	0.5815	4.587	192.82	194.00	-0.61
1.8831	0.6657	0.6400	4.019	186.35	187.60	-0.67
2.1615	0.7136	0.7409	-3.688	179.05	177.60	0.82
2.3795	0.7309	0.7882	-7.264	174.25	171.00	1.90

Table XXI   Calculated and Experimental Osmotic Coefficients and Vapor
            Pressures of NaI at 50° C Using the Pitzer Equation

molality moles per kg solvent	ϕ_{Pit}	ϕ_{exp}	relative % error	P_{Pit} mmHg	P_{exp} mmHg	relative % error
0.3367	0.5246	0.5208	0.729	217.90	217.93	-0.01
0.6603	0.5906	0.5824	1.417	213.66	213.77	-0.05
0.9881	0.6968	0.7421	-6.103	207.86	207.01	0.41
1.4196	0.8502	0.8217	3.471	198.17	198.91	-0.37
1.8329	0.9950	0.9777	1.769	187.22	187.77	-0.29
2.1313	1.0938	1.1106	-1.514	178.67	178.08	0.33
2.4837	1.2020	1.2014	0.053	168.21	168.24	-0.01
2.7552	1.2782	1.2826	-0.337	160.10	159.93	0.11

Table XXb   Calculated and Experimental Osmotic Coefficients and Vapor
Pressures of CaCl$_2$ at 50° C Using the Pitzer Equation

molality moles per kg solvent	ϕ_{Pit}	ϕ_{exp}	relative % error	P_{Pit} mmHg	P_{exp} mmHg	relative % error
0.2097	0.2250	0.2010	11.929	218.90	219.05	-0.07
0.3937	0.2371	0.2731	-13.175	217.51	217.08	0.20
0.6901	0.2894	0.2924	-1.018	214.33	214.27	0.03
0.8468	0.3304	0.3502	-5.644	211.97	211.48	0.23
1.0183	0.3819	0.3850	-0.808	208.80	208.71	0.04
1.2248	0.4480	0.4416	1.452	204.24	204.46	-0.11
1.4583	0.5220	0.4689	11.316	198.33	200.46	-1.06
1.9569	0.6507	0.6237	4.331	184.78	186.13	-0.73
2.4270	0.7068	0.7698	-8.182	173.82	170.19	2.14

Table XXII   Calculated and Experimental Osmotic Coefficients and Vapor
Pressures of LiCl at 50° C Using the Pitzer Equation

molality moles per kg solvent	ϕ_{Pit}	ϕ_{exp}	relative % error	P_{Pit} mmHg	P_{exp} mmHg	relative % error
0.7840	0.8603	0.8589	0.168	207.61	207.63	-0.01
1.7156	1.0732	1.0620	1.062	186.45	186.78	-0.18
2.4965	1.2680	1.3245	-4.263	165.03	162.90	1.31
3.4194	1.5196	1.4601	4.077	136.87	139.46	-1.86
3.7506	1.6141	1.6024	0.730	126.47	126.98	-0.40
4.3572	1.7911	1.8301	-2.130	107.63	105.96	1.58

Table XXIII   Calculated and Experimental Osmotic Coefficients and Vapor
Pressures of LiCl at 35° C Using the Pitzer Equation

molality moles per kg solvent	ϕ_{Pit}	ϕ_{exp}	relative % error	P_{Pit} mmHg	P_{exp} mmHg	relative % error
0.7840	0.6272	0.6284	-0.189	98.42	98.41	0.01
1.7156	0.7102	0.6952	2.156	92.04	92.26	-0.24
2.4965	0.8326	0.8793	-5.311	85.03	84.12	1.08
3.4194	1.0314	1.0131	1.803	74.41	74.84	-0.57
3.7506	1.1151	1.0692	4.295	70.05	71.17	-1.57
4.3572	1.2837	1.3289	-3.403	61.51	60.40	1.83

Table XXIV Calculated and Experimental Osmotic Coefficients and Vapor
Pressures of LiBr at 50° C Using the Pitzer Equation

molality moles per kg solvent	ϕ_{Pit}	ϕ_{exp}	relative % error	P_{Pit} mmHg	P_{exp} mmHg	relative % error
1.0950	0.7869	0.8845	-11.031	204.06	202.06	0.99
2.1652	1.3306	1.1006	20.902	169.42	177.37	-4.49
3.2221	1.8506	1.8637	-0.704	127.54	127.04	0.39
4.1475	2.2609	2.5485	-11.285	93.11	83.42	11.62
4.9489	2.5749	2.9637	-13.118	68.28	57.19	19.40
5.8547	2.8799	3.0792	-6.473	46.72	41.96	11.35
6.6974	3.1140	3.0815	1.053	32.34	32.99	-1.98
7.4944	3.2902	3.0142	9.154	22.78	27.56	-17.35

Table XXVa Calculated and Literature Osmotic Coefficients and Vapor
Pressures of $CaCl_2$ at 50° C Using the Bromley Equation and
the Average Value of ρ

molality moles per kg solvent	ϕ_{Brom}	ϕ_{lit}	relative % error	P_{Brom} mmHg	P_{exp} mmHg	relative % error
0.2415	0.1834	0.1899	-3.402	220.25	220.20	0.02
0.5759	0.2636	0.2867	-8.061	217.00	216.60	0.18
0.8104	0.3316	0.3660	-9.385	213.52	212.70	0.39
0.9776	0.3817	0.3838	-0.553	210.46	210.40	0.03
1.2235	0.4563	0.4489	1.637	205.14	205.40	-0.12
1.4704	0.5313	0.4973	6.845	198.92	200.30	-0.69
1.6551	0.5872	0.5815	0.990	193.74	194.00	-0.13
1.8831	0.6559	0.6400	2.480	186.82	187.60	-0.41
2.1615	0.7389	0.7409	-0.274	177.71	177.60	0.06
2.3795	0.8033	0.7882	1.916	170.15	171.00	-0.50

Table XXVb   Calculated and Experimental Osmotic Coefficients and Vapor Pressures of $CaCl_2$ at 50° C Using the Bromley Equation and the Average Value of ρ

molality moles per kg solvent	ϕ_{Brom}	ϕ_{exp}	relative % error	P_{Brom} mmHg	P_{exp} mmHg	relative % error
0.2097	0.1781	0.2010	-11.431	219.20	219.05	0.07
0.3937	0.2127	0.2731	-22.119	217.80	217.08	0.33
0.6901	0.2926	0.2924	0.057	214.27	214.27	0.00
0.8468	0.3381	0.3502	-3.464	211.78	211.48	0.14
1.0183	0.3888	0.3850	0.998	208.60	208.71	-0.05
1.2248	0.4505	0.4416	2.012	204.15	204.46	-0.15
1.4583	0.5203	0.4689	10.960	198.39	200.46	-1.03
1.9569	0.6682	0.6237	7.132	183.90	186.13	-1.20
2.4270	0.8051	0.7698	4.582	168.19	170.19	-1.18

Table XXVI Calculated and Experimental Osmotic Coefficients and Vapor
Pressures of NaI at 50° C Using the Bromley Equation and
the Average Value of ρ

molality moles per kg solvent	ϕ_{Brom}	ϕ_{exp}	relative % error	P_{Brom} mmHg	P_{exp} mmHg	relative % error
0.3367	0.6516	0.5208	25.102	217.05	217.93	-0.40
0.6603	0.6983	0.5824	19.900	212.27	213.77	-0.70
0.9881	0.7630	0.7421	2.807	206.62	207.01	-0.19
1.4196	0.8575	0.8217	4.360	197.98	198.91	-0.47
1.8329	0.9525	0.9777	-2.573	188.57	187.77	0.43
2.1313	1.0224	1.1106	-7.942	181.19	178.08	1.75
2.4837	1.1057	1.2014	-7.970	171.97	168.24	2.22
2.7552	1.1701	1.2826	-8.769	164.56	159.93	2.90

Table XXVII   Calculated and Experimental Osmotic Coefficients and Vapor
Pressures of LiCl at 50° C Using the Bromley Equation and
the Average Value of ρ

molality moles per kg solvent	ϕ_{Brom}	ϕ_{exp}	relative % error	P_{Brom} mmHg	P_{exp} mmHg	relative % error
0.7840	0.7783	0.8589	-9.379	208.84	207.63	0.58
1.7156	1.0383	1.0620	-2.229	187.48	186.78	0.37
2.4965	1.2700	1.3245	-4.110	164.95	162.90	1.26
3.4194	1.5474	1.4601	5.978	135.68	139.46	-2.71
3.7506	1.6471	1.6024	2.786	125.04	126.98	-1.53
4.3572	1.8296	1.8301	-0.028	105.98	105.96	0.02

Table XXVIII Calculated and Experimental Osmotic Coefficients and Vapor
Pressures of LiCl at 35° C Using the Bromley Equation and
the Average Value of ρ

molality moles per kg solvent	ϕ_{Brom}	ϕ_{exp}	relative % error	P_{Brom} mmHg	P_{exp} mmHg	relative % error
0.7840	0.6692	0.6284	6.499	98.12	98.41	-0.29
1.7156	0.7843	0.6952	12.823	90.97	92.26	-1.40
2.4965	0.8911	0.8793	1.337	83.89	84.12	-0.27
3.4194	1.0188	1.0131	0.567	74.70	74.84	-0.18
3.7506	1.0646	1.0692	-0.429	71.28	71.17	0.16
4.3572	1.1481	1.3289	-13.601	64.95	60.40	7.53

Table XXIX Calculated and Experimental Osmotic Coefficients and Vapor Pressures of LiBr at 50° C Using the Bromley Equation and the Average Value of ρ

molality moles per kg solvent	ϕ_{Brom}	ϕ_{exp}	relative % error	P_{Brom} mmHg	P_{exp} mmHg	relative % error
1.0950	0.9781	0.8845	10.585	200.16	202.06	-0.94
2.1652	1.3734	1.1006	24.791	167.98	177.37	-5.30
3.2221	1.7745	1.8637	-4.783	130.45	127.04	2.68
4.1475	2.1271	2.5485	-16.536	98.00	83.42	17.47
4.9489	2.4321	2.9637	-17.937	72.88	57.19	27.43
5.8547	2.7762	3.0792	-9.842	49.41	41.96	17.76
6.6974	3.0955	3.0815	0.454	32.71	32.99	-0.86
7.4944	3.3969	3.0142	12.694	21.16	27.56	-23.22

Table XXXa Calculated and Literature Osmotic Coefficients and Vapor Pressures of $CaCl_2$ at 50° C Using the Bromley Equation and the Optimum Value of ρ

molality moles per kg solvent	ϕ_{Brom}	ϕ_{lit}	relative % error	P_{Brom} mmHg	P_{lit} mmHg	relative % error
0.2415	0.1972	0.1899	3.880	220.14	220.20	-0.02
0.5759	0.2751	0.2867	-4.048	216.80	216.60	0.09
0.8104	0.3399	0.3660	-7.133	213.32	212.70	0.29
0.9776	0.3873	0.3838	0.896	210.30	210.40	-0.05
1.2235	0.4576	0.4489	1.932	205.10	205.40	-0.15
1.4704	0.5282	0.4973	6.210	199.05	200.30	-0.63
1.6551	0.5806	0.5815	-0.145	194.04	194.00	0.02
1.8831	0.6449	0.6400	0.774	187.36	187.60	-0.13
2.1615	0.7226	0.7409	-2.469	178.57	177.60	0.55
2.3795	0.7828	0.7882	-0.684	171.30	171.00	0.18

Table XXXb Calculated and Experimental Osmotic Coefficients and Vapor
Pressures of $CaCl_2$ at 50° C Using the Bromley Equation and
the Optimum Value of ρ

molality moles per kg solvent	ϕ_{Brom}	ϕ_{exp}	relative % error	P_{Brom} mmHg	P_{exp} mmHg	relative % error
0.2097	0.2087	0.2010	3.793	219.00	219.05	-0.02
0.3937	0.2405	0.2731	-11.945	217.47	217.08	0.18
0.6901	0.3094	0.2924	5.814	213.92	214.27	-0.16
0.8468	0.3477	0.3502	-0.714	211.54	211.48	0.03
1.0183	0.3899	0.3850	1.293	208.56	208.71	-0.07
1.2248	0.4408	0.4416	-0.175	204.49	204.46	0.01
1.4583	0.4980	0.4689	6.197	199.29	200.46	-0.58
1.9569	0.6178	0.6237	-0.941	186.43	186.13	0.16
2.4270	0.7277	0.7698	-5.467	172.61	170.19	1.42

Table XXXI Calculated and Experimental Osmotic Coefficients and Vapor
Pressures of NaI at 50° C Using the Bromley Equation and
the Optimum Value of ρ

molality moles per kg solvent	ϕ_{Brom}	ϕ_{exp}	relative % error	P_{Brom} mmHg	P_{exp} mmHg	relative % error
0.3367	0.5481	0.5208	5.240	217.74	217.93	-0.08
0.6603	0.5945	0.5824	2.080	213.61	213.77	-0.07
0.9881	0.6817	0.7421	-8.146	208.15	207.01	0.55
1.4196	0.8224	0.8217	0.088	198.89	198.91	-0.01
1.8329	0.9713	0.9777	-0.654	187.97	187.77	0.11
2.1313	1.0836	1.1106	-2.432	179.03	178.08	0.53
2.4837	1.2195	1.2014	1.508	167.54	168.24	-0.41
2.7552	1.3259	1.2826	3.383	158.18	159.93	-1.10

Table XXXII   Calculated and Experimental Osmotic Coefficients and Vapor
Pressures of LiCl at 50° C Using the Bromley Equation and
the Optimum Value of ρ

molality moles per kg solvent	ϕ_{Brom}	ϕ_{exp}	relative % error	P_{Brom} mmHg	P_{exp} mmHg	relative % error
0.7840	0.8495	0.8589	-1.091	207.77	207.63	0.07
1.7156	1.0839	1.0620	2.068	186.14	186.78	-0.35
2.4965	1.2857	1.3245	-2.928	164.36	162.90	0.90
3.4194	1.5246	1.4601	4.421	136.65	139.46	-2.01
3.7506	1.6102	1.6024	0.485	126.64	126.98	-0.27
4.3572	1.7666	1.8301	-3.471	108.70	105.96	2.58

Table XXXIII Calculated and Experimental Osmotic Coefficients and Vapor Pressures of LiCl at 35° C Using the Bromley Equation and the Optimum Value of ρ

molality moles per kg solvent	ϕ_{Brom}	ϕ_{exp}	relative % error	P_{Brom} mmHg	P_{exp} mmHg	relative % error
0.7840	0.5944	0.6284	-5.409	98.65	98.41	0.25
1.7156	0.7335	0.6952	5.505	91.71	92.26	-0.60
2.4965	0.8728	0.8793	-0.743	84.25	84.12	0.15
3.4194	1.0441	1.0131	3.060	74.11	74.84	-0.97
3.7506	1.1062	1.0692	3.458	70.26	71.17	-1.27
4.3572	1.2201	1.3289	-8.182	63.10	60.40	4.46

Table XXXIV   Calculated and Experimental Osmotic Coefficients and Vapor
Pressures of LiBr at 50° C Using the Bromley Equation and
the Optimum Value of ρ

molality moles per kg solvent	ϕ_{Brom}	ϕ_{exp}	relative % error	P_{Brom} mmHg	P_{exp} mmHg	relative % error
1.0950	0.8584	0.8845	-2.947	202.59	202.06	0.26
2.1652	1.2821	1.1006	16.499	171.06	177.37	-3.56
3.2221	1.7263	1.8637	-7.371	132.33	127.04	4.16
4.1475	2.1207	2.5485	-16.787	98.24	83.42	17.76
4.9489	2.4634	2.9637	-16.882	71.85	57.19	25.63
5.8547	2.8509	3.0792	-7.415	47.46	41.96	13.11
6.6974	3.2111	3.0815	4.205	30.45	32.99	-7.69
7.4944	3.5514	3.0142	17.820	19.02	27.56	-30.99

An examination of equation 69 for the Pitzer equation, indicates that in addition to the second virial coefficients β^0, β^1, and C^ϕ, the third virial coefficient, there are two other parameters, α and b which were assigned values of 2.0 and 1.2 respectively. This gives a total of five parameters which could be adjusted for a given salt.

The first term in equation 69 corresponds to the Debye-Huckel theory, the value of ρ in the Debye-Huckel theory is termed b by Pitzer. The second term, which contains the adjustable parameters, β^0, β^1, and α accounts for the transition between the Debye-Huckel region on a plot of $\gamma_\pm$ vs ionic strength. This term was found to work well for aqueous systems in both correlating the minimum as well as the linear portion. The relationship between these parameters is given following equation 69. It is in these expressions that the parameter α appears. For aqueous systems, this parameter is given a value of 2 and it appears to have no physical significance.

The parameter C^ϕ which is multiplied by the square of the molality, only serves to extend the Pitzer equation to higher concentrations. Its value is generally small and that has been observed here. Varying either α or b did not appear to have any significant effect on the results, therefore the were left at their original values.

Finally, the temperature dependence of the parameter B in the Bromley equation was investigated. The purpose was to see if some generalized correlation could be developed for this dependence in the ethanol systems. As shown in Figures 19 and 20 for the NaI and $CaCl_2$ systems, the slope of

both lines is in the opposite direction. Although each seem to correlate well with a simple straight line, the opposite sign on the slope caused any further investigation to stop.

CONCLUSIONS

The vapor pressure depression for $CaCl_2$, NaI, LiCl, and LiBr in ethanol at 50° C and also at 35° C for the LiCl system has been measured. From this data, osmotic coefficients for each electrolyte were calculated.

From the experimental osmotic coefficients, mean activity coefficients for the salts in ethanol were determined through the use of equations 83 and 84. This method was chosen over the graphical procedure for the reasons which have already been presented.

The experimental osmotic coefficient data were correlated with both the Pitzer equation and two forms of the Bromley. For 1-1 electrolytes, the Pitzer equation always performed better. For the $CaCl_2$ system, both Bromley methods out performed the Pitzer equation. On the basis of the parameters which were estimated from the experimental data, mean activity coefficients were generated by the three equations and compared to the experimental values.

Although all equations correlated the osmotic coefficient data, the calculated mean activity coefficients were much better for some systems than others. This was particularly evident with the Pitzer equation and the $CaCl_2$ system. One correlation method which was not tried, was to use the smoothed osmotic coefficients generated by equation 83.

Examination of the Bromley and Pitzer equations indicate that the parameters specific for ion-solvent interactions are, ρ, in the Bromley equation and α in the Pitzer equation. It has been shown that ρ can have a

significant impact on the correlation of that data. Evidence the fact that the Bromley (optimum ρ) always worked better than the Bromley (average ρ). Although it appears that α in the Pitzer equation should have an effect, none could be found for the ethanol system.

The temperature dependency of B in the Bromley equation was investigated. For the two systems for which data was available over a temperature range, a simple linear relationship existed between B and the temperature. No generalized correlation could be found between the temperature dependency and the individual salts. No attempt was made to find a relationship for the Pitzer equation as this would introduce too many parameters for practical purposes.

NOMENCLATURE

A_γ = Debye-Huckel constant for the activity coefficient

A_ϕ = Debye-Huckel constant for the osmotic coefficient

a = ion-size parameter or constant in equation 71 defined by equation 72

a_B = ion size defined in equation 61

a_1 = activity of solvent in solution

a_2 = activity of solute salt in solution

B = adjustable parameter in equations 74 and 75

Bo = adjustable parameter in equation 71

B^ϕ = second virial coefficient defined in equation 69

B^γ = second virial coefficient defined in equation 70

B_γ = constant defined in equation 55

b = constant in equations 69 and 70 and is equal to 1.2

C^ϕ = arbitrary constant in equations 69 and 70

c = concentration in moles salt/liter of solution

e = electronic charge

f = term defined for equations 69 and 70 which is a function of ionic strength

$\bar{G}$ = parital molal Gibbs free energy in solution

$\bar{G}^o$ = parital molal Gibbs free energy of the pure component

g_{ij} = radial distribution function

I = ionic strength

k = Boltzmann's constant

M_1 = molecular weight of solvent

m = molality, moles solute/kg of solvent

$m_{\pm}$ = mean molality, defined in equation 23

N_A = Avogadro's number

n_1 = number of moles of solvent

n_2 = number of moles of solute

n = equal to 2 in equation 71

P^S = vapor pressure of pure solvent

ΔP = vapor pressure depression

R = gas constant

S = Entropy

r = interionic distance

T = absolute temperature, °K

t = temperature, °C

U = internal energy

u_{ij} = interionic potential

V = volume of system

x_1 = mole fraction solvent

x_2 = mole fraction salt

z = charge on the ion; + refers to the cation and - refers to the anion

Greek Symbols

α = constant in equations 69 and 70 has a value of 1.2

β^0 = second virial coefficient in equations 69 and 70

β^1 = second virial coefficient in equations 69 and 70

ϵ = dielectric constant of the solvent

γ_1 = activity coefficient of the solvent

$\gamma_\pm$ = mean activity coefficient of the electrolyte

μ_1 = chemical potential of the solvent

$\mu^{\varnothing}$ = standard state chemical potential

μ_i = chemical potential defined in equation 2

ν_i = stoichiometeric number of ions of species i

ν = sum of stoichiometric number of ions

π = osmotic pressure or total system pressure

ρ = constant in equation 71, 74, 75, and 76

ϕ = osmotic coefficient

ψ = electrostatic potential

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APPENDIX A

Table XXXV   Coefficients Used in Equations 83 and 84 Obtained from
the Regression of Osmotic Coefficient vs Molality Data

System	A_1	A_2	A_3	A_4
$CaCl_2$ - EtOH[1]	44.71686	-73.90860	46.95961	-10.67691
$CaCl_2$ - EtOH	46.96611	-79.93294	52.26595	-12.22786
NaI - EtOH	4.490449	-3.250891	0.6860356	0.00000
LiCl - EtOH	7.494123	-7.687378	2.329779	0.00000
LiCl - EtOH[2]	6.086004	-6.321022	1.973240	0.00000
LiBr - EtOH	26.67349	-54.76918	40.04156	-9.848184

1 - Literature
2 - 35° C

Figure 21
Comparison of the Mean Activity Coefficient
Calculated by Graphical Integration and Eq 84
CaCl2 — EtOH at 50 deg C
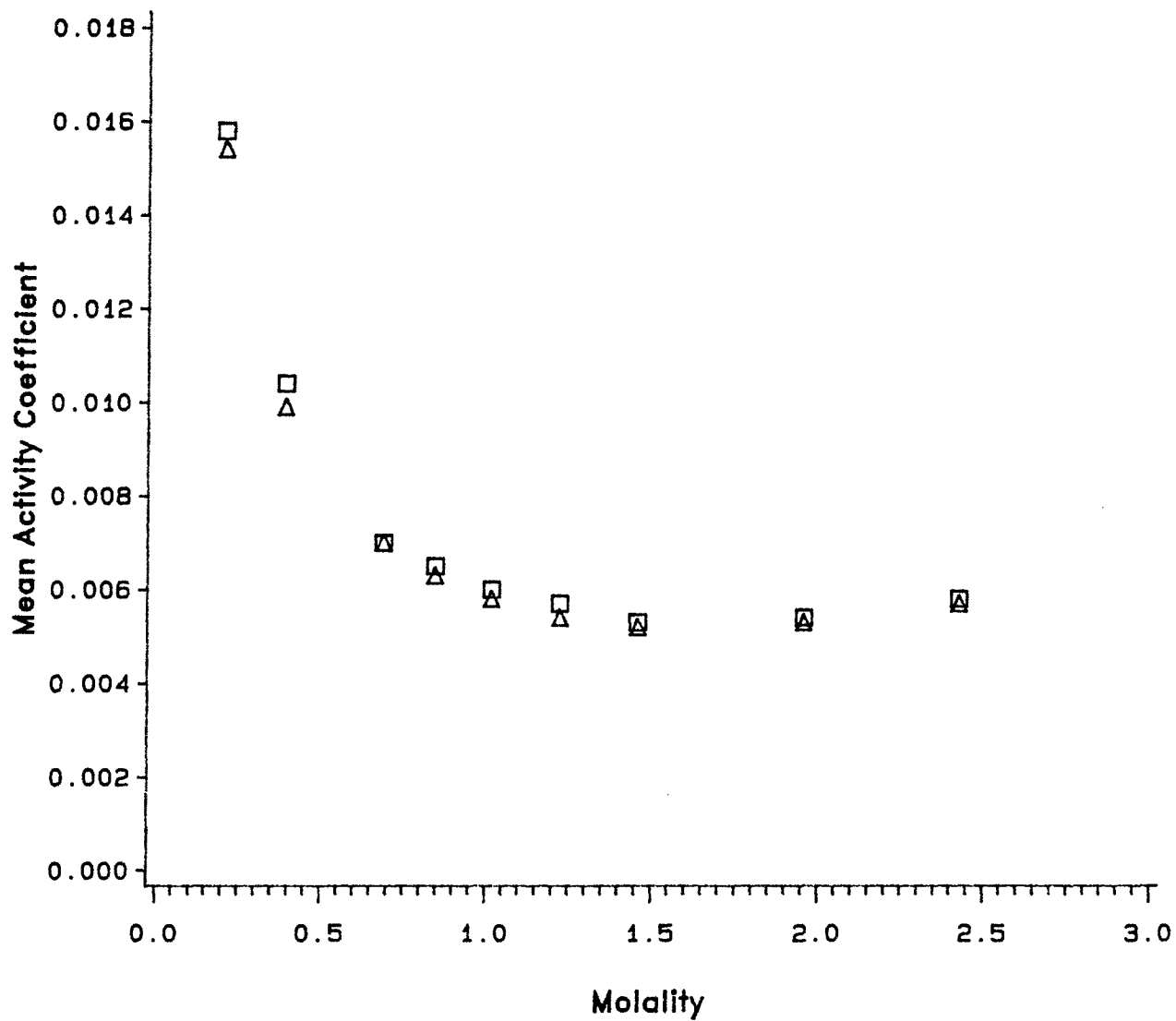
Graphically □
Equation 84 △

APPENDIX B

```
      PROGRAM POWLSALT
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
CCAT NO L40    POWELL METHOD
C
      INTEGER FZP,FZN
      DIMENSION TITLE(80),PE(50),P1(50),P2(50),PEP(50)
      DIMENSION GSOL(50),DP(50),SALTG(50),ORDY(50),ABSX(50)
      DIMENSION AA(50),F(50)
      COMMON /ONE/ X(10),Y(10),S(10),FX,FY
      COMMON/THREE/N,NFUNCT,NDRV,ITER,INDIC,IPRINT
      COMMON/MODEL/XS,GW,GCAL,NOPT,GEXP(50),NPHI,
     1 NP1,YY,NSYS,FNP,FNM,FZP,FZN,FK,XMOL(50),ADB,AMW,BB,ROW,MODL,
     2 GSALT,PCAL,PSM,VP,GER,PER,APHI(50),ADH,
     3 INDP,T
      COMMON/RESULT/PHI(50),GAMA(50),AOZ,IDEN
      DATA  A1,A2,A3,A4,A5 /5.9796E+01, -6.5950E+03, -5.0474E+00,
     1                      6.3000E-07, 2.0000E+00 /
      DATA ALFA /2.0/
      SUMT=0.D0
C
C     FNP IS THE NUMBER OF POSITIVE IONS
C     FNM IS THE NUMBER OF NEGATIVE IONS
C     FZP IS THE CHARGE OF THE POSITIVE ION
C     FZN IS THE CHARGE OF THE NEGATIVE ION
C     PSM IS THE VAPOR PRESSURE OF THE PURE COMPONENT
C     ADB IS THE DEBYE HUCKEL CONSTANT
C     NP1 IS THE NUMBER OF POINTS IN ONE SYSTEM
C     FK  IS THE TOTAL NUMBER OF IONS
C     AMWS IS THE MOLECULAR WEIGHT OF THE SALT
C     AMW IS THE MOLECULAR WEIGHT OF THE SOLVENT
C     ROW IS A VARIABLE IN BROMLEY'S EQUATION
C     N IS THE NUMBER OF PARAMETERS TO BE REGRESSED
C     NPG       0 - PHI VS MOLALITY
C               1 - GAMMA VS MOLALITY
C     AOZ IS A VARIABLE IN BROMLEY'S EQUATION
C
    1 READ(5,100,END=999) (TITLE(I),I=1,80)
C      READ(5,*) N,IPRINT,NPG,AOZ,IDEN
      READ(5,*) N,IPRINT,NPG,AOZ,PSM
      READ(5,*) (X(I),I=1,N)
      READ(5,*)ROW,T,ADB,AMW,AMWS,MODL,NP1,FK,FNP,FNM,FZP,FZN
      T1=T+273.15
      IF(PSM.EQ.0.)THEN
      PSM = EXP(A1 + (A2/T1) + (A3* LOG(T1)) + (A4*T1**A5))
      FAC1=760./101235.
      PSM=PSM*FAC1
      ELSE
      FAC1=760./101.325
      PSM=PSM*FAC1
      ENDIF
```

```fortran
      DO 20 I=1,NP1
      IF(NPG.EQ.0)THEN
      READ(5,*) APHI(I),XMOL(I)
      ELSE
      READ(5,*)GEXP(I),XMOL(I)
      ENDIF
   20 CONTINUE
      NFUNCT=0
      NDRV=0
      CALL MINI
      WRITE(6,10)
   10 FORMAT(1H1,'***** THE FINAL RESULTS ARE AS FOLLOWS *****'///)
      WRITE(6,11) ITER,NFUNCT,FX,(X(I),I=1,N)
   11 FORMAT(1X,'NUMBER OF ITERATIONS',12X,I3/1X,
     1 'NUMBER OF FUNCTION EVALUATIONS',2X,I3/1X,
     2 'FUNCTION VALUE',21X,G15.6/1X,
     3 'VALUE OF THE INDEPENDENT VARIABLES'/15X,4G15.6)
C     CALL ITIME(2)
      WRITE(3,36) (X(I),I=1,N),AOZ
   36 FORMAT(4G15.6)
      WRITE(6,35)
   35 FORMAT(2X,'THE FINAL RESULTS ARE'///)
      WRITE(6,100) (TITLE(I),I=1,80)
      WRITE(6,110)
      WRITE(6,500)
      SUM=0.0
      SUMPE=0.0
      DO 50 I=1,NP1
      IF(NPG.EQ.0)THEN
      DIF=PHI(I)-APHI(I)
      DIF1=ABS(PHI(I)-APHI(I))
      PE(I)=(DIF/APHI(I))*100D0
C
C     CALCULATE PRESSURE FROM OSMOTIC COEFFICENT
C
      ANS=1000D0/AMW
      AP=FNP*XMOL(I)
      AN=FNM*XMOL(I)
      XS=ANS/(ANS+AP+AN)
      RHS1=-PHI(I)*XMOL(I)*FK*AMW/1000D0
      RHS2=-APHI(I)*XMOL(I)*FK*AMW/1000D0
      P1(I)=PSM*EXP(RHS1)
      P2(I)=PSM*EXP(RHS2)
      DP(I)=PSM-P2(I)
      GSOL(I)=P2(I)/(XS*PSM)
      ABSX(I)=SQRT(XMOL(I))
      ORDY(I)=(1.0-APHI(I))/ABSX(I)
      PEP(I)=((P1(I)-P2(I))/P2(I))*100.D0
      SUMPE=SUMPE+ABS(PEP(I))
      ELSE
```

```
      DIF=GAMA(I)-GEXP(I)
      DIF1=ABS(GAMA(I)-GEXP(I))
      PE(I)=(DIF/GEXP(I))*100D0
      ENDIF
   50 SUM=SUM+ABS(PE(I))
      SUM=SUM/NP1
      SUMPE=SUMPE/NP1
      DO 30 I=1,NP1
      IF(NPG.EQ.0)THEN
      WRITE(6,40) XMOL(I),PHI(I),APHI(I),PE(I),P1(I),P2(I),PEP(I)
      ELSE
      WRITE(6,40) XMOL(I),GAMA(I),GEXP(I),PE(I)
      ENDIF
   30 CONTINUE
      DO 135 I=1,NP1
      WRITE(6,41) XMOL(I),P2(I),GSOL(I),APHI(I),DP(I),ORDY(I),ABSX(I)
   41 FORMAT(F12.4,F12.2,2F12.4,F12.3,2F12.4)
  135 CONTINUE
C
C     CALCULATE GAMMA SALT                           .
C
      IF(MODL.EQ.1)THEN
       B=X(1)
       DO 301 I = 1,NP1
       AA(I) = XMOL(I)*(FNP*FZP**2.+FNM*FZN**2.)/2.
       AT1 = -ADB*(FZP*FZN)*(AA(I)**0.5)/(1.+ROW*AA(I)**0.5)
       AT2 = (1.+1.5*AA(I)/(FZP*FZN))**2.
       SALTG(I) = EXP(2.303*(AT1+(0.06+0.6*B)*AA(I)*(FZP*FZN)/AT2
      1+B*AA(I)))
  301  CONTINUE
C
      ELSE IF(MODL.EQ.2)THEN
       B0=X(1)
       B1=X(2)
       C=X(3)
       FZPN=FZP+FZN-1
       BOM=4./3.
       CM=(2.**(2.5))/3
       DO590I=1,NP1
       AA(I)=XMOL(I)*(FNP*FZP**2.+FNM*FZN**2.)/2.
       A=1.+1.2*AA(I)**.5
       F(I)=-ADH*((AA(I)**.5)/A+(2./1.2)*LOG(A))
       T=EXP(-ALFA*AA(I)**.5)
       TA=2.*AA(I)
       GOTO(570,560),FZPN
  560  D=2.*BOM*B0+(.5*BOM*B1/AA(I))*(1.-T*(1.+2.*AA(I)**.5-TA))
       TERM=FZP*FZN*F(I)+XMOL(I)*2.*FNP*FNM*D/FK+2.*(XMOL(I)**2.)*
      * C*CM*((FNP*FNM)**1.5)/FK
       GOTO580
  570  D=2.*B0+(2.D0/ALFA**2)*B1/AA(I)*(1.-T*(1.+2.*AA(I)**.5-TA))
```

```fortran
      TERM=FZP*FZN*F(I)+2.*XMOL(I)*FNP*FNM*D/FK+2.*(XMOL(I)**2.)*
     * C*((FNP*FNM)**1.5)/FK
  580 SALTG(I)=EXP(TERM)
  590 CONTINUE
      ELSE IF(MODL.EQ.3)THEN
      CONTINUE
      ENDIF
      DO 600 I=1,NP1
      WRITE(6,610) XMOL(I),SALTG(I)
  600 CONTINUE
  610 FORMAT(2F12.4)
C  40 FORMAT(2X,3F12.4,G15.4,2F12.4)
   40 FORMAT(F9.4,F12.4,F12.4,F11.3,F9.2,F9.2,F10.2)
      WRITE(6,60) SUM,SUMPE
   60 FORMAT(//,5X,'   ABSOLUTE RELATIVE % ERROR IN PHI IS',F10.4,/
     1          5X,'   ABSOLUTE RELATIVE % ERROR IN P IS  ',F10.4)
  100 FORMAT(80A1)
  110 FORMAT(///)
  500 FORMAT(T2,'MOLALITY',T13,'PHI(CALC)',T26,'PHI(EXP)',T38,
     1 '% ERROR',T47,'P(CALC)',T57,'P(EXP)',T66,'% ERROR'/)
      SUMT=SUMT+SUM
      GOTO 1
  999 WRITE(6,61) SUMT
      WRITE(3,61) SUMT
   61 FORMAT(5X,'   TOTAL ABS. REL. % ERROR IS  ',F10.4)
      STOP
      END
      SUBROUTINE SEARCH
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
C  COGGIN METHOD OF UNDIMENSIONAL SEARCH
      COMMON /ONE/ X(10),Y(10),S(10),FX,FY
      COMMON /TWO/ H(10,10),DELX(10),DELG(10),GX(10)
      COMMON /THREE/ N,NFUNCT,NDRV,ITER,INDIC,IPRINT
C *** THE INITIAL VARIABLE VALUES ARE IN X, AND THE CORRESPONDING
C *** FUNCTION VALUE IS FX.
C *** THE SEARCH DIRECTION VECTOR IS S, AND THE INITIAL STEP SIZE STEP.
      IEXIT=0
      NTOL=4
      FTOL=.01D0
      FTOL2=FTOL/100.D0
      FA=FX
      FB=FX
      FC=FX
      DA=0.D0
      DB=0.D0
      DC=0.D0
      K=-2
      M=0
      STEP=1.0D0
      D=STEP
```

```
C   USE THE PARAMETER INDIC TO INDICATE HOW THE SEARCH VECTOR LENGTH
C   SHOULD BE SCALED.
C       INDIC=2  DO NOT SCALE.  TAKE LENGTH GIVEN BY MINI CALCULATION
C       INDIC=1 SCALE ONLY IF THE LENGTH OF THE LAST STEP WAS SHORTER THAN
C               THE LENGTH OF THE SEARCH VECTOR.  SCALE TO LENGTH OF LAST
C     INDIC=ANYTHING BUT 1 OR 2 RESULTS IN SCALING TO LENGTH OF LAST STEP
        IF(INDIC.EQ.2.OR.ITER.EQ.0)GOTO1
C   FIND NORM OF S AND NORM OF DELX
        DXNORM=0.
        SNORM=0.D0
        DO102I=1,N
        DXNORM=DXNORM+DELX(I)*DELX(I)
  102   SNORM=SNORM+S(I)*S(I)
        IF(INDIC.EQ.1.AND.DXNORM.GE.SNORM)GOTO1
        RATIO=DXNORM/SNORM
        STEP=DSQRT(RATIO)
        D=STEP
C *** START THE SEARCH THE BOUND THE MINIMUM
    1   DO2I=1,N
    2   Y(I)=X(I)+D*S(I)
        CALL FUN(Y,F)
        K=K+1
        IF(F-FA)5,3,6
C *** NO CHANGE IN FUNCTION VALUE. RETURN WITH VECTOR CORRESPONDING TO
C     FUNCTION VALUE OF FA. BECAUSE IF THE FUNCTION VALUE IS INDEPENDENT
C     OF THIS SEARCH DIRECTION, THEN CHANGES IN THE VARIABLE VALUES MAY
C     UPSET THE MAIN PROGRAM CONVERGENCE TESTING.
    3   DO4I=1,N
    4   Y(I)=X(I)+DA*S(I)
        FY=FA
        IF(IPRINT.EQ.1)WRITE(6,2100)
 2100   FORMAT('SEARCH FAILED.  FUNCTION VALUE INDEPENDENT OF SEARCH DIRE
      *CTION')
        GOTO326
C *** THE FUNCTION IS STILL DECREASING. INCREASE THE STEP SIZE BY
C     DOUBLE THE PREVIOUS INCREASE IN STEP SIZE.
    5   FC=FB
        FB=FA
        FA=F
        DC=DB
        DB=DA
        DA=D
        D=2.0D0*D+STEP
        GOTO1
C *** MINIMUM IS BOUNDED IN AT LEAST ONE DIRECTION.
    6   IF(K)7,8,9
C     MINIMUM IS BOUNDED IN ONE DIRECTION ONLY. REVERSE THE SEARCH
C     DIRECTION AND RECYCLE.
    7   FB=F
        DB=D
```

```
        D=-D
        STEP=-STEP
        GOTO1
C       MINIMUM IS BOUNDED IN BOTH DIRECTIONS AFTER ONLY TWO FUNCTION
C       EVALUATIONS 'ONE EITHER SIDE OF THE ORIGINZ.  PROCEED TO THE
C       PARABOLIC INTERPOLATION.
      8 FC=FB
        FB=FA
        FA=F
        DC=DB
        DB=DA
        DA=D
        GOTO21
C       THE MINIMUM IS BOUNDED AFTER AT LEAST TWO FUNCTION EVALUATIONS IN
C       THE SAME DIRECTION.  EVALUATE THE FUNCTION AT STEP SIZE=(DA+DB)/2.
C       THIS WILL YEILD 4 EQUALLY SPACED POINTS BOUNDING THE MINIMUM.
      9 DC=DB
        DB=DA
        DA=D
        FC=FB
        FB=FA
        FA=F
     10 D=0.5D0*(DA+DB)
        DO11I=1,N
     11 Y(I)=X(I)+D*S(I)
        CALL FUN(Y,F)
C *** NOW HAVE THAT FA*FB0FC AND THAT FA*F0FC ASSUMING THAT THE
C       FUNCTION IS UNIMODAL. REMOVE EITHER POINT A OR POINT B IN SUCH A
C       WAY THAT THE FUNCTION IS BOUNDED AND FA*FB0FC 'THE CORRESPONDING
C       STEP SIZES ARE DA*DB*DC OR DA0DB0DC Z.
     12 IF((DC-D)*(D-DB))15,13,18
C *** LOCATION OF MINIMUM IS LIMITED BY ROUNDING ERRORS.RETURN WITH B.
     13 DO14I=1,N
     14 Y(I)=X(I)+DB*S(I)
        FY=FB
        IF(IEXIT.EQ.1)GOTO32
        IF(IPRINT.EQ.1)WRITE(6,2200)
   2200 FORMAT('SEARCH FAILED.  LOCATION OF MINIMUM LIMITED BY ROUNDING')
        GOTO325
C *** THE POINT D IS IN THE RANGE DA TO DB
     15 IF(F-FB)16,13,17
     16 FC=FB
        FB=F
        DC=DB
        DB=D
        GOTO21
     17 FA=F
        DA=D
        GOTO21
C *** THE POINT D IS IN THE RANGE DB TO DC
```

```
   18 IF(F-FB)19,13,20
   19 FA=FB
      FB=F
      DA=DB
      DB=D
      GOTO21
   20 FC=F
      DC=D
C *** NOW PERFORM THE PARABOLIC INTERPOLATION.
   21 A=FA*(DB-DC)+FB*(DC-DA)+FC*(DA-DB)
      IF(A)22,30,22
   22 D=0.5D0*((DB*DB-DC*DC)*FA+(DC*DC-DA*DA)*FB+(DA*DA-DB*DB)*FC)/A
C     CHECK THAT THE POINT IS GOOD. IF SO, EVALUATE THE FUNCTION.
      IF((DA-D)*(D-DC))13,13,23
   23 DO24I=1,N
   24 Y(I)=X(I)+D*S(I)
      CALL FUN(Y,F)
C *** CHECK FOR CONVERGENCE. IF NOT ACHEIVED, RECYCLE.
      IF(DABS(FB)-FTOL2)25,25,26
   25 A=1.0D0
      GOTO27
   26 A=1.0D0/FB
   27 IF((DABS(FB-F)*A)-FTOL)28,28,12
C *** CONVERGENCE ACHEIVED. RETURN WITH THE SMALLER OF F AND FB.
   28 IEXIT=1
      IF(F-FB)29,13,13
   29 FY=F
      GOTO32
C *** THE PRABOLIC INTERPOLATION WAS PREVENTED BY THE DIVISOR BEING
C     ZERO.  IF THIS IS THE FIRST TIME THAT IT HAS HAPPENED. TRY AN
C     INTERMEDIATE STEP SIZE AND RECYCLED OTHERWISE GIVE UP AS IT LOOKS
C     LIKE A LOST CAUSE.
   30 IF(M)31,31,13
   31 M=M+1
      GOTO10
   32 DO99I=1,N
      IF(Y(1).NE.X(1))GOTO325
   99 CONTINUE
      GOTO33
  325 IF(NTOL.NE.0.AND.IPRINT.EQ.1)WRITE(6,3000)NTOL
 3000 FORMAT(1X,'TOLERANCE REDUCED',I1,'TIME(S)')
  326 IF(FY.LT.FX)RETURN
      IF((S(1).NE.-GX(1)).OR.(FY.LT.FX))RETURN
      WRITE(6,5000)
 5000 FORMAT('SEARCH FAILED ON A GRADIENT STEP.  JOB TERMINATED.')
      WRITE(6,5100) ITER,NFUNCT,NDRV,FY,(Y(I),I=1,N)
 5100 FORMAT(1X,3I7,E16.8,(5E16.8))
      STOP
   33 IF(NTOL.EQ.5)GOTO34
      IEXIT=0
```

```
      NTOL=NTOL+1
      FTOL=FTOL/2.D0
      GOTO12
   34 IF(IPRINT.EQ.1)WRITE(6,2000)
 2000 FORMAT(' A POINT BETTER THAN THE ENTERING POINT CANNOT BE FOUND.')
      RETURN
      END
      SUBROUTINE MINI
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
C   POWELL METHOD OF DIRECT SEARCH
C   SUBROUTINE TEST MUST BE PROVIDED FOR CONVERGENCE TESTING
      DIMENSION W(10),SECND(10)
      COMMON /ONE/ X(10),Y(10),S(10),FX,FY
      COMMON/TWO/ DIRECT(10,10),DUM(10),BEFORE(10),FIRST(10)
      COMMON/THREE/N,NFUNCT,NDRV,ITER,INDIC,IPRINT
      EQUIVALENCE (W,SECND)
C        CALL ITIME(1)
C *** N = THE NUMBER OF VARIABLES.
C      ICONVG=THE FINAL CONVERGENCE TEST DESIRED.
C           =1,TERMINATE AS SOON AS TESTING IS SATISFIED.
C           =2,AS SOON AS THE TESTING CRITERIA ARE SATISFIED INCREASE
C               ALL THE VARIABLES BY 10*ACC AND SOLVE PROBLEM AGAIN.
C      THEN PERFORM A LINE SEARCH BETWEEN THE SOLUTIONS IF DIFFERENT
C      SOLUTIONS ARE DEEMED TO BE FOUND.
C      STEP=THE INITIAL STEP SIZE.
C      ACC=THE REQUIRED ACCURACY IN THE FUNCTION AND VECTOR VALUES.
C      INSERT IPRINT=1 FOR COMPLETE PRINT OUT OR IPRINT=2 FINAL
C    1ANSWER ONLY
      ACC=.00001D0
      STEP=1.0D0
C   INDIC MUST BE SET TO 2
      INDIC=2
      ICONVG=2
      ITER=0
      NTRY=1
      N1=N-1
      STEPA=STEP
C *** SET UP THE INITIAL DIRECTION MATRIX (USING UNIT VECTORS).
      DO2I=1,N
      DO1J=1,N
    1 DIRECT(J,I)=0.D0
    2 DIRECT(I,I)=1.D0
C *** EVALUATED THE FUNCTION AT THE INITIAL VARIABLE VALUES.
  100 CALL FUN(X,FX)
      IF(IPRINT.EQ.1)WRITE(6,2000) ITER,NFUNCT,FX,(X(I),I=1,N)
 2000 FORMAT(1X,2I7,E16.8,(5E16.8))
      GOTO301
C *** SAVE THE FINAL FUNCTION VALUE (F1) AND THE FINAL VARIABLE VALUES
C      (BEFORE) FROM THE PREVIOUS CYCLE.
    3 ITER=ITER+1
```

```
              IF(IPRINT.EQ.1)WRITE(6,2000)ITER,NFUNCT,FX,(X(I),I=1,N)
      301 F1=FX
              DO4I=1,N
        4 BEFORE(I)=X(I)
              SUM=0.D0
C         AT THE END OF THE CYCLE, SUM WILL CONTAIN THE MAXIMUM CHANGE IN
C         THE FUNCTION VALUE FOR ANY SEARCH DIRECTION, AND ISAVE INDICATES
C         THE DIRECTION VECTOR TO WHICH IT CORRESPONDS.
              DO9I=1,N
C         S CONTAINS THE INITIAL STEP SIZES IN THE I-TH DIRECTION.
              DO5J=1,N
        5 S(J)=DIRECT(J,I)*STEP
C         FIND THE MINIMUM IN THE I-TH DIRECTION, AND THE CHANGE IN FUNCTION
C         VALUE.
              CALL SEARCH
              A=FX-FY
              IF(A-SUM)7,7,6
        6 ISAVE=I
              SUM=A
C         TRANSFER THE NEW FUNCTION AND VARIABLE VALUES TO FX AND X.
        7 DO8J=1,N
        8 X(J)=Y(J)
        9 FX=FY
C *** NOW INVESTIGATE WHETHER A NEW SEARCH DIRECTION SHOULD BE INCORPOR-
C         ATED INSTEAD OF THE ISAVE DIRECTION.
              F2=FX
              DO10I=1,N
       10 W(I)=2.0D0*X(I)-BEFORE(I)
              CALL FUN(W,F3)
              A=F3-F1
              IF(A)11,19,19
       11 A=2.0D0*(F1-2.0D0*F2+F3)*((F1-F2-SUM)/A)**2
              IF(A-SUM)12,19,19
C *** A NEW SEARCH DIRECTION IS REQUIRED. FIRST REMOVE ROW ISAVE.
       12 IF(ISAVE-N)13,15,15
       13 DO14I=ISAVE,N1
              II=I+1
              DO14J=1,N
       14 DIRECT(J,I)=DIRECT(J,II)
C         SET THE NITH DIRECTION VECTOR EQUAL TO THE NORMALISED DIFFERENCE
C         BETWEEN THE INITIAL AND FINAL VARIABLE VALUES FOR LAST CYCLE.
       15 A=0.D0
              DO16J=1,N
              DIRECT(J,N)=X(J)-BEFORE(J)
       16 A=DIRECT(J,N)**2+A
              A=1.0D0/DSQRT(A)
              DO17J=1,N
              DIRECT(J,N)=DIRECT(J,N)*A
       17 S(J)=DIRECT(J,N)*STEP
              CALL SEARCH
```

```
          FX=FY
          DO18I=1,N
       18 X(I)=Y(I)
C *** TEST FOR CONVERENCE.
       19 CALL TEST(F1,FX,BEFORE,X,FLAG,N,ACC)
          CALL DATSW(15,II)
          IF(II.EQ.1) RETURN
          IF(FLAG)22,22,20
C *** CONVERGENCE NOT YET ACHEIVED.  COMPUTE A NEW STEP SIZE
C     AND GO BACK TO 3.
       20 IF(F1-FX)121,120,120
      121 STEP=-0.4D0*DSQRT(DABS(F1-FX))
          GOTO123
      120 STEP=0.4D0*DSQRT(F1-FX)
      123 IF(STEPA-STEP)21,3,3
       21 STEP=STEPA
          GOTO3
C *** CONVERGENCE ACHEIVED. IF ICONVG=2, INCREASE ALL VARIABLES BY
C     10*ACC AND GO BACK TO 3.
       22 GOTO(23,24),ICONVG
       23 RETURN
       24 GOTO(25,27),NTRY
       25 NTRY=2
          IF(IPRINT.EQ.1)WRITE(6,816)
      816 FORMAT(' CONV ACHIEVED  INC VAR BY 1000*ACC***********'/)
          DO26I=1,N
          FIRST(I)=X(I)
       26 X(I)=X(I)+ACC*1000.D0
          FFIRST=FX
          GOTO100
C *** CONVERGENCE ATTAINED USING TWO DIFFERENT STARTING POINTS. CONSTRUC
C     UNIT VECTOR BETWEEN SOLUTIONS AND SEARCH DIRECTION FOR A MINIMUM.
       27 FSECND=FX
          A=0.D0
          DO28I=1,N
          SECND(I)=X(I)
          S(I)=FIRST(I)-SECND(I)
       28 A=A+S(I)**2
          IF(A)23,23,29
       29 A=STEP/DSQRT(A)
          DO30I=1,N
       30 S(I)=S(I)*A
          CALL SEARCH
C *** TEST IF NEW POINT IS SUFFICIENTLY CLOSE TO EITHER OF THE TWO
C     SOLUTIONS.  IF SO RETURN.
          CALL TEST(FFIRST,FY,FIRST,Y,FLAG,N,ACC)
          IF(FLAG)32,32,31
       31 CALL TEST(FSECND,FY,SECND,Y,FLAG,N,ACC)
          IF(FLAG)32,32,34
       32 DO33I=1,N
```

```fortran
   33 X(I)=Y(I)
      FX=FY
      RETURN
C *** FINAL SOLUTION NOT ACCURATE ENOUGH.  REPLACE THE FIRST DIRECTION
C     VECTOR BY INTER-SOLUTION VECTOR (NORMALIZED) AND RECYCLE.
   34 A=A/STEP
      DO35I=1,N
      DIRECT(I,1)=(FIRST(I)-SECND(I))*A
   35 FIRST(I)=SECND(I)
      GOTO3
      END
      SUBROUTINE TEST(FI,FF,RI,RF,FLAG,N,ACC)
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
C THIS SUBROUTINE IS PECULIAR TO THE POWELL METHOD OF DIRECT SEARCH
      DIMENSION RI(10),RF(10)
      FLAG=+2.D0
      IF(DABS(FI)-ACC)2,2,1
    1 IF(DABS((FI-FF)/FI)-ACC)3,3,7
    2 IF(DABS(FI-FF)-ACC)3,3,7
    3 DO6I=1,N
      IF(DABS(RI(I))-ACC)5,5,4
    4 IF(DABS((RI(I)-RF(I))/RI(I))-ACC)6,6,7
    5 IF(DABS(RI(I)-RF(I))-ACC)6,6,7
    6 CONTINUE
      FLAG=-2.D0
    7 RETURN
      END
      SUBROUTINE ITIME (M)
      CHARACTER*8 TYME(2)
      INTEGER*2 ST(2,3)
      L = 6
      IF (M .GT. 1) GO TO 10
      CALL TIME_INIT
      CALL TIME(TYME(1))
      CALL IDATE(ST(1,1),ST(1,2),ST(1,3))
      CALL SECOND(CPU)
      GO TO 20
   10 CONTINUE
      CALL TIME(TYME(2))
      CALL IDATE(ST(2,1),ST(2,2),ST(2,3))
      CALL SECOND(CPU)
      WRITE(L,50) TYME(1),(ST(1,J),J=1,3)
   50 FORMAT(///' JOB STARTED AT  ',A8,5X,I2,'/',I2,'/',
     1I2)
      WRITE(L,51) TYME(2),(ST(2,J),J=1,3)
   51 FORMAT(  /' JOB FINISHED AT ',A8,5X,I2,'/',I2,'/',
     1I2)
      WRITE(L,52) CPU
   52 FORMAT(/' CPU TIME FOR EXECUTION, SEC. ',F10.3)
   20 RETURN
```

```
                      END
                      SUBROUTINE FUN(Z,FX)
                      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
                      INTEGER FZP,FZN
                      DIMENSION Z(10),TM(6)
                      COMMON/RESULT/PHI(50),GAMA(50),AOZ,IDEN
                      COMMON/THREE/N,NFUNCT,NDRV,ITER,INDIC,IPRINT
                      COMMON/MODEL/XS,GW,GCAL,NOPT,GEXP(50),NPHI,
                     1 NP1,YY,NSYS,FNP,FNM,FZP,FZN,FK,XMOL(50),ADB,AMW,BB,ROW,MODL,
                     2 GSALT,PCAL,PSM,VP,GER,PER,APHI(50),ADH,
                     3 INDP,T
      C
      C     FNP IS THE NUMBER OF POSITIVE IONS
      C     FNM IS THE NUMBER OF NEGATIVE IONS
      C     FZP IS THE CHARGE OF THE POSITIVE ION
      C     FZN IS THE CHARGE OF THE NEGATIVE ION
      C     PSM IS THE VAPOR PRESSURE OF THE PURE COMPONENT
      C     ADB IS THE DEBYE HUCKEL CONSTANT
      C     NP1 IS THE NUMBER OF POINTS IN ONE SYSTEM
      C     FK  IS THE TOTAL NUMBER OF IONS
      C     AMWS = MOLECULAR WEIGHT OF SALT
      C     AMW = MOLECULAR WEIGHT OF SOLVENT
      C
      C     NOPT = 1 FOR DELTA P VS. MOLALITY
      C     NOPT = 2 FOR PHI VS. MOLALITY
      C     NOPT = 3 FOR GAMA OF SALT VS. MOLALITY
      C
      C     IND = 0  XMOL = WEIGHT FRACTION SALT
      C     IND = 1  XMOL = MOLE FRACTION SALT
      C     IND = 2  XMOL = MOLALITY
      C
      C     IF IONS = 1 MEAN IONIC CONCENTRATION IS USED FOR SALT MOLE FRACTIO
      C     IF IONS = 2 COMPLETE DISSOCIATION IS USED FOR SALT MOLE FRACTION
      C
      C     INDP = 1 DATA ARE VAPOR PRESSURE DEPRESSION VS. MOLE FRACTION
      C     INDP = 2 DATA ARE VAPOR PRESSURE VS. MOLE FRACTION
      C     INDP = 3 DATA ARE PHI VS. MOLALITY
      C
                      NPF=N
                      IND=2
                      TK=T+273.15
                      NOPT=2
                      GOTO(150,151,155,150,151),MODL
                150   XT1=Z(1)
                      XT2=Z(2)
                      XT3=Z(3)/(FZP*FZN)
                      IF(NPF.EQ.1.OR.NPF.EQ.2) XT3=AOZ/(FZP*FZN)
      C          IF(NPF.EQ.1.) XT2=0.647029-1.13911*XT1
                      NPHI=NPF
                      GOTO 161
```

```
C   151 IF(MODL.GT.2) GOTO 155
    151 CONTINUE
        CPHI=0.D0
        ALFA=2.0D0
        B0=Z(1)
        B1=Z(2)
        IF(NPF.EQ.3) CPHI=Z(3)
        IF(NPF.EQ.4) ALFA=Z(4)
        GOTO 161
    155 AAA=Z(1)
    161 CONTINUE
C
C       DIELECTRIC CONSTANT CALCULATED FOR METHANOL OR ETHANOL
C       T IS IN DEGREES C
C
        DIELEC=28.33288D0*EXP(-0.6186544D-2*T)
C
C       SATURATED LIQUID DENSITY CALCULATED FOR ETHANOL
C       T IS IN DEGREES C
C
C        IF(IDEN.EQ.1)THEN
C        DEN=2.3080/2.7192E-1**(1+(1-TK/512.58)**2.3310E-1)
C        ELSE
        DEN=1.5223/2.6395E-1**(1+(1-TK/516.25)**2.3670E-1)
C        ENDIF
        DO=DEN*46.07/1000.
        IF(ADB.EQ.0.00)THEN
        ADB=1.824829238D06*SQRT(DO)/(TK*DIELEC)**(1.5)
        ENDIF
        GOTO (171,172,173,174,175),MODL
    171 CALL FUNC (XT1,XT2,XT3,YS)
        GOTO 160
    172 CALL FN (B0,B1,CPHI,ALFA,YS)
        GOTO 160
    173 CALL FN1(AAA,DIELEC,DO,YS)
        GOTO 160
    174 CALL FUNCB (XT1,XT2,XT3,YS)
        GOTO 160
    175 CALL FNG (B0,B1,CPHI,ALFA,YS)
    160 FX=YS
    180 CONTINUE
C
        NFUNCT=NFUNCT+1
        RETURN
        END
        SUBROUTINE FUNC(XT1,XT2,XT3,YS)
C
C       CALCULATES PHI USING VARIOUS FORMS OF THE BROMLEY EQUATION
C
        IMPLICIT REAL*8 (A-H,O-Z)
```

```
      INTEGER FZP,FZN
      COMMON/RESULT/PHI(50),GAMA(50),AOZ,IDEN
      COMMON/MODEL/XS,GW,GCAL,NOPT,GEXP(50),NPHI,
     1 NP1,YY,NSYS,FNP,FNM,FZP,FZN,FK,XMOL(50),ADB,AMW,BB,ROW,MODL,
     2 GSALT,PCAL,PSM,VP,GER,PER,APHI(50),ADH,
     3 INDP,T
      GOTO(10,20,30),NPHI
   10 B=XT1
      AA=AOZ/(FZP*FZN)
C       BOMB=0.647029-1.13911*B
C       BOMB=1.097079-2.06475*B
      GOTO 40
C
C     FIND B AND ROW IN BROMLEY AA HELD TO VALUE GIVEN ON INPUT
C
   20 B=XT1
      ROW=XT2
      AA=AOZ/(FZP*FZN)
C       AA=ABS(XT3)
      GOTO 40
   30 B = XT1
      AA=ABS(XT3)
      BOMB=XT2
   40 CONTINUE
      YS=0D0
      DO 65 I=1,NP1
      AI  = XMOL(I)*(FNP*FZP**2.+FNM*FZN**2.)/2.
      AT  = AA*AI
      SAI = ((1.+2.*AT)/((1.+AT)**2.)-LOG(1.+AT)/(AT))*2./AT
      AT1 = 1.+ROW*(AI **0.5)
      AT2 = 3./((ROW*AI **0.5)**3.)
      SIG  = AT2*(AT1-1./AT1-2.*LOG(AT1))
      GOTO(50,50,60),NPHI
C
C     NORMAL BROMLEY EQUATION
C
   50 PHI(I) = 1.-2.303*ADB*(FZP*FZN)*(AI **0.5)*SIG /3.+
     1 2.303*(0.06+0.6*B)*(FZP*FZN)*AI *SAI /2.+2.303*B*AI /2.
      GOTO 61
C
C     USED TO FIND B0-B AS A FUNCTION OF TEMPERATURE
C
   60 PHI(I) = 1.-2.303*ADB*(FZP*FZN)*(AI **0.5)*SIG /3.+
     1 2.303*(BOMB)*AI*SAI /2.+2.303*B*AI /2.
   61 DIF=ABS(PHI(I)-APHI(I))
      Y=(DIF/APHI(I))**2
      YS=YS+Y
   65 CONTINUE
   70 RETURN
      END
```

```
      SUBROUTINE FN(B0,B1,CPHI,ALFA,YS)
C
C     CALCULATES PHI USING THE EXTENDED PITZER EQUATION
C
      IMPLICIT REAL*8 (A-H,O-Z)
      INTEGERFZP,FZN,FZPN
      COMMON/RESULT/PHI(50),GAMA(50),AOZ,IDEN
      COMMON/MODEL/XS,GW,GCAL,NOPT,GEXP(50),NPHI,
     1 NP1,YY,NSYS,FNP,FNM,FZP,FZN,FK,XMOL(50),ADB,AMW,BB,ROW,MODL,
     2 GSALT,PCAL,PSM,VP,GER,PER,APHI(50),ADH,
     3 INDP,T
      YS=0D0
      DO 65 I=1,NP1
      ADH=ADB*2.302585D0/3D0
      AI =XMOL(I) *(FNP*FZP**2.+FNM*FZN**2.)/2.
      FPHI =-(ADH*AI **.5)/(1.+ROW*AI **.5)
      BMX =B0+B1*EXP(-ALFA*AI **.5)
      C=CPHI
      PHI(I) =1.+FZP*FZN*FPHI +2.*XMOL(I)*FNP*FNM*BMX/FK+2.*
     * (XMOL(I) **2.)*((FNP*FNM)**1.5)*C/FK
      DIF=ABS(PHI(I)-APHI(I))
      Y=(DIF/APHI(I))**2
      YS=YS+Y
   65 CONTINUE
      RETURN
      END
      SUBROUTINE FN1(AAA,DIELEC,D0,YS)
C
C     CALCULATES PHI USING THE ONE PARAMETER PITZER EQUATION
C
      IMPLICIT REAL*8 (A-H,O-Z)
      INTEGERFZP,FZN,FZPN
      COMMON/RESULT/PHI(50),GAMA(50),AOZ,IDEN
      COMMON/MODEL/XS,GW,GCAL,NOPT,GEXP(50),NPHI,
     1 NP1,YY,NSYS,FNP,FNM,FZP,FZN,FK,XMOL(50),ADB,AMW,BB,ROW,MODL,
     2 GSALT,PCAL,PSM,VP,GER,PER,APHI(50),ADH,
     3 INDP,T
      YS=0D0
      TA=T+273.15D0
      ELEC=4.80223D-10
      AVOG=6.0238D23
      BOLTZ=1.380257D-16
      PI=3.14D0
      AK1=((8D0*PI*AVOG*ELEC**2)/(1000D0*DIELEC*BOLTZ*TA))**.5D0
      AL=(ELEC**2D0)/(DIELEC*BOLTZ*TA)
      FF=ABS(AAA)*1D-8
      W=(FNP*FZP**2D0+FNM*FZN**2D0)/FK
      TERM4=((2D0*PI*FF**(3D0))/3D0)
      BB=ABS(AAA)*AK1*1D-8
      DO 65 I=1,NP1
```

```
      AI=XMOL(I)*D0*(FNP*FZP**2D0+FNM*FZN**2D0)/2D0
      TERM5=(PI*FF*((AL)**2D0)*(W**2D0))/(3D0*(1D0+BB*AI**.5D0)**2D0)
      D=(XMOL(I)*D0*FK*AVOG)/(1000D0)
      T4=D*TERM4
      T5=D*TERM5
      C=-W*AL/6D0
      TERM1=C*((AK1*AI**.5D0)/(1D0+BB*AI**.5D0))
      PHI(I)=TERM1+T5+T4+1D0
      DIF=ABS(PHI(I)-APHI(I))
      Y=(DIF/APHI(I))**2
      YS=YS+Y
   65 CONTINUE
      RETURN
      END
      SUBROUTINE FUNCB(XT1,XT2,XT3,YS)
C
C     CALCULATES GAMMA USING VARIOUS FORMS OF THE BROMLEY EQUATION
C
      IMPLICIT REAL*8 (A-H,O-Z)
      INTEGER FZP,FZN
      COMMON/MODEL/XS,GW,GCAL,NOPT,GEXP(50),NPHI,
     1 NP1,YY,NSYS,FNP,FNM,FZP,FZN,FK,XMOL(50),ADB,AMW,BB,ROW,MODL,
     2 GSALT,PCAL,PSM,VP,GER,PER,APHI(50),ADH,
     3 INDP,T
      COMMON/RESULT/PHI(50),GAMA(50),AOZ,IDEN
      GOTO(10,20,30),NPHI
   10 B=XT1
      AA=AOZ/(FZP*FZN)
C       BOMB=0.647029-1.13911*B
C       BOMB=1.097079-2.06475*B
      GOTO40
   20 B=XT1
      BOMB=XT2
      AA=ABS(XT3)
      GOTO40
   30 B=XT1
      BOMB=XT2
      AA=ABS(XT3)
   40 CONTINUE
C
      YS=0.D0
      DO65I=1,NP1
      AI=XMOL(I)*(FNP*FZP**2.+FNM*FZN**2.)/2.
      AT1=-ADB*(FZP*FZN)*(AI**0.5)/(1.+ROW*AI**0.5)
      AT2=(1.+AA*AI)**2.
C       AT2=(1.+1.5*AI/(FZP*FZN))**2.
      GOTO(60,60,60),NPHI
   50 GAMA(I)=EXP(2.303*(AT1+(0.06+0.6*B)*AI*(FZP*FZN)/AT2+B*AI))
      GOTO61
   60 GAMA(I)=EXP(2.303*(AT1+(BOMB)*AI*(FZP*FZN)/AT2+B*AI))
```

```
   70 CONTINUE
   61 DIF=ABS(GAMA(I)-GEXP(I))
      Y=(DIF/GEXP(I))**2
      YS=YS+Y
   65 CONTINUE
      RETURN
      END
      SUBROUTINE FNG(B0,B1,CPHI,ALFA,YS)
C
C     CALCULATES GAMMA USING THE EXTENDED PITZER EQUATION
C
      IMPLICIT REAL*8 (A-H,O-Z)
      INTEGERFZP,FZN,FZPN
      COMMON/MODEL/XS,GW,GCAL,NOPT,GEXP(50),NPHI,
     1 NP1,YY,NSYS,FNP,FNM,FZP,FZN,FK,XMOL(50),ADB,AMW,BB,ROW,MODL,
     2 GSALT,PCAL,PSM,VP,GER,PER,APHI(50),ADH,
     3 INDP,T
      COMMON/RESULT/PHI(50),GAMA(50),AOZ,IDEN
      YS=0.D0
      DO65I=1,NP1
      ADH=ADB*2.302585D0/3D0
      AO=XMOL(I)*(FNP*FZP**2.+FNM*FZN**2.)/2.
      A=1.+ALFA*AO**.5
      F=-ADH*(AO**.5/A+(2./ALFA)*DLOG(A))
      T=EXP(-2.*AO**.5)
      TA=2.*AO
      BMX=2.*B0+.5*B1/AO*(1.-T*(1.+2.*AO**.5-TA))
      C=1.5*CPHI
      TERM=FZP*FZN*F+2.*XMOL(I)*FNP*FNM*BMX/FK+(XMOL(I)**2.)*2.*
     * (FNP*FNM)**1.5*C/FK
      GAMA(I)=EXP(TERM)
      DIF=ABS(GAMA(I)-GEXP(I))
      Y=(DIF/GEXP(I))**2
      YS=YS+Y
   65 CONTINUE
      RETURN
      END
```

APPENDIX C

In order to justify the use of equations 83 and 84, a trial run was made on the $CaCl_2$ - H_2O system for which accurate data is available for both the osmotic and mean activity coefficients. The purpose of this test was to determine what effect a perturbation in the last available osmotic coefficient would have, on the calculation of the mean activity coefficient.

The classical method of determining mean activity coefficients, from experimental osmotic coefficients, involves the graphical integration of equation 82. The problem with this method is that very often, sufficient data are not available at low concentrations. This makes the extrapolation to infinite dilution difficult. Another problem is that the lowest concentration data, are often subject to errors in pressure due to the small differences being measured. These differences do not have to be large in this region to cause significant errors in the quantity $(1-\phi)/m^{1/2}$. As pointed out by Tomasula (53) for the $KCl-H_2O$ system, a difference as small as 0.004 mmHg, at a concentration of 0.1m, can produce errors as large as $\pm 60\%$ in the value of $(1-\phi)/m^{1/2}$ when compared to the experimental value. This would translate into an error of about 20% in the mean activity coefficient.

To try and circumvent this problem, an alternative approach was sought. Equations 83 and 84 seemed to present that alternative. To test the method, the $CaCl_2-H_2O$ system was chosen since data were available from 0.0001m to 10m. The test involved the following steps: 1) delete all data less than 0.1m, 2) regress the data for the coefficients in equation 83,

and 3) use the constants along with equation 84 to calculate the mean activity coefficients. These steps were repeated two more times, once with the osmotic coefficient at 0.1m perturbed by a value of 1.1 and once by a value of 0.9. These 10% perturbations, correspond to a ±57% error in the value of $(1-\phi)/m^{\frac{1}{2}}$. Figure 24 shows what this looks like in terms of the graphical method. It can be seen that a significant error can occur in the extrapolation to zero concentration.

The results of the perturbations on equations 83 and 84 can be seen in Figures 22 and 23. These Figures represent a full range and partial range plot of the calculated and experimental mean activity coefficients. At no point on either plot do the $\gamma_{\pm}$ values disagree by more than 10%.

On the basis of these results and the problems encountered by both Bixon (55) and Tomasula (53), it was decided that equations 83 and 84 not only represented a faster way to determine the mean activity coefficients, but also a more accurate way.
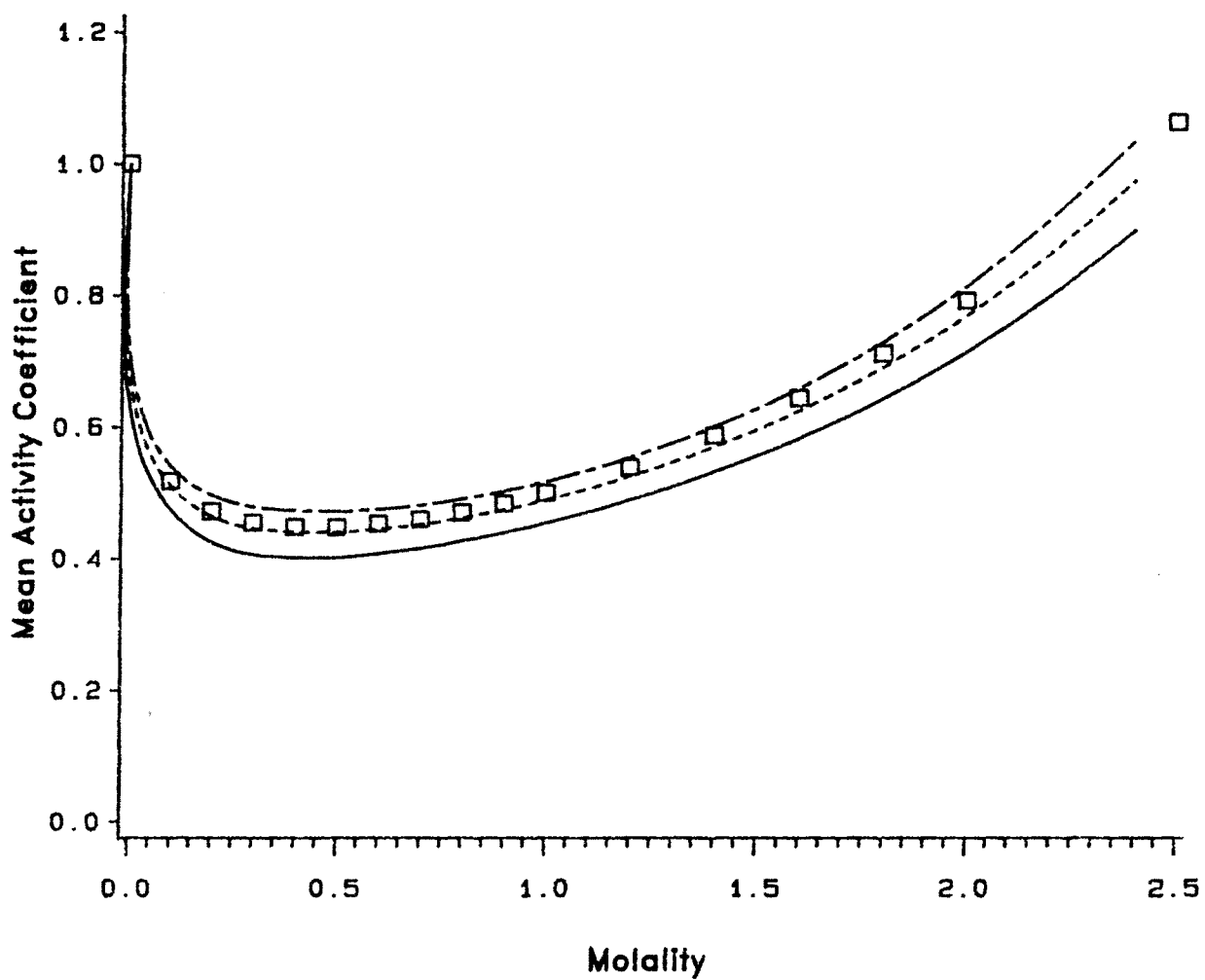
Figure 22
Comparison of Mean Activity Coefficient
System: CaCl2 — H2O at 25 deg C
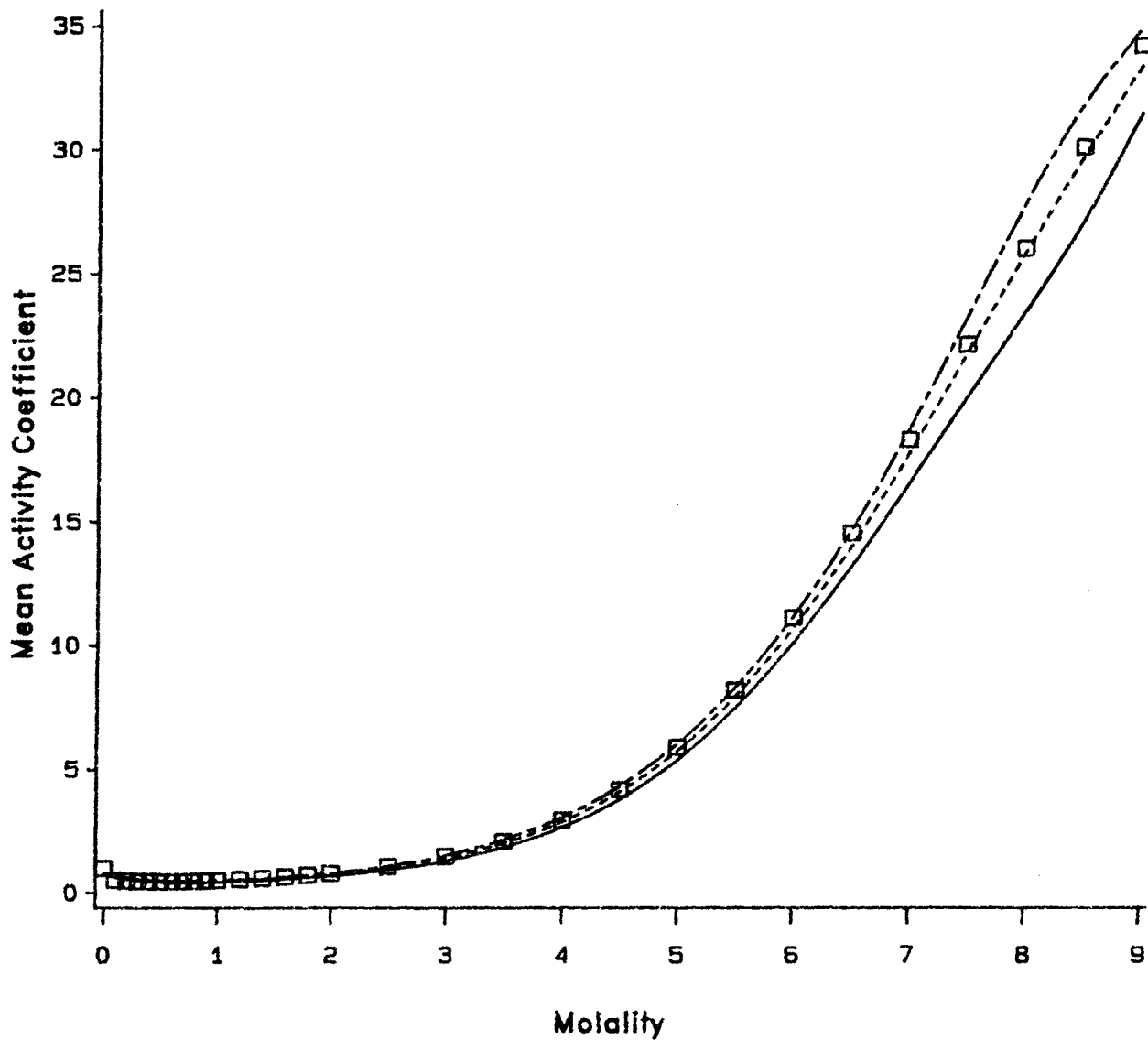
Using Phi at 0.1m 10% Low ————————

Using Phi at 0.1m — — — — — —

Using Phi at 0.1m 10% High — · — — · — ·

Literature Ref (32) ☐

Figure 23
Comparison of Mean Activity Coefficient
System: CaCl2 – H2O at 25 deg C

Using Phi at 0.1m 10% Low ————————

Using Phi at 0.1m — — — — — — —

Using Phi at 0.1m 10% High — — — — — — —

Literature Ref (32) □

Figure 24
Plot of Equation 82
CaCl2 — H2O 25 deg C