ABSTRACT

Vapor pressure depression data of LiBr and LiCl in methanol at temperatures of 25,35, and 45°C were measured in the molality range 0.1-4.4m using a static method, where the difference in vapor pressure of the electrolytic solution is compared to that of pure methanol.

Osmotic coefficients were calculated from the vapor pressure data. This data was then correlated with both the one parameter Bromley equation and the three parameter Pitzer equation. For all systems at all temperatures, the data were better correlated by the Pitzer equation than with the Bromley equation. Mean activity coefficients of the two salts at the three temperatures were calculated based on the parameters obtained by regression of the experimental osmotic coefficient data. They were also calculated using a graphical procedure. However, it was shown that if data are not available at low concentrations with which to extrapolate the data to infinite dilution, the mean activity coefficients determined graphically can be in error by 20%.

Although the Pitzer equation fit the experimental osmotic coefficient data better than the Bromley equation, it appears that the constants of both equations that reflect an aqueous media must be modified to reflect the properties

of the nonaqueous methanol.

The temperature dependency of B in the Bromley equation was investigated using a two parameter equation for both the LiBr and LiCl systems. Since the fit is good, the equation can be used to estimate the value of B in the range of 25-45 °C.

The temperature dependency of the parameters in the Pitzer equation was also studied. However, no relationship between the parameters and temperature could be found.

Since the temperature dependency of the parameter B in the Bromley equation can easily be expressed with a two parameter equation, it appears that this equation is more useful in the correlation of salt-solvent data over many temperatures than is Pitzer's equation.

OSMOTIC AND MEAN ACTIVITY COEFFICIENTS OF LiBr AND LiCl IN METHANOL AT 25,35, AND 45°C

by
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CHAPTER I

INTRODUCTION

Electrolytic solutions of nonaqueous-aqueous mixtures are often encountered in industrial applications, such as in solvent recovery in liquid wastes treatment; product separation through distillation; chemical reactions; and biological systems. The emergence of ethanol as a fuel constituent adds more importance to such systems. Yet, while thermodynamic data such as mean activity coefficients, vapor pressure depression, and osmotic coefficients are readily available for aqueous solutions,(17,18,20,36,38,42) data for nonaqueous electrolytic solutions are scarce.(24,39) Thermodynamic data of electrolytes in mixed solvents are even more limited.(40, 41)

Due to the infinite combinations existing for multicomponent systems, it is difficult to experimentally determine the thermodynamic data needed in the design of chemical processes. The prediction of the data through the use of an appropriate model and a limited amount of experimental data represents a significant advance in the application of thermodynamics to practical systems.

Several semi-empirical models(43,44,45) are available which allow the prediction of thermodynamic data for ternary nonelectrolytic solutions. These models were developed through the correlation of extensive binary data. However, comparable models for the prediction of ternary electrolytic systems consisting of an electrolyte in an aqueous-nonaqueous solvent from the binary data of an electrolyte in water and an electrolyte in a nonaqueous solvent are not available.

Two semi-empirical equations, the Pitzer and the Bromley equations, have recently been presented(14,16) and will be discussed in Chapter II. Both models have been used to generate parameters specific for an electrolyte in aqueous solution. Each model contains additional parameters which appear to be specific for the type of solvent and are obtained only through the regression of many salt-water systems.

It is for this reason that these models are not easily applied to electrolyte-nonaqueous systems. First of all, the extensive data necessary to establish the parameters in the semi-empirical equations which are specific for the solvent does not exist. Secondly, the existing models of electrolyte-water systems assume complete dissociation of the electrolyte. This is not true in the case of nonaqueous solvents where most electrolytes are incompletely dissociated.

It is the intention of this study to measure the osmotic and mean activity coefficients of LiCl and LiBr in methanol using the static method discussed later. These systems will then be used in a preliminary study to investigate the applicability of the Bromley and Pitzer equations to electrolyte-methanol systems. LiBr and LiCl were chosen in this study since both are completely dissociated in methanol.(46) This implies that the Bromley and Pitzer equations should be directly applicable to these systems since they were developed assuming complete dissociation.

CHAPTER II

THEORY

A. The Mean Activity Coefficient

In an attempt to explain the observed behavior of the chemical potential of dilute electrolytic solutions, early workers tended to treat electrolytic solutions as ideal nonelectrolytic solutions where the solute particles do not interact with each other or the solvent particles in the dilute solution. The classical equation for the chemical potential, μ_j, of an ideal nonelectrolytic solute is

$$\mu_j-\mu_j^0=RT\ln x_j \qquad (1)$$

where x_j is the mole fraction of the solute and μ_j^0 is the chemical potential of the standard state of particle j given by

$$\mu_j=\mu_j^0 \text{ when } x_j=1 \qquad (2)$$

Rewriting equation 1 for a dilute electrolytic solution, the following result is obtained

$$v_i\mu_i-v_i\mu_i^0=v_iRT\ln m_i \qquad (3)$$

where m_i is the molality of constituent i in the solution, v_i is the number of ions in the electrolytic solute of either positive or negative ions, and μ_i^0 is the chemical potential of the standard state given by

$$\mu_i=\mu_i^0 \text{ when } m_i=0 \qquad (4)$$

However, the application of equations 3 and 4 to experimental electrolytic systems neglects to predict the chemical potential change arising from long range ion-ion(Coulombic) interactions which are present in the most dilute solutions due to the positive and negative charges . Equation 3 applies only to dilute systems of noninteracting particles.

Lewis(1) modified equation (3) so that the chemical potential change arising from coulombic interactions is expressed as a function of the "effective concentration" or activity, a_i, of the free ions in the electrolytic solution. The chemical potential change of either a positive or negative ion is then

$$v_i\mu_i(\text{real})-v_i\mu_i^o=v_iRT\ln a_i \qquad (5)$$

where a_i is defined

$$a_i=\gamma_i m_i \qquad (6)$$

γ_i is the single ion activity coefficient or correction factor which accounts for the chemical potential change due to the addition of charged species i to a solvent. Upon substitution of equation 6 into equation 5, the following expression for the chemical potential of ionic species i is

$$v_i\mu_i(\text{real})-v_i\mu_i^o=v_iRT\ln\gamma_i m_i \qquad (7)$$

To show the physical significance of the activity coefficient, equation 3 is subtracted from equation 7 resulting in the following expression for γ_i

$$v_i\mu_i(\text{real})-v_i\mu_i(\text{ideal})=v_iRT\ln\gamma_i \qquad (8)$$

Equation 8 illustrates that the single ion activity coefficient is a measure of the deviation in the chemical potential of the ideal noninteracting solute due to the presence of an ionic solute.

It is impossible to measure the activity coefficient of a single ion in a solution since the change in the chemical potential of the electrolyte is due to contributions from the interacting positive and negative ions. It is possible though to measure the net change in the chemical potential of the electrolyte due to the influence of both ions. This measurable quantity is the mean activity coefficient of the electrolyte.

From equation 5, the chemical potential change of the positive ion (indicated by +) is

$$v_+\mu_+(\text{real})-v_+\mu_+^\circ=v_+RT\ln a_+ \tag{9}$$

and of the negative ion,(indicated by -), is given by

$$v_-\mu_-(\text{real})-v_-\mu_-^\circ=v_-RT\ln a_- \tag{10}$$

From equation 6, the activities of the positive and negative ions may be written

$$a_+=\gamma_+m_+ \tag{11a}$$

and

$$a_-=\gamma_-m_- \tag{11b}$$

Substitution of equations 11a and 11 b into equations 9 and 10 respectively yields the following expressions for the chemical potentials of the positive and negative ions.

$$v_+\mu_+(\text{real})-v_+\mu_+^\circ=v_+RT\ln\gamma_+m_+ \tag{12}$$

$$v_-\mu_-(\text{real})-v_-\mu_-^\circ=v_-RT\ln\gamma_-m_- \tag{13}$$

Adding equations 12 and 13 gives

$$(v_+\mu_+ +v_-\mu_-)\text{real}-(v_+\mu_+^\circ+v_-\mu_-^\circ)=RT\ln\gamma_+^{v+}\gamma_-^{v-}+RT\ln m_+^{v+}m_-^{v-} \tag{14}$$

Dividing equation 14 by the quantity

$$v=v_++v_- \tag{15}$$

where v is the total number of ions per salt, the following results are obtained

$$\mu_2-\mu_2^\circ=RT\ln(\gamma_+\gamma_-)^{1/v}+RT\ln(m_+m_-)^{1/v} \tag{16}$$

or

$$\mu_2(\text{real})-\mu_2^\circ=RT\ln m_\pm +RT\ln\gamma_\pm \tag{17}$$

where

$$\mu_2(\text{real})=\frac{v_+\mu_++v_-\mu_-}{v} \tag{18}$$

$$\mu_2^\circ=\frac{v_+\mu_+^\circ+v_-\mu_-^\circ}{v} \tag{19}$$

$$m_\pm=(m_+^{v+}m_-^{v-})^{1/v} \tag{20}$$

$$\gamma_\pm=(\gamma_+^{v+}\gamma_-^{v-})^{1/v} \tag{21}$$

μ_2, μ_2°, $m_\pm$, and $\gamma_\pm$ represent the chemical potential of the electrolyte, the chemical potential of the standard state, the mean molality, and the mean activity coefficient.

To show that the mean activity coefficient is a measure of ion-ion interactions in the solution, equation 3 for a system of noninteracting particles is written

$$v_+\mu_+(\text{ideal})-v_+\mu_+^\circ=v_+RT\ln m_+ \qquad (22)$$

and

$$v_-\mu_-(\text{ideal})-v_-\mu_-^\circ=v_-RT\ln m_- \qquad (23)$$

Adding equations 22 and 23 and dividing by v leads to the following result

$$\frac{v_+\mu_++v_-\mu_-}{v}(\text{ideal})-\frac{v_+\mu_+^\circ+v_-\mu_-^\circ}{v}=RT\ln(m_+^{v_+}m_-^{v_-})^{1/v} \qquad (24)$$

or from equations 19 and 20

$$\mu_2(\text{ideal})-\mu_2^\circ=RT\ln m_\pm \qquad (25)$$

where

$$\mu_2(\text{ideal})=\frac{v_+\mu_++v_-\mu_-}{v}(\text{ideal}) \qquad (26)$$

Subtracting equation 26 from 17, the following result is obtained

$$\mu_2(\text{real})-\mu_2(\text{ideal})=RT\ln Y_\pm \qquad (27)$$

which shows that the mean activity coefficient is a direct measure of the deviation of the chemical potential of the electrolyte from the ideal case of noninteracting particles due to the ion-ion interactions in the dilute solution.

B. The Gibbs-Duhem Equation

To obtain an expression for the activity and the osmotic coefficient of the solvent from the mean activity coefficient or chemical potential of the electrolyte, the Gibbs-Duhem equation must be utilized.

From thermodynamics, the change in internal energy, dU, for a heterogeneous open system is

$$dU=TdS-PdV+\sum_i \mu_i dn_i \tag{28}$$

For a binary system, equation 28 becomes

$$dU=TdS-PdV+\mu_1 dn_1+\mu_2 dn_2 \tag{29}$$

where subscript 1 refers to the solvent and subscript 2 refers to the electrolytic solute. n_1 and n_2 are the number of moles of the solvent and the solute respectively. Integrating equation 29 from a state of zero mass to a final state of finite mass at constant concentration, gives

$$U=TS-VP+\mu_1 n_1+\mu_2 n_2 \tag{30}$$

Equation 30 expresses the internal energy of the system as a function of the temperature, pressure, and composition of the system. Differentiating equation 3 to obtain a general expression for dU gives

$$dU=SdT+TdS-VdP-PdV+\mu_1 dn_1+n_1 d\mu_1+\mu_2 dn_2+n_2 d\mu_2 \tag{31}$$

Comparing this result with equation 29 yields the Gibbs-Duhem equation

$$SdT-VdP+n_1 d\mu_1+n_2 d\mu_2=0 \tag{32}$$

For a binary system at constant temperature and pressure equation 32 becomes

$$n_1 d\mu_1 + n_2 d\mu_2 = 0 \tag{33a}$$

or

$$n_1 d\mu_1 = -\frac{n_2}{n_1} d\mu_2 \tag{33b}$$

Differentiation of equation 17 for μ_2 gives

$$d\mu_2 = RT(d\ln(\Upsilon_\pm) + d\ln m_\pm)^{1/v} \tag{34}$$

Substituting this result in equation 33b gives

$$d\mu_1 = -\frac{n_2}{n_1} RT(d\ln \Upsilon_\pm + d\ln m_\pm)^{1/v} \tag{35a}$$

or

$$d\mu_1 = -\frac{n_2}{n_1} RT\ln(\Upsilon_\pm m_\pm)^{1/v} \tag{35b}$$

but

$$\frac{n_2}{n_1} = \frac{mM_1}{1000} \tag{36}$$

where M_1 is the molecular weight of the solvent. Substituting equation 36 into equation 35b gives

$$d\mu_1 = \frac{mM_1 RT}{1000} d\ln(\Upsilon_\pm m_\pm)^{1/v} \tag{37}$$

The chemical potential of the solvent may be written in terms of measurable quantities. From equation 5, the chemical potential of the solvent in terms of the activity of the solvent is

$$\mu_1(\text{real}) - \mu_1^\circ = RT\ln a_1 \tag{38}$$

Differentiation of equation 38 and insertion in equation 37 gives

$$d\ln a_1=\frac{vmM_1}{1000}d\ln \gamma_\pm m_\pm \qquad (39)$$

Since

$$m_\pm=(v_+^{v_+}v_-^{v_-})^{1/v}m \qquad (40)$$

equation 39 becomes after differentiation of equation 40

$$d\ln a_1=\frac{vmM_1}{1000}d\ln \gamma_\pm m \qquad (41)$$

Since the activity of the solvent differs very little from one, Bjerrum(2) introduced the function, ϕ, the osmotic coefficient, to better illustrate the deviation from ideality of the solvent. The osmotic coefficient is defined

$$\phi=\frac{-1000\ln a_1}{vmM_1} \qquad (42)$$

Differentiating equation 42 and substituting in equation 41 gives

$$-md\ln(\gamma_\pm m)=-d(\phi m) \qquad (43)$$

Performing the indicated differentiations, results in the following expression for the mean activity coefficient in terms of the osmotic coefficient

$$\ln\gamma_\pm=\phi-1+\ (\phi-1)d\ln m \qquad (44)$$

The use of equation 44 to determine mean activity coefficients from the measured osmotic coefficients is discussed in Chapter III.

C. Available Correlations for Osmotic and Mean Activity Coefficients

The Debye-Huckel limiting law(3) introduced in 1923, was the first successful attempt to define the chemical potential of the electrolyte solely due to ion-ion interactions. Central to this model are five assumptions:1) A central ion or reference ion is surrounded by an ionic cloud with a smeared out charge density many times the size of the ion. The ion may then be treated as a point charge. 2) Ions interact only through long range Coulombic forces. 3) The electrolyte is assumed to be completely dissociated. 4) The solvent is a medium of constant dielectric, and 5) the solution is dilute enough so that the electrostatic potential, Ψ, is minimal and a linearized form of the Boltzmann equation may be used to obtain an expression for the mean activity coefficient. Based on these assumptions, the following expression for the mean activity coefficient of an electrolyte was derived

$$\log \gamma_{\pm} = -A_{\gamma} |Z_+ Z_-| I^{\frac{1}{2}} \qquad (45)$$

where Z_+ and Z_- are the charges of the positive and negative ions, respectively; I is the ionic strength which is a measure of the total number of charges in the solution and is given by

$$I = \tfrac{1}{2} \sum_i m_i Z_i^{\,2} \qquad (46)$$

and A_{γ} is a proportionality constant arising from the theory which is a function of temperature only.

A_γ is calculated from the following expression where

$$A_\gamma = 1.824 \times 10^6 d^{\frac{1}{2}} / (\varepsilon T)^{3/2} \qquad (47)$$

ε is the dielectric constant of the solvent and d is the solvent density.

Equation 45 indicates that the log of the mean activity coefficient decreases in proportion with the square root of the ionic strength. The slope is dependent only on the temperature and the valence type of the electrolyte, not the kind of electrolyte.

The Debye-Huckel limiting law predicts the behavior of an infinitely dilute electrolytic solution. As the ionic strength approaches zero, the log of the activity coefficient goes to zero. Also, the limiting law correlates experimental data up to an ionic strength of 0.01 m.(4) At ionic strengths above 0.01 m, the limiting law begins to collapse. Plots of the mean activity coefficient as a function of the molality for experimental salt systems indicate that the activity coefficient goes through a minimum and then increases with increasing concentration. In addition, the activity coefficient is observed to be a function of the type of electrolyte, not only of the temperature and valency. Therefore, the limiting law must be reexamined for higher concentration.

At higher concentrations of electrolyte, the ions can no longer be treated as point charges, since the relative sizes of the ionic cloud and ion shrink with increasing concentration. The size of the ions must be taken into account.

This was accomplished in the Debye-Huckel theory through the introduction of a, the ion size parameter. As a result of this modification, a more precise expression was obtained for the electrostatic potential, Ψ. (See reference 17) The corresponding equation for the mean activity coefficient is

$$\log \gamma_{\pm} = - \frac{A_{\gamma}|Z_{+}Z_{-}|\, I^{\frac{1}{2}}}{1+\kappa a} \tag{47}$$

where

$$\kappa = \left(\frac{8\pi N_{A} e_{0}^{2}}{1000\,\varepsilon kT}\right)^{\frac{1}{2}} I^{\frac{1}{2}} \tag{48}$$

The introduction of the ion size parameter increases the range of validity of the Debye-Huckel theory to an ionic strength of 0.1m for 1-1electrolytes and makes the calculated value of $\gamma_{\pm}$ specific for each salt since each salt has a different value of a. Equation 47 reduces to equation 45 when $a \ll 1/\kappa$ in the dilute solution or physically, when the size of the ion is much smaller than the radius of the ionic cloud, where the ion may be treated as a point charge.

The values of the ion size parameter are determined by experiment. The lowest value that it can assume is one that corresponds to the sum of the crystallographic radii of the positive and negative ions making up the electrolyte. The maximum value that it can assume is the sum of the hydrated radii of the positive and negative ions if the salt is in aqueous solution. In aqueous solution, it is assumed that the solvation shells about the ions are crushed when the ions collide.(4) Since this distance would be difficult to measure, it is best to regard a as a mean distance of closest approach having a lower and upper bound as defined above.

The disadvantage of equation 47 is that the value of a changes with concentration and is purely an arbitrary value at ionic strengths above 0.1m. As an example, consider aqueous solutions of HCl. For ionic strengths up to 0.1m, the best value of a is 4.5Å. Increasing the ionic strength to 1.0m, changes the value of a to 13.8Å. At 2m, the value of a is -411.2Å, a physically impossible value. Therefore, it is clear that the concept of the ionic cloud fails at high concentration.

At concentrations above 0.1m, the mean activity coefficient reaches a minimum and then begins to increase with the square root of the ionic strength. The Debye-Huckel theory cannot predict this region due to the assumptions it is based on. First of all, the Debye-Huckel theory only considers long range ion-ion interactions. The short range ion-solvent interactions, such as dispersion forces, ion-dipole and ion-induced dipole forces, which become important as the concentration of electrolyte is increased were neglected in the development of the theory. Secondly, the Debye-Huckel theory assumes the electrolyte is completely dissociated into ions. However, it is possible for ions of opposite charge to form ion pairs or higher order clusters of ions with a net charge of zero. This would imply that an experimentally determined mean activity coefficient is less than that predicted by the theory due to the neutral entities in the solution which reduce the numbers of free ions. Third, the Debye-Huckel theory considers the solvent a constant dielectric medium in which the ions interact. However, as the concentration of electrolyte is increased, the dielectric constant of the solution decreases exponentially(5). The introduction of more and more electrolyte to a solution decreases the number of free solvent molecules since they are necessary in the solvation of the ions and are bound to them.

Due to the complexities of the electrolytic solution which must be considered in the construction of a model, empirical expressions were adopted to extend the range of the Debye-Huckel theory. In 1935, Guggenheim(6) defined an additional term,B, the specific ion interaction constant to account for the short range forces and the influence of the molecular nature of the solvent. B is a constant which is specific for each salt. In addition, he specified that the value of the ion size parameter,a, be 3Å for water. His modified form of the Debye-Huckel equation is

$$\log \gamma_{\pm} = -A_{\gamma}|Z_{+}Z_{-}|\frac{I^{\frac{1}{2}}}{1+I^{\frac{1}{2}}} + Bm \qquad (49)$$

and fits aqueous electrolytic experimental data up to .1m. The temperature and pressure dependency of B in this range was also investigated. Adding more terms to equation 49 permits the correlation of data at higher concentration.

It was not until, 1945, however, that McMillan and Mayer(7) used a statistical mechanical approach which showed that the systems of equations for molecules in imperfect gases could be applied to the salt solute in electrolytic solutions. Their model was a solution containing a solute in osmotic equilibrium with the pure solvent through a solute through a solute impermeable, solvent permeable membrane.

In 1968, Rasaiah and Friedman(8) applied the osmotic pressure equations of McMillan and Mayer to obtain an equation for the osmotic coefficient of a 1-1 electrolytic solution

$$\phi-1=\left(\frac{\pi}{ckT}\right)-1$$
$$=(6ckT)^{-1}\sum_i\sum_j c_i c_j\int_0^\infty r\frac{\partial u_{ij}}{\partial r}\, g_{ij}(r)4\pi r^2dr \qquad (50)$$

where π is the osmotic pressure; c_i and c_j are the concentrations of the ith and jth ions,respectively; r is the distance between the ions and c is the total concentration of all species in the solute. u_{ij} and g_{ij} are the interionic potential and the radial distribution functions, respectively. The integral represents the second virial coefficient accounting for deviations from the ideal solution due to short and long range interactions among the ions and the ions and the solvent.

Since a hard core model, where the radius of the hard core is a, is usually assumed for the radial distribution function, problems arise in evaluation of $\partial u_{ij}/\partial r$ when r=a. Barker and Henderson(9) solved this problem mathematically and equation(50) becomes

$$\phi - 1 = \left(\frac{\pi}{ckT}\right) - 1$$

$$= (6ckT)^{-1} \sum_i \sum_j c_i c_j \int_a^\infty r \frac{\partial u_{ij}}{\partial r} g_{ij} (4\pi r^2) dr + \frac{2\pi a^3}{3c} \sum_i \sum_j c_i c_j g_{ij}(a) \qquad (51)$$

where $g_{ij}(a) = g_{ij}(r)$ for r slightly greater than a.

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

The expression for the interionic potential is

$$u_{ij}(r) = u^*_{ij}(r) + \frac{z_i z_j e^2}{\varepsilon r} \qquad (52)$$

Using the primitive model for the interionic potential where

$$u^*_{ij} = \infty \qquad r_{ij} < a \qquad (53a)$$

$$u^*_{ij} = 0 \qquad r_{ij} > a \qquad (53b)$$

and Monte Carlo techniques to evaluate the radial distribution function, Card and Valleau(10) obtained values of the osmotic coefficients for several electrolytes in water at 25°C that agreed with experimental results up to 2m. Ramanthan and Friedman(11) used an ion-ion pair potential where in this case, u^*_{ij} in equation 52 is the sum of three effects: a core repulsion term proportinal to $1/r^9$; a dielectric repulsion term proportional to $1/r^4$; and a term to represent the effect of the overlap of spheres about the ions when the ions come close together. Their model agrees with experimental osmotic coefficients up to an ionic strength of 1m for 1-1 electrolytes.

If the primitive model of the interionic potential and the expanded form of the radial distribution function from the Debye-Huckel theory

$$g_{ij}(r)=1-q_{ij}(r)+1/2q_{ij}^{2}(r) \qquad \text{for } r>a \qquad (54)$$

where

$$q_{ij}(r)=\frac{z_i z_j e^2 \exp(\kappa a)\exp(-\kappa a)}{kT(1+\kappa a)r} \qquad (55)$$

is introduced into equation 51, the following expression is obtained for the osmotic coefficient of a 1-1 electrolyte,

$$\phi-1=\frac{-z^2 l\kappa}{6(1+\kappa a)}+c(\frac{2\pi a^3}{3}+\frac{\pi a z^4 l^2}{3(1+\kappa a)^2} \qquad (56)$$

where $l=e^2/\varepsilon kT$ and $\kappa=(8\pi Ne^2/1000\varepsilon kT)^{\frac{1}{2}}I^{\frac{1}{2}}$.

The first term in equation 56 is considered the primary electrostatic term since it comes from the second term of equation 54. This term also contains the Debye-Huckel limiting law. The second term of equation 56 is the hard core term or the second virial coefficient. The first term in the parenthesis, $2\pi a^3/3$, is the kinetic effect of the hard core arising from the first term of equation 54 and is independent of concentration. The second term in the parenthesis is the increased hard core repulsive effect caused by electrical interactions and arises from the term of equation 54. This term is a function of concentration and tends to decrease with increasing concentration or ionic strength due to a decrease in the average radial distribution function when the ions contact.

After substitution of the expressions for l and κ and after some rearrangement, equation 56, using the primitive model of the interionic potential and the radial distribution function of the Debye-Huckel theory, becomes

$$\phi - 1 = \frac{-z^2 A_\phi I^{\frac{1}{2}}}{1+bI^{\frac{1}{2}}} + B_{MX} m \tag{57}$$

where B_{MX} represents the terms in parenthesis of equation 56 and $b = a\kappa/I^{\frac{1}{2}}$.

Pitzer(12,13) proposed that B_{MX}, the second virial coefficient in equation 57 be replaced by a semi-empirical expression that reflects the constant term, $2\pi a^3/3$, and the second term in equation 56 which decreases with increasing ionic strength. He tested two expressions

$$B_{MX} = \beta^0 + \frac{\beta^1}{(1+\alpha I^{\frac{1}{2}})^2} \tag{58a}$$

and

$$B_{MX} = \beta^0 + \beta^1 \exp(-\alpha I^{\frac{1}{2}}) \tag{58b}$$

in equation 57 through regression of osmotic coefficient data for several electrolyte systems in water at 25°C. β^0 and β^1 were adjusted for each electrolyte while α and b were optimized over all the systems studied. Equation 58b was found to better represent all systems studied than equation 58a. The best values of α and b are 2.0 and 1.2, respectively.

Insertion of equation 58b into equation 57 gives Pitzer's result for the osmotic coefficient of an electrolyte in aqueous solution

$$\phi-1=-|z_+z_-|A_\varphi\frac{I^{\frac{1}{2}}}{1+bI^{\frac{1}{2}}}+2m\frac{V}{\nu}(\beta^0+\beta^1(\exp(-\alpha I^{\frac{1}{2}})))+m^2 2\frac{V^{3/2}}{\nu}C \qquad (59)$$

where the term in m^2 was added to equation 57 to fit data at higher concentrations. V is equal to $\nu_+\nu_-$. Pitzer defines C as the third virial coefficient, a variable which does not come from the theoretical results of equation 56.

Pitzer(14,15) used equation 59 to obtain values of β^0, β^1, and C for 1-1,2-2, and electrolytes with one or both ions univalent. The data are fit within experimental error up to an ionic strength of 6m in most cases.

He attempted to interpret the values of β^0 and β^1 for each electrolyte in respect of the hard core radii terms in equation 56 they were meant to represent. However, no correlation could be found between the parameters and the terms assuming that the ionic size parameter ie either represented by the crystallographic radii or the hard core radii. The values of C were found to be negligible or very small for most salts.

Using the appropiate thermodynamic equation, the expression for the mean activity coefficient is

$$\ln\gamma_{\pm}=|z_+z_-|f^\gamma+m\left(\frac{2V}{\nu}\right)B^\gamma+m^2 2\left(\frac{V}{\nu}\right)^{3/2}C \qquad (60)$$

where

$$f^\gamma=-A_\varphi\left(\frac{I^{\frac{1}{2}}}{1+bI^{\frac{1}{2}}}+\frac{2}{b}\ln(1+bI^{\frac{1}{2}})\right) \qquad (60a)$$

and

$$B^{\gamma}=2\beta^{0}+\frac{2\beta^{1}}{\alpha^{2}I}(1-\exp(-\alpha I^{\frac{1}{2}})(1+\alpha I^{\frac{1}{2}}-(1/2)\alpha^{2}I)) \qquad (60b)$$

Pitzer did not examine the temperature dependency of the second and third virial coefficients.

Bromley(16) extended Guggenheim's expression for the mean activity coefficient given in equation 49 so that one parameter could be used to fit experimental data up to high concentrations. He suggested the following equation

$$\log\gamma_{\pm}=\frac{-A_{\gamma}|z_{+}z_{-}|\,I^{\frac{1}{2}}}{1+\rho I^{\frac{1}{2}}}+\frac{(B_{0}-B)I}{(1+aI)^{n}}+BI+CI^{2} \qquad (61)$$

where $n=2$ and $\rho=1.0\pm0.2$. He found that the value of a, which is not the ion size parameter defined previously, is near one but it tends to decrease with an increase in the valence number. The value of a is represented well by

$$a=\frac{1.5}{|z_{+}z_{-}|} \qquad (61a)$$

The fit of the data is not sensitive to the value of a.

From regression of mean activity coefficient data and osmotic coefficient data for many electrolyte systems at 25°C, the relationship between B_0 and B was found to depend on Z_+ and Z_- where

$$B_{0}-B=(0.06+0.6B)Z_{+}Z_{-} \qquad (61b)$$

The value of C was zero in most cases or very small.

The temperature dependency of equation 61b was tested using data for the NaCl system from 0-100°C and no dependency was found. Substituting equations 61a and 61b into 61 along with the values of n and ρ give Bromley's final equation for the mean activity coefficient of an electrolyte

$$\log \gamma_{\pm} = \frac{-A_{\gamma} z_{+} z_{-} I^{\frac{1}{2}}}{1+\rho I^{\frac{1}{2}}} + \frac{(.06+.6B)Z_{+}Z_{-}I}{(1+(1.5/z_{+}z_{-})I)^{2}} + BI \qquad (62)$$

Examination of equation 62 shows that the first term is the Debye-Huckel term accounting for the long range forces between ions. Since the value of ρ is set at one, an ion size parameter of 3Å is assumed. The second term of the equation represents a transition term between the Debye-Huckel region of a plot of activity coefficient vs. the ionic strength and the linear portion of the curve at higher concentrations.

Using the appropriate thermodynamic function, the equation for the osmotic coefficient is

$$1-\phi=2.303A_{\gamma}|Z_{+}Z_{-}|\frac{I^{\frac{1}{2}}}{3}\sigma(\rho I^{\frac{1}{2}})-2.303(.06+.6B)Z_{+}Z_{-}\frac{I}{2}\Psi(aI)-2.303B\frac{I}{2} \qquad (63)$$

where

$$\sigma(\rho I^{\frac{1}{2}})=\frac{3}{(\rho I^{\frac{1}{2}})^{3}}\left(1+\rho I^{\frac{1}{2}}-\frac{1}{1+\rho I^{\frac{1}{2}}}-2\ln(1+\rho I^{\frac{1}{2}})\right) \qquad (63a)$$

and

$$\Psi(aI)=\frac{2}{aI}\left(\frac{1+2aI}{(1+aI)^{2}}-\frac{\ln(1+aI)}{aI}\right) \qquad (63b)$$

Using equations 62 and 63, Bromley regressed numerous aqueous electrolyte systems at 25°C to obtain the value of B specific for each electrolyte. Results indicated that the average relative percent error in the activity coefficient is 5.1% if data up to an ionic strength of 6m is used in the regression.

Bromley also investigated the temperature dependency of B through regression of heat capacity data. He proposed the following equations to express the variation of B with temperature

$$B=B^{*}\ln\left(\frac{T-243}{T}\right)+\frac{B_1}{T}+B_2+B_3\ln T \tag{64}$$

and

$$B=\frac{B^{*}}{T-243}+\frac{B_1}{T}+B_2+B_3\ln T \tag{65}$$

where B^{*}, B_1, B_2, and B_3 are arbitrary constants determined from the data. Both expressions were found to be satisfactory. If data at only two or three temperatures are available, B_2 and B_3 may be set to zero.

D. Experimental Methods Available to Measure the Osmotic and Mean Activity Coefficients

Several methods(17,18,19) are available which allow the determination of the osmotic and mean activity coefficients of an electrolyte in solution. Only the most common methods and their applicability to nonaqueous salt systems are discussed.

Electromotive Force Measurements

The electromotive force method relates, through the Nernst equation, the activity of an electrolyte in solution to the potential developed between a metal electrode and a reference electrode. Harned and Owen(20) and Robinson and Stokes(21) discuss the various types of cells, those with or without transport, used to measure the activity of an electrolyte in aqueous solution. The success of the Emf method, regardless of the experimental cell system, depends on an accurate determination of E^0, the standard cell potential for the electrode reactions at zero molality.

In cells without transport, where the positive electrode is generally comprised of a metal amalgam, Emf data are reliable above concentrations of 0.05 m for aqueous electrolytic solutions. Due to this limitation, an extended form of the Debye-Huckel equation must be used to extrapolate the data to infinite dilution to obtain E^0. Other limitations inherent in the use of this type of cell are the solubility of the metal electrode at high concentrations; difficulties in constructing the electrodes; and the irreproducibility of the metal electrode if used over a wide temperature range. The mean activity coefficients of many salts in water have been determined using this method.(22)

Mean activity coefficients of alkali chlorides in water have been determined in cells with transport at concentrations as low as 0.002m at various temperatures.(23) This method relates the potential of the cell to the transport numbers of the positive and negative ions. Only the alkali chlorides were investigated since the reversible behavior of the Ag|AgCl electrode is well established.

In cells with transport, the extrapolation of the data to infinite dilution to obtain E^0 is not as difficult as in cells without transport since an extended form of the Debye-Huckel equation is not required. The theory can be used directly without additional terms. A major limitation of this method is that transport number data are required over the entire concentration range of study.

The methods described above have been used to determine the mean activity coefficients of some electrolytes in methanol. Covington (24) reports values of E^0 and the mean activity coefficients of LiCl, KI, and NaCl in methanol using cells without transport. The mean activity coefficients are reported as low as 0.0008m for KI and 0.0062m for LiCl. This data is questionable since for the same salts in water using the same type of cell system, the data are reported only down to 0.1m. The cell reactions of salts in water are better understood than in methanol due to the many studies done by various workers using the two types of cells described above.

The Emf method was not chosen in this study to determine the mean activity coefficients of LiCl and LiBr in methanol for the following reasons:

1) It was desired to determine the mean activity coefficients of LiCl and LiBr in methanol over a wide range of concentration. This is impossible using cells without transport due to the solubility of the Li amalgam electrode at high concentrations of electrolyte. If a cell system, with transport was utilized, additional transport number data would be required.

2) The temperature dependency of the mean activity coefficients of LiCl and LiBr were also of interest. However, it is difficult to obtain reproducible data if the Li amalgam electrode is subjected to changes in temperature. A cell system with transport was rejected since transport number data at various temperatures would have to be measured in addition to the cell data.

Vapor Pressure Measurements

A. The Isopiestic Method

The isopiestic method, originally developed by Bousfield in 1918(25) and modified by Sinclair(26) allows the determination of the mean activity coefficient of an electrolyte through the measurement of the activity of the solvent. Essentially, a standard electrolytic solution, whose activity is known as a function of the concentration of the salt, is allowed to distill to an electrolytic solution of unknown activity and lower concentration. At equilibrium, the activity of the standard electrolytic solution is equal to the activity of the experimental solution. The concentrations of both solutions are determined and the activity of the standard electrolytic solution is determined from the activity-concentration curve. Since the activities of the standard and unknown solution are equal, the activity of the unknown is readily obtained. The experimental method is described in detail by Pitzer and Brewer(27) and Robinson and Stokes.

Due to its comparative nature, the value of the isopiestic method lies in the availability of precisely determined standard curves of activity as a function of concentration for at least one electrolyte in the solvent of study. For aqueous electrolytic solutions, the usual standards are NaCl,KCl, and $CaCl_2$. The activities of these salts over a wide concentration range are well established since they have been determined by many workers using a variety of methods.

The application of the isopiestic method to electrolytic solutions of methanol is impossible at this time since activity concentration data of not even one salt system have been investigated by a variety of methods, with the exception of LiCl in methanol.(28,29) This system was investigated by the Emf method up to 1m and by a static vapor pressure method from 0.3 to 12 m. However, the mean activity coefficients determined from the two sets of data differ by as much as 20%.

B. Still Methods

Through direct measurements of the vapor pressure of the pure solvent and of the electrolytic solution, the mean activity coefficient of the salt may be determined. These vapor pressure measurements are of two types: 1) the dynamic still method, and 2) the static method. Each is discussed below.

The Dynamic Method

The experimental apparatus used to measure the vapor pressures of electrolytic solutions are divided into two groups: 1) stills with circulation of the vapor phase and 2) stills with circulation of the vapor and liquid phases. Both types of stills are thoroughly discussed in Hala.(30)

In stills with circulation of the vapor phase, such as the Othmer still, the electrolytic solution is boiled at the desired temperature of study. The evolved vapor, which is solvent only since strong salts are nonvolatile, enters a portion of the still which leads to a condenser. The condensed vapor drops into a receptacle which recirculates the condensate back to the boiling liquid. This is an obvious disadvantage since the boiling of the solution does not guarantee thorough mixing of the liquid and concentration gradients in the still may result. Another problem with this still is superheating along the walls of the still caused by the external heating source which is usually a heating coil wrapped around the bottom leg of the still. The major difficulty with this still though, is the correct positioning of the thermometer. Placing the thermometer in the vapor space of the still results in a different temperature reading than in the boiling liquid.

In methods utilizing circulation of the liquid and vapor phases, a Cottrell pump is introduced to the still which serves to shoot a mixture of the liquid and the vapor onto the thermometer. This modification allows the measurement of the true boiling point of the electrolytic solution.

Even though a still utilizing circulation of the liquid and vapor phases eliminates the problems associated with a still utilizing only circulation of the vapor phase, there are still difficulties in determining the concentration of the electrolytic solution. Since the concentration of the solution cannot be determined by direct weighing, an alternate method must be used. If the electrolytic solution contains an alkali halide, the molarity of the solution may be determined through a Mohr titration and the molality of the solution determined if the density is measured. This technique was used by Bixon(31) who measured the vapor pressures of several electrolytes in methanol at 25°C. The technique is inferior to direct weighing since the red-yellow precipitate endpoint of a Mohr titration is difficult to discern. Also, the density of the electrolytic solution is difficult to measure using pycnometers due to the volatility of methanol. The electrolytic solutions could also be analyzed using a refractometer. However, there is the problem of the evaporation of the sample during analysis.

The still with circulation of the vapor phase was not chosen for this study due to the problems encountered with this apparatus described above. Although the still with circulation of the vapor and liquid phases would have been suitable for this study, it was rejected since the problem of the analysis of the solutions remains.

The Static Method

The static method allows the determination of the mean activity coefficient through measurements of the difference in vapor pressure between the pure solvent and the electrolytic solution using a differential manometer. The experimental method is described in detail in the experimental section.

Thorough degassing of the pure solvent, the electrolytic solution, and the manometer fluid, is essential in this method. The presence of air in the solutions results in vapor pressure readings which are higher than the true values. This is the only disadvantage of this method.

The static method was chosen in this study to determine the osmotic and mean activity coefficients of LiCl and LiBr in methanol due to its simplicity. The temperature of the solutions is not controlled through external heating tapes or indirectly through the pressure control by a manostat, but through immersion of the apparatus in a constant temperature bath. The molality of each solution is determined by direct weighing and not through titration and density experiments. Therefore, the static method is simple as well as accurate.

CHAPTER III

EXPERIMENTAL

1. Materials

The potassium chloride, lithium bromide, and lithium chloride, were Matheson reagent grade quality and were used without further purification. Each salt was dried at 110°C in an oven for 48 hours prior to use.

The water used to prepare the potassium chloride test solutions was obtained by passing distilled water through a mixed resin demineralizing column. J.T. Baker methanol of spectro-quality was used with no further purification. Analysis by a Karl-Fischer titration indicated the methanol contained 0.03% water.

The purities of the salts are shown in Table IIA in App.A.

2. Solution Preparation

Solutions were prepared by adding the appropiate salt to a preweighed flask. (In the case of lithium chloride and lithium bromide; salts which are hygroscopic in nature, the flasks were then placed in an oven at 110°C for three hours after the addition of salt and dried to constant weight.) The flasks were weighed again to determine the amount of salt added to the flask. Approximately thirty milliliters of either water or methanol was then added to each flask. The flasks were then attached to a degassing apparatus to be described below.

3. Apparatus

The differential vapor pressure measurements were carried out in a constant temperature water bath in which the flasks containing the pure solvent and the electrolytic solution were immersed. The fiberglass tank had a capacity of 40 gallons and had two glass walls for ease of observation. The temperature was controlled to ± 0.005°C using a HB7553 relay box and thermoregulator. Heating was accomplished by the use of one 1000 watt heater used in conjunction with the relay while cooling was done using water circulating in a copper coil distributed throughout the tank. The water was continuously mixed using a 1/10 hp. stirrer.

The temperature of the bath was determined using thermometers calibrated against a NBS standard thermometer to ±0.005°C. The difference in vapor pressures(ΔP) between the electrolytic solution and the pure solvent was measured with a differential manometer as originally described by Gibson and Adams(32) and Shankman and Gordon(33) and further modified by Oliver.(34) The apparatus is shown in Figure 1 along with the appropiate dimensions. The manometer used in this study differs from that described by Oliver in that the arms supporting the flasks were shortened for greater accessibility. Each flask, equipped with a magnetic stirrer, has a capacity of 100 cc.

4. Procedure

Due to the presence of residual air in the solvent, the flasks containing the pure solvent and the solvent-salt solution were first outgassed. The procedure for degassing is as follows: (1) The flasks containing either pure solvent or the solvent-salt solution are attached to the apparatus shown in Figure 2 which is connected to vacuum. (2) The stopcocks are opened and the entire apparatus is immersed in a refrigeration unit at -67 °C while boiling at high vacuum. (3) After the solvent or solvent-salt solutions subcool and a residual pressure of 0.001 mm Hg is indicated on a McLeod gauge, the flasks are removed from the refrigerant, the stopcocks are closed, and the contents of the flasks are warmed. (4) This procedure is repeated until air bubbles no longer rise from the solution.

a. Vapor Pressure Measurements

The vapor pressure depression was measured by direct comparison of the vapor pressure of the electrolytic solution to that of pure methanol. After degassing , the flasks containing the pure solvent and the solvent-salt solution were connented to the differential manometer. The entire apparatus was immersed in the constant temperature bath.

The vapor pressure difference was measured by opening stopcocks A and B to the arms of the manometer when equilibrium was reached.(It was assumed the system was at equilibrium when constant pressure readings were taken over a two hour interval.) The individual vapor pressure of the pure solvent was measured by opening stopcock A and connecting the other arm of the manometer to the vacuum. Closing stopcock A and connecting it to vacuum and opening stopcock B to the other arm of the manometer allowed the measurement of the vapor pressure of the of the electrolytic solution. (See Figure 1)

After a run at temperatures of 25, 35, and 45°C, the manometer was removed from the bath and the flask containing the electrolytic solution was removed and weighed to determine the molality of the solution.

The manometer fluid was Hg and was degassed before use. The pressure differential was measured with the aid of a cathetometer to ±0.06 mm Hg.

FIGURE 1 DIFFERENTIAL MANOMETER

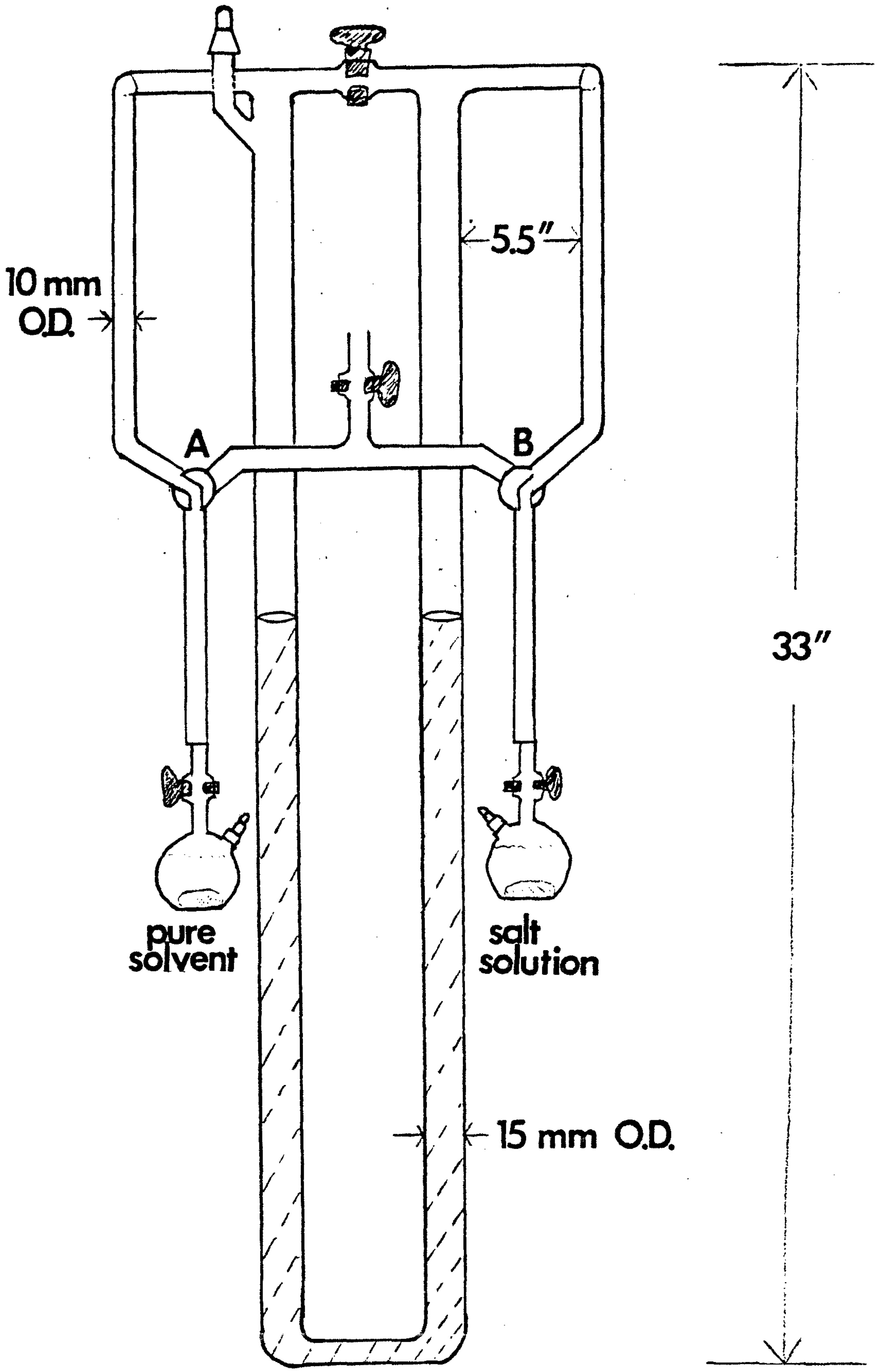
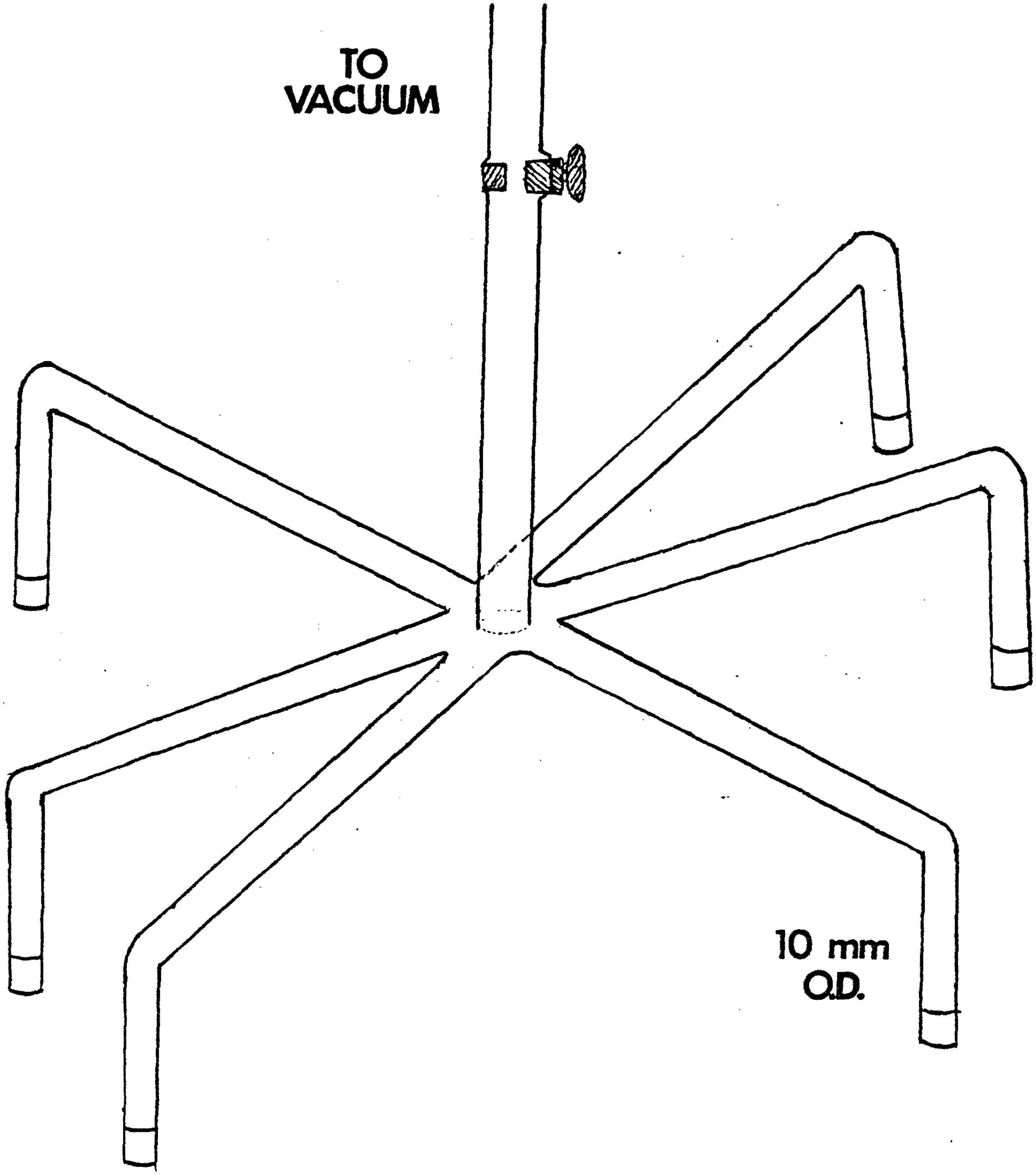


FIGURE 2 DEGASSING APPARATUS



5. Treatment of Experimental Results

The experimental quantity measured by the static method is ΔP, the difference between the vapor pressure of the solvent and the vapor pressure of the salt-solvent solution, or

$$\Delta P = P_0^s - P^s \qquad (66)$$

where P_0^s is the vapor pressure of the pure solvent and P^s is the vapor pressure of the electrolytic solution. Using equation (66), the activity of the solvent, a_1, is calculated from

$$a_1 = (P_0^s - P^s)/P_0^s \qquad (67)$$

The activity coefficient of the solvent, γ_1, is given by

$$\gamma_1 = a_1/x_1 \qquad (68)$$

where x_1 is the mole fraction of the solvent.

The osmotic coefficient, ϕ, is then calculated from the value of a_1 given in equation 67 and equation 42

$$\phi = -1000. \ln a_1/(vmM_1) \qquad (42)$$

To obtain the mean activity coefficient of the salt directly from the experimental data, the method of Randall and White(35) may be used. They rearranged the log term of equation 44 so that the following equation is obtained for the mean activity coefficient

$$\ln \gamma_{\pm} = \phi - 1 - 2\int_0^m (1 - \phi/m^{\frac{1}{2}})\, dm^{\frac{1}{2}} \qquad (69)$$

Plotting $1-\phi/m^{\frac{1}{2}}$ vs. $m^{\frac{1}{2}}$ allows the area under the curve to be evaluated and therefore the value of $\gamma_{\pm}$ at a particular molality of the electrolyte.

CHAPTER IV

RESULTS

A. Experimental Results

In order to check the performance of the differential manometer, the vapor pressure depression of KCl in water as a function of molality was measured at 25°C. The results are compared in Figure 3 to the values given by Robinson and Stokes. The values of ΔP agree to within ± 0.010 mm Hg.(TableIA)

The vapor pressure depressions of LiBr and LiCl in methanol were determined at temperatures of 25,35, and 45°C in the concentration range of 0.1m to 4.4m. The results are presented in Figures 4-9, where ΔP is plotted as a function of molality. In general, for a given system the vapor pressure depression increases with an increase in the concentration of the electrolyte. Increasing the temperature at a constant concentration of the electrolyte for either system results in a larger depression of the vapor pressure of methanol.

The experimental results obtained by Skabichevskii(29) for the LiBr and LiCl systems at 25°C are plotted with the experimental results obtained in this study in Figures 4 and 7, respectively. Agreement is excellent in both cases.

FIGURE 3 VAPOR PRESSURE DEPRESSION OF AQUEOUS KCL SOLUTIONS AT 25°C

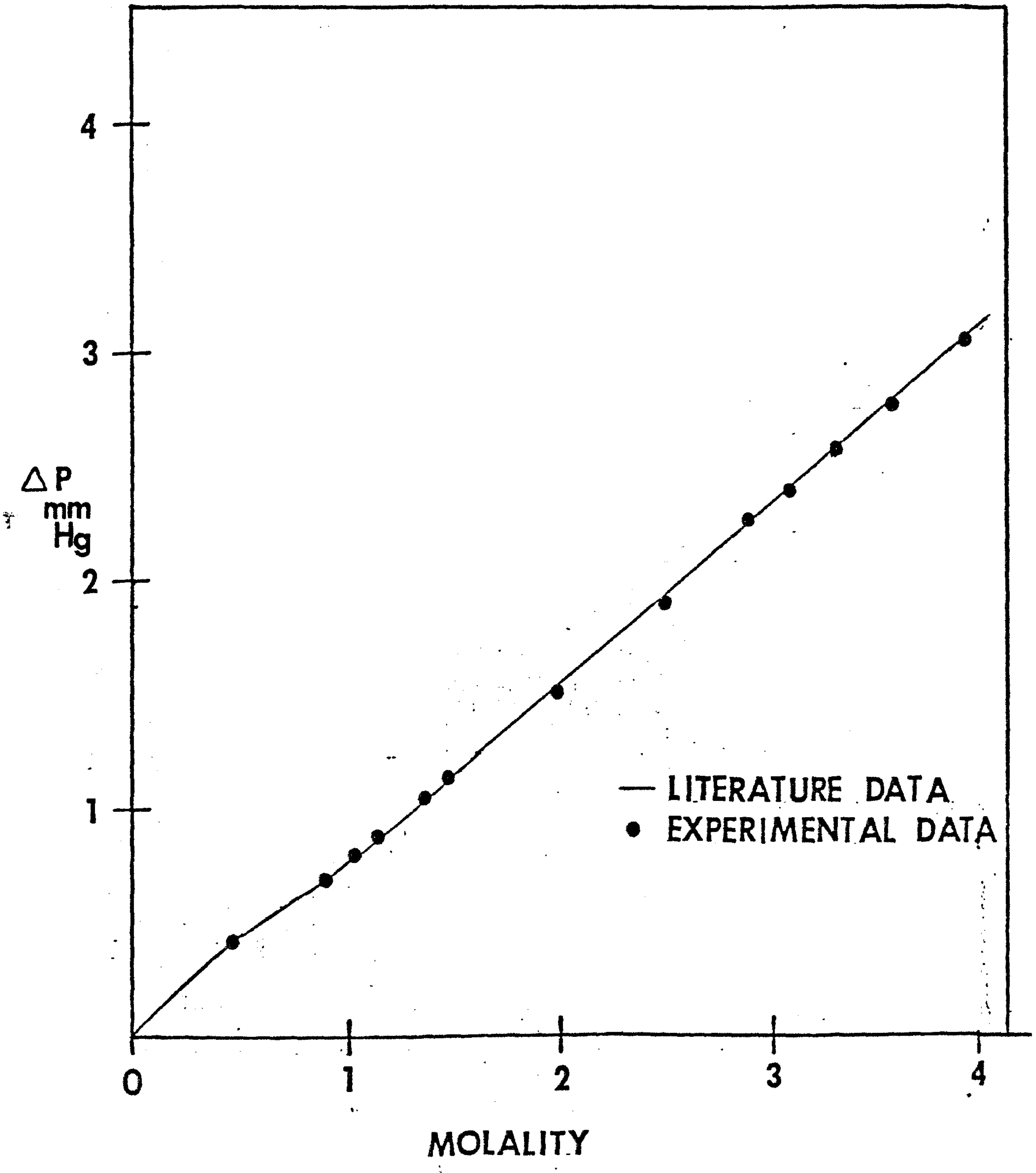


FIGURE 4 Vapor Pressure Depression as a Function of Molality for the LiBr-MeOH System at 25°C

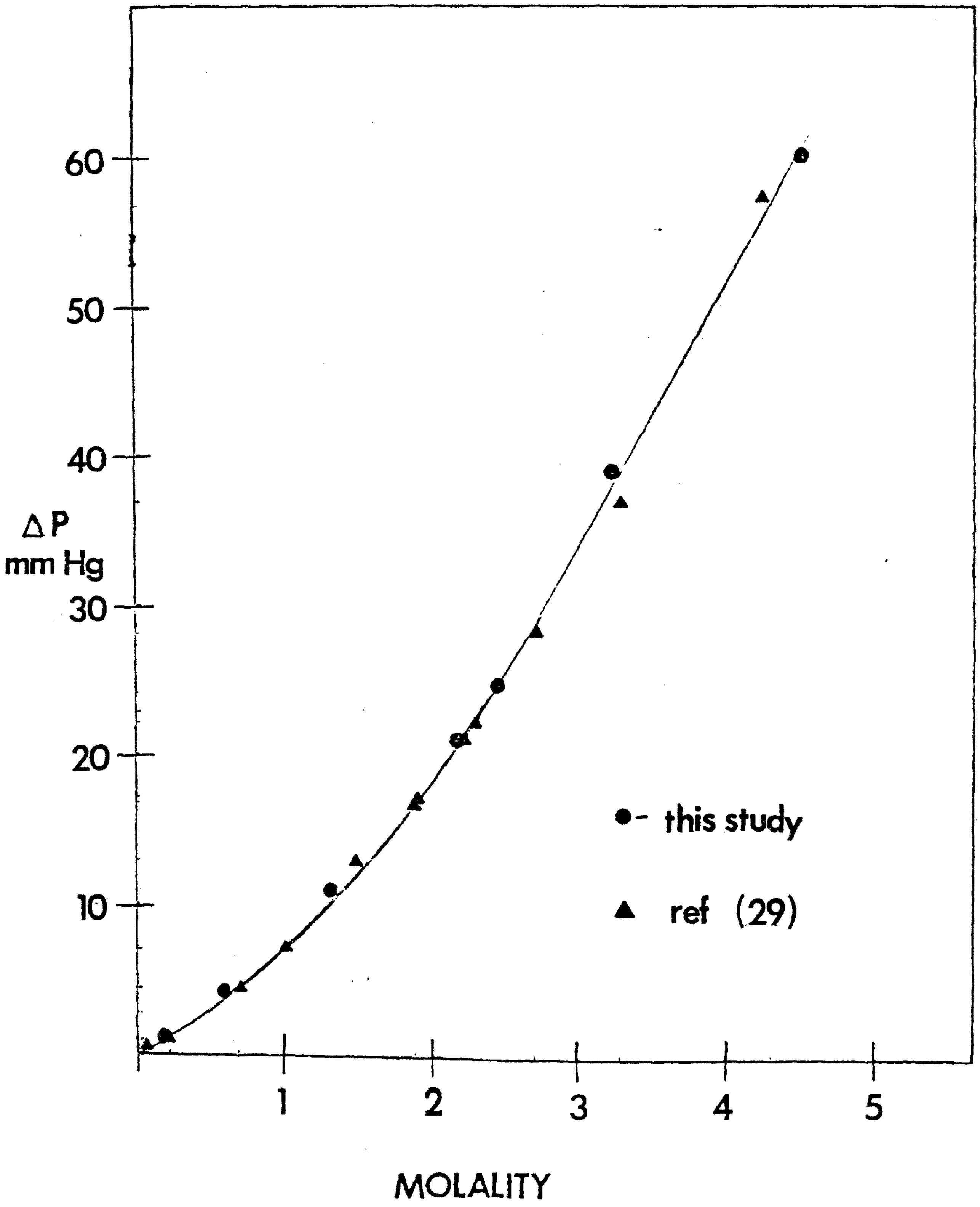


Figure 5 Vapor Pressure Depression as a Function of Molality for the LiBr-MeOH System at 35°C

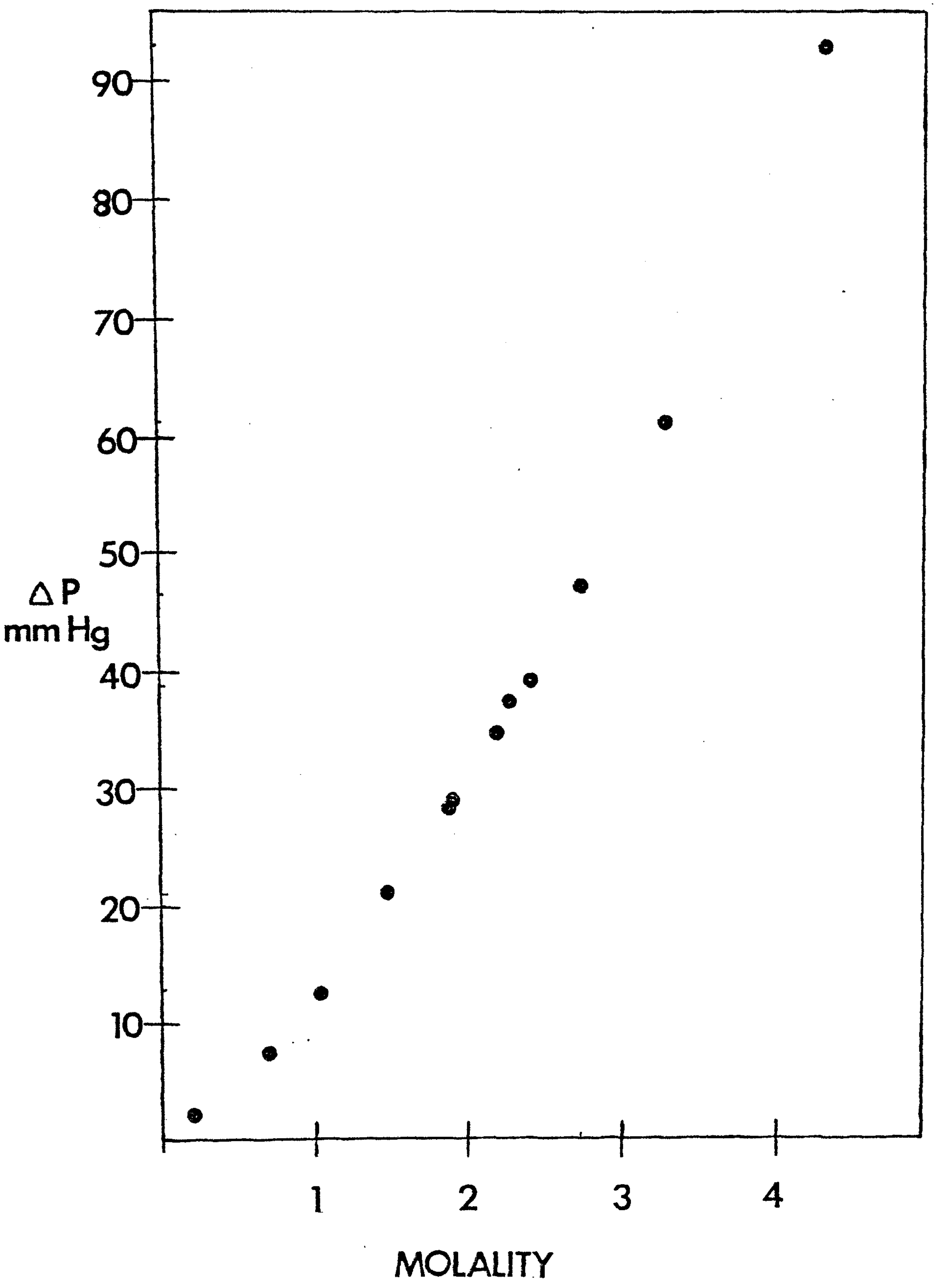


Figure 6 Vapor Pressure Depression as a Function of Molality for the LiBr-MeOH System at 45 °C.

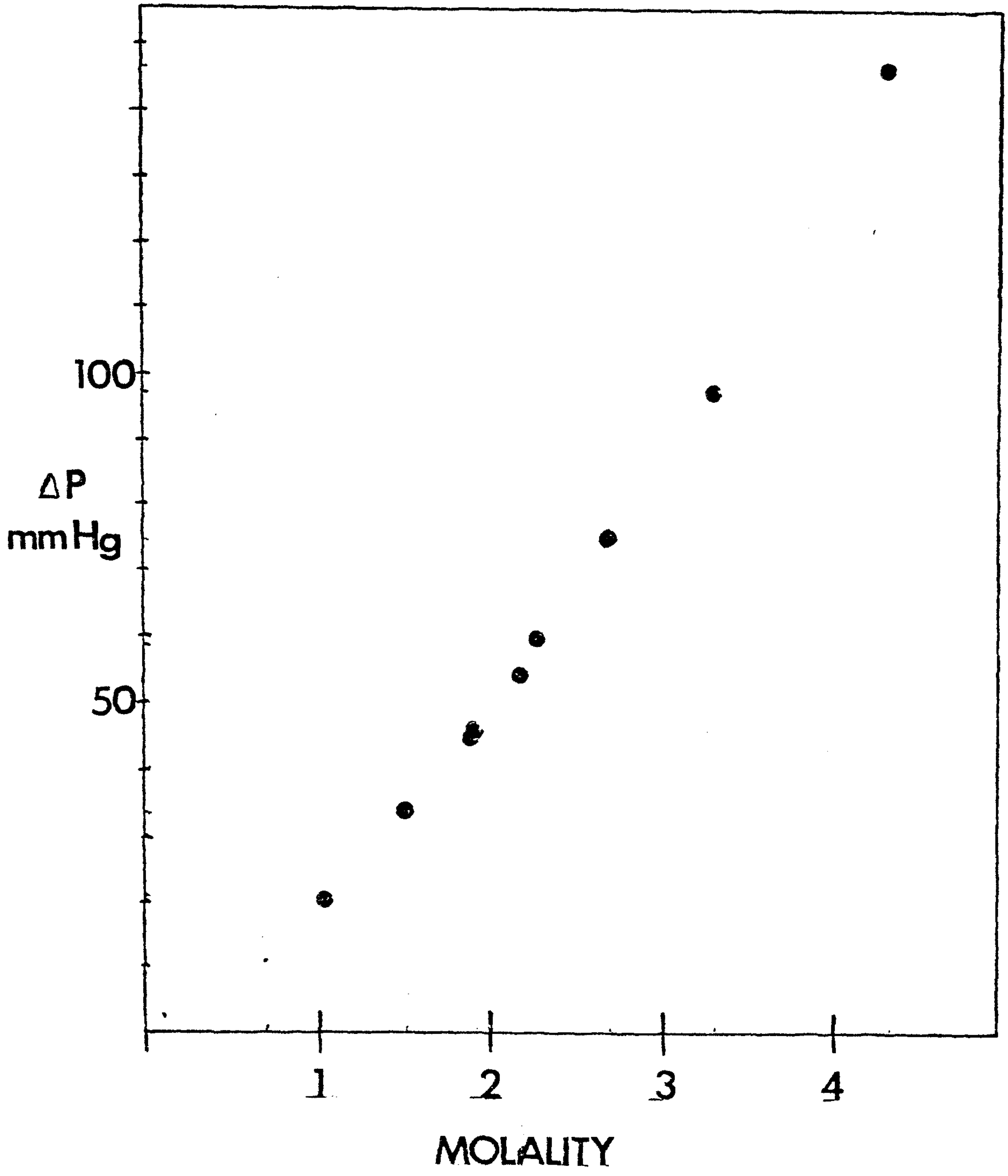


Figure 7 Vapor Pressure Depression as a Function of Molality for the LiCl-MeOH System at 25 °C

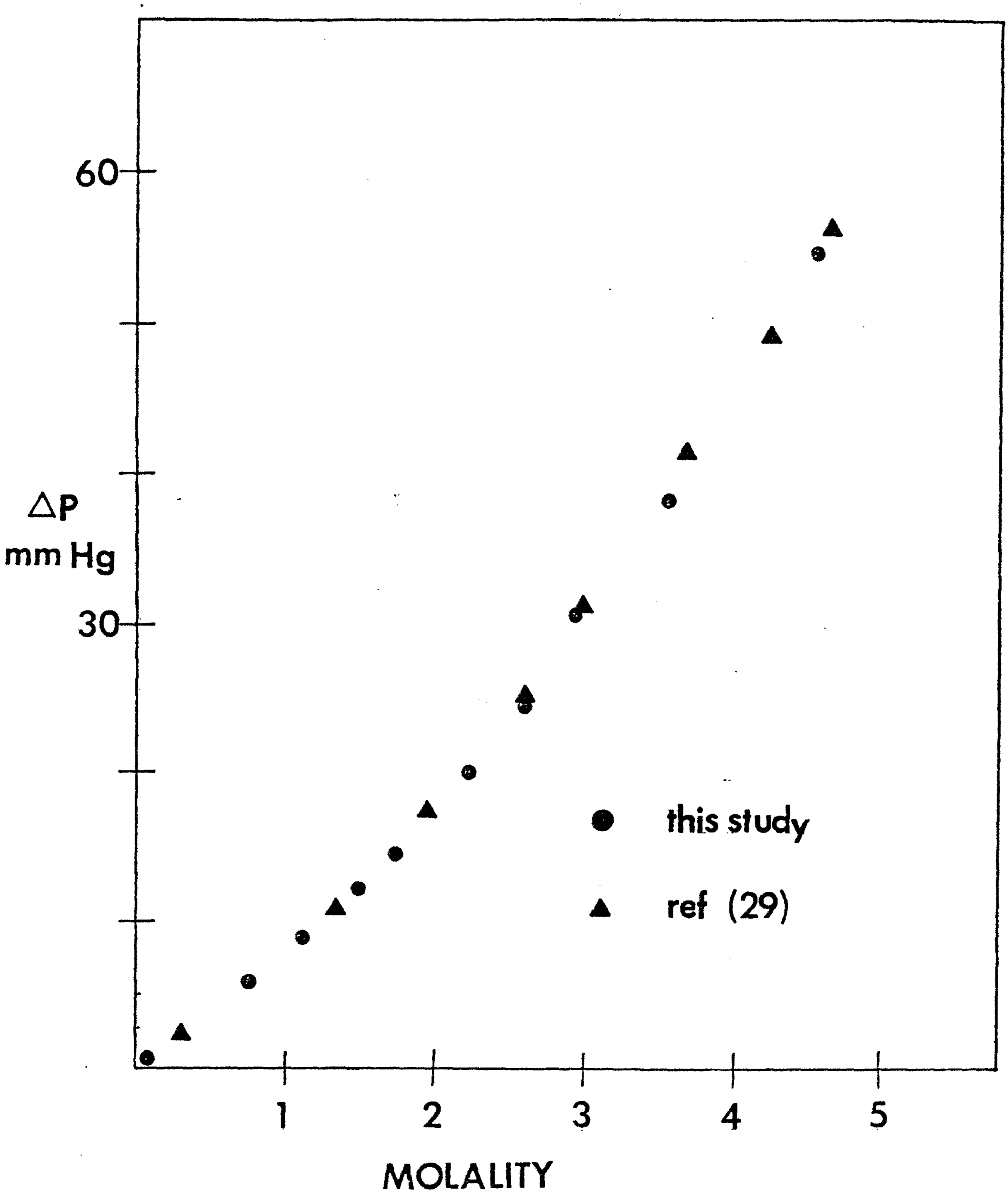


Figure 8 Vapor Pressure Depression as a Function of Molality for the LiCl-MeOH System at 35°C

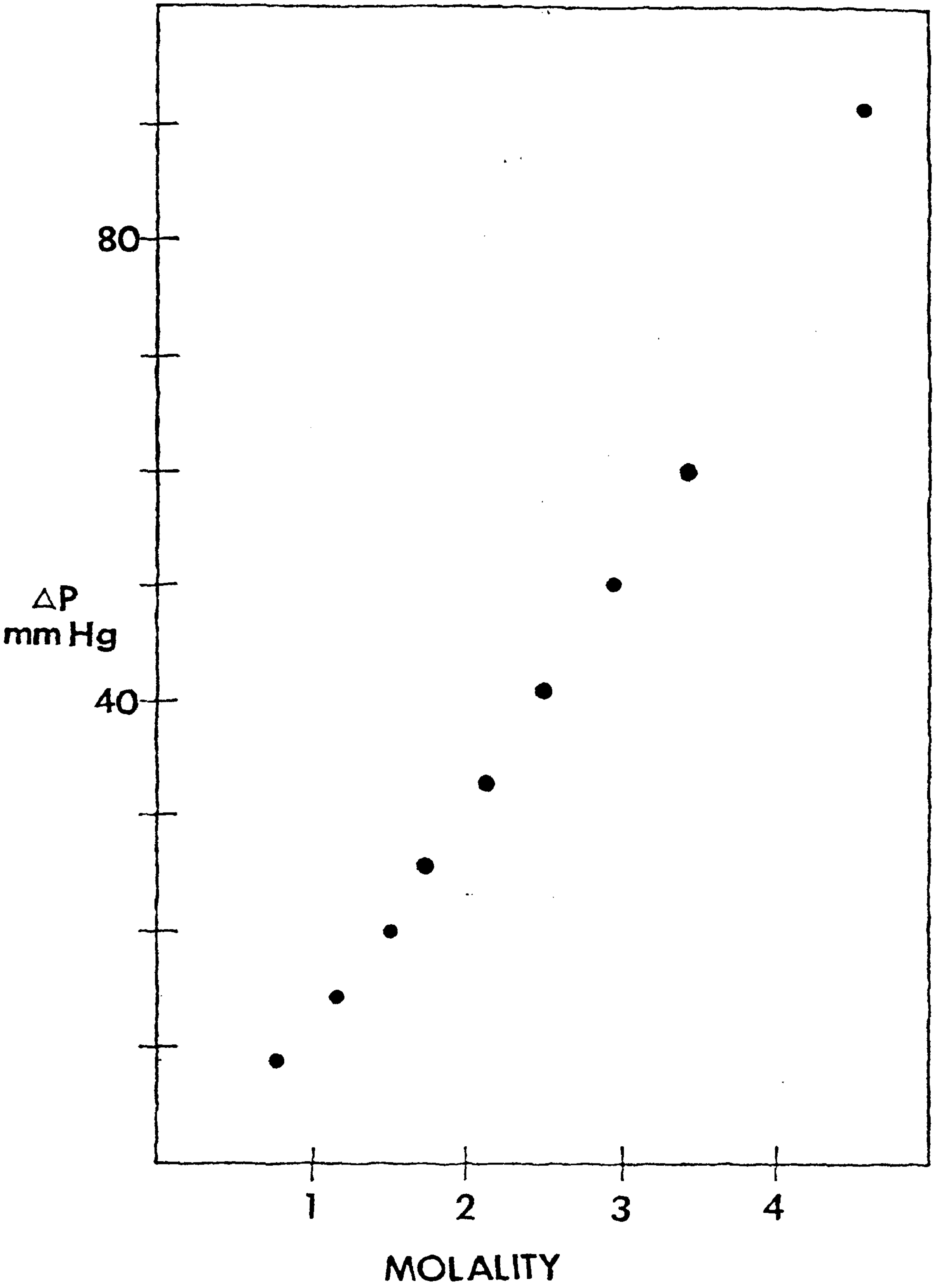
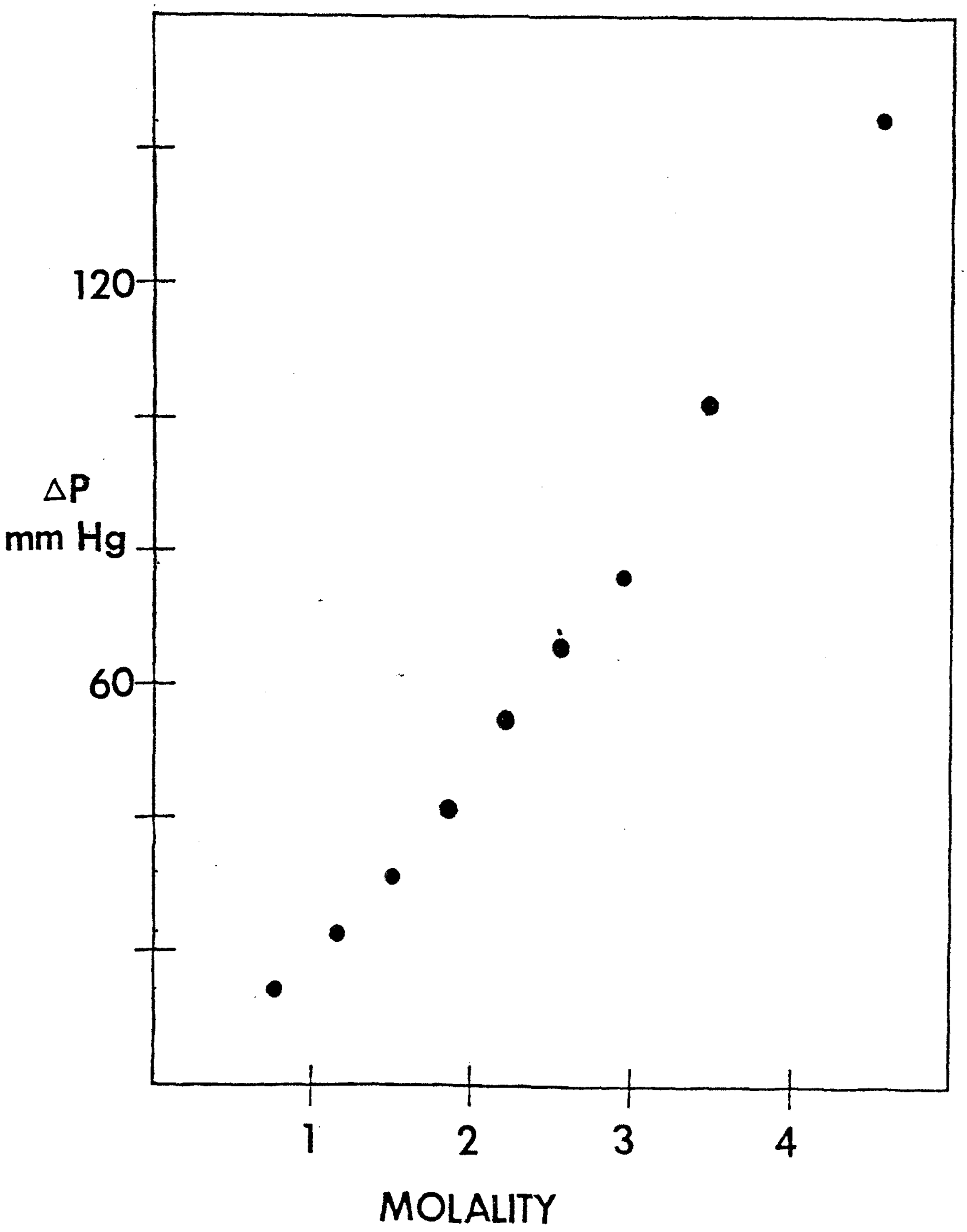


Figure 9 Vapor Pressure Depression as a Function of Molality for the LiCl-MeOH System at 45°C



Through the use of equations 67 and 68, the activity coefficient of the solvent, γ_1, is calculated for the two systems at 25,35, and 45°C. The results are presented in Tables I-VI. In general, as the mole fraction or the molality of the salt is increased, the solvent activity coefficient increases to a maximum value and then decreases. An increase in temperature results in a slight increase in the activity coefficient.

From equation 42, the osmotic coefficient of the electrolyte is calculated. The results are tabulated in the aforementioned tables. With an increase in electrolyte concentration, an increase in the osmotic coefficient is observed. An increase in temperature at a constant molality for either system indicates a decrease in the osmotic coefficient.

Using equation 69, the mean activity coefficients of the two salts were determined from plots of $1-\phi/m^{\frac{1}{2}}$ vs. $m^{\frac{1}{2}}$ and the osmotic coefficient at each concentration. A plot of $1-\phi/m^{\frac{1}{2}}$ vs. $m^{\frac{1}{2}}$ for the LiBr-MeOH system at 25°C is shown in Figure 10 for the purpose of illustration. The Debye-Huckel Limiting Law was used to extrapolate each plot in the limit of infinite dilution. The value of the limiting slope is calculated from

$$\text{slope}=-A_{\gamma}|Z_{+}Z_{-}|2.303/3 \qquad (70)$$

At 25°C, the value of the limiting slope is 1.29; at 35°C, it is 1.35; and at 45, the slope has a value of 1.40.

See Appendix B for the details of this extrapolation and its accuracy.

TABLE I Experimental Values of Vapor Pressure, Solvent Activity Coefficient, and Osmotic Coefficient for the LiBr-MeOH System at 25°C.

molality moles/kg.solv ±0.0001	P^s mm. Hg ±0.06mm	Solvent activity coeff.	osmotic coeff.	ΔP mm Hg ±0.06mm
0.1153	127.72	1.0052	0.307	0.29
0.2170	126.59	1.0027	0.802	1.42
0.6957	123.81	1.0103	0.748	4.20
1.0506	120.13	1.0016	0.944	7.88
1.5315	114.96	0.9862	1.096	13.05
1.9189	110.69	0.9711	1.182	17.31
1.9470	110.33	0.9695	1.191	17.68
2.1912	106.73	0.9509	1.295	21.28
2.3033	105.52	0.9460	1.309	22.49
2.4006	104.46	0.9416	1.321	23.55
2.7553	99.43	0.9139	1.431	28.58
3.3010	90.61	0.7093	1.633	37.40
4.3450	71.02	0.7093	2.116	56.99
0.0000	128.01	1.0000	0.000	0.00

TABLE II Experimental Values of Vapor Pressure, Solvent Activity Coefficient, and Osmotic Coefficient for the LiBr-MeOH System at 35°C.

molality ±0.0001	P^s mm Hg ±0.06 mm	solvent activity coeff.	osmotic coeff.	ΔP mm Hg ±0.06mm
0.0000	211.07	1.0000	0.000	0.00
0.1153	210.57	1.0050	0.321	0.50
0.2179	209.28	1.0054	0.610	1.79
0.6957	202.72	1.0033	0.905	8.35
1.0506	198.14	1.0019	0.939	12.93
1.5315	190.10	0.9890	1.066	20.97
1.9189	182.87	0.9729	1.166	28.20
1.9472	181.81	0.9688	1.196	29.26
2.1912	176.78	0.9552	1.263	34.29
2.3033	174.19	0.9471	1.301	36.88
2.4006	172.28	0.9418	1.320	38.79
2.7553	164.43	0.9166	1.414	46.64
3.3013	149.81	0.8717	1.620	61.26
4.3450	118.06	0.8225	2.087	93.01

TABLE III Experimental Values of Vapor Pressure, Solvent Activity Coefficient, and Osmotic Coefficient for the LiBr-MeOH system at 45°C.

molality ±0.0001	P^Smm Hg ±0.06	solvent activity coeff.	osmotic coeff.	ΔPmm Hg ±0.06
0.0000	337.48	1.0000	0.000	0.00
0.1153	335.56	1.0017	0.772	1.92
0.6957	326.48	1.0105	0.743	11.00
1.0506	316.35	1.0001	0.960	21.13
1.5315	304.00	0.9892	1.065	33.48
1.9189	293.01	0.9750	1.149	44.47
1.9472	291.36	0.9711	1.178	46.12
2.1912	282.89	0.9559	1.257	54.59
2.3033	278.77	0.9480	1.295	58.71
2.7553	263.23	0.9177	1.407	74.25
3.3013	240.59	0.8637	1.600	96.89
4.3450	190.05	0.7200	2.062	146.53

TABLE IV Experimental Values of Vapor Pressure, Solvent Activity Coefficient, and Osmotic Coefficient for the LiCl-MeOH System at 25°C.

molality ± 0.0001	P^s mm Hg ± 0.06	solvent activity coeff.	osmotic coeff.	ΔPmm Hg ± 0.06
0.0000	128.01	1.0000	0.000	0.00
0.1003	127.51	1.0025	0.609	0.50
6.7663	122.27	1.0013	0.951	5.84
1.1409	119.07	0.9982	0.990	8.94
1.4969	115.80	0.9914	1.045	12.21
1.7557	113.13	0.9832	1.098	14.88
2.2500	107.81	0.9636	1.191	20.20
2.6073	102.53	0.9348	1.328	25.48
2.9403	97.66	0.9067	1.436	30.35
3.5600	88.51	0.8492	1.617	39.50
4.5800	71.17	0.7192	2.000	56.84

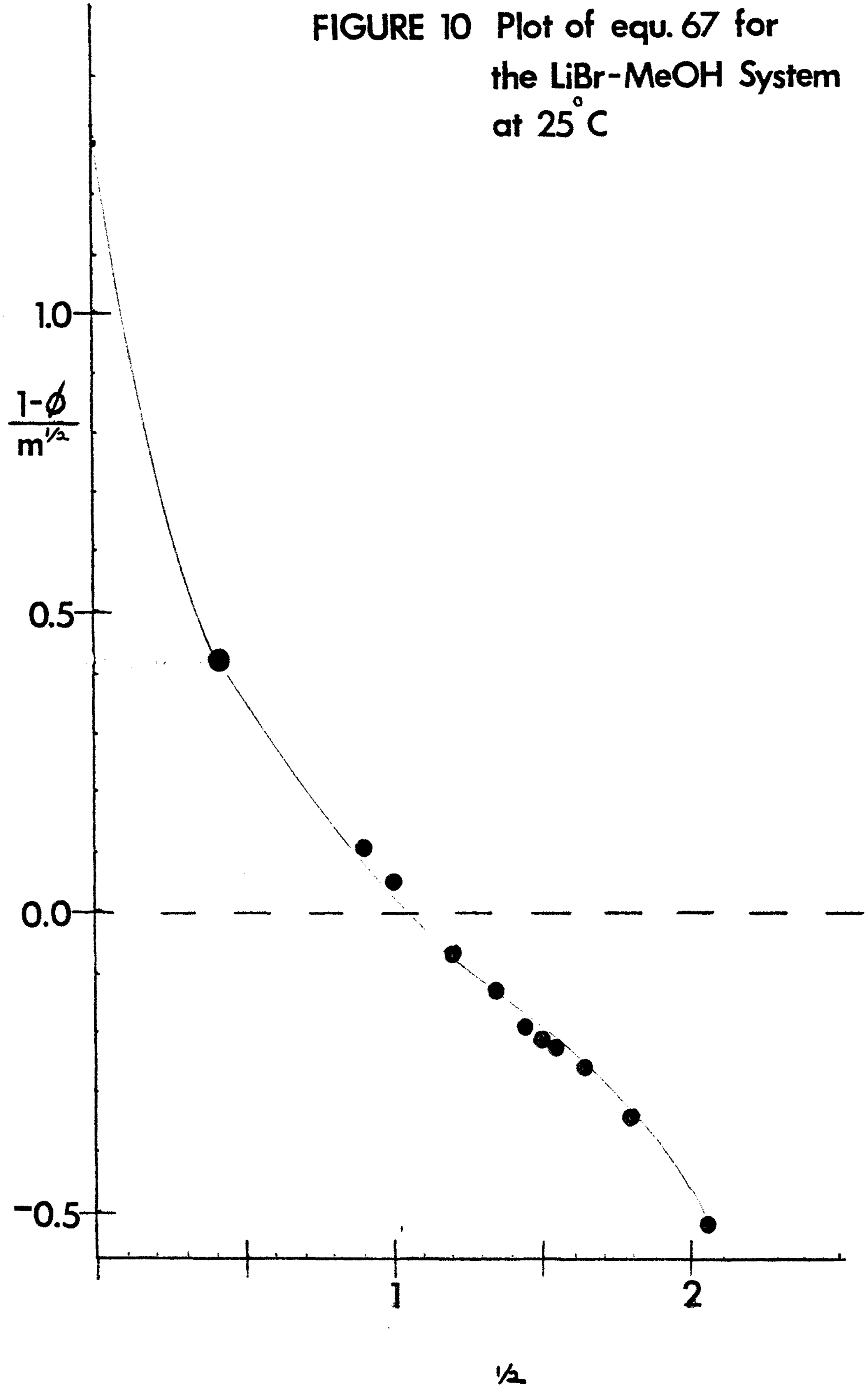
TABLE V Experimental Values of Vapor Pressure, Solvent Activity Coefficient, and Osmotic Coefficient for the LiCl-MeOH System at 35 °C.

molality ±0.0001	P^smm Hg ±0.06	solvent activity coeff.	osmotic coeff.	ΔPmm Hg ±0.06
0.0000	211.07	1.0000	0.000	0.00
0.1003	210.07	1.0016	0.739	1.00
0.7663	201.94	1.0037	0.901	9.13
1.1409	196.64	1.0002	0.962	14.43
1.4969	191.04	0.9919	1.039	20.03
1.7557	186.07	0.9807	1.1205	25.00
2.2500	177.57	0.9626	1.1986	33.50
2.6073	169.07	0.9349	1.328	42.00
2.9403	161.06	0.9068	1.435	50.01
3.5600	152.07	0.8848	1.437	59.00
4.5800	119.31	0.7312	1.943	91.76

TABLE VI Experimental Values of Vapor Pressure, Solvent Activity Coefficient, and Osmotic Coefficient for the LiCl-MeOH System at 45 °C.

molality ±0.0001	P^s mm Hg ±0.06	solvent activity coeff.	osmotic coeff.	ΔP mm Hg ±0.06
0.0000	337.48	1.0000	0.000	0.00
0.1003	335.38	1.0002	0.971	2.10
0.7663	322.98	1.0040	0.895	14.50
1.1409	314.61	1.0009	0.953	22.87
1.4969	305.84	0.9932	1.026	31.64
1.7557	297.77	0.9675	1.113	44.00
2.2500	280.63	0.9514	1.279	56.85
2.6073	268.38	0.9281	1.371	69.10
2.9403	258.54	0.9104	1.414	78.94
3.5600	234.58	0.8537	1.594	102.90
4.5800	193.72	0.7429	1.891	143.76

FIGURE 10 Plot of equ. 67 for the LiBr-MeOH System at 25°C



In Tables VII and VIII, are shown values of the experimental mean activity coefficients from equation 69 for the LiBr and LiCl systems at 25°C so that they can be compared with those values given by Skabichevskii.(29) For the LiBr system, the agreement between the mean activity coefficients at each concentration is good with the exception of the value of the mean activity coefficient at 4m. At this point, the relative percent error based on Skabichevskii's value is 13.9%. For the LiCl system, the agreement between the mean activity coefficients is good except at 0.3 and 4m, where the relative percent errors are 14.4 and 14.5%, respectively. No explanation can be given for these discrepancies since no other data from other sources are available.

In Tables IX and X, are plotted the mean activity coefficients for both systems at 35 and 45°C. As the temperature of the system is increased from 25 to 45°C, the mean activity coefficient decreases at a constant concentration. At a constant value of the temperature, the mean activity coefficients decrease and then begin to increase again with increasing concentration. Similar trends are also noted for these salts in water.

TABLE VII A Comparison of the Mean Activity Coefficients Obtained in this Study with those of Ref. 29 for the LiBr-MeOH System at 25°C.

Molality	$\gamma_\pm$	$\gamma_\pm$(ref.29)	rel. per. error
0.3	0.356	0.361	1.39
0.5	0.324	0.331	2.11
1.0	0.348	0.336	1.19
2.0	0.473	0.479	1.20
3.0	0.742	0.766	3.10
4.0	1.40	1.63	13.9

TABLE VIII A Comparison of the Mean Activity Coefficients Obtained in this Study with those of Ref. 29 for the LiCl-MeOH System at 25°C

Molality	$\gamma_\pm$	$\gamma_\pm$(ref.29)	rel. per. error
0.3	0.413	0.361	14.4
0.5	0.329	0.331	0.60
1.0	0.338	0.336	0.60
2.0	0.415	0.458	9.40
3.0	0.669	0.695	4.30
4.0	1.010	1.18	14.5

TABLE IX Experimental Values of the Mean Activity Coefficients for the LiBr-MeOH System at 35 and 45 °C

molality	$\gamma_{\pm}$ 35 °C	$\gamma_{\pm}$ 45 °C
0.1153	0.366	0.227
0.2170	0.261	0.258
0.6957	0.245	0.241
1.0506	0.243	0.235
1.5315	0.271	0.262
1.9189	0.304	0.297
2.1912	0.347	0.338
2.7553	0.434	0.425
3.3013	0.574	0.573
4.345	1.133	1.110

TABLE X Experimental Values of the Mean Activity Coefficients for the LiCl-MeOH System at 35 and 45°C.

molality	$\gamma_{\pm}$ 35 °C	$\gamma_{\pm}$ 45 °C
0.1003	0.509	0.382
0.7663	0.338	0.247
1.1409	0.348	0.254
1.4969	0.375	0.275
1.7557	0.414	0.301
2.2500	0.511	0.338
2.6073	0.583	0.401
2.9403	0.638	0.467
3.5600	0.844	0.509
4.5800	1.361	1.012

B. Correlation Results Using the Bromley and Pitzer Equations

The experimental ΔP-molality data for the LiBr-MeOH and and LiCl-MeOH systems at all temperatures were correlated using the Bromley and Pitzer equations, in order to test the applicability of these equations to nonaqueous electrolytic systems. Correlation of the data through the Bromley equation results in the determination of the parameter B, specific for each salt, while correlation of the data through the Pitzer equation results in the determination of the parameters, β_0, β_1, and C, which are specific for each salt.

To correlate the data using the Bromley equation, the following calculational procedure was utilized: 1) The ΔP data were converted to osmotic coefficient data through equations 66-68 and 42. 2) With the aid of a computer, the osmotic coefficient-molality data were substituted in the Bromley expression for the osmotic coefficient(equations 63-63b) using Bromley's values of ρ equal to unity, n equal to 2.0 and the value of a given by equation 61a. The data were then regressed to determine the optimum value of B for the particular system using the Fibonacci method. (The complete computer program is found in Appendix C) 3) The values of B, which were calculated for each system at the three temperatures, were then substituted into Bromley's expression for the mean activity coefficient(equation 62) to obtain values of this property based on this equation.

An approach similar to the above was used to determine the parameters β_0, β_1, and C, specific for the Pitzer correlation. Again, the experimentally determined values of ΔP were converted to the osmotic coefficient. The osmotic coefficient-molality data were substituted in the Pitzer equation for the osmotic coefficient(equation 59) and regressed using the LSQ2 subroutine to determine the optimum values of β_0, β_1, and C. (The complete computer program is found in Appendix D) The values of α and b were taken to be those of Pitzer. The regressed values of β_0, β_1, and C were then substituted in equations 60-60b to obtain the values of the mean activity coefficients of the salt based on the experimental data at 25, 35, and 45°C.

Since the Bromley and Pitzer equations were originally applied to aqueous electrolytic solutions and correlated the data satisfactorily up to 6m, it was assumed that in the case of an electrolyte in methanol that these equations would apply only up to 3m, since the dielectric constant of methanol at all temperatures is approximately half that of water. To test this assumption, data for a particular system using either equation were regressed over the entire molality range. The data points greater than 3m were eliminated and the system was regressed again. This procedure was done for the LiBr and LiCl systems at 25°C. Therefore, for each salt at 25°C, two values of B in the case of the Bromley equation were determined. One for the entire concentration range and one for the data up to 3m. Likewise, for the Pitzer equation, 6 parameters in all were determined for a system at 25°C. Three of the parameters, β_0, β_1, and C, correspond to the entire concentration range, while the other three correspond to values of the molality less than 3m.

Since the values of B in the case of the Bromley equation, and β_0, β_1, and C in the case of the Pitzer equation differed if the entire molality range or just those data points below 3m were considered, mean activity coefficients were calculated based on the two cases for the two systems at 25°C. These results are presented in Figures 11-14.

Examination of Figures 11 and 12 for the LiBr system indicate that the mean activity coefficients calculated by the Bromley equation do not change appreciably if all data are considered or data below 3m are considered. Referring to Figure 11, where the entire concentration range was considered in the regression, it is seen that the Bromley equation better represents the experimental. The Pitzer equation fails to correlate the minimum of the activity coefficient curve, and deviates greatly from the experimental curve at concentrations greater than 3m. In Figure 12, where data below 3m only are considered in the regression, the Bromley equation correlated the data well at low concentrations,(below 1m), while the Pitzer equation fits the data well at higher concentrations.(above 1.8m)

Figure 11 Values of the Mean Activity Coefficient of LiBr in Methanol at 25°C.(The entire concentration range is plotted)

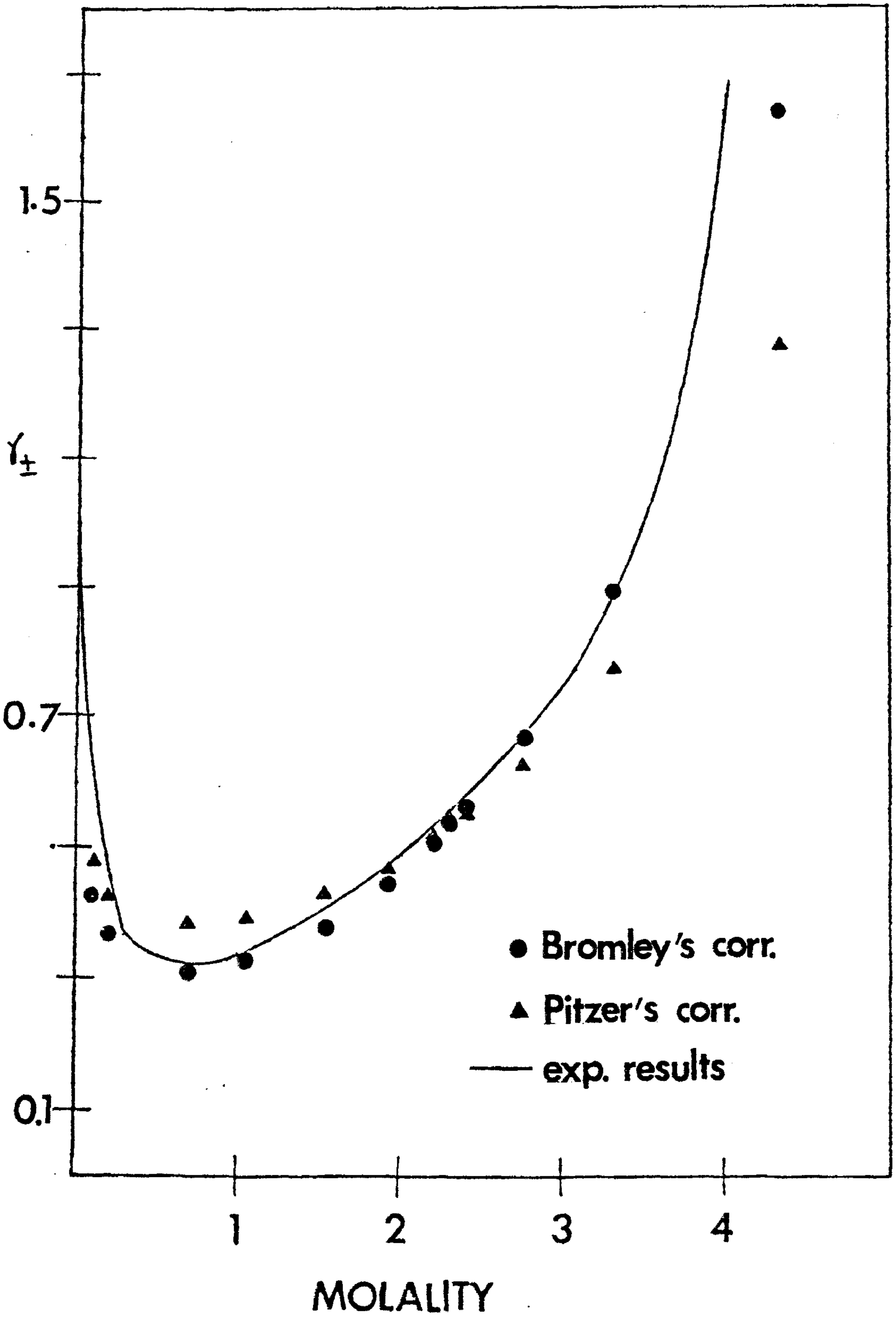


Figure 12 Values of the Mean Activity Coefficient of LiBr in Methanol at 25 °C.

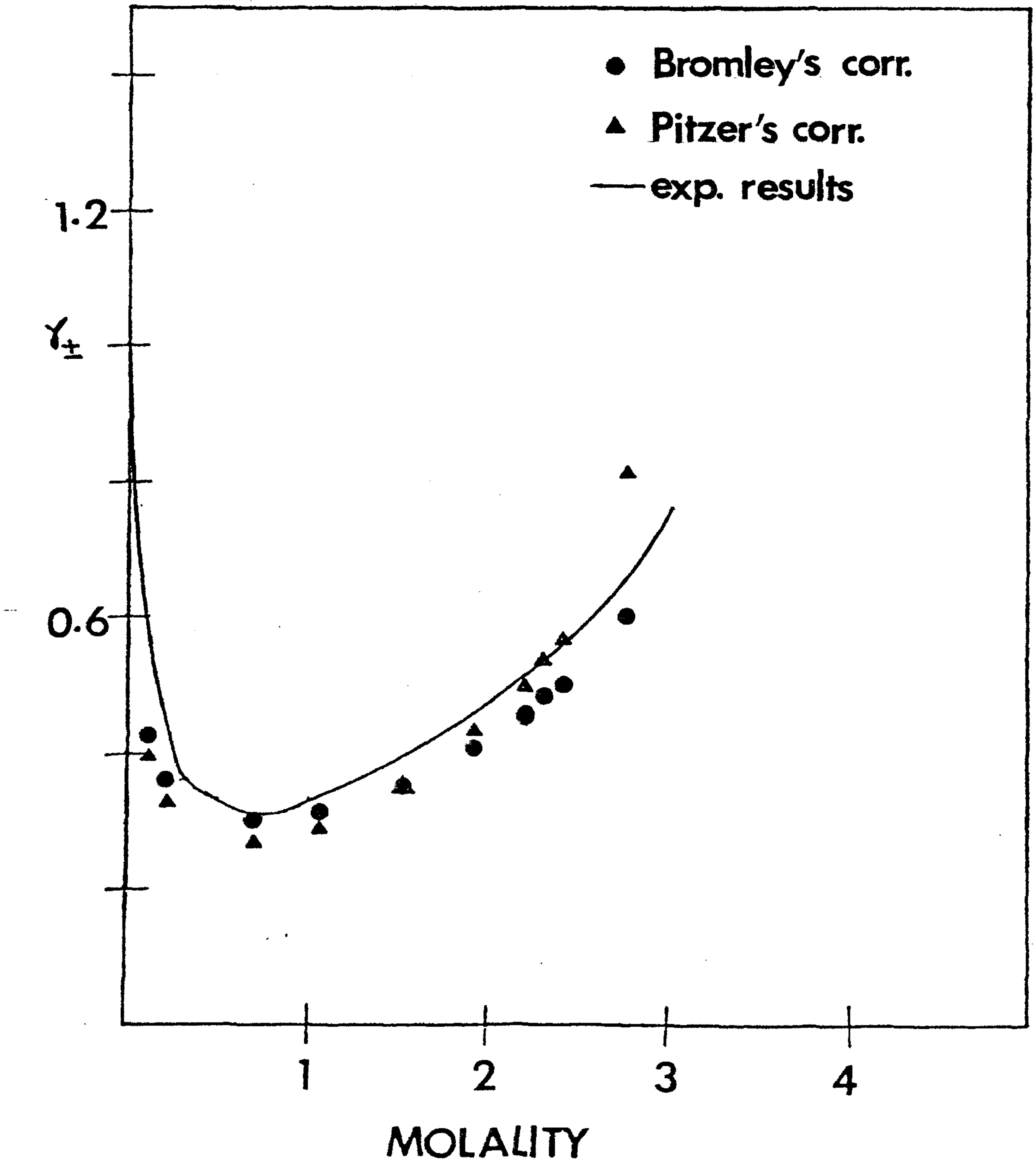


Figure 13 plots the mean activity coefficients for the LiCl-MeOH system at 25°C obtained from the Bromley and Pitzer equations over the entire concentration range. It is seen that the equations correlate the data at molalities from 1.0 to 2.0, but begin to deviate from the experimental curve at molalities greater than 2.0. In Figure 14 are plotted the activity coefficients for the same system but at concentrations below 3m. The Bromley equation follows the same trend as the experimental curve, but deviates from it by an average relative percent error of 14.0%. The Pitzer equation fails completely in correlating this data. It does not fit the minimum in the curve nor does it fit the data at molalities greater than 2.0.

Table XI presents values of the mean activity coefficients of the LiBr-MeOH system at 35°C generated using both the Bromley and the Pitzer equations. The relative percent error of each calculated value from the experimental value in Table X is also indicated. The results are plotted in Figure 15. Although both equations predicted the trend of the experimental mean activity curve, they did not correlate the data well. The average relative percent error in the activity coefficient predicted by the Bromley equation is 25.0% while that predicted by the Pitzer equation is 35.3%.

Table XII shows values of the mean activity coefficients of the LiBr-MeOH system at 45°C. calculated using the

TABLE XI Values of the Mean Activity Coefficient of LiBr in Methanol at 35°C calculated using the Bromley and Pitzer equations.(The relative percent error is compared to the experimental values in Table IX.

molality	$\gamma_{\pm}$ B	rel. per. error	$\gamma_{\pm}$P	rel. per. error
0.1153	0.407	11.2	0.466	27.0
0.2179	0.344	24.0	0.419	37.7
0.6957	0.284	13.7	0.378	54.3
1.0506	0.295	17.6	0.387	37.2
1.5315	0.340	20.3	0.418	35.2
1.9189	0.396	30.3	0.457	50.3
2.1912	0.448	29.1	0.493	42.1
2.7553	0.593	36.6	0.594	36.9
3.3013	0.797	38.9	0.733	27.7
4.3450	1.456	28.5	1.185	4.6

Figure 13 Values of the Mean Activity Coefficient of LiCl in Methanol at 25 °C.(The entire concentration is plotted)

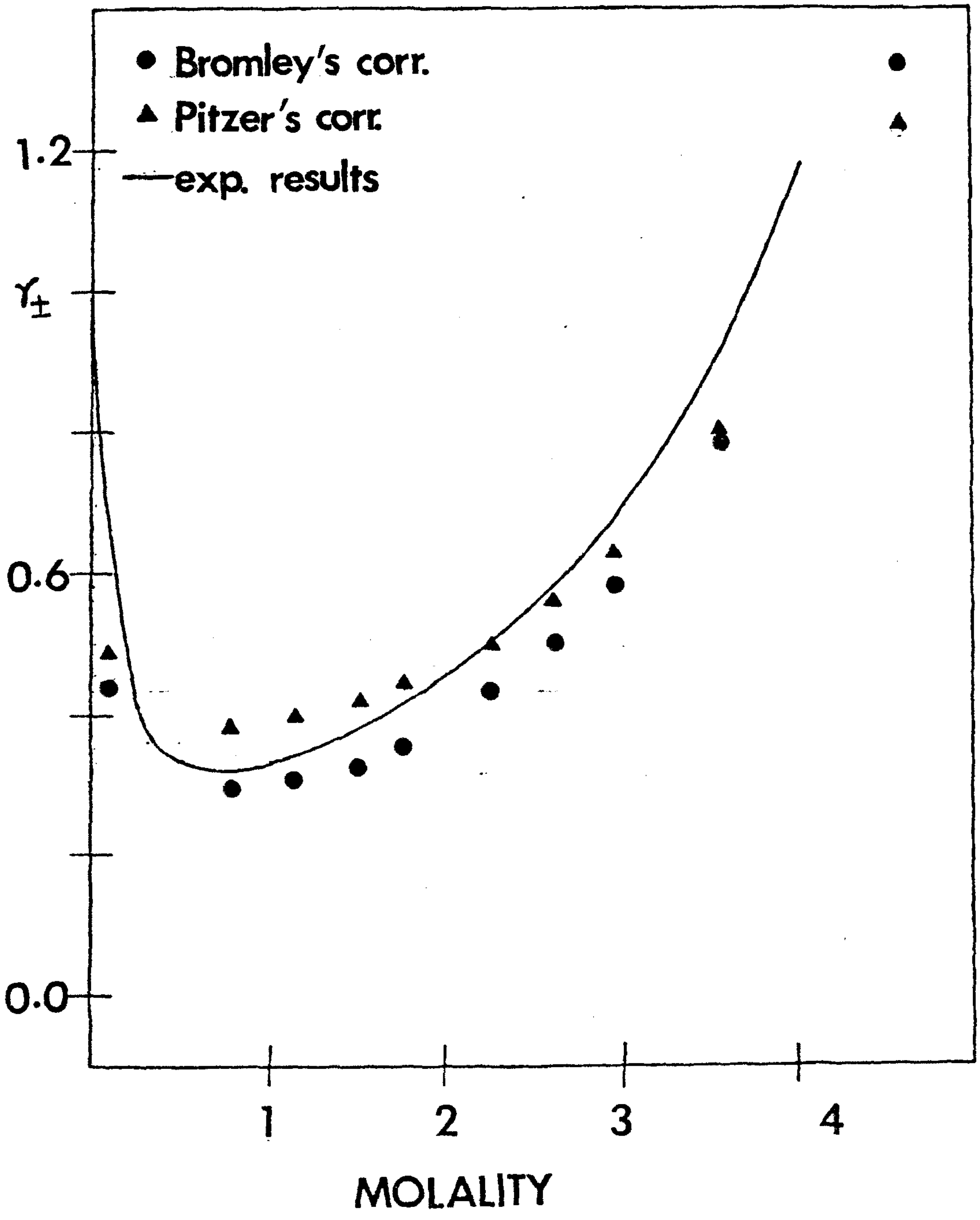


Figure 14. Values of the Mean Activity Coefficient of LiCl in Methanol at 25 °C.

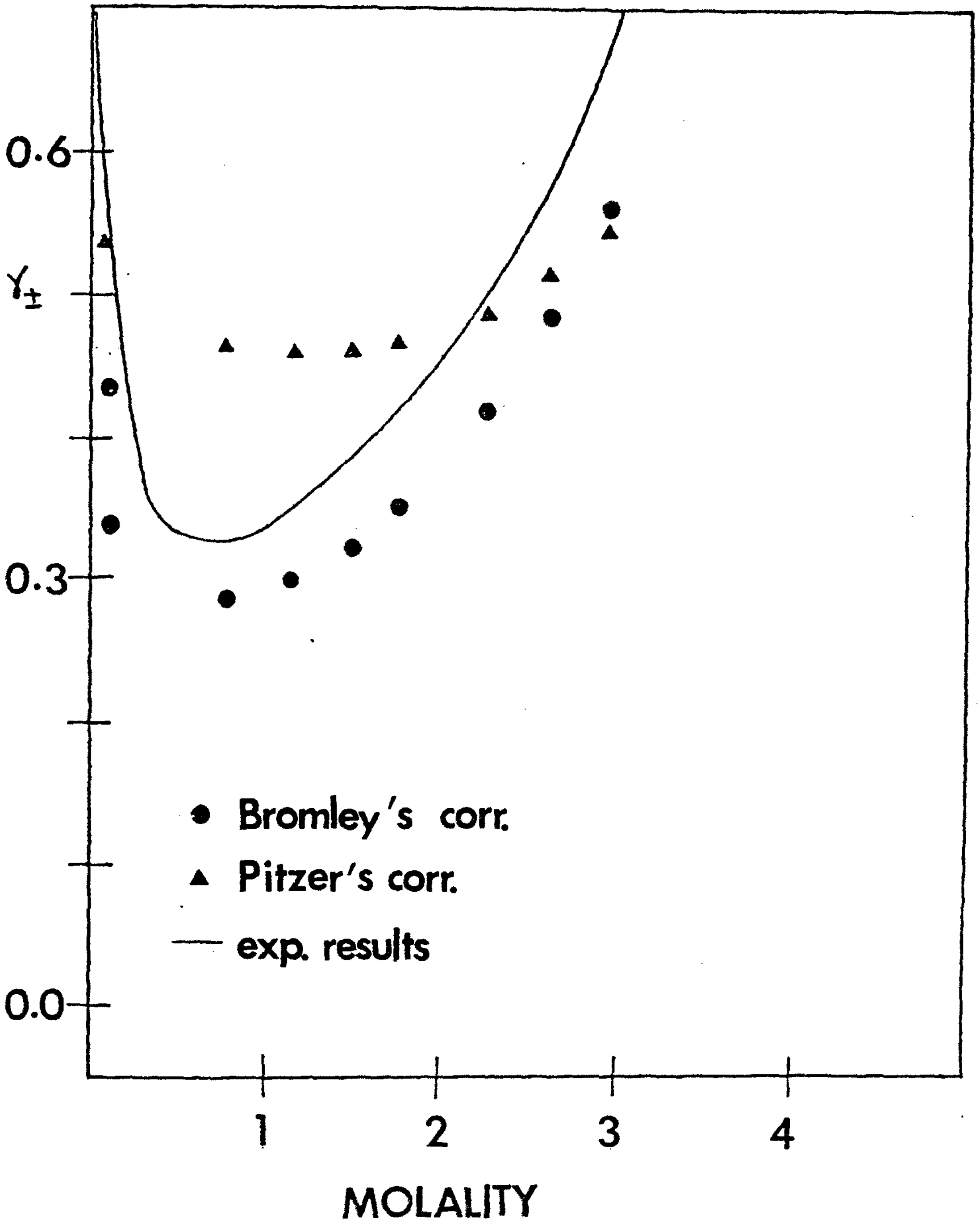
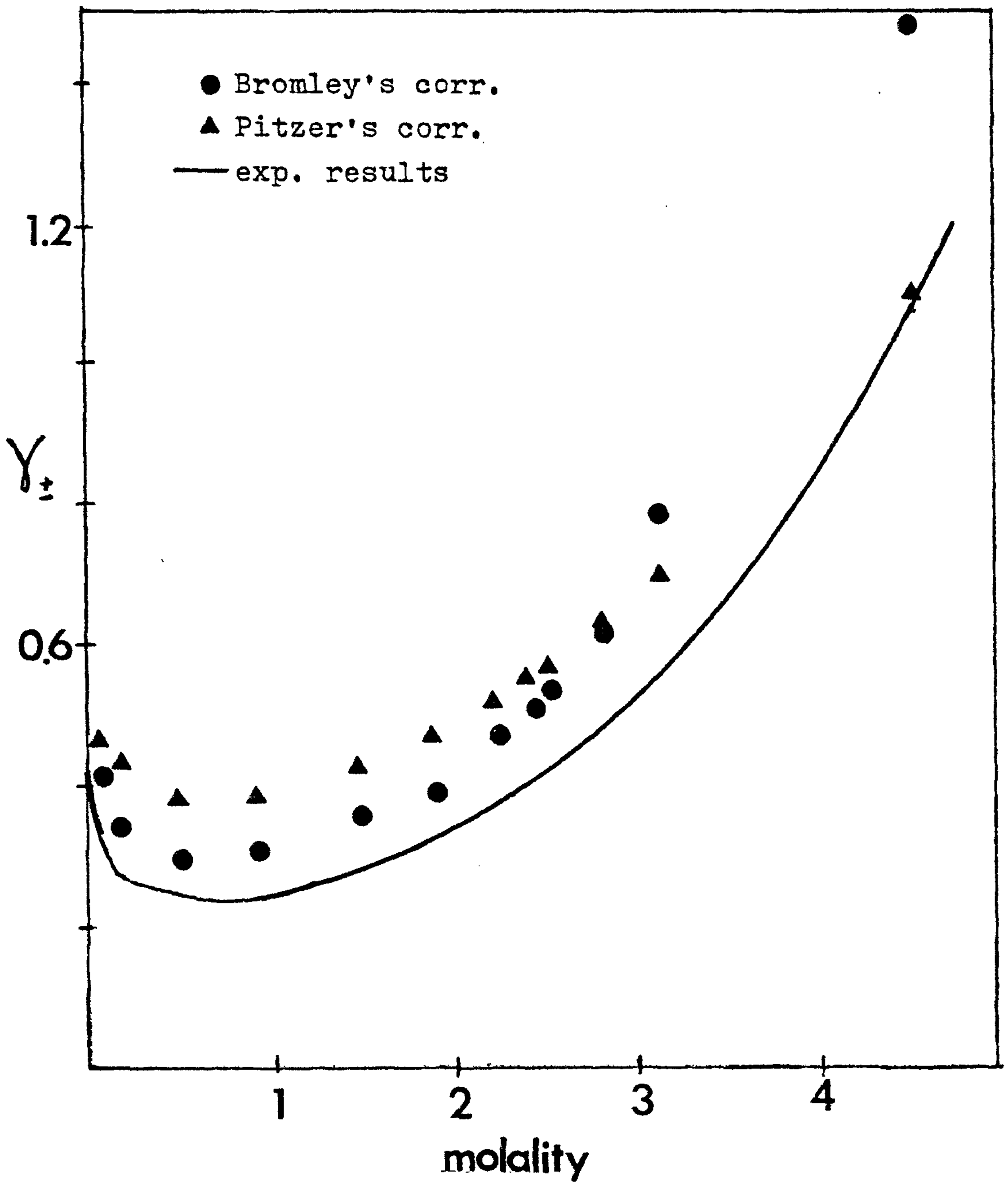


Figure 15 Values of the Mean Activity Coefficient of LiBr in Methanol at 35 C.



experimental data and the Bromley and the Pitzer equations. The relative percent error of each calculated value from the experimental value is also indicated. The results are illustrated in Figure 16. As in the case of this system at 35°C, both equations predict the trend of the experimental curve but fail to correlate the data. The average relative percent error in the mean activity coefficient calculated by the Bromley equation is 23.2% while the average relative percent error of the experimental data from the Pitzer equation is 39.9%.

Figure 17 presents the experimental values of the mean activity coefficients for the LiCl-MeOH at 35°C as well as those values generated from the Bromley and Pitzer equations through correlation of the experimental ϕ data. Table XIII tabulates the numerical values of the activity coefficients as well as the relative percent error of each data point from the experimental value shown in Table XI. As in the case of the LiBr-MeOH system, both equations predict the trend of the experimental data. The Bromley equation fits the experimental data with an average relative percent error of 15.8% while the Pitzer equation fits the data with an average relative percent error of 6.0%.

In Figure 18 are plotted the experimental values of the mean activity coefficients for the LiCl-MeOH system at 45°C as well as the values of the mean activity coefficients generated by the Bromley and Pitzer equations. As in all

TABLE XII Values of the Mean Activity Coefficient of LiBr in Methanol at 45 °C calculated using the Bromley and Pitzer equations. (The relative percent error is compared to the experimental values in Table IX.

molality	$\gamma_{\pm B}$	rel. per. error	$\gamma_{\pm P}$	rel. per. err.
0.1153	0.391	72.2	0.439	93.4
0.6957	0.264	2.30	0.341	32.2
1.0505	0.272	15.7	0.348	48.1
1.5315	0.310	18.3	0.380	45.0
1.9189	0.360	17.5	0.420	41.1
2.1912	0.405	16.5	0.456	34.9
2.7553	0.533	25.4	0.588	38.4
3.3013	0.712	24.3	0.699	22.0
4.3450	1.293	16.5	1.155	4.1

Figure 16 Values of the Mean Activity Coefficient of LiBr in Methanol at 45°C

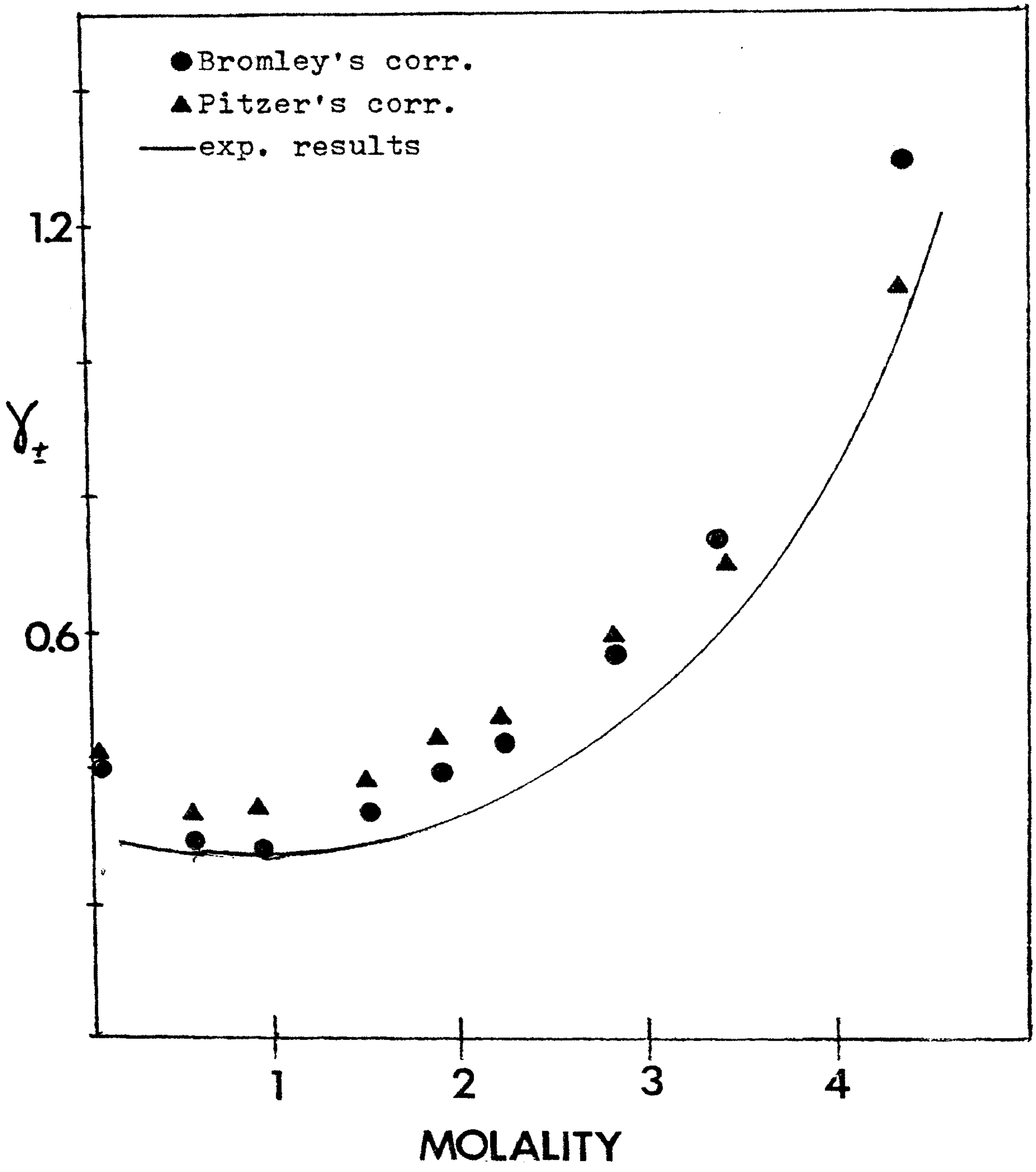


TABLE XIII Values of the Mean Activity Coefficient of LiCl in Methanol at 35°C calculated using the Bromley and Pitzer equations. (The relative percent error is compared to the experimental values in Table X.)

molality	$\gamma_{\pm B}$	rel. per. error	$\gamma_{\pm P}$	rel. per. error
0.1003	0.450	11.6	0.455	10.6
0.7663	0.266	21.3	0.358	5.90
1.1409	0.274	21.3	0.368	5.70
1.4969	0.297	20.8	0.388	3.50
1.7557	0.360	13.0	0.400	3.40
2.2500	0.400	21.7	0.508	0.60
2.6073	0.515	11.7	0.575	1.40
2.9403	0.518	18.8	0.585	8.30
3.5600	0.775	8.20	0.800	5.20
4.5800	1.172	13.9	1.150	15.5

Figure 17 Values of the Mean Activity Coefficient of LiCl in Methanol at 35°C.

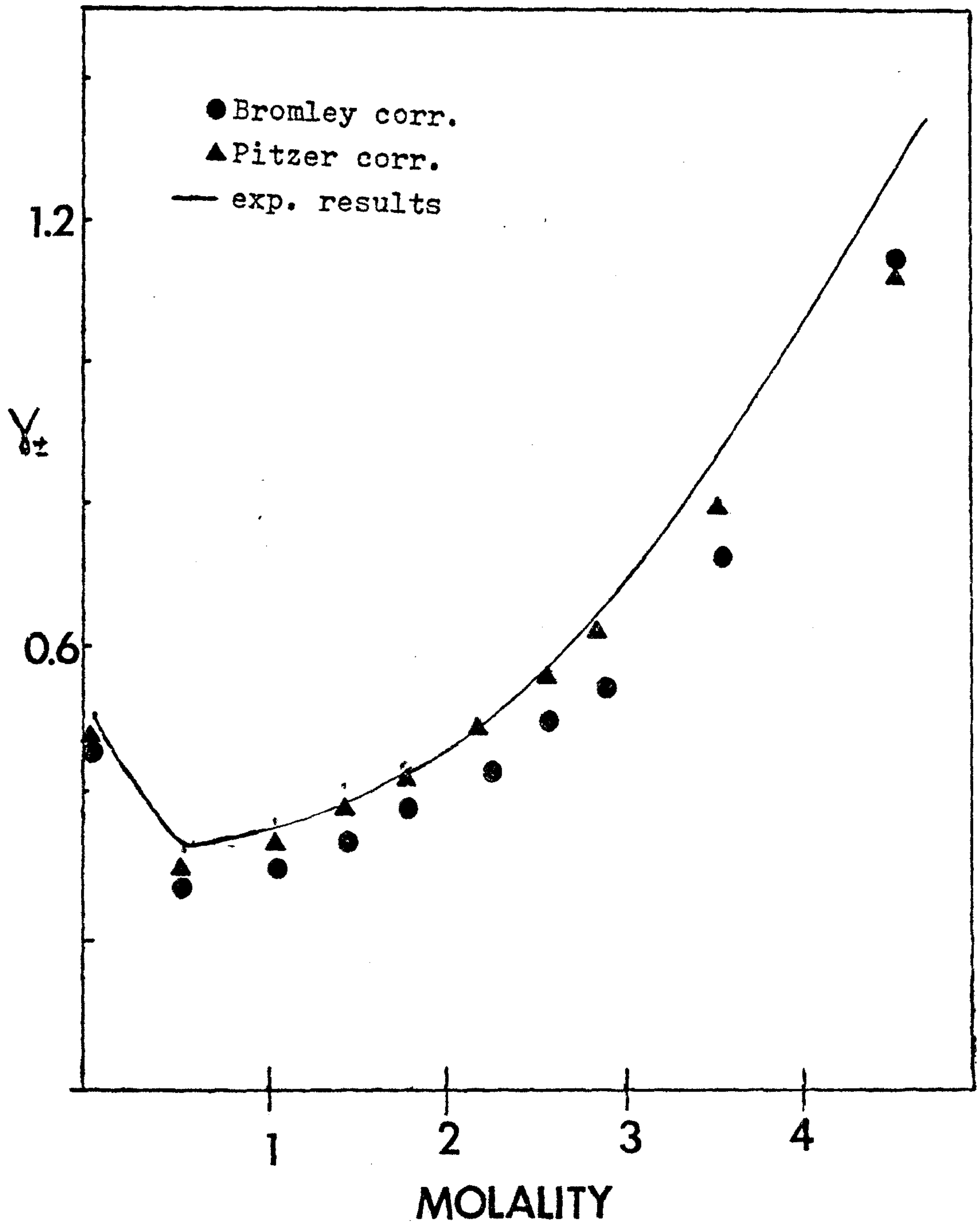
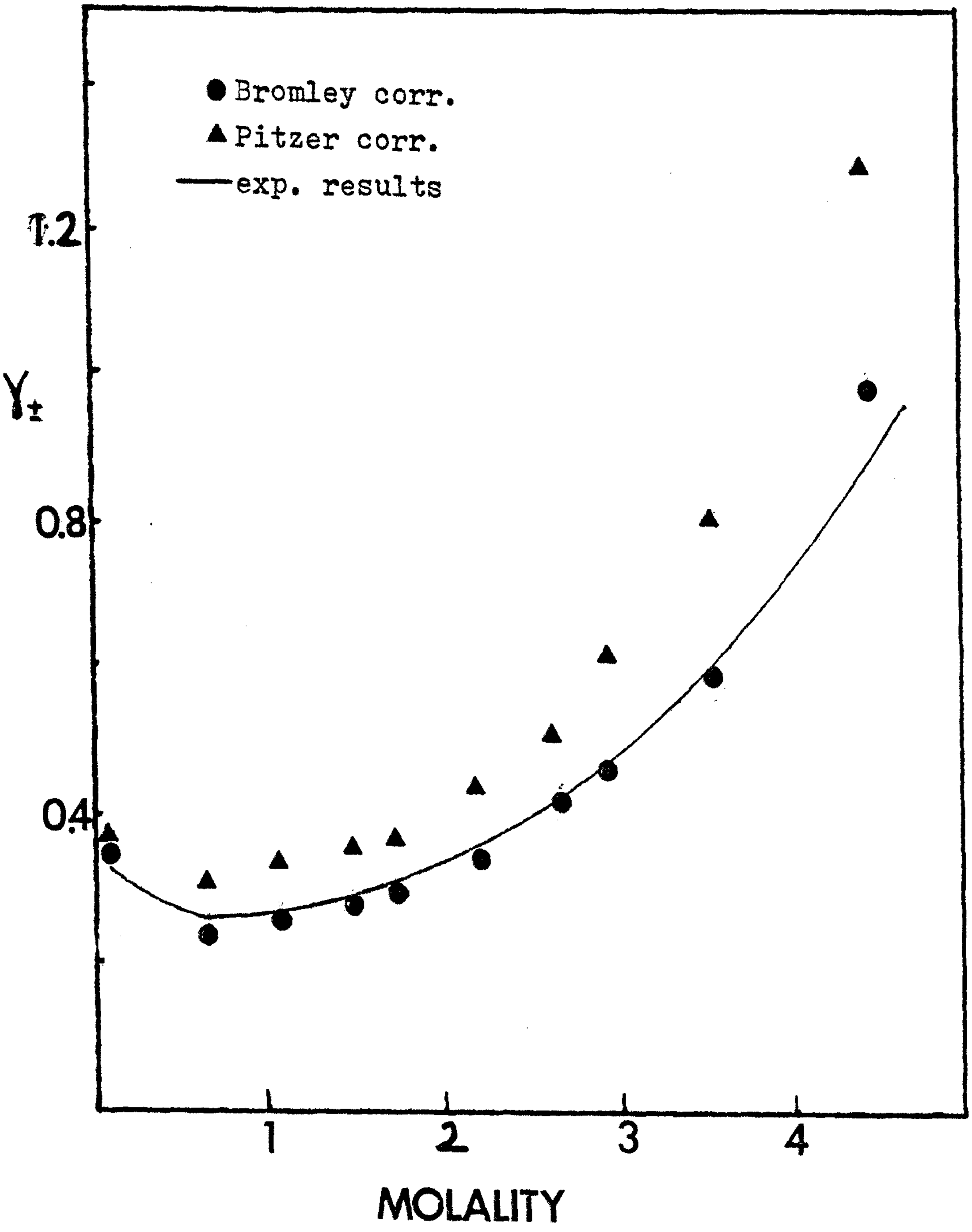


FIGURE 18 Values of the Mean Activity Coefficient of LiCl in Methanol at 45 °C.



the systems previously discussed, both the equations describe the trend in the experimental activity coefficient curve. However, the Bromley equation better correlates the experimental data than the Pitzer equation. The **mean activity** coefficients generated by the Bromley and Pitzer equations are shown in Table XIV along with the relative percent error of each point from the experimental value of the activity coefficient. In this system, the average relative error of the mean activity coefficients correlated by the Bromley equation is 1.54%, while that for the mean activity coefficients generated by the Pitzer equation is 29.1%.

In Table XV, the values of B calculated from the correlation of the LiBr and LiCl systems at 25, 35, and 45 °C over the entire molality range using the Bromley equation are presented. In general, as the temperature is increased, the value of B decreases, although slightly. A comparison of the two systems at a constant temperature shows that the value of B for the LiBr system is greater than that for the LiCl system. This same trend is exhibited for these salts in water.(16)

Table XVI shows the results for the LiBr and LiCl systems at 25 °C regressed using the Bromley equation at concentrations below 3m. Again, the B value for LiBr is larger than that of LiCl.

Using equation 64, the temperature dependency of B

TABLE XIV Values of the Mean Activity Coefficient of LiCl in Methanol at 45 °C calculated using the Bromley and Pitzer equations. (The relative percent error is compared to the experimental values in Table X.)

molality	$\gamma_{\pm B}$	rel. per. error	$\gamma_{\pm P}$	rel. per. error
0.1003	0.376	1.57	0.385	0.79
0.7663	0.245	0.81	0.316	27.9
1.1409	0.249	1.97	0.331	30.3
1.4969	0.267	2.91	0.359	30.6
1.7557	0.298	1.00	0.376	24.9
2.2500	0.336	0.59	0.430	27.2
2.6073	0.398	0.75	0.523	30.4
2.9403	0.451	3.43	0.605	29.5
3.5600	0.511	0.39	0.810	59.1
4.5800	0.992	1.98	1.320	30.4

TABLE XV Values of B in the Bromley Equation Obtained From Regression of the Experimental Data Using the Entire Concentration Range.

System	Temperature		
	25 °C	35 °C	45 °C
LiBr/MeOH	0.3069	0.3068	0.3056
LiCl/MeOH	0.2747	0.2731	0.2676

TABLE XVI Values of B in the Bromley Equation Obtained From Regression of the Experimental Data Using the Data Less than 3m for the systems at 25 °C.

	System	
	LiBr-MeOH	LiCl-MeOH
B	0.2925	0.2692

may be investigated. Since data are available at only three temperatures in this study, the values of B_2 and B_3 were set equal to zero. Equation 64 becomes then

$$B=B^*\mathrm{lN}((T-243)/T)+B_1/T \qquad 71$$

or in linear form

$$BT=B^*T\ln((T-243)/T)+B_1 \qquad 71a$$

From a plot of BT vs. $T\ln((T-243)/T)$, the constants B^* and B_1 are determined.

Equation 71a was applied to the data in Table XV for the LiBr and the LiCl systems and are plotted in Figure 19. The B data are correlated well by the equation. The values of B^* and B_1 are given in the figure.

In Table XVII, the values of β_0, β_1, and C obtained through the regression of the LiBr and LiCl data over the entire concentration range in the Pitzer equation are shown. As the temperature is increased from 25 to 35 °C, the value of β_0 for the LiBr system decreases and then increases as the temperature is increased to 45 °C. The values of β_0 for the LiCl system exhibit the opposite trend. The values of β_1 and C for the LiBr system increase as the temperature is increased from 25 to 35 °C and decrease as the temperature increases to 45 °C. Again, the LiCl system has the opposite trend.

The values of β_0, β_1, and C obtained for the LiBr and

FIGURE 19 Test of the Temperature Dependency of B for the LiBr and LiCl Systems

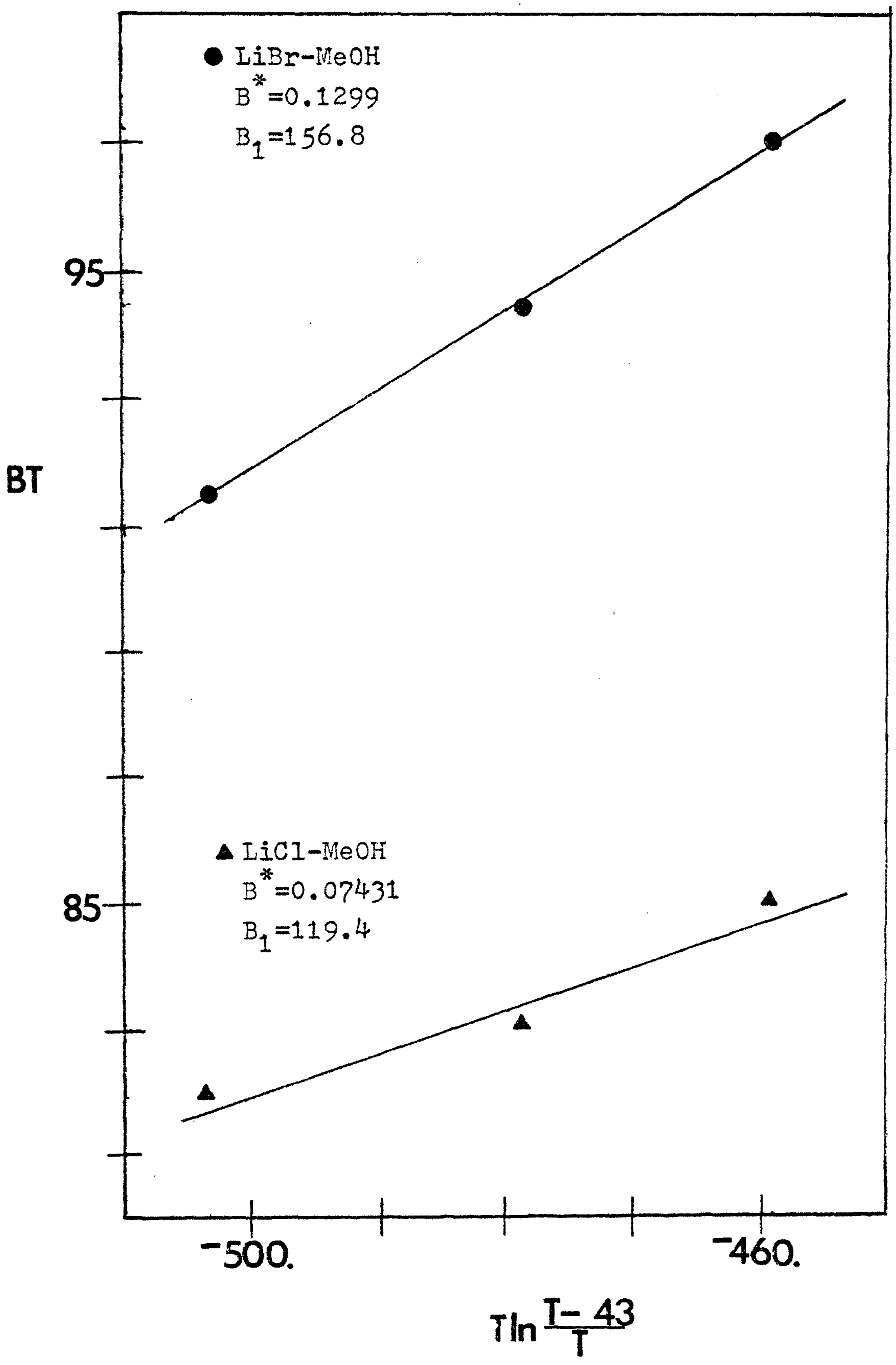


TABLE XVII Values of β_0, β_1, and C in the Pitzer Equation Obtained From Regression of the Experimental Data

System	T °C	β_0	β_1	C
LiBr/MeOH	25	0.2753	1.772	0.0296
	35	0.2692	2.016	0.0380
	45	0.3055	1.391	0.0226
LiCl/MeOH	25	0.2712	1.836	0.0199
	35	0.3538	1.391	0.00205
	45	0.3678	1.419	-0.00210

LiCl systems at 25 C for data less than 3m, are not shown since they do not describe the activity coefficient data well.

The temperature dependency of Pitzer's parameters were not investigated since no consistent trend in any of the parameters was observed as the temperature of the system was increased.

CHAPTER V

DISCUSSION OF RESULTS

The principal aims of this study were to 1) determine mean activity coefficients of LiBr and LiCl from experimental osmotic coefficient data at 25,35, and 45 °C. 2) test the applicability of the Bromley and Pitzer equations to the LiBr and LiCl salts in methanol, and 3)investigate the temperature dependency of the parameters in the Bromley and Pitzer equations. These three points are discussed in order.

The mean activity coefficients of LiBr and LiCl at 25,35, and 45°C as a function of molality are plotted in Figures 11-18. Their values are given in Tables VII-X. They were obtained through the use of the experimental osmotic coefficients and equation 69. Although no osmotic or mean activity coefficient below 0.1m were available to aid in the extrapolation of the integral of equation 69 to infinite dilution for these systems, a "French curve method" was adopted. As proven in Appendix B, this method allows the determination of mean activity coefficients from osmotic coefficient data if no data between zero molality and a molality of 0.1 are available. The mean activity coefficients determined by this method for the $KCl-H_2O$ system agreed with the values given in Robinson and Stokes with an average percent error of 1.24%. However, the rough extrapolation of the integral in equation 69 shown in Appendix B should not be expected to give reliable estimates of the mean activity coefficients due to the magnitude of the uncertainty in the vapor pressure measurement at low concentrations. As an example, consider the data point for the $KCl-H_2O$ system at $m=0.1$ given in Ref.29. The corresponding values of the vapor pressure and osmotic coefficient are 23.677 mm Hg and 0.9266, respectively. Since oil of specific gravity of .85 was the manometer fluid for the $KCl-H_2O$ system, the corresponding error in a vapor pressure measurement is ±0.004 mm Hg. Therefore, the true vapor pressure is in the range from 23.673 mm Hg to 23.681 mm Hg. The corresponding osmotic coefficients at the endpoints of this range are 0.9712 and 0.8792 with relative percent errors of 4.80 and 5.0, respectively, from the experimental value. Since the point at $m=0.1$ is the pivotal point in the extrapolation of plots of $1-\phi/m^{\frac{1}{2}}$ versus $m^{\frac{1}{2}}$, the quantity $1-\phi/m^{\frac{1}{2}}$ must be known with certainty or else the area under the curve will be over or under estimated. Insertion of the osmotic coefficients corresponding to vapor pressures of 23.673,23.677, and 23.681 mm Hg, give the values of $1-\phi/m^{\frac{1}{2}}$ of 0.0911,0.2321, and 0.3804, respectively, which correspond to relative percent errors from the experimental value of 0.2321 of -60.1 and 63.9, respectively. This large error would correspond to errors of at least 20% in the mean activity coefficients calculated from equation 69 compared to those given by other measurements.

Therefore it is concluded that the mean activity coefficients obtained from the experimental data in this study are good to only approximately 20% due to the unreliability of the vapor pressure measurements at the low concentrations which were used to extrapolate the integral in equation 69.

Due to the inadequacies of the graphical method in calculating mean activity coefficients described above and in Appendix B, experimental osmotic coefficients for the LiBr and LiCl-MeOH systems at 25,35, and 45°C, were regressed using both the Bromley and Pitzer equations. From the parameters obtained by regression using either equation, values of the mean activity coefficients for the two systems at the three temperatures were calculated. These values have already been shown in Tables XI through XIV and are plotted in Figures 11,13,15,16,17, and 18. However, since the mean activity coefficients obtained from the experimental osmotic coefficients and equation69 are unreliable due to difficulties in evaluating the integral of equation 69, the reliability of either the Bromley or Pitzer equations in generating mean activity coefficients can not be ascertained if these generated values are compared to the experimental values. Therefore, to determine the applicability of the Bromley and Pitzer equations to the LiBr and LiCl-MeOH systems, the parameters obtained from the regression of the experimental osmotic coefficient data were reinserted into these respective equations to obtain calculated values of the osmotic coefficients. From these calculated values of the osmotic coefficient, saturated vapor pressures of each system were calculated at each concentration from equation 42.

In Tables XVIII-XXIII, the vapor pressures calculated through the Bromley and Pitzer equations are shown for all systems and are compared to the experimental values.

Tables XVIII-XX present the vapor pressures calculated through the Bromley and Pitzer equations for the LiBr-MeOH systems at 25,35, and 45 °C. For this system at 25,35, and 45 °C, the average difference error in the vapor pressures generated by the Bromley equation from the experimental values are 0.52,0.73, and 0.90 mm Hg, respectively, while for the Pitzer equation, the average difference error in the vapor pressures are 0.26, 0.34, and 0.56 mm Hg, respectively.

In Tables XXI-XXIII, the vapor pressures calculated through the Bromley and Pitzer equations are shown for the LiCl-MeOH system at 25,35, and 45 °C. For this system at

TABLE XVIII Experimental and Calculated Vapor Pressures By the Bromley and Pitzer Equations for the LiBr-MeOH System at 25 °C

molality	P_{exp}(mm Hg)	P_{calB}(mm Hg)	$P_{exp}-P_{calB}$	P_{calP}(mm Hg)	$P_{exp}-P_{calP}$
0.1153	127.72	127.27	0.45	127.23	0.49
0.2170	126.59	126.65	-0.06	126.55	0.04
0.6957	123.81	123.29	0.52	122.98	0.83
1.0506	120.13	120.18	-0.05	119.94	0.19
1.5315	114.96	115.10	-0.14	115.18	-0.22
1.9189	110.70	110.31	0.39	110.74	-0.04
1.9470	110.33	109.95	0.39	110.39	-0.06
2.1912	106.73	106.63	0.11	107.27	-0.54
2.3033	105.52	105.04	0.48	105.76	-0.24
2.4006	104.46	103.63	0.82	104.41	0.05
2.7553	99.43	98.30	1.13	99.18	0.25
3.3010	90.61	89.58	1.03	90.27	0.34
4.3450	71.02	72.15	-1.13	71.11	-0.09

KEY: P_{calB}=vapor pressure generated by the Bromley equation

P_{calP}=vapor pressure generated by the Pitzer equation

TABLE XVIX Experimental and Calculated Values of the Vapor Pressure by the Bromley and Pitzer Equations for the LiBr-MeOH System at 35°C

molality	P_{exp}(mm Hg)	P_{calB}(mm Hg)	$P_{exp}-P_{calB}$	P_{calP}(mm Hg)	$P_{exp}-P_{calP}$
0.1153	210.57	209.88	0.69	209.79	0.78
0.2179	209.28	208.86	0.42	208.64	0.73
0.6957	202.72	203.45	-0.73	202.73	0.04
1.0506	198.14	198.42	-0.28	197.73	0.44
1.5315	190.10	190.15	-0.05	189.98	0.19
1.9189	182.87	182.34	0.52	182.78	0.09
1.9472	181.81	181.74	0.07	182.22	-0.35
2.1912	176.78	176.32	0.47	177.16	-0.29
2.3033	174.19	173.72	0.47	174.71	-0.44
2.4006	172.28	171.41	-0.86	172.52	-0.24
2.7553	164.43	162.66	1.77	164.03	0.44
3.3031	149.84	148.29	1.55	149.53	0.34
4.3450	118.06	119.64	-1.58	118.17	-0.10

TABLE XX Experimental and Calculated Values of the Vapor Pressure by the Bromley and Pitzer Equations for the LiBr-MeOH system at 45°C

$m(\frac{\text{moles}}{\text{kg MeOH}})$	P_{exp}(mm Hg)	P_{calB}(mm Hg)	$P_{exp}-P_{calB}$	P_{calP}(mm Hg)	$P_{exp}-P_{calP}$
0.1153	335.56	335.60	-0.04	335.48	0.08
0.6950	326.48	325.56	0.92	324.50	1.97
1.0506	316.35	317.67	-1.32	316.58	-0.23
1.5315	304.00	304.65	-0.65	304.17	-0.17
1.9180	293.01	292.32	0.69	292.62	0.41
1.9472	291.36	291.36	0.00	291.70	-0.34
2.1912	282.89	282.78	0.11	283.61	-0.72
2.3033	278.77	278.66	0.11	279.70	-0.92
2.7550	263.23	261.11	2.12	262.73	0.50
3.3013	240.59	238.34	2.25	239.89	0.70
4.3450	190.95	192.60	-1.65	191.12	-0.17

KEY: P_{calB}=vapor pressure calculated by the Bromley equation
P_{calP}=vapor pressure calculated by the Pitzer equation

25,35, and 45°C, the average difference error in the vapor pressure of the Bromley equation from the experimental results are 0.44,1.10, and 1.80 mm Hg, respectively, and is 0.16, 0.82, and 0.62 mm Hg, respectively, for the Pitzer equation.

In all cases, the Pitzer equation fit the experimental vapor pressure data better than the Bromley equation. Closer examination of the tables indicate that for the LiBr-MeOH system at all temperatures, the difference in vapor pressure between the experimental values and those generated by the Bromley equation begin to increase above 1 mm Hg at concentrations above 2.4006 molal suggesting that the Bromley equation applies only to molalities below this concentration range. Similar trends are not noted for the LiCl-MeOH system at 25 and 35°C. However, for this system at 45°C, the difference in vapor pressure between the experimental values and those generated by the Bromley equation are up to 4 mm Hg over most of the concentration range studied.

As shown previously, the values of the osmotic coefficients obtained from the static method at low concentrations must be known accurately or the values of the mean activity coefficients will be in error by approximately 20% if a graphical method is used to evaluate the integral in equation 69 when experimental data from other measurements are not available. However, in Appendix B, it was shown that the

TABLE XXI. Experimental and Calculated Values of the Vapor Pressure by the Bromley and Pitzer equations for the LiCl-MeOH system at 25°C.

$m(\frac{\text{moles}}{\text{kg MeOH}})$	P_{exp}(mm Hg)	P_{calB}(mm Hg)	$P_{exp}-P_{calB}$	P_{calP}	$P_{exp}-P_{calP}$
0.1003	127.51	127.37	0.14	127.33	0.18
0.7663	122.17	122.89	-0.72	122.40	-0.23
1.1409	119.07	119.68	-0.61	119.18	-0.11
1.4969	115.80	116.11	-0.31	115.77	0.03
1.7557	113.13	113.22	-0.09	113.06	0.07
2.2500	107.81	107.07	0.74	107.30	0.51
2.6073	102.53	102.18	0.35	102.65	-0.12
2.9403	97.66	97.35	0.31	97.97	-0.31
3.5600	88.51	87.88	0.63	88.45	0.06
4.5800	71.17	71.69	-0.52	71.16	0.01

TABLE XXII Experimental and Calculated Vapor Pressures By the Bromley and Pitzer Equations for the LiCl-MeOH System at 35°C

molality	P_{exp}(mm Hg)	P_{calB}(mm Hg)	$P_{exp}-P_{calB}$	P_{calP}(mm Hg)	$P_{exp}-P_{calP}$
0.1003	210.07	210.03	0.04	209.99	0.08
0.7663	201.94	202.83	-0.89	202.13	-0.19
1.1409	196.64	197.52	-0.88	196.61	0.03
1.4969	191.04	191.86	-0.82	190.92	0.11
1.7557	186.07	187.17	-1.10	186.29	-0.22
2.2500	177.57	177.15	0.42	176.54	1.03
2.6073	169.07	169.18	-0.11	168.79	0.28
2.9403	161.06	161.29	-0.23	161.09	-0.03
3.5600	152.07	145.77	6.30	145.85	6.22
4.5800	119.31	119.14	0.17	119.31	0.00

TABLE XXIII Experimental and Calculated Vapor Pressures By the Bromley and Pitzer Equations for the LiCl-MeOH System at 45°C

molality	P_{exp}(mm Hg)	P_{calB}(mm Hg)	$P_{exp}-P_{calB}$	P_{calP}(mm Hg)	$P_{exp}-P_{calP}$
0.1003	335.38	335.84	-0.46	335.77	-0.39
0.7663	322.98	324.67	-1.69	323.34	-0.36
1.1409	314.61	316.42	-1.80	314.59	0.02
1.4969	305.84	307.60	-1.16	305.58	-0.07
1.7557	297.77	300.23	-2.46	298.19	-0.42
2.2500	280.63	284.55	-3.92	282.80	-2.17
2.6073	268.38	272.04	-3.66	270.64	-2.26
2.9403	258.54	259.70	-1.76	258.61	0.26
3.5600	234.58	235.18	-0.60	234.86	-0.28
4.5800	193.72	193.14	0.58	193.71	0.01

Bromley and Pitzer equations correlate the osmotic coefficient data for the KCl-H_2O system at concentrations above 0.1m to allow the calculation of mean activity coefficient data which agree with the experimental mean activity coefficient data. Therefore, it was decided to evaluate the integral of equation 69 by the Bromley and Pitzer equations.

In Tables XXIV-XXIX, the values of the osmotic coefficients for the LiBr and LiCl-MeOH systems at 25,35, and 45°C, calculated by the Bromley and Pitzer euqations are presented and are compared to the experimental values. Examination of the tables indicate that both equations correlate the experimental data well, with the exception of some data points at the lower concentrations where the error in the experimental vapor pressure is large. For the LiBr-MeOH systems at 25,35, and 45°C, the average percent errors in the osmotic coefficients calculated by the Bromley equation are 2.48,2.59, and 2.68, respectively, while the average percent errors in the osmotic coefficient calculated by the Pitzer equation are 1.30,1.00, and 1.34, respectively. Data points with relative percent errors greater than 10% for a constant molality were omitted in the calculation of the average percent error if an error of this magnitude was shown by both equations. This would indicate errors in the experimental value of the osmotic coefficient and is not due to any inadequacy in either the Bromley or Pitzer equation.

TABLE XXIV Values of the Osmotic Activity Coefficient of LiBr in Methanol at 25°C calculated using the Bromley and Pitzer Equations. (The relative percent error is compared to the experimental values in Table I.)

molality	ϕ_B	rel. per. error	ϕ_P	rel. per. error
0.1153	0.785	155.7	0.827	169.4
0.2170	0.768	4.24	0.825	2.87
0.6957	0.843	12.7	0.899	20.2
1.0506	0.937	0.74	0.967	2.44
1.5315	1.083	1.19	1.076	1.82
1.9189	1.210	2.37	1.179	0.30
1.9470	1.219	2.35	1.187	0.34
2.1912	1.301	0.46	1.259	2.80
2.3033	1.339	2.29	1.294	1.18
2.4006	1.373	3.70	1.325	0.27
2.7553	1.496	4.54	1.445	0.98
3.3010	1.688	3.37	1.651	1.10
4.3450	2.059	2.06	2.111	0.24

TABLE XXV Values of the Osmotic Coefficient of LiBr in Methanol at 35°C calculated using the Bromley and Pitzer Equations.

molality	ϕ_B	rel. per. error	ϕ_P	rel. per. error
0.1153	0.765	138.4	0.823	156.4
0.2179	0.754	23.6	0.829	29.1
0.6957	0.825	8.87	0.904	-0.08
1.0506	0.918	2.24	0.970	3.27
1.5315	1.064	0.24	1.073	0.62
1.9189	1.190	2.04	1.170	0.37
1.9472	1.199	0.25	1.178	1.52
2.1912	1.282	1.41	1.247	1.25
2.3033	1.319	1.38	1.281	1.54
2.4006	1.353	2.50	1.311	0.68
2.7553	1.476	4.35	1.428	0.99
3.3013	1.668	2.94	1.628	0.49
4.3450	2.039	2.31	2.083	0.18

TABLE XXVI Values of the Osmotic Coefficient of LiBr in Methanol at 45°C calculated using the Bromley and Pitzer Equations. (The relative percent error is compared to the experimental values in Table III).

molality	ϕ_B	rel. per. error	ϕ_P	rel. per. error
0.1153	0.756	2.07	0.804	4.20
0.6957	0.807	8.56	0.880	18.4
1.0506	0.899	6.41	0.950	1.08
1.5315	1.043	2.08	1.059	0.58
1.9189	1.168	1.67	1.160	0.95
1.9472	1.178	0.03	1.168	0.82
2.1912	1.259	0.18	1.239	1.47
2.3033	1.298	0.19	1.272	1.78
2.7553	1.453	3.28	1.418	0.78
3.3013	1.644	2.75	1.613	0.81
4.3450	2.014	2.31	2.042	0.97

For the LiCl-MeOH systems at 25,35, and 45°C, the average percent errors in the osmotic coefficient calculated by the Bromley equation are 3.65, 7.20, and 5.39, respectively, and for the Pitzer equation are 1.19, 1.91, and 1.53, respectively. For both systems, the Pitzer equation better correlated the experimental osmotic coefficient data than the Bromley equation.

Even though both the Bromley and Pitzer equations correlate the experimental data well, with the Pitzer equation performing better than the Bromley equation, the relative percent errors comparing the experimental and calculated osmotic coefficients must be minimal if accurate values of the mean activity coefficients are to be obtained. This is especially true if the experimental osmotic coefficient data at high concentrations are to be used to generate mean activity coefficients from low to high concentrations. The impact of errors of the magnitude of 5% in the osmotic coefficient in the evaluation of the integral of equation 69 to obtain mean activity coefficients has already been demonstrated using the KCl-H_2O system.

To minimize the relative percent errors between the experimental osmotic coefficients and the osmotic coefficients generated by either the Bromley or Pitzer equations, the parameters which were given constant values specific for aqueous solutions must be reexamined in each equation.

Examination of equation 63, which is Bromley's ex-

TABLE XXVII Values of the Osmotic Coefficient of LiCl in Methanol at 25 °C calculated using the Bromley and Pitzer Equations. (The relative percent error is compared to the experimental values in Table IV.)

molality	ϕ_B	rel. per. error	ϕ_P	rel. per. error
0.1003	0.780	28.0	0.829	36.1
0.7663	0.831	12.7	0.913	4.04
1.1409	0.920	7.03	0.978	1.25
1.4969	1.019	2.48	1.048	0.26
1.7557	1.091	0.61	1.104	0.53
2.2500	1.239	4.03	1.224	2.76
2.6073	1.349	1.57	1.321	0.50
2.9403	1.453	1.18	1.419	1.16
3.5600	1.649	1.98	1.620	0.21
4.5800	1.975	1.25	2.001	0.03

TABLE XXVIII Values of the Osmotic Coefficient of LiCl in Methanol at 35 °C calculated using the Bromley and Pitzer Equations. (The relative percent error is compared to the experimental values in Table V.)

molality	ϕ_B	rel. per. error	ϕ_P	rel. per. error
0.1003	0.768	3.88	0.800	8.25
0.7663	0.811	10.0	0.881	2.19
1.1409	0.899	6.55	0.971	0.90
1.4969	0.995	4.27	1.046	0.67
1.7557	1.068	4.66	1.110	0.94
2.2500	1.215	1.37	1.239	3.37
2.6073	1.324	0.30	1.338	0.75
2.9403	1.917	33.6	1.434	0.06
3.5600	1.623	12.94	1.620	12.73
4.5800	1.947	0.21	1.944	0.03

TABLE XXIX Values of the Osmotic Coefficient of LiCl in Methanol at 45 °C calculated using the Bromley and Pitzer Equations. (The relative percent error is compared to the experimental values in Table VI.)

molality	ϕ_B	rel. per. error	ϕ_P	rel. per. error
0.1003	0.757	22.0	0.791	18.5
0.7663	0.789	11.8	0.872	-2.57
1.1409	0.875	8.18	0.961	0.84
1.4969	0.968	5.65	1.035	0.89
1.7557	1.040	6.60	1.100	1.17
2.2500	1.183	7.51	1.226	4.14
2.6073	1.290	5.91	1.321	3.72
2.9403	1.391	1.61	1.413	0.07
3.5600	1.583	0.69	1.589	0.31
4.5800	1.901	0.54	1.891	0.02

pression for the osmotic coefficient of a completely dissociated electrolyte, shows that in addition to the parameter B, which is specific for each electrolyte in a particular solvent, there are the three additional parameters a,n, and ρ. The value of a, as determined by Bromley is given by equation61a. He indicates that the fit of the data is not sensitive to the value of a. To prove that this is the case for methanol systems, the experimental values of the osmotic coefficient for the LiBr and LiCl systems obtained in this study were regressed using Bromley's equation for osmotic coefficient, setting ρ equal to one and n equal to 2.0. The value of a was varied from $0.5/|z_+z_-|$ to $2.0/|z_+z_-|$ and values of B were generated at each value of a. However, this change in a resulted in insignificant changes in the calculated values of the osmotic coefficient. Therefore, it is concluded that the value of a indicated by Bromley for aqueous systems may also be used for methanol systems.

The impact of the parameter n, can best observed in Bromley's equation for the mean activity coefficient.(Equation 62) The second term of this equation, which contains the parameter n, accounts for the transition from the Debye-Huckel region of a plot of the mean activity coefficient vs. the ionic strength and the linear portion of such a curve. It also defines the minimum of this curve. Bromley recommends a value of 2.0 for aqueous systems. Referring to Figures 11-18, it is seen that although the Bromley equation does not predict the same values of the mean activity coefficient as the Pitzer equation, it does predict the trends in the minima of the curves. This indicated that n is equal to 2.0 for electrolytic methanol systems as well as for aqueous electrolytic systems. Also, if the experimental osmotic coefficient data are regressed in the Bromley equation with other values of n, the fit of the data is not as good as with n equal to 2.0.

Bromley sets the value of ρ equal to 1.0. From the Debye-Huckel theory, the value of ρ is given by

$$\rho = \kappa a/I^{\frac{1}{2}} \frac{8\pi N_A e^{2}}{(1000\varepsilon kT}\Big)^{\frac{1}{2}} a \qquad (72)$$

where a is the ion size parameter. Since Bromley specifies that ρ is equal to 1.0, he assumes that the value of the ion size parameter is 3.04 Å for a salt in water. The value has been found to correlate aqueous mean activity coefficient data at low concentrations. However, if ρ is set equal to 1.0 for electrolytic methanol systems, a value of the ion size parameter of 2.2 Å is calculated from equation 72. This value, although smaller than that for an electrolyte in water, which is reasonable since an ion is not hydrated in a methanol solution, is too small since it is less than the sum of the crystallographic radii of all salts. This is a physically impossible value of a. The smallest value that a can have is 2.4 Å which was calculated for LiCl.(20)

Examination of equation 59 which is Pitzer's equation for the osmotic coefficient , indicates that in addition to the second virial coefficients, β^0 and β_1, and C, the third virial coefficient, there are two parameters α and b in which Pitzer assigned the values of α equal to 2.0 and b equal to 1.2, respectively. Therefore, there are a total of five parameters in Pitzer's expression for the osmotic coefficient of an electrolyte.

The first term of equation 59 corresponds to the Debye-Huckel theory.(The value of ρ in the Debye-Huckel theory is termed b by Pitzer.) Since Pitzer assigns b a value of 1.2, this corresponds to a value of the ion size parameter of 3.65Å, as calculated from equation 72. For electrolytic methanol solutions, this value of b would correspond to an ion size parameter of 2.65 Å which is a reasonable value since the ions in methanol are not hydrated as they are in aqueous solution. Therefore, it is believed that this value does not have to be modified in order to apply this equation to electrolytic methanol systems.

The second term of equation 59, which contains the two adjustable parameters, β_0 and β^1, and α, accounts for the transition from the Debye-Huckel region of a plot of the mean activity coefficient vs. the ionic strength. In aqueous electrolytic systems, this term was found to successfully correlate the minimum of such a curve as well as the linear portion as the ionic strength increases. The relationship among these parameters is given in equation 58b.

The first term of equation 58b, β^0, is the parameter which when multiplied by m in equation 60, define the linear portion of an activity coefficient vs. molality curve. Since this is an adjustable parameter depending on the type of salt, this term would not have to be modified in applying either equation 59 or 60 to methanol-salt systems. It is the second term of equation 58b which would have to be modified. This term is a function of β^1 and α. Since β^1 is allowed to vary freely in the regression of any experimental data, it is α, which Pitzer gives the value of 2.0 for aqueous systems, that would have to be modified for methanol-salt systems to minimize the error in the osmotic coefficients between the experimental values and those calculated by this equation. The exact value of α can only be ascertained through the regression of many methanol-salt systems, since the value of α appears to have no physical significance.

The value of C in equation 59 which is multiplied by the square of the molality, only serves to extend the Pitzer equation to higher concentrations. In aqueous systems, this value is very small or near zero compared to the values of β_0 and β^1. This same trend in C was observed in the methanol-salt systems.

The temperature dependency of the

parameters of the Bromley equation were investigated using equation 71a, which applies when data at three or less temperatures are available. The results are plotted in Figure 19. The values of B determined from regression of the experimental data were correlated well by this two parameter equation for both the LiBr and LiCl systems.

In the case of the LiBr-MeOH system, the values of B^* and B_1 are 0.1299 and 156.8, respectively. Inserting these values into equation 71a allows the calculation of B at the three temperatures. If this is done, the values of B from equation 71a at 25,35, and 45°C, are 0.3067, 0.3070, and 0.3054, respectively. This corresponds to relative percent errors in B(values shown in Table XV) of 0.07,0.07, and -0.07, respectively.

For the LiCl-MeOH system, the values of B^* and B_1, are 0.07431 and 119.4, respectively. Calculating values of B using equation 71a and the values of B^* and B_1 results in the values of 0.2751,0.2720, and 0.2681, at 25,35, and 45°C. This corresponds to relative percent errors from the regressed values of B shown in Table XV of 0.15,0.40, and 0.19, respectively.

No temperature relationship among the parameters of Pitzer's equation could be established since the parameters do not show any consistent trend as the temperature of the system is increased.(See Table XVI)

CONCLUSIONS

Values of the vapor pressure depression of LiBr and LiCl in methanol were measured at 25,35, and 45°C using a differential manometer. Values of the osmotic coefficients for each electrolyte at each temperature were calculated.

From the experimental osmotic coefficient data, mean activity coefficients for the LiBr and LiCl-MeOH systems at the three temperatures were determined graphically. However, it was shown that if experimental osmotic or mean activity coefficient data are not available at low concentrations with which to extrapolate the data to infinite dilution, the mean activity coefficients determined graphically can be in error by 20%.

The experimental osmotic coefficient data were correlated with both the Bromley and Pitzer equations for the osmotic coefficient. For all systems at all temperatures, the data were better correlated by the Pitzer equation than with the Bromley equation. Mean activity coefficients of the two salts at the three temperatures were calculated based on the parameters obtained by regression of the experimental osmotic coefficient data.

Although both equations correlated the experimental osmotic coefficients, it has been shown that the relative percent error between the experimental osmotic coefficients and those generated by either the Bromley and Pitzer equations must be minimal if reliable values of the mean activity coefficients are to be obtained.

An examination of the Bromley and Pitzer equations indicated that the parameters specific for ion-solvent interactions in the Bromley equation, ρ, and an adjustable parameter in the Pitzer equation which has no physical significance, α, must be modified to reflect the interactions of an ion in methanol. The values of these parameters can only be established through the regression of many methanol-salt systems. Once these modifications are made, it is sure that both the Bromley and the Pitzer equations would be useful in correlating experimental nonaqueous salt data.

The temperature dependency of the parameter B in Bromley's equation was investigated through a two parameter equation. The value of B calculated from the two parameter equation agreed well with the experimental values of B for the two systems at the three temperatures. The temperature dependency of the parameters in Pitzer's equation could not be established.

Since the temperature dependency of the parameter B in the Bromley equation could easily be expressed with a two parameter equation, it appears that Bromley's equation is more useful in the correlation of salt-solvent data over many temperatures than is Pitzer's equation. Even if a temperature dependency relationship was found for the three parameters of Pitzer's equation, this would not be of much value in the correlation of salt-solvent data because each parameter would require two parameters. This means that a total of six parameters would be needed to define the temperature dependency of a system as opposed to two for the Bromley equation.

NOMENCLATURE

A =Debye-Huckel constant for the activity coefficient

A =Debye-Huckel constant for the osmotic coefficient

a =ion-size parameter or constant in equation 61 defined by equation 61a.

a_1 =activity of the solvent in solution

a_2 =activity of the solute salt in solution

B =a constant for each salt in equation 62

B_0 =adjustable parameter in equation 61

B_1 =adjustable parameter in equation 64 and 65

B_2 =adjustable parameter in equation 64

B_3 =adjustable parameter in equation 64

B =adjustable parameter in equation 64 and 65

B_{MX} =the second virial coefficient defined in equations 58a and 58b.

B =the second virial coefficient defined in equation 60b

b =a constant in equations 59 and 60 and is equal to 1.2

C =arbitrary constant in equations 59,60 and 61

c =concentration is moles salt/liter of solution

E^0 =standard cell potential at zero molality.

e =electronic charge

f =term defined in equation 61a which is a function of the ionic strength

g_{ij} = radial distribution function

I =ionic strength defined in equation 46

k =Boltzmann's constant

M_1 =molecular weight of the solvent

m =molality, gmoles/kg solvent

N_A =Avogadro's number

n_1 =number of moles of solvent

n_2 =number of moles of solute

n =constant equal to 2 in equation 61

P =total pressure

P_0^s =vapor pressure of the pure solvent

P^s =vapor pressure of the salt solution

P =difference in vapor pressure between the pure solvent and the salt solution

q_{ij}=defined in equation 55

R =gas constant

r =interionic distance

S =entropy

T =temperature in °K

t =temperature in °C

U =internal energy

u_{ij}=interionic potential

V =volume of system

v =sum of stoichiometric number of ions in the salt

x_1 =mole fraction of the solvent

x_2 =mole fraction of the salt

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

Greek Letters

α =constant in equations 58a, 58b, and 59 with a value of 2.0

β_0 =second virial coefficient in equations 58a,58b,59, and 60b

β_1 =second virial coefficient in equations 58a,58b,59, and 60b

ε =dielectric constant of the solvent

γ_1 =activity coefficient of the solvent

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

κ =term defined in equation 48

μ_1 =chemical potential of the solvent

μ_2 =chemical potential of the electrolyte

π =osmotic pressure

ρ =constant in equation 62 which has a value of 1.0 for water.

$\sigma(\rho I^{\frac{1}{2}})$=function of $(\rho I^{\frac{1}{2}})$ in equation 63a

ϕ =osmotic coefficient

$\psi(aI)$=function of (aI) in equation 63b

ψ = electrostatic potential

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APPENDIX A

TABLE IA A Comparison of the Vapor Pressure Depressions of KCl in Water Obtained in this Study with those of Robinson and Stokes.(17)

molality	ΔP_{exp} mm Hg ± 0.06 mm	ΔP_{lit} mm Hg	$\lvert \Delta P_{exp} - \Delta P_{lit} \rvert$
0.5393	0.413	0.411	0.002
0.9178	0.694	0.694	0.000
1.0568	0.804	0.798	0.006
1.1498	0.873	0.868	0.005
1.3730	1.046	1.034	0.012
1.4935	1.133	1.126	-0.007
2.0247	1.562	1.529	0.033
2.0395	1.558	1.543	0.015
2.5094	1.908	1.904	0.004
2.9202	2.246	2.228	0.018
3.1046	2.383	2.370	0.013
3.3206	2.550	2.540	0.010
3.5660	2.740	2.736	0.004
3.9830	3.053	3.070	-0.017

TABLE IIA Purities of the Salts Used in this Study.

	KCl	LiBr	LiCl
Alkalinity		0.04%	0.03%
Barium	0.001%		
Bromide	0.01%		
Calcium	0.005%	0.01%	0.01%
Chlorate	0.003%		0.001%
Chloride		0.15%	
Heavy Metals(as Pb)	0.0005%		0.002%
Insoluble Matter	0.005%		0.01%
Iodide	0.002%		
Iron	0.0003%	0.002%	0.001%
Magnesium	0.005%	0.001%	
Nitrogen compounds	0.001%		0.001%
Phosphate	0.0005%		
Potassium			0.01%
Sodium	0.005%		0.20%
Sulfate	0.001%		0.01%
water		1.0%	

APPENDIX B

In order to obtain accurate values of the mean activity coefficient from experimental osmotic coefficient data, equation 69 is utilized where

$$\ln\gamma_{\pm}=\phi-1-2\int_{0}^{m}1-\phi/m^{\frac{1}{2}}dm^{\frac{1}{2}} \qquad (69)$$

A plot of $1-\phi/m^{\frac{1}{2}}$ vs. $m^{\frac{1}{2}}$ is constructed to evaluate the integral.

However, it is not possible to obtain accurate values of the osmotic coefficient below 0.1 molal with vapor pressure methods. This would imply that there is some uncertainty in extrapolating the integral of equation 69 from a molality of 0.1 to zero molality if no osmotic coefficient or mean activity coefficient data are available in this concentration region from other measurements.

Since no osmotic or mean activity coefficient data are available for the LiBr and LiCl systems below 0.1m, it is difficult to extrapolate the integral of equation 69 to infinite dilution with certainty. To determine how the extrapolation was to be done in this study, it was first done for the $KCl-H_2O$ system at 25°C using the data of Robinson and Stokes. However, since data between zero molality and a molality of 0.1 is not available from this study, it was assumed that osmotic coefficient data for the same concentration range for the $KCl-H_2O$ system did not exist.

The area under the curve of equation 69 for the KCl-

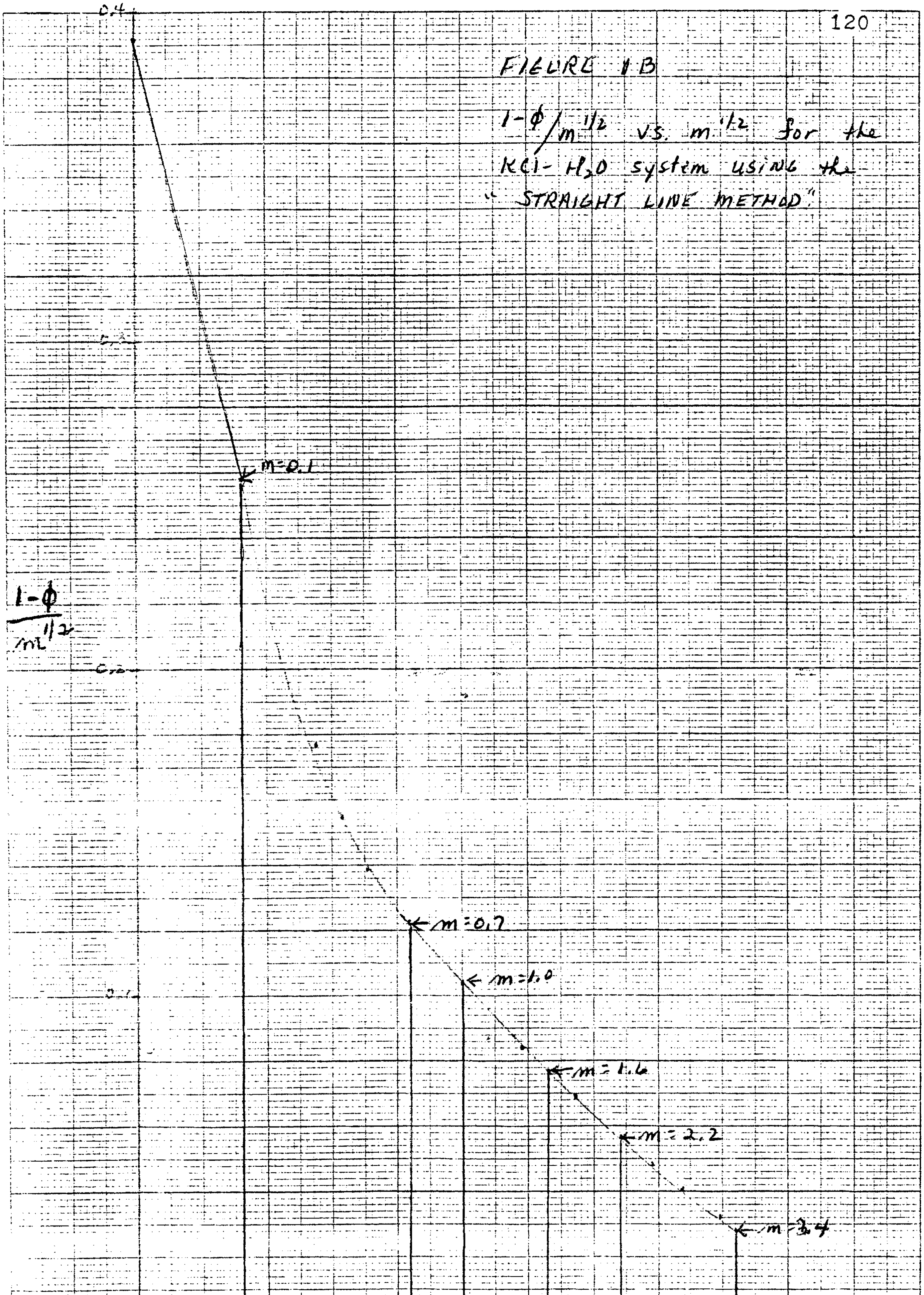
FIGURE 1B

$1-\phi / m^{1/2}$ vs. $m^{1/2}$ for the KCl-H_2O system using the "STRAIGHT LINE METHOD".

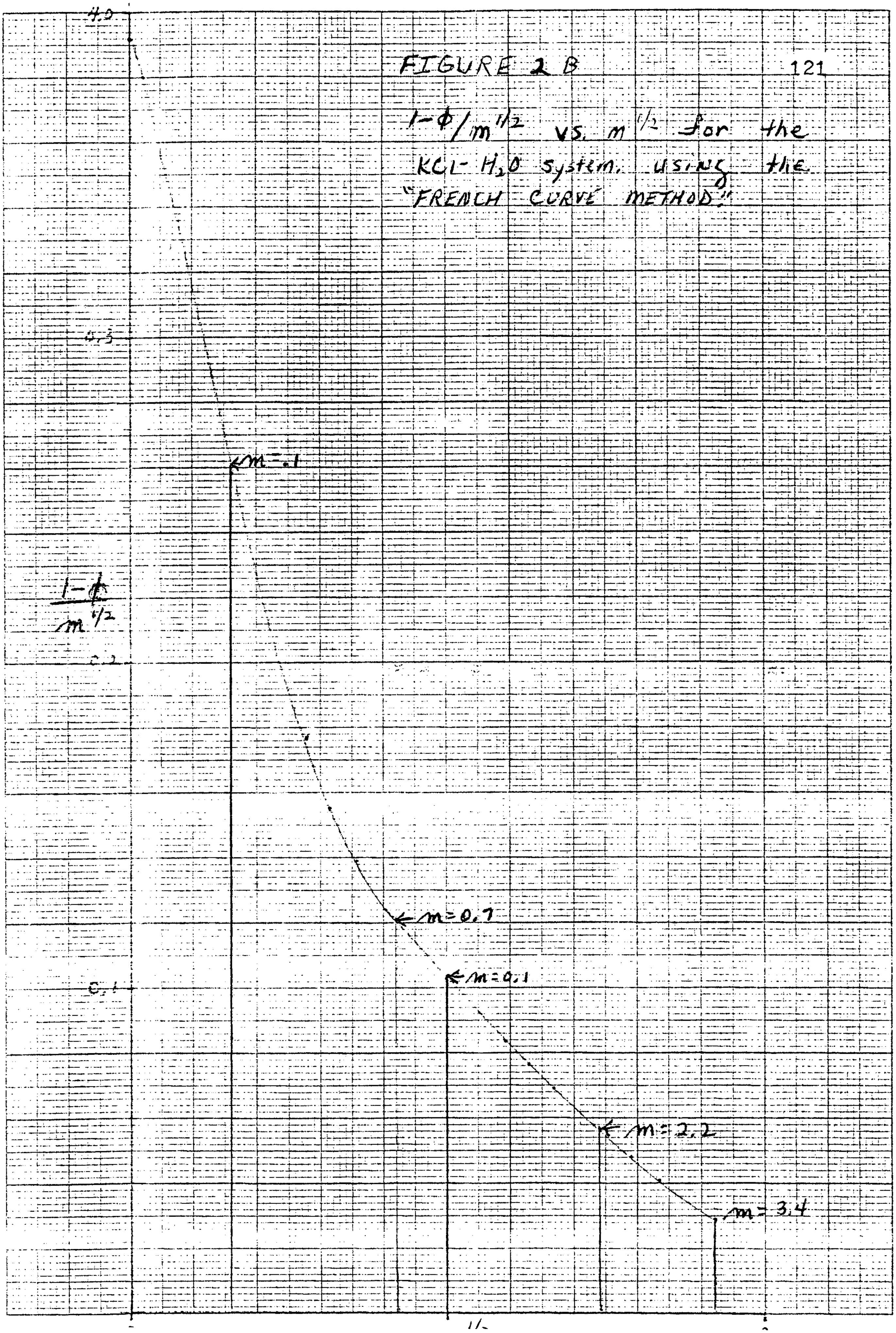

FIGURE 2 B

$1-\phi/m^{1/2}$ vs. $m^{1/2}$ for the KCL-H_2O system using the "FRENCH CURVE METHOD"

H_2O system was determined in two ways. In the first method, the plot of $1-\phi/m^{\frac{1}{2}}$ vs. $m^{\frac{1}{2}}$ was constructed omitting the data points between zero molality and a molality of 0.1. A straight line was then drawn from a molality of 0.1 or $m^{\frac{1}{2}}=.32$ to infinite dilution where $1-\phi/m^{\frac{1}{2}}$ is equal to 0.392 as determined from the Debye-Huckel limiting law for aqueous systems. At concentrations of 0.1,0.7,1.6,2.2, and 3.4m, the mean activity coefficients of aqueous KCl solutions were determined from the corresponding area indicated in the plot and the osmotic coefficient data. See Figure 1B. The results are compared to the values of the mean activity coefficients given by Robinson and Stokes and are shown in Table IB along with the relative percent error in the mean activity coefficient at each concentration. The average percent error in the mean activity coefficient using this method is 1.40%.

In the second method, a plot of $1-\phi/m^{\frac{1}{2}}$ vs. $m^{\frac{1}{2}}$ was again constructed omitting those data points between a molality of zero and a molality of 0.1. A french curve was then used to fit the data points from m equal to 0.1 to m equal to 3.8 with the limiting value of 0.392 at infinite dilution. At molalities of 0.1,0.7,1.0,1.6,2.2, and 3.4, the mean activity coefficients were determined from the corresponding areas indicated in Figure 2B and the osmotic coefficient data for aqueous KCl solutions. The results are compared to the values of the mean activity coefficients given by

Robinson and Stokes in Table IB. The relative percent errors in the mean activity coefficients for each data point is also indicated. The average percent error in the mean activity coefficient using this method is 1.24%.

Based on the above exercise using the $KCl-H_2O$ system as an example, it was decided to extrapolate the integral in equation 69 using the "French curve method" in order to obtain mean activity coefficients from the experimental osmotic coefficients for the LiCl and LiBr methanol systems. This method was chosen since the average percent error in the mean activity coefficients determined by this method for the $KCl-H_2O$ test system is less than that using the "Straight line method".

The osmotic coefficient data for the $KCl-H_2O$ system from 0.1-4.8m given by Robinson and Stokes were regressed using both the Bromley and Pitzer equations in order to generate mean activity coefficients. These values are compared in Table IIB with the values given by Robinson and Stokes. In all cases the relative percent errors of the mean activity coefficients calculated by these equations are less than those obtained from either the straight line or french curve methods. The average percent errors are 0.21 and 0.89 for the Bromley and Pitzer equations respectively, compared to 1.40 and 1.24 given by the straight line and French curve methods. This would indicate that more reliable activity coefficients are obtained from a

TABLE IB A Comparison of the Mean Activity Coefficients Calculated by the "Straight Line Method" and the "French Curve Method" with the Values given in Robinson and Stokes for the KCl-H_2O System.

m	$\gamma_{\pm R-S}$	$\gamma_{\pm str.}$	rel.% error	$\gamma_{\pm Fr.}$	rel.% error
0.1	0.770	0.748	-2.86	0.748	-2.86
0.7	0.626	0.618	-1.28	0.620	-0.96
1.0	0.604	0.595	-1.49	0.597	-1.16
1.6	0.580	0.580	0.00	0.584	0.69
2.2	0.571	0.563	-1.40	0.576	0.88
3.4	0.571	0.563	-1.40	0.576	0.88

TABLE IIB A Comparison of the Mean Activity Coefficients Calculated by the Bromley and Pitzer equations with the Values given in Robinson and Stokes for the KCl-H_2O System.

m	$\gamma_{\pm}$R-S	$\gamma_{\pm}$Brom.	rel. per. error	$\gamma_{\pm}$Pitz.	rel. per. error
0.1	0.770	0.767	0.39	0.765	0.65
0.7	0.626	0.625	0.16	0.620	0.96
1.0	0.604	0.603	0.17	0.594	1.66
1.6	0.580	0.579	0.17	0.575	0.86
2.2	0.571	0.570	0.18	0.566	0.88
3.4	0.571	0.570	0.18	0.569	0.35

correlation which fits the data over the entire concentration range of data, even though data were not taken from zero molality to a molality of 0.1, than from the graphical method.

Even though the French curve method was proven adequate in extrapolating the osmotic coefficient data through equ. 69 in order to obtain the mean activity coefficients for the KCl-H_2O system, and was used in extrapolating the LiCl and LiBr-MeOH systems, there is still some question about the reliability of the data at low concentrations. For example, referring to Tables I-VI, it is seen that the assumed error of measurement is ±0.06mm Hg. This implies, for example, that if the vapor pressure depression is only 1 mm Hg, that the true vapor pressure is in the range from 0.94 to 1.06 mm Hg. Referring to a specific example, the LiBr-MeOH system at 25°C at m=.2170 and ΔP=1.42 mm Hg, it is seen that within experimental error, the vapor pressure depression can range from 1.36 to 1.48 mm Hg. These values of the vapor pressure depression correspond to values of the osmotic coefficient of 0.768 and 0.836, respectively. For the LiBr-MeOH system at 25°C, the point at m= 0.2170 was used to extrapolate the experimental data using equation 69 since the value of the osmotic coefficient at m= .1153 was unreliable. If the curve is extrapolated using the value of the osmotic coefficient of .768 in equ. 69, the calculated value of the mean activity coefficient is 0.498, and is 0.325 if the osmotic coefficient is 0.836. The value of the osmotic coefficient used in this study was 0.802 for a ΔP of 1.42 mm Hg. The relative percent errors in the activity coefficient based on the experimental value of 0.425 are 17.2 and 23.5, respectively. This exercise indicates that a correlation that fits the data over the higher concentration ranges should be used to extrapolate the data to infinite dilution using equation 69 than a graphical method.

APPENDIX C

. THIS PROGRAM REGRESSES FOR B IN THE BROMLEY EQUATION

```
      COMMON XS(40),GEXP(40),ERROR(40),GCAL(40),NOPT
     %,NP,YD,FNP,FNM,FZP,FZN,FK,XMOL(40),ADB,AMW,B,ROW
     1,ERROP(40),PCAL(40),PSM,P(40)
      DIMENSION APHI(40),AA(40),SIG(40),ACT(40)
      DIMENSION AP(40),AN(40),XP(40),XN(40)
      REAL *8 NAME1,NAME2,NAME3
C     ******************************************
C     *                                        *
C     *  THIS PROGRAM REGRESSED FOR B IN BROMMEY'S     *
C     *   EQUATION GIVEN A VALUE OF ROW, WHICH IN THIS   *
C     *   PROGRAM VARIES TO FIND THE BEST VALUE.       *
C     *THE VALUE OF A IS CHOSEN AS DEFINED BY BROMLEY.   *
C     *******************************************
      INTEGER FZP,FZN
C     NOPT=1 FOR MOLALITY VS. DELTA P
C     NOPY=2 WHEN DATA ARE MOLALITY VS. P%HI
C     NOPT = 3 WHEN DATA ARE MOLALITY VS, GAMMA OF THE SALT
C     NDATA IS NO. OF DATA SET TO BE USED
C     FZP IS THE CHARGE ON THE POSITIVE ION
C     FZN IS THE CHARGE ON THE NEGATIVE ION(ABS. VALUE)
C     FK IS THE SUM OF THE POSITIVE AND NEGATIVE IONS AND
C        FK=FNP+FNM
C     FNP IS THE SUM OF THE NUMBER OF POSITIVE IONS
C     FNM IS THE SUM OF THE NEGATIVE IONS
C     NP IS THE NUMBER OF SYSTEM DATA POINTS
C     T IS THE TEMPERATURE OF THE SYSTEM
C     ADB IS THE DEBYE HUCKEL CONSTANT FOR THE ACTIVITY COEFFICIENT
C     AMWS IS THE MOLECULAR WEIGHT OF THE SALT
C     AMW IS THE MOLECULAR WEIGHT OF THE SOLVENT
C     PSM IS THE PURE SOLVENT VAPOR PRESSURE
C     XMOL IS THE MOLALITY OF THE SALT SOLUTION
C         AND IS A FUNCTION OF T
409   FORMAT(2F10.5)
406   FORMAT(4I5)
201   FORMAT(F10.7,2F10.4)
410      FORMAT('-', 5X,' THE TEMPERATURE OF THE SYSTEM=',F10.5)
931       FORMAT(8F10.4)
99         FORMAT('-')
1999        FORMAT(I5)
2000   FORMAT(3A8)
965         FORMAT(2I10)
1111       FORMAT(I5,3F5.1)
404       FORMAT(3F10.5)
7     FORMAT(2F10.5)
9     FORMAT(2F10.5)
932   FORMAT(8F10.4)
405   FORMAT('-','THE PURE COMPONENT VAPOR PRESSURE IS=',F10.5/'
     CTHE SOLVENT MOLECULAR WEIGHT IS=' ,F10.5/'THE SALT MOLECULAR W
     CEIGHT IS='F10.5)
```

```
407   FORMAT('-',5X,'NDATA=',I3,5X,'IND=',I2,5X,'INDP=',I2)
       READ(5,406)NDATA,IND,INDP,NIND
        WRITE(6,406)NDATA,IND,INDP,NIND
      READ(5,201)ALPHA,AX,BX
       WRITE(6,201)ALPHA,AX,BX
      DO 415 JJ=1,NDATA
      ROW=.8
       READ(5,1999)NOPT
       WRITE(6,1999)NOPT
       READ(5,409)T,ADB
        WRITE(6,409)T,ADB
      READ(5,2000)NAME1,NAME2,NA
       READ(5,1111)NP,FK,FNP,FNM
        WRITE(6,1111)NP,FK,FNP,FNM
         READ(5,965)FZP,FZN
         WRITE(6,965)FZP,FZN
      READ(5,404)PSM,AMW,AMWS
      ANS=1000./AMW
       WRITE(6,99)
       WRITE(6,410)T
       WRITE(6,405)PSM,AMW,AMWS
       WRITE(6,2000)NAME1,NAME2,NAME3
      N=NP
      GO TO(901,903,902),NOPT
901   DO 1391 I=1,N
       READ(5,7)XMOL(I),P(I)
1391  CONTINUE
       WRITE(6,6000)
6000  FORMAT('-','   XMOL      PEXP ')
      DO 403 I=1,N
      IF(IND-1)402,400,414
400   XMOL(I)=1000.*XMOL(I)/((100.-XMOL(I))*AMWS)
      GO TO 414
402   XMOL(I)=1000.*XMOL(I)/((1.-XMOL(I))*AMW)
414   IF(INDP.EQ.1) P(I)=PSM -P(I)
       WRITE(6,7)XMOL(I),P(I)
403   CONTINUE
      GO TO 910
C  IF IONS=1  MEAN IONIC CONCENTRATION IS USED FOR SALT MOLE FRACTI
C  IF IONS=2  COMPLETE DISSOCIATION IS USED FOR SAKT MOLE FRACTION
902   DO 962 I=1,N
       READ(5,9)XMOL(I),GEXP(I)
962   CONTINUE
      DO 942 I=1,N
       WRITE(6,9)XMOL(I),GEXP(I)
942   CONTINUE
      AXT=AX
      BXT=BX
      GO TO 10
```

```
903     READ(5,7)(XMOL(I),APHI(I),I=1,N)
        WRITE(6,972)(XMOL(I),APHI(I),I=1,N)
972    FORMAT('-',10X,'XMOL',15X,'APHI'//2(5X,E15.8))
911    DO 952 I=1,N
       ACT(I)=EXP(-FK*XMOL(I)*AMW*APHI(I)/1000.)
       P(I)=PSM*ACT(I)
952    CONTINUE
910    DO 4000 I=1,N
C  INDP=1  DATA ARE MOLE FRACTION VS. DEPRESSION IN VAPOR PRESSURE
C  INDP=2  DATA AREMOL.FRACTION VS. VAPOR PRESSURE
       AP(I)=FNP*XMOL(I)
       AN(I)=FNM*XMOL(I)
       XS(I)=ANS/(ANS+AP(I)+AN(I))
       XP(I)=AP(I)/(ANS+AP(I)+AN(I))
       AXT=AX
       BXT=BX
       XN(I)=AN(I)/(ANS+AP(I)+AN(I))
       GEXP(I)=P(I)/(XS(I)*PSM)
4000   CONTINUE
        WRITE(6,7000)
7000   FORMAT('-','                    XX                    GEXP')
        WRITE(6,4001)(XS(I),GEXP(I),I=1,N)
4001   FORMAT(2F20.8)
11     FORMAT(4F10.6)
910    DO 39 KK=1,6
       ALPHA=0.000005
       AXT=AX
       BXT=BX
        IF(NIND.EQ.1)GO TO 601
C     NIND=1  PARAMETER B IS ESTIMATED USING FIBONACCI PROCEDURE
C      NIND=2  PARAMETER B IS READ, OBTAINED FROM BROMLET'S PAPER
601    CALL FIBN(ALPHA,AXT,BXT)
603    N=NP
        WRITE(6,522)
522    FORMAT('-')
        WRITE(6,16)ROW
16     FORMAT('-',5X,'ROW OF THE SYSTEM='F10.5)
        WRITE(6,32)B
32     FORMAT('-',10X,'B=',E15.8)
       IF(NOPT.EQ.3.)GO TO 120
       WRITE(6,6)
6      FORMAT('-','       XX        GOBS        GCAL        ERROR ')
        WRITE(6,8)(XS(I),GEXP(I),GCAL(I),ERROR(I),I=1,N)
8      FORMAT(4F10.5)
       DO 301 I=1,N
        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.
        GCAL(I)=EXP(2.303*(AT1+(.06+.6*B)*AA(I)*(FZP*FZN)/AT2
```

```
     1+B*AA(I)))
301    CONTINUE
      WRITE(6,122)
122   FORMAT('-','    XM      POBS       PCAL       GSAL         ERROR')
       WRITE(6,123)(XMOL(I),P(I),PCAL(I),GCAL(I),ERROP(I),I=1,N)
123   FORMAT(5F10.5)
      GO TO 121
120    WRITE(6,8000)
8000  FORMAT('-','    XMOL      GEXP       GCAL       ERROR')
       WRITE(6,302)(XMOL(I),GEXP(I),GCAL(I),ERROP(I),I=1,N)
302   FORMAT(4F10.5)
121   ROW=ROW+.1
39    CONTINUE
415   CONTINUE
      STOP
      END
      SUBROUTINE FUNC(XT,YS)
      COMMON XS(40),GEXP(40),ERROR(40),GCAL(40),NOPT,
     1NP,YD,FNP,FNM,FZP,FZN,FK,XMOL(40),ADB,AMW,B,ROW,
     1ERROP(40),PCAL(40),PSM,P(40)
      DIMENSION AI(40),SAI(40),SIG(40),PHI(40),ACT(49)
      DIMENSION X(5)
       INTEGER FZP,FZN
      YY=0.0
      B=XT
      AA=1.5/(FZP*FZN)
      NN=NP
      DO 1 KK=1,NN
      AI(KK)=XMOL(KK)*(FNP*FZP**2.+FNM*FZN**2.)/2.
      GO TO(24,24,38),NOPT
 24   AT=AA*AI(KK)
      SAI(KK)=((1.+2.*AT)/((1.+AT)**2.)-ALOG(1.+AT)/(AT))*2./AT
      AT1=1.+ROW*(AI(KK)**0.5)
      AT2=3./((ROW*AI(KK)**0.5)**3.)
      SIG(KK)=AT2*(AT1-1./AT1-2.*ALOG(AT1))
       PHI(KK)=1.-2.303*ADB*(FZP*FZN)*(AI(KK)**0.5)*SIG(KK)/3.+
     12.303*(0.06+0.6*B)*(FZP*FZN)*AI(KK)*SAI(KK)/2.+2.303*B*AI(KK)/2.
      ACT(KK)=EXP(-FK*XMOL(KK)*AMW*PHI(KK)/1000.)
      GCAL(KK)=ACT(KK)/XS(KK)
      PCAL(KK)=GCAL(KK)*XS(KK)*PSM
      ERROP(KK)=P(KK)-PCAL(KK)
      GO TO 48
 38   AT1=-ADB*(FZP*FZN)*(AI(KK)**0.5)/(1.+ROW*AI(KK)**0.5)
      AT2=(1.+1.5*AI(KK)/(FZP*FZN))**2.
      GCAL(KK)=EXP(2.303*(AT1+(0.06+0.6*B)*AI(KK)*(FZP*FZN)/AT2
     1+B*AI(KK)))
 48   DIFF=ABS(GEXP(KK)-GCAL(KK))
      Y=(DIFF/GEXP(KK))**2.
      ERROR(KK)=(DIFF/GEXP(KK))*100.
```

```
      YY=Y+YY
1     CONTINUE
      YS=YY
      RETURN
      END
      SUBROUTINE FIBN(ALPHA,A,B)
      DIMENSION FIB(50)
C
C     SUBROUTINE FOR FIBONACCI PROCEDURE
C
      DEL=B-A
      WRITE(6,001)
001   FORMAT(1H1,10X,35HFIBONACCI SINGLE-VARIABLE PROCEDURE )
C
C     DEFINE THE FIRST THREE FIBONACCI NUMBERS
C
      FIBO=1.0
      FIB(1)=1.0
      FIB(2)=2.0
C
C     CALCULATE THE REMAINING FIBONACCI NUMBERS
C
5     BB=1.0/ALPHA
      IF(BB-2.)10,10,11
10    GO TO 14
11    CONTINUE
      JJ=2
12    JJ=JJ+1
      FIB(JJ)=FIB(JJ-1)+FIB(JJ-2)
       CC=FIB(JJ)
       IF(CC-BB)13,15,15
13    GO TO 12
14     WRITE(6,002)
002   FORMAT(///,10X,' ACCURACY SPECIFIED IN FUNC NOT SUFFICIENT.',
     1//,10X,' PROGRAM RESET ALPHA,ALPHA=0.01')
      ALPHA=0.01
      GO TO 5
C
C     FIRST STEP IN THE TABLEAU
15    I=0
      KK=JJ-2
      IK=JJ-2
      BL=B-A
      ALL=FIB(IK)*BL/FIB(JJ)
      W=A+ALL
      V=B-ALL
      CALL FUNC(W,T)
      CALL FUNC(V,U)
      JK=1
```

```
$$    WRITE(6,003)
003   FORMAT(//,1X,1HK,5X,2HLK,12X,2HAK,13X,2HBK,12X,3HLLK,9X,1HX,
     18X,1HY)
       WRITE(6,004)JK,BL,A,B,ALL,W,T
004   FORMAT(/,I3,6G11.4)
006   FORMAT(41X,E12.4,2X,E12.4)
C
C     SUCCEEDING STEPS IN THE TABLEAU
C
      IK=IK-1
      JJ=JJ-1
      DO 70 I=1,KK
      IF(U-T)20,20,22
20    A=A+ALL
      BL=B-A
      W=V
      CALL FUNC(W,T)
      ALL=FIB(IK)*BL/FIB(JJ)
      V=B-ALL
      CALL FUNC(V,U)
      II=I+1
      IK=IK-1
      JJ=JJ-1
      IF(IK-1)28,29,29
28    IK=1
29    CONTINUE
      WRITE(6,004)II,BL,A,B,ALL,W,T
      WRITE(6,006)V,U
      GO TO 70
22    B=B-ALL
      BL=B-A
      V=W
      CALL FUNC(V,U)
      ALL=FIB(IK)*BL/FIB(JJ)
      W=A+ALL
      CALL FUNC(W,T)
      II=I+1
      IK=IK-1
      JJ=JJ-1
      IF(IK-1)30,31,31
30    IK=1
31    CONTINUE
      WRITE(6,004)II,BL,A,B,AL,V,U
      WRITE(006)W,T
      GO TO 70
70    CONTINUE
C
C     CALCULATION OF THE FINAL RANGE OF THE DEPENENT VARIABLE
      EPS=0.001*W
```

APPENDIX D

THIS PROGRAM REGRESSES FOR β_0, β_1, AND C IN THE PITZER EQUATION

```
       COMMON XS(35),GW(35),ERROR(35),GCAL(35),NOPT,GEXP(35)
      C,M,N,NP,YD,FNP,FNM,FZP,FZN,FK,XMOL(35),ADB,AMW,B,ROW,
      CGSALT(35),ERRO(35),GSAL(35),ALPH,EE,ERROP(35),P(35),PSM
      C,PCAL(35),B0,B1,CPHI,APHI(35),PHI(35),C
       DIMENSION AA(35),SIG(35),ACT(35)
       DIMENSION XT(12),DX(12),Y(8),X(7,10)
       DIMENSION AK(35),F(35)
       DIMENSION AP(35),AN(35),XP(35),XN(35)
       REAL *8 NAME1,NAME2,NAME3
       INTEGER FZP,FZN
409    FORMAT(2F10.5)
C      NDATA IS NO. OF DATA SET TO BE USED
406    FORMAT(4I5)
        READ(5,406)NDATA,IND,INDP,NIND
        READ(5,201)ALPHA,AX,BX
6000   FORMAT(F10.7,2F10.4)
C      IND =0FORWEIGHT FRAC,=1 FOR MOLE FRAC,=2 FOR MOLALITY
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      NP IS THE NUMBER OF POINTS IN ONE SYSTEM
C      FK IS THE TOTAL NUMBER OF IONS
201     FORMAT(F10.7,2F10.4)
410    FORMAT('-', 3X,' TEMPERATURE OF THE SYSTEM =',F10.5)
931    FORMAT(8F10.4)
       DO [illegible] JJ=1,NDATA
        WRITE(6,99)
99     FORMAT('1')
        READ(5,1999)NOPT
1999   FORMAT(I5)
        READ(5,409)T,ROS
        ADB ,13382.303*ADB
        READ(5,2000)NAME1,NAME2,NAME3
        WRITE(6,2000)NAME1,NAME2,NAME3
2000   FORMAT(1X,3A8)
        READ(5,1111)NP,FK,FNP,FNM
        READ(5,965)FZP,FZN
965    FORMAT(2I10)
          WRITE(6,425)FZP,FZN
425       FORMAT(2I10)
        WRITE(6,410)T
1111   FORMAT(I5,3F5.1)
C   AMWS    MOLECULAR WEIGHT OF SALT
C    AMW    MOLECULAR WEIGHT OF SOLVENT
        READ(5,404)PSM,AMW,AMWS
        WRITE(6,405)PSM,AMW,AMWS
```

```
404   FORMAT(3F10.5)
      ANS=1000./AMW
405   FORMAT('-','PURE COMPONENT VAPOR PRESSURE =',F10.5//'SOLVENT MOLECU
     1LAR WEIGHT=',F10.5//'SOLUTE MOLECULAR WEIGHT =',F10.5)
       WRITE(6,407)NDATA,IND,INDP
407   FORMAT('-',5X,'NDATA=',I3,5X,'IND=',I2,5X,'INDP=',I2)
      N=NP
      GO TO (901,903,902),NOPT
C     NOPT=1 DATA ARE MOL VS.VAPOR PRESSURE
C     NOPT=2 DATA ARE MOLALITY VS PHI
C     NOPT = 3 DATA ARE MOL VS. GAMMA OF SALT
901   DO 1391 I=1,N
       READ(5,7)XMOL(I),P(I)
1391  CONTINUE
      DO 403 I=1,N
      IF(IND-1)402,400,414
400   XMOL(I)=1000.*XMOL(I)/((100.-XMOL(I))*AMWS)
      GO TO 414
402   XMOL(I)=1000.*XMOL(I)/((1.-XMOL(I))*AMW)
414   IF(INDP.EQ.1) P(I)=PSM -P(I)
       WRITE(6,7)XMOL(I),P(I)
403   CONTINUE
7     FORMAT(2F10.5)
      GO TO 953
C  IF IONS=1  MEAN IONIC CONCENTRATION IS USED FOR SALT MOLE FRACTION
C  IF IONS=2  COMPLETE DISSOCIATION IS USED FOR SAKT MOLE FRACTION
903    READ(5,7)(XMOL(I),APHI(I),I=1,N)
932   FORMAT(8F10.4)
       WRITE(6,972)(XMOL(I),APHI(I),I=1,N)
972   FORMAT('-',10X,'XMOL',15X,'APHI'//2(5X,E15.8))
911   DO 952 I=1,N
      ACT(I)=EXP(-FK*XMOL(I)*AMW*APHI(I)/1000.)
      P(I)=PSM*ACT(I)
952   CONTINUE
953   DO 4000 I=1,N
C  INDP=1  DATA ARE MOLE FRACTION VS. DEPRESSION IN VAPOR PRESSURE
C  INDP=2  DATA AREMOL.FRACTION VS. VAPOR PRESSURE
      AP(I)=FNP*XMOL(I)
      AN(I)=FNM*XMOL(I)
      XS(I)=ANS/(ANS+AP(I)+AN(I))
      XP(I)=AP(I)/(ANS+AP(I)+AN(I))
      XN(I)=AN(I)/(ANS+AP(I)+AN(I))
      GW(I)=P(I)/(XS(I)*PSM)
      TERM=GW(I)*XS(I)
      TERM1=ALOG(TERM)
      APHI(I)=-1000.*TERM1/(XMOL(I)*FK*AMW)
4000  CONTINUE
      GO TO 501
902   DO 1997 I=1,N
```

```
       READ(5,9)XMOL(I),GEXP(I)
1997  CONTINUE
      DO 1996 I=1,N
       WRITE(6,9)XMOL(I),GEXP(I)
1996  CONTINUE
9     FORMAT(2F10.5)
501   DO 21 J=1,7
      DO 21 K=1,10
      X(J,K)=0.0
21    CONTINUE
      M=3
       XT(1)=0.0
       XT(2)=0.0
       XT(3)=0.0
      DO 507 I=1,M
      DX(I)=0.1
507   CONTINUE
      M1=M+1
      M3=M+3
      L=200
      E=0.0001
       WRITE(6,4)E
4     FORMAT(///,10X,'E=',F10.8)
       WRITE(6,301)(I,XT(I),I=1,M)
301   FORMAT(///,5X,'INITIAL VALUES FOR XT(',I2,')=',F15.5)
      CALL LSQ2(XT,X,DX,Y,M,M1,M3,L,E)
      N=NP
       WRITE(6,5)(I,XT(I),I=1,M)
5     FORMAT(///,5X,'FINAL VALUES FOR XT(',I2,')=',F15.5)
       WRITE(6,401)(I,Y(I),I=1,M1)
401   FORMAT('-',10X,'Y(',I2,')=',F10.5)
       WRITE(6,31)YD
31    FORMAT('-','MEAN=',F10.5)
       WRITE(6,32)B0
32    FORMAT('-',10X, 'B0=',E15.8)
       WRITE(6,5000)B1
5000  FORMAT('-',10X    'B1=',E15.8)
       WRITE(6,596)CPHI
596   FORMAT( '-' ,10X            'CPHI=',E15.8)
       WRITE(6,523)
523   FORMAT('-')
      IF(NOPT.EQ.3.) GO TO 45
11    FORMAT(4F10.6)
       WRITE(6,522)
522   FORMAT('-')
       WRITE(6,6)
6     FORMAT('-',' XX          GOBS            GCAL               ERROR  ' )
       WRITE(6,8)(XS(I),GW(I),GCAL(I),ERROR(I),I=1,N)
8     FORMAT(///,4F10.5)
```

```
       DO 598 I=1,N
        AA(I)=XMOL(I)*(FNP*FZP**2.+FNM*FZN**2.)/2.
       A=1.+1.2*AA(I)**.5
        ADH=.333*2.303*ADB
       F(I)=-ADH*((AA(I)**.5)/A+(2./1.2)*ALOG(A))
       T=EXP(-2.*AA(I)**.5)
       TA=2.*AA(I)
        D=2.*B0+.5*B1/AA(I)*(1.-T*(1.+2.*AA(I)**.5-TA))
        CG=.667*C
       TERM=FZP*FZN*F(I)+2.*XMOL(I)*FNP*FNM*D/FK+2.*(XMOL(I)**2.)*CG*
      C((FNP*FNM)**1.5)/FK
       GSALT(I)=EXP(TERM)
598    CONTINUE
        WRITE(6,122)
122      FORMAT('-','      XM       POBS       PCAL       GSAL       ERROR')
        WRITE(6,123)(XMOL(I),P(I),PCAL(I),GSALT(I),ERROP(I),I=1,N)
123     FORMAT(5F10.5)
        GO TO 415
 45     WRITE(6,1003)(XMOL(I),GEXP(I),GSAL(I),ERRO(I),I=1,N)
        WRITE(6,4004)(XMOL(I),AK(I),I=1,N)
4004   FORMAT(2F20.8)
1003   FORMAT(//,4F10.5)
        WRITE(6,4020)AVRGE
4020   FORMAT('-',10X,      'AVRGE=',E15.8)
415    CONTINUE
       STOP
       END
       SUBROUTINE FN(YY,XT,LIC)
       COMMON XS(35),GW(35),ERROR(35),GCAL(35),NOPT,GEXP(35)
      C,M,N,NP,YD,FNP,FNM,FZP,FZN,FK,XMOL(35),ADB,AMW,S,ROW,
      CGSALT(35),ERRO(35),GSAL(35),ALPH,EE,ERROP(35),P(35),PSM
      C,PCAL(35),B0,B1,CPHI,APHI(35),PHI(35),C
       DIMENSION AI(35),SAI(35),SIG(35),ACT(35)
       DIMENSION XT(12)
       DIMENSION AO(35),F(35),BMX(35)
       DIMENSION FPHI(35)
        INTEGER FZP,FZN
        ADH=.333*2.303*ADB
       YS=0.0
        B0=XT(1)
       B1=XT(2)
       CPHI=XT(3)
       NN=NP
       GO TO (36,36,38),NOPT
36     DO 1 KK=1,NN
       AI(KK)=XMOL(KK)*(FNP*FZP**2.+FNM*FZN**2.)/2.
       FPHI(KK)=-(ADH*AI(KK)**.5)/(1.+1.2*AI(KK)**.5)
        BMX(KK)=B0+B1*EXP(-2.*AI(KK)**.5)
       C=CPHI
```

```
      PHI(KK)=1.+FZP*FZN*FPHI(KK)+2.*XMOL(KK)*FNP*FNM*BMX(KK)/FK
     C+2.*(XMOL(KK)**2.)*((FNP*FNM)**1.5)*C/FK
      ACT(KK)=EXP(-FK*XMOL(KK)*AMW*PHI(KK)/1000.)
      GCAL(KK)=ACT(KK)/XS(KK)
      PCAL(KK)=GCAL(KK)*XS(KK)*PSM
      ERROP(KK)=P(KK)-PCAL(KK)
      ERROR(KK)=(GCAL(KK)-GW(KK))*100./GW(KK)
      DIFF=ABS(GCAL(KK)-GW(KK))
      Y=(DIFF/GW(KK))**2.
      YS=Y+YS
1     CONTINUE
      GO TO 24
38    DO 2 KK=1,NN
      A0(KK)=XMOL(KK)*(FNP*FZP**2.+FNM*FZN**2.)/2.
      A=1.+1.2*A0(KK)**.5
      F(KK)=-ADH*(A0(KK)**.5/A+(2./1.2)*ALOG(A))
      T=EXP(-2.*A0(KK)**.5)
      TA=2.*A0(KK)
       BMX(KK)=2.*B0+.5*B1/A0(KK)*(1.-T*(1.+2.*A0(KK)**.5-TA))
      C=1.5*CPHI
      TERM=FZP*FZN*F(KK)+2.*XMOL(KK)*FNP*FNM*BMX(KK)/FK+
     C(XMOL(KK)**2.)*2.*(FNP*FNM)**1.5*C/FK
      GSAL(KK)=EXP(TERM)
      ERRO(KK)=(GEXP(KK)-GSAL(KK))*100./GEXP(KK)
      DIF=ABS(GEXP(KK)-GSAL(KK))
      SUM=0.0
      Y=(DIF/GEXP(KK))**2.
      YS=Y+YS
2     CONTINUE
24    YY=YS
      YD=YY
      RETURN
      END
      SUBROUTINE LSQ2(XT,X,DX,Y,M,M1,M3,L,E)
       DIMENSION XT(12),DX(12),X(7,10),Y(8),JJ(3),A(3,3)
      IL=0
      IH=0
      LIC=0
      IF(L.LE.0) GO TO 50
      IHC=M1+1
      EN=M
      EN=EN*1.5
      L1=L
      L=-L
      L2=(3*M)/2+5
      K3=2
       IF(M.GE.3)K3=3
      K4=K3-1
      G=K3*2
```

```
      G=1.0/G
      DO 100 I=1,M
100   X(I,1)=XT(I)
      CALL FN(Y(1),XT,LIC)
      DO 106 J=2,M1
      XT(J-1)=XT(J-1)+DX(J-1)
      DO 104 I=1,M
104   X(I,J)=XT(I)
      CALL FN(Y(J),XT,LIC)
      XT(J-1)=X(J-1,1)
106    CONTINUE
      L2C=0
      FLG=1.0
      GO TO 50
108   LIC=LIC+1
      IF(LIC.GE.L1)GO TO 400
50    YL=1.0E38
      YH=-YL
      Y2=YH
      Y3=YL
      DO 110 J=1,M1
      IF(Y(J).LT.YH)GO TO 1091
      Y2=YH
      I2=IH
      YH=Y(J)
      IH=J
      GO TO 109
1091   IF(Y(J).LT.Y2)GO TO 109
      Y2=Y(J)
      I2=J
109   IF(Y(J).GT.YL)GO TO 1101
      Y3=YL
      I3=IL
      IL=J
      YL=Y(J)
      GO TO 110
1101   IF(Y(J).GT.Y3)GO TO 110
      Y3=Y(J)
      I3=J
110    CONTINUE
      L2C=L2C+1
      IF(L2C.LT.L2)GO TO 111
      L2C=0
      JJ(1)=IL
      JJ(2)=I2
       JJ(3)=I3
      DO 60 K1=1,K3
      J1=JJ(K1)
      DO 60 K2=K1,K3
```

```
      J2=JJ(K2)
      S=0.0
      DO 55 I=1,M
55    S=S+(X(I,J1)-X(I,IH))*(X(I,J2)-X(I,IH))
60     A(K1,K2)=S
      D=A(1,1)*A(2,2)-A(1,2)**2
      GO TO (62,61),K4
61     D1=A(1,1)*A(2,3)-A(1,2)*A(1,3)
      IF(A(1,1).EQ.0.0)A(1,1)=1.0E-5
      D=((A(1,1)*A(3,3)-A(1,3)**2)*D-D1*D1)/(A(1,1)*9.0)
62     IF(D.EQ.0.0)GO TO 65
      IF(D.LE.0.0)D=ABS(D)
      D=(D/4.0)**G
      IF(D.LT.E)GO TO 65
      FLG=1.0
      GO TO 111
65     IF(FLG.LT.0.0)GO TO 400
      FLG=-1.0
111    DO 115 I=1,M
      XT(I)=0.0
      DO 112 J=1,M1
      IF(J.NE.IH)XT(I)=XT(I)+X(I,J)
112   CONTINUE
115    XT(I)=(3.0*XT(I)+X(I,I2)-X(I,IL))/EN-X(I,IH)
121    CALL FN(YT,XT,LIC)
      IF(YT.GE.Y2)GO TO 167
      IHC=M1+1
      IF(YT.GE.YL)GO TO 140
      YTT=YT
      DO 135 I=1,M
135    XT(I)=1.5*XT(I)-0.5*X(I,IH)
      CALL FN(YT,XT,LIC)
      IF(YT.LE.YL)GO TO 140
      DO 138 I=1,M
138    X(I,IH)=(2.0*XT(I)+X(I,IH))/3.0
      Y(IH)=YTT
      GO TO 108
140    DO 142 I=1,M
142    X(I,IH)=XT(I)
      Y(IH)=YT
      GO TO 108
167    IHC=IHC-1
      IF(IHC.EQ.0)GO TO 300
      IF(YT.GE.YH)GO TO 173
       DO 168 I=1,M
      XS=XT(I)
      XT(I)=X(I,IH)
168    X(I,IH)=XS
173    DO 174 I=1,M
```

```
174      XT(I)=0.75*X(I,IH)+0.25*XT(I)
         CALL FN(YT,XT,LIC)
        IF(YT.GT.YH)GO TO 180
        Y(IH)=YT
        DO 175 I=1,M
175     X(I,IH)=XT(I)
        GO TO 108
180     DO 185 J=1,M1
        IF(J.EQ.IL)GO TO 185
        DO 182 I=1,M
        XT(I)=(X(I,J)+X(I,IL))/2.0
182     X(I,J)=XT(I)
        CALL FN(Y(J),XT,LIC)
185     CONTINUE
        GO TO 108
300     IHC=2*M1
        IF(M.GE.3)GO TO 350
        S=0.0
        DO 302 I=1,M
        X(I,M+2)=X(I,IH)-X(I,IL)
        X(I,M+3)=X(I,IH)-X(I,I3)
302     S=S+X(I,M+2)**2
303     S=SQRT(S)
        IF(S.EQ.0.0)S=1.0E-5
304     U=-X(2,M+2)/S
        X(2,M+2)=X(1,M+2)/S
        X(1,M+2)=U
        S=X(1,M+2)*X(1,M+3)+X(2,M+2)*X(2,M+3)
        DO 305 I=1,M
305     X(I,M+2)=X(I,M+2)*S
306     DO 307 I=1,M
307     XT(I)=X(I,IH)+X(I,M+2)
        CALL FN(YT,XT,LIC)
        DO 309 I=1,M
309     XT(I)=X(I,IH)-X(I,M+2)
        CALL FN(YTT,XT,LIC)
        IF(YTT.LE.YT)GO TO 320
        DO 311 I=1,M
311     XT(I)=X(I,IH)+X(I,M+2)
        YTT=YT
320     Y(IH)=YTT
        DO 321 I=1,M
321     X(I,IH)=XT(I)
        GO TO 108
350     DO 352 I=1,M
        XT(I)=X(I,IH)-X(I,IL)
        X(I,M+2)=X(I,IH)-X(I,I2)
352     X(I,M+3)=X(I,IH)-X(I,I3)
        S=0.0
```

```
      S1=0.0
      DO 355 I=1,M
      S=S+XT(I)**2
355   S1=S1+X(I,M+3)**2
      S=SQRT(S)
      S1=SQRT(S1)
      S2=0.0
      DO 357 I=1,M
      IF(S.EQ.0.0)S=1.0E-5
      XT(I)=XT(I)/S
      S2=S2+XT(I)*X(I,M+2)
      IF(S1.EQ.0.0)S1=1.0E-5
357   X(I,M+3)=X(I,M+3)/S1
      DO 360 I=1,M
360   X(I,M+2)=X(I,M+2)-XT(I)*S2
      S1=0.0
      DO 362 I=1,M
362   S1=S1+X(I,M+2)**2
      S1=SQRT(S1)
      DO 365 I=1,M
      IF(S1.EQ.0.0)S1=1.0E-5
365   X(I,M+2)=X(I,M+2)/S1
      S1=0.0
      S2=0.0
      DO 367 I=1,M
      S1=S1+XT(I)*X(I,M+3)
367   S2=S2+X(I,M+2)*X(I,M+3)
      DO 370 I=1,M
370   X(I,M+2)=S*(S1*XT(I)+S2*X(I,M+2)-X(I,M+3))
      GO TO 306
400   S=Y(1)
      Y(1)=Y(IL)
      Y(IL)=S
      DO 402 I=1,M
      XT(I)=X(I,IL)
      X(I,IL)=X(I,1)
402   X(I,1)=XT(I)
      WRITE(6,772) LIC
772   FORMAT('-','LIC=',I5)
      RETURN
```

```
C
      DL=W+EPS
      CALL FUNC(DL,YL)
      IF(YL-T)80,80,81
80    CALL FUNC (B,BF)
      WRITE(6,007)W,B
007   FORMAT(///,25HTHE FINAL FEASIBLE REGION ,2X,2HX=,E15.4,2X,2HX=,
     1E15.4)
     $WRITE(6,008)T,BF
008   FORMAT(/    ,20HWITH FUNCTION VALUES,7X,2HY=,E10.4,2X,2HY=,E10.4)
      GO TO 87
81    CALL FUNC(A,AF)
      WRITE(6,009)W,A
009   FORMAT(///    ,25HTHE FINAL FEASIBLE REGION,2X,2HX=,E15.4,2X,2HX=,
     1E15.4)
      WRITE(6,017)T,AF
017   FORMAT(/     ,20HWITH FUNCTION VALUES,7X,2HY=,E10.4,2X,2HY=,E10.4)
87    ACC=(W-A )/(DEL)
      WRITE(6,018)ACC
018   FORMAT(/    ,     15HTHE ACCURACY IS,12X,E10.4)
      WRITE(6,019)ALPHA
019     FORMAT(/         ,'THE REQUIRED ACCURACY WAS =',E10.4)
C
      RETURN
      END
```