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IN MIXED SOLVENTS

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Equation of State for Solutions of Electrolytes
in Mixed Solvents

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Abstract

Based on molecular theory, an equation of state (EOS) is derived for a mixture containing two solvents and a salt. The equation of state follows from an expression for the Helmholtz energy; parameters are fitted to vapor pressure-, density-, and osmotic-coefficient data between -10 and 120°C from infinite dilution to 15 mole% salt. For the binary systems (methanol-water, methanol-lithium bromide, water-lithium bromide) deviations in vapor pressure are about 2-4%. When applied to the ternary system, using only binary parameters, the EOS predicts vapor pressures with a mean deviation of 6% and vapor compositions with a mean deviation of less than 1.5 mole%.

1. Introduction

While much attention has been given to the thermodynamics of aqueous electrolyte solutions /1,2,6,7,22/, much less is known about the thermodynamics of those solutions which contain an electrolyte in a mixed solvent /5,8/. This work is concerned with such a solution: lithium bromide in methanol-water in the temperature range -10° to 120°C at concentrations to 15 mole% salt. This system is of interest for heat-pump technology /16/. Experimental thermophysical properties are reported by Raatschen /26/.

To represent the experimental data, this work presents a new expression for the Helmholtz energy of the mixture as a function of temperature, density and composition. The new expression gives an equation of state which is not limited to the liquid phase; it covers the entire fluid-density range from zero to liquid-like densities. For calculation of vapor-liquid equilibria, the new expression is therefore applicable to both phases.

It is desirable to correlate thermodynamic properties of solutions with an equation of state, because it is then easily possible to include not only condensable components but also supercritical gases. Further, an equation of state facilitates calculation of vapor-liquid equilibria at high pressures.

Essentially all previous thermodynamic work on electrolyte solutions uses activity coefficients for describing liquid-phase properties; a separate model (usually ideal-gas law) is used to describe vapor-phase properties. To our best knowledge, this work is the first attempt to establish a correlation of thermodynamic properties of electrolyte solutions, using a single equation of state applicable to both phases.

2. Thermodynamic Framework

Our basic framework is an extension of that discussed by Hu et al /13,14/. Helmholtz energy A is a function of temperature T, total volume V and mole number n_i; it is given by

$$A = \sum_{i=1}^{L} n_i a_i^0 + \Delta A_I + \Delta A_{II} + \Delta A_{III} + \Delta A_{IV} + \Delta A_V + \Delta A_{VI} \qquad (1)$$

where a_i^0 is the molar Helmholtz energy of pure species i in the ideal-gas state at system temperature T and 1 bar, and L is the number of molecular species. We write for the residual Helmholtz energy

$$A^r = A - \sum_{i=1}^{L} n_i a_i^0 - \Delta A_I = \Delta A_{II} + \Delta A_{III} + \Delta A_{IV} + \Delta A_V + \Delta A_{VI} \qquad (2)$$

Residual here means relative to a mixture of ideal gases at the same temperature T, volume V, and composition n_i.

From residual Helmholtz energy A^r we compute fugacity coefficient ϕ_i and pressure P according to

$$\ln \phi_i = \left(\frac{\partial A^r/RT}{\partial n_i}\right)_{V,T,n_{j \neq i}} - \ln Z \; ; \qquad Z = \frac{PV}{nRT} \qquad (3)$$

$$P = -\left(\frac{\partial A^r}{\partial V}\right)_{T,n_i} + \frac{nRT}{V} \qquad (4)$$

where Z is the compressibility factor, R is the gas constant, and n is the total number of moles. We consider the salt to be completely dissociated into ions.

ΔA_I is the change in Helmholtz energy when the pure ideal gases at 1 bar are mixed at constant temperature and compressed to total volume V:

$$\Delta A_I = \sum_{i=1}^{L} n_i RT \ln\left(\frac{n_i RT}{V}\right) \qquad (5)$$

ΔA_{II} is the change in Helmholtz energy when the ideal-gas molecules are inflated to hard spheres at constant temperature, volume and composition. For each species i, there is a hard-sphere diameter σ_i. Using the Boublik-Mansoori extension /4,18/ of the Carnahan-Starling equation,

$$\Delta A_{II} = nRT \left[\frac{\frac{3DE}{F}\xi - \frac{E^3}{F^2}}{(1-\xi)} + \frac{\frac{E^3}{F^2}}{(1-\xi)^2} + \left(\frac{E^3}{F^2} - 1\right)\ln(1-\xi) \right] \qquad (6)$$

where $D = \sum_{i=1}^{L} x_i \sigma_i$

$$E = \sum_{i=1}^{L} x_i \sigma_i^2$$

$$F = \sum_{i=1}^{L} x_i \sigma_i^3 \qquad \xi = \frac{\pi}{6} \rho N_{Av} F \qquad \rho = \frac{n}{V}$$

Here ρ is the molar density of the mixture, N_{Av} is Avogadro number, and $x_i = n_i/n$ is the mole fraction of species i.

ΔA_{III} is the contribution to A from all intermolecular forces of attraction except those that are due to the permanent electric charges on ions. Calculation of ΔA_{III} is similar to that described by Hu, based on a Lennard-Jones potential and on a radial distribution function which assumes that the structure of a fluid mixture can be described through a short-range coordination shell followed by a long-range random environment, as shown in Figure 1.

Following Hu's method, ΔA_{III} can be written as

$$\Delta A_{III} = \frac{N_{Av}^2}{2} \sum_{i=1}^{L} \sum_{j=1}^{L} n_i \left[\left(\frac{4}{3}\right) \pi \frac{(r_{ji}^{**3} - \sigma_{ji}^3)}{V} n_j \Gamma_{ji}(r_{ji}^*) + \int_{r_{ji}^{**}}^{\infty} n_j \Gamma_{ji}(r) \frac{4\pi r^2}{V} dr \right] \tag{7}$$

where Γ_{ji} is the two-body potential function; r_{ji}^{**} is the distance from the center of central molecule i to the outer border of the first shell formed by molecules j; and where r_{ji}^* is the center-to-center distance of molecule i to molecule j in the first shell. As in eqn. (6), σ_i is the hard-sphere diameter of molecule i and σ_{ji} is the collision diameter of molecules i and j.

The expression $4/3 \pi (r_{ji}^{**3} - \sigma_{ji}^3)(n_j N_{Av}/V)$ gives the number of molecules j surrounding the central molecule i in the first shell. If we multiply this expression by the potential function $\Gamma_{ji}(r_{ji}^*)$, sum over all molecules and then divide by a factor of two to avoid double-counting of interactions, we obtain the change in Helmholtz energy for the first shell. All other molecules around central molecule i are in the long-range random en-

vironment. Their contribution to ΔA_{III} is given by the integral in eqn. (7).

The Lennard-Jones potential function is

$$\Gamma_{ji}(r) = 4\ \varepsilon_{ji}\ [(\frac{\sigma_{ji}}{r})^{12} - (\frac{\sigma_{ji}}{r})^{6}] \tag{8}$$

The ratios $\dfrac{\sigma_{ji}}{r_{ji}^{*}} = \dfrac{1}{K^{*}}$ and $\dfrac{\sigma_{ji}}{r_{ji}^{**}} = \dfrac{1}{K^{**}}$ are universal constants; based on data from computer simulation, Hu gives $K^{*}=1.15$ and $K^{**}=1.575$. Since the lower limit of the integral in eqn. (7) is r_{ji}^{**}, the Lennard-Jones potential, as used here, provides only contributions from attractive forces. We here use the Lennard-Jones potential to account for all attractive forces other than those due to permanent electric charges. Therefore, for hydrogen-bonded fluids such as water and methanol and their mixtures, parameter ε_{ji} is temperature-dependent.

ΔA_{IV} is the change in Helmholtz energy which follows from giving to some of the molecules electric charges to form ions; ΔA_{V} and ΔA_{VI} account for ion-ion interactions. We return later to these contributions to A.

We consider first the pure solvents and then the salt-free mixture methanol-water. For these cases, ΔA_{IV}, ΔA_{V}, and ΔA_{VI} are zero.

3. EOS for Pure Methanol and Pure Water

To fit parameters to experimental data, we use computer programs prepared by Topliss /30/.

For pure methanol and pure water, adjustable parameters are diameter σ_i and energy parameter ε_i. They are obtained by fitting to experimental pure-component vapor pressures and saturated-liq-

uid and saturated-vapor densities. To represent the temperature dependence of ε_i, we use the relation

$$\frac{\varepsilon_i}{k} = \frac{\varepsilon_i^{(0)} + \varepsilon_i^{(1)} \left(\frac{T_{ci}}{T}\right)^2}{1 + \varepsilon_i^{(2)} \left(\frac{T_{ci}}{T}\right)^2} \tag{9}$$

where T_{ci} is the critical temperature and k is Boltzmann's constant. Table 1 gives the adjusted parameters and values for T_{ci}. Table 2 gives mean deviations for pure-component properties.

For methanol, ε/k is in the range 445-475 K; for water, ε/k is in the range 540-570 K. With rising temperature the energy parameter decreases, as expected for a hydrogen-bonded fluid.

4. EOS for the Mixture Methanol(1)-Water(2)

For distance parameter σ_{12} we use

$$\sigma_{12} = \frac{1}{2} \left(\sigma_1 + \sigma_2 \right) \tag{10}$$

For energy parameter ε_{12} we use a corrected geometric-mean combining rule:

$$\varepsilon_{12} = \sqrt{\varepsilon_1 \varepsilon_2} \left(1 - k_{12}\right) \quad \text{with} \quad k_{12} = k_{21} = k_{12}^{(1)} + \frac{k_{12}^{(2)}}{T} \tag{11}$$

We obtain k_{12} by fitting phase-equilibrium data from the collection of Gmehling and Onken /10/.

$$k_{12}^{(1)} = 0.01738 ; \qquad k_{12}^{(2)} = -16.063 \text{ K}$$

Given liquid-phase mole fraction x and temperature T, the mean deviation in calculated vapor pressure is less than 2.7%; the mean deviation in vapor-phase mole fraction is $\Delta y_1 = 0.011$. Figure 2 shows experimental and calculated vapor pressures for methanol-water mixtures as a function of concentration at three temperatures.

5. Ions

In the next steps we charge some of the molecules to become ions, apply a modified Debye-Hückel equation to very dilute solutions and extend it to salt concentrations of 7 mole% using an equation proposed by Pitzer. Finally, for higher salt concentrations, we make an empirical modification in Pitzer's equation.

5.1 Charging Molecules to Become Ions

The change in Helmholtz energy ΔA_{IV} accounts for assigning a permanent electric charge to those species which exist as ions in the solution. For this step, we use an expression derived by Born /3/:

$$\Delta A_{IV} = \frac{N_{Av} e^2}{D} \sum_{i=1}^{L} \frac{n_i z_i^2}{\sigma_i^*} \tag{12}$$

Here e is the unit charge and z_i is the ionic charge. We assume that the salt molecule lithium bromide completely dissociates into a $Li^+(3)$ and a $Br^-(4)$-ion. For Li^+, $z_3 = +1$, and for Br^-, $z_4 = -1$. For solvent molecules, z_i is zero. For the mixture, dielectric constant D is a function of density, composition, and temperature[‡]; this function, described by Harvey /11/, is briefly

summarized in Appendix I. For the ionic diameter σ_i^* in eqn. (12), we use corrected diameters proposed by Rashin et al /27/, who argue that in Born's equation, it is appropriate to use the cavity diameter which an ion forms in the solvent.

5.2 The Debye-Hückel Equation

For dilute solutions we introduce the Debye-Hückel equation (DHE), extended by Pitzer /23/ to slightly higher salt concentrations. The change in Helmholtz energy ΔA_V is

$$\Delta A_V = - nRT \left(\frac{4}{3}\right) \sqrt{2\pi N_{Av}} \left(\frac{e^2}{DkT}\right)^{1.5} \frac{I}{\rho b} \ln(1+b\sqrt{I}) \tag{13}$$

$$I = \frac{1}{2} \rho \sum_{i=1}^{L} x_i z_i^2 \qquad\qquad b = (1.2) \cdot \sqrt{1000} \left[\left(\frac{cm^3}{mole}\right)^{0.5}\right]$$

where I is the ionic strength in concentration units, here moles/cm^3. For $b\sqrt{I}<<1$, we can expand the logarithm in eqn. (13) in a power series; if we truncate after the first term, we obtain the original Debye-Hückel equation, which holds to molalities $m=0.01$ for water-lithium bromide solutions with deviations in the osmotic coefficient less than 1%. The modified Debye-Hückel equation (eqn. (13)) allows predictions to $m=0.05$. Figure 3 compares the DHE and the modified DHE with experimental data.

Eqns. (12) and (13) contain no adjustable parameters. For methanol-lithium bromide solutions, the validity range of both equations is much smaller due to the smaller dielectric constant of methanol.

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‡Dielectric constant D is not to be confused with D in eqn. (6).

5.3 Pitzer Equation and Its Modification

The Pitzer equation, discussed in /24,25/, describes inter-actions between ions. We use here an empirically modified form of Pitzer's equation for ΔA_{VI}; we use

$$\Delta A_{VI} = nRT \rho \sum_{i=1}^{L} \sum_{j=1}^{L} x_i x_j (B_{ij} + H^3 C_{ij}) \qquad (14)$$

with

$$B_{ij} = \beta_{ij}^{(0)} + \left[\frac{2}{\alpha^2 I} \left(1 - e^{-\alpha\sqrt{I}} (1 + \alpha\sqrt{I}) \right) \right] \beta_{ij}^{(1)}$$

$$H = \frac{1}{2} \rho \sum_{i=1}^{L} x_i |z_i| \; ; \qquad \alpha = 2 \cdot \sqrt{1000} \; \left[\left(\frac{cm^3}{mole} \right)^{0.5} \right]$$

In his original equation, Pitzer uses molalities rather than mole fractions and the exponent on H is unity, not 3. Parameters $\beta_{ij}^{(0)}$, $\beta_{ij}^{(1)}$, and C_{ij} are adjustable. They are zero for solvent-ion interactions and when i and j are ions of the same species. For a binary electrolyte solution, there are three adjustable binary parameters; they account for interactions between Li^+ and Br^- ions due to the permanent electric charge. In our work we consider these parameters to be independent of temperature.

6. Evaluation of Parameters

For solutions containing ions, it is necessary to specify parameters σ_{ij} and ε_{ij} for those interactions where either i or j (or both) is an ion. These parameters are needed for ΔA_{II} and ΔA_{III}. We use eqn. (10) and (11) with $k_{ij}=0$.

The literature gives a variety of distance parameters σ_i for ions. Once σ_i is fixed, we can use Mavroyannis-Stephen dispersion theory /20,21/ to estimate energy parameter ε_i for the ion:

$$\frac{\varepsilon_i}{k} = 2.2789 \cdot 10^{-8} \, \alpha_i^{1.5} \, z_i^{*0.5} \, \frac{1}{\sigma_i^6} \quad [K] \tag{15}$$

Here z_i^* is the number of electrons and α_i denotes polarizability for ion $i^{\ddagger}$. As the ionic diameter influences the energy parameter with the sixth power, a small variation in σ changes ε drastically. Figure 4 shows possible values for σ and ε for the Li^+ and Br^- ions. Table 3 gives literature data for diameters and Table 4 gives polarizabilities for ions.

As binary parameters $\beta_{ij}^{(0)}$, $\beta_{ij}^{(1)}$, and C_{ij} depend on the solvent, we use a volume-fraction mixing rule to obtain parameters for ion-ion interactions for the ternary system.

$$\beta_M^{(0)} = \frac{x_1 \sigma_1^3}{x_1 \sigma_1^3 + x_2 \sigma_2^3} \, \beta_1^{(0)} + \frac{x_2 \sigma_2^3}{x_1 \sigma_1^3 + x_2 \sigma_2^3} \, \beta_2^{(0)} \tag{16}$$

Parameter $\beta_M^{(0)}$ stands for parameter $\beta^{(0)}$ for Li^+ and Br^- interactions in a mixed solvent of methanol(1) and water(2). $\beta_1^{(0)}$ denotes parameter $\beta^{(0)}$ in methanol(1) while $\beta_2^{(0)}$ denotes the same parameter in water(2). The same mixing rule applies to parameters $\beta^{(1)}$ and C.

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‡Polarizability α is not to be confused with α in eqn. (14)

7. Results and Discussion

Ionic diameters for Li^+ and for Br^- are optimized using binary and ternary data. With these optimum values, vapor pressures of the ternary system are fitted with mean deviations under 6%, and vapor-phase mole fractions with mean deviations $\Delta y = 0.015$. Table 5 gives the optimum ionic diameters and energy parameters for the ions and Table 6 shows the optimum binary parameters. Table 7 gives literature sources for thermophysical properties of lithium-bromide solutions in methanol and water.

The Pitzer equation with $C_{ij}=0$ gives deviations in osmotic coefficient of less than 2% for salt concentrations to 7 mole% for both binary salt solutions. Including the additional empirical term, we obtain good agreement to salt concentrations of 22 mole% for a constant temperature, as shown in Figure 5. As we included no temperature dependence in the binary parameters, the valid salt-concentration range of eqn. (14) is smaller if we cover the entire temperature range from -10 to 120°C.

Figure 6 shows the influence of the salt on vapor-phase composition. With increasing salt concentration, the vapor-phase mole fraction of methanol increases. This increase is consistent with the usual observation that the solvent with the lower dielectric constant is salted out. Table 8 shows experimental and calculated vapor pressures and vapor compositions for the ternary solution.

Using eqn. (4), pressure P is related to the reduced molar residual Helmholtz energy $\tilde{A}$ by

$$P = \rho RT \left[1 + \rho \sum_{t=II}^{VI} \left(\frac{\partial \tilde{A}_t}{\partial \rho} \right)_{T,x_i} \right] = P_{ideal} + \sum_{t=II}^{VI} P_t \qquad (17)$$

$$\text{with} \quad \tilde{A} = \frac{A^r}{nRT} \quad ,$$

where the summation includes contributions II to VI to the Helmholtz energy.

The derivatives of these terms with respect to density give very large positive and negative contributions to the pressure, as shown in Figure 7. These large contributions combine to give a relatively small total pressure. When adding and subtracting large numbers, small errors in any one of these numbers may produce a large error in the final result. Unfortunately, this disadvantage is unavoidable when using an equation of state. It is therefore necessary to exercise care when writing a computer program to calculate vapor-liquid equilibria.

Vapor-liquid equilibria are calculated using the relations

$$\phi_i^V y_i = \phi_i^L x_i \qquad \text{for every } i$$

$$T^V = T^L$$

$$P^V = P^L$$

Fugacity coefficients are obtained from eqn. (3) and the pressure is obtained from eqn. (4). We extended computer programs prepared by Topliss /30/ to apply to electrolyte solutions. While it is common to assume that there are no ions in the vapor phase (and this is a good assumption for all of the conditions considered in this work), the thermodynamic framework developed here is sufficiently general to permit calculations where ions are present in both phases.

Table 2 suggests that the proposed model represents pure-solvent properties reasonably well. However, for the binary methanol-water system, deviations are significant at low temperatures and at methanol concentrations smaller than 15 mole%, where non-idealities are largest. Using only one binary parameter k_{12}, the proposed model does not give satisfactory results in this region.

Liquid-density data have a large influence on fitting pure-

component parameters. A good representation of the density is important because at high densities, the density strongly influences the dielectric constant and its derivatives, which are used in the Born expression and in the Debye-Hückel equation. Calculated liquid densities for methanol-water mixtures (which were not included in fitting binary parameter k_{12}) show mean deviations of 1.8% with maximum deviations of 4.5% in the dilute-methanol region.

Methanol/lithium-bromide and water/lithium-bromide solutions are fairly well represented in this model to 22 mole% salt when T=298K. Using temperature independent parameters ($\beta^{(0)}$, $\beta^{(1)}$ and C) in the modified Pitzer equation, good representation is obtained to 15 mole% for the entire temperature range. These results might be improved and perhaps extended to higher salt concentrations upon introducing temperature-dependent parameters in eqn. (14).

Vapor pressures and vapor-phase mole fractions of the ternary solution are well represented, if we consider the simplicity of the model and the uncertainties of the ionic parameters. For the ternary system, largest deviations in P, y_i, and ρ occur at low methanol concentrations and at low temperatures. Therefore, it is likely that an improvement in describing the ternary solution may be achieved from a better model for the solvent mixture.

8. Conclusions

A model has been established for calculating equilibrium properties of an electrolyte solution with mixed solvents. An equation is presented for the Helmholtz energy as a function of temperature, volume and mole numbers. Phase equilibria of binary electrolyte solutions are well represented by this model for salt concentrations to 15 mole% in the temperature range -10 to 120°C. Using only binary parameters, results for the ternary system methanol-water-lithium bromide are fairly good; they might be im-

proved if a better representation of the methanol-water mixture can be achieved.

Acknowledgements

APPENDIX I

Brief Description of the Calculation of the Dielectric Constant
of a Mixture as a Function of Temperature, Density and
Composition

Harvey /11/ estimates the static dielectric constant of a
fluid mixture by a linear volume-fraction mixing rule in which
pure components are mixed isothermally at constant reduced densi-
ty. The mixing rule is written for p_m, the polarization per unit
volume of the mixture:

$$p_m = \sum_{i=1}^{L} \phi_i^{\ddagger} \, p_i^{\ddagger} \qquad (A-1)$$

where $\phi_i^{\ddagger}$ is a volume fraction based on molecular diameters σ:

$$\phi_i^{\ddagger} = \frac{x_i \, \sigma_i^3}{\sum\limits_{j=1}^{L} x_j \, \sigma_j^3} \qquad (A-2)$$

and where $p_i^{\ddagger}$ is the polarization per unit volume of pure compo-
nent i at temperature T and at density $\rho_i^{\ddagger}$ which corresponds to
the reduced density of the mixture. Kirkwood's theory /15/ re-
lates the polarization to the dielectric constant D:

$$p = \frac{(D - 1)(2D + 1)}{9 \, D} \qquad (A-3)$$

Eqn. (A-3) applies to both the mixture polarization p_m and
to the pure-component polarization $p_i^{\ddagger}$. The pure-component values
of $p_i^{\ddagger}$ are calculated depending on the nature of species i. For
nonpolar molecules or ions, we calculate the polarization from
Kirkwood's theory:

$$p_i^{\ddagger} = \rho_i^{\ddagger} \frac{4\pi \ N_{Av} \alpha_i}{3} \qquad\qquad (A-4)$$

where α_i is the polarizability of component i. For water, we use
the equation of Uematsu and Franck /31/ which applies to a wide
range of temperatures and to densities from zero to liquid-like
densities. For other polar or associating fluids, we use the
known functionality for water (as given by Uematsu and Franck) to
extend existing dielectric-constant data to the desired tempera-
ture and density for use in eqn. (A-1). The use of water as a
model fluid permits calculations at temperatures and/or densities
for which no dielectric-constant data exist.

In this work, we simplify Harvey's procedure by averaging
the dielectric constants instead of the polarizations. Eqn. (A-1)
is then replaced by:

$$D = \sum_{i=1}^{L} \phi_i^{\ddagger} D_i^{\ddagger} \qquad\qquad (A-5)$$

The two averaging processes are nearly equivalent, particu-
larly for systems with large dielectric constants such as those
for methanol-water mixtures.

Because of the analytic form of the equation of Kirkwood and
that of Uematsu and Franck, eqn. (A-5) can be differentiated with
respect to density or composition to provide the derivatives re-
quired by the equation of state.

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Table 8: Comparison of Experimental and Calculated Pressures and Vapor-phase Mole Fractions for Methanol(1)-Water(2)-Lithium Bromide(s) Solutions

Table 1: Pure-component Parameters for Methanol and for Water		
Parameter	Methanol(1)	Water(2)
$\sigma_i \quad \times 10^{-8} [cm]$	3.9591	3.0787
$\epsilon_i^{(0)} \times 10^4 \ [K]$	-4.4029	-9.4464
$\epsilon_i^{(1)} \times 10^5 \ [K]$	1.6135	5.0803
$\epsilon_i^{(2)} \times 10^2$	3.0983	8.6378
$T_{ci} \quad \times 10^2 \ [K]$	5.126	6.473

Table 2: Mean Deviations for Pure-component Properties					
Component	Temp. Range [°C]	Pressure range [Bar]	Deviation in		
			P [%]	ρ_{Liquid} [%]	ρ_{Vapor} [%]
Methanol	-10 to 100	0.021-3.455	0.9	0.8	3.0
Water	0 to 140	0.006-3.518	1.8	1.7	0.8

Table 3: Literature Data for Ionic Diameters of Li^+ and Br^- Ions

Author	σ [$\cdot 10^{-8}$cm]	
	Li^+	Br^-
Goldschmidt in /19/	1.56	3.92
Pauling in /19/	1.2	3.9
Gourary in /19/	1.88	3.6
Marcus /19/	1.36	3.88
Rashin* /27/	2.632	4.174
* only used in Born expression		

Table 4: Literature Data for Polarizabilities of Li^+ and Br^- Ions

Author	α [$\cdot 10^{-25}$cm^3]	
	Li^+	Br^-
Fajans et al in /17/	0.8	49.7
Pauling in /17/	0.313	47.7
Mayer in /17/	0.25	41.7

Table 5: Optimum Ionic Diameters and Energy Parameters

Parameters	Li^+	Br^-
$\sigma_i \times 10^{-8}$[cm]	1.35	3.75
ε_i/k [K]	140.	480.

Table 6: Optimum Binary Parameters

Parameters	LiBr in methanol	LiBr in water
$\beta^{(0)}$ ×10³	0.66840	0.43129
$\beta^{(1)}$ ×10⁴	-0.16618	-0.56624
C ×10⁸	12.0210	-0.78599

Table 7: Literature Sources for Thermophysical Properties of Lithium Bromide Solutions in Methanol and Water

Author		Methanol – LiBr	Water – LiBr
Renz	/28/	-10° to 120°C; $0.09 < x_s < 0.3$	20° to 140°C; $0.065 < x_s < 0.35$
Eichholz	/9/	20° to 100°C; $0.008 < x_s < 0.085$	-----
Skabichevski	/29/	20°,25°,30°C; $0.05 < x_s < 0.14$	-----
Hamer/Wu	/12/	-----	25°C; $0 < x_s < 0.265$

x_s = salt concentration (undissociated)

Table 8: Comparison of Experimental and Calculated Pressures and Vapor-phase Mole Fractions for Methanol(1)-Water(2)-Lithium Bromide(s) Solutions

T [K]	x_1	x_2	x_s	P_{ex} [bar]	P_{calc} [bar]	$\Delta P/p$ [%]	y_1	y_{calc}	Δy
293.15	0.3824	0.6047	0.0129	0.076	0.074	-2.6	0.8037	0.7917	0.0121
333.14	0.3713	0.6148	0.0139	0.528	0.516	-2.4	0.7530	0.7411	0.0119
378.86	0.4640	0.3953	0.1407	1.433	1.494	4.3	0.8400	0.8325	0.0075
331.00	0.7047	0.1725	0.1228	0.401	0.370	-7.7	0.9268	0.9429	0.0161
362.98	0.7444	0.1234	0.1322	1.322	1.299	-1.7	0.9552	0.9520	0.0032
349.84	0.7723	0.1094	0.1183	0.925	0.928	-1.3	0.9446	0.9617	-0.0171
300.61	0.7344	0.1408	0.1248	0.085	0.085	-0.3	0.9550	0.9608	-0.0058
344.04	0.1230	0.7977	0.0793	0.535	0.510	-4.7	0.5929	0.6259	-0.0330
315.86	0.1313	0.7904	0.0783	0.137	0.144	5.6	0.5780	0.6552	-0.0700
351.77	0.2396	0.7275	0.0329	0.938	0.940	0.3	0.6532	0.6591	-0.0050

Nomenclature:

A	Helmholtz energy
B	defined in eqn. (14)
C	adjustable binary parameter
D,E,F	defined in eqn. (6)
D	dielectric constant
H	defined in eqn. (14)
I	ionic strength
K^*, K^{**}	distance ratio
L	number of components
N_{Av}	Avogadro number
P	pressure
R	gas constant
T	temperature
V	total volume
Z	compressibility factor
a	molar Helmholtz energy
b	constant
e	unit charge
k	Boltzmann constant
k_{ij}	adjustable binary parameter
m	molality
n	total number of moles
n_i	number of moles of component i
p	polarization
r	distance
x	mole fraction in liquid phase
y	mole fraction in vapor phase
z	charge number
z^*	number of electrons of ion

Greek Letters:

α	constant
α_i	polarizability of component i
β	adjustable binary parameter
ϵ	energy parameter
ϕ	fugacity coefficient
κ	defined in Figure 6
ρ	molar density
σ	hard-sphere diameter
σ^*	corrected diameter of ions used in eqn. (12)
ξ	reduced density
ϕ	volume fraction
Γ	potential function
Ω	osmotic coefficient

Superscripts:

r	residual
°	standard state
~	reduced molar residual Helmholtz energy
‡	evaluated at a density corresponding to the reduced density of the mixture (Appendix)

Subscripts:

i,j	component i (or j)
ji	molecule j around central molecule i
m	mean
s	salt (undissociated)
t	index in eqn. (17)
I...VI	contributions to A^r and P

$a = r_{ii}^{**}$

$b = r_{ii}^{*}$

$c = r_{ji}^{**}$

$d = r_{ji}^{*}$
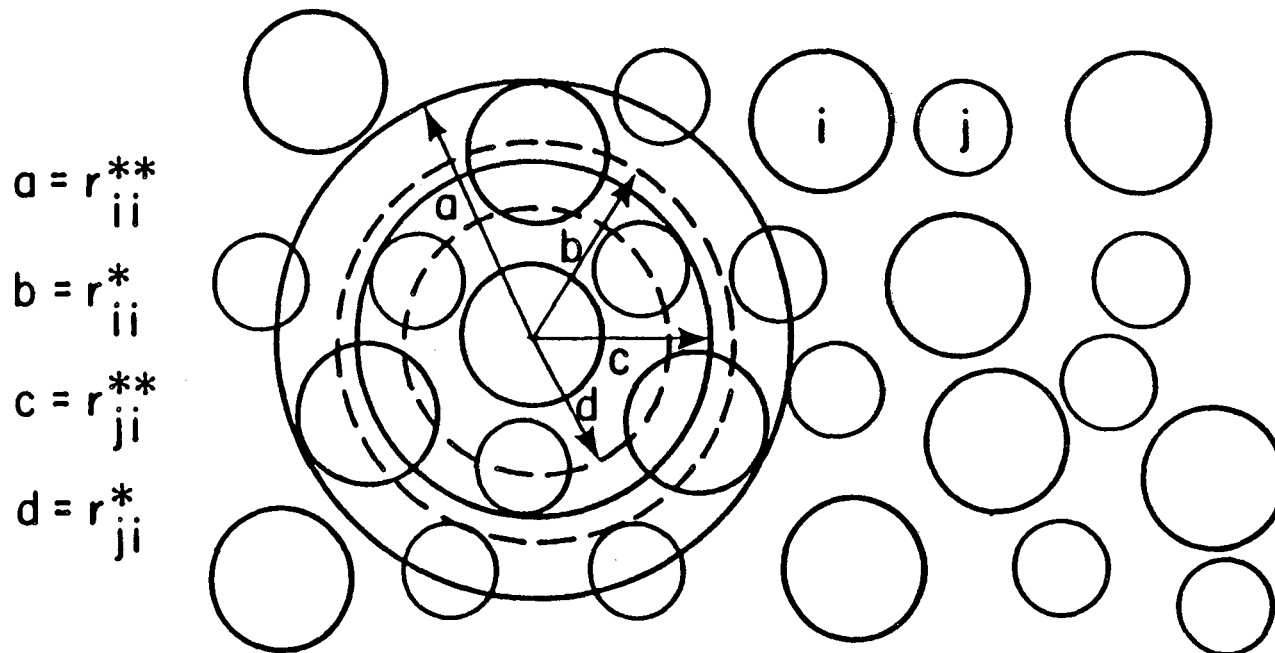
FIRST COORDINATION SHELL AROUND CENTRAL
MOLECULE i AND RANDOM ENVIRONMENT
OUTSIDE COORDINATION SHELL

FIGURE 1

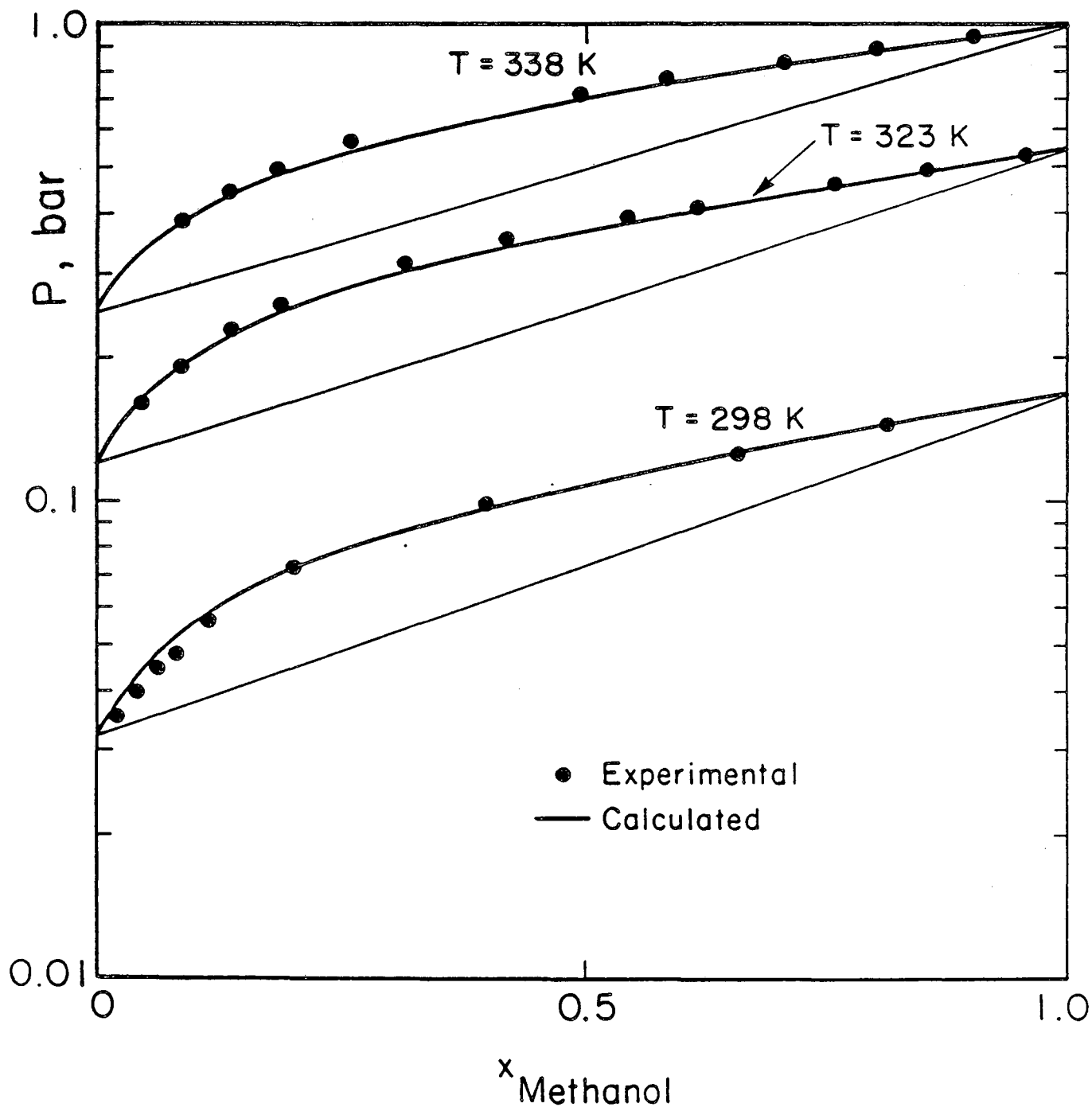# EXPERIMENTAL AND CALCULATED VAPOR PRESSURES OF METHANOL-WATER MIXTURES AT THREE TEMPERATURES

FIGURE 2

EXPERIMENTAL AND CALCULATED OSMOTIC COEFFICIENT
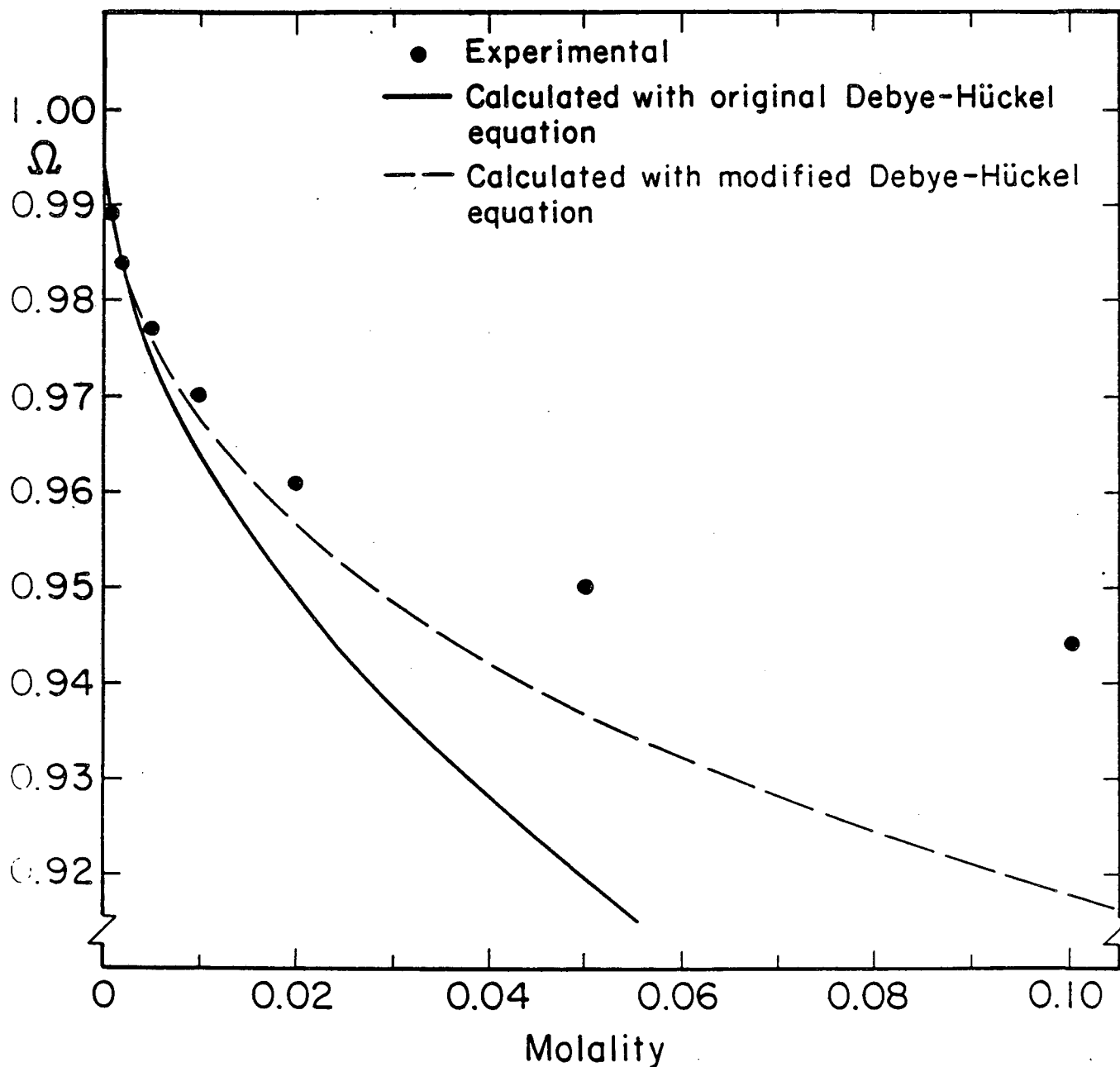## Ω FOR VERY DILUTE H_2O-LiBr SOLUTIONS AT 298 K

FIGURE 3

RANGE OF IONIC DIAMETER σ AND ENERGY PARAMETER
ϵ/k FOR Li^+, Br^- IONS ACCORDING TO LITERATURE DATA
(GIVEN IN TABLES 3 AND 4). ϵ/k VALUES CALCULATED
BY MAVROYANNIS/STEPHEN DISPERSION THEORY
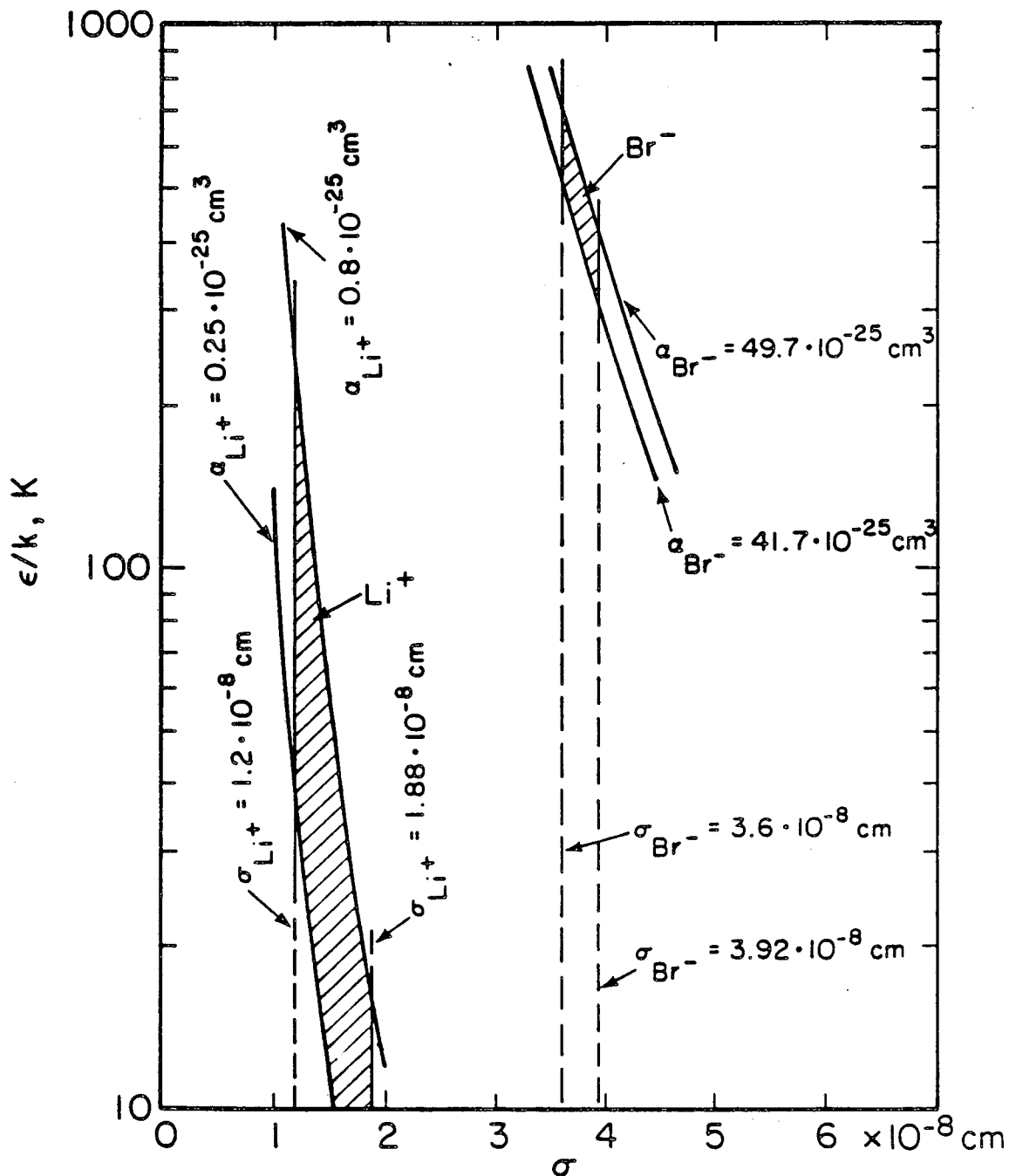
FIGURE 4

EXPERIMENTAL AND CALCULATED OSMOTIC COEFFICIENT Ω FOR H_2O-LiBr SOLUTIONS AT 298 K
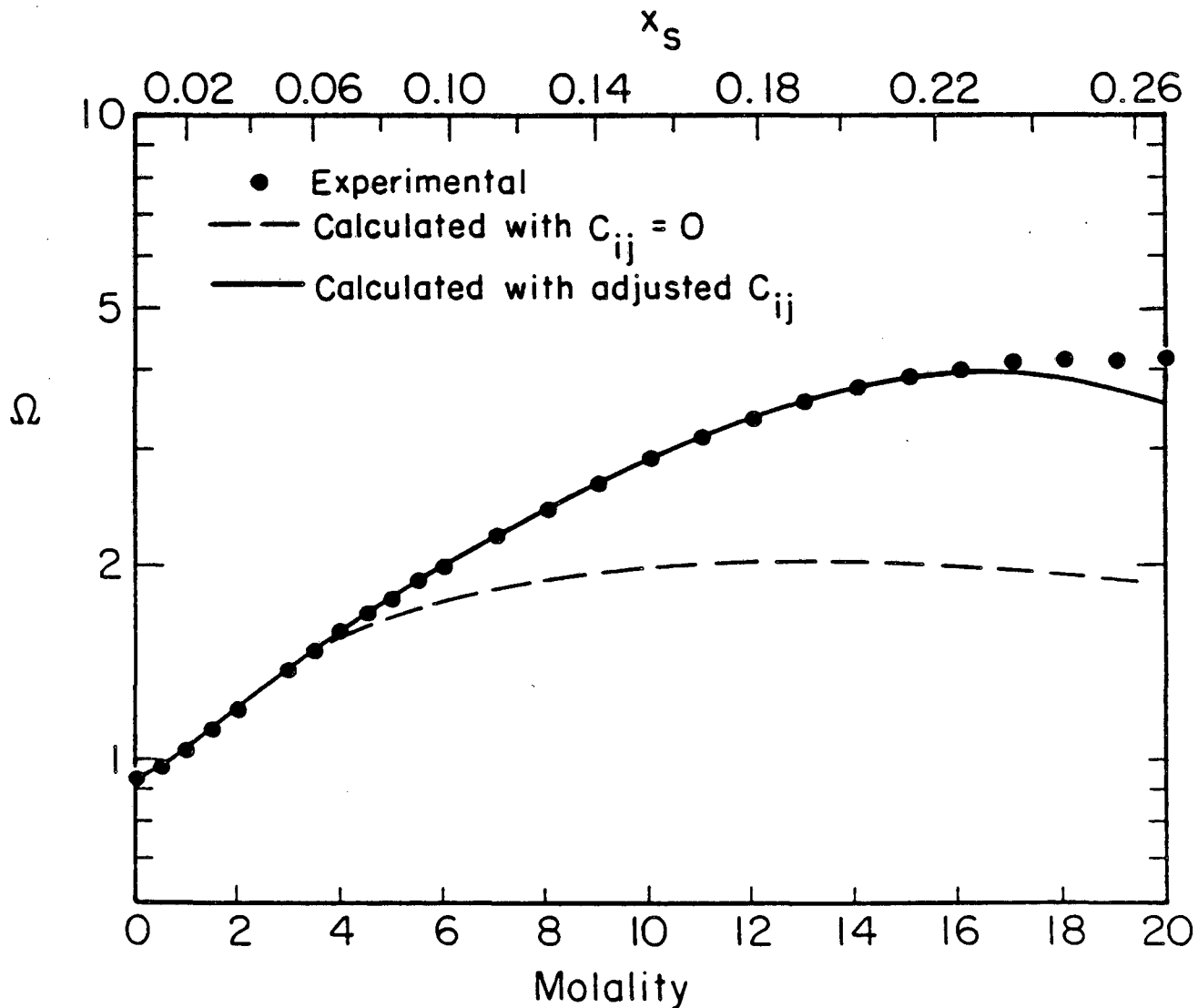
FIGURE 5

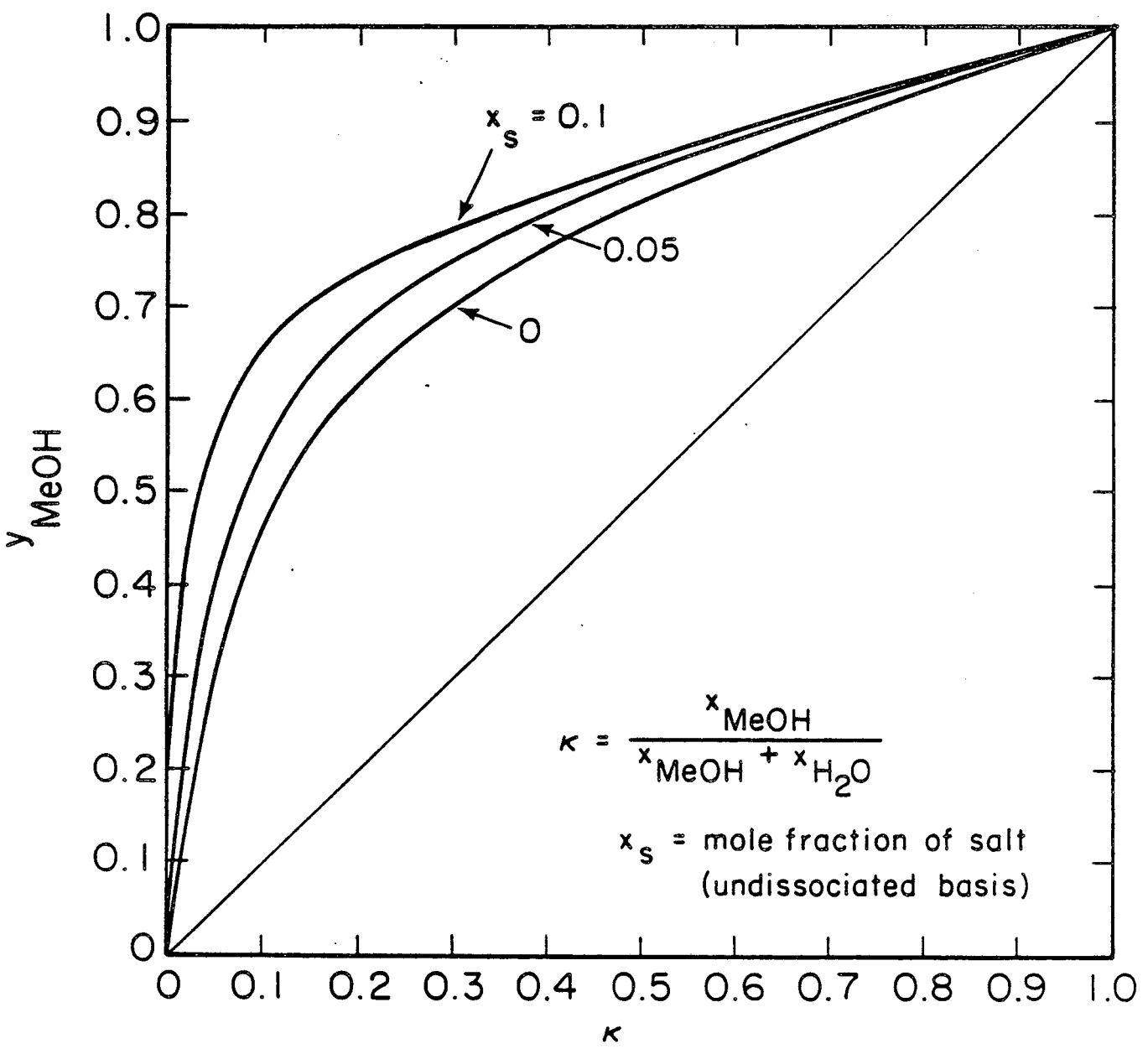# VAPOR-PHASE COMPOSITIONS FOR CH$_3$OH-H$_2$O-LiBr SOLUTIONS AT 313 K

$$\kappa = \frac{x_{MeOH}}{x_{MeOH} + x_{H_2O}}$$

x_s = mole fraction of salt
(undissociated basis)

FIGURE 6

CONTRIBUTIONS TO THE CALCULATED TOTAL
PRESSURE AT 323.15 K

$$P_{calc} = P_{ideal} + P_{II} + P_{III} + P_{IV} + P_{V} + P_{VI}$$

$P_{expt} = 0.301$ bar; $P_{calc} = 0.286$ bar

$x_{MeOH} = 0.3486$; $x_{H_2O} = 0.5098$;

$x_{Li^+} = x_{Br^-} = 0.0708$

☐ Positive Contribution

▨ Negative Contribution

P, bar

$P_{ideal} = 1029.328$

$P_{II} = 10533.415$

$P_{III} = -11435.005$

$P_{IV} = -704.447$

$P_{V} = 377.752$

$P_{VI} = 199.243$

FIGURE 7