Thermodynamics of High-Pressure Aqueous Systems Containing Gases and Salts

This work provides a new method for calculating phase equilibria for systems where conventional activity-coefficient models are not suitable. A procedure is presented for superimposing ionic effects on a conventional equation of state for nonelectrolytes. A modification of Born's equation is used to describe charging the ions; ion-ion interactions are described with the Mean Spherical Approximation, coupled with an adjustable salt/solvent parameter that is obtained from osmotic-coefficient data at room temperature. The equation of state is used to predict gas solubilities in aqueous salt solutions at high pressures. While this method produces qualitative agreement with the experimental solubility data, quantitative agreement requires a salt/gas parameter obtained from Setchenow-constant data. When Setchenow constants are used, agreement with experiment is good except at high salt concentrations, where salting-out is usually underpredicted. Good results are obtained for phase equilibria in a natural-gas/brine system at high pressures.

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Introduction

Dissolved salts have an important effect on phase equilibria in a variety of chemical and geological processes. For many of these systems, phase equilibria can be described adequately using an activity-coefficient model for the liquid phase and a separate model (often an ideal gas) for the vapor phase. Useful activity-coefficient models for strong electrolytes include those of Meissner and coworker (1972, 1980), Bromley (1973), Pitzer (1973, 1979, 1987), Cruz and Renon (1978), Chen et al. (1982, 1986), and Haghtalab and Vera (1988); a review is given by Zemaitis et al. (1986).

A molecular-thermodynamic description becomes more difficult when the solvent is not water alone. [The volumes edited by Furter (1976, 1979) discuss salt effects at low pressures in many aqueous mixed-solvent systems.] While some activity-coefficient models have been extended to mixed solvents (Mock et al., 1986; Sander et al., 1986), their success has been limited. This limitation may be due, in part, to an inconsistency when electrostatic terms are improperly superimposed on conventional excess-Gibbs-energy models, as pointed out by Cardoso and O'Connell (1987).

Even greater difficulty arises for systems containing supercritical components at high pressures. One important example of such a system is provided by geopressurized aquifers where deposits of natural gas are in equilibrium with brine at high pressures and temperatures. Activity-coefficient models are not suitable for systems containing supercritical components, because it is not posible to select a truly useful standard state for the supercritical components (Prausnitz et al., 1986). Henry's law may be used at low pressures, but not at the high pressures with which we are concerned in this work.

An alternate description of high-pressure phase equilibria is provided by a single equation of state (EOS) to calculate the fugacity of each species in each phase. Such equations of state have been successful for nonelectrolyte systems; the problem for salt-containing systems is to superimpose properly the electrostatic effects on an EOS for nonelectrolytes.

Efforts along these lines were reported by Raatschen et al. (1987) and Copeman and Stein (1987). Raatschen's work was concerned with the mixed-solvent problem; while good results were obtained for the system water/methanol/lithium bromide, some of the expressions for the ionic effects were not in a form suitable for extension to systems containing supercritical gases. Copeman and Stein used the Mean Spherical Approximation (MSA) to describe ion-ion interactions; while they reported results for the activity coefficients of several salts at 25°C and for two mixed-solvent systems, discussion was limited to pressures near atmospheric. Recently Jin and Donohue (1988) have extended the Perturbed-Anisotropic-Chain Theory to systems

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containing electrolytes. Although their work is concerned mostly with aqueous salt solutions at room temperature, they also show calculations for two systems with dissolved gases, one at high pressures. The work of Ball et al. (1985) is also relevant: a model was developed mainly for electrolytes [the nonprimitive MSA model of Planche and Renon (1981)] and then adapted into an equation-of-state form suitable for vapor-liquid equilibrium calculations. However, the only calculations reported were for osmotic coefficients of salts in water at 25°C.

This work differs in emphasis from earlier studies: we focus primarily on high-pressure vapor-liquid equilibria for aqueous systems containing supercritical gases as well as salts. In practice, these are the electrolyte systems for which an equation of state is useful; we do not, therefore, devote significant attention to the low-pressure, single-solvent systems for which existing activity-coefficient models are satisfactory.

The aim of this work is to provide a framework in which easily available data (e.g., binary vapor-liquid equilibria for nonelectrolytes and osmotic coefficients for single salts in water at 25°C) can be used to predict vapor-liquid equilibria in salt-containing systems at high pressures. Since our emphasis is on correctly describing the ionic effects, we choose a relatively simple model for interactions between uncharged species. However, since our method for incorporating the effects of charged species is general, it can be adapted for use with any molecular-based equation of state.

Theoretical Framework: Helmholtz Energy

The EOS is obtained readily upon differentiating the Helmholtz energy with respect to density:

$$\frac{P}{\rho RT} = 1 + \rho\left(\frac{\partial \tilde{A}}{\partial \rho}\right)_{T,\underline{x}} \tag{1}$$

Here P is the pressure, ρ is the molar density, R is the gas constant, T is the absolute temperature, and the differentiation is performed at constant temperature and composition. $\tilde{A}$ is the reduced residual Helmholtz energy:

$$\tilde{A} = A^r/nRT \tag{2}$$

where n is the total number of moles and the residual Helmholtz energy A^r is defined relative to a mixture of uncharged ideal gases at the same temperature, density, and composition. Efficient computation of phase equilibria from the quantity $\tilde{A}$ is described by Topliss (1985); extensions of these computational procedures to electrolyte systems are described by Harvey (1988).

We divide the residual Helmholtz energy into three parts:

$$\tilde{A} = \tilde{A}^I + \Delta\tilde{A}^{II} + \Delta\tilde{A}^{III} \tag{3}$$

$\tilde{A}^I$ is the "nonelectrolyte" contribution, i.e., that arising from all intermolecular forces other than those due to the permanent electric charges on ions; it can be calculated with any equation of state suitable for nonelectrolytes. $\Delta\tilde{A}^{II}$ is the contribution to the Helmholtz energy from charging the ions and $\Delta\tilde{A}^{III}$ accounts for charge-charge interactions.

Except for interactions arising from permanent electric charges, we describe intermolecular forces with a relatively simple model: the intermolecular potential for all species (ions included) is given by the Lennard-Jones potential

$$u_{ii}(r) = 4\epsilon_{ii}\left[\left(\frac{\sigma_{ii}}{r}\right)^{12} - \left(\frac{\sigma_{ii}}{r}\right)^{6}\right] \tag{4}$$

where $u_{ii}(r)$ is the potential energy between two molecules of species i at distance r and where ϵ_{ii} and σ_{ii} are characteristic molecular energy and size parameters, respectively. For polar or nonspherical fluids ϵ_{ii} is temperature-dependent according to:

$$\epsilon_{ii}(T)/k = \epsilon_{ii}^{(0)} + \epsilon_{ii}^{(1)} \exp\left(\epsilon_{ii}^{(2)} \frac{T}{T_{c,i}}\right) \tag{5}$$

where k is Boltzmann's constant and $T_{c,i}$ is the critical temperature of component i.

$\tilde{A}^I$ for the mixture of Lennard-Jones molecules is computed using the Barker-Henderson form (Barker and Henderson, 1967; Leonard et al., 1970) of thermodynamic perturbation theory. Details are presented in Appendix I. Adjustable binary parameters k_{ij} and k_{ji} are introduced in the combining rule for the attractive-energy parameter ϵ_{ij} for the interaction between unlike molecules:

$$\epsilon_{ij} = (\epsilon_{ii}\epsilon_{jj})^{1/2}\left[1 - k_{ij} + (k_{ij} - k_{ji})\frac{x_i}{x_i + x_j}\right] \tag{6}$$

This results in a cubic mixing rule similar to that of Panagiotopoulos and Reid (1986). For many mixtures it is adequate to set $k_{ij} = k_{ji}$; in that case, the correction to the geometric-mean combining rule becomes the familiar $(1 - k_{ij})$. However, the extra flexibility of the two-parameter mixing rule is required to fit highly asymmetric binary mixtures of water and nonpolar gases. If necessary, k_{ij} can be made temperature-dependent according to

$$k_{ij} = k_{ij}^{(1)} + k_{ij}^{(2)}/T \tag{7}$$

For gas/water binaries it was found that it was sufficient to make only $k_{\text{gas-water}}$ temperature-dependent.

For uncharged species, $\epsilon_{ii}(T)$ and σ_{ii} are obtained from experimental pure-component data for vapor pressures, saturated-vapor and saturated-liquid densities, and densities in the one-phase region. Values for the binary parameters k_{ij} and, if necessary, k_{ji} are fitted to binary vapor-liquid equilibrium data. Appendix II presents fitted parameters for several pure components and binary systems.

Ion-Charging Contribution

The reversible work required to charge an ion in solution was first calculated by Born (1920), who modeled the ions as charged hard spheres in a continuum of uniform dielectric constant. We use this "primitive model" approximation with a slight modification as suggested by Rashin and Honig (1985): the ions are considered to be charged hard spheres centered in a cavity inside a dielectric continuum, resulting in the following expression for $\Delta\tilde{A}^{II}$:

$$\Delta\tilde{A}^{II} = \frac{N_A e^2}{RT}\sum_i x_i z_i^2\left(\frac{1}{D\sigma_{c,i}} + \frac{1}{\sigma_{ii}} - \frac{1}{\sigma_{c,i}}\right) \tag{8}$$

where N_A is Avogadro's number, e is the unit electronic charge, z_i is the charge on ion i, D is the static dielectric constant, and $\sigma_{c,i}$ is the diameter of the cavity for ion i. For anions, following Rashin and Honig, we take $\sigma_{c,i} = \sigma_{ii}$ which results in Born's original expression. For cations, however, we have $\sigma_{c,i} > \sigma_{ii}$ which accounts for the larger cavity formed by cations in aqueous solution. One could argue that $\sigma_{c,i}$ might be different in the vapor phase; however, the effect of such a difference is negligible unless there is a significant concentration of ions in the vapor and the vapor-phase dielectric constant is not near unity.

The second and third terms in parentheses in Eq. 8 do not affect phase equilibria because they are the same in both phases. The first term has a large effect on the ions because the dielectric constant D is typically much higher in the liquid phase; it is this effect which keeps the ions in the liquid under most conditions. In some previous work (Copeman and Stein, 1987; Jin and Donohue, 1988), $\Delta\tilde{A}^{II}$ has been omitted and the ions have simply been constrained to the liquid phase. This produces essentially the same effect for the ions as Eq. 8, but $\Delta\tilde{A}^{II}$ also produces an effect on the fugacities of the uncharged species through the composition dependence of the dielectric constant D. This effect was the basis of the earliest theory for the salting-out of gases (Debye and McAulay, 1925). We find that this effect on the fugacities of the uncharged species is small (in comparison to the hydration effect discussed below), but not negligible.

Charge-Charge Interactions

We use the primitive model to describe also charge-charge interactions. No exact solution is known for the thermodynamic properties of this model, but reasonable results are obtained from the Mean Spherical Approximation (MSA), which has been solved for mixtures of ions with arbitrary sizes and charges (Blum, 1980). However, Blum's solution is too unwieldy for efficient use in iterative equation-of-state calculations. We therefore use an approximation: the mixture of ions is replaced by one in which all ions have a single effective diameter σ_{mix} given by

$$\sigma_{\text{mix}} = \frac{\sum_{\text{ions}} x_i \sigma_{ii}}{\sum_{\text{ions}} x_i} \tag{9}$$

where the sums are taken only over ionic species. This approximation has been tested (Harvey et al., 1988) and found to give accurate thermodynamic properties for ion-size ratios characteristic of most salts, including those considered in this work. The resulting expression for $\Delta\tilde{A}^{III}$ is

$$\Delta\tilde{A}^{III} = -\frac{(2\Gamma)^3(1 + 1.5\sigma_{\text{mix}}\Gamma)}{12\pi N_A \rho} \tag{10}$$

where Γ is the MSA screening parameter; it is given by

$$\Gamma = \frac{1}{2\sigma_{\text{mix}}}\left[(1 + 2\sigma_{\text{mix}}\kappa)^{1/2} - 1\right] \tag{11}$$

$$\kappa^2 = \frac{4\pi e^2 N_A \rho}{DkT}\sum_i x_i z_i^2 \tag{11a}$$

Here κ is the familiar inverse Debye length; the MSA reduces to the Debye-Hückel expression in the limit $\rho\sigma_{\text{mix}}^3 \rightarrow 0$.

Dielectric Constant

Both $\Delta\tilde{A}^{II}$ and $\Delta\tilde{A}^{III}$ require the static dielectric constant D of the fluid mixture; D must be calculated as a function of temperature, density and composition. For this calculation, a systematic procedure has been given elsewhere (Harvey and Prausnitz, 1987). The only information required is a size parameter for each species (σ_{ii}^3 is used as the size parameter for species i in our EOS calculations) and the polarizability of each nonpolar component. The dielectric constant for water is given by the equation of Uematsu and Franck (1980) over a wide range of temperature and density. For polar substances other than water, water is used as a model fluid in a corresponding-states formulation to extrapolate whatever dielectric-constant data are available to the required temperature and density. The final result is an analytic form for the dielectric constant and, as required for EOS calculations, its derivatives with respect to density and composition.

Parameters for Ions

For ions, estimates are required for Lennard-Jones parameters σ_{ii} and ϵ_{ii} because there are no pure-component data to fit them. In addition to these parameters, we require the cavity diameter $\sigma_{c,i}$ for the modified Born expression and also the polarizability α_i for estimating the dielectric constant and, as explained below, for estimating ϵ_{ii}.

Ion diameters σ_{ii} are taken from crystal radii given in *Lange's Handbook* (1985). As suggested by Rashin and Honig (1985), cavity diameters for cations are taken from values for covalent radii in *Lange's Handbook*. Ion polarizabilities α_i are taken from Coker (1976). Lennard-Jones energy parameters ϵ_{ii} are calculated using the dispersion theory of Mavroyannis and Stephen (1962) as adapted by Shoor and Gubbins (1969):

$$\epsilon_{ii}/k = 2.2789 \times 10^{-8}\alpha_i^{1.5} Z_i^{1/2} \sigma_{ii}^{-6} \tag{12}$$

where Z_i is the number of electrons on the ion. The numerical constant in Eq. 12 has units of (K · cm$^{1.5}$). Ion parameters are given in Appendix II.

Ion-Water Interactions

It is commonly recognized (see, for example, Stokes, 1972; Pailthorpe et al., 1984) that the primitive model alone is inadequate to describe the thermodynamics of real electrolyte solutions. The main deficiency is the neglect of the discrete nature of the solvent; in the primitive model, specific ion/solvent interactions (i.e., hydration) are not taken into account.

There is as yet no practical molecular theory which can properly describe ionic solvation, particularly when water is the solvent. It may, however, be viewed in an oversimplified manner as coming from an "extra" short-range force between ions and solvent molecules. (The long-range portions of the ion-solvent interactions are, presumably, accounted for in $\Delta\tilde{A}^{II}$.) We therefore approximate this effect by adjusting the attractive energy parameter ϵ_{ij} between solvent and ionic species. Binary parameter $k_{ij}(=k_{ji})$ in combining rule (Eq. 6) is fitted to osmotic-coefficient data for single salts in water at 25°C. Since the effects of the individual ions cannot be separated, we set $k_{\text{cation-water}} = k_{\text{anion-water}}$; there is therefore only one adjustable parameter for a given salt in water. Table 1 shows parameters for several salts obtained from osmotic-coefficient data. For 1:1 salts, data from

Table 1. Binary Water/Salt Parameters Obtained from Osmotic Coefficients at 25°C

Salt	k_{ij}
LiCl	−0.512
LiBr	−0.368
NaCl	−0.268
NaBr	−0.209
KCl	−0.152
KBr	−0.118
$MgCl_2$	−0.406
$CaCl_2$	−0.283

the compilation of Hamer and Wu (1972) were used up to a molality of six or to saturation, whichever came first. For 2:1 salts, data up to 3 molal were taken from the compilation of Goldberg and Nuttall (1978).

Figure 1 compares calculated and observed results for the system $NaCl/H_2O$ at 25°C. The fit of the data is comparable to that of other one-parameter correlations; the same is true for the other salts in Table 1. The goal of this work, however, is not to reproduce these data but to use them to provide the necessary information to calculate high-pressure VLE in aqueous systems containing electrolytes and supercritical gases.

Utilization of Setchenow-Constant Data

For VLE at high pressures in salt-containing systems, calculations based on only a single salt/water parameter from Table 1 (in addition to the normal parameters for the nonelectrolyte binaries) give only qualitative agreement with experiment. The EOS correctly predicts salting out (i.e., a lowering of the solubility of a gas by the addition of a salt), but the magnitude of this effect may be over- or underestimated. This is not surprising because the effect of a salt on gas solubility depends on the gas that is salted out. That effect can be attributed to differences in the direct ion/gas interactions or to the different structural/hydration behavior of different solute gases; we do not have a clear understanding of these phenomena. In any event, the EOS using only ion/water parameters incorrectly predicts approximately the same salting-out effect regardless of the solute gas.

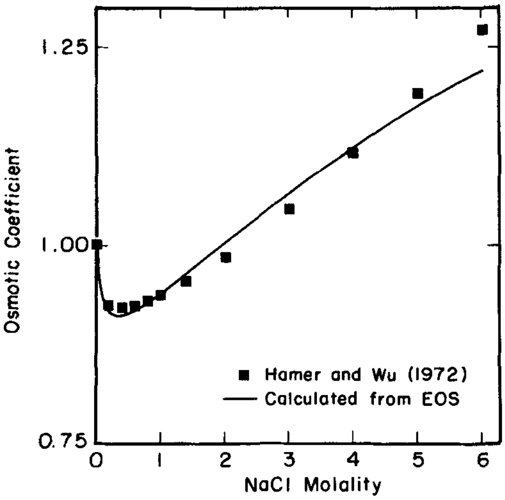

Figure 1. Osmotic coefficient for sodium chloride in water at 25°C.

We correct for this deficiency by introducing an adjustable ion/gas interaction in the same manner as that used for ion/water interactions: we use an adjustable k_{ij} in the combining rule (Eq. 6) for ϵ_{ij} between ions and solute gases. In keeping with our goal of using only easily available data to predict high-pressure VLE, we choose the value of k_{ij} which reproduces the experimental Setchenow constant at room temperature. The Setchenow constant k_s for the salting-out of a solute in aqueous solution is defined by

$$k_s = \lim_{C_s \to 0} \left[C_s^{-1} \log_{10} \frac{\phi^{\infty}_{i,s}}{\phi^{\infty}_{i,w}} \right] \qquad (13)$$

where $\phi^{\infty}_{i,s}$ and $\phi^{\infty}_{i,w}$ are the fugacity coefficients of component i at infinite dilution in the salt solution and in pure water, respectively, and C_s is the salt concentration. C_s is usually expressed in molality units; therefore, k_s has units of (molality^{-1}). Table 2 presents values of k_{ij} obtained from published experimental Setchenow constants at room temperature. A review with a large amount of Setchenow-constant data is given by Long and McDevit (1952); more recent work is reviewed by Zemaitis et al. (1986).

Results

Figure 2 shows calculated and observed results for the salting-out of carbon dioxide by sodium chloride at 150°C and pressures to 1,400 bar; experimental data are from Takenouchi and Kennedy (1965). Only the liquid-phase compositions are shown; none of the data we found on salt-containing systems at high pressures contained vapor compositions. Our relatively simple nonelectrolyte model does a fair job for the CO_2/H_2O binary, although there is some deviation at higher pressures. More importantly, the effect of the salt on gas solubility is predicted very well for the 6 wt.% salt solution and fairly well for the solution with 20 wt.% salt.

Figure 3 shows results for carbon dioxide solubility in calcium chloride solutions at 121°C and pressures to 700 bar; experimental data are from Prutton and Savage (1945). Again, salting out is predicted very well at the lower salt concentration (10.1 wt.%). The salting effect for a 30.2% solution is somewhat underpredicted.

Figures 4 and 5 are for nitrogen and methane, respectively, in sodium chloride solutions at 102.5°C and pressures to 600 bar; data are from O'Sullivan and Smith (1970). In both cases, the effect of a 1-molal salt solution is predicted fairly well, while the effect of the more concentrated (4 m) solution is substantially

Table 2. Binary Gas/Salt Parameters Obtained from Aqueous Setchenow Constants at or near 25°C

Gas	Salt	k_{ij}	Reference for k_s
Nitrogen	NaCl	0.369	Morrison and Billett (1952)
Carbon Dioxide	NaCl	−0.127	Long and McDevit (1952)
Methane	NaCl	0.342	Cramer (1984)
Ethane	NaCl	0.282	Morrison and Billett (1952)
Propane	NaCl	0.244	Morrison and Billett (1952)
n-Butane	NaCl	0.175	Morrison and Billett (1952)
Carbon Dioxide	$CaCl_2$	−0.601	Yasunishi and Yoshida (1979)
Methane	$CaCl_2$	−0.308	Pawlikowski and Prausnitz (1983)*

*Setchenow constant estimated from correlation.

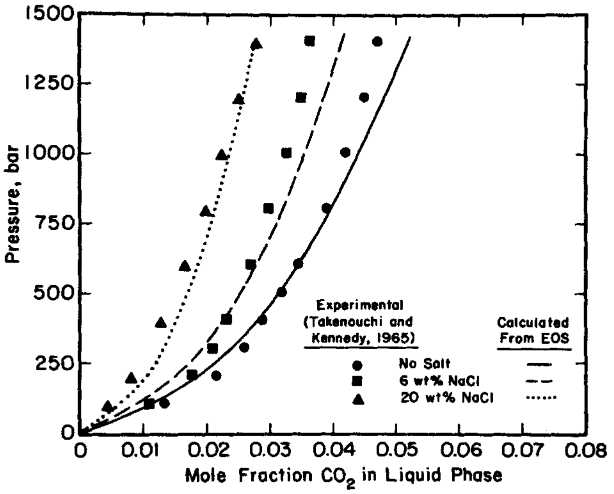

Figure 2. Salting-out of carbon dioxide by sodium chloride at 150°C.

underpredicted. Similar results are obtained for the CH_4/NaCl/H_2O data of Price et al. (1982); Figure 6 shows calculated and observed results at 170°C to pressures above 1,500 bar. Figure 7 shows the salting-out of methane by calcium chloride at 102.5°C; here only one salt concentration was studied experimentally (Blanco and Smith, 1978) and the EOS somewhat underpredicts the salting-out effect.

For engineering applications, a more interesting calculation is shown in Figure 8. Dodson and Standing (1944) measured the solubility of a real natural gas in two oil-field brines at elevated temperatures and pressures. The compositions of the brines and of the dry gas were also reported.

The ion content of the brines was over 95% sodium chloride; for simplicity, the calculations were performed using a concentration of sodium chloride at an ionic strength equal to that of the brine. [Our model, however, is not limited to single salts.] Values of k_{ij} and k_{ji} for gas components with water were obtained from binary experimental data; these binary parameters are given in Appendix II. Due to a lack of binary data, the isobutane fraction in the gas was assumed to be *n*-butane and

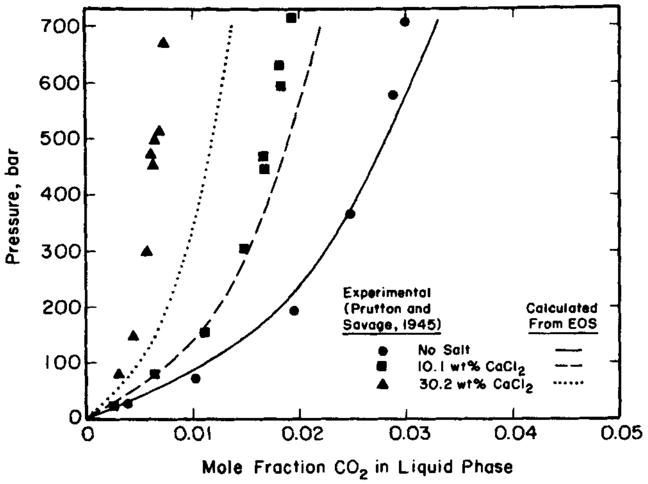

Figure 3. Salting-out of carbon dioxide by calcium chloride at 121°C.

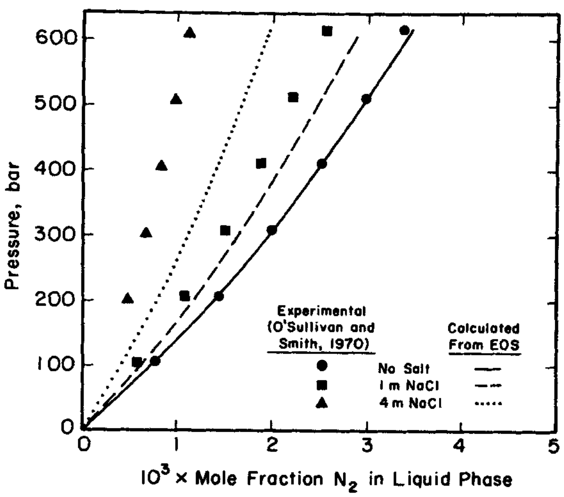

Figure 4. Salting-out of nitrogen by sodium chloride at 102.5°C.

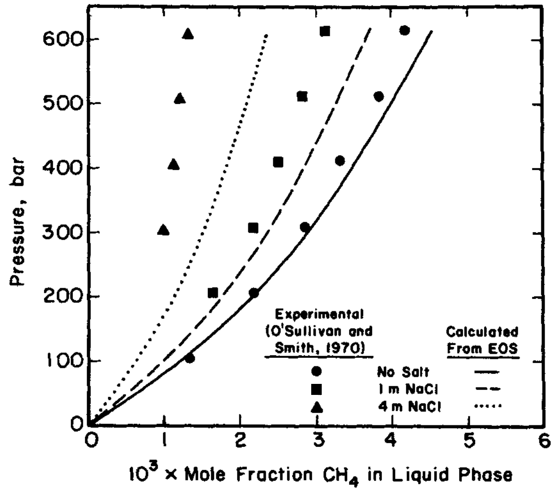

Figure 5. Salting-out of methane by sodium chloride at 102.5°C.

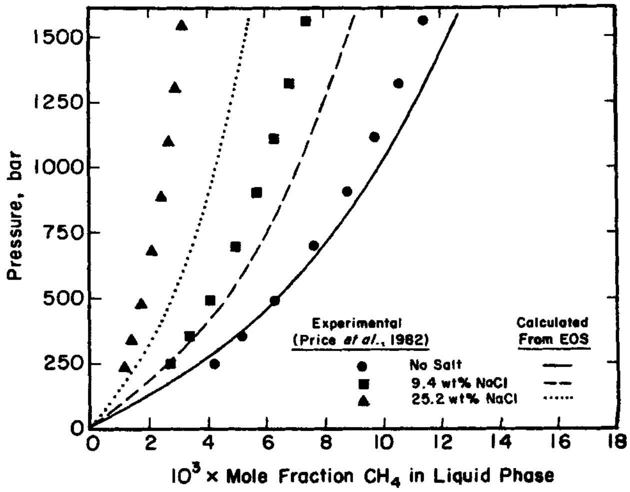

Figure 6. Salting-out of methane by sodium chloride at 170°C.

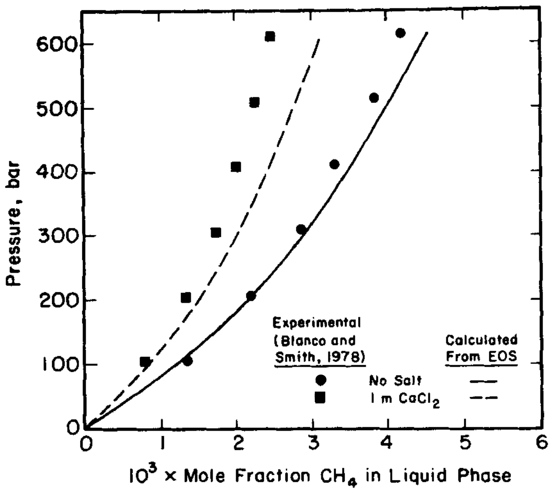

Figure 7. Salting-out of methane by calcium chloride at 102.5°C.

the "isopentanes and heavier" fraction was assumed to be *n*-pentane. Values for k_{ij} between gas components and sodium chloride were taken from Table 2, except for the value for *n*-pentane which was extrapolated using Setchenow-constant data for the lower alkanes. Values for k_{ij} between pairs of gas components can be fitted to experimental data for these binaries, but these parameters are unimportant for our purposes here and were set to zero.

Figure 8 compares calculated and experimental gas solubilities at 93.3°C (200°F) in brine "B" which, at approximately 0.6 molal, is the more concentrated of the two brines. The salt effect is estimated with good accuracy, although salting out is slightly underpredicted through the entire range of pressures. The underprediction is not surprising since it was observed also in Figures 5 and 6 for methane, the primary component of the natural-gas mixture.

Discussion

Very good results are obtained for salt effects on VLE at high temperatures and pressures at low to moderate salt concentrations (1 molal or less) when binary parameters are obtained from room-temperature data for osmotic coefficients and Setchenow constants. At higher salt concentrations the prediction is less reliable; the salt effect is significantly underpredicted at very high salt concentrations for all systems studied with the exception of $CO_2/NaCl/H_2O$.

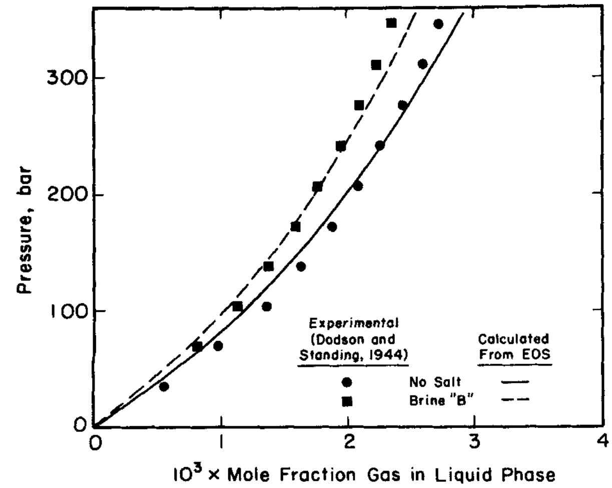

Figure 8. Salting-out of a natural-gas mixture by sodium chloride at 93.3°C.

The source of this underprediction is not clear. Certainly the MSA is an imperfect approximation to the primitive model. Stell and Larsen (1979) expanded the Helmholtz energy of the primitive model in powers of the ion density and the reciprocal temperature. The MSA is the lowest-order (and the dominant) term in this series; the higher-order terms are comparatively very small for conditions characteristic of aqueous electrolytes. Henderson and Blum (1980, 1983) used perturbation theory to obtain the MSA and a similar series of corrections in powers of reciprocal temperature. The corrections from perturbation theory were included in the model of Jin and Donohue (1988), but this series does not include the lowest-order density correction to the second ionic virial coefficient (ΔB_2 in the notation of Stell and Larsen). Both the study of Stell and Larsen and that of Henderson state that this is the most important correction to the MSA in the aqueous electrolyte regime. In any event, any corrections to the MSA appear likely to be negligible in comparison to the inadequacies of the primitive model itself.

A more likely source of error at high salt concentrations is the somewhat *ad hoc* manner in which the adjustable parameters for ion/water and ion/gas interactions were introduced into the Lennard-Jones term. This simplistic description of complicated hydration phenomena is at best a first approximation; it is evident from Figure 1 that the ion/water interaction is not described correctly at high salt concentrations. A possible method for improvement would be provided by a composition-dependent ion/water k_{ij}, but that method would come at the expense of requiring a second adjustable salt/water parameter.

Because experimental data are readily available at or near 25°C, we used these data to obtain the binary parameters in Tables 1 and 2; it is not clear if these values are valid at much higher temperatures. For sodium chloride, where data are available also at high temperatures, the salt/water k_{ij} could be made temperature-dependent. If Setchenow-constant data are also available at higher temperatures for a given system, it would probably be best to use the higher-temperature data to obtain the salt/gas k_{ij}.

Finally, there is much room for improvement in the simple model used for $\tilde{A}^l$. For example, it is likely that incorporation of polar effects into the nonelectrolyte portion of the EOS (as in the PACT model used by Jin and Donohue, 1988) would improve the correlation of the salt-free systems; it is possible that it would also improve the predictions of the salting-out effect. A proper treatment of hydrogen bonding and structural effects in water and aqueous solutions would provide much improvement, but a practical theory for these complex phenomena is still far from realization.

Despite the limitations mentioned above, we now have a reliable method for predicting high-pressure VLE for aqueous systems containing salts (in low or moderate concentrations) and supercritical gases. Using data which are relatively easily available, the method predicts VLE in these complex systems. It should therefore be a useful tool for the design engineer who encounters high-pressure VLE for aqueous systems containing gases and salts. The thermodynamic model presented here can also be used as the basis for an equation of state for systems containing weak electrolytes (Krei et al., 1988).

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Notation

A = Helmholtz energy
C_s = salt concentration
d = additive hard-sphere diameter
D = static dielectric constant
D, E, F = defined in Eqs. AI5abc
e = unit electronic charge
g = radial distribution function
k = Boltzmann's constant
k_{ij} = adjustable binary parameter for interaction beween i and j
k_s = Setchenow constant
n = number of moles
N_A = Avogadro's number
r = distance between molecular centers
R = molar gas constant
T = absolute temperature
u = intermolecular potential energy
x = mole fraction
z = charge on ion
Z = number of electrons on ion

Greek letters

α = molecular polarizability
Γ = MSA screening parameter
δ = nonadditive hard-sphere diameter
ϵ = intermolecular potential-energy parameter
η_n = defined in Eq. AI7a
κ = inverse Debye length defined in Eq. 11a
ξ = reduced density in Eq. AI5
ρ = molar density
σ = intermolecular size parameter
ϕ = fugacity coefficient

Subscripts

c = cavity
i = species i
ij = interaction between species i and j
i, s = species i in salt solution
i, w = species i in pure water
HS = additive hard-sphere contribution
NA = nonadditive hard-sphere contribution
pert = attractive-energy (perturbation) contribution

Superscripts

I = contribution from nonelectrolyte EOS
II = contribution from charging ions
III = contribution from charge-charge interactions
r = residual
$\sim$ = reduced quantity
∞ = infinite dilution

Appendix I: Implementation of Barker-Henderson Perturbation Theory

When the Barker-Henderson perturbation theory is implemented for mixtures, the Helmholtz energy is given as the sum of three terms (Leonard et al., 1970):

$$\tilde{A}^I = \tilde{A}_{HS} + \Delta\tilde{A}_{NA} + \Delta\tilde{A}_{\text{pert}} \tag{AI1}$$

$\tilde{A}_{HS}$ and $\Delta\tilde{A}_{NA}$ both come from the mixed-hard-sphere reference system which takes into account the repulsive portion of the intermolecular potential. The equivalent hard-sphere diameter δ_{ij}, characterizing the repulsive interaction between species i and j is related to the Lennard-Jones parameter, σ_{ij} by

$$\delta_{ij} = \sigma_{ij}\int_0^1 \{1 - \exp[-u_{ij}(z)/kT]\}\,dz; \quad z = r/\sigma_{ij} \tag{AI2a}$$

We replace this integral with the analytic approximation obtained for the Lennard-Jones potential by Cotterman et al. (1986):

$$\delta_{ij} = \sigma_{ij}\frac{1 + 0.29770\tilde{T}_{ij}}{1 + 0.33163\tilde{T}_{ij} + 0.0010477\tilde{T}_{ij}^2} \tag{AI2b}$$

where the reduced temperature $\tilde{T}_{ij}$ is defined by

$$\tilde{T}_{ij} = kT/\epsilon_{ij} \tag{AI3}$$

It is not necessarily true that $\delta_{ij} = \frac{1}{2}(\delta_{ii} + \delta_{jj})$, even if $\sigma_{ij} = \frac{1}{2}(\sigma_{ii} + \sigma_{jj})$. We therefore define an additive hard-sphere diameter d_{ij} by

$$d_{ij} = \tfrac{1}{2}(\delta_{ii} + \delta_{jj}) \tag{AI4}$$

The Helmholtz energy for the reference system can then be expressed in two parts: $\tilde{A}_{HS}$ is the Helmholtz energy of an additive hard-sphere mixture (one in which $\delta_{ij} = d_{ij}$ for all i and j) and $\Delta\tilde{A}_{NA}$ is a first-order correction for nonadditivity.

An accurate expression for the Helmholtz energy of a mixture of additive hard spheres has been given by Boublik (1970) and by Mansoori et al. (1971):

$$\tilde{A}_{HS} = \frac{\dfrac{3DE}{F}\xi - \dfrac{E^3}{F^2}}{(1-\xi)} + \frac{\dfrac{E^3}{F^2}}{(1-\xi)^2} + \left(\frac{E^3}{F^2} - 1\right)\ln(1-\xi) \tag{AI5}$$

$$D = \sum_i x_i d_{ii}; \quad E = \sum_i x_i d_{ii}^2; \quad F = \sum_i x_i d_{ii}^3 \tag{AI5abc}$$

where $\xi = (\pi/6)\,N_A\rho F$ is a reduced density.

The first-order correction for nonadditivity is given by:

$$\Delta\tilde{A}_{NA} = 2\pi N_A\rho \sum_i\sum_j x_i x_j d_{ij}^2 g_{ij}(d_{ij})(\delta_{ij} - d_{ij}) \tag{AI6}$$

where $g_{ij}(d_{ij})$ is the contact value of the radial distribution function for the additive hard-sphere system. A good estimate of $g_{ij}(d_{ij})$ for additive hard-sphere mixtures is given by Grundke and Henderson (1972):

$$g_{ij}(d_{ij}) = \frac{1}{1-\eta_3} + \frac{3\eta_2}{2(1-\eta_3)^2}\left(\frac{d_{ii}d_{jj}}{d_{ij}}\right) + \frac{\eta_2^2}{2(1-\eta_3)^3}\left(\frac{d_{ii}d_{jj}}{d_{ij}}\right)^2 \tag{AI7}$$

$$\eta_n = \frac{\pi}{6} N_A \sum_i \rho_i d_{ii}^n \qquad \text{(AI7a)}$$

For the perturbation term $\Delta\tilde{A}_{\text{pert}}$, we employ a simplification introduced by Cotterman et al. (1986). Rather than evaluating integrals over radial distribution functions as required in the original theory, Cotterman fitted polynomials to the Barker-Henderson results for the first- and second-order perturbation terms. The result is:

$$\Delta\tilde{A}_{\text{pert}} = \frac{A^{(1)}}{\tilde{T}_{\text{mix}}} + \frac{A^{(2)}}{\tilde{T}^2_{\text{mix}}} \qquad \text{(AI8)}$$

$$A^{(1)} = -6.0782\tilde{\rho} - 2.2712\tilde{\rho}^2 - 0.75194\tilde{\rho}^3 + 2.5713\tilde{\rho}^4 \qquad \text{(AI8a)}$$

$$A^{(2)} = -1.3488\tilde{\rho} + 4.9862\tilde{\rho}^2 - 7.8545\tilde{\rho}^3 + 3.9760\tilde{\rho}^4 \qquad \text{(AI8b)}$$

where $\tilde{\rho} = (6/\pi)\,\xi$ is another measure of the reduced density. The reduced temperature $\tilde{T}_{\text{mix}}$ is defined for a mixture by a one-fluid mixing rule for energy parameter ϵ:

$$\tilde{T}_{\text{mix}} = kT/\epsilon_{\text{mix}} \qquad \text{(AI9)}$$

$$\epsilon_{\text{mix}} = \frac{\sum_i \sum_j x_i x_j d_{ij}^3 \epsilon_{ij}}{F} \qquad \text{(AI10)}$$

where ϵ_{ij} is given by Eq. 6.

Appendix II: Pure-Component Parameters and Binary Parameters for Nonelectrolyte-Water Interactions

Table AII-1. Pure-Component Parameters for Nonelectrolytes

Component	$\epsilon_{ii}^{(0)}$ (K)	$\epsilon_{ii}^{(1)}$ (K)	$\epsilon_{ii}^{(2)}$	σ_{ii} (10^{-8} cm)
Water	100.00	597.76	0.31616	3.0049
Nitrogen	98.526	0.0	0.0	3.5954
Carbon Dioxide	150.00	177.28	0.93909	4.1254
Methane	147.08	0.0	0.0	3.7384
Ethane	204.24	61.52	0.61000	4.2334
Propane	248.61	101.89	0.91759	4.6868
n-Butane	281.54	147.30	1.0288	5.0778
n-Pentane	311.37	200.84	1.2077	5.4182

Table AII-2. Pure-Component Parameters for Ions

Ion	$\epsilon_{ii}^{(0)}$ (K)	σ_{ii} (10^{-8} cm)	$\sigma_{c,i}$ (10^{-8} cm)	α (10^{-24} cm^3)
Li^+	25.0	1.36	2.46	0.0285
Na^+	96.0	1.90	3.14	0.158
K^+	214.0	2.66	4.05	0.85
Mg^{2+}	328.0	1.30	2.72	0.0784
Ca^{2+}	605.0	1.98	3.48	0.522
Cl^-	336.0	3.62	3.62	3.94
Br^-	449.0	3.92	3.92	5.22

For all ions, $\epsilon_{ii}^{(1)} = \epsilon_{ii}^{(2)} = 0$.

Table AII-3. Binary Parameters for Gases (Component 1) with Water (Component 2)

Gas	$k_{12}^{(1)}$	$k_{12}^{(2)}$	$k_{21}^{(1)}$	Data Sources
Nitrogen	0.2298	−221.9	0.7603	Wiebe et al. (1933) O'Sullivan and Smith (1970)
Carbon Dioxide	−0.0639	−80.04	0.0714	Wiebe and Gaddy (1939, 1940, 1941) Tödheide and Franck (1963)
Methane	0.2378	−172.6	0.3524	Culberson and McKetta (1951) Olds et al. (1942)
Ethane	0.2728	−143.1	0.3963	Culberson and McKetta (1950) Reamer et al. (1943)
Propane	0.2839	−139.0	0.4476	Kobayashi and Katz (1953)
n-Butane	0.3414	−155.3	0.4887	Reamer et al. (1952)
n-Pentane	0.3271	−140.4	0.4584	Gillespie and Wilson (1982)

For all systems, $k_{21}^{(2)} = 0$.

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