Phase Equilibria and Volumetric Properties of Aqueous CACl$_2$ by an Equation of State

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A comprehensive equation of state was developed to represent the phase equilibria and volumetric properties of aqueous calcium chloride solutions at temperatures above 523 K. The equation consists of a reference part and a perturbation contribution. The reference function is developed from the statistical mechanical theory for mixtures of dipolar and quadrupolar hard spheres, which agrees well with the Monte Carlo simulation results. In this treatment, calcium chloride is described by the completely undissociated model. The empirical perturbation function is a truncated series of virial expansion terms. Thus, mixing rules are guided by those of virial coefficients, which are derived rigorously from statistical mechanics. The equation reproduces experimental saturated vapor pressures and volumetric data within experimental uncertainty for temperatures to 623 K. At higher temperatures, few and less accurate experimental data are available, but values of the saturated vapor pressures of the liquid have been reported and are represented satisfactorily.

Introduction

Calcium chloride ($CaCl_2$) is a major constituent of natural waters and is important in many industrial fluids. In addition, $CaCl_2$ is the premier example of an electrolyte of the 2–1 charge type and its aqueous solution has been used considerably as an isopiestic standard. Therefore, understanding of the behavior of the system $CaCl_2$–H_2O over wide ranges of temperature and pressure is important.

The thermodynamic properties of aqueous $CaCl_2$ have been measured over a wide range of temperature. Reviews of experimental results below 373 K were given by Garvin et al. (1987) and Ananthaswamy and Atkinson (1985) together with equation-of-state representations based on excess Gibbs energy models. Pitzer and Shi (1993) presented a treatment for $CaCl_2$ that extended to saturated solution and equilibrium with hydrated crystals for the temperature range to 373 K. Holmes et al. (1994) presented a comprehensive equation of state, which gives an accurate representation of various properties to 523 K and 4.75 molal, while Pitzer and Oakes (1994) proposed a thermodynamic treatment in the range from 4.75 molal to saturation and from 323 to 523 K. The combination of the equations of Holmes et al. (1994) and Pitzer and Oakes (1994) yields a complete treatment for aqueous $CaCl_2$ below 523 K.

Saturated vapor pressures of aqueous $CaCl_2$ solutions were measured by Wood et al. (1984), Zarembo et al. (1980), and Crovetto et al. (1993) from 423 to 623 K up to 6 molal. There is an important set of vapor pressure measurements by Ketsko et al. (1984) from 523 to 673 and up to saturation molalities (as high as 51.0 molal at 673 K). Densities of $CaCl_2$ solutions in the one-phase region were measured by Oakes et al. (1995), Gates and Wood (1989), Tsay et al. (1989), and Crovetto et al. (1993) from 323 to 643 K and at pressures up to 400 bar. Compositions of coexisting vapor and liquid were measured by Tkachenko and Shmulovich (1992), Tkachenko (personal communication), and Bischoff and Rosenbauer (personal communication) between 673 and 873 K. There is only one set of density measurements of coexisting vapor and liquid available in the literature between 523 and 613 K (Rodnyanskii et al., 1962). However, their data were found to be fairly unreliable, especially above 573 K (Potter and Brown, 1976). Aqueous $CaCl_2$ was also studied by Zhang and Frantz (1987, 1989) using the synthetic fluid inclusion method up to 973 K and 3,000 bar.

It is desirable to have a comprehensive equation of state describing thermodynamic properties of aqueous $CaCl_2$ solutions over a wide range of temperature and pressure. Over the full range of temperature, pressure, and composition, $CaCl_2$ shifts from a fully ionized state in dilute solutions at

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temperatures below 523 K to that of nearly complete ion pairing at higher temperatures as the dielectric constant of H_2O decreases. At high concentration this picture becomes ambiguous because a given ion can have several near neighbors of the opposite sign. While it is possible to include an ion-association equilibrium in a comprehensive treatment, we have chosen to use the fully associated basis for the present treatment. This precludes accuracy in the dilute region at high pressure when dielectric constant is large enough to allow substantial dissociation, but is quite satisfactory for more concentrated solutions and for dilute solutions at saturation pressure. Therefore, at higher temperatures (e.g., above 523 K), the $CaCl_2$ is treated approximately as a linear molecule with a very large quadrupole, while the solvent molecules can be approximated by dipoles. A reference function was developed from thermodynamic perturbation theory for mixtures of dipolar hard spheres and quadrupolar hard spheres. Then, an empirical perturbation function was added to obtain accurate agreement with various experimental data. The empirical perturbation function was based on a truncated virial expansion, and mixing rules were thus based on the rigorously known composition dependence of virial coefficient as proposed by Anderko and Pitzer (1991). Similar treatments involving reference and perturbation functions were successful for NaCl–H_2O and KCl–H_2O (Anderko and Pitzer, 1993a, b).

Thermodynamic Model

At higher temperatures an excess Gibbs energy model becomes inconvenient, especially for the vapor–liquid phase equilibria and the near-critical region where the condition of mechanical stability cannot be derived from the excess Gibbs energy surface. A residual Helmholtz energy model is more suitable (Levelt-Sengers, 1991). The molar residual Helmholtz energy is defined as the difference between the molar Helmholtz energy of the system and that of an ideal gas mixture at the same (ρ, T, x):

$$a^{\text{res}}(\rho,T,x) = a(\rho,T,x) - a^{\text{id}}(\rho,T,x). \qquad (1)$$

It is useful to divide the molar Helmholtz energy into a reference term and a perturbation term:

$$a^{\text{res}} = a^{\text{ref}} + a^{\text{per}}. \qquad (2)$$

The reference term is modeled by mixtures of dipolar hard spheres and quadrupolar hard spheres. The dipolar hard spheres are the reference for water, while the quadrupolar hard spheres are the reference for calcium chloride. The perturbation contribution is given by a truncated virial expansion.

With a mixture of dipolar hard spheres and quadrupolar hard spheres as the reference system, the molar Helmholtz energy can be expressed as

$$a^{\text{ref}} = a^{hs} + a^{es} \qquad (3)$$

where a^{hs} is the residual Helmholtz energy of mixtures of hard spheres and a^{es} is the electrostatic contribution to the Helmholtz energy (or the excess Helmholtz energy relative to simple hard sphere mixtures). For mixtures of dipolar hard spheres and quadrupolar hard spheres, the electrostatic interaction includes dipolar–dipolar, dipolar–quadrupolar, and quadrupolar–quadrupolar interactions.

Repulsive contribution

The residual Helmholtz energy with respect to a mixture of ideal gas at the same (ρ, T, and x) of a mixture of hard spheres was given by Boublik (1970) and Mansoori et al. (1971)

$$\frac{a^{hs}}{RT} = \frac{(3DE/F)\eta - (E^3/F^2)}{1-\eta} + \frac{E^3/F^2}{(1-\eta)^2} + \left(\frac{E^3}{F^2} - 1\right)\ln(1-\eta), \qquad (4)$$

where

$$D = \sum_{i=1}^{n} x_i \sigma_i \qquad (5)$$

$$E = \sum_{i=1}^{n} x_i \sigma_i^2 \qquad (6)$$

$$F = \sum_{i=1}^{n} x_i \sigma_i^3. \qquad (7)$$

The reduced density η and the van der Waals covolume parameter b (for simple hard sphere mixtures) are given by

$$\eta = \frac{b\rho}{4} \qquad (8)$$

and

$$b = \frac{2}{3}\pi N_A F. \qquad (9)$$

For mixtures of equal-sized spheres, the Boublik–Mansoori form is identical to that of Carnahan and Starling (1969). However, for other mixtures, the Boublik–Mansoori form is superior as demonstrated by Dimitrelis and Prausnitz (1986).

Electrostatic contribution

In thermodynamic perturbation theory, first proposed by Pople (1954), the Helmholtz energy is expanded in powers of the perturbing potential

$$a^{\text{res}} = a_0 + a_2 + a_3 + \cdots, \qquad (10)$$

where a_0 is the value for the reference system, a_2 is the second-order perturbation term, and so on (the first-order term a_1 vanishes). General expressions for a_2 and a_3 for an arbitrary intermolecular potential have been worked out by Flytzani-Stephanopoulos et al. (1975). When Eq. 10 is terminated at the third-order term, it is found to give good results for moderately polar fluids, but fails for strong dipoles. Similar results are found for quadrupole forces. The slow convergence of Eq. 10 for strong multipole strengths led Stell et al.

(1974) to suggest the simple Padé approximation for the Helmholtz energy. For mixtures of dipolar hard spheres and quadrupolar hard spheres, the Padé approximation for the electrostatic contribution to the Helmholtz energy is given by

$$a^{es} = a_2\left[\frac{1}{1-(a_3/a_2)}\right], \tag{11}$$

where a_3 can be divided into the two-body and three-body terms

$$a_3 = a_{3,2} + a_{3,3}. \tag{12}$$

Explicit expressions for a_2, $a_{3,2}$, and $a_{3,3}$ are given by (Gubbins and Twu, 1978)

$$\frac{a_2}{RT} = -\frac{3\rho}{2\pi}\left[\frac{x_1^2\mu_1^{*4}b_1}{6}I_6^{hs}(\rho^*) + \frac{x_1x_2\mu_1^{*2}Q_2^{*2}b_1b_2^{5/3}}{2b_{12}^{5/3}}I_8^{hs}(\rho^*) + \frac{7x_2^2Q_2^{*4}b_2}{10}I_{10}^{hs}(\rho^*)\right] \tag{13}$$

$$\frac{a_{3,2}}{RT} = \frac{3\rho}{2\pi}\frac{36x_2^2Q_2^{*6}b_2}{245}I_{15}^{hs}(\rho^*) \tag{14}$$

$$\frac{a_{3,3}}{RT} = \left(\frac{3\rho}{2\pi}\right)^2 \times\left[\frac{x_1^3\mu_1^{*6}b_1^2}{54}I_{ddd}^{hs}(\rho^*) + \frac{x_1^2x_2\mu_1^{*4}Q_2^{*2}b_1^{5/3}b_2^{5/3}}{480b_{12}^{4/3}}I_{ddq}^{hs}(\rho^*) + \frac{x_1x_2^2\mu_1^{*2}Q_2^{*4}b_1b_2^{7/2}}{640b_{12}^{4/3}}I_{dqq}^{hs}(\rho^*) + \frac{x_2^3Q_2^{*6}b_2^2}{6{,}400}I_{qqq}^{hs}(\rho^*)\right], \tag{15}$$

where $I_m^{hs}(\rho^*)$ and $I_{\text{triple}}^{hs}(\rho^*)$ are the pair and triple integrals of the hard sphere distribution function. An approximation for $I_m^{hs}(\rho^*)$ and $I_{\text{triple}}^{hs}(\rho^*)$ was constructed in the form of the extended virial series

$$I_k^{hs}(\rho^*) \simeq \sum_{i=0}^{5} J_{i,k}\,\rho^{*i} \quad (k = 6, 8, 10, 15, ddd, ddq, dqq, qqq). \tag{16}$$

The coefficients were given by Larsen et al. (1977) and are listed in Table 1. For mixtures, these integrals are evaluated using the van der Waals one-fluid theory (Gubbins and Twu, 1978),

$$\rho^* = \frac{3\rho}{2\pi}\sum_{i=1}^{n}\sum_{j=1}^{n}x_ix_jb_{ij}^3 \equiv \frac{3\rho}{2\pi}b. \tag{17}$$

Table 1. Coefficients of the Extended Virial Series Approximation for $I_m^{hs}(\rho^*)$ and $I_{\text{triple}}^{hs}(\rho^*)$ (Eq. 16)*

m	$J_{0,m}$	$J_{1,m}$	$J_{2,m}$	$J_{3,m}$	$J_{4,m}$	$J_{5,m}$
6	4.1888	2.8287	0.8331	0.0317	0.0858	−0.0846
8	2.5133	2.1795	1.0423	0.2596	0.1097	−0.0573
10	1.7952	1.7551	1.0376	0.3890	0.1561	−0.0082
15	1.0472	1.1631	0.8552	0.4506	0.1913	0.1465
ddd	16.4493	19.8096	6.3321	−0.0932	−1.1741	−0.8321
ddq	139.4906	241.9354	163.9581	57.0537	13.2686	−22.3827
dqq	139.4906	298.9225	283.4908	161.7222	81.7788	−35.8868
qqq	532.9586	1287.3491	1447.9762	1026.3847	608.4235	−20.5065

*Taken from Larsen et al. (1977).

It is important to note that the one-fluid assumption has been made here for the electrostatic term. The repulsive term is not based on a one-fluid assumption. Other reduced quantities and cross terms used in Eqs. 13–15 are defined as follows

$$\mu_1^{*2} = \frac{\mu_1^2}{kT\sigma_1^3},$$

$$Q_2^{*2} = \frac{Q_2^2}{kT\sigma_2^5},$$

$$b_{12} = \left(\frac{b_1^{1/3} + b_2^{1/3}}{2}\right)^3. \tag{18}$$

It has been shown (Jiang and Pitzer, 1994) that the perturbation theory based on the Padé approximation yields good agreement in compressibility factor, chemical potential, Helmholtz energy, and configuration energy for a mixture of dipolar hard spheres and quadrupolar hard spheres with Monte Carlo calculations.

Perturbation contribution

Following Dohrn and Prausnitz (1990), and Anderko and Pitzer (1993a), a generalized van der Waals attractive term using a truncated virial expansion is used

$$\frac{a^{\text{per}}}{RT} = -\frac{4a}{RTb}\eta(1 + c\eta + d\eta^2 + e\eta^3) \tag{19}$$

where b is the van der Waals covolume and the perturbation term parameters a, c, d, and e are required to represent the properties of pure water. For pure $CaCl_2$, only two parameters (a and b) are needed to describe vapor pressures and molar volumes of pure liquid $CaCl_2$.

To extend Eq. 19 to mixtures, we follow the technique developed by Anderko and Pitzer (1993a). Equation 19 is rewritten in terms of density:

$$\frac{a^{\text{per}}}{RT} = -\frac{1}{RT}\left(a\rho + \frac{acb\rho^2}{4} + \frac{adb^2\rho^3}{16} + \frac{aeb^3\rho^4}{64}\right), \tag{20}$$

where a, acb, adb^2, and aeb^3 are related to the second, third, fourth, and fifth virial coefficients, respectively. According to statistical mechanics, the second virial coefficient of a mixture should be a quadratic function of composition, the third virial coefficient a cubic, and so on. Therefore, the following mixing rules are adopted

$$a = \sum_{i=1}^{n}\sum_{j=1}^{n}x_ix_ja_{ij} \tag{21}$$

$$acb = \sum_{i=1}^{n} \sum_{j=1}^{n} \sum_{k=1}^{n} x_i x_j x_k (ac)_{ijk} b_{ijk} \tag{22}$$

$$adb^2 = \sum_{i=1}^{n} \sum_{j=1}^{n} \sum_{k=1}^{n} \sum_{l=1}^{n} x_i x_j x_k x_l (ad)_{ijkl} b_{ijkl}^2 \tag{23}$$

$$aeb^3 = \sum_{i=1}^{n} \sum_{j=1}^{n} \sum_{k=1}^{n} \sum_{l=1}^{n} \sum_{m=1}^{n} x_i x_j x_k x_l x_m a_{ij} (ae)_{ijklm} b_{ijklm}^3. \tag{24}$$

The specific combining rules are needed to describe the cross terms from pure fluid parameters. For the van der Waals covolume parameters, the pair parameter b_{ij} is defined by Eq. 18

$$b_{ijk} = \left[\left(b_i^{1/3} + b_j^{1/3} + b_k^{1/3}\right)/3\right]^3 \tag{25}$$

$$b_{ijkl} = \left[\left(b_i^{1/3} + b_j^{1/3} + b_k^{1/3} + b_l^{1/3}\right)/4\right]^3 \tag{26}$$

$$b_{ijklm} = \left[\left(b_i^{1/3} + b_j^{1/3} + b_k^{1/3} + b_l^{1/3} + b_m^{1/3}\right)/5\right]^3. \tag{27}$$

In our treatment, the parameters (c_2, d_2, and e_2) for pure $CaCl_2$ are set to zero. Therefore, the combining rules originally proposed by Anderko and Pitzer (1991, 1993a) are modified. In the present study, the parameters a_{ij}, $(ac)_{ijk}$, $(ad)_{ijkl}$, and $(ae)_{ijklm}$ are related to pure fluid parameters according to the prescription of

$$a_{ij} = (a_i a_j)^{1/2} \alpha_{ij} \tag{28}$$

$$(ac)_{ijk} = [a_i a_j a_k]^{1/3} \gamma_{ijk} \tag{29}$$

$$(ad)_{ijkl} = [a_i a_j a_k a_l]^{1/4} \delta_{ijkl} \tag{30}$$

$$(ae)_{ijklm} = [a_i a_j a_k a_l a_m]^{1/5} \epsilon_{ijklm} \tag{31}$$

where α_{ij}, γ_{ijk}, δ_{ijkl}, and ϵ_{ijklm} are parameters to correct for deviation from the combining rules for the cross terms.

Equations for the other thermodynamic properties (e.g., compressibility factor and fugacity coefficients) can be readily obtained by applying the usual thermodynamic identities to the Helmholtz energy presented in the three previous subsections on contributions. The compressibility factor is given by

$$Z = \rho \left[\frac{\partial (a^{\text{res}}/RT)}{\partial \rho}\right]_{T,\eta_i} + 1. \tag{32}$$

The fugacity coefficient is given by

$$\ln \phi_i = \left[\frac{\partial (n a^{\text{res}}/RT)}{\partial n_i}\right]_{\rho,T,n_{j \neq i}} + (Z-1) - \ln Z. \tag{33}$$

Explicit expressions for hard-sphere and perturbation contributions to the compressibility factor and fugacity coefficient (or chemical potential) were given by Dimitrelis and Prausnitz (1990), and Anderko and Pitzer (1993a), respectively. The expressions for the electrostatic contribution are given in the Appendix.

Evaluation of Parameters

Water

The dipole moment of water ($\mu_1 = 1.85\ D$) was taken from McClellan (1963–1989). The parameters b_1, a_1, c_1, d_1, and e_1, were fitted to data generated from the comprehensive equation of state of Hill (1990) by Anderko and Pitzer (1993a). The parameters are

$$b_1 = 28.4959 \quad (\text{cm}^3/\text{mol}) \tag{34}$$

$$a_1 = (1.718248 + 1.828379/T_r + 1.546648/T_r^2 + 0.107189/T_r^4 \cdot 10^6 \quad (\text{bar} \cdot \text{cm}^6/\text{mol}^2) \tag{35}$$

$$c_1 = 2.953548 - 8.874823/T_r + 3.179334/T_r^2 - 0.168698/T_r^4 \tag{36}$$

$$d_1 = 2.139339 + 9.442203/T_r - 3.144017/T_r^2 + 0.149539/T_r^4 \tag{37}$$

$$e_1 = -9.0, \tag{38}$$

where T_r is the reduced temperature:

$$T_r = T/T_c = T/647.067. \tag{39}$$

The equation with parameters listed in Eqs. 34–39 represents the properties of water with very good accuracy. The details were discussed in the original article by Anderko and Pitzer (1993a).

Calcium chloride

The quadrupole moment for $CaCl_2$ is not available in the literature. It is estimated in this article by a method similar to that proposed by Rittner (1951) for estimating the dipole moment of a molecule. For the linear molecule of $CaCl_2$, the quadrupole moment is given by

$$Q = \sum_i e_i^- r_i^2, \\ = 2e^- (r_e - \Delta r)^2 \tag{40}$$

where r_e is the equilibrium distance between the Ca^{2+} and Cl^- nuclei; it has a value of 2.51 Å taken from Kim and Gordon (1974). Δr is the change of the effective interatomic distance of the Cl^- charge due to polarization by the electric field and can be calculated from the induced moment (Rittner, 1951)

$$p_{Cl} E_{Cl} = e^- \Delta r, \tag{41}$$

where p_{Cl} is the polarizability of Cl^-, and has a value of 3.69 Å^3 taken from Pauling (1936). E_{Cl} is the electrostatic field at the center of Cl^-. The expression for the electrostatic field was given by Guido and Gigli (1976). For the linear molecule of $CaCl_2$, the expression for E_{Cl} can be simplified as

$$E_{\mathrm{Cl}} = -\left[e^{+}\cos\beta + \frac{e^{-}\sin(\theta+\beta)}{4\sin\theta^{2}}\right]e^{+}/r_e^{2} - \frac{2\sin(\theta+\beta)^{2}+\cos(\theta+\beta)^{2}}{8\sin\theta^{3}}p_{\mathrm{Cl}}E_{\mathrm{Cl}}/r_e^{3} \quad (42)$$

where θ and β are 90°C and 180°C for $CaCl_2$ (Guido and Gigli, 1976), respectively.

From Eqs. 40–42, the quadrupole moment for $CaCl_2$ is obtained to be -22.84×10^{26} esu. This value was used in our equation.

Vapor pressures of pure liquid $CaCl_2$ above its melting point were measured by several workers whose results are summarized by Chase et al. (1985). Over the temperature range of our interest, the vapor pressures can be represented by the equation

$$\log P\,(\mathrm{bar}) = 6.3435 - \frac{13{,}579}{T(\mathrm{K})}. \quad (43)$$

Molar volumes of pure liquid $CaCl_2$ can be represented by a linear function of temperature (Janz et al., 1974)

$$v(\mathrm{cm^3/mol}) = 42.252 + 0.01054T(\mathrm{K}). \quad (44)$$

The parameters c_2, d_2, and e_2 were set to zero and the parameters a_2 and b_2 were obtained by fitting vapor pressures and molar volumes of liquid $CaCl_2$ to the equation. The final parameters for pure liquid $CaCl_2$ are given below

$$a_2 = (5.834 + 0.007235T - 1.913\times10^{-6}T^{2})\cdot10^{7} \quad (\mathrm{bar\cdot cm^6/mol^2}) \quad (45)$$

$$b_2 = 138.810 - 0.005109T + 1.732\times10^{-6}T^{2}\,(\mathrm{cm^3/mol}) \quad (46)$$

$$c_2 = 0.0 \quad (47)$$

$$d_2 = 0.0 \quad (48)$$

$$e_2 = 0.0. \quad (49)$$

Figures 1 and 2 show comparisons of vapor pressures and molar volumes of pure liquid (and subcooled liquid) $CaCl_2$ from the equation of state with the smoothed experimental data from Eqs. 43 and 44, respectively. The melting point of pure $CaCl_2$ is 1,055.15 K taken from the *CRC Handbook* (1990). Both vapor pressures and molar volumes are well reproduced. The use of this equation below 1,055.15 K is an extrapolation into the subcooled range, however, and the absolute value of the fugacity of $CaCl_2$ becomes increasingly uncertain.

Calcium chloride–water mixtures

Preliminary trials showed that all ϵ_{ijklm} coefficients are 0 and six parameters (α_{12}, γ_{112}, γ_{122}, δ_{1112}, δ_{1122}, and δ_{1222}) are required to fit the following data of mixtures to the equation.

- Saturated vapor pressures of aqueous $CaCl_2$ solutions between 523 and 623 K and up to 6 molal from Wood et al. (1984) and Zarembo et al. (1980), and between 523 and 673 K and up to saturation by Ketsko et al. (1984).
- Densities of $CaCl_2$ aqueous solutions in the one-phase region from Oakes et al. (1995) and Gates and Wood (1989) from 523 to 643 K and at pressures up to 400 bar.
- Compositions of coexisting vapor and liquid from Tkachenko and Shmulovich (1992), Tkachenko (personal communication), and Bischoff and Rosenbauer (personal communication) between 673 and 874 K.

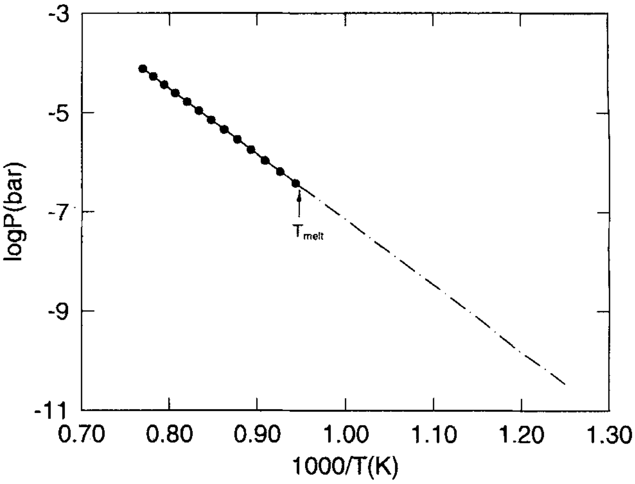

Figure 1. Vapor pressures of pure liquid $CaCl_2$ calculated from the equation of state (——) vs. smoothed experimental data from Eq. 43 (●).

The saturated vapor pressure of subcooled liquid $CaCl_2$ calculated from the equation of state is denoted by – – –.

The Levenberg–Marquardt method was used in the nonlinear least-squares fitting of the parameters. In the Levenberg–Marquardt scheme, the steepest descent method is used far from the minimum, switching continuously to the inverse-Hessian method as the minimum is approached (Press

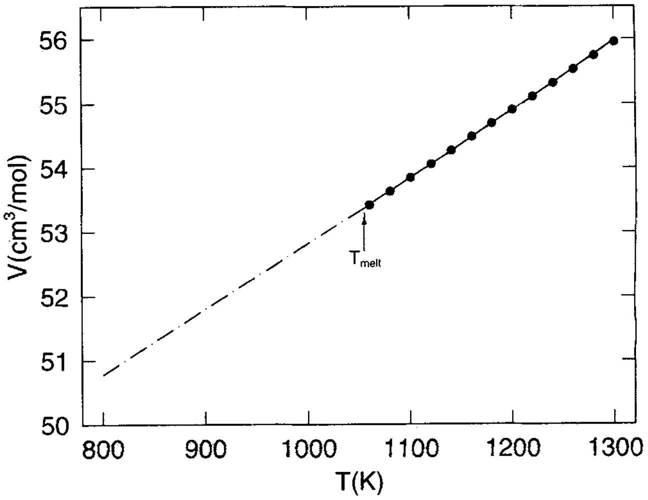

Figure 2. Molar volumes of pure liquid $CaCl_2$ calculated from the equation of state (——) vs. smoothed experimental data from Eq. 44 (●).

The molar volume of subcooled liquid $CaCl_2$ calculated from the equation of state is denoted by – – –.

et al., 1989). The resulting parameters for $CaCl_2$-H_2O mixtures are

$$\alpha_{12} = 3.2768 - 0.0034513T + 4.6766 \times 10^{-6}T^2 \quad (50)$$

$$\gamma_{112} = 0.57560 + 0.0021377T \quad (51)$$

$$\gamma_{122} = 5.0441 - 0.013455T + 2.0706 \times 10^{-5}T^2 \quad (52)$$

$$\delta_{1112} = 0.3521 + 2.2826 \times 10^{-9}(T - 523.15)^3 \quad (53)$$

$$\delta_{1122} = 6.2630 - 0.024806T + 3.2981 \times 10^{-5}T^2 \quad (54)$$

$$\delta_{1222} = -1.8157 + 0.005383T \quad (55)$$

$$\epsilon_{11112} = \epsilon_{11122} = \epsilon_{11222} = \epsilon_{12222} = 0.0 \quad (56)$$

Results and Discussion

Vapor-liquid equilibria

Saturated vapor pressures in aqueous $CaCl_2$ solutions have been measured by Wood et al. (1984), Zarembo et al. (1980), and Ketsko et al. (1984) between 523.15 and 623.15 K. In this region the equation reproduces the data up to saturation with very good accuracy, as shown in Figures 3–5. At these temperatures, the vapor phase contains essentially pure water and the curves for x_{CaCl_2} in the vapor phase are not distinguishable from zero on these figures.

Vapor–liquid equilibrium data become scarce and much less precise above the critical point of water. There are experimental data available from Ketsko et al. (1984) at 673.15 K, and from Tkachenko and Shmulovich (1992), Tkachenko (personal communication), and Bischoff and Rosenbauer (personal communication) at several temperatures. The measurements of Bischoff and Rosenbauer (personal communication) indicate increasing hydrolysis with decrease in pressure at 673 K and higher temperatures. Near the critical pressure this effect is negligible, but at lower pressure at a given temperature the analysis of the vapor shows more than 2 Cl per Ca. Indeed, at pressures half of the critical or less, the solute in the vapor is primarily HCl. The resulting $Ca(OH)_2$ must be in the liquid phase. However, the fraction $Ca(OH)_2$ in the liquid remains small.

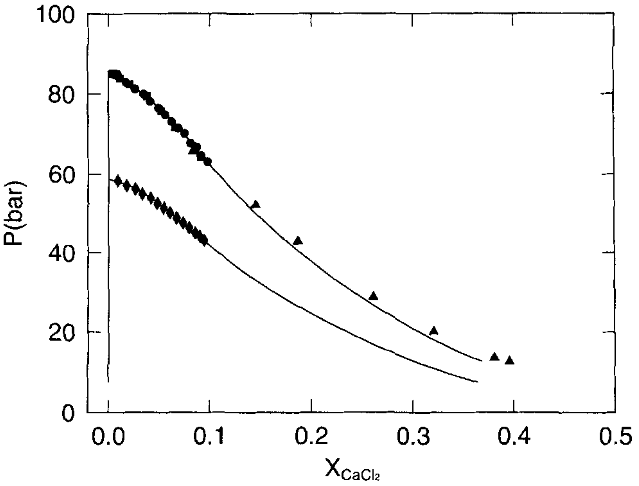

Figure 4. Comparison of saturated vapor pressures of aqueous $CaCl_2$ solutions calculated from the equation of state (——) vs. experimental data by Wood et al. (♦) at 548.15 K, and by Wood et al. (●), Zarembo et al. (■), and Ketsko et al. (▲) at 573.15 K.

The equation represents the saturated vapor pressures of liquid phase satisfactorily at 673.15 K where there are extensive data as shown on Figure 6, but fails to represent the vapor compositions and the near critical region. At higher temperatures the only experimental data for the liquid are at near-critical pressure, and reasonable agreement with the equation is shown on Figure 7. The vapor composition at near-critical pressure is fairly well represented, but some improvements are needed. At lower pressures, hydrolysis becomes a very serious problem. For the vapor at lower pressures, the measurements of the Ca content should constitute

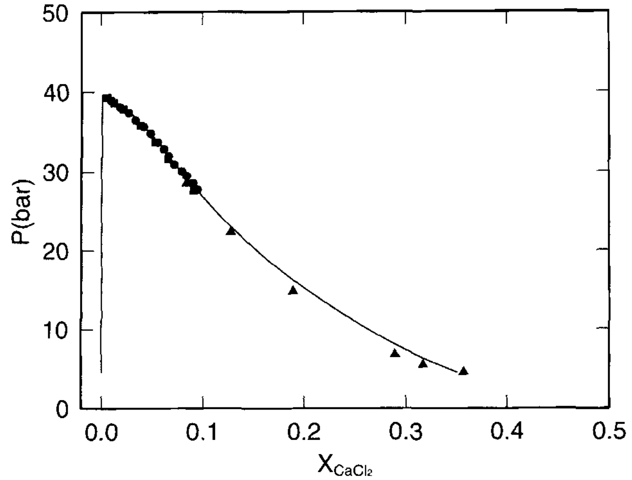

Figure 3. Saturated vapor pressures of aqueous $CaCl_2$ solutions calculated from the equation of state (——) vs. experimental data by Wood et al. (●), Zarembo et al. (■), and Ketsko et al. (▲) at 523.15 K.

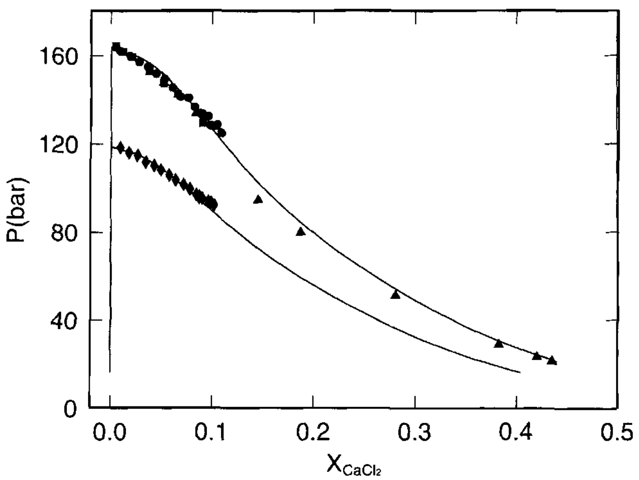

Figure 5. Saturated vapor pressures of aqueous $CaCl_2$ solutions calculated from the equation of state (——) vs. experimental data by Wood et al. (♦) at 598.15 K, and by Wood et al. (●), Zarembo et al. (■), and Ketsko et al. (▲) at 623.15 K.

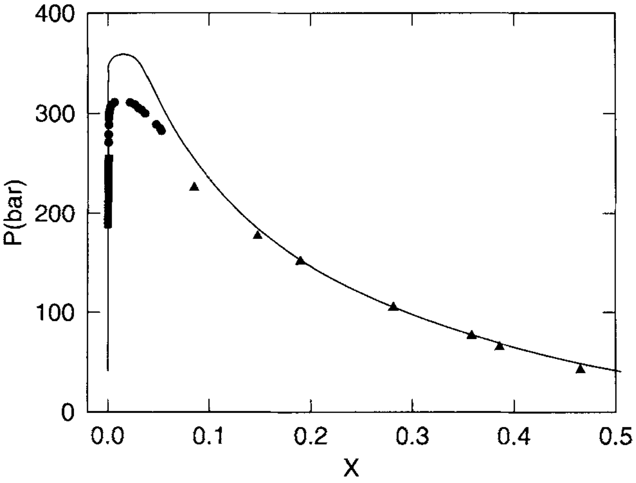

Figure 6. Vapor-liquid equilibria of aqueous $CaCl_2$ solutions calculated from the equation of state (——) vs. experimental data by Tkachenko and Shmulovich (1992) (●), Bischoff et al. (1996) (■), and Ketsko et al. (1984) (▲) at 673.15 K.

a first approximation for unhydrolyzed $CaCl_2$, but the uncertainty is large and the differences from our equation become large on a percentage basis but very small as to the amount of $CaCl_2$. Indeed, the vapor in this range is nearly pure H_2O with HCl as the primary impurity. It remains for further research to fully represent the vapor in this range.

Densities

Oakes et al. (1995) and Gates and Wood (1989) reported liquid density data in the one-phase region at temperatures between 523 and 623 K and pressures up to 400 bar. The equation of state represents these data essentially within experimental uncertainty. Such comparisons are shown in Figures 8–12 for temperatures between 523 and 623 K.

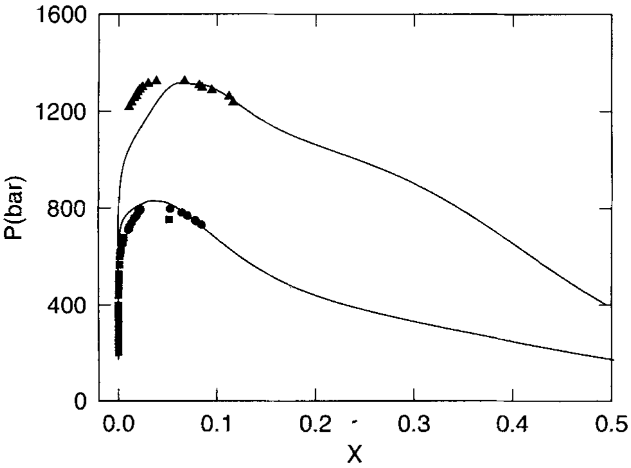

Figure 7. Vapor-liquid equilibria of aqueous $CaCl_2$ solutions calculated from the equation of state (——) vs. experimental data by Tkachenko and Shmulovich (1992) (●), Bischoff et al. (1996) (■) at 773.15 K, and by Tkachenko and Shmulovich (1992) (▲) at 873.15 K.

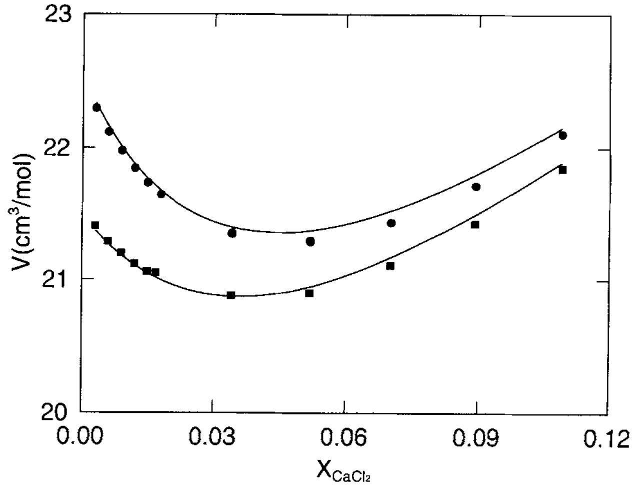

Figure 8. Molar volumes of aqueous $CaCl_2$ solutions calculated from the equation of state (——) vs. experimental data by Oakes et al. 525.36 K and 75.0 bar (●), and at 522.46 K and 405.0 bar (■).

Conclusions

A comprehensive equation of state is developed to provide accurate representation of saturated vapor pressures and densities of aqueous calcium chloride solutions at temperatures from 523 to 623 K. At higher temperatures there are no density data and the *P-T-x* data are less precise, but the saturated vapor pressures of liquid are represented satisfactorily. The completely undissociated model has proved to be convenient and rather successful.

However, the equation fails to represent vapor compositions in the range where there is substantial hydrolysis of the salt. A model, which takes this reaction into account, may be needed in order to accurately describe the vapor phase. On the other hand, more experimental data for vapor–liquid

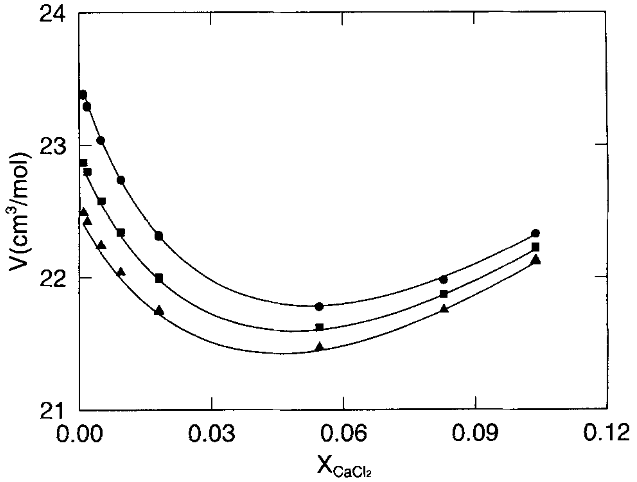

Figure 9. Molar volumes of aqueous $CaCl_2$ solutions calculated from the equation of state (——) vs. experimental data by Gates and Wood at 548.05 K and 108.6 bar (●), at 548.05 K and 247.2 bar (■), and at 548.05 K and 372.6 bar (▲).

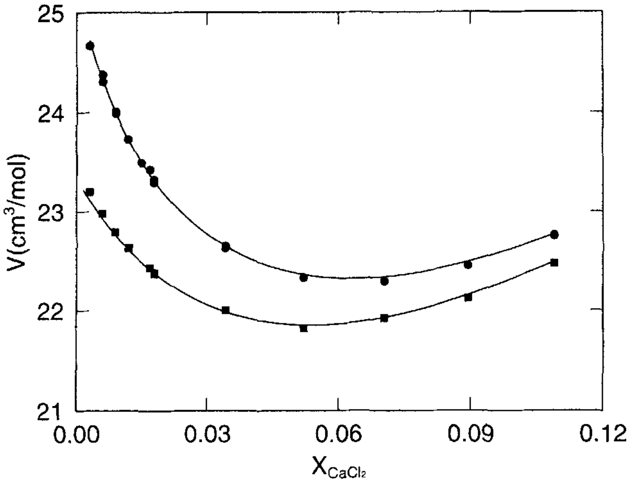

Figure 10. Molar volumes of aqueous $CaCl_2$ solutions calculated from the equation of state (——) vs. experimental data by Oakes et al. at 574.07 K and 104.0 bar (●), and at 572.05 K and 402.0 bar (■).

equilibria and densities, especially above the critical temperature of water, are needed for further development of an improved equation of state, which will be more accurate for extrapolation to a wider range of conditions and for prediction of vapor compositions as well.

Acknowledgments

This research was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Div. of Chemical Sciences and Div. of Engineering and Geosciences of the U.S. Department of Energy under contract No. DE-AC03-76SF00098. We would like to thank J. L. Bischoff and R. J. Rosenbauer for providing their unpublished results, S. T. Tkachenko for numerical data of their experimental results, and A. Anderko for helpful discussions.

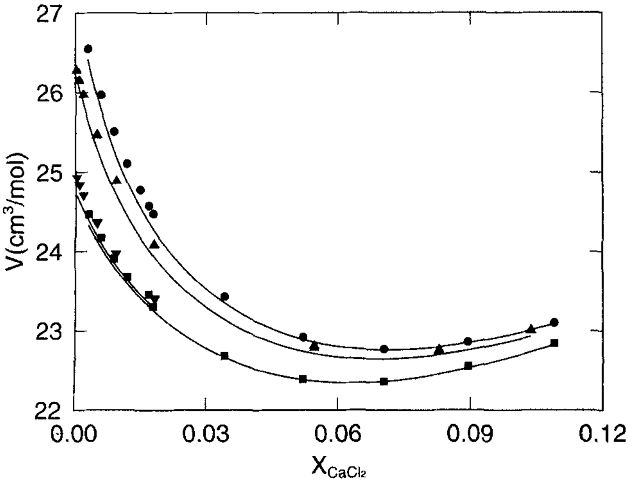

Figure 11. Molar volumes of aqueous $CaCl_2$ solutions calculated from the equation of state (——) vs. experimental data by Oakes et al. at 596.99 K and 124.0 bar (●), at 597.05 K and 397.0 bar (■), and by Gates and Wood at 597.45 K and 206.5 bar (▲), at 597.45 K and 388.5 bar (▼).

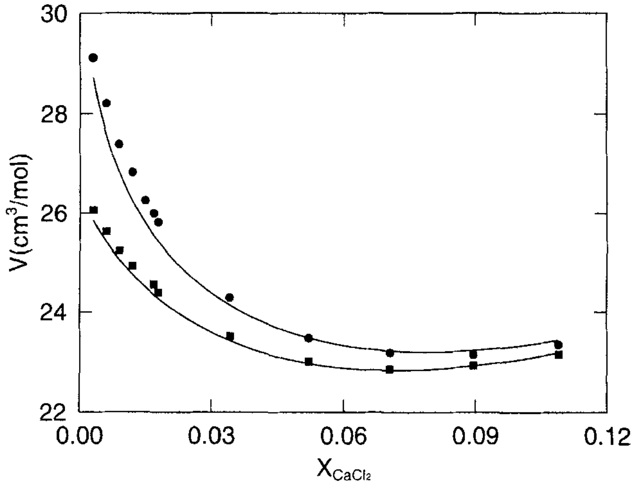

Figure 12. Molar volumes of aqueous $CaCl_2$ solutions calculated from the equation of state (——) vs. experimental data by Oakes et al. at 621.65 K and 172.0 bar (●), and at 621.75 K and 400.0 bar (■).

Notation

e^+, e^- = charge on a positive, negative ion
J = coefficient of the approximation for I
n = number of component; number of moles
N_A = Avogadro's number
P = pressure
Q = quadrupole moment
R = gas constant
x = mole fraction
Z = compressibility factor
π = constant (3.1415926)
ρ = density
σ = hard-sphere diameter

Superscripts and subscripts

ig = ideal gas
$*$ = reduced properties
c = critical
ddd = triple dipole
ddq = dipole–dipole–quadrupole
dqq = dipole–quadrupole–quadrupole
qqq = triple quadrupole

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Appendix

The electrostatic contribution to the compressibility factor for mixtures of dipolar hard spheres and quadrupolar hard spheres is given by

$$Z^{es} = \rho^* \left[\frac{\partial (a^{es}/RT)}{\partial \rho^*} \right]_{T,n_i}$$

$$= \rho^* \frac{\left(1 - \dfrac{2a_3}{a_2}\right) \dfrac{\partial (a_2/RT)}{\partial \rho^*} + \dfrac{\partial (a_3/RT)}{\partial \rho^*}}{\left(1 - \dfrac{a_3}{a_2}\right)^2} \tag{A1}$$

where

$$\frac{\partial (a_2/RT)}{\partial \rho^*} = -\frac{3}{2\pi} \left[\frac{x_1^2 \mu_1^{*4} b_1}{6b} \left(I_6^{hs} + \rho^* \frac{\partial I_6^{hs}}{\partial \rho^*} \right) + \frac{x_1 x_2 \mu_1^{*2} Q_2^{*2} b_1 b_2^{5/3}}{2 b_{12}^{5/3} b} \left(I_8^{hs} + \rho^* \frac{\partial I_8^{hs}}{\partial \rho^*} \right) + \frac{7 x_s^2 Q_2^{*4} b_1}{10b} \left(I_{10}^{hs} + \rho^* \frac{\partial I_{10}^{hs}}{\partial \rho^*} \right) \right] \tag{A2}$$

$$\frac{\partial(a_{3,2}/RT)}{\partial\rho^*} = \frac{3}{2\pi}\frac{36x_2^2Q_2^{*6}b_2}{245b}\left(I_{15}^{hs} + \rho^*\frac{\partial I_{15}^{hs}}{\partial\rho^*}\right) \quad \text{(A3)}$$

$$\frac{\partial(a_{3,3}/RT)}{\partial\rho^*} = \left[\frac{x_1^3\mu_1^{*6}b_1^2}{54b^2}\left(2I_{ddd}^{hs} + \rho^*\frac{\partial I_{ddd}^{hs}}{\partial\rho^*}\right)\right.$$

$$+ \frac{x_1^2x_2\,\mu_1^{*4}Q_2^{*2}b_1^{5/3}b_2^{5/3}}{480b_{12}^{4/3}b^2}\left(2I_{ddq}^{hs} + \rho^*\frac{\partial I_{ddq}^{hs}}{\partial\rho^*}\right) + \frac{x_1x_2^2\,\mu_1^{*2}Q_2^{*4}b_1b_2^{7/3}}{640b_{12}^{4/3}b^2}$$

$$\left.\times\left(2I_{dqq}^{hs} + \rho^*\frac{\partial I_{dqq}^{hs}}{\partial\rho^*}\right) + \frac{x_2^3Q_2^{*6}b_2^2}{6{,}400b^2}\left(2I_{qqq}^{hs} + \rho^*\frac{\partial I_{qqq}^{hs}}{\partial\rho^*}\right)\right]\rho^*. \quad \text{(A4)}$$

$(\partial I_k^{hs}/\partial\rho^*)$ (k = 6, 8, 10, 15, *ddd*, *ddq*, *dqq*, *qqq*) can be readily obtained by differentiating Eq. 16 with respect to the density ρ^* and coefficients of Eq. 16 are listed in Table 1.

The electrostatic contribution to the chemical potential of component 1 is given by

$$\frac{\mu_1^{es}}{RT} = \left[\frac{\partial(na^{es}/RT)}{\partial n_1}\right]_{\rho,T,n_{j\neq1}}$$

$$= \frac{\left(1-\dfrac{2a_3}{a_2}\right)\dfrac{\partial(na_2/RT)}{\partial n_1} + \dfrac{\partial(na_3/RT)}{\partial n_1}}{\left(1-\dfrac{a_3}{a_2}\right)^2} \quad \text{(A5)}$$

where

$$\frac{\partial(na_2/RT)}{\partial n_1} = -\frac{3\rho}{2\pi}\left\{\frac{\mu_1^{*4}b_1}{6}\left[2x_1I_6^{hs} + x_1^2\left(n\frac{\partial I_6^{hs}}{\partial n_1}\right)\right]\right.$$

$$+ \frac{\mu_1^{*2}Q_2^{*2}b_1b_2^{5/3}}{2b_{12}^{5/3}}\left[x_2I_8^{hs} + x_1x_2\left(n\frac{\partial I_8}{\partial n_1}\right)\right] + \frac{7Q_2^{*4}b_2}{10}$$

$$\left.\times\left[x_2^2\left(n\frac{\partial I_{10}^{hs}}{\partial n_1}\right)\right]\right\} \quad \text{(A6)}$$

$$\frac{\partial(na_{3,2}/RT)}{\partial n_1} = \frac{3\rho}{2\pi}\frac{36Q_2^{*6}b_2}{245}\left[x_2^2\left(n\frac{\partial I_{15}^{hs}}{\partial n_1}\right)\right] \quad \text{(A7)}$$

$$\frac{\partial(na_{3,3}/RT)}{\partial n_1} = \frac{3\rho^2}{2\pi}\left\{\frac{\mu_1^{*6}b_1^2}{54}\left[3x_1^2I_{ddd}^{hs} + x_1^3\left(n\frac{\partial I_{ddd}^{hs}}{\partial n_1}\right)\right]\right.$$

$$+ \frac{\mu_1^{*4}Q_2^{*2}b_1^{5/3}b_2^{5/3}}{480b_{12}^{4/3}}\left[2x_1x_2I_{ddq}^{hs} + x_1^2x_2\left(n\frac{\partial I_{ddq}^{hs}}{\partial n_1}\right)\right]$$

$$+ \frac{\mu_1^{*2}Q_2^{*4}b_1b_2^{7/3}}{640b_{12}^{4/3}}\left[x_2^2I_{dqq}^{hs} + x_1x_2^2\left(n\frac{\partial I_{dqq}^{hs}}{\partial n_1}\right)\right]$$

$$\left.+ \frac{Q_2^{*6}b_2^2}{6{,}400}\left[x_2^3\left(n\frac{\partial I_{qqq}^{hs}}{\partial n_1}\right)\right]\right\} \quad \text{(A8)}$$

and

$$n\frac{\partial I_k^{hs}}{\partial n_1} = \left[\frac{\partial(n\rho^*)}{\partial n_1} - \rho^*\right]\frac{\partial I_k^{hs}}{\partial\rho^*}$$

$$(k = 6, 8, 10, 15, ddd, ddq, dqq, qqq) \quad \text{(A9)}$$

$$\frac{\partial(n\rho^*)}{\partial n_1} = \frac{3\rho}{\pi}(x_1b_1 + x_2b_{12}). \quad \text{(A10)}$$

The electrostatic contribution to the chemical potential of component 2 is given by

$$\frac{\mu_2^{es}}{RT} = \left[\frac{\partial(na^{es}/RT)}{\partial n_2}\right]_{\rho,T,n_{i\neq2}}$$

$$= \frac{\left(1-\dfrac{2a_3}{a_2}\right)\dfrac{\partial(na_2/RT)}{\partial n_2} + \dfrac{\partial(na_3/RT)}{\partial n_2}}{\left(1-\dfrac{a_3}{a_2}\right)^2} \quad \text{(A11)}$$

where

$$\frac{\partial(na_2/RT)}{\partial n_2} = -\frac{3\rho}{2\pi}\left\{\frac{\mu_1^{*4}b_1}{6}\left[x_1^2\left(n\frac{\partial I_6^{hs}}{\partial n_2}\right)\right]\rho\right.$$

$$+ \frac{\mu_1^{*2}Q_2^{*2}b_1b_2^{5/3}}{2b_{12}^{5/3}}\left[x_1I_8^{hs} + x_1x_2\left(n\frac{\partial I_8}{\partial n_2}\right)\right]$$

$$\left.+ \frac{7Q_2^{*4}b_2}{10}\left[2x_2I_{10} + x_2^2\left(n\frac{\partial I_{10}^{hs}}{\partial n_2}\right)\right]\right\} \quad \text{(A12)}$$

$$\frac{\partial(na_{3,2}/RT)}{\partial n_2} = \frac{3\rho}{2\pi}\frac{36Q_2^{*6}b_2}{245}\left[2x_2I_{15} + x_2^2\left(n\frac{\partial I_{15}^{hs}}{\partial n_2}\right)\right] \quad \text{(A13)}$$

$$\frac{\partial(na_{3,3}/RT)}{\partial n_2} = \left(\frac{3\rho}{2\pi}\right)^2\left\{\frac{\mu_1^{*6}b_1^2}{54}\left[x_1^3\left(n\frac{\partial I_{ddd}^{hs}}{\partial n_2}\right)\right]\right.$$

$$+ \frac{\mu_1^{*4}Q_2^{*2}b_1^{5/3}b_2^{5/3}}{480b_{12}^{4/3}}\left[x_1^2I_{ddq}^{hs} + x_1^2x_2\left(n\frac{\partial I_{ddq}^{hs}}{\partial n_2}\right)\right] + \frac{\mu_1^{*2}Q_2^{*4}b_1b_2^{7/3}}{640b_{12}^{4/3}}$$

$$\times\left[2x_1x_2I_{dqq}^{hs} + x_1x_2^2\left(n\frac{\partial I_{dqq}^{hs}}{\partial n_2}\right)\right] + \frac{Q_2^{*6}b_2^2}{6{,}400}$$

$$\left.\times\left[3x_2^2I_{qqq} + x_2^3\left(n\frac{\partial I_{qqq}^{hs}}{\partial n_2}\right)\right]\right\} \quad \text{(A14)}$$

and

$$n\frac{\partial I_k^{hs}}{\partial n_2} = \left[\frac{\partial(n\rho^*)}{\partial n_2} - \rho^*\right]\frac{\partial I_k^{hs}}{\partial\rho^*}$$

$$(k = 6, 8, 10, 15, ddd, ddq, dqq, qqq) \quad \text{(A15)}$$

$$\frac{\partial(n\rho^*)}{\partial n_2} = \frac{3\rho}{\pi}(x_1b_{12} + x_2b_2). \quad \text{(A16)}$$

Manuscript received Nov. 28, 1994, and revision Mar. 2, 1995.