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EQUATION OF STATE FOR PURE SODIUM CHLORIDE

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ABSTRACT

An equation of state for pure sodium chloride has been developed on the basis of experimental data and results of Monte Carlo simulations for the restricted primitive model (RPM). The experimental data base included limited vapor pressure and saturated liquid density data as well as dimerization equilibrium constants. The liquid densities have been extrapolated to the supercooled region using liquid-phase Monte Carlo data. For this purpose, the parameters of the primitive model have been calculated by assuming that sodium chloride and RPM obey the corresponding states principle over a limited range of conditions. In the near-critical region Monte Carlo data as well as results of cluster calculations have been used with parameters scaled to reproduce the critical temperature obtained by extrapolating saturation data. The RPM parameters employed in the calculations are close to those for crystalline NaCl. The experimental and scaled Monte Carlo data have been reproduced within their accuracy using a van der Waals-type equation of state with two temperature-dependent parameters a and b. The functions representing the temperature dependence of the parameters have been designed to ensure reliable extrapolation to lower and higher temperatures. Formation of Na_2Cl_2 clusters has been allowed for by using a closed-form term representing the effect of association on the compressibility factor. The performance of the equation has been additionally verified by predicting compressibility factors at low reduced temperatures outside the saturation region and comparing them with scaled Monte Carlo data.

INTRODUCTION

Much attention has been focussed on the high-temperature, high-pressure behavior of aqueous mixtures containing sodium chloride primarily because of their importance in many geological as well as steam-power processes. Although several successful thermodynamic models are available for some restricted ranges of P, T, and x, it is desirable to develop a more comprehensive method of treating such

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mixtures. For this purpose, it is prerequisite to have a convenient representation of the properties of pure fluid sodium chloride. In an earlier paper, Pitzer (1984) analyzed the properties of pure sodium chloride with emphasis on the estimation of critical properties. In this study, we shall extend this treatment by including critically evaluated experimental data as well as results of simulations for the restricted primitive model (RPM) as a model ionic fluid. The results will be summarized in the form of a simple analytical equation of state that is suitable for interpolating as well as extrapolating the available PVT data.

EXPERIMENTAL DATA

Only fragmentary experimental data are available for pure fluid NaCl. Liquid densities are available from the melting point (1073 K) to 1720 K. In this study, the most extensive data of Kirshenbaum et al. (1962) have been used. These data are in reasonable agreement with results of earlier investigations cited by Kirshenbaum et al. The liquid densities can be satisfactorily reproduced by a linear function of temperature.

$$d/(\mathrm{g{\cdot}cm^{-3}}) = 2.061(1 - T/4330.7) \qquad (1)$$

In general, a linear relationship between liquid density and temperature is frequently found for molten alkali halides at temperatures not too near the critical value (e.g. Adams and McDonald, 1975).

The available vapor pressure data show some lack of agreement. The discrepancies between the data of Wartenberg and Albrecht (1921), Ruff and Mugden (1921) and Barton and Bloom (1956) are about 5-10% between 1430 and 1540 K, with Barton and Bloom's data having intermediate values. At higher temperatures (1540 - 1720 K) the data of Wartenberg and Albrecht and Ruff and Mugden are in closer agreement (ca 2%). The data of Fiock and Rodebush (1926) are significantly different than the remaining data sets. Therefore, we adopted the data of Barton and Bloom in the temperature range of 1340-1540 K and the data of Wartenberg and Albrecht (1921) and Ruff and Mugden (1921) in the range 1540-1720 K. Unfortunately, no vapor pressure data are available above the normal boiling point of NaCl, which is around 1720 K.

Sodium chloride is known to dimerize in the vapor phase:

$$2\mathrm{NaCl} = \mathrm{Na_2Cl_2} \qquad (\mathrm{A})$$

Molecular parameters are available from spectroscopic measurements for the monomer NaCl and the dimer Na_2Cl_2, although the dimer's properties are subject to a greater uncertainty because of the absence of vibrational anharmonicity data (Stull and Prophet, 1971). The molecular parameters permit a statistical calculation of the ideal-gas thermodynamic properties of both NaCl and Na_2Cl_2. We used the K_f(NaCl) and K_f(Na_2Cl_2) values reported by Stull and Prophet (1971) to calculate the equilibrium constants for the dimerization reaction

$2NaCl = Na_2Cl_2$. The dimerization constants can be represented over the temperature range 600-4000 K by the equation:

$$\ln K = c_1/T + c_2 + c_3 \ln T + c_4 T \qquad (2)$$

The parameters $c_1, \ldots c_4$ are listed in Table 1. Mass spectrometric studies suggest that higher multimers can be neglected (c.f. Stull and Prophet, 1971), although cluster calculations indicate small but significant amounts of trimer at higher temperatures (Pitzer and Schreiber, 1987; Gillan, 1983).

TABLE 1

Parameters of the equation of state for sodium chloride (eqs. 2 and 12-13)

i	c_i	A_i	B_i
1	205737.	0.41815	27.458
2	-189.21	0.31509	20.064
3	8.267	1.6069	89.268
4	-0.685 e-3	0.78029	0.73792
5		-24.904	-16.535

It should be noted that the present equation does not allow for the equilibrium between ion pairs (NaCl) and ions (Na^+ and Cl^-). An explicit treatment of ionic dissociation would unduly complicate the proposed equation; it can be treated by a separate calculation for any condition where it is significant. The dimerization of ion pairs (reaction A), however, is well documented and should be taken into account.

THE USE OF SIMULATION DATA

In view of the scarcity of experimental data, results of molecular simulation are also of value for establishing an equation of state for NaCl. As simple ionic fluids can be expected to follow the principle of corresponding states (Reiss et al., 1961), the simulated properties of model ionic fluids can be mapped on the real fluid properties using the corresponding-states techniques.

To make a corresponding-states analysis possible, it is necessary to use a considerably simplified intermolecular potential model. However, the model should take into account the essential characteristics of the physical system. Adams and McDonald (1975) analyzed the applicability of one-parametric corresponding states relations to molten salts. Although such relations are not accurate for a large group of salts, they are more appropriate when the class of salts is more restricted. Larsen (1976) showed that the thermodynamic properties of the restricted primitive model are in very good qualitative agreement with real molten salt properties, although the model parameters cannot be adjusted to quantitatively reproduce all properties of interest.

In this study, we will utilize the restricted primitive model because it fulfills the requirements for corresponding states behavior, i.e., it differs for various substances only by energy and distance scaling factors. Moreover, numerical data are available for the restricted primitive model in several regions of the PVT space including the liquid-like and near-critical regions. The restricted primitive model implies the potential

$$u_{ij} = z^2e^2/4\pi\epsilon_0\epsilon r \quad \text{for} \quad r > \sigma \tag{3}$$

$$u_{ij} = \infty \quad \text{for} \quad r < \sigma \tag{4}$$

Consequently, reduced variables can be defined as

$$c^* = N\sigma^3/V \tag{5}$$

$$\beta^* = \beta z^2e^2/4\pi\epsilon_0\epsilon\sigma \tag{6}$$

$$P^* = P\sigma^4(4\pi\epsilon_0\epsilon/z^2e^2) \tag{7}$$

with $\beta = 1/kT$, ϵ the dielectric constant (relative permittivity); in this case $\epsilon = 1$.

As discussed by Larsen (1976) and Pitzer (1984), it is not possible to adjust the parameters z and σ to accurately map the complete phase diagram of the restricted primitive model on the phase diagram of a real ionic fluid. The parameters cannot be uniquely determined because of their density and temperature dependence caused by interactions not represented by eqs. (3-4). However, if the ionic environment is similar in two states, these interactions are likely to cancel and a corresponding-states mapping may be possible. Therefore, we will use the corresponding-states technique separately for two regions: the high-density and near-critical regions.

Simulation data in the high-density region

Gillan (1983) obtained an equation for the saturated liquid density of the restricted primitive model:

$$c^* = 0.951(1 - 15.56/\beta^*) \tag{8}$$

Equation (8) is based on the Monte Carlo data of Larsen (1976) which are valid within the ranges $1.4 < \beta^* < 94$ and $0.29 < c^* < 0.75$.

Pitzer (1984) noted that eqs. (8) and (1) have identical forms, thus facilitating a numerical comparison based on the principle of corresponding states. A comparison of numerical coefficients leads to the model parameters $\sigma = 2.81_8$ Å and $z = 1.06_6$. The value of σ is close to the nearest neighbor distance in crystalline NaCl, and z is not much different from the true value of 1. These values of z and σ make it possible to evaluate from eq. (6) the lower limit of the temperature range for which eq. (1) can be assumed to be valid. This limit is around 720 K and is well below the melting temperature of NaCl (1073 K). Therefore, eq. (1) can be extrapolated by about 350 K into the supercooled liquid region, thus providing reliable estimates of supercooled liquid volumes. The availability of such estimates is important because our equation of state is intended to be used for mixture fluid phase equilibrium calculations at temperatures lower than the melting point of NaCl.

Simulation data in the near-critical region

Gillan (1983) calculated the properties of various clusters in the vapor phase for the restricted primitive model. Pitzer and Schreiber (1987) extended Gillan's theory by including the effects of inter-cluster interactions. They located the critical point by interpolating between their results for the vapor phase and Larsen's (1976) results for the liquid phase. Very recently, Valleau (1991) obtained Monte Carlo simulation data. The data of Pitzer and Schreiber (1987) and Valleau (1991) cover the temperature range $14 < \beta^* < 17$. They are shown in Figure 1 in the $1/\beta^*$ - c^* projection. Pitzer (1984) presented an estimate of the critical point of real fluid NaCl by interpolating between estimates of vapor density and extrapolated liquid densities obtained from the (1962) data of Kirshenbaum et al. This estimate is more reliable for critical temperature than for critical density or pressure.

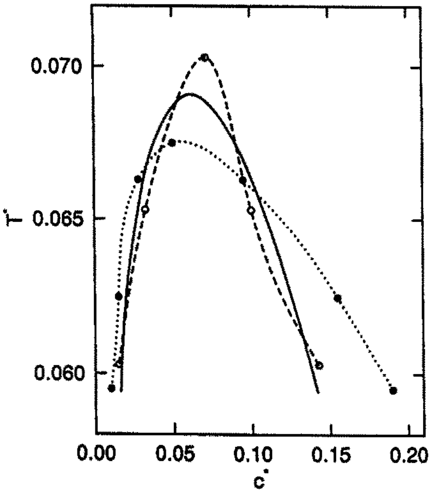

Figure 1. Vapor-liquid coexistence curve for an ionic fluid. The solid curve denotes the proposed equation of state with variables recalculated from T and V into $T^* = 1/\beta^*$ and c^*. The solid and open circles denote the results for the restricted primitive model obtained by Schreiber and Pitzer (1987) and Valleau (1991), repectively.

To include the near-critical data in the development of the equation of state, it was assumed that $z = 1$ and σ was allowed to vary in the vicinity of the value $\sigma = 2.8$ obtained from liquid density data. The equation-of-state parameters as well as σ were evaluated in the near-critical region by using the (β^*, c^*_{liq}, c^*_{vap}) values of Pitzer and Schreiber and those of Valleau, with a higher statistical weight for the latter. Additionally, the critical temperature was constrained to lie within the interval $3700 < T_c < 4000$ K, as suggested by Pitzer's (1984) analysis.

EQUATION OF STATE

The proposed analytical equation of state includes dimerization equilibria in an explicit form (Anderko, 1989)

$$z = z^{(ph)} + z^{(ch)} - 1 \tag{9}$$

where

$$z^{(ph)} = \frac{v}{v-b} - \frac{av}{RT[v(v+b)+b(v-b)]} \tag{10}$$

and

$$z^{(ch)} = \frac{2 - 2RTK/v}{1 - 4RTK/v + \sqrt{1+8RTK/v}} \tag{11}$$

The physical contribution to the compressibility factor $z^{(ph)}$ has a simple two-parameter form due to Peng and Robinson (1976), as a more sophisticated form would not be justified by the experimental data available. The chemical contribution $z^{(ch)}$ is calculated using the dimerization constant K defined by eq. (2). The method of including association equilibria into explicit van der Waals-type equations as well as the derivation of eq. (11) have been described by Anderko (1989, 1990, 1991). The temperature dependence of the parameters "a" and "b" has been expressed as

$$a \cdot 10^{-7} = A_1 + A_2 T_r + \frac{A_3}{1 + \exp[A_5(T_r - A_4)]} \tag{12}$$

$$b = B_1 + B_2 T_r + \frac{B_3}{1 + \exp[B_5(T_r - B_4)]} \tag{13}$$

where $T_r = T/T_c$ and v is the molar volume in $cm^3 \cdot mol^{-1}$. The coefficients $A_1, \ldots A_5$ and $B_1, \ldots B_5$ are listed in Table 1. The functions (12-13) have been designed so that both the "a" and "b" parameters could be safely extrapolated beyond the range of experimental data. The parameters are almost linear functions of temperature at low or high T_r with an s-shaped curvature in the intermediate range. Both parameters increase with temperature, which is unusual behavior in comparison with the temperature dependence of the van der Waals parameters for nonelectrolytes.

In the near-critical region, the simulation data have been represented with $\sigma = 3.01$. This value is close to the nearest neighbor distance in crystalline NaCl and is not much different from the value $\sigma = 2.818$ used to scale the high-density simulation data. The calculated critical coordinates of the proposed EOS are: T_c = 3841 K, V_c = 539 cm^3/mol and P_c = 182 bar. If these coordinates are recalculated into reduced variables (eqs. 5-7) using the values σ = 3.01 and z = 1, we obtain the reduced density $c_c^* = 0.061$, reduced reciprocal temperature $\beta_c^* = 14.5$ and reduced pressure $P_c^* = 0.00065$. These values can be compared with the estimates of Pitzer and Schreiber (1987): $c_c^* = 0.05$, $\beta_c^* = 14.7$ and $P_c^* = 0.0005$ and those of Valleau (1991): $c_c^* = 0.07$, $\beta_c^* = 14.2$ and $P_c^* = 0.0007$. It is evident that the critical point of the equation of state for NaCl agrees very well with the critical point of the restricted primitive model. Figure 1 compares the near-critical coexistence curve of our equation with those obtained from Pitzer and Schreiber's and Valleau's data.

The quality of representing experimental data (not the scaled simulation data) using the proposed EOS is illustrated in Table 2. The obtained deviations are well within experimental uncertainty.

TABLE 2

Representation of experimental data by means of the proposed EOS

$$(\delta Q = \frac{100}{N} \sum_{i=1}^{N} |1 - Q_i^{cal}/Q_i^{exp}|)$$

Property, Q	Ref.	T/K	δQ
Vapor pressure	a+b+c	1340-1723	2.5
Saturated liquid volume	d	1075-1670	0.1
Supercooled liquid volume	e	700-1075	0.3

a - Wartenberg and Albrecht (1921); b - Ruff and Mugden (1921); c - Barton and Bloom (1956); d - Kirshenbaum et al. (1962); e - extrapolated (see text).

A question may arise whether the proposed equation with the temperature dependence of parameters expressed by eqs. 12 and 13 is justified for the representation of the limited amount of data available. In fact, the Peng-Robinson EOS with the original temperature dependence of the "a" parameter and without the dimerization term can correlate the available vapor pressure and liquid density data with fairly good accuracy. The critical temperature and pressure values obtained from such correlation are ca. 3840 K and 650 bar, respectively. However, this critical pressure cannot be reconciled with the simulation data. For example, the critical temperature T_c = 3840 K and the critical parameter β_c^* = 14.5 can be matched using σ = 3.01 Å. If we use this value of σ and assume that P = 650 bar, we obtain $P_c^* = 0.0023$ from eq. (7). This value is very different from those obtained by Pitzer and Schreiber (1987) and Valleau (1991). Alternatively, we can assume that $P_c^* = 0.00065$ (which is an intermediate value between those reported by Pitzer and Schreiber and Valleau), $\beta_c^* = 14.5$ and $P_c = 650$ bar and calculate σ from eq. (7). The result is $\sigma = 1.97$ Å, which is much smaller than any reasonable value estimated from crystalline nearest-neighbor distances.

On the other hand, the more complex temperature dependencies of "a" and "b" (eqs. 12 and 13) make it possible to reproduce both experimental and simulation data as well as to include the dimerization equilibria.

DISCUSSION

It has been shown that simulation data, coupled with the corresponding states principle, can be used to supplement the scarce experimental data for sodium chloride. In order to additionally verify the adopted procedure, liquid-like volumes have been calculated outside the saturation region and compared with those obtained from scaled Monte Carlo data of Larsen (1976). Larsen's data have been recalculated from the β^* and c^* variables into the real-fluid T and V variables using the σ and z parameters determined from the corresponding-states treatment of saturated liquid volumes (i.e. $\sigma = 2.818$ Å and $z = 1.066$). Subsequently, volumes have been calculated from the proposed EOS to match the compressibility factor values tabulated by Larsen (1976).

The comparison has been limited to liquid-like volumes and the temperature range of experimental saturated liquid volume data. The results are shown in Table 3. Taking into account the high sensitivity of the compressibility factor to V and T in this region and the approximations involved in the corresponding-states treatment, the results can be considered as satisfactory.

TABLE 3

Liquid-like volumes outside the saturation calculated from the proposed EOS and those obtained from the restricted primitive model with the "σ" and "z" parameters scaled to reproduce saturated liquid volumes

c^*	β^*	T	$v/cm^3\ mol^{-1}$	
			RPM	EOS
0.4788	39.68	1698	56.32	56.28
0.6690	70.95	950	40.31	40.21
0.6690	35.48	1899	40.31	44.91
0.7534	68.17	988	35.80	35.51

It is believed that this equation summarizes all available information about sodium chloride in the fluid state. There remain many uncertainties, however, especially in the region above 1700 K, where there are no experimental data and we depend on extrapolations and various calculations for simplified models.

SUPPLEMENTARY NOTE

At the Eleventh Symposium on Thermophysical Properties where the present paper was presented, Panagiotopoulos presented Monte Carlo calculations for the RPM; his results, $\beta_c^* = 17.9$, $c_c^* = 0.04$, can be compared with those listed above. The difference from those of Valleau (1991) is surprisingly large. The two Monte Carlo calculations differed in several respects; the most likely cause of the discrepancy lies in the different methods used to account for interactions with particles outside the cell that was calculated in detail. For neutral particles with short range interparticle potentials, this is a small effect, while for ionic crystals with very high symmetry, special methods are known to be satisfactory. For the irregular structure of the ionic liquid, however, the methods used for crystals may be inaccurate. While the method of Pitzer and Schreiber (1987) is less precise, it appears to be reliable in indicating phase separation for β^* above 16. Thus, we believe the present treatment is optimum until the discrepancy between the two near-critical Monte Carlo calculations is resolved.

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