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Prediction of Densities of Concentrated Brines by Pitzer Theory[†]

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The virial coefficient approach of Pitzer has been used to estimate the densities and mean apparent molal volumes of very concentrated brines composed of aqueous NaCl-KCl-$MgCl_2$-$CaCl_2$ in the ionic strength range 8.3-9.6 mol kg^{-1} at 20-40 °C. The theory successfully predicts these properties in mixtures based on the coefficients of pure salts. The inclusion of binary interaction term improves the degree of prediction.

Introduction

The recently developed Pitzer formalism (*1*, *2*) can accurately predict the volume properties of single and mixed (aqueous NaCl-$CaCl_2$) electrolyte solutions. The purpose of this paper is to examine the applicability of Pitzer formalism to more complicated systems composed of concentrated brines like NaCl-KCl-$MgCl_2$-$CaCl_2$ at 20-40 °C, using experimental data of Krumgalz and Millero (*3*).

Pitzer Treatment and Method of Calculations

***Single Electrolytes*.** The Pitzer relation between apparent molal volume ϕ_V and molality of a salt type ${}^{M}\nu_m{}^{X}\nu_x$ can be given by

$$\phi_V = \phi_V{}^0 + \nu|Z_m Z_x|\frac{A_V}{2b}\ln(1 + bI^{1/2}) + 2\nu_m\nu_x RT[mB_{MX}{}^V + m^2(\nu_m\nu_x)^{1/2}C_{MX}{}^V] \quad (1)$$

where

$$B_{MX}{}^V = \left(\frac{\partial\beta^{(0)}}{\partial P}\right)_T + \left(\frac{\partial\beta^{(1)}}{\partial P}\right)_T(2/\alpha^2 I) \times [1 - (1 + I^{1/2})\exp(-\alpha I^{1/2})] \quad (2)$$

and

$$C_{MX}{}^V = \left(\frac{\partial C^\phi}{\partial P}\right)_T/2 \quad (3)$$

$$\alpha = 2.0\ (\mathrm{kg/mol})^{1/2}$$

$$b = 1.2\ (\mathrm{kg/mol})^{1/2}$$

$$R = 83.1441\ \mathrm{cm^3\ bar\ mol^{-1}\ K^{-1}}$$

A_V, Pitzer-Debye-Hückel limiting law slope (*4*), can be defined as

$$A_V = -4RT\left(\frac{\partial A_\phi}{\partial P}\right)_T \quad (4)$$

$$= 6RTA_\phi\left(\frac{\partial \ln D}{\partial P}\right) - \frac{\beta}{3} \quad (5)$$

The values of A_V used in the computations are 1.793, 1.875, 1.962, 2.055, and 2.153 $cm^3\ kg^{1/2}\ mol^{-3/2}$ at 20, 25, 30, 35, and 40 °C, respectively.

Pitzer coefficients $(\partial\beta^{(0)}/\partial P)_T$, $(\partial\beta^{(1)}/\partial P)_T$, and $(\partial C^\phi/\partial P)_T$ are evaluated for each salt by using eq 1 and holding $\phi_V{}^0$ constant.

***Mixtures of Electrolytes*.** The apparent molal volume ϕ_{Vi} of an ion in mixture can be written as

$$\phi_{Vi} = \phi_{Vi}{}^0 + \frac{Z_i{}^2 A_V}{2b}\ln(1 + bI^{1/2}) + RT\sum_i B_{ij}m_j + \frac{RT}{2|Z_i|^{1/2}}\sum_i C_{ij}m_J{}^2|Z_j|^{1/2} \quad (6)$$

where the sums are over all j ions of opposite charge to the i ion.

In eq 6, the interactions between cation and anion are considered. The present system has four cations and one anion, and thus it is necessary to evaluate the mixing term arising due to possible interactions between any two cations ($\theta_{ik}{}^V$) and two cations with anion ($\psi_{ijk}{}^V$). For an ion, one can write

$$\Delta\phi_{Vi} = RTm_k\theta_{ik}{}^V \quad (7)$$

where i and k are two different cations. Also

$$\theta_{ii}{}^V = \theta_{kk}{}^V = 0$$

The mixing term $\theta_{ik}{}^V$ is calculated from the difference ($\Delta\phi_V{}^*$) between experimental and predicted $\phi_V{}^*$ (mean apparent molal volume) as

$$\theta_{ik}{}^V = \frac{\Delta\phi_V{}^*(m_1 + m_2)}{RTm_1m_2(\nu_i + \nu_k)} \quad (8)$$

where m_1 and m_2 are molalities of salts whose cations are under consideration for interactions and ν_i and ν_k are moles of i and k, respectively, in moles of salt 1 and 2.

The ternary interaction term $\psi_{ijk}{}^V$ for the interaction among any two cations and one anion can be derived the same way.

$$\Delta\phi_{Vi} = RT\sum_k m_k\sum_j m_j\psi_{ijk}{}^V \quad (9)$$

where k = same charge as on i and j = opposite charge as on i. The extended Pitzer equation for ϕ_{Vi} can be written as

$$\phi_{Vi} = \text{right-hand side of eq 6} + RT\sum_k\theta_{ik}{}^V m_k + RT\sum_k m_k\sum_j m_j\psi_{ijk}{}^V \quad (10)$$

where in the second term $\sum_k$ indicates sum over all the ions of the same charge as on i. In the third term, the sum is over all the ions of the same charge as on i.

General Equations

ϕ_{Vi}, evaluated by eq 6, can be combined to give the apparent molal volume of a salt (ϕ_{Vj}) in a mixture of ionic strength I as

$$\phi_{Vj} = \sum_i\nu_i\phi_{Vi} \quad (11)$$

which could be converted to mean apparent molal volume of mixtures, $\phi_V{}^*$ by

$$\phi_{V_{pred}}{}^* = \sum_j m_j\phi_{Vj}/\sum_j m_j \quad (12)$$

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Table I. Pitzer Coefficients

salt	terms	20 °C	25 °C	30 °C	35 °C	40 °C
NaCl	$\phi_v{}^0$, cm^3/mol^{-1}	15.91 ± 0.02	16.58 ± 0.04	17.01 ± 0.01	17.30 ± 0.07	17.70 ± 0.01
	$\partial\beta^{(0)}/\partial P \times 10^5$	1.37 ± 0.02	1.14 ± 0.04	1.28 ± 0.02	0.95 ± 0.09	1.03 ± 0.02
	$\partial\beta^{(1)}/\partial P \times 10^5$	1.21 ± 0.17	1.15 ± 0.39	2.88 ± 0.13	0.04 ± 0.73	2.90 ± 0.11
	$\partial C^\phi/\partial P \times 10^6$	−1.51 ± 0.03	−1.11 ± 0.08	−1.45 ± 0.05	−1.03 ± 0.20	−1.09 ± 0.04
	σ, $cm^3\ mol^{-1}$	0.005	0.005	0.01	0.02	0.005
KCl	$\phi_v{}^0$, $cm^3\ mol^{-1}$	26.90 ± 0.01	26.90 ± 0.03	27.03 ± 0.02	27.36 ± 0.01	27.56 ± 0.02
	$\partial^{(0)}/\partial P \times 10^5$	1.68 ± 0.08	1.57 ± 0.24	1.59 ± 0.06	1.60 ± 0.04	1.61 ± 0.07
	$\partial\beta^{(1)}/\partial P \times 10^6$	0.42 ± 0.30	−0.11 ± 0.80	−0.16 ± 0.32	0.18 ± 0.29	−0.19 ± 0.35
	$\partial C^\phi/\partial P \times 10^6$	−2.75 ± 0.50	−2.74 ± 1.02	−2.69 ± 0.25	2.81 ± 0.22	−3.10 ± 0.27
	σ, $cm^3\ mol^{-1}$	0.005	0.02	0.01	0.005	0.01
$MgCl_2$	$\phi_v{}^0$, $cm^3\ mol^{-1}$	15.76 ± 0.02	14.16 ± 0.01	14.11 ± 0.08	14.67 ± 0.09	15.04 ± 0.10
	$\partial\beta^{(0)}/\partial P \times 10^5$	2.34 ± 0.05	1.78 ± 0.01	1.76 ± 0.06	1.87 ± 0.05	1.99 ± 0.08
	$\partial\beta^{(1)}/\partial P \times 10^5$	−11.11 ± 1.3	−6.38 ± 0.13	−10.20 ± 8.1	−14.26 ± 1.00	−18.32 ± 8.10
	$\partial C^\phi/\partial P \times 10^6$	−3.05 ± 0.18	−1.82 ± 0.03	−2.04 ± 0.15	−2.36 ± 0.08	−2.69 ± 0.20
	σ, $cm^3\ mol^{-1}$	0.01	0.02	0.008	0.005	0.01
$CaCl_2$	$\phi_v{}^0$, $cm^3\ mol^{-1}$	17.13 ± 0.16	18.53 ± 0.28	18.51 ± 0.30	19.50 ± 0.88	20.45 ± 0.75
	$\partial\beta^{(0)} \times 10^6$	14.99 ± 0.84	15.64 ± 1.91	13.61 ± 1.05	16.62 ± 2.04	11.95 ± 0.94
	$\partial\beta^{(1)}/\partial P \times 10^5$	0.59 ± 0.17	−10.48 ± 3.37	−6.50 ± 2.12	−1.10 ± 7.35	−12.09 ± 1.90
	$\partial C^\phi/\partial P \times 10^7$	−8.45 ± 1.63	−8.82 ± 3.20	−8.08 ± 2.04	−8.61 ± 3.20	−6.01 ± 1.83
	σ, $cm^3\ mol^{-1}$	0.01	0.30	0.10	0.25	0.20

Table II. Standard Deviation (σ) of Fit of Mixture Data at Various Temperatures

temp, °C	$(d - d_0) \times 10^3$, g cm^{-3}	ϕ_V,[a] $cm^3\ mol^{-1}$
20	0.36 (0.10)	0.07 (0.03)
25	0.31 (0.08)	0.05 (0.02)
30	0.30 (0.08)	0.05 (0.02)
35	0.31 (0.08)	0.06 (0.03)
40	0.33 (0.09)	0.06 (0.03)

[a] Values in parentheses are σ, calculated by using mixing terms listed in Table III.

Table III. Values of $\theta_{ik}{}^V$ Used in the Mixture Calculations

i	k	$\theta_{ik}{}^V \times 10^6$	i	k	$\theta_{ik}{}^V \times 10^6$
Na	K	7.1	K	Mg	7.2
Na	Mg	1.4	K	Ca	9.1
Na	Ca	3.3	Mg	Ca	3.4

where $\sum_j$ indicates sum over salts. The density of mixture, d, is then computed by employing the following equation

$$d = \frac{1000 + \sum_j m_j M_j}{1000 d_0 + \sum_j m_j \phi_{Vj}} \tag{13}$$

d_0, the density of pure water at various temperatures, is given elsewhere (*5*).

The experimentally measured densities of Krumgalz and Millero (*3*) were converted to $\phi_{V_{\text{exptl}}}{}^*$ as

$$\phi_{V_{\text{exptl}}}{}^* = \frac{1000(d_0 - d)}{\sum_j m_j d d_0} + \frac{\sum_j m_j M_j}{d \sum_j m_j} \tag{14}$$

Results and Discussion

The Pitzer coefficients of NaCl, KCl, $MgCl_2$, and $CaCl_2$ calculated by using nonlinear least-squares method and eq 1–3 are listed in Table I. ϕ_V data for these pure salts were taken from elsewhere (*2*, *6*, *7*) or calculated by the equation of Lo Sourdo et al. (*8*). Except for $CaCl_2$, Pitzer equation gives a good fit up to concentrated solution at various temperatures. Phutela and Pitzer (*9*) have recently discussed the problem associated with the concentrated solutions of $CaCl_2$, supported by neutron scattering studies (*10*). A more accurate ϕ_V equation is needed for $CaCl_2$ in future. Unlike NaCl and KCl, $MgCl_2$ and $CaCl_2$ gave better fit with $(\partial\beta^{(1)}/\partial P)_T$ term. We have used all these terms in our calculations.

Table II summarizes the results of calculations in mixtures (75 data points) at various temperatures in terms of standard deviation between experimental values of Krumgalz and Millero (*3*) and predicted ones. Apparent molal volume of an ion ϕ_{Vi} in mixture was calculated from eq 6 and by using the Pitzer coefficients evaluated by eq 1–3. It is clear from this table that relative densities can be predicted within 0.1% and $\phi_V{}^*$ to 0.25%—a good estimation for most practical purposes. These predictions are based solely on the Pitzer coefficients derived from single salt analysis.

Since the ionic strengths of various solutions were reasonably high, we attempted to evaluate various binary ($\theta_{ik}{}^V$) and ternary ($\psi_{ijk}{}^V$) terms. $\theta_{ik}{}^V$ terms determined by eq 8 are listed in Table III. In the present study, these terms were considered ionic strength independent due to the narrow ionic strength range. These terms showed a very mild change with temperature and their values varied within 8% in the temperature range of 20–40 °C. Equation 10 minus the last term was employed in computing ϕ_{Vi} in the mixture to account for the effect of the binary mixing term in fitting the data. The use of these terms, determined at 30 °C, made a remarkable improvement in fit; one now can predict the relative density and $\phi_V{}^*$ to within 0.04 and 0.11%, respectively. The contribution due to ternary interaction terms was negligible.

The excess volumes of these systems were also examined by using the following expression.

$${}_mV^E = \phi_{V_{\text{exptl}}}{}^* \sum_j m_j - \sum_j \phi_{Vj} m_j \tag{15}$$

The excess volumes were negative throughout and very small. They could not yield any substantial information due to the narrow range of ionic strength.

In the foregoing, the Pitzer theory emerges as a powerful working tool for predicting the volume properties of a concentrated mixture of four salts.

Registry No. NaCl, 7647-14-5; KCl, 7447-40-7; $MgCl_2$, 7786-30-3; $CaCl_2$, 10043-52-4.

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