Extension of Chen's (1982) Theory to Correlate Densities of Aqueous Electrolytes

The model proposed by Chen et al. for treating nonideality in concentrated electrolyte solutions has been extended to the correlation of the densities of solutions of single electrolytes (1:1, 2:1, 1:2, and 2:2) in terms of Chen's energy interaction parameters $\tau_{ca,m}$ and $\tau_{m,ca}$. At any single temperature, only three adjustable parameters, $\overline{V}_2^\circ$ (the partial molar volume of the solute at infinite dilution), and the pressure derivatives $(\partial\tau_{ca,m}/\partial p)_T$ and $(\partial\tau_{m,ca}/\partial p)_T$ are required for correlating the density as effectively as the conventional treatment employing a power series in (molality)$^{1/2}$. For some electrolytes, only the latter two parameters are required, as tabulated $\overline{V}_2^\circ$ values also lead to satisfactory correlations. The treatment can be extended to cover the temperature range 0-100°C, using either $\tau_{ca,m}$ and $\tau_{m,ca}$ values derived from activity or osmotic coefficients, or constant $\tau_{ca,m}$ and $\tau_{m,ca}$ values, but the irregular variation with temperature of the pressure derivatives precludes their representation by simple analytical functions, and individual values of the pressure derivatives at each temperature are necessary.

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Introduction

The PVT properties of concentrated aqueous electrolytes, singly and in mixtures, are of considerable practical and theoretical importance, and much work has gone into data correlation of solution densities (Rogers and Pitzer, 1982; Lo Surdo et al., 1982; Kumar and Atkinson, 1983; Kumar, 1986; Connaughton et al., 1986). A power series in (molality)$^{1/2}$ is usually employed for correlation, the coefficients in the equations being polynomial functions of temperature. An adequate description may require a large number of parameters; for example, for $MgCl_2$, over the molality range 0–5 *m*, six parameters are required to fit the density at 25°C, rising to 16 parameters to cover the range 0–95°C (Connaughton et al., 1986). Apparent molar volumes and specific volumes are well correlated by Pitzer's equations (Rogers and Pitzer, 1982), $MgCl_2$ requiring four parameters at 25°C, and 15 parameters for the range 0–95°C (Connaughton et al., 1986).

The objective in the present work was to extend a recently developed theory for nonideality in electrolyte solutions (Chen et al., 1982), which employed only two adjustable parameters, to the correlation of the densities of concentrated electrolyte solutions, with the aims of both reducing the number of parameters necessary for a satisfactory correlation, and of decreasing the number of figures requiring tabulation. Because some of the coefficients for the power series treatment are positive, and some negative, many figures are lost in the calculations, and some 10 significant figures need to be tabulated for each coefficient (Connaughton et al., 1986).

Differentiation of Chen's expression for Gibbs energy led to an equation for the volume of a solution, from which (and the molality) the density could be evaluated. Using Chen's energy interaction parameters $\tau_{ca,m}$ and $\tau_{m,ca}$, three adjustable parameters, $\overline{V}_2^\circ$ (the partial molar volume of the solute at infinite dilution), and the pressure derivatives, $(\partial\tau_{ca,m}/\partial p)_T$ and $(\partial\tau_{m,ca}/\partial p)_T$, were required for density correlation at each temperature, comparable in precision to that from the power series treatment. Because the equations for Gibbs energy in Chen's treatment are nonlinear in the energy interaction parameters $\tau_{ca,m}$ and $\tau_{m,ca}$, these parameters remain in the equations for density, leading to the intriguing possibility of evaluating these energy parameters, and hence of evaluating activity or osmotic coefficients, from density measurements alone. Unfortunately, the strong cross-correlation between the τ values, and their pressure derivatives, leads to an inherently ill-conditioned situation, requiring the provision of the two τ values in order to evaluate the three adjustable parameters. However, simplification was possible, in that Chen's published τ values could be replaced by constant values within a wide range, without significant deterioration of the correlation, at any temperature from 0 to 100°C. The parameter $\bar{V}_2^\circ$ could be replaced by a tabulated value or could be represented by a three-parameter equation, over this temperature range, but the pressure derivatives, $(\partial\tau_{ca,m}/\partial p)_T$ and $(\partial\tau_{m,ca}/\partial p)_T$ showed irregular behavior and could not be adequately represented as a simple analytical function of temperature.

Using the method described herein, the density of a solution of a 1:1, 1:2, 2:1, or 2:2 electrolyte can be satisfactorily correlated by an equation with only two adjustable parameters, if $\bar{V}_2^\circ$ is obtained from tables, or, at most, three parameters (three to four significant figures each) at any temperature in the range 0–100°C, and at ionic strength up to about 6 *m*.

Extension of Chen's Model to Densities

Recently, Chen et al. (1982) developed a local composition model for electrolyte solutions and successfully applied it to data correlation for activity coefficients and osmotic coefficients, vapor pressures, solubilities, and phase equilibria (Chen and Evans, 1986; Mock et al., 1986). The model covers the entire concentration range up to fused salts, and applies to mixed as well as single-component solvents. In aqueous solutions, with the nonrandom parameter α fixed at 0.2, only two energy parameters, $\tau_{ca,m}$ and $\tau_{m,ca}$ (readily evaluated from experimental activity or osmotic coefficients or vapor pressures), are required for each electrolyte; the numerical values vary somewhat depending on which observed property is used for regression. Thus, for NaCl at 25°C, the values of $\tau_{c,am}$ and $\tau_{m,ca}$ are -4.549 and 8.885 from activity coefficients (Chen et al., 1982), -4.5916 and 9.0234 from osmotic coefficients (Chen and Evans, 1986), and -4.678 and 9.693 from vapor pressures (Mock et al., 1986).

The most extensive list of τ values is that obtained from regression on (ln) activity coefficients (Chen et al., 1982), hereafter referred to as τ_a values. For NaCl, and other 1:1 electrolytes, activity and osmotic coefficients can be estimated with comparable precision using either these τ_a values or τ values obtained by regression on osmotic coefficients (Chen and Evans, 1986); the latter are denoted here as τ_o values. τ_v values, evaluated from regression on vapor pressures but omitting the long-range interactions, give good results for osmotic coefficients, but poorer agreement for activity coefficients. The list of τ_v values is not extensive, and only that for NaCl is used here.

In extending the treatment to mixtures in the second and third papers, Chen found it convenient to employ a redefined local composition. For other than 1:1 electrolytes, this alters the expressions for free energy, activity, and osmotic coefficients so that, for such electrolytes, Chen's τ_a values can only be used with equations of the form of Eqs. 23–25 (Chen et al., 1982), while τ_o and τ_v values are appropriate for equations of the form of Eqs. 34–36 (Chen and Evans, 1986); for 1:1 electrolytes the two sets of equations are equivalent. It is shown below that Chen's model can be extended to provide satisfactory density correlations for single electrolytes, and that the choice of τ values is much less critical than it is for evaluating activity or osmotic coefficients. Three additional parameters are required, namely the pressure derivatives $(\partial\tau_{ca,m}/\partial p)_T$ and $(\partial\tau_{m,ca}/\partial p)_T$, and $\bar{V}_2^\circ$, the partial molar volume of the solute at infinite dilution. These parameters are readily evaluated from density vs. molality data.

Evaluation of the Pressure Derivatives and $\bar{V}_2^\circ$

Following Pitzer (Rogers and Pitzer, 1982) the Gibbs energy G of an aqueous electrolyte solution of molality m containing n_2 moles of solute dissolved in n_1 moles of water is given by

$$G = n_1\bar{G}_1^\circ + n_2\bar{G}_2^\circ + G^{ex} + \nu n_2 RT(\ln m - 1) \tag{1}$$

Here $\bar{G}_1^\circ$ and $\bar{G}_2$ are the molar Gibbs energies of water and salt respectively, G^{ex} the excess Gibbs energy, and ν the number of moles of ions produced from one mole of salt. Further, the volume V is given by

$$V = (\partial G/\partial p)_T = n_1\bar{V}_1^\circ - n_2\bar{V}_2^\circ + (\partial G^{ex}/\partial p)_T \tag{2}$$

where $\bar{V}_1^\circ$ and $\bar{V}_2^\circ$ are the molar volumes of pure water and salt, respectively. At 25°C, for 1 kg of water, with volumes in cm^3,

$$V = 1{,}002.964 + m\bar{V}_2^\circ + (55.508 + \nu m)(\partial g^{ex*}/\partial p)_T \tag{3}$$

where g^{ex*} is the molar excess Gibbs energy, normalized to the hypothetical ideal unimolal standard state, and the value of $n_1\bar{V}_1^\circ$ is calculated from Kell's equation (Kell, 1975).

Chen's local composition model gives, for the molar excess Gibbs energy of an electrolyte solution, the expression

$$g^{ex*} = g^{ex*,pdh} + g^{ex*,lc} \tag{4}$$

For a solution containing 1 kg of water, the long-range interaction contribution $g^{ex*,pdh}$, based on the Pitzer-Debye-Huckel treatment, is given by

$$g^{ex*,pdh} = -4RT\frac{7.45}{\rho}A_\phi I_x \ln(1 + \rho I_x^{1/2}) \tag{5}$$

where A_ϕ and ρ are the Debye-Huckel parameters for osmotic coefficient and ion size, respectively, and I_x is the ionic strength on the mole fraction scale, $I_x = \frac{1}{2}\Sigma x_i z_i^2$. From Eq. 5,

$$(\partial g^{ex*,pdh}/\partial p)_T = DH = \frac{7.45}{\rho}A_v I_x \ln(1 + \rho I_x^{1/2}) \tag{6}$$

where $A_v = -4RT(\partial A_\phi/\partial p)_T = 1.875\ \text{cm}^3 \cdot \text{mol}^{-1}$ at 25°C (Rogers and Pitzer, 1982). Chen's expression for $g^{ex*,lc}$, after separating the $\tau_{ca,m}$ and $\tau_{m,ca}$ terms, and using the modified definition of local composition adopted in the two later papers (Chen and Evans, 1986; Mock et al., 1986), becomes

$$g^{ex*,lc} = 2RTX_c\left[G_{ca,m}\tau_{ca,m}\left(\frac{X_m}{\theta_1} - 1\right) - \frac{\tau_{m,ca}X_c}{\theta_2}\right] \tag{7}$$

where

$$\theta_1 = X_m + 2X_cG_{ca,m} = X_m + 2X_aG_{ca,m}$$

and

$$\theta_2 = X_a + X_mG_{m,ca} = X_c + X_mG_{m,ca}$$

The definition of local composition given by Chen et al. (1982) leads to the equation,

$$\begin{aligned} g^{ex*,lc} = RT\Bigg\{&G_{ca,m}\tau_{ca,m}(x_c + x_a)\left[\frac{x_m}{\beta_1} - 1\right] \\ &+ \tau_{m,ca}\left[x_mG_{m,ca}\left(\frac{z_cx_c}{\beta_2} + \frac{z_ax_a}{\beta_3}\right) - (z_cx_c + z_ax_a)\right]\Bigg\} \end{aligned} \tag{8}$$

where

$$\beta_1 = x_m + (x_c + x_a)G_{ca,m}$$

$$\beta_2 = x_a + x_m G_{m,ca}$$

$$\beta_3 = x_c + x_m G_{m,ca}$$

Appropriate differentiation of Eq. 7 or 8 leads to the expressions mentioned above for evaluation of activity or osmotic coefficients, (Chen and Evans, 1986, Eqs. 34–36 from Eq. 7, and Chen et al., 1982, Eqs. 23–25 from Eq. 8). The volume of the solution, and from it the density, can be evaluated, as in Eq. 2 or 3 above, by combining the pressure derivatives of Eq. 7 or 8 with Eq. 6.

Differentiation, with respect to p at constant T, of Eq. 7 gives

$$(\partial g^{ex*,lc}/\partial p)_T = RT[A_1(\partial \tau_{ca,m}/\partial p)_T + B_1(\partial \tau_{m,ca}/\partial p)_T] \quad (9)$$

where

$$A_1 = 2X_c G_{ca,m}\left[\frac{X_m}{\theta_1}\left(1 - \frac{\alpha \tau_{ca,m} X_m}{\theta_1}\right) - (1 - \alpha \tau_{ca,m})\right] \quad (10)$$

and

$$B_1 = 2X_c\left[\frac{X_m G_{m,ca}}{\theta_2}\left(1 - \frac{\alpha X_c \tau_{m,ca}}{\theta_2}\right) - 1\right] \quad (11)$$

while Eq. 8 gives

$$(\partial g^{ex*,lc}/\partial p)_T = RT[A_2(\partial \tau_{ca,m}/\partial p)_T + B_2(\partial \tau_{m,ca}/\partial p)_T] \quad (12)$$

where

$$A_2 = G_{ca,m}(x_c + x_a)\left[\frac{x_m}{\beta_1}\left(1 - \frac{\alpha \tau_{ca,m} x_m}{\beta_1}\right) - (1 - \alpha \tau_{ca,m})\right] \quad (13)$$

and

$$B_2 = x_m G_{m,ca}\left[\frac{z_c x_c}{\beta_2}\left(1 - \frac{\alpha x_a \tau_{m,ca}}{\beta_2}\right) + \frac{z_a x_a}{\beta_3}\left(1 - \frac{\alpha x_c \tau_{m,ca}}{\beta_3}\right) - (z_c x_c + z_a x_a)\right] \quad (14)$$

Hence, at 25°C,

$$V = 1{,}002.964 + m\overline{V}_2^\circ + (55.508 + \nu m) \cdot \{DH + RT[A_i(\partial \tau_{ca,m}/\partial p)_T + B_i(\partial \tau_{m,ca}/\partial p)_T]\} \quad (15)$$

using A_1 and B_1 or A_2 and B_2, depending on the definition adopted for local composition.

Also

$$\Delta d = d - d_o = \frac{1{,}000(1 + m\mathrm{Ms})}{V} - d_o \quad (16)$$

with M_s the solute molecular weight in kg · mol^{-1}. Alternatively,

$$1/d = \frac{V}{1{,}000(1 + m\mathrm{Ms})} \quad (17)$$

Results and Discussion

The parameters $\overline{V}_2^\circ$, $(\partial \tau_{ca,m}/\partial p)_T$, and $(\partial \tau_{m,ca}/\partial p)_T$ can be obtained by regression on Eq. 16 or 17, after substituting for V from Eq. 15 and for A_i and B_i, as appropriate, from Eqs. 10 and 11, or 12 and 13; note, however, that this requires values for $\tau_{ca,m}$ and $\tau_{m,ca}$. With the nonrandom parameter α fixed at 0.2, Eq. 17, linear in $\overline{V}_2^\circ$, $(\partial \tau_{ca,m}/\partial p)_T$; and $(\partial \tau_{m,ca}/\partial p)_T$ generally gives a better fit to the data (smaller standard deviation) than does Eq. 16, which is nonlinear in these parameters, but often the difference is small. The sum of squares objective functions used in data correlation are, for Eq. 17

$$S_1 = \Sigma[(d_{\text{obs}})^{-1} - (d_{\text{calc}})^{-1}]^2 \quad (18)$$

and, for Eq. 16

$$S_2 = \Sigma(\Delta d_{\text{obs}} - \Delta d_{\text{calc}})^2 \quad (19)$$

It should be possible, in principle, to evaluate as well the $\tau_{ca,m}$ and $\tau_{m,ca}$ parameters, which are included in the A_i and B_i terms, thus leading to the evaluation of activity or osmotic coefficients directly from measured densities. The problem appears, however, to be inherently ill-conditioned because of the strong correlation between the τ values and their pressure derivatives, and to the small fraction of the volume (and hence the density) from which the regression parameters are estimated. Thus, for NaCl at 25°C, the last term on the righthand side of Eq. 15 constitutes only 0.4% of the total volume at $m = 1$, rising to only 2.5% at $m = 6$; the sum of the A_i and B_i components of this term, from which the four parameters would have to be evaluated, constitutes 0.08% of V at $m = 1$, and 1.6% of V at $m = 6$. It has not proved possible to evaluate all five parameters simultaneously nor, by fixing $\overline{V}_2^\circ$ (e.g., from additivity), to evaluate the other four, but fixing of either the two τ values, or the two pressure derivatives permits evaluation of the other three parameters. Apart from the values of the correlation coefficients, standard deviations, and residuals, a measure of the appropriateness of fit is gained by comparison of the value obtained for $\overline{V}_2^\circ$ with the value from conventional extrapolation procedures, for example, the Redlich-Meyer equation (Redlich and Meyer, 1964), or from additivity.

NaCl at 25°C

Parameters obtained by regression on Eqs. 16 and 17 are shown in Table 1. The standard deviations indicate that the fit is satisfactory; also, the agreement of $\overline{V}_2^\circ$ with the accepted value of 16.68 cm^3 · mol^{-1} (Rogers and Pitzer, 1982) is adequate, and the residuals appear randomly distributed, with close to half positive and half negative, for each set of density data. Included in Table 1 are parameters calculated using τ_a, τ_o, and τ_v values, also using $\tau_{m,ca} = -2\tau_{ca,m}$, with $\tau_{ca,m} = -4.5$ (arbitrarily selected as a rounded value close to the mean of τ_a, τ_o, and τ_v) and with $\tau_{ca,m} = -4$ and -6, (to check the sensitivity to the value

Table 1. Parameters of Density Correlation of NaCl at 25°C

$\bar{V}_2^o/\mathrm{cm^3 \cdot mol^{-1}}$	$(\partial\tau_{ca,m}/\partial p)_T \times 10^5$	$(\partial\tau_{m,ca}/\partial p)_T \times 10^6$	$\tau_{ca,m}$[a]	Eq. No.	σ[b] × 10^5	Ref.
16.642	−2.86	−28.1	τ_o	17	1.8	c
16.634	−2.81	−0.99	τ_o	16	1.8	c
16.642	−2.86	−0.65	τ_a	17	1.8	c
16.634	−2.81	−2.335	τ_a	16	2.3	c
16.644	−2.81	2.21	τ_v	17	1.8	c
16.636	−2.79	1.11	τ_v	16	2.3	c
16.634	−2.83	−3.39	−4.5[f]	16	2.3	c
16.68 (fixed)[g]	−3.04	4.86	τ_a	16	2.5	c
	−3.07	5.64	τ_a	17	2.0	c
	−3.05	−1.47	−4.0[f]	17	2.0	c
	−1.96	14.8	−6.0[f]	17	1.4	c
16.633	−2.66	−4.81	τ_o	17	1.6	d
16.626	−2.62	−5.97	τ_o	16	2.1	d
16.633	−2.66	−6.40	τ_a	17	1.6	d
16.626	−2.62	−7.65	τ_a	16	2.1	d
16.630	−2.28	−34.1	−4.0[f]	16	2.0	d
16.633	−2.68	−7.14	−4.5[f]	17	1.6	d
16.676	−1.92	13.4	−6.0[f]	17	1.4	d
16.710	−3.03	5.56	τ_o	17	0.9	e
16.708	−3.02	5.09	τ_o	16	1.1	e
16.714	−2.94	5.72	τ_v	17	0.9	e

[a] τ_a (from ln γ), τ_o (from ϕ), τ_v (from vapor pressure);
[b] units: Eq. 16 $\mathrm{cm^3 \cdot g^{-1}}$, Eq. 17 $\mathrm{g \cdot cm^{-3}}$
[c] Rogers and Pitzer (1982); [d] Lo Surdo et al. (1982): [e] Perron et al. (1981)
[f] $\tau_{m,ca} = -2\tau_{ca,m}$; [g] conventional value (from Rogers and Pritzer, 1982)

employed for τ). It is evident that the goodness of fit is little affected by either the numerical values used for $\tau_{ca,m}$ and $\tau_{m,ca}$, or whether Eq. 16 or 17 is employed. Millero and coworkers (Lo Surdo et al., 1982) quoted a standard deviation of fit, using a power series in $m^{1/2}$ with three adjustable coefficients, of 1.93×10^{-5} g · cm^{-3} for NaCl at 25°C, while the range of standard deviations in Table 1, for the same data with three adjustable parameters [$\bar{V}_2^o$, $(\partial\tau_{ca,m}/\partial p)_T$, and $(\partial\tau_{m,ca}/\partial p)_T$] is 1.4–2.1 × 10^{-5} g · cm^{-3}. Thus, at 25°C, density correlation of adequate precision requires only three parameters derived from the density. Furthermore, little loss of precision results, if $\bar{V}_2^o$ is fixed, from additivity, and $(\partial\tau_{ca,m}/\partial p)_T$ and $(\partial\tau_{m,ca}/\partial p)_T$ evaluated from Eq. 16 or 17.

Na_2SO_4 and $MgCl_2$ at 25°C

A representative list of parameters obtained by regression on Eq. 17 is shown in Table 2; more detailed listings illustrating the effects of employing Eq. 16 are available in Tables SM 1 and SM 2 in the Supplementary Material. As for NaCl, the standard deviations and residuals indicate that the fits are satisfactory and are little affected by the τ values employed.

The values obtained for $\bar{V}_2^o$ for Na_2SO_4 show only a small spread, but are all considerably larger than the conventional value (a range of 11.56–11.76 for Lo Surdo et al., 1982, but 11.48 for Connaughton et al., 1986). This contrasts with the situation for $MgCl_2$, for which the opposite trend, $\bar{V}_2^o$ (calc) < $\bar{V}_2^o$ (conventional), is observed. For Na_2SO_4, fixing $\bar{V}_2^o$ within the conventional range causes a marked increase in the standard deviation of fit, so that three adjustable parameters are required for adequate precision; the power series treatment with three adjustable coefficients is superior, having a standard deviation of only 0.95×10^{-5} g · cm^{-3} (Lo Surdo et al., 1982).

The opposite tendency for the 2:1 electrolyte $MgCl_2$ to underestimate $\bar{V}_2^o$ suggests that the discrepancies may arise from having arbitrarily fixed α at 0.2 for both cations and anions, as originally suggested by Chen. For $MgCl_2$, three adjustable parameters give an adequate fit, or if $\bar{V}_2^o$ is set to about 14.2 cm^3 · mol^{-1}, two parameters suffice; for comparison, Millero and coworkers quote, at 25°C, a standard deviation of 1.99 × 10^{-5} g · cm^{-3} for a power series fit, with six adjustable coefficients (Lo Surdo et al., 1982).

$MgSO_4$ at 25°C

Results are shown in Table 3, from which it is immediately evident that the fit is poorer than for the three previous cases, but consistent over a wide range of τ values. The fit is also much poorer than that from the power series treatment with four adjustable coefficients, which gives a standard deviation of 1.28×10^{-5} g · cm^{-3} (Lo Surdo et al., 1982). The values obtained for $\bar{V}_2^o$ show wider variation among themselves, and greater deviation from the conventional value, −7.39 cm^3 · mol^{-1} (Connaughton et al., 1986), which, however, cannot be obtained directly from densities but must be obtained by additivity treatments, because of the effects of ion-pairing.

Extension to cover 0–100°C

Values for $\tau_{ca,m}$ and $\tau_{m,ca}$ for NaCl over the temperature range 0–100°C were evaluated by regression from the osmotic coefficients for NaCl tabulated at 10°C intervals by Rogers and Pitzer (1982). The values obtained for $\tau_{ca,m}$ varied from −4.65 to −4.49, a range of only 0.16, while those for $\tau_{m,ca}$ covered a range of 0.6, from 9.29 to 8.69. In each case the variation with temperature was smooth, and the results were fitted to an equa-

Table 2. Parameters for Density Correlation of Na_2SO_4 and $MgCl_2$ at 25°C

$\bar{V}_2^\circ$/cm³ · mol⁻¹	$(\partial\tau_{ca,m}/\partial p)_T \times 10^5$	$(\partial\tau_{m,ca}/\partial p)_T \times 10^4$	$\tau_{ca,m}$[a]	Eq. No.	σ[b] × 10⁵
		Na_2SO_4			
12.632	5.16	3.23	τ_a	12, 17	1.8
12.645	10.0	4.03	τ_o	12, 17	1.9
12.639	4.98	2.02	τ_o	9, 17	1.8
12.613	−3.10	0.85	−4.5[c]	9, 17	1.8
12.579	−3.43	0.012	−6.0[c]	9, 17	1.8
11.56 (fixed)[d]	12.5	5.27	τ_a	12, 17	6.8
11.56 (fixed)[d]	19.4	6.17	τ_o	9, 17	6.9
		$MgCl_2$			
14.203	2.26	4.95	τ_a	9, 17	1.2
13.977	2.96	3.89	τ_o	9, 17	2.2
13.779	4.08	3.98	−4.5[c]	9, 17	3.8
14.267	2.30	3.81	−6.0[c]	9, 17	1.
14.188[e]	2.22	4.78	τ_a	9, 17	1.4
13.964[e]	2.90	3.73	τ_o	9, 17	2.9
13.741[f]	2.01	0.66	τ_a	12, 17	1.8
13.796[f]	1.63	2.00	τ_a	9, 17	1.4
13.742[f]	2.07	1.00	τ_o	9, 17	1.7

[a] τ_a (from $\ln \gamma$), τ_o (from ϕ); [b] units: g · cm⁻³
[c] $\tau_{m,ca} = -2\tau_{ca,m}$; [d] conventional value
Data from Lo Surdo et al. (1982), except
[e] Perron et al. (1981), [f] Gates and Wood (1985)

tion of the form

$$\tau = a + b\left(\frac{1}{T} - \frac{1}{298.15}\right) + c\left(\frac{298.15 - T}{T} + \ln\frac{T}{298.15}\right) \quad (20)$$

as recommended by Chen. The coefficients obtained by least squares were:

for $\tau_{ca,m}$ $a = -4.6267, b = -104.6540, c = 2.8798$

for $\tau_{m,ca}$ $a = 9.1279, b = 564.1498, c = -2.4991$

Values of $\tau_{ca,m}$ and of $\tau_{m,ca}$ for NaCl, calculated from Eq. 20 at 10°C intervals from 0 to 100°C, and at 25°C, were used to fit densities from the tabulation of Rogers and Pitzer. The correlations gave fits of equal to or slightly poorer precision than those at 25°C, except at 0°C, where the standard deviation was about 7×10^{-5} cm³ · g⁻¹ (see Table SM 3 in the Supplementary Material). $\bar{V}_2^\circ$ values agreed well with those of Rogers and Pitzer, but plots of $(\partial\tau_{ca,m}/\partial p)_T$ and $(\partial\tau_{m,ca}/\partial p)_T$ against temperature both showed several inflections. With six parameters already required to evaluate $\tau_{ca,m}$ and $\tau_{m,ca}$ over the temperature range, an unacceptably large number of parameters would be required to correlate $\bar{V}_2^\circ$ and the pressure derivatives, and thus the densities, from 0 to 100°C. However, the small variation with temperature of $\tau_{ca,m}$ and $\tau_{m,ca}$ and the ability of the pressure derivatives to compensate for changes in these parameters suggested that a satisfactory correlation would be achieved by arbitrarily fixing

Table 3. Parameters of Density Correlation of $MgSO_4$ at 25°C

$\bar{V}_2^\circ$/cm³ · mol⁻¹	$(\partial\tau_{ca,m}/\partial p)_T \times 10^5$	$(\partial\tau_{m,ca}/\partial p)_T \times 10^5$	$\tau_{ca,m}$[a]	Eq. No.	σ[b] × 10⁵
3.748	7.89	5.83	τ_a	12, 16	5.5
3.819	7.40	4.65	τ_a	12, 17	4.6
3.582	3.78	10.3	τ_a	9, 16	6.9
3.687	3.66	9.62	τ_a	9, 17	5.6
3.730	9.00	−10.6	τ_o	12, 16	5.5
3.796	5.14	−15.1	τ_o	12, 17	4.6
3.749	10.0	10.1	τ_o	9, 16	5.5
3.822	9.44	9.15	τ_o	9, 17	4.6
3.833	45.2	54.6	−2.0[c]	9, 17	4.4
3.816	17.1	14.7	−3.0[c]	9, 17	4.4
3.822	10.1	9.1	−4.0[c]	9, 17	4.5
3.810	7.82	7.33	−4.5[c]	12, 16	4.7
3.785	6.11	6.05	−5.0[c]	9, 17	4.9
3.664	3.83	4.48	−6.0[c]	9, 17	5.7
2.813	1.63	3.60	−8.0[c]	9, 17	9.6

[a] τ_a (from $\ln \gamma$), τ_o (from ϕ); [b] Units: Eq. 16 cm³ · g⁻¹; Eq. 17 g · cm⁻³
[c] $\tau_{m,ca} = -2\tau_{ca,m}$
Data from Lo Surdo et al. (1982)

$\tau_{ca,m}$ at -4.5, (and $\tau_{m,ca}$ at $-2\tau_{ca,m}$) at all temperatures over the range 0–100°C. At 25°C, densities from Rogers and Pitzer and from Lo Surdo et al. (1982) were fitted with comparable precision, but the fit was better to Rogers and Pitzer's smoothed values at other temperatures. The $\bar{V}_2^\circ$ values for both sets of data (complete listing in Table SM 3) show a common trend, as do $(\partial\tau_{ca,m}/\partial p)_T$ and $(\partial\tau_{m,ca}/\partial p)_T$ over most of the temperature range, the notable exception being the divergence of both these parameters at 85 and 95°C. Over the whole temperature range, the differences between the parameters for the two sets of density data are sufficiently great that no simple analytical expression can be deduced for $(\partial\tau_{ca,m}/\partial p)_T$ and $(\partial\tau_{m,ca}/\partial p)_T$ as functions of temperature. Thus, although the number of adjustable parameters can be reduced by employing constant values of -4.5 for $\tau_{ca,m}$ and 9 for $\tau_{m,ca}$, to give reasonable correlation of densities of NaCl solutions over the temperature range 0–100°C (or at least 5–100°C), at each temperature the appropriate values of $\bar{V}_2^\circ$, $(\partial\tau_{ca,m}/\partial p)_T$, and $(\partial\tau_{m,ca}/\partial p)_T$ are required.

The Na_2SO_4 activity coefficient data of Rogers and Pitzer (1985) from 25 to 100°C permitted evaluation of $\tau_{ca,m}$ and $\tau_{m,ca}$ values over this temperature range, and fitting to an equation of the type of Eq. 20. The parameters obtained were:

$$\text{for } \tau_{ca,m} \quad a = -3.6656, b = -335.2, c = 1.527$$

$$\text{for } \tau_{m,ca} \quad a = 7.4746, b = 1324.3, c = 4.9611$$

Densities were correlated from 25 to 95°C using τ values thus evaluated, also using $\tau_{ca,m} = -4.5$ and $\tau_{m,ca} = 9$, or $\tau_{ca,m} = -6$ and $\tau_{m,ca} = 12$, over the range 15–95°C. At each temperature the fit was comparable to that at 25°C and was little affected by the τ values employed. A striking improvement in the fit results at 35°C if the results of Connaughton et al. are excluded (see Table SM 4 for complete tabulation).

For $MgCl_2$ and $MgSO_4$ extensive tabulations of activity coefficients or osmotic coefficients are not available over a wide temperature range, but reasonable correlation of densities for both salts at each temperature from 5 to 95°C is achieved using constant $\tau_{ca,m} = -6$ and $\tau_{m,ca} = 12$, or, for $MgSO_4$ using $\tau_{ca,m} = -4.5$ and $\tau_{m,ca} = 9$ (see Tables SM 5 and 6). At 75°C the final entry in the $MgCl_2$ density tabulation by Connaughton et al. is obviously erroneous and so was omitted from the correlation. For $MgCl_2$, $(\partial\tau_{ca,m}/\partial p)_T$ was almost constant from 35 to 95°C, but decreased significantly below 35°C, while $(\partial\tau_{m,ca}/\partial p)_T$ showed several inflections. For $MgSO_4$, the largest standard deviation was at 65°C (using only seven data points).

Conclusions

Using constant τ values in the range $\tau_{ca,m} = -4.5$ to -6, with $\tau_{m,ca} = -2\,\tau_{ca,m}$, *at any single temperature*, only three adjustable parameters $[\bar{V}_2^\circ$, $(\partial\tau_{ca,m}/\partial p)_T$, and $(\partial\tau_{m,ca}/\partial p)_T]$ are required to provide satisfactory density correlation for NaCl, Na_2SO_4, and $MgCl_2$, and somewhat poorer correlation for $MgSO_4$, with standard deviations of comparable magnitude to those obtained using the power series in $m^{1/2}$ treatment. Other electrolytes—for example, LiCl, $CaCl_2$, and the alkali hydroxides—give good correlations and the procedure should be generally applicable. The most suitable procedure at 25°C is to use Chen's tabulated τ_a values (Chen, 1982), because they provide the most extensive list. If τ values are not available, a satisfactory correlation can be sought for any $\tau_{ca,m}$ in the range -4.5 to -6, with $\tau_{m,ca} = -2\,\tau_{ca,m}$; these values can be applied at any other temperature, obviating the need for osmotic or activity coefficients as functions of temperature.

Recently Ball et al. (1985) spoke optimistically about developing a one-parameter model for osmotic coefficients, valid up to a molality of 6. A model of this type, by avoiding the problem of the strong cross-correlation between parameters, may permit the evaluation of osmotic and/or activity coefficients from density measurements alone; it is to be hoped that this additional application will be put to the test when such a model is developed.

Notation

a, b, c = coefficients in equation for temperature effect on τ values
A_ϕ = Debye-Huckel constant for osmotic coefficient
A_v = $-4RT(\partial A_\phi/\partial p)_T = 1.875$ cm^3 · mol^{-1} at 25°C
d, d_o = density of solution, solvent, g · cm^{-3}
g^{ex} = molar excess Gibbs energy
G = Gibbs energy
I_x = ionic strength on mole fraction scale
m = molality, gmol solute/kg solvent
M_s = solvent molecular weight, kg · mol^{-1}
n = mole number
p = pressure
R = gas constant
T = temperature, K
V = volume
$\bar{V}_1^\circ$, $\bar{V}_2^\circ$ = partial molar volumes of components 1 (solvent) and 2 (solute)
x = true liquid phase mole fraction based on all species, molecular and ionic
X = effective liquid phase mole fraction
z = absolute value of ionic charge

Greek letters

α = NRTL nonrandomness factor
γ = activity coefficient
ν = moles of ions from one mole solute
ρ = closest approach parameter of Pitzer-Debye-Huckel equation, = 14.9
σ = standard deviation
τ = NRTL binary interaction energy parameter
ϕ = osmotic coefficient

Superscripts

* = unsymmetric convention
pdh = long-range contribution, represented by Pitzer-Debye-Huckel equation
lc = short-range contribution, represented by local composition model

Subscripts

a = anion
c = cation
ca = salt Ca
m = molecular species
a, o, v = subscripts to τ to indicate source: activity, osmotic coefficients, or vapor pressures

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Manuscript received June 3, 1988, and revision received Sept. 7, 1988.

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