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The Pitzer Formalism vis-à-vis the Mixture Rule for the Estimation of Apparent Molal Volumes of Aqueous NaCl-KCl, NaCl-KBr, and NaCl-K_2SO_4 Mixtures at 298.15 K

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The density data reported by Wirth for aqueous solutions of KCl, KBr, and K_2SO_4 in NaCl solutions of five different fixed concentrations at 298.15 K have been used to calculate the apparent molal volumes of the mixtures; the results have been compared with those calculated by the Pitzer formalism as also the Young and Smith's mixture rule.

Recently, attention has been drawn to the successful extension of the Pitzer formalism[1,2] by Kumar[3–5] for the calculation of volume properties of a number of mixed electrolytes in aqueous solutions. Humffray[6] has also proposed a comparatively simpler treatment by adopting the Young and Smith's "mixture rule"[7] for estimating the densities and apparent molal volumes of mixtures of electrolytes from those of the individual components, and obtained a better agreement for NaCl–KBr mixtures than from Pitzer's equations. Kumar[8a] has however observed that the good agreement obtained by Humffray is due to the fact that the variation of the densities of the mixtures happens to be linear with respect to the component densities. It is the purpose of this investigation to extend such studies to a number of other electrolyte mixtures in order to investigate further the extent of agreement between the experimental values and those calculated from the mixture rule, and the Pitzer's equations.

For this purpose, we have made use of the entire set of precise density data reported by Wirth (for the mixtures: NaCl–KCl, NaCl–KBr, and NaCl–K_2SO_4)[9] by suitable interpolation of the data, without and with proper reformulation of the empirical equations given for the representation of the mixture density, so that the latter could be represented for constant total ionic strengths within the range: 0.25 to 1 mol kg^{-1}.

Calculations and Results

Wirth's reported density data in terms of molarity have been converted to molality for meaningful comparison with the recent data, by means of the following conversion formula deduced in analogy with that for the pure components:[10]

$$\frac{\sum c_i}{\sum m_i} = d_{\mathrm{mix}} - \frac{\sum c_i M_i}{1000}. \tag{1}$$

The experimental ϕ_{V}^{*} values for the mixtures are then calculated with the help of the following equation

$$\phi_{\mathrm{V}}^{*} = \frac{1000(d_0 - d_{\mathrm{mix}})}{d_{\mathrm{mix}}\, d_0 \sum m_i} + \frac{\sum m_i M_i}{d_{\mathrm{mix}} \sum m_i}. \tag{2}$$

Here d_{mix} and d_0 are the densities of the mixture and the solvent respectively, m_i is the molality and M_i the molecular weight of the *i*th component in the mixture.

Wirth[9] reported the density values of KCl, KBr, and K_2SO_4 in NaCl solutions of five fixed concentrations [viz., 0.04, 0.16, 0.35, 0.62, and 0.97 equiv] in which the concentration of the first electrolyte generally varied from 0.04 to 0.64 equiv except in the case of K_2SO_4. All density values of the mixtures of different electrolytes were represented by means of least square equations:[9]

$$(d_3 - d_2)/c_3 = a - b(\mu_{\mathrm{V}}^{1/2} - c_2^{\circ\,1/2}). \tag{3}$$

From the experimental data as reported by Wirth in Tables 2, 3, and 4, Ref. 9, it has been possible to interpolate the experimental densities and apparent molal volumes of the different mixed electrolytes at a number of constant total ionic strengths between 1 and 0.25 mol kg^{-1}. However, such calculations with Wirth's reported equations produce only a set of three to four density values for each ionic strength, which is inadequate for the present purpose. In order to obtain more data for meaningful comparison, we have introduced the following technique. Instead of a fixed concentration of NaCl in the mixtures as reported by Wirth, the concentration of the other electrolyte is now made fixed, so as to vary the concentration of NaCl in the mixtures. All these density values are then represented in the form of equations analogous to Wirth's equation by the computerized least squares method with proper '*a*' and '*b*' values.

With the help of these reformulated equations it is now possible to calculate the densities or apparent molal volumes at suitable ional fractions other than those calculated directly from Wirth's reported equations. The thus calculated values of densities [or rather, the density differences ($\Delta d = d_3 - d_2$)] and apparent molal volumes, at the total ionic strengths of 1, 0.75, 0.50, and 0.25 mol kg^{-1}, are shown in columns 3 and 4 of Table 1, for the NaCl—KCl mixture only (two 1—1 type electrolytes with common anion). The consistency of the density values obtained from our reformulated equation with those calculated using Wirth's equations, has been tested and found to be excellent.

Table 1. Experimental Δd and ϕ_V^* Values (Wirth's data) together with the Corresponding Estimated ϕ_V^* Values by Young's Rule and Pitzer's Equation for NaCl–KCl Mixtures at 298.15 K

m_{NaCl}	m_{KCl}	$\Delta d \times 10^3$ / g cm^{-3}	ϕ_V^*/cm^3 mol^{-1} (Wirth)	ϕ_V^*/cm^3 mol^{-1} (Pitzer)	ϕ_V^*/cm^3 mol^{-1} (Young's rule)
			m=1.0		
1.0000	0.0000	39.189	18.47	—	—
0.9926	0.0074	39.220	18.55	18.54	18.55
0.9605	0.0395	39.362	18.93	18.86	18.88
0.8792	0.1208	39.708	19.87	19.67	19.72
0.7577	0.2423	40.269	21.23	20.89	20.97
0.6285	0.3715	40.842	22.50	22.28	22.30
0.4810	0.5190	41.675	24.15	23.73	23.82
0.3501	0.6499	42.317	25.37	25.09	25.17
0.0000	1.0000	44.451	28.78	—	—
				σ_1=0.12	σ_3=0.20
				σ_2=0.05	σ_4=0.04
			m=0.75		
0.7500	0.0000	29.716	18.22	—	—
0.7105	0.0395	29.902	18.81	18.75	18.76
0.6285	0.1215	30.269	19.98	19.84	19.89
0.5077	0.2423	30.904	21.77	21.61	21.54
0.3898	0.3602	31.528	23.41	23.08	23.16
0.2310	0.5190	32.416	25.54	25.28	25.34
0.1557	0.5943	32.824	26.47	26.33	26.37
0.0000	0.7500	33.773	28.51	—	—
				σ_1=0.12	σ_3=0.17
				σ_2=0.03	σ_4=0.03
			m=0.50		
0.5000	0.0000	20.052	17.92	—	—
0.4605	0.0395	20.255	18.78	18.71	18.73
0.3501	0.1499	20.827	21.08	20.94	21.00
0.2577	0.2423	21.344	23.05	22.83	22.90
0.1557	0.3443	21.905	25.08	24.93	24.99
0.0386	0.4614	22.588	27.45	27.37	27.40
0.0000	0.5000	22.837	28.19	—	—
				σ_1=0.08	σ_3=0.09
				σ_2=0.03	σ_4=0.02
			m=0.25		
0.2500	0.0000	10.168	17.53	—	—
0.2105	0.0395	10.390	19.18	19.12	19.18
0.1557	0.0943	10.696	21.43	21.36	21.39
0.1292	0.1208	10.851	22.54	22.45	22.48
0.0386	0.2114	11.371	26.22	26.17	26.19
0.0077	0.2423	11.558	27.46	27.45	27.45
0.0000	0.2500	11.604	27.77	—	—
				σ_1=0.04	σ_3=0.04
				σ_2=0.01	σ_4=0.01

Table 2. ϕ_V° Values of the Electrolytes and Pitzer Coefficients (Pressure Derivatives) for the Different Cation–Anion Interactions (least squares fit to Pitzer equation[5])

Cation–Anion	ϕ_V° / cm^3 mol^{-1}	$\left(\frac{\partial \beta^0}{\partial P}\right)_T \times 10^5$	$\left(\frac{\partial \beta^1}{\partial P}\right)_T \times 10^5$	$\left(\frac{\partial C^\phi}{\partial P}\right)_T \times 10^5$	σ / cm^3 mol^{-1}
Na–Cl	16.62 (16.60)[a]	2.41	−1.74	−1.31	0.00
K–Cl	26.96 (26.86)[a]	4.31	−6.42	−2.42	0.02
Na–Br	23.83 (23.37)[a]	1.69	−4.66	−0.31	0.01
K–Br	34.17 (34.04)[a]	4.33	−7.74	−2.50	0.03
Na–SO$_4$	11.40	5.94	15.55	−1.29	0.00
K–SO$_4$	32.26	−1.45	31.80	8.21	0.06

a) From Redlich-Meyer equation.

Table 3. Pitzer Mixing Parameters Obtained by Best Fit to θ_v Expression, for NaCl-KCl, NaCl-KBr, and NaCl-K_2SO_4 Mixtures at 298.15 K

I mol kg^{-1}	$\theta_{Na^+-K^+}\times10^5$	$\theta_{Cl^--Br^-}\times10^5$	$\theta_{Cl^--SO_4^{2-}}\times10^5$
1.0	1.55	0.56	−0.06
0.75	1.54	0.44	0.81
0.50	2.00	0.25	2.56
0.25	1.71	1.01	4.85

Pitzer's Equation. The form of the Pitzer equation[11] which was used by Kumar[5] has also been utilized here. The apparent molal volume of an ith type ion in a mixture can be estimated by the following equation (which is slightly different from that of Kumar[8]):

$$\phi_{v_i}=\phi^\circ_{v_i}+\frac{z_i^2 A_v}{2b}\ln(1+bI^{1/2})+RT\sum_j B^v_{ij}m_j + \frac{BT}{|z_i|^{1/2}}\sum_j C^v_{ij}m_j^2|z_j|^{1/2}, \tag{4}$$

where

$$B^v_{ij}=B^\circ_{ij}+\frac{1}{2I}B^1_{ij}[1-(1+2I^{1/2})\exp(-2I)^{1/2}];$$

$$B^\circ_{ij}=\left(\frac{\partial\beta^{(0)}_{ij}}{\partial P}\right)_T,\ B^1_{ij}=\left(\frac{\partial\beta^{(1)}_{ij}}{\partial P}\right)_T;$$

$$C^v_{ij}=\left(\frac{\partial C^\phi_{ij}}{\partial P}\right)_T\Big/2;\ A_v=1.8743,\ b=1.2.$$

The apparent molal volume of the Jth salt in a mixture can then be obtained by summing over the component ionic values: $\phi_{v_J}=\sum_i \nu_i\phi_{v_i}$ which in turn calculates the theoretical mean apparent molal volumes ϕ^*_v of the mixtures: $\phi^*_{v_{cal}}=(\sum_J m_J\phi_{v_J})/\sum_J m_J$.

In order to calculate the ϕ^*_v values of the different mixtures by the Pitzer formalism the values of the pure electrolyte parameters $(\partial\beta^{(0)}/\partial P)_T$, $(\partial\beta^{(1)}/\partial P)_T$, and $(\partial C^\phi/\partial P)_T$ (as also ϕ°_v) for the different cation–anion pairs such as Na–Cl, K–Cl, Na–Br, Na–SO_4, and K–SO_4 are required. The experimental ϕ_v values at different concentrations over the range 0.01—1.04 M (1 M=1 mol dm^{-3}) were directly calculated for NaCl, KCl, KBr, and K_2SO_4 from Wirth's reported pure electrolyte density values, using 10—15 data points, whereas those for NaBr and Na_2SO_4 were obtained from Isano's data[12] using five data points for each in the concentration range 0.05—4 M. The values of the pressure derivative parameters and ϕ°_v for the individual electrolytes were then calculated with the help of the Pitzer equation by the nonlinear least squares method. The calculated values for the individual electrolytes, together with the standard deviations of fit (σ) are shown in Table 2. The calculated values of ϕ^*_v at the specified ionic strengths for all the systems mentioned have been incorporated in column 5 of Table 1.

In the Pitzer equation (Eq. 4) the contributions arising out of the interactions between like charges were ignored. However, the consideration of such interactions, called the "mixing terms", gives a better representation for the data studied here. The different binary mixing terms $\theta^v[\equiv\theta_{ik}(m_A m_k\nu_i+m_B m_i\nu_k)+\theta_{jl}(m_A m_l\nu_j+m_B m_j\nu_l)]$ both for cation–cation and anion–anion types, are calculated from the difference between the experimental and estimated ϕ^*_v values as usual: $\theta^v=[(\phi^*_{v_{exp}}-\phi^*_{v_{cal}})(m_A+m_B)]/RT$, where m_A, m_B are the molalities of the salts whose cations as well as anions are under consideration for interaction, the ν's being the moles of ionic species produced per mole of the salts (assumed that θ^v_{ii} etc.=0). The θ_{ik} and θ_{jl} values for the NaCl–KCl, NaCl–KBr, and NaCl–K_2SO_4 mixtures considered are shown in Table 3. The extended Pitzer equation for calculating ϕ_{v_i} in a mixture with the use of the mixing terms is obtained by simply adding the term $RT\sum_k\theta_{ik}m_k$ to Eq. 4. Also included in Table 1are the various standard deviations of fit without and with the binary mixing terms for the systems studied (σ_1 and σ_2 respectively).

Mixture Rule. For the calculation of the mean apparent molal volume using Young and Smith's mixture rule,[7] the following equation has been used:

$$\phi^*_v=\frac{n_A\phi_A+n_B\phi_B}{n_A+n_B}, \tag{5}$$

where ϕ^*_v, ϕ_A, and ϕ_B are respectively the apparent molal volumes of the mixtures and the components A and B, all at the same ionic strength. The calculated values of ϕ^*_v at different ional fractions of various systems are shown in column 6 of Table 1. For the calculation of the "mixing terms", the excess volumes of mixing ΔV^{ex}_{mix} for the systems mentioned, which are related to interactions of like charged ions, were calculated by using Millero's equation:[13,14]

$$\Delta V^{ex}_{mix}/\sum_J m_J=\phi^*_{v_{exp(mix)}}-\sum_J m_J\phi'_{v_J}/\sum_J m_J,$$

where ϕ'_{v_J} indicates the $\phi_{v_{exp}}$ value of each individual electrolyte in the mixture at the ionic strength of the

Table 4. Friedman Mixing Parameters Obtained by Least Squares Fit of Eq. 6, for the Three Systems NaCl-KCl, NaCl-KBr, and NaCl-K_2SO_4 at 298.15 K

I	NaCl-KCl		NaCl-KBr		NaCl-K_2SO_4	
mol kg^{-1}	ν_0	ν_1	ν_0	ν_1	ν_0	ν_1
1.0	1.1006	−0.1711	1.2670	−0.1354	1.2007	−0.3062
0.75	1.2089	−0.0882	1.1105	−0.0791	1.0278	−0.3438
0.50	1.0011	0.0252	0.5723	−0.2406	1.4368	−0.5413
0.25	0.8618	0.0595	0.8525	0.0747	1.3815	−0.0631

mixture. The $\Delta V_{\mathrm{mix}}^{\mathrm{ex}}$ values thus obtained are fitted to an equation of the form:[15)]

$$\Delta V_{\mathrm{mix}}^{\mathrm{ex}}=I^2 y_{\mathrm{B}}(1-y_{\mathrm{B}})[\nu_0+\nu_1 I(1-2y_{\mathrm{B}})], \tag{6}$$

where ν_0 and ν_1 are related to the ionic interaction parameters[16)] (ν_0 to θ_{MN}) and their values are shown in Table 4; (y_{B}=the ionic strength fraction of component B).

The $\Delta V_{\mathrm{mix}}^{\mathrm{ex}}$ values thus obtained are now incorporated in the ϕ_{v}^{*} values estimated from the mixture rule; thus:

$$\phi_{\mathrm{v_{cal}}}^{*}=(\sum_J m_J \phi_{\mathrm{v}_J})/\sum_J m_J+\Delta V_{\mathrm{mix}}^{\mathrm{ex}}/\sum_J m_J, \tag{7}$$

and the standard deviations of fit with the $\phi_{\mathrm{v_{exp}}}^{*}$ values, without and with the mixing terms (σ_3 and σ_4 respectively), are also shown in Table 1 for the NaCl–KCl system mentioned.

Discussion

The $\phi_{\mathrm{v}}^{\circ}$ values for NaCl, KBr, NaBr, and KCl obtained in this study are slightly higher than those reported by Kumar for the same systems. We have also calculated the $\phi_{\mathrm{v}}^{\circ}$ values using the Redlich–Meyer equation:[17)] $\phi_{\mathrm{v}}=\phi_{\mathrm{v}}^{\circ}+S_{\mathrm{v}}\sqrt{c}+hc$, where S_{v} is the theoretical limiting slope (=1.868 cm³ dm$^{3/2}$ for 1—1 electrolytes at 25 °C) and 'h' is an empirical constant. The different $\phi_{\mathrm{v}}^{\circ}$ values obtained from the least squares plots of $(\phi_{\mathrm{v}}-S_{\mathrm{v}}\sqrt{c})$ vs. c are also included in Table 2.

The standard deviations of fit for the ϕ_{v}^{*} values of the different mixtures without using the mixing parameters (i.e., σ_1 and σ_3) (Table 1) indicate that for all the mixtures, the Pitzer approach gives better agreement with the experimental values than does the "mixture rule" at the higher two ionic strengths, while at the lower two ionic strengths the agreement is evenly balanced. For the NaCl-KBr mixtures, Humffray[6)] observed better agreement using Pitzer's equation at I=1—3 m, while at I=4 m the mixture rule gave a better fit. With the addition of the "volume mixing terms" to Young's rule, as also the interaction terms θ to Pitzer equation, the estimated values of ϕ_{v}^{*} in both cases have improved considerably, as is evident from the σ_2 and σ_4 values shown in Table 1. We now find that both the "mixture rule" and the "Pitzer approach" are almost equally successful in predicting the ϕ_{v}^{*} values for the mixtures considered.

Figure 1 illustrates the variation of $\phi_{\mathrm{v}}^{\circ,*}$ values of NaCl in the three binary electrolyte mixtures, with different fixed concentrations of KCl, KBr, and K_2SO_4 respectively. The different $\phi_{\mathrm{v}}^{\circ,*}$ values of NaCl in the mixtures containing fixed concentration of the other electrolyte were obtained from the intercepts of various reformulated equations representing the density data. It is interesting to note that the extrapolated $\phi_{\mathrm{v}}^{\circ}$ values of pure NaCl obtained by the nonlinear least squares method for the above three types of mixtures containing KCl, KBr, or K_2SO_4 all agree excellently well with the experimental $\phi_{\mathrm{v}}^{\circ}$ value of pure NaCl solution.

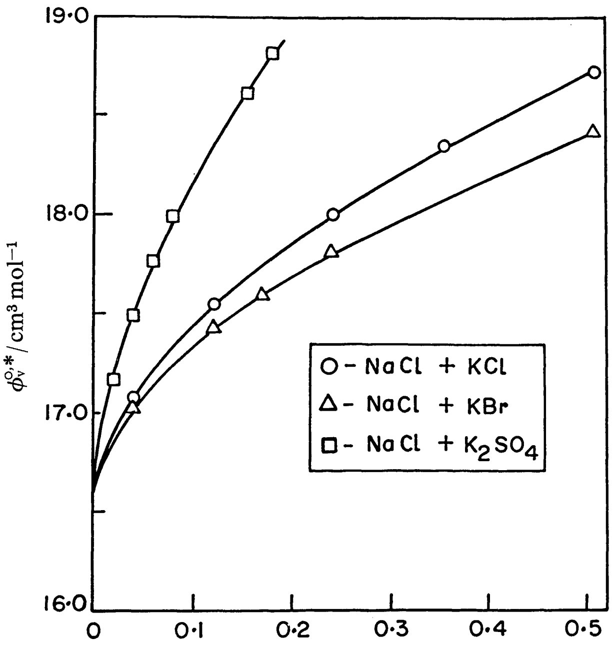

Fig. 1. Variation of $\phi_{\mathrm{v}}^{\circ,*}$ values of NaCl in three binary electrolyte mixtures, with different fixed concentrations of KCl, KBr, and K_2SO_4.

Very recently Connaughton, Millero, and Pitzer[18)] have summarized the Pitzer equations for the volume change on mixing any combination of the four sea salts NaCl, Na_2SO_4, $MgSO_4$, $MgCl_2$ at constant ionic strength. They find that the inclusion of mixing terms based on the differences in the interactions of ions of the same sign is of marginal value at 25 °C. At other temperatures the agreement without the mixing terms is good, but significant improvement is obtained by inclusion of some binary mixing terms. Among the three different mixtures considered by us only the NaCl-K_2SO_4 mixture resembles, as regards the charge type, one of the mixtures considered by Connaughton et al.,[18)] namely NaCl-Na_2SO_4 (though the former has no common ions while the latter is a common cation mixture); our other two mixtures are of different charge types than the ones considered by the said authors. The $\overset{\mathrm{v}}{\theta}_{\mathrm{Cl^-,SO_4^{2-}}}$ value found by Millero is approximately equal to 2×10⁻⁶ at 25 °C. The values found by us for the same vary from −0.6×10⁻⁶ to 48×10⁻⁶ over the ionic strength range 1.0—0.25 mol kg⁻¹.

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