October, 1989] Bull. Chem. Soc. Jpn., 62, 3311—3314 (1989)

Concentrated Mixtures of 1:1 Electrolytes: Densities and Excess Volumes of Aqueous KBr with KCl and NaBr

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(Received December 9, 1988)

Densities of aqueous KCl–KBr and NaBr–KBr mixtures are reported from the ionic strengths 0.5 to 4 mol kg^{-1} of water. The results are analyzed in the light of Pitzer theory of specific interactions. The deviations of experimental quantities from the Young rule (excess volumes) are discussed in terms of interactions between the ions of like charges. The excess volumes showed weak dependence on temperature.

In recent years there has been upsurge in interest in the thermodynamic properties of aqueous concentrated electrolyte mixtures. This upsurge has most probably been caused due to the development of ion-interactions or specific interactions approach of Pitzer,[1,2] which describes various thermodynamic properties like osmotic, activity coefficients, and enthalpies of both pure and mixed electrolyte solutions of high concentrations.[3] However, the understanding of volume properties of concentrated aqueous mixed electrolytes is still very poor, as evidenced by little amount of work in this direction,[4–9] where the studies were carried out in diluted solutions.

The present article describes the densities and apparent molal volumes of mixtures of aqueous KBr with KCl, and with NaBr up to the constant ionic strength of 4 mol kg^{-1} of water. The results are analyzed with the help of Pitzer theory.[1,2] The ion-ion interactions are also discussed in relation to the excess volumes of mixing. Besides detailed study at 298.15 K, the article also discusses the temperature dependence of the excess volumes.

Materials and Methods

KBr, KCl, and NaBr were Baker analyzed and were crystallized twice before preparing solutions on molality basis in deionized water. The concentrations of the solutions were determined by volumetric analysis. The mixtures of different compositions were prepared by mixing appropriate amounts of stock solutions as $y_B = m_B/I$, and remembering that $y_A + y_B = 1$. y corresponds to ionic strength fraction, and B refers to KBr. The symbols m and I are molality and ionic strength, respectively.

The experimental density differences, Δd, were measured using a Paar vibrating tube densimeter. The difference between density of solution, d, and of pure water, d_0, is called the density difference, Δd. The densimeter was calibrated using the densities of pure water[10] and of aqueous NaCl solutions.[11] The temperature of thermostat bath was maintained constant to ±0.005 K, and the Δd values were accurate to within 3×10^{-6} g cm^{-3}.

Data Treatment

The Pitzer theory is based on the evaluation of three adjustable parameters from constituent pure electrolytes and then using them in the ionic equations of mixtures. The estimation of ionic property in mixture primarily is based on the cation–anion pair interactions. Subsequently, the corrections arising out of two like charged ion interactions (binary) and three-ion interactions are treated as difference parameters. The volumetric equations of Pitzer as derived from the pressure dependence of the equations applicable to activity coefficients are summarized below. The details of the Pitzer equations are given elsewhere.[12]

Apparent molal volume, ϕ_V, of a single electrolyte is related to its molality, m, as

$$\phi_V = \phi_V^\circ + \nu\,|Z_M Z_X|\,\frac{A_V}{2b}\ln(1+bI^{1/2}) + 2\nu_M\nu_X RT\,[mB_{MX}^V + m^2(\nu_M\nu_X)^{1/2}C_{MX}^V] \tag{1}$$

where

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

and

$$C_{MX}^V = (\partial C^\phi/\partial P)/2. \tag{3}$$

In these equations $I = 1/2\sum_i m_i Z_i^2$, $\nu = \nu_M + \nu_X$, $R =$ 83.1441 cm^3 bar mol^{-1} K^{-1}, $\alpha = 2$ and $b = 1.2$, A_V is the Pitzer-Debye-Hückel slope having value of 1.874 cm^3 kg$^{1/2}$ mol$^{-3/2}$ at 298.15 K. ϕ_V° is the partial molal volume of an electrolyte at infinite dilution. $(\partial\beta^{(0)}/\partial P)_T$, $(\partial\beta^{(1)}/\partial P)_T$, and $(\partial C^\phi/\partial P)_T$ are the virial coefficients in the Pitzer equations.

Rogers and Pitzer[13] have suggested that the term $(\partial\beta^{(1)}/\partial P)_T$ could be neglected, as it is not possible to obtain it accurately from volumetric results. Thus, the omission of $(\partial\beta^{(1)}/\partial P)_T$ from Eq. 2 yields into a very simple expression as Eq. 1 with two unknown parameters as $(\partial\beta^{(0)}/\partial P)_T$ and $(\partial C^\phi/\partial P)_T$.

The apparent molal volume of an ion in the mixture, ϕ_{Vi}^* (considering cation–anion pairwise interactions only) is given by

$$\phi_{Vi}^* = \phi_{Vi}^\circ + \frac{Z_i A}{2b}\ln(1+bI^{1/2})RT\sum_j B_{ij}\,m_j + \frac{RT}{2|Z_i|^{1/2}}\sum_j C_{ij}\,m_j^2\,|Z_j|^{1/2} \tag{4}$$

where the summations over j are over ions of opposite charge.

ϕ^*_{Vi} then yields the apparent molal volume of an electrolyte in mixture, ϕ_{VJ}, as

$$\phi_{VJ}=\sum_{i}\nu_i\,\phi^*_{Vi} \tag{5}$$

which in turn calculates theoretical mean apparent molal volumes ϕ^*_{Vth} by

$$\phi^*_{Vth}=\sum_{J}m_J\,\phi_{VJ}/\sum m_J. \tag{6}$$

Theoretical density, d_{th}, of the mixture is obtained from

$$d_{th}=(1000+\sum_{J}m_J M_J/(1000/d_0)+\sum_{J}m_J\phi_{VJ} \tag{7}$$

where M_J is molecular weight of an electrolyte.

The experimental densities, d_{exp}, may be converted to experimental mean apparent molal volumes ϕ^*_{Vexp} by the relationship

$$\phi^*_{Vexp}=\frac{1000(d_0-d_{exp})}{\sum_{J} m_J\,d_{exp}d}+\frac{\sum_{J} m_J M_J}{d_{exp}\sum_{J} m_J}. \tag{8}$$

Equation 4 does not include the interactions due to the ions of like charge. These interactions i.e. Na^+ and K^+; Cl^--Br^- designated by θ^V_{ik} (i, k are ions with like charges) can be evaluated in the form of difference parameter as:

$$\theta^V_{ik}=(\phi^*_{Vexp}-\phi^*_{Vth})\,(m_i+m_k)/2RT\,m_i\,m_k. \tag{9}$$

It may be noted that Eq. 9 is consistent with Eq. 17 of reference by Pitzer and Kim,[2)] who described the mixing therms θ_{ik} for osmotic and activity coefficients of aqueous mixed electrolytes.

An additional term $RT\sum_{k}\theta^V_{ik}m_k$ may be appended to Eq. 4 in order to obtain ϕ^*_{Vi} with both the cation-anion pair and cation-cation or anion-anion pair interactions as

$$\phi^*_{Vi,corr}=\text{R. H. S. of Eq. }4+RT\sum_{k}\theta^V_{ik}m_K. \tag{10}$$

Results and Discussion

Table 1 lists the experimental density differences for both KCl-KBr and NaBr-KBr as a function of y_{KBr} at constant ionic strengths of 0.5, 1, 2, 3, and 4 mol kg^{-1} of water. The values of ϕ^*_{Vexp} can readily be obtained from Eq. 8. The density values for pure constituent electrolytes, i.e. KCl, KBr, and NaBr were in excellent agreement with recent literature.[14-18)]

In order to employ the virial coefficients equation of Pitzer, it is essential to obtain the $(\partial\beta^{(0)}/\partial P)_T$, $(\partial\beta^{(1)}/\partial P)_T$, and $(\partial C^\phi/\partial P)_T$ parameters of pure electrolytes from Eqs. 1 to 3. The $(\partial\beta^{(0)}/\partial P)_T$ and $(\partial C^\phi/\partial P)_T$ terms for KCl, KBr, and NaBr were taken from our earlier work[19,20)] or calculated from the coefficients cited therein. The values of pure electrolyte parameters are listed in Table 2. The use of these parameters

Table 1. Experimental Relative Densities of Aqueous KCl-KBr and NaBr-KBr at 298.15 K

y_B	$\Delta d\times10^3$/g cm^{-3}	y_B	$\Delta d\times10^3$/g cm^{-3}
KCl-KBr		NaBr-KBr	
I=0.5		I=0.5	
0	22.73	0	33.53
1.1432	25.37	0.1988	39.06
0.2957	28.19	0.4021	39.59
0.4119	30.33	0.5012	39.85
0.5594	33.05	0.6119	40.14
0.6937	35.52	0.8095	40.67
0.8231	37.91	1	41.17
1	41.16		
I=1		I=1	
0	44.28	0	75.72
0.1533	49.83	0.2043	76.66
0.3139	55.64	0.4122	76.68
0.4638	61.07	0.5099	78.12
0.5982	65.92	0.6065	78.58
0.7492	71.38	0.8033	79.50
0.8925	76.55	1	80.43
1	80.43		
I=2		I=2	
0	84.46	0	146.20
0.1123	92.28	0.2055	147.75
0.2194	99.72	0.4079	149.27
0.3452	108.45	0.5005	149.97
0.4298	114.32	0.6663	151.22
0.5389	121.88	0.8065	152.28
0.6721	131.10	1	153.75
0.7690	137.79		
0.8992	146.78		
1	153.74		
I=3		I=3	
0	121.28	0	212.27
0.1243	133.77	0.1992	214.06
0.2395	145.34	0.4040	215.89
0.3701	158.44	0.4998	216.74
0.4695	168.39	0.6045	217.68
0.5921	180.64	0.8013	219.45
0.7119	192.58	1	221.23
0.8399	205.31		
0.9342	214.69		
1	221.23		
I=4		I=4	
0	155.14	0	274.39
0.0981	167.83	0.2022	276.18
0.1952	180.36	0.4045	277.98
0.2666	189.56	0.5017	278.84
0.3531	200.69	0.6061	279.78
0.4555	213.86	0.7998	281.52
0.5521	226.26	1	283.33
0.6661	240.81		
0.8444	263.53		
1	283.33		

Table 2. Pitzer Coefficients for Pure Electrolytes for Correlating ϕ_V and Molality

Electrolyte	ϕ^0_V / cm^3 mol^{-1}	$(\partial\beta^{(0)}/\partial P)$ $\times10^6$	$(\partial C^\phi/\partial P)T$ $\times10^7$	Standard deviation σ/cm^3 mol^{-1}
KCl	27.11	11.82	−11.61	0.01
KBr	33.84	11.45	−14.33	0.01
NaBr	23.52	8.70	−8.70	0.01

in Eqs. 4 to 7 yields the calculated ϕ^*_{Vth} and d_{th} of the mixtures. It is interesting to note that these calculations are manifestation of a simple Young's rule,[21] where the mixture properties are computed from the properties of the individual ions at the same ionic strength. The results of calculations are shown in Table 3 in terms of average deviations of fits, indicating systematic negative deviations for Δd values as demonstrated for example at the highest ionic strength I=4 mol kg^{-1} for both the systems in Fig. 1. In view of these deviations, the interactions between like charged ions were taken into account with the use of Eq. 10, where the $\theta^{\mathrm{V}}_{\mathrm{ik}}$ values (Table 4) were obtained from Eq. 9. The results of calculations are shown in Table 3. Figure 1 also depicts the results for both the systems at I=4 mol kg^{-1} with the use of $\theta^{\mathrm{V}}_{\mathrm{ik}}$ terms. An examination of Table 3 indicates a remarkable improvement in the fits, and, also the systematic deviations are removed. In general, the average deviations for KCl-KBr and NaBr-KBr are reduced to 7 and 5 ppm respectively with the use of $\theta^{\mathrm{V}}_{\mathrm{ik}}$.

Very recently, Patwardhan and Kumar[22,23] have derived a simple equation from the concept of reduced inoic activity coefficient for estimating densities of concentrated mixed electrolyte solutions. The equation is

$$d=\sum_J(1000y_J+m_JM_J)/\sum_J(1000y_J+m_JM_J/d^0_J). \tag{11}$$

Table 3. Average Deviations, δ, from Experimental Data as Obtained by Pitzer Equations without (Also by Equation of Patwardhan and Kumar) and with Mixing Term, $\theta^{\mathrm{V}}_{\mathrm{ik}}$ at 298.15 K

I	−δ/ppm			
mol kg^{-1}	KCl-KBr		MaBr-KBr	
	Without $\theta^{\mathrm{V}}_{\mathrm{ik}}$	With $\theta^{\mathrm{V}}_{\mathrm{ik}}$	Without $\theta^{\mathrm{V}}_{\mathrm{ik}}$	With $\theta^{\mathrm{V}}_{\mathrm{ik}}$
0.5	3	2	3	2
1	28	5	10	3
2	89	7	29	6
3	185	9	56	7
4	294	11	85	9

Table 4. Binary Mixing Terms of Pitzer ($\theta^{\mathrm{V}}_{\mathrm{iK}}$) and Friedman ($v^0$) Equations at 298.15 K

I	$\theta^{\mathrm{V}}_{\mathrm{ik}}\times10^6$	v^0
	i=Cl$^-$, k=Br$^-$	
0.5	1.94	0.096
1	2.74	0.136
2	2.44	0.121
3	2.16	0.107
4	1.84	0.091
	i=Na$^+$, k=K$^+$	
0.5	0.97	0.048
1	0.81	0.040
2	0.71	0.035
3	0.61	0.030
4	0.52	0.026

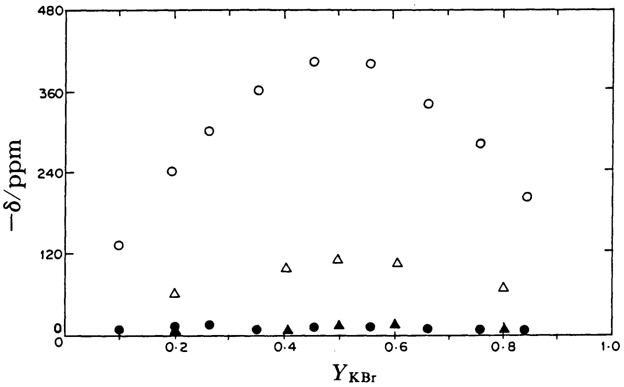

Fig. 1. Deviaition of experimental density data from calculated ones by Pitzer Equations without and with $\theta^{\mathrm{V}}_{\mathrm{ik}}$ values for KCl-KBr and NaBr-KBr at I=4 and T=298.15 K; KCl-KBr ○ without ● with; NaBr-KBr △ without ▲ with.

In this equation, d^0_J is density of constituent Jth electrolyte at the ionic strength of the mixture. Their equation neglects any interactions due to like charged ions and, thus, is again equivalent to Young's rule.[21] The results, hence, listed in Table 3 without the $\theta^{\mathrm{V}}_{\mathrm{ik}}$ are also applicable to Eq. 11.

The excess volumes of mixing, ΔV_{m}, for these mixtures can be obtained as

$$\Delta V_{\mathrm{m}}=\phi^*_{\mathrm{V\,exp}}\,m_J-\sum_J m_J\,\phi''_{\mathrm{V}J} \tag{12}$$

where $\phi''_{\mathrm{V}J}$ is apparent molal volume of Jth electrolyte at the ionic strength of mixture. The ΔV_{m} values can be fitted to the Friedman equation.[24]

$$\Delta V_{\mathrm{m}}=y_{\mathrm{B}}(1-y_{\mathrm{B}})I^2[v^0+v^1(1-2y_{\mathrm{B}})] \tag{13}$$

where v^0 and v^1 are the Friedman parameters indicating binary (ik) and ternary (ijk) interactions, respectively. The use of Eq. 13 fitted, the ΔV_{m} with good accuracy and v^1 values were found negligible. The values of v^0 values as a function of I can conveniently be represented as

$$v^0=15.3\times10^{-2}-15.0\times10^{-3}I\,(\text{for KCl-KBr}) \tag{14}$$

and

$$v^0=4.5\times10^{-2}-4.75\times10^{-3}I\,(\text{for NaBr-KBr}). \tag{15}$$

One should note that data of I=0.5 are not included in the fit, as the error becomes significantly large at lower ionic strengths.

Wood and Smith[25] reported the heats of mixing data up to I=1 for these mixtures, and fitted the data to analogous equation of Friedman in order to obtain RTh_0 and $\mathrm{RTh_1}$ as we did to Eq. 13. Negligible RTh_1 values from their study support our negligible v^1 values for both the systems. A study of their data shows that h_0 value is approximately ten times higher in the case of aq. NaBr-KBr than that of aq. KCl-KBr. The present study on volume indicates the relationships inversed by three times. The former effect is

Table 5. Temperature Dependence of v^0 Values for Aqueous KCl-KBr and NaBr-KBr Systems at Low and High Ionic Strengths

I	Temperature	
mol kg^{-1}	278.15 K	318.15 K
	KCl-KBr	
1	0.131	0.144
4	0.084	0.100
	NaBr-KBr	
1	0.036	0..046
4	0.022	0.032

obtained from the temperature dependence of activity coefficients, while the latter from pressure dependence.

Friedman[24,26,27] using Mayer's ionic cluster expansion method estimated the excess properties of mixing of aqueous mixed electrolytes with a common ion. The equations incorporated the primitive model consisting of hard spheres in a continuous dielectric. According to him, the interaction terms RTg_0 and RTh_0 for excess free energy and enthalpy of mixing, respectively, are finite for common ion mixtures even at infinite dilution. The values of intercepts in Eqs. 14 and 15 confirm Friedman's results of calculations for excess volumes of mixing too. One clearly notes the absence of high order limiting law[28] in the symmetric mixtures like these under study. A survey of v_0 values for both the mixtures indicates a slow variation of v_0 with I or total molality. Thus, v_0 values arising out of like-charged ion-interactions are more important than v^1 which is an indication of ternary interaction. This observation is confirmed both by enthalpy of mixing data of Wood and Smith[25] and by the present work on volumes.

The binary mixing term of Pitzer, $\theta^{\mathrm{V}}_{\mathrm{ik}}$ could be correlated with v^0 term of Friedman using Eqs. 9, 12, and 13 to give

$$\theta^{\mathrm{V}}_{\mathrm{ik}}=v^0/2RT. \tag{16}$$

It is natural that $\theta^{\mathrm{V}}_{\mathrm{ik}}$ will have same ionic strength dependence.

Since the ΔV_{m} values at 298.15 K showed maxima at $y_{\mathrm{B}}=0.5$, we conducted one experiment each for $I=1$ and 4 mol kg^{-1} for both the systems at 278.15 and 318.15 K in order to obtain temperature dependence of ΔV_{m}. Table 5 lists the results in terms of v^0, which indicate poor temperature dependence in both the cases. The values of $\partial v^0/\partial T$ for aqueous KCl-KBr and aqueous NaBr-KBr were found to be 3.6×10^{-4} and 2.5×10^{-4}, respectively in the temperature range of 278.15 to 318.15 K. In view of this, we deferred conducting further experimentations at other intermediate ionic strengths and temperatures.

To summarize, the densities of concentrated aqueous mixed electrolytes can be estimated with accuracy with the Pitzer theory of specific interactions, provided both the interactions (cation-anion and cation-cation or anion-anion) are explicitly considered. Ternary interactions are negligible throughout, although they could be significant in many other systems. In near future, we shall present complete description of the symmetric and asymmetric mixtures, for which we are collecting experimental data. Also, the experimental data, for the treatment of which, ternary interaction term is required, will be presented.

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