Densities and Excess Volumes of Aqueous KCl–NaBr up to Ionic Strength of 4 mol kg^{-1}

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Densities of aqueous mixtures of KCl with NaBr are reported at ionic strengths of 0.5, 1, 2, 3, and 4 mol kg^{-1} and at 298.15 K from pure KCl to pure NaBr solutions. The excess volumes of mixing, which are negative, can be fitted to Friedman's equation. Mixing experiments at equimolal concentration and ionic strengths 1 and 4 mol kg^{-1} were also conducted at 278.15 and 318.15 K. The results indicate weak temperature dependence of the excess volumes. The densities of these mixtures can be estimated accurately with Young's rule, if the excess volumes are taken into account.

Introduction

In continuation of our earlier work (*1–4*) on densities of concentrated aqueous mixed electrolyte solutions, we now extend our studies to an aqueous mixture of four different ions and report density measurements for the system KCl–NaBr–H_2O at constant ionic strengths of 0.5, 1, 2, 3, and 4 mol kg^{-1} water. Initially, all the measurements were made at a constant temperature of 298.15 K, but after study of the results, a single mixing experiment each at ionic strengths of 1 and 4 mol kg^{-1} water was conducted at two additional temperatures, i.e., 278.15 and 318.15 K, with a view to understanding temperature dependence.

Experimental Section

The differences in densities ($\Delta d = d - d_0$) were measured by using a Paar densimeter, where d and d_0 were the densities of solution and pure water, respectively. The densimeter was calibrated with pure water and NaCl solutions by using the precise density data of Kell (*5*) and Lo Surdo et al. (*6*), respectively. The temperature of thermostat bath was controlled to $\pm 5 \times 10^{-3}$ K, and the densities were precise to $\pm 3 \times 10^{-6}$ g cm^{-3}. The stock solutions of both KCl and NaBr (oven dried at 140 °C), obtained from Baker (reagent grade), were made by dissolving a definite mass into degassed ion-exchanged water. The mixtures with different compositions were prepared at constant ionic strength as $y_{NaBr} = m_{NaBr}/I$, where y and m refer to the ionic strength fraction and molality, respectively.

Results and Discussion

In Table I are reported the values of the density differences, Δd, as a function of y_{NaBr} at various constant ionic strengths and at 298.15 K. Our results on densities for pure electrolytes are in good agreement with those available in literature. Vaslow (*7*) and Gucker et al. (*8*) reported very precise density data on aqueous KCl. Our data agree with those of Vaslow and of Gucker et al. on interpolation to appropriate molalities to within 30×10^{-6} g cm^{-3} with the maximum residual being 95×10^{-6} g cm^{-3}. Interestingly, our data were in excellent agreement (15×10^{-6} g cm^{-3}) with those of Romankiw and Chou (*9*). Similarly our data compared well with very recent work of Gates and Wood (*10*). However, there are remarkable differences between our data and those of Nickels and Allmand (*11*), Fabuss and Korosi (*12*), and International Critical Tables (*13*) by 992×10^{-6}, 360×10^{-6}, and 250×10^{-6} g cm^{-3}, respectively. Similarly our data on pure NaBr solutions were in excellent agreement with those of Gates and Wood (*10*), Isono (*14*), and Gucker et al. (*15*).

Table I. Experimental Density Differences (Δd/g cm^{-3}) of Aqueous KCl–NaBr at 25 °C

Y_{NaBr}	$10^3\Delta d$	Y_{NaBr}	$10^3\Delta d$	Y_{NaBr}	$10^3\Delta d$
		$I = 0.5$ mol kg^{-1}			
0	22.723	0.4992	30.627	0.8117	35.564
0.1652	25.339	0.6301	32.695	1	38.539
0.3451	28.187				
		$I = 1.0$ mol kg^{-1}			
0	44.296	0.4050	57.017	0.7511	67.889
0.1421	48.756	0.5001	60.004	0.8723	71.695
0.2851	53.252	0.6139	63.578	1	75.703
		$I = 2.0$ mol kg^{-1}			
0	84.479	0.5002	115.354	0.7914	133.328
0.1951	96.523	0.6038	121.749	1	146.199
0.4018	109.281				
		$I = 3.0$ mol kg^{-1}			
0	121.260	0.3814	155.970	0.7494	189.455
0.1239	132.539	0.4989	166.692	0.8810	201.432
0.2561	144.569	0.6301	178.604	0	212.263
		$I = 4.0$ mol kg^{-1}			
0	155.139	0.3701	199.269	0.7661	246.493
0.1208	169.540	0.5005	214.829	0.8951	261.884
0.2495	184.898	0.6198	229.055	1	274.390

The apparent molal volumes of pure electrolyte solutions, ϕ_V, were calculated as

$$\phi_V = (M/d) - [10^3(d - d_0)/dd_0m] \tag{1}$$

where M is the molecular weight of an electrolyte. Similarly, the mean apparent molal volumes, $\phi_V{}^*$, of mixtures were obtained as

$$\phi_V{}^* = (M_T/m_Td) - [10^3(d - d_0)/dd_0m_T] \tag{2}$$

where

$$M_T = (m_{KCl}M_{KCl} + m_{NaBr}M_{NaBr})$$

and

$$m_T = m_{KCl} + m_{NaBr}$$

The excess volumes of mixing Δ_mV (cm^3 kg^{-1} H_2O) were obtained from the relationship

$$\Delta_mV = \phi_V{}^*m_T - \phi_V{}'_{KCl}m_{KCl} - \phi_V{}'_{NaBr}m_{NaBr} \tag{3}$$

where $\phi_V{}'$ refers to the apparent molal volume of an individual electrolyte solution at ionic strength of the mixture.

The Δ_mV values, if plotted against y_{NaBr}, show fairly symmetrical parabola. The Δ_mV values can be treated with Friedman's equation (*16*):

$$\Delta_mV = y_{NaBr}(1 - y_{NaBr})I^2[v_0 + v_1(1 - 2y_{NaBr})] \tag{4}$$

In this equation, v_0 and v_1 are the parameters related to binary and ternary interactions, respectively. The Δ_mv values, which are negative throughout, could be represented with the help of a single Friedman parameter v_0 (cm^3 mol^{-2} kg) to within experimental error, thus indicating the negligible magnitude of ternary interaction (v_1) term. The values of v_0 obtained are -0.240, -0.130, -0.122, -0.117, and -0.116 with standard deviation of 0.005 for I = 0.5, 1, 2, 3, and 4 mol kg^{-1}, respectively. The average standard deviation of fit for the $\Delta_m V$ values is 0.003 cm^3 kg^{-1} with maximum standard deviation 0.008 cm^3 kg^{-1} at $I = 4$.

Wood and Smith (*17*) reported heats of mixing data on this system and fitted their data to analogous Friedman's equation in order to obtain RTh_0 and RTh_1 values. The negligible values of RTh_1 reported by them support our negligible v_1 values. Further, the negative sign of RTh_0 values confirms the nature of our v_0 values. Comparison at high ionic strengths is, however, not possible, as their data do not extend beyond I = 1 mol kg^{-1}.

An examination of v_0 as a function of ionic strength suggests finite value at zero ionic strength. This confirms the theoretical predictions made by Friedman (*16*, *18*, *19*) using Mayer's ionic cluster expansion method. The slow variation of v_0 with ionic strength ($I > 1$) suggests that like-charged ion pair interactions (e.g., Na^+, K^+; Cl^-, Br^-) are more important than triplet interactions. It may be noted that in the dilute region ($I < 1$), the error in v_0 is enlarged and that is the case at $I = 0.5$.

Since the $\Delta_m V$ versus y_{NaBr} plots are nearly a symmetric parabola, we conducted temperature dependence for $y_{NaBr} = 0.5$ at lower and high ionic strengths, i.e., 1 and 4, by taking measurements at 278.15 and 318.15 K. Thus, the values of v_0 at $I = 4$ are -0.126 ± 0.005 and -0.105 ± 0.004 at 278 and 318.15 K, respectively. Similarly at $I = 1$, v_0 varies as -0.137 ± 0.004 and -0.121 ± 0.004 at 278 and 318.15 K, respectively. These results along with those at 298.15 K show that $\Delta_m V$ values of this system are weakly dependent on temperature.

One can demonstrate the need of considering the $\Delta_m V$ values by comparing the experimental densities with those obtained by

$$d = (M_T + 1000)/(m_T\, \phi_V{}^*{}_{est} + 1000/d_0) \tag{5}$$

where

$$\phi_V{}^*{}_{est} = x_{KCl}\phi_V{}'_{KCl} + x_{NaBr}\phi_V{}'_{NaBr} + \Delta_m V/m_T \tag{6}$$

with $x = m/m_T$.

The values of $\phi_V{}^*{}_{est}$ are obtained without and with $\Delta_m V$ values. The former case is the direct application of famous Young's rule (*20*). Very recently, Patwardhan and Kumar (*21*, *22*) derived an equation for estimating densities of aqueous mixed electrolyte. Their equation, which neglects any mixing term arising out of interaction of like-charged ions, is

$$d = \sum_J \psi_J / \sum_J \psi_J / d_J{}^0 \tag{7}$$

where

$$\psi_J = 1000 + m_J M_J$$

and $d_J{}^0$ is density of pure electrolyte solution at the ionic strength of mixture. Thus, the results obtained from eq 5 and 7 are the same, provided the former equation is used without $\Delta_m V$ values. Table II shows that if the $\Delta_m V$ values are not considered for calculating the densities of mixtures, the differences, δ, become very large. The use of $\Delta_m V$ values reduced δ values greatly. For example, values are reduced to 9 ppm with the use, as compared to 316 ppm obtained without the use, of $\Delta_m V$ at I = 4 mol kg^{-1}. As an average from $I = 0.5$ to 4, the δ values are reduced remarkably to 6 ppm from 145 ppm.

Table II. Differences, δ, between Experimental Densities and Those without (Also by Eq 7) and with the use of $\Delta_m V$

I	δ/ppm without $\Delta_m V$	δ/ppm with $\Delta_m V$
1	11	3
2	22	5
3	180	8
4	316	9
av	145	6

To summarize, we have presented experimental density differences for aqueous KCl–NaBr up to ionic strength of 4 mol kg^{-1} water. The densities can accurately be predicted with Young's rule, provided the correction term, $\Delta_m V$, is taken into consideration.

Registry No. KCl, 7447-40-7; NaBr, 7647-15-6.

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