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Isopiestic Studies on the Quaternary System (Water + Ethanol + Sodium Bromide + Ammonium Bromide) at the Temperature 298.15 K: Comparison with the Ideal-Like Solution Model[†]

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Isopiestic measurements have been carried out for the quaternary system (water + ethanol + sodium bromide + ammonium bromide) with a mass ratio of water to ethanol of 9:1 or 4:1 at the temperature 298.15 K. The results are well represented by the ideal-like solution model.

Introduction

Zdanovskii discovered an empirical rule for ternary electrolyte solutions under isopiestic equilibrium[1]

$$m_B/m_B^{OB} + m_C/m_C^{OC} = 1 \tag{1}$$

where m_B and m_C denote molalities of solute B and solute C in the ternary solutions, while m_B^{OB} and m_C^{OC} denote molalities of B and C, respectively, in the binary subsystems at constant activity of water. Equation 1 was first derived by Stokes and Robinson for aqueous nonelectrolyte solutions in their semi-ideal hydration model.[2] Starting from the Zdanovskii rule, Wang[3,4] presented a general linear concentration rule and the corresponding partial ideal solution model, which hold good for the real system {A+B+C+... +Z} having zero interchange energy among B, C,... Z at constant chemical potential of A. Since 1998, Wang[5] has extended the partial ideal solution model and proposed the ideal-like solution model, which hold good for the real system {A_1+A_2+... +A_q+B+C+... +Z} having zero interchange energy among B, C,..., Z at constant chemical potentials of A_1, A_2,..., A_q. On the other hand, isopiestic measurements are known to be the most accurate method for unsaturated aqueous and nonaqueous solutions. By using the isopiestic technique, accurate activity data have been determined for hundreds of binary and ternary aqueous solutions at T = 298.15 K.[6] To check the partial ideal solution model and the ideal-like solution model, isopiestic determinations have been made for unsaturated ternary and quaternary aqueous solutions[7−9] and ternary methanol solutions[10] and been extended to alloys,[11−14] molten salt mixtures,[15,16] slags,[17] saturated aqueous solutions,[5,18−20] and unsaturated (water + methanol)[21] and (water + methanol + ethanol)[22] mixed solvent solutions. Our previously reported measurements[21,22] have presented evidence for the advantages of the isopiestic technique in the easy and accurate determination of solute molalities in isotonic equilibrium samples in mixed solvent solutions over other vapor−liquid equilibrium techniques. In this study, extensive isopiestic measurements are reported for the unsaturated mixed solvent quaternary system {water (A_1) + ethanol (A_2) + sodium bromide (B) + ammonium bromide (C)} with the mass ratios w_{A1}/w_{A2} = 9 and w_{A1}/w_{A2} = 4 at the temperature T = 298.15 K and to compare the results with the ideal-like solution model.[5]

Experimental

Isopiestic measurements were made by the method described previously.[7−10,21,22] Sodium bromide and ammonium bromide were ultrapure grade, and ethanol was HPLC grade from Aldrich and used without further treatment. The salts were stored over P_2O_5 in a vacuum desiccator before use. Triple-distilled water was used. A mixed solvent {water (A_1) + ethanol (A_2)} with the mass ratio w_{A1}/w_{A2} = 9 or w_{A1}/w_{A2} = 4 was prepared by weighing. Then, a quaternary system {water (A_1) + ethanol (A_2) + sodium bromide (B) + ammonium bromide (C)} or its ternary subsystems {water (A_1) + ethanol (A_2) + sodium bromide (B)} and {water (A_1) + ethanol (A_2) + ammonium bromide (C)} were prepared by adding the mixed solvent into the salt mixture (sodium bromide + ammonium bromide) or the pure salt. The quaternary system was run against both of its ternary subsystems, and no reference standard could be used in this study for the lack of relatively accurate vapor−liquid equilibrium data for the mixed solvent systems and the relatively large difficulties in determining accurately the mass ratios of water to ethanol in the equilibrium samples. Preliminary experiments showed that the isopiestic equilibrium might be achieved within (4 to 6) days. Therefore, the formal equilibrium period was (6 to 9) days for each run. At the end of each run, after pressing a lid onto all the cups, the isopiestic apparatus was placed in a dry container where the temperature was kept to T = 273 K. After opening the isopiestic apparatus, individual caps were immediately placed on the cups before they were weighed. According to Rard and Platford,[6] an individual isopiestic molality at equilibrium can be determined to ± $(0.0005 \cdot m)$ to ± $(0.001 \cdot m)$. The isopiestic equilibrium reported in this study for each sample was the average between the duplicates, and an individual isopiestic molality at equilibrium was reproducible to ± $(0.0005 \cdot m)$.

Results and Discussion

Let m denote molality, and let the superscript ^{oo} denote the behavior for the ternary subsystems {water (A_1) + ethanol (A_2) + nonvolatile solute (B)} and {water (A_1) + ethanol (A_2) +

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Table 1. Isopiestic Results for the {Water (A_1) + Ethanol (A_2) + Sodium Bromide (B) + Ammonium Bromide (C)} Quaternary System with a Mass Ratio $w_{A1}/w_{A2} = 9$ at $T = 298.15$ K and $m° = 1$ mol·kg^{-1}[a]

$m_B/m°$	$m_C/m°$	Δ
1.0056	0	
0	1.0299	
0.8476	0.1626	0.0008
0.6778	0.3366	0.0009
0.5074	0.5111	0.0008
0.3374	0.6846	0.0002
0.1675	0.8588	0.0004
2.0168	0	
0	2.1546	
1.7048	0.3354	0.0010
1.3682	0.6953	0.0011
1.0276	1.0587	0.0009
0.6864	1.4227	0.0006
0.3417	1.7902	0.0003
2.9932	0	
0	3.2947	
2.5342	0.5090	0.0011
2.0366	1.0561	0.0010
1.5352	1.6074	0.0008
1.0297	2.1634	0.0006
0.5194	2.7253	0.0007
4.0195	0	
0	4.6879	
3.4383	0.6776	−0.0001
2.8229	1.4005	0.0010
2.1878	2.1421	0.0012
1.4766	2.9691	0.0007
0.7506	3.8125	0.0000

[a] Δ denotes the experimental deviation from eq 2.

Table 2. Isopiestic Results for the {Water (A1) + Ethanol (A2) + Sodium Bromide (B) + Ammonium Bromide (C)} Quaternary System with a Mass Ratio $w_{A1}/w_{A2} = 4$ at $T = 298.15$ K and $m° = 1$ mol·kg^{-1}[a]

$m_B/m°$	$m_C/m°$	Δ
1.0198	0	
0	1.0012	
0.8550	0.1617	−0.0001
0.6806	0.3334	0.0004
0.5086	0.5018	−0.0001
0.3361	0.6702	−0.0010
0.1672	0.8361	−0.0009
2.0278	0	
0	2.0744	
1.7124	0.3242	0.0007
1.3712	0.6737	0.0010
1.0294	1.0228	0.0007
0.6858	1.3727	−0.0001
0.3406	1.7261	0.0001
3.0188	0	
0	3.1467	
2.5489	0.4879	−0.0006
2.0501	1.0124	0.0008
1.5358	1.5503	0.0014
1.0371	2.0683	0.0008
0.5146	2.6116	0.0004
4.0556	0	
0	4.4295	
3.4348	0.6777	−0.0001
2.8020	1.3752	0.0014
2.1622	2.0742	0.0014
1.4522	2.8477	0.0010
0.7313	3.6267	−0.0009

[a] Δ denotes the experimental deviation from eq 2.

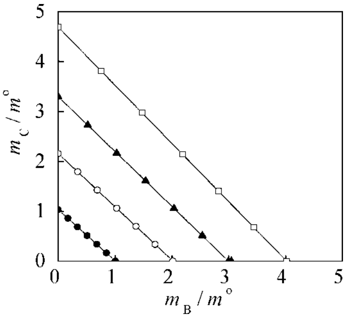

Figure 1. Isopiestic lines of the quaternary system {water (A_1) + ethanol (A_2) + sodium bromide (B) + ammonium bromide (C)} with a mass ratio $w_{A1}/w_{A2} = 9$ at $T = 298.15$ K: $m° = 1$ mol·kg^{-1}.

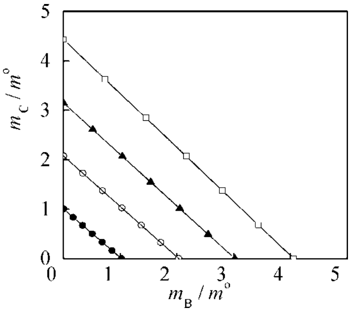

Figure 2. Isopiestic lines of the quaternary system {water (A_1) + ethanol (A_2) + sodium bromide (B) + ammonium bromide (C)} with a mass ratio $w_{A1}/w_{A2} = 4$ at $T = 298.15$ K: $m° = 1$ mol·kg^{-1}.

nonvolatile solute (C)}. Isopiestic behavior of a quaternary system {water (A_1) + ethanol (A_2) + nonvolatile solute (B) + nonvolatile solute (C)}, which obeys the ideal-like solution model[5] due to completely random distribution and zero interchange energy between B and C, may be expressed as

$$(m_B/m_B^{oo}) + (m_C/m_C^{oo}) = 1 \qquad (2)$$

at constant activities of A_1 and A_2 and within $0 \le (m_C/m_C^{oo}) \le 1$. In other words, if a quaternary system which follows the ideal-like solution model and two of its ternary subsystems are isotonic (the solvent activities of all three are equal), then this quaternary system has such a composition that can be prepared by mixing these two ternary subsystems. The deviation of a real system from eq 2 can then be defined by

$$\Delta = [(m_B/m_B^{oo}) + (m_C/m_C^{oo})] - 1 \qquad (3)$$

at constant activities of A_1 and A_2 and within $0 \le (m_C/m_C^{oo}) \le 1$. Table 1 shows four sets of isopiestic results for the {water (A_1) + ethanol (A_2) + sodium bromide (B) + ammonium bromide (C)} quaternary system with the mass ratio $w_{A1}/w_{A2} = 9$. Table 2 shows four sets of isopiestic results for the same quaternary system but with the mass ratio $w_{A1}/w_{A2} = 4$. The first and second columns give the molalities m_B of NaBr and m_C of NH_4Br. The third column gives the values of the Δ function defined by eq 3. It can be seen that $|\Delta| \le 0.0014$, similar to those for the (water + methanol)[21] and (water + methanol + ethanol)[22] mixed solvent systems and the aqueous solutions.[7−9,18−20] According to Rard and Platford,[6] an individual isopiestic molality at equilibrium can be determined to ± $(0.0005 \cdot m)$ to ± $(0.001 \cdot m)$, and the molality ratio of the reference standard to the test solution can be determined to ± 0.001 to ± 0.002 at $T = 298.15$ K for aqueous solutions under favorable conditions. Thus, the value of $|\Delta| \le 0.0014$ would indicate that the {water (A_1) + ethanol (A_2) + sodium bromide (B) + ammonium bromide (C)} quaternary system follows the ideal-like solution model within experimental errors.

Figure 1 and Figure 2 show the isopiestic lines that are well represented by eq 2 or ZSR graphs for the {water (A_1) + ethanol (A_2) + sodium bromide (B) + ammonium bromide (C)} quaternary system with the mass ratios $w_{A1}/w_{A2} = 9$ and $w_{A1}/w_{A2} = 4$, respectively.

The result reported here is consistent with our previous reports that the {water (A_1) + methanol (A_2) + bromide (B) + ammonium bromide (C)}[21] and {water (A_1) + methanol (A_2) + ethanol (A_3) + bromide (B) + ammonium bromide (C)}[22] mixed solvent systems fit the ideal-like solution model, indicating the negligible interchange energy between sodium bromide and ammonium bromide. This study further shows that the ideal-like solution model holds good predictive function for the isopiestic equilibria of mixed solvent mixed solute systems and that if the interchange energy between the unsaturated solutes can be neglected the interactions among the solvent components and between one of the solvent components and one of the solute components may have no effect on the linear isopiestic behavior.

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