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Vapor Pressures for 1,4-Dioxane + Tetrabutylammonium Nitrate, Water + Tetrabutylammonium Nitrate, and 1,4-Dioxane + Water + Tetrabutylammonium Nitrate

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The vapor pressures of the 1,4-dioxane + tetrabutylammonium nitrate and water + tetrabutylammonium nitrate systems have been measured at different salt molalities. The vapor pressures of the 1,4-dioxane + water + tetrabutylammonium nitrate system have also been measured at 11 constant salt molalities (0.100, 0.250, 0.500, 0.750, 1.000, 1.500, 2.000, 2.500, 3.000, 3.500, and 4.000) $\mathrm{mol \cdot kg^{-1}}$. These systems have been studied at (288.15, 298.15, and 308.15) K with a modified Othmer still. The electrolyte nonrandom two-liquid model was used for the calculation of the activity coefficients of solvents in the binary systems.

Introduction

Organic salts are important and are usually used as intermediate chemicals, reaction catalysts, inhibitors to undesired reactions, supporting electrolytes, and surfactants. The electrolyte systems containing large organic ions (ammonium, borate, phosphonium, sulfonium, arsonium, hydrazinium, pyridinium, other organic salts, and ionic liquids) continue to represent an important area of theoretical interest as well.[1]

Recently, the vapor pressures of the aqueous and nonaqueous solutions of several alkylammonium salts have been reported.[2–10] In this study, the vapor pressures of the 1,4-dioxane + tetrabutylammonium nitrate (TBAN), water + TBAN, and 1,4-dioxane + water + TBAN systems were measured at different salt molalities at (288.15, 298.15, and 308.15) K with an Othmer-type equilibrium cell. No vapor pressure data for these systems were found in the literature, but there are many experimental data for the binary 1,4-dioxane + water system. The electrolyte nonrandom two-liquid (NRTL) model of Chen et al.[11] was used to calculate solvent activity coefficients in the binary systems.

Experimental Section

Materials. The 1,4-dioxane ($w \geq 99.9$ %, Aldrich) was stored above 3 Å molecular sieves. Double-distilled and deionized water was used. Tetrabutylammonium nitrate ($w \geq 99.0$ %, Fluka) was previously dried at 75 °C in a vacuum oven until a constant mass was reached.

Procedure. Mixtures consisting of 1,4-dioxane, water, and TBAN were prepared gravimetrically using an analytical balance (Ohaus Explorer Pro Balance) with an uncertainty of ± 0.1 mg. Known masses of salt were dissolved in 0.5 $\mathrm{dm^3}$ of solvent (or mixed solvent), and the solution was placed in the still. Then the system was closed and the still was heated until constant pressure and temperature were attained. The average uncertainty of the mole fraction is ± 0.005. For a fixed liquid-phase composition, at least three data points were taken of the total pressure at the target temperature of (288.15, 298.15, and 308.15) K. The uncertainty of the measured temperature was ± 0.1 K. Vapor pressure data for pure water and 1,4-dioxane are presented in Table 1.

Table 1. Vapor Pressures for Pure 1,4-Dioxane (1) and Water (2) from T = (288.15 to 308.15) K

	p_1/kPa		p_2/kPa	
T/K	lit.[a]	exptl[b]	lit.[a]	exptl[b]
288.15	2.691	2.703	1.669	1.706
298.15	4.986	4.975	3.166	3.172
308.15	8.129	8.119	5.547	5.556

[a] Refs 16 and 17. [b] This work.

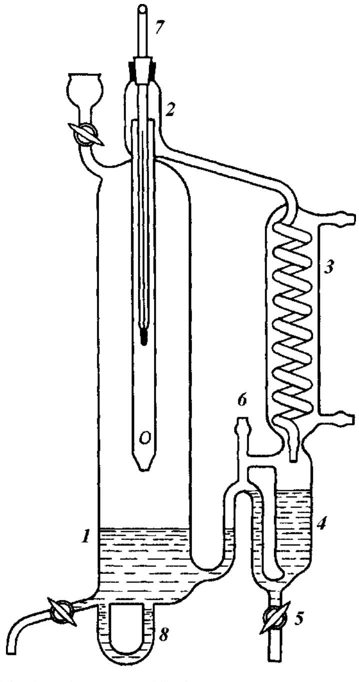

Figure 1. Modified Othmer's still for vapor pressure measurement: 1, distillation still; 2, steam jacket; 3, condenser; 4, condensed vapor receiver; 5, stopcock; 6, to manometer; 7, thermometer; 8, heating loop.

Apparatus. A modified static Othmer-type condensed vapor recirculating still[12] used for the present study is shown in Figure 1. The heating loop (8) ensures mixing and prevents bumping.

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Table 2. Experimental and Literature Vapor Pressure Data of the Benzyltributylammonium Chloride (1) + Water (2) System from T = (298.15 to 303.15) K as a Function of Salt Molality m_1

	T/K = 298.15		T/K = 303.15	
m_1/(mol·kg^{-1})	p_{exptl}/kPa[a]	p_{lit}/kPa[b]	p_{exptl}/kPa[a]	p_{lit}/kPa[b]
0.1	3.153	3.14	4.205	4.19
0.5	3.116	3.12	4.153	4.15
1.0	3.091	3.09	4.110	4.10
1.5	3.074	3.08	4.071	4.08
2.0	3.032	3.03	4.006	4.01
3.0	2.971	2.95	3.854	3.87
3.5	2.893	2.91	3.807	3.81
4.0	2.820	2.83	3.762	3.77

[a] This work. [b] Ref 3.

Table 3. Activity Coefficients of 1,4-Dioxane γ_1, Vapor Pressure p of the 1,4-Dioxane (1) + Tetrabutylammonium Nitrate (2) System from T = (288.15 to 308.15) K as a Function of Salt Molality m_2

	T/K = 288.15		T/K = 298.15		T/K = 308.15	
m_2/(mol·kg^{-1})	p/kPa	γ_1	p/kPa	γ_1	p/kPa	γ_1
0.100	2.907	1.0198	4.899	1.0212	7.987	1.0073
0.250	2.884	1.0112	4.854	1.0180	7.914	1.0014
0.500	2.853	1.0020	4.800	1.0104	7.802	0.9750
0.750	2.825	0.9814	4.751	1.0010	7.698	0.9610
1.000	2.796	0.9792	4.692	0.9814	7.601	0.9512
1.500	2.768	0.9670	4.639	0.9475	7.545	0.9370

Table 4. Activity Coefficients of Water γ_1, Vapor Pressure p of the Water (1) + Tetrabutylammonium Nitrate (2) System from T = (288.15 to 308.15) K as a Function of Salt Molality m_2

	T/K = 288.15		T/K = 298.15		T/K = 308.15	
m_2/(mol·kg^{-1})	p/kPa	γ_1	p/kPa	γ_1	p/kPa	γ_1
0.100	1.691	1.0601	3.150	1.0203	5.607	1.0170
0.250	1.684	1.0560	3.135	1.0244	5.579	1.0110
0.500	1.674	1.0420	3.122	0.9918	5.534	0.9807
0.750	1.665	1.0307	3.100	0.9722	5.506	0.9630
1.000	1.657	1.0097	3.078	0.9643	5.472	0.9489
1.500	1.638	0.9707	3.043	0.9414	5.410	0.9211
2.000	1.621	0.9240	3.008	0.9291	5.348	0.9013
2.500	1.608	0.8935	2.983	0.9179	5.303	0.8892
3.000	1.593	0.8681	2.958	0.8908	5.258	0.8784
3.500	1.581	0.8492	2.939	0.8804	5.213	0.8760
4.000	1.565	0.8305	2.904	0.8713	5.157	0.8688

The electrical heating system is Y6-VFP (Grant Instruments Ltd., U.K.). The temperature was measured with a mercury-in-glass thermometer. A device consisting of a 2200-type pressure sensor and PDRC-1C/2C type display supplied by the MKS Corporation (Andover MA, USA) was used to measure the pressure directly. The uncertainty of the measured pressure was 0.013 kPa. This apparatus was tested by measuring the vapor pressure of benzyltributylammonium chloride aqueous solutions at different concentrations from (298.15 to 303.15) K as given in Table 2. The average absolute deviations of the experimental data sets were less than 0.02 kPa compared to the published data.[3] This test showed the reliability of this apparatus and experimental procedure.

Results and Discussion

The vapor pressures of the binary systems 1,4-dioxane + TBAN and water + TBAN have been measured at (288.15, 298.15, and 308.15) K. In these systems for each temperature, 6 or 11 vapor pressure measurements of different salt concentrations have been studied. The molalities of TBAN ranged from (0.100 to 4.000) mol·kg^{-1}. The vapor pressures of the 1,4-dioxane + water + TBAN system have also been measured at 11 constant salt molalities (0.100, 0.250, 0.500, 0.750, 1.000, 1.500, 2.000, 2.500, 3.000, 3.500, and 4.000) mol·kg^{-1} at (288.15, 298.15, and 308.15) K. All the experimental data are given in Tables 3 to 5 and in Figure 2 and Figure 3. The vapor pressures of 1,4-dioxane and water decrease with an increase of salt molality in the binary systems.

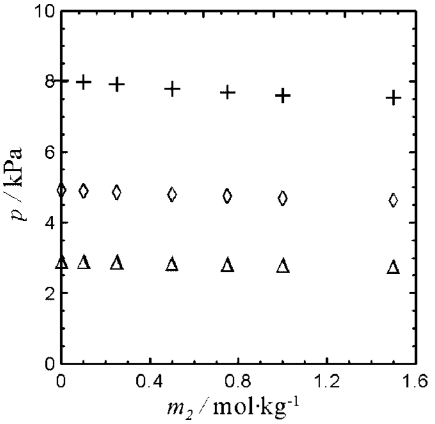

Figure 2. Vapor pressure p of 1,4-dioxane in the 1,4-dioxane (1) + tetrabutylammonium nitrate (2) system: Δ, 288.15 K; ◊, 298.15 K; +, 308.15 K. m_2 is the salt molality.

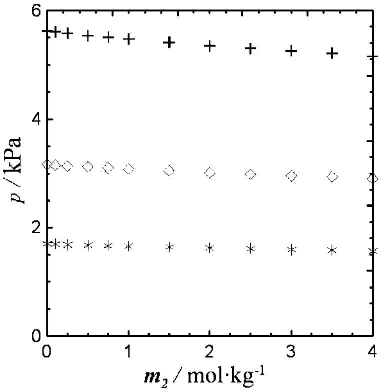

Figure 3. Vapor pressure p of water in the water (1) + tetrabutylammonium nitrate (2) system: ∗, 288.15 K; ◊, 298.15 K; +, 308.15 K. m_2 is the salt molality.

Calculation of the Activity Coefficients of Solvents for the Binary Systems. Vapor–liquid equilibrium data for the binary systems 1,4-dioxane (1) + TBAN (2) and water (1) + TBAN (2) were correlated by using the electrolyte NRTL model of Chen et al.[11] This model is usually used for correlation and prediction of phase equilibria of the binary electrolyte + solvent systems. The vapor phase was assumed as an ideal gas. For salt-containing binary systems, the salt was regarded as a nonvolatile component ($y_2 = 0$ and $y_1 = 1$). The formula of the vapor–liquid equilibrium is

$$y_i P = \gamma_i x_i p_i^0 \tag{1}$$

The saturation vapor pressure of pure solvent i (p_i^0) at system temperature was calculated with the published Antoine constants.[13] x_i is the liquid-phase mole fraction of solvent i based on the assumption of total dissociation of salt.

The parameters of the electrolyte NRTL model were taken from the published data[14] and are shown in Table 6. This model was often used to calculate the activity coefficients of solvents γ_i in the binary solvent + electrolyte systems. The activity coefficients of solvents of the studied binary systems are presented in Table 3 and Table 4. The expressions for calculation of the activity coefficients of solvents were directly taken from the electrolyte NRTL model of Chen et al.[11]

Table 5. Total Vapor Pressure p of the 1,4-Dioxane (1) + Water (2) + Tetrabutylammonium Nitrate (3) System from T = (288.15 to 308.15) K as a Function of Liquid Mole Fraction of 1,4-Dioxane x'_1 on a Salt-Free Basis and Salt Molality m_3

	p/kPa				p/kPa		
m_3/(mol·kg^{-1})	T/K = 288.15	T/K = 298.15	T/K = 308.15	m_3/(mol·kg^{-1})	T/K = 288.15	T/K = 298.15	T/K = 308.15
		$x'_1 = 0.050$				$x'_1 = 0.500$	
0.000	2.352	4.157	7.238	0.000	3.657	6.357	10.735
0.100	2.369	4.197	7.215	0.100	3.640	6.342	10.684
0.250	2.389	4.194	7.186	0.250	3.596	6.234	10.589
0.500	2.390	4.150	7.126	0.500	3.529	6.135	10.388
0.750	2.381	4.114	7.003	0.750	3.490	5.993	10.190
1.000	2.352	4.090	6.947	1.000	3.437	5.876	10.068
1.500	2.309	4.053	6.839	1.500	3.344	5.682	9.824
2.000	2.264	4.014	6.787	2.000	3.257	5.482	9.645
2.500	2.216	3.966	6.743	2.500	3.196	5.336	9.486
3.000	2.172	3.922	6.696	3.000	3.122	5.192	9.363
3.500	2.136	3.884	6.654	3.500	3.041	5.094	9.227
4.000	2.108	3.846	6.607	4.000	2.968	5.002	9.091
		$x'_1 = 0.100$				$x'_1 = 0.700$	
0.000	2.709	4.930	8.617	0.000	3.749	6.359	10.828
0.100	2.724	4.965	8.593	0.100	3.718	6.342	10.774
0.250	2.736	4.949	8.542	0.250	3.669	6.257	10.696
0.500	2.730	4.890	8.461	0.500	3.610	6.181	10.543
0.750	2.694	4.828	8.358	0.750	3.562	6.069	10.370
1.000	2.660	4.742	8.245	1.000	3.521	5.965	10.263
1.500	2.576	4.590	8.002	1.500	3.421	5.773	10.042
2.000	2.514	4.441	7.842	2.000	3.338	5.637	9.839
2.500	2.452	4.336	7.663	2.500	3.254	5.542	9.679
3.000	2.386	4.233	7.511	3.000	3.201	5.464	9.541
3.500	2.317	4.141	7.366	3.500	3.158	5.400	9.430
4.000	2.260	4.078	7.216	4.000	3.088	5.336	9.331
		$x'_1 = 0.170$				$x'_1 = 0.900$	
0.000	2.984	5.482	9.703	0.000	3.386	6.027	9.914
0.100	2.992	5.481	9.661	0.100	3.374	6.001	9.854
0.250	2.980	5.441	9.563	0.250	3.357	5.997	9.823
0.500	2.925	5.348	9.447	0.500	3.332	5.945	9.745
0.750	2.868	5.290	9.349	0.750	3.309	5.862	9.691
1.000	2.814	5.208	9.258	1.000	3.294	5.801	9.626
1.500	2.686	5.032	9.133	1.500	3.264	5.681	9.469
2.000	2.620	4.882	9.007	2.000	3.216	5.549	9.335
2.500	2.537	4.728	8.849	2.500	3.162	5.456	9.155
3.000	2.456	4.585	8.694	3.000	3.108	5.352	9.042
3.500	2.349	4.442	8.509	3.500	3.066	5.285	8.925
4.000	2.300	4.336	8.351	4.000	3.032	5.246	8.806

Table 6. Energy Parameters Δg_{ij} and Δg_{ji} and Nonrandomness Factors α_{ij} for the Electrolyte NRTL Model

component			Δg_{ij}	Δg_{ji}
i	j	α_{ij}	J·mol^{-1}	J·mol^{-1}
water	TBAN	0.2	2613.158	−134.126
1,4-dioxane	TBAN	0.1	3369.516	−822.603

The activity coefficients of solvents in the ternary system 1,4-dioxane + water + TBAN were earlier[14] calculated by using the electrolyte NRTL model of Mock et al.[15] which is used for the ternary mixed-solvent electrolyte systems.

Conclusion

The vapor pressures of the 1,4-dioxane + tetrabutylammonium nitrate, water + tetrabutylammonium nitrate, and 1,4-dioxane + water + tetrabutylammonium nitrate systems have been measured at different salt molalities at (288.15, 298.15, and 308.15) K with a modified Othmer-type equilibrium cell. The activity coefficients of solvents in the binary systems were calculated by using the electrolyte NRTL model.

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