J. Chem. Eng. Data **2009,** *54,* 1049–1051

Short Articles

Vapor Pressures for the Acetonitrile + Tetrabutylammonium Bromide, Water + Tetrabutylammonium Bromide, and Acetonitrile + Water + Tetrabutylammonium Bromide Systems

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The vapor pressures of the acetonitrile + tetrabutylammonium bromide, water + tetrabutylammonium bromide, and acetonitrile + water + tetrabutylammonium bromide systems have been measured at five constant salt molalities [(0.200, 0.400, 0.600, 0.800, and 1.000) $\text{mol}\cdot\text{kg}^{-1}$]. These systems have been studied at (298.15 and 323.15) K with a modified Othmer still.

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 salts with large organic ions (fatty acid anions, ammonium, phosphonium, sulfonium, arsonium, hydrazinium, pyridinium, borates, and others), betaines, and ionic liquids continue to represent an important area of theoretical interest as well.

Recently, the vapor pressures of the aqueous and nonaqueous solutions of several alkylammonium salts have been reported.[1−8] In this study, the vapor pressures of the acetonitrile + tetrabutylammonium bromide (TBAB), water + TBAB, and acetonitrile + water + TBAB systems were measured at different salt molalities [(0.200, 0.400, 0.600, 0.800, and 1.000) $\text{mol}\cdot\text{kg}^{-1}$] at (298.15 and 323.15) K with an Othmer-type equilibrium cell. The vapor pressure data for the acetonitrile + TBAB system at 298.15 K were found in the literature.[5,7]

Experimental Section

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

Procedure. Mixtures consisting of acetonitrile, water, and TBAB 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 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 was 0.005. For a fixed liquid-phase composition, at least three data points were taken of the total pressure at the target temperature of (298.15 and 323.15) K. The uncertainty of measured temperature was ± 0.1 K.

Table 1. Vapor Pressure p and Osmotic Coefficients Φ_1 of Acetonitrile in the Acetonitrile (1) + Tetrabutylammonium Bromide (2) System at $T = 323.15$ K as a Function of Salt Molality m_2

$m_2/(\text{mol}\cdot\text{kg}^{-1})$	p/kPa	Φ_1
0.000	33.860	–
0.200	33.008	0.812
0.400	32.504	0.767
0.600	32.020	0.738
0.800	31.487	0.716
1.000	31.022	0.695

Table 2. Vapor Pressure p of the Water (1) + Tetrabutylammonium Bromide (2) System from $T = (298.15$ to $323.15)$ K as a Function of Salt Molality m_2

	T/K = 298.15	T/K = 323.15
$m_2/(\text{mol}\cdot\text{kg}^{-1})$	p/kPa	p/kPa
0.000	3.166	12.348
0.200	3.055	12.006
0.400	2.959	11.704
0.600	2.864	11.358
0.800	2.779	10.907
1.000	2.701	10.532

Apparatus. A modified static Othmer-type condensed vapor recirculating still used for the present study is the same as the one presented earlier.[1,8] 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 measured pressure was 0.013 kPa. The experimental setup and apparatus testing are described in detail in our previous work.[1]

Results and Discussion

The vapor pressures of the binary systems acetonitrile + TBAB and water + TBAB were measured at (298.15 and 323.15) K. In these systems for each temperature, six vapor pressure measurements at different salt molalities were studied. The vapor pressures of the acetonitrile + water + TBAB system were also measured at (298.15 and 323.15) K. All the

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10.1021/je800557h CCC: $40.75

Table 3. Total Vapor Pressure p of the Acetonitrile (1) + Water (2) + Tetrabutylammonium Bromide (3) System from T = (298.15 to 323.15) K as a Function of Liquid Mole Fraction of Acetonitrile x'_1 on a Salt-Free Basis and Salt Molality m_3

	P/kPa	
m_3/(mol·kg^{-1})	T/K = 298.15	T/K = 323.15
	x'_1 = 0.020	
0.000	5.488	18.622
0.200	4.023	14.134
0.400	3.720	12.935
0.600	3.546	12.164
0.800	3.336	11.163
1.000	3.260	10.461
	x'_1 = 0.050	
0.000	8.398	27.002
0.200	6.236	17.920
0.400	5.425	15.916
0.600	4.916	14.927
0.800	4.611	14.196
1.000	4.273	13.636
	x'_1 = 0.100	
0.000	11.127	32.267
0.200	7.923	21.071
0.400	7.188	18.304
0.600	6.336	16.841
0.800	5.767	15.410
1.000	5.182	14.707
	x'_1 = 0.200	
0.000	12.441	35.890
0.200	10.867	27.844
0.400	9.839	24.554
0.600	8.742	21.855
0.800	7.657	20.062
1.000	6.933	18.037
	x'_1 = 0.300	
0.000	12.663	36.791
0.200	11.124	29.985
0.400	10.280	26.243
0.600	9.528	24.054
0.800	8.763	22.019
1.000	8.099	20.670
	x'_1 = 0.400	
0.000	12.702	37.457
0.200	11.798	31.550
0.400	11.119	29.447
0.600	10.428	27.572
0.800	9.744	26.057
1.000	8.976	25.083
	x'_1 = 0.500	
0.000	12.749	37.601
0.200	12.121	34.189
0.400	11.620	31.573
0.600	11.141	30.090
0.800	10.664	28.623
1.000	10.176	27.289
	x'_1 = 0.650	
0.000	12.793	37.991
0.200	12.267	36.043
0.400	11.795	35.564
0.600	11.299	32.977
0.800	10.862	31.379
1.000	10.330	30.081
	x'_1 = 0.750	
0.000	12.899	38.124
0.200	12.456	36.725
0.400	11.995	35.294
0.600	11.483	34.216
0.800	11.042	33.242
1.000	10.607	32.211
	x'_1 = 0.850	
0.000	12.797	37.629
0.200	12.330	36.288
0.400	11.886	35.002
0.600	11.427	33.593
0.800	11.019	32.320
1.000	10.648	31.009
	x'_1 = 0.950	
0.000	12.264	35.340
0.200	11.865	34.229
0.400	11.531	33.225
0.600	11.188	32.069
0.800	10.859	31.165
1.000	10.577	30.063

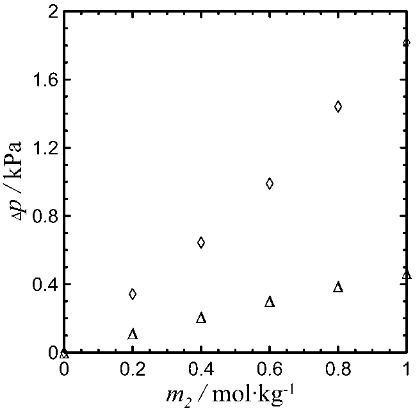

Figure 1. Vapor pressure lowering Δp of water as a function of salt molality m_2 in the water (1) + tetrabutylammonium bromide (2) system: Δ, 298.15 K; ◇, 323.15 K.

experimental data are given in Tables 1 to 3 and in Figure 1. Vapor pressures of acetonitrile and water decrease with an increase of salt molalities in the binary systems. Total vapor pressures decrease with an increase of salt concentration and liquid mole fraction of acetonitrile in the ternary system.

Calculation of Activities and Osmotic Coefficients of Acetonitrile in the Acetonitrile + TBAB System. Osmotic coefficients (Φ_s) as a function of salt molality were calculated from vapor pressure lowering as described by Barthel and Kunz[5]

$$\Phi_s = -\frac{\ln a_s}{\nu m M_s} \tag{1}$$

$$\ln a_s = \ln \frac{p}{p^*} + \frac{(B - V_s^*)(p - p^*)}{RT} \tag{2}$$

M_s is the molecular weight of acetonitrile; m is the salt molality; B is the second virial coefficient; and V_s is the molar volume of acetonitrile. The saturation vapor pressure of pure acetonitrile (p^*) was calculated with the published Antoine constants.

The calculated data are presented in Table 1.

The activity coefficients of solvents in the ternary system acetonitrile + water + TBAB were earlier[9] calculated by using the electrolyte NRTL model of Mock et al.[10] which is used for the ternary mixed-solvent electrolyte systems.

Conclusion

The vapor pressures of the acetonitrile + tetrabutylammonium bromide, water + tetrabutylammonium bromide, and acetonitrile + water + tetrabutylammonium bromide systems have been measured at different salt molalities at (298.15 and 323.15) K with a modified Othmer-type equilibrium cell.

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Received for review July 17, 2008. Accepted November 23, 2008. A.N.E. thanks the Government of Saint-Petersburg for the financial support [Grant for young PhD (Reg. No MKN-39/191-08)].

JE800557H