Vapor−Liquid Equilibria of Water + Methanol in the Presence of Mixed Salts

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Vapor−liquid equilibria of water + methanol, in the presence of binary salts of sodium chloride, potassium chloride, and sodium bromide, were studied at 298.15 K. The single salt−mixed solvent systems were also reported. A modified Othmer still was employed. The estimated accuracy of the pressure measurements was 0.12 kPa. The experimental results were compared with the predictions of the method of Lee et al.

Introduction

Experimental data are relatively abundant for single or mixed electrolyte aqueous systems and single electrolyte mixed solvent systems. However, few data are available for mixed solvent mixed electrolyte systems. Such systems may be of practical importance or of interest in developing a general electrolyte solution model. Activity coefficients (Shim et al., 1991) and solubilities (Shim and Lee, 1991) of mixed salts in water + methanol have been reported by the authors. Isothermal vapor−liquid equilibria are experimentally studied in the present work.

Experimental Section

Isopiestic measurements are known to be the most accurate method for single solvent electrolyte systems. Use of the isoteniscope is also limited to single solvent systems. Morrison et al. (1990) modified the Othmer still to measure the vapor−liquid equilibria of water + ethanol + single electrolyte systems. In the present work a slightly modified Morrison's apparatus was employed.

The modified Othmer still used in the present study is shown in Figure 1. The heating loop (1) ensures mixing and prevents bumping. The liquid sampling stopcock (4) is located such that condensed vapor remains condensed. The 3 dm^3 ballast bulb minimizes pressure fluctuation. The calibrated thermometer is the model 8502-12 from Cole-Palmer whose accuracy is claimed to be less than 0.2 K. The pressure transducer was from Data Instrument and calibrated against the vapor pressure of triple-distilled water. For salt-containing mixtures, frequent calibration was needed. Calibration curves were repeatedly determined by fitting two adjacent calibration measurements between which data were taken. The overall uncertainty as a sum of calibration error and equipment precision was estimated to be less than 0.05 kPa. The condensed vapor was sampled and analyzed using model 580 gas chromatography from Gow-Mac. The standard error of repeated calibration data points from the best-fitted curve was 0.002 in mole fraction.

Potassium chloride, sodium chloride, and sodium bromide were ultrapure grade from Junsei Chemical. They were kept in a desiccator for more than 24 h before use. Methanol was HPLC grade from Merck and used without further treatment. Triple-distilled water was used.

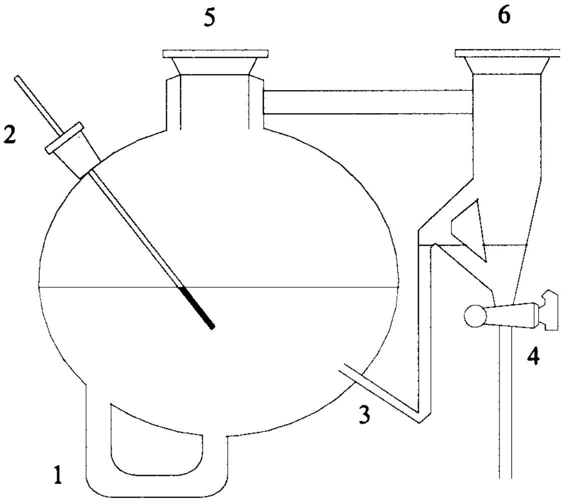

Figure 1. Modified Othmer's still for vapor−liquid equilibrium measurement of mixed electrolyte−mixed solvent systems (1, heating loop; 2, thermometer probe; 3, capillary tube; 4, two-way stopcock; 5, to condenser; 6, from condenser).

Known masses of salts were dissolved in 0.5 dm^3 of water + methanol, and the solution was placed in the still and degassed until a metallic clicking sound became audible (Fischer and Gmehling, 1994). The change of composition during degassing was compensated by empirically adjusting the initial composition. The deviation of final composition from the desired value was found to be less than 0.002 in mole fraction by chromatographic analysis. Then the system was closed and the still was heated until constant pressure and temperature were attained. After equilibrium is reached, the system was open to air and vapor condensate of about 1 cm^3 was taken promptly for the determination of vapor composition. For a fixed liquid-phase composition, at least three data points were taken for total pressure and vapor composition in the temperature range of 298.15 ± 1.0 K by adjusting the heating rate. From these measurements values at 298.15 K were determined.

Prediction Method

Lee et al. recently proposed an electrolyte solution model for aqueous mixed solvents−mixed electrolytes (Lee et al.,

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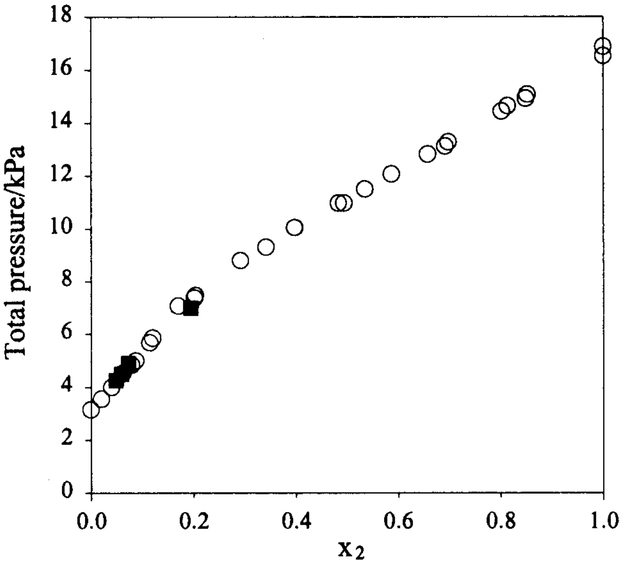

Figure 2. Comparisons of experimental total pressure with data from Gmehling et al. for water (1) + methanol (2) at 298.15 K: (○) data from Gmehling et al. (1977); (■) experimental data.

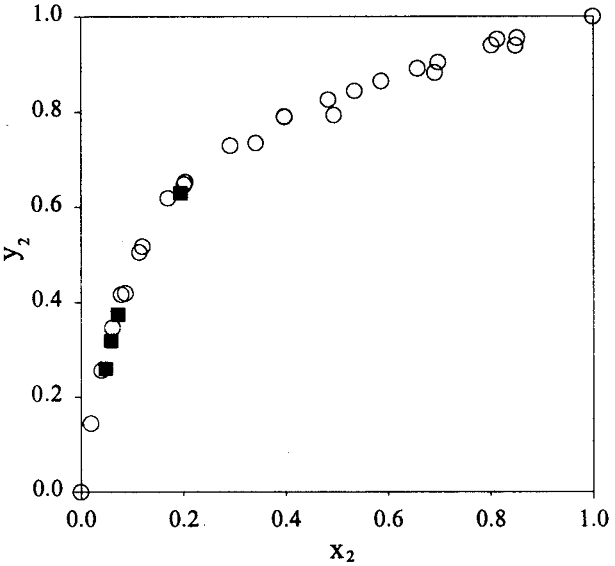

Figure 3. Comparisons of experimental mole fraction of methanol with data from Gmehling et al. for water (1) + methanol (2) at 298.15 K: (○) data from Gmehling et al.(1977); (■) experimental data.

1996). This model provides activity coefficients for solvents. With the activity coefficients, a standard thermodynamic method can be used to predict total pressures and vapor mole fractions.

Results and Discussions

Vapor mole fraction and pressure at 298.15 K were determined by interpolation using linear least-squares fitted curves. This procedure introduces uncertainties of 0.03 kPa in pressure and 0.002 in mole fraction. To summarize, the overall uncertainties are 0.004 in mole fractions of both phases and 0.08 kPa in pressure.

To test the reliability of the present method, the total pressure and the vapor compositions for water + methanol were measured. The maximum methanol concentration was 40 wt %. They were compared with three sets of data of Hall et al. (1979), Butler et al. (1933), and Dulitskaya (1945) from Gmehling et al. (1977) in Figures 2 and 3. The standard errors for Gmehling data from the best-fitted curve were 0.019 in vapor mole fraction and 0.17 kPa, whereas error values for present data were 0.018 and 0.14 kPa. This indicates that the present data are within error bounds and that the present uncertainties are probably somewhat underestimated.

Table 1. Results of Equilibrium Composition and Pressure Measure for Single Solute (1) + MeOH (2) + Water (3) at 298.15 K

solute	$w_2{}^a$	m_1/mol·kg^{-1}	y_2	P/kPa
NaCl	0.10	0.0	0.319	4.507
		1.0	0.368	4.526
		2.0	0.412	4.668
		3.0	0.441	4.808
		4.0	0.469	4.825
	0.30	0.0	0.629	7.044
		1.0	0.670	7.302
		2.0	0.682	7.570
		3.0	0.721	7.799
KCl	0.10	0.0	0.319	4.507
		0.5	0.353	4.566
		1.0	0.363	4.658
		1.5	0.389	4.766
	0.30	0.0	0.629	7.044
		0.5	0.655	7.177
		1.0	0.662	7.345
		1.5	0.683	7.472
NaBr	0.236	0.0	0.581	6.411
		2.0	0.630	6.888
		4.0	0.678	6.791
		6.0	0.703	6.369
	0.423	0.0	0.718	8.812
		2.0	0.763	9.069
		4.0	0.801	8.946

[a] Weight fraction on salt-free basis.

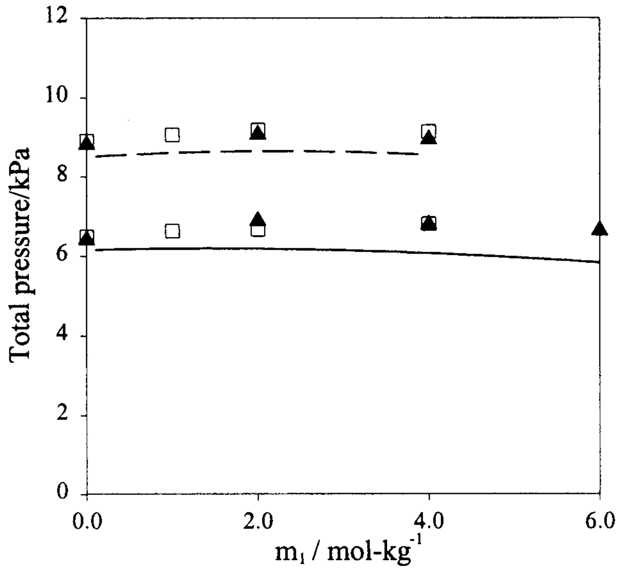

Figure 4. Comparisons of experimental total pressure with data of Ciparis and prediction of Lee et al. for NaBr (1) + methanol (2) + water (3) at 298.15 K: (□) data of Ciparis (1966); (▲) experimental data; (solid line) w_2 = 0.236, prediction of Lee et al.; (dashed line) w_2 = 0.423, prediction of Lee et al.

Vapor−liquid equilibrium data for single salt water + methanol are given in Table 1. Results for the sodium bromide system are reported by Ciparis (1966), and they are compared with present data in Figures 4 and 5. Standard deviations for identical salt compositions were 0.004 in vapor mole fraction and 0.12 kPa in total pressure. Again we find the error in pressure is larger than the

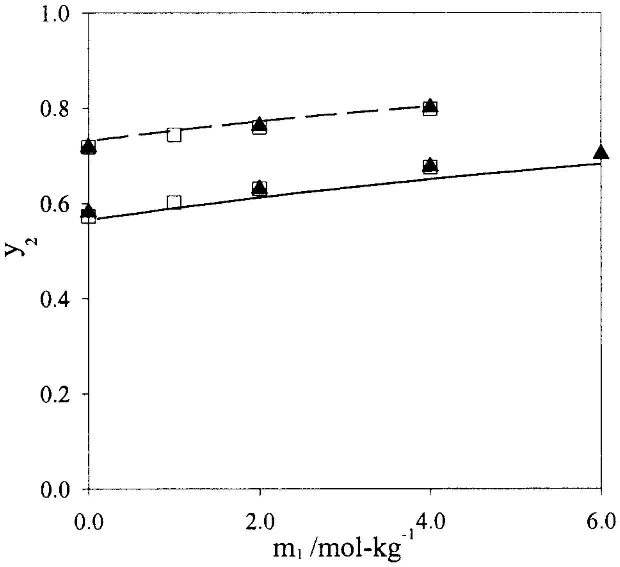

Figure 5. Comparisons of experimental mole fraction of methanol with data of Ciparis and prediction of Lee et al. for NaBr (1) + methanol (2) + water (3) at 298.15 K: (□) data of Ciparis (1966); (▲) experimental data; (solid line) $w_2 = 0.236$, prediction of Lee et al.; (dashed line) $w_2 = 0.423$, prediction of Lee et al.

Table 2. Results of Equilibrium Composition and Pressure Measure for Solute (1) + Solute (2) + MeOH (3) + Water (4) System at 298.15 K

solute 1	solute 2	w_3[a]	m_2/mol·kg^{-1}	y_3	P/kPa
KCl 1.0 mol·kg^{-1}	NaCl	0.30	0.5	0.662	7.288
			1.0	0.673	7.621
			1.5	0.691	7.742
			2.0	0.713	7.840
			2.5	0.725	7.960
KCl 1.0 mol·kg^{-1}	NaBr	0.236	1.0	0.624	6.738
			2.0	0.646	6.849
			3.0	0.666	6.847
			4.0	0.701	6.626
NaCl 1.0 mol·kg^{-1}	NaBr	0.236	1.0	0.624	6.821
			2.0	0.650	6.886
			3.0	0.678	6.962
			4.0	0.691	6.762

[a] Weight fraction on salt-free basis.

estimated uncertainty. This is probably due to uncertainties in temperature and liquid mole fractions. Therefore the uncertainty in pressure for fixed temperature and liquid composition may be revised as 0.12 kPa. Data for mixed salts water + methanol systems are given in Table 2. For these systems no other isothermal data are known to the authors.

In both single and binary salt systems, the vapor mole fraction of methanol is seen to increase as the ionic strength increases. However, the total pressure may increase, remain almost constant, or decrease depending on the system. These tendencies are generally reproduced by the prediction method. Experimental data are compared with predictions in Figures 4, 5, 6, and 7. The total pressure is not sensitive to salt molalities despite the strong nonideality of the solution. In Table 3 prediction errors are listed. The table shows that prediction errors in total pressure are generally greater for mixed salt systems than for pure salt solutions. Average root-mean-square deviations are 0.025 in vapor mole fractions and 0.5 kPa in total pressure. These values are larger than those for corresponding salt-free systems, which are 0.011 in vapor mole fractions and 0.1 kPa in total pressure.

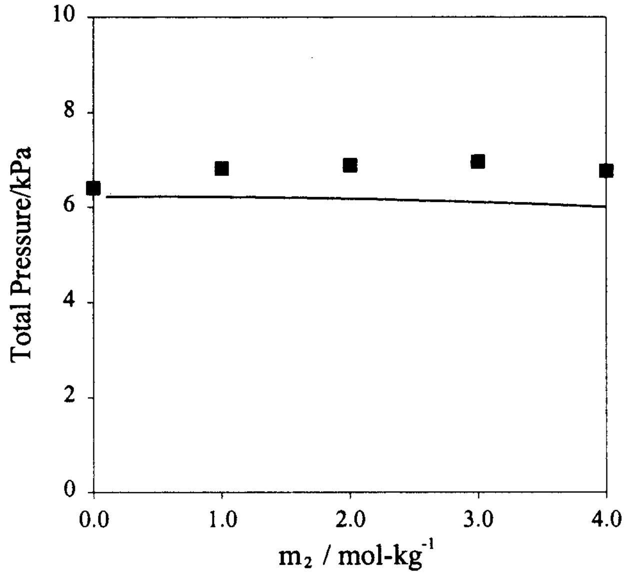

Figure 6. Comparisons of experimental total pressure with prediction of Lee et al. for NaCl (1, $m_1 = 1.0$ mol·kg^{-1}) + NaBr (2) + methanol (3) + water (4) at 298.15 K: $w_3 = 0.236$; (■) experimental data; (solid line) prediction of Lee et al.

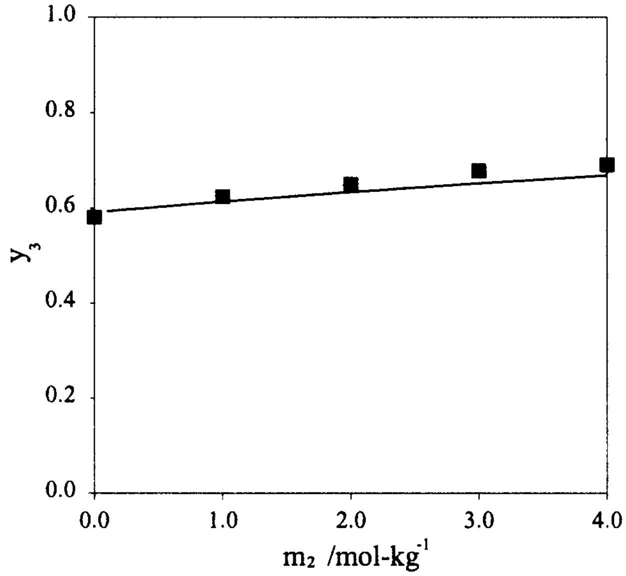

Figure 7. Comparisons of experimental mole fraction of methanol with prediction of Lee et al. for NaCl (1, $m_1 = 1.0$ mol·kg^{-1}) + NaBr (2) + methanol (3) + water (4) at 298.15 K: $w_3 = 0.236$; (■) experimental data; (solid line) prediction of Lee et al.

Table 3. Results of Comparison of Experimental Mixed Salt/Mixed Solvent Equilibrium Data with Prediction Value

solute	w_2[a]	maximum ionic strength/mol·kg^{-1}	σ_P/kPa[b]	σ_y[b]
NaCl	0.1	4.0	0.42	0.048
NaCl	0.3	3.0	0.42	0.018
NaBr	0.236	4.0	0.58	0.029
NaBr	0.423	4.0	0.38	0.004
KCl	0.1	1.5	0.30	0.024
KCl	0.3	1.5	0.34	0.025
NaCl−NaBr	0.236	5.0	0.74	0.031
KCl−NaBr	0.236	5.0	0.69	0.034
KCl−NaCl	0.3	3.5	0.68	0.019
average			0.51	0.026

[a] Weight fraction of methanol on salt-free basis. [b] Root-mean-square deviations defined as $\sigma_f = [\Sigma(f_{\mathrm{calc}} - f_{\mathrm{exp}})^2/N]^{1/2}$ where f is either P or y.

Summary

Vapor−liquid equilibria were measured for water + methanol + single salt and water + methanol + mixed salt by using a modified Othmer still at 298.15 K. Reliability of the present data were confirmed against data of Gmehling et al. and of Ciparis for salt-free systems and NaBr + methanol + water. The comparison showed that the present measurements are accurate probably within error bounds. The estimated uncertainties were about 0.12 kPa in pressure for fixed temperature and liquid composition. The present data were compared with Lee et al.'s prediction.

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