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Isobaric Vapor−Liquid Equilibria for Ethanol + Benzene + Magnesium Chloride

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The effect of magnesium chloride on the vapor−liquid equilibria for the system ethanol + benzene at different salt concentrations was studied at 100.0 kPa. The measured mole fractions in the vapor phase were correlated by the Johnson−Furter and Sada models. Thermodynamic consistency was checked by the restricted range area test with satisfactory results.

Introduction

The effect of salts on the vapor−liquid equilibrium (VLE) of solvent mixtures has been of considerable interest in separation processes. There are many cases where a salt is generated in the process before final product purification. Salts may be added to a system to alter the VLE behavior in the extractive or azeotropic distillation. The salt effect on the VLE behavior has been studied by many researchers. Review papers have been published on the chemistry (Furter, 1976), the thermodynamic consistency test (Jaques and Furter, 1972; Jaques, 1974), correlations and predictive models (Schmitt and Vogelpohl, 1982; Chen et al., 1982; Fürst and Renon, 1993; Kumar, 1993), and the economic and technical aspects of salt distillation (Furter and Cook, 1967; Furter, 1977; Tan, 1987). The effect of lithium chloride, potassium acetate, and copper nitrate on the VLE of the ethanol + benzene system was studied by Alvarez Gonzalez and Vega Zea (1967). Sada et al. (1974) also studied the effect of addition of lithium chloride, calcium chloride, and zinc chloride to the ethanol + benzene system at atmospheric pressure. In this work, the effect of magnesium chloride on the VLE of the ethanol + benzene system was experimentally determined.

Experimental Section

Vapor−liquid equilibrium measurements were carried out in a recirculating equilibrium still manufactured by Fischer Labor-und-Verfahrenstechnik (Germany). The still allows good mixing of the vapor and liquid phases and good separation of the phases once they reach equilibrium, and it prevents entrainment of liquid drops and partial condensation in the vapor phase. A detailed description of the apparatus and operation procedure has been reported elsewhere (Tsai and Chen, 1988).

About 100 mL of liquid mixture was heated in the heating section of the still. The boiling liquid rose through a Cottrell pump and ejected out of the nozzle onto the thermometer wall in the equilibrium chamber, where the liquid and vapor were separated into different paths out of the chamber. The vapor was totally condensed, allowing sampling as a liquid. Condensed vapor and liquid were mixed and sent to the heating section to be boiled again. The pressure in the system was maintained constant to within ±0.1 kPa by an electronic regulator. Temperature in the equilibrium chamber was measured with a standard mercury-in-glass thermometer, having an accuracy of ±0.1 K. The attainment of a constant temperature for about 1 h was the sign that equilibrium had been reached. Once equilibrium was achieved, the pressure and temperature were recorded and samples of both phases were withdrawn for analysis.

Since the liquid phase contained magnesium chloride, it was analyzed after separation of magnesium chloride from it by evaporation. The liquid sample was analyzed for magnesium chloride by titration with EDTA, using eriochrome black T as the indicator. It was found that the presence of the organic compounds had no effect on the titration.

The compositions of the liquid x_i and vapor y_i phases were determined by using a Hewlett-Packard 5880 A gas chromatograph equipped with a flame-ionization detector. The chromatographic column (6 ft × 1/8 in.) was packed with 20% bis(2-ethylhexyl) sebacate on 80/100 Chromosorb W AW-DMCS, and operated isothermally at 373 K. Both injector and detector temperatures were 473 K. Nitrogen gas was used as the carrier gas at a flow rate of 30 mL min^{-1}. The gas chromatograph was calibrated by using mixtures of known composition that were prepared gravimetrically. An injection volume of 0.4 μL was used. At least two injections were made for both standard as well as unknown mixtures. The uncertainty of the composition measurements was estimated to be ±0.001 mole fraction.

The chemicals were absolute ethanol (Merck, 99.8+ mass %), benzene (Merck, 99.7+ mass %), and magnesium chloride (Fluka, 98+ mass %). They were used without further purification.

Results and Discussion

The VLE data of ethanol (1) + benzene (2) + magnesium chloride (3) are presented in Table 1. The concentration of ethanol is expressed as the mole fraction of the binary mixture (salt-free basis), and that of magnesium chloride is expressed as the mass percent of the mixture by the equation mass % = $[m_3/(m_1 + m_2)] \times 100\%$, where m_i is the mass of component i. Figure 1 reveals that our salt-free data agree well with those measured by Tyrer (1912). It can be seen from Table 1 that by adding magnesium chloride the relative volatility of benzene increases. Thus, the azeotropic composition shifts to a higher composition of benzene in the ethanol + benzene system.

In this work the ternary system of ethanol (1) + benzene (2) + magnesium chloride (3) can be treated as a pseudobinary system. One component is ethanol dissolved with magnesium chloride; the other is benzene. The activity coefficients of ethanol and benzene in solution were calcu-

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Table 1. Vapor–Liquid Equilibrium Data and Calculated Results for Ethanol (1) + Benzene (2) + Magnesium Chloride (3) at 100.0 kPa

					$y_{1,\mathrm{calcd}}$	
T/K	x_1	$y_{1,\mathrm{exptl}}$	γ_1	γ_2	J–F model	Sada model
			0 mass % $MgCl_2$			
341.3	0.261	0.410	2.355	1.157		
341.0	0.367	0.423	1.748	1.335		
340.9	0.466	0.436	1.426	1.552		
341.0	0.502	0.452	1.368	1.610		
341.1	0.560	0.466	1.257	1.771		
341.5	0.593	0.485	1.215	1.822		
342.0	0.733	0.548	1.087	2.398		
			1 mass % $MgCl_2$			
344.5	0.129	0.299	3.090	1.048	0.329	0.304
340.9	0.407	0.418	1.574	1.443	0.421	0.416
341.1	0.578	0.471	1.240	1.828	0.474	0.472
342.0	0.736	0.538	1.070	2.473	0.549	0.549
343.7	0.814	0.608	1.016	2.829	0.610	0.610
345.3	0.874	0.672	0.980	3.298	0.675	0.676
346.6	0.912	0.733	0.971	3.680	0.741	0.742
348.0	0.940	0.793	0.963	4.011	0.797	0.797
			2 mass % $MgCl_2$			
343.3	0.234	0.331	1.981	1.184	0.381	0.352
340.9	0.447	0.430	1.486	1.514	0.425	0.416
341.3	0.653	0.489	1.136	2.134	0.491	0.489
342.6	0.778	0.567	1.046	2.703	0.569	0.570
344.2	0.864	0.646	1.002	3.421	0.653	0.655
346.3	0.901	0.725	0.989	3.403	0.711	0.713
347.6	0.945	0.796	0.981	4.391	0.794	0.796
348.8	0.965	0.850	0.978	4.814	0.853	0.854
			4 mass % $MgCl_2$			
343.5	0.260	0.348	1.878	1.189	0.373	0.334
341.7	0.482	0.419	1.314	1.605	0.419	0.408
341.8	0.662	0.486	1.103	2.167	0.486	0.484
342.3	0.730	0.537	1.080	2.406	0.527	0.528
343.5	0.812	0.600	1.031	2.864	0.594	0.596
345.5	0.873	0.671	0.987	3.267	0.654	0.657
347.0	0.912	0.738	0.976	3.572	0.719	0.726
348.0	0.934	0.793	0.983	3.645	0.766	0.769
			8 mass % $MgCl_2$			
342.6	0.518	0.386	1.112	1.768	0.412	0.398
342.2	0.656	0.452	1.040	2.244	0.457	0.456
342.7	0.727	0.514	1.044	2.465	0.500	0.504
343.8	0.799	0.576	1.015	2.818	0.557	0.563
345.5	0.869	0.654	0.986	3.342	0.640	0.648
347.1	0.906	0.716	0.725	3.631	0.702	0.709

lated by using eqs 1–5, where n_i is the mole of component i and ν_c and ν_a are the number of moles of cation and anion dissociated from 1 mol of salt, respectively.

$$\ln \gamma_i = \ln\frac{y_i P}{x_i P_i^\circ} + \frac{(B_{ii} - V_i^{\mathrm{L}})(P - P_i^\circ)}{RT} + \frac{(1 - y_i)^2 P\delta}{RT} \tag{1}$$

$$\delta = 2B_{12} - B_{11} - B_{22} \tag{2}$$

$$P_1^\circ = P_1^{\mathrm{s}}(1 - N') \tag{3}$$

$$P_2^\circ = P_2^{\mathrm{s}} \tag{4}$$

$$N' = \frac{(\nu_c + \nu_a)n_3}{n_2 + (\nu_c + \nu_a)n_3} \tag{5}$$

The second virial coefficients B_{ii} and B_{ij} were calculated from the Tsonopoulos (1974) empirical correlation. The modified Rackett equation (Spencer and Adler, 1978) was used to calculate the molar volume V_i^{L} of the saturated liquid. The vapor pressure of the pure component P_i^{s} was obtained by use of the Antoine equation with the constants from Reid et al. (1987). The activity coefficients of ethanol and benzene calculated from eqs 1–5 are listed in Table 1.

The experimental salt-free VLE data were tested for thermodynamic consistency by using the area test of Herington (1951, 1968) as described by Gmehling and Onken (1977). Some of the VLE data of the salt-containing system do not cover the entire liquid composition range. For such a system, the restricted range area method (Jaques and Furter, 1972) was used to test the VLE data for thermodynamic consistency. The results of the consistency test as shown in Table 2 indicate that the experimental data are thermodynamically consistent except for the system containing 2 mass % $MgCl_2$.

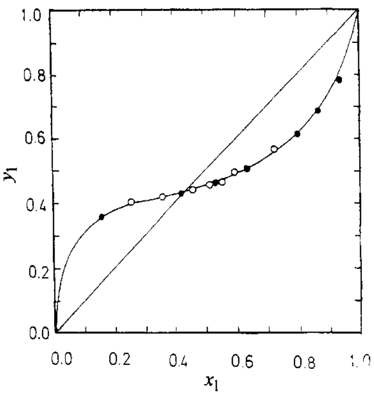

Figure 1. Vapor–liquid equilibrium data for the ethanol (1) + benzene (2) system at 100.0 kPa: (○) this work; (●) Tyrer (1912); (—) Wilson equation.

Table 2. Application of the Thermodynamic Consistency Test to the Ethanol + Benzene + Magnesium Chloride System at 100.0 kPa

mass % $MgCl_2$	*D*/%	*J*/%	(*D* – *J*)/%
0	2.53	4.75	–2.22
1	1.46	4.76	–3.30
2	6.09	4.81	1.28
4	4.59	4.69	–0.10
8	3.93	4.17	–0.24

Table 3. Average Deviations between Calculated and Experimental Vapor-Phase Mole Fractions

	$(\Delta y/y)^a$/%			$(\Delta y/y)^a$/%	
mass % $MgCl_2$	J–F model	Sada model	mass % $MgCl_2$	J–F model	Sada model
1	1.93	0.86	4	2.35	1.99
2	2.54	1.69	8	3.00	1.70

[a] $\Delta y/y = (1/n)\sum_{i=1}^{n} |(y_{1,\mathrm{exptl}} - y_{1,\mathrm{calcd}})/y_{1,\mathrm{exptl}}|_i \times 100\%$.

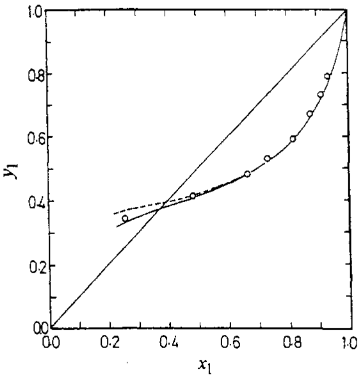

Figure 2. Comparison of the calculated mole fraction y_1 with experimental data for the ethanol (1) + benzene (2) + 4 mass % $MgCl_2$ system: (○) this work; (- - -) J–F model; (—) Sada model.

Various methods (Kumar, 1993) have been developed to correlate the VLE data of salt-containing systems. The correlation proposed by Johnson and Furter (1960) is expressed as

$$\log(\alpha_s/\alpha) = kx_3 \tag{6}$$

where α_s and α are the relative volatilities with and without salt, respectively, and x_3 is the salt mole fraction. In the calculation of α the Wilson equation (Gmehling and Onken, 1977) with A_{12} = 1310.0706 cal mol^{-1} and A_{21} = 220.7486 cal mol^{-1} was used. The VLE data were fitted to eq 6 by the method of least squares, and the best correlation was obtained by using the value of k as 1.81. The values of y_1 calculated from eq 6 are listed in Table 1.

Sada et al. (1974) suggested the equation

$$\ln(\alpha_s/\alpha) = N' \tag{7}$$

to predict the VLE data of salt-containing systems. In their work the VLE data for the ethanol + benzene system containing salts were correlated, and the standard deviations of 0.0287, 0.0156, and 0.0315 for LiCl, $CaCl_2$, and $ZnCl_2$, respectively, were obtained. In eq 7 there is no empirical constant. The values of y_1 calculated from eq 7 for this work are also listed in Table 1.

Table 3 lists the average deviations in y_1 calculated by the Johnson–Furter (J–F) and Sada models. As observed from Figure 2, the predicted results using the Sada model are superior to the J–F model.

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