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Isobaric Vapor–Liquid Equilibrium for Ethanol + Water + Strontium Chloride

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Isobaric vapor–liquid equilibrium for ethanol (1) + water (2) + strontium chloride (3) at different mole fractions of strontium chloride has been measured at 100.0 kPa. The results were correlated by assuming that the salt was in ionic form and was associated only with the water.

Introduction

The study of the effects produced by the addition of an electrolyte to a solvent mixture on vapor–liquid equilibrium is an open and most challenging area of research within chemical engineering, in view of the important industrial applications of such systems.

The addition of salt to a mixed solvent has a pronounced effect on the relative volatility of the mixture components, depending on the interactions between the ions of the dissociated electrolyte and the molecules of both solvents.

Several methods for the correlation of the activity coefficients of the solvents in this kind of ternary mixture have appeared in the literature. Some of them consider that solvent mixtures can be treated as pseudobinary systems (Natarajan, 1980; Schmitt and Vogelpohl, 1983). More recently, different correlations based on modifications of the vapor–liquid equilibrium local composition model have been proposed (Chen et al., 1982; Chen and Evans, 1986; Sander et al.,1986; Tan, 1987; Kikic et al., 1991).

The present work studies the vapor–liquid equilibrium of ethanol + water + strontium chloride with varying concentrations of salt. The addition of strontium chloride to this solvent mixture increases the amount of alcohol present in the vapor phase at equilibrium, even eliminating the azeotrope. This indicates a preferential association of the salt with the less volatile component of the mixed solvent.

Researchers have previously studied the effect produced by strontium chloride. The vapor–liquid equilibrium of acetic acid + water + strontium chloride has been studied by Ramalho et al. (1964), Sabarathinam et al. (1975), and Ohe (1976), but only at saturation. Furthermore, this system is quoted in the reviews by Ciparis (1966, 1973). The vapor–liquid equilibrium of ethanol + water saturated with strontium chloride has been studied by Galán et al. (1976), but we have not found any reported vapor–liquid equilibrium for ethanol + water with varying concentrations of strontium chloride below saturation.

Experimental Section

The chemicals were absolute ethanol (Baker-analyzed reagent, >99.5 mass %), distilled water, and strontium chloride (Probus, >99.5 mass %). They were used without further purification.

The equilibrium apparatus was a recirculating still of the Labodest model, manufactured by Fischer. The vapor–liquid equilibrium data were obtained at 100.00 ± 0.04 kPa. The vapor pressure of water with a varying concentration of salt was also measured with the same apparatus.

Every experimental point was obtained from an initial sample prepared gravimetrically by using a Sartorius analytical balance with a precision of ±0.0001 g and, afterwards, by adding different quantities of ethanol or water. Each experiment was kept at the boiling point for 15 min or more to ensure equilibrium conditions. The accuracy of the temperature measurement was ±0.1 K.

Compositions of the condensed vapor phase were analyzed by a Hewlett-Packard 5700 A gas chromatograph with a thermal conductivity detector, connected to a Hewlett-Packard 3394 A integrator. The chromatographic column (2 m × 1/8 in.) was packed with Porapak P. The gas carrier was helium flowing at 50 cm^3/min, and the column temperature was 383 K. The calibration was carried out with gravimetrically prepared standard solutions. The accuracy of the measured vapor-phase mole fraction was ±0.002.

The liquid phase was composed of ethanol, water, and strontium chloride. The salt mass fraction in the liquid phase was gravimetrically determined after separating the volatile components from a known mass of sample by evaporation to dryness. Also, the density of the liquid phase was determined with an Anton Paar DMA 55 densimeter matched to a Julabo circulator with proportional temperature control and an automatic drift correction system that kept the samples at 298.15 ± 0.01 K. Previously, the density of a set of standard solutions with known amounts of ethanol, water, and salt in the ternary mixtures had been measured, and a correlation that allowed the mass fraction of ethanol in the sample to be determined, given the density and the mass fraction of salt in the solution, had been obtained. The mass fractions are then translated into mole fractions. The accuracy in the determination of the ethanol, water, and strontium chloride mole fractions in the liquid phase was ±0.002. This method of analyzing the composition of salt-containing mixtures was found to be reproducible and of consistent accuracy, as described in a previous work (Vercher, 1994).

Results and Discussion

In Table 1, the vapor–liquid equilibrium for ethanol (1) + water (2) + strontium chloride (3) at a pressure of 100.0 kPa is reported. Included are the equilibrium temperature (T), the mole fractions of ethanol (x_1), water (x_2), and salt (x_3) in the ternary liquid phase, and the mole fraction of ethanol in the vapor phase (y_1).

To make possible the thermodynamic treatment of vapor–liquid equilibrium, we postulate that the salt is in ionic form and is associated only with the water (Vercher, 1991). Therefore, the ternary system can be treated as a

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Table 1. Vapor–Liquid Equilibrium for Ethanol + Water + Strontium Chloride at 100.0 kPa

T/K	x_1	x_2	x_3	y_1	γ_I	γ_{II}	T/K	x_1	x_2	x_3	y_1	γ_I	γ_{II}
362.6	0.031	0.938	0.032	0.434	8.914	0.939	353.5	0.299	0.680	0.021	0.662	1.957	1.095
362.5	0.033	0.943	0.023	0.419	7.952	0.935	353.4	0.302	0.671	0.028	0.675	1.987	1.118
363.1	0.034	0.951	0.015	0.378	6.984	0.946	353.9	0.307	0.684	0.010	0.631	1.794	1.116
359.3	0.047	0.915	0.039	0.531	8.076	0.938	353.6	0.323	0.663	0.014	0.647	1.764	1.135
359.3	0.055	0.916	0.029	0.507	6.577	0.944	353.3	0.326	0.653	0.021	0.673	1.840	1.122
359.6	0.056	0.922	0.021	0.490	6.141	0.933	353.3	0.335	0.646	0.019	0.668	1.777	1.136
357.6	0.063	0.901	0.036	0.563	6.741	0.937	353.2	0.340	0.635	0.025	0.686	1.805	1.141
356.9	0.066	0.889	0.045	0.596	7.004	0.950	353.6	0.343	0.649	0.008	0.639	1.642	1.162
357.8	0.093	0.894	0.013	0.521	4.214	0.948	353.4	0.361	0.627	0.012	0.654	1.607	1.181
357.2	0.094	0.886	0.020	0.547	4.482	0.945	353.1	0.365	0.615	0.020	0.686	1.688	1.155
355.6	0.100	0.863	0.037	0.619	5.061	0.938	353.0	0.377	0.606	0.017	0.681	1.628	1.173
356.5	0.100	0.874	0.026	0.571	4.494	0.955	353.4	0.382	0.612	0.007	0.647	1.507	1.208
355.8	0.105	0.863	0.032	0.602	4.639	0.948	352.9	0.388	0.590	0.022	0.696	1.624	1.193
355.0	0.116	0.843	0.040	0.642	4.605	0.944	353.2	0.391	0.598	0.010	0.659	1.507	1.225
356.0	0.125	0.857	0.018	0.576	3.718	0.958	353.3	0.403	0.592	0.005	0.652	1.441	1.235
356.5	0.127	0.861	0.012	0.553	3.449	0.966	353.2	0.419	0.577	0.004	0.651	1.392	1.270
355.1	0.132	0.839	0.029	0.616	3.879	0.961	352.9	0.419	0.566	0.015	0.687	1.483	1.232
354.8	0.136	0.830	0.034	0.632	3.906	0.964	353.1	0.420	0.571	0.009	0.666	1.424	1.257
355.5	0.137	0.840	0.024	0.595	3.577	0.972	352.7	0.423	0.557	0.020	0.703	1.515	1.235
355.7	0.164	0.825	0.010	0.576	2.858	0.985	352.9	0.457	0.535	0.007	0.674	1.333	1.316
355.2	0.166	0.818	0.016	0.595	2.970	0.987	352.7	0.463	0.524	0.013	0.698	1.374	1.291
354.2	0.170	0.793	0.036	0.654	3.304	0.995	352.5	0.469	0.514	0.017	0.713	1.398	1.294
354.9	0.171	0.808	0.021	0.611	3.004	0.990	352.7	0.492	0.502	0.006	0.682	1.264	1.373
354.6	0.172	0.801	0.027	0.629	3.098	0.989	352.5	0.499	0.491	0.010	0.703	1.296	1.349
354.3	0.179	0.791	0.030	0.643	3.075	0.989	352.4	0.508	0.477	0.015	0.722	1.310	1.349
355.1	0.206	0.786	0.009	0.586	2.375	1.032	352.5	0.525	0.470	0.005	0.691	1.209	1.432
354.1	0.215	0.761	0.025	0.642	2.584	1.021	352.3	0.535	0.453	0.012	0.723	1.251	1.398
354.5	0.216	0.770	0.014	0.612	2.414	1.029	352.3	0.547	0.445	0.008	0.719	1.218	1.413
354.0	0.216	0.757	0.027	0.648	2.606	1.021	352.0	0.554	0.433	0.013	0.740	1.252	1.412
353.9	0.219	0.748	0.033	0.661	2.632	1.036	352.1	0.581	0.409	0.010	0.738	1.185	1.468
354.3	0.229	0.752	0.019	0.626	2.347	1.040	352.1	0.598	0.395	0.007	0.735	1.146	1.509
354.7	0.242	0.751	0.007	0.597	2.088	1.064	351.9	0.599	0.389	0.012	0.756	1.186	1.482
353.8	0.256	0.721	0.023	0.651	2.220	1.058	351.9	0.621	0.371	0.008	0.750	1.134	1.552
353.7	0.258	0.716	0.025	0.659	2.237	1.062	351.8	0.651	0.344	0.005	0.753	1.092	1.629
354.2	0.259	0.728	0.013	0.622	2.067	1.070	351.6	0.652	0.338	0.011	0.775	1.131	1.595
353.6	0.262	0.708	0.030	0.670	2.257	1.073	351.5	0.698	0.295	0.008	0.793	1.085	1.664
354.5	0.271	0.723	0.006	0.604	1.900	1.090	351.6	0.700	0.295	0.005	0.780	1.060	1.711
353.9	0.280	0.704	0.016	0.638	1.984	1.089	351.5	0.724	0.272	0.004	0.790	1.040	1.773
354.3	0.299	0.697	0.005	0.607	1.747	1.128	351.4	0.739	0.255	0.007	0.813	1.055	1.744
353.4	0.299	0.677	0.024	0.671	1.995	1.095							

pseudobinary system composed of pure ethanol (I) and water + salt (II) components. This assumption is acceptable in this case in the entire range of compositions, because the solubility of strontium chloride, which expressed as salt mole fraction is 0.0596 in water at 25 °C, decreases almost linearly when the mole fraction of ethanol in the mixed solvent increases, to become practically null in pure ethanol (Jankovic, 1958).

When equilibrium is established between the vapor and liquid phases, the activity coefficients of both pseudocomponents will be given by the following expressions:

$$\gamma_I = \frac{y_I \phi_I P}{x_I P_I^\circ} \qquad \gamma_{II} = \frac{y_{II} \phi_{II} P}{x_{II} P_{II}^\circ} \tag{1}$$

where x_I is the mole fraction of pseudocomponent I in the liquid phase ($=x_1$), x_{II} is the mole fraction of pseudocomponent II in the liquid phase ($=x_2 + x_3$), y_I is the mole fraction of ethanol in the vapor phase ($=y_1$), y_{II} is the mole fraction of water in the vapor phase ($=1 - y_1$), ϕ_I is the fugacity coefficient of pseudocomponent I in the vapor phase, ϕ_{II} is the fugacity coefficient of pseudocomponent II in the vapor phase, P is the system pressure, and P_I° is the vapor pressure of pure ethanol ($=P_1^\circ$) and P_{II}° the vapor pressure of pseudocomponent II, both calculated at the equilibrium temperature. The value of P_{II}° depends on the temperature and on the salt concentration. Jaques and Furter (1972) propose that this dependency can be expressed as

$$P_{II}^\circ = P_2^\circ(T)\,\epsilon(x_3^*) \tag{2}$$

Table 2. Boiling Points of Water + Strontium Chloride Mixtures at 100.0 kPa

x_3^*	T/K	x_3^*	T/K
0.002	373.1	0.028	375.5
0.003	373.2	0.030	375.8
0.005	373.3	0.032	376.0
0.007	373.4	0.034	376.4
0.008	373.5	0.036	376.7
0.011	373.7	0.039	377.1
0.014	374.0	0.042	377.6
0.016	374.2	0.045	378.3
0.019	374.4	0.049	378.9
0.020	374.6	0.055	379.9
0.022	374.8	0.060	380.9
0.024	375.0	0.061	381.3
0.026	375.3		

where P_2° is the vapor pressure of pure water (kPa) and ϵ is the vapor pressure correction factor, which only depends on x_3^*, the mole fraction of the component salt in the pseudocomponent II ($=x_3/(x_2 + x_3)$).

The vapor pressure correction factor was computed by the method of Jaques and Furter (1972) from results of the vapor pressure of water with different amounts of salt that we have obtained, given in Table 2, and the vapor pressure of pure water obtained from the Antoine equation with the parameters given in the literature (Gmehling et al., 1981), both at the same temperature.

The correlation equation obtained from experimental results for the vapor pressure correction factor (ϵ) with the salt mole fraction in pseudocomponent II (x_3^*), for the entire range of salt concentrations studied, is

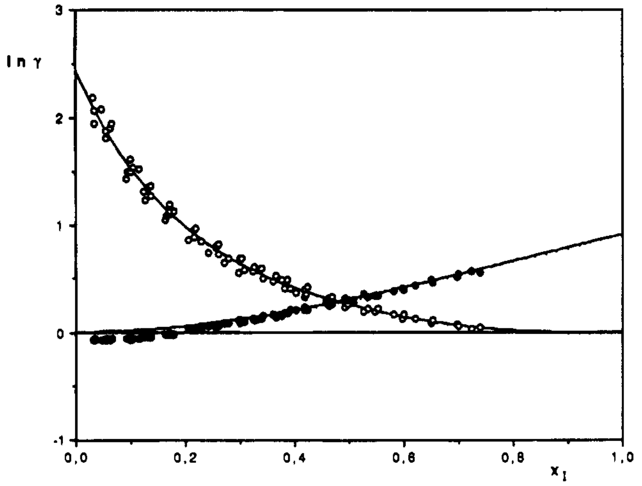

Figure 1. Experimental solvent activity coefficients for the system ethanol + water + strontium chloride at 100.0 kPa: (○) ln γ_I, (●) ln γ_{II}.

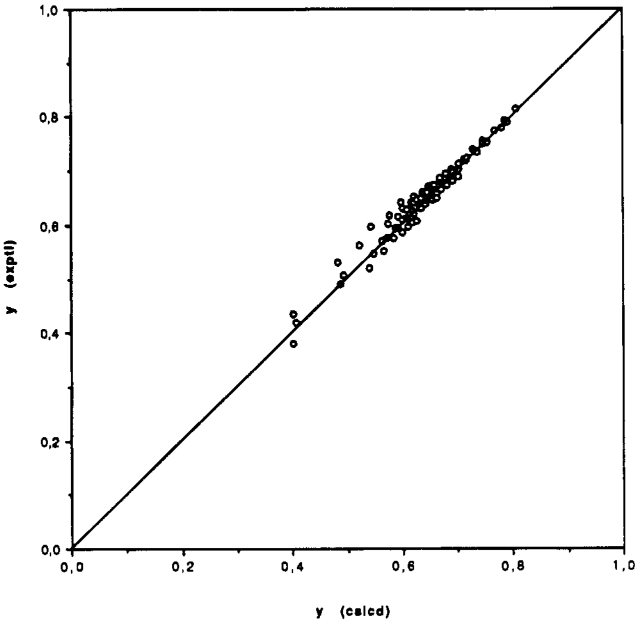

Figure 2. Comparison of calculated vapor composition, y_{calcd}, with experimental values, y_{exptl}.

$$\epsilon = 1 - 2.511x_3^* - 27.7125(x_3^*)^2 \qquad (3)$$

The fugacity coefficients ϕ_I and ϕ_{II} were calculated by means of the virial equation of state, and the second virial coefficients were calculated from the Pitzer and Curl (1957) equations and the Tsonopoulos (1974) correlation correction for polar compounds.

For each experimental value, the activity coefficients of pseudocomponents I and II in the liquid phase have been calculated following the above procedure. The obtained values of γ_I and γ_{II} are shown in columns 6 and 7 of Table 1.

In Figure 1, the logarithms of γ_I and γ_{II} are plotted against x_I. In this figure, the logarithms of activity coefficients for both pseudocomponents can be adjusted to one curve whatever the salt concentration may be. This fact implies that the pseudobinary model proposed explains the behavior of the system.

In order to reproduce experimental data, the activity coefficients obtained for every pseudocomponent were adjusted against their composition in the liquid phase, and the equations found were:

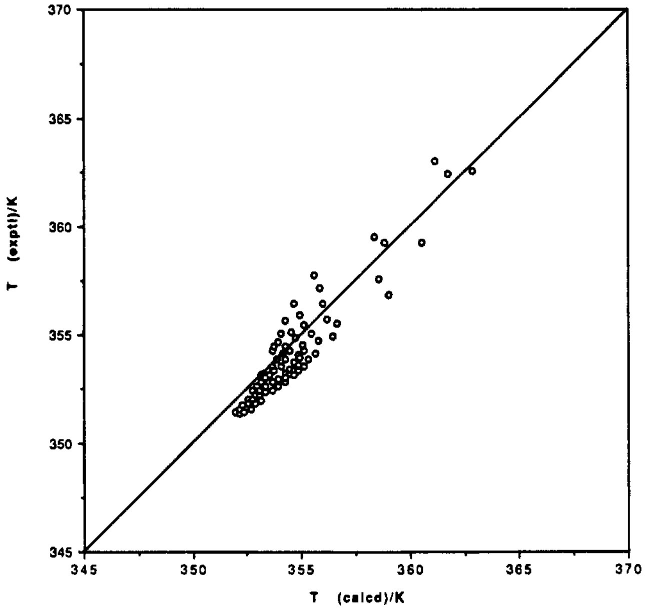

Figure 3. Comparison of calculated bubble points with experimental values.

$$\ln \gamma_I = (2.4497 - 6.5749x_I + 11.509x_I^2 - 7.9717x_I^3)(1 - x_I)^2 \qquad (4)$$

$$\ln \gamma_{II} = (0.90598 + 0.59469x_{II})(1 - x_{II})^2 \qquad (5)$$

These equations were used to recalculate the vapor composition and temperature values in equilibrium from the liquid-phase composition. From comparison of experimental and calculated values, we found

$y_{exptl} - y_{calcd}$: mean, 0.013
standard deviation, 0.016

$T_{exptl} - T_{calcd}$: mean, 0.83 K
standard deviation, 0.89 K

The experimental values are plotted against the corresponding calculated ones in Figure 2 for the vapor composition and in Figure 3 for the temperature. In these figures, the agreement between both experimental and calculated values can be noted.

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