Isobaric Vapor−Liquid Equilibrium for Ethanol + Water + Strontium Nitrate

Ernesto Vercher, M. Pilar Peña, and Antoni Martinez-Andreu*

Departamento de Ingenieria Quimica, Facultad de Quimica, Universitat de València, 46100 Burjassot, Valencia, Spain

Isobaric vapor−liquid equilibrium for ethanol (1) + water (2) + strontium nitrate (3) at various concentrations of salt and with ethanol mole fractions from 0 to 0.672, has been measured at 100.0 kPa. The results were correlated by assuming that the salt was in ionic form and it was associated only with the water.

Introduction

The effect of salts on the vapor−liquid equilibrium of solvent mixtures is of considerable interest in the separation of close boiling and azeotropic mixtures. The salt effect has been studied by many researchers. Most investigations have been limited to measurements on the saturated salt solutions.

Some proposed methods for the experimental data correlation consider that the mixtures can be treated as pseudobinary systems (Natarajan, 1980; Schmitt and Vogelpohl, 1982; Vercher *et al.*, 1991, 1994; Peña *et al.*, 1994). Other correlations are based on modifications of the vapor−liquid equilibrium local composition model (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 nitrate at different concentrations of salt below saturation. The addition of strontium nitrate to this solvent mixture increases the amount of alcohol present in the vapor phase at equilibrium. This indicates a preferential association of the salt with the less volatile component of the mixed solvent.

The vapor−liquid equilibrium of the ethanol + water system saturated with strontium nitrate has been determined by Galán *et al.* (1980) and Mondeja (1977), but we have not found any reported vapor−liquid equilibrium for this system at salt concentrations below saturation.

Experimental Section

The chemicals were absolute ethanol (Baker-analyzed reagent, >99.8 mass %), distilled water, and strontium nitrate (Merck GR, >99 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 various concentrations of salt was also measured with the same apparatus.

Every experimental point was obtained from an initial sample prepared gravimetrically by using a Mettler AE 200 analytical balance with a precision of ±0.0001 g and, afterward, by adding different quantities of ethanol, water, or ethanol + water mixture. Each experiment was kept at the boiling point for 15 min or more to ensure the stationary state. The accuracy of the temperature measurement was ±0.1 K.

Compositions of the condensed vapor phase were analyzed by using a Varian STAR 3400 CX gas chromatograph with a thermal conductivity detector. The GC response was treated with a Star Chromatography Station. The chromatographic column (2 m × $^1/_8$ in.) was packed with Porapak P. The gas carrier was helium flowing at 50 $cm^3 \cdot min^{-1}$ 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 salt mass fraction in the liquid phase was gravimetrically determined after the volatile components were separated from a known mass of sample by evaporation to dryness. 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 between the density and the mass fraction of ethanol and salt in the solution had been obtained. The mass fraction of ethanol in the liquid phase was obtained from this correlation, the density of solution, and the mass fraction of salt. The mass fractions were then translated into mole fractions. The accuracy in the measurement of the ethanol, water, and strontium nitrate mole fractions in the liquid phase was ±0.003. 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 *et al.*, 1994).

Results and Discussion

In Table 1, the vapor−liquid equilibrium for the ethanol (1) + water (2) + strontium nitrate (3) system 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, in the range of liquid-phase salt compositions studied, the salt is in ionic form and it is associated only with the water (Vercher *et al.*, 1991). Therefore, the ternary system can be treated as a 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,

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Table 1. Vapor−Liquid Equilibrium for Ethanol (1) + Water (2) + Strontium Nitrate (3) at 100.0 kPa

T/K	x_1	x_2	x_3	y_1	γ_I	γ_{II}
369.8	0.013	0.933	0.053	0.228	8.395	0.980
367.8	0.014	0.965	0.021	0.228	8.530	0.962
368.7	0.015	0.956	0.029	0.215	7.303	0.966
367.0	0.016	0.971	0.013	0.230	7.746	0.973
368.6	0.017	0.933	0.050	0.258	7.853	0.976
364.5	0.028	0.926	0.047	0.374	8.003	0.964
364.8	0.030	0.944	0.026	0.333	6.487	0.959
363.9	0.033	0.948	0.019	0.346	6.311	0.957
362.4	0.038	0.909	0.053	0.436	7.280	0.973
362.4	0.041	0.915	0.044	0.421	6.543	0.970
361.4	0.054	0.929	0.017	0.411	5.005	0.966
361.1	0.056	0.920	0.024	0.438	5.226	0.953
361.4	0.056	0.911	0.033	0.439	5.167	0.962
359.6	0.058	0.895	0.047	0.498	6.095	0.968
360.3	0.058	0.902	0.040	0.470	5.563	0.971
359.8	0.070	0.916	0.014	0.449	4.493	0.973
359.3	0.073	0.897	0.029	0.488	4.733	0.963
358.0	0.074	0.879	0.046	0.530	5.336	0.980
358.8	0.084	0.895	0.022	0.494	4.298	0.961
359.2	0.087	0.907	0.006	0.450	3.689	0.994
357.7	0.089	0.875	0.036	0.528	4.492	0.983
357.6	0.102	0.872	0.026	0.521	3.885	0.985
357.4	0.112	0.870	0.018	0.522	3.555	0.983
357.6	0.113	0.876	0.012	0.503	3.391	0.997
357.8	0.118	0.879	0.004	0.486	3.114	1.010
356.5	0.120	0.847	0.032	0.560	3.672	0.988
355.9	0.128	0.833	0.039	0.579	3.649	0.999
356.6	0.130	0.847	0.023	0.543	3.296	1.004
356.7	0.135	0.850	0.015	0.535	3.103	1.001
356.8	0.137	0.856	0.007	0.520	2.969	1.013
355.9	0.145	0.826	0.029	0.569	3.181	1.011
355.4	0.154	0.810	0.036	0.590	3.159	1.016
355.9	0.156	0.823	0.021	0.557	2.886	1.027
356.2	0.164	0.831	0.005	0.533	2.605	1.036
355.4	0.167	0.807	0.026	0.577	2.846	1.032
355.9	0.170	0.818	0.012	0.551	2.622	1.033
355.0	0.182	0.785	0.033	0.598	2.751	1.039
355.8	0.184	0.813	0.003	0.543	2.401	1.051
355.3	0.190	0.793	0.018	0.575	2.504	1.046
355.4	0.202	0.790	0.009	0.561	2.294	1.064
354.9	0.205	0.772	0.023	0.589	2.417	1.064
354.6	0.207	0.763	0.030	0.604	2.478	1.067
354.9	0.223	0.763	0.015	0.579	2.186	1.088
354.4	0.236	0.738	0.026	0.611	2.215	1.086
354.9	0.237	0.757	0.006	0.575	2.038	1.094
354.5	0.241	0.740	0.020	0.601	2.128	1.093
354.6	0.246	0.742	0.012	0.585	2.019	1.113
354.7	0.255	0.741	0.004	0.577	1.915	1.117
354.0	0.269	0.708	0.023	0.617	1.990	1.128
354.2	0.270	0.713	0.016	0.606	1.934	1.126
354.4	0.277	0.714	0.009	0.591	1.825	1.146
353.9	0.302	0.684	0.013	0.610	1.760	1.172
353.8	0.307	0.674	0.020	0.623	1.777	1.169
354.0	0.308	0.685	0.007	0.598	1.685	1.189
353.7	0.338	0.652	0.011	0.617	1.605	1.213
353.5	0.341	0.643	0.016	0.629	1.634	1.216
353.7	0.348	0.648	0.005	0.610	1.542	1.231
353.5	0.362	0.635	0.003	0.613	1.498	1.255
353.4	0.378	0.614	0.008	0.627	1.476	1.264
353.2	0.383	0.604	0.014	0.639	1.494	1.271
353.1	0.417	0.577	0.006	0.639	1.377	1.314
353.0	0.423	0.567	0.011	0.649	1.385	1.322
352.8	0.452	0.544	0.003	0.648	1.302	1.372
352.8	0.453	0.538	0.009	0.657	1.317	1.367
352.4	0.499	0.495	0.007	0.670	1.240	1.450
352.2	0.539	0.456	0.005	0.686	1.184	1.505
352.0	0.576	0.420	0.004	0.701	1.140	1.566
351.8	0.601	0.396	0.003	0.710	1.115	1.622
351.5	0.672	0.326	0.002	0.743	1.056	1.764

because the solubility of strontium nitrate, which, expressed as the salt mole fraction, is 0.0633 in water at 25 °C, decreases almost linearly when the mole fraction of ethanol in the mixed solvent increases, to become practically zero when the mole fraction of alcohol in the ethanol + water mixed solvent is 0.85 (Linke, 1965).

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

x_3*	T/K	x_3*	T/K	x_3*	T/K	x_3*	T/K
0.0621	377.4	0.0428	375.7	0.0251	374.4	0.0109	373.4
0.0580	377.0	0.0388	375.4	0.0223	374.2	0.0078	373.2
0.0547	376.7	0.0353	375.1	0.0190	374.0	0.0054	373.0
0.0505	376.4	0.0322	374.9	0.0164	373.7	0.0039	372.9
0.0474	376.1	0.0284	374.6	0.0136	373.5		

Table 3. Antoine Coefficients[a] of Pure Components (Gmehling *et al.*, 1981)

component	A	B	C
ethanol	8.11220	1592.864	226.184
water	8.07131	1730.630	233.426

[a] $\log(P_i°/\text{mmHg}) = A - B/((T/°\text{C}) + C)$.

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

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

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 (kPa), $P_I°$ is the vapor pressure of pure ethanol ($=P_1°$), and $P_{II}°$ is the vapor pressure of pseudocomponent II, both calculated at the equilibrium temperature (kPa). 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

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

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

The vapor pressure correction factor was computed according to 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 Table 3 (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

$$\epsilon = 1 - 1.891x_3* - 8.63(x_3*)^2 \tag{3}$$

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 the pseudocomponents I and II in the liquid phase have been calculated following the above procedure. The obtained results 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

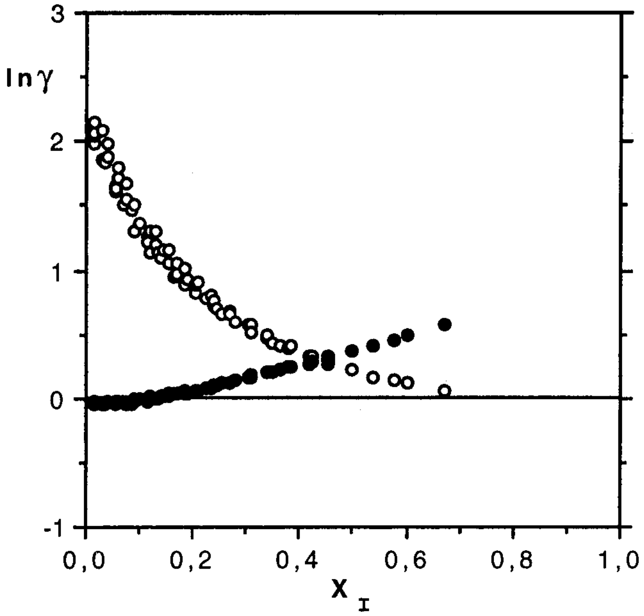

Figure 1. Experimental solvent activity coefficients for the system ethanol (1) + water (2) + strontium nitrate (3) at 100.0 kPa: (○) ln γ_{I}; (●) ln γ_{II}.

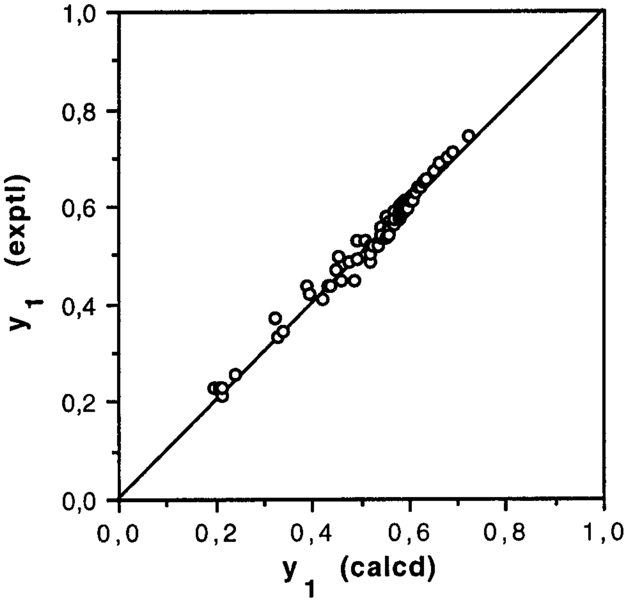

Figure 2. Comparison of the calculated ethanol vapor composition, y_1(calcd), with experimental values, y_1(exptl).

one curve whatever the salt concentration may be. This fact implies that the pseudobinary model proposed explains the behavior of the system in the range of compositions established.

For the purpose of reproducing experimental data, the activity coefficients obtained for every pseudocomponent were adjusted to the Van Laar model. The obtained parameters are $A_{12} = 2.121$ and $A_{21} = 1.042$.

The Van Laar model and the pseudobinary approach were used to recalculate the vapor composition and temperature results in equilibrium from the liquid-phase composition. From comparison of experimental and calculated results, we found the following:

$y_{\mathrm{exptl}} - y_{\mathrm{calcd}}$: mean, 0.015; standard deviation, 0.016

$T_{\mathrm{exptl}} - T_{\mathrm{calcd}}$:

mean, 0.78 K; standard deviation, 0.83 K

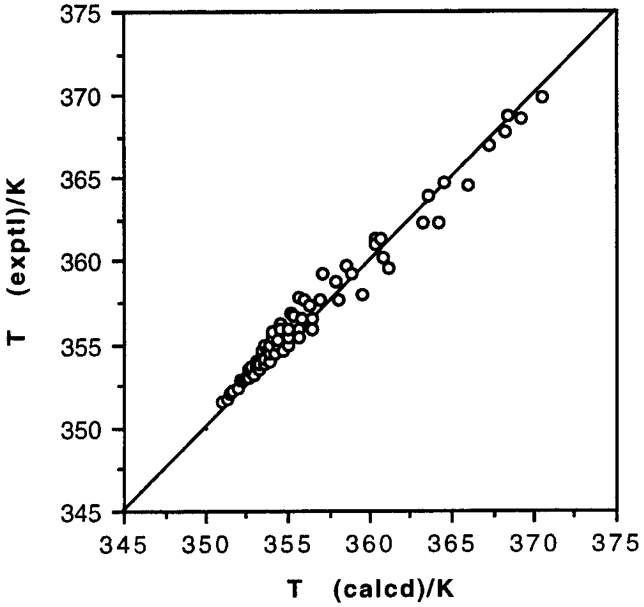

Figure 3. Comparison of calculated bubble points, T(calcd), with experimental values, T(exptl).

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

The same equations were used to reproduce the results obtained by Galán *et al.* (1980) for this system in saturation conditions, finding a mean deviation in the molar fraction of ethanol in the vapor phase of 0.023 and a mean deviation in the equilibrium temperature of 1.05 K.

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