

# Isobaric Vapor–Liquid Equilibrium for Ethanol + Water + Potassium Nitrate

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Isobaric vapor–liquid equilibrium for ethanol (1) + water (2) + potassium nitrate (3) at various concentrations of salt and with ethanol mole fractions from 0 to 0.642 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.

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## Introduction

An increasing research interest in the determination of the salt effect in the vapor–liquid equilibrium of binary systems has developed over the last few decades due to the importance of distillation with salts in the separation of close boiling and azeotropic mixtures. Most investigations on the salt effect are limited to the presentation of experimental data with no attempt to develop correlations. Furthermore, in nearly all cases only saturated salt solutions were studied, with the idea that under these conditions a more pronounced effect would be observed.

Some methods for the correlation of the activity coefficients of the solvents in these ternary mixtures consider that the mixtures can be treated as pseudobinary systems (Natarajan, 1980; Schmitt and Vogelpohl, 1983; Vercher *et al.*, 1991, 1994; Peña *et al.*, 1994). Another approach uses correlations 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 + potassium nitrate at different concentrations of salt below saturation. The addition of potassium 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 potassium nitrate has been determined by Rieder and Thompson (1950), and this system is quoted in the reviews by Ciparis (1966, 1973), but we have not found any reported vapor–liquid equilibrium for ethanol + water with various concentrations of potassium nitrate below saturation. The effect of potassium nitrate addition in the vapor–liquid equilibrium of other binary systems has also been studied: propionic acid + water (Ramalho, 1964); methanol + water (Schuberth, 1974); 1-propanol + water (Santhanam, 1975); 2-propanol + water (Tan, 1985); 1,4-dioxane + water (Rao, 1988).

## Experimental Section

The chemicals were absolute ethanol (Baker-analyzed reagent, >99.8 mass %), distilled water, and potassium 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  $(100.00 \pm 0.04)$  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  $\pm 0.0001$  g and, afterward, by adding different quantities of ethanol, water, ethanol + salt solution, or water + salt solution. 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  $\pm 0.1$  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  $\times$  1/8 in.) was packed with Porapak P. The gas carrier was helium flowing at 50  $\text{cm}^3 \cdot \text{min}^{-1}$ , 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  $\pm 0.002$ .

The liquid phase was composed of ethanol, water, and potassium nitrate. 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. 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  $(298.15 \pm 0.01)$  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 determination of the mass fraction of ethanol in the sample, given the density and the mass fraction of salt in the solution, had been obtained. The mass fractions were then translated into mole fractions. The accuracy in the measurement of the ethanol, water, and potassium nitrate mole fractions in the liquid phase was  $\pm 0.004$ . 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) + potassium nitrate (3) system at a pressure of 100.0 kPa is reported. Included are the equilibrium

**Table 1. Vapor–Liquid Equilibrium for Ethanol (1) + Water (2) + Potassium Nitrate (3) at 100.0 kPa**

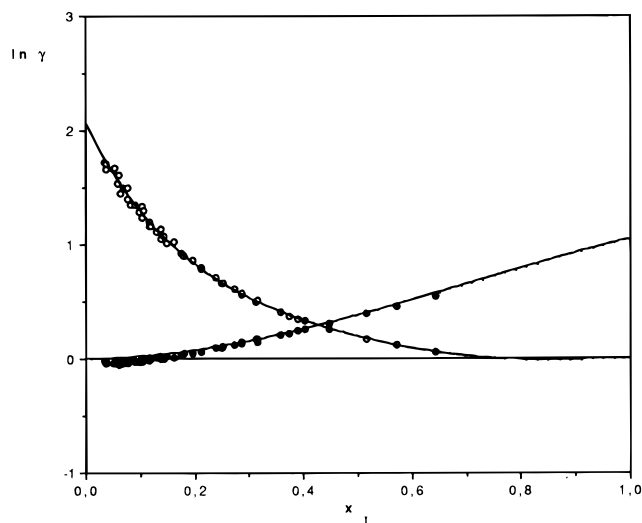
<i>T</i> /K	$x_1$	$x_2$	$x_3$	$y_1$	$\gamma_1$	$\gamma_{II}$
364.0	0.035	0.950	0.016	0.320	5.584	0.976
363.7	0.037	0.937	0.026	0.343	5.576	0.971
363.7	0.038	0.953	0.009	0.329	5.263	0.968
361.8	0.050	0.927	0.023	0.402	5.275	0.960
361.3	0.053	0.912	0.035	0.424	5.352	0.962
361.3	0.057	0.929	0.014	0.399	4.646	0.976
360.5	0.061	0.907	0.032	0.448	5.041	0.955
361.2	0.062	0.930	0.008	0.401	4.284	0.974
360.0	0.070	0.910	0.020	0.451	4.478	0.961
359.8	0.076	0.912	0.012	0.444	4.068	0.975
359.0	0.078	0.893	0.029	0.482	4.468	0.964
359.6	0.081	0.912	0.007	0.442	3.842	0.984
358.7	0.091	0.892	0.017	0.481	3.856	0.974
358.5	0.097	0.893	0.010	0.480	3.621	0.980
358.3	0.102	0.892	0.006	0.475	3.440	0.995
357.7	0.102	0.871	0.026	0.516	3.811	0.971
357.4	0.107	0.869	0.024	0.513	3.669	0.990
357.7	0.116	0.879	0.005	0.488	3.180	1.007
357.5	0.116	0.870	0.014	0.510	3.338	0.989
357.4	0.120	0.871	0.008	0.505	3.217	0.996
357.2	0.128	0.868	0.004	0.505	3.031	1.007
356.5	0.137	0.842	0.020	0.540	3.107	0.999
356.9	0.138	0.859	0.003	0.504	2.843	1.032
356.7	0.142	0.847	0.011	0.529	2.925	1.006
356.6	0.149	0.844	0.007	0.523	2.766	1.023
356.0	0.161	0.821	0.018	0.554	2.776	1.012
356.0	0.174	0.817	0.010	0.544	2.526	1.036
355.8	0.180	0.815	0.006	0.544	2.454	1.047
355.4	0.196	0.789	0.015	0.566	2.382	1.049
355.3	0.210	0.782	0.008	0.563	2.215	1.067
355.3	0.211	0.785	0.004	0.560	2.201	1.068
354.8	0.238	0.750	0.012	0.576	2.044	1.103
354.8	0.250	0.744	0.007	0.576	1.946	1.109
354.7	0.251	0.746	0.004	0.574	1.936	1.116
354.4	0.273	0.717	0.010	0.588	1.846	1.139
354.3	0.286	0.711	0.003	0.584	1.755	1.161
354.3	0.286	0.709	0.005	0.592	1.779	1.143
354.0	0.312	0.686	0.002	0.593	1.655	1.189
354.0	0.314	0.678	0.008	0.601	1.662	1.185
354.0	0.315	0.680	0.004	0.605	1.666	1.168
353.6	0.357	0.640	0.003	0.613	1.515	1.233
353.6	0.357	0.637	0.006	0.614	1.515	1.240
353.5	0.372	0.626	0.002	0.615	1.464	1.259
353.3	0.389	0.610	0.001	0.620	1.424	1.285
353.2	0.402	0.593	0.004	0.627	1.397	1.305
352.9	0.447	0.550	0.003	0.645	1.306	1.359
352.4	0.516	0.482	0.002	0.665	1.191	1.491
352.0	0.572	0.426	0.001	0.690	1.129	1.590
351.6	0.642	0.357	0.001	0.721	1.068	1.737

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

$x_3^*$	<i>T</i> /K	$x_3^*$	<i>T</i> /K
0.0681	375.6	0.0338	374.2
0.0660	375.5	0.0281	374.0
0.0625	375.4	0.0243	373.8
0.0563	375.1	0.0204	373.6
0.0521	375.0	0.0162	373.4
0.0485	374.8	0.0122	373.2
0.0425	374.6	0.0085	373.1
0.0376	374.4		

temperature (*T*/K), 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,

**Figure 1.** Experimental solvent activity coefficients for the system ethanol (1) + water (2) + potassium nitrate (3) at 100.0 kPa: (○)  $\ln \gamma_I$ ; (●)  $\ln \gamma_{II}$ ; (—) results calculated using eqs 4 and 5.

because the solubility of potassium nitrate, which expressed as the salt mole fraction is 0.0625 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 0.80 (Linke, 1965).

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

$$\gamma_I = \frac{y_I \phi_I P}{x_I P_I^0} \quad \gamma_{II} = \frac{y_{II} \phi_{II} P}{x_{II} P_{II}^0} \quad (1)$$

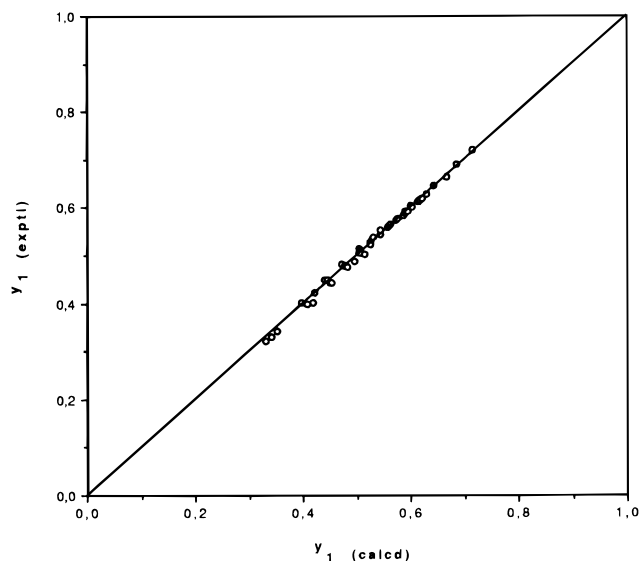
where  $x_I$  is the mole fraction of pseudocomponent I in the liquid phase ( $=x_1$ ),  $x_{II}$  is the mole fraction of pseudocomponent II in the liquid phase ( $=x_2 + x_3$ ),  $y_1$  is the mole fraction of ethanol in the vapor phase ( $=y_1$ ),  $y_{II}$  is the mole fraction of water in the vapor phase ( $=1 - y_1$ ),  $\phi_I$  is the fugacity coefficient of pseudocomponent I in the vapor phase,  $\phi_{II}$  is the fugacity coefficient of pseudocomponent II in the vapor phase,  $P$  is the system pressure (kPa),  $P_I^0$  is the vapor pressure of pure ethanol ( $=P_1^0$ ), and  $P_{II}^0$  is the vapor pressure of pseudocomponent II, both calculated at the equilibrium temperature (kPa). The value of  $P_{II}^0$  depends on the temperature and on the salt concentration. Jaques and Furter (1972) propose that this dependency can be expressed as

$$P_{II}^0 = P_2^0(T) \epsilon(x_3^*) \quad (2)$$

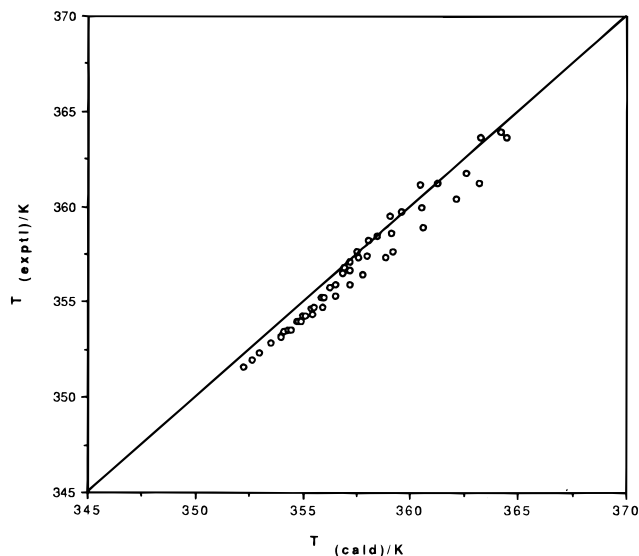
where  $P_2^0$  is the vapor pressure of pure water (kPa) and  $\epsilon$  is the vapor pressure correction factor, which depends only on  $x_3^*$ , the mole fraction of the salt component in the pseudocomponent II [ $=x_3/(x_2 + x_3)$ ].

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 literature (Gmehling *et al.*, 1981), both at the same temperature.

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



**Figure 2.** Comparison of the calculated ethanol vapor composition,  $y_1(\text{calcd})$ , with experimental values,  $y_1(\text{exptl})$ .



**Figure 3.** Comparison of calculated bubble points,  $T(\text{calcd})/\text{K}$ , with experimental values,  $T(\text{exptl})/\text{K}$ .

$$\epsilon = 1 - 1.4152x_3^* + 0.9510(x_3^*)^2 \quad (3)$$

The fugacity coefficients  $\phi_I$  and  $\phi_{II}$  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  $\gamma_I$  and  $\gamma_{II}$  are shown in columns 6 and 7 of Table 1.

In Figure 1, the logarithms of  $\gamma_I$  and  $\gamma_{II}$  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 the range of compositions established.

For the purpose of reproducing experimental data, the activity coefficients obtained for every pseudocomponent were adjusted against their composition in the liquid phase,

and the equations found were

$$\ln \gamma_I = (2.0729 - 5.6966x_I + 10.709x_I^2 - 8.8191x_I^3)(1 - x_I)^2 \quad (4)$$

$$\ln \gamma_{II} = (1.0437 + 0.9464x_{II})(1 - x_{II})^2 \quad (5)$$

These equations 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:

$Y_{\text{exptl}} - Y_{\text{calcd}}$ :	mean 0.005
	standard deviation 0.008
$T_{\text{exptl}} - T_{\text{calcd}}$ :	mean 0.72 K
	standard deviation 0.57 K

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.

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