

# Vapor–Liquid Equilibrium for the Hexane + 2-Propanol + Calcium Chloride System at 101.33 kPa

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Vapor–liquid equilibrium measurements have been performed at isobaric conditions for the hexane + 2-propanol + calcium chloride system at different mole fractions of salt with a recirculating still. Relative volatilities and activity coefficients of the solvents were calculated. Even though the effect of the electrolyte on the relative volatility is significant, the azeotrope was not destroyed.

## Introduction

The study of the influence of a salt on vapor–liquid equilibrium (VLE) of a binary organic mixture is of interest because of its application to breaking azeotropes and improving the relative volatilities. There have been many investigations (Slusher et al., 1995; Morrison et al., 1990) concerning the experimental determination of salt effect on aqueous solutions. In the area of binary organic mixtures, however, few studies have been reported. The low solubility of salts in such systems could be the reason for the scarcity of such studies.

The purpose of this work was to study the effect of calcium chloride on the VLE of hexane + 2-propanol. This system was chosen because it is nonaqueous and presents azeotropic behavior at the conditions studied.

## Experimental Section

**Apparatus.** VLE measurements were performed under isobaric conditions by means of a two-phase recirculating still, which has been described previously (Zemp and Francesconi, 1992). The temperature was measured with a platinum resistance thermometer in conjunction with a Fischer Model Dt 4 digital instrument. Pressure was determined from measured differences in height of the mercury in a U-tube manometer using a cathetometer. The pressure measurement device was tested by measuring the vapor pressure of pure hexane over the range 312.55 K to 341.65 K and the vapor pressure of pure 2-propanol over the range 325.15 K to 353.05 K with the present apparatus. The normal boiling temperatures measured were 341.65 K for hexane and 355.35 K (obtained from the Antoine equation) for 2-propanol, while the literature values (Smith and Srivastava, 1986a,b) are 341.886 K and 355.390 K, respectively. The composition of the liquid phase and vapor-phase condensate samples for both hexane and 2-propanol was determined by using a CG3537 gas chromatograph (Instrumentos Científicos CG, Brazil) with a thermal conductivity detector connected to a CG300 integrator. The chromatographic column (1.8 m × 1/8 in.) was packed with Chromosorb 102. The gas carrier was hydrogen flowing at 35 cm<sup>3</sup>/min, and the column temperature was 110 °C. For the salt mole fraction in the liquid phase, gravimetry was used. A small aliquot from a liquid sample was placed in a preweighed volumetric flask and then weighed. After evaporation of solvents, the sample was

reweighed and the salt mass determined. With the results of the chromatographic analysis of the liquid phase, salt composition was then determined.

The uncertainty in the pressure measurement was about ±0.007 kPa, in temperature about ±0.01 K, and in mass about ±0.000 05 g. The uncertainty in the final mole fractions caused by the above uncertainties is estimated to be ±0.004.

**Materials.** Hexane (analytical grade, Carlo Erba), 2-propanol (analytical grade, Merck), and calcium chloride (analytical grade, Nuclear) were used without further purification.

## Results and Discussion

The effect of calcium chloride on the VLE of hexane + 2-propanol was studied at 101.33 kPa at different salt mole fractions. The results are given in Table 1. Experimental activity coefficients for hexane and 2-propanol on a three-component basis were obtained from the equation (Morrison et al., 1990)

$$\ln \gamma_i = \ln \left( \frac{y_i P}{x_i P_i^v} \right) + \frac{(B_{ii} - V_i)(P - P_i^v)}{RT} + \frac{(1 - y_i)^2 P \delta}{RT} \quad (1)$$

where  $\delta = 2B_{ij} - B_{ii} - B_{jj}$ . Second virial coefficients  $B_{ii}$ ,  $B_{jj}$ , and  $B_{ij}$  were estimated using correlations suggested by Tsonopoulos (1974). The pure liquid molar volumes  $V_i$  were obtained by the modified Rackett equation (Smith and Srivastava, 1986a,b). For the vapor pressure  $P_i^v$  data for this work were used. Pure component thermodynamic quantities used in these calculations are given in Table 2. The relative volatility of hexane (1) to propanol (2)

$$\alpha_{1,2} = \frac{y_1/x_1}{y_2/x_2} \quad (2)$$

was also calculated.

Adding calcium chloride to hexane + 2-propanol system caused no change in the azeotropic point at 101.33 kPa, probably because of the limited solubility of the salt in the hydrocarbon-rich side.

The activity coefficient for the hexane was increased with increasing salt concentration, while that of 2-propanol decreased. Relative volatilities  $\alpha_{1,2}$  are improved, indicating that hexane is salted-out.

**Table 1. Vapor-Liquid Equilibria and Activity Coefficients  $\gamma$  for the System Hexane (1) + 2-Propanol (2) + Calcium Chloride (3) at 101.33 kPa;  $x_1$  Is the Salt-free Mole Fraction of Hexane, and  $\alpha_{12}$  Is the Relative Volatility of Hexane to 2-Propanol**

$T/K$	$x_3$	$x_1$	$y_1$	$\gamma_1$	$\gamma_2$	$\alpha_{1,2}$
335.95	0.000	0.894	0.779	1.030	4.699	0.420
336.25	0.001	0.871	0.811	1.090	3.550	0.598
335.75	0.002	0.845	0.792	1.050	3.124	0.685
335.45	0.004	0.818	0.780	1.144	2.797	0.789
334.95	0.000	0.793	0.753	1.157	2.836	0.793
334.95	0.006	0.778	0.766	1.199	2.504	0.932
334.75	0.007	0.759	0.749	1.210	2.470	0.955
334.55	0.008	0.734	0.750	1.260	2.261	1.092
334.75	0.010	0.715	0.743	1.274	2.177	1.141
334.65	0.012	0.691	0.732	1.303	2.057	1.238
335.35	0.000	0.585	0.680	1.401	1.799	1.506
335.85	0.010	0.612	0.703	1.363	1.721	1.517
335.65	0.014	0.626	0.729	1.390	1.647	1.623
335.75	0.015	0.614	0.730	1.415	1.582	1.718
335.85	0.017	0.596	0.728	1.449	1.516	1.832
336.15	0.000	0.550	0.670	1.434	1.649	1.660
336.25	0.011	0.557	0.699	1.472	1.492	1.881
336.55	0.012	0.530	0.691	1.516	1.427	2.015
336.65	0.013	0.488	0.674	1.601	1.367	2.218
336.85	0.014	0.428	0.661	1.781	1.275	2.634
336.35	0.000	0.512	0.673	1.538	1.491	1.966
336.25	0.018	0.513	0.711	1.625	1.307	2.369
336.45	0.019	0.472	0.697	1.722	1.251	2.611
336.75	0.021	0.426	0.685	1.858	1.187	2.959
337.55	0.024	0.324	0.596	2.080	1.244	3.094
336.95	0.000	0.477	0.660	1.591	1.412	2.124
336.95	0.005	0.469	0.655	1.606	1.401	2.162
337.55	0.016	0.360	0.638	2.002	1.169	3.193
337.75	0.017	0.353	0.633	2.014	1.156	3.244
336.85	0.000	0.474	0.662	1.610	1.402	2.167
336.45	0.022	0.371	0.615	1.936	1.254	2.704
337.25	0.024	0.357	0.603	1.927	1.250	2.722
337.95	0.027	0.316	0.586	2.073	1.204	3.075
337.45	0.000	0.415	0.652	1.780	1.261	2.642
338.15	0.006	0.354	0.617	1.935	1.218	2.936
337.85	0.016	0.356	0.642	2.019	1.144	3.277
338.75	0.025	0.274	0.565	2.252	1.173	3.435
338.05	0.000	0.327	0.625	2.128	1.153	3.424
340.65	0.012	0.235	0.578	2.541	1.008	4.497
341.15	0.020	0.212	0.556	2.672	1.003	4.728
342.15	0.024	0.180	0.514	2.831	1.012	4.902
338.25	0.000	0.306	0.603	2.183	1.172	3.444
340.05	0.011	0.242	0.585	2.541	1.009	4.512
342.35	0.019	0.175	0.519	2.923	0.995	5.110
343.05	0.020	0.164	0.511	3.011	0.969	5.332
338.65	0.000	0.301	0.608	2.210	1.129	3.600
340.65	0.009	0.224	0.590	2.721	0.973	4.990
343.55	0.019	0.155	0.500	3.075	0.959	5.455
339.75	0.000	0.229	0.593	2.745	1.014	4.892
341.45	0.006	0.195	0.566	2.932	0.964	5.364
344.85	0.013	0.132	0.466	3.247	0.940	5.785
342.35	0.000	0.159	0.497	3.083	1.029	5.208
346.85	0.006	0.104	0.394	3.305	0.992	5.572
349.25	0.010	0.065	0.290	3.659	1.012	5.877
343.35	0.000	0.148	0.494	3.200	0.979	5.609
348.45	0.005	0.073	0.320	3.670	1.021	6.014
345.35	0.000	0.101	0.418	3.760	0.984	6.359
348.85	0.005	0.064	0.310	4.012	1.018	6.432
348.55	0.000	0.077	0.302	3.277	1.010	5.191
351.05	0.010	0.045	0.210	3.658	1.011	5.582
351.25	0.011	0.043	0.202	3.664	1.012	5.598

VLE data for the hexane + 2-propanol system at 101.33 kPa have been measured. The thermodynamic consistency of the data was tested using Herington's method. The data sets were considered consistent according to the value of  $(D-J) = -8.30$ .

**Table 2. Critical Temperature ( $T_c$ ), Critical Pressure ( $P_c$ ), Critical Compressibility Factor ( $Z_c$ ), Rackett's Parameter ( $Z_{RA}$ ), Acentric Factor ( $\omega$ ), Tsonopoulos Constants ( $a$ ,  $b$ ), and Parameters of the Antoine Equation ( $A$ ,  $B$ ,  $C$ )**

quantity	hexane	2-propanol
$T_c^a/K$	507.680	508.300
$P_c^a/MPa$	3.040	4.762
$Z_c^a$	0.2640	0.2480
$Z_{RA}$	0.2633 <sup>a</sup>	0.2540 <sup>b</sup>
$\omega^a$	0.3018	0.6648
$a^a$	0.0000	0.8780
$b^a$	0.0000	0.053
$A^c$	15.6553	17.6340
$B^c/K$	2692.1788	3004.0954
$C^c/K$	-43.2037	-82.1904

<sup>a</sup> Smith and Srivastava (1986a,b). <sup>b</sup> Prausnitz et al. (1980). <sup>c</sup> This work.

VLE data for hexane-2-propanol in the absence of salt are reported by Gmehling et al. (1977). The average deviation between the vapor composition reported here and those of literature is less than 0.050 in mole fraction. The comparison was made using a  $y-x$  plot by assuming liquid mole fractions  $x_i$  and comparing the corresponding vapor mole fractions  $y_i$ .

## Conclusions

Isobaric vapor-liquid equilibrium measurements on the hexane + 2-propanol + calcium chloride system have been performed at 101.33 kPa over a wide range of salt concentration. The system was chosen because is nonaqueous and presents an azeotropic point at 101.33 kPa. The effect of the electrolyte on the relative volatility of hexane to 2-propanol is significant, but the azeotropic point of the binary system is not influenced by adding salt.

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Received for review June 11, 1997. Accepted September 24, 1997.  
JE970141P

© Abstract published in *Advance ACS Abstracts*, November 15, 1997.