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Isobaric Vapor−Liquid Equilibria of 3-Pentanone with Acetone and Isopropyl Ether at 101.3 kPa

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Vapor−liquid equilibrium at 101.3 kPa has been determined for the binary systems of acetone + 3-pentanone and isopropyl ether + 3-pentanone. The two systems exhibit positive deviations from ideal behavior. The activity coefficients were correlated by the Wilson equation. The results are thermodynamically consistent according to the method of Van Ness. Neither system shows an azeotrope.

Introduction

One of the commercially important ways to manufacture acetone is by the catalytic dehydrogenation of 2-propanol. Acetone is relatively easy to separate from the mixture formed by rectification; however, a concurrent reaction takes place in which some of the 2-propanol dehydrates to form isopropyl ether. This, with acetone, forms a minimum azeotrope containing 61 mass % acetone (Berg *et al.*, 1984).

It is therefore impossible to produce pure acetone from acetone + isopropyl ether mixtures by rectification. Extractive distillation would be an attractive method of effecting the separation of acetone from isopropyl ether if agents can be found that will break the azeotrope which are also easy to recover from the acetone.

In this work, we have selected possible solvents by means of Scheibel's criterion, which suggests the compounds be selected from the same homologous series. These solvents were tested by UNIFAC (Fredenslund *et al.*, 1977), and from that prediction we have selected the 3-pentanone.

In this paper, the vapor−liquid equilibria of the acetone + 3-pentanone and isopropyl ether + 3-pentanone systems were measured at 101.3 kPa. Data of the isopropyl ether + 3-pentanone system are not found in the literature, and new data of acetone + 3-pentanone are shown and compared with the literature (Glukhareva *et al.*, 1974). A check of the patent literature shows that 3-pentanone is not covered as an extractive distillation agent.

Experimental Section

Materials. Acetone (99.8+ mol %) and 3-Pentanone (99.7+ mol %) were supplied by Fluka. Analytical grade isopropyl ether (Fluka) was purified by distillation in a laboratory column. The purity of the materials was checked by GLC, and the purities obtained were better than 99.7 mol % and were compared with the literature values from the TRC tables (TRC, 1994). Densities, refractive indexes and boiling points of the substances are displayed in Table 1.

Apparatus and Procedure. Vapor−liquid equilibrium measurements were carried out using a dynamic recirculating all-glass still described previously (Resa *et al.*, 1994). The boiling temperature in the equilibrium still was measured with a platinum 100 resistance thermometer with a four-conductor circuit with an accuracy of ±0.1 K. The pressure *P* was maintained constant with a digital regulator, and it is measured with an accuracy of ±0.1 kPa.

Analysis. The compositions of equilibrium samples of the acetone + 3-pentanone system were obtained by gas chromatography on a Perkin-Elmer Series 3920-B apparatus provided with a flame ionization detector and a Hewlett-Packard Model 3390-A electronic integrator. The column used was a 2 m long and 0.32 cm diameter stainless steel tube with Carbowax 20M.

Table 1. Physical Properties of Pure Compounds (Densities, Refractive Indexes at 298.15 K, and Normal Boiling Points)

	ρ/(kg·m^{-3})		n$_D$		T_b/K	
	obsd	lit.	obsd	lit.	obsd	lit.
acetone	784.35	785.47	1.3559	1.35596	329.3	329.23
isopropyl ether	718.56	718.2	1.3651	1.36550	341.4	341.5
3-pentanone	809.50	809.45	1.3904	1.39002	375.4	375.14

Table 2. Density of Isopropyl Ether + 3-pentanone Mixtures as a Function of the Mole Fraction (x_1) of Isopropyl Ether at 298.15 K

x_1	ρ/(kg·m^{-3})	x_1	ρ/(kg·m^{-3})	x_1	ρ/(kg·m^{-3})
0.000	809.50	0.347	774.36	0.723	740.60
0.052	803.97	0.400	769.38	0.787	734.35
0.099	799.13	0.451	764.66	0.839	731.00
0.151	793.78	0.499	760.35	0.900	726.21
0.198	789.08	0.549	755.73	0.954	721.90
0.251	783.74	0.571	753.76	1.000	718.56
0.298	779.09	0.648	747.23		

The analysis for the isopropyl ether + 3-pentanone system was carried out by densimetry using an Anton-Paar (DMA 58 vibrating-tube densimeter, accuracy ±0.00001 g·cm^{-3}) and employing standard curves for the density−mole fraction of each mixture at the temperature 298.15 K. All samples were prepared by mass by means of a Sartorius balance (model Bosch 5200, accuracy 0.0001 g). The uncertainty of comparation measurements was estimated to be ±0.001 mole fraction. Table 2 shows the density−composition values.

Results and Discussion

The vapor−liquid equilibrium data for the acetone + 3-pentanone and isopropyl ether + 3-pentanone systems at 101.3 kPa are reported in Tables 3 and 4 with an accuracy in the mole fraction of ±0.001.

Fugacity coefficients are close to unity for all compositions according to Reid *et al.* (1987), so we have calculated the activity coefficients γ_i by

$$\gamma_i = y_i P / x_i P_i^{\circ} \qquad (1)$$

where x_i and y_i are liquid and vapor mole fractions, respectively, P is the total pressure, and P_i° is the vapor pressure of pure component *i*. Both binary systems show positive deviations from Raoult's law, and no azeotropes

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Table 3. Vapor–Liquid Equilibrium Data for the Acetone + 3-Pentanone System: Liquid-Phase Mole Fraction (x_1), Vapor-Phase Mole Fraction (y_1), Boiling Temperature (T), and Activity Coefficients (γ_1 and γ_2) at 101.3 kPa

T/K	x_1	y_1	γ_1	γ_2
375.4	0.000	0.000		
371.0	0.041	0.172	1.2155	0.9822
362.0	0.143	0.442	1.1385	0.9886
356.7	0.236	0.592	1.0722	0.9681
353.9	0.290	0.650	1.0386	0.9838
350.5	0.336	0.724	1.1035	0.9345
344.8	0.476	0.817	1.0439	0.9662
342.1	0.519	0.853	1.0875	0.9312
340.7	0.573	0.862	1.0403	1.0403
338.0	0.686	0.905	0.9946	1.0811
336.7	0.735	0.916	0.9808	1.1863
335.1	0.782	0.946	1.0025	0.9886
333.4	0.850	0.965	0.9952	0.9958
331.8	0.913	0.973	0.9857	1.4085
331.0	0.936	0.984	0.9985	1.2055
330.3	0.963	0.988	0.9978	1.5581
329.9	0.979	0.992	0.9997	1.8276
329.3	1.000	1.000		

Table 4. Vapor–Liquid Equilibrium Data for the Isopropyl Ether + 3-Pentanone System: Liquid-Phase Mole Fraction (x_1), Vapor-Phase Mole Fraction (y_1), Boiling Temperature (T), and Activity Coefficients (γ_1 and γ_2) at 101.3 kPa

T/K	x_1	y_1	γ_1	γ_2
375.4	0.000	0.000		
369.9	0.049	0.090	1.6817	1.0023
367.4	0.082	0.283	1.5801	0.9958
365.5	0.127	0.329	1.2574	1.0406
364.2	0.155	0.381	1.2349	1.0349
363.2	0.181	0.413	1.1776	1.0470
361.5	0.209	0.456	1.1871	1.0608
359.8	0.263	0.507	1.0983	1.0924
356.0	0.390	0.620	1.0126	1.1571
351.9	0.508	0.735	1.0414	1.1539
349.7	0.580	0.764	1.0155	1.2984
346.6	0.707	0.829	0.9947	1.5101
345.9	0.741	0.849	0.9938	1.5460
344.9	0.793	0.875	0.9878	1.6650
344.2	0.831	0.894	0.9854	1.7704
343.6	0.865	0.909	0.9814	1.9412
342.2	0.906	0.951	1.0249	1.5869
341.1	1.000	1.000		

Table 5. Antoine Coefficients, Eq 2 (Riddick *et al.*, 1986)

compound	A_i	B_i	C_i
acetone	6.254 78	1216.689	−42.875
isopropyl ether	5.976 78	1143.073	−53.810
3-pentanone	6.145 70	1307.927	−59.184

Table 6. Wilson's Constants Λ_{12}, and Λ_{21} and Thermodynamic Consistency Values from the Van Ness and Herington Test

system	Wilson's constants	Van Ness results	Herington results
acetone + 3-pentanone	$\Lambda_{12} = 0.9121$ $\Lambda_{21} = 1.0854$	$\Delta y^a = 0.009$	$D - J = 4.95$
isopropyl ether + 3-pentanone	$\Lambda_{12} = 2.3416$ $\Lambda_{21} = 0.1662$	$\Delta y^a = 0.006$	$D - J = 3.23$

[a] $\Delta y = \Sigma|y_{\text{exptl}} - y_{\text{calcd}}|/N$ (N = number of data points).

are found for these systems at 101.3 kPa. The pure component vapor pressures P_i° were calculated according to the Antoine equation:

$$\log(P/\text{kPa}) = A_i - \frac{B_i}{(T/\text{K}) + C_i} \qquad (2)$$

where the constants A_i, B_i, and C_i are reported in Table 5.

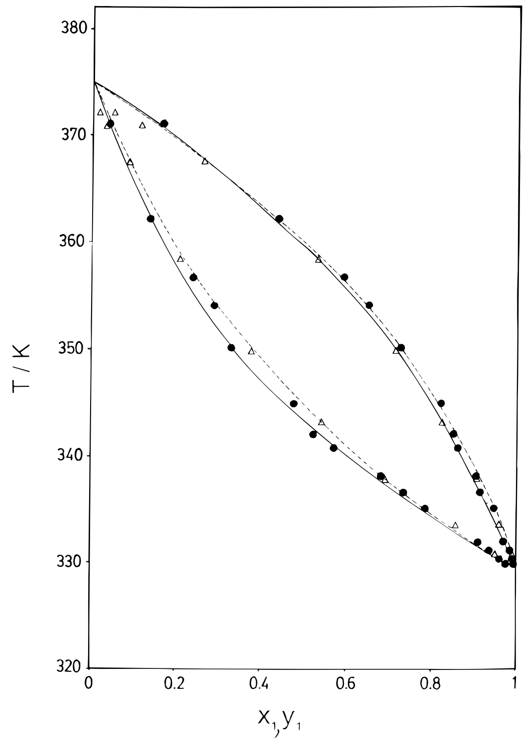

Figure 1. T–x_1–y_1 diagram for acetone + 3-pentanone: (●) experimental data at 101.3 kPa; (- - -) Wilson equation; (—) UNIFAC prediction; (△) Glukhareva *et al.* (1974).

The activity coefficients were correlated with Wilson's equation (Wilson, 1964) and results were compared with the UNIFAC results. To determine Wilson's constants, the method suggested by Apelblat (Apelblat and Wisniak, 1989) was used. The constants are given in Table 6.

The thermodynamic consistency of the experimental data was tested by means of the point-to-point method (Van Ness *et al.*, 1973) using a fifth-order Legendre polynomial where the objective function was the sum of the squared relative deviations in total pressure $F(P)$:

$$F(P) = \sum\left(\frac{P_{\text{exptl}} - P_{\text{calcd}}}{P_{\text{exptl}}}\right)^2 \qquad (3)$$

According to this test, the data are considered consistent if the average absolute deviation in y, Δy, is less than 0.01. In this work, for the two systems, the Δy values obtained fulfill this condition as shown in Table 6. The results were also assessed for thermodynamic consistency by applying the Herington test (Herington, 1951), and the data are consistent if $D - J < 10$, where

$$D = 100|I|/\Sigma \qquad (4)$$

$$J = 150(T_{\max} - T_{\min})/T_{\min} \qquad (5)$$

where $T_{\max}$ and $T_{\min}$ are the maximum and minimum temperatures and

$$I = \int_0^1 \ln(\gamma_1/\gamma_2)\, dx = A - B \qquad (6)$$

$$\Sigma = |A| + |B| \qquad (7)$$

corresponding to the areas above (A) and below (B) the x-axis for the plot of $\ln(\gamma_1/\gamma_2)$ versus x_1. Table 6 gives these values. Since D is less than J, the results are thermodynamically consistent.

The activity coefficients were predicted by using the UNIFAC method (Fredenslund *et al.*, 1977), and the

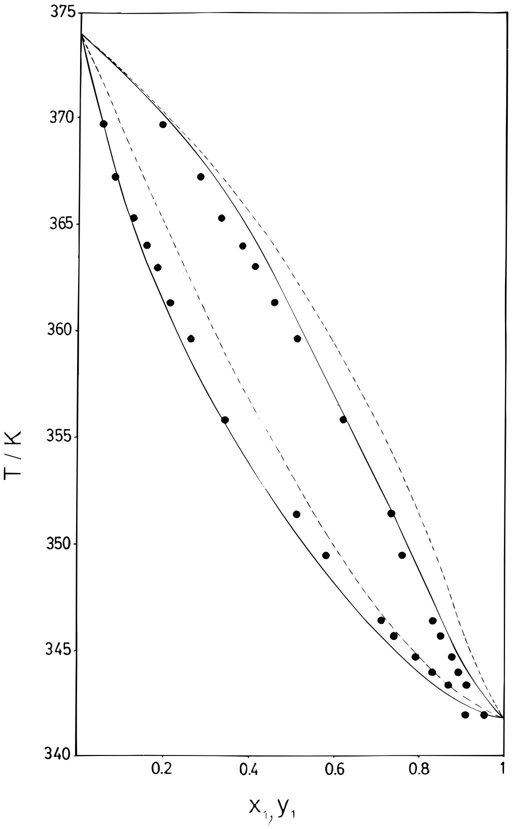

Figure 2. $T-x_1-y_1$ diagram for isopropyl ether + 3-pentanone: (●) experimental data at 101.3 kPa; (- - -) Wilson equation; (—) UNIFAC prediction.

predicted results agree reasonably well with the experimental values (Figures 1 and 2).

Experimental equilibrium data for the acetone + 3-pentanone system agree properly with literature values (Glukhareva *et al.*, 1974), as can be shown in Figure 1. For the isopropyl ether + 3-pentanone system, the Wilson equation does not correctly fit the experimental data. Although in the compositions x_1-y_1 the fit is good, there is an important deviation in the boiling temperatures of the mixture. The acetone−acetone molecules are strongly associated by dipole−dipole bonds. When the mixture acetone−ether occurs, the nonpolar molecules of ether intervene between the strongly polar acetone molecules and the molecules can be dissociated. These molecules can pass easily to the vapor phase, and accordingly the mixture boils at a lower temperature than the mixture of apolar molecules.

The liquid−vapor equilibria acetone + 3-pentanone and isopropyl ether + 3-pentanone are presented, and it is suggested that 3-pentanone can be used as a solvent for extractive distillation.

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