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Isobaric Vapor−Liquid Equilibria in the Systems 2-Butanone + Heptane and 2-Butanone + Oxolane

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Vapor−liquid equilibrium at 94 kPa has been determined for the binary systems 2-butanone + heptane and 2-butanone + oxolane. The system 2-butanone + heptane deviates strongly from ideal behavior and presents an azeotrope that boils at 348.4 K and contains 75.0 mol % 2-butanone. The system 2-butanone + oxolane behaves like a regular solution and does not have an azeotrope. The activity coefficients and boiling points of both binary systems were well-correlated with its composition by the Redlich−Kister, Wohl, Wilson, UNIQUAC, NRTL, and Wisniak −Tamir equations.

Vapor−liquid equilibrium for the system 2-butanone + heptane has been measured at 101.3 kPa and 323.15 K by Aristovich et al. (1965): at 101.3 kPa the azeotrope contained 76.7 mol % 2-butanone and boiled at 350.25 K; at 322.15 K the azeotrope contained 76.5 mol % 2-butanone and had a vapor pressure of 39.1 kPa. Steinhauser and White (1949) measured the phase equilibrium at 101.3 kPa and found the system had an azeotrope that boiled at 350.2 K and contained 76.6 mol % 2-butanone. The authors indicated that the boiling point of the pure components and of the azeotrope changed over a long period of time even though the materials were carefully repurified in a manner identical with previous purifications. Dallinga et al. (1993) measured the infinite dilution activity coefficients of the system over the temperature range 303 to 403 K. Takeo et al. (1970) measured the vapor−liquid equilibria at 318.15 K, and at that temperature they found an azeotropic point that contained 75.6 mol % fraction 2-butanone and a vapor pressure of 31.92 kPa. Wilson and Wilding (1994) have measured $T-x$ equilibria data for the system 2-butanone + oxolane at 288.15 and 423.15 K and determined the vapor compositions by integration of the Gibbs−Duhem equation and use of the Soave equation of state. The present work was undertaken to measure vapor−liquid equilibria (VLE) data for the title systems for which isobaric data are either not very accurate or unavailable.

Experimental Section

Purity of Materials. 2-Butanone (99.68 mass %), heptane (99.95 mass %), and oxolane (tetrahydrofuran, 99.9 mass %) were purchased from Aldrich. The reagents were used without further purification after gas chromatography failed to show any significant impurities. The properties and purity (as determined by GLC) of the pure components appear in Table 1.

Apparatus and Procedure. An all glass vapor−liquid-equilibrium apparatus model 602, manufactured by Fischer Labor-und Verfahrenstechnik (Germany), was used in the equilibrium determinations. In this circulation method apparatus, a volume of about 100 mL of the solution is heated to its boiling point by a 250 W immersion heater (Cottrell pump). The vapor−liquid mixture flows through an extended contact line that guarantees an intense phase exchange and then enters a separation chamber whose construction prevents an entrainment of liquid particles into the vapor phase. The separated gas and liquid phases are condensed and then returned to a mixing chamber, where they are stirred by a magnetic stirrer, and returned again to the immersion heater. The equilibrium temperature is measured with a Lauda thermometer, model R42/2, provided with a 4 mm diameter Pt-100 temperature sensor, with an accuracy of ±0.01 K. The total pressure of the system is controlled by a vacuum pump capable to work at pressures down to 0.25 kPa. The pressure is measured by a Vac Probs with an accuracy of ±0.07 kPa. On the average the system reaches equilibrium conditions after 0.5−1 h of operation. Samples, taken by syringing out 0.7 μL after the system had achieved equilibrium, were analyzed by gas chromatography on a Gow-Mac series 550P apparatus equipped with a thermal conductivity detector and a Spectra Physics model SP 4290 electronic integrator. The column was 3 m long and 0.2 cm in diameter, packed with SE-30. Injector and detector temperatures for both binaries were 493.15 and 543.15 K, respectively, and column temperatures were 353.15 K for the system 2-butanone + heptane and 323.15 K for the system 2-butanone + oxolane. Very good separation was achieved under these conditions, and calibration analyses were carried out to convert the peak ratio to the mass composition of the sample. The pertinent polynomial fits had a correlation coefficient R^2 better than 0.99. Concentration measurements were accurate to better than ±0.005 mole fraction.

Table 1. Mole Percent GLC Purities (mass %), Refractive Index n_D at the Na D Line, and Normal Boiling Points T of Pure Components

component (purity/mass %)	n_D (298.15 K)	T/K
2-butanone (99.68)	1.3764^a	352.71^a
	1.3764^b	352.79^b
heptane (99.95)	1.3851^a	371.5^a
	1.38511^d	371.553^e
oxolane (99.9)	1.4045^a	339.15^a
	1.4049^f	339.12^f

^{a} Measured. ^{b} TRC a-5920, 1994. ^{d} TRC fa-1460, 1991. ^{e} TRC k-1460, 1991. ^{f} TRC a-6170, 1985.

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Table 2. Experimental Vapor–Liquid Equilibrium Data for 2-Butanone (1) + Heptane (3) at 94 KPa

T/K	x_1	y_1	γ_1	γ_3	$-B_{11}$/ (cm^3 mol^{-1})	$-B_{33}$/ (cm^3 mol^{-1})	$-B_{13}$/ (cm^3 mol^{-1})
369.02	0	0					
367.15	0.010	0.057	3.342	1.005	985	1574	1256
366.05	0.019	0.097	3.239	1.002	992	1586	1266
365.45	0.024	0.123	3.306	0.995	996	1593	1271
364.15	0.036	0.173	3.214	0.987	1005	1608	1283
363.45	0.040	0.192	3.274	0.988	1010	1616	1289
363.25	0.044	0.203	3.165	0.985	1012	1618	1291
361.95	0.058	0.240	2.945	0.990	1021	1634	1303
361.35	0.070	0.270	2.792	0.981	1025	1641	1309
360.35	0.088	0.303	2.564	0.984	1033	1653	1318
358.05	0.122	0.364	2.375	1.000	1050	1681	1340
357.35	0.133	0.390	2.382	0.993	1055	1689	1347
355.85	0.162	0.439	2.301	0.990	1067	1708	1362
354.55	0.198	0.477	2.126	1.004	1077	1725	1375
353.35	0.236	0.500	1.938	1.046	1086	1741	1387
352.65	0.256	0.517	1.887	1.061	1092	1750	1395
349.75	0.466	0.633	1.387	1.233	1116	1789	1426
348.90	0.582	0.677	1.219	1.426	1123	1801	1435
348.41	0.639	0.703	1.171	1.543	1127	1807	1440
348.26	0.716	0.737	1.101	1.745	1128	1810	1442
348.13	0.743	0.751	1.085	1.834	1129	1811	1443
348.27	0.814	0.793	1.041	2.097	1128	1809	1442
348.65	0.890	0.850	1.009	2.538	1125	1804	1437
349.32	0.944	0.913	1.000	2.830	1119	1795	1430
349.67	0.968	0.944	0.998	3.152	1116	1790	1426
350.00	0.985	0.971	0.999	3.445	1114	1786	1423
350.42	1	1					

Table 3. Experimental Vapor–Liquid Equilibrium Data for 2-Butanone (1) + Oxolane (3) at 94 KPa

T/K	x_2	y_2	g_2	g_3	$-B_{22}$/ (cm^3 mol^{-1})	$-B_{33}$/ (cm^3 mol^{-1})	$-B_{23}$/ (cm^3 mol^{-1})
336.82	0	0					
337.29	0.004	0.003	1.119	0.986	1907	573	947
337.80	0.063	0.045	1.091	0.988	1899	571	943
338.09	0.097	0.070	1.081	0.989	1894	569	940
338.55	0.146	0.107	1.077	0.990	1886	567	936
339.53	0.238	0.177	1.060	0.991	1871	563	928
340.27	0.306	0.231	1.049	0.994	1859	559	922
340.55	0.342	0.254	1.020	1.009	1854	558	920
341.85	0.451	0.344	1.003	1.022	1834	552	910
342.62	0.513	0.399	0.997	1.031	1821	549	904
343.39	0.569	0.453	0.994	1.037	1809	545	898
344.25	0.628	0.513	0.992	1.043	1796	541	892
345.02	0.679	0.564	0.984	1.057	1784	538	886
345.81	0.734	0.625	0.983	1.073	1772	535	880
346.33	0.767	0.665	0.984	1.080	1764	533	876
347.03	0.816	0.728	0.991	1.086	1754	530	871
347.99	0.871	0.802	0.992	1.099	1740	526	864
348.94	0.919	0.871	0.992	1.109	1726	522	857
349.69	0.966	0.943	0.999	1.124	1715	519	852
350.05	0.984	0.973	1.000	1.133	1709	518	849
350.42	1	1					

Results

The temperature T and liquid-phase x_i and vapor-phase y_i mole fraction measurements at $P = 94$ kPa are reported in Tables 2 and 3 and Figures 1–4, together with the activity coefficients γ_i which were calculated from the following equation (Van Ness and Abbott, 1982)

$$\ln \gamma_i = \ln \frac{y_i P}{x_i P_i^0} + \frac{(B_{ii} - V_i^{\mathrm{L}})(P - P_i^0)}{RT} + y_j^2 \frac{\delta_{ij} P}{RT} \qquad (1)$$

where T and P are the boiling point and the total pressure, V_i^{L} is the molar liquid volume of component i, P_i^0 is the pure component vapor pressure, B_{ii} and B_{jj} are the second virial coefficients of the pure gases, B_{ij} is the cross second virial coefficient, and

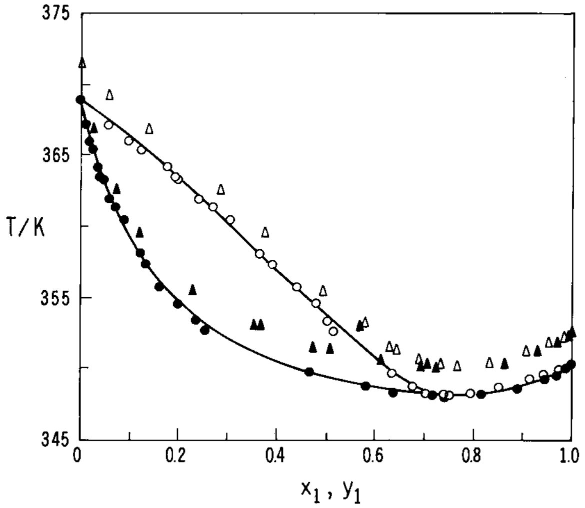

Figure 1. Boiling temperature diagram for the system 2-butanone (1) + heptane (2) at 94 kPa (●, ○, —); data of Steinhauser and White at 101.3 kPa (▲, △).

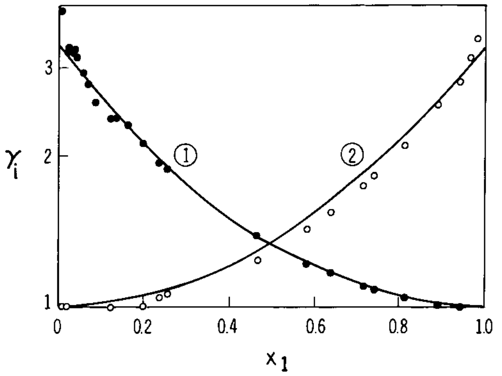

Figure 2. Activity coefficients for the system 2-butanone (1) + heptane (2) at 94 kPa. Experimental data (●, ○); predicted by the Wohl model (—).

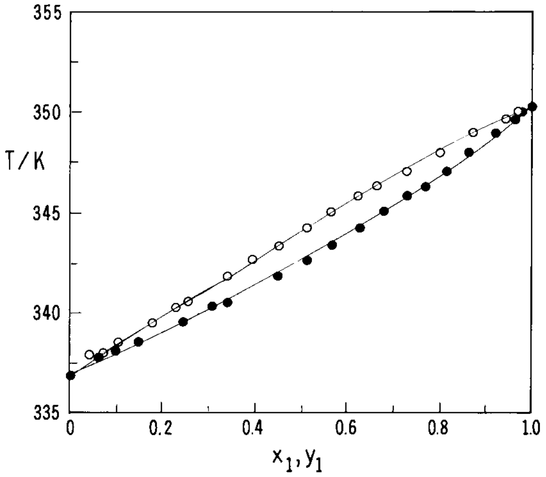

Figure 3. Boiling temperature diagram for the system 2-butanone (1) + oxolane (3) at 94 kPa (●,○, —).

$$\delta_{ij} = 2B_{ij} - B_{jj} - B_{ii} \qquad (2)$$

The standard state for calculation of activity coefficients is the pure component at the pressure and temperature of the solution. Equation 1 is valid at low and moderate pressures when the virial equation of state truncated after

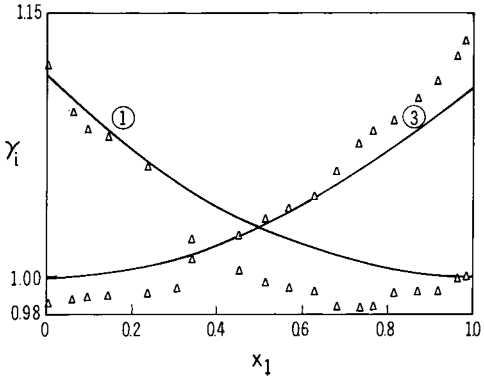

Figure 4. Activity coefficients for the system 2-butanone (1) + oxolane (3) at 94 kPa. Experimental data (▲, △); predicted by the Wilson model (—).

Table 4. Antoine Coefficients, Eq 3

compound	A_i	B_i	C_i
2-butanone[a]	6.333 57	1368.21	36.65
heptane[b]	6.020 23	1263.909	56.718
oxolane[a]	6.120 043	1202.29	46.90

[a] TRC k-5920, 1981. [b] Reich (1996).

the second coefficient is adequate to describe the vapor phase of the pure components and their mixtures, and liquid volumes of the pure components are incompressible over the pressure range under consideration. The pure component vapor pressures P_i^0 were calculated according to the Antoine equation

$$\log (P_i^0/\text{kPa}) = A_i - \frac{B_i}{(T/\text{K} - C_i)} \quad (3)$$

where the Antoine constants A_i, B_i, and C_i are reported in Table 4. The molar virial coefficients B_{ii} and B_{ij} were estimated by the method of O'Connell and Prausnitz (1967) using the molecular parameters suggested by the authors and assuming the association parameter η to be zero. The last two terms in eq 1, particularly the second one that expresses the correction due to the nonideal behavior of the vapor phase, contributed between 2 and 3% to the activity coefficients of both binary systems; in general, their influence was important only at very dilute concentrations. The calculated activity coefficients are reported in Tables 2 and 3 and are estimated accurate to within ±3%. The results reported in these tables indicate that the binary system 2-butanone + heptane deviates strongly from ideal behavior and presents an azeotrope that boils at 348.4 K and contains 75.0 mol % 2-butanone (determined by double interpolation of the data). For the sake of comparison, the vapor−liquid data reported by Steinhauser and White (1949) for the system 2-butanone + heptane at 101.3 kPa are also included in Figure 2. The results of Aristovich et al. (1965) and Steinhauser and White (1949) indicate that at 101.3 kPa the azeotrope contains a larger concentration of 2-butanone; hence, according to Wrewski's law (Malesinski, 1965), the heat of vaporization of the ketone from the solution must be larger than that of heptane. The results for the system 2-butanone + oxolane indicate that the system deviates slightly from ideal behavior and that no azeotrope is present. The vapor−liquid equilibria data reported in Tables 2 and 3 were found to be thermodynamically consistent by the $L-W$ point-to point and area method of Wisniak (1993), except at the very dilute ends, and the point-to-point method of Van Ness et al. (1973) as modified by Fredenslund et al. (1977). For both binaries, the residuals of the Fredenslund test were randomly distributed, as measured by the Durbin−Watson statistic. The activity coefficients of both binary systems were correlated well with the Redlich−Kister, Wohl, Wilson, NRTL, and UNIQUAC equations (Walas, 1985). The following expression was used for the Redlich−Kister (1948) expansion

$$\log (\gamma_1/\gamma_2) = B\,(x_2 - x_1) + C\,(6x_1x_2 - 1) + D(x_2 - x_1)(8x_1x_2 - 1) \quad (4)$$

The values of the constants B, C, and D were determined by multilinear regression and appear in Table 5 together with the pertinent statistics. It is seen that the Redlich−Kister model gives a good representation of the data for both systems and that the system 2-butanone + oxolane behaves like a regular solution. The parameters of the Wohl, Wilson, NRTL and UNIQUAC equations were obtained by minimizing the following objective function (OF)

$$\text{OF} = \sum_{i=1}^{N} \left(\frac{\gamma_{1,i}^{\text{exptl}} - \gamma_{1,i}^{\text{calc}}}{\gamma_{1,i}^{\text{exptl}}}\right)^2 + \left(\frac{\gamma^{\text{exptl}}{}_{2,i} - \gamma_{2,i}^{\text{calc}}}{\gamma_{2,i}^{\text{exptl}}}\right)^2 \quad (5)$$

and are reported in Table 5, together with the relative deviation of the vapor composition. Inspection of the

Table 5. Parameters and Deviations between Experimental and Calculated Values for G^E-Different Models

A. Redlich−Kister, Eq 4

system	B	C	D	max dev %[a]	avg dev %[b]	rmsd[c]
2-butanone (1) + heptane (2)	0.5113	−0.0005	0.0385	5.5	2.8	0.02
2-butanone (1) + oxolane (3)	0.0568			3.3	1.5	0.004
	0.0569	−0.0045	2.8	1.6	0.004	

B. Other Models[d]

model	system	A_{12}	A_{21}	q_1/q_2	α	$\delta(y)$[e]
Wohl	1 + 2	1.2044	1.1794	1.0214		0.005
	1 + 3	0.1118	0.0963	1.0120		0.002
Wilson	1 + 2	3853.42[f]	357.39			0.005
	1 + 3	−36.48	337.7			0.003
NRTL	1 + 2	3353.87[f]	−3.8894[f]		−0.087	0.007
	1 + 3	305.21	−3.913		0.355	0.002
UNIQUAC	1 + 2	−642.13[f]	2093.33[f]			0.006
	1 + 3	767.33	993.61			0.002

[a] Maximum deviation %. [b] Average deviation %. [c] Root-mean-square deviation. [d] All equations in ln γ_i form. [e] $\delta(y) = \sum|y_{\text{exptl}} - y_{\text{calcd}}|/N$ (N = number of data points). [f] J/mol.

Table 6. Coefficients in Correlation of Boiling Points, Eq 6, Average % Deviation, and Root-Mean-Square Deviations in Temperature, rmsd (T/K)

system	C_0	C_1	C_2	C_3	max dev %[a]	avg dev %[b]	rmsd[c]
2-butanone (1) + heptane (3)	−33.119 16	0.101 65	−58.302 96	52.236 00	3.0	0.7	0.2
2-butanone (1) + oxolane (3)	1.293 7				2.1	1.2	0.2

[a] Maximum deviation % /K. [b] Average deviation %/K. [c] Root-mean-square deviation/K.

results given in Table 5 shows that the four models give a good fit of the experimental data. For the system 2-butanone + heptane the Wohl model gave the best fit, while for the binary 2-butanone + oxolane the best fit was that of the Wilson model. The simultaneous capability of predicting the vapor-phase composition and the bubble-point temperature was used as the ranking factor. The apparent large deviations that appear in Figure 4 are due to the scale factor of the activity coefficients axis.

The boiling points of the two binaries were correlated by the equation proposed by Wisniak and Tamir (1976):

$$T/\mathrm{K} = x_1 T_1^0 + x_2 T_2^0 + x_1 x_2 \sum_{k=1}^{m} Ck(x_1 - x_2)k \qquad (6)$$

In this equation T_i^0/K is the boiling point of the pure component i at the operating pressure and m is the number of terms in the series expansion of $(x_1 - x_2)$. The various constants of eq 6 are reported in Table 6, which also contains information indicating the degree of goodness of the correlation.

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