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Isobaric Vapor–Liquid Equilibria in the Binary System Hexane + 2-Propanol

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New vapor–liquid equilibrium data have been obtained for the binary system hexane + 2-propanol at 94.4 kPa to compare with previously reported data assumed to be thermodynamically inconsistent. The system exhibits large positive deviations from ideal behavior and an azeotrope that boils at 332.92 K and contains 73.3 mol % hexane. The activity coefficients and boiling point of the solution were correlated with its composition by the Redlich–Kister, Wilson, UNIFAC, UNIQUAC, and Wisniak–Tamir models.

The properties of hydrogen-bonding substances such as alcohols may be explained by the concept of multispecies association. It is observed experimentally that associated solutions exhibit large deviations from ideal behavior, and the major part of these deviations may be attributed to interactions leading to the formation of associated complexes. In mixtures of alcohols and saturated hydrocarbons one group is self-associating and interacts with the other only by physical forces. Solutions of alcohols and hydrocarbons are known to deviate strongly from ideal behavior. Mixtures of alcohols and saturated hydrocarbons are complex because the degree of alcohol bonding is strongly dependent on the composition, particularly in the region dilute with respect to the alcohol. An expression of the complexity of these mixtures is the fact that they normally require four terms in the Redlich–Kister expansion. Various aspects of the theory of alcohol + hydrocarbon solutions have been considered by Scatchard (1949), Kretschmer and Wiebe (1954), and Renon and Prausnitz (1967). The latter concluded that, in spite of its simplifying assumptions, the Flory–Scatchard model of associated solutions gives a group representation of the properties of concentrated solutions of alcohols in saturated hydrocarbons. For these solutions the complexes cannot be regarded as simple chains, but must to some extent be in the form of closed rings or, more likely, two- and three-dimensional aggregates.

The system hexane + 2-propanol has been studied at constant pressure (Govindaswamy et al., 1976; Morozov et al., 1978; Rotter and Knickle, 1977; Vijayaraghavan et al., 1964) and constant temperature (Barraza and Edwards, 1982; Berro and Neau, 1981). Only the isothermal data are considered by DECHEMA (Gmehling and Onken, 1977) to be thermodynamically consistent; all the isobaric data sets fail to pass the Fredenslund test (Fredenslund et al., 1977). In addition, the data published by Rotter and Knickle (1977) present a maximum in the curve that describes the variation of the activity coefficient of 2-propanol with concentration without a corresponding minimum value in the curve of the second component. This behavior contradicts the one predicted by the Gibbs–Duhem equation, and the anomaly reported is probably a result of experimental errors. Extreme values in the $\gamma(x)$ curves do appear sometimes in highly asymmetric systems, which is not the case of the system in question.

Experimental Section

Purity of Materials. Hexane (99.5 + mol %) was purchased from Phillips and 2-propanol (99.6+ mol %) from Frutarom. 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, the solution is heated to its boiling point by a 250 W immersion heater. The vapor–liquid mixture flows through an extended contact line which 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 returned to a mixing chamber, where they are stirred by a magnetic stirrer, and return again to the immersion heater. Temperature control is achieved by a 5 mm diameter Pt-100 temperature sensor, with an accuracy of ±0.1 K. The total pressure of the system is controlled by a vacuum pump capable to work under vacuum up to 0.25 kPa. The pressure is measured by a Vac Probs with an accuracy of ±0.1 kPa. On the average the system reaches equilibrium conditions after 1–2 h of operation.

Samples, taken by syringing 0.7 μL after the system had achieved equilibrium, were analyzed by gas chromatography on a Gow-Mac series 550P apparatus provided 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 and operated at 323.15 K; injector and detector temperatures were 493.15 and 523.15 K, respectively. 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. Concentration measurements were accurate to better than ±0.008 mole fraction unit. The analytical method used in this work (GLC) is assumed to be more reliable than the density one used by Govindaswamy et al. (1976) and Rotter and Knickle (1977).

Results

The temperature T and liquid-phase x_i and vapor-phase y_i mole fraction measurements at P = 94.4 kPa are reported in Table 2 and Figures 1 and 2, together with the activity coefficients γ_i that were calculated from the following

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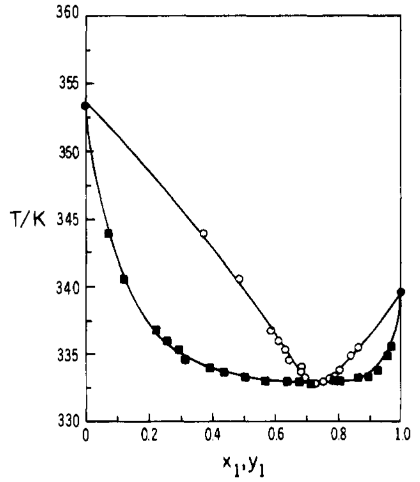

Figure 1. Boiling temperature diagram for the system 2-propanol (1) + hexane (2) at 94.40 kPa.

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

component (purity/(mol %))	n_D(298.15 K)	T/K
hexane (99.9)	1.3731[a]	341.84[a]
	1.3723[b]	341.89[b]
2-propanol (99.79)	1.3752[a]	355.50[a]
	1.3752[b]	355.41[b]

[a] Measured. [b] TRC (1974).

Table 2. Experimental Vapor–Liquid Equilibrium Data for Hexane (1) + 2-Propanol (2) at 94.4 kPa

T/K	x_1	y_1	γ_1	γ_2	$-B_{11}$	$-B_{22}$	$-B_{12}$
353.45	0	0	0				
343.85	0.071	0.371	4.6315	1.0055	1304	1094	1219
340.45	0.120	0.485	3.9331	1.0060	1337	1128	1253
336.75	0.221	0.587	2.9051	1.0688	1375	1166	1293
335.95	0.257	0.610	2.6598	1.0960	1383	1175	1302
335.25	0.293	0.631	2.4633	1.1249	1391	1182	1309
334.55	0.315	0.645	2.3990	1.1515	1398	1190	1317
333.95	0.395	0.675	2.0378	1.2285	1405	1196	1324
333.65	0.440	0.677	1.8530	1.3350	1408	1200	1327
333.25	0.504	0.694	1.6795	1.4556	1412	1204	1332
333.05	0.567	0.704	1.5246	1.6257	1414	1206	1334
332.95	0.638	0.714	1.3781	1.8887	1416	1208	1335
332.95	0.676	0.723	1.3166	2.0444	1416	1208	1335
332.85	0.709	0.731	1.2729	2.2225	1417	1209	1337
333.05	0.787	0.750	1.1694	2.7938	1414	1206	1334
332.95	0.804	0.752	1.1519	3.0224	1416	1208	1335
333.15	0.858	0.769	1.0960	3.8588	1413	1205	1333
333.15	0.861	0.769	1.0925	3.9431	1413	1205	1333
333.25	0.893	0.785	1.0720	4.7352	1412	1204	1332
333.75	0.924	0.805	1.0452	5.9477	1407	1199	1326
334.75	0.959	0.838	1.0172	8.5829	1396	1188	1315
335.45	0.969	0.863	1.0127	9.5221	1389	1180	1307
339.60	1	1	1				

equation (Van Ness and Abbott, 1982):

$$\ln \gamma_i = \ln \frac{y_i P}{x_i P_i^\circ} + \frac{(B_{ii} - V_i^L)(P - P_i^\circ)}{RT} + \gamma_j^2 \frac{\delta_{ij} P}{RT} \quad (1)$$

where x_i and y_i are the equilibrium molar concentrations of component i in the liquid and vapor phases, T and P are the boiling point and the total pressure, V_i^L is the molar liquid volume of component i, B_{ij} and B_{jj} are the second virial coefficients of the pure gases, B_{ij} is the cross section virial coefficient, and

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

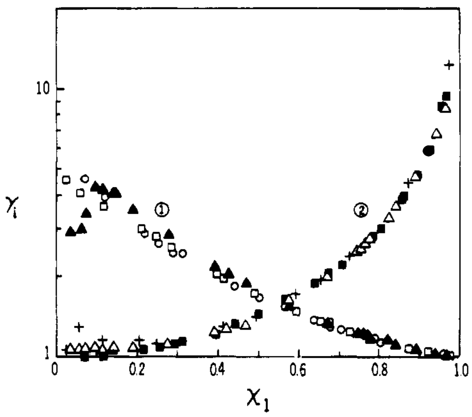

Figure 2. Activity coefficients for the system 2-propanol (1) + hexane (2) at 94.40 kPa: present work (○, ■), data of Rotter and Knickle at 101.3 kPa (□, +) and 50.7. kPa (▲, △).

Table 3. Antoine Coefficients, Eq 3 (TRC, 1974)

compound	a_i	B_i	C_i
hexane	6.000 91	1171.17	48.74
2-propanol	7.242 68	1580.92	53.54

The standard state for calculation of activity coefficients is the pure component at the pressure and temperature of the solution. The pure component vapor pressures P_i° were calculated according to the Antoine equation

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

where the constants A_i, B_i, and C_i are reported in Table 3. 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 contributed less than 3% to the activity coefficients, and their influence was important only at very dilute concentrations. The calculated activity coefficients are reported in Table 2 and are estimated accurate to within ±3%. Inspection of Figure 1 points to an azeotrope in the system hexane + 2-propanol which contains 73.3 mol % hexane and boils at 332.92 K.

The vapor–liquid equilibrium data reported in Table 2 were found to be thermodynamically consistent by the Redlich–Kister area test (1948) (Figure 3), the Herington test as modified by Wisniak (1994), and by the L–W point-to-point and area method of Wisniak (1993). From Figures 1 and 2 it is seen that the system presents strong positive deviations from ideality. The molar liquid volumes (mL/mol) are 76.92 for 2-propanol and 131.29 for hexane; the large ratio between the two is indicative of the degree of nonideality. Similarly, the solubility parameters (mPa$^{-0.5}$) are 23.68 for hexane and 14.87 for 2-propanol, indicating that the solutions should be highly nonideal and deviate positively from ideal behavior. The positive values of G^E/RT over the entire composition range can also be taken as another proof of strong interaction between molecules through hydrogen bonding. The variation of G^E/RT with composition appears in Figure 4; the value of $G^E(x=0.5)$ is 1240 J/mol.

Although the data of Rotter and Knickle were obtained at a slightly different pressure, we feel that the difference in results cannot account for the abnormal behavior of Rotter and Knickle's data and that the latter are in error. For comparison purposes the data of Rotter and Knickle are also plotted in Figure 2.

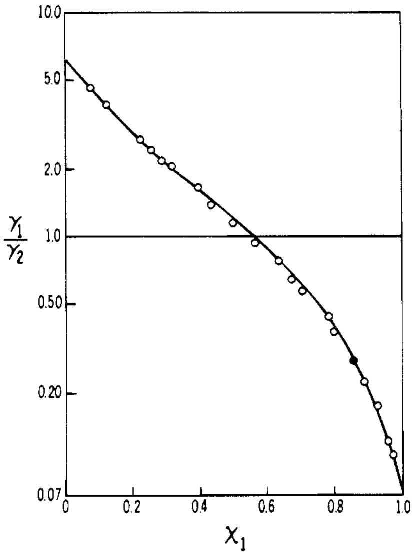

Figure 3. Redlich–Kister test of consistency.

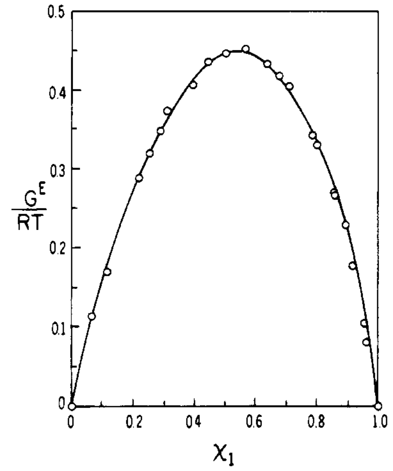

Figure 4. Variation of G^E/RT with composition.

The activity coefficients were correlated by the Redlich–Kister and Wilson equations, and the UNIQUAC and UNIFAC group-contribution methods, as follows.

(a) Redlich–Kister (1948) Equation.

$$\log\frac{\gamma_1}{\gamma_2} = B(x_2 - x_1) + C(6x_1x_2 - 1) + D(x_2 - x_1)(8x_1x_2 - 1) + E(x_2 - x_1)^2(10x_1x_2 - 1) \quad (4)$$

where $B = 0.7719$, $C = 0.081\,80$, $D = 0.1213$, and $E = 0.1486$. The average percent deviation was 3.1%, and the root mean square deviation (rmsd) was 0.02.

(b) Wilson Equation (Van Ness and Abbott, 1982).

$$\ln\gamma_1 = -\ln(x_1 + A_{12}x_2) + x_2\left[\frac{A_{12}}{x_1 + A_{12}x_2} - \frac{A_{21}}{A_{21}x_1 + x_2}\right] \quad (5)$$

$$\ln\gamma_1 = -\ln(x_2 + A_{21}x_1) - x_1\left[\frac{A_{12}}{x_1 + A_{12}x_2} - \frac{A_{21}}{A_{21}x_1 + x_2}\right] \quad (6)$$

The values of the constants $A_{12} = 0.466\,28$ and $A_{21} = 0.122\,41$ were obtained using the method of Apelblat and Wisniak (1989). Govindaswamy et al. (1976) report the values $A_{12} = 0.478\,06$ and $A_{21} = 0.121\,29$ without indicating the procedure by which they were obtained. An attempt to recover the original equilibrium data of Govindaswamy et al. indicated that their Wilson constants reproduced the values of γ_1 rather well but that errors of up to 20% were obtained when trying to recover the values of γ_2.

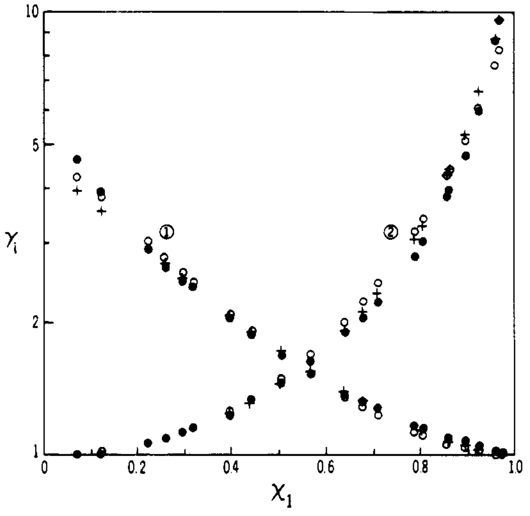

Figure 5. Comparison of predicted vs experimental activity coefficients: UNIQUAC (○); UNIFAC (+); experimental (●).

(c) Group Contribution Methods. Both the UNIQUAC (Abrams and Prausnitz, 1975) and the Larsen et al. (1987) modifications of the UNIFAC group contribution methods were capable of reproducing the values of the activity coefficients. As shown in Figure 5, the UNIQUAC method produced slightly better results.

The boiling point of the solution was correlated with its composition by the equation proposed by Wisniak and Tamir (1976):

$$T/\mathrm{K} = x_1T_1^\circ + x_2T_2^\circ + x_1x_2\sum_{k=1}^{m} C_k(x_1 - x_2)^k \quad (7)$$

In this equation T_i°/K is the boiling point of the pure component i and m is the number of terms in the series expansion of $x_1 - x_2$. The values of the constants obtained by multilinear regression are $C_1 = -43.092\,32$, $C_2 = 14.994\,65$, and $C_3 = -104.072\,81$. Equation 7 predicts the boiling points with an average percent deviation of 2 and rmsd of 0.31.

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