Phase Equilibria in the Systems Oxolane + Octane and Methyl 1,1-Dimethylethyl Ether + Hex-1-ene

Jaime Wisniak,* Eti Fishman, and Rotem Shaulitch

Department of Chemical Engineering, Ben-Gurion University of the Negev, Beer-Sheva, Israel 84105

Vapor−liquid equilibrium at 94 kPa has been determined for the binary system oxolane + octane and methyl 1,1-dimethylethyl ether + hex-1-ene. The system oxolane + octane deviates strongly from ideality with no azeotrope formation. The system methyl 1,1-dimethylethyl ether + hex-1-ene presents ideal behavior. The activity coefficients of the system oxolane + octane were correlated reasonable well with its composition by the Redlich−Kister, Wohl, Wilson, UNIQUAC, and NRTL models. The boiling point of both binary systems were correlated with the Wisniak−Tamir equation.

This work is part of our program to determine vapor−liquid equilibria (VLE) in systems formed by oxygenates and gasoline components. Phase-equilibrium data of oxygenated mixtures are important for predicting the vapor-phase composition that would be in equilibrium with hydrocarbon mixtures. No isothermal or isobaric vapor−liquid equilibria data are available for both of the systems investigated here.

Experimental Section

Purity of Materials. Methyl 1,1-dimethylethyl ether (MTBE) (99.71), hex-1-ene (99.84 mass %), octane (99.80 mass %), and oxolane (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. Details of the equipment and its operation appear in a previous publication (Wisniak et al., 1997). 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; a 5-L Erlenmeyer flask connected between the separating chamber and the Vac Probs dampens the pressure variations to no more than 0.01 kPa. 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 478.15 K for the system oxolane + octane and 323.15 K for the system methyl 1,1-dimethylethyl ether. 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
methyl 1,1-dimethylethyl ether (99.71)	1.3661[a]	328.29[a]
	1.3663[b]	328.35[b]
hex-1-ene (99.84)	1.3851[a]	336.5[a]
	1.38502[c]	336.635[c]
octane (99.80)	1.3948[a]	398.50[a]
	1.39512[d]	398.83[d]
oxolane (99.9)	1.4045[a]	339.15[a]
	1.4049[e]	339.12

[a] Measured. [b] TRC a-6040. [c] TRC a-2630. [d] TRC a-1490. [e] TRC a-6170.

Table 2. Experimental Vapor−Liquid Equilibrium Data for Oxolane (1) + Octane (2) at 94 KPa

T/K	x_1	y_1	γ_1	γ_2	$-B_{11}$/ (cm^3 mol^{-1})	$-B_{22}$/ (cm^3 mol^{-1})	$-B_{12}$/ (cm^3 mol^{-1})
396.20	0	0					
388.27	0.025	0.143	1.368	1.000	671	1825	1134
381.80	0.044	0.232	1.349	0.997	684	1864	1157
377.95	0.088	0.392	1.319	0.997	713	1950	1208
372.33	0.118	0.476	1.305	0.997	731	2004	1240
367.34	0.163	0.587	1.333	0.986	758	2087	1288
360.39	0.217	0.674	1.303	0.976	784	2166	1335
352.35	0.312	0.77	1.241	0.989	822	2285	1403
348.60	0.471	0.863	1.150	1.018	870	2436	1491
347.28	0.586	0.905	1.079	1.032	894	2512	1535
346.08	0.628	0.919	1.063	1.035	903	2540	1551
344.90	0.661	0.928	1.056	1.059	911	2565	1565
343.92	0.689	0.932	1.054	1.139	919	2591	1580
342.75	0.729	0.942	1.038	1.145	926	2613	1593
341.49	0.771	0.949	1.023	1.257	934	2639	1608
339.95	0.819	0.96	1.013	1.319	943	2668	1624
338.68	0.882	0.969	0.996	1.641	954	2704	1645
338.04	0.933	0.981	0.991	1.869	964	2734	1662
338.04	0.960	0.986	0.989	2.365	968	2750	1671
336.82	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 1−3, together with the

---

* To whom correspondence should be addressed. Email: wisniak@bgumail.bgu.ac.il.

S0021-9568(97)00284-7 CCC: $15.00

Table 3. Experimental Vapor−Liquid Equilibrium Data for Methyl 1,1-Dimethylethyl Ether (3) + Hex-1-ene (4) at 94 KPa

T/K	x_3	y_3	γ_3	γ_3	$-B_{33}$/ (cm^3 mol^{-1})	$-B_{44}$/ (cm^3 mol^{-1})	$-B_{34}$/ (cm^3 mol^{-1})
334.29	0	0					
333.82	0.017	0.024	1.077	1.008	1075	1280	1174
333.62	0.044	0.060	1.054	1.004	1076	1282	1176
333.15	0.083	0.110	1.050	1.005	1080	1286	1180
332.87	0.106	0.139	1.048	1.006	1083	1289	1183
332.14	0.170	0.218	1.043	1.007	1089	1296	1189
331.18	0.257	0.319	1.041	1.009	1097	1306	1198
330.23	0.355	0.423	1.030	1.014	1105	1315	1207
329.34	0.453	0.525	1.028	1.014	1112	1324	1215
328.15	0.609	0.663	1.005	1.043	1123	1337	1227
327.75	0.667	0.718	1.004	1.041	1126	1341	1230
327.16	0.754	0.793	0.999	1.056	1132	1347	1236
326.63	0.837	0.865	0.999	1.055	1136	1352	1241
326.12	0.928	0.940	0.997	1.064	1141	1358	1246
326.00	0.955	0.963	0.995	1.068	1142	1359	1248
325.72	0.996	0.997	0.996	1.080	1145	1362	1250
325.75	1	1					

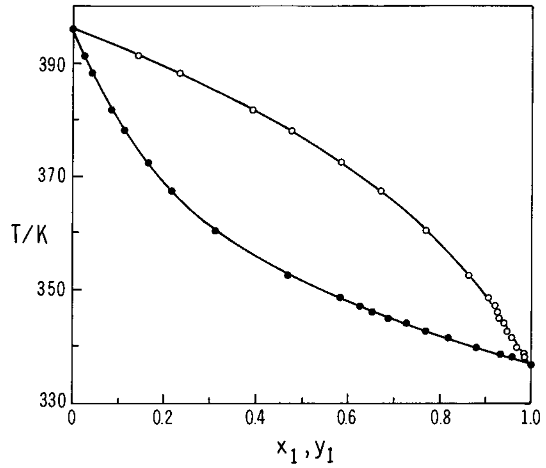

Figure 1. Boiling-temperature diagram for the system oxolane (1) + octane (2) at 94 kPa.

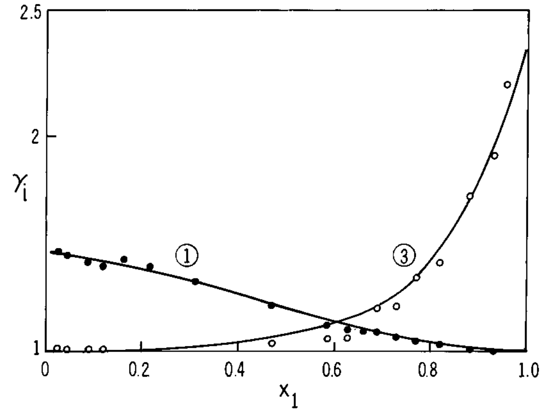

Figure 2. Activity coefficients for the system oxolane (1) + octane (2) at 94 kPa.

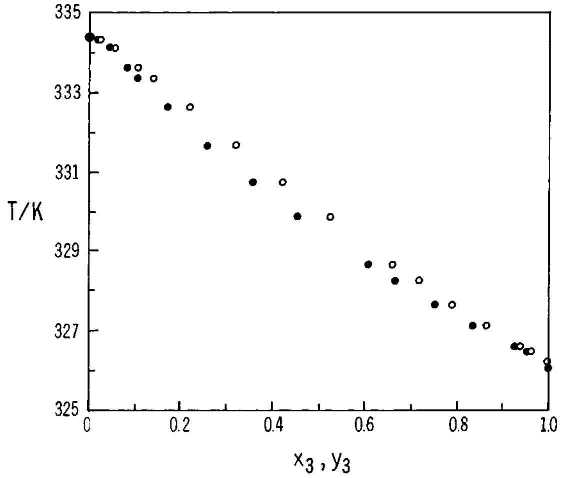

Figure 3. Boiling-temperature diagram for the system methyl 1,1-dimethylethyl ether (3) + hex-1-ene (4) at 94 kPa.

Table 4. Antoine Coefficients, Eq 3

compound	A_i	B_i	C_i
methyl 1,1-dimethylethyl ether[a]	5.860 78	1032.988	59.876
hex-1-ene[b]	5.982 60	1148.62	47.81
oxolane[c]	6.121 42	1203.11	46.795
octane[d]	6.050 75	1356.36	63.515

[a] Reich et al. (1998). [b] TRC k-2500. [c] TRC k-6170. [d] TRC k-1490.

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

A. Redlich−Kister, Eq 4

system	B	C	D	E	max dev %[a]	avg dev %[b]	rmsd[c]
oxolane (1) + octane (2)	0.2112	0.1051	0.0768	0.0612	5.6	2.0	0.005

B. Other Models[d]

model	system	A_{12}	A_{21}	q_1/q_2	α	$\delta(y)$[e]
Wohl	1 + 2	0.2682	1.0821	0.2478		0.008
Wilson	1 + 2	372.09[f]	3152.8[f]			0.007
NRTL	1 + 2	1330.06[f]	−0.71199[f]		0.2	0.008
UNIQUAC	1 + 2	1835.4[f]	−950.35[f]			0.006

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

activity coefficients γ_i, which were calculated from the following equation (Van Ness and Abbott, 1982)

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

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

$$\delta_{ij} = 2B_{ij} - B_{jj} - B_{ii} \tag{2}$$

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 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

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

where the Antoine constants A_i, B_i, and C_i are reported in

Table 6. Coefficients in Correlation of Boiling Points, Eq 6, Average Percent 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]
oxolane (1) + octane (2)	−60.595 36	41.638 99	−19.244 79	8.800 98	0.5	0.2	0.04
MTBE (3) + hex-1-ene (4)	−4.637 66	−10.126 63	4.099 20	25.550 35	1.3	0.6	0.1

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

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. Critical properties of MTBE were taken from a publication by Ambrose et al. (1974). 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 1 and 8% 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 oxolane (1) + octane (2) deviates strongly from ideality and no azeotrope is present. The system 1,1-dimethylethyl ether (3) + hex-1-ene (4) exhibits ideal behavior. 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 the oxolane + octane 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 of the system. The parameters of the Wohl, Wilson, NRTL, and UNIQUAC equations were obtained by minimizing the following objective function (OF)

$$\mathrm{PF} = \sum_{i=1}^{N}\left(\frac{\gamma_{1,i}^{\mathrm{exptl}} - \gamma_{1,i}^{\mathrm{calcd}}}{\gamma_{1,i}^{\mathrm{exptl}}}\right)^2 + \left(\frac{\gamma_{2,i}^{\mathrm{exptl}} - \gamma_{2,i}^{\mathrm{calcd}}}{\gamma_{2,i}^{\mathrm{exptl}}}\right)^2 \quad (5)$$

and are reported in Table 5, together with the relative deviation of the vapor composition. Inspection of the results given in Table 5 shows that the four models fitted the system oxolane + octane reasonable well. The capability of predicting the vapor-phase composition has been used as the ranking factor.

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

$$T/\mathrm{K} = x_1T_1^0 + x_2T_2^0 + x_1x_2\sum_{k=1}^{m}C_k(x_1 - x_2)^k \quad (6)$$

In this equation T_1^0/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.

Literature Cited

Ambrose, D.; Broderick, B. E. The Critical Temperature and Pressure of Thirty Organic Compounds. *J. Appl. Chem. Biotechnol.* **1974**, *24*, 359−372.

Fredenslund, A.; Gmehling, J.; Rasmussen, P. *Vapor−Liquid Equilibria Using UNIFAC*; Elsevier: Amsterdam, 1977.

O'Connell, J. P.; Prausnitz, J. M. Empirical Correlations of Second Virial Coefficients for Vapor−Liquid Equilibrium Calculations. *Ind. Eng. Chem. Process Des. Dev.* **1967**, *6*, 245−250.

Redlich, O.; Kister, A. T. Algebraic Representation of Thermodynamic Properties and the Classification of Solutions. *Ind. Eng. Chem.* **1948**, *40*, 345−348.

Reich, R.; Cartesa, M.; Wisniak, J.; Segura, H. Phase Equilibria in the Systems Methyl 1,1-Dimethylethyl Ether + Benzene and + Toluene. *J. Chem. Eng. Data* **1998**, *43*, 299−303.

TRC−Thermodynamic Tables−Hydrocarbons; Thermodynamics Research Center: Texas A&M University System, College Station, TX, extant 1996; a-1490, 1990; a-2630, 1991; k-1490, 1990; k-2500, 1986.

TRC−Thermodynamic Tables−Non-Hydrocarbons; Thermodynamics Research Center: Texas A&M University System, College Station, TX, extant 1996; a-6040, 1963; a-6170, 1985.

Van Ness, H. C.; Abbott, M. M. *Classical Thermodynamics of Non-electrolyte Solutions*; McGraw-Hill Book Co.: New York, 1982.

Van Ness, H. C.; Byer, S. M.; Gibbs, R. E. Vapor−Liquid Equilibrium: Part I. An Appraisal of Data Reduction Methods. *AIChE J.* **1973**, *19*, 238.

Walas, S. M. *Phase Equilibria in Chemical Engineering*, Butterworth Publishers: Boston, MA, 1985.

Wisniak, J. A New Test for the Thermodynamic Consistency of Vapor-Liquid Equilibrium. *Ind. Eng. Chem. Res.* **1993**, *32*, 1531−1533.

Wisniak, J.; Tamir, A. Correlation of the Boiling Point of Mixtures. *Chem. Eng. Sci.* **1976**, *31*, 631−635.

Wisniak, J.; Embon, G.; Shafir, R.; Segura, S.; Reich, R. Isobaric Vapor-Liquid Equilibria in the Systems Methyl 1,1-Dimethylethyl Ether + Octane and Heptane + Octane. *J. Chem. Eng. Data*, **1997**, *42*, 1191−1194.

Received for review November 25, 1997. Accepted January 20, 1998.

JE970284B