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Isobaric Vapor−Liquid Equilibria in the Systems Methyl 1,1-Dimethylethyl Ether + Octane and Heptane + Octane

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Vapor−liquid equilibrium at 94 kPa has been determined for the binary systems methyl 1,1-dimethylethyl ether (MTBE) + octane and heptane + octane. Both binary systems deviate slightly from ideal behavior, and neither system presents an azeotrope. The system MTBE + octane behaves like a regular solution. 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.

Use of oxygenated fuels in winter has become compulsory in the United States and other countries in the world. Since 1990 reformulated gasolines must contain at least 2% mass oxygen and a Reid vapor pressure below 59.3 kPa. In most cases the required oxygen is provided by alcohols such as methanol and ethanol or ethers such as methyl *tert*-butyl ether (MTBE), and ethyl *tert*-butyl ether (ETBE). MTBE is the primary oxygenated compound being used to reformulate gasolines to improve their octane rating and pollution-reducing capability. Phase equilibrium data of oxygenated mixtures are important for predicting the vapor phase composition that would be in equilibrium with hydrocarbon mixtures. Vapor−liquid equilibria for the system heptane + octane has been measured by Leslie and Carr (1925) at (12.3, 19.9, 31.1, 47.3, 70.1, and 101.3) kPa, by Beatty and Calingaert (1934) at 370.35 K, by Duty and Mayberry (1966) at (327.85, 337.15, 352.25, and 370.15) K, by Han et al. (1993), at (293.5, 312.75, and 328.15) K, by Kudryatseva et al. (1971) at 328.15 K, and by Zielkiewicz (1992) at 313.15 K. Hutchings and Van Hook (1985) determined the values of the excess Gibbs molar energy of the binary system at 323.15 K, and Golik and Baranovskii (1961) determined the enthalpies of vaporization of the same as a function of the composition of the system. The isobaric data reported by Leslie and Carr (1925) were obtained in order to build the Dühring graph of the system. The data reported are the boiling point of solutions at rounded values of the liquid composition (every 10 mol %), no indication is given regarding the thermodynamic consistency of the same. According to Zielkiewicz (1992) at 313.15 K the system heptane + octane presents small positive deviations from ideality and may be considered a regular solution. The same behavior has been reported by Han et al. (1993) at four temperature levels. No isothermal or isobaric vapor−liquid equilibria data are available for the system MTBE + octane. 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. Methyl 1,1-dimethylethyl ether (99.93 mass %), heptane (99.57 mass %), and octane (99.80 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.

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 (99.93)	1.3661[a]	328.3[a]
	1.3663[b]	327.85[b]
		328.31[c]
heptane (99.57)	1.3851[a]	371.5[a]
	1.38511[d]	371.553[e]
octane (99.80)	1.3948[a]	398.5[a]
	1.3952[f]	398.83[g]

[a] Measured. [b] TRC a-6040, 1963. [c] Zykmundova et al. (1990). [d] TRC fa-1460, 1991. [e] TRC k-1460, 1991. [f] TRC fa-1490, 1990. [g] TRC k-1490, 1990.

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 returned to a mixing chamber, where they are stirred by a magnetic stirrer, and returned 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 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

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Table 2. Experimental Vapor−Liquid Equilibrium Data for Methyl 1,1-Dimethylethyl Ether (1) + Octane (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})
395.95	0	0					
387.65	0.044	0.243	1.139	0.994	741	1872	1185
385.25	0.060	0.312	1.117	0.985	752	1904	1204
384.65	0.064	0.318	1.088	0.997	755	1912	1209
381.25	0.089	0.407	1.071	0.984	772	1958	1237
379.15	0.104	0.443	1.049	1.000	783	1987	1254
375.85	0.129	0.513	1.047	0.995	800	2035	1282
373.05	0.154	0.566	1.029	0.996	814	2076	1307
368.75	0.188	0.638	1.046	0.993	838	2144	1347
364.85	0.226	0.693	1.035	1.004	860	2208	1384
354.05	0.353	0.820	1.024	1.022	927	2402	1497
352.35	0.374	0.836	1.029	1.022	938	2436	1516
350.85	0.403	0.850	1.010	1.037	948	2466	1533
348.05	0.442	0.878	1.024	1.002	967	2523	1566
346.75	0.457	0.888	1.037	0.993	976	2551	1582
344.35	0.504	0.906	1.026	0.999	994	2603	1612
342.05	0.549	0.922	1.023	0.996	1010	2655	1641
340.75	0.579	0.931	1.015	0.994	1020	2685	1658
332.45	0.782	0.972	1.003	1.099	1086	2892	1773
329.35	0.883	0.987	0.992	1.077	1112	2976	1820
325.75	1	1					

Table 3. Experimental Vapor−Liquid Equilibrium Data for Heptane (2) + Octane (3) at 94 KPa

T/K	x_2	y_2	γ_2	γ_3	$-B_{22}$/(cm^3 mol^{-1})	$-B_{33}$/(cm^3 mol^{-1})	$-B_{23}$/(cm^3 mol^{-1})
395.95	0	0					
394.45	0.033	0.072	1.116	1.005	1313	1788	1532
394.05	0.040	0.084	1.112	1.009	1317	1793	1536
393.65	0.061	0.125	1.086	0.996	1320	1798	1540
393.25	0.070	0.140	1.074	0.999	1323	1802	1544
393.05	0.071	0.142	1.076	1.004	1325	1805	1546
391.25	0.118	0.221	1.044	1.009	1341	1827	1564
389.65	0.167	0.293	1.020	1.013	1355	1847	1581
388.65	0.200	0.339	1.009	1.015	1363	1860	1592
386.35	0.274	0.444	1.022	1.003	1384	1889	1616
384.95	0.328	0.503	1.001	1.009	1397	1908	1632
382.25	0.401	0.585	1.021	1.021	1422	1944	1662
381.65	0.443	0.626	1.004	1.008	1428	1952	1669
379.65	0.502	0.685	1.021	1.008	1447	1980	1692
376.05	0.639	0.795	1.025	1.008	1483	2032	1735
374.95	0.712	0.841	1.002	1.016	1494	2048	1748
373.85	0.756	0.869	1.005	1.021	1505	2064	1762
373.35	0.784	0.885	1.000	1.031	1511	2072	1768
371.95	0.841	0.918	1.006	1.040	1525	2093	1786
370.65	0.906	0.953	1.005	1.045	1539	2113	1803
369.55	0.962	0.982	1.005	1.043	1551	2131	1817
368.55	1	1					

SE−30. Injector and detector temperatures for both binaries were 493.15 and 543.15 K, respectively, and column temperatures were 399.25 K for the system methyl 1,1-dimethylethyl ether (MTBE) + octane and 393.15 K for the system heptane + octane. 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.

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 and 2, together with the activity coefficients γ_i that were calculated from the following equation (Van Ness and Abbott, 1982)

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

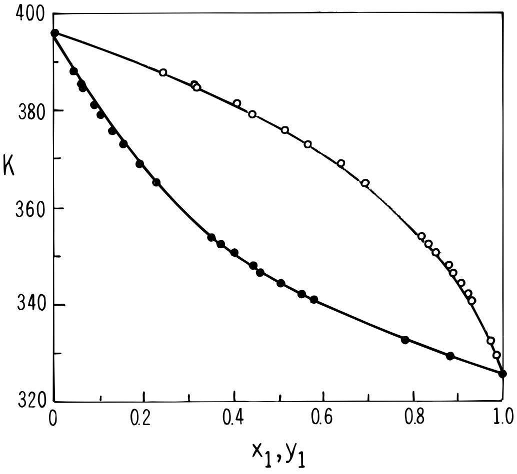

Figure 1. Boiling temperature diagram for the system methyl 1,1-dimethylethyl ether (1) + octane (3) at 94 kPa (—).

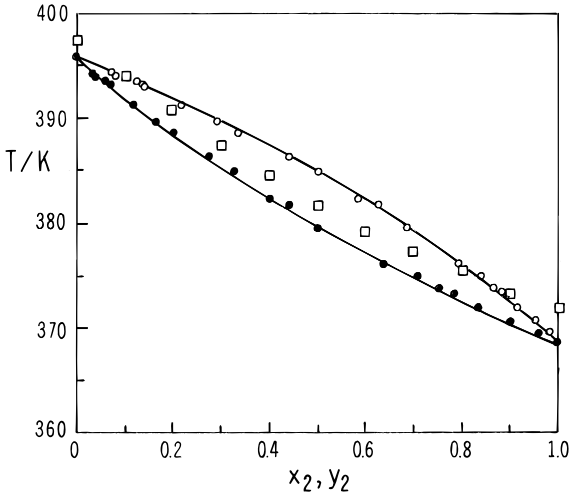

Figure 2. Boiling temperature diagram for the system heptane (2) + octane (3); this work at 94 kPa (—), data of Leslie and Carr at 101.3 kPa (□).

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
heptane[b]	6.020 23	1263.909	56.718
octane[a]	6.051 41	1354.107	63.888

[a] Reich (1996). [b] TRC k-1460, 1991.

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

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

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

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

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]
methyl 1,1-dimethylethyl ether (1) + octane (3)	0.0425			4.6	2.6	0.007
	0.0425	−0.0001		4.6	2.6	0.007
heptane (2) + octane (3)	0.0181	−0.0089	0.0235	2.3	1.8	0.003

B. Other Models[d]

model	system	A_{12}	A_{21}	q_1/q_2	α	$\delta(y)$[e]
Wohl	1 + 3	0.1244	0.0417	3.7145		0.017
	2 + 3	0.1494	0.0248	3.6681		0.006
Wilson	1 + 3	−35.67[f]	543.3[f]			0.018
	2 + 3	−40.51	391.7			0.009
NRTL	1 + 3	31.75[f]	29.85[f]		0.308	0.018
	2 + 3	51.64	−1.437		0.537	0.007
UNIQUAC	1 + 3	67.64[f]	20.04[f]			0.018
	2 + 3	34.59	14.31			0.007

[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]
methyl 1,1-dimethylethyl ether (1) + octane (3)	−65.082 60	21.854 33	−13.396 09	28.421 98	0.8	0.3	0.07
heptane (2) + octane (3)	−9.535 48	−0.222 96	0.510 07	9.833 63	0.4	0.1	0.04

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

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. Critical properties of MTBE were taken from a publication by Ambrose and Broderick (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 5 and 10% 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 ±2%. The results reported in these tables indicate that both binary systems deviate slightly from ideal behavior. For the sake of comparison, the vapor−liquid data reported by Leslie and Carr (1925) for the system heptane + octane at 101.3 kPa are also included in Figure 2. Inspection of Table 2 shows that the large difference in boiling point temperatures between MTBE and octane reflects a vapor phase very rich in MTBE; the relative volatility $\alpha = (y_1/x_1)/(y_2/x_2)$ is 6.8 at $x_1 = 0.1$ and 10.1 at $x_1 = 0.88$.

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 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 behavior of the system MTBE + heptane approximates that of a regular solution. The parameters of the Wohl, Wilson, NRTL and UNIQUAC equations were obtained by minimizing the following objective function (OF)

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

and are reported in Table 5, together with the relative deviation of the vapor composition. Inspection of the results given in Table 5 shows that although the four models fitted both binary systems well the fit for the system heptane + octane was much better than that for the system MTBE + octane, probably because of the smaller difference between the boiling points of the pure components. 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_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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