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Isobaric Vapor−Liquid Equilibria in the Systems Methyl 1,1-Dimethylethyl Ether + 1,3-Dioxolane and Methyl 1,1-Dimethylethyl Ether + 2,2′-Oxybis[propane]

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Vapor−liquid equilibrium at 94 kPa has been determined for the binary systems of methyl 1,1-dimethylethyl ether (MTBE) + 1,3-dioxolane and methyl 1,1-dimethylethyl ether + 2,2′-oxybis[propane] (diisopropyl ether). The binary system with 1,3-dioxolane deviates moderately from ideal behavior, and the system with 2,2′-oxybis[propane] behaves almost ideally; neither system presents an azeotrope. The activity coefficients and boiling points of the binary system methyl 1,1-dimethylethyl ether + 1,3-dioxolane were well correlated with its composition by the Redlich−Kister, Wohl, Wilson, UNIQUAC, NRTL, and Wisniak−Tamir equations.

The three compounds involved in this study here are oxygenates that may be considered as additives for gasoline. Methyl 1,1-dimethylethyl ether (MTBE) is the primary oxygenated compound being used to reformulate gasolines to improve their octane rating and pollution-reducing capability. In addition, MTBE is finding acceptance as an effective replacement for methylene chloride, aromatics, and others, as well as a commercial outlet for the 2-methyl-2-propanol used in its synthesis. Cyclic and aliphatic ethers are frequenly used in the chemical industry as solvents and intermediates. Phase equilibrium data of oxygenated mixtures are important for predicting the vapor phase composition that would be in equilibrium with hydrocarbon mixtures. The present work was undertaken to measure vapor−liquid equilibria (VLE) data for the title systems for which no isobaric data are available.

Experimental Section

Purity of Materials. Methyl 1,1-dimethylethyl ether (99.93 mass %), and 2,2′-oxybis[propane] (99.75 mass %) were purchased from Aldrich; 1,3-dioxolane (99.94 mass %) was purchased from Merck. 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 (Cottrell pump). 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 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 under vacuum up 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 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 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. Column, injector, and detector temperatures for both binaries were (323.15, 493.15, 543.15) K. 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 fit had a correlation coefficient R^2 better than 0.99. Mole fractions were accurate to better than ±0.005.

Table 1. Mole % 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]	328.29[a]
	1.3663[b]	328.35[b]
1,3-dioxolane (99.94)	1.3980[a]	348.60[a]
	1.3984[c]	348.55[d]
2,2′-oxybis[propane] (99.75)	1.3654[a]	341.55[a]
	1.3655[b]	341.45[b]

[a] Measured. [b] TRC, 1996. [c] Castellari et al. (1984). [d] Wu and Sandler (1989).

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

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

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

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Table 2. Experimental Vapor–Liquid Equilibrium Data for Methyl 1,1-Dimethylethyl Ether (1) + 1,3-Dioxolane (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})	G^E/RT
346.30	0	0						0
345.15	0.014	0.046	1.8127	1.0048	681	897	713	0.013
341.55	0.073	0.207	1.7310	1.0032	697	932	736	0.043
339.15	0.122	0.288	1.5535	1.0486	707	957	751	0.086
338.45	0.145	0.329	1.5288	1.0228	710	964	756	0.081
338.05	0.163	0.357	1.4910	1.0150	712	968	759	0.078
337.05	0.186	0.380	1.4306	1.0662	717	979	766	0.105
335.35	0.248	0.453	1.3466	1.0568	725	998	777	0.115
335.35	0.255	0.465	1.3414	1.0450	725	998	777	0.108
333.65	0.317	0.510	1.2463	1.1093	733	1017	790	0.141
332.95	0.358	0.553	1.2231	1.1040	736	1025	795	0.136
330.65	0.503	0.655	1.1078	1.1974	748	1053	812	0.141
329.75	0.553	0.694	1.0984	1.2207	753	1064	819	0.141
328.75	0.606	0.729	1.0860	1.2749	758	1076	827	0.146
327.95	0.684	0.777	1.0527	1.3463	762	1086	834	0.129
327.15	0.792	0.851	1.0216	1.4089	767	1097	840	0.088
326.85	0.840	0.880	1.0053	1.4947	768	1101	843	0.069
326.25	0.905	0.925	1.0002	1.6101	772	1108	848	0.045
325.95	0.939	0.949	0.9983	1.7352	773	1112	850	0.032
325.75	1	1						0
γ_i^{∞} [a]			1.93	1.66				

[a] Calculated according to Wisniak et al. (1996).

Table 3. Experimental Vapor–Liquid Equilibrium Data for Methyl 1,1-Dimethylethyl Ether (1) + 2,2′-Oxybis[propane] (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})	G^E/RT
339.12	0	0						0
338.05	0.025	0.038	1.0372	1.0213	712	1033	861	0.021
337.15	0.088	0.127	1.0067	1.0200	716	1039	866	0.019
336.95	0.097	0.141	1.0200	1.0204	717	1041	868	0.020
336.15	0.145	0.204	1.0090	1.0250	721	1047	872	0.022
335.35	0.23	0.31	0.9911	1.0129	725	1053	877	0.008
334.35	0.295	0.383	0.9869	1.0209	730	1060	883	0.011
331.55	0.499	0.598	0.9896	1.0302	744	1082	901	0.010
330.15	0.608	0.703	0.9994	1.0169	751	1094	910	0.006
328.65	0.738	0.81	0.9944	1.0257	759	1106	920	0.003
327.35	0.861	0.905	0.9938	1.0030	766	1117	929	−0.005
326.15	0.955	0.971	0.9976	1.0142	772	1128	937	−0.002
325.95	0.973	0.982	0.9973	1.0360	773	1129	938	−0.001
325.75	1	1						0

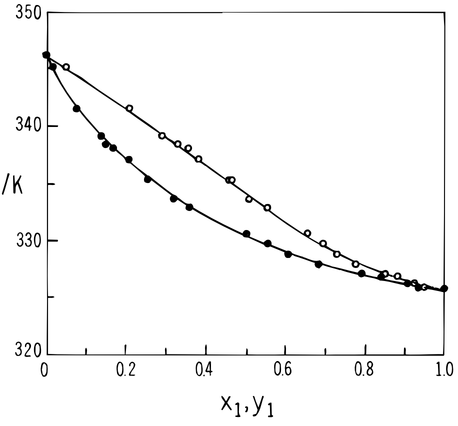

Figure 1. Boiling temperature diagram for the system methyl 1,1-dimethylethyl ether (1) + 1,3-dioxolane (2) at 94 kPa.

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° were calculated according to the Antoine equation

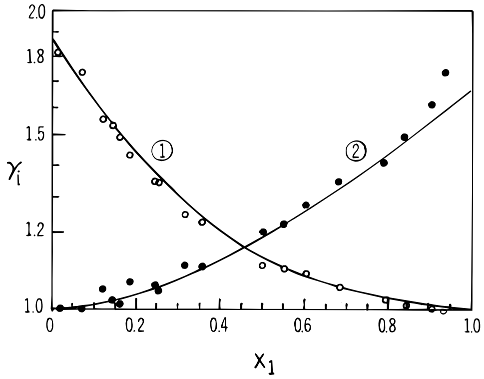

Figure 2. Activity coefficients for the system methyl 1,1-dimethylethyl ether (1) + 1,3-dioxolane (2) at 94 kPa: (○, ●) experimental, (—) predicted by UNIQUAC.

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

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

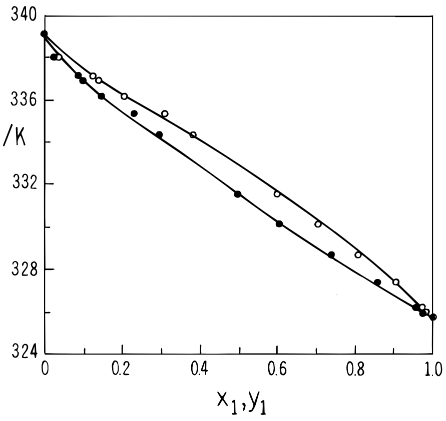

Figure 3. Boiling temperature diagram for the system methyl 1,1-dimethylethyl ether (1) + 2,2′-oxybis[propane] (3) at 94 kPa.

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
1,3-dioxolane[b]	6.231 82	1236.7	55.91
2,2′-oxybis[propane][c]	6.222 00	1257.60	43.14

[a] Reich (1996). [b] Wu and Sandler (1984). [c] Reid et al. (1977).

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 less than 2% 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 Figure 2 and are estimated accurate to within ±2%. The results reported in these tables indicate that the binary system methyl 1,1-dimethylethyl ether + 1,3-dioxolane deviates moderately from ideal behavior and the system methyl 1,1-dimethylethyl ether + 2,2′-oxybis[propane] behaves almost ideally; neither system presents an azeotrope. Table 2 contain also the activity coefficients at infinite dilution calculated by the method suggested by Wisniak et al. (1996).

The vapor−liquid equilibria data reported in Tables 2 and 3 were found to to be thermodynamically consistent by the L−W (point-to point and area) method of Wisniak (1993) 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 binary system methyl 1,1-dimethylethyl ether (1) + 1,3-dioxolane (2) 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 the system in question, with the largest deviations occurring at the dilute end of the components. The parameters of the Wohl, Wilson, NRTL, and UNIQUAC equations were obtained by minimizing the following objective function (OF)

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

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 all four models fitted the binary system methyl 1,1-dimethylethyl ether (1) + 1,3-dioxolane (2), the best fit corresponding to the UNIQUAC correlation. The capability of predicting the vapor phase composition has been used as the ranking factor.

The excess Gibbs function G^E of the two binary systems is presented in Tables 2 and 3 as the variation of the dimensionless function G^E/RT with concentration of MTBE. The value of G^E ($x = 0.5$) for the system MTBE + 1,3-dioxolane is more than 10 times that of the system MTBE + 2,2′-oxybis[propane], MTBE and 1,3-dioxolane are both polar compounds with very different steric configuration, and the large values of G^E are probably due to the disruption by MTBE of the packed layered arrangement

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) + 1,3-dioxolane (2)	0.2434	−0.0172	0.0285	6.0	3.0	0.009

B. Other Models[d]

model	system	A_{12}	A_{21}	q_1/q_2	α	$\delta(y)$[e]
Wohl	1 + 2	0.6170	0.5378	1.014		0.0096
Wilson	1 + 2	−38.83[f]	1785.6[f]			0.0103
NRTL	1 + 2	403.96[f]	1414.6[f]		0.578	0.0086
UNIQUAC	1 + 2	604.81[f]	15.018[f]			0.0078

[a] Maximum deviation %. [b] Average deviation %. [c] Root-mean-square deviation. [d] All equations in ln γ_i form. [e] $\delta(y) = \sum|y_{\mathrm{exptl}} - y_{\mathrm{calcd}}|/N$ (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_4	max dev %[a]	avg dev %[b]	rmsd[c]
methyl 1,1-dimethylethyl ether (1) + 1,3-dioxolane (2)	−21.116 23	7.220 48	−16.251 11	16.559 17	0.6	0.25	0.04
methyl 1,1-dimethylethyl ether (1) + 2,2′-oxybis[propane] (3)	−0.537 42	−7.211 91	−14.521 43	19.628 32	1.3	0.51	0.11

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

present in 1,3-dioxolane; for this reason it is reasonable that this binary will present a large exothermic mixing effect.

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

$$T/\mathrm{K} = x_1 T_1^\circ + x_2 T_2^\circ + x_1 x_2 \sum_{k=1}^{m} C_k (x_1 - x_2)^k \tag{6}$$

In this equation T_i°/K is the boiling point of the pure component at the operating pressure and i and m are 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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Literature Cited

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

Castellari, C.; Francesconi, R.; Comelli, F.; Ottani, S. Vapor-Liquid Equilibria in Systems Containing 1,3-Dioxolane at Isobaric Conditions. 6. Binary Mixtures of 1,3-Dioxolane with Acetone. *J. Chem. Eng. Data* **1984**, *29*, 283−284.

Fredenslund, A.; Gmehling, J.; Rasmussen, P. *Vapor−Liquid Equilibrium 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. Develop.* **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. Personal communication, 1996.

Reid, R. C.; Prausnitz, J. M.; Sherwood, T. K. *The Properties of Gases and Liquids*; McGraw-Hill Book Co.: New York, 1977.

TRC-Thermodynamic Tables−Non-Hydrocarbons; Thermodynamics Research Center, The Texas A & M University System: College Station, TX, 1963; a-6060 (loose-leaf data sheets, extant 1996).

Van Ness, H. C.; Abbott, M. M. *Classical Thermodynamics of Nonelectrolyte 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.; Segura, H.; Reich, R. Prediction of Activity Coefficients at Infinite Dilution by Using the Weighted Volatility Function. *Phys. Chem. Liq.* **1996**, *32*, 1−24.

Wu, H. S.; Sandler, S. I. Vapor-Liquid Equilibrium of 1,3-Dioxolane Systems *J. Chem. Eng. Data* **1989**, *34*, 209−213.

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