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Vapor−Liquid Equilibria in the Systems Oxolane + Methyl 1,1-Dimethylethyl Ether and Oxolane + 2-Propanol

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Vapor−liquid equilibrium at 94 kPa has been determined for the binary systems of oxolane (tetrahydrofuran) with methyl 1,1-dimethylethyl ether (MTBE) and 2-propanol. Both systems deviate slightly from ideal behavior and do not present an azeotrope. The activity coefficients and boiling point of the solutions were correlated with their composition by the Redlich−Kister, Wohl, Wilson, UNIQUAC, NRTL, and Wisniak−Tamir equations.

Oxolane is an intermediate for the production of hexamethylenediamine and adipic acid used in the manufacture of nylon 6 and may also be used for the production of 1,4-butanediol. It possesses a high dipole moment (1.7 D) and is used in many processes as a solvent. The three compounds tested 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 2-methyl-2-propanol. Unlike most ethers, MTBE has minimal handling and storage concerns associated with peroxide formation and exhibits excellent oxidative stability, resisting peroxide formation without added inhibitors. Vapor−liquid equilibrium for the binary system MTBE (1) + oxolane (2) at nine compositions has been measured by Zykmundova et al. (1990) at 101.3 kPa, the system was found to deviate slightly from ideality, and the data were represented well by the Redlich−Kister and Wilson models; no activity coefficients were reported. Vapor−liquid equilibrium for the binary system oxolane (2) + 2-propanol (3) has been measured at 79.9 and 101.32 kPa by Shnitko et al. (1969), Shnitko and Kogan (1977), and Yoshikawa et al. (1980). Shnitko et al. have interpolated their data and reported them at even intervals of the composition; their values for the normal boiling points of the pure components differ from those given in reliable sources like TRC (1974). In addition, their equilibrium data fail to pass the Fredenslund et al. (1977) test for thermodynamic consistency. Yoshikawa et al. measured the vapor−liquid data indirectly as part of the testing of a new ebulliometer, and no measurements were made of the composition of the vapor phase. 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 isobaric data are incomplete or are unreliable.

Experimental Section

Purity of Materials. Methyl *tert*-butyl ether (99.93 mass %), oxolane (99.9 mass %), and 2-propanol (99.5 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]	328.29[a]
	1.3663[b]	327.83[b]
oxolane (99.9)	1.4050[a]	339.15[a]
	1.4049[b]	339.12[b]
2-propanol (99.5)	1.3754[a]	355.51[a]
	1.3752[b]	355.41[b]

[a] Measured. [b] TRC, 1974.

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 ±0.1 kPa. On the average the system reaches equilibrium conditions after 1−2 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 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. Column, injector, and detector temperatures for both binaries were (333.15, 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. Concentration

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Table 2. Experimental Vapor–Liquid Equilibrium Data for Methyl 1,1-Dimethylethyl Ether (1) + Oxolane (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
336.82	0	0						0
336.50	0.019	0.030	1.1070	1.0010	720	577	597	0.003
335.90	0.052	0.079	1.0980	1.0030	722	580	599	0.008
334.70	0.120	0.173	1.0800	1.0100	728	587	605	0.018
333.70	0.191	0.261	1.0590	1.0140	733	592	609	0.022
332.60	0.274	0.359	1.0500	1.0170	738	597	614	0.025
332.10	0.313	0.402	1.0480	1.0180	741	600	617	0.027
331.60	0.351	0.438	1.0310	1.0320	744	603	619	0.031
330.40	0.447	0.532	1.0240	1.0480	750	609	625	0.036
329.90	0.507	0.586	1.0100	1.0570	752	612	627	0.032
329.40	0.563	0.633	0.9970	1.0760	755	615	630	0.030
329.00	0.604	0.674	1.0020	1.0700	757	617	632	0.028
328.20	0.682	0.744	1.0050	1.0750	761	622	636	0.026
327.90	0.732	0.782	0.9940	1.0970	763	623	637	0.020
327.40	0.772	0.815	0.9970	1.1150	766	626	640	0.023
327.20	0.803	0.842	0.9970	1.1120	767	627	641	0.018
326.80	0.847	0.877	0.9970	1.1300	769	630	643	0.016
326.40	0.877	0.902	1.0030	1.1370	771	632	645	0.018
326.30	0.909	0.927	0.9980	1.1480	772.	633	646	0.011
326.20	0.929	0.942	0.9960	1.1670	772	633	646	0.007
326.10	0.946	0.956	0.9960	1.1700	773	634	647	0.004
326.00	0.956	0.964	0.9970	1.1720	773	635	647	0.004
325.90	0.962	0.969	0.9990	1.1750	774	635	648	0.005
325.59	1	1						0
γ_i^{∞} [a]		1.13	1.07					

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

Table 3. Experimental Vapor–Liquid Equilibrium Data for Oxolane (2) + 2-Propanol (3) at 94 kPa

T/K	x_2	y_2	γ_2	γ_3	$-B_{22}$/ ($cm^3 mol^{-1}$)	$-B_{33}$/ ($cm^3 mol^{-1}$)	$-B_{23}$/ ($cm^3 mol^{-1}$)	G^E/RT
353.55	0	0					0	
352.3	0.034	0.069	1.2665	1.0125	509	676	606	0.02
352.09	0.053	0.106	1.2494	1.0008	510	677	607	0.013
351.22	0.091	0.175	1.2360	0.9958	513	682	611	0.015
349.52	0.152	0.273	1.2147	1.0073	520	693	620	0.036
346.86	0.287	0.453	1.1545	1.0053	530	709	634	0.045
346.56	0.302	0.469	1.1484	1.0086	532	711	636	0.048
345.82	0.329	0.499	1.1466	1.0208	535	716	640	0.059
344.87	0.376	0.552	1.1399	1.0224	539	722	645	0.063
343.8	0.441	0.612	1.1147	1.0335	543	730	651	0.066
342.61	0.508	0.665	1.0902	1.0673	549	738	658	0.076
341.78	0.561	0.710	1.0820	1.0726	552	743	663	0.075
341.73	0.576	0.715	1.0625	1.0935	553	744	663	0.073
341.44	0.604	0.731	1.0463	1.1163	554	746	665	0.071
340.71	0.661	0.771	1.0305	1.1504	557	751	669	0.067
339.79	0.721	0.814	1.0270	1.1777	561	757	675	0.065
339.54	0.732	0.823	1.0311	1.1826	563	759	676	0.067
339.23	0.757	0.839	1.0268	1.2004	564	762	678	0.064
338.96	0.783	0.856	1.0211	1.2184	565	764	680	0.059
338.64	0.825	0.881	1.0077	1.2631	567	766	682	0.047
337.93	0.872	0.914	1.0121	1.2833	570	771	687	0.042
336.82	1	1						0
γ_i^{∞} [a]			1.36	1.41				

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

measurements were accurate to better than ±0.009 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 3, together with the activity coefficients γ_i which were calculated from the following equation (Van Ness and Abbott, 1982)

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

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

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

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 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

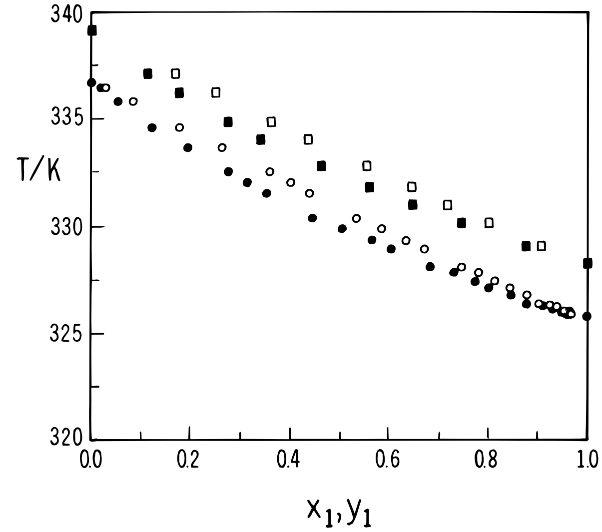

Figure 1. Boiling temperature diagram for the system methyl 1,1-dimethylethyl ether (1) + oxolane (2) at 94 kPa (○, ●). Comparison with the data of Zykmundova et al. (1990) at 101.325 kPa (□, ■).

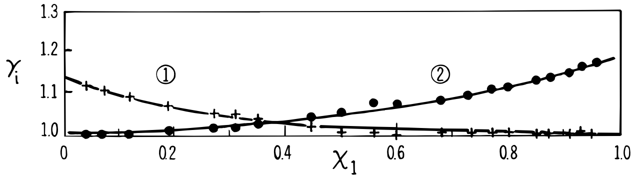

Figure 2. Activity coefficients for the system methyl 1,1-dimethylethyl ether (1) + oxolane (2) at 94 kPa.

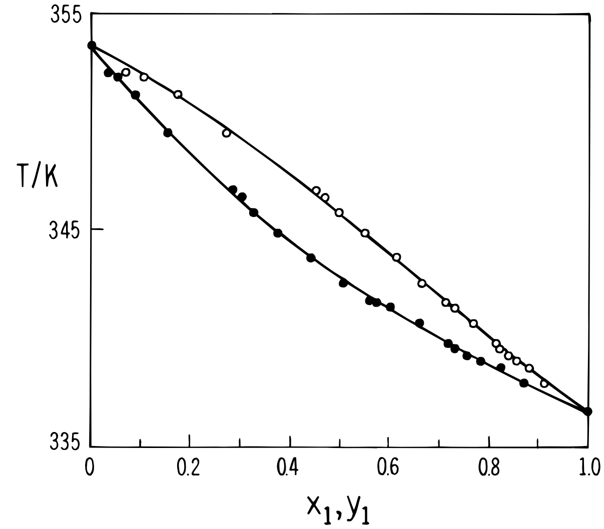

Figure 3. Boiling temperature diagram for the system oxolane (2) + 2-propanol (3) at 94 kPa.

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
oxolane[b]	6.120 043	1202.29	46.90
2-propanol[b]	7.242 683	1580.92	53.54

[a] Reich (1996). [b] TRC (1974).

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	0.0653			5.8	3.3	0.007
ether (1) + oxolane (2)	0.0644	0.0052		6.4	3.2	0.007
oxolane (2) + 2-propanol (3)	−0.1320	0.0215	0.0131	2.7	0.8	0.003

B. Other Models[d]

model	system	A_{12}	A_{21}	q_1/q_2	α	$\delta(y)$[e]
Wohl	1 + 2	0.0969	0.0760	0.2209		0.0079
	2 + 3	0.2473	0.3732	1.035		0.0022
Wilson	1 + 2	−42.12[f]	564.93[f]			0.0075
	2 + 3	922.38[f]	−25.10[f]			0.0053
NRTL	1 + 2	228.75[f]	173.49[f]		0.378	0.0072
	2 + 3	1185.24[f]	−138.45[f]		0.762	0.0035
UNIQUAC	1 + 2	179.16[f]	−11.391[f]			0.0067
	2 + 3	−101.47[f]	400.81[f]			0.0034

[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.

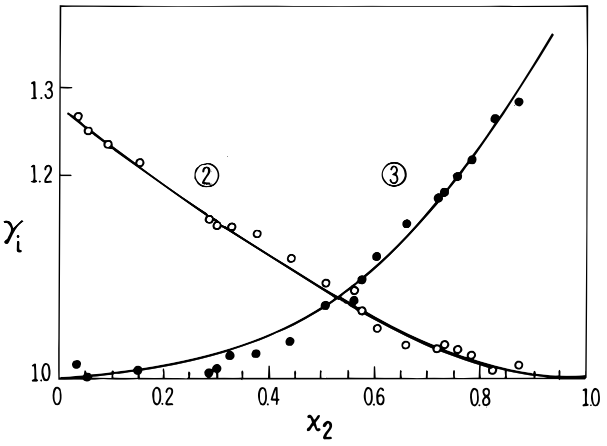

Figure 4. Activity coefficients for the system oxolane (2) + 2-propanol (3) at 94 kPa. (○,●), (—) according to Wohl.

component vapor pressures P_i^0 were calculated according to the Antoine equation

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

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 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 less than 1% 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 Figures 2 and 4 and are estimated accurate to within ±3%. The results reported in these tables indicate that both systems exhibit small positive deviations from ideal behavior and that no azeotrope is present. Tables 2 and 3 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 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

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) + oxolane (2)	−5.329 81	2.966 23	−0.456 61	−5.401 81	0.25	0.10	0.02
oxolane (2) + 2-propanol (3)	−8.521 62	−2.671 39	−3.601 76		0.42	0.19	0.04

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

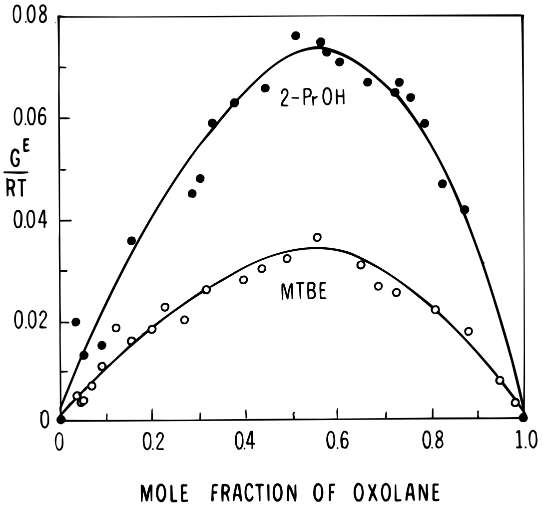

Figure 5. Variation of dimensionless number G^E/RT with the mole fraction of oxolane.

measured by the Durbin−Watson statistic. The activity coefficients were correlated 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 binary systems, with the largest deviations occurring at the dilute end of the components. In addition, it is seen that the binary system MTBE (1) + oxolane (2) can be well approximated by regular solution behavior. 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 well both systems, the best fit corresponding to the UNIQUAC correlation for the MTBE + oxolane system and the Wohl model for the oxolane + 2-propanol system. 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 and Figure 5 as the variation of the dimensionless function G^E/RT with concentration of oxolane. The value of G^E (x = 0.5) for the system MTBE + 2-propanol is more than twice that of the system MTBE + oxolane, probably due to associating effects present in systems containing alcohols.

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 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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