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Isobaric Vapor−Liquid Equilibria in the Systems 2,2′-Oxybis[propane] + Propanol and Methyl Ethanoate + 2,2′-Oxybis[propane]

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Vapor−liquid equilibrium at 92 kPa has been determined for the binary systems 2,2′-oxybis[propane] (diisopropyl ether) + propanol and methyl ethanoate + 2,2′-oxybis[propane]. Both systems exhibit moderate positive deviations from ideal behavior; the system methyl ethanoate + 2,2′-oxybis[propane] forms an azeotrope that boils at 360.05 K and contains 79.3 mol % methyl ethanoate. The activity coefficients and boiling point of the solution were correlated with its composition by the Redlich−Kister, Wohl, Wilson, UNIQUAC, NRTL, and Wisniak−Tamir equations.

The vapor−liquid equilibrium for the binary system 2,2′-oxybis[propane] (1) + propanol (2) has been measured at 91.2 kPa by Vijayaraghavan et al. (1966) and at 101.3 kPa by González Benito and Cartón López (1992). Vijayaraghavan et al. have indicated that their data are not consistent because of the highly nonideal nature of the solution, as evidenced by the large difference in boiling points of their components. In addition, the DECHEMA data bank indicates that the data of Vijayaraghavan et al. fail to pass the Fredenslund (1977) point-to-point and the Herington (1951) area tests for thermodynamic consistency. Analysis of the data of González Benito and Cartón López indicate that they pass the thermodynamic consistency tests of Fredenslund and Wisniak (1993). No vapor−liquid equilibrium data are available for the binary system methyl ethanoate (3) + 2,2′-oxybis[propane] (1). The components of both systems have large dipole moments (>1.2 D). The present work was undertaken to measure vapor−liquid equilibria (VLE) data for the title systems for which isobaric data are not available or are not reliable.

Experimental Section

Purity of Materials. 2,2′-Oxybis[propane] (99.75+ mass %), propanol (99.66+ mass %), and methyl ethanoate (99.89+ mass %) were purchased from Aldrich. The reagents were used without further purification after gas chromatography failed to show any significant impurities. The properties and purities (as determined by GLC) of the pure components appear in Table 1.

Apparatus and Procedure. An all-glass modified Dvorak and Boublik recirculation still (Boublikova and Lu, 1969) was used in the VLE measurements. The general experimental features have been described in a previous paper (Wisniak and Tamir, 1975). The temperature was measured with a Lauda Model R42/2 digital thermometer provided with a PT-10 probe, and the total pressure of the system was determined from the boiling temperature of distilled water in a Swietoslawski ebulliometer. All analyses were carried out 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 1.8 m long and 0.2 cm in diameter packed with SE-30 on 80-100 mesh SUPELCOPORT and operated at 323.15 K for the binary with propanol and 333.15 K for the binary with methyl ethanoate. The temperatures at the injector and detector were 493.15 and 543.15 K, respectively. Very good separation for the binary systems was achieved under these conditions, and repetitive gravimetric calibration analyses were carried out with synthetic mixtures to convert the peak ratio to the mass composition of the sample. Concentration measurements were accurate to better than ±0.008 mole fraction. The pertinent polynomial fit had a correlation coefficient R^2 better than 0.99. The accuracies in the determination of the pressure P and temperature T was at least ±0.1 kPa and ±0.02 K, respectively.

Table 1. Mole Percent GLC Purities, 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
propanol (99.66)	1.3836[a]	370.35[a]
	1.38370[b]	370.35[b]
2,2′-oxybis[propane] (99.75)	1.3654[a]	341.55[a]
	1.3655[b]	341.45[b]
methyl ethanoate (99.89)	1.3588[a]	330.09[a]
	1.3589[b]	330.09[b]

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

Results

The temperature T and liquid-phase x_i and vapor-phase y_i mole fraction measurements at $P = 92$ kPa are reported in Tables 2 and 3 and Figures 1−4, together with the activity coefficients γ_i which were calculated from the following equation (Van Ness and Abbott, 1982):

$$\ln \gamma_i = \ln \frac{y_i P}{x_i P_i^0} + \frac{(B_{ii} - V_i^L)(P - P_i^0)}{RT} + y_j^2 \frac{\delta_{12} P}{RT} \qquad (1)$$

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_{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

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Table 2. Experimental Vapor–Liquid Equilibria Data for 2,2′-Oxybis[propane] (1) + Propanol (2) at 92 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
367.45	0	0						0
366.55	0.008	0.046	2.6015	1.0134	836	671	706	0.0208
365.05	0.022	0.117	2.5215	1.0076	843	679	713	0.0277
356.75	0.119	0.460	2.2797	0.9516	884	731	757	0.0539
356.15	0.125	0.474	2.2646	0.9568	887	735	760	0.0635
353.85	0.169	0.550	2.0665	0.9498	899	751	773	0.0800
351.65	0.208	0.570	1.8501	1.0448	911	766	786	0.1629
346.95	0.342	0.708	1.6055	1.0440	939	801	816	0.1900
344.55	0.441	0.765	1.4411	1.1024	953	821	832	0.2157
342.95	0.528	0.796	1.3143	1.2183	964	834	843	0.2375
341.45	0.638	0.837	1.1966	1.3596	973	846	854	0.2257
339.75	0.776	0.873	1.0828	1.8405	985	861	866	0.1986
338.25	0.955	0.963	1.0167	2.8307	995	875	877	0.0632
337.85	1	1						0
γ_i^{∞} [a]			3.10	6.72				

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

Table 3. Experimental Vapor–Liquid Equilibrium Data for Methyl Ethanoate (3) + 2,2′-Oxybis[propane] (1) at 92 kPa

T/K	x_3	y_3	γ_3	γ_1	$-B_{33}$/cm^3 mol^{-1}	$-B_{11}$/cm^3 mol^{-1}	$-B_{13}$/cm^3 mol^{-1}	G^E/RT
337.85	0	0						0
336.95	0.019	0.055	2.1346	1.0108	541	1004	678	0.0248
336.35	0.035	0.093	1.9873	1.0054	544	1008	681	0.0290
335.25	0.059	0.143	1.8677	1.0093	549	1016	687	0.0455
334.35	0.085	0.195	1.8255	1.0030	553	1022	691	0.0538
332.75	0.150	0.287	1.5954	1.0089	560	1034	699	0.0775
331.45	0.209	0.358	1.4897	1.0186	566	1044	706	0.0981
330.45	0.257	0.412	1.4453	1.0263	571	1052	712	0.1139
329.95	0.299	0.447	1.3700	1.0404	573	1056	714	0.1219
328.55	0.387	0.524	1.2974	1.0765	580	1067	722	0.1460
327.75	0.458	0.572	1.2324	1.1229	584	1073	727	0.1586
327.25	0.515	0.615	1.1976	1.1504	587	1077	729	0.1609
326.95	0.561	0.644	1.1632	1.1877	588	1080	731	0.1603
326.45	0.636	0.688	1.1168	1.2746	591	1084	734	0.1586
326.25	0.694	0.727	1.0886	1.3369	592	1086	735	0.1478
326.15	0.744	0.762	1.0682	1.3972	592	1087	736	0.1348
326.05	0.793	0.797	1.0503	1.4870	593	1087	736	0.1209
326.05	0.823	0.817	1.0389	1.5584	593	1087	736	0.1100
326.05	0.848	0.840	1.0365	1.5874	593	1087	736	0.1007
326.35	0.923	0.906	1.0153	1.8368	591	1085	735	0.0607
326.65	0.961	0.950	1.0120	1.9133	590	1082	733	0.0365
326.85	0.979	0.971	1.0085	2.0345	589	1081	732	0.0232
327.32	1	1						0
g_i^{∞} [a]			2.43	2.36				

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

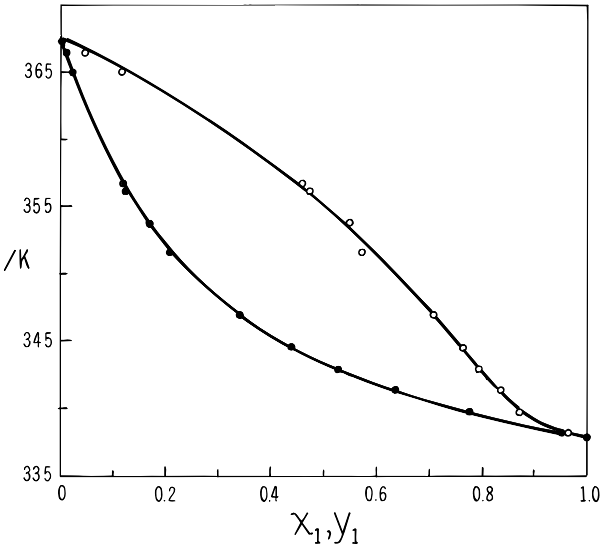

Figure 1. Boiling temperature diagram for the system 2,2′-oxybis[propane] (1) + propanol (2) at 92 kPa.

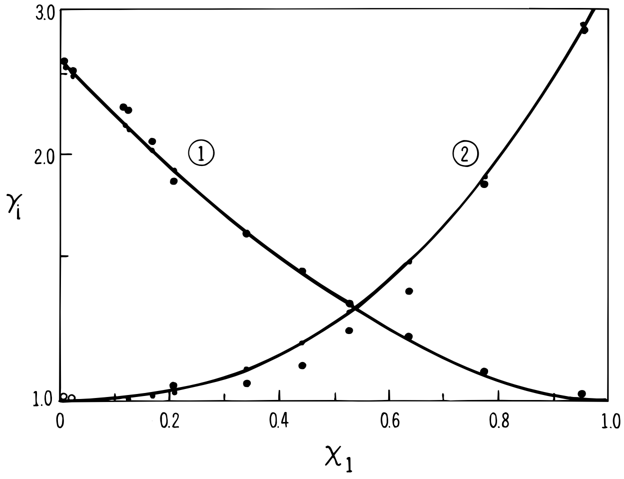

Figure 2. Activity coefficients for the system 2,2′-oxybis[propane] (1) + propanol (2) at 92 kPa: experimental (●); predicted by Wohl (—).

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

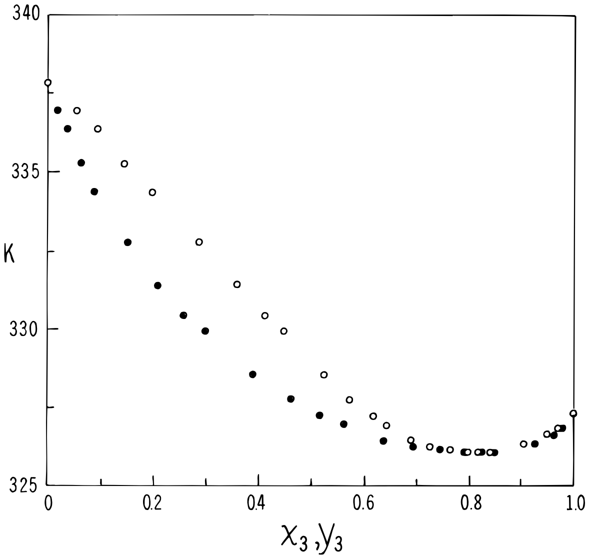

Figure 3. Boiling temperature diagram for the system methyl ethanoate (3) + 2,2′-oxybis[propane] (1) at 92 kPa.

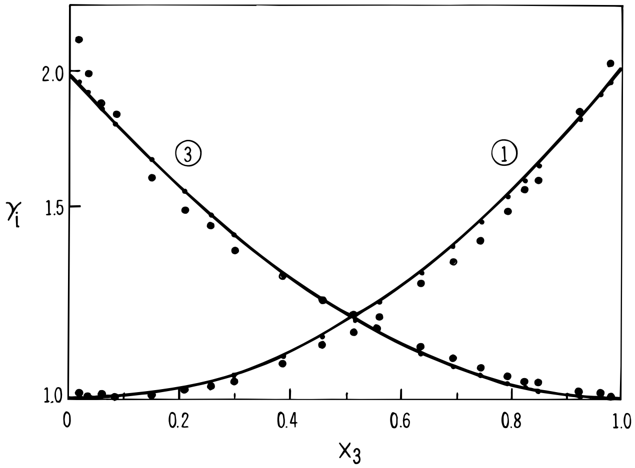

Figure 4. Activity coefficients for the system methyl ethanoate (3) + 2,2′-oxybis[propane] (1) + at 92 kPa: experimental (●); predicted by Wohl (—).

Table 4. Antoine Coefficients,[a] Eq 3

compound	A_i	B_i	C_i
propanol	6.972 839	1499.21	68.51
2,2′-oxybis[propane]	6.222 00	1257.60	43.14
methyl ethanoate	6.186 21	1156.43	53.46

[a] TRC (1974).

to the Antoine equation

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

where the constants A_i, B_i, and C_i (TRC, 1974) are reported in Table 4. The molar virial coefficients B_{ii} and B_{ij} were estimated according to the method of O'Connell and Prausnitz (1967) using the molecular parameters suggested by the authors and assuming the association parameter η to be 0.5 (Prausnitz et al., 1980). The last two terms in eq 1 contributed less than 4% to the activity coefficients in the binary of 2,2′-oxybis[propane] with propanol and less than 2% in the binary with methyl ethanoate; 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 ±6% and ±3%, respectively; the higher relative error for the system 2,2′-oxybis[propane] + propanol is due to the larger boiling temperature difference between the two pure components. The results reported in these tables indicate that both systems exhibit moderate positive deviations from ideal behavior and that the system methyl ethanoate + 2,2′-oxybis[propane] forms an azeotrope that boils at 360.05 K and contains 79.3 mol % methyl ethanoate. Tables 2 and 3 contain also the activity coefficients at infinite dilution calculated by the method suggested by Wisniak et al. (1996).

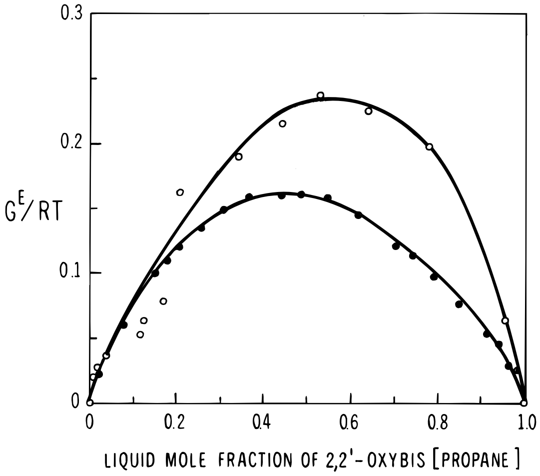

Figure 5. Variation of G^E/RT with the liquid composition of 2,2′-oxybis[propane]: (○) solutions with propanol; (●) solutions with methyl methanoate.

The vapor−liquid equilibria data reported in Tables 2 and 3 were found 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 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 Redlich−Kister expansion was used (1948):

$$\ln \gamma_1/\gamma_2 = B(x_2 - x_1) + C(6x_1x_2 - 1) + D(x_2 - x_1)(1 - 8x_1x_2) \tag{4}$$

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 fair representation of the data for the system 2,2′-oxybis[propane] + propanol and a good fit of the second binary system, 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):

$$\text{OF} = \sum_{i=1}^{N,2}\left(\frac{\gamma_{i,\text{exptl}} - \gamma_{i,\text{calc}}}{\gamma_{i,\text{exptl}}}\right)^2 \tag{5}$$

They 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 Wohl correlation. A comparison of the experimental activity coefficients and the ones predicted by the Wohl model is presented in Figures 2 and 3.

Table 5. Parameters and Deviations between Experimental and Calculated Values for the Different Models

A. Redlich−Kister, Eq 4

system	*B*	*C*	*D*	max dev %[a]	avg dev %[b]	rmsd[e]
2,2′-oxybis[propane] (1) + propanol (2)	0.4775	0.0628		11.4	6.2	0.03
methyl ethanoate (3) + 2,2′-oxybis[propane] (1)	0.2859	0.0050	0.0420	5.2	2.7	0.008

B. Other Models[d]

model	system	A_{12}	A_{21}	q_1/q_2	α	$\delta(y)$[e]
Wohl	1 + 2	0.9355	1.2027	0.8171		0.0079
	3 + 1	0.6796	0.7125	0.9325		0.0046
Wilson	1 + 2	−688.80[f]	4318.6[f]			0.0108
	3 + 1	3274.7[f]	−1159.06[f]			0.0067
NRTL	1 + 2	2563.64[f]	1274.04[f]		0.572	0.0099
	3 + 1	1061.94[f]	1088.53[f]		0.628	0.0053
UNIQUAC	1 + 2	38.110[f]	729.12[f]			0.0229
	3 + 1	−595.70[f]	1467.04[f]			0.0051

[a] Maximum deviation. [b] Average deviation. [c] Root mean square deviations. [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, and 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]
2,2′-oxybis{propane] (1) + propanol (2)	−36.8243	24.862 6	−16.1640	7.466 89	0.24	0.08	0.03
methyl ethanoate (3) + 2,2′-oxybis{propane] (1)	−19.3917	3.720 32	−15.0197		0.66	0.29	0.04

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

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 number G^E/RT (Gibbs number) with the concentration of 2,2′-oxybis[propane]. It is seen that the value of the parameter at $x = 0.5$ for the system with propanol is much larger than that for the system with methyl ethanoate, probably due to homo- and heteroassociation effects caused by hydrogen bonding of the alcohol.

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

$$T/\mathrm{K} = \sum_{i=1}^{2} T_i^0/\mathrm{K} + x_1 x_2 \sum_{m=0}^{m} C_k (x_i - x_j)^k \qquad (6)$$

In this equation T_i^0 is the boiling point of the pure component i and m is the number of terms in the series expansion of $x_i - x_j$. 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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