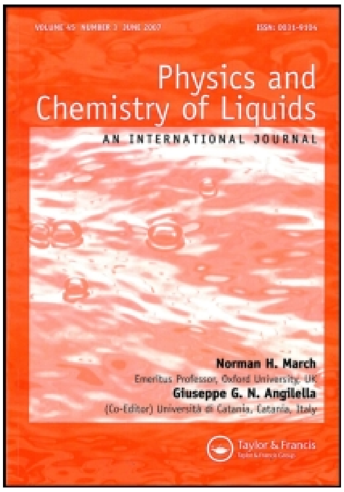

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VAPOR-LIQUID EQUILIBRIA IN THE BINARY SYSTEMS OF 1,3-DIOXOLANE WITH CYCLOHEXANE, *n*-HEPTANE AND DIETHYL CARBONATE

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Vapor-liquid equilibrium at 101.3 kPa has been determined for the binary systems of 1,3-dioxolane with cyclohexane, *n*-heptane and diethyl carbonate. The binary systems of 1,3-dioxolane with cyclohexane and *n*-heptane exhibit positive deviations from ideal behavior and present azeotropic points with 57% mole 1,3-dioxolane, 341.04 K and 80% mole, 345.6 K respectively. The binary system 1,3-dioxolane–diethyl carbonate behaves almost ideally. The activity coefficients and boiling point of the solution were correlated with its composition by the Redlich-Kister and Wisniak-Tamir equations.

KEY WORDS: Vapor-liquid equilibrium, activities, organic solutions.

Cyclic ethers and diethyl carbonate are frequently used in the chemical industry as solvents and intermediates. The present work was undertaken to measure vapor-liquid equilibria (VLE) data for the title systems for which no isobaric data are available. This is part of a program to determine UNIFAC parameters for organic compounds.

EXPERIMENTAL

Purity of materials

1,3-dioxolane (99.94 + mole %), cyclohexane (99.9 + mole %), *n*-heptane (99.8 + mole %) and diethyl carbonate (99.9%) were purchased from Merck. The reagents were used without further purification after gas chromatography failed to show any significant impurities. Properties and purity (as determined by GLC) of the pure components appear in Table 1.

Apparatus and procedure

An all-glass modified Dvorak and Boublik recirculation still (1) was used in the VLE measurements. The experimental features have been described in a previous

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Table 1 Mole % GLC Purities, Refractive Index n_D at Na D line, and Normal Boiling Points T of Pure Components.

Component (Purity, mole %)	*n_D(298.15 K)*	*T/K*
1,3-dioxolane (99.94)	1.3980^a 1.3984^b	348.60^a 348.55^c
cyclohexane (99.9)	1.4233^a 1.42354^d	353.82^a 353.88^d
heptane (99.8)	1.3851^a 1.38511^d	371.46^a 371.574^d
diethyl carbonate (99.9)	1.3821^a 1.3824^e	352.71^a 352.79^f

[a] Measured
[b] Reference 9
[c] Reference 8
[d] Reference 10
[e] Reference 11
[f] Reference 12

publication (2). 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 2 m long and 0.2 cm in diameter, filled with 10% Carbowax 20M, the injector and detector temperatures were 523.15 K; the column temperature was 353.15 K for the systems of 1,3-dioxolane with cyclohexane and *n*-heptane, and 368.15 K for the system with diethyl carbonate. Very good separation was achieved under these conditions, and calibration analyses with gravimetrically prepared samples were carried to convert the peak ratio to the weight composition of the sample. Concentration measurements were accurate to better than ± 0.008 mole fraction units. The accuracy in determination of pressure P and temperature T was at least ± 0.1 kPa and 0.02 K, respectively.

RESULTS

The temperature T and liquid-phase x_i and vapor-phase y_i mole fraction measurements at $P = 101.3$ kPa are reported in Tables 2–4 and Figures 1–5, together with the activity coefficients γ_i which were calculated from the following equation (3):

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

where:

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

The standard state for the calculation of activity coefficients is the pure component at the pressure and temperature of the solution. The pure component vapor pressures P_i^0 were calculated according to the Antoine equation:

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

where the constants A_i, B_i, C_i are reported in Table 5. The molar virial coefficients B_{ii}

Table 2 Experimental Vapor-liquid equilibrium data for 1,3-Dioxolane (1) + Cyclohexane (2) at 101.3 kPa.

T/K	x_1	y_1	γ_1	γ_2	$-B_{11}$ ($cm^3 mol^{-1}$)	$-B_{22}$ ($cm^3 mol^{-1}$)	$-B_{12}$ ($cm^3 mol^{-1}$)
348.67	0.062	0.180	2.8928	1.0186	818	1151	978
346.34	0.120	0.280	2.5073	1.0227	832	1170	995
344.29	0.189	0.356	2.1655	1.0569	844	1188	1009
342.58	0.273	0.428	1.9084	1.1043	855	1202	1022
341.83	0.340	0.464	1.7037	1.1670	860	1209	1028
341.16	0.471	0.536	1.4533	1.2873	864	1215	1033
341.04	0.522	0.552	1.3600	1.3808	865	1216	1034
341.05	0.621	0.594	1.2261	1.5777	865	1216	1034
341.18	0.691	0.639	1.1801	1.7137	864	1215	1033
341.44	0.725	0.650	1.1341	1.8516	862	1212	1031
341.58	0.744	0.667	1.1286	1.8841	861	1211	1030
341.58	0.750	0.672	1.1280	1.9004	861	1211	1030
342.48	0.828	0.735	1.0840	2.1696	856	1203	1023
344.27	0.914	0.831	1.0458	2.6179	844	1188	1010
345.89	0.952	0.893	1.0227	2.8258	834	1174	998
347.03	0.979	0.949	1.0182	2.9739	828	1165	990

Table 3 Experimental Vapor-liquid equilibrium data for 1,3-Dioxolane (1) + *n*-Heptane (2) at 101.3 kPa.

T/K	x_1	y_1	γ_1	γ_2	$-B_{11}$ ($cm^3 mol^{-1}$)	$-B_{22}$ ($cm^3 mol^{-1}$)	$-B_{12}$ ($cm^3 mol^{-1}$)
364.59	0.052	0.210	2.4853	1.0166	733	1607	1119
359.26	0.116	0.371	2.2985	1.0172	760	1670	1162
356.08	0.164	0.451	2.1745	1.0351	776	1710	1188
351.63	0.267	0.566	1.9232	1.0741	801	1768	1228
348.78	0.380	0.642	1.6778	1.1489	817	1807	1254
347.27	0.485	0.695	1.4941	1.2387	826	1828	1268
346.82	0.528	0.705	1.4127	1.3269	829	1834	1272
345.97	0.663	0.755	1.2443	1.6334	834	1847	1280
345.84	0.701	0.759	1.1827	1.7685	835	1849	1282
345.58	0.772	0.785	1.1202	2.0874	836	1852	1284
345.63	0.804	0.801	1.0958	2.2440	836	1852	1284
345.94	0.886	0.852	1.0468	2.8408	834	1847	1281
346.65	0.938	0.904	1.0250	3.3103	830	1837	1274
347.86	0.979	0.961	1.0037	3.8164	827	1820	1262

Table 4 Experimental Vapor-liquid equilibrium data for 1,3-Dioxolane (1) + Diethyl Carbonate (2) at 101.3 kPa.

T/K	x_1	y_1	γ_1	γ_2	$-B_{11}$ ($cm^3 mol^{-1}$)	$-B_{22}$ ($cm^3 mol^{-1}$)	$-B_{12}$ ($cm^3 mol^{-1}$)
393.32	0.053	0.194	1.0572	1.0055	434	1198	660
387.61	0.119	0.367	1.0213	1.0131	451	1248	683
382.36	0.183	0.489	1.0089	1.0437	466	1298	706
378.27	0.239	0.572	1.0044	1.0744	479	1339	725
373.77	0.320	0.680	1.0052	1.0480	494	1387	748
367.49	0.443	0.786	0.9987	1.0674	517	1460	782
364.81	0.503	0.828	1.0004	1.0596	527	1493	797
358.50	0.672	0.912	0.9937	1.0395	552	1577	837
355.20	0.755	0.942	1.0106	1.0412	566	1623	859
353.94	0.810	0.956	0.9941	1.0670	571	1642	868
352.59	0.852	0.967	0.9974	1.0862	577	1662	877
350.46	0.926	0.985	1.0002	1.0748	587	1695	893

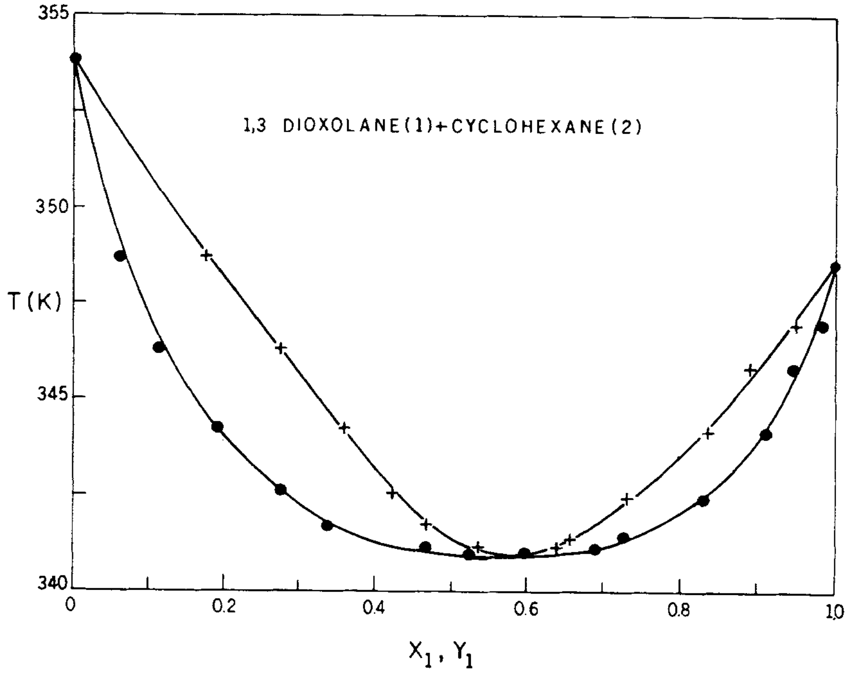

Figure 1 Boiling temperature diagram for the system 1,3-dioxolane (1) - cyclohexane (2) at 101.3 kPa.

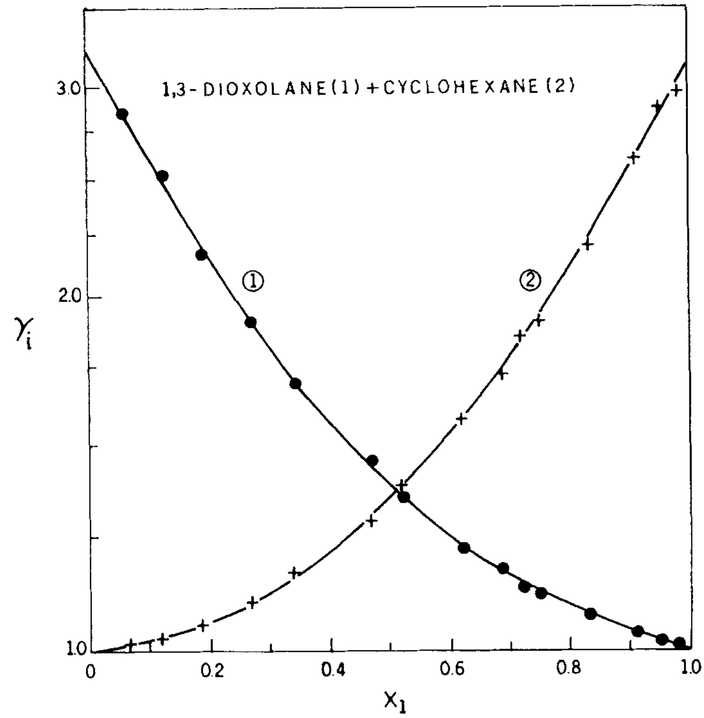

Figure 2 Activity coefficients for the system 1,3-dioxolane (1) - cyclohexane (2) at 101.3 kPa.

and B_{ij} were estimated by the method of O'Connell and Prausnitz (4) using the molecular parameters suggested by the authors and assuming the association parameter η to be zero. The last two terms in Eq. 1 contributed less than 3% to the activity coefficient and their influence was important only at very dilute concentrations. The calculated activity coefficients are reported in Tables 2–4 and are estimated accurate to within $\pm 3\%$.

The vapor-liquid equilibria data reported in Tables 2–4 were found to be thermodynamically consistent by the Redlich-Kister test (5) and by the L-W method of Wisniak (6). Inspection of Figures 1–4 shows that the binary systems of 1,3-dioxolane with cyclohexane and *n*-heptane exhibit positive deviations from ideal behavior and present azeotropic points with 57% mole 1,3-dioxolane, 341.04 K and 80% mole,

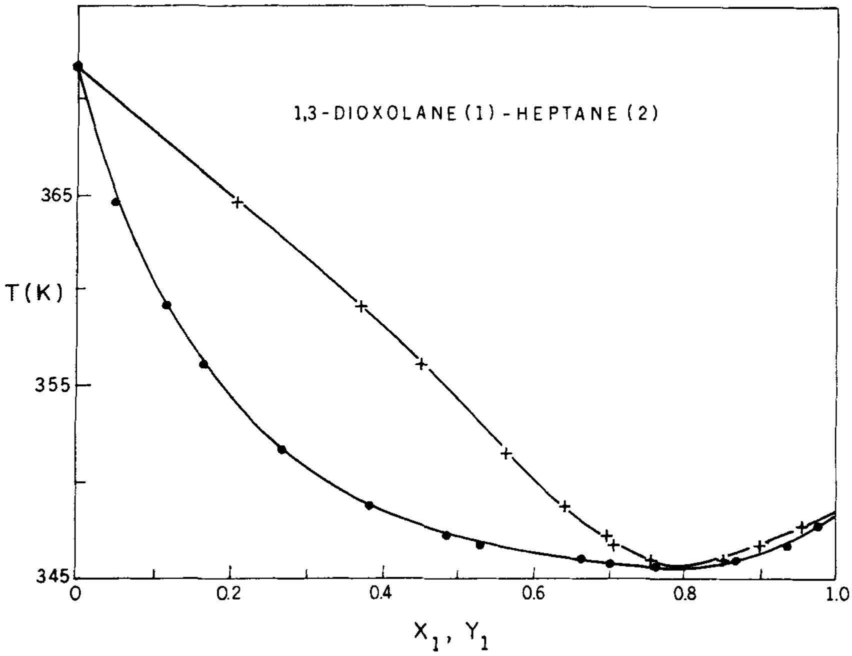

Figure 3 Boiling temperature diagram for the system 1,3-dioxolane (1) - *n*-heptane (2) at 101.3 kPa.

Table 5 Antoine Coefficients, Eq. 3.

Compound	A_i	B_i	C_i
1,3-dioxolane[1]	6.23182	1236.7	55.91
cyclohexane[1]	5.96407	1200.31	50.65
heptane[1]	6.02167	1264.90	56.61
diethyl carbonate[1]	6.77616	1721.904	37.96

[1] Reference 8
[2] Reference 10
[3] Reference 12

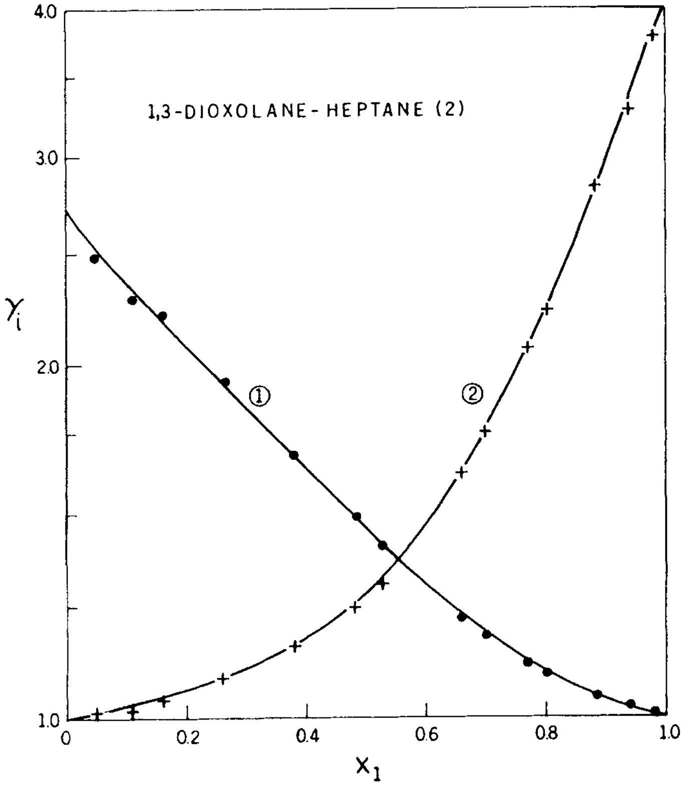

Figure 4 Activity coefficients for the system 1,3-dioxolane (1) - *n*-heptane (2) at 101.3 kpa.

345.6 K respectively. The binary system 1,3-dioxolane–diethyl carbonate behaves almost ideally.

The activity coefficients for the 1,3-dioxolane-cyclohexane and *n*-heptane binaries were correlated by the Redlich-Kister expansion (5):

$$\ln \gamma_1/\gamma_2 = B(x_2 - x_1) + C(6x_1x_2 - 1) + D(x_2 - x_1)(1 - 8x_1x_2) + E(x_2 - x_1)^2(10x_1x_2 - 1) \qquad (4)$$

The values of the pertinent parameters and statistics appear en Table 6.

The excess Gibbs function of these two systems are presented in Table 7 and Figure 5 as the variation of the dimensionless number (Gibbs number) $\Delta G^E/RT$ with composition. The values of the parameter are positive over the entire composition range, the values at $x = 0.5$ are essentially the same for both systems indicating a similar balance between thermal and entropic effects.

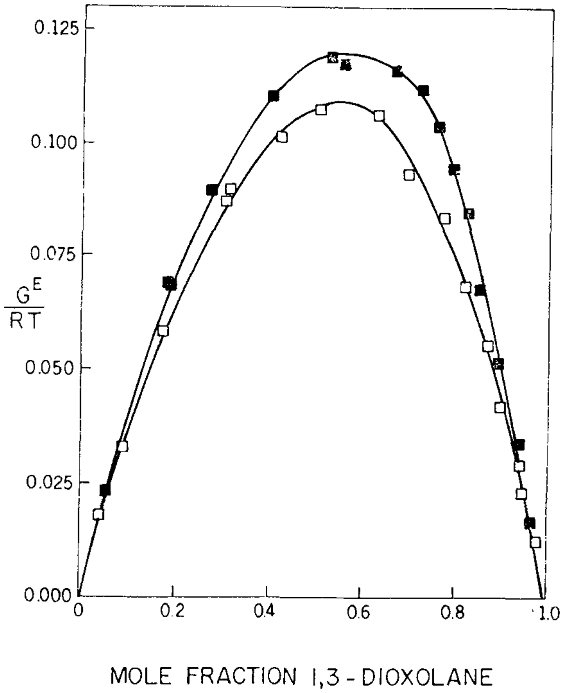

Figure 5 Variation of $\Delta G^E/RT$ with composition for 1,3-dioxolane + cyclohexane and 1,3 dioxolane + *n*-heptane.

Table 6 Redlich-Kister Coefficients, Eq. 4.

System	*B*	*C*	*D*	*rmsd*	$\%^1$
1,3-dioxolane (1) + cyclohexane (2)	0.4857	−0.0016	0.0154	0.01	3.0
1,3-dioxolane (1) + heptane (2)	0.5047	0.1065	0.00948	0.005	1.2

[1] average % deviation

The boiling points of the three binaries were correlated by the equation proposed by Wisniak and Tamir (7):

$$\frac{T}{K} = \sum_{i=1}^{2} x_i T_i^0/K + x_1 x_2 \sum^{m} C_k (x_i - x_j)^k \tag{5}$$

In this equation T_i^0 is the boiling point of the pure component *i* (K or °C) and *m* is the

Table 7 Variation of $\Delta G^E/RT$ with composition.

1,3-dioxolane + cyclohexane		*1,3-dioxolane + n-heptane*	
x_1	$\Delta G^E/RT$	x_1	$\Delta G^E/RT$
0.000	0.000	0.000	0.000
0.062	0.083	0.052	0.063
0.120	0.130	0.116	0.112
0.189	0.191	0.164	0.156
0.273	0.249	0.267	0.227
0.340	0.283	0.380	0.283
0.471	0.310	0.485	0.305
0.522	0.313	0.528	0.316
0.621	0.299	0.660	0.298
0.691	0.281	0.701	0.288
0.725	0.261	0.772	0.255
0.744	0.252	0.804	0.232
0.750	0.251	0.886	0.160
0.828	0.200	0.938	0.097
0.914	0.124	0.979	0.032
0.952	0.071	1.000	0.000
0.979	0.041		
1.000	0.000		

Table 8 Coefficients in Correlation of Boiling Points, eq 5, average %deviation and Root Mean Square Deviations in Temperature, rmsd (T/K).

System	C_0	C_1	C_2	*r msd*	%[1]
1,3-dioxolane (1) + cyclohexane (2)	−37.574	6.6099	−45.756	0.10	0.34
1,3-dioxolane (1) + heptane (2)	−50.075	28.323	−40.952	0.07	0.21
1,3-dioxolane (1) + diethyl carbonate (2)	−35.184	15.567	− 8.386	0.05	0.12

[1] average %deviation

number of terms in the series expansion of $(x_i - x_j)$. The various constants of Equation 5 are reported in Table 8, which also contains information indicating the degree of goodness of correlation.

Acknowledgement

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Glossary

A_i, B_i, C_i	Antoine constants, Eq. 3
B_{ii}, B_{ij}	second molar virial coefficients, Eqs. 1, 2
C_k	constants, Eq. 5

ΔG^E	excess Gibbs function
N	number of measurements
P	total pressure
P_i^0	vapor pressure of pure component i
R	gas constant
$rmsd(T)$	root mean square deviation, $\{\Sigma(T_{\text{expt}} - T_{\text{calc}})^2\}^{0.5}/N$
t, T	boiling temperature of a mixture
t_i^0	boiling temperature of pure component i
v_i^L	molar volume of liquid component i
x_i, y_i	mole fraction of component i in the liquid and vapor phases
γ_i	activity coefficient of component i

Subscripts

expt	experimental value
calc	calculated value
i	component i

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