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Isobaric Vapor—Liquid Equilibria in the Binary Systems of 1,3-Dioxolane, 1-Chlorobutane and 2-Chlorobutane

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ISOBARIC VAPOR–LIQUID EQUILIBRIA IN THE BINARY SYSTEMS OF 1,3-DIOXOLANE, 1-CHLOROBUTANE AND 2-CHLOROBUTANE

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Vapor-liquid equilibrium at 101.3 kPa has been determined for the binary systems of 1,3-dioxolane, 1-chlorobutane and 2-chlorobutane. The binary systems 1,3-dioxolane-chlorobutanes exhibit positive deviations from ideal behavior while the binary 1-chlorobutane-2-chlorobutane behaves 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 chlorobutanes 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 halogenated organic compounds.

EXPERIMENTAL

Purity of Materials

1, 3-dioxolane (99.4 + mole%), 1-chlorobutane (99.84 + mole%) and 2-chlorobutane (99.9 + mole%) 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 I.

Apparatus and Procedure

An all-glass modified Dvorak and Boublik recirculation still¹ was used in the VLE measurements. The experimental features have been described in a previous

Table I Gas-chromatography analysis.

System	Column filling	Temperature (K)		
		Injector	Column	Detector
1, 3-dioxolane-1-chlorobutane	OV-17	358.15	333.15	533.15
2-chlorobutane-1, 3-dioxolane	Carbowax 20M	573.15	573.15	533.15
2-chlorobutane-1-chlorobutane	SE-30	423.15	333.15	533.15

Table II 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	348.60 ^a
	1.3984 ^b	348.55 ^c
1-chlorobutane (99.8)	1.3999 ^a	351.58 ^a
	1.4000 ^b	351.58 ^a
2-chlorobutane (99.9)	1.3941 ^a	341.24 ^a
	1.3941 ^d	341.25 ^d

^a Measured; ^b Reference 8; ^c Reference 9; ^d Reference 10

publication². 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, and the apparatus was operated under the conditions given in Table II. 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 III–V and Figure 1–4, together with the activity coefficients γ_i which were calculated from the following Eq. (3):

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

where:

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

Table III Experimental vapor-liquid equilibria data for 1,3-dioxolane (1)+ 1-chlorobutane (2) at 101.3 kPa.

T/K	x_1	y_1	γ_1	γ_2	$-B_{11}$ ($\text{cm}^3 \text{mol}^{-1}$)	$-B_{22}$ ($\text{cm}^3 \text{mol}^{-1}$)	$-B_{12}$ ($\text{cm}^3 \text{mol}^{-1}$)
350.73	0.041	0.060	1.3656	1.0057	585	648	600
350.02	0.088	0.122	1.3233	1.0094	589	651	603
348.88	0.173	0.225	1.2876	1.0175	594	657	608
347.63	0.306	0.359	1.2094	1.0424	600	662	614
347.55	0.315	0.369	1.2108	1.0422	600	663	614
346.94	0.424	0.463	1.1513	1.0751	603	666	617
346.61	0.505	0.528	1.1153	1.1100	605	667	618
346.32	0.630	0.628	1.0724	1.1824	606	669	620
346.40	0.696	0.684	1.0496	1.2142	605	668	619
346.60	0.770	0.749	1.0368	1.2725	605	667	619
346.93	0.822	0.801	1.0274	1.2903	603	666	617
347.13	0.873	0.847	1.0168	1.3765	602	665	616
347.44	0.898	0.872	1.0062	1.4313	601	663	615
347.77	0.939	0.921	1.0060	1.4566	600	662	613
347.93	0.947	0.931	1.0031	1.4570	599	661	612
347.21	0.975	0.966	1.0017	1.5091	597	660	611

Table IV Experimental vapor-liquid equilibrium data for 2-chlorobutane-(1),3-dioxolane(2) at 101.3 kPa.

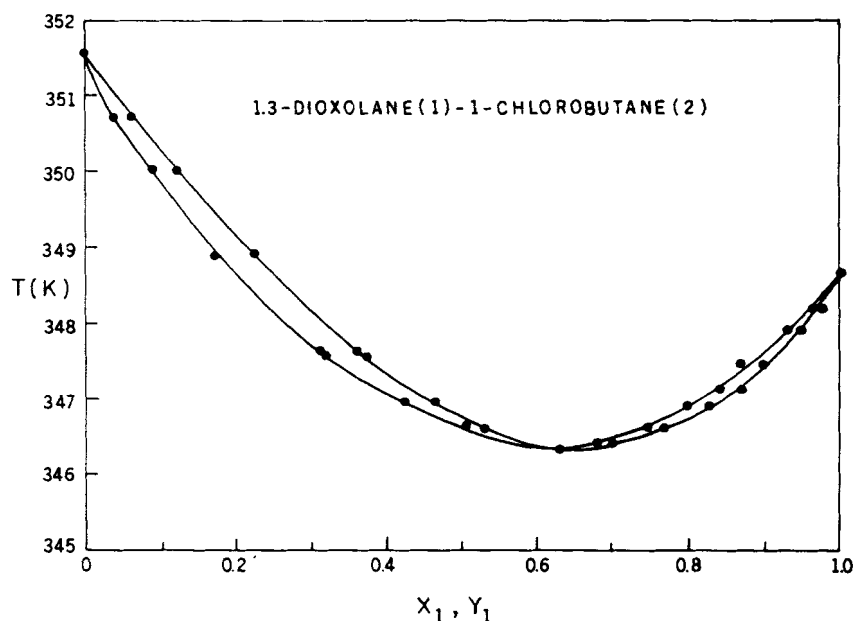
T/K	x_1	y_1	γ_1	γ_2	$-B_{11}$ ($\text{cm}^3 \text{mol}^{-1}$)	$-B_{22}$ ($\text{cm}^3 \text{mol}^{-1}$)	$-B_{12}$ ($\text{cm}^3 \text{mol}^{-1}$)
347.61	0.033	0.058	1.4544	1.0043	687	663	673
346.80	0.059	0.099	1.4217	1.0136	692	666	678
345.73	0.108	0.173	1.4005	1.0167	698	671	683
344.98	0.146	0.217	1.3286	1.0307	702	675	687
344.40	0.174	0.238	1.2439	1.0573	705	678	690
343.83	0.204	0.275	1.2469	1.0639	708	681	693
343.31	0.239	0.312	1.2265	1.0747	711	683	696
342.84	0.277	0.348	1.1971	1.0891	714	686	698
342.33	0.333	0.404	1.1739	1.0979	717	688	701
341.60	0.443	0.501	1.1187	1.1284	721	692	705
341.36	0.469	0.526	1.1175	1.1336	722	693	706
341.83	0.591	0.624	1.0692	1.1888	725	696	709
340.54	0.723	0.729	1.0301	1.2777	727	698	711
340.57	0.808	0.805	1.0169	1.3250	727	698	711
340.51	0.813	0.805	1.0125	1.3632	727	698	711
340.91	0.946	0.940	1.0032	1.4449	725	696	709

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:

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

Table V Experimental vapor-liquid equilibrium data for 2-chlorobutane (1)-1-chlorobutane (2) at 101.3 kPa.

T/K	x_1	y_1	γ_1	γ_2	$-B_{11}$ ($\text{cm}^3 \text{mol}^{-1}$)	$-B_{22}$ ($\text{cm}^3 \text{mol}^{-1}$)	$-B_{12}$ ($\text{cm}^3 \text{mol}^{-1}$)
350.43	0.092	0.121	1.0034	1.0024	673	650	660
349.77	0.146	0.189	1.0064	1.0033	676	653	663
348.59	0.255	0.317	0.9998	1.0043	682	658	669
347.85	0.315	0.386	1.0069	1.0046	686	661	672
346.94	0.411	0.483	0.9916	1.0120	691	666	677
345.82	0.511	0.583	0.9948	1.0183	697	671	682
345.48	0.542	0.616	1.0001	1.0119	699	673	684
343.78	0.728	0.788	1.0027	0.9928	708	681	693
342.81	0.822	0.863	1.0012	1.0113	714	686	698
341.91	0.927	0.946	1.0000	1.0005	719	691	703

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

where the constants A_i , B_i , C_i are reported in Table VI. The molar virial coefficients B_{ii} and B_{ij} were estimated by the method of O'Connell and Prausnitz⁴ 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 III-V and are estimated accurate to within $\pm 3\%$. Inspection of Figures 1 and 3 points to the possibility of an azeotrope

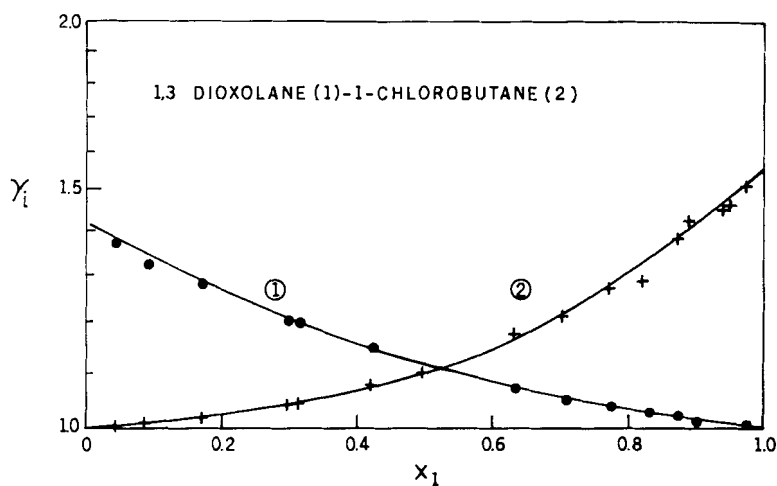


Figure 2 Activity coefficients for the system 1, 3-dioxolane (1)-1-chlorobutane (2) at 101.3 kPa.

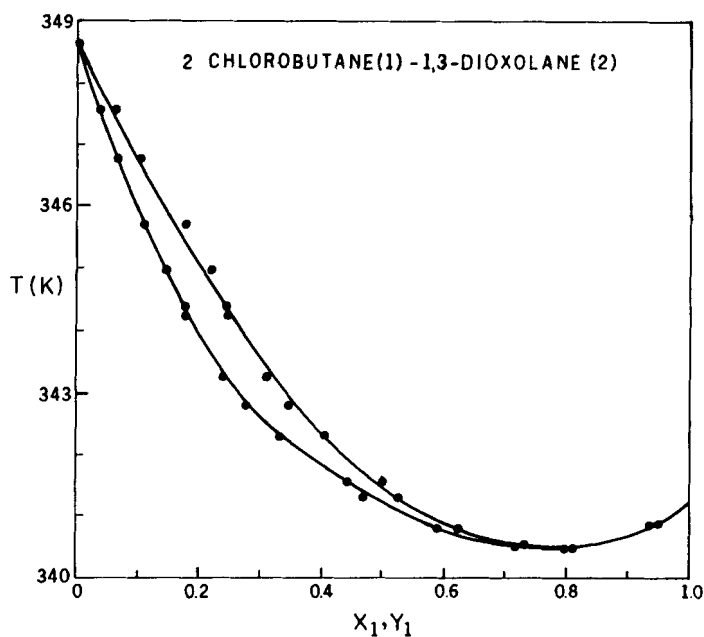


Figure 3 Boiling temperature diagram for the system 2-chlorobutane (1)-1, 3-dioxolane (2) at 101.3 kPa.

in the systems of 1,3-dioxolane-chlorobutanes, which could not be investigated further because of limitations of the analytical method employed. The vapor-liquid equilibria data reported in Tables III-V were found to be thermodynamically consistent by the Redlich-Kister test⁵ and by the L-W method of Wisniak⁶. The activity coefficients for

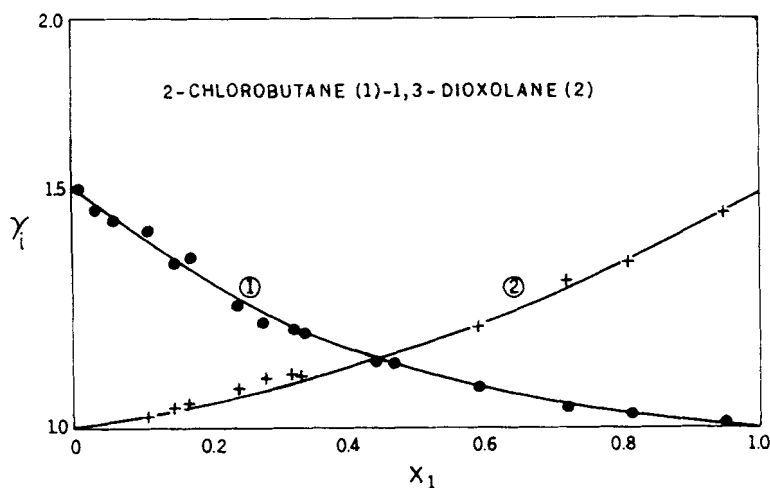


Figure 4 Activity coefficients for the system 2-chlorobutane (1)-1, 3-dioxolane (2) at 101.3 kPa.

Table VI Antoine Coefficients, Eq. 3.

compound	A_i	B_i	C_i
1, 3-dioxolane ¹	6.23182	1236.700	55.915
1-chlorobutane ²	6.05154	1216.82	50.82
2-chlorobutane ²	6.12220	1245.2	38.75

¹ Reference 9; ² Reference 10

the 1,3-dioxolane-chlorobutane binaries were correlated by the Redlich-Kister expansion⁵:

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

The values of the pertinent parameters and statistics appear in Table VII.

The excess Gibbs function of the two systems are presented in Table VIII and Figure 5 as the variation of the dimensionless number (Gibbs number) $\Delta G^E/RT$ with

Table VII Redlich-Kister coefficients, Eq. 4.

System	B	C	D	E	rmsd	% ¹
1, 3-dioxolane + 1-chlorobutane (2)	0.1648	0.0219	—	—	0.003	2.8
2-chlorobutane (1) + 1, 3-dioxolane (2)	0.1569	0.0043	0.0160	-0.0457	0.01	5.9

¹ average % deviation

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

<i>1,3-dioxolane + 1-chlorobutane</i>		<i>1,3-dioxolane + 2-chlorobutane</i>	
x_1	$\Delta G^E/RT$	x_1	$\Delta G^E/RT$
0.000	0.000	0.000	0.000
0.041	0.018	0.033	0.016
0.088	0.033	0.059	0.034
0.173	0.058	0.108	0.051
0.306	0.087	0.146	0.067
0.315	0.089	0.174	0.084
0.424	0.101	0.204	0.094
0.505	0.107	0.239	0.104
0.630	0.106	0.277	0.111
0.696	0.093	0.333	0.116
0.770	0.083	0.443	0.117
0.822	0.068	0.469	0.119
0.873	0.055	0.591	0.110
0.898	0.042	0.723	0.089
0.939	0.029	0.808	0.068
0.947	0.023	0.813	0.068
0.975	0.012	0.946	0.023
1.000	0.000	1.000	0.000

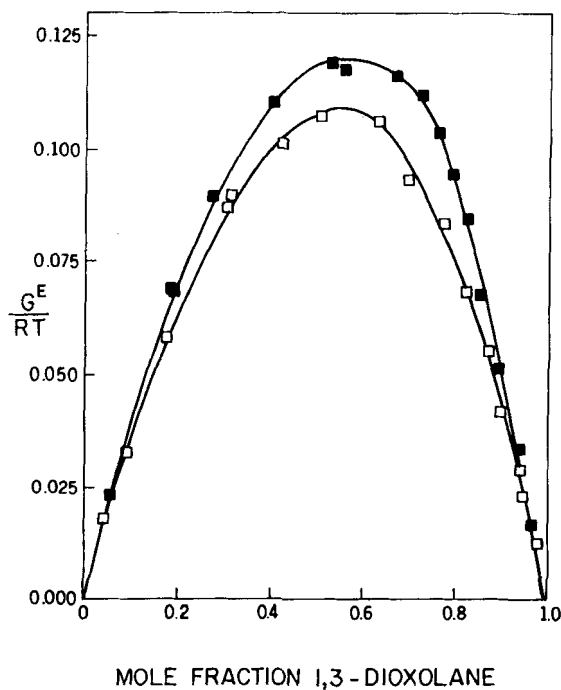

Figure 5 Variation of $\Delta G^E/RT$ with composition for 1-chlorobutane + 1,3-dioxolane (□) and 2-chlorobutane + 1,3-dioxolane (■).

Table IX 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	C_3	rmsd	% ¹
1,3-dioxolane (1) + 1-chlorobutane (2)	-13.596	0.01049	-4.8658	-	0.01	0.05
2-chlorobutane (1) + 1,3-dioxolane (2)	-14.899	5.3845	-5.1755	-	0.01	0.04
2-chlorobutane (1) + 1-chlorobutane (2)	-1.8554	0.5540	-	-	0.01	0.04

¹ average % deviation

composition. The values of the parameter are positive over the entire composition range and fall in the order 2-chlorobutane > 1-chlorobutane due to the larger steric effects of the 2-chloro isomer.

The boiling points of the three binaries were correlated by the equation proposed by Wisniak and Tamir⁷:

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

In this equation T_i^0 is the boiling point of the pure component i (K or $^{\circ}C$) and m is the number of terms in the series expansion of $(x_i - x_j)$. The various constants of equation 5 are reported in Table IX, which also contains information indicating the degree of goodness of the correlation.

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, $\{\sum (T_{\text{expt}} - T_{\text{calc}})^2\}^{0.5}/N$
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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