Table I. 6-Methyl-5-hepten-2-one (1)/Ethyl 3-Oxobutanoate (2) System at 2.7 kPa

X_1	Y_1	temp, °C	X_1	Y_1	temp, °C
1.0000	1.0000	71.5	0.5755	0.6550	72.8
0.9500	0.9585	71.3	0.4610	0.5660	73.6
0.8990	0.9130	71.2	0.3325	0.4255	75.0
0.8435	0.8670	71.5	0.1820	0.2890	76.5
0.7910	0.8265	71.7	0.0620	0.1155	79.0
0.6760	0.7293	72.1	0.0000	0.0000	80.2

Table II. Methanol (1)/1,6-Hexanediol (2) System at 100.0 kPa

X_1	Y_1	temp, °C	X_1	Y_1	temp, °C
1.0000	1.0000	64.3	0.3800	0.9996	92.7
0.9715	1.0000	64.9	0.1370	0.9935	132.5
0.9555	0.9999	65.1	0.0665	0.9640	166.3
0.9260	0.9999	66.1	0.0390	0.8775	191.5
0.8925	0.9999	67.3	0.0275	0.7860	204.5
0.7670	0.9999	71.0	0.0230	0.7240	210.2
0.6915	0.9999	73.4	0.0170	0.6335	218.8
0.5860	0.9999	78.2	0.0060	0.3255	236.5
0.4655	0.9998	85.5	0.0000	0.0000	248.5

Redlich and Kister equation cannot be applied to these data, due to the large temperature difference between the two farthest experimental points. An analogous check with the isobaric Gibbs–Duhem equation is also impossible since the enthalpic data for 1,6-hexanediol are not reported in the literature. The obtained results, however, appear to be coherent on the basis of their graphical representation (Figure 7). All the products used in this work were of 99+ mol% purity.

Concluding Remarks

A flow apparatus represents the most versatile approach presently available for the vapor–liquid determinations at low pressure. The favorable features of flow systems in terms of fast equilibrium attainment and accurate results can be fully exploited by replacing the Cottrell pump with the device proposed in the paper.

The following main advantages of the new apparatus can be stressed: simplified operations under vacuum and at moderate pressures; wide application field for both low- and high-boiling substances and their mixtures; temperature determinations of outstanding accuracy; reduced overheating time, which enables vapor–liquid determinations with temperature-sensitive compounds; applicability to systems showing miscibility gaps.

Finally, high-pressure work can be carried out with the proposed apparatus by simply replacing the glass parts with similar metallic ones, as is currently performed in our laboratories.

Registry No. 6-Methyl-5-hepten-2-one, 110-93-0; ethyl 3-oxobutanoic acid, 141-97-9; methanol, 67-56-1; 1,6-hexanediol, 629-11-8.

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Vapor–Liquid Equilibria in Binary Systems Containing 1,3-Dioxolane at Isobaric Conditions. 5. Binary Mixtures of 1,3-Dioxolane with Cyclohexanone and Cyclohexanol

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This paper presents vapor–liquid equilibrium (VLE) data at 300, 500, and 740 mmHg for the binary systems of 1,3-dioxolane (1)–cyclohexanone and –cyclohexanol. The activity coefficients in the liquid phase are correlated from experimental t,x data by using the Redlich–Kister equation with temperature-dependent parameters. Both systems show deviation from ideality with activity coefficients up to 2.5.

Introduction

As a continuation of earlier works (*1–5*) on isobaric VLE data of binary mixtures containing 1,3-dioxolane (1,3-$C_3H_6O_2$) as a common component, new data for the two systems containing cyclohexanone ($C_6H_{10}O$) and cyclohexanol ($C_6H_{12}O$) as noncommon components are reported.

Measurements are taken in order to detect the effect of a six-membered cyclic ketone and alcohol on a five-membered cyclic ether.

Materials Used

The source and the treatment of 1,3-dioxolane have been given previously (*1*). Cyclohexanone and cyclohexanol (from Carlo Erba, Milan; purity > 99 wt %) were used without further purification. Major impurities were water (0.1 wt %) and cyclohexanol (0.5 wt %) in cyclohexanone and water (0.2 wt %) in cyclohexanol.

Experimental Section

The experimental apparatus was the same as that previously employed (*1–5*). The pressures were measured with an ac-

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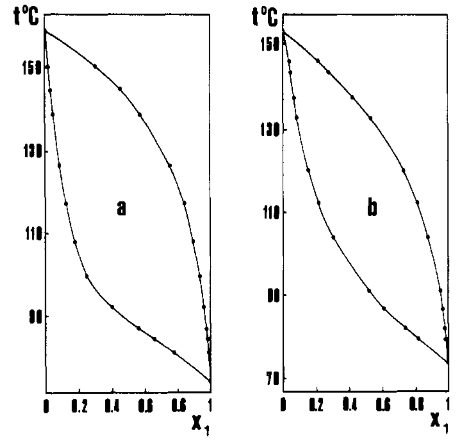

Figure 1. VLE data at 740 mmHg: (●) experimental and (—) smoothed data for (a) 1,3-dioxolane-cyclohexanol and (b) 1,3-dioxolane-cyclohexanone.

Table I. Refractive Index-Composition Data

x_1	$n^{25}{}_D$	x_1	$n^{25}{}_D$
1,3-Dioxolane-Cyclohexanone			
0.0000	1.4517	0.5352	1.4282
0.1163	1.4464	0.6454	1.4225
0.1715	1.4442	0.7163	1.4186
0.2327	1.4418	0.8328	1.4117
0.4169	1.4337	0.9570	1.4036
		1.0000	1.3997
1,3-Dioxolane-Cyclohexanol			
0.0000	1.4660	0.4376	0.4406
0.0984	1.4608	0.5798	1.4315
0.2186	1.4541	0.7335	1.4205
0.3076	1.4486	0.8115	1.4149
0.4095	1.4424	0.9431	1.4045
		1.0000	1.3997

curacy of ±1 mmHg with a mercury manometer. The temperatures were measured by a mercury thermometer to within 0.1 °C.

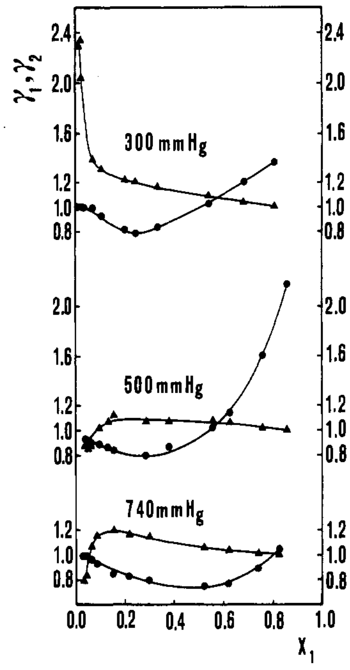

Figure 2. Experimental activity coefficients of the system 1,3-dioxolane-cyclohexanone at P = 300, 500, and 740 mmHg.

The compositions of the liquid and vapor phases were determined by the refractive indexes at 25 °C and with a sodium lamp. An Abbe refractometer was used having an error of ±0.0002 refractive unit. The refractive index-composition data of the two systems are reported in Table I.

Results and Conclusions

Table II presents the experimental P, t, x_1, y_1 data for the two binary systems; x_1 and y_1 are the mole fractions of 1,3-dioxolane in the liquid and vapor phases, respectively. As an example, the VLE data at 760 mmHg are shown in Figure 1.

Table II. P-t-x-y Data

P = 300 mmHg			P = 500 mmHg			P = 740 mmHg		
t/°C	x_1	y_1	t/°C	x_1	y_1	t/°C	x_1	y_1
			1,3-Dioxolane-Cyclohexanone					
49.0	1.000	1.000	62.4	1.000	1.000	73.8	1.000	1.000
53.8	0.808	0.980	66.4	0.855	0.975	79.4	0.820	0.983
57.0	0.687	0.967	69.3	0.755	0.965	81.9	0.740	0.977
61.5	0.540	0.950	73.2	0.625	0.955	86.5	0.620	0.965
72.1	0.333	0.905	75.8	0.555	0.947	91.0	0.520	0.950
79.2	0.245	0.870	86.7	0.378	0.905	103.9	0.300	0.877
83.6	0.200	0.827	94.3	0.285	0.867	112.3	0.215	0.813
94.9	0.107	0.673	107.7	0.157	0.735	120.3	0.153	0.730
101.0	0.070	0.560	112.3	0.130	0.673	132.7	0.085	0.535
109.2	0.025	0.370	119.3	0.097	0.567	137.5	0.065	0.425
111.7	0.017	0.310	128.0	0.065	0.405	143.7	0.047	0.275
114.0	0.013	0.247	130.2	0.055	0.350	146.3	0.035	0.207
122.6	0.000	0.000	132.2	0.043	0.297	153.2	0.000	0.000
			139.3	0.000	0.000			
			1,3-Dioxolane-Cyclohexanol					
49.0	1.000	1.000	62.4	1.000	1.000	73.8	1.000	1.000
52.8	0.850	0.990	68.5	0.770	0.980	81.1	0.773	0.983
55.0	0.745	0.987	71.4	0.665	0.975	84.5	0.655	0.975
59.3	0.555	0.983	77.2	0.480	0.973	86.9	0.560	0.970
70.2	0.270	0.965	88.4	0.287	0.935	92.0	0.400	0.955
78.3	0.170	0.935	99.0	0.187	0.887	99.6	0.250	0.933
83.6	0.123	0.910	109.0	0.130	0.825	108.0	0.175	0.890
98.0	0.065	0.810	116.0	0.090	0.730	117.2	0.123	0.837
107.2	0.045	0.700	112.0	0.065	0.623	126.4	0.087	0.753
115.2	0.027	0.523	129.5	0.040	0.465	138.5	0.047	0.575
118.7	0.020	0.425	135.9	0.025	0.305	144.7	0.031	0.455
123.0	0.015	0.300	142.0	0.010	0.133	150.0	0.020	0.305
131.5	0.000	0.000	146.3	0.000	0.000	158.7	0.000	0.000

Table III. Values of Constants A and B in the Vapor Pressure Expression $\log P°_i = A + B/T$ for Cyclohexanone and Cyclohexanol

	cyclohexanone	cyclohexanol
A	7.8155	8.8322
B	-2110.4	-2572.9

In Figures 2 and 3 the experimental liquid-phase activity coefficients γ_1 and γ_2 are reported for the systems 1,3-dioxolane-cyclohexanone and 1,3-dioxolane-cyclohexanol, respectively. The activity coefficients were calculated with the expression $\gamma_i = y_iP/(x_iP°_i)$, $i = 1, 2$, where the vapor pressures of the pure substances $P°$ were correlated by the usual expression $\log P°_i = A + B/T$ ($P°_i$ in mmHg and T the absolute temperature). The constants A and B, relative to the noncommon components, were obtained by fitting experimental data of this work with a least-squares method and are presented in Table III. The values of A and B for 1,3-dioxolane are those quoted in ref *4*. The system 1,3-dioxolane-cyclohexanone at 300 mmHg and the system 1,3-dioxolane-cyclohexanol at 740 mmHg satisfy Herington's test ($D < J$). All other VLE data of the two systems do not satisfy this test, and the presence of associations may be suspected owing to the limited scattering of x,y points after rechecking the analytical procedure and the duplication of experiments. Furthermore, the wide difference between the boiling points of the pure compounds casts some doubt on the validity of Herington's test (*6*).

The activity coefficients were correlated by the Redlich-Kister equations (*7*)

$$\ln \gamma_1 = x_2^2[C + D(3x_1 - x_2) + E(x_1 - x_2) \times (5x_1 - x_2) + F(x_1 - x_2)^2(7x_1 - x_2)] \quad (1)$$

$$\ln \gamma_2 = x_1^2[C + D(x_1 - 3x_2) + E(x_1 - x_2) \times (x_1 - 5x_2) + F(x_1 - x_2)^2(x_1 - 7x_2)] \quad (2)$$

with three adjustable, temperature-dependent parameters C, D, and E, of the form

$$C = C_1 + C_2/T \qquad D = D_1 + D_2/T \qquad E = E_1 + E_2/T \quad (3)$$

and the temperature-independent parameter F_1.

The adjustable parameters of eq 2 and 3 are calculated with a least-squares method and listed in Table IV, together with their estimated standard errors and the root-mean-square deviation σ. In the calculations, a computer program, based on the algorithms of Nelder and Mead (*9*) and Fletcher (*10*), was used and the objective function is minimized

$$\Phi = \sum_{k=1}^{n} (P_{\text{exptl}} - P_{\text{calcd}})^2 \quad (4)$$

where n is the number of experimental points and P_{calcd} is evaluated from

$$P_{\text{calcd}} = \sum_{k=1}^{2} Py_k = \sum_{k=1}^{2} \gamma_k x_k P°_k \quad (5)$$

with γ_k given by eq 1.

A number of parameters higher or lower than seven causes an increase of Φ and σ, as happens when the most appropriate order of the polynomial fitting experimental data is to be found (*11*).

The activity coefficients γ_1 and γ_2 were also correlated by using Wilson, LEMF, and NRTL equations, but, in these cases,

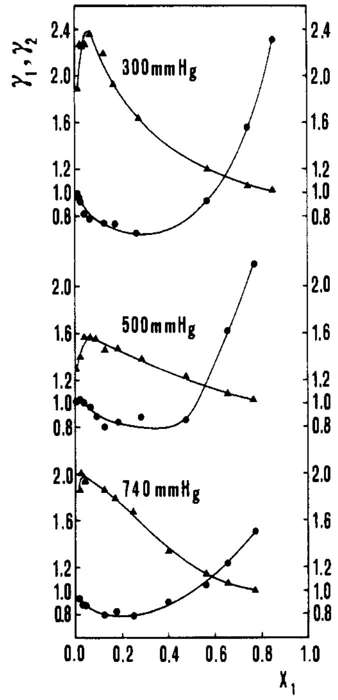

Figure 3. Experimental activity coefficients for the system 1,3-dioxolane-cyclohexanol at P = 300, 500, and 740 mmHg.

Table IV. Values of the Parameters Obtained from VLE Data by the Redlich-Kister Equation 1[a]

parameters	P = 300 mmHg	P = 500 mmHg	P = 740 mmHg
		1,3-Dioxolane (1)-Cyclohexanone (2)	
C_1	1.323 ± 0.001	-0.272 ± 0.001	-0.234 ± 0.001
C_2	359.4 ± 0.5	199.5 ± 0.3	187.7 ± 0.2
D_1	-1.135 ± 0.003	2.824 ± 0.001	2.533 ± 0.001
D_2	474 ± 1	-1001.2 ± 0.3	-979.6 ± 0.5
E_1	9.788 ± 0.005	-14.599 ± 0.001	-6.764 ± 0.002
E_2	-3379 ± 2	5325 ± 3	2546.6 ± 0.8
F_1	0.471 ± 0.007	-1.136 ± 0.001	-0.423 ± 0.005
σ	2.6	3.9	9.7
		1,3-Dioxolane (1)-Cyclohexanol (2)	
C_1	-0.94 ± 0.03	0.557 ± 0.001	-0.22 ± 0.08
C_2	669 ± 12	-16 ± 3	377 ± 33
D_1	3.0 ± 0.1	-1.12 ± 0.02	0.5 ± 0.2
D_2	-1078 ± 41	472 ± 9	-243 ± 73
E_1	-1.79 ± 0.07	3.0 ± 0.1	-0.80 ± 0.03
E_2	677 ± 26	-1135 ± 50	206 ± 7
F_1	-0.32 ± 0.01	0.21 ± 0.01	-0.05 ± 0.01
σ	1.9	2.7	6.4

[a] The uncertainty of a parameter is defined as the variation of the parameter giving rise to a variation of σ_P^2 in the objective function Φ in the minimum (*12*), where σ_P^2 is the (estimated) variance of P (σ_P = 1 mmHg). $\sigma = \{\Sigma_{k=1}^{n}(P_{\text{exptl}} - P_{\text{calcd}})^2/(n - n_P)\}^{1/2}$. n_P = 7 = number of adjustable parameters.

the values of σ were 2–3 times those given in Table IV. This result is not surprising if we consider Figures 2 and 3 showing activity coefficients with maximum and minimum as a function of composition, particularly for the system 1,3-dioxolane–cyclohexanol. Moreover, both systems have activity coefficients up to 2.5 and present, for a wide composition range, deviations from the Raoult law which are positive for 1,3-dioxolane ($\gamma_1 >$ 1) and negative for the six-membered cyclic compounds ($\gamma_2 <$ 1).

Registry No. 1,3-Dioxolane, 646-06-0; cyclohexanone, 108-94-1; cyclohexanol, 108-93-0.

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NEW COMPOUNDS

Synthesis and High-Resolution Mass-Spectral Analysis of Isotopically Labeled 2,4,6-Trinitrotoluene

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The high-resolution electron impact spectra of 2,4,6-trinitrotoluene (TNT) and its ^2H and ^{15}N isotopic derivatives have been determined. 2,4,6-Trinitrotoluene loses an OH group to form the major ion, *m/e* 210, which undergoes various fragmentation reactions. The parent ion of 2,4,6-trinitrotoluene, *m/e* 227, loses three NO_2 groups to form the second most abundant ion, $C_7H_5^+$, which then rearranges to form a tropylium-like ion. The $C_7H_5^+$ species then undergoes loss of C_2H_2 to form $C_5H_3^+$, in a manner similar to tropylium.

Introduction

In previous years, this laboratory has undertaken various studies (*1–3*) to determine the mechanism of the thermochemical decomposition reactions of 2,4,6-trinitrotoluene (TNT). Recently, we reported the results of quantum-mechanical calculations and X-ray crystallographic studies of TNT (*4*). This latter investigation established that TNT exists in two different forms within the unit cell, and both forms are stabilized by extensive hydrogen bonding. With the above in mind, we have synthesized several ^{15}N and ^2H isotopic versions of TNT, to observe the effects of such substitution on the mass-spectral degradation of TNT.

Experimental Section

Instrumentation. All high-resolution mass spectra reported herein were obtained with a Kratos MS-50 double-focusing mass spectrometer operating at 70 eV with a resolution of 180 000 (10% valley), coupled to an INCOS data system. Samples were introduced via the direct insertion probe at ambient temperature. The source temperature was set at 250 °C for the measurement of normal spectra. Metastables were observed in the second field-free region between the electrostatic analyzer and magnet and were recorded with a light beam oscillographic recorder. Fragmentation pathways were confirmed by using mass-analyzed kinetic energy spectrometry (MIKES) and helium collisionally activated MIKES.

^1H NMR spectra were obtained with a Varian T-60A spectrometer operating at ambient temperature. The melting points were determined with a Reichert micro hot stage melting point apparatus equipped with a calibrated thermometer.

Synthesis of TNT. This was synthesized by using a modified version of a previous method (*5*). A 75-mL sample of fuming sulfuric acid (15% oleum) was cooled to 0 °C, and 27 mL of 90% nitric acid was added dropwise. This mixed acid solution was warmed to room temperature and 35.4 g of 2,4-dinitrotoluene was added. Gentle stirring was started and continued from this point on. The temperature was slowly raised to 90 °C (60 min), at which point the resulting exothermic reaction required cooling to keep the temperature below 120 °C. The reaction was maintained at 90–100 °C for the next 2 h. The reaction was then cooled and allowed to stand overnight at 25 °C. The resulting mixture was then extracted with 800 mL of methylene chloride. The methylene chloride layer was neutralized with 500 mL of saturated sodium carbonate solution and washed twice with 500 mL of distilled water. The methylene chloride was removed with a roto-vac, and the solid TNT recrystallized from ethanol and CCl_4; 27.2 g of product (mp 81.5–82.0 °C) was obtained (62% yield).

Synthesis of α-d_3-TNT. This was synthesized by a modified version of a previous method (*1*) as follows: A solution was prepared containing 0.5 g of TNT, 15 mL of $(CD_3)_2CO$, 6 mL of CH_3OD, and 3 mL of D_2O; 0.1 mL of triethylamine was added to the above solution and the mixture at room temperature for

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