the adiabatic sound frequency, ω_s. The adiabatic sound frequency is given by the frequency shift of the Brillouin peaks from the laser frequency relative to the splitting between adjacent orders of the Brillouin spectra. The splitting between the adjacent orders is the FSR and is used to calibrate the frequency shift of the digitized data.

The sound velocity was calculated with eq 1

$$C_s = 2\pi\omega_s/q \qquad (1)$$

where C_s is the sound velocity and q is the scattered wave vector. The scattered wave vector is given by

$$q = (4\pi n/\lambda)\sin(\theta/2) \qquad (2)$$

where n is the refractive index, λ is the wavelength of the incident light, and θ is the scattering angle. For our measurements the scattering angle was 90°. The refractive indices were obtained from published values (*3*).

A thousand data points were taken over two spectral orders. All the spectra were fitted to a Lorentzian line shape by using a Simplex fitting routine from which the ω_s values were obtained (*4*).

The isentropic compressibility, χ_s, was calculated with

$$\chi_s = C_s^{-2}\rho^{-1} \qquad (3)$$

where ρ is the density. Values for the density as a function of temperature were also obtained from the literature (*5*). The refractive indices and densities were interpolated from the values in the literature. From the given uncertainty in the reported values of density and refractive indices the error is much less than 1% and does not contribute significantly to the error in the reported velocities. The major source of error is in the uncertainty in the FSR (±2%) which produces systematic error in all the data.

The quoted value in the literature of the speed of sound for formamide at 298 K was 1622 ms^{-1} (*6*). This value was determined by ultrasonic methods and is within the quoted error of our value.

Registry No. Formamide, 75-12-7.

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Vapor–Liquid Equilibria in Binary Systems Containing 1,3-Dioxolane at Isobaric Conditions. 4. Binary Mixtures of 1,3-Dioxolane with 1,4-Dioxane and 1,1,2,2-Tetrachloroethane

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Isobaric vapor–liquid equilibria (VLE) for the binary systems 1,3-dioxolane–dioxane and 1,3-dioxolane–tetrachloroethane were measured at 150, 300, 500, 650, and 740 mmHg by using a Stage–Müller distilling apparatus. The Redlich–Kister equation, with temperature-dependent parameters, was used to correlate the VLE data. A one-temperature-dependent-parameter equation is sufficient for the system 1,3-dioxolane–dioxane and for the system 1,3-dioxolane–tetrachloroethane at P = 150 and P = 740 mmHg, whereas a two-temperature-dependent-parameter equation is needed for the second system at P = 300, 500, and 650 mmHg.

Isobaric vapor–liquid equilibria (VLE) data at several subatmospheric pressures were determined for the binary systems of 1,3-dioxolane (1) with 1,4-dioxane (2) and with 1,1,2,2-tetrachloroethane (tetrachloroethane) (2). This study is a continuation of the systematic acquisition of isobaric VLE data for binary systems containing 1,3-dioxolane as a common component (*1–4*).

Table I. Refractive Index–Composition Data for 1,3-Dioxolane–Dioxane

x_1	n^{25}_D	x_1	n^{25}_D
1.0000	1.3992	0.4446	1.4123
0.9189	1.4012	0.3720	1.4139
0.8305	1.4035	0.2306	1 4168
0.7197	1.4062	0.1662	1.4181
0.6272	1.4084	0.0951	1.4195
0.5410	1.4103	0.0000	1.4214

Experimental Section

The Fluka product 1,3-dioxolane (analytical grade, 99%) was purified by refluxing on sodium in inert gas flow and fractionated on a Vigreux column, following the procedure given in ref *1*. Dioxane and tetrachloroethane (C. Erba RPE products) were used without purification. Their major impurity is water (0.02% and 0.05%, respectively). The refractive indices of dioxane and tetrachloroethane are n^{20}_D = 1.4224 (lit. (*5*) n^{20}_D = 1.4224) and n^{20}_D = 1.4944 (lit. (*5*) n^{20}_D = 1.4940), respectively. The isobaric VLE data were determined with a Stage–Müller distilling

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Table II. Refractive Index-Composition Data for 1,3-Dioxolane-Tetrachloroethane

x_1	n^{25}_D	x_1	n^{25}_D
1.0000	1.3992	0.5277	1.4545
0.9521	1.4052	0.4442	1.4620
0.9123	1.4107	0.3480	1.4698
0.8296	1.4223	0.2680	1.4758
0.7046	1.4368	0.2573	1.4763
0.6003	1.4476	0.1176	1.4855
		0.0000	1.4922

Table III. Values of Constants A and B in the Vapor Pressure Expression $\log P^\circ = A + B/T$ for Dioxane and Tetrachloroethane

	dioxane	tetrachloroethane
A	7.9864	7.9649
B	−1907.7	−2129.6

apparatus (*6*), with the procedure used in previous works (*1–4*), at the pressures P = 150, 300, 500, 650, and 740 mmHg, with a maximum estimated uncertainty of 2 mmHg. The composition x and y of the liquid phase and the vapor condensate samples was determined by a precision Abbe refractometer (Galileo, Milan, Italy), thermostated at 25 ± 0.01 °C, with an accuracy of 5×10^{-5} unit. Refractive index-composition data for the mixtures of 1,3-dioxolane with dioxane and tetrachloroethane are reported in Tables I and II, respectively. The equilibrium temperature t was measured to within 0.1 °C.

Results

The vapor pressures of the pure compounds were correlated by the usual expression $\log P^0 = A + B/T$ (P^0 in mmHg and T the absolute temperature). The constants A and B of dioxane and tetrachloroethane, obtained from VLE data of this work with a least-squares method, are reported in Table III. Table IV shows the experimental t-x_1-y_1 data for the two systems studied. The set of isobaric VLE data, determined at P = 740 mmHg, is also reported, as an example, in Figure 1 (curve a, 1,3-dioxolane–tetrachloroethane; curve b, 1,3-dioxolane–dioxane).

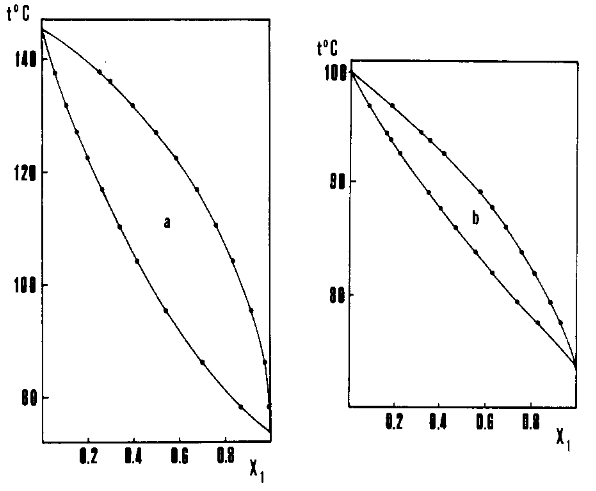

Figure 1. t-x_1-y_1 values: (a) system 1,3-dioxolane–tetrachloroethane, P = 740 mmHg; (b) system 1,3-dioxolane–dioxane, P = 740 mmHg.

The activity coefficients γ_k in the liquid phase were evaluated from the experimental data by means of the formula

$$\gamma_k = Py_k/P_k{}^0x_k \qquad (k = 1, 2) \tag{1}$$

where P is the total pressure on the system. The activity coefficient γ_k of the two systems satisfied the semiintegral consistency criterion (*1*), with the assumption of no association in the vapor phase. The activity coefficients γ_k were correlated by using the Redlich–Kister equation (equivalent to the Margules equation (*6*)):

$$\ln \gamma_k = x_j^2[C + (-1)^j D(3x_k - x_j)] \qquad (k, j = 1,2;\ k = j) \tag{2}$$

where C and D are adjustable parameters obtained with the least-squares method. The objective function used, Φ, is the sum of the squared deviations between the experimental

Table IV. t-x-y Data for 1,3-Dioxolane–Tetrachloroethane and 1,3-Dioxolane–Dioxane

P = 150 mmHg			P = 300 mmHg			P = 500 mmHg			P = 650 mmHg			P = 740 mmHg		
t/°C	x_1	y_1	t/°C	x_1	y_1	t/°C	x_1	y_1	t/°C	x_1	y_1	t/°C	x_1	y_1
						1,3-Dioxolane–Tetrachloroethane								
32.4	1.000	1.000	48.8	1.000	1.000	62.4	1.000	1.000	69.9	1.000	1.000	73.8	1.000	1.000
34.1	0.948	0.999	50.9	0.891	0.998	73.2	0.703	0.978	73.7	0.875	0.999	78.0	0.870	0.995
36.4	0.866	0.998	55.9	0.752	0.988	81.8	0.558	0.948	78.6	0.775	0.995	85.9	0.702	0.978
40.3	0.764	0.995	62.8	0.608	0.962	89.8	0.488	0.912	85.0	0.645	0.976	95.2	0.540	0.915
45.0	0.657	0.982	67.8	0.529	0.957	96.0	0.370	0.845	92.0	0.527	0.946	104.0	0.420	0.835
50.0	0.558	0.968	76.0	0.430	0.900	103.7	0.280	0.730	102.0	0.395	0.855	110.2	0.356	0.755
62.4	0.382	0.859	84.3	0.333	0.808	110.9	0.200	0.616	110.0	0.312	0.764	116.8	0.260	0.680
68.7	0.281	0.778	90.4	0.262	0.722	115.1	0.156	0.546	115.7	0.254	0.682	122.3	0.200	0.585
74.6	0.216	0.646	95.8	0.200	0.595	120.0	0.115	0.415	121.5	0.202	0.580	127.0	0.155	0.500
82.5	0.128	0.458	106.1	0.095	0.346	124.7	0.066	0.244	130.2	0.096	0.337	131.6	0.110	0.394
85.8	0.090	0.377	108.2	0.080	0.275	127.0	0.044	0.186	133.1	0.079	0.257	136.0	0.065	0.300
88.0	0.070	0.310	110.1	0.058	0.240	128.4	0.038	0.150	134.4	0.062	0.219	137.3	0.052	0.250
98.0	0.000	0.000	115.1	0.000	0.000	130.9	0.000	0.000	140.2	0.000	0.000	144.9	0.000	0.000
						1,3-Dioxolane–Dioxane								
32.4	1.000	1.000	48.8	1.000	1.000	62.4	1.000	1.000	69.9	1.000	1.000	73.8	1.000	1.000
35.4	0.820	0.928	52.3	0.811	0.907	66.3	0.796	0.907	73.6	0.842	0.940	77.6	0.830	0.930
37.4	0.701	0.867	53.9	0.714	0.859	68.7	0.671	0.839	75.8	0.730	0.884	79.4	0.734	0.883
39.0	0.610	0.815	55.8	0.596	0.800	71.1	0.555	0.780	78.2	0.628	0.812	82.0	0.625	0.810
41.0	0.484	0.751	57.7	0.508	0.738	72.8	0.476	0.715	80.6	0.508	0.726	83.8	0.550	0.755
43.9	0.373	0.637	61.4	0.312	0.585	76.8	0.326	0.586	82.6	0.440	0.658	86.0	0.464	0.692
45.3	0.322	0.578	63.0	0.260	0.512	78.5	0.269	0.488	84.4	0.364	0.590	87.8	0.402	0.628
46.7	0.270	0.502	64.6	0.206	0.440	81.0	0.196	0.382	85.8	0.316	0.526	89.2	0.344	0.577
48.3	0.216	0.435	66.0	0.160	0.373	82.3	0.150	0.316	88.5	0.216	0.398	92.6	0.222	0.407
50.6	0.136	0.293	67.8	0.100	0.278	83.3	0.124	0.269	89.8	0.176	0.340	93.7	0.170	0.350
51.4	0.104	0.246	68.8	0.080	0.231	84.6	0.080	0.196	90.9	0.144	0.284	94.4	0.150	0.312
56.8	0.084	0.196	69.9	0.060	0.180	86.0	0.045	0.115	92.7	0.084	0.186	96.8	0.080	0.186
54.0	0.040	0.105	70.0	0.050	0.155	87.8	0.000	0.000	95.7	0.000	0.000	99.7	0.000	0.000
56.0	0.000	0.000	72.6	0.000	0.000									

Table V. Redlich-Kister Parameters[a]

parameters	press., mmHg 150	300	500	650	740
			1,3-Dioxolane (1)-Dioxane (2)		
c	0.63 ± 0.07	6.92 ± 0.04	−0.47 ± 0.20	2.55 ± 0.17	3.01 ± 0.15
γ	−200 ± 24	−2253 ± 1	172 ± 70	−940 ± 60	−1121 ± 53
			1,3-Dioxolane (1)-Tetrachloroethane (2)		
c	2.87 ± 0.15	3.27 ± 0.03	−0.47 ± 0.04	−0.79 ± 0.03	1.65 ± 0.01
γ	−1290 ± 52	−1484 ± 1	9.0 ± 14	13.9 ± 1.5	−861.3 ± 0.3
d		−247 ± 0.13	−1.26 ± 0.07	0.032 ± 0.01	
δ		1003 ± 45	459 ± 26	8.5 ± 4	

[a] The uncertainty of the 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 (*11*), where σ_P^2 is the (estimated) variance of $P(\sigma_P = 2 \text{ mmHg})$.

pressure and the pressure calculated from eq 1, with γ_k given by eq 2:

$$\Phi = \sum_{k=1}^{n} (P_{\text{exptl}} - P_{\text{calcd}})^2 \qquad (3)$$

where n is the number of experimental points.

The minimization is first performed by using the Nelder and Mead method (*7*), which generally converges for a wider class of functions, but gives only estimates of the parameter errors and is then repeated by using the Fletcher algorithm (*8*), in order to obtain better precision and a more complete covariance matrix.

The goodness of fit was tested by the average deviation $\Delta\gamma_k$ between the γ_k's obtained by eq 1 from experimental data and the γ_k's calculated by eq 2 with parameters drawn from least squares. We believe that we have a satisfactory correlation of γ_k when $\Delta\gamma_k$ compares with the standard error of the γ_k's, calculated from eq 1 with the well-known rules of estimation (*9*).

The Redlich-Kister equation 2 leads to a good correlation of the γ_k's for the system 1,3-dioxolane-dioxane, whereas γ_k's of the system 1,3-dioxolane-tetrachloroethane were badly correlated (the resulting $\Delta\gamma_k$'s were very large, up to 100%). Hence, as was done in ref *10*, the parameters C and D were allowed to vary with the temperature, according to the expressions

$$C = c + \gamma/T \qquad (4)$$

$$D = c + \delta/T \qquad (5)$$

In this way, a notable improvement in the correlation of the γ_k's for the system 1,3-dioxolane-tetrachloroethane was realized. The one-temperature-dependent-parameter equation

$$\ln \gamma_k = x_j^2(c + \gamma/T) \qquad (6)$$

was sufficient to correlate the γ_k's for the system 1,3-dioxolane-tetrachloroethane at $P = 150$ and $P = 740$ mmHg, whereas the two-temperature-dependent-parameter equation

$$\ln \gamma_k = x_j^2[(c + \gamma/T) + (-1)^j(3x_k - x_j)(d + \delta/T)] \qquad (7)$$

was needed for the same system at $P = 300$, 500, and 650 mmHg. Equations 6 and 7 were used to correlate the γ_k's of the system 1,3-dioxolane-dioxane, in order to make a comparison with the results obtained previously with eq 2. No significant differences were found in the values of $\Delta\gamma$ and σ but the parameters of the three equations 2, 6, and 7 had different uncertainties; the lowest of them (referring to the parameters c and γ of eq 6) are shown in Table V.

The Redlich-Kister parameters C, D, c, γ, d, δ obtained with the least-squares method are presented in Table V, together with their estimated standard errors.

Table VI. Average Deviations between Experimental and Calculated Activity Coefficients, $\Delta\gamma$, and Standard Deviations, σ

	press., mmHg 150	300	500	650	740
		1,3-Dioxolane (1)-Dioxane (2)			
$\Delta\gamma_1$[a]	0.032	0.044	0.062	0.030	0.053
$\Delta\gamma_2$[a]	0.035	0.040	0.046	0.039	0.044
σ[b]	1.5	2.2	2.1	3.8	4.4
		1,3-Dioxolane (1)-Tetrachloroethane (2)			
$\Delta\gamma_1$[a]	0.009	0.005	0.024	0.015	0.014
$\Delta\gamma_2$[a]	0.084	0.027	0.110	0.095	0.062
σ[b]	0.7	2.53	4.07	4.67	3.65

[a] $\Delta\gamma = \sum_{k=1}^{n} |\gamma_{k,\text{exptl}} - \gamma_{k,\text{calcd}}|/n$. [b] $\sigma = [\sum_{k=1}^{n}(P_{\text{exptl}} - P_{\text{calcd}})^2/(n - n_{\text{p}})]^{1/2}$. n_{p} = number of adjustable parameters.

Table VI shows the average deviation $\Delta\gamma_k$ between calculated and experimental γ_k and $\sigma = \Phi_{\text{min}}/(n - n_{\text{p}})$, where n_{p} is the number of the adjustable parameters and Φ_{min} is the minimum value of the objective function obtained from regression. Also Wilson, NRTL, and LEMF equations were tested in order to correlate the experimental γ_k. Again, we find that the γ_k's of the system 1,3-dioxolane-dioxane are fairly correlated by these equations, particularly by the LEMF equation (which gives values of $\Delta\gamma_k$ and σ practically coincident with the ones of the Redlich-Kister equation 2). On the other hand, none of these equations were able to interpolate adequately the γ_k's of the system 1,3-dioxolane-tetrachloroethane: both $\Delta\gamma_k$ and σ were markedly higher than those obtained from the temperature-dependent-parameter Redlich-Kister equation.

Registry No. 1,3-Dioxolane, 646-06-0; tetrachloroethane, 79-34-5; dioxane, 123-91-1.

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