Table I. Solubility of Substances in Liquid Xenon at 60-95-atm Pressure and 0-40 °C Temperatures

substance	soluble	insoluble	estimated amount dissolved, g mL^{-1}
picric acid	X		5×10^{-3}
picrate ion (both DABH$^+$ and H$^+$ as counterions)		X	
p-nitrophenol	X		3×10^{-3}
p-nitrophenolate ion (protonated triethylamine counterion)		X	
p-nitrophenolate-protonated triethylamine (ion pair)		X	
p-nitrophenol-triethylamine (neutral complex)	X		4×10^{-3}
(dimethylamino)azobenzene (DAB)	X		1.6×10^{-5}
DABH$^+$ (picrate counterion)		X	
tetrabutylammonium picrate (ion pair)		X	
fluorenyl anion-dibenzo-30-crown-10/K$^+$ complex		X	
crystal violet (chloride salt)		X	
crystal violet (perchlorate salt)		X	

and fittings from High Pressure Equipment Co., Erie, PA, were used to connect the cell to the pressurizing apparatus. The xenon was pressurized by condensing into a cylinder from the supply cylinder using liquid nitrogen, closing off the supply, and then allowing the cylinder to warm back up to room temperature. Final pressurization was achieved with a volume reducing hand crank pressure generator. The cell was thermostated by circulating fluid through the inside of the top of the cell. Solubility observations were made spectrophotometrically with a Cary 14 spectrophotometer.

Discussion and Results

Solutes were selected for study on the basis of their promise for producing weak electrolyte equilibria involving ion pairs that would be susceptible to rate studies by the spectrophotometric electric field jump relaxation technique (*4*). It was hoped that a spreading of electrical charge over larger ions would enhance their solubility in xenon.

The solubility observations are summarized in Table I. Problems were experienced with the materials coating the bottom of the cell and the cell windows, so the reported quantitative solubilities are not intended to represent the maximum molar solubility of the materials. The values are intended only as a rough guide. All observations of actual dissolution were confirmed by at least one repetition of the experiment. Solubility in all cases was observed to improve drastically when the pressure was increased from 60 to 80 atm, and then more slowly from 80 to 95 atm. From these solubility data it appears that xenon in the pressure regimes studied here will not be a useful solvent for kinetic investigations of weak electrolyte equilibria.

Acknowledgment

The possible use of xenon as a solvent in E-jump kinetic studies was drawn to our attention by Peter Rentzepis of Bell Labs. Jiri Jonas, University of Illinois, made helpful suggestions regarding the construction of high-pressure sample cells.

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Vapor-Liquid Equilibria in Binary Systems Containing 1,3-Dioxolane at Isobaric Conditions. 1. Binary Mixtures of 1,3-Dioxolane with 1,2-*trans*-Dichloroethylene, Trichloroethylene, and Tetrachloroethylene

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The vapor-liquid equilibrium data of the binary mixtures of 1,3-dioxolane with 1,2-*trans*-dichloroethylene, trichloroethylene, and tetrachloroethylene were obtained with a Stage-Müller apparatus at isobaric subatmospheric pressures. The values of the activity coefficients were correlated by means of the Wilson expression, whose parameters show a marked dependence on the temperature.

In two previous papers (*1*, *2*) the system 1,3-dioxolane-water was studied with the aim of finding satisfactory correlations both of the vapor-liquid data and of the liquid-phase enthalpy of mixing ΔH_m. We chose this system on account of the strong nonideality in the liquid phase and of the anomalous ΔH_m curve showing an inversion of sign as a function of the

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Table I. *t-x-y* Data for 1,3-Dioxolane-1,2-*trans*-Dichloroethylene

$P = 740$ mmHg			$P = 650$ mmHg			$P = 500$ mmHg			$P = 300$ 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
73.8	1.000	1.000	69.9	1.000	1.000	62.4	1.000	1.000	49.0	1.000	1.000
72.7	0.960	0.906	69.1	0.968	0.920	60.2	0.937	0.854	46.5	0.922	0.830
69.0	0.864	0.710	64.9	0.852	0.682	55.6	0.804	0.618	44.0	0.855	0.690
65.9	0.774	0.562	61.8	0.754	0.560	53.1	0.724	0.498	41.8	0.784	0.586
64.0	0.698	0.482	60.1	0.701	0.477	51.2	0.658	0.419	39.9	0.730	0.498
61.8	0.636	0.390	58.6	0.651	0.415	50.2	0.616	0.374	38.3	0.668	0.426
59.6	0.559	0.312	57.1	0.601	0.360	49.0	0.566	0.326	37.0	0.622	0.376
56.5	0.440	0.226	52.0	0.417	0.195	46.0	0.457	0.229	32.4	0.450	0.210
55.6	0.401	0.190	50.5	0.350	0.158	44.5	0.400	0.182	30.4	0.364	0.156
53.9	0.338	0.143	49.4	0.310	0.125	43.3	0.348	0.146	29.0	0.312	0.119
52.9	0.296	0.119	48.5	0.269	0.096	42.1	0.306	0.116	27.8	0.264	0.089
51.8	0.229	0.092	46.1	0.158	0.049	39.7	0.249	0.086	26.4	0.205	0.055
50.0	0.158	0.042	42.8	0.000	0.000	38.4	0.158	0.042	25.3	0.150	0.036
46.6	0.000	0.000				35.4	0.000	0.000	22.2	0.000	0.000

Table II. *t-x-y* Data for 1,3-Dioxolane-Trichloroethylene

$P = 740$ mmHg			$P = 650$ mmHg			$P = 500$ mmHg			$P = 300$ mmHg			$P = 150$ 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
73.8	1.000	1.000	69.9	1.000	1.000	62.4	1.000	1.000	49.0	1.000	1.000	32.7	1.000	1.000
74.0	0.988	0.992	70.1	0.980	0.983	62.6	0.976	0.982	49.2	0.974	0.976	32.9	0.976	0.980
74.1	0.977	0.984	70.4	0.933	0.946	63.0	0.900	0.919	49.4	0.917	0.930	33.2	0.906	0.920
74.3	0.942	0.953	70.7	0.866	0.892	63.3	0.841	0.873	49.6	0.864	0.888	33.6	0.808	0.843
74.5	0.892	0.920	71.1	0.806	0.847	63.7	0.777	0.825	50.0	0.788	0.827	34.0	0.724	0.779
74.7	0.844	0.896	71.6	0.726	0.786	64.3	0.692	0.758	50.4	0.702	0.760	34.5	0.642	0.710
75.0	0.795	0.836	72.1	0.659	0.732	64.8	0.630	0.707	50.9	0.638	0.708	34.9	0.560	0.655
75.5	0.712	0.768	72.8	0.569	0.665	65.4	0.555	0.646	51.4	0.574	0.639	36.2	0.400	0.503
75.9	0.659	0.728	74.5	0.426	0.530	67.0	0.396	0.505	52.8	0.414	0.519	37.1	0.317	0.410
76.7	0.583	0.656	75.8	0.335	0.445	68.0	0.326	0.432	53.8	0.332	0.440	37.7	0.258	0.349
77.3	0.520	0.615	76.5	0.279	0.385	68.7	0.275	0.378	54.5	0.287	0.368	38.2	0.215	0.298
79.3	0.372	0.474	77.7	0.201	0.285	69.3	0.236	0.335	55.0	0.228	0.319	39.0	0.144	0.208
80.3	0.299	0.412	78.5	0.155	0.234	69.6	0.214	0.317	56.0	0.156	0.229	39.5	0.098	0.150
80.9	0.258	0.361	78.8	0.140	0.210	70.4	0.164	0.242	56.7	0.107	0.169	39.8	0.072	0.110
81.5	0.223	0.312	79.3	0.107	0.174	71.0	0.132	0.200	58.5	0.000	0.000	40.8	0.000	0.000
83.0	0.127	0.195	81.8	0.000	0.000	71.5	0.102	0.164						
83.6	0.100	0.150				73.3	0.000	0.000						
84.0	0.079	0.130												
86.3	0.000	0.000												

Table III. *t-x-y* Data for 1,3-Dioxolane-Tetrachloroethylene

$P = 740$ mmHg			$P = 650$ mmHg			$P = 500$ mmHg			$P = 300$ mmHg			$P = 150$ 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
73.8	1.000	1.000	69.9	1.000	1.000	62.4	1.000	1.000	49.0	1.000	1.000	32.7	1.000	1.000
74.7	0.955	0.980	70.8	0.963	0.981	63.2	0.957	0.980	49.5	0.973	0.983	33.0	0.989	0.995
76.4	0.849	0.938	72.8	0.835	0.933	64.7	0.855	0.944	50.7	0.876	0.948	33.5	0.944	0.974
78.1	0.747	0.904	74.8	0.717	0.893	66.1	0.753	0.908	51.6	0.805	0.924	34.4	0.880	0.950
79.7	0.660	0.876	76.2	0.634	0.870	67.8	0.663	0.881	52.7	0.725	0.901	35.2	0.801	0.926
87.5	0.377	0.756	81.4	0.388	0.783	69.7	0.562	0.856	53.8	0.648	0.882	35.8	0.718	0.906
91.3	0.291	0.698	85.5	0.282	0.721	75.3	0.337	0.761	55.3	0.553	0.864	37.0	0.620	0.878
94.0	0.238	0.652	88.5	0.218	0.670	77.9	0.278	0.721	59.2	0.395	0.789	38.2	0.542	0.859
96.7	0.192	0.605	90.9	0.193	0.632	80.2	0.230	0.688	62.8	0.291	0.729	42.3	0.356	0.783
104.4	0.086	0.443	97.9	0.104	0.488	83.2	0.188	0.620	68.1	0.189	0.630	44.5	0.282	0.748
106.5	0.073	0.395	101.0	0.084	0.422	91.2	0.094	0.448	71.1	0.152	0.565	46.4	0.240	0.708
108.4	0.060	0.346	103.0	0.068	0.381	94.6	0.071	0.370	73.3	0.122	0.515	48.5	0.197	0.666
110.7	0.043	0.292	106.7	0.043	0.285	96.3	0.059	0.332	75.8	0.096	0.450	55.8	0.103	0.497
111.8	0.038	0.254	108.6	0.035	0.230	100.0	0.035	0.220	79.9	0.063	0.336	58.3	0.080	0.426
112.5	0.032	0.240	110.1	0.029	0.186	103.9	0.013	0.089	82.7	0.045	0.259	60.8	0.060	0.354
118.3	0.011	0.062	113.1	0.012	0.078	106.0	0.000	0.000	87.2	0.008	0.102	62.0	0.051	0.320
119.9	0.000	0.000	115.2	0.000	0.000				90.1	0.000	0.000	68.1	0.006	0.118
												70.8	0.000	0.000

1,3-dioxolane molar fraction.

Though both vapor–liquid and ΔH_m data were correlated only by a Redlich–Kister equation, with five temperature-dependent parameters, vapor–liquid data of this complex were fairly well correlated by a two-parameter equation, that is, Wilson's.

In this paper we extend our study to other systems containing 1,3-dioxolane and consider the mixtures with 1,2-*trans*-dichloroethylene, trichloroethylene, and tetrachloroethylene. Again we try to correlate the vapor–liquid data by means of the Wilson equation.

Experimental Section

The 1,3-dioxolane (Fluka product, analytical grade, 99%) was purified following the procedure given in ref *1*. The chloro compounds (Carlo Erba RPE products) were used without purification. The vapor–liquid measurements were carried out with a Stage–Müller apparatus, described elsewhere (*3*). The mixture 1,3-dioxolane (1)–1,2-*trans*-dichloroethylene (2) was measured at $P =$ 300, 500, 650, and 740 mmHg. The mixtures 1,3-dioxolane (1)–trichloroethylene (2) and 1,3-dioxolane (1)–

Table IV. Refractive Index-Composition Data

1,2-*trans*-dichloroethylene		1,3-dioxolane (1) with trichloroethylene		tetrachloroethylene	
x_1	n^{25}_D	x_1	n^{25}_D	x_1	n^{25}_D
0.0000	1.4412	0.0000	1.4737	0.0000	1.5021
0.0677	1.4389	0.0963	1.4681	0.0780	1.4964
0.1544	1.4360	0.2189	1.4606	0.1519	1.4907
0.2096	1.4339	0.2288	1.4598	0.1813	1.4882
0.2444	1.4325	0.2721	1.4571	0.2597	1.4815
0.3123	1.4297	0.4202	1.4467	0.3056	1.4776
0.4083	1.4256	0.5036	1.4405	0.3736	1.4714
0.4749	1.4226	0.6460	1.4292	0.4227	1.4665
0.5786	1.4178	0.6921	1.4249	0.4668	1.4625
0.6578	1.4140	0.7795	1.4173	0.5304	1.4560
0.7692	1.4085	0.7962	1.4158	0.6020	1.4483
0.9251	1.4004	0.8999	1.4059	0.7002	1.4371
1.0000	1.3871	0.9519	1.4008	0.7595	1.4298
		1.0000	1.3971	0.8304	1.4207
				0.8912	1.4125
				0.9683	1.4010
				1.0000	1.3971

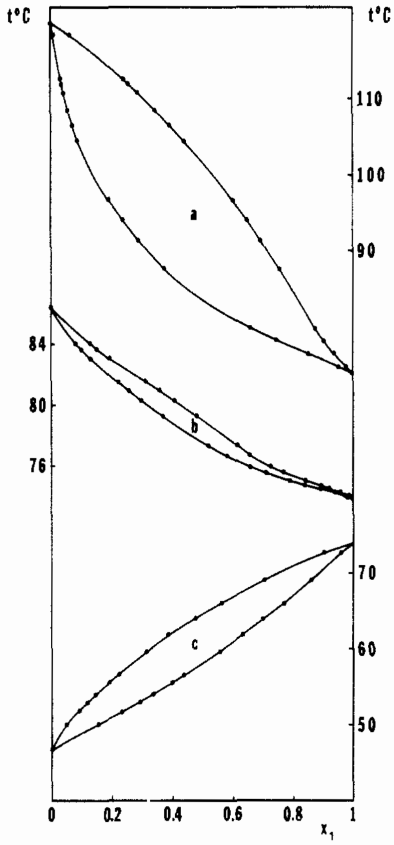

Figure 1. *t*, x_1, and y_1 values for the mixture of 1,3-dioxolane with (a) 1,2-*trans*-dichloroethylene, (b) trichloroethylene, and (c) tetrachloroethylene at P = 740 mmHg.

tetrachloroethylene (2) were measured at P = 150, 300, 500, 650, and 740 mmHg.

Tables I–III and Figure 1 collect the experimental *t*, x_1, and y_1 values (where *t* is the temperature and x_1 and y_1 are the mole fractions of 1,3-dioxolane in the liquid and vapor phases, respectively). The values of x_1 and y_1 were determined with an Abbe refractometer; the refractive index–composition data are shown in Table IV. The refractive indexes of the pure chloro compounds given by the literature are as follows: 1,2-*trans*-dichloroethylene, n^{25}_D = 1.4432 (*4*); trichloroethylene, n^{25}_D = 1.47457 (*5*); tetrachloroethylene, n^{25}_D = 1.50284 (*5*).

Results

The parameters of the Wilson equation were evaluated from the data of Tables I–III by means of a least-squares procedure. The objective function, to be minimized for each isobaric set of data, is

$$\Phi = \sum_{r=1}^{N} [P - \sum_{k=1}^{2} P_k^{0}(r)\, x_k(r)\, \gamma_k(r)]^2 \qquad (1)$$

Table V. 1,3-Dioxolane-Tetrachloroethylene. Values of γ_i Calculated from the Wilson Equation

x_1	γ_1	γ_2	x_1	γ_1	γ_2
150 mmHg[a]					
0.000	1.956	1.000	0.550	1.102	1.120
0.050	1.387	1.001	0.600	1.082	1.148
0.100	1.354	1.003	0.650	1.064	1.181
0.150	1.322	1.007	0.700	1.048	1.219
0.200	1.290	1.013	0.750	1.034	1.263
0.250	1.258	1.020	0.800	1.022	1.315
0.300	1.228	1.030	0.850	1.013	1.374
0.350	1.200	1.042	0.900	1.006	1.444
0.400	1.173	1.057	0.950	1.002	1.525
0.450	1.147	1.075	1.000	1.000	2.390
0.500	1.124	1.095			
300 mmHg[b]					
0.000	1.857	1.000	0.550	1.101	1.113
0.050	1.365	1.001	0.600	1.082	1.141
0.100	1.336	1.003	0.650	1.064	1.173
0.150	1.306	1.006	0.700	1.048	1.210
0.200	1.277	1.012	0.750	1.034	1.254
0.250	1.248	1.019	0.800	1.023	1.304
0.300	1.220	1.028	0.850	1.013	1.364
0.350	1.194	1.039	0.900	1.006	1.434
0.400	1.168	1.053	0.950	1.002	1.516
0.450	1.144	1.070	1.000	1.000	2.378
0.500	1.122	1.090			
500 mmHg[c]					
0.000	1.930	1.000	0.550	1.100	1.123
0.050	1.395	1.001	0.600	1.080	1.151
0.100	1.361	1.003	0.650	1.062	1.184
0.150	1.326	1.007	0.700	1.047	1.222
0.200	1.293	1.013	0.750	1.033	1.266
0.250	1.260	1.021	0.800	1.022	1.316
0.300	1.229	1.031	0.850	1.012	1.374
0.350	1.199	1.044	0.900	1.006	1.441
0.400	1.172	1.059	0.950	1.001	1.518
0.450	1.146	1.077	1.000	1.000	2.242
0.500	1.122	1.098			
650 mmHg[d]					
0.000	2.102	1.000	0.550	1.102	1.142
0.050	1.462	1.001	0.600	1.080	1.173
0.100	1.415	1.004	0.650	1.062	1.208
0.150	1.370	1.009	0.700	1.045	1.248
0.200	1.327	1.017	0.750	1.032	1.293
0.250	1.286	1.026	0.800	1.020	1.343
0.300	1.248	1.038	0.850	1.012	1.400
0.350	1.213	1.053	0.900	1.005	1.464
0.400	1.181	1.071	0.950	1.001	1.537
0.450	1.152	1.091	1.000	1.000	2.313
0.500	1.125	1.115			
740 mmHg[e]					
0.000	1.918	1.000	0.550	1.084	1.124
0.050	1.398	1.001	0.600	1.066	1.151
0.100	1.356	1.004	0.650	1.051	1.180
0.150	1.316	1.008	0.700	1.037	1.212
0.200	1.277	1.015	0.750	1.026	1.249
0.250	1.242	1.024	0.800	1.017	1.289
0.300	1.209	1.035	0.850	1.009	1.333
0.350	1.180	1.048	0.900	1.004	1.383
0.400	1.152	1.063	0.950	1.001	1.437
0.450	1.127	1.081	1.000	1.000	1.803
0.500	1.105	1.101			

[a] λ_{12} = 1741 ± 52 J mol^{-1}, λ_{21} = 580 ± 62 J mol^{-1}, σ = 2.57 mmHg. [b] λ_{12} = 1584 ± 30 J mol^{-1}, λ_{21} = 791 ± 38 J mol^{-1}, σ = 1.68 mmHg. [c] λ_{12} = 2035 ± 19 J mol^{-1}, λ_{21} = 368 ± 21 J mol^{-1}, σ = 5.62 mmHg. [d] λ_{12} = 2781 ± 16 J mol^{-1}, λ_{21} = −252 ± 14 J mol^{-1}, σ = 6.04 mmHg. [e] λ_{12} = 2903 ± 20 J mol^{-1}, λ_{21} = −739 ± 16 J mol^{-1}, σ = 9,95 mmHg.

Table VI. 1,3-Dioxolane-Trichloroethylene. Values of γ_i Calculated from the Wilson Equation

x_1	γ_1	γ_2	x_1	γ_1	γ_2
150 mmHg[a]					
0.000	1.254	1.000	0.550	1.028	1.052
0.050	1.162	1.001	0.600	1.021	1.060
0.100	1.141	1.002	0.650	1.016	1.070
0.150	1.122	1.004	0.700	1.012	1.080
0.200	1.105	1.008	0.750	1.008	1.090
0.250	1.090	1.012	0.800	1.005	1.101
0.300	1.076	1.017	0.850	1.003	1.113
0.350	1.064	1.022	0.900	1.001	1.125
0.400	1.053	1.029	0.950	1.000	1.137
0.450	1.044	1.036	1.000	1.000	1.106
0.500	1.035	1.043			
300 mmHg[b]					
0.000	1.305	1.000	0.550	1.030	1.047
0.050	1.145	1.000	0.600	1.024	1.056
0.100	1.129	1.002	0.650	1.018	1.066
0.150	1.114	1.004	0.700	1.013	1.076
0.200	1.100	1.006	0.750	1.009	1.088
0.250	1.087	1.010	0.800	1.006	1.100
0.300	1.075	1.014	0.850	1.003	1.113
0.350	1.064	1.019	0.900	1.001	1.127
0.400	1.054	1.025	0.950	1.000	1.142
0.450	1.045	1.031	1.000	1.000	1.225
0.500	1.037	1.039			
500 mmHg[c]					
0.000	1.222	1.000	0.550	1.025	1.031
0.050	1.096	1.000	0.600	1.020	1.038
0.100	1.087	1.001	0.650	1.015	1.046
0.150	1.079	1.002	0.700	1.012	1.054
0.200	1.071	1.004	0.750	1.008	1.064
0.250	1.063	1.006	0.800	1.005	1.074
0.300	1.056	1.008	0.850	1.003	1.086
0.350	1.049	1.012	0.900	1.001	1.099
0.400	1.042	1.016	0.950	1.000	1.113
0.450	1.036	1.020	1.000	1.000	1.257
0.500	1.030	1.025			
650 mmHg[d]					
0.000	1.195	1.000	0.550	1.024	1.028
0.050	1.085	1.000	0.600	1.019	1.034
0.100	1.078	1.001	0.650	1.015	1.041
0.150	1.071	1.002	0.700	1.011	1.049
0.200	1.064	1.003	0.750	1.008	1.058
0.250	1.057	1.005	0.800	1.005	1.068
0.300	1.051	1.007	0.850	1.003	1.079
0.350	1.045	1.010	0.900	1.001	1.092
0.400	1.039	1.014	0.950	1.000	1.106
0.450	1.034	1.018	1.000	1.000	1.253
0.500	1.028	1.022			
740 mmHg[e]					
0.000	1.162	1.000	0.550	1.023	1.024
0.050	1.075	1.000	0.600	1.019	1.030
0.100	1.069	1.001	0.650	1.015	1.037
0.150	1.063	1.001	0.700	1.011	1.044
0.200	1.058	1.002	0.750	1.008	1.053
0.250	1.053	1.004	0.800	1.005	1.063
0.300	1.047	1.006	0.850	1.003	1.075
0.350	1.042	1.008	0.900	1.001	1.088
0.400	1.037	1.011	0.950	1.000	1.103
0.450	1.032	1.015	1.000	1.000	1.257
0.500	1.028	1.019			

[a] $\lambda_{12} = 2622 \pm 314$ J mol^{-1}, $\lambda_{21} = -1760 \pm 167$ J mol^{-1}, $\sigma = 1.04$ mmHg. [b] $\lambda_{12} = 1829 \pm 182$ J mol^{-1}, $\lambda_{21} = -1070 \pm 135$ J mol^{-1}, $\sigma = 1.50$ mmHg. [c] $\lambda_{12} = 747 \pm 107$ J mol^{-1}, $\lambda_{21} = -110 \pm 118$ J mol^{-1}, $\sigma = 1.29$ mmHg. [d] $\lambda_{12} = 480 \pm 78$ J mol^{-1}, $\lambda_{21} = 172 \pm 95$ J mol^{-1}, $\sigma = 1.76$ mmHg. [e] $\lambda_{12} = 59 \pm 58$ J mol^{-1}, $\lambda_{21} = 684 \pm 83$ J mol^{-1}, $\sigma = 2.42$ mmHg.

where P is the pressure on the system in mmHg, N is the number of the experimental isobaric points, $P_k{}^0$ is the vapor pressure of the pure component k, and the γ_k values are the Wilson expressions containing the two adjustable parameters λ_{12} and λ_{21}, that is

Table VII. 1,3-Dioxolane-1,2-*trans*-Dichloroethylene. Values of γ_i Calculated from the Wilson Equation

x_1	γ_1	γ_2	x_1	γ_1	γ_2
300 mmHg[a]					
0.000	0.864	1.000	0.550	1.007	1.000
0.050	1.002	1.000	0.600	1.007	1.001
0.100	1.004	1.000	0.650	1.006	1.002
0.150	1.005	1.000	0.700	1.005	1.004
0.200	1.006	0.999	0.750	1.004	1.007
0.250	1.007	0.999	0.800	1.003	1.011
0.300	1.008	0.999	0.850	1.002	1.016
0.350	1.008	0.999	0.900	1.001	1.023
0.400	1.008	0.999	0.950	1.000	1.032
0.450	1.008	0.999	1.000	1.000	0.919
0.500	1.008	0.999			
500 mmHg[b]					
0.000	0.912	1.000	0.555	1.013	1.006
0.050	1.021	1.000	0.600	1.011	1.008
0.100	1.021	1.000	0.650	1.010	1.011
0.150	1.021	1.000	0.700	1.008	1.015
0.200	1.021	1.000	0.750	1.006	1.020
0.250	1.020	1.000	0.800	1.004	1.027
0.300	1.020	1.001	0.850	1.003	1.035
0.350	1.019	1.001	0.900	1.001	1.044
0.400	1.018	1.002	0.950	1.000	1.056
0.450	1.016	1.003	1.000	1.000	1.000
0.500	1.015	1.004			
650 mmHg[c]					
0.000	0.947	1.000	0.550	0.994	0.992
0.050	0.975	1.000	0.600	0.995	0.990
0.100	0.977	1.000	0.650	0.996	0.988
0.150	0.980	0.999	0.700	0.997	0.986
0.200	0.982	0.999	0.750	0.998	0.984
0.250	0.984	0.998	0.800	0.999	0.982
0.300	0.986	0.998	0.850	0.999	0.979
0.350	0.987	0.997	0.900	1.000	0.976
0.400	0.989	0.996	0.950	1.000	0.973
0.450	0.991	0.995	1.000	1.000	0.940
0.500	0.992	0.993			
740 mmHg[d]					
0.000	0.944	1.000	0.550	0.993	0.992
0.050	0.974	1.000	0.600	0.995	0.990
0.100	0.977	1.000	0.650	0.996	0.988
0.150	0.979	0.999	0.700	0.997	0.986
0.200	0.981	0.999	0.750	0.998	0.983
0.250	0.983	0.998	0.800	0.999	0.981
0.300	0.985	0.998	0.850	0.999	0.978
0.350	0.987	0.997	0.900	1.000	0.975
0.400	0.989	0.996	0.950	1.000	0.972
0.450	0.990	0.994	1.000	1.000	0.936
0.500	0.992	0.993			

[a] $\lambda_{12} = -1816 \pm 52$ J mol^{-1}, $\lambda_{21} = 2657 \pm 147$ J mol^{-1}, $\sigma = 1.92$ mmHg. [b] $\lambda_{12} = -1710 \pm 3$ J mol^{-1}, $\lambda_{21} = 2622 \pm 7$ J mol^{-1}, $\sigma = 4.40$ mmHg. [c] $\lambda_{12} = -561 \pm 2$ J mol^{-1}, $\lambda_{21} = 523 \pm 3$ J mol^{-1}, $\sigma = 3.77$ mmHg. [d] $\lambda_{12} = -605 \pm 92$ J mol^{-1}, $\lambda_{21} = 571 \pm 125$ J mol^{-1}, $\sigma = 2.90$ mmHg.

$$\ln \gamma_k = -\ln (x_k + \Lambda_{kj}x_j) + x_j\{\Lambda_{kj}/(x_k + \Lambda_{kj}x_j) - \Lambda_{jk}/(x_j + \Lambda_{jk}x_k)\} \qquad (2)$$

with

$$\Lambda_{kj} = (v_j/v_k) \exp[-\lambda_{kj}/(RT)] \qquad (3)$$

where k, j = 1, 2, $k \neq j$, and v_k is the molar volume of the pure liquid component k, obtained from the density of pure component at 20 °C (*6*). The ratio v_j/v_k in eq 1 is assumed to be independent of temperature.

The vapor pressures of the pure chloro compounds are expressed by the usual relation $\log P^0 = A + B/T$ (P^0 in mmHg), obtained with a least-squares method from the vapor-liquid data of this work. We have the following: 1,2-*trans*-dichloroethylene, A = 7.6140, B = −1517.5; trichloroethylene, A =

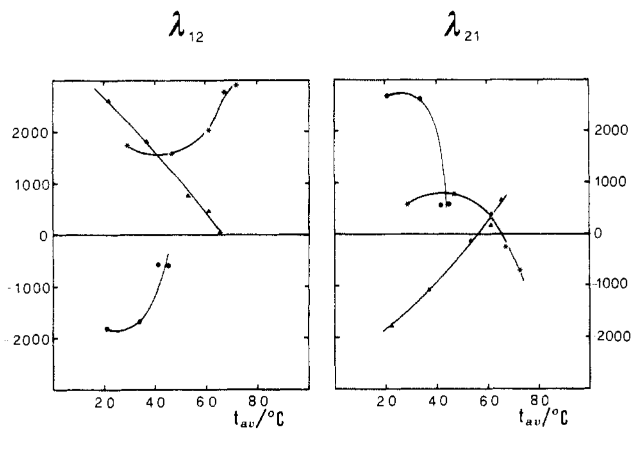

Figure 2. Values of the parameters λ_{12} and λ_{21} of the Wilson equation as a function of the average temperature in the isobaric groups of the vapor-liquid data for the binary mixtures of 1,3-dioxolane with (●) dichloroethylene, (▲) trichloroethylene, and (*) tetrachloroethylene.

7.7597, $B = -1754.4$; tetrachloroethylene, $A = 7.5966$, $B = -1855.3$. The vapor pressure of 1,3-dioxolane is given in ref *1*. The values of parameters λ_{12} and λ_{21} appear in Tables V-VII together with their estimated standard errors and the root-mean-square deviation $\sigma = [\Phi/(N-2)]^{0.5}$ evaluated at the minimum of the objective function Φ. The estimation of the standard errors of the parameters is obtained with the procedure outlined in ref *2*. Moreover, Tables V-VII give the values of the activity coefficients γ_1 and γ_2 calculated from eq 2 and 3 with the parameters λ_{12} and λ_{21}. The values of the activity coefficients lead to the conclusion that the binary mixtures of 1,3-dioxolane with 1,2-*trans*-dichloroethylene and trichloroethylene are nearly ideal in the liquid phase, whereas the mixture with tetrachloroethylene shows a notable departure from ideality with activity coefficients up to ~2. Parameters λ_{12} and λ_{21} are strongly dependent on the temperature, as can be seen in Figure 2, which shows the parameters as a function of the average values of the temperature in each isobaric group of the data. Thus, the mixtures of chloro compounds with 1,3-dioxolane exhibit a behavior exactly opposite to that of the mixture 1,3-dioxolane-water, where the parameters are fairly independent of temperature, whereas the activity coefficients of components are very large—up to 15 (*1*).

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NEW COMPOUNDS

Synthesis of Cycloalkylhydroxamic Acids and Their N-Substituted Derivatives

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The preparation of a series of cycloalkylhydroxamic acids (C_3–C_7 rings) and their *N*-methyl and *N*-cyclohexyl derivatives are reported. Some of their copper complexes are also prepared and characterized. The IR and NMR spectral results are tabulated and discussed.

Hydroxamic acids of the general formula RCONHOH have been known earlier and considered to be good complexing agents with a number of metal ions (*1*). They have been used widely for the colorimeteric determination of trace metals (*2*). Although a large number of these ligands have been prepared for these purposes, they were mainly aromatic and to a lesser extent alicyclic hydroxamic acids (*3*). The aim of the present work is to prepare a number of small-sized cycloalkylhydroxamic acids and their N-substituted derivatives (I–XV) (see Table I).

Some of the prepared hydroxamic acids that could not be purified by the usual methods were purified through their copper chelates. The physical and spectral data of I–XV are given in Table II.

Table I

$$\underset{\text{I-XV}}{\mathrm{RCOCl + R'NHOH \rightarrow RCONR'OH + HCl}}$$

R (cycloalkyl)	R' H	R' CH_3	R' C_6H_{11}
C_3H_5	I	II	III
C_4H_7	IV	V	VI
C_5H_9	VII	VIII	IX
C_6H_{11}	X	XI	XII
C_7H_{13}	XIII	XIV	XV

Experimental Section

Infrared spectra were recorded on an IR 10 Beckman infrared spectrophotometer, and ^1H NMR spectra with a Varian T 60 A spectrometer using Me_4Si as internal standard. CHN elementary analyses were obtained by using a 185 HP analyzer. Melting points were obtained on a Kofler block and were uncorrected. The purities of different products were checked by TLC using glass plates coated with silica.