Isothermal Vapor–Liquid Equilibria, Densities, Refractive Indexes, Excess Enthalpies, and Excess Volumes of 1,3-Dioxolane or Oxolane + Isooctane at 298.15 K

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Isothermal vapor–liquid equilibria, excess molar enthalpies, and excess molar volumes at 298.15 K have been determined for 1,3-dioxolane or oxolane + isooctane mixtures. Also the excess Gibbs energies for the two systems have been calculated from the vapor–liquid equilibrium data.

Introduction

As a continuation of a long-term study on the thermodynamic properties of liquid mixtures containing cyclic ethers, this paper deals with 1,3-dioxolane or oxolane + isooctane (2,2,4-trimethylpentane) mixtures. Vapor–liquid equilibria, excess molar enthalpies H^E, and excess molar volumes V^E of the two systems have been determined. The purpose of this study is to correlate the experimental data and find a relationship between the chemical structure of the compounds and their physicochemical properties.

The molar excess Gibbs energies G^E have been calculated from the VLE data. A literature survey shows no evidence of these data for these systems.

Experimental Section

Materials. 1,3-Dioxolane, oxolane, and isooctane, Aldrich products, analytical grade, 99.5, 99.9, and 99.7 mol %, respectively, were used without further purification. They were previously dried by using Union Carbide type 4A molecular sieves (Fluka) and kept in dark bottles after this treatment. The substances were carefully degassed prior to each measurement.

The experimental densities ρ, vapor pressures P, and refractive indexes $n(D)$ of the pure liquids are reported in Table I and compared with literature data (*1–3*).

Apparatus and Procedure. An equilibrium still manufactured by Fritz Gmbh (Normag) Hofheim (Germany) was used for the determination of the vapor–liquid equilibria. The details of the still and its operations were described elsewhere (*4*). The temperature T and pressure P were measured by digital instruments with an accuracy of ±0.05 K and ±0.05 kPa, respectively.

The vapor pressures of pure components $P_i°$ were obtained with the same still used for the determination of the other VLE data, and parameters A and B were adjusted to the Clausius–Clapeyron equation

$$\log(P_i°/\text{kPa}) = A + B/T\ (\text{K}) \qquad (1)$$

by means of a least-squares analysis and are reported in Table II.

Vapor condensate y_i and liquid-phase x_i compositions were determined by refractometry (Abbe refractometer, Carl Zeiss-Jena, precision 0.0001) at 298.15 ± 0.1 K using calibration curves constructed from $n(D)$ vs x_1 data; see Table III. All samples were prepared by weighing with a Mettler balance, model AE 160 (precision 0.0001 g).

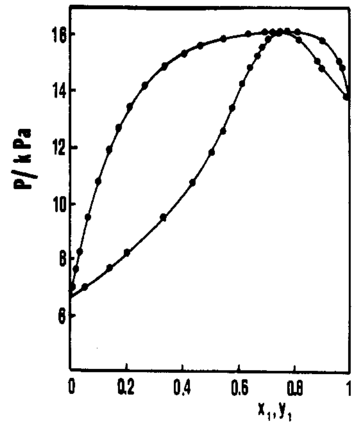

Figure 1. VLE data for the mixture 1,3-dioxolane (1) + isooctane (2) at 298.15 K.

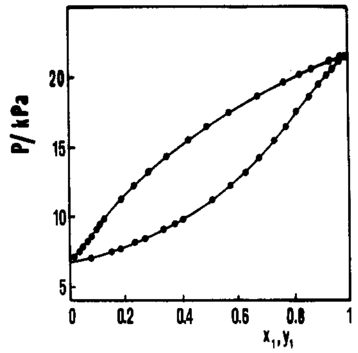

Figure 2. VLE data for the mixture oxolane (1) + isooctane (2) at 298.15 K.

Table IV and Figures 1 and 2 show the VLE data.

Excess molar volumes V^E were calculated from densities measured by means of an Anton Paar digital density meter (model DMA 60/602, resolution of 10^{-6} g cm^{-3}). The apparatus and the operating procedure are described in ref 5.

The apparatus was calibrated with doubly distilled and degassed water and dehumidifed air at atmospheric pressure. A temperature constancy of less than 0.005 K was achieved

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Table I. Densities ρ, Vapor Pressures P, and Refractive Indexes n(D) of the Pure Liquid Components at Temperature T

	1,3-dioxolane		oxolane		isooctane	
T/K	exptl	lit.	exptl	lit.	exptl	lit.
			ρ/(g cm^{-3})			
293.15	1.064 533	1.0647 (*1*)				
298.15	1.058 593	1.058 65 (*2*)	0.882 190	0.882 300 (*3*)	0.687 698	0.687 81 (*1*)
			P/kPa			
293.15	10.9	11.0 (*1*)				
298.15			21.7	21.6 (*1*)	6.6	6.5 (*1*)
			n(D)			
293.15	1.3994	1.3992 (*1*)				
298.15			1.4050	1.404 96	1.3890	1.388 98 (*1*)

Table II. Values of Constants A and B in the Clausius–Clapeyron Vapor Pressure Equation (1), Number of Experimental Points N, and Temperature Range ΔT/K[a]

	1,3-dioxolane	oxolane	isooctane
A	7.2494	6.9488	6.8613
B	−1823.4	−1673.2	−1800.7
N	13	10	10
ΔT/K	20–74	20–92	19–93

[a] Correlation coefficient $|R| = 0.9999$.

Table III. Indexes of Refraction n(D) of the Binary Mixtures at 298.15 K as a Function of the Mole Fraction x_1

x_1	n(D)	x_1	n(D)	x_1	n(D)
		1,3-Dioxolane (1) + Isooctane (2)			
0.027 23	1.3892	0.631 60	1.3920	0.864 95	1.3954
0.093 52	1.3893	0.662 62	1.3923	0.868 52	1.3955
0.175 27	1.3894	0.700 08	1.3929	0.932 97	1.3967
0.328 06	1.3895	0.728 16	1.3932	0.962 23	1.3973
0.402 90	1.3900	0.775 36	1.3938	0.982 36	1.3978
0.564 76	1.3912	0.792 65	1.3941	0.994 76	1.3980
0.567 26	1.3913	0.829 73	1.3948		
		Oxolane (1) + Isooctane (2)			
0.018 12	1.3895	0.555 97	1.3952	0.800 21	1.3997
0.083 94	1.3900	0.601 44	1.3960	0.834 07	1.4005
0.175 17	1.3907	0.627 63	1.3965	0.865 57	1.4013
0.316 48	1.3922	0.662 49	1.3970	0.896 01	1.4020
0.391 23	1.3930	0.688 95	1.3974	0.963 64	1.4038
0.442 44	1.3937	0.713 66	1.3980	0.991 88	1.4047
0.501 49	1.3944				

by using a bath circulator (Hetotherm type 01DBT623); the measurements were carried out by a DT 100-25 digital thermometer (Anton Paar, Graz, Austria) calibrated previously. The procedure for preparing the mixtures from degassed pure liquids and for correcting the vapor space are the same as described in ref 6.

Furthermore, the test system benzene + cyclohexane (*7*) at 298.15 K was studied to evaluate the accuracy of the experimental technique, and the results obtained are in agreement with those of the literature (discrepancy of less than 3×10^{-6} g cm^{-3}).

Excess molar enthalpies H^E were determined in an LKB flow microcalorimeter (model 2107) in a manner described elsewhere (*8*). Studies of the test system cyclohexane + hexane (*9*) indicate that the precision of the H^E values is better than 0.5% over the central range of composition. The experimental procedure and further details of the apparatus are described in ref 10.

Results and Discussion

Table IV and Figures 1 and 2 give the measured VLE data, that is, mole fractions x_1 and y_1 in the liquid and vapor phases, respectively, and the measured vapor pressure P.

The excess molar enthalpies H^E are reported in Table V and the excess molar volumes V^E in Table VI.

Table IV. Experimental Vapor–Liquid Equilibrium Data at 298.15 K for the Binary Mixtures 1,3-Dioxolane (1) + Isooctane (2) and Oxolane (1) + Isooctane (2): Pressure P, Liquid Phase, x_1, and Vapor Phase, y_1, Mole Fraction Compositions, and Calculated Activity Coefficients, γ_i

P/kPa	x_1	y_1	γ_1	γ_2	P/kPa	x_1	y_1	γ_1	γ_2
				1,3-Dioxolane (1) + Isooctane (2)					
6.6	0.000	0.000	3.26	1.00					
7.0	0.010	0.055	3.31	1.00	15.6	0.470	0.688	1.65	1.36
7.7	0.020	0.140	3.38	1.00	15.9	0.548	0.710	1.49	1.51
8.3	0.035	0.205	3.45	1.00	16.0	0.636	0.726	1.35	1.75
9.5	0.065	0.335	3.50	1.00	16.1	0.696	0.740	1.26	1.99
10.8	0.100	0.440	3.42	1.00	16.1	0.748	0.748	1.19	2.31
11.8	0.140	0.516	3.22	1.00	16.1	0.806	0.770	1.12	2.84
12.6	0.170	0.540	3.03	1.02	15.8	0.900	0.812	1.04	4.55
13.4	0.215	0.586	2.74	1.06	15.0	0.960	0.886	1.02	6.78
14.2	0.270	0.613	2.40	1.09	14.9	0.975	0.897	1.00	7.58
14.9	0.340	0.650	2.06	1.17	13.8	0.995	0.980	1.00	8.87
15.3	0.410	0.672	1.81	1.26	13.6	1.000	1.000	1.000	9.80[a]
				Oxolane (1) + Isooctane (2)					
6.6	0.000	0.000	1.29[a]	1.00					
7.0	0.018	0.080	1.31	1.00	14.2	0.349	0.679	1.25	1.04
7.4	0.044	0.154	1.34	1.00	15.5	0.427	0.731	1.18	1.07
7.7	0.050	0.188	1.35	1.00	16.4	0.488	0.775	1.14	1.10
8.2	0.070	0.242	1.36	1.00	17.5	0.566	0.813	1.10	1.15
8.4	0.078	0.275	1.37	1.00	18.5	0.673	0.860	1.06	1.22
9.0	0.099	0.340	1.38	1.00	19.5	0.766	0.892	1.04	1.30
9.4	0.110	0.380	1.38	1.00	20.1	0.825	0.920	1.02	1.36
9.8	0.127	0.405	1.38	1.00	20.5	0.866	0.946	1.01	1.42
11.2	0.190	0.510	1.36	1.00	21.1	0.939	0.966	1.00	1.58
12.3	0.234	0.575	1.34	1.00	21.4	0.969	0.985	1.00	1.68
13.2	0.286	0.634	1.30	1.01	21.7	1.000	1.000	1.00	1.79[a]

[a] Extrapolated.

Table V. Excess Molar Enthalpies H^E as a Function of The Mole Fraction x_1 at 298.15 K and Atmospheric Pressure

x_1	H^E/(J mol^{-1})	x_1	H^E/(J mol^{-1})	x_1	H^E/(J mol^{-1})
		1,3-Dioxolane (1) + Isooctane (2)			
0.0691	357	0.3724	1585	0.7636	1299
0.0900	461	0.4417	1704	0.8255	1019
0.1651	825	0.5427	1762	0.8769	753
0.2288	1088	0.6128	1721	0.9344	392
0.2835	1321	0.7036	1502	0.9661	221
		Oxolane (1) + Isooctane (2)			
0.0597	55	0.3368	492	0.7714	474
0.0780	78	0.4037	574	0.8025	437
0.1447	166	0.5039	652	0.8591	322
0.2025	287	0.5753	659	0.9242	171
0.2529	363	0.6701	606	0.9606	87

The Excess molar Gibbs energies G^E were calculated by means of the five-parameter Redlich–Kister expression as described in ref 11. The adjustable parameters obtained by least-squares analysis are listed in Table VII.

The objective function to be minimized was

$$\phi = \sum_{k=1}^{N} \eta_k^{\,2} \qquad (2)$$

Table VI. Densities ρ and Excess Molar Volumes V^E as a Function of the Mole Fraction x_1 at 298.15 K and Atmospheric Pressure

x_1	ρ/(g cm^{-3})	V^E/(cm^3 mol^{-1})	x_1	ρ/(g cm^{-3})	V^E/(cm^3 mol^{-1})
		1,3-Dioxolane (1) + Isooctane (2)			
0.027 15	0.691 636	0.0875	0.727 92	0.881 906	0.2529
0.093 29	0.701 919	0.2656	0.775 14	0.905 461	0.1907
0.174 90	0.716 100	0.4174	0.792 43	0.914 585	0.1781
0.327 60	0.747 891	0.5345	0.829 54	0.935 499	0.1384
0.402 44	0.766 472	0.5317	0.864 78	0.957 021	0.1021
0.564 37	0.815 632	0.4144	0.868 35	0.959 302	0.0984
0.566 89	0.816 444	0.4211	0.932 87	1.003 990	0.0376
0.631 28	0.840 348	0.3471	0.962 18	1.026 760	0.0129
0.662 331	0.852 834	0.3217	0.982 33	1.043 260	0.0100
0.699 84	0.869 056	0.2764	0.994 75	1.053 901	0.0069
		Oxolane (1) + Isooctane (2)			
0.018 12	0.689 430	0.0039	0.662 49	0.783 116	0.0026
0.083 94	0.695 964	0.0263	0.688 95	0.789 000	−0.0004
0.175 17	0.705 866	0.0456	0.713 66	0.794 712	−0.0022
0.316 48	0.723 523	0.0430	0.800 21	0.816 653	−0.0122
0.391 23	0.734 159	0.0383	0.834 07	0.826 126	−0.0137
0.442 44	0.742 047	0.0353	0.865 67	0.835 452	−0.0136
0.501 49	0.751 862	0.0258	0.896 01	0.844 972	−0.0126
0.555 97	0.761 624	0.0204	0.963 64	0.868 147	−0.0065
0.601 44	0.770 410	0.0096	0.991 88	0.878 742	−0.0011
0.627 63	0.775 704	0.0087			

Table VII. Least-Squares Parameters a_k of the Polynomial Equations for Binary Mixtures of Cyclic Ethers + Isooctane

mixture	function	a_0	a_1	a_2	a_3	a_4	σ
1,3-dioxolane + isooctane	G^E/(J mol^{-1})	1.605	0.251	0.281	0.294	−0.189	0.08
	H^E/(J mol^{-1})	7079	764.4	−1300			12.6
	V^E/(cm^3 mol^{-1})	1.917	−1.475				0.005
oxolane + isooctane	G^E/(J mol^{-1})	0.460	0.052	−0.058	0.118	0.022	0.08
	H^E/(J mol^{-1})	2599	842.3	−1121			6.5
	V/(cm^3 mol^{-1})	0.106	−0.294				0.002

where N is the number of experimental points and

$$\eta_k = \ln(\gamma_1/\gamma_2)^{\mathrm{exptl}} - \ln(\gamma_1/\gamma_2)^{\mathrm{calcd}} \qquad (3)$$

with $\ln \gamma_i^{\mathrm{calcd}}$ calculated from the Redlich–Kister expression and $\ln \gamma_{i\mathrm{exptl}}$ evaluated by means of the formula

$$\gamma_i^{\mathrm{exptl}} = Py_i/P_i^{\circ\prime}x_i \qquad (4)$$

where $P_i^{\circ\prime}$ are the "corrected" vapor pressures (*12*), obtained from the virial coefficients calculated with the Wohl formula (*13*), following the method described in ref 14.

Experimental values of excess molar enthalpies H^E and excess molar volumes V^E have been fitted to Redlich–Kister polynomials of the form

$$Q^E/x_1x_2 = \sum_{k\geq 0} a_k(x_1 - x_2)^k \qquad (5)$$

(where $Q^E = H^E$ or V^E), by least-squares analysis with unit statistical weight assigned to each point.

Parameters a_k, based on the lowest values of standard deviation σ

$$\sigma|\ln(\gamma_1/\gamma_2),H^E,V^E| = |\phi/(N-n)|^{0.5} \qquad (6)$$

where ϕ is given by eq 2, with $\eta_k = (H^E \text{ or } V^E)_{\mathrm{exptl}} - (H^E \text{ or } V^E)_{\mathrm{calcd}}$, are listed in Table VII.

The solid curves of Figures 3 and 4 were calculated from eq 2 with these parameters.

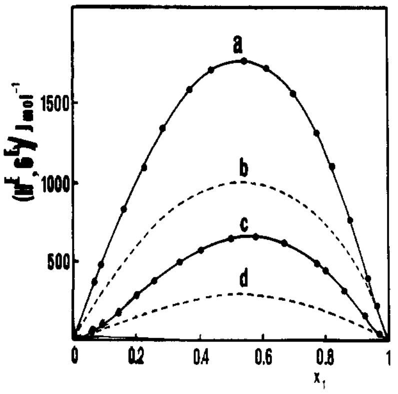

Figure 3. Excess molar enthalpies H^E and excess molar Gibbs energies G^E of cyclic ethers (1) + isooctane (2) at 298.15 K: ●, experimental H^E points; curves, calculated; (a) H^E and (b) G^E of 1,3-dioxolane + isooctane; (c) H^E and (d) G^E of oxolane + isooctane.

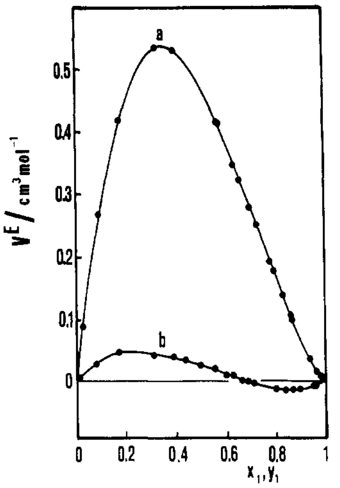

Figure 4. Excess molar volumes V^E of binary mixtures at 298.15 K: ●, experimental points; curves, calculated; (a) 1,3-dioxolane (1) + isooctane (2); (b) oxolane (1) + isooctane (2).

Discussion of the Results. The isothermal VLE curves reflect the different trends of mono- and diethers in mixtures with isooctane. The diether shows a very marked nonideal behavior with formation of an azeotrope close to $x_1 = 0.8$.

Similarly, the H^E and V^E curves show larger values for 1,3-dioxolane + isooctane. In particular, the V^E values for oxolane + isooctane are very low with a sign inversion close to $x_1 = 0.66$.

The positive deviations from ideality seem to indicate that interactions between similar molecules prevail over the ones between dissimilar molecules; the two O of 1,3-dioxolane are most probably responsible for the strong intermolecular interactions giving raise to the large nonideality observed.

The same behavior was observed with cyclic ethers + *n*-alkanes or + cyclohexane (*15*).

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