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Isothermal Vapor−Liquid Equilibria of 1,3-Dioxolane or 1,4-Dioxane + Hexane or + Cyclohexane or + Ethanol Mixtures at T = 308.15 K

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Isothermal vapor−liquid equilibria (VLE) at 308.15 K have been measured for liquid 1,3-dioxolane or 1,4-dioxane + hexane or + cyclohexane or + ethanol mixtures. The VLE data were reduced using the Redlich−Kister equation, taking into consideration the vapor-phase imperfection in terms of the second molar virial coefficients. The excess molar Gibbs energies of all the studied mixtures are positive and range from 653 J·mol^{-1} for 1,4-dioxane + ethanol and 1020 J·mol^{-1} for 1,3-dioxolane + hexane.

Introduction

The thermodynamic behavior of mixtures containing cyclic ethers is of considerable interest because they represent a class of technically important compounds frequently used as solvents in the chemical industry. In this paper we report isothermal vapor−liquid equilibrium (VLE) data, at 308.15 K, for 1,3-dioxolane ($C_3H_6O_2$) or 1,4-dioxane ($C_4H_8O_2$) + hexane (C_6H_{14}) or + cyclohexane (C_6H_{12}) or + ethanol (C_2H_5OH). Several studies of vapor−liquid equilibria of these systems are present in the literature: 1,3-dioxolane + cyclohexane (Wu and Sandler, 1989) at T = 313.15 K and T = 333.15 K, 1,3-dioxolane + ethanol (Wu and Sandler, 1989) at T = 313.15 K and 338.15 K, 1,4-dioxane + hexane (Tassios and Van Winkle, 1967) at T = 353.15 K and (Suryanarayana and Van Winkle, 1966) at P = 101.32 kPa, 1,4-dioxane + cyclohexane (Nath, 1991) at T = 288.15 K, (Vierk, 1950) at T = 293.15 K, T = 303.15 K, and T = 313.15 K, (Deshpande and Oswal, 1975) at T = 298.15 K and T = 313.15 K, and 1,4-dioxane + ethanol (Balcázar-Ortiz et al., 1979; González and Van Ness, 1983) at T = 323.15 K and (Kato et al., 1971; Hopkins et al., 1939) at P = 101.33 kPa. No vapor−liquid equilibria measurements have been published for T = 308.15 K.

Experimental Section

Materials. 1,3-Dioxolane (purity > 99 mol %), 1,4-dioxane (purity > 99.8 mol %), hexane (purity > 99.5 mol %), and cyclohexane (purity > 99.8 mol %) were obtained from Fluka AG Buchs; ethanol (purity > 99.8 mol %) was obtained from Normasolv. All of the liquids were used without further purification.

In Table 1, we compare the measured densities and vapor pressures of the products with literature values.

Apparatus and Procedure. Vapor−liquid equilibrium data were taken at constant temperature in a dynamic still designed by Berro et al. (1982). The temperature T inside the equilibrium cell was measured with a precision of 0.01 K by means of a Digitec digital thermometer (Digitec Corp.) Model 5831. The pressure P was measured by means of a Digiquartz Transmitter of Paroscientific Inc., Model 1015A, calibrated in the pressure range 0−0.1 MPa. The accuracy of the pressure measurements is 0.01%. Liquid and vapor mole fractions x_1 and y_1, respectively, were determined by densimetric analysis using an Anton Paar Model DMA 60 densimeter equipped with a DMA 602 cell in a flow system, as described in Muñoz Embid et al. (1991). The densimeter calibration was performed, at atmospheric pressure, by using doubly distilled and degassed water, benzene, and dry air. The vibrating-tube temperature was measured by means of a Anton Paar DM 100−30 digital thermometer and was regulated to better than 0.01 K using a Neslab RTE−210 thermostat. The uncertainty of the composition measurements was estimated to be ±0.001 mole fraction. Molar excess volumes have been determined previously (Calvo, 1997) from density measurements, carried out with the same densimeter.

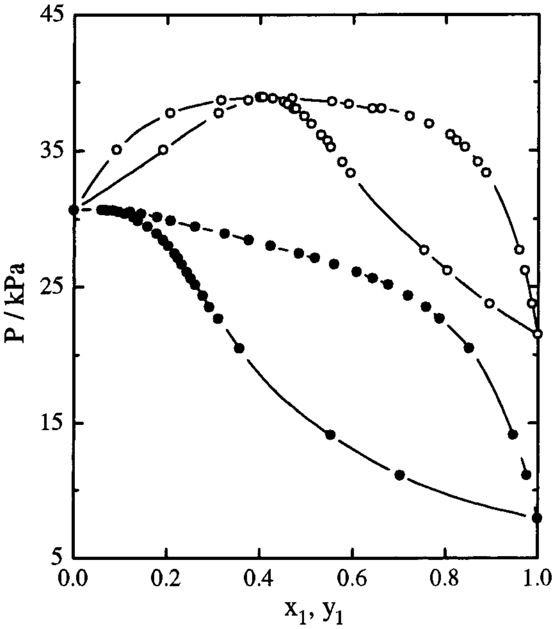

Figure 1. Vapor−liquid equilibrium diagrams at 308.15 K. Pressure, P, as a function of mole fraction in liquid, x_1, or vapor, y_1, phase: continuous curves, smoothed values, eq 1; points, direct experimental values (○, 1,3-dioxolane (1) + hexane (2); ●, 1,4-dioxane (1) + hexane (2)).

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Table 1. Densities $\rho_i°$, Vapor Pressure $P_i°$, Molar Second Virial Coefficients B_{ii}, and Liquid Molar Volumes $V_i°$ of Pure Components

	$\rho_i°$(298.15 K)/(g·cm^{-3})		$P_i°$(308.15 K)/kPa		B_{ii}(308.15K)/(cm^3·mol^{-1})	$V_i°$(308.15K)/(cm^3·mol^{-1})
	this work	lit.[a]	this work	lit.[b]	this work[d]	this work
1,3-dioxolane	1.06273[c]	1.0647[c]	21.457	21.52	−1439	71
1,4-dioxane	1.02772	1.02797	7.899	8.069	−1701	86
hexane	0.65470	0.65484	30.636	30.63	−1726	132
cyclohexane	0.77365	0.77389	20.140	20.08	−1573	110
ethanol	0.78566	0.78493	13.771	13.76	−1974	59

[a] From Riddick et al. (1986). [b] From TRC Thermodynamic Tables (1994). [c] Value at different temperature, $T = 293.15$ K. [d] Estimated by the method of Tsonopoulos (1974, 1975).

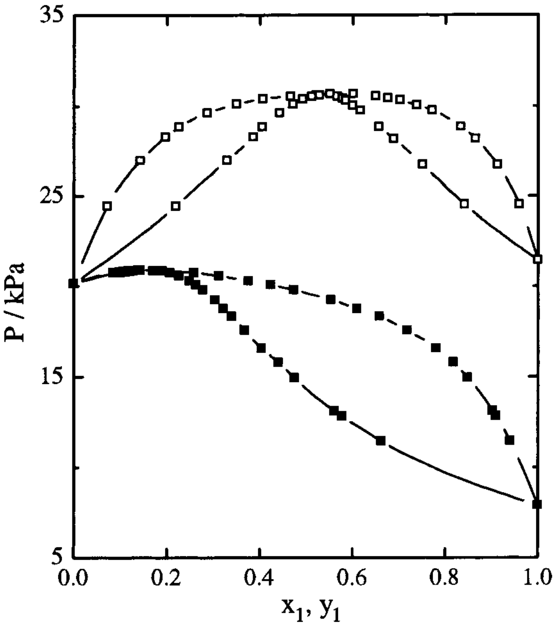

Figure 2. Vapor−liquid equilibrium diagrams at 308.15 K. Pressure, P, as a function of mole fraction in liquid, x_1, or vapor, y_1, phase: continuous curves, smoothed values, eq 1; points, direct experimental values (□, 1,3-dioxolane (1) + cyclohexane (2); ■, 1,4-dioxane (1) + cyclohexane (2)).

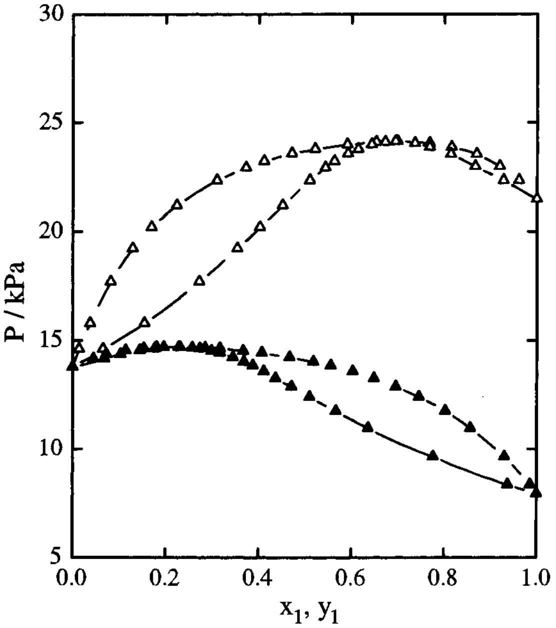

Figure 3. Vapor−liquid equilibrium diagrams at 308.15 K. Pressure, P, as a function of mole fraction in liquid, x_1, or vapor, y_1, phase: continuous curves, smoothed values, eq 1; points, direct experimental values (△, 1,3-dioxolane (1) + ethanol (2); ▲, 1,4-dioxane (1) + ethanol (2)).

Results and Discussion

The experimental vapor−liquid equilibrium data are listed in Table 2 and plotted as a function of the mole fraction in the liquid or vapor phase in Figures 1−3.

Excess molar Gibbs energies G_M^E were calculated by reduction of the experimental $P-x_1$ data with the Redlich−Kister equation. Vapor-phase nonideality and the variation of the Gibbs energy of the pure liquid components with pressure were accounted for in terms of the molar second virial coefficients B_{ij}, estimated by the method of Tsonopoulos (1974, 1975) and the liquid molar volumes. The critical constants for 1,3-dioxolane ($P_c = 58$ bar, $V_c = 188$ cm^3·mol^{-1}, and $T_c = 554$ cm^3·mol^{-1}) were estimated by the Joback method (modification of Lydersen's method) (Reid et al., 1986).

A smoothing equation of the type

$$G^E_{m,calc}/\{x_1(1 - x_1)RT\} = \sum A_j(2x_1 - 1)^{j-1} \qquad (1)$$

was fitted by the method of least squares.

The values of the root-mean-squared deviations $\sigma(Q)$ calculated with

$$\sigma(Q) = [\sum(Q - Q_{cal})^2/N]^{1/2} \qquad (2)$$

where N is the number of experimental values are reported in Table 2 and Q can be either pressure P or composition y_1. The A_j parameters are given in Table 3.

The thermodynamic consistency of the experimental data was checked by means of the test of Van Ness et al. (1973) in the version of Fredenslund et al. (1977). According to this test, the data are considered consistent if the mean absolute deviation in y, $\delta(y)$, is less than 0.01. In this work, the $\delta(y)$ values obtained range from $\delta(y) = 0.0026$ for 1,3-dioxolane + hexane to $\delta(y) = 0.0061$ for 1,4-dioxane + hexane, which shows these data to be thermodynamically consistent. In this study, all the systems present an azeotrope: 1,3-dioxolane + hexane ($x_1 = 0.4130$ and $P = 38.849$ kPa), 1,3-dioxolane + cyclohexane ($x_1 = 0.5391$ and $P = 30.636$ kPa), 1,3-dioxolane + ethanol ($x_1 = 0.6903$ and $P = 24.130$ kPa), 1,4-dioxane + hexane ($x_1 = 0.0322$ and $P = 30.687$ kPa), 1,4-dioxane + cyclohexane ($x_1 = 0.1520$ and $P = 20.874$ kPa), and 1,4-dioxane + ethanol ($x_1 = 0.2220$ and $P = 14.684$ kPa).

The excess molar Gibbs energies for the studied systems are plotted as a function of the mole fraction of the liquid phase in Figure 4. The calculated excess molar Gibbs energies of all the mixtures are positive but larger in the case of mixtures with hexane or cyclohexane than in the case of the corresponding mixtures with ethanol (about 250 J·mol^{-1} at the maximum). On the other hand, 1,3-dioxolane containing mixtures exhibit values of G_M^E slightly higher

Table 2. Experimental Vapor−Liquid Equilibrium Pressure P and Vapor Mole Fraction y_1 at 308.15 K as a Function of Liquid Mole Fraction x_1, Root Mean Squared $\sigma(P)$ and $\sigma(y_1)$, Equation 2, and Molar Second Virial Coefficients B_{ij}

x_1	y_1	P/(kPa)	x_1	y_1	P/(kPa)	x_1	y_1	P/(kPa)
			1,3-Dioxolane (1) + Hexane (2)					
0.0912	0.1916	35.031	0.6418	0.4718	38.051	0.8703	0.5772	34.143
0.2073	0.3106	37.699	0.6618	0.4777	38.023	0.8879	0.5956	33.349
0.3156	0.3739	38.644	0.7226	0.4950	37.453	0.9597	0.7552	27.689
0.4000	0.4059	38.861	0.7646	0.5101	36.895	0.9720	0.8046	26.156
0.4694	0.4268	38.789	0.8098	0.5311	36.096	0.9874	0.8958	23.740
0.5545	0.4507	38.530	0.8245	0.5446	35.694			
0.5915	0.4594	38.345	0.8419	0.5522	35.223			
			$\sigma(P)$/Pa = 31; $\sigma(y_1)$ = 0.0026					
			B_{12}/(cm^3·mol^{-1}) = −1396					
			1,4-Dioxane (1) + Hexane (2)					
0.0671	0.0603	30.666	0.3765	0.1912	28.421	0.7198	0.2773	24.361
0.0845	0.0729	30.620	0.4231	0.2020	28.026	0.7588	0.2919	23.487
0.1202	0.0956	30.495	0.4846	0.2163	27.444	0.7876	0.3100	22.629
0.1447	0.1102	30.342	0.5181	0.2227	27.126	0.8511	0.3568	20.499
0.1792	0.1272	30.126	0.5598	0.2316	26.661	0.9479	0.5529	14.094
0.2083	0.1378	29.836	0.6095	0.2433	26.075	0.9762	0.7030	11.055
0.2612	0.1575	29.415	0.6438	0.2509	25.629			
0.3239	0.1774	28.884	0.6763	0.2610	25.122			
			$\sigma(P)$/Pa = 40; $\sigma(y_1)$ = 0.0061					
			B_{12}/(cm^3·mol^{-1}) = −1673					
			1,3-Dioxolane (1) + Cyclohexane (2)					
0.0721	0.2196	24.460	0.4662	0.5122	30.515	0.7726	0.6173	29.745
0.1433	0.3297	26.956	0.5227	0.5289	30.571	0.8336	0.6574	28.834
0.1966	0.3857	28.274	0.6018	0.5513	30.661	0.8659	0.6884	28.162
0.2260	0.4049	28.829	0.6498	0.5663	30.526	0.9119	0.7513	26.712
0.2875	0.4435	29.600	0.6764	0.5773	30.426	0.9596	0.8415	24.523
0.3497	0.4719	30.091	0.7027	0.5853	30.304			
0.4070	0.4937	30.361	0.7391	0.6006	30.040			
			$\sigma(P)$/Pa = 45; $\sigma(y_1)$ = 0.0058					
			B_{12}/(cm^3·mol^{-1}) = −1354					
			1,4-Dioxane (1) + Cyclohexane (2)					
0.0841	0.0995	20.752	0.3123	0.2267	20.562	0.7174	0.3679	17.536
0.0974	0.1109	20.790	0.3757	0.2488	20.275	0.7805	0.4043	16.555
0.1074	0.1205	20.826	0.4233	0.2629	20.061	0.8179	0.4397	15.748
0.1165	0.1274	20.843	0.4741	0.2774	19.779	0.8491	0.4752	14.915
0.1370	0.1425	20.866	0.5535	0.3043	19.228	0.9029	0.5610	13.120
0.1909	0.1706	20.851	0.6103	0.3226	18.744	0.9094	0.5771	12.845
0.2583	0.2070	20.730	0.6586	0.3403	18.289	0.9405	0.6626	11.469
			$\sigma(P)$/Pa = 19; $\sigma(y_1)$ = 0.0047					
			B_{12}/(cm^3·mol^{-1}) = −1611					
			1,3-Dioxolane (1) + Ethanol (2)					
0.0138	0.0648	14.587	0.3720	0.5432	22.921	0.7687	0.7358	24.023
0.0372	0.1544	15.776	0.4113	0.5622	23.208	0.8148	0.7682	23.863
0.0816	0.2719	17.686	0.4708	0.5921	23.546	0.8690	0.8141	23.515
0.1297	0.3536	19.210	0.5215	0.6138	23.779	0.9189	0.8671	22.982
0.1691	0.4030	20.182	0.5903	0.6436	23.984	0.9607	0.9271	22.336
0.2234	0.4519	21.186	0.6534	0.6726	24.100			
0.3095	0.5095	22.334	0.6992	0.6951	24.122			
			$\sigma(P)$/Pa = 13; $\sigma(y_1)$ = 0.0035					
			B_{12}/(cm^3·mol^{-1}) = −1236					
			1,4-Dioxane (1) + Ethanol (2)					
0.0440	0.0687	14.160	0.3163	0.2733	14.619	0.6483	0.4366	13.244
0.0723	0.1021	14.340	0.3670	0.2982	14.509	0.6958	0.4704	12.865
0.1136	0.1439	14.522	0.4073	0.3172	14.412	0.7464	0.5104	12.381
0.1526	0.1758	14.621	0.4668	0.3449	14.192	0.8030	0.5665	11.733
0.1810	0.1961	14.667	0.5174	0.3686	13.999	0.8572	0.6365	10.947
0.2299	0.2279	14.689	0.5558	0.3877	13.815	0.9311	0.7761	9.614
0.2847	0.2574	14.654	0.6026	0.4110	13.551	0.9855	0.9371	8.322
			$\sigma(P)$/Pa = 10; $\sigma(y_1)$ = 0.0035					
			B_{12}/(cm^3·mol^{-1}) = −1452					

(about 100 J·mol^{-1} at the maximum) than for the corresponding 1,4-dioxane mixtures.

Our results of G_M^E for the studied mixtures show good agreement with those of Wu and Sandler (1989) for 1,3-dioxolane + cyclohexane ($G_M^E(x_1{=}0.5)$ = 966 J·mol^{-1} at 313 K and $G_M^E(x_1{=}0.5)$ = 910 J·mol^{-1} at 333 K) and for 1,3-dioxolane + ethanol ($G_M^E(x_1{=}0.5)$ = 780 J·mol^{-1} at 313 K) and with those of Balcázar-Ortiz et al. (1979) and González and Van Ness (1983) at T = 323.15 K ($G_M^E(x_1{=}0.5)$ = 624 J·mol^{-1} and $G_M^E(x_1{=}0.5)$ = 619 J·mol^{-1}, respectively). For 1,4-dioxane + cyclohexane our results agree with those of Nath (1991) ($G_M^E(x_1{=}0.5)$ = 848 J·mol^{-1} at

Table 3. Coefficients A_j, Equation 1

	A_1	A_2	A_3	A_4
1,3-dioxolane (1)				
+ Hexane (2)	1.5928	0.2071	0.1244	0.0396
+ Cyclohexane (2)	1.5213	0.1049	0.0700	
+ Ethanol (2)	1.1828	−0.0201	0.0582	
1,4-dioxane (1)				
+ Hexane (2)	1.4502	0.0982	0.0936	
+ Cyclohexane (2)	1.3332	−0.0044	0.0657	
+ Ethanol (2)	1.0196	−0.0863	0.0444	

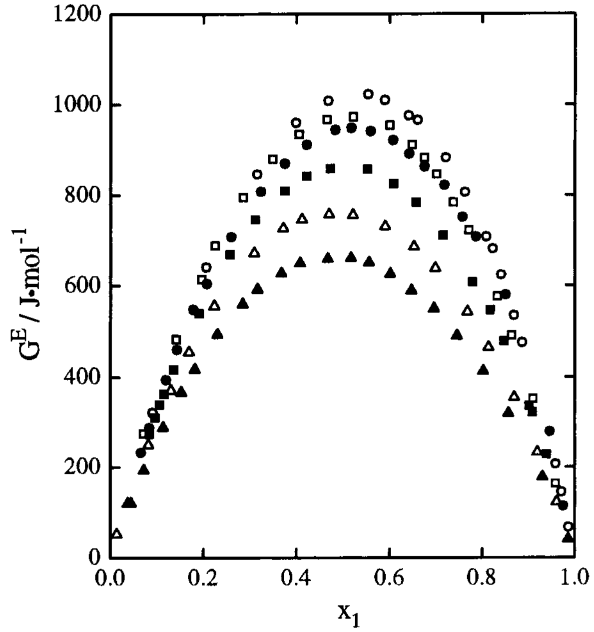

Figure 4. Excess molar Gibbs energies at 308.15 K as a function of mole fraction, x_1: ○, 1,3-dioxolane (1) + hexane (2); ●, 1,4-dioxane (1) + hexane (2); □, 1,3-dioxolane (1) + cyclohexane (2); ■, 1,4-dioxane (1) + cyclohexane (2); △, 1,3-dioxolane (1) + ethanol (2); ▲, 1,4-dioxane (1) + ethanol (2).

288 K) and show some discrepancy with those of Deshpande and Oswal (1975) ($G^E_M(x_1{=}0.5) = 1033$ J•mol^{-1} at 298 K and $G^E_M(x_1{=}0.5) = 962$ J•mol^{-1} at 313 K).

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