larger than v_w, in a constant extent, because of some intrinsic geometrical factors; hence, the volume $V - 1.6v_w$ may be equated to the void volume, which should be modified by interactions. This void volume should be $\sim 3.3\ \mathrm{cm^3 \cdot mol^{-1}}$ in the case of *n*-alkanoic acids, as calculated from our measurements, both in the pure state and in sulfolane solutions.

Acknowledgment

We are indebted to Lisbo Parella Luigi for technical assistance.

Registry No. Sulfolane, 126-33-0; acetic acid, 64-19-7; propionic acid, 79-09-4; butyric acid, 107-92-6; valeric acid, 109-52-4; caproic acid, 142-62-1.

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Isobaric Vapor-Liquid Equilibria in Binary Systems Containing 1,3-Dioxolane. The System 1,3-Dioxolane-Chlorobenzene

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The isobaric vapor-liquid equilibria of the system 1,3-dioxolane-chlorobenzene was studied with a Stage-Muller apparatus at pressures P = 300, 500, 650, 740 mmHg. The P-t-x-y data were analyzed by means of the Wilson expressions and show a poor thermodynamic consistency when checked with the area test, accounting for the deviation of the vapor phase from the ideal gas behavior and neglecting the contribution of the small values of the heat of mixing. A better consistency is obtained if association between the components is assumed.

Introduction

This paper pursues our systematic research on vapor-liquid (VLE) measurements of the binary systems containing 1,3-dioxolane, with the aim of comparing the thermodynamic properties of a set of binary mixtures having one component unchanged and the other chosen with varying functional groups. We shall focus our attention on the correlability of the VLE data by means of the same expression (we have considered the Wilson relationship to be particularly important), on the possible trend of the energy parameters in the correlation equation, on the volatility of components, etc. (*1-6*). Since some VLE data have shown unsatisfactory thermodynamic consistency (area test), we have set up an LKB flow microcalorimeter to obtain heat of mixing data that are necessary to have the enthalpy term in the Gibbs-Duhem equation. The mixture 1,3-dioxolane-chlorobenzene studied in this paper, though revealing small values of the heat of mixing (*7*) and therefore the best conditions for application of the area test, has shown a complicated interaction pattern of the molecules which is referred to in the Conclusions.

Experimental Section

Chemicals Used. The 1,3-dioxolane (Fluka product, analytical grade, 99%) was purified following the procedure given in ref 1. Chlorobenzene was C. Erba (Milan, Italy) RPE product; purity 99.5%. The major impurity, water 0.1%, was removed by drying with molecular sieve 3A followed by distillation.

The refractive index of purified 1,3-dioxolane is n^{25}_{D} = 1.3990: the literature values are n^{20}_{D} = 1.3974 (*8*) and n^{20}_{D} = 1.4000 (*9*). For purified chlorobenzene we have n^{25}_{D} = 1.5219 and n^{20}_{D} = 1.5245, whereas the literature value is n^{20}_{D} = 1.5241 (*8*).

1,3-Dioxolane (dioxolane) is component 1.

VLE Measurements

The isobaric VLE data P-t-x-y were obtained at pressures P = 300, 500, 650, 740 mmHg, with a Stage-Muller apparatus described in ref 10 (Figure 1). For further details on the equipment see also ref 11.

The equilibrium temperature was measured by a standard mercury-in-glass thermometer having an accuracy of ±0.1 °C.

The pressure was measured with a mercury filled U-tube manometer. The maximum error in the pressure measurement

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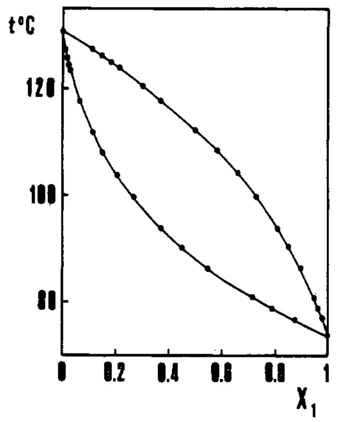

Figure 1. Isobar at P = 740 mmHg for the mixture 1,3-dioxolane (1)–chlorobenzene (2).

Table I. Refractive Index–Composition Data for the Mixture 1,3-Dioxolane (1)–Chlorobenzene (2)

x_1	n^{25}_D	x_1	n^{25}_D
0.0000	1.5219	0.5776	1.4640
0.0788	1.5156	0.6636	1.4529
0.1755	1.5070	0.7244	1.4444
0.2429	1.5010	0.8437	1.4264
0.4216	1.4826	0.9715	1.4043
0.4873	1.4750	1.0000	1.3990

was estimated to be 1 mmHg.

The mole fractions x, y of dioxolane were measured with an Abbe refractometer (Na lamp) having an accuracy of 0.0002 refractive unit at 25 °C.

The calibration curve was obtained by measuring the refractive index of weighed samples of the 1,3-dioxolane–chlorobenzene mixture. The estimated standard deviation in the composition measurements is approximately 0.002 mole fraction.

Table I gives the refractive index–composition values. The vapor pressures of the pure components were correlated by the usual Clausius–Clapeyron expression $\log P^0 = A + B/T$ (P^0 in mmHg and T absolute temperature), with constants A and B obtained by a least-squares analysis. For chlorobenzene A = 7.62107, B = −1918.37, and the root-mean-square deviation between calculated and experimental vapor pressures was about 0.6 mmHg. The boiling point of chlorobenzene was 131.5 °C at 760 mmHg (the literature values are 131.7 (*12*) and 132 (*13*)). The constants A and B for dioxolane were obtained in a previous paper (*1*). The boiling points of 1,3-dioxolane were 74.4 °C at P = 756 mmHg and 73.7 °C at P = 738 mmHg (the literature values are 74–75 °C at P = 756 (*14*), 74.5–75 °C at P = 755 mmHg (*14*), and 74 °C at P = 738 mmHg (*14*).

Correlation of the VLE Data

The VLE data of Table II were correlated by means of the Wilson expression, and the energy parameters λ_{12}, λ_{21} were evaluated with the least-squares method. Details of calculations are given in ref 3. The values of λ_{12}, λ_{21}, their estimated errors, and the root-mean-square deviation σ are given in Table III showing also a comparison between the activity coefficients calculated from the least-squares parameters and the ones evaluated from the experimental data by means of the formula

$$\gamma = Py_k/P_k'^0x_k \quad k = 1, 2 \tag{1}$$

where $P_k'^0$ is the "corrected vapor pressure" (*15*) accounting for deviations of the vapor phase from the ideal gas behavior and was calculated from

$$P_k'^0 = P_k^0 \exp[(v_k - B_k)(P - P_k^0)/RT] \quad k = 1, 2 \tag{2}$$

where R = gas constant, v_k = molar volume of component, and B_k = second virial coefficient obtained from Wohl formula (*16*) with v_k and critical temperature and pressure of chlorobenzene taken from ref 8, while the corresponding critical values for dioxolane were evaluated by the Eduljee method in a previous paper (*1*).

The ranges of the ratio $P_k'^0/P_k^0$ are 0.93–1 and 1–1.05 for components 1 and 2, respectively.

The thermodynamic consistency of the VLE data was checked with the area test (*17*)

$$\int_0^1 \ln(\gamma_1/\gamma_2)\,dx_1 - \int_0^1 \frac{\Delta H_m}{RT^2}\left(\frac{\partial T}{\partial x_1}\right)_P dx_1 = 0 \tag{3}$$

with ΔH_m = molar heat of mixing.

The small values of ΔH_m for the system 1,3-dioxolane–chlorobenzene (*7*), not exceeding 40 J mol^{-1} at 40 °C, allow us to disregard the enthalpy term in eq 3.

The criterion assumed here is that $|I|$ must be $\leqslant \Delta I$, the estimated error on the integral, to ensure a satisfactory test for thermodynamic consistency of the isobaric VLE data. Table III gives the values of I and ΔI, with ΔI obtained by applying the general rules of variance analysis (*18*) to the integral I evaluated numerically with the trapezoidal rule and taking account of the sample variance of each term. $s(P_k^0)$, $s(x)$, and $s(y)$

Table II. P–t–x–y Data for 1,3-Dioxolane (1)–Chlorobenzene (2)

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
48.9	1.000	1.000	62.4	1.000	1.000	69.9	1.000	1.000	73.8	1.000	1.000
50.2	0.923	0.989	64.3	0.922	0.987	71.7	0.934	0.986	75.9	0.913	0.982
51.3	0.867	0.978	65.9	0.854	0.975	73.7	0.852	0.973	77.6	0.842	0.970
52.8	0.802	0.966	68.3	0.755	0.955	75.8	0.765	0.928	80.6	0.719	0.944
55.1	0.726	0.949	70.9	0.654	0.933	81.3	0.564	0.905	86.4	0.541	0.898
56.9	0.645	0.931	74.7	0.543	0.896	83.4	0.506	0.880	90.2	0.443	0.855
59.8	0.560	0.906	77.9	0.453	0.859	87.1	0.418	0.845	93.7	0.366	0.819
62.6	0.483	0.873	81.0	0.383	0.823	91.4	0.336	0.791	99.7	0.271	0.730
67.1	0.348	0.805	88.9	0.258	0.714	98.9	0.217	0.681	104.1	0.207	0.658
70.5	0.276	0.757	93.2	0.193	0.639	104.5	0.155	0.581	108.3	0.149	0.581
73.4	0.232	0.705	91.6	0.153	0.582	108.3	0.119	0.507	112.2	0.111	0.503
80.2	0.145	0.573	99.4	0.114	0.510	112.1	0.085	0.425	117.5	0.068	0.380
83.9	0.107	0.494	105.0	0.065	0.372	115.0	0.065	0.359	120.4	0.048	0.307
86.6	0.088	0.430	107.0	0.055	0.308	118.0	0.045	0.274	123.5	0.027	0.220
89.8	0.059	0.350	108.4	0.049	0.272	120.6	0.032	0.190	124.6	0.021	0.180
91.7	0.046	0.287	111.9	0.023	0.155	122.4	0.018	0.125	126.0	0.014	0.148
93.3	0.036	0.240	113.2	0.014	0.114	125.8	0.000	0.000	127.0	0.010	0.113
94.0	0.028	0.210	114.0	0.009	0.092				130.5	0.000	0.000
96.4	0.015	0.127	116.6	0.000	0.000						
98.6	0.000	0.000									

Table III. Results of Least-Squares and Thermodynamic Consistency Calculations on the Mixture 1,3-Dioxolane (1)–Chlorobenzene (2)

	P = 300 mmHg					P = 500 mmHg			
	γ_1		γ_2			γ_1		γ_2	
x_1	exptl	calcd	exptl	calcd	x_1	exptl	calcd	exptl	calcd
0.923	1.01	1.00	1.01	1.33	0.922	1.01	1.00	0.92	1.31
0.867	1.03	1.00	0.94	1.29	0.854	1.02	1.01	0.89	1.27
0.802	1.04	1.01	0.92	1.25	0.755	1.05	1.02	0.88	1.21
0.726	1.04	1.02	0.91	1.21	0.654	1.08	1.04	0.84	1.16
0.645	1.07	1.04	0.88	1.17	0.543	1.11	1.06	0.86	1.11
0.560	1.08	1.06	0.86	1.13	0.453	1.15	1.10	0.87	1.08
0.483	1.10	1.09	0.89	1.10	0.383	1.19	1.13	0.87	1.06
0.348	1.21	1.15	0.91	1.05	0.258	1.22	1.19	0.91	1.02
0.276	1.28	1.20	0.90	1.03	0.193	1.29	1.24	0.92	1.01
0.232	1.29	1.23	0.93	1.02	0.153	1.37	1.27	0.92	1.01
0.145	1.35	1.29	0.95	1.01	0.114	1.45	1.29	0.92	1.00
0.107	1.41	1.33	0.95	1.00	0.070	1.48	1.33	0.95	1.00
0.088	1.38	1.34	0.96	1.00	0.055	1.48	1.34	0.97	1.00
0.059	1.52	1.37	0.95	1.01	0.049	1.41	1.36	0.97	1.00
0.046	1.51	1.38	0.97	1.00	0.023	1.57	1.37	0.99	1.00
0.036	1.55	1.39	0.97	1.00	0.016	1.60	1.37	0.99	1.00
0.028	1.70	1.40	0.97	1.00	0.009	1.94	1.38	0.98	1.00
0.015	1.80	1.41	0.98	1.00					
λ_{12} = 2211 ± 78		λ_{21} = 1114 ± 67			λ_{12} = 2131 ± 58		λ_{21} = −1075 ± 51		
σ = 3.43		I = −0.23 ± 0.04			σ = 4.97		I = −0.26 ± 0.04		

	P = 650 mmHg					P = 740 mmHg			
	γ_1		γ_2			γ_1		γ_2	
x_1	exptl	calcd	exptl	calcd	x_1	exptl	calcd	exptl	calcd
0.934	1.00	1.00	1.15	1.45	0.913	1.02	1.00	1.09	1.31
0.852	1.02	1.01	0.92	1.34	0.842	1.03	1.00	0.94	1.28
0.756	1.05	1.03	0.89	1.25	0.719	1.06	1.02	0.88	1.22
0.564	1.13	1.09	0.84	1.11	0.541	1.13	1.06	0.80	1.15
0.506	1.15	1.11	0.87	1.09	0.443	1.18	1.10	0.83	1.11
0.418	1.20	1.14	0.84	1.05	0.366	1.22	1.14	0.83	1.08
0.336	1.23	1.18	0.87	1.03	0.271	1.28	1.21	0.90	1.05
0.217	1.33	1.24	0.88	1.01	0.207	1.35	1.28	0.92	1.03
0.155	1.37	1.27	0.91	1.01	0.149	1.46	1.36	0.91	1.02
0.119	1.41	1.28	0.91	1.00	0.111	1.54	1.41	0.92	1.01
0.085	1.50	1.30	0.92	1.00	0.068	1.66	1.49	0.94	1.00
0.065	1.54	1.31	0.92	1.00	0.048	1.77	1.53	0.95	1.00
0.045	1.57	1.32	0.94	1.00	0.032	1.77	1.56	0.97	1.00
0.025	1.85	1.32	0.96	1.00	0.026	1.74	1.57	0.98	1.00
0.018	1.62	1.33	0.98	1.00	0.021	1.71	1.58	0.98	1.00
					0.015	1.79	1.60	0.99	1.00
λ_{12} = 944 ± 33		λ_{21} = 341 ± 45			λ_{12} = 3623 ± 57		λ_{21} = −1921 ± 35		
I = −0.26 ± 0.04		σ = 3.73			I = −0.28 ± 0.04		σ = 6.90		

were given the values of the uncertainties on P, x, and y reported in the Experimental Section.

Conclusions

As can be seen from Table III, at all pressures $\Delta I > |I|$. Experimental data were checked for any inaccuracy by means of a duplication of the experiments carried out randomly, confirming the previous data within the limits of the experimental errors. Since ΔI exceeds $|I|$ by about an order of magnitude, we have assumed associations of components as a possible reason for the relatively high values of $|I|$. Thus, we have turned to the consistency criterion obtained in ref 19 and applied in ref 10, 16 to binary mixtures with associating components in the vapor phase. We have assumed, in the vapor phase, dimerization of chlorobenzene, A_2, (self-association of dioxolane was never encountered in previous works and was not considered) and the formation of mixed complexes AB, A_1B_2, and A_2B_1, where A and B are components 2 and 1. The assumption of complexes of the AB and A_1B_2 type leads always to a value of $|I|$ greater than the ones calculated in the absence of associates, whereas the assumed prevalence of dimers A_2 in the chlorobenzene-rich mixtures and of associates A_2B_1 in the dioxolane-rich mixtures resulted in a reduction of the values of $|I|$ to half their size.

The equilibrium constant K_2 for the dimerization reaction was taken as the one of acetic acid (*10*), and the ln K_{21} for the formation of A_2B_1 was given the value −11, corresponding to the lowest $|I|$, with practically no dependence on temperature.

Registry No. Chlorobenzene, 108-90-7; 1,3-dioxolane, 646-06-0.

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Thermodynamic and Transport Properties of *o*-Chlorophenol with Aniline and *N*-Alkylanilines

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Densities and viscosities at five temperatures were determined for the systems *o*-chlorophenol with aniline, *N*-methylaniline, *N*,*N*-dimethylaniline, *N*-ethylaniline, and *N*,*N*-diethylaniline. From the experimental data, the excess volumes, excess viscosities, partial molar excess volumes, and partial molar volumes were calculated. Various thermodynamic parameters of activation of viscous flow were calculated from the dependency of viscosity on temperature. The results are discussed in terms of theories of nonelectrolyte solutions and also the type and strength of interaction between the two components in solution.

This present paper continues our investigations of the thermodynamic and transport properties of binary acid–base mixtures (*1*–*3*). The systems *o*-chlorophenol (CP) with aniline (A), *N*-methylaniline (MA), *N*,*N*-dimethylaniline (DMA), *N*-ethylaniline (EA), and *N*,*N*-diethylaniline (DEA) were chosen to represent the acid–base interactions and were also chosen because of their polar characteristics, and the ability to form hydrogen bonding. Solutions of nonelectrolytes were classified by Barker and Smith (*4*) as (i) "nonpolar" solutions, (ii) "polar" solutions, and (iii) "associated" solutions. The above systems could be classified as ii and iii.

In the present paper, densities and viscosities of the five systems at different mole fractions were measured at 298, 303, 308, 313, and 318 K. From the experimental results the following thermodynamic functions have been calculated: V^E (excess volume), η^E (excess viscosity), G^{*E} (excess molar free energy of activation of flow), ΔH^{*E}, ΔS^{*E} (excess enthalpy and entropy of activation), and $\bar{V}_1$ partial molar quantities in solution. The results were discussed in terms of the type of interaction between CP with various substituted anilines. Viscosity and density measurements on *o*-chlorophenol with aniline and *N*,*N*-dimethylaniline at 25 °C were reported by Solimo et al. and our results agree well with published data (*5*).

Experimental Section

Densities of pure liquids and of mixtures were determined with an Anton-Paar DMA 45 densitometer with an accuracy in density measurements of ±0.0001 g/cm³. A thermostatically controlled bath (SODEV), constant to ±0.001 °C, was used.

Viscosity measurements at various temperatures were done using modified Ostwald or Cannon–Fenske viscometers and a viscosity bath (Koehler Instrumentation). Viscometers were calibrated against pure liquids (acetone and benzene), and the accuracy was found to be ±0.005 cP. All chemicals used were either B.D.H. or Aldrich and were purified by the standard procedures described by Weissberger (*6*). Only colorless middle fractions were collected and used to prepare the mixtures, which were prepared by mixing weighed amounts of the pure liquids.

Results

The experimental values of density, ρ, and viscosity η for the five systems are listed in Tables I–V. The molar volume (V) of the solution was obtained from the expression

$$V = (X_1M_1 + X_2M_2)/\rho \tag{1}$$

where M_1, M_2 are molecular masses of the pure components 1 and 2 and X_1 and X_2 are their mole fractions.

Excess properties Y^E were calculated by the equation

$$Y^E = Y - [X_1Y_1 + X_2Y_2] \tag{2}$$

where Y, Y_1, and Y_2 are the specific properties of the mixture and of the pure components 1 and 2, respectively.

Excess molar free energy of activation of flow, G^{*E}, was calculated by using the equation

$$G^{*E} = RT\,[\ln \eta V - (X_1 \ln \eta_1 V_1 + X_2 \ln \eta_2 V_2)] \tag{3}$$

where η and V are the viscosity and molar volume respectively of the mixtures, η_1, η_2 and V_1, V_2 are the viscosities and molar volumes of the pure components 1 and 2, respectively, R is the gas constant, and T is the absolute temperature (*7*). The excess functions were fitted with a Redlich–Kister (*8*) form of the type

$$X^E = X_1\,(1 - X_1) \sum_{j=1}^{n} a_j (1 - 2X_1)^{j-1} \tag{4}$$

where X^E represents the excess property under consideration. The least-squares method was used to determine the values of the coefficients a_j. In each case the optimum number of coefficients was ascertained from an examination of the variation of the standard error of estimate (σ) with n

$$\sigma_x = [(X^E{}_{\text{obsd}} - X^E{}_{\text{calcd}})^2/(n_{\text{obsd}} - n)]^{1/2} \tag{5}$$

The values of these coefficients along with the standard error of estimate at five different temperatures have been given in Tables VI–VIII. Figures 1–3 show the values of η^E, V^E, and G^{*E} as a function of the mole fraction of *o*-chlorophenol. The continuous curves were generated by the computer aided plotter and the coefficients in Tables VI–VIII.

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