

Vapor-Liquid Equilibria in Binary Systems Containing 1,3-Dioxolane at Isobaric Conditions. 6. Binary Mixtures of 1,3-Dioxolane with Acetone

Carlo Castellari* and Romolo Francesconi

Istituto Ciamician, Università di Bologna, 40126 Bologna, Italy

Fabio Comelli and Stefano Ottani

Centro di Studio per la Fisica delle Macromolecole del CNR, 40126 Bologna, Italy

This paper presents vapor-liquid equilibrium (VLE) data at 300, 500, and 740 mmHg for the binary system 1,3-dioxolane (1)-acetone (2). The values of the activity coefficients show that the system deviates from ideality in the liquid phase with activity coefficients up to 1.4. The activity coefficients are correlated from experimental t , x data by using the NRTL equation.

Introduction

As a continuation of earlier works (1-6) on isobaric VLE of binary mixtures containing 1,3-dioxolane (1,3-C₃H₆O₂) as a common component, new data for the binary mixtures of 1,3-dioxolane (1) with acetone (2) are shown.

Experimental Section

The source and treatment of 1,3-dioxolane have been given previously (1). Acetone (from Carlo Erba, Milan, purity >99 wt %) was used without further purification. The major impurity was water (0.2 wt %).

The experimental apparatus was the same as previously employed (1-6). The pressures were measured with an accuracy of ± 1 mmHg with a mercury manometer. The temperatures were measured with a mercury thermometer to within 0.1 °C. The compositions of the liquid and vapor phases were determined by the refractive indexes at 25 °C and with a sodium lamp. An Abbe refractometer was used having a reproducibility of ± 0.0001 refractive unit. The refractive index-composition data are reported in Table I.

Results

Table II presents the experimental P , t , x_1 , y_1 , data; x_1 and y_1 are respectively the mole fractions of 1,3-dioxolane in the liquid and vapor phases. In Figure 1 the experimental liquid-phase activity coefficients γ_1 and γ_2 are shown. The activity coefficients were evaluated with the expression

$$\gamma_i = yP/(x_i P_i^\circ) \quad i = 1, 2 \quad (1)$$

The vapor pressures of the pure acetone over the temperature range 32-59.9 °C are represented by the expression

$$\log P^\circ(\text{mmHg}) = 7.93 - 1663/T(\text{K}) \quad (2)$$

whose constants were evaluated by the least-squares method from the experimental data of this work. A similar expression, obtained in ref 1, was employed for the vapor pressure of 1,3-dioxolane. The system 1,3-dioxolane-acetone shows positive deviations from the Raoult law with activity coefficients

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

x_1	n_D^{25}	x_1	n_D^{25}
1.000	1.3984	0.2908	1.3697
0.9536	1.3967	0.2230	1.3666
0.7874	1.3904	0.1327	1.3626
0.6059	1.3832	0.0640	1.3593
0.5153	1.3795	0.0000	1.3563
0.4385	1.3759		

Table II. P - t - x - y Data for 1,3-Dioxolane-Acetone

$P = 300$ mmHg			$P = 500$ mmHg			$P = 740$ mmHg		
$t/^\circ\text{C}$	x_1	y_1	$t/^\circ\text{C}$	x_1	y_1	$t/^\circ\text{C}$	x_1	y_1
48.9	1.000	1.000	62.4	1.000	1.000	73.9	1.000	1.000
47.2	0.938	0.844	60.3	0.926	0.840	72.2	0.929	0.848
44.8	0.856	0.698	56.8	0.784	0.626	70.0	0.848	0.724
42.3	0.744	0.546	54.8	0.686	0.502	68.2	0.777	0.621
40.2	0.633	0.482	53.2	0.599	0.423	64.3	0.601	0.428
38.6	0.546	0.345	51.9	0.532	0.354	63.0	0.534	0.359
37.7	0.490	0.305	50.5	0.446	0.286	61.8	0.460	0.301
36.9	0.440	0.265	49.3	0.382	0.232	60.6	0.399	0.250
36.0	0.385	0.225	48.6	0.334	0.196	59.8	0.340	0.208
35.2	0.340	0.185	47.9	0.286	0.170	59.0	0.274	0.163
34.5	0.283	0.149	47.4	0.243	0.143	58.3	0.232	0.136
34.1	0.256	0.139	44.6	0.000	0.000	57.7	0.190	0.110
33.5	0.210	0.110				57.1	0.154	0.092
33.1	0.172	0.092				56.0	0.070	0.050
32.0	0.000	0.000				54.9	0.000	0.000

Table III. Values of the Parameters Obtained from VLE Data by the NRTL Equation for 1,3-Dioxolane (1)-Acetone (2)

parameters	$P = 300$ mmHg	$P = 500$ mmHg	$P = 740$ mmHg
$\lambda_{12}/(\text{J mol}^{-1})$	250 ± 26	230 ± 18	-2068 ± 9
$\lambda_{21}/(\text{J mol}^{-1})$	1808 ± 300	1119 ± 127	3149 ± 34
$-\alpha$	3.8 ± 0.3	6.3 ± 0.4	0.34 ± 0.05

up to 1.4. The activity coefficients were correlated by the NRTL equation

$$\ln \gamma_k = x_j^2 [\tau_{jk} G_{jk}^2 / (x_k + G_{jk} x_j)^2 + \tau_{jk} G_{kj} / (x_j + G_{kj} x_k)^2] \quad (3)$$

where

$$\tau_{kj} = \lambda_{kj} / RT \quad (4)$$

$$G_{kj} = \exp(-\alpha \tau_{kj}) \quad (5)$$

$$\lambda_{kj} = g_{kj} - g_{kk} \quad (6)$$

which g_{kj} and g_{jj} are interaction energies between molecules. The adjustable parameters λ_{12} , λ_{21} , and α in eq 3 are calculated with a least-squares method and listed in Table III, to-

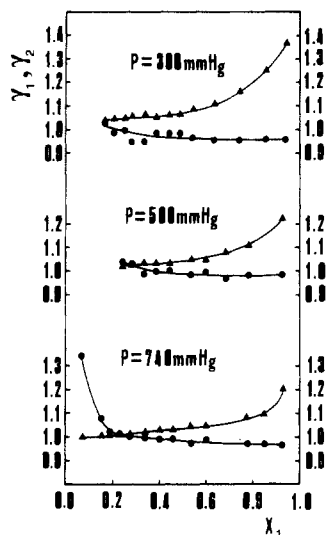


Figure 1. Experimental activity coefficients of the system 1,3-dioxolane (1)-acetone (2) at $P = 300, 500,$ and 740 mmHg: (Δ , \bullet) experimental values, (—) graphical smoothing.

Table IV. Standard Deviation σ and Average Deviation $\Delta\gamma$ between Experimental and Calculated Activity Coefficients for 1,3-Dioxolane (1)-Acetone (2)

press./mmHg	NRTL eq		
	σ^a	$\Delta\gamma_1^b$	$\Delta\gamma_2^b$
300	0.9	0.07	0.06
500	1.5	0.04	0.02
740	2.1	0.03	0.04

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

gether with their estimated standard errors. The objective function in the least-squares method is

$$\Phi = \sum_{k=1}^n (P_{k,\text{exptl}} - P_{k,\text{calcd}})^2 \quad (7)$$

$$P_{\text{calcd}} = P^0_1 x_1 \gamma_1 + P^0_2 x_2 \gamma_2 \quad (8)$$

where n is the number of experimental points and γ_1 and γ_2 are given by eq 3.

The uncertainty of the parameters is defined as the variation of the parameter giving rise to a variation of σ_p^2 (1 mmHg) for Φ at its minimum. In the calculations, a computer program, based on the algorithms of Nelder and Mead (7) and Fletcher (8), was used. In Table IV the root-mean-square deviation σ and the average deviations $\Delta\gamma$ between experimental and calculated activity coefficients γ_1 and γ_2 are shown. The activity coefficients γ_1 and γ_2 were also correlated by using the Wilson, LEMF, and Redlich-Kister equations.

Wilson and LEMF equations lead to values of σ slightly higher than the ones given in Table IV and values of $\Delta\gamma$ up to twice those of the NRTL equation. On the other hand, the minimization of the experimental data made with the Redlich-Kister equation with two temperature-dependent parameters gives rise to values of σ ($\sigma = 1.0, 0.9,$ and 1.8 for the pressures of 300, 500, and 740, respectively) comparable with those obtained by using the NRTL equation, but leads to higher values of $\Delta\gamma_1$ and $\Delta\gamma_2$ ($\Delta\gamma_1 = 10\%, 5\%,$ and 4% ; $\Delta\gamma_2 = 6\%, 2\%,$ and 5% for the pressures of 300, 500, and 740 mmHg, respectively). For this reason only the parameters of the NRTL equation are shown in Table III.

Registry No. 1,3-Dioxolane, 646-06-0; acetone, 67-64-1.

Literature Cited

- (1) Francesconi, R.; Castellari, C.; Arcelli, A.; Comelli, F. *Can. J. Chem. Eng.* **1980**, *58*, 1113.
- (2) Comelli, F.; Castellari, C.; Francesconi, R. *J. Chem. Eng. Data* **1981**, *26*, 334.
- (3) Francesconi, R.; Comelli, F.; Castellari, C. *J. Chem. Eng. Data* **1982**, *27*, 53.
- (4) Castellari, C.; Francesconi, R.; Comelli, F. *J. Chem. Eng. data* **1982**, *27*, 156.
- (5) Castellari, C.; Francesconi, R.; Comelli, F. *J. Chem. Eng. Data* **1984**, *29*, 126.
- (6) Castellari, C.; Francesconi, R.; Comelli, F. *J. Chem. Eng. Data* **1984**, *29*, 90.
- (7) Nelder, J. A.; Mead, R. *Comput. J.* **1958**, *6*, 163.
- (8) Fletcher, R.; Powell, M. J. D. *Comput. J.* **1963**, *6*, 163.

Received for review August 5, 1983. Accepted November 30, 1983.

Conductance of Electrolytes in 1,2-Dichloro-1,1-difluoroethane

Patricia H. Smith,* William P. Kilroy, and Stanley D. James

Electrochemistry Branch, Naval Surface Weapons Center, White Oak, Maryland 20910

Conductivities are presented for solutions of tetrabutylammonium tetrafluoroborate and tetrabutylphosphonium bromide in 1,2-dichloro-1,1-difluoroethane at 25 °C. For a given concentration, solutions of tetrabutylammonium salt were found to be more conductive than the tetrabutylphosphonium salt. Molar conductances display a distinct minimum at about 0.02 mol L⁻¹.

Introduction

The conductance of R₄ZX salt solutions, where R = alkyl group, and Z = N or P and X is an anion, has been widely studied (1-5). However, these same measurements employing halocarbons as the solvent are relatively rare. The present

paper investigates the conductivity of such salts in 1,2-dichloro-1,1-difluoroethane for evaluation in an experimental battery.

Experimental Section

1,2-Dichloro-1,1-difluoroethane (obtained from PCR Research Chemicals, Inc.) was dried over molecular sieves for 12 h prior to distillation under nitrogen. Only the middle fraction (bp 47 °C) was retained.

Tetrabutylammonium tetrafluoroborate and tetrabutylphosphonium bromide obtained from Aldrich Chemical Co. were purified by recrystallization from a mixture of ethyl acetate and diethyl ether. Both salts were vacuum dried at 60-70 °C for 48 h. Due to the hygroscopic nature of these salts, extreme care was taken to avoid contact of these salts with water va-