Vapor-Liquid Equilibrium with Association of the Components. The Acetic Acid-1,3-Dioxolane Mixture

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The vapor-liquid equilibrium data of the mixture acetic acid-1,3-dioxolane have been obtained at pressures ranging from 150 to 740 mmHg. The dimerization of acetic acid is taken into account when checking the thermodynamic consistency of $P-t-x-y$ data with an integral test derived in a previous paper. Vapor-phase deviations from ideal gas behavior have also been accounted for. Experimental data are correlated with the two-parameter Wilson expression.

Introduction

Usual methods to test the thermodynamic consistency of vapor-liquid equilibrium (VLE) data must overcome, when an associating substance is present, the obstacles of defining the number of chemical species in the phases and of estimating physical properties (such as vapor pressure) of monomers and complexes which are not easily isolated.

Marek and Standart (1, 2) have correlated VLE data of systems containing dimer associate in both phases, an alternative approach was given by Meehan and Murphy (3), and other kinds of associations were accounted for by Apelblat (4) and by Taha and Christian (5). The thermodynamic properties of a solvating binary mixture were considered by Harris and Prausnitz (6).

More recently, Inoue et al. (7) have studied the keto-enol equilibrium of acetylacetone in organic solvents and have correlated the VLE data of the mixtures with the Wilson equation for a three-component system.

In this paper, we determine the VLE data for the mixture acetic acid-1,3-dioxolane, where the acid association is generally accepted, and we test our data with the criterion proposed in a previous work (8) and applied to the systems acetic acid-trichloroethylene (9), acetic acid-acetone, and water-pyridine (10).

The advantages of this criterion are that it requires the knowledge of the detailed composition in the vapor phase only and permits the description of the binary systems with associating compounds in terms of two liquid-phase "macroscopic activity coefficients". The Gibbs-Duhem equation can now be written in terms of the "macroscopic activity coefficients" and we have, at isobaric conditions (8)

$$x_A \, d \ln \frac{y_1}{(P_A{}^0)_c y_1(1)} + x_B \, d \ln \frac{y_1'}{(P_B{}^0)_c} = -\frac{\Delta H}{RT^2} \, dT \quad (1)$$

where $(P^0)_c$ = "corrected vapor pressure" (11), ΔH = liquid-phase enthalpy of mixing of pure A and B, y_1 and y_1' = molar fractions of monomer of A and B in the vapor phase, and y_1 (1) and y_1' (1) = values of y_1 and y_1' at $x_A = 1$ and $x_B = 1$, x_A being the molar fraction of A in the liquid.

The system acetic acid-1,3-dioxolane studied in this paper is assumed to present dimerization of acid (A) (8) with dioxolane as an inert solvent.

The dependence of y_1, y_1', $y_1(1)$, and $y_1'(1)$ on the measurable molar fraction y_A in the vapor phase is given in ref 8. Finally, ideality of the vapor phase is assumed and hence the equilibrium constant k_2 for dimerization is

$$k_2 = y_2/(y_1{}^2 P) \quad (2)$$

where y_2 is the molar fraction of the dimer in the vapor.

Now, if eq 1 is rewritten as

$$x_A \, d \ln y_1/y_1(1) + x_B \, d \ln y_1' - x_A \, d \ln (P_A{}^0)_c -$$
$$x_B \, d \ln (P_B{}^0)_c + \frac{\Delta H}{RT^2} \, dT = 0 \quad (3)$$

from the Clausius-Clapeyron equation we have that $d \ln P_k{}^0 = (L_k/RT^2) \, dT$, with L_k = latent heat of vaporization, and the following expression holds

$$x_A L_A + x_B L_B \geq L \gg \Delta H \quad (4)$$

where L is smallest between L_A and L_B.

The validity of eq 4 has been discussed in ref 12 and was checked considering the more recent data on heat of mixing given in ref 13.

Since the ΔH's of the mixture 1,3-dioxolane-acetic acid are not available, we have considered the binary aqueous mixtures containing 1,3-dioxolane and the acid.

At a mole fraction 0.5, the heat of mixing of the systems H_2O-1,3-dioxolane and H_2O-acetic acid are 200 (14) and 24 cal/(mol of mixture) (15) whereas L_A and L_B are of the order of 8000 cal/mol (see Table III), and if the ΔH values for the system 1,3-dioxolane-acetic acid compare with the ordinary values of heat of mixing, eq 1, remembering eq 3 and 4, becomes, at least at first approximation

$$x_A \, d \ln \frac{y_1}{(P_A{}^0)_c y_1(1)} + x_B \, d \ln \frac{y_1'}{(P^0)_c} = 0 \quad (5)$$

the integral of which, between $x_B = 0$ and $x_B = 1$, is the thermodynamic relation we assume VLE data must satisfy.

If the dimerization of acetic acid is ignored, eq 5 simplifies to

$$x_A \, d \ln \frac{y_A}{(P_A{}^0)_c} + x_B \, d \ln \frac{y_B}{(P_B{}^0)_c} = 0 \quad (6)$$

which, when integrated, provides a convenient check: in fact, if I_{ass} and I are the absolute values of integrals of eq 5 and 6 between $x_B = 0$ and $x_B = 1$, then $I_{ass} < I$ is a necessary condition for the existence of associations among the components.

Chemicals Used

1,3-Dioxolane (Fluka Product, analytical grade 99%) was purified with the method described in ref 16. Acetic acid (C.Erba RPE Product, 99.8%) was used without purification: major impurity is formic acid 0.01%.

Table I. P-t-x_B-y_B Data for Acetic Acid (A)-1,3-Dioxolane (B) System

t °C	x_B	y_B	t °C	x_B	y_B	t °C	x_B	y_B	t °C	x_B	y_B	t °C	x_B	y_B
P = 150 mmHg			P = 300 mmHg			P = 500 mmHg			P = 650 mmHg			P = 740 mmHg		
32.4	1.000	1.000	48.9	1.000	1.000	62.4	1.000	1.000	69.9	1.000	1.000	73.8	1.000	1.000
33.2	0.962	0.995	50.9	0.937	0.981	64.8	0.922	0.986	73.6	0.862	0.976	76.5	0.903	0.985
36.0	0.848	0.976	54.0	0.800	0.962	69.3	0.758	0.962	76.4	0.764	0.961	80.6	0.769	0.960
37.9	0.764	0.962	56.9	0.687	0.932	71.9	0.670	0.927	79.8	0.654	0.915	84.0	0.666	0.923
41.0	0.646	0.927	59.1	0.630	0.908	74.7	0.591	0.890	83.6	0.550	0.870	87.9	0.572	0.866
43.4	0.564	0.889	61.6	0.548	0.866	77.5	0.504	0.848	86.6	0.470	0.817	90.8	0.485	0.817
46.3	0.470	0.839	63.4	0.496	0.848	80.4	0.429	0.775	89.8	0.399	0.745	93.5	0.422	0.752
51.9	0.322	0.693	69.8	0.330	0.687	87.0	0.284	0.596	95.3	0.290	0.587	99.6	0.298	0.587
54.9	0.260	0.603	72.6	0.274	0.602	89.7	0.241	0.510	97.5	0.250	0.534	102.4	0.247	0.510
57.2	0.218	0.530	74.6	0.238	0.542	91.6	0.210	0.455	99.4	0.218	0.475	104.6	0.210	0.440
59.1	0.187	0.475	76.2	0.204	0.478	93.2	0.184	0.406	101.1	0.195	0.410	106.4	0.183	0.390
61.0	0.156	0.410	78.5	0.173	0.415	94.7	0.156	0.350	103.1	0.156	0.340	107.6	0.162	0.350
65.3	0.091	0.230	83.6	0.090	0.224	98.6	0.084	0.204	107.4	0.086	0.190	111.8	0.087	0.180
71.9	0.000	0.000	89.4	0.000	0.000	104.1	0.000	0.000	112.3	0.000	0.000	116.8	0.000	0.000

Table II. Refractive Index–Composition Data for Acetic Acid (A)-1,3-Dioxolane (B)

x_B	n^{25}_D	x_B	n^{25}_D	x_B	n^{25}_D
0.0000	1.3682	0.2023	1.3760	0.7763	1.3920
0.0552	0.3705	0.4673	1.3840	0.8803	1.3942
0.1455	1.3738	0.6731	1.3885	1.0000	1.3968

Table III. Values of Constants α and β in the Clausius–Clapeyron Expression $\log P^0 = \alpha + \beta/T$ (P^0 in mmHg, T in K) for Vapor Pressures of Pure Components

	acetic acid	1,3-dioxolane
α	8.080871	7.974263
β	-2032.357	-1770.877

Table IV. I and I_{ass}, the Integrals of Eq 6 and 5 Taken over the Range of the Experimental Values of x of Table I

P, mmHg	I	I_{ass}
150	0.105	0.042
300	0.047	0.017
500	0.131	0.012
650	0.120	0.006
740	0.121	0.038

Figure 1. Isobar at P = 740 mmHg for the mixture acetic acid (A)-1,3-dioxolane (B).

Figure 2. Mixture acetic acid (A)-1,3-dioxolane (B) at P = 740 mmHg. Thermodynamic consistency plots: $Z = \ln \gamma_1/\gamma_2$ vs. x_B (a); $Z = \ln y_1'/(P_B^0)_C$ vs. x_B (b); $Z = \ln y_1'/(P_A^0)_C y_1(1)$ vs. x_B (c).
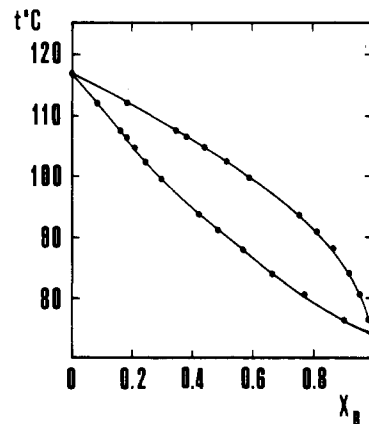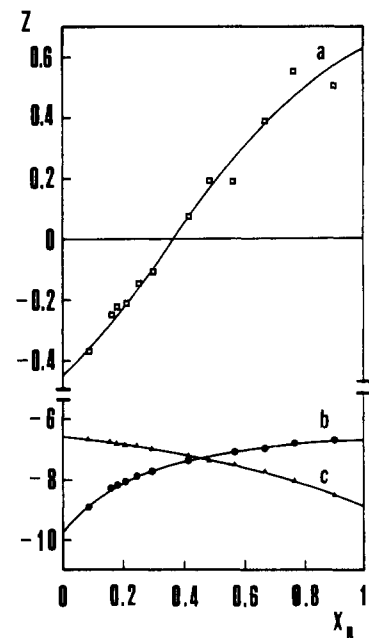
Experimental Section

The VLE data were obtained at pressures p = 150, 300, 500, 650, and 740 mmHg, with a Stage–Muller apparatus (9). Table I gives the P-t-x_B-y_B values, while Figure 1 shows the isobar at 740 mmHg, as an example. The mole fractions x_B and y_B of 1,3-dioxolane were measured with an Abbe refractometer (at 25 °C, with Na lamp), having an error of ∓ 0.0002 refractive units. Table II reports the refractive index–composition data. Uncertainties in P and t are ∓ 0.5 mmHg and ∓ 0.1 °C, respectively. Table III gives the constants α and β for the correlations of vapor pressures of pure components.

Correlations and Results

The thermodynamic consistency of the VLE data of Table I was checked by comparing the integrals I_{ass} and I of eq 5 and 6. Table IV reports the values of I_{ass} and I. The limits of integration were restricted to the lowest and highest experimental values of x_B in order to avoid uncertainties connected with the extrapolation of the logarithmic terms in eq 5 and 6. Figure 2 shows the thermodynamic consistency plots.

The results seem to confirm the presence of dimers of acetic acid in the vapor phase with 1,3-dioxolane, since I_{ass} is invariably less than I at all pressures, in agreement with the theoretical considerations of the Introduction. Moreover, the values of I_{ass} are of the same order as errors on these integrals evaluated according to ref 9 with the uncertainties given in this paper for the measured quantities.

We have tried to correlate the "macroscopic activity coefficients" γ_A and γ_B with the Wilson expression, considering the mixture 1,3-dioxolane–acetic acid as a binary system with activity coefficients "corrected" to allow for dimerization of the acid.

The values of the parameters and the root-mean-square deviation σ are comparable with those of other systems (17), where associations were not suspected, which would seem to confirm the validity of the Wilson expression, purely as a cor-

relating tool, also in the presence of association.

However, the activity coefficients γ_A of acetic acid, calculated from the Wilson expression, show large deviation from the ones evaluated from the experimental data especially at the lowest values of x_A (when $x_A \rightarrow 1$ then $\gamma_A \rightarrow 1$ and deviations are less evident). This seems to indicate difficulties of the Wilson expression in correlating the activity coefficients of the associating substance, though the overall result of the least squares, σ, is acceptable. The second virial coefficients s_1 and s_1' of monomer of A and B, appearing in $(P_k^0)_c$, were calculated with the Wohl formula (9) assuming, for acetic acid, that the virial coefficient of the monomer can be estimated from physical properties of the acid (clearly a mixture of at least monomer and dimer). The equilibrium constant k_2 in eq 2 is the same used in ref 9. In the calculation of s_1 and s_1' the critical values of the components are needed: the ones of acetic acid were taken from ref 15, whereas for dioxolane they were estimated in a previous work (16).

Other forms of associations of the acetic acid in the vapor (such as trimer and tetramer) and A–B associates were not accounted for in this paper, following the conclusions of ref 9 and 10.

Glossary

A, B	pure components
k_2	equilibrium constant for the acetic acid dimerization
L	latent heat of vaporization
P	pressure on the system, mmHg
s	second virial coefficient
t	temperature, °C
T	temperature, K
x, y	molar fractions in the liquid and vapor phases
y_1, y_1'	molar fractions of monomer of A and B in the vapor phase
$y_1(1)$, $y_1'(1)$	values of y_1 and y_1' at $y_A = 1$ and $y_B = 1$

Greek

α, β	constants in the Clausius–Clapeyron equation
ΔH	liquid-phase enthalpy of mixing
γ	activity coefficient
σ	root-mean-square deviation, mmHg

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Thermal Expansion Coefficients of the Mixture Benzene + 1-Heptanol

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The thermal expansion coefficients for the mixtures of benzene with 1-heptanol were determined from density measurements between 298.15 and 313.15 K. The data obtained are compared with those evaluated from equations derived by differentiation of the Gladstone–Dale, Lorentz–Lorenz, and Eykman relationships.

Introduction

The object of the present work is to determine the thermal expansivities of the binary mixtures of benzene with 1-heptanol at moderate temperatures and to verify the applicability to the binary mixtures of the empirical formulas reported in a previous paper (1) for some pure substances. This involved measuring the densities and refractive indices of the mixtures mentioned at the entire range of concentration and at temperatures of 298.15, 303.15, 308.15, and 313.15 K.

The results obtained experimentally for the thermal expansion coefficients of the pure compounds and mixtures thereof were then compared with those predicted from empirical equations taken from the Gladstone–Dale, Lorentz–Lorenz, and Eykman relationships. In order to facilitate data analysis, the experimental values of densities and refractive indices of this study were correlated with the most suitable equations in each case.

Experimental Section

Both the benzene (puriss >99.5 mol %) and 1-heptanol (puriss >99.0 mol %) were from Fluka and were used without further purification.

The densities were measured with an Anton Paar DMA-55 digital vibrating tube densimeter with a reproducibility of ±0.000 01 $g \cdot cm^{-3}$ The temperature of the vibrating tube was controlled within ±0.01 K by using a thermistor previously calibrated according to the regulation IPTS-68. Before each series of measurements, the instrument was calibrated for each temperature with redistilled and deaerated water and benzene. The values of the densities of water at the different temperatures were derived from ref 2 and those corresponding to benzene (Table I) were confirmed by a precision pycnometer.