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Excess Thermodynamic Properties for the Binary System 1,3-Dioxolane–Acetonitrile at t = 40 °C

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Isothermal vapor–liquid equilibrium data P-x_1-y_1 are obtained for the mixture 1,3-dioxolane–acetonitrile at t = 40 °C and are correlated by a two-parameter Redlich–Kister equation. Also liquid-phase enthalpies of mixing H^E are determined as a function of composition and the excess functions G^E and TS^E are calculated therefrom. A comparison of the thermodynamic properties of this mixture with those of 1,4-dioxane–acetonitrile is then made.

Introduction

Data for the vapor–liquid equilibrium (VLE) and the liquid-phase enthalpy of mixing are determined at t = 40 °C for the binary mixture 1,3-dioxolane–acetonitrile, with the aim of comparing the thermodynamic properties of this system with those of 1,4-dioxane–acetonitrile (*1*).

Experimental Section

Chemicals Used. 1,3-Dioxolane (dioxolane), Fluka product, analytical grade 99%, was purified following the method described in ref *2*. Acetonitrile was a C. Erba (Milan, Italy) RPE-ACS 99.9% product. The major impurity, water 0.1% was removed by distillation. The refractive indexes $n^{25}{}_D$ of purified products are for dioxolane 1.3985 (literature values 1.3974 (3) and 1.4000 (4)) and for acetonitrile 1.3418 (literature values 1.3416 (5) and 1.3419 (6)). Dioxolane is component 1.

VLE Measurements. The VLE data P-x_1-y_1 at t = 40 °C were obtained by using the equilibrium still manufactured by Fritz GmbH (Normag) Hofheim (West Germany). For details of the apparatus and check of the equipment, see ref *7* and *8*. The VLE data are shown in Table I and Figure 1.

Temperature and pressure were controlled by digital instruments, allowing an accuracy of 0.1 °C and 1 mbar, respectively.

The vapor pressure of pure dioxolane was evaluated by the expression

$$\log P_1{}^0 \text{ (mmHg)} = 8.13821 - 1826.87/T \text{ (K)}$$

fitting our experimental points $P_1{}^0$, T with a rms deviation of 0.3 mmHg between calculated and experimental $P_1{}^0$. The vapor pressure of acetonitrile was taken from ref *1*.

Table I. P-x_1-y_1 Data for the Mixture Dioxolane (1)-Acetonitrile (2), at t = 40 °C

P, mmHg	x_1	y_1	P, mmHg	x_1	y_1
171.0	0.000	0.000	195.0	0.462	0.511
173.3	0.035	0.049	197.3	0.520	0.562
174.8	0.057	0.077	199.1	0.578	0.610
176.3	0.083	0.110	200.6	0.643	0.665
178.5	0.115	0.150	201.8	0.716	0.728
181.5	0.163	0.209	202.5	0.780	0.785
183.8	0.200	0.249	202.2	0.870	0.858
186.4	0.255	0.309	202.3	0.935	0.928
189.0	0.309	0.366	202.2	0.963	0.952
193.1	0.412	0.462	201.8	1.000	1.000

Table II. Liquid-Phase Enthalpy of Mixing for the Mixture Dioxolane (1)-Acetonitrile (2), at t = 40 °C

x_1	H^E, J·mol^{-1}	x_1	H^E, J·mol^{-1}
0.0230	-4.5	0.6031	-78.9
0.0590	-14.4	0.6950	-72.7
0.115	-24.4	0.7532	-66.3
0.1585	-35.9	0.8201	-56.1
0.2021	-45.8	0.8603	-46.0
0.2747	-56.8	0.9023	-36.3
0.3362	-65.0	0.9486	-19.1
0.4317	-77.4	0.9610	-15.7
0.5326	-80.1		

The mole fractions x_1 and y_1 for component 1 in the liquid and vapor phases were obtained by using a precision Abbe refractometer having an accuracy of 0.0002 refractive unit. The refractive index–composition data were correlated by the expression

$$x_1 = N_1 + N_1N_2 \sum_{k\geq0} a_k(N_1 - N_2)^k \qquad (1)$$

where

$$N_1 = (n - n_2)/(n_1 - n_2) \qquad N_2 = 1 - N_1 \qquad (2)$$

and n_1, n_2 are the refractive indexes of pure components. Thus, eq 1 gives the mole fraction x_1 directly from the measured refractive index $n = n^{25}{}_D$. The parameters a_k were determined with a least-squares method. The objective function to be minimized is

$$\phi_n = \sum_{k=1}^{N_n} \eta^2$$

where the residual η is given by the difference between $(x_1 - N_1)/N_1N_2$ and the summation in eq 1 and N_n is the number of the refractive index–mole fraction points. With four parameters, the maximum deviation between calculated and experimental x_1 is of the same order as the error on x_1 evaluated through the approximated formula

$$dx_1 \simeq dN_1 = dn/(n_1 - n_2) = 0.0002/0.0567 = 3.5 \times 10^{-3} \qquad (3)$$

obtained by taking the derivative of eq 1 and retaining only the first term.

Calorimetric Measurements. The liquid-phase enthalpies of mixing (excess molar enthalpies) H^E for the mixture dioxolane–acetonitrile at t = 40 °C were measured by a flow microcalorimeter Model 2107, LKB-Produkter AB (Bromme, Sweden), which is described in ref *9*). Details on the calibration of the equipment and the accuracy of the measurements are also reported (*10*). Table II and Figure 2 show values of H^E as a function of the mole fraction of dioxolane. Densities of pure components, which are necessary to obtain fluxes in the

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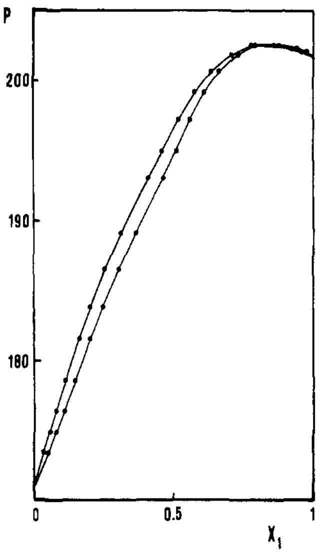

Figure 1. VLE data for the mixture dioxolane (1)–acetonitrile (2) at t = 40 °C. P in mmHg.

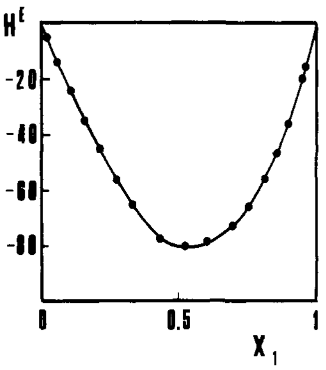

Figure 2. Liquid-phase enthalpy of mixing H^E (J·mol^{-1}) for the mixture dioxolane (1)–acetonitrile (2), as a function of the mole fraction of dioxolane, at t = 40 °C: (●) experimental points; (—) calculated with eq 10.

calorimetric measurements, were taken from ref *1* and *10*.

Correlation of VLE and H^E Data

The thermodynamic consistency of the VLE data was checked by the area test

$$I = \int_0^1 \ln(\gamma_1/\gamma_2)\,dx_1, \quad |I| \leq \Delta I \tag{4}$$

where the activity coefficients γ_1 and γ_2 are evaluated from the experimental data of Table I through the formula

$$\gamma_k = Py_k/P_k^{0\prime}x_i \qquad k = 1, 2 \tag{5}$$

where $P^{0\prime}$ is the corrected vapor pressure of pure component (*11*), taking into account the nonideality of the vapor phase. Figure 3 shows the ln (γ_1/γ_2) vs x_1 plot. The estimated error ΔI on I was obtained from knowledge of the uncertainties in x_1, y_1, P, T by the variance analysis given in ref *12*. We have $I = -0.027 \pm 0.10$.

An uncertainty in x_1 2.5 times the value obtained from eq 3 would be necessary to have a ΔI comparable with I and agreement with eq 4. This situation was met with other mixtures (*13*, *14*) and was attributed to possible associations between the components. Owing to the lack of any information on the species really present in the mixture considered here, we did not try to apply the procedure of ref *13* to correct the activity coefficients of components dioxolane and acetonitrile.

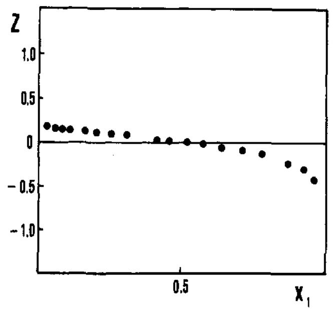

Figure 3. Plot of $Z = \ln(\gamma_1/\gamma_2)$ vs x_1 for the mixture dioxolane (1)–acetonitrile (2).

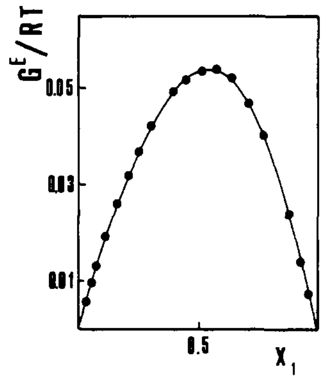

Figure 4. G^E/RT plot for the mixture dioxolane (1)–acetonitrile (2), as a function of the mole fraction of dioxolane, at t = 40 °C: (●) experimental points; (—) calculated with the two-parameter Redlich–Kister expression, eq 6.

The VLE data of Table I were correlated by a two-parameter Redlich–Kister expression

$$\ln\gamma_1 = x_2^2[C + D(3x_1 - x_2)]$$
$$\ln\gamma_2 = x_1^2[C + D(x_1 - 3x_2)] \tag{6}$$

The parameters C and D were calculated by using a least-squares method, to minimize the objective function

$$\phi_G = \sum_{k=1}^{N_G} \eta^2 \tag{7}$$

with

$$\eta = \sum_{j=1}^{2} x_j \ln(\gamma_j^{\text{exptl}}/\gamma_j^{\text{calcd}}) \tag{8}$$

where N_G is the number of the VLE experimental points, the γ^{exptl}'s and the γ^{calcd}'s being given by eq 5 and 6, respectively.

An increased number of parameters in eq 6 leaves practically unchanged the minimum of ϕ_G, whereas the parameters exceeding C and D are close to zero with estimated standard errors larger than the values of parameters. The fair correlation of VLE data by eq 6 is reflected by the small values of the mean deviations $\overline{\Delta\gamma}$'s

$$\overline{\Delta\gamma} = \sum_{k=1}^{N_G} |\gamma^{\text{calcd}} - \gamma^{\text{exptl}}|/N_G$$

which are 0.007 and 0.029, respectively, for dioxolane and acetonitrile.

The molar excess free energy divided by RT

$$G^E/RT = x_1 \ln\gamma_1 + x_2 \ln\gamma_2 \tag{9}$$

is shown in Figure 4, where experimental and calculated values are compared.

The two-parameter Wilson expression was also considered

Table III. Results of the Least-Squares Analysis for the Mixture Dioxolane–Acetonitrile at t = 40 °C[a]

$C = 0.213 \mp 0.006$	$a_0 = -0.371790$	$b_0 = -318.0 \mp 1.8$
$D = 0.033 \mp 0.001$	$a_1 = -0.085699$	$b_1 = -61.6 \mp 5.6$
	$a_2 = -0.101128$	$b_2 = -9.2 \mp 5.1$
	$a_3 = -0.070404$	$b_3 = -42.0 \mp 9.9$
$\sigma_G = 0.0014$	$\sigma_n = 0.0026$	$\sigma_H = 1.0$

[a] C and D are the parameters in the Redlich–Kister expression 6, correlating VLE data; a_k (k = 0, 1, 2, 3) and b_k (k = 0, 1, 2, 3) are the parameters in the expressions 1 and 10, correlating refractive index–composition and H^E data, respectively. Uncertainties are the estimated standard errors, σ_G, σ_n, and σ_H are the rms deviations in the least-squares procedure leading to the parameters C, D, a_k, and b_k, defined by $\sigma = (\phi_{min}/(N - N_p))^{0.5}$ with ϕ_{min} the minimum of the objective function; ϕ, N, and N_p are the number of experimental points and of adjustable parameters.

for correlating the VLE data but larger values of ϕ_G and $\overline{\Delta\gamma}$ were obtained.

The H^E's data were correlated by the Redlich–Kister expression

$$H^E = x_1x_2\sum_{k\geq 0} b_k(x_1 - x_2)^k \tag{10}$$

and the parameters b_k were obtained by the least-squares procedure used in ref *10*. Four parameters allow eq 10 to fit experimental data with a rms deviation σ_H close to 1 J mol^{-1}. Figure 2 compares the experimental H^E's and those calculated by eq 10.

Table III shows all calculated parameters, together with the rms deviations between calculated and experimental values.

Figure 5 shows the calculated excess functions G^E, H^E and $TS^E = H^E - G^E$.

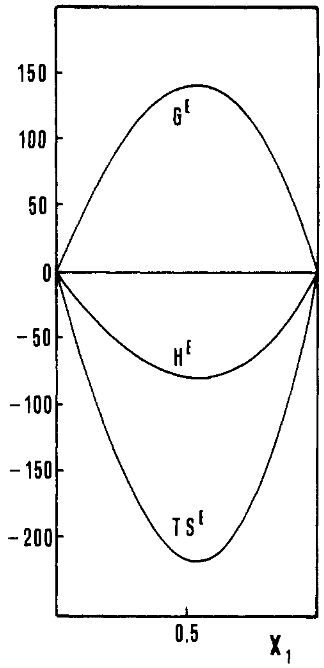

Figure 5. Excess functions (J·mol^{-1}) for the mixture dioxolane (1)–acetonitrile (2) at t = 40 °C.

Conclusions

In spite of the fact that dioxane and dioxolane have very similar molecular structures, both being cyclic (with 6 and 5 members, respectively) saturated, and inclusive of two in-cycle ethereal groups, the thermodynamic properties of their binary mixtures with the same compound, acetonitrile, are quite different and can be summarized as follows.

1. The binary system acetonitrile–dioxane does not give an azeotrope whereas the acetonitrile–dioxolane shows one, although not marked.

2. The liquid-phase enthalpy of mixing H^E of dioxane–acetonitrile shows a sign inversion as a function of the composition. Instead, the H^E's of dioxolane–acetonitrile are always negative with a minimum whose absolute value is about twice the maximum value of the acetonitrile–dioxane mixture. The graph of H^E vs composition for the dioxane–acetonitrile mixture is similar to that for dioxane–water, but with lower values of H^E since the energies corresponding to the water–water hydrogen bonds are larger than the mainly electrostatic interaction energies between acetonitrile molecules. However, the latter prevail over dioxane–dioxane and dioxane–acetonitrile interaction energies, on account of the unusually large dipole moment (3.4 D) of acetonitrile (*15*).

The calorimetric behavior of the mixture dioxolane–acetonitrile (not showing the sign inversion in H^E displayed by dioxolane–water) may be accounted for on the basis of interactions stronger than the mixture acetonitrile–dioxane and of electrostatic nature. In fact, the symmetric molecule of dioxane has no appreciable dipole moment, while dioxolane has a dipole moment of 1.47 D (*16*). Furthermore, in the latter the carbon atom in position 2, neighbor to two oxygen atoms, should have a fractional positive charge larger than that of the carbon atoms of dioxane, where such a situation cannot occur. As a consequence, when dioxolane and acetonitrile are mixed, the energy adsorbed in breaking acetonitrile–acetonitrile bonds is lower than the energy released in the formation of acetonitrile–dioxolane bonds and the H^E's are always negative.

3. Though the activity coefficients of the components in both mixtures show positive deviations from Raoult law, the G^E's of dioxane–acetonitrile are about twice the values for dioxolane–acetonitrile, owing to the relative larger γ's of dioxane.

Glossary

a_k	parameters in the empirical expression correlating refractive index–composition data, eq 1
b_k	parameters in the Redlich–Kister expression correlating the H^E's, eq 10
C, D	parameters in the Redlich–Kister expression correlating VLE data, eq 6
G^E	excess molar free energy
H^E	excess molar enthalpy (liquid-phase enthalpy of mixing)
I	integral in the area test, eq 4
N_1	$(n - n_2)/(n_1 - n_2)$
N_n, N_G, N_H	number of experimental points
N_p	number of adjustable parameters
n	$= n^{25}{}_D$, refractive index at t = 25 °C with Na lamp
n_1, n_2	refractive index of pure components
P	pressure
$P^{0\prime}$	"corrected" vapor pressure of pure component
R	gas constant
S^E	excess molar entropy
T	absolute temperature, K
t	temperature, °C
x_1, y_1	mole fraction of dioxolane in the liquid or in the vapor phases
γ	activity coefficient
$\overline{\Delta\gamma}$	mean deviation between calculated and experimental γ
ΔI	estimated error on I
ϕ_n, ϕ_G, ϕ_H	objective functions in the least-squares method
σ_n, σ_G, σ_H	rms deviation, defined as $(\phi_{min}/(N - N_p))^{0.5}$, with N the number of experimental points N_n, N_G, N_H

Indexes

n, G, H	refer to refractive index–composition, VLE, and H^E data, respectively

Registry No. 1,3-Dioxolane, 646-06-0; acetonitrile, 75-05-8.

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Solubility of Aromatic Hydrocarbons in Water and Sodium Chloride Solutions of Different Ionic Strengths: Benzene and Toluene

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The solubilities of benzene and toluene in aqueous sodium chloride solutions having ionic strengths ranging from 0 to 5.00 have been determined at 25.00 °C. The solubilities were determined by headspace analysis using a multiple injection interrupted flow (MIIF) technique. The values for the Henry's law constants and partition coefficients for benzene and toluene in the solutions studied are also given. The activity coefficients of benzene and toluene in the solutions studied can be calculated from the solubility data.

Determining solubilities of substances with appreciable vapor pressures can be complicated by the partition of such substances between the solvent and free gas space present above the solvent. A modification of the headspace analysis technique developed by Massaldi and King (*1*) was selected as the method used for this study because of its ease of execution and because solute partition is not a problem since headspace methods make use of partition.

Theory

Volatile solutes tend to obey Henry's law

$$p = kx \tag{1}$$

The Henry's law constant is dependent upon the solute, solvent, and temperature but is independent of x over the range for which the law holds. Since conformity with Henry's law increases as $x \rightarrow 0$, substances of limited solubilities tend to obey it over their solubility range.

When a sample from above a solution of a volatile solute, which obeys Henry's law, is analyzed by gas chromatography (GC) the peak area of the solute is directly proportional to its mole fractions in both the vapor and solution through the relationship

$$A = Cy = Cx/K_p \tag{2}$$

The total number of moles of solute in the system is given by

$$n_s = n_x + n_y \tag{3}$$

Table I. Symbols Employed[a]

p	partial pressure of substance in the vapor
x, y	mole fraction of substance in the solution and vapor, respectively
k	Henry's law constant
A_x, A_y	integrated GC peak area of vapor from above solution samples and from vapor-only samples, respectively
K_p	partition coefficient ($=x/y$)
C	GC correlation constant
n_x, n_y, n_s	moles of substance in the solution, vapor, and system, respectively
v_x, v_y, v_s	liquid volume of substance in the solution, vapor, and system, respectively
S	solubility in any units
γ	activity coefficient
μ	ionic strength

[a] Zeroed quantities refer to system as well as solvent saturation.

If n_s^0 and n_y^0 can be determined then n_x^0 can be computed. The method of Massaldi and King was modified, in part, in the way n_s^0 was determined. Table I defines the terms used in the determinations.

Experimental Section

Instrumentation. Measurements were made using a headspace attachment constructed specifically for a Varian Model 3700 gas chromatograph (*2*).

Materials. Benzene and toluene (Baker Instra-Analyzed grade) were analyzed by gas chromatography and were 99.97 and 99.83% pure, respectively. Sodium chloride (Baker Analyzed Reagent grade) was dried at 110 °C prior to use. The deionized water used had a conductivity of $<10^{-6}$ (ohm cm)$^{-1}$ at 20 °C.

Sample Preparation. Samples were prepared in 125-mL septum bottles (Wheaton "400" clear glass) which have a mean volume of 160.10 ± 0.87 mL at room temperature. Two types of samples were used: one contained 50.00 mL of water or aqueous NaCl solution plus the hydrocarbon of interest, added from a microliter syringe (Hamilton Model 700 RN); the other contained only hydrocarbon vapor. A small 6.4 mm by 22.2 mm Pyrex glass coated magnetic stirring bar with a mean volume of 0.70 mL (Bel-Art Products) was present in the liquid

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