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Excess Thermodynamic Properties for the Binary System 1,4-Dioxane–Acetonitrile at 40 °C

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Vapor–liquid equilibrium (VLE) and heat of mixing data for the binary system 1,4-dioxane–acetonitrile were determined at 40 °C. Measurements of vapor pressure and density were taken on pure components. The excess thermodynamic properties G^E and TS^E were calculated from the experimental data, which were correlated by means of Redlich–Kister expressions. Thermodynamic consistency of the VLE data is checked by the area test.

Introduction

Isothermal vapor–liquid equilibrium (VLE) data and liquid-phase enthalpy of mixing data were determined for the binary mixtures of 1,4-dioxane and acetonitrile at 40 °C. The measurements reported in this paper, together with the VLE data from the system 1,3-dioxolane–1,4-dioxane, previously obtained (*1*), and from 1,3-dioxolane–acetonitrile (following article in this issue), constitute a complete study of the three binary mixtures and supply a thermodynamic basis for the description of the corresponding ternary mixture. Furthermore, a comparison between thermodynamic properties of the binary mixtures of acetonitrile with 1,3 dioxolane and 1,4 dioxane is of interest due to the size of dipole moments of the three molecules considered. In fact, acetonitrile has an unusually large dipole moment, 3.4 D(*2*), to be compared with the one of 1,2 dioxolane, 1.47 D (*3*), whereas the symmetric molecule 1,4-dioxane has no appreciable dipole moment.

The experiments were carried out at 40 °C, which is the maximum working temperature for the calorimetric equipment. Since the enthalpy of mixing H^E is necessary to test correctly the thermodynamic consistency of isobaric VLE data, values of H^E at high temperatures are generally needed over the range of pressure 100–760 mmHg, which is usually explored. Isothermal VLE at 25 °C for 1,4 dioxane–acetonitrile mixtures was investigated by D'Avolio et al. (*4*).

Table I. Refractive Index–Composition Data for the Mixture Dioxane–Acetonitrile

X_1	n^{25}_D	X_1	n^{25}_D	X_1	n^{25}_D	X_1	n^{25}_D
0.000	1.3417	0.123	1.3567	0.396	1.3835	0.911	1.4163
0.005	1.3423	0.155	1.3603	0.455	1.3881	1.000	1.4206
0.038	1.3467	0.205	1.3658	0.527	1.3935		
0.074	1.3510	0.289	1.3740	0.736	1.4069		

Experimental Section

Chemicals Used. 1,4-Dioxane (dioxane) and acetonitrile were C. Erba (Milan, Italy) RPE-ACS 99.9% products. The major impurity, water 0.1% for acetonitrile and 0.02% for dioxane, was removed by distillation. The refractive indexes n^{25}_D of purified products are for dioxane 1.4206, (literature value 1.4202 (*4*, *5*)) and for acetonitrile 1.3417 (literature values 1.3419 (*4*), 1.3416 (*5*)). Dioxane is component 1. Molecular sieves 3A were added to the solvents to prevent moisture from contaminating them. Syringes were used to fill the still and to bring microsamples of liquid and condensed vapor to the refractometer. Since acetonitrile is toxic in contact with skin, use of gloves was necessary in handling this compound. Ordinary precautions were taken against inflammability of both materials.

VLE Measurements. The isothermal VLE data P-X-Y at 40 °C were obtained with the equilibrium still manufactured by Fritz GmbH (Normag) Hofheim (West Germany) described in detail by Gmehling (*6*). Equilibrium temperature t and pressure P in the still were measured with digital instruments declaring accuracy of 0.1 °C and 1 mbar (0.75 mmHg), respectively. These values were confirmed by repeated experiments on pure water and are assumed as the estimated errors for VLE data of this paper. A check of the equipment was performed following the procedure given in ref *7*.

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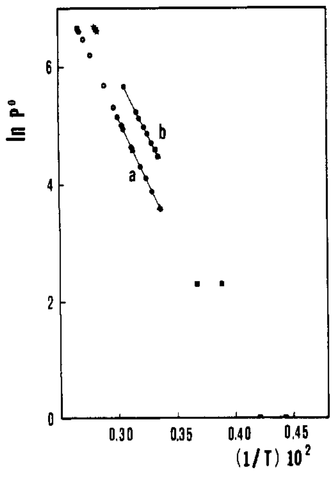

Figure 1. Vapor pressure of pure dioxane and acetonitrile, P^0 (mmHg), as a function of temperature T (K): (a) dioxane; (b) acetonitrile; (○) Castellari et al. (*1*); (▲) D'Avolio et al. (*4*); (★) Beilstein (*8*); (■) Dreisbach (*9*); (●) this work; (—) calculated from parameters A and B of Table II.

Table II. Experimental Vapor Pressure of Pure Components[a]

T, K	P_1^0, mmHg	T, K	P_1^0, mmHg
	Dioxane		
298.2	35.6	320.3	104.3
304.2	48.8	327.5	142.5
309.0	61.5	332.5	175.5
313.2	75.0	336.0	202.5
	Acetonitrile		
298.2	88.9	313.2	171.0
303.6	113.3	316.0	191.3
306.5	129.0	320.0	225.0
310.1	150.0	326.4	288.8

[a] A and B are the constants in the Clausius–Clapeyron expression $\ln P^0 = A + B/T$ (P^0 in mmHg, T in K) and were obtained by a least-squares method. σ is the rms deviation between calculated and experimental values. For dioxane, σ = 0.2 mmHg, A = 18.9685, and B = −4587.74. For acetonitrile, σ = 0.2 mmHg, A = 18.1090, and B = −4060.98.

The mole fractions of the samples, X and Y, in the liquid and vapor phases, were measured with a precision Abbe refractometer having an accuracy of 0.0002 refractive unit. The refractive index–composition data are reported in Table I. Mixtures were prepared by weighing and an estimate of the uncertainty in the mole fraction may be calculated through the formula $\Delta X = \Delta n/|n_1 - n_2|$ where $\Delta n = 0.0002$ is the accuracy of the refractometer and n_1 and n_2 are the refractive indexes of pure compounds. Hence $\Delta X = 3 \times 10^{-3}$.

Figure 1 compares the vapor pressures of the pure components obtained in this paper with the ones from the literature (*1*, *2*, *4*, *9*). Table II lists the experimental vapor pressures of pure components and the results of correlation of the vapor pressure data by a Clausius–Clapeyron expression. Table III collects the VLE data.

Calorimetric Measurements. The liquid-phase enthalpies of mixing (excess molar enthalpies) H^E for the system dioxane–acetonitrile at 40 °C were obtained with the flow microcalorimeter Model 2107, LKB-Produkter AB. Bromme, Sweden, described in ref (*10*). Details on calibration, analytical measurements and accuracy of the results are given in ref *11*.

Figure 2 and Table IV show the values of H^E as a function of the mole fraction of dioxane.

Density Measurements. Density measurements of pure liquid components, ρ_1 and ρ_2, are necessary to evaluate fluxes in the calorimetric experiments and were obtained with a two-capillary glass pycnometer, calibrated with distilled mercury.

Table III. P-X-Y Data and Experimental Activity Coefficients for the Mixture Dioxane (1)-Acetonitrile (2) at 40 °C

P, mmHg	X_1	Y_1	γ_1	γ_2
165.0	0.099	0.062	1.37	1.01
161.3	0.151	0.094	1.33	1.01
156.8	0.211	0.129	1.27	1.01
153.0	0.268	0.163	1.23	1.02
147.0	0.343	0.211	1.20	1.03
142.1	0.405	0.254	1.18	1.04
138.8	0.450	0.282	1.15	1.06
132.8	0.517	0.339	1.12	1.08
123.8	0.622	0.413	1.09	1.13
117.8	0.687	0.470	1.07	1.17
113.3	0.737	0.521	1.06	1.21
105.0	0.816	0.610	1.04	1.31
98.3	0.872	0.691	1.04	1.39
96.0	0.890	0.718	1.03	1.45
88.1	0.940	0.820	1.02	1.56
81.8	0.974	0.906	1.01	1.74

Table IV. Isothermal Liquid-Phase Enthalpy of Mixing H^E for the Mixture Dioxane (1)-Acetonitrile (2) at 40 °C

X_1	H^E, J·mol^{-1}	X_1	H^E, J·mol^{-1}	X_1	H^E, J·mol^{-1}	X_1	H^E, J·mol^{-1}
0.015	−2.1	0.292	−32.0	0.650	9.4	0.937	30.2
0.025	−1.9	0.314	−31.6	0.712	21.8	0.952	25.5
0.049	−5.5	0.382	−28.8	0.788	33.2	0.961	22.7
0.094	−15.6	0.452	−23.4	0.832	37.7	0.980	11.4
0.134	−23.6	0.553	−7.6	0.881	38.7		
0.236	−31.1	0.623	3.9	0.908	35.6		

Table V. Experimental Densities of Pure Components as a Function of Temperature

dioxane		acetonitrile	
T, K	ρ_1, kg·m^{-3}	T, K	ρ_2, kg·m^{-3}
308.5	1015.5	305.4	767.9
310.4	1013.1	310.3	762.6
314.0	1009.1	314.9	757.6
315.8	1007.0	319.3	752.7

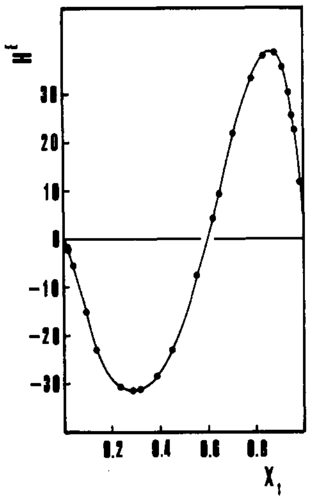

Figure 2. Liquid-phase enthalpy of mixing H^E (J·mol^{-1}) for the mixture dioxane (1)–acetonitrile (2) as a function of the mole fraction of dioxane, at 40 °C: (●) experimental points; (—) calculated with eq 7.

The experimental data, measured at variable temperatures and at saturation pressures, are reported in Table V and are fitted by the following straight lines

$$\rho_1\ (\mathrm{kg \cdot m^{-3}}) = 1056.61 - 1.16882t\ (^\circ\mathrm{C}) \qquad 15\text{–}43\ ^\circ\mathrm{C} \qquad (1)$$

$$\rho_2\ (\mathrm{kg \cdot m^{-3}}) = 803.971 - 1.09539t\ (^\circ\mathrm{C}) \qquad 16\text{–}81\ ^\circ\mathrm{C} \qquad (2)$$

over the temperature ranges indicated, with a mean deviation of 0.3 and 1 kg·m^{-3} between calculated and experimental

Table VI. Results of the Least-Squares Analysis for the Mixture Dioxane-Acetonitrile[a]

		$a_0 = -64.17 \pm 0.4$
$C = 0.3858 \mp 0.014$	$\lambda_{12} = -1954.4$	$a_1 = 290.99 \pm 1.5$
$D = 0.2325 \mp 0.058$	$\lambda_{12} = 3635.0$	$a_2 = 144.22 \pm 4.8$
$E = 0.3685 \mp 0.085$		$a_3 = 105.36 \pm 3.1$
		$a_4 = 232.94 \pm 6.2$
$\sigma_{RK} = 0.003$	$\sigma_W = 0.009$	$\sigma_H = 0.84$

[a] C, D, and E are the parameters in the Redlich-Kister expression 3 and λ_{12} and λ_{21} are parameters of the Wilson expression in the correlation of VLE data; a_k ($k = 0, ..., 4$) are the parameters in the Redlich-Kister expression 7 correlating H^E data. Uncertainties are the estimated standard errors. σ_{RK}, σ_W and σ_H are the rms deviations in the least-squares procedure referring to calculation of C, D, E, λ_{12}, λ_{21}, and a_k, respectively.

values of density, respectively. More significant figures than the ones indicated by the mean deviation have been retained in eq 1 and 2, to avoid rounding-off errors in the calculated values. The same procedure was followed for the other parameters calculated.

Correlation of VLE and H^E data

The VLE data of Table III were correlated by means of the three-parameter Redlich-Kister expressions

$$\ln \gamma_1 = X_2^2[C + D(3X_1 - X_2) + E(X_1 - X_2)(5X_1 - X_2)]$$
$$\ln \gamma_2 = X_1^2[C + D(X_1 - 3X_2) + E(X_1 - X_2)(X_1 - 5X_2)] \tag{3}$$

The adjustable parameters C, D, and E were determined by a least-squares method with the objective function ϕ_G to be minimized chosen as

$$\phi_G = \sum_{k=1}^{N_G} \eta^2$$
$$\eta = \sum_{j=1}^{2} X_j \ln (\gamma_j^{\text{exptl}}/\gamma_j^{\text{calcd}}) \tag{4}$$

where N_G is the number of experimental points, the γ_j^{calcd}'s are given by eq 3, and the γ_j^{exptl}'s are evaluated through the formula

$$\gamma_j = PY_j/p_j^{0\prime}X_j \tag{5}$$

with $P^{0\prime}$ the corrected vapor pressure of pure component, taking into account the nonideality of the vapor phase (*12*, *13*). The fugacity coefficients are in the range 1-1.01 and 1-0.994 for dioxane and acetontrile, respectively. The activity coefficients of dioxane and acetonitrile, evaluated from eq 5, are listed in Table III.

A four-parameter Redlich-Kister expression was also tried, with no detectable improvement of the rms deviation $\sigma_{RK} = (\phi_{G,\min}/(N - N_G))^{0.5}$, where $\phi_{G,\min}$ is the minimum value of ϕ_G, eq 4. A two-parameter Wilson expression gives $\sigma_W = 0.009$, to be compared with $\sigma_{RK} = 0.003$ for the three-parameter Redlich-Kister equation. The Wilson equation was used in view of the good results obtained in correlating VLE data of several mixtures previously studied (*14*-*18*). No other empirical expression was used since the simple Redlich-Kister eq 3 was able to correlate well the data. This can be seen from Figure 3 and from the value of σ in Table VI, , where the adjusted parameters, their estimated errors, and values of rms deviations are collected. Critical temperatures and pressures, which are necessary for the calculation of $P^{0\prime}$, where taken from ref 19. The molar excess free energy G^E (divided by RT)

$$G^E/RT = X_1 \ln \gamma_1 + X_2 \ln \gamma_2 \tag{6}$$

obtained from the calculated parameters C, D, and E is shown in Figure 3, together with the corresponding G^E/RT for the two-parameter Wilson expression, and compared with the experimental value.

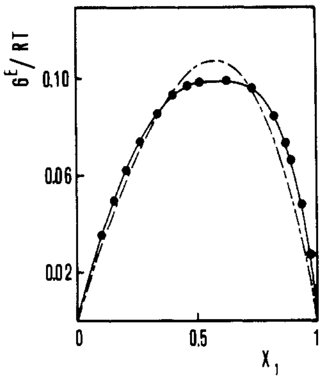

Figure 3. G^E/RT plot for the mixture dioxane (1)-acetonitrile (2) as a function of the mole fraction of dioxane at 40 °C: (●) experimental points; (- -) calculated with Wilson expression; (—) calculated with three-parameter Redlich-Kister expression.

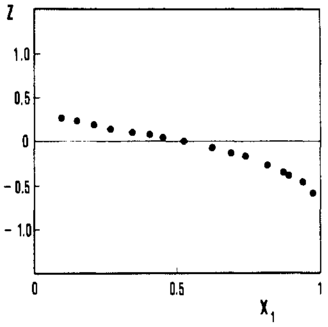

Figure 4. Plot of $Z = \ln (\gamma_1/\gamma_2)$ vs X_1 for the mixture dioxane (1)-acetonitrile (2) at 40 °C.

Correlation of H^E data was carried out by means of the Redlich-Kister expression

$$H^E = X_1X_2\sum_{k\geq 0} a_k(X_1 - X_2)^k \tag{7}$$

and the parameters a_k were obtained with the usual least-squares procedure. The objective function is the same used in ref *11*. Five parameters were needed for eq 7 to fit the experimental H^E data with a sample standard deviation $\sigma_H = 0.84$. σ_H is defined as $(\phi_{H,\min}/(N - 5))^{0.5}$ where $\phi_{H,\min}$ is the minimum value of the sum of the weighed squared differences between the experimental H^E's and the ones calculated through eq 7. Table VI reports parameters a_k's together with their estimated standard errors and the rms deviation.

The thermodynamic consistency of the VLE data for the mixture dioxane-acetonitrile at 40 °C was checked by means of the area test

$$I = \int_0^1 \ln (\gamma_1/\gamma_2)\, dX_1 = 0 \tag{8}$$

neglecting the contribution of the volume-term to the Gibbs-Duhem equation (*12*). An estimate of the error ΔI on integral I was obtained following the procedure given in ref *18*.

Since $I = -0.071 \pm 0.088$, we may conclude that, within the limits of experimental errors, the VLE are consistent. Figure 4 shows the plot $\ln (\gamma_1/\gamma_2)$ vs X_1.

Figure 5 shows calculated excess properties G^E, H^E, and $TS^E = H^E - G^E$. Let us briefly comment on the calorimetric behavior of dioxane, a six-membered ring molecule with two etheric groups. The liquid-phase enthalpy of mixing H^E of the mixture dioxane-acetonitrile, displayed in Figure 2, exhibits a sign inversion as a function of composition, the same profile being shown by the dioxane-water (*2*) system. Also 1,3-dioxolane, a five-membered ring molecule with two etheric groups, gives aqueous binary mixtures showing a sign inversion in the H^E values (*20*). For aqueous mixtures, this profile is the

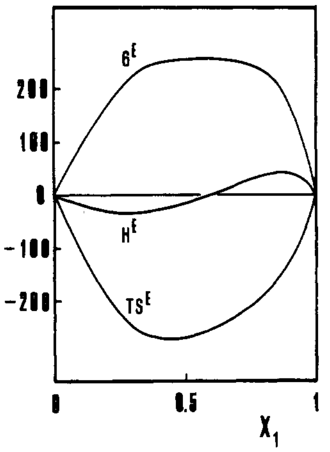

Figure 5. Excess functions (J·mol^{-1}) for the mixture dioxane (1)–acetonitrile (2) at 40 °C.

effect of a particular balance between strong hydrogen bonds broken by the solute molecules and the subsequent solute–water bonds formed, when mixing the components (*2*). High values of H^E are measured, in the order of 500–1000 J·mol^{-1}.

In the case of acetonitrile, since this solute is unable to form hydrogen bonds, a possible explanation of the anomalous H^E profile may be sought in the unusually large dipole moment of acetonitrile (*2*), which gives rise to interactions of lesser strength than the hydrogen bonds and, consequently, lower values of H^E, not exceeding 40 J·mol^{-1}.

Glossary

A, B	parameters in the Clausius–Clapeyron expression for the vapor pressure of pure components
C, D, E	parameters in the Redlich–Kister expression correlating VLE data, eq 3
a_k	parameters in the Redlich–Kister expression correlating H^E data, eq 7 (k = 0, ..., 4)
G^E	exess molar free energy
H^E	excess molar enthalpy (liquid-phase enthalpy of mixing)
I	integral in the area test, eq 8
n_G, n_H	number of adjustable parameters in the VLE or H^E data correlation expressions
N_G, N_H	number of experimental VLE or H^E points
P	pressure
$P^{0\prime}$	"corrected" vapor pressure of pure component
R	gas constant
S^E	excess molar entropy
t	temperature, °C
T	absolute temperature, K
X, Y	mole fraction in the liquid or in the vapor phase
γ	activity coefficient
ρ	density
λ_{12}, λ_{21}	parameters in the Wilson equation
ΔI	estimated error on I
ϕ	objective functions in the least-squares method
σ	rms deviation, defined as $\sigma = (\phi_{\min}/(N - n))^{0.5}$ where $\phi_{\min}$ is the value of ϕ at its minimum

Indexes

H	refers to H^E data
RK	refers to VLE data (Redlich–Kister expression)
W	refers to VLE data (Wilson expression)

Registry No. 1,4-Dioxane, 123-91-1; acetonitrile, 75-05-8.

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