γ_f^∞	corrected activity coefficient
γ_A^∞	athermal contribution to activity coefficient
γ_T^∞	thermal contribution to activity coefficient
γ_p^∞	activity coefficient
γ_{F-H}^∞	Flory–Huggins size effect correction
γ_{I-S}^∞	size-corrected athermal contribution

Registry No. 1, 108-87-2; 2, 111-65-9; 3, 124-18-5; 4, 71-43-2; 5, 108-88-3; 6, 100-41-4; 7, 103-65-1; 8, 104-51-8; 9, 95-47-6; 10, 108-38-3; 11, 106-42-3; 12, 611-14-3; 13, 620-14-4; 14, 622-96-8; 15, 526-73-8; 16, 95-63-6; 17, 108-67-8; 18, 98-82-8; 19, 98-06-6; 20, 100-42-5; 21, 100-66-3; 22, 462-06-6; 23, 108-90-7; 24, 108-86-1; 25, 591-50-4; 26, 95-49-8; 27, 108-41-8; 28, 106-43-4; 29, 118-69-4; 30, 25186-47-4; 1,3-propanediyl-(PrTCTP)$_2$, 36640-96-7; 1,3-propanediyl-(BuTCTP)$_2$, 36640-93-4; bis(3-((4-propoxycarbonyl)-2,3,5,6-tetrachlorobenzoyl)oxy)tetrachloroterephthalate, 36640-98-9.

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Liquid-Phase Enthalpy of Mixing for Binary Mixtures with Associated Components. The Mixture 1,3-Dioxolane–Acetic Acid

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The liquid-phase enthalpies of mixing for the system 1,3-dioxolane–acetic acid have been determined at 298.15, 306.15, and 313.15 K as a function of composition. Correlation of the calorimetric data was obtained by the Redlich–Kister empirical expression.

Introduction

The present work, an extension of our previous studies on binary mixtures of 1,3-dioxolane with associated components (*1*, *2*), deals with the calorimetric determination of the liquid-phase enthalpy of mixing (heat of mixing) for the system 1,3-dioxolane (D)–acetic acid (A). The aim of the present work is to determine and correlate the calorimetric data for the mixture D–A in the temperature range 298.15–313.15 K. The upper limit of 313.15 K is imposed by our LKB flow microcalorimeter; the lower limit of 298.15 K is due to the melting point of A (289.75 K).

Chemicals

1,3-Dioxolane (Fluka product, analytical grade 99%) was purified by refluxing for about 10 h on Na wires in N_2 flow, excluding moisture. It was then fractionated on a Vigreux column. For further details see also ref *3*. Acetic acid (C. Erba product, 99.8%) was used without purification: the major impurity is formic acid, 0.01%.

Table I. Values of the Experimental Enthalpies of Mixing ΔH for the System D–A as a Function of the Mole Fraction of D, at Three Temperatures

T = 298.15 K		T = 306.15 K		T = 313.15 K	
N_D	ΔH, J·mol^{-1}	N_D	ΔH, J·mol^{-1}	N_D	ΔH, J·mol^{-1}
0.0250	18.4	0.0249	18.6	0.0307	16.0
0.0330	24.7	0.0331	25.3	0.0405	22.0
0.0641	48.7	0.0641	48.2	0.0778	43.4
0.1205	87.9	0.1204	87.0	0.1204	72.8
0.1705	119.1	0.1704	113.2	0.1724	108.0
0.2151	144.8	0.2150	141.4	0.2149	132.2
0.2913	182.3	0.2912	176.3	0.2910	169.0
0.3539	207.4	0.3539	198.0	0.3537	192.5
0.4512	231.2	0.4510	225.5	0.4509	215.3
0.5522	237.5	0.5521	230.3	0.5519	222.4
0.6218	233.2	0.6217	225.9	0.6215	217.2
0.7115	213.2	0.7115	205.2	0.7196	200.6
0.7668	192.3	0.7667	185.8	0.7595	187.7
0.8315	161.4	0.8314	154.4	0.8313	154.9
0.8680	136.8	0.8679	132.2	0.8679	132.6
0.9080	103.3	0.9079	103.0	0.9079	102.6
0.9518	60.4	0.9517	60.4	0.9517	60.7
0.9634	48.7	0.9634	47.4	0.9633	47.1

Table II. Values of the Experimental Densities ρ_A of Acetic Acid as a Function of Temperature

T, K	ρ_A, kg·m^{-3}	T, K	ρ_A, kg·m^{-3}	T, K	ρ_A, kg·m^{-3}
290.70	1052.50	297.00	1045.45	307.25	1033.89
290.85	1052.45	299.65	1042.54	309.10	1031.82
291.10	1052.16	300.65	1041.35	310.30	1030.46
292.95	1049.94	304.65	1036.18	311.55	1029.04
293.65	1049.18	306.00	1035.33	313.15	1027.15

Liquid-Phase Enthalpy of Mixing: Calorimetric Measurements

The enthalpies of mixing ΔH for the mixture D–A were determined by a flow microcalorimeter Model 2107, LKB-Producter AB (Bremme, Sweden) described in ref *4*. Details of the calibration of the equipment and accuracy of measurements are given in ref *5*. Figure 1 and Table I gather the ΔH values as a function of the mole fraction of D. The calorimetric experiments were performed at 298.15, 306.15, and 313.15 ± 0.01 K (IPTS-68).

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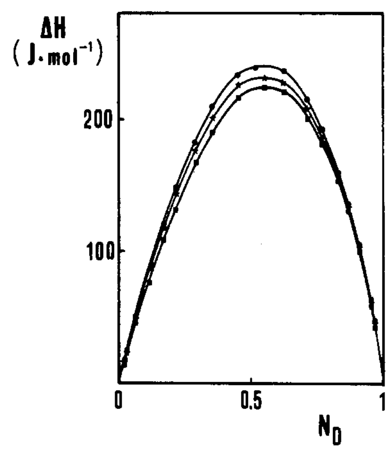

Figure 1. Enthalpies of mixing for the system D–A as a function of the mole fraction of D, at three temperatures: experimental values (●) at 298.15 K; (★) at 306.15 K; (■) at 313.15 K; (—) calculated by the right-hand side of eq 2 with parameters a_k of Table III.

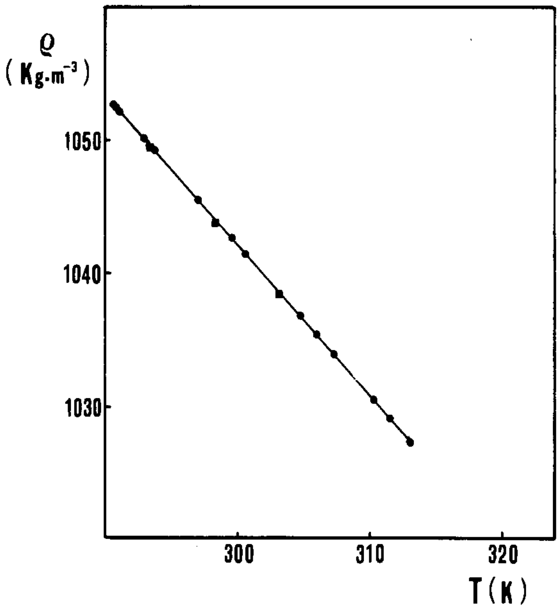

Figure 2. Experimental density measurements of pure A as a function of temperature: (●) this paper; (▲) ref *8*; (■) ref *7*; (—) calculated by eq 1.

Our calorimetric data at 298.15 K were compared with the ones obtained by Grolier and Inglese (*6*). The mean deviation between the two sets of data is about 1%.

Densities of pure components enter the calculations to obtain ΔH and were taken from ref *6* for D and measured for A by using a two-capillary glass pycnometer, calibrated with distilled mercury. The experimental densities were obtained in the temperature range 291–313 ± 0.01 K, at saturation pressures.

The density values of pure A are fitted by the straight line

$$\rho_A(\mathrm{kg \cdot m^{-3}}) = 1380.58 - 1.1284T(\mathrm{K}) \quad (1)$$

with the correlation coefficient being 0.999 986 and the sample standard deviation 0.05 kg·m^{-3}. Table II shows the experimental values of ρ_A in this paper as a function of temperature, and Figure 2 compares these values with the ones in literature (*7*, *8*).

The three isothermal sets of calorimetric data of Table I were correlated by the Redlich–Kister empirical expression

$$\Delta H = N_A N_D \sum_{k \geq 0} a_k (N_A - N_D)^k \quad (2)$$

and parameters a_k are obtained by the least-squares method,

Table III. Parameters a_k in the Correlation of the Heat of Mixing Data, According to Eq 2

n_H	T, K	a_0	a_1	a_2	a_3	a_4	σ_H[a]
18	298.15	954.22	142.22	84.29	196.38	65.01	0.85
18	306.15	916.48	135.66	33.97	190.53	159.82	1.34
18	313.15	880.11	126.63	136.63	343.48	74.18	0.81

[a] σ is the root-mean-square deviation between experimental and calculated values, $\sigma_H = (\phi_{\min}/(n_H - n_p))^{0.5}$, with n_H the number of experimental points, n_p the number of adjustable parameters, and $\phi_{\min}$ the value of ϕ_H at the minimum.

with the following objective function to be brought to a minimum:

$$\phi_H = \sum_{j=1}^{n_H} \eta_j^2 \quad (3)$$

$$\eta_j = \frac{\Delta H}{N_A N_D} - \sum_{k \geq 0} a_k (N_A - N_D)^k \quad (4)$$

where n_H is the number of calorimetric experimental points for each set of data.

The calculated parameters are shown in Table III for the mixtures at different temperatures, together with the root-mean-square deviations σ_H between calculated and experimental values of enthalpies.

The number of adjusted parameters was chosen so that σ_H compares with the mean error on experimental enthalpies as calculated according to the equations reported in ref *5*. In Figure 1 the calculated curves are compared against the experimental data.

Conclusions

As can be seen from Figure 1, the system 1,3-dioxolane–acetic acid shows positive values for the enthalpy of mixing ΔH with a maximum value of about 240 J·mol^{-1} and a feeble dependence on temperature.

In terms of interaction energies between molecules, positive values of ΔH may result when the (positive) energy required from breaking A–A and D–D bonds exceeds that (negative) released when A–D bonds are formed during mixing if, for simplicity, only nearest-neighbor interactions are appreciable.

Thus the high positive values of ΔH for the mixtures of acetic acid with hexane, heptane, and cyclohexane (*9*) are probably due to the dominant interaction energy of hydrogen bonds in the acid, leading to dimers (*1*, *2*). On the contrary, the mixtures of acetic acid with cyclic ethers oxane, oxolane, and dioxane (*10*) show negative values since the ethereal groups may interact with the OH groups of the acid to give hydrogen bonding with consequent energy release, which seems to overcome the energy taken up for breaking acetic acid dimers.

The positive value of ΔH for the system dioxolane–acetic acid may be originated by the ether–ether interactions stronger than those of the other cyclic ethers since the carbon atom in position 2 for dioxolane should have a fractional positive charge larger than that of the carbon atoms of dioxane, oxane, and oxolane (*11*) with consequent larger electrostatic attraction between opposite charged positions of two molecules.

However, these qualitative considerations can be definitively confirmed by spectroscopic measurements which will be performed in a future work with the aim of ascertaining possible associations between the components in addition to the well-known dimerization of acetic acid.

Glossary

A	acetic acid
a_k	parameters in eq 2
D	1,3-dioxolane
ΔH	molar enthalpy of mixing, J·mol^{-1}

n_H	number of enthalpy-of-mixing experimental points
T	temperature, K

Greek Letters

ρ	density, kg·m^{-3}
ϕ	objective function, eq 3
σ	root-mean-square deviation between calculated and experimental values
η	residual, eq 3

Registry No. 1,3-Dioxolane, 646-06-0; acetic acid, 64-19-7.

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Solubilities of *n*-Octadecane, Phenanthrene, and *n*-Octadecane/Phenanthrene Mixtures in Supercritical Propane at 390 and 420 K and Pressures to 60 bar

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Solubility data were obtained for *n*-octadecane, phenanthrene, and a nearly equimolar *n*-octadecane/phenanthrene mixture in supercritical propane. Solubilities were measured in a flow apparatus at 390 and 420 K over the pressure range 35–60 bar. The experimental data have been correlated using the perturbed-hard-chain equation of state. Agreement between experiment and correlation is good.

Introduction

Supercritical-fluid extraction has received wide attention during the past few years for potential application in the specialty-chemicals, pharmaceutical, and petroleum industries (*1*). At the center of this new technology lies enhanced solubility of the solute near the solvent's critical point. Experimental information on selected model systems is required to utilize molecular-thermodynamic models for representing the complex systems encountered in industrial applications.

Model systems using carbon dioxide or ethylene as the supercritical solvent have been studied extensively (*2–5*). However, only a few studies have reported data for systems where the gaseous solvent has a critical temperature significantly above that of carbon dioxide (304.2 K) (*6*, *7*). In this work we present solubilities of two model compounds (*n*-octadecane and phenanthrene) in supercritical propane.

Propane's critical point (369.8 K and 41.9 bar) makes it a suitable solvent for deasphalting processes in the petroleum industry. *n*-Octadecane and phenanthrene represent two classes of hydrocarbon compounds, aliphatic and aromatic, found in heavy fossil fuels. Both are liquids in the temperature range investigated in this work; both exhibit essentially identical vapor pressures within this temperature range.

Experimental Apparatus

Figure 1 shows a modified version of an apparatus described previously (*8*). Propane is pumped through the apparatus by a positive-displacement liquid pump from a cylinder. The desired pressure is adjusted by a back-pressure regulator. High-pressure propane reaches the desired temperature upon flowing through a heat exchanger inserted in a constant-temperature fluidized-sand bath. Propane then passes through a packed-bed cell where it equilibrates with the heavy hydrocarbon at measured temperature and pressure. The temperature of the saturated fluid leaving the packed bed is raised to approximately 150 deg above the bath temperature to avoid precipitation of the heavy hydrocarbons; the fluid is then expanded and directed through a heated gas-sampling valve to take samples intermittently as discussed below. Gas samples are analyzed in a gas chromatograph; the area of the peaks is measured by an electronic integrator and displayed on a chart recorder. Thermal cracking was insignificant; we ascertain the absence of cracking reactions in the equilibrium cell or the heated downstream portion of the equipment by monitoring the gas-chromatograph signal for extraneous peaks. Finally, the propane stream passes through a condenser where the heavy hydrocarbon precipitates. Subsequently, the pure-propane stream passes through a flowmeter where its cumulative volume is measured. The experimental procedure is automated once steady-state fluid flow is reached. Complete vaporization of the heavy hydrocarbon is signaled by a sharp decrease in the chromatogram peak area. To increase the rate of data acquisition, we use two flow systems in parallel.

When using a flow-solubility apparatus to study supercritical fluid-phase equilibria, it is necessary to exercise care when expanding from the experimental pressure to ambient pressure as required to facilitate downstream chemical or gravimetric

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