W_{13} weight fraction of water (1) in the solvent phase
W_{23} weight fraction of acetic acid (2) in the solvent phase
W_{33} weight fraction of cyclohexyl acetate (3) in the solvent phase

Greek Letter

σ standard deviation

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Liquid-Phase Excess Enthalpies for the Binary Mixtures 1-Chloronaphthalene + Cyclic Ethers

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The molar excess enthalpies H^E for binary liquid mixtures of 1-chloronaphthalene + cyclic ethers (1,3-dioxolane, oxane, oxolane, or 1,4-dioxane) were determined at atmospheric pressure, at 298.15 K. H^E is negative for all the mixtures, with the exception of 1-chloronaphthalene + 1,3-dioxolane. The experimental data have been correlated by means of the Redlich-Kister equation.

Introduction

The molar excess enthalpies H^E of a series of n-alkanes with a common solvent, 1-chloronaphthalene, have been determined by Inglese et al. (*1*). In this paper the study of this solvent has been extended to cyclic ethers with the aim of correlating the experimental H^E data and assessing the influence of ring size and proximity of oxygen atoms in diethers on the calorimetric behavior of the mixtures. We have found no H^E data for these systems in the literature.

Experimental Section

Materials. 1-Chloronaphthalene (Kodak product, analytical grade, purity 99.5%) was purified by fractional distillation followed by fractional crystallization of the middle fraction. Cyclic ethers were Aldrich products, with the exception of oxane, which was from Fluka. 1,4-Dioxane (99.97%) and oxolane (99.9%) were used without further purification. Oxane (purum, 99%) was fractionally distilled over sodium wires. All the liquids were stored in the dark over molecular sieves (Union Carbide: type 4A $^1/_{16}$-in. pellets).

Density Measurements. The densities ρ of 1-chloronaphthalene, oxane, and oxolane, required to evaluate fluxes and hence mole fractions in the calorimetric experiments, were measured at atmospheric pressure by means of a two-capillary glass pycnometer calibrated with distilled mercury. The experimental data were obtained in the range 288.15-313.40 K, and the estimated uncertainty in these measurements is ±0.2 kg m^{-3}.

Table I. Densities ρ of 1-Chloronaphthalene, Oxane, Oxolane as a Function of Temperature T, Coefficients A and B, Equation 1, Standard Deviation $\sigma(\rho)$ (kg m^{-3}) and Correlation Coefficient R

1-chloronaphthalene		oxane		oxolane	
T/K	ρ/(kg m^{-3})	T/K	ρ/(kg m^{-3})	T/K	ρ/(kg m^{-3})
288.15	1197.8[a] (1197.6)[b]	288.15	885.6	290.15	892.4
289.85	1196.5	289.15	884.5	290.95	891.5
292.45	1194.4	291.65	882.6	293.15	889.2[a] (889.2)[b]
293.15	1193.7[a] (1193.8)[b]	293.15	881.4[a] (881.4)[c]	294.95	887.1
295.50	1191.9	293.55	881.0	298.85	883.0
296.65	1191.0	297.00	878.1	299.45	882.3
298.15	1189.8	299.15	876.3	300.25	881.4
300.15	1187.9	301.20	874.7	300.90	880.7
302.60	1186.2	301.65	874.2	301.50	880.0
306.70	1182.9	302.85	873.2	302.55	879.0
309.65	1180.7	303.45	872.8	303.20	878.2
312.15	1178.6				
313.15	1177.7[a] (1177.8)[b]				
313.40	1177.5				
A	1209.8		898.1		910.8
B	−0.8012		−0.8386		−1.0844
$\sigma(\rho)$	0.06		0.05		0.04
$\|R\|$	≥0.99995				

[a] Interpolated, eq 1. [b] Reference 6. [c] Reference 7.

The densities were fitted to the equation

$$\rho/(\text{kg m}^{-3}) = A + B((T/\text{K}) - 273.15) \qquad (1)$$

Parameters A and B, correlation coefficient R, standard deviation $\sigma(\rho)$, and the agreement with literature data are shown in Table I. The densities of 1,3-dioxolane and 1,4-dioxane

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Table II. Experimental Liquid-Phase Molar Excess Enthalpies H^E for the 1-Chloronaphthalene (1) + Cyclic Ether (2) Systems as a Function of the Mole Fraction x_1 of 1-Chloronaphthalene at 298.15 K, Coefficients a_k, Equation 2, and Standard Deviations $\sigma(H)$ (J mol^{-1})

	1,3-dioxolane		oxane		oxolane		1,4-dioxane	
	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})
	0.0409	17.1	0.0564	−156.8	0.0474	−196.3	0.0497	−201.3
	0.0601	22.4	0.0745	−199.0	0.0694	−278.1	0.0727	−286.9
	0.0786	27.9	0.1069	−267.7	0.0905	−348.0	0.0947	−361.9
	0.1134	35.3	0.1522	−355.7	0.1299	−459.1	0.1356	−477.1
	0.1457	42.4	0.1932	−422.1	0.1660	−566.6	0.1730	−574.6
	0.2038	47.9	0.2643	−501.2	0.2299	−692.3	0.2388	−717.4
	0.2544	49.6	0.3238	−547.2	0.2847	−764.5	0.2949	−788.6
	0.3385	44.2	0.4181	−570.8	0.3738	−832.3	0.3855	−858.4
	0.4284	37.4	0.5187	−533.2	0.4724	−813.5	0.4984	−852.7
	0.5058	30.9	0.5896	−485.3	0.5442	−765.8	0.5565	−802.1
	0.6056	21.4	0.6831	−399.0	0.6417	−652.3	0.6531	−676.2
	0.6718	17.5	0.7418	−329.2	0.7048	−545.4	0.7151	−556.0
	0.7544	12.9	0.8117	−240.1	0.7818	−391.4	0.7901	−413.6
	0.8037	10.1	0.8518	−187.4	0.8269	−291.7	0.8339	−316.3
	0.8600	8.1	0.8961	−115.6	0.8776	−183.1	0.8828	−200.9
	0.9247	4.3	0.9452	−62.7	0.9348	−92.2	0.9378	−103.1
a_0	122.9		−2188.2		−3232.8		−3390.3	
a_1	−191.1		930		1317.5		1173.9	
a_2	181.9		155.8		450.4		519.8	
a_3	54.5				417.5		349.8	
$\sigma(H^E)$	0.7		4.1		6.6		4.8	

were reported in previous papers (*2*, *3*).

Calorimetric Measurements. Table II reports the H^E data obtained with an LKB flow microcalorimeter Model 2107, LKB Produkter AB (Bromma, Sweden), described elsewhere (*4*). The microcalorimeter was electrically calibrated before use (*2*) and the calibration subsequently checked by using the standard cyclohexane + hexane mixture (*5*). The discrepancy between H values was less than 0.5% over the central range of mole fraction.

The Redlich–Kister polynomial

$$H^E/(\mathrm{J\ mol^{-1}}) = x_1x_2\sum_{k=0}^{n-1} a_k(x_1 - x_2)^k \qquad (2)$$

where n is the number of adjustable parameters a_k and x_1, x_2 are the mole fractions of 1-chloronaphthalene (component 1) and cyclic ethers (component 2), respectively, was fitted to our results. The values of the a_k parameters, determined by least-squares analysis, with all points equally weighted, and their standard deviations $\sigma(H^E)$ are presented in Table II. Figure 1 shows the H^E vs x_1 curves for the four mixtures.

Results and Discussion

As can be seen from the figure, when an O atom substitutes a CH_2 group of oxane to give 1,4-dioxane, H^E decreases, whereas the same substitution on the five-membered ring of oxolane to give 1,3-dioxolane leads to increased H^E. Again, when oxane reduces to oxolane, after subtraction of a CH_2 group, H^E decreases, whereas subtraction of a CH_2 group from 1,4-dioxane leads to 1,3-dioxolane with increased H^E. These results seem to indicate no simple correlation of calorimetric properties with the functional groups in the molecules.

Glossary

a_k	parameters in eq 2
A,B	parameters in eq 1
H^E	liquid-phase molar excess enthalpy, J mol^{-1}
T	temperature, K
x_i	mole fraction of component i (i = 1,1-chloronaphthalene; i = 2, cyclic ether)

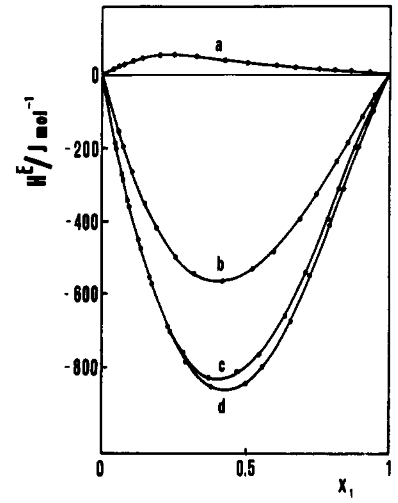

Figure 1. Liquid-phase molar excess enthalpies H^E for 1-chloronaphthalene + 1,3-dioxolane (a), + oxane (b), + oxolane (c), or + 1,4-dioxane (d) at 298.15 K: (●) experimental values; (—) results calculated by eq 2 with the parameters a_k of Table II.

Greek Letters

ρ	density, kg m^{-3}
$\sigma(X)$	standard deviation, $\sigma(X) = \lvert\Sigma(X_{\mathrm{calc}} - X_{\mathrm{expt}})^2/(N - n)\rvert^{1/2}$, ($X = \rho$ or H^E); N, number of experimental points; n, number of parameters)

Registry No. 1-Chloronaphthalene, 90-13-1; 1,3-dioxolane, 646-06-0; oxane, 75-21-8; oxolane, 109-99-9; 1,4-dioxane, 123-91-1.

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