binary systems were identical with the values given earlier in Table IV.

With use of the binary parameters of Table VI and eqs 3 and 4, the ternary parameters of eq 4 were obtained by Barker's method. These parameter values are given in Table VI. No evidence was found for strong correlation between any of the parameters. The average deviation between calculated, P_{calc}, and measured, P_{expt}, pressures was 0.09 kPa with a maximum deviation of 0.28 kPa. A plot of the pressure residuals, $P_{expt} - P_{calc}$, for the ternary system is given in Figure 4.

On the basis of the parameter values given in Table VI, the P-x surface for the ternary system was calculated and is shown in Figure 5. The parameter C which appears in this figure is defined by

$$C = \frac{x_2}{x_2 + x_3} \tag{7}$$

Glossary

A_{ij}, A_{ji}	binary parameters for G^E, eq 2
B_{ij}	molar second virial coefficient for species i and j, $cm^3\ mol^{-1}$
C	ternary composition parameter, eq 7
C'	ternary composition parameter, eq 1
C_0	ternary parameter for G^E, eq 4
C_{ij}	ternary parameter for G^E, eq 4
F	ternary function for G^E, eq 3
G^E	molar excess Gibbs free energy, $kJ\ mol^{-1}$
P	pressure, kPa
P_i°	vapor pressure of pure species i, kPa
P_{calc}	calculated total pressure, kPa
P_{expt}	measured total pressure, kPa
R	universal gas constant, $kJ\ mol^{-1}\ K^{-1}$
T	temperature, K
V_i^L	saturated molar volume of pure liquid i, $cm^3\ mol^{-1}$
x_i	liquid-phase mole fraction of species i
z_i	overall mole fraction of species i in equilibrium cell

Greek Letters

α_{ij}, α_{ji}	binary parameters for G^E, eq 2
η_{ij}	binary parameter for G^E, eq 2
$\sigma_{p,i}$	weighting factor for ith data point, eq 5, kPa

Registry No. n-Pentane, 109-66-0; methanol, 67-56-1; 2-butanol, 78-92-2.

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Received for review September 14, 1990. Accepted May 21, 1991. This work was supported, in part, by the University of South Florida Research and Creative Scholarship Grant Program under Grant No. RCS-25. S.T. was supported by a National Science Foundation REU Grant No. EID-9000720.

Liquid–Liquid Equilibria of the Water + Acetic Acid + Cyclohexyl Acetate Ternary

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Liquid–liquid equilibria for the water + acetic acid + cyclohexyl acetate system were measured at 298.16 ± 0.20, 308.16 ± 0.20, and 318.16 ± 0.20 K. Tie-line compositions were correlated by the reduced Eisen–Joffe equation. Reliability of data was ascertained through Othmer–Tobias plots. Distribution coefficients and separation factors were evaluated over the immiscibility region, and it is concluded that the high-boiling solvent, cyclohexyl acetate, is a suitable separating agent for dilute aqueous acetic acid solutions. In addition, the temperature dependence of solubility and tie-line compositions is insignificant from 298 to 318 K, except at very low acetic acid concentrations.

Introduction

Major advantages of high-boiling separating agents for the extraction of acetic acid from its aqueous solutions have been recently reported (*1–3*). It has also been predicted that cyclohexyl acetate could be used as solvent (*4*).

The objective of this study was to determine the experimental solubility and tie-line compositions of the water + acetic acid + cyclohexyl acetate ternary at 298.16 ± 0.20, 308.16 ± 0.20, and 318.16 ± 0.20 K, at atmospheric pressure. Complete phase diagrams were obtained by evaluating together the solubility and the tie-line compositions for each temperature. In addition, the tie-line compositions were correlated by using the reduced Eisen–Joffe equation (*5*). Their thermodynamic consistency was ascertained by making Othmer–Tobias plots (*6*) and applying an independent material balance check.

In order to determine the most suitable process temperature, free-solvent-based selectivity diagrams at 298.16, 308.16, and

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0021-9568/91/1736-0378$02.50/0

Table I. Physical Properties of Chemicals

property	measd	lit.	ref
Acetic Acid			
density at 293.16 K/(kg·m^{-3})	1050.0	1049.8	7
refractive index at 293.16 K (n_D)	1.3720	1.3718	7
boiling point at 1 atm/K	391.20	391.26	7
Cyclohexyl Acetate			
density at 293.16 K/(kg·m^{-3})	970.3	969.8	8
refractive index at 293.16 K (n_D)	1.4410	1.4401	8
boiling point at 1 atm/K	446.26	446.16	8

318.16 K were plotted and compared graphically. The temperature dependence was investigated by evaluating distribution coefficients and separation factors for each case.

Experimental Section

Chemicals. Acetic acid (100 mass %) and cyclohexyl acetate (reagent grade, 99 mass %) were furnished by Merck. The acetic acid was distilled with the middle 80% collected. The cyclohexyl acetate was distilled under moderate vacuum with the middle 60% collected. Gas-liquid chromatography showed that the major peak area exceeds 99.7%.

The purity of the chemicals was checked on the basis of their refractive indexes and densities at 293.16 ± 0.20 K and their boiling points at 101.325 ± 0.067 kPa.

Refractive indexes were measured with an Abbé-Hilger refractometer; its stated accuracy is $\pm 0.0001 n_D$. Densities were measured with a Westphal balance. Boiling point measurements were obtained by using a Fischer boiling point apparatus. The estimated uncertainties in the density and boiling point measurements were ±0.1 kg·m^{-3} and ±0.1 K, respectively. The measured physical properties are listed in Table I, along with literature values (*7*, *8*).

Deionized water was further distilled before use.

Procedure. Solubility determinations were performed in an equilibrium cell equipped with a magnetic stirrer and isothermal fluid jacket. The solution temperature was regulated by a thermostated bath with an accuracy of ±0.2 K. The inner temperature of the cell was measured within an accuracy of ±0.1 K by a certified Fischer thermometer.

The cell designed to contain a solution of 50-200 cm^3 was filled with heterogeneous water + cyclohexyl acetate mixtures prepared by weighing. An electronic Sauter balance accurate to ±0.1 mg was used. The acid was added by means of an automatic microburet with an accuracy of ±0.005 cm^3. The end point was determined by observing the transition from heterogeneity to a clear and stable solution. The pattern was convenient to provide the left and central portions of the curves. The data for the right part of the curves were therefore obtained by titrating homogeneous water + acetic acid binaries with cyclohexyl acetate until the turbidity had appeared. Composition determinations were accurate to ±0.0005 weight fraction.

The mutual solubilities of the water + cyclohexyl acetate system were determined by using a synthetic method (*9*). A weighted amount of one component was placed in the cell; then the other component was added until a permanent heterogeneity had been observed. An ultraaccurate titrator of ±0.001 cm^3 was used. The content of solute was generally accurate to ±0.0002 weight fraction. The tie-line compositions were obtained by using the equilibrium apparatus described above. Eight ternary mixtures with compositions within the heterogeneous gap were prepared for each temperature. A mixture was added to the cell and vigorously stirred for 1 h under isothermal conditions. After the stirrer was turned off, the content was immediately allowed into the vertical settler equipped also with an isothermal jacket. After the complete break of the phases, a suitable amount of each layer was withdrawn for analysis.

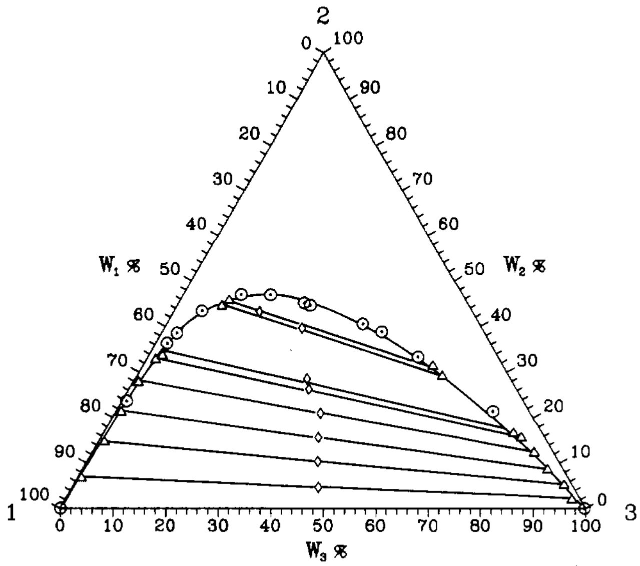

Figure 1. Ternary diagram for experimental LLE of water (1) + acetic acid (2) + cyclohexyl acetate (3) at 298.16 K: ⊙, solubility results; △, tie-line data; ◇, overall compositions for tie-line. (Concentrations are expressed in weight percent.)

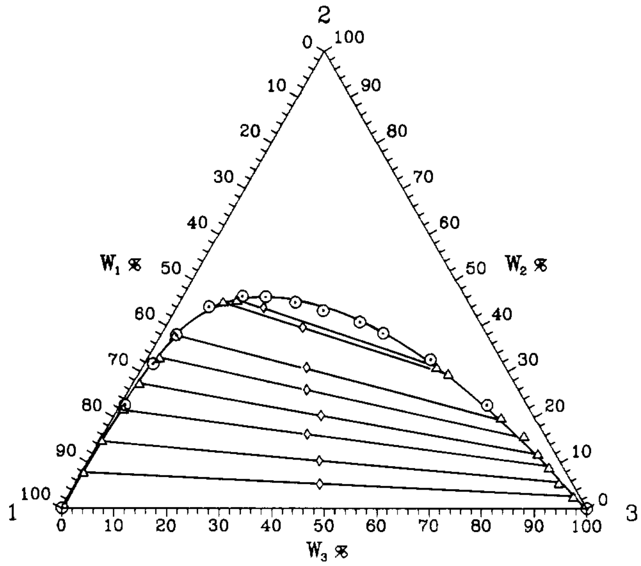

Figure 2. Ternary diagram for experimental LLE of water (1) + acetic acid (2) + cyclohexyl acetate (3) at 308.16 K: ⊙, solubility results; △, tie-line data; ◇, overall compositions for tie-line. (Concentrations are expressed in weight percent.)

The acid contents of the samples were determined by volumetric titration with 0.1 M NaOH solution to the ethanolic phenolphtalein end point. Several check determinations on known samples showed that the accuracy of the method was of ±0.001 weight fraction.

Results

The experimental tie-line compositions and solubilities for the water + acetic acid + cyclohexyl acetate system at 298.16 ± 0.20, 308.16 ± 0.20, and 318.16 ± 0.20 K are plotted in Figures 1-3. Distribution coefficients D_i for acetic acid (i = 2) and water (i = 1) and separation factors S were determined:

$$D_i = \frac{\text{weight fraction in solvent phase } (W_{i3})}{\text{weight fraction in aqueous phase } (W_{i1})} \tag{1}$$

$$S = D_2/D_1 \tag{2}$$

The results are listed in Table II.

The measured values for solubility curves and experimental mutual solubilities are reported in Table III. The tie-line com-

Table II. Experimental Distribution Coefficients D_i of Water (i = 1) and Acetic Acid (i = 2) and Separation Factors $S = D_2/D_1$

T/K	D_2	D_1	S
298.16	0.318	0.017	18.71
	0.364	0.017	21.41
	0.411	0.038	10.82
	0.452	0.049	9.23
	0.482	0.067	7.19
	0.500	0.082	6.10
	0.657	0.268	2.45
	0.687	0.297	2.31
308.16	0.334	0.013	25.67
	0.378	0.028	13.49
	0.415	0.035	11.86
	0.440	0.046	9.58
	0.482	0.062	7.79
	0.528	0.106	4.98
	0.653	0.250	2.61
	0.678	0.301	2.25
318.16	0.358	0.005	71.60
	0.365	0.015	24.33
	0.403	0.025	16.14
	0.435	0.049	8.88
	0.478	0.079	6.06
	0.549	0.118	4.65
	0.629	0.247	2.55
	0.675	0.302	2.23

Table III. Solubility Results for Water (1) + Acetic Acid (2) + Cyclohexyl Acetate (3)[a]

T/K	W_1/%	W_2/%	W_3/%
298.16	0.07		99.93 ms
	7.03	21.34	71.63
	15.36	33.26	51.38
	19.51	38.77	41.72
	22.26	40.50	37.24
	30.23	44.56	25.21
	31.09	45.09	23.82
	36.61	46.85	16.54
	42.20	46.92	10.88
	51.44	43.34	5.22
	58.67	38.47	2.86
	61.64	36.25	2.11
	75.67	23.57	0.76
	99.93		0.07 ms
308.16	0.08		99.92 ms
	7.74	22.61	69.65
	13.54	32.52	53.94
	19.70	38.28	42.02
	23.27	40.42	36.31
	28.70	43.23	28.07
	33.04	45.03	21.93
	38.10	46.24	15.66
	42.45	46.36	11.19
	49.97	44.03	6.00
	59.26	37.90	2.84
	66.78	31.60	1.62
	76.65	22.62	0.73
	99.93		0.07 ms
318.16	0.10		99.90 ms
	7.91	24.45	67.64
	13.44	31.32	55.24
	19.16	36.81	44.03
	25.15	40.55	34.30
	29.28	42.53	28.19
	34.48	44.75	20.77
	38.20	45.54	16.26
	42.86	45.54	11.60
	50.76	43.05	6.19
	62.06	34.80	3.14
	66.26	31.95	1.79
	81.13	18.20	0.67
	99.92		0.08 ms

[a] ms = mutual solubility.

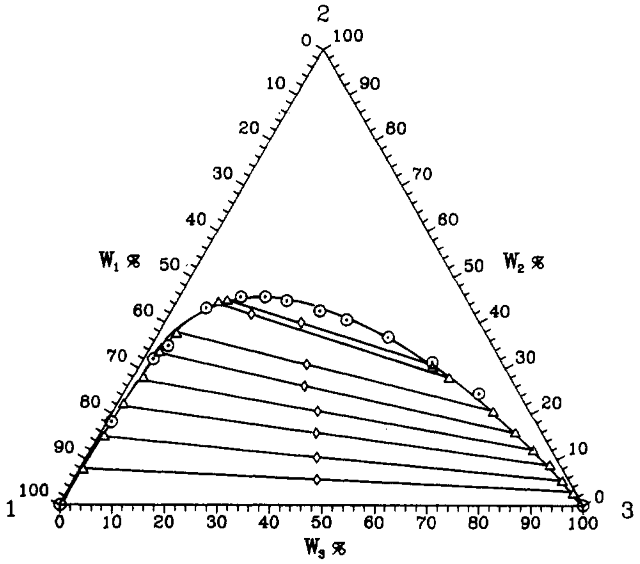

Figure 3. Ternary diagram for experimental LLE of water (1) + acetic acid (2) + cyclohexyl acetate (3) at 318.16 K: ⊙, solubility results; △, tie-line data; ◇, overall compositions for tie-line. (Concentrations are expressed in weight percent.)

Table IV. Tie-Line Compositions for Water (1) + Acetic Acid (2) + Cyclohexyl Acetate (3)

	water-rich phase			solvent-rich phase		
T/K	W_{11}/%	W_{21}/%	W_{31}/%	W_{13}/%	W_{23}/%	W_{33}/%
298.16	92.43	7.01	0.56	1.60	2.23	96.17
	84.12	14.98	0.90	1.45	5.45	93.10
	77.73	21.49	0.78	2.95	8.84	88.21
	71.10	28.08	0.82	3.47	12.69	83.84
	65.36	33.03	1.61	4.39	15.93	79.68
	63.69	33.89	2.42	5.27	16.93	77.80
	46.92	44.72	8.36	12.60	29.40	58.00
	44.90	45.99	9.11	13.36	31.58	55.06
308.16	91.93	7.94	0.16	1.23	2.65	96.12
	84.85	14.96	0.19	2.41	5.65	91.94
	77.28	21.82	0.90	2.67	9.06	88.27
	71.46	27.44	1.10	3.28	12.06	84.66
	64.82	33.03	2.15	4.04	15.95	80.01
	59.63	37.75	2.63	6.33	19.94	73.73
	46.60	45.25	8.15	11.65	29.53	58.82
	43.74	45.66	10.60	13.18	30.94	55.88
318.16	91.56	7.90	0.54	0.49	2.83	96.68
	83.92	15.18	0.90	1.24	5.54	93.22
	76.67	22.24	1.09	1.88	8.97	89.15
	70.04	28.05	1.91	3.42	12.21	84.37
	64.18	33.67	2.15	5.05	16.09	78.86
	59.02	37.64	3.34	6.96	20.65	72.39
	47.62	44.60	7.78	11.77	28.07	60.16
	45.71	44.98	9.31	13.83	30.34	55.83

Table V. Constants of Reduced Eisen–Joffe Equation for Water + Acetic Acid + Cyclohexyl Acetate Systems

T/K	C_1	C_2	σ	RMSD
298.16	−0.6883	1.2287	8.16×10^{-2}	7.06×10^{-2}
308.16	−0.7234	1.1988	7.25×10^{-2}	6.28×10^{-2}
318.16	−0.7271	1.1991	10.60×10^{-2}	9.18×10^{-2}

positions are given in Table IV.

Reliability of measured tie-line compositions was ascertained by making Othmer–Tobias plots at each temperature. The linearity of the plot indicates the degree of consistency of the data. The plots are shown in Figures 4–6.

Correlation of Data. Experimental tie-line compositions were correlated with the reduced Eisen–Joffe equation:

$$\ln (W_{23}/W_{33}) = C_1 + C_2[\ln (W_{21}/W_{11})] \qquad (3)$$

The coefficients C_1 and C_2 were estimated by linear regression.

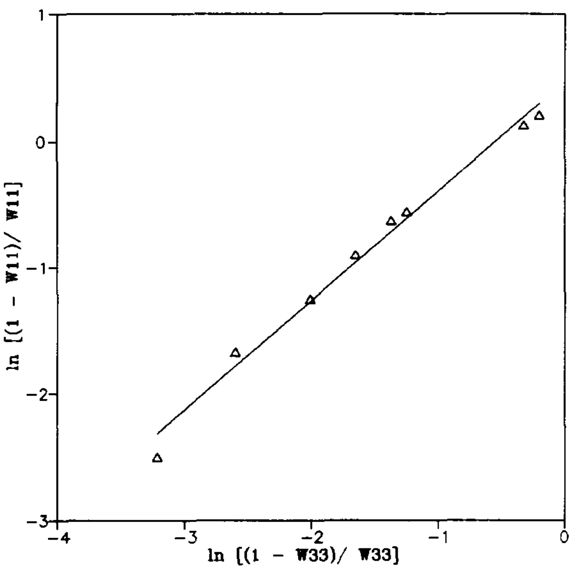

Figure 4. Othmer–Tobias plot at 298.16 K: Δ, tie-line results.

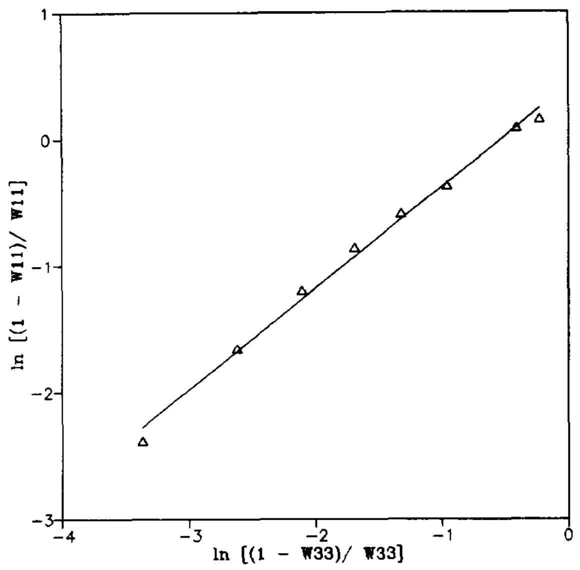

Figure 6. Othmer–Tobias plot at 318.16 K: Δ, tie-line results.

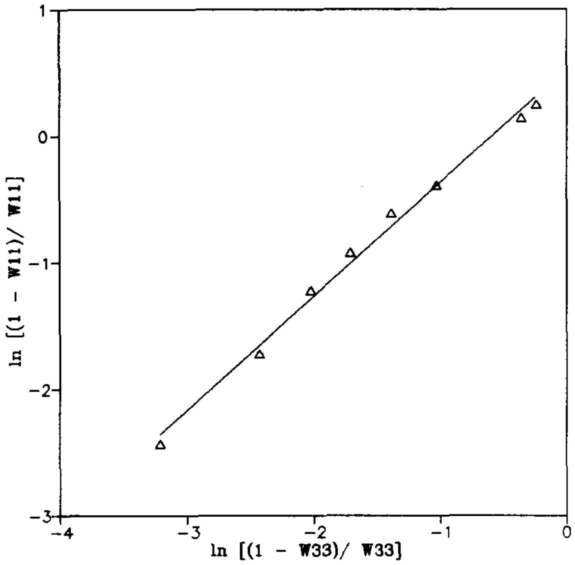

Figure 5. Othmer–Tobias plot at 308.16 K: Δ, tie-line results.

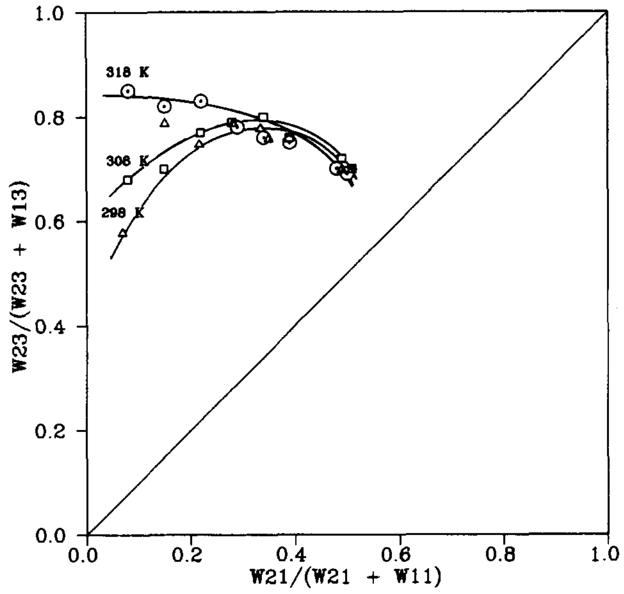

Figure 7. Selectivity diagram at investigated temperature values (free-solvent basis): Δ, 298.16 K; □, 308.16 K; ⊙, 318.16 K.

The results are given in Table V.

Selectivity. Selectivity diagrams on a solvent-free basis are plotted for 298.16, 308.16, and 318.16 K in Figure 7. The effect of a temperature change on the selectivity values was generally found to be insignificant. However, it is observed that an increase of temperature favors slightly the distribution of acetic acid in cyclohexyl acetate for the mixtures with up to 5% acetic acid.

Conclusions

It is concluded that because cyclohexyl acetate shows extremely low solubilities in water it may serve as an adequate solvent to extract acetic acid from its dilute aqueous solutions. Distribution coefficients greater than 0.25 and separation factors varying between 70 and 2 make this solvent a candidate as a separating agent.

Distribution coefficients varying between 0.318 and 0.687 require relatively larger solvent amounts. However, the recovery of a high-boiling solvent necessitates the solute to be volatilized. Another noteworthy observation is that the complete break of conjugate phases was never hindered by density-, viscosity-, and interfacial-tension-related phenomena during the settling process. Sedimentation and coalescence of dispersed phases were so rapid that a few minutes up to ten minutes were sufficient to obtain absolutely clear layers with a very thin dispersion band. It is seen that the elevation of temperature decreases slightly the settling time. It is observed that the effect of the temperature changes on the shape and the size of the immiscibility gap was insignificant over the investigated range. In spite of this, it can be stated that the increase of temperature favors slightly the distribution of acetic acid when the acid concentration is very low.

Glossary

C_1,C_2	coefficients of the reduced Eisen–Joffe equation, eq 3
D_i	distribution coefficient of the *i*th component, eq 1
n_D	refractive index
RMSD	root mean square deviation
S	separation factor, eq 2
W_i	weight fraction of *i*th component
W_{11}	weight fraction of water (1) in the aqueous phase
W_{21}	weight fraction of acetic acid (2) in the aqueous phase
W_{31}	weight fraction of cyclohexyl acetate (3) in the aqueous phase

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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Received for review November 17, 1990. Accepted April 15, 1991.

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

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

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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