J. Chem. Eng. Data **1990**, *35*, 172-174

Table IV. Second Molar Virial Coefficients B_{ij} and Liquid Molar Volumes V_i (cm^3 mol^{-1}) as a Function of Temperature T

component	T/K	V_i	B_{ii}	B_{12}
pyrrolidine (i = 1)	313.15	84.7	-1235	
	313.35	84.7	-1233	
	333.15	86.6	-1054	
	333.35	86.6	-1052	
	353.15	88.4	-914	
cyclohexane (i = 2)	313.15	111.9	-1691	-1278
	333.15	114.6	-1423	-1081
water (i = 2)	333.15	18.4	-912	-479
	353.15	18.8	-637	-415
ethanol (i = 2)	313.15	59.2	-1652	-985
	333.35	60.9	-1201	-847
tetrahydrofuran (i = 2)	313.35	83.4	-1118	-1101
	333.35	84.8	-958	-937

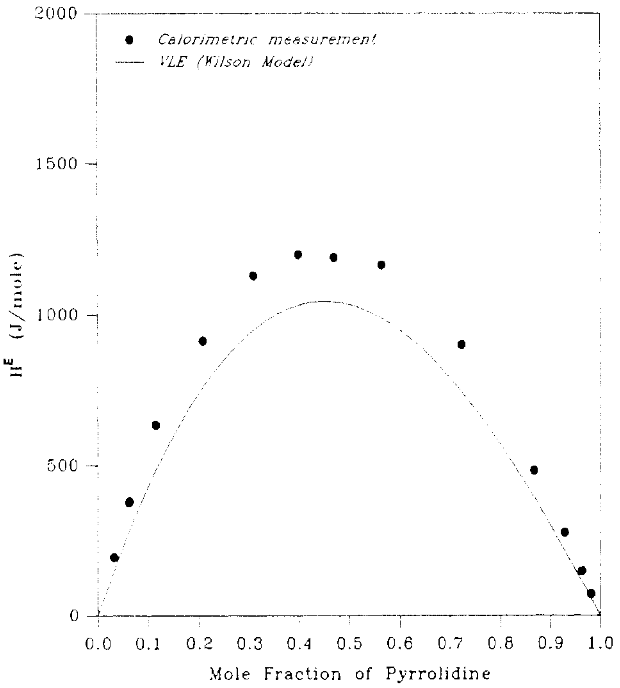

Figure 5. Molar excess enthalpy, H^E, for the pyrrolidine (1) + cyclohexane (2) system. The points are direct calorimetric measurements (*13*), and the lines resulted from the values of G^E generated from our vapor-liquid equilibrium measurements.

Tine and Kehiaian (*16*) that the cyclic secondary amine group in pyrrolidine may have to be considered a different functional group from the noncyclic secondary amine group in future improvements of the UNIFAC model. It is also worth noting that our VLE data reported here can be reproduced by the DISQUAC model with reported parameters (*17*), with average deviations in pressure of the order of 0.5 kPa and in composition of 0.01 or better.

Acknowledgment

We thank Dr. H. Kehiaian for his comments and for providing us with the results of the DISQUAC calculations.

Registry No. Pyrrolidine, 123-75-1; cyclohexane, 110-82-7; ethanol, 64-17-5; tetrahydrofuran, 109-99-9.

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Thermodynamics of Binary Mixtures Containing Alkanenitriles. 1. Excess Enthalpies of Some *n*-Alkanenitrile + *n*-Alkane or + Cyclohexane Mixtures

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A Tian-Calvet-type calorimeter was used to determine excess enthalpies, H^E, as a function of concentration at atmospheric pressure and 298.15 K for some binary liquid mixtures containing linear alkanenitriles of the general formula $CH_3(CH_2)_{n-2}CN$ (n = 2, 3, 4, 5) with n-alkanes (hexane, heptane) or cyclohexane.

Introduction

This work is part of a systematic study of the thermodynamic properties of organic mixtures, TOM Project (*1*-*16*), with the purpose of characterizing the type and magnitude of molecular interactions in binary liquid mixtures and to improve the group contribution models currently used to predict thermodynamic

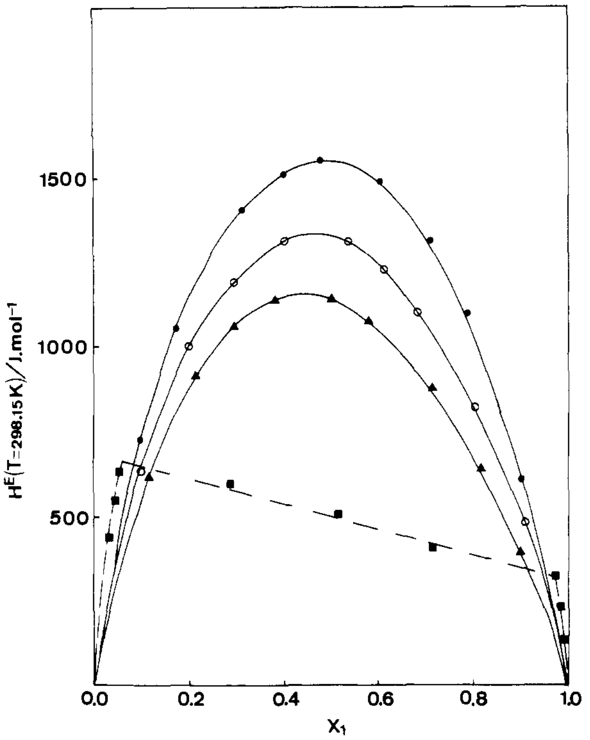

Figure 1. Experimental molar excess enthalpies, H^e, of alkanenitrile (1) + heptane (2) mixtures at 298.15 K vs x_1, the mole fraction of alkanenitrile: ■, ethanenitrile; ●, propanenitrile; O, butanenitrile; ▲, pentanenitrile.

properties. Mixtures containing short-chain nitriles + *n*-alkanes or + cyclohexane exhibit large positive deviations from ideality, often reflected in partial miscibility.

As the chain length of the nitrile increases, the positive deviations from ideality decrease and total miscibility becomes more common.

McLure et al. (*7*) reported the upper critical solution temperatures (UCST) for binary mixtures of ethanenitrile, propanenitrile, or butanenitrile with *n*-alkanes containing 5–18 carbon atoms.

The liquid–liquid equilibrium of ethanenitrile + cyclohexane has been carefully investigated by Vani et al. (*8*).

A search of the literature reveals that thermodynamic studies on alkanenitrile + alkane or + cyclohexane are rather scarce, and moreover some discordances exist in the results reported by different authors.

Molar excess enthalpies, H^E, of alkanenitrile + *n*-alkane or + cyclohexane have been measured calorimetrically by several authors (*9*–*14*).

In order to better characterize the behavior of the CN group, we decided to measure, or remeasure, H^E in a systematic way for mixtures of *n*-alkanenitriles [$CH_3(CH_2)_{n-2}CN$ (n = 2–5)] + *n*-alkanes [$CH_3(CH_2)_{m-2}CH_3$ (m = 6, 7)] or + cyclohexane [C_6H_{12}].

Experimental Section

The enthalpies of mixing have been measured with use of a Tian–Calvet ("CRMT") type calorimeter manually tilted. The batch mixing cell and the experimental procedure are described elsewhere (*15*). The calorimeter was calibrated by Joule effect, and the calibration was repeated after each experiment.

The reliability of the apparatus and procedure adopted were checked by performing H^E measurements on the test system benzene + cyclohexane. Our results differed by <2% from literature data (*16*) over the entire composition range.

Table I. Experimental Molar Excess Enthalpies, H^E, at 298.15 K for Binary Mixtures of *n*-Alkanenitriles [$CH_3(CH_2)_{n-2}CN$ (1)] + *n*-Alkanes [$CH_3(CH_2)_{m-2}CH_3$] or + Cyclohexane (2); Coefficients a_j, Equation 1; and Standard Deviations, $\sigma(H^E)$, Equation 2

x_1	H^E, J mol^{-1}	x_1	H^E, J mol^{-1}	x_1	H^E, J mol^{-1}
		CH_3CN (1) + C_7H_{16} (2)			
0.0295	452	0.2857[a]	595	0.9711	322
0.0403	550	0.5143[a]	501	0.9808	227
0.0507	634	0.7140[a]	403	0.9894	130
		CH_3CH_2CN (1) + C_6H_{14} (2)			
0.1059	724	0.3892	1435	0.7103	1191
0.1889	1071	0.4906	1459	0.8269	842
0.3136	1363	0.5844	1397	0.9035	519
a_0 = 5822; a_1 = −636; a_2 = 1573; a_3 = −707; $\sigma(H^E)$ = 2.4 J mol^{-1}					
		CH_3CH_2CN (1) + C_7H_{16} (2)			
0.0975	720	0.3988	1515	0.7050	1310
0.1712	1055	0.4802	1545	0.7836	1095
0.3107	1410	0.6021	1483	0.9037	594
a_0 = 6164; a_1 = −292; a_2 = 1978; a_3 = −852; $\sigma(H^E)$ = 4.8 J mol^{-1}					
		CH_3CH_2CN (1) + C_6H_{12} (2)			
0.1018	731	0.4047	1515	0.7069	1229
0.1929	1129	0.5035	1522	0.7933	977
0.2815	1371	0.6043	1430	0.9217	433
a_0 = 6088; a_1 = −808; a_2 = 1401; a_3 = −693; $\sigma(H^E)$ = 2.8 J mol^{-1}					
		$CH_3(CH_2)_2CN$ (1) + C_6H_{14} (2)			
0.1058	630	0.4090	1249	0.7031	945
0.2051	966	0.4992	1235	0.8002	690
0.3044	1160	0.6025	1138	0.9027	359
a_0 = 4934; a_1 = −1052; a_2 = 627; a_3 = −896; $\sigma(H^E)$ = 5.8 J mol^{-1}					
		$CH_3(CH_2)_2CN$ (1) + C_7H_{16} (2)			
0.0950	614	0.3977	1300	0.6809	1120
0.2011	1011	0.5349	1285	0.8005	833
0.2938	1206	0.6082	1225	0.9073	449
a_0 = 5217; a_1 = −669; a_2 = 1541; a_3 = −672; $\sigma(H^E)$ = 2.6 J mol^{-1}					
		$CH_3(CH_2)_2CN$ (1) + C_6H_{12} (2)			
0.1059	690	0.4025	1276	0.7346	912
0.2123	1051	0.4952	1260	0.8182	674
0.3070	1215	0.6190	1138	0.8958	415
a_0 = 5028; a_1 = −1103; a_2 = 1290; a_3 = −1131; $\sigma(H^E)$ = 3.3 J mol^{-1}					
		$CH_3(CH_2)_3CN$ (1) + C_6H_{14} (2)			
0.0997	560	0.3949	1077	0.7041	810
0.2019	876	0.4997	1050	0.7908	632
0.2932	1019	0.6012	960	0.8899	355
a_0 = 4207; a_1 = −1102; a_2 = 1141; a_3 = −813; $\sigma(H^E)$ = 3.0 J mol^{-1}					
		$CH_3(CH_2)_3CN$ (1) + C_7H_{16} (2)			
0.1151	625	0.3804	1137	0.7066	877
0.2158	924	0.4979	1133	0.8135	635
0.2928	1061	0.5762	1075	0.9011	380
a_0 = 4517; a_1 = −999; a_2 = 1045; a_3 = −377; $\sigma(H^E)$ = 5.9 J mol^{-1}					
		$CH_3(CH_2)_3CN$ (1) + C_6H_{12} (2)			
0.1088	630	0.4157	1129	0.6976	854
0.2136	941	0.4891	1108	0.7984	623
0.3142	1086	0.5987	1011	0.8960	345
a_0 = 4405; a_1 = −1178; a_2 = 1094; a_3 = −975; $\sigma(H^E)$ = 2.8 J mol^{-1}					

[a] Two-phase region.

All the measurements were carried out at 298.15 ± 0.10 K.

The experimental, H_{exp} values, reported in Table I, were fitted to the smoothing equation

$$H^E_{sm}/(J\ mol^{-1}) = x_1x_2\sum a_j(x_1 - x_2)^j \qquad (1)$$

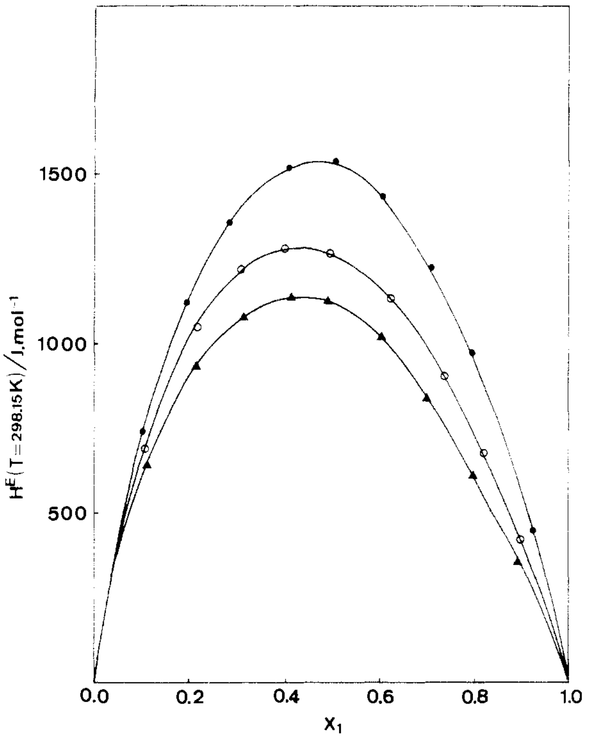

Figure 2. Experimental molar excess enthalpies, H^E, of alkanenitrile (1) + cyclohexane (2) mixtures at 298.15 K vs x_1, the mole fraction of alkanenitrile: ●, propanenitrile; ○, butanenitrile; ▲, pentanenitrile.

where x_1 is the mole fraction of alkanenitrile and x_2 the mole fraction of n-alkane or cyclohexane.

The values of the coefficients a_j and the standard deviations $\sigma(H^E)$,

$$\sigma(H^E) = [\sum(H^E_{sm} - H^E_{exp})/(N - n)]^{1/2} \qquad (2)$$

where N is the number of experimental points and n the number of coefficients a_j, were determined by a least-squares fit and are reported in Table I.

Our H^E measurements on propanenitrile or butanenitrile + hexane and butanenitrile + hexane agree to better than 3% with the data reported by McLure et al. (*13*).

Discussion

As shown in Figures 1 and 2, the values of H^E are large and positive; this behavior is mainly due to breaking of dipole-dipole interactions between the alkanenitrile molecules. Since the dipole moments (*17*) of the alkanenitriles are similar, it is the decreasing surface fraction of the CN group that determines the decrease of H^E with increasing number of $-CH_2-$ groups in the alkanenitriles.

A detailed interpretation of these results in terms of the DISQUAC group contribution model (*6*) will be presented separately.

Glossary

a_j	coefficients in eq 1
H^E	molar excess enthalpy, J mol^{-1}
n	number of coefficients a_j in eq 1
N	number of experimental points
T	temperature, K
x_i	mole fraction in liquid phase of component i (i = 1, alkanenitrile; i = 2, n-alkane or cyclohexane)
$\sigma(H^E)$	standard deviation, eq 2, J mol^{-1}

Subscripts

exp	experimental value
sm	smoothed value

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Solubilities of 2,5- and 2,6-Xylenols in Supercritical Carbon Dioxide

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The solubilities of 2,5- and 2,6-xylenols in supercritical carbon dioxide were measured by using a flow-type apparatus at 308.15 K up to 27 MPa. The appearance of a liquid phase was seen for the CO_2 + 2,6-xylenol system though the equilibrium temperature was lower than the melting point of 2,6-xylenol. The solubilities of 2,5-xylenol were correlated by a three-constant cubic equation of state with the two characteristic parameters.

Introduction

Separation methods for coal-derived components have received considerable attention recently (*1*) for use as the raw materials of fine chemicals. The supercritical fluid extraction is showing promise as a separation method (*2*). Solubility data of coal-derived components in supercritical fluids are very important as a fundamental knowledge. Correlation methods are also important in the design of a supercritical extraction pro-

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