Thermodynamic Properties of Binary Mixtures Containing Cycloalkanones. 2. Excess Volumes of Cycloalkanones + *n*-Alkanes

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Molar excess volumes have been measured by means of a vibrating tube densimeter for binary liquid mixtures of cycloalkanones (cyclopentanone and cyclohexanone) + *n*-alkanes. The V^E data are reported over the complete mole fraction range at 298.15 K. An inversion of the sign of V^E is observed over some concentrations for mixtures of cyclopentanone with *n*-hexane and *n*-heptane and cyclohexanone with *n*-heptane.

Introduction

This work is part of a systematic study on thermodynamic properties of binary mixtures containing cycloalkanone with organic solvents in order to characterize the behavior of the cyclocarbonyl group with respect to the main functional groups of organic chemistry. In fact, we have recently studied the excess enthalpies of cycloalkanones with *n*-alkanes, cyclohexane, benzene, and carbon tetrachloride (*1*). There are many intricate problems related with binary liquid mixtures containing *n*-alkanes (*2*, *3*) and it could be useful to provide additional V^E experimental data.

Experimental Section

Excess volumes were determined from densities measured by use of a vibrating densimeter (Model DMA 602 Anton Paar). The measuring cell of the apparatus was thermostated with a Heto-Birkerod ultrathermostat with an accuracy of ±0.01 K.

The imprecision in density measurements was less than 3×10^{-6} g cm^{-3}. The V^E values were accurate to ±0.003 cm^3 mol^{-1}. Purities of the components were as follows (wt %): cyclopentanone (Fluka) 99.5; cyclohexanone (Fluka) 99.5; *n*-hexane (Merck) 99; *n*-heptane (Carlo Erba) 99.5; *n*-dodecane (Fluka) 99.5; *n*-hexadecane (Merck) 99. Densities of pure components were measured before preparing sample mixtures and are listed in Table I with literature values for comparison (*4*-*6*).

The excess volumes V^E were calculated from the equation (*7*)

$$V^E = \frac{x_1M_1 + x_2M_2}{\rho} - \frac{x_1M_1}{\rho_1} - \frac{x_2M_2}{\rho_2} \qquad (1)$$

where x_1 and x_2 are the mole fractions, M_1 and M_2 are the molecular weights, ρ_1 and ρ_2 are the densities of the two components, and ρ is the density of mixtures.

Results

Excess volumes were determinated at 298.15 K for binary mixtures of cyclopentanone or cyclohexanone with *n*-hexane, *n*-heptane, *n*-dodecane, and *n*-hexadecane. The results are given in Table II and are graphically represented in Figures 1

Table I. Densities of the Pure Components at 298.15 K

component	ρ, g cm^{-3} this work	ρ, g cm^{-3} lit.
cyclopentanone	0.944 004	
cyclohexanone	0.942 212	
n-hexane	0.654 929	0.654 89 (*4*)
n-heptane	0.679 483	0.679 48 (*5*)
n-dodecane	0.745 163	0.745 16 (*6*)
n-hexadecane	0.769 967	0.769 96 (*6*)

Table II. Values of V^E for the Binary Mixtures of Cyclopentanone and Cyclohexanone with *n*-Alkanes at 298.15 K

x_1[a]	V^e, cm^3 mol^{-1}	x_1[a]	V^e, cm^3 mol^{-1}	x_1[a]	V^e, cm^3 mol^{-1}
Cyclopentanone + C_6H_{14}					
0.0908	0.032	0.2987	−0.094	0.6208	−0.220
0.1707	−0.010	0.3957	−0.139	0.7811	−0.208
0.1813	−0.022	0.5022	−0.187	0.8895	−0.135
Cyclopentanone + C_7H_{16}					
0.0633	0.105	0.4023	0.117	0.7934	−0.010
0.1117	0.142	0.5191	0.082	0.9286	−0.012
0.2227	0.162	0.6257	0.042		
0.3126	0.145	0.7272	0.003		
Cyclopentanone + $C_{12}H_{26}$					
0.0920	0.273	0.4441	0.650	0.7973	0.444
0.2073	0.487	0.5415	0.644	0.9145	0.235
0.3095	0.601	0.6789	0.567		
Cyclopentanone + $C_{16}H_{34}$					
0.1000	0.331	0.3950	0.832	0.7005	0.764
0.2249	0.621	0.4708	0.876	0.8200	0.589
0.2905	0.720	0.6018	0.845	0.9119	0.350
Cyclohexanone + C_6H_{14}					
0.0258	−0.003	0.2843	−0.189	0.7116	−0.292
0.0506	−0.005	0.3704	−0.268	0.8260	−0.201
0.1257	−0.055	0.4508	−0.309	0.9224	−0.106
0.2058	−0.129	0.6053	−0.325		
Cyclohexanone + C_7H_{16}					
0.0814	0.043	0.3772	−0.0005	0.6871	−0.058
0.1407	0.064	0.4848	−0.039	0.8087	−0.052
0.2590	0.047	0.5509	−0.046	0.9145	−0.022
Cyclohexanone + $C_{12}H_{26}$					
0.0754	0.212	0.3932	0.631	0.7754	0.486
0.1551	0.390	0.5367	0.640	0.9007	0.301
0.2405	0.522	0.6439	0.602		
Cyclohexanone + $C_{16}H_{34}$					
0.1168	0.361	0.5242	0.925	0.7879	0.677
0.2135	0.581	0.5636	0.928	0.9280	0.295
0.3947	0.863	0.6922	0.824		

[a] Subscript 1 denotes the cycloalkanone.

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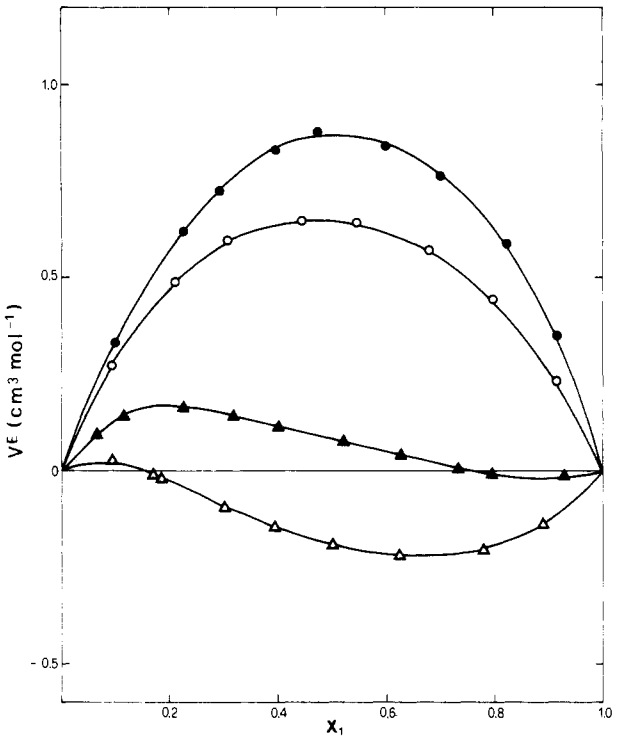

Figure 1. V^E vs. mole fraction (x_1) for the system cyclopentanone with n-C_6H_{14} (△), n-C_7H_{16} (▲), n-$C_{12}H_{26}$ (○), n-$C_{16}H_{34}$ (●).

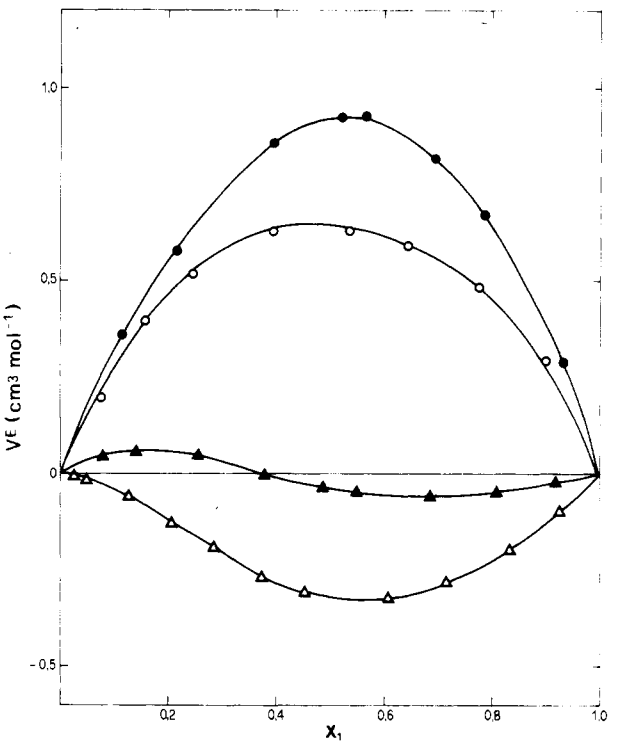

Figure 2. V^E vs. mole fraction (x_1) for the system cyclohexanone with n-C_6H_{14} (△), n-C_7H_{16} (▲), n-$C_{12}H_{26}$ (○), n-$C_{16}H_{34}$ (●).

Table III. Values of Parameters in Eq 2 and the Standard Deviations $\sigma(V^E)$

system	a_0	a_1	a_2	a_3	$\sigma(V^E)$
cyclopentanone–n-C_6H_{14}	−0.763	−0.674	0.206	−0.587	0.008
cyclopentanone–n-C_7H_{16}	0.328	−0.706	0.460	−0.573	0.006
cyclopentanone–n-$C_{12}H_{26}$	2.600	−0.210	0.764		0.004
cyclopentanone–n-$C_{16}H_{34}$	3.478	0.104	0.742	0.479	0.007
cyclohexanone–n-C_6H_{14}	−1.130	−0.563	0.619		0.007
cyclohexanone–n-C_7H_{16}	−0.152	−0.554	0.480		0.005
cyclohexanone–n-$C_{12}H_{26}$	2.577	−0.221	0.921	0.613	0.006
cyclohexanone–n-$C_{16}H_{34}$	3.686	−0.483	0.266		0.007

and 2. The equation used to express the dependence of the excess volume on composition was

$$V^E_{calcd}\ (cm^3\ mol^{-1}) = x_1x_2\sum_{j=0}^{3} a_j(x_1 - x_2)^j \qquad (2)$$

The coefficients a_j are listed in Table III along with the standard deviations $\sigma\ (V^E)$

$$\sigma(V^E) = |\sum(V^E_{calcd} - V^E)^2/(N - n)|^{1/2} \qquad (3)$$

The numerical values of the excess volumes for the cycloalkanones with the n-alkanes decrease in the order n-hexadecane > n-dodecane > n-heptane > n-hexane. An inversion of the sign of V^E values is observed over part of the concentration range for both the cycloalkanones with n-heptane and for only cyclopentanone with n-hexane. The behavior of V^E shown in Figures 1 and 2 may be ascribed to a balance between positive effects due to the disruption of the molecular order existing in pure n-alkanes by the cycloalkanone molecules and negative effects arising from interstitial accommodation of molecules in the mixtures.

Glossary

a_j	coefficients, eq 2
M	molecular weight
N	number of experimental values
n	number of coefficients, eq 2
V^E	excess volume, cm^3 mol^{-1}
X	mole fraction
ρ	density, g cm^{-3}
$\sigma(V^E)$	standard deviation

Registry No. C_6H_{14}, 110-54-3; C_7H_{16}, 142-82-5; $C_{12}H_{26}$, 112-40-3; $C_{16}H_{34}$, 544-76-3; cyclopentanone, 120-92-3; cyclohexanone, 108-94-1.

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