θ reduced sample size

Registry No. *n*-Hexane, 110-54-3; *n*-heptane, 142-82-5; *n*-octane, 111-65-9; *n*-nonane, 111-84-2; cyclohexane, 110-82-7; benzene, 71-43-2; toluene, 108-88-3; *p*-xylene, 106-42-3; 2-butanone, 78-93-3; 3-pentanone, 96-22-0; fluorene, 86-73-7; dibenzofuran, 132-64-9; *n*-hexadecane, 544-76-3.

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Thermodynamic Properties of Binary Mixtures Containing Cycloalkanones. 3. Excess Volumes of Cycloalkanones + Cyclohexane, + Benzene, and + Tetrachloromethane

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Molar excess volumes have been determined by means of a vibrating-tube densimeter for binary liquid mixtures of cycloalkanones (cyclopentanone and cyclohexanone) + cyclohexane, + benzene, and + tetrachloromethane. The V^E data are reported over the complete mole fraction range at 288.15, 298.15, and 308.15 K. The obtained excess volumes are positive for mixtures of cyclopentanone with cyclohexane and are negative for mixtures of the cycloalkanones with benzene and tetrachloromethane; for the system cyclohexanone-cyclohexane the V^E values are positive for a wide range of mole fraction, but at very low cyclohexane mole fraction an inversion of the sign of V^E is observed. The data show that in the considered range of temperature the values of the temperature coefficient $(\partial V^E/\partial T)$ are negative for mixtures of the cycloalkanones with benzene and are almost zero for mixtures with cyclohexane and with tetrachloromethane.

Introduction

This paper can be considered as a continuation of our previous studies on the excess thermodynamic properties of the binary mixtures containing cycloalkanone with organic solvents (*1*, *2*).

In the present paper we have studied mixtures of cyclopentanone or cyclohexanone with cyclohexane that present rather unspecific interaction and mixtures of these cycloalkanones with tetrachloromethane and with benzene that show specific interactions. We took a specific interest in the examination of the temperature dependence of V^E in these mixtures.

Table I. Experimental Measurements of Liquid Density

component	ρ_s, g cm^{-3} 288.15 K	298.15 K	308.15 K	lit.[a]
cyclopentanone	0.953 714	0.944 004	0.935 958	0.943 83 (*3*)
cyclohexanone	0.951 130	0.942 212	0.934 841	0.942 47 (*4*)
				0.942 01 (*5*)
cyclohexane	0.783 120	0.773 860	0.765 645	0.773 85 (*6*)
benzene	0.884 134	0.873 608	0.864 327	0.873 60 (*7*)
tetrachloromethane	1.603 597	1.584 440	1.567 498	1.584 39 (*8*)

[a] At 298.15 K.

Experimental Section

Excess volumes were determined from densities measured by use of a vibrating densimeter (Model DMA 602, Anton Paar) with a reproducibility within $\pm 1.5 \times 10^{-6}$ g cm^{-3} at 288.15, 298.15, and 308.15 K.

The measuring cell of the apparatus was thermostated with a Heto-Birkerod ultrathermostat with an accuracy of ± 0.01 K. The liquid mixtures were prepared by weight in a septum-capped vial of approximately 5-mL capacity. The two components were injected through the septum into the vial without allowing any vapor to escape, and then the sample was injected into the cell of the densimeter where its density was recorded. The temperature fluctuations in the cell were ± 0.005 K during the course of a run. The mole fraction error is estimated to be less than 1×10^{-4}. The error limit of the density $\Delta\rho$ is estimated to be $\pm 1 \times 10^{-5}$ g cm^{-3}. The V^E values were accurate to ± 0.003 cm^3 mol^{-1}. All liquids were of the best quality available from Fluka (AG, puriss. grade).

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Table II. Values of V^E for the Binary Mixtures of Cyclopentanone and Cyclohexanone with Cyclohexane, with Benzene, and with Tetrachloromethane

T, K	X_1	V^E, cm^3 mol^{-1}	X_1	V^E, cm^3 mol^{-1}	X_1	V^E, cm^3 mol^{-1}	T, K	X_1	V^E, cm^3 mol^{-1}	X_1	V^E, cm^3 mol^{-1}	X_1	V^E, cm^3 mol^{-1}
Cyclopentanone (1)–Cyclohexane (2)							Cyclohexanone (1)–Cyclohexane (2)						
288.15	0.0357	0.106	0.2389	0.367	0.7021	0.305	288.15	0.0247	0.044	0.3055	0.174	0.6970	0.085
	0.0556	0.146	0.2971	0.399	0.7840	0.236		0.0521	0.085	0.4041	0.165	0.8119	0.049
	0.0902	0.209	0.4225	0.419	0.8834	0.128		0.0963	0.125	0.5064	0.143	0.9006	0.023
	0.1297	0.266	0.5168	0.403	0.9264	0.073		0.2062	0.166	0.6020	0.125	0.9570	−0.008
	0.1709	0.312	0.6123	0.360			298.15	0.0516	0.082	0.3125	0.169	0.7121	0.080
298.15	0.0540	0.150	0.4066	0.425	0.7713	0.242		0.0585	0.091	0.4118	0.154	0.7953	0.054
	0.1211	0.263	0.4985	0.409	0.7882	0.229		0.1222	0.137	0.5522	0.133	0.9509	−0.005
	0.2323	0.371	0.5957	0.368	0.8854	0.130		0.2076	0.167	0.6052	0.102	0.9751	−0.001
	0.3232	0.413	0.6778	0.320	0.9585	0.048	308.15	0.0299	0.063	0.4065	0.033	0.9421	−0.002
308.15	0.0531	0.153	0.4021	0.433	0.8002	0.216		0.1014	0.136	0.6076	0.104	0.9748	−0.010
	0.1171	0.216	0.4874	0.415	0.8855	0.121		0.1995	0.179	0.7070	0.066		
	0.2200	0.372	0.5837	0.378	0.9569	0.047		0.3053	0.181	0.8094	0.033		
	0.3111	0.419	0.6782	0.320									
Cyclopentanone (1)–Benzene (2)							Cyclohexanone (1)–Benzene (2)						
288.15	0.0311	−0.042	0.3782	−0.299	0.7972	−0.201	288.15	0.0419	−0.042	0.3613	−0.212	0.7704	−0.131
	0.0838	−0.102	0.4857	−0.318	0.9032	−0.110		0.0714	−0.070	0.4338	−0.205	0.8865	−0.073
	0.1781	−0.193	0.5850	−0.303	0.9587	−0.052		0.1736	−0.143	0.5590	−0.190	0.9390	−0.041
	0.2773	−0.258	0.6868	−0.268				0.2654	−0.190	0.6600	−0.164		
298.15	0.0370	−0.050	0.3812	−0.323	0.7988	−0.216	298.15	0.0431	−0.048	0.3656	−0.235	0.7814	−0.143
	0.1006	−0.130	0.4954	−0.340	0.8704	−0.150		0.1015	−0.111	0.4584	−0.236	0.8793	−0.104
	0.1913	−0.217	0.5848	−0.327	0.9556	−0.060		0.1885	−0.173	0.5818	−0.216	0.9611	−0.054
	0.2975	−0.290	0.6945	−0.285				0.2803	−0.217	0.6782	−0.187		
308.15	0.0391	−0.058	0.4019	−0.360	0.7982	−0.231	308.15	0.0252	−0.031	0.4049	−0.266	0.8165	−0.140
	0.1053	−0.148	0.5013	−0.369	0.9009	−0.129		0.0788	−0.097	0.4882	−0.265	0.9296	−0.067
	0.2020	−0.248	0.5967	−0.351	0.9485	−0.071		0.1977	−0.198	0.5944	−0.241		
								0.2900	−0.244	0.7093	−0.197		
Cyclopentanone (1)–Tetrachloromethane (2)							Cyclohexanone (1)–Tetrachloromethane (2)						
288.15	0.0300	−0.052	0.2958	−0.413	0.7912	−0.354	288.15	0.0266	−0.059	0.2963	−0.468	0.6347	−0.526
	0.0564	−0.094	0.4056	−0.494	0.8888	−0.217		0.0510	−0.103	0.3993	−0.553	0.7250	−0.445
	0.1044	−0.173	0.5080	−0.523	0.9384	−0.131		0.0984	−0.190	0.4838	−0.569	0.8227	−0.318
	0.1489	−0.241	0.5998	−0.505				0.1860	−0.337	0.5273	−0.570	0.9306	−0.135
	0.2158	−0.336	0.6958	−0.446			298.15	0.0437	−0.089	0.3928	−0.541	0.7901	−0.364
298.15	0.0423	−0.077	0.4035	−0.502	0.7936	−0.350		0.0923	−0.177	0.4775	−0.562	0.9021	−0.191
	0.1860	−0.174	0.5038	−0.530	0.9032	−0.195		0.1903	−0.343	0.5900	−0.537	0.9743	−0.055
	0.2192	−0.334	0.6020	−0.501	0.9584	−0.098	308.15	0.0367	−0.080	0.3800	−0.535	0.8304	−0.291
	0.3030	−0.429	0.6948	−0.456				0.0961	−0.197	0.4834	−0.565	0.9323	−0.133
308.15	0.0396	−0.067	0.4093	−0.501	0.7867	−0.343		0.1904	−0.353	0.5865	−0.538		
	0.1026	−0.170	0.5071	−0.526	0.8920	−0.207		0.2834	−0.468	0.6840	−0.470		
	0.2088	−0.325	0.6068	−0.507	0.9499	−0.108							
	0.3079	−0.438	0.6995	−0.435									

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

system	T, K	a_0	a_1	a_2	a_3	$\sigma(V^E)$
cyclopentanone (1)–cyclohexane (2)	288.15	1.620	−0.450	0.377	−0.544	0.004
	298.15	1.627	−0.543	0.430	−0.451	0.004
	308.15	1.649	−0.575	0.411	−0.515	0.004
cyclopentanone (1)–benzene (2)	288.15	−1.259	0.051	−0.055		0.001
	298.15	−1.357	0.051	−0.0043		0.001
	308.15	−1.474	0.086	−0.0041		0.001
cyclopentanone (1)–tetrachloromethane (2)	288.15	−2.080	−0.176	0.095		0.004
	298.15	−2.100	−0.083	0.103	−0.262	0.005
	308.15	−2.099	−0.000	0.190	−0.285	0.005
cyclohexanone (1)–cyclohexane (2)	288.15	0.580	−0.394	0.327	−0.607	0.005
	298.15	0.537	−0.419	0.368	−0.578	0.004
	308.15	0.559	−0.576	0.321	−0.558	0.005
cyclohexanone (1)–benzene (2)	288.15	−0.813	0.239	−0.126		0.004
	298.15	−0.918	0.337	−0.278	−0.384	0.005
	308.15	−1.048	0.252	−0.140		0.003
cyclohexanone (1)–tetrachloromethane (2)	288.15	−2.289	0.030	0.229		0.002
	298.15	−2.245	0.029	0.137		0.004
	308.15	−2.250	0.153	0.137		0.002

The estimated purities as determined by gas–liquid chromatographic analysis were in all cases better than 99.5 mol %. The densities ρ of the pure liquids were found in good agreement with values published in the literature and are shown in Table I (*3–8*). The excess volumes V^E were calculated from the equation

$$V^E = \frac{X_1M_1 + X_2M_2}{\rho} - \frac{X_1M_1}{\rho_1} - \frac{X_2M_2}{\rho_2} \qquad (1)$$

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 the mixture.

Results

Excess volumes were determined at 288.15, 298.15, and 308.15 K for mixtures of cyclopentanone or cyclohexanone with

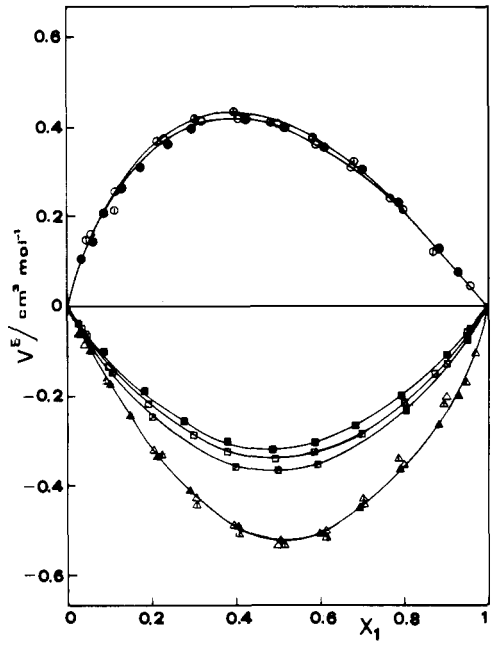

Figure 1. V^E vs mole fraction (X_1) for the systems cyclopentanone with cyclohexane at 288.15 (●), 298.15 (○), and 308.15 K (⦶); with benzene at 288.15 (■), 298.15 (□), and 308.15 K (⧅); with tetrachloromethane at 288.15 (▲), 298.15 (△), and 308.15 K (⧋).

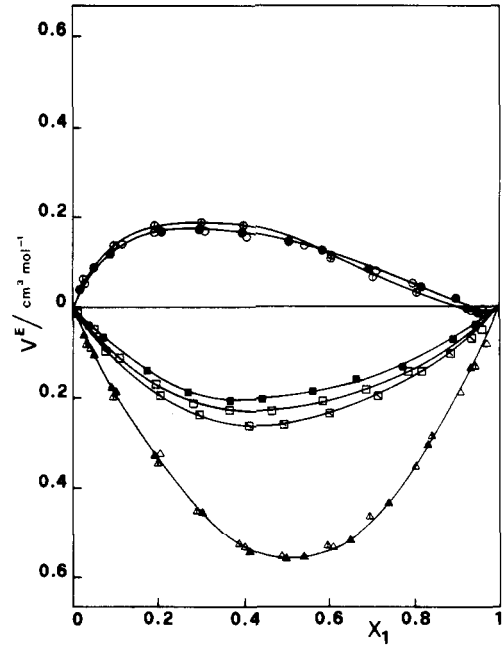

Figure 2. V^E vs mole fraction (X_1) for the systems cyclohexanone with cyclohexane at 288.15 (●), 298.15 (○), and 308.15 K (⦶); with benzene at 288.15 (■), 298.15 (□), and 308.15 K (⧅); with tetrachloromethane at 288.15 (▲), 298.15 (△), and 308.15 K (⧋).

cyclohexane, with benzene, and with tetrachloromethane. The results are given in Table II and are graphically represented in Figures 1 and 2.

The equation used to express the dependence of the molar excess volume on composition was

$$V^E_{calcd}(\text{cm}^3\ \text{mol}^{-1}) = X_1X_2\sum_{i=0}^{3}a_i(x_1 - x_2)^i \qquad (2)$$

The coefficients a_i 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 system cyclopentanone–cyclohexane exhibits positive V^E over the complete mole fraction range at the three temperatures examined, and no appreciable temperature effect is noted in this range. The same negligible temperature effect has been noted for the systems cyclopentanone–tetrachloromethane and cyclohexanone–tetrachloromethane, but these mixtures present negative V^E. The binary systems cyclopentanone–benzene and cyclohexanone–benzene show negative V^E and also negative values of the temperature coefficient. In the case of the cyclohexanone–cyclohexane system, positive values of V^E for a wide range of mole fraction are observed. Only at very low cyclohexane mole fraction does V^E have small negative values, hardly measurable at 308.15 K, so further V^E data at higher temperatures will be measured in the near future.

Glossary

a_i	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. Cyclopentanone, 120-92-3; cyclohexanone, 108-94-1; cyclohexane, 110-82-7; benzene, 71-43-2; tetrachloromethane, 56-23-5.

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