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EXCESS MOLAR VOLUMES OF BINARY LIQUID MIXTURES OF
CYCLOHEXANE - CARBON TETRACHLORIDE AND TOLUENE - BENZENE AT
VARIOUS TEMPERATURES

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Abstract: Excess molar volumes of binary mixtures of cyclohexane - carbon tetrachloride at 288.15, 293.15, 298.15 K and of toluene - benzene at 293.15, 298.15, 308.15 K have been determined using a vibrating tube densimeter.

Flory's theory of liquid mixture has been applied to calculate the excess enthalpy of cyclohexane - carbon tetrachloride at 298,15 K; the calculated value for the equimolar mixture is in fairly good agreement with experimental results.

INTRODUCTION

Excess molar volumes of binary mixtures of cyclohexane - carbon tetrachloride and toluene - benzene are presented in this paper. The toluene - benzene system which forms nearly ideal solutions has been used as reference system.

The aim of our work was to calculate the excess enthalpy from measured excess volumes, using the statistical Flory's theory of liquid mixtures [1]. Flory has developed an approach which relates the excess properties of a mixture to measurable macroscopic properties of pure liquid components by a partition function. This theory has been very useful in predicting the thermodynamic properties of binary mixtures of nonpolar

molecules such as hydrocarbons (normal, branched, cyclic and aromatic) and halocarbons [2,3]. In this work we use this approach to the mixture of cyclohexane - carbon tetrachloride with a moderate polarity.

EXPERIMENTAL

Cyclohexane (Kemika, Zagreb), carbon tetrachloride (Carlo Erba), toluene (Kemika) and benzene (Riedel - de Haen), with p.a. stated purity, were used without further purification. The investigation of sources of errors in V^E by Lepory et al. [4] showed namely, that purity of substances was not a crucial factor in V^E measurements.

Densities were measured, using a vibrating tube densimeter A.Paar DMA 60/602, at 288.15, 293.15, 298.15 and 308.15 K. Temperature control of the cell was $\pm 5 \cdot 10^{-3}$ °C. Before each series of measurements, the instrument was calibrated with doubly distilled water and dry air at atmospheric pressure. The density d , of any liquid relative to the density of pure water d_w , is given by

$$d = d_w + k (T^2 - T_w^2) \quad (1)$$

where k is the characteristic of a particular oscillator. T^2 and T_w^2 are vibration periods of the tube, filled with liquid and with water, respectively. The determined densities [5,6] are accurate to at least $\pm 10^{-5}$ g cm⁻³. For pure cyclohexane, benzene, toluene and carbon tetrachloride they agreed well with literature values [7-10,12-14]. The mixtures were prepared by weight. The values of V^E determined from density measurements are accurate within ± 0.0005 cm³ mol⁻¹.

RESULTS AND DISCUSSION

Excess molar volumes V^E of binary mixtures of cyclohexane (1)- carbon tetrachloride (2) and toluene (1) - benzene (2) were calculated from the corresponding density measurements using the equation

$$V^E (\text{cm}^3 \text{mol}^{-1}) = x_1 M_1 (d_m^{-1} - d_1^{-1}) + x_2 M_2 (d_m^{-1} - d_2^{-1}) \quad (2)$$

where x_i is the molar fraction of component i , and d_m and d_i are the densities of the mixture and pure component i , respectively. M_i are the molar masses of the pure components. The obtained results are listed in Table 1 and Table 2.

Table 1: Densities and excess molar volumes V^E of binary mixtures of toluene(1) - benzene(2) at 293.15, 298.15 and 308.15 K

293.15 K			298.15 K			308.15 K		
X_2	d (g cm ⁻³)	V^E (cm ³ mol ⁻¹)	X_2	d (g cm ⁻³)	V^E (cm ³ mol ⁻¹)	X_2	d (g cm ⁻³)	V^E (cm ³ mol ⁻¹)
0.00000	0.86685	0.0000	0.00000	0.86223	0.0000	0.00000	0.85299	0.0000
0.10676	0.86771	0.0280	0.09093	0.86291	0.0238	0.07520	0.85346	0.0209
0.16292	0.86818	0.0421	0.16471	0.86349	0.0415	0.24456	0.85459	0.0645
0.23090	0.86876	0.0593	0.23253	0.86403	0.0585	0.26568	0.85461	0.0851
0.29499	0.86937	0.0696	0.24830	0.86416	0.0621	0.28276	0.85486	0.0736
0.34447	0.86987	0.0752	0.29065	0.86456	0.0662	0.31242	0.85507	0.0809
0.38214	0.87027	0.0779	0.33250	0.86494	0.0728	0.37459	0.85559	0.0875
0.40612	0.87050	0.0828	0.37787	0.86536	0.0797	0.40639	0.85587	0.0898
0.45288	0.87099	0.0882	0.41849	0.86578	0.0814	0.47647	0.85652	0.0922
0.48365	0.87135	0.0880	0.48448	0.86647	0.0849	0.59077	0.85766	0.0910
0.51775	0.87175	0.0882	0.52499	0.86691	0.0861	0.59490	0.85770	0.0912
0.54412	0.87202	0.0931	0.57627	0.86751	0.0837	0.68986	0.85876	0.0817
0.58951	0.87264	0.0851	0.59444	0.86772	0.0835	0.73848	0.85933	0.0755
0.65377	0.87346	0.0820	0.63416	0.86821	0.0801	0.75586	0.85955	0.0717
0.75732	0.87492	0.0667	0.69181	0.86894	0.0746	0.80325	0.86016	0.0612
0.81199	0.87572	0.0580	0.73162	0.86947	0.0689	0.85483	0.86082	0.0515
0.86405	0.87641	0.0588	0.79248	0.87032	0.0577	0.90854	0.86159	0.0341
0.90216	0.87717	0.0339	0.85753	0.87128	0.0425	0.95616	0.86229	0.0182
0.94521	0.87777	0.0338	0.89630	0.87187	0.0328	1.00000	0.86298	0.0000
1.00000	0.87888	0.0000	0.95441	0.87282	0.0132			
			1.00000	0.87356	0.0000			

Table 2: Densities and excess molar volumes V^E of binary mixtures of cyclohexane(1) - carbon tetrachloride(2) at 288.15, 293.15 and 298.15 K

288.15 K			293.15 K			298.15 K		
X_2	d (g cm ⁻³)	V^E (cm ³ mol ⁻¹)	X_2	d (g cm ⁻³)	V^E (cm ³ mol ⁻¹)	X_2	d (g cm ⁻³)	V^E (cm ³ mol ⁻¹)
1.00000	1.60374	0.000	1.00000	1.59311	0.000	1.00000	1.58427	0.000
0.95162	1.55895	0.035	0.95243	1.55008	-0.008	0.95118	1.53959	0.039
0.89768	1.50984	0.063	0.89964	1.50223	0.026	0.89982	1.49347	0.062
0.85224	1.46883	0.096	0.85152	1.45925	0.051	0.84930	1.44861	0.088
0.80115	1.42346	0.121	0.79943	1.41332	0.077	0.79976	1.40527	0.106
0.69971	1.33524	0.154	0.69900	1.32651	0.116	0.70118	1.32036	0.156
0.59972	1.25030	0.191	0.59972	1.24271	0.156	0.59743	1.23358	0.174
0.49878	1.16713	0.179	0.49878	1.16003	0.150	0.49892	1.15360	0.146
0.39881	1.08633	0.192	0.40045	1.08070	0.198	0.40045	1.07416	0.235
0.30000	1.00839	0.190	0.30077	1.00295	0.160	0.29962	0.99606	0.187
0.20020	0.93158	0.166	0.15004	0.88850	0.099	0.20087	0.92094	0.168
0.14949	0.89325	0.145	0.09949	0.85101	0.067	0.15021	0.88361	0.086
0.10266	0.85857	0.081	0.05004	0.81477	0.028	0.10291	0.84864	0.064
0.04667	0.81738	0.023	0.00000	0.77838	0.000	0.04739	0.80818	0.019
0.00000	0.78320	0.000				0.00000	0.77386	0.000

Each set of experimental results as fitted to the Redlich - Kister equation [11]

$$V^E (\text{cm}^3 \text{mol}^{-1}) = x_1 x_2 \sum_{i=0}^n A_i (1 - 2 x_2)^i \quad (3)$$

Values of coefficients A_i are listed in Table 3, together with the standard deviation of the fit, σV^E , defined as

$$\sigma V^E = \left[\sum (V_{\text{exp}}^E - V_{\text{calc}}^E)^2 / (N - n) \right]^{1/2} , \quad (4)$$

where N is the number of data points and n is the number of coefficients.

Table 3: Coefficients A_i and standard deviation σV^E of equation (3)

	$T(K)$	A_0	A_1	A_2	A_3	$\sigma V^E (\text{cm}^3 \text{mol}^{-1})$
cyclohexane-carbon tetrachloride	288.15	0.7967	0.2549	0.1356	-0.1290	0.013
	293.15	0.6903	0.2970	-0.2709	-0.1113	0.012
	298.15	0.8129	0.5045	-0.1836	-0.8788	0.022
toluene-benzene	293.15	0.3535	-0.0356	-0.0218	-0.0320	0.0052
	298.15	0.3465	-0.0291	-0.0491	0.0090	0.0012
	308.15	0.3770	-0.0092	-0.0211	-0.0867	0.0167

The V^E of both mixtures are positive throughout. However, they are significantly smaller for toluene-benzene mixture, which is nearly ideal solution, than for the cyclohexane-carbon tetrachloride system. Positive values can be explained by the predominance of expansion in volume, caused by the loss of dipolar association and difference in size and shape of component molecules, over contraction in volumes, due to the dipole-dipole and dipole-induced dipole interactions.

Ocon, Tojo, Espada [12] have determined V^E of cyclohexane-carbon tetrachloride at 293.15 K. Our results for this mixture at 293.15 K are compared with literature ones in Fig.1; it can be seen, that our values are higher in a part of the curve ($X_2 = 0.4-0.5$). The reason may be in additional purification of chemicals [12].

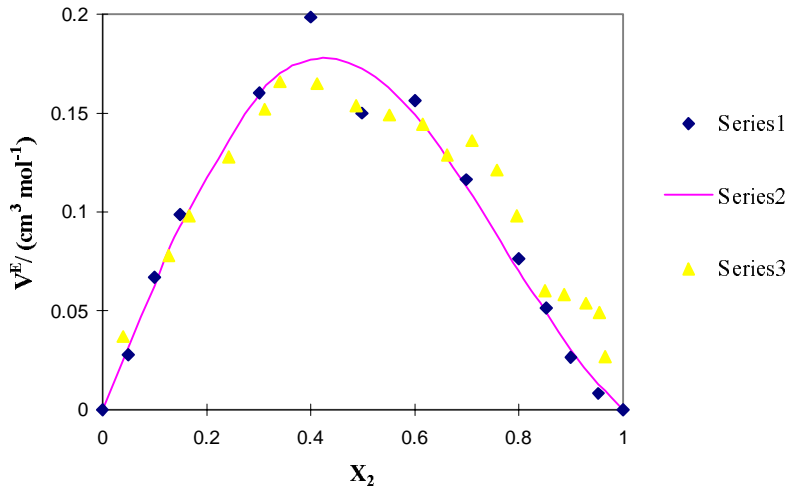


Fig.1: Experimental V^E for cyclohexane-carbon tetrachloride at 293.15 K (series 1); Ocon, Tojo, Espada (series 3); calculated values based upon equ. 3 (series 2)

Analysis in terms of the Flory theory

The interaction parameter χ_{12} in Flory's theory can be calculated from experimental excess volume data and should be used further to obtain H^E . Details were given by Flory (1965) and Abe, Flory (1965). Symbols in the following equations have their usual meaning and are explained at the end of the text:

$$V^E = \frac{(\tilde{v}^0)^{7/3}}{(4/3) - (\tilde{v}^0)^{1/3}} (\tilde{T} - \tilde{T}^0) (X_1 V_1^* + X_2 V_2^*), \quad (5)$$

$$H^E = X_1 P_1^* V_1^* (1/\tilde{v}_1 - 1/\tilde{v}) + X_2 P_2^* V_2^* (1/\tilde{v}_2 - 1/\tilde{v}) + X_1 V_1^* \Theta_2 \chi_{12} / \tilde{v}, \quad (6)$$

$$\text{where } \tilde{v}^0 = \Phi_1 \tilde{v}_1 + \Phi_2 \tilde{v}_2, \quad (7)$$

$$\tilde{T} = \frac{\Phi_1 P_1^* T_1 + \Phi_2 P_2^* \tilde{T}}{\Phi_1 P_1^* + \Phi_2 P_2^* - \Phi_1 \Theta_2 \chi_{12}}, \quad (8)$$

$$\tilde{v}_i^{1/3} - 1 = \frac{\alpha_i T}{3(1 + \alpha_i T)}, \quad (9)$$

$$\Phi_1 = 1 - \Phi_2 = \frac{X_1 V_1^*}{X_1 V_1^* + X_2 V_2^*} \quad (10)$$

The key quantity of the theory, the interchange energy parameter χ_{12} , was fitted to equimolar experimental values of V^E for cyclohexane-carbon tetrachloride at 298.15 K. The resulting χ_{12} was used to calculate H^E , along with the pure component parameters

(α_i from Wood, Gray [14] and γ_i from Holder, Whalley [15]) as given in Table 4. Comparison between calculated and experimental (Adcock and McGlashan [16]) excess enthalpy, and TS^E is given in Table 5.

Table 4: The parameters of pure liquid component used in Flory's theory

component	c-C ₆ H ₁₂	CCl ₄
V_i (cm ³ / mol)	108.75	97.08
$\alpha_i \cdot 10^3$ (K ⁻¹)	1.217	1.229
γ_i (J / cm ³ K)	1.067	1.143
\tilde{V}_i	1.2904	1.2927
\tilde{T}_i	0.06314	0.06345
P_i^* (J / cm ³)	532	569
V_i^* (cm ³ / mol)	84.28	75.10
T_i^* (K)	4720	4697
Φ_i	0.5288	0.4712
Θ_i	0.5192	0.4808

Table 5: Calculated (Flory's theory) and experimental H^E (X=0.5) and TS^E (X=0.5) values for the cyclohexane-carbon tetrachloride system, at 298.15 K

χ_{12}	H^E (J/mol)		TS^E (J/mol)	
	calc.	exp.	calc.	exp.
7.9	167	149	78.3	46.5

From Table 5 it can be seen, that the theory predicts H^E reasonably well, even though the calculated value exceeds the experimental by 12%. The agreement in excess entropy is worse; but it is well known, that Flory's theory can not provide a better conformity for a moderate polarity of molecules.

LIST OF SYMBOLS

H^E	excess molar enthalpy
P_i^*	characteristic pressure of pure component
T_i^*	characteristic temperature of pure component
\tilde{T}_i	reduced temperature of component I
V^E	excess molar volume
V_i	molar volume of pure component
V_i^*	characteristic volume of pure component
\tilde{v}_i	reduced volume of pure component
X_2	mole fraction of component 2
Θ_2	site fraction of component 2
Φ_2	segment fraction of component 2
γ	thermal pressure coefficient
α	thermal volume coefficient
χ_{12}	interaction parameter

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Povzetek: Z gostotomerom smo izmerili gostote raztopin cikloheksana z ogljikovim tetrakloridom pri 288,15, 293,15 in 298,15 K ter raztopin toluena z benzenom pri 293,15, 298,15 in 308,15 K in iz njih izračunali presežne molske volumne.

S pomočjo Flory-jeve teorije za raztopine smo za sistem cikloheksan-ogljikov tetraklorid pri 298,15 K izračunali presežno molsko entalpijo; izračunana vrednost za ekvimolarno mešanico se relativno dobro ujema z experimentalno določeno.