

# Densities and Excess Molar Volumes of the Binary Mixtures of Cyclopentanone with Chloroalkanes at $T = (288.15, 298.15, 308.15, \text{ and } 318.15) \text{ K}$

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The experimental densities of binary mixtures of cyclopentanone with 1,1,2,2-tetrachloroethane, 1,1,1-trichloroethane, trichloromethane, 1,2-dichloroethane, 1,3-dichloropropane, 1,4-dichlorobutane, and 1-chlorobutane have been measured at  $T = (288.15, 298.15, 308.15, \text{ and } 318.15) \text{ K}$  and atmospheric pressure, over the whole composition range. From these results, excess molar volumes,  $V^E$ , have been calculated and fitted to the Redlich–Kister polynomial equation. The excess molar volumes are negative for the cyclopentanone + 1,1,2,2-tetrachloroethane, 1,1,1-trichloroethane, trichloromethane, and 1-chlorobutane systems and positive for the other three systems over almost the whole mole fraction range and temperatures studied. The variation of these properties with composition of the binary mixtures is discussed in terms of molecular interactions between components and structural effects.

## Introduction

In a first part of our experimental study concerning the volumetric properties of cyclic ketones with chloroalkanes we have investigated the binary systems of cyclohexanone with 1,1,2,2-tetrachloroethane, 1,1,1-trichloroethane, trichloromethane, 1,2-dichloroethane, 1,3-dichloropropane, 1,4-dichlorobutane, and 1-chlorobutane.<sup>1</sup> In the present work, we are concerned with the same binary chloroalkane systems but with cyclopentanone, as a homologue of cyclohexanone.

This choice allows one to make a comparison with the aim of analyzing the influence of cycloketone structure or of their basicity (electron-donor activity) on the studied properties of the corresponding binary mixtures. On the other hand, some of us determined excess properties of linear ketones (propan-2-one, pentan-3-one)<sup>2,3</sup> with several chloroalkanes, which means that interesting data are available to improve the discussion.

We present here densities and excess molar volumes for seven binary systems of cyclopentanone with 1,1,2,2-tetrachloroethane, 1,1,1-trichloroethane, trichloromethane, 1,2-dichloroethane, 1,3-dichloropropane, 1,4-dichlorobutane, and 1-chlorobutane at temperatures between (288.15 and 318.15) K. To the best of our knowledge, no density and excess molar volume data of these systems are available in literature.

Both cyclopentanone and chloroalkanes are polar and practically unassociated liquids, and their mixtures are interesting from the point of view of both theoretical and engineering applications. The values of the excess molar volumes of the studied systems are discussed in terms of structural effects and molecular interactions between components.

## Experimental Section

**Materials.** All used substances were first grade purity commercial products from Aldrich. Their purity, checked by gas chromatography, was better than 0.998 in mole fraction.

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**Table 1. Comparison of Measured Densities with Literature Values for Pure Components at  $T = (298.15 \text{ and } 308.15) \text{ K}$**

component	$10^{-3} \rho/\text{kg}\cdot\text{m}^{-3}$			
	$T/\text{K} = 298.15$		$T/\text{K} = 308.15$	
	exptl	lit.	exptl	lit.
cyclopentanone	0.94435	0.9453 <sup>4,5</sup> 0.94386 <sup>6</sup>	0.93469	
1,1,2,2-tetrachloroethane	1.58919	1.58655 <sup>7</sup> 1.588539 <sup>8</sup>	1.57359	1.572901 <sup>8</sup>
1,1,1-trichloroethane	1.32949	1.3287 <sup>5</sup> 1.3314 <sup>9</sup> 1.32955 <sup>10</sup>	1.31265	
trichloromethane	1.47343	1.47988 <sup>7</sup> 1.472435 <sup>8</sup> 1.4717 <sup>11</sup> 1.47156 <sup>12</sup>	1.45433	1.460025 <sup>13</sup>
1,2-dichloroethane	1.24580	1.24561 <sup>3</sup> 1.2458 <sup>7</sup> 1.245290 <sup>8</sup> 1.2455 <sup>14</sup>	1.23115	1.230566 <sup>8</sup> 1.2309 <sup>14</sup>
1,3-dichloropropane	1.17956	1.1818 <sup>9</sup> 1.17922 <sup>15</sup> 1.17908 <sup>16</sup>	1.16714	
1,4-dichlorobutane	1.13250	1.13402 <sup>3</sup> 1.1328 <sup>7</sup> 1.1353 <sup>9</sup> 1.1337 <sup>14</sup>	1.12154	1.1224 <sup>14</sup>
1-chlorobutane	0.88112	0.8809 <sup>4,7</sup> 0.8810 <sup>11</sup> 0.88079 <sup>17</sup>	0.86993	0.86962 <sup>17</sup>

The liquids were dried and stored over 4A molecular sieves and used without further purification. Experimental densities of the pure components are in agreement with the literature values, as can be seen in Table 1.

**Apparatus and Procedure.** The binary mixtures were prepared by mixing the appropriate volumes of liquids in airtight glass bottles and weighed using a HR-120 (A&D Japan) electronic balance with a precision of  $0.1 \cdot 10^{-6} \text{ kg}$ . The experimental uncertainty in mole fraction was estimated to be less than  $\pm 0.0002$ . The density measurements of the pure solvents and of the mixtures were performed by means of an Anton Paar DMA 4500 densimeter with a precision of  $\pm 0.05$

**Table 2. Experimental Densities,  $\rho$ , and Molar Excess Volumes,  $V^E$ , for Binary Mixtures of Chloroalkanes with Cyclopentanone at Temperatures of (288.15, 298.15, 308.15, and 318.15) K**

$x_1$	$T/K = 288.15$		$T/K = 298.15$		$T/K = 308.15$		$T/K = 318.15$	
	$10^{-3} \rho$ kg·m <sup>-3</sup>	$10^6 V^E$ m <sup>3</sup> ·mol <sup>-1</sup>	$10^{-3} \rho$ kg·m <sup>-3</sup>	$10^6 V^E$ m <sup>3</sup> ·mol <sup>-1</sup>	$10^{-3} \rho$ kg·m <sup>-3</sup>	$10^6 V^E$ m <sup>3</sup> ·mol <sup>-1</sup>	$10^{-3} \rho$ kg·m <sup>-3</sup>	$10^6 V^E$ m <sup>3</sup> ·mol <sup>-1</sup>
1,1,2,2-Tetrachloroethane (1) + Cyclopentanone (2)								
0.0000	0.95399	0.000	0.94435	0.000	0.93469	0.000	0.92499	0.000
0.1209	1.04722	-0.168	1.03691	-0.189	1.02654	-0.207	1.01611	-0.223
0.2041	1.10907	-0.272	1.09828	-0.301	1.08744	-0.329	1.07653	-0.355
0.3218	1.19326	-0.384	1.18179	-0.421	1.17029	-0.459	1.15870	-0.494
0.4139	1.25669	-0.457	1.24471	-0.500	1.23266	-0.540	1.22054	-0.579
0.5120	1.32138	-0.479	1.30882	-0.521	1.29619	-0.561	1.28350	-0.601
0.6132	1.38546	-0.469	1.37229	-0.508	1.35906	-0.545	1.34577	-0.582
0.7097	1.44391	-0.415	1.43016	-0.449	1.41637	-0.482	1.40250	-0.513
0.7901	1.49055	-0.329	1.47632	-0.357	1.46203	-0.383	1.44769	-0.408
0.9004	1.55195	-0.178	1.53702	-0.193	1.52206	-0.208	1.50705	-0.221
1.0000	1.60478	0.000	1.58919	0.000	1.57359	0.000	1.55795	0.000
1,1,1-Trichloroethane (1) + Cyclopentanone (2)								
0.0000	0.95399	0.000	0.94435	0.000	0.93469	0.000	0.92499	0.000
0.1165	1.00637	-0.157	0.99599	-0.166	0.98556	-0.175	0.97508	-0.184
0.2125	1.04824	-0.258	1.03723	-0.274	1.02617	-0.289	1.01504	-0.305
0.3002	1.08547	-0.330	1.07388	-0.349	1.06222	-0.369	1.05049	-0.389
0.4003	1.12673	-0.381	1.11446	-0.404	1.10211	-0.427	1.08970	-0.454
0.4938	1.16410	-0.403	1.15118	-0.427	1.13819	-0.453	1.12509	-0.480
0.5938	1.20279	-0.394	1.18917	-0.419	1.17546	-0.445	1.16164	-0.472
0.6952	1.24070	-0.354	1.22635	-0.377	1.21189	-0.400	1.19732	-0.426
0.7988	1.27798	-0.274	1.26286	-0.291	1.24762	-0.310	1.23224	-0.329
0.9110	1.31670	-0.141	1.30071	-0.149	1.28460	-0.160	1.26834	-0.171
1.0000	1.34617	0.000	1.32949	0.000	1.31265	0.000	1.29566	0.000
Trichloromethane (1) + Cyclopentanone (2)								
0.0000	0.95399	0.000	0.94435	0.000	0.93469	0.000	0.92499	0.000
0.1249	1.01696	-0.108	1.00656	-0.124	0.99612	-0.141	0.98560	-0.156
0.2266	1.06907	-0.164	1.05803	-0.194	1.04693	-0.224	1.03575	-0.255
0.3255	1.12083	-0.223	1.10911	-0.262	1.09732	-0.304	1.08543	-0.346
0.4011	1.16110	-0.267	1.14882	-0.312	1.13646	-0.360	1.12398	-0.410
0.5001	1.21466	-0.315	1.20157	-0.365	1.18838	-0.417	1.17507	-0.473
0.5919	1.26500	-0.339	1.25109	-0.390	1.23705	-0.443	1.22287	-0.500
0.6900	1.31945	-0.340	1.30453	-0.386	1.28948	-0.435	1.27426	-0.488
0.8070	1.38463	-0.272	1.36839	-0.308	1.35197	-0.346	1.33537	-0.386
0.9060	1.43989	-0.158	1.42236	-0.178	1.40464	-0.200	1.38700	-0.241
1.0000	1.49231	0.000	1.47343	0.000	1.45433	0.000	1.43497	0.000
1,2-Dichloroethane (1) + Cyclopentanone (2)								
0.0000	0.95399	0.000	0.94435	0.000	0.93469	0.000	0.92499	0.000
0.1186	0.98657	0.017	0.97653	0.010	0.96645	0.004	0.95632	-0.002
0.1945	1.00790	0.026	0.99759	0.015	0.98723	0.005	0.97681	-0.006
0.3015	1.03860	0.036	1.02787	0.022	1.01708	0.008	1.00623	-0.006
0.4044	1.06885	0.045	1.05769	0.028	1.04646	0.012	1.03516	-0.006
0.5004	1.09768	0.055	1.08609	0.037	1.07443	0.019	1.06267	0.001
0.6009	1.12864	0.060	1.11655	0.043	1.10439	0.025	1.09212	0.007
0.6915	1.15724	0.059	1.14468	0.043	1.13202	0.028	1.11926	0.011
0.7932	1.19015	0.054	1.17701	0.041	1.16376	0.029	1.15040	0.015
0.8997	1.22570	0.035	1.21187	0.029	1.19794	0.021	1.18389	0.012
1.0000	1.26033	0.000	1.24580	0.000	1.23115	0.000	1.21635	0.000
1,3-Dichloropropane (1) + Cyclopentanone (2)								
0.0000	0.95399	0.000	0.94435	0.000	0.93469	0.000	0.92499	0.000
0.1064	0.98050	0.044	0.97062	0.040	0.96068	0.038	0.95070	0.036
0.1972	1.00292	0.069	0.99280	0.064	0.98263	0.060	0.97241	0.057
0.2925	1.02613	0.094	1.01576	0.088	1.00535	0.082	0.99487	0.078
0.3865	1.04887	0.103	1.03826	0.096	1.02759	0.090	1.01686	0.085
0.4831	1.07197	0.108	1.06110	0.100	1.05016	0.095	1.03917	0.089
0.5793	1.09477	0.103	1.08363	0.096	1.07243	0.091	1.06116	0.086
0.6743	1.11706	0.091	1.10564	0.086	1.09417	0.082	1.08263	0.078
0.7804	1.14170	0.070	1.12998	0.067	1.11821	0.064	1.10636	0.061
0.8756	1.16359	0.045	1.15159	0.043	1.13954	0.042	1.12741	0.041
1.0000	1.19192	0.000	1.17956	0.000	1.16714	0.000	1.15465	0.000
1,4-Dichlorobutane (1) + Cyclopentanone (2)								
0.0000	0.95399	0.000	0.94435	0.000	0.93469	0.000	0.92499	0.000
0.1103	0.97925	0.030	0.96945	0.029	0.95963	0.027	0.94976	0.025
0.2151	1.00202	0.054	0.99209	0.051	0.98211	0.048	0.97209	0.045
0.3024	1.02017	0.068	1.01012	0.065	1.00002	0.060	0.98987	0.058
0.3909	1.03787	0.076	1.02770	0.073	1.01748	0.067	1.00721	0.065
0.4900	1.05687	0.080	1.04656	0.079	1.03622	0.072	1.02582	0.069
0.5868	1.07468	0.078	1.06425	0.078	1.05378	0.070	1.04326	0.068
0.6976	1.09422	0.068	1.08364	0.070	1.07304	0.062	1.06239	0.059
0.8036	1.11213	0.050	1.10143	0.053	1.09070	0.045	1.07993	0.042

Table 2. Continued

$x_1$	$T/K = 288.15$		$T/K = 298.15$		$T/K = 308.15$		$T/K = 318.15$	
	$10^{-3} \rho$ kg·m <sup>-3</sup>	$10^6 V^E$ m <sup>3</sup> ·mol <sup>-1</sup>	$10^{-3} \rho$ kg·m <sup>-3</sup>	$10^6 V^E$ m <sup>3</sup> ·mol <sup>-1</sup>	$10^{-3} \rho$ kg·m <sup>-3</sup>	$10^6 V^E$ m <sup>3</sup> ·mol <sup>-1</sup>	$10^{-3} \rho$ kg·m <sup>-3</sup>	$10^6 V^E$ m <sup>3</sup> ·mol <sup>-1</sup>
0.9190	1.13080	0.023	1.11997	0.028	1.10910	0.021	1.09819	0.020
1.0000	1.14343	0.000	1.13250	0.000	1.12154	0.000	1.11054	0.000
1-Chlorobutane (1) + Cyclopentanone (2)								
0.0000	0.95399	0.000	0.94435	0.000	0.93469	0.000	0.92499	0.000
0.0970	0.94769	-0.060	0.93794	-0.068	0.92814	-0.074	0.91829	-0.081
0.2041	0.94085	-0.115	0.93096	-0.128	0.92102	-0.142	0.91100	-0.155
0.3226	0.93338	-0.159	0.92332	-0.175	0.91320	-0.192	0.90301	-0.212
0.4106	0.92800	-0.189	0.91783	-0.208	0.90758	-0.228	0.89724	-0.250
0.4991	0.92246	-0.190	0.91215	-0.209	0.90177	-0.230	0.89129	-0.253
0.6050	0.91599	-0.187	0.90553	-0.205	0.89469	-0.226	0.88433	-0.248
0.7051	0.91000	-0.176	0.89939	-0.192	0.88868	-0.209	0.87786	-0.230
0.7934	0.90456	-0.131	0.89382	-0.144	0.88297	-0.158	0.87198	-0.172
0.8965	0.89844	-0.084	0.88754	-0.091	0.87652	-0.099	0.86536	-0.109
1.0000	0.89218	0.000	0.88112	0.000	0.86993	0.000	0.85858	0.000

kg·m<sup>-3</sup>, between (288.15 and 318.15) K. The DMA cell was calibrated with dry air and ultra pure water at atmospheric pressure. The sample thermostating was controlled to  $\pm 0.01$  K. The uncertainty in the density determination is an absolute average of  $\pm 0.1$  kg·m<sup>-3</sup> and for the  $V^E$  calculation is less than  $\pm 10^{-8}$  m<sup>3</sup>·mol<sup>-1</sup>.

## Results and Discussion

The measured densities,  $\rho$ , for the binary mixtures of cyclopentanone with chloroalkanes at  $T = (288.15, 298.15, 308.15, \text{ and } 318.15)$  K over the whole composition range are listed in Table 2.

The experimental excess molar volumes,  $V^E$ , for these binary mixtures were obtained from the following relation:

$$V^E = x_1 M_1 \left( \frac{1}{\rho} - \frac{1}{\rho_1} \right) + x_2 M_2 \left( \frac{1}{\rho} - \frac{1}{\rho_2} \right) \quad (1)$$

where  $x_1$  and  $x_2$  are the mole fractions,  $M_1$  and  $M_2$  are molar masses, and  $\rho_1$  and  $\rho_2$  are the densities of the pure liquid components 1 and 2, respectively. The determined  $V^E$  values are indicated also in Table 2.

The experimental values of  $V^E$  were fitted to the Redlich–Kister type polynomials:

$$V^E = x_1 x_2 \sum_{k=0}^2 A_k (x_1 - x_2)^k \quad (2)$$

The adjustable parameters  $A_k$  obtained by fitting the equations to the experimental values with a least-squares type algorithm are given in Table 3, along with the standard deviation,  $\sigma$ , defined as follows:

$$\sigma = \left[ \sum_{i=1}^n (V_{\text{exp},i}^E - V_{\text{calc},i}^E)^2 / (n - m) \right]^{0.5} \quad (3)$$

where  $n$  is the number of experimental data and  $m = 3$  is the number of parameters.

From the experimental results shown in Table 2 and Figures 1 to 4, it can be observed that at investigated temperatures the excess molar volume values are negative for the cyclopentanone + 1,1,2,2-tetrachloroethane, 1,1,1-trichloroethane, trichloromethane, and 1-chlorobutane systems and positive for the cyclopentanone + 1,2-dichloroethane, 1,3-dichloropropane, and 1,4-dichlorobutane systems over almost the whole composition range. Except for the cyclopentanone + trichloromethane and cyclopentanone + 1,2-dichloroethane systems, the excess volume curves for the other five systems are symmetric about  $x = 0.5$ .

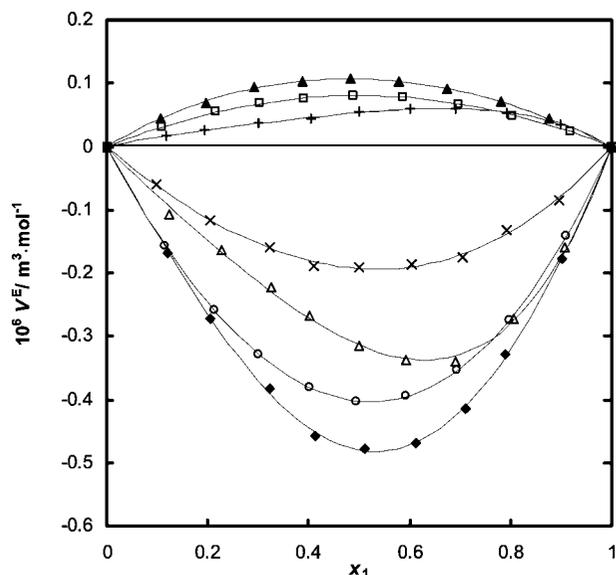
Table 3. Coefficients  $A_k$  of the Fitting Equation 2 and Standard Deviations  $\sigma$ 

$T$ K	$10^6 A_0$ m <sup>3</sup> ·mol <sup>-1</sup>	$10^6 A_1$ m <sup>3</sup> ·mol <sup>-1</sup>	$10^6 A_2$ m <sup>3</sup> ·mol <sup>-1</sup>	$10^6 \sigma$ m <sup>3</sup> ·mol <sup>-1</sup>
1,1,2,2-Tetrachloroethane + Cyclopentanone				
288.15	-1.9199	-0.2866	0.2435	0.004
298.15	-2.0883	-0.2730	0.2274	0.004
308.15	-2.2508	-0.2600	0.2223	0.004
318.15	-2.4098	-0.2519	0.2292	0.004
1,1,1-Trichloroethane + Cyclopentanone				
288.15	-1.6117	-0.1369	-0.0250	0.001
298.15	-1.7110	-0.1466	-0.0324	0.001
308.15	-1.8146	-0.1717	-0.0355	0.001
318.15	-1.9239	-0.1945	-0.0310	0.001
Trichloromethane + Cyclopentanone				
288.15	-1.2552	-0.6824	-0.2391	0.007
298.15	-1.4561	-0.7367	-0.2237	0.007
308.15	-1.6665	-0.7961	-0.2043	0.007
318.15	-1.8811	-0.8973	-0.2723	0.005
1,2-Dichloroethane + Cyclopentanone				
288.15	0.2145	0.1404	0.0966	0.001
298.15	0.1435	0.1333	0.0919	0.001
308.15	0.0725	0.1214	0.0938	0.001
318.15	-0.0003	0.1057	0.0828	0.001
1,3-Dichloropropane + Cyclopentanone				
288.15	0.4296	-0.0347	0.0048	0.001
298.15	0.3998	-0.0217	0.0046	0.001
308.15	0.3754	-0.0206	0.0063	0.001
318.15	0.3530	-0.0165	0.0164	0.001
1,4-Dichlorobutane + Cyclopentanone				
288.15	0.3212	-0.0013	-0.0095	0.001
298.15	0.3024	0.0085	-0.0135	0.001
308.15	0.2881	0.0086	-0.0144	0.001
318.15	0.2784	0.0074	-0.0229	0.001
1-Chlorobutane + Cyclopentanone				
288.15	-0.7728	-0.1058	-0.0063	0.004
298.15	-0.8486	-0.1046	-0.0145	0.005
308.15	-0.9321	-0.1102	-0.0083	0.005
318.15	-1.0243	-0.1206	-0.0019	0.005

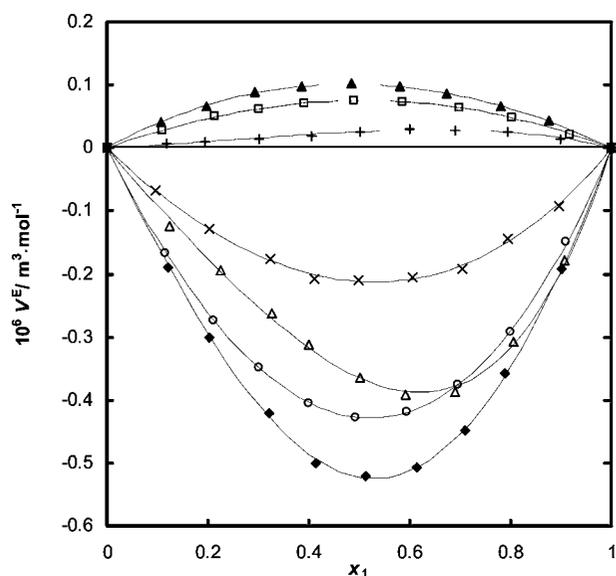
Similarly to the cyclohexanone + chloroalkane systems,<sup>1</sup> the interactional factor seems to be predominant for the systems with negative excess molar volumes, while for the systems with small positive  $V^E$  values, the structural effects prevail.

The general tendency of the present investigated systems is to have a smaller deviation from ideality comparative with the corresponding systems with cyclohexanone, except for the system with 1,1,2,2-tetrachloroethane, for which the  $V^E$  values are practically the same for both cyclohexanone and cyclopentanone mixtures, within its experimental uncertainties.

The carbonyl group of cyclohexanone is more basic than the carbonyl group of cyclopentanone.<sup>18</sup> Therefore, the (CH<sub>2</sub>)<sub>4</sub>



**Figure 1.** Excess molar volumes,  $V^E$ , for the chloroalkanes (1) + cyclopentanone (2) mixtures at 288.15 K:  $\blacklozenge$ , 1,1,2,2-tetrachloroethane;  $\circ$ , 1,1,1-trichloroethane;  $+$ , 1,2-dichloroethane;  $\blacktriangle$ , 1,3-dichloropropane;  $\square$ , 1,4-dichlorobutane;  $\times$ , 1-chlorobutane;  $\triangle$ , trichloromethane; solid line, Redlich–Kister correlation.

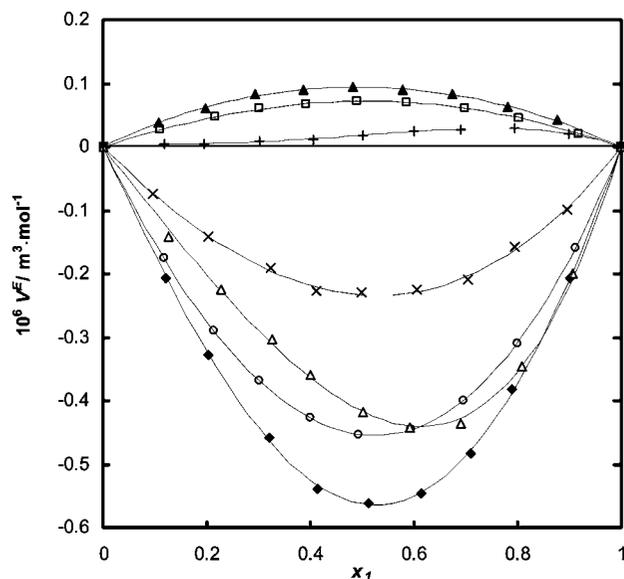


**Figure 2.** Excess molar volumes,  $V^E$ , for the chloroalkanes (1) + cyclopentanone (2) mixtures at 298.15 K:  $\blacklozenge$ , 1,1,2,2-tetrachloroethane;  $\circ$ , 1,1,1-trichloroethane;  $+$ , 1,2-dichloroethane;  $\blacktriangle$ , 1,3-dichloropropane;  $\square$ , 1,4-dichlorobutane;  $\times$ , 1-chlorobutane;  $\triangle$ , trichloromethane; solid line, Redlich–Kister correlation.

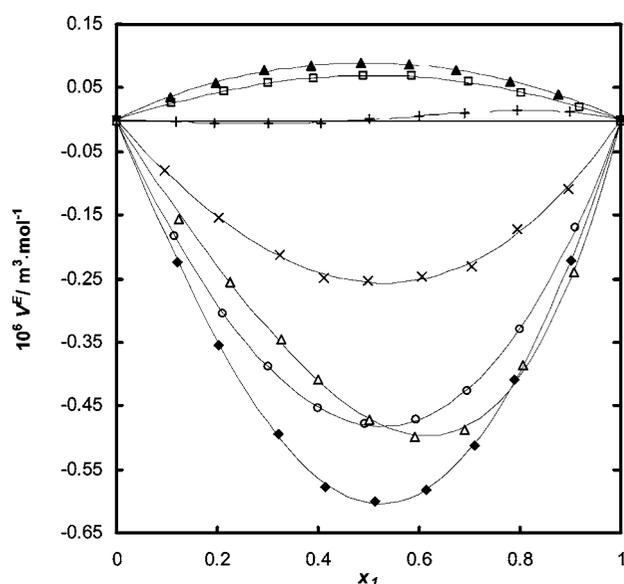
groups contribute with more electrons to the C=O group in cyclohexanone than they do in cyclopentanone, so the formation of hydrogen bonds is enhanced in the first case. This explains the variation of excess molar volumes with composition for the investigated systems containing 1,1,1-trichloroethane, trichloromethane, and 1-chlorobutane: they are more negative for the cyclohexanone case.

The calorimetric measurements also indicate the more pronounced basicity of cyclohexanone than cyclopentanone; in literature we have found, for example, that the excess equimolar enthalpy value for chloroform with cyclohexanone is more negative than for the corresponding system with cyclopentanone.<sup>19</sup>

In the case of cyclopentanone + 1,2-dichloroethane, 1,3-dichloropropane, and 1,4-dichlorobutane systems, the  $V^E$  values



**Figure 3.** Excess molar volumes,  $V^E$ , for the chloroalkanes (1) + cyclopentanone (2) mixtures at 308.15 K:  $\blacklozenge$ , 1,1,2,2-tetrachloroethane;  $\circ$ , 1,1,1-trichloroethane;  $+$ , 1,2-dichloroethane;  $\blacktriangle$ , 1,3-dichloropropane;  $\square$ , 1,4-dichlorobutane;  $\times$ , 1-chlorobutane;  $\triangle$ , trichloromethane; solid line, Redlich–Kister correlation.



**Figure 4.** Excess molar volumes,  $V^E$ , for the chloroalkanes (1) + cyclopentanone (2) mixtures at 318.15 K:  $\blacklozenge$ , 1,1,2,2-tetrachloroethane;  $\circ$ , 1,1,1-trichloroethane;  $+$ , 1,2-dichloroethane;  $\blacktriangle$ , 1,3-dichloropropane;  $\square$ , 1,4-dichlorobutane;  $\times$ , 1-chlorobutane;  $\triangle$ , trichloromethane; solid line, Redlich–Kister correlation.

are less positive than for the corresponding systems with cyclohexanone. For these mixtures, this can be explained by the steric effects which seem to become more important than the very weak H-bond interaction effects: the cyclopentanone molecules are smaller than those of cyclohexanone, which means that its mixtures with  $\alpha,\omega$ -dichloroalkanes are more dense than corresponding cyclohexanone mixtures (free volumes are smaller). In the homologous series of  $\alpha,\omega$ -dichloroalkanes, because of the size of chloroalkane molecules, the compacting is stronger for 1,2-dichloroethane than for 1,3-dichloropropane and 1,4-dichlorobutane, and this is visible in variation of  $V^E$ , too.

Comparing the  $V^E$  values for cyclopentanone and cyclohexanone + 1,1,2,2-tetrachloroethane systems, we can say that the better packing compensates the weaker H-bond interaction effects for the cyclopentanone system, since similar values of  $V^E$  are obtained.

The isothermal excess equimolar volume of the studied binary mixtures of cyclopentanone with chloroalkanes follow the general order: 1,4-dichlorobutane  $\approx$  1,3-dichloropropane > 1,2-dichloroethane > 1-chlorobutane > trichloromethane > 1,1,1-trichloroethane > 1,1,2,2-tetrachloroethane, with both positive and negative observed values, similarly to cyclohexanone + chloroalkane systems.<sup>1</sup>

The  $V^E$  values obtained for cyclopentanone + 1,1,2,2-tetrachloroethane, + 1,2-dichloroethane, + 1,3-dichloropropane, and + 1,4-dichlorobutane at 298.15 K are more positive than those reported previously for 3-pentanone with the same chloroalkanes,<sup>3</sup> and for 1,1,1-trichloroethane and trichloromethane they are more negative. We may conclude that the cyclization of the linear ketone decreases the H-bond interaction intensity and/or increases free volume except for the trichloroalkane mixtures where interactions and/or in-bulk accommodation seem to become stronger. This was observed in literature for similar systems.<sup>20</sup> Besides, our excess volume interpolated data at 303.15 K for the 1,2-dichloroethane + cyclopentanone system agree well with those previously reported in literature,<sup>21</sup> with deviation of  $0.7 \cdot 10^{-8} \text{ m}^3 \cdot \text{mol}^{-1}$ .

The  $V^E$  values become more negative for all of the present studied systems as the temperature increases from (288.15 to 318.15) K. Such behavior could be explained by the bulkier effect of cyclopentanone, which became more dominant and increased with temperature, as it was observed previously for cyclohexanone + chloroalkane<sup>1</sup> and for other systems refereed in literature.<sup>22</sup>

## Conclusion

The densities of the binary cyclopentanone with 1,1,2,2-tetrachloroethane, 1,1,1-trichloroethane, trichloromethane, 1,2-dichloroethane, 1,3-dichloropropane, 1,4-dichlorobutane, and 1-chlorobutane systems have been measured as a function of composition at temperatures between (288.15 and 318.15) K and atmospheric pressure. The excess molar volumes obtained from densities are negative for the cyclopentanone + 1,1,2,2-tetrachloroethane, 1,1,1-trichloroethane, trichloromethane, and 1-chlorobutane systems and positive for the cyclopentanone + 1,2-dichloroethane, 1,3-dichloropropane, and 1,4-dichlorobutane systems and become more negative as the temperature increases from (288.15 to 318.15) K.

The general tendency of the investigated systems is to have smaller deviations from ideality compared with the corresponding systems with cyclohexanone. For the studied mixtures of cyclic ketones (cyclopentanone, cyclohexanone) with chloroalkanes, the excess molar volumes have been explained in terms of some physicochemical and structural effects (basicity, free volume, and in-bulk accommodation).

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