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Densities and Excess Molar Volumes of the Binary Mixtures of Cyclohexanone with Chloroalkanes at Temperatures between (288.15 and 318.15) K

Oana Ciocirlan,^{*,†} Mariana Teodorescu,[‡] Dana Dragoescu,[‡] Olga Iulian,[†] and Alexandru Barhala[‡]

Department of Applied Physical Chemistry and Electrochemistry, Politehnica University of Bucharest, 1-7 Gh. Polizu Street, 011061 Bucharest, Romania, and Ilie Murgulescu Institute of Physical Chemistry, Splaiul Independentei 202, 060021 Bucharest, Romania

The experimental densities of binary mixtures 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 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 Redlich–Kister polynomial equation. The excess molar volumes are negative for the cyclohexanone + 1,1,2,2-tetrachloroethane, 1,1,1-trichloroethane, trichloromethane, and 1-chlorobutane systems and positive for the other three systems, over the whole composition range and at all investigated temperatures. The variation of these properties with the composition of the binary mixtures is discussed in terms of molecular interactions between components and structural effects.

Introduction

The physicochemical properties of liquid mixtures have attracted much attention from the point of view of both theoretical and engineering applications. Many engineering applications require quantitative data on the density of liquid mixtures. They also provide information about the nature and molecular interactions between liquid mixture components.

Cyclohexanone is a versatile solvent, having a globular molecule and being used in the synthesis of pharmaceuticals, in agricultural chemistry, and as a solvent for polymers. Mono- and polychloroalkanes represent a class of technically important compounds, used in industry as intermediates or as final products. Both cyclohexanone and chloroalkanes are polar and practically unassociated liquids. These compounds are also interesting from a theoretical aspect because of the inter- and intramolecular effects. A fundamental understanding of the mixture behavior of cyclohexanone with chloroalkanes is therefore important from the technical and engineering standpoint.

The present work is a continuation of the studies devoted to the physicochemical properties of various nonelectrolyte systems.^{1–3} Concerning the volumetric behavior of ketones with chloroalkanes mixtures, so far we have studied systems of linear ketones (propan-2-one, pentan-3-one) with several chloroalkanes,^{1,3} and here we report density data for mixtures of a cyclic ketone with mono-, di-, tri-, and tetrachloroalkanes at temperatures between (288.15 and 318.15) K and atmospheric pressure. The values of the excess molar volumes of the studied systems are reported with the aim to discuss the results in terms of structural effects and molecular interactions between components.

A survey of the literature indicates that volumetric properties of binary mixtures of cyclohexanone + 1,1,1-trichloroethane, trichloromethane, and 1,2-dichloroethane have been studied by other authors^{4–10} at (298.15, 303.15, and 308.15) K. For the

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

component	$10^{-3} \rho/\text{kg} \cdot \text{m}^{-3}$			
	$T = 298.15 \text{ K}$		$T = 308.15 \text{ K}$	
	exptl	lit.	exptl	lit.
cyclohexanone	0.94276	0.94251 ⁸ 0.9424 ¹¹ 0.94207 ¹²	0.93380	
1,1,2,2-tetrachloroethane	1.58918	1.58655 ¹² 1.588539 ¹³ 1.5876 ¹⁴	1.57357	1.572901 ¹³
1,1,1-trichloroethane	1.32827	1.32929 ⁸ 1.3314 ¹⁵ 1.32955 ¹⁶ 1.3287 ¹⁷	1.31145	
trichloromethane	1.47316	1.47988 ¹² 1.472435 ¹³ 1.4717 ¹⁸ 1.47156 ¹⁹	1.45407	1.460025 ²⁰
1,2-dichloroethane	1.24548	1.24561 ³ 1.2458 ¹² 1.245290 ¹³ 1.2455 ²¹	1.23083	1.230566 ¹³ 1.2309 ²¹
1,3-dichloropropane	1.17958	1.1818 ¹⁵ 1.17922 ²² 1.17908 ²³	1.16716	
1,4-dichlorobutane	1.13257	1.13402 ³ 1.1353 ¹⁵ 1.1337 ²¹ 1.1328 ²⁴	1.12161	1.1224 ²¹
1-chlorobutane	0.88105	0.8809 ^{12,24} 0.8810 ¹⁸ 0.88079 ²⁵	0.86986	0.86962 ²⁵

other four systems presented here, the density data are not available in literature.

Experimental Section

Materials. All of the substances used were commercial products from Aldrich of the first grade purity. The purity of substances, checked by gas chromatography, was not less than 99.8 % in mole fraction. The liquids were dried and stored over

* Corresponding author: E-mail: ciocirlan_o@yahoo.com. Tel.: +40214023855.

[†] Politehnica University of Bucharest.

[‡] Ilie Murgulescu Institute of Physical Chemistry.

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

x_1	$T = 288.15 \text{ K}$		$T = 298.15 \text{ K}$		$T = 308.15 \text{ K}$		$T = 318.15 \text{ K}$	
	$10^{-3} \rho$	$10^6 V^E$	$10^{-3} \rho$	$10^6 V^E$	$10^{-3} \rho$	$10^6 V^E$	$10^{-3} \rho$	$10^6 V^E$
	$\text{kg} \cdot \text{m}^{-3}$	$\text{m}^3 \cdot \text{mol}^{-1}$	$\text{kg} \cdot \text{m}^{-3}$	$\text{m}^3 \cdot \text{mol}^{-1}$	$\text{kg} \cdot \text{m}^{-3}$	$\text{m}^3 \cdot \text{mol}^{-1}$	$\text{kg} \cdot \text{m}^{-3}$	$\text{m}^3 \cdot \text{mol}^{-1}$
1,1,2,2-Tetrachloroethane (1) + Cyclohexanone (2)								
0.0000	0.95169	0.000	0.94276	0.000	0.93380	0.000	0.92482	0.000
0.1147	1.02934	-0.181	1.01979	-0.198	1.01020	-0.214	1.00058	-0.230
0.2121	1.09487	-0.295	1.08477	-0.322	1.07462	-0.348	1.06444	-0.374
0.3045	1.15678	-0.383	1.14613	-0.416	1.13543	-0.448	1.12470	-0.481
0.4052	1.22380	-0.447	1.21252	-0.482	1.20120	-0.519	1.18984	-0.555
0.4996	1.28607	-0.469	1.27418	-0.505	1.26226	-0.543	1.25030	-0.581
0.5909	1.34580	-0.463	1.33331	-0.499	1.32077	-0.534	1.30820	-0.570
0.6868	1.40773	-0.410	1.39458	-0.442	1.38138	-0.474	1.36814	-0.505
0.7820	1.46850	-0.323	1.45464	-0.347	1.44076	-0.373	1.42683	-0.398
0.8798	1.53011	-0.197	1.51552	-0.213	1.50089	-0.229	1.48623	-0.245
1.0000	1.60475	0.000	1.58918	0.000	1.57357	0.000	1.55794	0.000
1,1,1-Trichloroethane (1) + Cyclohexanone (2)								
0.0000	0.95169	0.000	0.94276	0.000	0.93380	0.000	0.92482	0.000
0.1151	0.99674	-0.137	0.98713	-0.146	0.97749	-0.157	0.96781	-0.168
0.2288	1.04175	-0.271	1.03143	-0.289	1.02106	-0.308	1.01065	-0.329
0.3155	1.07619	-0.352	1.06528	-0.374	1.05433	-0.398	1.04333	-0.425
0.4163	1.11630	-0.419	1.10468	-0.445	1.09301	-0.474	1.08128	-0.505
0.5167	1.15617	-0.447	1.14381	-0.475	1.13139	-0.507	1.11890	-0.542
0.6059	1.19152	-0.442	1.17845	-0.470	1.16533	-0.502	1.15212	-0.537
0.7081	1.23185	-0.398	1.21794	-0.424	1.20395	-0.453	1.18986	-0.485
0.8062	1.27030	-0.314	1.25552	-0.334	1.24064	-0.357	1.22564	-0.382
0.8979	1.30581	-0.186	1.29016	-0.198	1.27441	-0.214	1.25851	-0.229
1.0000	1.34495	0.000	1.32827	0.000	1.31145	0.000	1.29447	0.000
Trichloromethane (1) + Cyclohexanone (2)								
0.0000	0.95169	0.000	0.94276	0.000	0.93380	0.000	0.92482	0.000
0.1198	1.00415	-0.086	0.99458	-0.103	0.98497	-0.122	0.97532	-0.141
0.2362	1.05819	-0.182	1.04793	-0.213	1.03761	-0.249	1.02725	-0.287
0.3050	1.09164	-0.241	1.08094	-0.281	1.07016	-0.325	1.05932	-0.372
0.4235	1.15188	-0.331	1.14029	-0.379	1.12862	-0.434	1.11688	-0.493
0.5103	1.19822	-0.384	1.18589	-0.435	1.17348	-0.495	1.16097	-0.559
0.6047	1.25045	-0.399	1.23716	-0.446	1.22378	-0.503	1.21028	-0.564
0.6953	1.30306	-0.412	1.28880	-0.457	1.27442	-0.513	1.25990	-0.573
0.8109	1.37210	-0.312	1.35630	-0.341	1.34036	-0.381	1.32423	-0.423
0.9089	1.43335	-0.188	1.41612	-0.204	1.39868	-0.227	1.38101	-0.252
1.0000	1.49186	0.000	1.47316	0.000	1.45407	0.000	1.43472	0.000
1,2-Dichloroethane (1) + Cyclohexanone (2)								
0.0000	0.95169	0.000	0.94276	0.000	0.93380	0.000	0.92482	0.000
0.1142	0.97881	0.046	0.96950	0.039	0.96016	0.032	0.95078	0.026
0.2318	1.00861	0.067	0.99888	0.054	0.98910	0.040	0.97928	0.027
0.3197	1.03210	0.078	1.02200	0.063	1.01186	0.046	1.00167	0.029
0.4227	1.06102	0.091	1.05047	0.072	1.03986	0.053	1.02919	0.032
0.5190	1.08950	0.105	1.07846	0.085	1.06736	0.065	1.05619	0.043
0.6155	1.11970	0.107	1.10812	0.089	1.09648	0.067	1.08475	0.046
0.7061	1.14967	0.103	1.13752	0.086	1.12530	0.067	1.11298	0.048
0.8134	1.18743	0.084	1.17453	0.071	1.16153	0.056	1.14842	0.042
0.9145	1.22550	0.052	1.21176	0.046	1.19792	0.039	1.18396	0.030
1.0000	1.26001	0.000	1.24548	0.000	1.23083	0.000	1.21604	0.000
1,3-Dichloropropane (1) + Cyclohexanone (2)								
0.0000	0.95169	0.000	0.94276	0.000	0.93380	0.000	0.92482	0.000
0.1276	0.97976	0.042	0.97050	0.037	0.96122	0.031	0.95190	0.026
0.2270	1.00199	0.077	0.99246	0.070	0.98290	0.061	0.97330	0.053
0.3268	1.02479	0.100	1.01495	0.093	1.00509	0.083	0.99519	0.073
0.4189	1.04627	0.111	1.03615	0.102	1.02599	0.092	1.01578	0.082
0.5140	1.06886	0.116	1.05841	0.108	1.04794	0.097	1.03741	0.087
0.6112	1.09238	0.116	1.08163	0.105	1.07082	0.094	1.05994	0.085
0.7147	1.11803	0.101	1.10686	0.094	1.09564	0.087	1.08436	0.080
0.8103	1.14226	0.076	1.13071	0.072	1.11911	0.066	1.10745	0.061
0.8979	1.16489	0.049	1.15299	0.045	1.14103	0.042	1.12899	0.039
1.0000	1.19193	0.000	1.17958	0.000	1.16716	0.000	1.15467	0.000
1,4-Dichlorobutane (1) + Cyclohexanone (2)								
0.0000	0.95169	0.000	0.94276	0.000	0.93380	0.000	0.92482	0.000
0.1063	0.97311	0.038	0.96400	0.035	0.95486	0.030	0.94569	0.027
0.1969	0.99109	0.070	0.98182	0.064	0.97251	0.058	0.96317	0.053
0.2901	1.00939	0.096	0.99994	0.089	0.99046	0.081	0.98095	0.074
0.3808	1.02704	0.111	1.01742	0.103	1.00776	0.095	0.99807	0.087
0.4803	1.04624	0.115	1.03641	0.108	1.02655	0.101	1.01666	0.093
0.5814	1.06555	0.110	1.05552	0.104	1.04546	0.096	1.03537	0.088
0.6763	1.08346	0.102	1.07323	0.097	1.06297	0.090	1.05268	0.084
0.7751	1.10196	0.082	1.09152	0.078	1.08105	0.073	1.07054	0.069
0.8849	1.12233	0.048	1.11166	0.046	1.10096	0.043	1.09021	0.040
1.0000	1.14349	0.000	1.13257	0.000	1.12161	0.000	1.11061	0.000
1-Chlorobutane (1) + Cyclohexanone (2)								
0.0000	0.95169	0.000	0.94276	0.000	0.93380	0.000	0.92482	0.000
0.1152	0.94558	-0.086	0.93647	-0.098	0.92734	-0.112	0.91817	-0.127
0.2084	0.94043	-0.134	0.93118	-0.154	0.92188	-0.176	0.91254	-0.200
0.3068	0.93495	-0.179	0.92551	-0.203	0.91603	-0.232	0.90650	-0.264
0.4067	0.92927	-0.212	0.91965	-0.241	0.90997	-0.275	0.90022	-0.311
0.5041	0.92360	-0.229	0.91378	-0.260	0.90389	-0.295	0.89392	-0.333
0.5841	0.91886	-0.233	0.90886	-0.263	0.89878	-0.297	0.88863	-0.336
0.6920	0.91228	-0.216	0.90202	-0.242	0.89168	-0.273	0.88125	-0.308
0.7881	0.90618	-0.173	0.89571	-0.196	0.88512	-0.221	0.87442	-0.249
0.8820	0.90011	-0.117	0.88937	-0.129	0.87854	-0.147	0.86757	-0.166
1.0000	0.89210	0.000	0.88105	0.000	0.86986	0.000	0.85852	0.000

4A molecular sieves and were 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 $0.1 \cdot 10^{-6}$ kg. The experimental uncertainty in mole fractions was estimated to be less than ± 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 $\pm 0.05 \text{ kg} \cdot \text{m}^{-3}$, 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 ± 0.01 K. The uncertainty in the density determination is $\pm 0.05 \text{ kg} \cdot \text{m}^{-3}$ and for the V^E calculation is less than $\pm 10^{-8} \text{ m}^3 \cdot \text{mol}^{-1}$.

Results and Discussion

The measured densities, ρ , for the binary mixtures of cyclohexanone with chloroalkanes at $T = (288.15, 298.15, 308.15, \text{ and } 318.15) \text{ K}$ 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 ρ_1 and ρ_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:

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

where $p = 2$ is the degree of polynomial expansion. 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, σ , 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.

It can be observed from the experimental results in Table 2 and Figures 1, 2, 3, and 4 that the excess molar volume values are negative for the cyclohexanone + 1,1,2,2-tetrachloroethane, 1,1,1-trichloroethane, trichloromethane, and 1-chlorobutane systems and positive for the cyclohexanone + 1,2-dichloroethane, 1,3-dichloropropane, and 1,4-dichlorobutane systems over the whole composition range at $T = (288.15, 298.15, 308.15, \text{ and } 318.15) \text{ K}$. Except for the cyclohexanone + 1,1,2,2-tetrachloroethane system, the excess volume curves for the other six systems are slightly asymmetric about $x = 0.5$.

It seems that intermolecular interactions are the predominant factors in deciding the sign of V^E for the mixtures of cyclohexanone with the studied tetra- and trichloroalkanes. The most negative values of V^E for cyclohexanone + 1,1,2,2-tetrachloroethane, + 1,1,1-trichloroethane, or + trichloromethane systems show that strong intermolecular complexes are formed between components, probably favored by an increased number of

Table 3. Coefficients A_k of the Fitting Equation (2) and Standard Deviations σ

T K	$10^6 A_0$ $\text{m}^3 \cdot \text{mol}^{-1}$	$10^6 A_1$ $\text{m}^3 \cdot \text{mol}^{-1}$	$10^6 A_2$ $\text{m}^3 \cdot \text{mol}^{-1}$	$10^6 \sigma$ $\text{m}^3 \cdot \text{mol}^{-1}$
1,1,2,2-Tetrachloroethane + Cyclohexanone				
288.15	-1.8821	0.1058	0.1272	0.003
298.15	-2.0279	0.1058	0.1100	0.003
308.15	-2.1773	0.0898	0.0965	0.003
318.15	-2.3270	0.0832	0.0895	0.003
1,1,1-Trichloroethane + Cyclohexanone				
288.15	-1.7860	0.4085	0.1322	0.003
298.15	-1.8963	0.4343	0.1208	0.003
308.15	-2.0216	0.4683	0.1084	0.003
318.15	-2.1588	-0.5062	0.1069	0.003
Trichloromethane + Cyclohexanone				
288.15	-1.5070	0.9382	0.0013	0.007
298.15	-1.7090	0.9587	0.0521	0.008
308.15	-1.9436	-1.0225	0.0673	0.009
318.15	-2.1957	-1.0893	0.0907	0.010
1,2-Dichloroethane + Cyclohexanone				
288.15	0.4005	0.1469	0.2041	0.003
298.15	0.3229	0.1333	0.2063	0.003
308.15	0.2388	0.1165	0.2086	0.003
318.15	0.1518	0.0973	0.2142	0.003
1,3-Dichloropropane + Cyclohexanone				
288.15	0.4698	0.0663	-0.0225	0.002
298.15	0.4331	0.0714	-0.0213	0.002
308.15	0.3901	0.0815	-0.0264	0.002
318.15	0.3516	0.0908	-0.0272	0.002
1,4-Dichlorobutane + Cyclohexanone				
288.15	0.4641	0.0141	0.0243	0.002
298.15	0.4361	0.0275	0.0304	0.002
308.15	0.4059	0.0275	0.0304	0.002
318.15	0.3736	0.0413	0.0327	0.002
1-Chlorobutane + Cyclohexanone				
288.15	-0.9137	0.2019	0.0849	0.002
298.15	-1.0370	0.2123	0.0819	0.002
308.15	-1.1753	0.2263	0.0994	0.002
318.15	-1.3308	0.2478	-0.1082	0.002

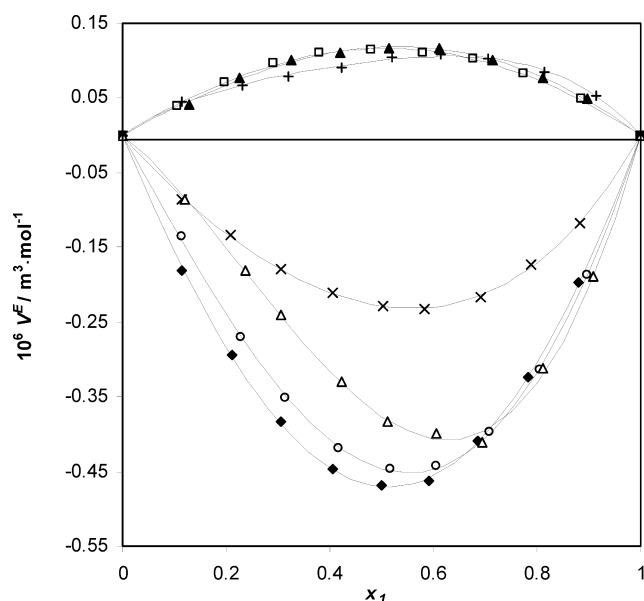


Figure 1. Excess molar volumes, V^E , for the chloroalkanes (1) + cyclohexanone (2) mixtures at 288.15 K: \blacklozenge , 1,1,2,2-tetrachloroethane; \circ , 1,1,1-trichloroethane; $+$, 1,2-dichloroethane; \blacktriangle , 1,3-dichloropropane; \square , 1,4-dichlorobutane; \times , 1-chlorobutane; \triangle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

chlorine atoms to one carbon atom in these chloroalkanes. The cyclohexanone + 1-chlorobutane system presents less negative values for V^E , comparative with the above-mentioned systems.

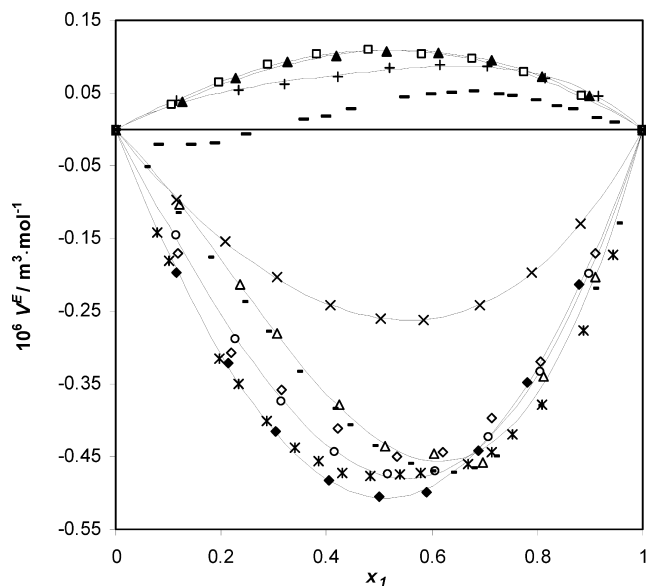


Figure 2. Excess molar volumes, V^E , for the chloroalkanes (1) + cyclohexanone (2) mixtures at 298.15 K: \blacklozenge , 1,1,2,2-tetrachloroethane; \circ , 1,1,1-trichloroethane; $+$, 1,2-dichloroethane; \blacktriangle , 1,3-dichloropropane; \square , 1,4-dichlorobutane; \times , 1-chlorobutane; \triangle , trichloromethane; solid line, Redlich-Kister correlation; $*$, 1,1,1-trichloroethane (ref 6); short dashed line, trichloromethane (ref 6); long dashed line, 1,2-dichloroethane (ref 6); \diamond , 1,1,1-trichloroethane (ref 8).

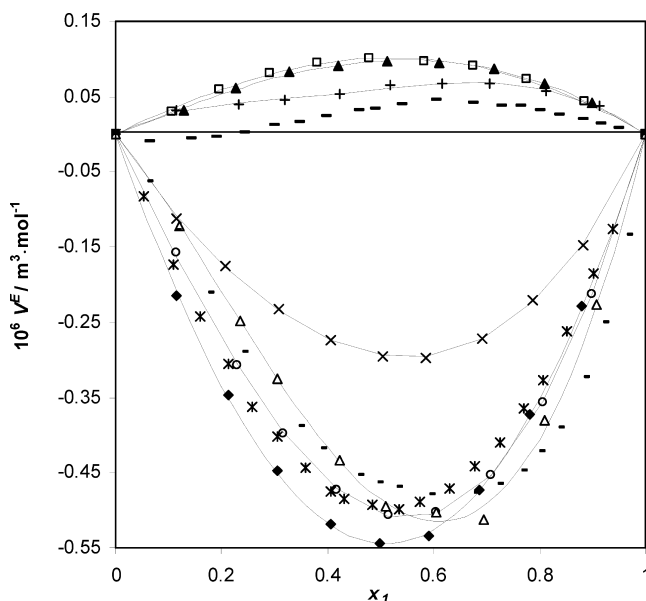


Figure 3. Excess molar volumes, V^E , for the chloroalkanes (1) + cyclohexanone (2) mixtures at 308.15 K: \blacklozenge , 1,1,2,2-tetrachloroethane; \circ , 1,1,1-trichloroethane; $+$, 1,2-dichloroethane; \blacktriangle , 1,3-dichloropropane; \square , 1,4-dichlorobutane; \times , 1-chlorobutane; \triangle , trichloromethane; solid line, Redlich-Kister correlation; $*$, 1,1,1-trichloroethane (ref 5); short dashed line, trichloromethane (ref 5); long dashed line, 1,2-dichloroethane (ref 5).

Surprisingly, the values of V^E for the systems of cyclohexanone with 1,2-dichloroethane, 1,3-dichloropropane, and 1,4-dichlorobutane are small, positive, and nearly identical. For such systems of cyclohexanone with α,ω -dichloroalkanes, the positive values of V^E suggest the presence of weak interaction between the component molecules and the unfavorable packing of unlike molecules into each other's structure because of almost equal molar volumes: cyclohexanone ($10.4 \cdot 10^{-5} \text{ m}^3 \cdot \text{mol}^{-1}$), 1,2-dichloroethane ($7.9 \cdot 10^{-5} \text{ m}^3 \cdot \text{mol}^{-1}$), 1,3-dichloropropane ($9.5 \cdot 10^{-5} \text{ m}^3 \cdot \text{mol}^{-1}$), and 1,4-dichlorobutane ($11.2 \cdot 10^{-5} \text{ m}^3 \cdot \text{mol}^{-1}$).

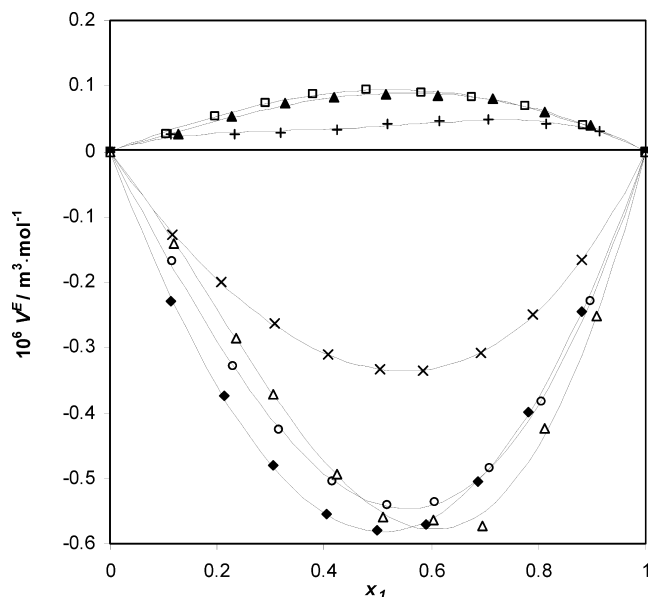


Figure 4. Excess molar volumes, V^E , for the chloroalkanes (1) + cyclohexanone (2) mixtures at 318.15 K: \blacklozenge , 1,1,2,2-tetrachloroethane; \circ , 1,1,1-trichloroethane; $+$, 1,2-dichloroethane; \blacktriangle , 1,3-dichloropropane; \square , 1,4-dichlorobutane; \times , 1-chlorobutane; \triangle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

$\text{m}^3 \cdot \text{mol}^{-1}$) at 298.15 K. Besides, a possible explanation of the positive values of V^E could be the breaking of dipole-dipole interactions between the α,ω -dichloroalkanes molecules from the pure state.

The excess molar volumes of the studied binary mixtures of cyclohexanone with chloroalkanes follow the general order: 1,4-dichlorobutane \cong 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.

For a better illustration of the system's nonideality and a better evaluation of the uncertainty in the data at high and low mole fractions,²⁶ we also plot the quantity $V^E/x_1(1-x_1)$ versus x_1 at, for example, 298.15 K in Figure 5. In addition, this plot furnishes an approximation of the partial molar excess quantities at infinite dilution when no measurement has been made in the dilute regions. Crude extrapolations yield different values of $V^E/x_1(1-x_1)$ for cyclohexanone at infinite dilution, indicating that the behavior of the cyclohexanone in the solvent bulk is influenced by the shape and nature of the chlorocompound, being less significant in the series of α,ω -dichloroalkanes.

From the Figures 2 and 5 it is obvious that our V^E data compare well with literature data⁸ for the 1,1,1-trichloroethane system, when the same experimental method is used. Also, the comparison with other sources^{5,6} indicate satisfactory results at (298.15 and 308.15) K (Figures 2 and 3) for the trichloromethane and 1,1,1-trichloroethane systems, when the dilatometric method is involved. The differences between our and literature data^{5,6} for the 1,2-dichloroethane system could be due to the very small V^E values. Other literature data²⁷ for the trichloromethane system at 308.15 K do not compare well with neither our or above-mentioned data.⁵ They are more negative, with a deviation of about $0.13 \cdot 10^{-6} \text{ m}^3 \cdot \text{mol}^{-1}$ around equimolar composition.

The V^E values become more negative for all of the studied systems as the temperature of the systems increase from (288.15 to 318.15) K. Such behavior could be explained by the packing effect which became more dominant and increases with temperature, as it was observed for other systems in literature.²⁸

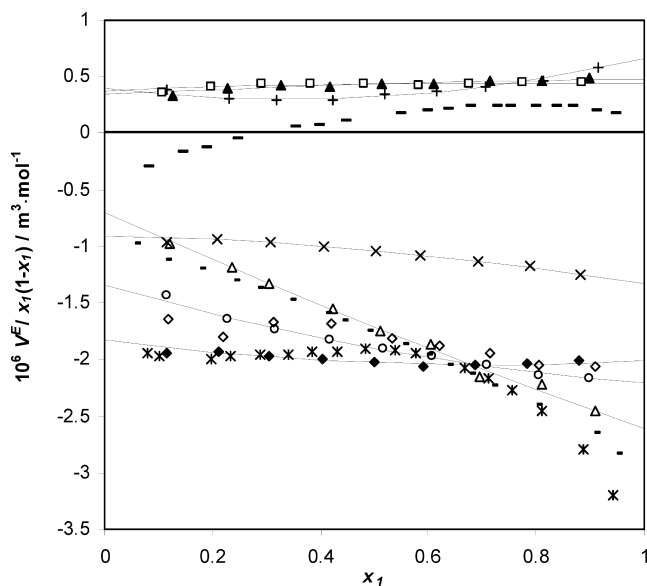


Figure 5. Plot of $V^E/x_1(1-x_1)$ at 298.15 K for chloroalkanes (1) + cyclohexanone (2) mixtures: \blacklozenge , 1,1,2,2-tetrachloroethane; \circ , 1,1,1-trichloroethane; $+$, 1,2-dichloroethane; \blacktriangle , 1,3-dichloropropane; \square , 1,4-dichlorobutane; \times , 1-chlorobutane; \triangle , trichloromethane; solid line, Redlich–Kister correlation; $*$, 1,1,1-trichloroethane (ref 6); short dashed line, trichloromethane (ref 6); long dashed line, 1,2-dichloroethane (ref 6); \diamond , 1,1,1-trichloroethane (ref 8).

Conclusion

The densities of the binary cyclohexanone 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 cyclohexanone + 1,1,2,2-tetrachloroethane, 1,1,1-trichloroethane, trichloromethane, and 1-chlorobutane systems and positive for the cyclohexanone + 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 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.

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