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Excess Molar Volume for Cyclohexanone ($C_6H_{10}O$) with Chloroalkanes at 303.15K

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ABSTRACT
Measurements on excess molar volume by using dilatometer have been made for mixtures of Cyclohexanone with 1-chlorobutane, acetylene tetrachloride, Chloroform and 1,3 dichloropropane at 303.15K and under atmospheric pressure in the liquid state. The obtained data have been fitted with the help of polynomial Redlich-Kister equation and discussed with the point view of molecular interactions in the liquid state. The values of V^E have been found to be negative in sign for the mixtures of Cyclohexanone with 1-chlorobutane, acetylene tetrachloride, and chloroform whereas it is positive in sign with 1,3-dichloropropane. The results obtained may be attributed to donor-acceptor interaction for all components in the liquid state.

Keywords: Excess Volume, Cyclohexanone, Interaction, H-bonding, Physicochemical Properties

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INTRODUCTION

From the viewpoint of thermodynamic and manufacturing applications, the physico-chemical properties of liquid mixtures are very important. Excess volume data are needed in these applications. The interactions between different molecules are obtained by using these excess properties.

Cyclohexanone used as solvent for polymers, intermediates in industrial applications and also in the synthesis of pharmaceuticals. $C_6H_{10}O$ and alkanes containing chloro groups are polar liquids and provide the effects between like and unlike molecules.

A literature survey disclosed that data on excess volumes of binary mixtures of $C_6H_{10}O$ + methylchloroform, chloroform, and ethylene dichloride have been studied (Nath J. et.al, 1998, 1999) at 298.15, 303.15, and 308.15K. But vast studies concerning interaction of cyclohexanone with chlorobutane have not been undertaken in the literature. Thus, in the current program we have undertaken determination of excess volumes for the mixtures of cyclohexanone with 1-chlorobutane, acetylene tetrachloride, chloroform and 1,3 dichloropropane at 303.15K

in the liquid state and the data obtained have been analyzed and discussed.

EXPERIMENTAL

1,3-dichloropropane (B.D.H.) and 1-chlorobutane (A.R. grade) used as such but activated by means of $4A^0$ molecular sieves before use**.**

For removing ethanol, chloroform ($CHCl_3$) was treated with distilled water, kept over anh. $CaCl_2$ and distillated fractionally. Acetylene tetrachloride of AR quality with mass fraction purity of 0.99 were washed with 10 % K_2CO_3 solution, dried over anh. $CaCl_2$ and then distilled. Purity of the chemicals were ascertained by checking the densities of chemicals, which were compared with the available literature data (Riddick and Bungar, 1970).

The experimental values of V^E were determined with reproducibility of ± $2X10^{-3}$ cm^3 mol^{-1}, using a two-armed dilatometer as given by Nath and Tripathi,1983. Weighed quantities of the two components were locked up above Hg in the nonappearance of air bubbles in the two arms of a dilatometer. The whole assembly was built up on a stand (made up of wood) and kept in water of thermostat at required temperature (adjusted to ±0.1 K). The two liquids were mixed by swinging the cell in backward and forward direction through a specific angle, and the height of Hg- levels in the capillary of instrument dilatometer were read by means of a cathetometer (reproducibility ±$1X10^{-3}$ cm).

RESULTS AND DISCUSSION

The experimental values obtained from dilatometric results for systems of Cyclohexanone with 1-chlorobutane,acetylene tetrachloride, and chloroform and 1,3-dichloropropane are listed in Table 1 and plotted in Fig. 1.

Redlich-Kister type polynomials (eq.1) are used for fitting all these data as under:

$$V^E/(cm^3.mol^{-1}) = x_1x_2\sum_{i=0}^{m} A_i\,(x_{1-}x_2)^i \qquad (1)$$

Where x_1 represents mole fraction of 1-chlorobutane or acetylene tetrachloride or chloroform or 1,3- dichloropropane and x_2 for cyclohexanone in the liquid state at desired temperature. The different coefficients, along with standard deviations, σ, are collected in Table 2. The values of standard deviation of the fit, σ, are obtained by means of eq. 2.

$$\sigma = \left[\frac{\Sigma\left(V^E - V^E_{calc}\right)^2}{(m^*-n^*)}\right]^{1/2} \qquad (2)$$

Where, V^E is experimental values and V^E_{calc} refers to calculated excess volume with the help of eq. (1), m* represents no. of data measured experimentally & n* is no. of constants which are distinctive of a binary system.

Table 1: Excess volumes for various mixtures at 303.15K

1-chlorobutane (1) + Cyclohexanone (2)		**Acetylene tetrachloride (1) + Cyclohexanone (2)**		**$CHCl_3$+ Cyclohexanone (2)**		**1,3-Dichloropropane (1) + Cyclohexanone (2)**	
x_1	V^E / (cm^3 mol^{-1})	x_1	V^E / (cm^3 mol^{-1})	x_1	V^E / (cm^3 mol^{-1})	x_1	V^E / (cm^3 mol^{-1})
0.1002	-0.113	0.1234	-0.226	0.0987	-0.087	0.0876	0.027
0.1765	-0.180	0.2176	-0.357	0.1333	-0.122	0.1566	0.046
0.2034	-0.200	0.3098	-0.448	0.2091	-0.203	0.2099	0.060
0.3553	-0.273	0.4234	-0.510	0.3212	-0.320	0.2675	0.074
0.4567	-0.287	0.4987	-0.519	0.3678	-0.365	0.3123	0.083
0.5198	-0.282	0.5543	-0.511	0.4211	-0.410	0.4054	0.097
0.6244	-0.253	0.6176	-0.484	0.5098	-0.466	0.4578	0.103
0.6789	-0.229	0.7234	-0.404	0.5567	-0.483	0.5089	0.105
0.7034	-0.216	0.8065	-0.310	0.6123	-0.491	0.5412	0.106
0.7687	-0.178	0.8555	-0.243	0.6956	-0.473	0.6001	0.104
0.8192	-0.143	0.9042	-0.168	0.7444	-0.443	0.6521	0.100
0.8798	-0.098	0.9331	-0.120	0.8022	-0.387	0.7001	0.094
0.9043	-0.079			0.8654	-0.298	0.7577	0.084
0.9332	-0.056			0.9064	-0.223	0.8034	0.073
						0.8672	0.054
						0.9012	0.042

Table 2: Least Squares Coefficients of Eq 1 for the Excess Molar Volumes, and the standard deviations, σ, of 1-Chlorobutane (1) + Cyclohexanone (2); acetylene tetrachloride (1) + Cyclohexanone (2); Chloroform (1) + Cyclohexanone (2) and, 1,3-dichloropropane (1) + Cyclohexanone (2) at the temperature 303.15 K.

System	**A_0**	**A_1**	**A_2**	**A_3**	**σ/(cm^3 mol^{-1})**
1-Chlorobutane (1)+ Cyclohexanone (2)	-1.138	0.2154	0.0852	-0.008	0.0002
Acetylene tetrachloride (1)+ Cyclohexanone (2)	-2.077	-0.006	0.097	0.0068	0.0003
Chloroform (1) + Cyclohexanone (2)	-1.844	-1.021	0.0661	-0.006	0.0003
1,3-dichloropropane (1)+ Cyclohexanone (2)	0.4196	0.0793	-0.0235	0.0104	0.003

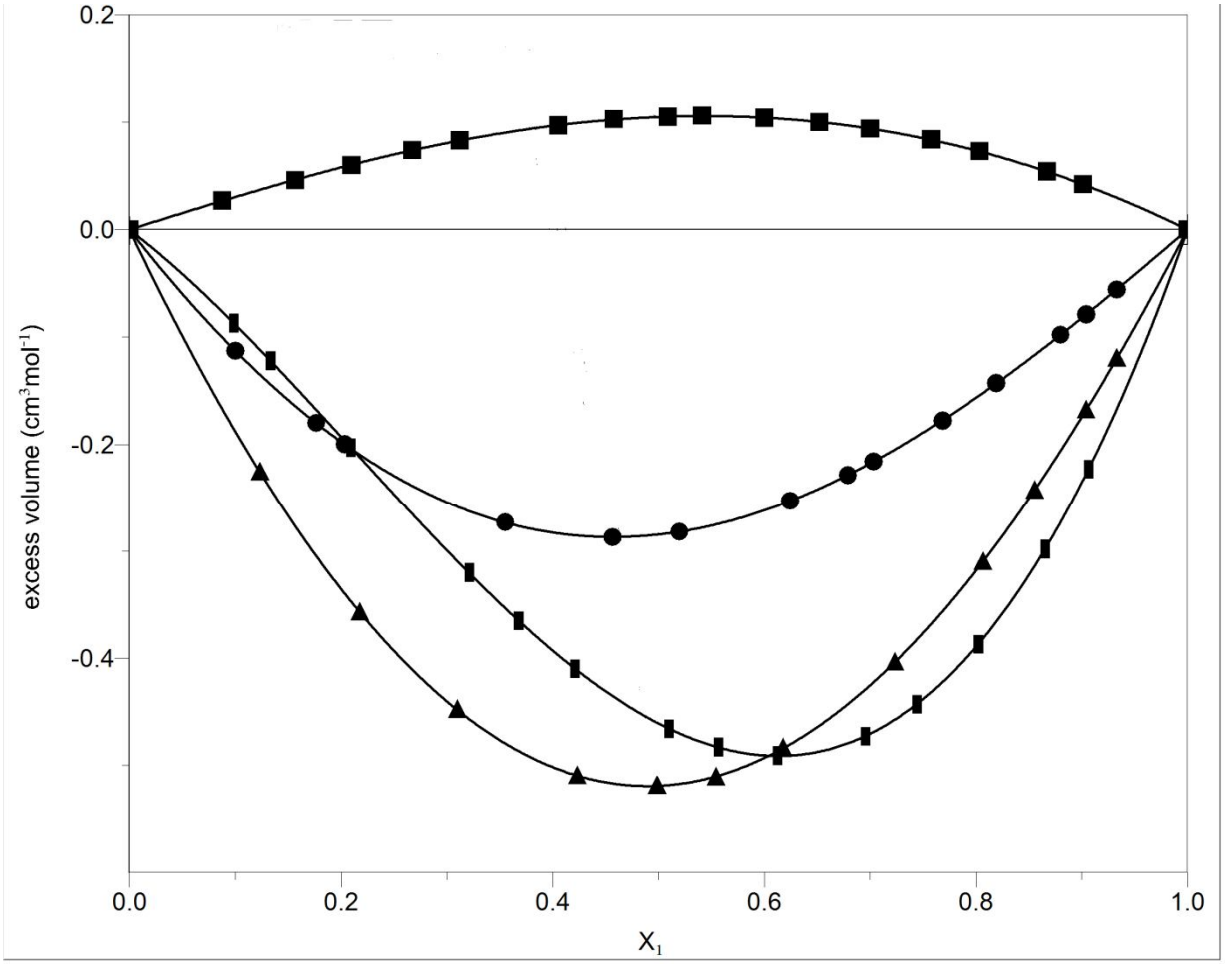

Figure 1: Excess volumes for various mixtures at 303.15K. 1-Chlorobutane (1)+Cyclohexanone (2)(●), acetylene tetrachloride (1) + Cyclohexanone (2) (▲), Chloroform + Cyclohexanone (2) (▮) and, 1,3-dichloropropane+ Cyclohexanone (2) **(■)**

The values of V^E decrease in the following sequence:

1,3-dichloropropane>1-Chlorobutane> Chloroform >Acetylene tetrachloride

Table 1 shows that the values of V^E are positive in sign for the system of cyclohexanone with 1, 3 -dichloropropane whereas it is negative for other systems. As the number of Cl atom increases, negativity in the values of V^E increases for those systems which show negative values of excess volume as indicated by our results. The more negativity indicates much more intermolecular interactions leading to the creation of H-bonding in the liquid state. The positive sign in V^E values might be due to the infringement of dipole-dipole interactions between the R, ω-dichloroalkanes molecules from the uncontaminated state.

The mixing of any above-mentioned chlorobutane of these compounds with cyclohexanone directs to three types of interactions: (1) Rupture of self-associated cyclohexanone molecules by other molecules. (2) Infringement of specific interactions of the second compound by cyclohexanone (3) Interactions, prevailing H-bond creation, between $C_6H_{10}O$ and the other compound.

The first two types of interactions are endothermic while the last is an exothermic reaction. The values obtained for excess volumes are the total effect of two positive and one negative.

Because excess molar volume is a packing effect between the C and D components of an (C +D) mixture, and because the values of excess molar volume of the cyclohexanone with 1-chlorobutane, acetylene tetrachloride, and Chloroform are negative throughout the entire composition range of cyclohexanone, this suggests that more compact packing of the molecules occur due to higher dipole-dipole chemical interaction between the two dissimilar molecules.

The complexation of cyclohexanone is attributed to the existence of isolated pair of electrons on O atom, which forms hydrogen bonding complex with interaction of hydrogen atom of 1-chlorobutane or acetylene tetrachloride or chloroform in the liquid state. There is also possibility of creation of charge transfer complex between lone pair of electrons present on O atom of cyclohexanone and Cl atom of alkane compounds in the present case. Cyclohexanone will act as n-donor and alkane compounds will perform as σ-acceptors toward cyclohexanone.

CONCLUSION

In the present study cyclohexanone performs as n-donor towards 1-chlorobutane, acetylene tetrachloride, chloroform and 1,3-dichloropropane, due to the existence of lone pair of electrons on the O atom. The latter compounds act as σ-acceptors. The value of excess volume obtained is the net effect of all types of effects observed during interaction of two types of components. The negative value of excess volume is an indication of creation of strong complex formation between the components. The specific interaction occurs between the components when the values of excess volume are negative in sign. Positive excess molar volume values are shown in the system where structural effects succeed.

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