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**VOLUMETRIC PROPERTIES OF THE BINARY LIQUID MIXTURES OF
CYCLOHEXANOL + 1,2-DICHLOROBENZENE, +1,3- DICHLOROBENZENE,
+ 1,2,4-TRICHLOROBENZENE AT DIFFERENT TEMPERATURES**

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Abstract

The densities of pure liquids cyclohexanol, 1,2-dichlorobenzene, 1,3-dichlorobenzene, 1,2,4-trichlorobenzene and binary liquid mixtures of cyclohexanol with 1,2-dichlorobenzene, 1,3-dichlorobenzene and 1,2,4-trichlorobenzene over the entire composition range were measured at four different temperatures (303.15K, 308.15 K, 313.15 K, 318.15 K). From this experimental data, the excess molar volume values were calculated over whole composition range. Excess molar volume values were found positive for all the mixtures at each temperature studied and the extent of positive deviation in excess molar volume values follows the order 1,2,4-Trichlorobenzene > 1,3-Dichlorobenzene > 1,2-Dichlorobenzene.

Keywords: Cyclohexanol, Binary organic liquid mixtures, Specific interactions, Excess molar volumes.

Introduction:

To the best of our knowledge, no excess molar volume data in the literature for the mixtures cyclohexanol with 1,2-dichlorobenzene, 1,3-dichlorobenzene, 1,2,4-trichlorobenzene at different temperatures are available. Therefore in this paper, we present the densities (ρ) of pure liquids cyclohexanol, 1,2-dichlorobenzene, 1,3-dichlorobenzene, 1,2,4-trichlorobenzene and Binary organic liquid mixtures cyclohexanol + 1,2-dichlorobenzene, cyclohexanol +1,3-dichlorobenzene, Cyclohexanol+ 1,2,4-trichlorobenzene at different temperatures (303.15 K, 308.15 K, 313.15 K, 318.15 K) covering the entire range of composition. The experimental values of densities (ρ) were used to calculate the excess molar volumes [2]. Recently many papers have appeared on thermodynamic properties of chlorine substituted benzenes with organic liquids [3-5]. The present investigated mixtures include cyclohexanol as a

common component and chlorine substituted benzenes as non-common components. The experimental results are analyzed in terms of hydrogen bonds, dipole-dipole interactions and size differences.

Experimental

All the organic liquids used in this work were supplied from S.D. Fine Chemicals Ltd., India, AR grade. The method of purification has been described in the literature [6-8]. The purity of all the four organic liquids is checked by comparing their experimental densities with their literature values [9]. These are reported in table-1.

Table-1: Densities at 303.15 K temperature of pure components and comparison with the literature value.

| Component | Density (ρ) | |
|------------------------|--------------------|--------------------|
| | Present work | Literature |
| Cyclohexanol | 0.948 | 0.962 ^a |
| 1,2-Dichlorobenzene | 1.29920 | 1.29922 |
| 1,3-Dichlorobenzene | 1.27708 | 1.27718 |
| 1,2,4-Trichlorobenzene | 1.44235 | 1.44215 |

^a at 298.15 K

Results and Discussion

All Binary organic liquid mixtures samples were prepared by mass using a digital electronic balance (ACCULAB-ALC-210.4) with the precision of ± 0.1 mg. To diminish the partial degassing, the samples were weighed and stored in air tight glass stopper bottles. The uncertainties in the molefractions was estimated to be less than $\pm 1 \times 10^{-4}$. The densities were measured for the liquid mixtures over the entire composition range by using Rudolph Research Analytical digital densimeter (DDH-2911 model), with precision $\pm 2 \times 10^{-5}$ g cm⁻³ at different temperatures (303.15K, 308.15 K, 313.15 K, 318.15 K) with accuracy of ± 0.03 K. Doubly distilled, deionized water and air were used to calibrate the density meter.

The excess molar volume values for the Binary organic liquid mixtures at different temperatures were calculated from the densities (ρ) of liquid mixtures, pure components (ρ_i), molar masses (m_i) and molefractions (x_i) by using the equation

$$V_m^E = \left[\frac{x_1 M_1 + x_2 M_2}{\rho} \right] - \left[\frac{x_1 M_1}{\rho_1} + \frac{x_2 M_2}{\rho_2} \right]$$

Where subscript 1 is cyclohexanol and 2 is second component in the liquid mixture. The results are summarized in

Table 2 and graphs are showed in figures 1, 2 and 3.

Table-2: The least squares parameters, standard deviation values and extreme values at different temperatures.

| T in K | A ₀ | A ₁ | A ₂ | σ | x | V _m ^E in c.c. mol ⁻¹ |
|----------------------------------------------|----------------|----------------|----------------|-------|--------|-------------------------------------------------------|
| Cyclohexanol + 1,2-Dichlorobenzene | | | | | | |
| 303.15 | 3.8937 | -1.4407 | 0.2004 | 0.003 | 0.4730 | 0.7757 |
| 308.15 | 3.8215 | -1.3843 | -0.0567 | 0.002 | 0.4111 | 0.9185 |
| 313.15 | 3.7324 | -1.3139 | -0.3058 | 0.002 | 0.4132 | 0.9480 |
| 318.15 | 3.6338 | -1.2687 | -0.3967 | 0.004 | 0.4036 | 0.9834 |
| Cyclohexanol + 1,3-Dichlorobenzene | | | | | | |
| 303.15 | 3.5205 | -0.161 | -0.3099 | 0.003 | 0.0895 | 0.7129 |
| 308.15 | 3.318 | -0.0399 | -0.2656 | 0.003 | 0.4778 | 0.7586 |
| 313.15 | 3.0518 | 0.0307 | -0.0147 | 0.002 | 0.4769 | 0.8204 |
| 318.15 | 2.8768 | -0.0504 | -0.1746 | 0.004 | 0.4752 | 0.8715 |
| Cyclohexanol + 1,2,4-Trichlorobenzene | | | | | | |
| 303.15 | 3.6403 | -1.086 | 0.1192 | 0.002 | 0.4154 | 0.8234 |
| 308.15 | 3.522 | -1.0929 | -0.0991 | 0.002 | 0.4133 | 0.8606 |
| 313.15 | 3.4124 | -1.0569 | -0.345 | 0.004 | 0.4111 | 0.8901 |
| 318.15 | 3.2434 | -1.0546 | -0.2819 | 0.002 | 0.4085 | 0.9303 |

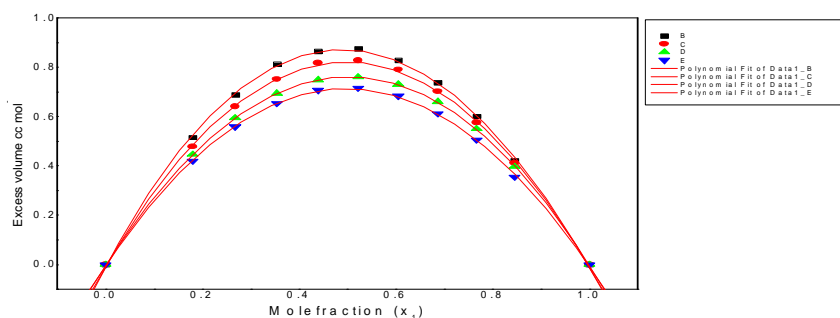


Fig.1: Molefraction of cyclohexanol versus Excess volumes of cyclohexanol + metadichlorobenzene at 303.15K (▼), 308.15K (▲), 313.15K (●) and 318.15K (■)

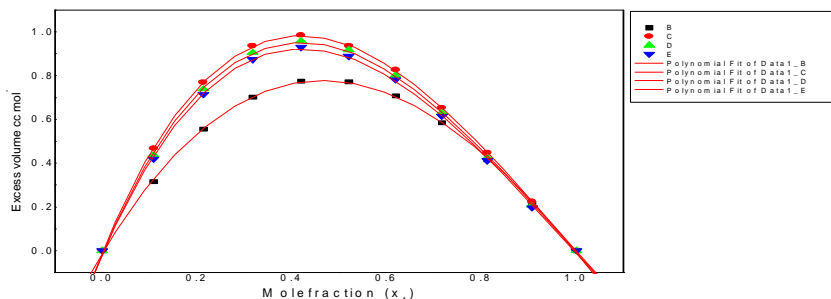


Fig.2: Molefraction of cyclohexanol versus Excess volumes of cyclohexanol + orthodichlorobenzene at 303.15K (▼), 308.15K (▲), 313.15K (●) and 318.15K (■)

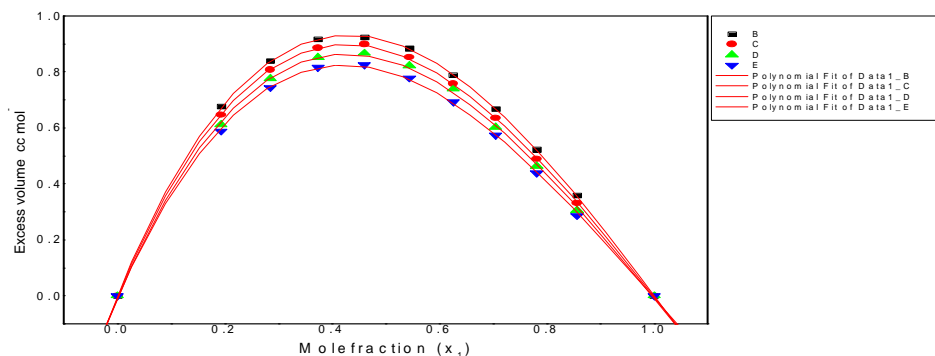


Fig.3: Molefraction of cyclohexanol versus Excess volumes of cyclohexanol + trichlorobenzene at 303.15K (▼), 308.15K (▲), 313.15K (●) and 318.15K (■)

The Redlich-Kister polynomial equation

$$V_m^E (\text{cm}^3 \text{mol}^{-1}) = x_1 (1 - x_1) \sum_{i \geq 0}^p [A_i (1 - 2x_2)^i] \quad \text{Was used to fit the excess molar volume data.}$$

In the Redlich-Kister polynomial equation, A_i is polynomial co-efficient, p is the polynomial degree. The standard deviation (σ) values for excess molar volume were calculated by using the equation.

$$\sigma (V_m^E) = \left[\frac{\sum_{i=1}^n (V_{cal}^E - V_{exp}^E)^2}{n - p} \right]^{1/2}$$

Where n is the number of experimental data points. The value of excess molar volume, values of parameters obtained by least squares method and the extreme values of excess molar volume are reported in table 2 along with standard deviation (σ) values.

Figures 1,2 & 3 show the variation of excess molar volume with the molefraction of cyclohexanol (x_1) over the entire composition range at 303.15K, 308.15 K, 313.15 K, 318.15 K. The excess molar volume versus molefraction of cyclohexanol (x_1) curves for the present investigated Binary organic liquid mixtures of cyclohexanol with 1,2-Dichlorobenzene, 1,3-Dichlorobenzene and 1,2,4-Trichlorobenzene reveal that all are positively deviated. This is probably due to the disruption of hydrogen bond in cyclohexanol and due to the formation of hydrogen bonds between chlorine atom of chlorine substituted benzenes and hydrogen atom of OH group of cyclohexanol. But the former is dominant than later. It means expansion factors are dominating the contraction factors and the excess molar volume values are 1,2,4-Trichlorobenzene > 1,3-Dichlorobenzene > 1,2-Dichlorobenzene and interactions are

less in the Binary organic liquid mixtures of cyclohexanol with 1,2,4-Trichlorobenzene when compared to dichlorobenzenes. It is because of sterichindrance, geometry and also size. Due to more sterichindrance in 1,2,4-Trichlorobenzene the specific molecular interactions are weak.

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