Molecular interactions in non-electrolyte binary liquid mixtures of cyclohexanol with 2-nitrotoluene and 3-nitrotoluene at four different temperatures

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ABSTRACT

The densities were measured over the entire molefraction range for the binary liquid mixtures of Cyclohexanol with 2-Nitrotoluene & 3- Nitrotoluene at four different temperatures (303.15 K, 308.15 K, 313.15 K, 318.15 K). From the experimental data, excess molar volumes $\left(V_m^E\right)$ values were calculated. These values are negative for Cyclohexanol + 2-Nitrotoluene and positive for Cyclohexanol + 3-Nitrotoluene. The excess molar volumes $\left(V_m^E\right)$ values are analysed on the basis of molecular interactions between unlike non-electrolyte molecules.

Keywords: Cyclohexanol, molecular interaction, non-electrolytes, excess molar volumes, temperature dependence.
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INTRODUCTION

Thermodynamic properties provide important information for the design of industrial processes and also supply the knowledge about inter component interactions in binary liquid mixtures [1]. A fundamental understanding of the behaviour of Cyclohexanol in its binary liquid mixtures with non-electrolyte liquids is useful in polymer industry. To the best of our knowledge, excess molar volumes data for the liquid mixtures is not available in the literature. Recently many papers are published on thermodynamic properties of isomeric nitrotoluenes with organic liquids [2] and [3]. New experimental data for the excess volumes of two binary liquid mixtures namely Cyclohexanol +2-Nitrotoluene and Cyclohexanol + 3-Nitrotoluene are reported.

EXPERIMENTAL SECTION

Cyclohexanol obtained from S.D. Fine Chemicals Ltd, India was used as supplied. 2-Nitrotoluene and 3-Nitrotoluene also obtained from S.D. Fine Chemicals Ltd., India were purified as described in references [4], [5] and [6]. The purity of all the present investigated organic liquids was ascertained by comparing their experimental densities with the corresponding literature values [7]. The values are listed in table 1.

All organic liquid mixtures were prepared by mass and aliquots were transferred into glass stopper bottles via syringe to avoid the preferential evaporation. A digital electronic balance (Acculab ALC-210.4) was used for this purpose with the precision of ±0.1 mg. All molar quantities are based on the relative atomic mass table of 1986

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issued by International Union of Pure and Applied Chemistry (IUPAC). The uncertainity in the molefraction (x) was estimated to be less than $\pm 10^{-4}$. Densities of binary liquid mixtures were measured by using Rudolph Research Analytical digital densimeter (DDH-2911 model) with density precision $\pm 2 \times 10^{-5}$ g.cm^{-3} at different temperatures with accuracy of ± 0.03 K temperature. Densimeter was calibrated with doubly distilled, deionized water and with air as standards.

RESULTS AND DICUSSION

From the experimental values of density of liquid mixtures (ρ) of Cyclohexanol + Nitrotoluene, density of pure components (ρ_i) of Cyclohexanol, 2-Nitrotoluene & 3-Nitrotoluene, molefraction (x_i), excess molar volumes $\left(V_m^E\right)$ were calculated at different temperatures by using the formula

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

Where x_1 is molefraction of Cyclohexanol, x_2 is molefraction of nitrotoluene, M_1 is gram molecular weight of Cyclohexanol and M_2 is gram molecular weight of nitrotoluene.

The relation between excess molar volume & polynomial co-efficient was explained based on Redlich-Kister polynomial equation. The Reddlich-Kister polynomial equation is

$$V_m^E = x_1 (1-x_1) \sum_{i \geq 0}^{p} \left[A_i (1-2x_2)^i\right]$$

Where A_i is polynomial co-efficient, p is the polynomial degree, x_1 is the molefraction of Cyclohexanol, x_2 is molefraction of nitrotoluene and i is 0, 1, 2, ………

The standard deviation values were calculated by using the equation

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

Where n is the number of experimental data points.

The extreme values of excess molar volumes, the values of parameters obtained by least – squares method and the $\sigma\left(V_m^E\right)$ values are reported in table 2. Excess molar volumes curves were showed as graphs by taking molefraction of Cyclohexanol (x_1) on x-axis and excess molar volumes $\left(V_m^E\right)$ on y-axis in figures (1) & (2).

Experimentally measured excess molar volumes data for the binary liquid mixtures Cyclohexanol + 2-Nitrotoluene and Cyclohexanol + 3-Nitrotoluene is given in Table 2. The sign of excess molar volumes of a system depends on the relative magnitude of expansion or contraction on mixing of liquids. If the factors causing expansion dominate the factors causing the contraction then excess molar volumes values become positive. On the other land the factors causing contraction dominate the factors causing the expansion then excess molar volume values become negative. The factors causing expansion are disruption of hydrogen bonds in Cyclohexanol. The factors causing contraction are formation of Hydrogen bonds (-O----HO-) between oxygen atom of nitrotoluene and Hydrogen atom of OH group of Cyclohexanol.

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The factors causing expansion are dominant than the factors causing contraction in 3-Nitrotoluene thus excess molar volume values are positive. Where as in 2-Nitrotoluene the factors causing contraction are dominant than the factors causing expansion, thus the excess molar volume values are negative. Therefore the excess molar volume values are in the order 3-Nitrotoluene> 2-Nitrotoluene where as the molecular interactions are in the order 3-Nitrotoluene < 2-Nitrotoluene. Moreover the high interaction of 2-Nitrotoluene when compared to 3-Nitrotoluene can be explained on the basis of polar nature. 2-Nitrotoluene is more polar, due to the presence of electron attracting nitro (-NO$_2$) group and electron repelling methyl (-CH$_3$) group, which are very near to each other. Thus formation of hydrogen bond is easy in the binary liquid mixture of Cyclohexanol+2-Nitrotoluene, when compared to binary liquid mixture of Cyclohexanol 3-Nitrotoluene, since 3-Nitrotoluene is less polar because of presence of nitro and methyl group are faraway when compared to 2-Nitrotoluene.

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]
2-Nitrotoluene	1.15319	1.15321
3-Nitrotoluene	1.14761	1.14766

[a] at 298.15 K

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$^-$
Cyclohexanol + 2-Nitrotoluene						
303.15	-5.3189	1.0469	-0.5371	0.001	0.4634	-1.3396
308.15	-5.2203	1.0379	-0.0169	0.002	0.4586	-1.3131
313.15	-5.1535	0.9664	0.5689	0.003	0.4538	-1.2787
318.15	-5.0541	0.9891	0.9392	0.003	0.4421	-1.2394
Cyclohexanol + 3-Nitrotoluene						
303.15	2.1614	1.2219	0.2611	0.005	0.6229	0.4983
308.15	2.096	1.1888	-0.0538	0.001	0.6112	0.5170
313.15	1.9937	1.067	-0.3446	0.002	0.6064	0.5563
318.15	1.897	1.1302	-0.3491	0.004	0.6037	0.5854
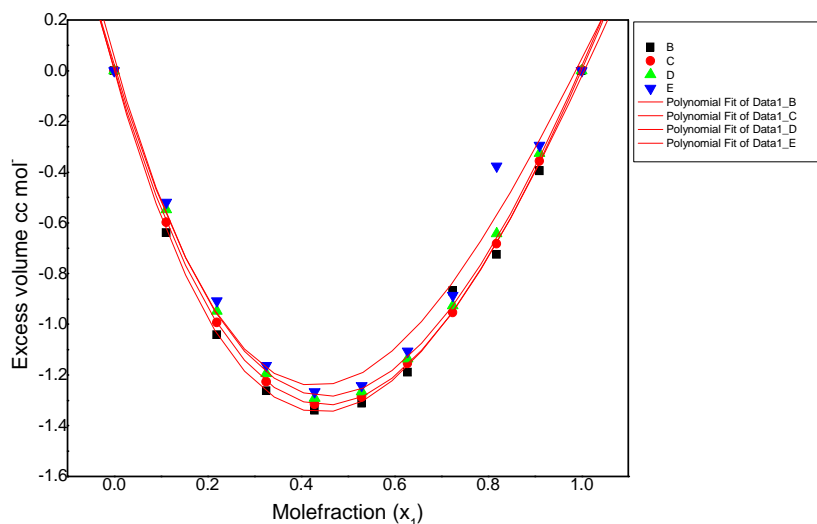
Fig.1: Molefraction of cyclohexanol versus Excess volumes of cyclohexanol + 2-nitrotoluene at 303.15K (■), 308.15K (●), 313.15K (▲) and 318.15K (▼)
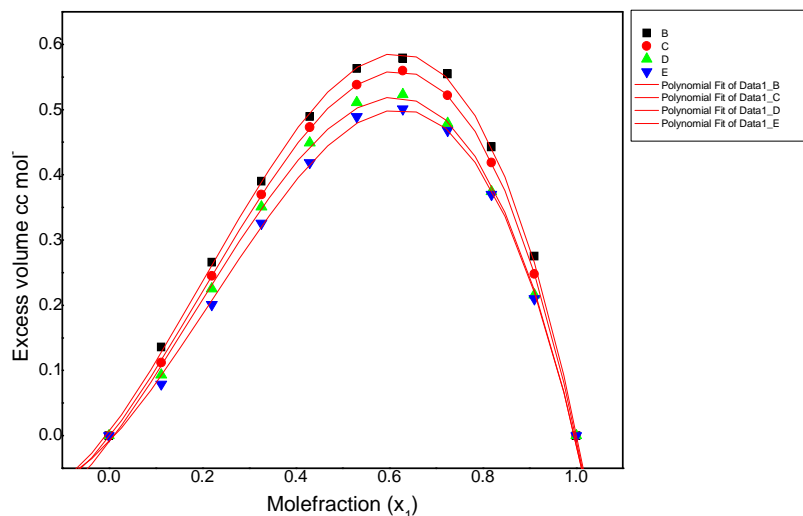
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Fig.2: Molefraction of cyclohexanol versus Excess volumes of cyclohexanol + 3-nitrotoluene at 303.15K (▼), 308.15K (▲), 313.15K (●) and 318.15K (■)

REFERENCES

[1] M V Ratnam; R K Singh. *Ind. J. Chem. Tech*, **2004**, 11, 526-530.

[2] V Syamala; K. Siva Kumar; P. Venkateswarlu. *J. Chem. Thermodynamics*, **2006**, 38, 1553-1562.

[3] V Syamala; K Siva Kumar, P Venkateswarlu, *Chinese Journal of Chemistry*, **2007**, 25, 32-43.

[4] A I Vogel, Text book of practical organic chemistry, 5th edn, Longman, London (**1989**).

[5] J.A.Riddick, W Bunger, T K Sakano: Techniques of Chemistry, Organic Solvents, Physical Properties and methods of purification, 4th edn, Wiley interscience, New York (**1987**).

[6] C Wojtowccz, Utradzwiekowe badanica mieszanincieczy silinie zasocjowanych: gliceryna – cyclohexanol 15, MSc. Thesis University Staski, Katowice (**1988**).

[7] J Timmermans: Physico-chemical constants of pure organic compounds, Elsevier, Amsterdam (**1950**).