

## CHAPTER IV

### **Investigation on Viscous Synergism and Antagonism Prevailing in Binary Mixtures of Cyclohexylamine with Isomeric Butanols by Volumetric, Viscometric, Refractive Index and Ultrasonic Speed Measurements**

Densities,  $\rho$ , viscosities,  $\eta$ , speeds of sound,  $u$ , and refractive indices,  $n_D$ , were measured for the binary systems of cyclohexylamine with 1-butanol, 2-butanol, isobutanol and *t*-butanol at 298.15 K over the entire composition range. From the experimental results, the excess volume,  $V^E$ , the deviations in viscosity,  $\Delta\eta$ , and synergic index ( $Is$ ) are derived by the equation developed by Kalentunc–Gencer, Peleg and Howell, respectively. Excess isentropic compressibility,  $K_s^E$ , and deviation in refractive indices,  $\Delta n_D$ , were also calculated. The above functions show deviations from the additivity law, which depend on the nature of the carbon chain of the alcohols.

*Keywords:* Density; Viscosity; Speed of Sound; Refractive Index; Cyclohexylamine; Butanol.

#### **4.1. Introduction:**

Many engineering problems require quantitative data on the viscosity and density of liquid mixtures. The thermodynamic and transport properties of liquid and liquid mixtures have been used to understand the molecular interactions between the components of the mixture and also for engineering applications concerning heat transfer, mass transfer, and fluid flow. During the last few years the thermodynamic properties of binary mixtures of alcohols with different solvents have been studied extensively.<sup>1-4</sup> Binary systems of cyclohexylamine with alcohols are interesting from the viewpoint - the type of interaction between the components of the mixture. The mixtures included

cyclohexylamine as a common component and four isomeric alcohols as uncommon components. The four isoalcohols were 1-butanol, 2-butanol, isobutanol and *t*-butanol. The tendency of cyclohexylamine to form hydrogen bonds with alcohols via the participation of the amine group i.e.  $-NH_2$  functionality and oxygen of the  $-OH$  functionality have attracted the attention of many experimental investigations on amine + alcohol binary mixtures dealing with the measurements especially of the excess properties. These studies show that the properties vary with the lengthening of the carbon chain length and branching of alcohols for amine + alcohol mixtures. Cyclohexylamine is a strong base which is completely miscible with water and common organic solvents.

The compound is widely employed in the industrial processing of pharmaceuticals, plastics, paper, rubber, insecticides, textiles, dyestuff, petroleum and some synthetic sweeteners. Butanol sees use as a solvent for a wide variety of chemical and textile processes, in organic synthesis and as a chemical intermediate. It is also used as a paint thinner and a solvent in other coating applications where it is used as a relatively slow evaporating latent solvent in lacquers and ambient-cured enamels. 2-butanol occurs naturally as a product of fermentation of carbohydrates. It is also used for the production of fruit essences, as a flavouring in food, and as a solvent. Isobutanol is used as insecticides for agric, garden and health service use, miscellaneous paint-related products, other art materials inclay, water & tempera colours, finger paint, and other automotive chemicals. Being relatively hydrophobic cosolvents, *t*-butanol is attractive compound in the study of hydration phenomena and may serve as models for more complicated aqueous systems like surfactants, emulsions, biopolymers and petroleum streams. Other uses of these compounds are as surfactants, additives in detergents, and agriculture products. <sup>5</sup> In the hope of obtaining an overall picture of these binary solutions we have studied the whole composition range. The most important use of this kind of compound is for removal of sour gases from natural gas and as an extension of the work we have measured the densities and viscosities for the same isomers over the entire range of composition at 298.15 K.

Thermodynamic and transport properties of binary liquid mixtures containing protic, aprotic, and associated liquids have been studied. The calculated excess quantities from such data have been interpreted in terms of the differences in the size of molecules and the strength of specific and nonspecific interactions taking place between components of the mixtures. Alkanols exist in associated form. When alkanols are mixed with cyclohexylamine, mixing properties with varying intermolecular interactions may be generated. To investigate this effect, in the present investigation, the density ( $\rho$ ), viscosity ( $\eta$ ), speed of sound, ( $u$ ), and refractive index, ( $n_D$ ), of the binary mixtures have been studied. The measured experimental values of the speed of sound along with those of density are used to calculate the isentropic compressibility,  $K_s^E$ , which provides useful information about the interactions that take place between the components of the mixture. Also, from the experimental values deviations in relative viscosity, ( $\Delta\eta$ ), and refractive indices, ( $\Delta n_D$ ), have been estimated. Such results should give some insight into the interactions among the -OH and -NH<sub>2</sub> groups.

In addition, the rheological and molecular behaviour of a formulation can influence aspects such as, patient acceptability, since it has been well demonstrated that viscosity and density both influence the absorption rate of such products in the body.<sup>6, 7</sup> The present study investigates and quantifies viscous synergy and volume contraction in binary mixtures of cyclohexylamine and isomeric butanols and their relation to concentration.

## 4.2. Experimental Section:

### 4.2.1. Method:

Densities ( $\rho$ ) were measured with an Ostwald-Sprengel-type pycnometer having a bulb volume of about 25 cm<sup>3</sup> and an internal diameter of the capillary of about 0.1 cm. The pycnometer was calibrated at 298.15 K with doubly distilled water and benzene. The pycnometer with experimental liquid was equilibrated in a glass-walled thermostated water bath maintained at 0.01 K of the desired temperature. The pycnometer was then removed from the

thermostat, properly dried, and weighed in an electronic balance with a precision of (0.01 mg). Adequate precautions were taken to avoid evaporation losses during the time of measurements. An average of triplicate measurements was taken into account. The density values were reproducible to  $\pm 3 \times 10^{-4} \text{ g}\cdot\text{cm}^{-3}$ . The viscosity was measured by means of a suspended Ubbelohde-type viscometer, calibrated at 298.15 K with doubly distilled water and purified methanol. A thoroughly cleaned and perfectly dried viscometer filled with the experimental liquid was placed vertically in the glass-walled thermostat maintained to ( $\pm 0.01$ ) K. After attainment of thermal equilibrium, efflux times of flow were recorded with a stopwatch correct to (0.1) s. At least three repetitions of each data reproducible to (0.1) s were taken to average the flow times. The accuracy of the viscosity measurements, based on our work on several pure liquids, was (0.003) mPa·s. The details of the methods and measurement techniques have been described elsewhere.<sup>8-10</sup> The mixtures were prepared by mixing known volumes of pure liquids in air-tight stoppered bottles. The weights were taken on a Mettler electronic analytical balance (AG 285, Switzerland) accurate to 0.0002 g. The ultrasonic speeds ( $u$ ) were determined using a single crystal variable path ultrasonic interferometer (Mittal Enterprises, New Delhi) working at 2 MHz<sup>11</sup> which was calibrated and the temperature stability was maintained within ( $\pm 0.01$ ) K by circulating thermostatic water around the cell with a circulating pump. The uncertainties in the liquid composition of sound measurements were estimated to be  $0.2 \text{ ms}^{-1}$ . The refractive indices of pure liquids and their binary mixtures were measured by using a thermostated Abbe refractometer. The refractometer was calibrated by measuring the refractive indices of triply distilled water and toluene at desired temperatures. The values of refractive index were obtained using sodium D light. The uncertainty of refractive index measurements was within (0.0002). The reliability of experimental measurements of  $n_D$  was ascertained by comparing the experimental data of pure liquids with the corresponding values available in the literature at 298.15 K.

#### 4.2.2. Source and purity of samples:

The monoalkanols; 1-butanol, 2-butanol, isobutanol and *t*-butanol with richness values of over 98% by volume (Merck, India) were purified by the methods as described in other papers.<sup>12, 13</sup> The solvents finally obtained after purification was 99.9% pure. Cyclohexylamine with richness values of over 99% by volume was obtained from Thomas Baker Chemicals Limited and used without further purification. The purity of the liquids was checked by measuring their densities, viscosities and refractive indices at 298.15 K which was quite in agreement with the literature values.

#### 4.3. Results and Discussion:

The comparison of the experimentally determined densities, viscosities and speeds of sound at 298.15 K of the pure components, along with their literature values,<sup>14-23</sup> are presented in Table 1, the experimental values of densities ( $\rho$ ) and the excess molar volumes,  $V^E$ , of the binary mixtures of cyclohexylamine (A), and monoalkanols (B), i.e., 1-butanol, 2-butanol, isobutanol, and *t*-butanol, have been presented along with the mole fractions of (A) and (B) in Table 2. The excess molar volumes,  $V^E$ , are calculated from density of these solvent mixtures according to the following equation:<sup>24</sup>

$$V^E = \sum_{i=1}^n x_i M_i (1/\rho - 1/\rho_i) \quad \text{.....(1)}$$

where  $x_i$ ,  $M_i$ ,  $\rho_i$  and  $\rho$  are the mole fraction, molar mass of the  $i^{\text{th}}$  component, density of the  $i^{\text{th}}$  component and density of the solution mixture respectively.

Viscous synergy is the term used in application to the interaction between the components of a system that causes the total viscosity of the system to be greater than the sum of the viscosities of each component considered separately. In contraposition to viscous synergy, viscous antagonism is defined as the interaction between the components of a system causing the net viscosity of the latter to be less than the sum of the viscosities of each

component considered separately. <sup>16</sup> Accordingly, when  $\eta_{exp} > \eta_{calc}$ , viscous synergy exists, while, when  $\eta_{calc} > \eta_{exp}$ , the system is said to exhibit viscous antagonism. If the total viscosity of the system is equal to the sum of the viscosities of each component considered separately, the system is said to lack interaction. <sup>25, 26</sup> This procedure is used when Newtonian fluids are involved, since in non-Newtonian systems shear rate must be taken into account, and other synergy indices are defined in consequence. <sup>27</sup> The viscosity in the absence of interaction,  $\eta_{calc}$ , is defined by the simple mixing rule:

$$\eta_{calc} = \sum_{i=1}^n x_i \eta_i \quad \text{..... (2)}$$

where  $x_i$ ,  $\eta_i$  are respectively the mole fraction and viscosity of component  $i$ .

The method used to analyze volume contraction and expansion is similar to that applied to viscosity, i.e., the density of the mixture is determined experimentally,  $\rho_{exp}$ , and a calculation is made for  $\rho_{calc}$  based on the following expression:

$$\rho_{calc} = \sum_{i=1}^n x_i \rho_i \quad \text{..... (3)}$$

where  $x_i$ ,  $\rho_i$  are, respectively the mole fraction and density of component  $i$ .

Viscosity deviation,  $(\Delta\eta)$ , values presented in Table 3 for clear comparison among the alcohols that appears to be different properties with mole fraction of A. The method most widely used to analyze the synergic behaviour of the ternary liquid mixtures used here is that developed by Kalentunc-Gencer and Peleg <sup>28</sup> allowing quantification of the synergy and interactions taking place in the mixtures involving variable proportions of the constituent components. Quantitatively, as per the absolute reaction rates theory, <sup>29</sup> the deviations of viscosities from the ideal mixture values can be calculated as:

$$\Delta\eta = \eta_{exp} - \sum_{i=1}^n x_i \eta_i \quad \text{..... (4)}$$

where  $\eta_{exp}$  is the viscosity of the mixture and  $x_i$ ,  $\eta_i$  are, respectively the mole fraction and viscosity of component  $i$ .

In order to secure more comparable viscous synergy results, the so called synergic interaction index introduced by Howell<sup>30</sup> is taken into account:

$$I_S = (\eta_{exp} - \eta_{calc}) / \eta_{calc} = \Delta\eta / \eta_{calc} \quad \text{..... (5)}$$

Table 3 also gives the data for the  $I_S$  of the mixtures against  $x_A$ . The negative value of  $I_S$  gives antagonic interaction index ( $I_A$ ).

Isentropic compressibilities,  $K_S$  and excess isentropic compressibilities,  $K_S^E$  are calculated from  $\rho_{exp}$  and speeds of sound,  $u$ , using the following equations:<sup>31-33</sup>

$$K_S = 1 / (u^2 \rho) \quad \text{..... (6)}$$

$$K_S^E = K_S - \sum_{i=1}^n x_i K_{S,i} \quad \text{..... (7)}$$

where  $x_i$ ,  $K_{S,i}$  are the mole fraction and isentropic compressibility of component  $i$  respectively. The experimental values of  $u$ ,  $K_S$  and  $K_S^E$  are compiled in Table 4 along with  $x_A$  and results have been depicted graphically in Figure 3.

Table 5, represents the  $\Delta n_D$  along with  $\Delta n_{Dcalc}$  and  $\Delta n_{Dexp}$  values for the four binary mixtures under examination. The deviations in refractive index from the mole fraction average ( $\Delta n_D$ ) are given by:

$$\Delta n_D = n_D - \sum_{i=1}^n x_i n_{D,i} \quad \text{..... (8)}$$

where  $n_D$ , is the refractive index of the mixture and  $x_i$ ,  $n_{D,i}$  are the mole fraction and refractive index of component  $i$ , respectively. Figure 4, shows the results of  $\Delta n_D$  for the four mixtures at 298.15 K.

Again, the  $V^E$ ,  $\Delta\eta$ ,  $K_S^E$  and  $\Delta n_D$  values can be fitted to Redlich-Kister equation<sup>34</sup> to derive the binary coefficient,  $A_k$ :

$$Y_{ij}^E = x_i x_j \sum_{k=1}^m A_k (x_i - x_j)^k \quad \text{..... (9)}$$

where  $Y_{ij}^E$  refers to an excess property for each  $i$ - $j$  binary pair, and  $x_i$  is the mole fraction of the  $i^{\text{th}}$  component, and  $A_k$  represents the coefficients.

The standard deviation for all the semiempirical models or equations used was calculated using the relation:

$$\sigma = \left[ \sum_{i=1}^n (Y_{exp}^E - Y_{calc}^E)^2 / (n - m) \right]^{1/2} \quad \text{..... (10)}$$

where  $n$  is the number of experimental points and  $m$  is the number of adjustable parameters.

The results in Table 2 and the curves in Figure 1 show that the excess volume is negative over the whole range of composition in the four mixtures. The  $V^E$  values fall in the order:



The more negative value found for 1-butanol and to those of all the other butanol isomers may be attributed to their more spherical shape. This spherical shape makes it difficult to form hydrogen bond between themselves, so that hydrogen bonding is mainly established with smaller molecules having -OH group at the terminal carbon atom. Comparing the  $V^E$  data obtained in this experiment with the corresponding values obtained in a work for benzylamine + the pentanol isomers, the same trend was observed.<sup>35</sup> The negative values of excess molar volume,  $V^E$  suggest specific interactions<sup>36-39</sup> between the mixing components in the mixtures while its positive values suggest dominance of dispersion forces between them. The negative  $V^E$  values indicate the specific interactions such as intermolecular hydrogen bonding between the mixing components and also the interstitial accommodation of the mixing components because of the difference in molar volumes. Several effects may contribute to the value of  $V^E$  and three different effects may be considered as being important — (a) disruption of liquid order on mixing and unfavourable interactions

between unlike molecules producing a positive contribution to  $V^E$ , (b) differences in molecular volumes and free volumes <sup>40</sup> between liquid components and (c) the possible association due to hydrogen bond interactions between the unlike molecules. The actual volume change would, therefore, depends on the relative strength of these effects. Thus negative values of  $V^E$  may be attributed to the presence of strong intermolecular hydrogen bond interactions between the cyclohexylamine and the isomeric butanols.

The minimum  $V^E$  values for all the mixtures appear near the equimolecular composition. The diagrams in which the excess volumes for the binary systems (Figure 1) are represented have the same shape. Knowing that excess volume is the result of several effects – chemical, structural and physical, our present investigation may be discussed in terms of specific interaction between constituent molecules and structural effects that would lead to the subsequent formation of bonds between –OH and –NH<sub>2</sub> groups that will yield a greater packing and therefore a negative excess volume for the mixture alkanol + cyclohexylamine. Mixing alcohols with cyclohexylamine has the consequence that hydrogen bondings of the self-association of alcohols are broken and new hydrogen bonds (–HO– –H–N–) with cyclohexylamine are generated. Since the bonding (–HO– –H–N–) is stronger than (–HO– –HO–) and has a more negative excess volume, the resulting excess volume reflects this balance leading to a negative contribution. The excess molar volume depends also on the degree of cross-association between the alcohol and the cyclohexylamine.

The values in Table 3 are graphically represented in Figures 2(a), 2(b) and 2(c).

In Figure 2(a) the viscosity is seen to increase in case of the system cyclohexylamine + 1-butanol and cyclohexylamine + isobutanol non-linearly for the entire composition range, and from Table 3 it is observed that where  $\eta_{exp} > \eta_{calc}$  for the binary mixtures, synergy prevails as mentioned earlier reaching maximum values (saturation point) at different concentrations in each case and thereafter decreases. Further, it has been also observed that antagonism comes into play for the system cyclohexylamine + *t*-butanol and  $\eta_{exp} < \eta_{calc}$ .  $\eta_{exp}$  have lower values than  $\eta_{calc}$  but higher for the last four composition range for the

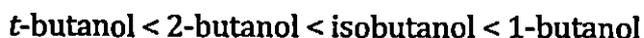
system cyclohexylamine + 2-butanol. This may be attributed to the known phenomenon of solvation, as a consequence of the hydrogen bonds formed between the molecules of the components of the mixture-producing an increasing in size of the resulting molecular package, which legally implies rise in viscosity. In case of isomers, the H-bonds in tertiary is weakest than in secondary which is weaker than primary alkanols, i.e., the monoalkanols with –OH group at terminal position other than primary C-atom, attracts more unlike molecules. This type of characteristic behaviour is a manifestation of strong specific interaction <sup>18</sup> between the unlike molecules predominated by H-bonding interaction. Similar results were reported in earlier papers. <sup>16</sup>

A perusal of Table 3 shows that the values of viscosity deviation,  $\Delta\eta$ , are positive over the entire composition range for the system cyclohexylamine + 1-butanol and isobutanol except one composition. Whereas  $\Delta\eta$  values are negative over the entire composition range for the system cyclohexylamine + *t*-butanol but in case of 2-butanol after attaining a minima shows to obtain positive viscosity deviation,  $\Delta\eta$ . The estimated uncertainty for viscosity deviation,  $\Delta\eta$ , is (0.004 mPa·s). The negative values imply the presence of dispersion forces between the mixing components in these mixtures, while positive values may be attributed to the presence of specific interactions <sup>41</sup> between them. The plots of viscosity deviation,  $\Delta\eta$ , versus mole fraction,  $x_A$ , for the different binary mixtures have been presented in Figure 2(b). The decrease of mixture viscosities indicates the weakening of self-association of alkanols in presence of cyclohexylamine. According to Fort and Moore <sup>41</sup> excess viscosities are negative in mixtures of components having unequal size and in which dispersion forces are present. As expected, the values of  $\Delta\eta$  become more negative as the chain length of the alkanols <sup>42</sup> and branching in chain length of the concerned molecule increases and one shifts from primary to secondary alcohols. This suggests that the strength of interaction in the mixtures is in the order:



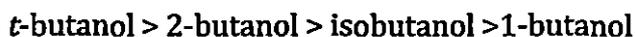
indicating same result as obtained in case of excess molar volume.

In Figure 2(c) the synergic index values for the ternary mixtures are presented in the following trend:



Here steric effect becomes the deciding factor. Due to large and complex size of the tertiary and secondary alkanols compared to the primary ones, cyclohexylamine molecules cannot easily disrupt the molecular package formed between like molecules. Thus, the mutual attraction remains lower for the 3°- and 2°-isomers. The explanation of this behaviour is based on the known phenomenon of molecular dissociation, as a consequence of weakening the H-bond formed between the molecules producing a decrease in size of the molecular package which logically implies the decrease in  $I_S$ . Thus, the molecular package decreases gradually with the branching of alcohols which implies a decrease in  $I_S$ .

Figure 3 shows that  $K_S^E$  values are negative for all the mixtures, and fall in the order:



It is interesting to note that the trend observed is just the reverse of that obtained for  $I_S$  values for the mixtures. This trend is justified by the presence of weak interaction or structure disruptive effects between the mixing liquids for the binary mixtures of isomeric butanols and by the presence of strong hydrogen bond interactions between the mixing liquids for the binary mixtures. As stated earlier alkanols in pure state remains in associate form. These structures can thus resist the structure disruptions in the presence of cyclohexylamine and this effect probably increases with the branching in the alkanols. The largest negative value is observed for the system cyclohexylamine with 1-butanol and the minimum for the studied binary systems remains at  $x_A = 0.4277$ . The  $K_S^E$  values may be attributed to (i) an increase in free spaces in mixtures compared to those in pure components due to the depolymerization of alcohol aggregates with the addition of cyclohexylamine and (ii) a decrease in free spaces as a result of hydrogen-bonding interactions of the type  $(-\text{HO}-----\text{H-N}-)$  between unlike molecules and interstitial accommodation of cyclohexylamine in hydrogen bonded aggregates of alcohols. The former factor

leads to positive  $K_S^E$  values, and the latter effect contributes to negative values of  $K_S^E$ . The actual deviation in isentropic compressibility would be the resultant of the later effect. The algebraic values of  $K_S^E$  at equimolar mixtures fall in the order.

$$t\text{-butanol} > 2\text{-butanol} > \text{isobutanol} > 1\text{-butanol}$$

These observations are further supported by  $V^E$  (Figure 1) and  $\Delta\eta$  (Figure 2(b)) values.

The  $\Delta n_D$  values, which increase as the branching increases, are negative for all of the systems over the entire range of composition. The values of  $\Delta n_D$  follow the order:

$$t\text{-butanol} > 2\text{-butanol} > \text{isobutanol} > 1\text{-butanol}$$

Figure 4 represents variation of deviation in refractive index  $\Delta n_D$ , against mole fraction ( $x_A$ ) of cyclohexylamine at 298.15 K.  $\Delta n_D$  values are negative for the whole range of composition and for all the considered binary systems. The negative values of this property through the Maxwell equation show that the mixture has a permittivity at the Na D-line wavelength smaller than that in the ideal case. This behaviour could be explained by considering that when the packing effect decreases ( $V^E > 0$ ), the number of dipoles per unit volume diminishes and therefore  $n_D$  also becomes smaller, originating negative  $\Delta n_D$ . It would imply the influence of  $V^E$  in the polarization mechanisms at high frequency, just as seems to be reflected in the results obtained by the theoretical models for the prediction of  $n_D$ ,<sup>43</sup> which improve when the real volume is considered ( $V^E \neq 0$ ).

The values of coefficients  $A_k$ , were determined by a multiple-regression analysis based on the least-squares method and were summarized along with their standard deviations between the experimental and fitted values of the respective functions in Table 6. The small  $\sigma$  values for excess or deviation properties indicated that the fits are good and in the present study,  $V^E$ ,  $\Delta\eta$ ,  $K_S^E$  and  $\Delta n_D$  are quite systematic and function of the composition of the binary mixtures.

#### 4.4. Conclusion:

In summary, cyclohexylamine + isomeric butanol systems are characterized by the presence of strong hydrogen bond interaction between the mixing liquids and the strength of interaction follows the order: cyclohexylamine + *t*-butanol < cyclohexylamine + 2-butanol < cyclohexylamine + isobutanol < cyclohexylamine + 1-butanol; also steric and other effects play a pivotal role in this regard. On the contrary, alkanol + amine systems are characterized by the presence of hydrogen bond interaction in the studied binary systems. The reason is probably due to presence of strong hydrogen bond interaction in these molecules by the interaction of the alcoholic oxygen and hydrogen of  $-NH_2$  group in the cyclohexylamine molecule. The monoalkanols with the hydroxyl group positioned at the first carbon atom accept more cyclohexylamine than those with the hydroxyl group at secondary or tertiary alcohols and their  $I_5$  values are, therefore, considerably higher.

## References

1. J. Troncoso, E. Carballo, C.A. Cerdeiriña, D. González, and L. Román, *J. Chem. Eng. Data* **2000**, *45*, 594.
2. C. Lafuente, J. Pardo, V. Rodríguez, F.M. Royo, and J.S. Uribe, *J. Chem. Eng. Data* **1993**, *38*, 554.
3. L. Pikkarainen, *J. Chem. Eng. Data* **1988**, *33*, 299.
4. D. Venkatesulu, P. Venkatesu, and M.V. Prabhakara Rao, *J. Chem. Eng. Data* **1997**, *42*, 1145.
5. G. Astarita, D.W. Savage, A. Bisio, *Gas Treating with Chemical Solvents*. (Wiley, New York, 1983).
6. C. Faulí i Trillo. *Tratado de Farmacia Galénica*. (Luzán. 5, Madrid, 1993).
7. J. Swarbrick and J.C. Boyland, *Encyclopedia of Pharmaceutical Technology*. (Marcel Dekker, New York, 1993).
8. M.N. Roy, D.K. Hazra, *Indian J. Chem. Technol.* **1994**, *1*, 93.
9. P.S. Nikam, M. Hosan, *J. Chem. Eng. Data* **1988**, *33*, 165.
10. M.N. Roy, A. Sinha, *Fluid Phase Equil.* **2006**, *243*, 133.
11. C.H. Tu, H.C. Ku. *J. Chem. Eng. Data* **2005**, *50*, 608.
12. D.D. Perrin, W.L.F. Armarego, *Purification of Laboratory Chemicals*, third ed. (Pergamon Press, Australia, 1988).
13. S.L. Oswal, H.S. Desai, *Fluid Phase Equil.* **1998**, *149*, 359.
14. M.N. Roy, B. Sinha, V.K. Daku. *J. Mol. Liq.* **2007**, *136*, 128.
15. P. Haraschka, A. Heintz, J.K. Lehmann, and A. Peters, *J. Chem. Eng. Data* **1999**, *44*, 932.
16. J.V. Herraiz, R. Belda, *J. Solution Chem.* **2004**, *33*, 117.
17. J.M. Resa, C.G. Iz, J.M. Goenaga, and M. Iglesias, *J. Chem. Eng. Data* **2004**, *49*, 804.
18. A. Anso'n, R. Garriga, S. Martínez, P. Pérez, and M. Gracia, *J. Chem. Eng. Data* **2005** *50*, 677.
19. T.M. Aminabhavi' and B. Gopalkrishna, *J. Chem. Eng. Data* **1994**, *39*, 865.
20. J.A. Riddick, W.B. Bunger, *Organic Solvents Techniques of Chemistry*, 4th ed.; Vol. II. (Wiley, New York, 1986).

21. J. Troncoso, C.A. Tovar, C.A. Cerdeirina, E. Carballo, and L. Romani, *J. Chem. Eng. Data* **2001**, *46*, 312.
22. C. Lafuente, J. Pardo, V. Rodriguez, F.M. Royo, and J.S. Urieta, *J. Chem. Eng. Data* **1993**, *38*, 554.
23. T.M. Aminabhavi, M.Y. Aralaguppi, S.B. Harogoppad, R.H. Balundgi, *J. Chem. Eng. Data* **1993**, *38*, 31.
24. Z. Atik, *J. Solution Chem.* **2004**, *33*, 1447.
25. J. Pellicer, Sinergia viscosa. *Fundamentos de reología. Los materiales viscoelásticos. Aplicaciones a las industrias alimentarias y quimico-farmacéuticas.* (Universidad Internacional Menéndez Pelayo, Valencia, Spain, 1997).
26. G. Copetti, R. Lapasin, E.R. Morris, *Proceedings of the Fourth European Rheology Conference.* (Seville, Spain, 1994).
27. D.D. Christianson, *Hydrocolloidal Interactions with Starche.* (AVI Publishing Company, Westport, 1982).
28. G. Kalentunc-Gencer, M. Peleg, *J. Texture Studies* **1986**, *17*, 61.
29. S. Glasstone, K.J. Laidler, H. Eyring. *The Theory of Rate Process.* (McGraw-Hill, New York, 1941).
30. N.K. Howell, *Elucidation of protein-protein interactions in gels and foms.* *Proc. 7th Intern. Conf. Wales 1993*, G.O. Phillips, P.A. Williams, and D.J. Wdlock, Eds. (Oxford University Press, New York, 1994).
31. C. Lafuente, B. Ginar, A. Villares, I. Gascon, P. Cea, *Int. J. Thermophys.* **2004**, *25*, 1735.
32. G. Douheret, A. Pal, M.I. Davis, *J. Chem. Thermo.* **1990**, *22*, 99.
33. I. Gascon, S. Martin, P. Cea, M.C. Lopez, F.M. Royo, *J. Solution Chem.* **2002**, *31*, 905.
34. O. Redlich, A.T. Kister, *Ind. Eng. Chem.* **1948**, *40*, 345.
35. W.L. Weng, L.T. Chang, and I.M. Shiah, *J. Chem. Eng. Data* **1999**, *44*, 994.
36. M.N. Roy, A. Sinha, and B. Sinha, *J. Solution Chem.* **2005**, *34*, 1311.
37. M.N. Roy, B. Sinha, and V. Dakua, *J. Chem. Eng. Data* **2006**, *51*, 590.
38. V.K. Dakua, B. Sinha, and M.N. Roy, *Indian J. Chem.* **2006**, *45A*, 1381.
39. Ku Hsu-Chen and Tu Chein-Hsiun, *J. Chem. Eng. Data* **2005**, *50*, 608.

40. M.G. Prolongo, R.M. Mesagosa, H.I. Fuentes, and A. Horta, *J. Phys. Chem.* **1984**, *88*, 2163.
41. R.J. Fort and W.R Moore, *Trans. Faraday Soc.* **1966**, *62*, 1112.
42. N.V. Sastry and S.R. Patel, *Int. J. Thermophys.* **2000**, *21*, 1153.
43. T.P. Iglesias, J.L. Legido, S.M. Pereira, B. Cominges, and M.I. Paz Andrade, *J. Chem. Thermo.* **2000**, *32*, 923.

**Table 1.** Physical properties of pure components at 298.15 K

Solvents	$\rho \times 10^{-3} / (\text{kg}\cdot\text{m}^{-3})$		$\eta / (\text{mPa}\cdot\text{s})$		$u / \text{m}\cdot\text{s}^{-1}$		$n_D$	
	Exp.	Lit.	Exp.	Lit.	Exp.	Lit.	Exp.	Lit.
cyclohexylamine	0.8628	0.8668 <sup>14</sup>	1.7727	1.7530 <sup>14</sup>	1416.36	1416.4 <sup>14</sup>	1.4565	-
1-butanol	0.8051	0.8059 <sup>22</sup>	2.5749	2.5420 <sup>16</sup>	1240.00	1240.00 <sup>23</sup>	1.3971	1.3975 <sup>19</sup>
2-butanol	0.8022	0.8024 <sup>22</sup>	2.9924	2.8571 <sup>15</sup>	1210.45	1210.43 <sup>21</sup>	1.3951	1.3950 <sup>20</sup>
isobutanol	0.7974	0.7980 <sup>22</sup>	3.4298	3.4350 <sup>18</sup>	1187.09	1185.63 <sup>17</sup>	1.3939	1.3937 <sup>17</sup>
t-butanol	0.7782	0.7648 <sup>22</sup>	4.4449	4.3719 <sup>15</sup>	1116.09	-	1.3852	1.3826 <sup>19</sup>

**Table 2.** Experimental values of density,  $\rho \times 10^{-3} / (\text{kg}\cdot\text{m}^{-3})$ , excess molar volume,  $V^E \times 10^6 / (\text{m}^3\cdot\text{mol}^{-1})$  for the binary mixtures under investigation at 298.15 K

$x_A$	$x_B$	$\rho \times 10^{-3} / (\text{kg}\cdot\text{m}^{-3})$	$V^E \times 10^6 / (\text{m}^3\cdot\text{mol}^{-1})$
cyclohexylamine(A)+1-butanol(B)			
0	1	0.8061	0
0.0767	0.9233	0.8144	-0.3412
0.1574	0.8426	0.8236	-0.7851
0.2426	0.7574	0.8317	-1.1008
0.3325	0.6675	0.8391	-1.3342
0.4277	0.5723	0.8453	-1.4225
0.5285	0.4715	0.8504	-1.3726
0.6355	0.3645	0.8543	-1.1641
0.7493	0.2507	0.8572	-0.8115
0.8706	0.1294	0.8598	-0.3939
1	0	0.8628	0
cyclohexylamine(A)+2-butanol(B)			
0	1	0.8022	0
0.0767	0.9233	0.8101	-0.2584
0.1574	0.8426	0.8181	-0.5245
0.2426	0.7574	0.8258	-0.7504
0.3325	0.6675	0.8333	-0.9487
0.4277	0.5723	0.8400	-1.0450
0.5285	0.4715	0.8455	-0.9880
0.6355	0.3645	0.8502	-0.8188
0.7493	0.2507	0.8539	-0.5047
0.8706	0.1294	0.8583	-0.2568
1	0	0.8628	0
cyclohexylamine(A)+isobutanol(B)			
0	1	0.7974	0
0.0767	0.9233	0.8059	-0.2827
0.1574	0.8426	0.8147	-0.5949
0.2426	0.7574	0.8240	-0.9595
0.3325	0.6675	0.8322	-1.1892

0.4277	0.5723	0.8395	-1.3032
0.5285	0.4715	0.8455	-1.2502
0.6355	0.3645	0.8504	-1.0464
0.7493	0.2507	0.8549	-0.7714
0.8706	0.1294	0.8584	-0.3418
1	0	0.8628	0
cyclohexylamine(A)+t-butanol(B)			
0	1	0.7782	0
0.0767	0.9233	0.7876	-0.2077
0.1574	0.8426	0.7970	-0.3993
0.2426	0.7574	0.8069	-0.6339
0.3325	0.6675	0.8166	-0.8272
0.4277	0.5723	0.8254	-0.8893
0.5285	0.4715	0.8333	-0.8188
0.6355	0.3645	0.8406	-0.6479
0.7493	0.2507	0.8476	-0.4105
0.8706	0.1294	0.8548	-0.1678
1	0	0.8628	0

**Table 3.** Calculated,  $\eta_{calc}$  / (mPa·s), and experimental,  $\eta_{exp}$  / (mPa·s), values of viscosity, deviation in viscosity  $\Delta\eta$  / (mPa·s) along with synergic index,  $I_s$ , for the binary mixtures under investigation at 298.15 K

$x_A$	$x_B$	$\eta_{calc}$ / (mPa·s)	$\eta_{exp}$ / (mPa·s)	$\Delta\eta$ / (mPa·s)	$I_s$
cyclohexylamine(A)+1-butanol(B)					
0	1	2.5749	2.5749	0	0
0.0767	0.9233	2.5134	2.5577	0.0443	0.0176
0.1574	0.8426	2.4486	2.5551	0.1065	0.0435
0.2426	0.7574	2.3803	2.5642	0.1839	0.0773
0.3325	0.6675	2.3082	2.5736	0.2654	0.1150
0.4277	0.5723	2.2318	2.5494	0.3176	0.1423
0.5285	0.4715	2.1509	2.4811	0.3302	0.1535
0.6355	0.3645	2.0651	2.3794	0.3143	0.1522
0.7493	0.2507	1.9738	2.2482	0.2744	0.1390
0.8706	0.1294	1.8765	2.0617	0.1852	0.0987
1	0	1.7727	1.7727	0	0
cyclohexylamine(A)+2-butanol(B)					
0	1	2.9924	2.9924	0	0
0.0767	0.9233	2.8988	2.8039	-0.0949	-0.0327
0.1574	0.8426	2.8004	2.6191	-0.1813	-0.0647
0.2426	0.7574	2.6965	2.4718	-0.2247	-0.0833
0.3325	0.6675	2.5868	2.3694	-0.2174	-0.0840
0.4277	0.5723	2.4707	2.3025	-0.1682	-0.0681
0.5285	0.4715	2.3478	2.2499	-0.0979	-0.0417

0.6355	0.3645	2.2173	2.2243	0.0070	0.0032
0.7493	0.2507	2.0785	2.1480	0.0695	0.0334
0.8706	0.1294	1.9305	2.0022	0.0717	0.0371
1	0	1.7727	1.7727	0	0
cyclohexylamine(A)+isobutanol(B)					
0	1	3.4298	3.4298	0	0
0.0767	0.9233	3.3027	3.2736	-0.0291	-0.0088
0.1574	0.8426	3.1690	3.1827	0.0137	0.0043
0.2426	0.7574	3.0278	3.1254	0.0976	0.0322
0.3325	0.6675	2.8788	3.0672	0.1884	0.0654
0.4277	0.5723	2.7211	2.9756	0.2545	0.0935
0.5285	0.4715	2.5540	2.8595	0.3055	0.1196
0.6355	0.3645	2.3767	2.6813	0.3046	0.1282
0.7493	0.2507	2.1881	2.4473	0.2592	0.1185
0.8706	0.1294	1.9871	2.165	0.1779	0.0895
1	0	1.7727	1.7727	0	0
cyclohexylamine(A)+t-butanol(B)					
0	1	4.4449	4.4449	0	0
0.0767	0.9233	4.2399	4.0394	-0.2005	-0.0473
0.1574	0.8426	4.0243	3.7217	-0.3026	-0.0752
0.2426	0.7574	3.7966	3.4437	-0.3529	-0.0930
0.3325	0.6675	3.5564	3.2026	-0.3538	-0.0995
0.4277	0.5723	3.302	2.9739	-0.3281	-0.0994
0.5285	0.4715	3.0326	2.7489	-0.2837	-0.0936
0.6355	0.3645	2.7467	2.5193	-0.2274	-0.0828
0.7493	0.2507	2.4426	2.3092	-0.1334	-0.0546
0.8706	0.1294	2.1185	2.1060	-0.0125	-0.0059
1	0	1.7727	1.7727	0	0

**Table 4.** Experimental values of ultrasonic speed,  $u/\text{m}\cdot\text{s}^{-1}$ ; isentropic compressibility,  $K_S \times 10^{12}/(\text{Pa}^{-1})$  and deviation in isentropic compressibility,  $K_S^E \times 10^{12}/(\text{Pa}^{-1})$  of binary mixtures at 298.15 K

$x_A$	$u/\text{m}\cdot\text{s}^{-1}$	$K_S \times 10^{12}/(\text{Pa}^{-1})$	$K_S^E \times 10^{12}/(\text{Pa}^{-1})$
cyclohexylamine(A)+1-butanol(B)			
0	1240.0	806.80	0
0.0767	1254.7	779.98	-0.9
0.1574	1277.7	743.75	-2.7
0.2426	1299.7	711.78	-4.0
0.3325	1323.7	680.15	-5.1
0.4277	1345.8	653.17	-5.6
0.5285	1365.5	630.66	-5.5
0.6355	1379.0	615.55	-4.6
0.7493	1388.8	604.84	-3.1

0.8706	1398.8	594.42	-1.3
1	1416.4	577.72	0
cyclohexylamine(A)+2-butanol(B)			
0	1210.5	850.72	0
0.0767	1225.4	822.06	-0.8
0.1574	1245.0	788.60	-1.9
0.2426	1265.7	755.90	-2.9
0.3325	1288.7	722.60	-3.8
0.4277	1312.8	690.75	-4.3
0.5285	1331.5	667.12	-4.0
0.6355	1350.4	644.99	-3.3
0.7493	1370.2	623.77	-2.3
0.8706	1390.5	602.59	-1.1
1	1416.4	577.72	0
cyclohexylamine(A)+isobutanol(B)			
0	1187.1	889.92	0
0.0767	1203.7	856.41	-1.0
0.1574	1225.7	817.02	-2.4
0.2426	1248.8	778.19	-3.6
0.3325	1272.8	741.74	-4.5
0.4277	1298.7	706.26	-5.0
0.5285	1321.8	676.95	-4.8
0.6355	1342.6	652.35	-3.9
0.7493	1364.3	628.44	-2.8
0.8706	1388.1	604.60	-1.4
1	1416.4	577.72	0
cyclohexylamine(A)+t-butanol(B)			
0	1116.1	1031.58	0
0.0767	1132.8	989.44	-0.8
0.1574	1152.1	945.28	-1.5
0.2426	1175.2	897.34	-2.5
0.3325	1200.9	849.14	-3.2
0.4277	1228.6	802.63	-3.5
0.5285	1257.2	759.26	-3.3
0.6355	1287.9	717.21	-2.6
0.7493	1323.4	673.64	-1.8
0.8706	1363.8	628.98	-0.8
1	1416.4	577.72	0

**Table 5.** Experimental and calculated values of refractive index,  $n_D$ , and deviation in refractive index  $\Delta n_D$  of binary mixtures at 298.15 K

$X_A$	$X_B$	$n_{Dexp}$	$n_{Dcalc}$	$\Delta n_D$
<b>cyclohexylamine(A)+1-butanol(B)</b>				
0	1	1.3971	1.3971	0
0.0767	0.9233	1.3992	1.4017	-0.0024
0.1574	0.8426	1.3999	1.4064	-0.0065
0.2426	0.7574	1.4000	1.4115	-0.0115
0.3325	0.6675	1.4005	1.4169	-0.0164
0.4277	0.5723	1.4042	1.4225	-0.0183
0.5285	0.4715	1.4105	1.4285	-0.0180
0.6355	0.3645	1.4191	1.4348	-0.0157
0.7493	0.2507	1.4312	1.4416	-0.0104
0.8706	0.1294	1.4451	1.4488	-0.0037
1	0	1.4565	1.4565	0
<b>cyclohexylamine(A)+2-butanol(B)</b>				
0	1	1.3951	1.3951	0
0.0767	0.9233	1.3989	1.3998	-0.0009
0.1574	0.8426	1.4011	1.4048	-0.0037
0.2426	0.7574	1.4032	1.4100	-0.0068
0.3325	0.6675	1.4049	1.4156	-0.0106
0.4277	0.5723	1.4088	1.4214	-0.0126
0.5285	0.4715	1.4158	1.4275	-0.0117
0.6355	0.3645	1.4254	1.4341	-0.0087
0.7493	0.2507	1.4365	1.4411	-0.0046
0.8706	0.1294	1.4472	1.4486	-0.0014
1	0	1.4565	1.4565	0
<b>cyclohexylamine(A)+isobutanol(B)</b>				
0	1	1.3939	1.3939	0
0.0767	0.9233	1.3972	1.3987	-0.0015
0.1574	0.8426	1.3995	1.4038	-0.0043
0.2426	0.7574	1.4009	1.4091	-0.0082
0.3325	0.6675	1.4028	1.4148	-0.0119
0.4277	0.5723	1.4060	1.4207	-0.0147
0.5285	0.4715	1.4126	1.4270	-0.0144
0.6355	0.3645	1.4220	1.4337	-0.0117
0.7493	0.2507	1.4333	1.4408	-0.0075
0.8706	0.1294	1.4460	1.4484	-0.0024
1	0	1.4565	1.4565	0
<b>cyclohexylamine(A)+<i>t</i>-butanol(B)</b>				
0	1	1.3852	1.3852	0
0.0767	0.9233	1.3901	1.3907	-0.0006
0.1574	0.8426	1.3932	1.3964	-0.0032
0.2426	0.7574	1.3972	1.4025	-0.0053
0.3325	0.6675	1.4016	1.4089	-0.0073
0.4277	0.5723	1.4079	1.4157	-0.0078

0.5285	0.4715	1.4161	1.4229	-0.0068
0.6355	0.3645	1.4255	1.4305	-0.0050
0.7493	0.2507	1.4356	1.4386	-0.0030
0.8706	0.1294	1.4459	1.4473	-0.0014
1	0	1.4565	1.4565	0

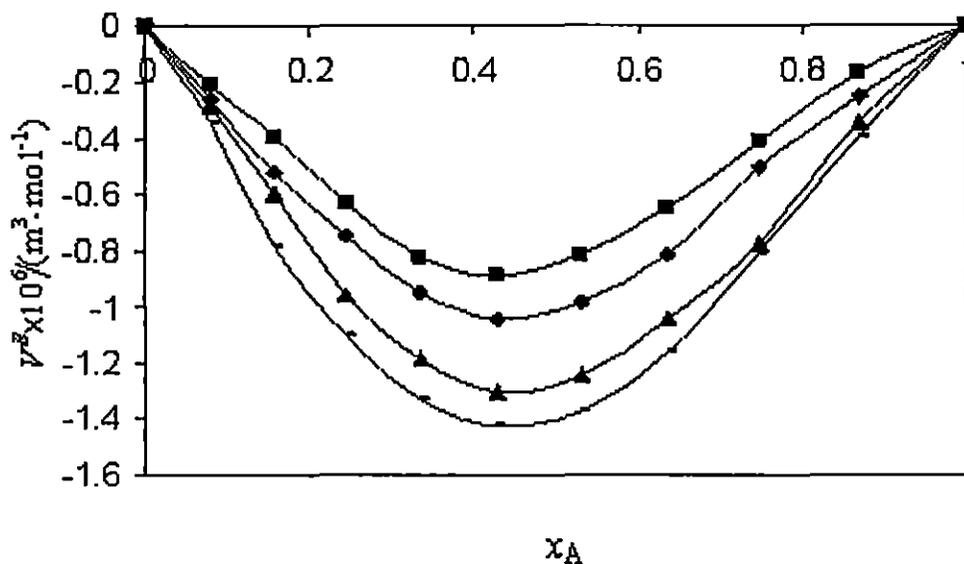
**Table 6.** Correlation coefficients of viscosity, density, speed of sound and refractive index of the binary mixtures at 298.15 K

$V^E \times 10^6 / (\text{m}^3 \cdot \text{mol}^{-1})$				
	cyclohexylamine (A)+1-butanol(B)	cyclohexylamine (A)+2-butanol(B)	cyclohexylamine (A)+isobutanol(B)	cyclohexylamine (A)+t-butanol(B)
A <sub>0</sub>	-5.6454	-4.1118	-5.0932	-3.4000
A <sub>1</sub>	0.4498	1.4281	1.8980	1.9397
A <sub>2</sub>	-2.9509	3.4263	1.2903	1.5877
A <sub>3</sub>	-2.7363	0.5136	-4.3926	-3.1240
A <sub>4</sub>	2.9966	-2.7391	2.2929	3.9854
A <sub>5</sub>	-	-2.1320	4.6146	2.4063
A <sub>6</sub>	-	-	-	-5.2370
$\sigma$	0.0288	0.0129	0.0150	0.0014
$\Delta\eta / (\text{mPa}\cdot\text{s})$				
	cyclohexylamine (A)+1-butanol(B)	cyclohexylamine (A)+2-butanol(B)	cyclohexylamine (A)+isobutanol(B)	cyclohexylamine (A)+t-butanol(B)
A <sub>0</sub>	1.3226	-0.4581	1.1740	-1.1878
A <sub>1</sub>	0.1050	1.7380	0.6430	0.8786
A <sub>2</sub>	-0.3622	0.1764	-0.7724	-0.9036
A <sub>3</sub>	1.6278	-0.6904	0.8137	1.1396
A <sub>4</sub>	0.2014	-	-	2.3104
A <sub>5</sub>	-1.2550	-	-	0.2282
A <sub>6</sub>	-	-	-	-1.7517
$\sigma$	0.0015	0.0053	0.0041	0.0017
$K_S^E \times 10^{12} / (\text{Pa}^{-1})$				
	cyclohexylamine (A)+1-butanol(B)	cyclohexylamine (A)+2-butanol(B)	cyclohexylamine (A)+isobutanol(B)	cyclohexylamine (A)+t-butanol(B)
A <sub>0</sub>	-22.4903	-16.5361	-19.4956	-13.5190
A <sub>1</sub>	5.5854	5.8001	6.8588	5.6187
A <sub>2</sub>	17.7912	9.2690	8.9161	7.8033
A <sub>3</sub>	1.8980	-6.3863	-7.2164	-4.9994
A <sub>4</sub>	-32.0063	-	-	-
A <sub>5</sub>	-6.4066	-	-	-
A <sub>6</sub>	44.4602	-	-	-
$\sigma$	0.0657	0.0637	0.0562	0.0806
$\Delta n_D$				
	cyclohexylamine (A)+1-butanol(B)	cyclohexylamine (A)+2-butanol(B)	cyclohexylamine (A)+isobutanol(B)	cyclohexylamine (A)+t-butanol(B)

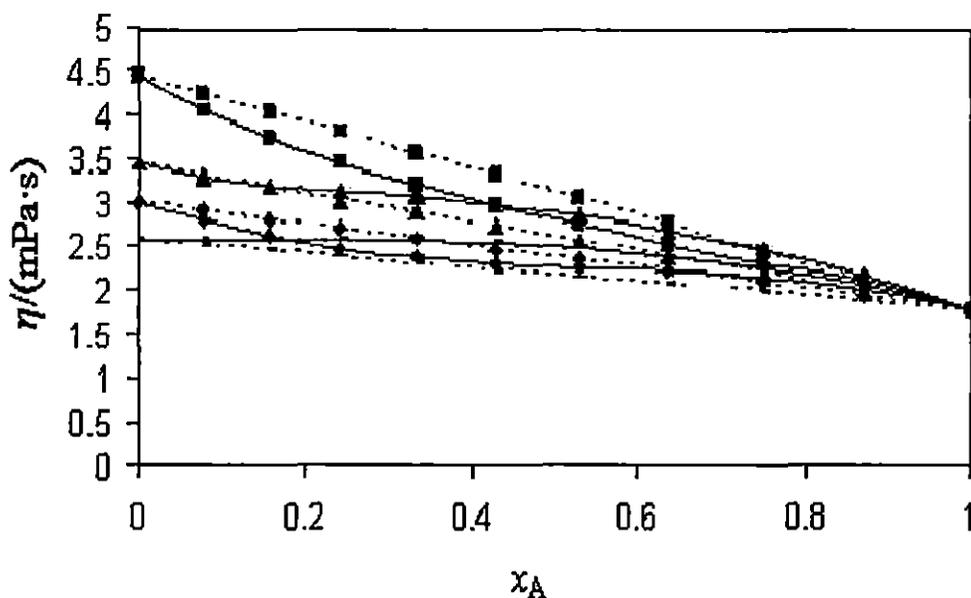
---

$A_0$	-0.0750	-0.0491	-0.0585	-0.0289
$A_1$	0.0092	0.0235	0.0065	0.0231
$A_2$	0.0646	0.0802	0.0625	0.0239
$A_3$	-	-0.0315	-	-0.0345
$A_4$	-	-0.0409	-	-
$A_5$	-	-	-	-
$A_6$	-	-	-	-
$\sigma$	0.0004	0.0002	0.0003	0.0002

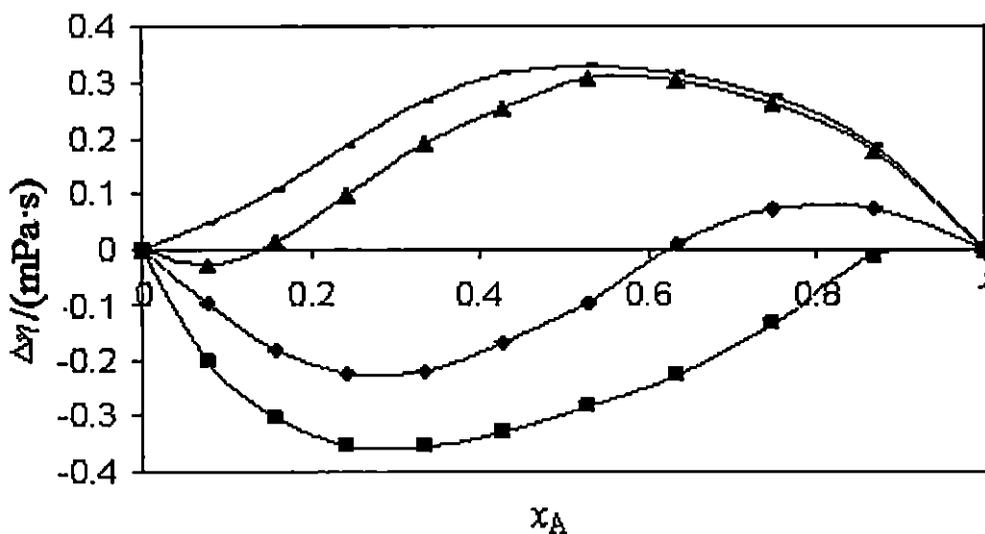
---



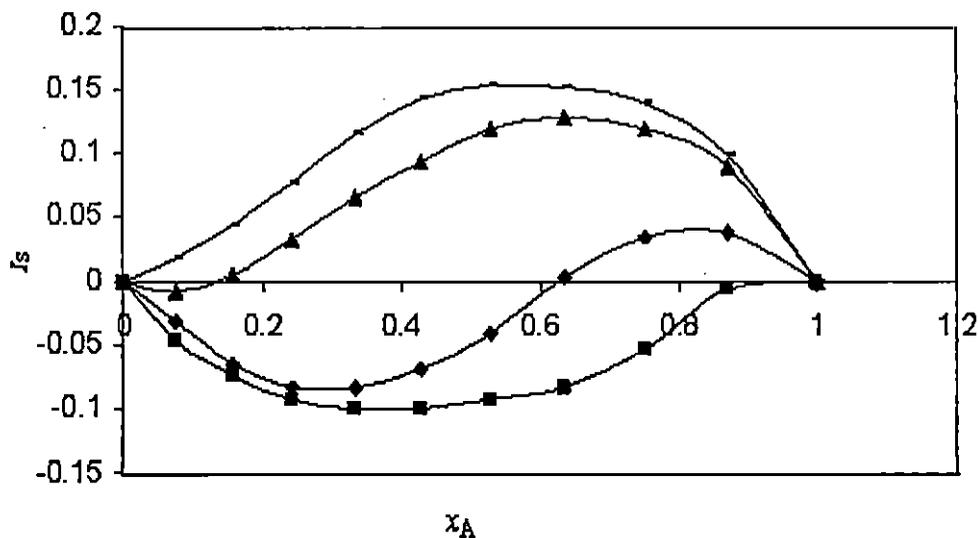
**Figure 1.** Variation of excess molar volumes,  $V^E \times 10^6 / (\text{m}^3 \cdot \text{mol}^{-1})$  against mole fraction ( $x_A$ ) of cyclohexylamine at 298.15 K with *t*-butanol (■), 2-butanol (◆), isobutanol (▲), 1-butanol (-).



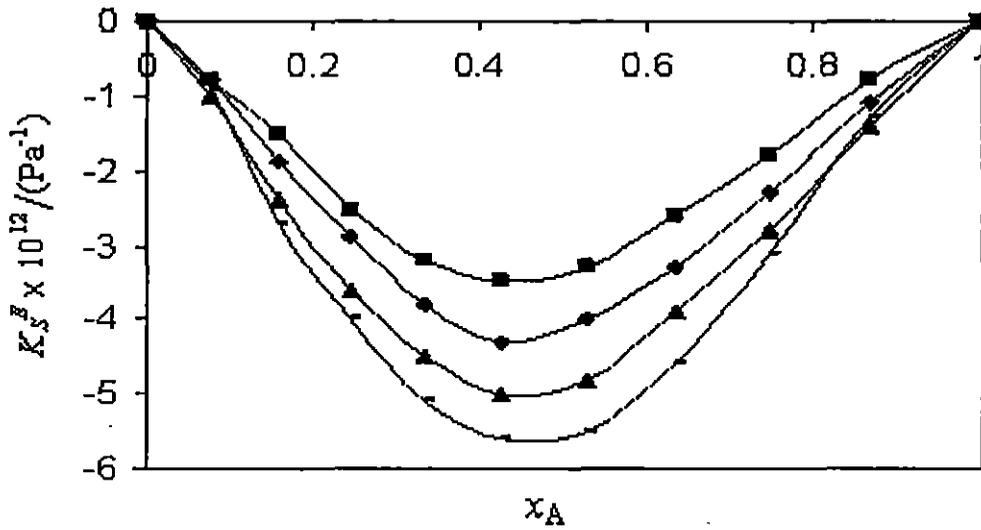
**Figure 2(a).** Experimental,  $\eta_{exp} / (\text{mPa} \cdot \text{s})$ , (—) and calculated,  $\eta_{calc} / (\text{mPa} \cdot \text{s})$ , (---) viscosity against mole fraction ( $x_A$ ) of cyclohexylamine at 298.15 K with *t*-butanol (■), 2-butanol (◆), isobutanol (▲), 1-butanol (-).



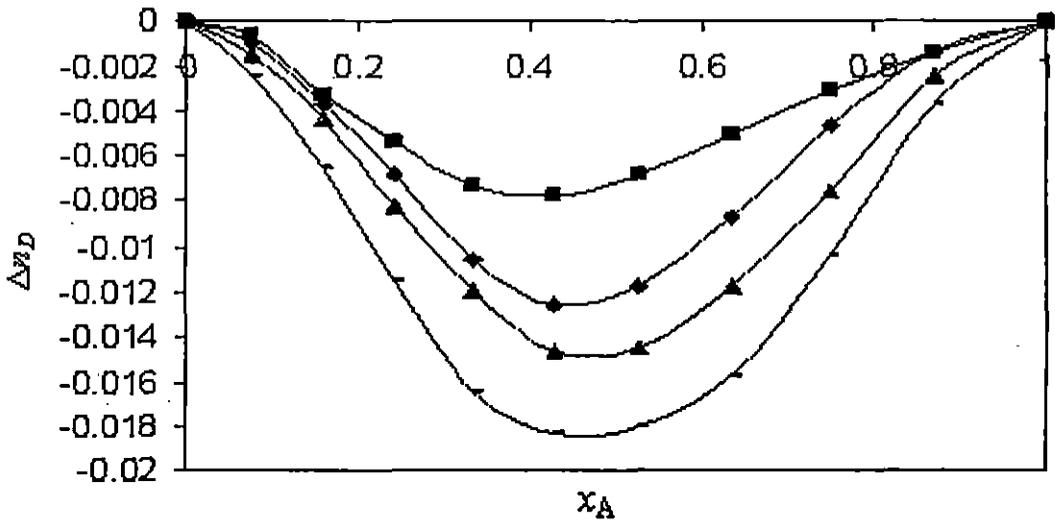
**Figure 2(b).** Variation of deviation in viscosity  $\Delta\eta/(\text{mPa}\cdot\text{s})$  against mole fraction ( $x_A$ ) of cyclohexylamine at 298.15 K. with *t*-butanol (■), 2-butanol (◆), isobutanol (▲), 1-butanol (-).



**Figure 2(c).** Synergic index values ( $I_s$ ) against mole fraction ( $x_A$ ) of cyclohexylamine at 298.15 K with *t*-butanol (■), 2-butanol (◆), isobutanol (▲), 1-butanol (-).



**Figure 3.** Variation of deviation in isentropic compressibility  $K_S^E \times 10^{12} / (\text{Pa}^{-1})$  against mole fraction ( $x_A$ ) of cyclohexylamine at 298.15 K with *t*-butanol (■), 2-butanol (◆), isobutanol (▲), 1-butanol (-).



**Figure 4.** Variation of deviation in refractive index  $\Delta n_D$  against mole fraction ( $x_A$ ) of cyclohexylamine at 298.15 K with *t*-butanol (■), 2-butanol (◆), isobutanol (▲), 1-butanol (-).