August 2015

IJPSS Volume 5, Issue 8 ISSN: 2249-5894

Intermolecular interactions in binary mixtures of 2-Chloroethanol with 2-Dimethylaminoethanol and 2-Diethylaminoethanol at different temperatures: Optical and Internal pressure study

Puneet Kumar Pandey[1], Vrijesh Kumar Pandey[2], Reetesh Srivastava[3], Rajiv Kumar Tripathi[4], S.K. Shukla[5], Anjali Awasthi[6] and Aashees Awasthi[7]

Material Science Research Laboratory,

Department of Physics, University of Lucknow, Lucknow-226 007, India

4, 5 - D. A. V. P. G. College, Lucknow

Abstract

The refractive indices (n_D) and density (ρ) of binary liquid mixtures of 2-Chloroethanol (2-CletOH) with 2-Dimethylaminoethanol (DMAE) and 2-Diethylaminoethanol (DEAE) have been measured over the entire concentration range at temperatures 293.15, 303.15 and 313.15 K. The experimental values of refractive index and density data are used to calculate the molar refraction (R_m), reduced molar free volume (V_m/R_m), molecular radii (r) and internal pressure (P_{int}). The deviations of refractive index (Δn_D), molar refractions (ΔR_m) and reduced molar free volumes $\Delta(V_m/R_m)$ have been also calculated. The variations of these parameters with composition and temperature of the mixtures are discussed in terms of molecular interactions between the unlike molecules of binary liquid mixtures. The applicability of different mixing rules of refractive index is tested against the experimentally measured values.

Keywords: 2-Chloroethanol; molecular interaction; internal pressure; refractive index

1. Introduction

Experimental thermophysical properties are used to obtain information about the molecular level structures of liquid mixtures, as well as about the intermolecular interactions and structural features leading to the behaviour and macroscopic properties of fluids [1]. Moreover, experimental values of thermophysical properties allow establishing new predictive models to determinate the properties necessary for the industry in a fast, reliable and economical way. Intermolecular interactions are a very complex subject, and thus, experimental results and theoretical models have to be combined to elucidate the fluid structure [2]. Prediction of n_D of liquid mixtures is essential for many physicochemical calculations, which include correlation of n_D with density [3] excess molar volume [4, 5] and surface tension [5]. In continuation to our previous works [6–8] in this study, we report the results of our studies on refractive properties of binary mixtures of 2-Chloroethanol (2-CletOH) with 2-Dimethylaminoethanol (DMAE) and 2-Diethylaminoethanol (DEAE). Literature survey [9–15] indicates that refractive index and related properties have been used to study the solute-solvent interactions in the liquid mixtures.

2-Chloroethanol is a polar compound, consisting of both an alkyl chloride and alcohol functional groups. It is a versatile solvent used in many industrial areas. Halogenoalcohols are different from aliphatic alcohols in that halogenoalcohols possess an additional proton-accepting group other than the hydroxyl group. This is significant as they are potentially able to act not only as bi-functional hydrogen bonding solvent but also as a strong proton-donating acid. The protein denaturation ability of halogenoalcohols is much higher than that of aliphatic alcohols. Vapors of 2-chloroethanol possess highly toxic properties, therefore, it should be handled only under extreme precautions for the protection against skin and breathing [16, 17]. Amino-alcohols are bi-functional organic compounds having two kinds of polar groups, hydroxyl and amino

groups, leading to complicated intermolecular interactions with the molecules having polar groups. They are used as chemical intermediates for the pharmaceutical industry [18].

The binary systems of 2-CletOH with DMAE and DEAE are of considerable interest for investigating the intra- and inter-molecular behaviour of given solvent systems. To the best of our knowledge, there has been no temperature-dependent study on these systems from the view point of their refractive index behaviour. This fact allows us to plan some extensive studies in this research field in order to investigate the closest interactions between the unlike molecules by examining the optical and thermodynamic parameters. In this study, we have reported a detailed investigation on the refractive indices (n_D) of binary mixtures of 2-CletOH with DMAE and DEAE at 293.15, 303.15 and 313.15K covering the entire miscibility range ($0 \leq x \leq 1$).

2. Experimental

The chemicals used were of AR grade, 2-Chloroethanol (HiMedia Laboratories Pvt. Ltd., mass fraction purity > 0.980), 2-Dimethylaminoethanol (HiMedia Laboratories Pvt. Ltd., mass fraction purity > 0.980) and 2-Diethylaminoethanol (HiMedia Laboratories Pvt. Ltd., mass fraction purity > 0.990) and were purified by gas chromatography as described in literature [19, 20]. Mixtures were stored in glass stoppered flasks to avoid contamination and evaporation. All mixtures were prepared by mass using Sartorius Electronic balance, Model-CPA225D with a precision of ± 0.01 mg. Density measurements were made using a single-capillary pycnometer made of Borosil glass having a bulb capacity of 13.5 cm^3. The precision of density measurement was ± 0.00001 $g.cm^{-3}$. The measurements were replicated atleast three times for each measurement, and the results reported are the average values. The refractive indices of pure liquids and their binary mixtures were measured using a thermostated Abbe's refractometer. The

refractometer was calibrated by measuring refractive indices of triply distilled water and toluene at known temperatures. The sample mixtures were directly injected into the prism assembly of the instrument by means of an air-tight hypodermic syringe. The refractometer containing the sample to be tested was allowed to stand for around 30 minutes in a thermostatic water bath so as to minimise any possible thermal fluctuations in the refractometer. A minimum of three independent readings were taken for each composition. The temperature was maintained by an electronically controlled thermostated water bath supplied by Orbit. The purity of solvents and reliability of experimental measurements of density and refractive index data was ascertained by comparing the data of pure liquids with the corresponding values, which were available in the literature at 293.15, 303.15 and 313.15 K.

3. Results and discussion

The experimentally measured values of refractive indices (n_D), molar refraction (R_m), reduced molar free volume (V_m/R_m), molecular radii (r) and internal pressure (P_{int}) of both the binary mixtures of 2-CletOH with DMAE and DEAE at different temperatures are shown in Tables 1 and 2, respectively. The deviations of refractive index (Δn_D), molar refractions (ΔR_m) and reduced molar free volumes $\Delta(V_m/R_m)$ are shown in Figures 1–3 (a and b), respectively. The deviations in refractive index (Δn_D) also known as synergy of refractive index has been calculated using the following relation:

$$\Delta n_D = n_{(mix)} - (\emptyset_1 n_{D1} + \emptyset_2 n_{D2}) \quad (1)$$

where, $\emptyset_1$, $\emptyset_2$, n_{D1} and n_{D2} represents the volume fractions and refractive indices of components 1 and 2, respectively.

The molar refraction (R_m) gives information about the presence of specific intermolecular interactions in the binary liquid mixture. The experimental molar refractions (R_m) is obtained by the relation given as:

$$R_m = \left(\frac{n_D^2 - 1}{n_D^2 + 2}\right)\left(\frac{M_1x_1 + M_2x_2}{\rho_m}\right) \quad (2)$$

where, ρ_m is the density of the mixture, x_1 and x_2 are mole fractions and M_1 and M_2 are the molecular weights of component 1 and 2, respectively. Deviations in molar refractions have been calculated using the relation as [21]:

$$\Delta R_m = R_m - (x_1R_{m1} + x_2R_{m2}) \quad (3)$$

where, R_{m1} and R_{m2} are the molar refractions of pure components 1 and 2, respectively. The deviations of reduced molar free volumes have been calculated using the relation [21]:

$$\Delta\left(\frac{V_m}{R_m}\right) = \left(\frac{n_D^2 + 2}{n_D^2 - 1}\right) - \left(\frac{x_1V_1 + x_2V_2}{x_1R_{m1} + x_2R_{m2}}\right) \quad (4)$$

The theoretical estimation of molecular radii of pure liquids can be successfully done by using the values of refractive index as:

$$r = \left[\left\{\left(\frac{3}{4\pi N_A}\right)\left(\frac{n_D^2 - 1}{n_D^2 + 2}\right)\right\}V_m\right]^{1/3} \quad (5)$$

Internal pressures of binary liquid mixture can be evaluated using the well-known Buchler–Hirschfelder–Curtiss equation of state given as [22]:

$$P_{int} = \frac{2^{1/6}RT}{2^{1/6}V_m - 2rN_A^{1/3}V_m^{2/3}} \quad (6)$$

Various mixing rules are used to predict the refractive index of binary mixtures from density of the mixtures together with refractive indices of the pure components. In this study, we

Various mixing rules are used to predict the refractive index of binary mixtures from density of the mixtures together with refractive indices of the pure components. In this study, we have applied nine different mixing rules [23,24], viz, Arago - Biot (A-B), Newton (Nw), Heller (H), Gladstone-Dale (G-D), Eyring-John (E-J) [25], Eykman (Eyk), Lorentz-Lorenz (L-L), Weiner (W) and Oster (Os) to test their validities for the present systems.

It is observed that the experimental refractive index of 2-CletOH + DMAE and 2-CletOH + DEAE systems increases linearly with an increase in mole fractions of 2-CletOH. Figures 1 (a & b) exhibit that Δn_D values are positive and nonlinear over the entire composition range at all temperatures for both the systems. The Δn_D value shows maximum at $x_1 \sim 0.5001$ for (2-CletOH + DMAE) and $x_1 \sim 0.4984$ for (2-CletOH + DEAE) binary system. It is well known that the refractive index deviation depend on several energetic and structural effects [26, 27]. The positive deviations Δn_D (on volume fraction dependence basis) is considered due to the presence of significant interactions in the mixtures, whereas negative deviations Δn_D indicates weak interactions between the contributing components of the mixtures [28]. The observed variations of Δn_D values indicate the presence of significant interactions in these mixtures.

Figure 2 (a & b) show the deviation in molar refraction (ΔR_m) with mole fractions (x_1) of 2-CletOH. The molar refraction is a sensitive function of wavelength, temperature and solution composition. A negative non-linear trend is observed in ΔR_m values, for both the binary liquid mixtures, over the entire concentration range. The negative value of ΔR_m suggest the presence of strong intermolecular interactions between the components of the liquid mixtures. The values of ΔR_m slightly decrease with increase in the temperature [23].

Figure 3(a & b) present the deviations of reduced molar free volume versus mole fraction of 2-CletOH. The values of deviations of reduced molar free volume $\Delta(V_m/R_m)$ are negative and nonlinear over the whole concentration range, at all temperatures, for both the systems. Brocos et al. [21] stated that the molar refraction deviation function must be calculated on mole fraction basis and refractive index deviation function on volume fraction basis, which makes it directly interpretable as a sign-reversed measure of the deviations of reduced free volumes from ideality. According to their suggestions, we have evaluated all the deviation functions, Δn_D, ΔR_m and $\Delta(V_m/R_m)$ and found that deviations in refractive index Δn_D have the opposite sign to the

deviation in reduced free molar volume, $\Delta(V_m/R_m)$, for the present binary system [5, 28]. Negative values of $\Delta(V_m/R_m)$ show the minima at the same concentrations where positive values of Δn_D maxima occur. Negative values of $\Delta(V_m/R_m)$ show strong molecular interactions between the components of the liquid mixtures [23].

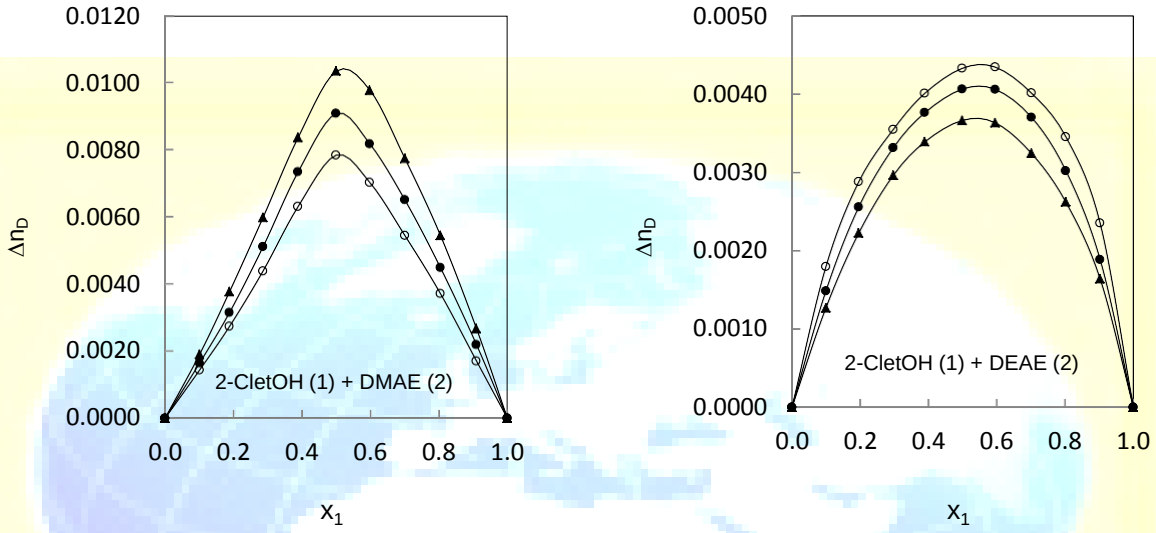

Fig. 1(a, b): Plots of refractive index (Δn_D) versus mole fraction (x_1) of 2-Chloroethanol for binary systems at (o) 293.15 K, (•) 303.15 K, ( ) 313.15 K.

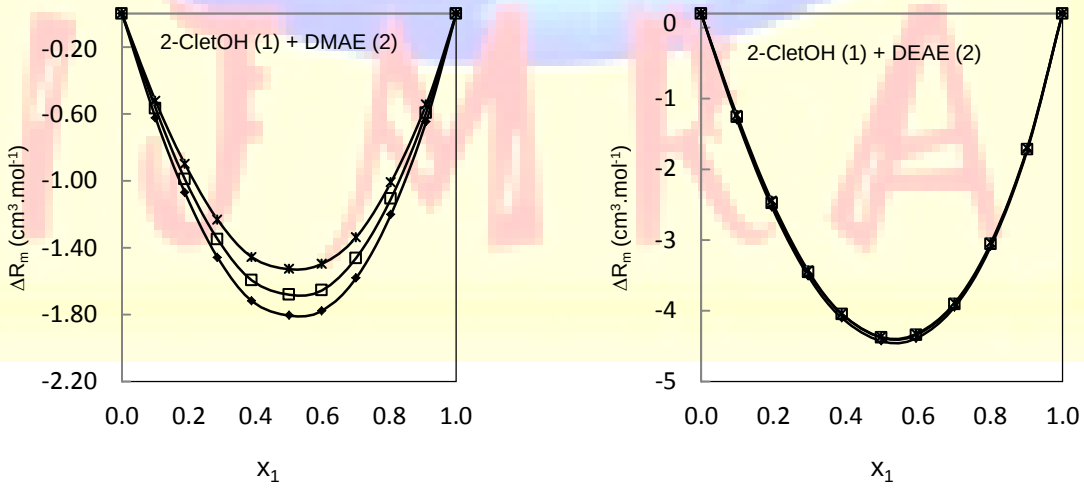

Fig. 2 (a, b): Plots of excess molar refraction (ΔR_m) versus mole fraction (x_1) of 2-Chloroethanol for binary systems at (o) 293.15 K, (•) 303.15 K, ( ) 313.15 K.

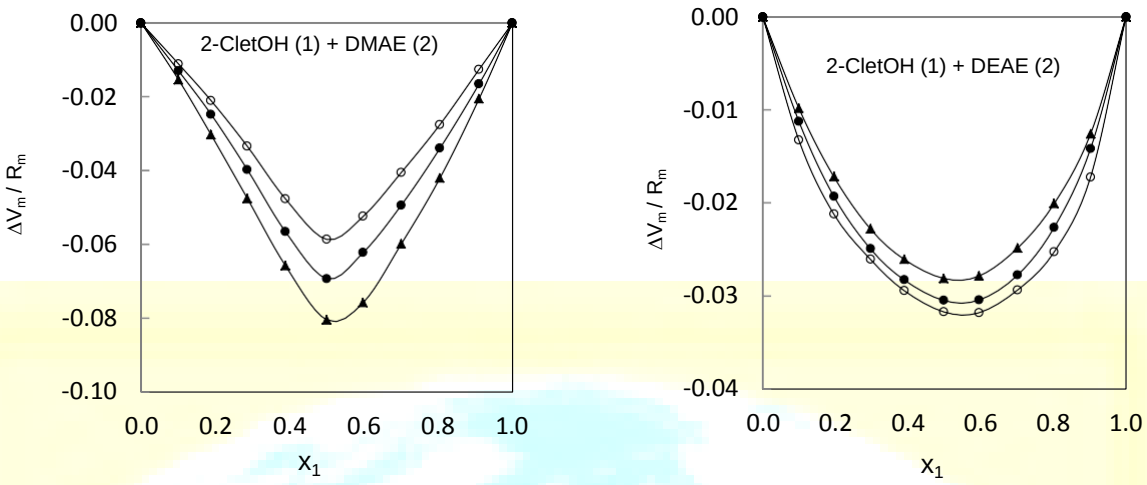

Fig. 3 (a, b): Plots of deviations of reduced molar free volume $\Delta(V_m/R_m)$ versus mole fraction (x_1) of 2-Chloroethanol for binary systems at (o) 303.15 K, (•) 313.15 K, ( ) 323.15 K.

The predicted refractive indices of the binary mixtures at each temperature studied were compared with the experimentally measured values and the results are presented in terms of APD. A close perusal reveals that all the mixing rules show good agreement with experimental values for the both 2-CletOH + DMAE and 2-CletOH + DEAE systems. The results show the W, Nw, Os, A-B, G-D, Eyk and E-J relations with minimum percentage deviations, providing excellent agreement for the present systems. This may be because W's relation is based on the assumption that the molecules are spherically symmetrical, whereas in the case of Nw's and Os's relations, this is not so. Furthermore, the APD values of A-B and G-D are similar for the systems studied, as expected for volume additivity. However, L-L and H relations show relatively large percentage deviations for the both systems.

4. Conclusions

In this article, the refractive indices (n_D) of binary mixtures of 2-Chloroethanol with DMAE and DEAE have been measured over the whole composition range at 293.15, 303.15 and 313.15 K. The variations of refractive index and related parameters with composition and temperature of the mixtures are discussed in terms of molecular interactions due to physical, chemical and structural effects between the unlike molecules. The results were analysed in terms

of the molecular characteristics of the interacting molecules and found significant interactions in the given binary mixtures.

References

[1] Y. Marcus, *Solvent Mixtures, Properties and Selective Solvation*, Marcel Dekker, New York,2002.

[2] J. N. Murrell, A. D. Jeankins, *Properties of Liquids and Solutions*, John-Wiley & Sons Ltd., Chichester, 1994.

[3] A. F. Fucaloro, J. Chem. Educ. 79 (2002) 865.

[4] B. Giner, C. Lafuente, A. Villares, M. Haro, C. M. Lopez, J. Chem. Thermodyn. 39 (2007)148.

[5] A. Pineiro, P. Brocos, A. Amigo, M. Pintos, R. Bravo, Phys. Chem. Liqs. 38 (2000) 251.

[6] P. K. Pandey, A. Awasthi, A. Awasthi, Chem. Phys. 423 (2013) 119.

[7] P. K. Pandey, A. Awasthi, A. Awasthi, J. Mol. Liq. 187 (2013) 343.

[8] P. K. Pandey, A. Awasthi, A. Awasthi, Phys. Chem. Liqs. (In Press) (2013).

[9] P. Pradhan, M. N. Roy, Phys. Chem. Liqs. 49 (2011) 286.

[10] Y. C. Kao, C. H. Tu, J. Chem. Thermodyn. 43 (2011) 216.[11]

A. K. Nain, J. Mol. Liq. 140 (2008) 108.

[12] R. Francesconi, S. Ottam, J. Mol. Liq. 133 (2007) 125.

[13] T. M. Aminabhavi, B. Gopalakrishna, J. Chem. Eng. Data 40 (1995) 462.

[14] J. D. Pandey, P. Jain, V. Vyas, Can. J. Chem. 72 (1994) 2486.

[15] T. M. Aminabhavi, B. Gopalakrishna, J. Chem. Eng. Data 40 (1995) 856.

[16] K. Mizuno, H. Kaido, K. Kimura, K. Miyamoto, N. Yoneda, T. Kawabata, T. Tsurusaki, N. Hashizume, Y. Shindo, J. Chem. Soc., Faraday Trans. 1 80 (1984) 879.

[17] J. A. Gordon, W. P. Jencks, Biochemistry 2 (1963) 47.

[18] M. W. Sanders, L. Wright, L. Tate, G. Fairless, L. Crowhurst, N. C. Bruce, A. J. Walker, G. A. Hembury, S. Shimizu, J. Phys. Chem. A 113 (2009) 10143.

[19] J. A. Riddick, W. B. Bunger, T. Sakano, *Organic Solvents: Physical Properties and Methodsof Purification*, Wiley Interscience, New York, 1986.

[20] A. I. Vogel, *Text Book of Practical Organic Chemistry*, Longman Green, London, 1989.

[21] P. Brocos, A. Pineiro, R. Bravo, A. Amigo, Phys. Chem. Chem. Phys. 5 (2004) 550.

[22] J. O. Hirschfelder, C. F. Curtiss, R. B. Bird, *Molecular Theory of Gases and Liquids* , John-Wiley, New York, 1964.

[23] A. Ali, M. Tariq, Chem. Eng. Comm. 195 (2008) 43.

[24] H. Eyring, M. S. John, *Significant Liquid Structure*, John-Wiley & Sons, New York, 1969.

[25] H. Eyring, J. F. Kinkaid, J. Chem. Phys. 6 (1938) 620.

[26] L. M. Cases, G. Marino, E. Mascato, M. Iglesias, B. Orge, J. Tojo, Phys. Chem. Liqs. 43 (2005) 473.

[27] B. Giner, I. Gason, H. Artigas, A. Villares, C. Lafuente, J. Therm. Anal. Cal. 83 (2006) 735.

[28] A. K. Nain, J. Chem. Eng. Data 53 (2008) 1208.