



# Studies of physical properties on molecular interactions in binary liquid mixtures of 3-chloroaniline with isomeric butanols at different temperatures



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## ABSTRACT

The thermophysical parameters, viz. excess molar volume ( $V^E$ ), viscosity ( $\eta$ ), speed of sound ( $u$ ) and spectroscopic parameter (FTIR) have been measured for binary mixtures of 3-chloroaniline with isomeric butanols (1-butanol, 2-butanol and 2-methyl-2-propanol) over the entire range of mole fraction at 303.15, 308.15, 313.15 K and 318.15 K. The excess isentropic compressibility, deviation in excess viscosity and excess Gibbs energy of activation of viscous flow have also been estimated and analyzed. The spectroscopic measurement confirms that the interaction between unlike molecules takes place through hydroxyl groups of isomeric butanols. A good agreement is obtained between excess quantities and spectroscopic data.

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## 1. Introduction

The physicochemical properties of binary mixtures have been studied for several reasons, one of the most important of which is that these properties provide information about molecular interactions. Further such data are required in many chemical engineering calculations involving mass-transfer, fluid flow, and heat-transfer operations. The present investigation is a continuation of our earlier research [1–5] on thermodynamic properties of binary liquid mixtures. The liquids were chosen in the present study on the basis of their industrial importance. 3-Chloroaniline is chosen as a polar solvent and self associated through hydrogen bonding of its amine group. The amino group in 3-chloroaniline is an electron donor and  $-NH_2$  group can also play the role of proton-acceptor center. 3-Chloroaniline is used as an intermediate in the production of a number of products, including agricultural chemicals, azo dyes and pigments, bactericide or biocide and pharmaceuticals. Isomeric butanols are used as hydraulic fluids in pharmaceutical and cosmetics, in medications for animals, in manufacturing perfumes, paint removers, flavors and dye-stuffs, as defrosting and as an antiseptic agent. The aim of the present work consists of knowing the effect of the position of the  $-OH$  group in the isomeric butanol molecule which can affect both the sign and magnitude of various thermodynamic functions when mixed with 3-chloroaniline. For this, measurements of density, speed of sound and

viscosity of the binary mixtures (3-chloroaniline + isomeric butanols) were performed over the entire range of composition in the temperature range of 303.15–318.15 K at intervals of 5 K. In the present paper we report densities ( $\rho$ ), speed of sounds ( $u$ ) and viscosities ( $\eta$ ) of the binary mixtures of 3-chloroaniline with isomeric butanols including pure liquids at different temperatures over the entire composition range. By using this data, excess volume ( $V^E$ ), excess isentropic compressibility ( $\kappa_s^E$ ), deviation in viscosity ( $\Delta\eta$ ) and excess Gibbs free energy of activation of viscous flow ( $G^{*E}$ ) of isomeric butanols in 3-chloroaniline have been calculated and are fitted to the Redlich–Kister polynomial equation. The variations of the excess properties with composition are discussed from the strong association between the isomeric butanols and 3-chloroaniline molecules through the hydrogen bond. Generally, FT-IR spectral technique [6] offers the advantages to measure the association properties and hydrogen bonding capability and to assess the interaction of alcohol with water and polar by analyzing band shifts and changes of band shape. Furthermore, FT-IR is also advantageous to evaluate the vibrational properties of bonds through very thin solution films which are usefully difficult to handle for the floating properties of solution.

## 2. Experimental

### 2.1. Materials

All the chemicals used in the present work were of analytical reagent grade produced from Merck and their purities were as follows:

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3-chloroaniline (0.995), 1-butanol (0.996), 2-butanol (0.996) and 2-methyl-2-propanol (0.996). The source, purity and water contents of solvents used in this work are listed in Table 1. Prior to making experimental measurements, all the liquids were used after double distillation and partially degassed with a vacuum pump under an inert atmosphere. The purity of all these solvents was compared with the measured density and viscosity of the pure liquids with the literature [7–10] and it is given in Table 2. The water content of solvents used in this work was measured by Analab (MicroAqua Cal 100) Karl Fischer Titrator. It can detect water content from less than  $10 \times 10^{-6}$  to 100% by conductometric titration with dual platinum electrodes. All the binary liquid mixtures were prepared by weighing an amount of pure liquids in an electric balance (ER-120A, Afoset, and India) with a precision of  $\pm 0.1$  mg by syringing each component into air-tight stopper bottles to minimize evaporation losses. The uncertainty of the mole fraction was  $\pm 1 \times 10^{-4}$ .

## 2.2. Apparatus and procedure

Densities of the pure liquids and their mixtures were measured by using Rudolph Research Analytical digital densimeter (DDH-2911 Model), and these measurements were carried by carefully filling the sample into the U-tube of the densimeter through a syringe. We have also ensured that there was no bubble formation during the measurement since the cell should be air-free. The density was measured automatically at the specified temperature with an accuracy of  $\pm 0.00005$  K. The uncertainty in the density measurement is  $\pm 5 \times 10^{-5} \text{ g}\cdot\text{cm}^{-3}$ . Proper calibration at each temperature was achieved with doubly distilled deionized water and with air as standards. The viscosities of pure liquids and their mixtures were determined at atmospheric pressure and at  $T = 303.15$  to  $318.15$  K by using an Ubbelohde viscometer, which was calibrated with benzene, carbon tetrachloride, acetonitrile, and doubly distilled water. The kinetic energy corrections were calculated from these values and they were found to be negligible. The Ubbelohde viscometer bulb has a capacity of 15 ml and the capillary tube has a length of about 90 mm with 0.5 mm internal diameter. The viscometer was thoroughly cleaned and perfectly dried, filled with the sample liquid by fitting the viscometer to about  $30^\circ$  from the vertical and its limbs are closed with Teflon caps to avoid the evaporation. The viscometer was kept in a transparent walled bath with a thermal stability of  $\pm 0.01$  K for about 20 min to obtain thermal equilibrium. An electronic digital stopwatch with an uncertainty of  $\pm 0.01$  s was used for flow time measurements. The uncertainty of viscosity thus estimated was found to be  $\pm 0.005 \text{ mPa}\cdot\text{s}$ . The speed of sound measurements was performed using a commercially available single crystal ultrasonic interferometer (Model F-05), from Mittal Enterprise, New Delhi, India operated at 2 MHz frequency at various temperatures. A thermostatically controlled, well-stirred circulated water bath with a temperature controlled at  $\pm 0.01$  K was used for all the speed of sound measurements. The uncertainty in the measured speed of sound is  $\pm 0.5 \text{ m}\cdot\text{s}^{-1}$ . The working of the interferometer was tested by making measurements for pure samples of benzene, toluene, chloroform, chlorobenzene and acetone and the measured speeds of sound of these liquids were in good agreement with those reported in the literature [11].

## 3. Results and discussion

Measured data of density and viscosity are used to calculate excess molar volumes ( $V^E$ ), deviation in viscosity ( $\Delta\eta$ ), and excess Gibbs energy of activation of viscous flow ( $G^{*E}$ ) using the following equations:

$$V^E(\text{cm}^3/\text{mol}) = [x_1M_1 + x_2M_2]/\rho - [x_1M_1/\rho_1 + x_2M_2/\rho_2] \quad (1)$$

$$\Delta\eta/\text{mPa}\cdot\text{s} = \eta - [x_1\eta_1 + x_2\eta_2] \quad (2)$$

$$G^{*E}(\text{J/mol}) = RT[\ln\eta V - (x_1 \ln\eta_1 V_1 + x_2 \ln\eta_2 V_2)] \quad (3)$$

where for each equation,  $\rho$ ,  $V$ , and  $\eta$  are the density, the molar volume and the dynamic viscosity of the mixtures and  $x_i$ ,  $V_i$ ,  $M_i$ , and  $\eta_i$  ( $i = 1, 2$ ) are the mole fraction, molar volume, the molar mass and the dynamic viscosity of the components 3-chloroaniline (1) and isomeric butanols (2), respectively.  $R$  is the gas constant and  $T$  is the absolute temperature.

The excess isentropic compressibilities ( $\kappa_s^E$ ) were obtained from the relation [12]

$$\kappa_s^E = \kappa_s - \kappa_s^{\text{id}} \quad (4)$$

where,  $\kappa_s$  is the isentropic compressibility and was calculated using Laplace relation,

$$\kappa_s = u^{-2}\rho^{-1} \quad (5)$$

where,  $\kappa_s^{\text{id}}$  is the ideal value of the isentropic compressibility and was calculated from the following equation [12]

$$\kappa_s^{\text{id}} = \sum_{i=1}^2 \phi_i [\kappa_{s,i} + TV_i(\alpha_i^2)/C_{p,i}] - \left\{ T \left( \sum_{i=1}^2 x_i V_i \right) \left( \sum_{i=1}^2 \phi_i \alpha_i \right)^2 / \sum_{i=1}^2 x_i C_{p,i} \right\} \quad (6)$$

where,  $\phi_i$  is ideal state volume fraction of component  $i$  in the mixture and is defined by relation,

$$\phi_i = x_i V_i^0 / (\sum x_i V_i^0). \quad (7)$$

$T$  is temperature and  $\kappa_{s,i}$ ,  $V_i^0$ ,  $\alpha_i^0$  and  $C_{p,i}$  are isentropic compressibility, molar volume, coefficient of isobaric thermal expansion and molar heat capacity respectively, for pure component  $i$ .  $\alpha_i^0$  is calculated from measured densities by relation,

$$\alpha_i^0 = [(\rho_1/\rho_2) - 1]/(T_2 - T_1). \quad (8)$$

The experimental values of density ( $\rho$ ), viscosity ( $\eta$ ) and speed of sound ( $\mu$ ) of the binary liquid mixtures of 3-chloroaniline with isomeric butanols at temperatures  $T = 303.15$  to  $318.15$  K are given in Table 3.

The excess molar volume ( $V^E$ ), deviation in viscosity ( $\Delta\eta$ ) and excess isentropic compressibility ( $\kappa_s^E$ ) values are given in Table 4. The negative  $V^E$  values indicate the presence of strong molecular interactions between the components of the mixtures. Several effects may contribute to the value of  $V^E$ , such as (i) dipolar interactions, (ii) interstitial accommodation of one component into the other and (iii) hydrogen bond interactions between unlike molecules. The actual volume change,

**Table 1**

Provenance and purity of the materials used.

Chemical name	CAS Number	Source	Water content (%)	Mass fraction purity
3-chloroaniline	108-42-9	S.D. Fine Chemicals, India	0.042	0.995
1-butanol	71-36-3	S.D. Fine Chemicals, India	0.040	0.996
2-butanol	78-92-2	S.D. Fine Chemicals, India	0.038	0.996
2-methyl-2-propanol	75-65-0	S.D. Fine Chemicals, India	0.038	0.996

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