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Specific Molecular Interactions of Dihydropyridine Moiety in Polar and Non-Polar Solvents at Various Concentrations and Temperatures 303–318 K on Ultrasonic Data[1]

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Abstract—Ultrasonic studies of compounds of dihydropyridine series in polar and non-polar solvents at various concentrations and temperatures 303–318 K. Density and ultrasonic velocity and different thermoacoustical parameters measured. Rao's constant, molar volume, Wada's constant, isothermal compressibility reported with the help of these data using standard formulae. Ethanol and DMF selected as polar and non-polar solvents respectively. The variation in thermoacoustical parameters with temperature and concentration shows that the solute–solute molecular interaction takes place in solution which is more in DMF.

Keywords: dihydropyridine, adiabatic compressibility, intermolecular free length, acoustic impedance, surface tension, Rao's constant, molar volume, Wada's constant, isothermal compressibility

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INTRODUCTION

Ultrasonic velocity measurements are used in understanding the molecular interactions in liquids. We already reported the ultrasonic studies on molecular interactions in *N*-phenyl-3-(pyridin-4-yl) prop-2-enamide as well as pyridoxine solutions in polar and non-polar solvents at different temperatures [1, 3]. Acoustical study on molecular interaction is also reported by Kukade et al. [2], Kharat [4] and Sasaki et al. [5]. Many researchers used IR spectroscopy to illustrate hydrogen bonding [6–9].

EXPERIMENTAL

Digital ultrasonic pulse echo velocity meter (Vi Microsystems Pvt. Ltd., India, Model no. VCT 70) used to measure the ultrasonic velocity of solutions. Here, ultrasonic studies of compounds of dihydropyridine series i.e. diethyl 1-(2-(1,3-dioxoisoindolin-2-yl)butanoyl)-2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (C-DHP-1), diethyl 1-(2-(1,3-dioxoisoindolin-2-yl)-3-methylbutanoyl)-2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (C-DHP-2) and diethyl 1-(2-(1,3-dioxoisoindolin-2-yl)-3-methylbutanoyl)-2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (C-DHP-3) studied in ethanol and DMF at various concentrations and temperatures viz. 303, 308, 313, and 318 K. Structures of solutes are given in Fig. 1.

By measuring ultrasonic velocity and density, various acoustic parameters are calculated which are mentioned below. The variations of these properties with concentration and different temperature are represented by graphs.

From ultrasonic velocity and density data, various acoustic parameters are calculated using following formulae:

ultrasonic velocity

$$\upsilon,\ \mathrm{ms^{-1}} = f\lambda,$$

where f is frequency of ultrasonic waves, λ is wave length;

adiabatic compressibility

$$\kappa,\ \mathrm{kg^{-1}\ ms^{2}} = 1/\upsilon^2\rho,$$

where υ is ultrasonic velocity, ρ is density of the solution;

acoustic impedance

$$Z,\ \mathrm{kg\ m^{-2}\ s^{-1}} = \upsilon\rho,$$

where υ is ultrasonic velocity, ρ is density of the solution;

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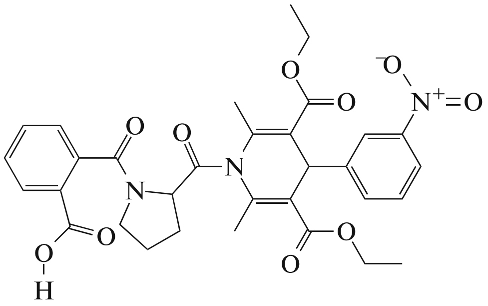
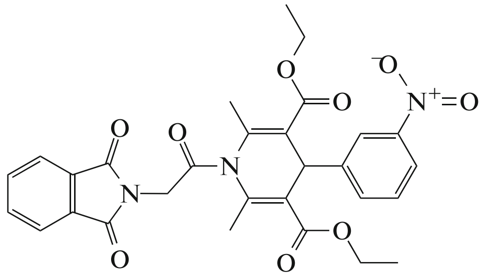
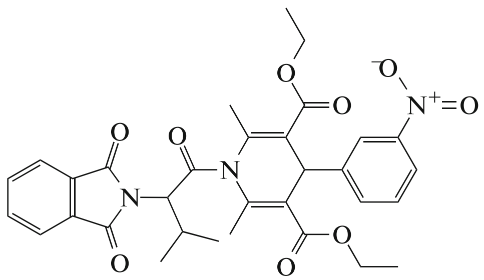


Diethyl 1-(2-(1,3-dioxoisoindolin-2-yl)butanoyl)-2,6-dimethyl-
4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (C-DHP-1)



Diethyl 1-(2-(1,3-dioxoisoindolin-2-yl)-3-methylbutanoyl)-2,6-dimethyl-
4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (C-DHP-2)



Diethyl 1-(2-(1,3-dioxoisoindolin-2-yl)-3-methylbutanoyl)-2,6-dimethyl-
4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (C-DHP-3)

Fig. 1. Structure of solutes.

free length

$$L_{\mathrm{f}},\ \mathrm{m} = K/\upsilon\rho^{1/2},$$

where υ is ultrasonic velocity, ρ is density, K (Jacobson temperature dependent constant) = $(93.875 + 0.345T) \times 10^{-8}$;

isothermal compressibility (β_T):

$$\beta_{T,n\text{–mix}} = \frac{17.1\times10^{-4}}{\nu_{n\text{–mix}}^{2}T^{4/9}\rho_{n\text{–mix}}^{4/3}},$$

where ρ is density, ν is velocity;

Rao's constant

$$R = M/\rho v^{1/3},$$

where ρ is density, v is molar volume, and M is molecular weight;

surface tension (v)

$$v = (S/6.3\times10^{-4}\rho)^{2/3};$$

molar volume (it is the ratio of density and molecular weight)

$$V_{\mathrm{m}} = \frac{\rho}{M};$$

Wada's constant

$$W = (M\beta^{-1/7})/\rho,$$

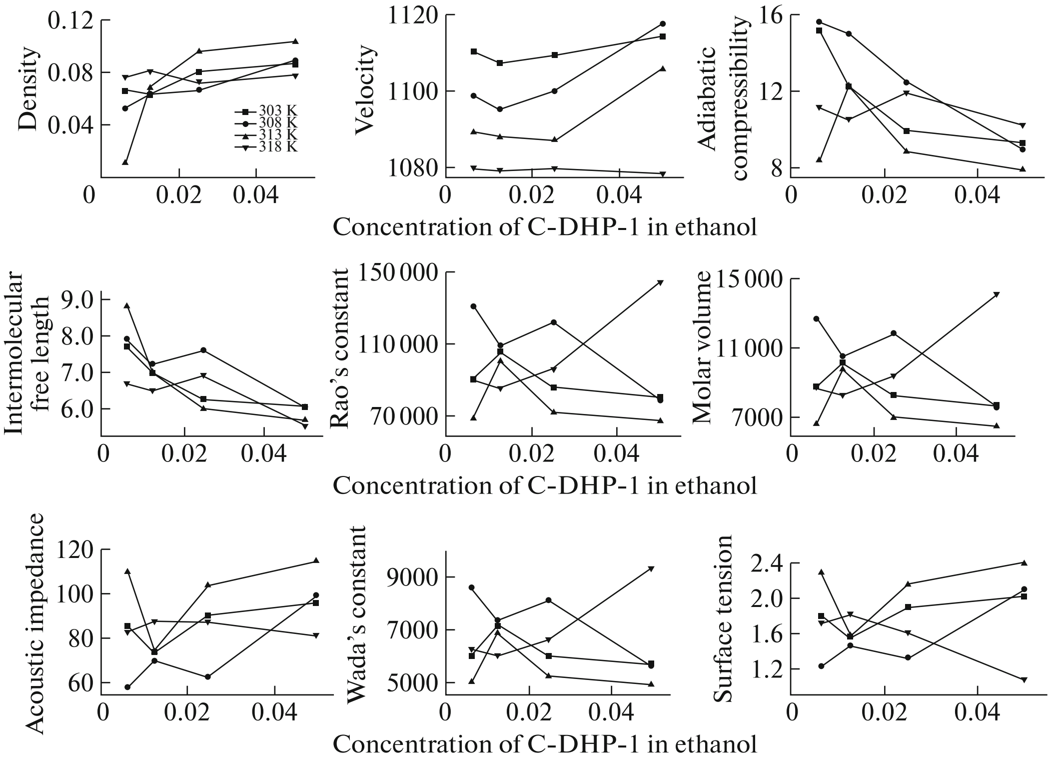


Fig. 2. Density, velocity, adiabatic compressibility, intermolecular free length, acoustic impedance, molar volume, Rao's constant, Wada's constant, surface tension at various temperature and concentration for (C-DHP-1 in ethanol).

where ρ is density, β is adiabatic compressibility, and *M* is molecular weight.

FTIR spectra were recorded on Bruker Alpha FTIR spectrometer at Department of Chemistry, Jankidevi Bajaj College of Science, Wardha.

RESULT AND DISCUSSION

Acoustical Study

The increase in velocity with concentrations, indicates the increase in cohesive forces due to solute-solvent interactions and it also suggests the intermolecular attractions, macromolecular motion in solution. Moreover, the increase in ultrasonic velocity also indicates the possibility of H-bond formation between solute and solvent. Density is measure of solvent–solvent and solute–solvent interaction. If value of density increases with increase in concentration, it indicates increase in solvent–solvent and solute–solvent interaction due to structure making ability of solute in presence of solvent. Adiabatic compressibility has the inverse relation with the ultrasonic velocity. The decrease in compressibility takes place due to a closer packing which leads to a decrease of intermolecular free length.

Free length or intermolecular free length (L_f) is the distance between the surfaces of the adjacent molecules. Intermolecular free length (L_f) changes due to intermolecular attraction or repulsion. With increase in concentration, number of ions or particles increases in a given solution which leads to decrease in the gap (intermolecular free length) between two species. The intermolecular free length values decreases with the increasing values of ultrasonic velocity. It indicates significant interaction among solute and solvent molecules, due to which the structural arrangements in the adjacent constituent ions is considerably affected. The closer packing molecule suggests the dipole-dipole interaction between solute and solvent.

When an acoustic wave travels in any medium, pressure varies from particle to particle. The ratio of the instantaneous pressure excess at any particle in medium to the instantaneous velocity of that particle in medium is acoustic impedance of that medium. The increase in impedance values also suggests effective solute–solvent interactions. Positive values of molar volume suggests the effective interaction between the solute and solvent molecules because of increase in pressure and cohesive energy of the system due to strong interaction. Further, the increasing trends of apparent molar volume of systems with increase in molarity confirms the presence of strong solute–solvent as well as ion–solvent interactions

The molar sound velocity (Rao's constant) and molar compressibility (Wada's constant) increases with increase in temperature. This variation confirms

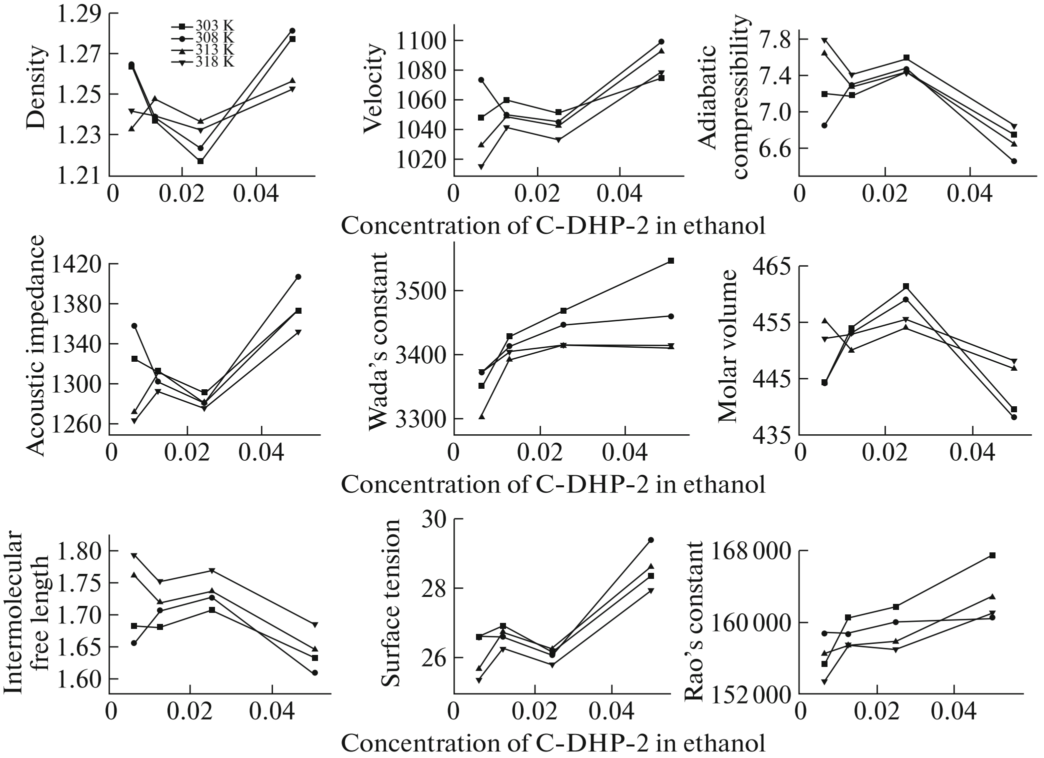


Fig. 3. Density, velocity, adiabatic compressibility, intermolecular free length, acoustic impedance, molar volume, Rao's constant, Wada's constant, surface tension at various temperature and concentration for (C-DHP-2 in ethanol).

the change in molecular interaction. The values of surface tension also increase with increase in concentration and temperatures. Surface tension is used to study the surface composition in aqueous solution. A variation of surface tension supports the attractive interactions between the solute and solvent.

In the present ultrasonic study of C-DHP-1, C-DHP-2, and C-DHP-3, observations are as follows.

1. For C-DHP-1 in ethanol: values of density, ultrasonic velocity, acoustic impedance and surface tension increases with increase in concentration and values of adiabatic compressibility as well as intermolecular free length decreases with increase in concentration which indicates strong solute–solvents interaction. Values of Rao's constant, molar volume and Wada's constant increases with increase in concentration for temperature 318 K which indicate more solute–solvent interaction than other temperatures (Fig. 2).

2. For C-DHP-2 in ethanol : values of density, ultrasonic velocity, acoustic impedance, surface tension, Rao's constant, molar volume (up to 0.025% concentration), Wada's constant increases with increase in concentration and values of adiabatic compressibility as well as intermolecular free length decreases with increase in concentration indicates strong solute–solvents interaction (Fig. 3).

3. For C-DHP-3 in ethanol : values of density, ultrasonic velocity, acoustic impedance, surface tension increases with increase in concentration &values of adiabatic compressibility as well as intermolecular free length decreases with increase in concentration indicates strong solute–solvents interaction. Upto 0.025% concentration, values of Rao's constant, molar volume, wada's constant increases with increase in concentration for 308 K temperature indicates strong more solute–solvents interaction at that temperature than other temperature where these parameters shows opposite trends (Fig. 4).

4. For C-DHP-1 in DMF : with increase in concentration, values of parameters such as density, ultrasonic velocity, acoustic impedance, surface tension, molar volume (except Rao's constant and Wada's constant) increases and values of adiabatic compressibility as well as intermolecular free length decreases which indicates strong solute–solvents interaction (Fig. 5).

5. For C-DHP-2 in DMF : with increasing concentration, increasing values of parameters such as density, ultrasonic velocity, acoustic impedance, surface tension, molar volume (at 303 K), Rao's constant (at 303 K) and wada's constant (at 303 K) indicates strong solute–solvent interaction. Decreasing values of adiabatic compressibility as well as intermolecular free length also indicates strong solute–solvents interaction (Fig. 6).

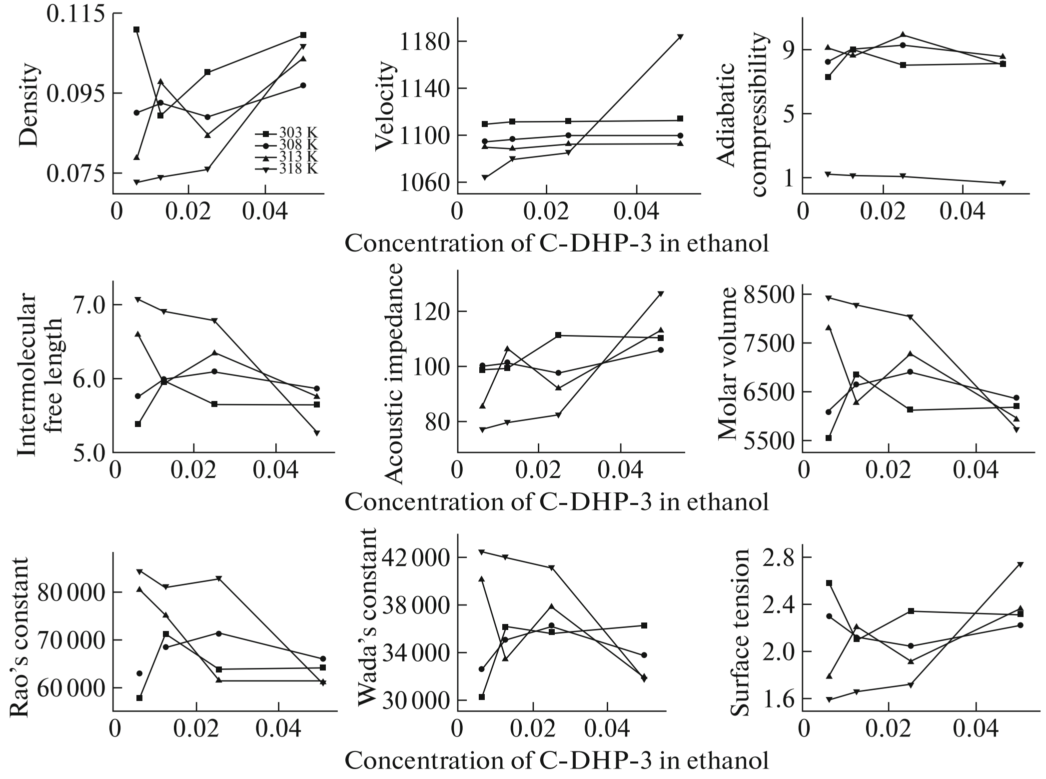


Fig. 4. Density, velocity, adiabatic compressibility, intermolecular free length, acoustic impedance, molar volume, Rao's constant, Wada's constant, surface tension at various temperature and concentration for (C-DHP-3 in ethanol).

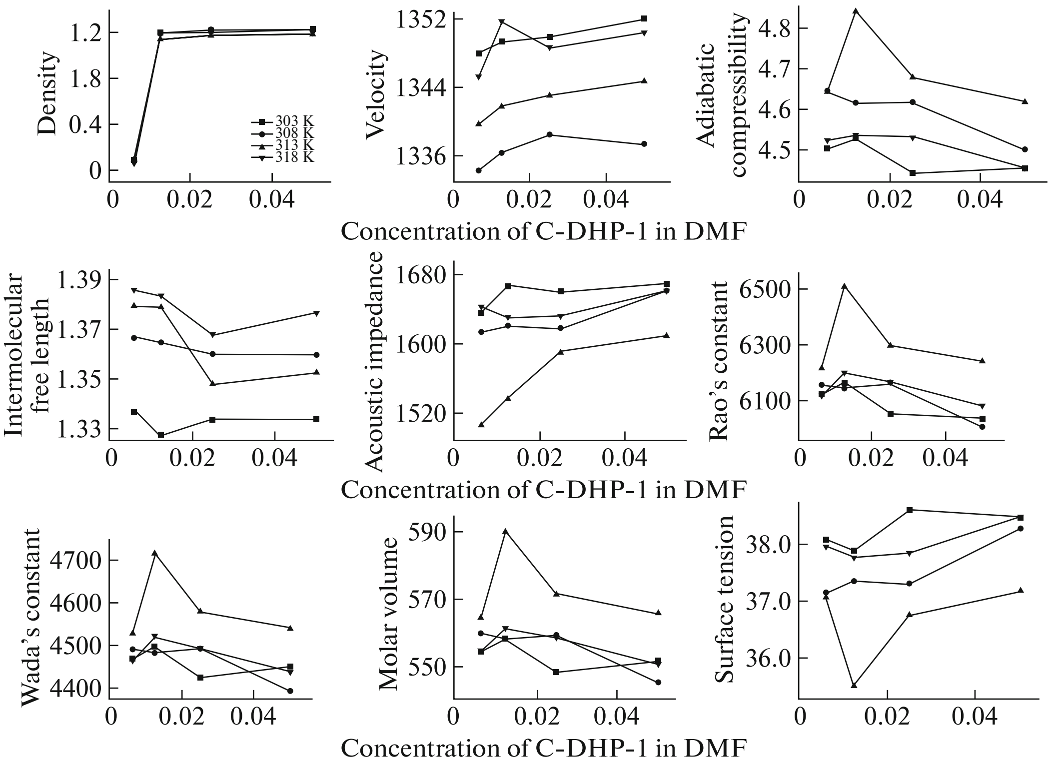


Fig. 5. Density, velocity, adiabatic compressibility, intermolecular free length, acoustic impedance, molar volume, Rao's constant, Wada's constant, surface tension at various temperature and concentration for (C-DHP-1 in DMF).

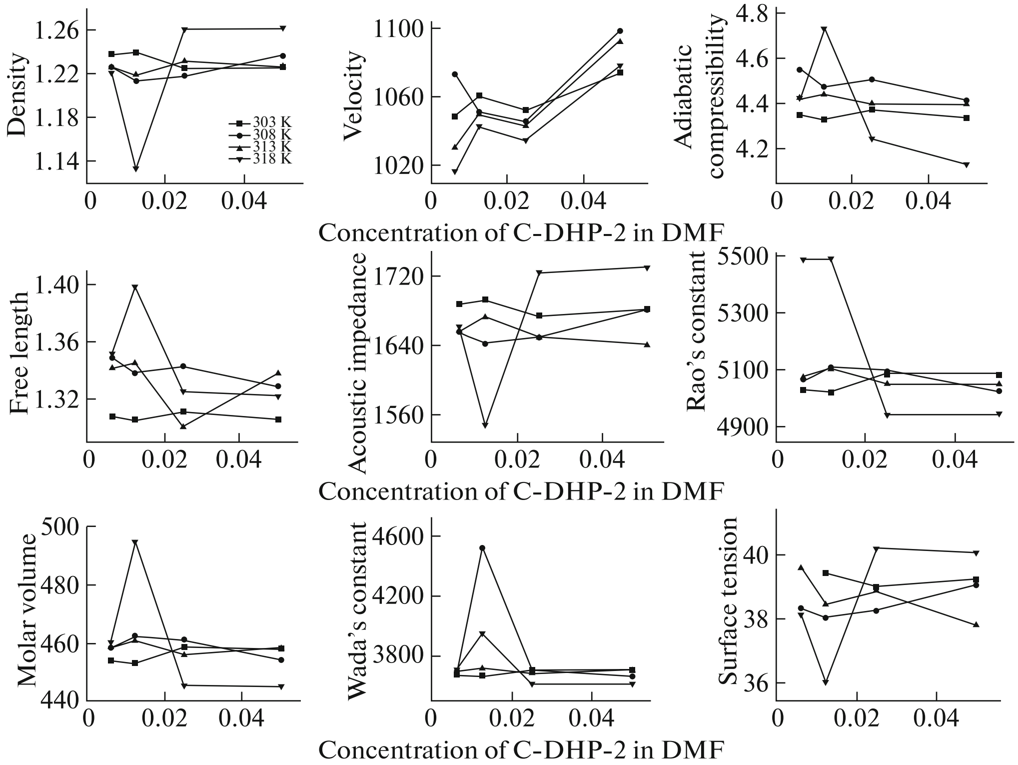


Fig. 6. Density, velocity, adiabatic compressibility, intermolecular free length, acoustic impedance, molar volume, Rao's constant, Wada's constant, surface tension at various temperature and concentration for (C-DHP-2 in DMF).

6. For C-DHP-3 in DMF : values of density, ultrasonic velocity, acoustic impedance (except 318 K), surface tension, Rao's constant (at 303 K), molar volume (at 303 K), Wada's constant (at 303 K) increases and values of adiabatic compressibility as well as intermolecular free length decreases with increase in concentration indicates strong solute–solvents interaction (Fig. 7).

FTIR Analysis

Results of ultrasonic velocity and density measurement are further supported by FTIR spectral analysis. The change in transmittance and shift in frequency of the representative peaks –OH and other functional groups present in the compounds in FTIR spectra gives interferences about the complex formation between solute and solvent by molecular interaction. Here All the three solutes i.e., C-DHP-1, C-DHP-2, and C-DHP-3 has carbonyl/hydroxyl/carboxylic acid functional group and solvent has hydroxyl/carbonyl functional group. So hydrogen bonding between solute and solvent is possible as shown in Figs. 8–11. In Figs. 8–11, frequency is expressed in terms of wave number. In IR spectra, when solute dissolved in solvent (ethanol/DMF) then value of its IR absorption frequency is found to be different from the IR absorption frequency of pure solute. Alteration in value of frequency in presence of solvents supports hydrogen bonding between solute and solvent. The complex formation can be illustrated through the molecular structures of compounds and solvent.

Figure 8 clearly indicates frequency shifts from 3326.31 cm^{-1} (solute) to 3485.19 cm^{-1} (mixture of solute + solvent DMF). In Fig. 9 the FTIR spectrum of compound shows –OH stretching band at 3326.31 cm^{-1} and the FTIR spectrum of the solution of this compound in ethanol shows a broad band for –O–H stretching at 3348.95 cm^{-1}. Although, there are various hetero atoms present in the structure of the compound which are also available for the hydrogen bonding with the hydrogen atom of ethanol, but it is observed from the FTIR spectrum that there is a strong hydrogen bonding in –OH group of compound with oxygen atom of ethanol, which supports the presence of specific molecular interaction in solute and solvent.

In Fig. 10 the FTIR spectrum shows the enol form of the structure due to the presence of a band for –O–H stretching at 3342.12 cm^{-1}. When it is compared with the FTIR spectrum of solute in DMF solvent, it is observed that the frequency of –O–H band alters which is seen at 3463.87 cm^{-1}. Figure 11 clearly indicates that in mixture 1, the –O–H band appears at frequency 3347.33 cm^{-1}. When it is compared with the

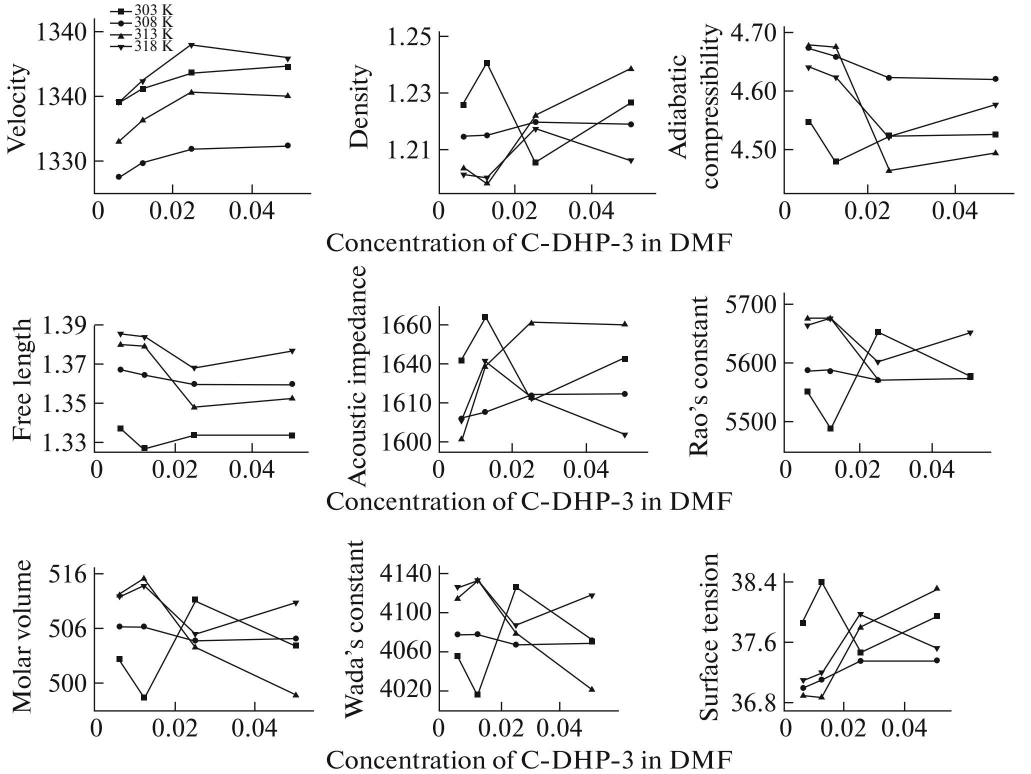


Fig. 7. Density, velocity, adiabatic compressibility, intermolecular free length, acoustic impedance, molar volume, Rao's constant, Wada's constant, surface tension at various temperature and concentration for (C-DHP-3 in DMF).

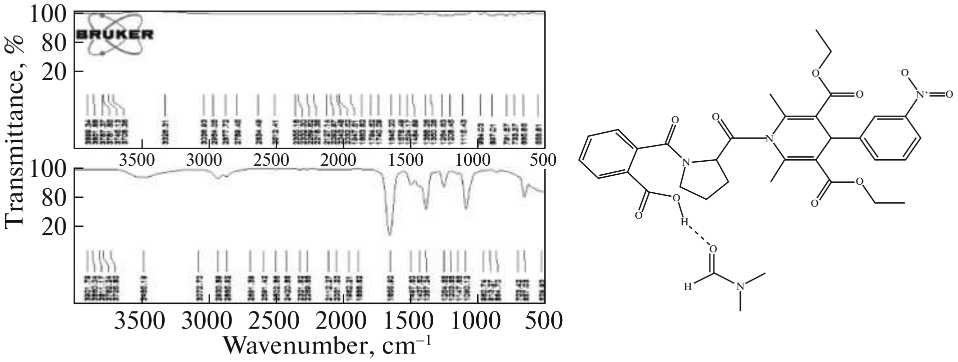


Fig. 8. FTIR spectrum of C-DHP-1 in DMF and hydrogen bonding of C-DHP-1 with DMF.

FTIR spectrum of the solute, it is observed that the frequency shifts from 3334.12 cm^{-1} (solute-enol form) to 3347.33 cm^{-1} (mixture of solute + ethanol solvent) Although, various oxygen and nitrogen atoms are there in the structure of the compound, which are also available for hydrogen bonding with the hydrogen atom in –O–H group of ethanol. It is seen from the FTIR spectrum of binary mixture that, the shift in the frequency of –OH group is more pronounced as that of other groups. Therefore, it can be concluded that the –OH group form a hydrogen bond.

CONCLUSION

From the present study it may be concluded that Interaction of solute with DMF is higher than that with ethanol, since values of acoustical parameters viz. density, ultrasonic velocity, acoustic impedance, surface tension are more in case of DMF except Rao's constant, Wada's constant as well as molar volume (for C-DHP-1 and C-DHP-3) and values of acoustical parameters viz. adiabatic compressibility and intermolecular free length are less for DMF. The com-

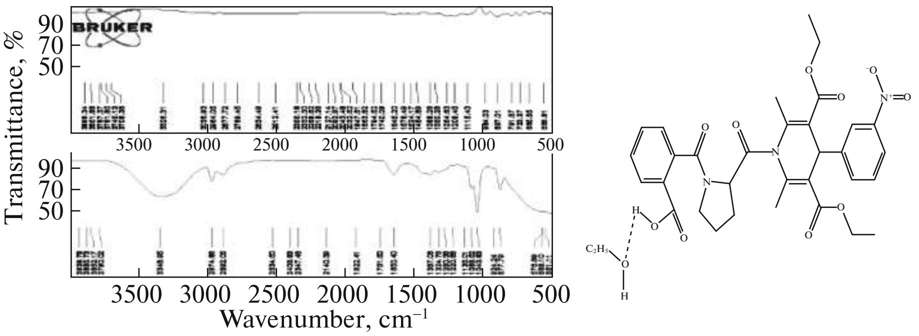


Fig. 9. FTIR spectrum of C-DHP-1 in ethanol and hydrogen bonding of C-DHP-1 with ethanol.

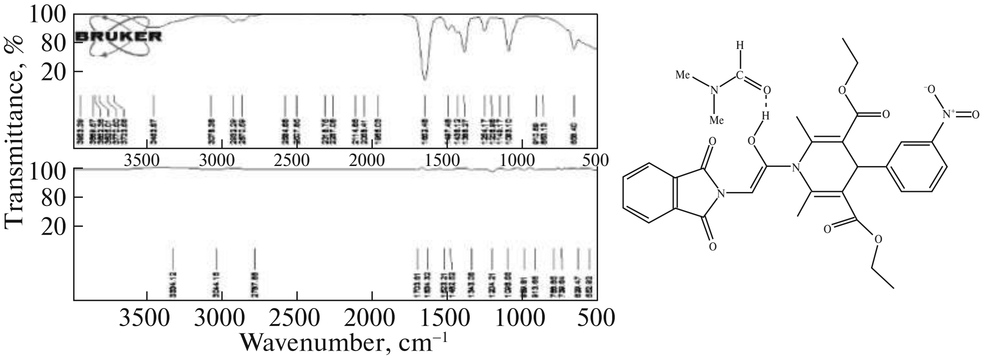


Fig. 10. FTIR spectrum of C-DHP-2 in DMF and hydrogen bonding of C-DHP-2 with DMF.

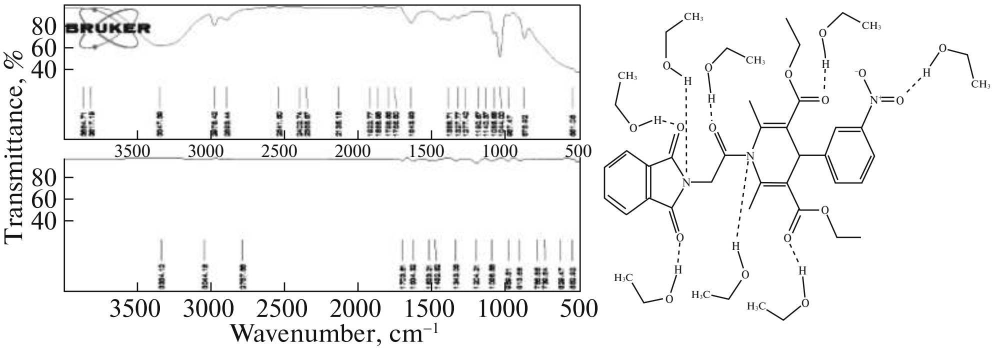


Fig. 11. FTIR spectrum of C-DHP-2 in ethanol and hydrogen bonding of C-DHP-2 with ethanol.

pressibility values are more for polar solvent, i.e., ethanol than non-polar solvent, i.e., DMF because solute in ethanol forms polar–polar molecule interaction, resulting in higher values of compressibility. But in DMF, the interaction is polar (solute)–non-polar (solvent), which leads to the decrease in compressibility. Similarly values of free length are more for ethanol because of less solute–solvent interaction. Thus the variation in thermoacoustical parameters with temperature and concentration shows that the solute–solute molecular interaction also takes place in solution.

The resultant interaction in a solution is not only because of molecular structure of components of solution but also due to other factors like dispersion forces, dipole–dipole interaction, dipole–induced dipole interaction, hydrogen bonding, charge transfer interaction and complex formation etc. In graphical representation of various thermo-acoustical parameters, non-linear variation of these parameters over the whole composition and temperature in all cases indicates a strong solute-solvent interaction. On addition of solute to solvents, non-specific physical interactions and unfavorable interactions takes place between unlike component molecules thereby giving the nonlinear variation in various thermo-acoustical parameters at different temperature and concentration of binary solvent mixtures.

All values of acoustical parameters shows strong correlation with each other. The solute–solute molecular association takes place due to dipole–dipole interaction and the polar nature of various molecular species in the mixture. The solute–solvent association takes place due to slightly polar solute and polar/nonpolar nature of the solvent. The association in this mixture is because of hydrogen bonding between solute and solvent. An analysis of these values supports strong intermolecular interaction which may be due to hydrogen bond, dipole–dipole, hyperconjugation and charge transfer. Thus, the concept of intermolecular interaction explained by variation of acoustical parameter.

The results of ultrasonic velocity measurements were further examined using FTIR spectra for C-DHP-1 and C-DHP-2 in polar and non-polar solvents. FTIR study shows alteration in the frequency values for O–H stretching of the compound in binary solution which indicates the molecular interaction between solute–solvent (compound with ethanol and DMF) and solvent–solvent (ethanol and DMF). Thus, the interaction of solute with ethanol is more than DMF.

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