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Ultrasonic studies on molecular interaction in polyvinyl chloride solution

Priyanka Tabhane[1], Omprakash P. Chimankar[1], Chandragupt M. Dudhe[2] and Vilas A. Tabhane[3]

[1]Department of Physics, R. T. M. Nagpur University, Nagpur, India
[2]Department of Physics, Institute of Science, Nagpur, India
[3]Department of Physics, University of Pune, Ganeshkhind, Pune, India

ABSTRACT

The ultrasonic technique provides a powerful, effective and reliable probe to investigate properties of polymer solution. In the present investigation, ultrasonic velocities, densities and viscosities have been measured in 0.1M solution using pulse echo overlap technique at 293K at different concentrations of polyvinyl chloride in tetrahydrofuran. Thermoacoustical parameters viz., adiabatic compressibility, relaxation time, molar sound velocity, molar compressibility, acoustic impedance, van der Waals' constant and internal pressure have been computed from the experimental data. The variation of ultrasonic velocity and other thermo-acoustical parameters shows nonlinear increase or decrease with molar concentration. The nature of polymer-solvent interaction and the effect of concentration on the molecular interaction of polyvinyl chloride in tetrahydrofuran have been studied.

Keywords: *Poly vinyl chloride, Tetrahydrofuran, Pulse echo overlap technique.*

INTRODUCTION

Ultrasonic studies in liquids and polymer solutions have been the subject of research in recent years [1-8]. Recently many workers have carried out pioneering work on polymer solution using ultrasonic technique. An acoustical study provides a useful technique to understanding the physico-chemical properties of the interacting components in polymer solution. The different acoustical parameters interpret the nature and strength of molecular interaction that exist in the system. The present paper deals with the ultrasonic studies of polymer solution of polyvinyl chloride (PVC) in tetrahydrofuran as a function of increasing molar concentration at temperature 293K. Polyvinyl chloride is a thermoplastic polymer. It is a vinyl polymer constructed of repeating vinyl groups (ethenyls) having one hydrogen replaced by chloride. PVC is widely used in construction because it is cheap, durable, and easy to assemble.

MATERIALS AND METHODS

The polyvinyl chloride solution was prepared by adding a known weight of polyvinyl chloride to a fixed volume of tetrahydrofuran and then stirring until clear solution were obtain[9]. The molecular weight of polyvinyl chloride is 62.5gm/mol. The concentration range chosen in the solution are 0, 0.02, 0.04, 0.06, 0.08 & 0.1M. The ultrasonic velocity, density and viscosity measurements are carried out using pulse echo overlap technique at fixed frequency of 4MHz at temperature 293K. The density and viscosity were measured by hydrostatic sinker method and Oswald's viscometer respectively. Thermostatically controlled water circulation system is used to maintain the temperature at 293K with an accuracy of 0.05^0C.

By using experimental data on ultrasonic velocity, density and viscosity, various acoustical parameters are calculated according to standard relationship [10].

1) Adiabatic compressibility (β_a) is given by the relation

$$\beta_a = \frac{1}{u^2 \times \rho} \quad \text{cm}^2/\text{dyne}$$

Where, u is the u.s. velocity and ρ is the density of the polymer solution.

2) Relaxation time (τ) is given by,

$$\tau = \frac{4}{3}\eta \cdot \beta_a \ \text{sec}$$

Where, η is the experimental viscosity of the polymer solution.

3) Molar sound velocity (R) is evaluated using the formula,

$$R = (M/\rho)\, u^{1/3} \quad \text{cm}^{10/3}/\text{sec}^{1/3}$$

Where, M is the molecular weight of the polymer solution.

4) Molar compressibility (W) can be found out from the expression

$$W = (M/\rho)\, \beta_s^{-1/7} \quad \text{cm}^{19/7}/\text{dyne}^{1/7}$$

5) Acoustic impedance (Z) is given by

$$Z = u.\rho \quad \frac{\text{gm}}{\text{cm}^2 \cdot \text{sec}}$$

6) Van der Waals' constant (b) is calculated by the formula

$$b = V\left[1 - \left(\frac{RT}{Mu^2}\right)\left(1 + \frac{Mu^2}{3RT}\right)^{1/2}\right] \quad \text{cm}^3/\text{mole}$$

Where, R is the gas constant = 8.3143×10^7 erg · mol^{-1} · K^{-1}

7) Internal pressure (P_i) is evaluated by the relation

$$P_i = bRT^3\left[\left(\frac{K\eta}{u}\right)^{1/2}\left(\frac{\rho^{2/3}}{M^{1/6}}\right)\right] \quad \text{dyne/cm}^2$$

RESULTS AND DISCUSSION

The values of β_a, τ, R, W, Z, b and P_i were calculated using equations (1)-(7). Figure 1-10 shows the plots of experimental velocity, density, viscosity and the calculated values of all the above acoustical parameters at different molar concentration for polymer solution of polyvinyl chloride with tetrahydrofuran.

The variation of ultrasonic velocity with concentration is non-linear with concentration (Fig. 1), with anomalous behaviour at 0.04 concentration. Initial increase in velocity with concentration suggests increase in cohesive forces due to powerful polymer-solvent interaction [11]. Then decrease in ultrasonic velocity after 0.02 concentration suggests breaking up of molecules when the concentration of polyvinyl chloride is more in the solution. This suggests dissociation of molecules. Then, the same behaviour is observed in case of acoustic impedance, van der Waals' constant, molar sound velocity and molar compressibility (Fig. 6, Fig. 8, Fig. 9 and Fig. 10) which supports the existence of strong molecular interaction in the polymer solution [12].

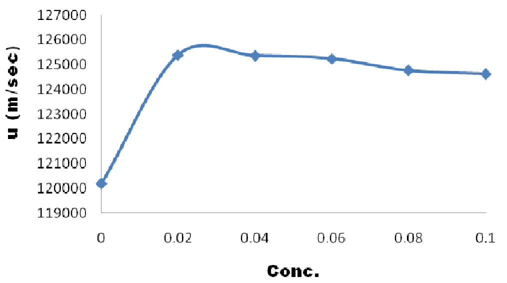

Figure 1 Variation of *v* with concentration

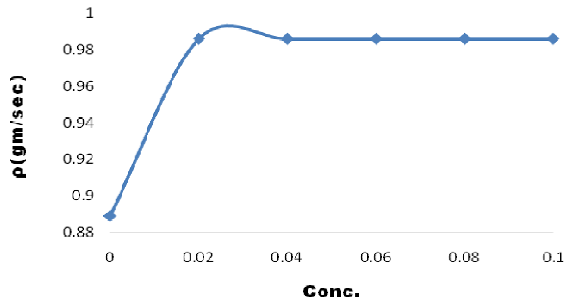

Figure 2 Variation of *ρ* with concentration

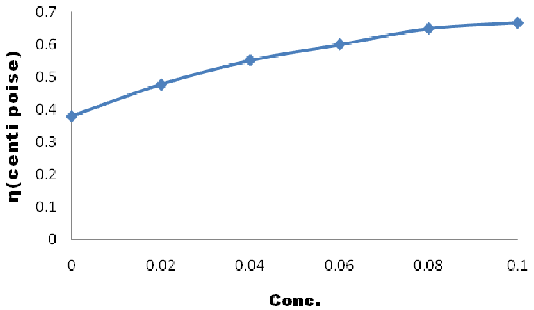

Figure 3 Variation of *η* with concentration

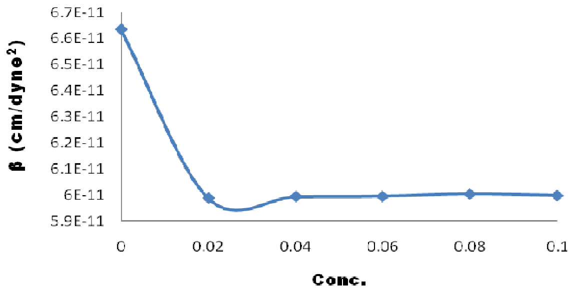

Figure 4 Variation of *β* with concentration

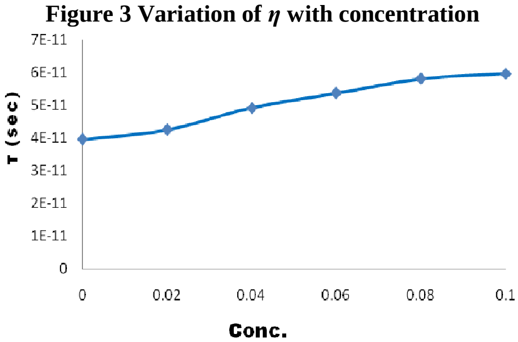

Figure 5 Variation of τ with concentration

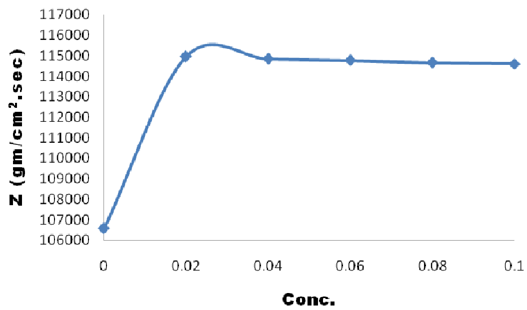

Figure 6 Variation of *Z* with concentration

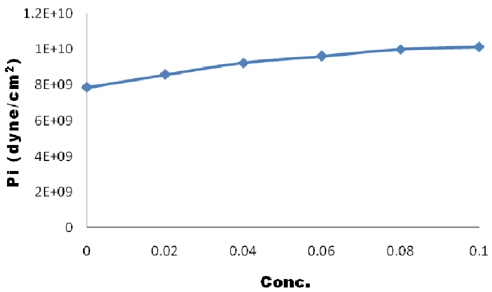

Figure 7 Variation of *Pi* with concentration

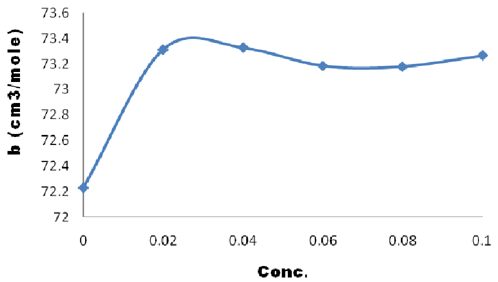

Figure 8 Variation of *b* with concentration

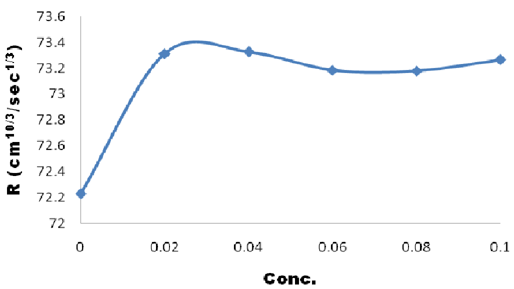

Figure 9 Variation of *R* with concentration

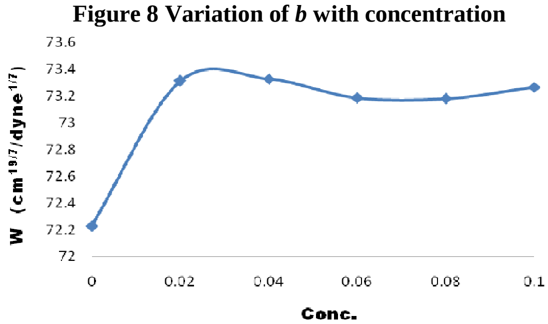

Figure 10 Variation of *W* with concentration

Variation of density with concentration is shown in fig. 2, which is increasing after addition of poly vinyl chloride in tetrahydrofuran. Increase in density is due to the fact that the number of polymer chains added to the solution increases with increase in polymer concentration. Polymers are characterized by the large molecular weight compared to the solvents. This also contributes to the increase in the density of the solution [13]. The same phenomenon can be applied to the increase in viscosity with concentration (fig. 3). The adiabatic compressibility (fig. 4) shows opposite nature to velocity, density and viscosity. It decreases with increasing molar concentration. These all nonlinear behaviour with molar concentration is may be attributed to molecular association and complex formation. The variation of relaxation time is increasing with concentration as shown in figure 5. This indicates that the solution is highly ordered due to outstanding hydration and such solution generally absorbs more ultrasonic energy [14]. The variation in internal pressure is given in figure 7. The internal pressure of a liquid reflects the molecular interaction and a sensitive parameter. As stated above, the internal pressure increases with increase in concentration of polyvinyl chloride and thus it can be concluded that it shows attractive forces between the solvent – polymer molecules.

CONCLUSION

The non-linear variation in ultrasonic velocity and other acoustical parameters indicates that there is a strong molecular interaction between polyvinyl chloride in tetrahydrofuran solution.

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