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RESEARCH ARTICLE

Acoustical Study of Poly Methyl Methacrylate in Tetrahydrofuran

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Abstract

Ultrasonic techniques are powerful and effective tool for investigation of polymer solution properties and behaviour of polymer chains in ultrasonic field. Extensive uses of polymers have promoted ultrasonic studies to understand structures of polymers and furnish knowledge on solvophilic or solvophobic nature of polymers. It provides a wealth of information about molecular interactions, nature and strength of interactions. It is a rapid non-destructive method for characterizing materials. In the present work, the ultrasonic velocity, density and viscosity measurements have been made for different concentrations of Poly (methyl methacrylate) (PMMA) in Tetrahydrofuran at the temperatures 308K, 313K, 318 K and 323 K. From the experimentally measured parameters, the acoustical parameters such as Adiabatic compressibility, Specific acoustic impedance, Relaxation time, Free volume and Internal Pressure were determined to study the nature of interaction in polymer solutions. Variations in acoustical parameters with changes in concentration and temperature are studied.

Keywords: Polymers, Ultrasonic technique, Adiabatic compressibility, Acoustic impedance, Internal pressure, Relaxation time, Free volume.

Introduction

Today a wide range of polymeric materials are used in our daily life. Polymers perform a great variety of functions. In medical field, they are widely applied as plasma substitutes, for stabilization and purification of some ferment and for the controlled release of drugs. Polymer science is a fascinating subject and there are many demanding challenges awaiting scientists who venture into the study of polymers.

Solutions of synthetic polymers find widespread technological applications rather than the solid polymers. For example, adhesives, coatings, cast films, spun fibers, sealants etc., are from the solutions of polymers. The polymer solutions are of considerable practical and theoretical interest, because of the specific interaction between solvent and polymer chain. The solvent effects have large influence on the properties of the polymer.

As the solution properties of polymers form the basis for the quantitative characterization of polymer molecules, knowledge about the molecular interactions and the changes in physical properties of polymer solutions is needed.

The ultrasonic study of polymer solutions is a powerful method for exploring molecular interactions and understanding the behavior of polymers in different solvents. (Kalyanasundaram S et al.1997) Ultrasonic waves, which travel through the solution, are influenced by various factors such as the solution's density, viscosity and compressibility. By measuring the velocity of these waves and related acoustic parameters, researchers can gain valuable insights into the molecular interactions, solubility and structure of polymer solutions

Materials And Methods

Ultrasonic technique is found to be a suitable method for the molecular interaction study because the waves just perturb the physico- chemical equilibrium of the medium. Due to its useful wavelength range, the ultrasonic technique could provide valuable information about the weak molecular interactions also. The use of ultrasonic waves does not result in the change in the structure of polymer materials and destruction of the sample being studied. (Kalyanasundaram

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S.et al,2000). PMMA, also known as acrylic or plexi glass is utilized because it is affordable, durable and easy to form. It is resistant to UV rays and has the capacity to maintain a light beam reflected within the surface. Acrylic glass is used in many items, including aquariums, car windows, and screens for digital devices

Adiabatic Compressibility

When an acoustic wave passes through the medium, adiabatic compressions and rarefactions take place. This results in a change in pressure (∂P) and a corresponding change in volume (∂V). These changes are related to the compressibility of the medium by a thermo dynamical relation.

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S$$

Using the equation of Newton and Laplace, the adiabatic compressibility can be calculated employing velocity (U) and density (ρ)

$$\beta = \left(\frac{1}{U^2\rho}\right) \quad (1)$$

Acoustic Impedance

Acoustic impedance is a characteristic property of the medium, representing the resistance an object or medium offers to the transmission of sound waves. It's defined as the product of the medium's density and the speed of sound within it. The importance of acoustic impedance lies in its role in understanding how sound waves interact with different materials. It is calculated as,

$$Z=U\rho. \quad (2)$$

Relaxation Time

The amount of energy passed to a given compartment grows exponentially with time to a final value and is characterized by a time constant which is known as the relaxation time τ and is given by the relation

$$\tau=4\eta/ 3\rho U^2 \quad (3)$$

Free Volume

The free volume is defined as the average volume in which the centre of the molecules can move inside the hypothetical cell due to the repulsion of the surrounding molecules. C.V. Suryanarayana and Kuppusamy (Suryanarayana C. V and J.Kuppusamy 1976) derived a formula for free volume of a liquid system based on dimensional analysis. The ultrasonic velocity U in a liquid is a function of molecular weight M, viscosity η and free volume V_f.

$$V_f = \left(\frac{M_{eff}U}{k\eta}\right)^{3/2} \quad (4)$$

Internal Pressure

Internal pressure is the resultant of the forces of attraction and the forces of repulsion between the molecules in a liquid. Internal pressure is the parameter which depends on all types of interactions such as solvent-solvent, solute-solvent and solute-solute. Also, it is closely related to the solubility parameters which determine the mode of interaction in the system.

The internal pressure is measured through the equation,

$$\pi_i = bRT\left(\frac{k\eta}{U}\right)^{1/2}\left(\frac{\rho^{2/3}}{M_{eff}^{7/6}}\right) \quad (5)$$

Experimental

In the present research work, PMMA of monomer weight 100.1158 has been used. The solutions of various concentrations have been prepared by dissolving a known quantity of PMMA in 100 ml of tetrahydrofuran. The sound velocity through the solution is measured with the fixed frequency Mittal type ultrasonic interferometer at 2 MHz. The density of the solution is measured with 10ml specific gravity bottle. The viscosity is found using Ostwald's viscometer. All the measurements have been carried out at 308 K, 313K,

318 K and 323 K using a thermostatically controlled water bath with an accuracy of ±0.1°C.

Results And Discussion

The decrease in adiabatic compressibility of a polymer solution with increasing concentration is mainly due to enhanced intermolecular interactions and structural organization of the polymer chains in solution. (Richa Saxena.et al, 2022) As concentration rises, polymer chains become more closely packed, reducing free volume and limiting the ability of the solution to compress under pressure.

In contrast, an increase in adiabatic compressibility with rising temperature occurs because thermal energy disrupts intermolecular interactions and reduces structural order in the solution. Higher temperatures lead to increased molecular motion, creating more free volume and thus enhancing the solution's compressibility. (Seetharaman et al 2004)

In liquids, specific acoustic impedance can be used to evaluate the strength of intermolecular attraction. (Subhraraj Panda 2023, 2025) As the strength of these attractions increases, ultrasonic velocity also rises. Consequently, the acoustic impedance value also increases (Figure 1).

The variations of internal pressure and free volume are studied with respect to concentration and temperature. It is observed that the internal pressure increases with concentration of the solute while the free volume decreases at all temperatures, showing the cohesion between the components. (Figures 2 & 3) With increase of temperature, the internal pressure is found to decrease while the free volume is found to increase. This implies the weakening of the cohesive forces on increasing the temperature.

The values of relaxation time are found to increase with increase in concentration at all temperatures studied. At a fixed concentration, the value of τ is found to decrease with increase in temperature (Figure 4).

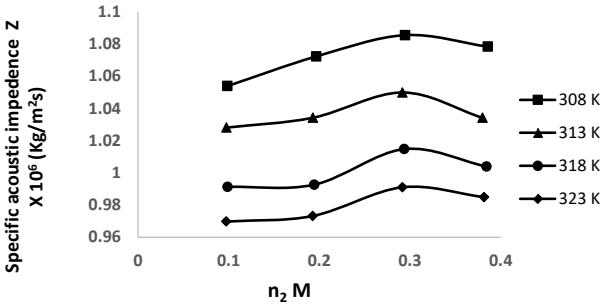


Figure 1: Variation of Specific Acoustic Impedence with concentration

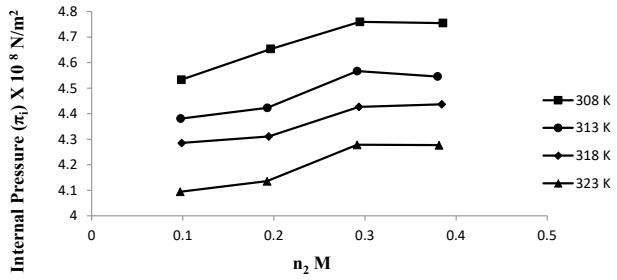


Figure 2: Variation of Internal pressure with concentration

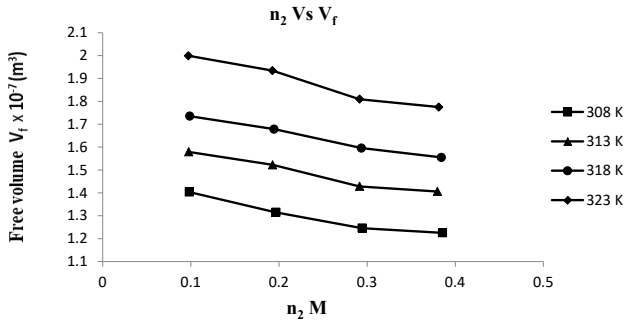


Figure 3: Variation of Free volume with concentration

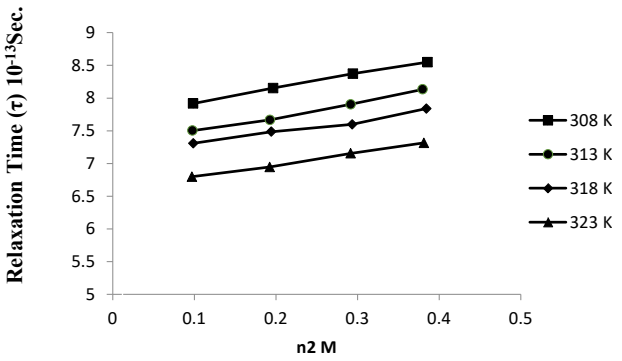


Figure 4: Variation of Relaxation time with concentration

Conclusion

Acoustical studies offer an in-depth investigation into molecular associations within polymer solutions. Analysis of the trends and variations in acoustical parameters with changes in concentration and temperature reveals that cohesion between components increases with concentration, though it remains relatively weak. As temperature rises, these cohesive forces weaken further.

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