

Study of Miscibility of Aqueous Polyacrylamide (PAA) Solution

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Abstract— The ultrasonic technique provides an effective and reliable tool to investigate properties of polymer solutions in the light of phase separation studies. The propagation of ultrasonic waves and the measurement of their velocity in solution form an important tool for the evaluation of various acoustical and thermo- dynamical parameters which give an insight into the nature of miscibility/compatibility and molecular interactions in polymer solution. The phenomenon polymer- solvent miscibility may arise due to any specific molecular interactions such as hydrogen bonding, dipole- dipole interactions and charge transfer complexes for homogeneous polymer- solvent mixture. Miscibility is an important phenomenon in polymer solution to achieve mechanical integrity, better adhesion, better processing and optimum property gain. In present system polyacrylamide is a carbon- carbon chain polymer which is water-soluble and is used as a thickening agent and a flocculent. Polyacrylamide (PAA) solutions of different concentrations have been prepared with water and there miscibility has been investigated by using ultrasonic pulse echo technique. Various thermo acoustic parameters such as viscosity (η), refractive index (μ), density (ρ) and ultrasonic velocity (u) for polyacrylamide solutions are measured at different concentrations (Wt%) i.e. 0.05 Wt% 0.3 Wt% . All the measurements were made at 288K to 308K and at two different frequencies 2MHz and 5MHz. The results are discussed. Variations in ultrasonic velocity (u), density (ρ), viscosity (η) and refractive index (μ) were found to be linear. These linear variations predict the miscibility of polyacrylamide in water solution at that concentration range.

Keywords: Acoustic parameters, miscibility, polyacrylamide (PAA), Ultrasonic pulse echo techniques, etc.

I. INTRODUCTION

Polyacrylamide is a carbon-carbon chain polymer having molecular formula $(C_3H_5NO)_n$ [1]. It is formed from acryl amide subunits. It can be synthesized as a simple linear-chain structure or cross-linked. It is water- soluble and is used as a thickening agent and flocculent. It is highly water-absorbent, forming a soft gel when hydrated, used in such applications as polyacrylamide gel electrophoresis and in manufacturing soft contact lenses. In the straight-chain form, it is also used as a thickener and suspending agent. More recently, it has been used as sub dermal filler for aesthetic facial surgery. Structural analysis of polymer is a subject of considerable interest in polymer science. A review of literature reveals that ultrasonic parameters, such as adiabatic compressibility (β_a), relaxation time (τ), acoustic impedance (z), free length (L_f), isothermal compressibility (β_i), volume expansivity (α) and Moelwyn-Hughes parameter (C_1) have been used to

study the molecular interactions in polymer solutions [2]-[5]. In present work, the authors have prepared the polyacrylamide solutions at different concentrations in water solutions and have measured the solutions ultrasonic velocity, density and viscosity using ultrasonic pulse echo technique at temperature range 288K- 308K and at three different frequencies 1MHz, 2MHz and 5MHz in order to study the structural changes to the solutions, if any.

II. EXPERIMENTAL

Polyacrylamide (AR grade) from Otto Chemi was used. Ultrasonic velocity, density and viscosity values are estimated in the aqueous polyacrylamide solution. The solution was prepared by adding a known weight of polyacrylamide to a fixed volume of distilled water and then stirring until clear solution were obtain. The concentration range chosen in the solution are 0.05, 0.1, 0.15, 0.2, 0.25, & 0.3 wt. %. **Velocity measurements are carried out using ultrasonic pulse echo technique by using MHF-400 High frequency pulser-receiver supplied by Roop Telsonic Ultrasonic Limited; Mumbai- (India) at different frequencies of 1 MHz, 2MHz & 5MHz and at temperature range 288K-308K with an accuracy of ± 0.1 m/sec.** Density has been measured by pycnometer method. The viscosity of liquid was measured by Oswald's viscometer. Temperature is maintained at a constant range by Plasto Crafts Thermostat and other related parameters calculated by standard formulae.

III. FORMULAE

1. Density
$$\rho = \frac{M_l}{M_w} \rho_w$$
 Where M_l - mass of experimental liquid, M_w - mass of water & ρ_w - density of water
2. Viscosity
$$\eta = \frac{\rho_l t_l}{\rho_w t_w} \eta_w$$
3. Adiabatic compressibility
$$\beta_a = \frac{1}{u^2 \rho}$$
4. Relaxation Time
$$\tau = \frac{4}{3} \eta \cdot \beta_a$$
5. Acoustic Impedance
$$Z = \rho \cdot u$$
6. Free Length
$$L_f = K_j \beta_a^{1/2}$$
 Where, K_j - Jacobson's constant
7. Volume Expansivity
$$\alpha = -\frac{1}{\rho} \left(\frac{\partial \rho}{\partial T} \right)$$
 Where, T - temperature
8. Moelwyn-Hughes parameter

$$C_1 = [13/3 + (\alpha T)^{-1} + 4/3 \alpha T]$$

IV. EXPERIMENTAL RESULTS AND DISCUSSION

The ultrasonic velocity (u), density (ρ) and viscosity (η) of the various concentrations at 298K and at three different frequencies of PAA in water are presented in following table. The increase or decrease in adiabatic compressibility (β_a), relaxation time (τ), free length (L_f) and acoustic impedance (z) according to solution concentrations studied indicates significant interactions between polyacrylamide and water molecules [6]. The ultrasonic velocity (u) increases linearly with the concentration of PAA in water. It is maximum at higher concentration (0.3 wt. %). This linear relationship between velocity and concentration of solution suggest its miscible behavior [7]. In PAA solutions, hydrogen bonds are formed between the solute and solvent molecules. When PAA is dissolved in water, the ultrasonic velocity increases, because at this stage polyacrylamide must be well dispersed hence at this stage compressibility is minimum, demonstrating the association of PAA particle with water. It is observed that density increases with increase in concentration of polyacrylamide (PAA) in water, increase in density decreases the volume indicating association in component molecules. This increase in density is due to the fact that the number of polymer chain added to the solution increases with increase in concentration of polymer solution. Polymers are characterized by large molecular weight compared to the solvents. This also contributes to increase in the density of the solution [8]. It is observed that viscosity linearly increases with increase in concentration (wt. %) of polyacrylamide (PAA) in water. According to Kauzman and Eyring [9], the viscosity of a mixture strongly depends on the entropy of mixture, which is related with the liquid structure as well as molecular interactions between the components of the mixtures. Thus the viscosity depends upon the molecular interaction as well as on the shape and size of the molecules.

TABLE-I

Polyacrylamide + water at $f=2\text{MHz}$ and $T=298\text{K}$
Measurement of ultrasonic velocity, density, viscosity, adiabatic compressibility, relaxation time, acoustic impedance, relaxation time, volume expansivity and Moelwyn-Hughes parameter

Conc. (wt.%)	u (m/sec)	ρ (Kg/m^3)	$\eta \times 10^{-3}$ (Pa. sec)	$\beta_a \times 10^{-10}$ ($\text{Kg}^{-1}\text{m}^2.\text{S}$)
0.00	1482	996.798	0.89	4.52
0.05	1486	1008.94	0.99	4.49
0.1	1490	1009.35	2.04	4.46
0.15	1494	1009.75	3.04	4.43
0.2	1498	1010.16	4.76	4.4
0.25	1502	1010.56	5.85	4.37
0.3	1506	1010.97	7.15	4.34

Conc. (wt.%)	$\tau \times 10^{13}$ (sec)	$Z \times 10^6$ ($\text{Kg. m}^{-2} \text{s}^{-1}$)	$L_f \times 10^{-11}$ (m)	$\alpha \times 10^{-4}$ (K^{-1})	C_1
0.00	5.36	1.48	4.19	10.1	8.06

0.05	5.92	1.5	4.17	9.73	8.17
0.1	12.1	1.51	4.16	9.73	8.17
0.15	20.1	1.51	4.15	9.72	8.17
0.2	27.9	1.52	4.13	9.47	8.25
0.25	34.1	1.52	4.12	9.48	8.25
0.3	41.4	1.53	4.1	9.48	8.25

TABLE-II

Polyacrylamide + water at $f=5\text{MHz}$ and $T=298\text{K}$
Measurement of ultrasonic velocity, density, viscosity, adiabatic compressibility, relaxation time, acoustic impedance, relaxation time, volume expansivity and Moelwyn-Hughes parameter

Conc. (wt.%)	u (m/sec)	ρ (Kg/m^3)	$\eta \times 10^{-3}$ (Pa. sec)	$\beta_a \times 10^{-10}$ ($\text{Kg}^{-1}\text{m}^2.\text{S}$)
0.00	1485	996.798	0.89	4.5
0.05	1489	1008.94	0.99	4.47
0.1	1494	1009.35	2.04	4.44
0.15	1498	1009.75	3.04	4.41
0.2	1503	1010.16	4.76	4.38
0.25	1507	1010.56	5.85	4.36
0.3	1511	1010.97	7.15	4.33

Conc. (wt.%)	$\tau \times 10^{-13}$ (sec)	$Z \times 10^6$ ($\text{Kg. m}^{-2} \text{s}^{-1}$)	$L_f \times 10^{-11}$ (m)	$\alpha \times 10^{-4}$ (K^{-1})	C_1
0.00	5.34	1.49	4.16	10.1	8.06
0.05	5.9	1.51	4.14	9.73	8.17
0.1	12.1	1.51	4.13	9.73	8.17
0.15	20	1.52	4.12	9.72	8.17
0.2	27.8	1.52	4.11	9.47	8.25
0.25	34	1.53	4.1	9.48	8.25
0.3	41.3	1.53	4.09	9.48	8.25

The adiabatic compressibility decreases as the concentration of PAA in water solution increases. The increase in velocity and decrease in adiabatic compressibility in this concentration range indicates that the molecules are forming a more tightly bonded system. The closer packing of molecules caused by hydrogen bonds between the PAA and water molecules has an even greater influence on the overall compressibility of the system. In our investigation we have observed that relaxation time slightly increases with increase in the concentration of polyacrylamide in water indicating high stability of polyacrylamide molecules. Polyacrylamide (PAA) is a highly polar & a cross-linked polymer of acrylamide having compact structure and hence molecules are not stable which increases the relaxation time. Motion of amide side groups on the polyacrylamide polymer chain may also contribute to relaxation processes. In this case energy exchange can occur between the wave and vibrational and rotational energy associated with motion of the side chain groups. With increase in the concentration of amide side chain groups increases and also the pathways for energy dissipation. In this system, acoustic impedance increases with increase in concentration (Wt %). This behavior may caused by complex formations in the solution that may be result of interactions between solute and solvent molecules [10]. In the case of impedance, the relation is linear. It is also evident for solute-solvent interactions. The similar observations were made by Rao [11] in their study of ultrasonic velocities of PVP in water

at various temperatures. The variation of ultrasonic velocity depends on intermolecular free length at mixing [12], something affected by the structural changes. In our investigation, we have observed the intermolecular free length decreases with increase in concentration of PAA in water. It shows the strong interactions between solute and solvents. The minimum free length indicates closer packing of the molecules. the variation of C_1 and volume expansivity (α) shows the opposite behavior with increase of concentration. If C_1 increases then α is found to be decrease with concentration and vice-versa. This may be due to associating tendency of the liquid molecules.

V. CONCLUSION

- In diluted solution of polyacrylamide with water up to given concentration range, interactions between solute and solvent molecules are strong.
- The linear variation of ultrasonic velocity with concentration gives the evidence to enhance the compatibility among the molecules presence in the PAA solution.
- The linear decrease in adiabatic compressibility and free length with increase in concentration of PAA solution indicates the strong interactions, association and non-dominance of PAA in water.
- The hydration state and its dynamic behavior are also explained in the light of formation of inter or intra-molecular hydrogen bonds between adjacent OH groups.
- The linearity in all the parameters indicates there is a single phase formation. It predicts strong polymer-solvent interaction and strong association in the PAA solution.

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