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Acoustic, Thermal and molecular interactions of Polyethylene Glycol (2000, 3000, 6000)

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Abstract

Polyethylene Glycol (PEG) is a condensation polymer of ethylene oxide and water. PEG find its application as emulsifying agents, detergents, soaps, plasticizers, ointments, etc. Though the chemical and physical properties of PEG are known, still because of their uses in day to day life, it becomes necessary to study few physical properties like ultrasonic velocity, viscosity and hence adiabatic compressibility, free length, etc. In the present study, an attempt has been made to compute the activation energy and hence to analyse the molecular interactions of aqueous solutions of Polyethylene Glycol of molar mass 2000, 3000 and 6000 at different concentrations (2%, 4%, 6%, 8% and 10%) at different temperatures (303K, 308K, 313K, 318K) by determining relative viscosity, ultrasonic velocity and density. Various parameters like adiabatic compressibility, viscous relaxation time, inter molecular free length, free volume, internal pressure, etc are calculated at 303K and the results are discussed in the light of polymer-solvent interaction. This study helps to understand the behavior of macro-molecules with respect to changing concentration and temperature. Furthermore, viscosity and activation energy results are correlated to understand the increased entanglement of the polymer chains due to the increase in the concentration of a polymer solution that leads to an increase in viscosity and an increase in the activation energy of viscous flow.

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1. Introduction

Polyethylene Glycol has variety of applications like preparation of detergents, soaps, pharmaceutical preparations, metal costing process and cosmetics (Syal et al. (2005)). Ultrasonic studies in liquids and polymer

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solutions have been the subject of research in recent years (Upmanyu et al. (2014); Priyanka Tabhane et al. (2012)). Ultrasonic study provides a useful technique in understanding the physico-chemical properties of the interacting components in polymer solution. Various acoustical parameters interpret the nature and strength of molecular interaction that exists in the system. Activation energy is the minimum energy required to initiate a chemical reaction. Many researchers (Al-Furhood et al. (2014); Venkatramanan et al. (2006)) have observed that the activation energy of flow and the pre exponential term depend not only on the molecular weight and concentration but also on polymer chain stiffness and coil expansion. Niezette et al. (1977) have reported that the difference between the activation energy for the solutions and for the solvent is much higher than for flexible chains. In the present paper, an attempt has been made to compute the activation energy and hence to analyse the molecular interactions of aqueous solutions of Polyethylene Glycol of molar mass 2000, 3000 and 6000 by determining relative viscosity, ultrasonic velocity and density values. Various molecular interaction parameters are discussed in the light of polymer-solvent interaction.

2. Methods and Materials

Polyethylene glycol (PEG) 2000, 3000 and 6000 (Spectra grade) were obtained from KAVIN SCIENTIFIC, Chennai, India. The polymer solutions were prepared by dissolving the polymers (PEG 2000, 3000 & 6000) in double distilled water to get desired concentrations (2%, 4%, 6%, 8% and 10%). Magnetic stirrer [REMI make] was used for this purpose at a rate of 1000 rpm. The relative viscosity of the polymer solutions was studied at 303K, 308K, 313K & 318K for different concentrations (2%, 4%, 6%, 8% & 10% w/v) using Brookfield viscometer [accuracy ± 0.01 cP]. The density values are measured using specific gravity method. The mass of the liquid was measured using a K-ROY make Electronic balance, with an accuracy of ± 0.001 gm. The ultrasonic velocity measurements are performed using Mittal make single frequency Ultrasonic interferometer at 2 MHz (F-81 model) (uncertainty ± 0.01 m/s). The temperature of viscometer and interferometer are maintained at 303K by circulating water from a thermostat with a thermal stability of ± 0.05 K.

3. Results and Discussion

3.1. Activation Energy Studies

Viscosity studies are performed for aqueous solutions of PEG (2000, 3000, 6000) for different concentrations from 2% to 10% at temperatures 303K, 308K, 313K and 318K. In all the cases, the relative viscosity is increasing with the increase in concentration and decreases with the increase in temperature (Table 1). It may be due to more frictional force that is developed between the layers of the solution. Arrhenius expression is valid for pure solvents and also for dilute polymer solutions. It is given by

$$\eta = A e^{Q/RT} \quad (1)$$

where Q is the apparent activation energy of flow and A is the pre-exponential term with an activation entropy significance. The logarithm of this equation leads to a straight-line type given by

$$\ln \eta = \ln A + \left(\frac{Q}{R}\right) \left(\frac{1}{T}\right) \quad (2)$$

The plot between logarithm of relative viscosity against inverse of temperature for PEG (2000, 3000, 6000) gives the values of activation energy. The variation of activation energy (Q) with concentration (C) of aqueous solutions of PEG is shown in Table 1 which shows that the activation energy increases with increase in concentration. From this, it may be concluded that more energy is required to move the molecules inside the structure with increase in concentration (Guadalupe Olayo et al. (2010)).

It is observed that the density of the system increases with increase in concentration (Table 1). This 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 (Priyanka Tabhane et al. (2012)). The increase in ultrasonic velocity (Table 1) with concentration suggests powerful solute-solvent interaction. As density increases, number of particles in given region is also increased, which leads to quick transfer of sound velocity and hence ultrasonic velocity increases with concentration.

Table 1. Values of Relative viscosity, Density, Ultrasonic Velocity and Activation Energy for Aqueous Solutions of PEG

System	Concentration (gm/dL)	Relative Viscosity ($\times 10^{-3}$ N s m ⁻²)				Density at 303 K (kg m ⁻³)	Ultrasonic Velocity at 303K (m s ⁻¹)	Activation Energy (KJ mol ⁻¹)
		303 K	308 K	313 K	318 K			
PEG 2000	2	1.19	1.08	1.03	1.00	997.29	1473.87	9.1540
	4	1.45	1.32	1.19	1.10	1001.90	1483.53	14.1622
	6	1.73	1.56	1.42	1.33	1006.61	1492.71	14.9448
	8	2.07	1.87	1.70	1.56	1008.32	1501.37	15.1286
	10	2.42	2.18	1.98	1.80	1012.03	1510.77	15.7703
PEG 3000	2	1.17	1.08	1.04	1.01	999.29	1475.07	7.6979
	4	1.45	1.31	1.20	1.10	1000.70	1482.92	14.6636
	6	1.72	1.56	1.42	1.29	1004.91	1492.71	15.3325
	8	2.02	1.84	1.66	1.51	1006.61	1502.00	15.6326
	10	2.45	2.17	1.97	1.79	1009.22	1510.14	16.6462
PEG 6000	2	1.29	1.18	1.07	1.01	1000.80	1471.67	13.3430
	4	1.74	1.54	1.41	1.30	1003.92	1481.10	15.4437
	6	2.15	1.95	1.77	1.62	1007.74	1490.56	15.1585
	8	2.60	2.34	2.10	1.92	1010.16	1500.13	16.3120
	10	3.28	2.91	2.62	2.38	1012.78	1507.63	17.1081

3.2. Molecular Interaction Studies

From Table 2, it is evident that, adiabatic compressibility decreases with the increase of concentration. This attributes to closed packing of molecules and decreased ionic repulsion. This also indicates the enhancement of the bond strength at this concentration. Adiabatic compressibility shows an inverse behaviour to ultrasonic velocity. This indicates that there is a significant interaction between solute and solvent molecules. It can be taken as an indication for formation of complexes. The intermolecular free length decreases with increase in concentration as shown in Table 2. At lower concentration range the molecules exhibit weak interaction due to dominant repulsive force and at higher concentration there is a specific interaction among the molecules. In view of greater forces of interaction between solute and solvent molecules forming hydrogen bonding, there will be a decrease in free length in the mixture (Asghar et al. (2010); Jayakumar et al. (1996)). Free volume may be defined as the average volume in which the central molecule can move inside the hypothetical cell freely without affected by the repulsion of surrounding molecules. The free volume follows reverse trend of viscosity. Therefore viscosity rather than velocity determines the free volume of the present system. Since the viscosity of the polymer is varied due to molecular interaction or polymer salvation, same parameters are influencing the free volume also. Free volume reduces when the internal pressure increases. In the present case, free volume for aqueous solutions of PEG (2000, 3000, 6000) is maximum at 2% and minimum at 10% [Table 2]. Viscous relaxation time increases with increasing concentration which shows that viscous forces play a dominant role in the relaxation process. This indicates that the solution is highly ordered due to outstanding hydration and such solution generally absorbs more ultrasonic energy (Priyanka Tabhane et al. (2012)). The internal pressure of a liquid reflects the molecular interaction. Internal pressure increases with increase in concentration of polyethylene glycol and thus it may be due to the presence of attractive forces between the solvent –polymer molecules.

4. Conclusion

Aqueous solutions of polyethylene glycol (PEG 2000, 3000 and 6000), at different concentrations are prepared and relative viscosity is determined for different temperatures (303K, 308K, 313K and 318K). Density and ultrasonic studies are done at 303K. It is found that the activation energy increased with increase in concentration for all the systems. Density and ultrasonic velocity found to increase with increase in concentration. Variation of molecular interaction parameters with concentration suggested the presence of strong polymer-solvent interaction at higher concentration and the effect of concentration is analysed.

Table 2. Molecular Interaction Parameters for Aqueous solutions of PEG at 303 K

System	Concentration (gm/dL)	Adiabatic Compressibility ($\times 10^{10} \text{ m}^2 \text{ N}^{-1}$)	Intermolecular free length ($\times 10^{11} \text{ m}$)	Free Volume ($\times 10^{-9} \text{ m}^3 \text{ mol}^{-1}$)	Relaxation time ($\times 10^{-13} \text{ s}$)	Internal Pressure ($\times 10^9 \text{ atm}$)
PEG 2000	2	4.6159	4.4580	12.2960	7.3239	2.7915
	4	4.5350	4.4188	9.5415	8.7677	3.0028
	6	4.4584	4.3813	7.6318	10.2840	3.1987
	8	4.3997	4.3524	6.0705	12.1430	3.4081
	10	4.3292	4.3174	4.9997	13.9690	3.5950
PEG 3000	2	4.5992	4.4500	12.629	7.1747	2.7703
	4	4.5442	4.4233	9.5375	8.7855	3.0005
	6	4.4660	4.3851	7.7009	10.2420	3.1851
	8	4.4035	4.3542	6.3038	11.8600	3.3611
	10	4.3449	4.3252	4.9076	14.1930	3.6098
PEG 6000	2	4.6135	4.4569	10.871	7.9352	2.9152
	4	4.5407	4.4216	7.2421	10.5340	3.2960
	6	4.4645	4.3843	5.5001	12.7980	3.5700
	8	4.3989	4.3520	4.3088	15.2490	3.8245
	10	4.3440	4.3247	3.1603	18.9980	4.1902

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