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Dielectric relaxation and molecular dynamics in poly(vinyl pyrrolidone)–ethyl alcohol mixtures in pure liquid state and in non-polar solvent

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Abstract

Dielectric relaxation and molecular dynamics in poly(vinyl pyrrolidone)–ethyl alcohol (PVP–E) mixtures with varying concentration in pure state and also in very dilute solutions of benzene were studied for their molecular conformation at 35 °C. Dielectric permittivity ε' and dielectric loss ε'' of PVP–E mixtures were measured by a time domain reflectometry technique in the frequency range 10 MHz to 10 GHz. The value of static dielectric constant ε_0, dielectric relaxation time τ, and dielectric free energy of activation ΔF_τ has been evaluated by fitting the complex dielectric data into Debye equation. The variation in ε_0 was discussed by considering the volume effect and the structuring effects of the PVP on ethyl alcohol molecules. The formation of cooperative domains between PVP and ethyl alcohol molecules, $\mathrm{CD_{PVP-E}}$ and between the ethyl alcohol–ethyl alcohol molecules $\mathrm{CD_E}$ and their dynamics in the PVP–E mixtures were explored by using the evaluated values of τ and ΔF_τ.

The PVP–E mixtures of low PVP concentration were also studied in very dilute solutions of benzene at 10.1 GHz. The value of average relaxation time τ_0, distribution parameter α, and relaxation time corresponding to the motion of small multimer species of alcohol molecules τ_1 and group rotation τ_2 has been determined. It has been observed that in dilute solution of benzene the value of τ_0 and τ_1 increases with the increase in concentration of PVP in PVP–E mixture but the τ_2 value is found independent of the mixture constituent concentration. The entanglement of the $\mathrm{CD_{PVP-E}}$ and the increase in the length of $\mathrm{CD_E}$ in dilute solution of benzene due to dissociation of the complexes between carbonyl and hydroxyl groups has been explored. The value of τ_2 is assigned to the rotation of –OH group about C–O bond in the ethyl alcohol species in dynamic equilibrium with larger steric hindrance due to hydrogen bonding.

Keywords: Dielectric relaxation; Dynamic equilibrium; Intermolecular interaction

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1. Introduction

Conformational changes originating in macromolecules as a consequence of their interaction with solvent have been the subject of large number of investigations [1,2]. Micro-Brownian motion of polymer chain is one of the most important subject in polymer physics [3]. Predicting molecular dynamics and intra-molecular rotations for associating macromolecules are challenging problems that have received considerable attention both experimentally and theoretically over the last two decades. Dielectric relaxation phenomena of the macromolecule are dominated by its dynamics. Dielectric relaxation measurement is a reliable method of investigating the motion if the polymer is polar. Further, dielectric relaxation study of binary liquid mixture systems can be utilize to gather information on solute–solvent interactions because the dielectric relaxation time of the macromolecule depends on the flexibility and coiling of the molecular chain, mobility of the polymer segments, intra-molecular group rotations and the steric hindrance to internal rotations due to intra and intermolecular interactions.

Over the past few years, considerable attention has been focused on the dielectric behavior and relaxation studies of associating polymers and their oligomers molecules of poly(ethylene glycol)s (PEG) [4–8], poly(propylene glycol)s (PPG) [9–12], poly(vinyl alcohol) (PVA) [13] and poly(vinyl pyrrolidone) (PVP)[14–17] in different environments for their conformations. These polymers and their oligomers have a wide range of biological and technological

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applications. Among these associating polymers, PVP, has several useful properties including very low toxicity, good film forming and adhesive properties, and solubility in a broad range of hydroxyl group containing solvents. Recently, Feldstein et al. [18,19] studied the PVP blends with ethyl alcohol, water, glycerol and the short-chain poly(ethylene glycol) for their use in transdermal drug delivery system (TDDS) by FTIR spectroscopy, DSC, and optical microinterference. Adhesive, transport, reservoir and biological properties of polymer composites constitute a general basis for their use as TDDS [20]. Intramolecular dynamics and the nature of intra- and intermolecular hydrogen bonding in the heterogeneous network of binary mixture of polymer in polar solvent govern the adhesive, transport and reservoir properties of the polymer matrix. The solubility of PVP in hydroxyl group/s containing solvents depends upon the formation of hydrogen bonds between the carbonyl groups of the PVP monomer units and the hydroxyl group/s of the solvent. In case of PVP, the plasticization of PVP depends on the fraction of hydroxyl groups in the blend rather than on the plasticizer weight fractions. The study of the molecular dynamics and the exploration of the behavior of complex formation density in the matrix of PVP–plasticizer over the entire compositional range is very interesting for their use in TDDS. Further it is useful to study the PVP–plasticizer network in dilute solutions of non-polar solvent to gather the information about the elongation of the PVP–plasticizer network and also the dissociation of the solute–solvent complexes. Earlier, microwave dielectric relaxation studies of the binary mixtures of PVP–PEG [21] and ternary mixtures of PVP–PEG–PPG [16] has been studied over wide compositional range to confirm the effect of the concentration of hydroxyl groups on the elongation of the dynamical network in dilute solutions.

The purpose of the present paper is to carry out the microwave dielectric relaxation study of the poly(vinyl pyrrolidone)–ethyl alcohol (PVP–E) mixtures of varying concentration in pure state and also in dilute solutions of benzene. Using the experimentally evaluated dielectric relaxation times, an attempt has been made to explore the formation of homogeneous and heterogeneous cooperative domains due to intermolecular hydrogen bonding in binary mixtures. Further, the elongation of PVP–E network in dilute solution at different concentration of hydroxyl and carbonyl groups in PVP–E mixtures has been examined.

2. Experimental

2.1. Materials

The samples of poly(vinyl pyrrolidone) (PVP) 40,000 g mol^{-1} and ethyl alcohol (E) of LR grade were obtained from Loba Chemie, India. The binary mixtures of PVP–E were made gravimetrically. The concentrations of PVP employed were 5, 10, 15, 20, 30, 50, 60, 80, 100 and 140 wt%, respectively in the weight of ethyl alcohol. The weight fraction of PVP, w_{PVP} corresponding to these mixtures is 0.048–0.583.

2.2. Dielectric measurements

2.2.1. PVP–E mixtures

The permittivity ε' and dielectric loss ε'' of the PVP–E mixtures in the frequency range 10 MHz to 10 GHz were performed by a time domain reflectometry (TDR) technique at 35 °C. A Hewlett Packard HP 54750A sampling oscilloscope with HP 54754A TDR plug-in module was used. The detailed explanations of the apparatus and the procedures of the system have been previously reported [22].

2.2.2. PVP–E mixtures in benzene solution

The permittivity ε' and dielectric loss ε'' of E and each 5, 10, 15, 20, 30 and 50 wt% PVP in PVP–E mixtures as solute in the weight fraction range 0.005–0.06 in benzene solution at five concentrations were measured at 10.1 GHz. The values of ε' and ε'' were determined by the precise waveguide method suggested by Heston et al. [23] adapted to short-circuited termination. The heterodyne beat method was used for determination of the static dielectric constant ε_0 at 1 MHz. The high frequency dielectric constant ε_∞, was taken as the square of the refractive index n_D which was measured with an Abbe's refractometer at wavelength of sodium light. All measurements were made at 35 °C and the temperature was controlled thermostatically within ±0.5 °C. Due to starting of dissociation of complexes at higher concentration of PVP in PVP–E mixtures in benzene solution, the measurements were restricted up to 50 wt% of PVP. It has been observed that ε_0, ε', ε'' and ε_∞ are linear functions of the weight fraction of PVP–E solute in dilute solutions of benzene. The linear slopes a_0, a', a'' and a_∞ corresponding to ε_0, ε', ε'' and ε_∞ versus weight fraction of solute (i.e. PVP–E mixture) are recorded in Table 1.

Table 1
Values of the slopes of ε_0, ε', ε'' and ε_∞ versus weight fraction of solute (PVP–E mixture) in dilute solution of benzene at 35 °C

PVP wt% in PVP–E mixture	a_0	a'	a''	a_∞
0	7.76	6.40	1.55	−0.42
5	8.33	6.20	1.57	−0.48
10	8.18	5.71	1.48	−0.39
15	8.09	5.26	1.27	−0.40
20	8.00	4.73	1.17	−0.33
30	7.89	4.23	1.12	−0.23
50	7.14	3.33	1.00	−0.29

2.3. Data analysis

2.3.1. PVP–E mixtures

To evaluate various dielectric parameters, the frequency dependent complex permittivity data of E and PVP–E mixtures were fitted with the Debye expression [24]

$$\varepsilon^*(\omega) = \varepsilon_\infty + [(\varepsilon_0 - \varepsilon_\infty)/(1 + j\omega\tau)] \tag{1}$$

with ε_0, ε_∞ and τ as fitting parameters. It has been found that the complex dielectric data of pure ethyl alcohol and the binary mixtures of PVP–E obey the Debye dispersion model faithfully. The values of dielectric parameters ε_0, ε_∞ and τ obtained from fitting into Eq. (1) for the E and PVP–E mixtures with wt% of PVP are recorded in Table 2. The activation free energy of dielectric relaxation process ΔF_τ of these binary mixtures were also determined using Eyring's rate equation [25] and the observed values of ΔF_τ are also recorded in Table 2.

2.3.2. PVP–E mixtures in benzene solution

The linear slopes a_0, a', a'' and a_∞, given in Table 1, were used for the determination of average relaxation time τ_0 and distribution parameter α in dilute solution of benzene. The values of τ_0 and α were evaluated by Higasi's [26] single frequency measurement equations and these values are given in Table 2. The observed large values of distribution parameter α suggest, that in dilute solution of benzene there is a significant contribution of the segmental motion and group rotation to the relaxation processes in the E and PVP–E mixtures. Because of the high value of α, relaxation times corresponding to segmental motion τ_1 and group rotation τ_2 were determined using the values of τ_0 and α in the equations of Higasi et al. [27], proposed for dilute solutions. The evaluated values of τ_0, α, τ_1, τ_2 and ΔF_τ of PVP–E mixtures in dilute solutions of benzene are recorded in Table 2. The ratio R of the hydroxyl groups of ethyl alcohol molecules to the carbonyl groups of PVP monomer units were also determined using the weights of PVP and E in each PVP–E mixture prepared for their dielectric relaxation study. The value of R (Table 2) decreases with increase in concentration of PVP in PVP–E mixtures and up to 140 wt% of PVP, the R is greater than unity which shows that the prepared PVP–E mixtures are hydroxyl group rich mixtures.

3. Results and discussion

3.1. PVP–E mixtures

The value of static dielectric constant ε_0 of pure ethyl alcohol obtained from TDR measurements is in good agreement with the earlier reported values [28,29] at 35 °C. Further, it is observed that the value of ε_0 decreases gradually with increase in concentration of PVP in the PVP–E binary mixture. The physical basis of the lowering of the static dielectric constant of ethyl alcohol by dissolved PVP seems to be more than a single volume effect arising from the addition of large particles. The PVP is known to bind and orient the alcohol molecules around it, thereby probably reducing their ability to orient in the applied field and so reducing the dielectric constant. Further the structuring effects of the PVP on ethyl alcohol is also important for the static dielectric constant of ethyl alcohol in the PVP mixture than the particle volume effects. Earlier, dielectric studies [15,30,31] of PVP 10000 and PVP 12700 g mol^{-1} in ethyl alcohol and water solvent also confirmed the gradual decrease in ε_0 with increase in concentration of PVP in the polar solvent mixture.

Shinyashiki et al. [14,15,17,30] extensively studied the dielectric behavior of different polymers in polar solvents. They interpreted the wide frequency range dielectric data of PVP–ethyl alcohol and PVP–water mixtures by the sum of the two types of relaxations in the lower frequency region and in the high frequency region corresponding to the local chain motion and the reorientation of the solvent (i.e. attributed to the primary process of solvent). But Zaslavsky et al. [31] used the single Debye behavior of PVP–water

Table 2

Values of dielectric constants of PVP–E mixtures in their pure liquid state and also in dilute solutions of benzene at 35 °C

PVP wt% in PVP–E mixture	PVP–E mixture				PVP–E mixture in benzene solution					R = OH/C=O
	ε_0	ε_∞	τ (ps)	ΔF_τ (kcal mol^{-1})	τ_0 (ps)	α	τ_1 (ps)	τ_2 (ps)	ΔF_{τ_0} (kcal mol^{-1})	
0	23.9	3.00	117.9	4.04	2.6	0.32	13.8	3.6	1.73	
5	23.2	3.12	119.9	4.05	2.8	0.45	21.4	3.7	1.76	48.2
10	22.6	3.08	126.0	4.08	3.3	0.51	26.3	3.8	1.86	24.1
15	22.2	3.13	133.1	4.11	3.4	0.59	35.1	3.5	1.89	16.1
20	21.3	3.16	141.9	4.15	5.2	0.64	44.0	3.6	2.14	12.1
30	20.5	3.12	139.4	4.14	9.3	0.65	51.5	4.0	2.49	8.0
50	18.5	3.14	137.4	4.13	18.2	0.67	60.0	4.4	2.90	4.8
60	17.3	3.10	126.5	4.08						4.0
80	16.2	3.08	132.4	4.11						3.0
100	15.0	3.06	127.8	4.09						2.4
140	13.8	3.13	135.3	4.12						1.7

mixtures for the interpretation of the measured microwave dielectric data. In the present study only one relaxation peak related to Debye relaxation processes is observed for ethyl alcohol and PVP–E mixtures in the frequency range 10 MHz to 10 GHz. The Debye type relaxation in ethyl alcohol and the PVP–E mixture reflects the behavior of hydrogen-bonded clusters of molecules as large species. Further, the Debye process in case of pure ethyl alcohol molecules also suggests the cooperative process involving the relaxation of the structure. Furthermore, it seems that in the PVP–E mixture, the individual principal relaxation processes of the components coalesce, and hence the mixture exhibits a single relaxation time. Single relaxation behavior were also found in the mixtures of associating molecules of poly(propylene glycol)–propylene glycol [11], poly(vinyl alcohol)–water [13], propylene glycol–water [12] etc. Rohmann and Stockhausen [32] analyzed the dielectric data of frequency range 2 MHz to 72 GHz of PVP–pyrrolidone mixtures in terms of multiple Debye type components to explore the unaffected, loosely affected and tightly bound molecules of pyrrolidone with PVP chain. Although the investigators used different relaxation processes, dielectric results are discussed in similar manner and identical conclusions were drawn regarding the polymer–solvent interactions.

In the present study, evaluated τ value of PVP–E mixture increases gradually with the increase in concentration of PVP up to 20 wt% but above this concentration there is a monotonous variation in τ value. The high value of τ (117.9 ps) for pure ethyl alcohol is due to the reorientational motion of hydrogen bonded linear polymeric structure, which is already confirmed by earlier dielectric relaxation studies [28,29]. At lower concentration of PVP in PVP–E mixtures, the observed τ value confirms that the steric hindrance to the reorientational motion of the ethyl alcohol structure increases due to the formation of hydrogen bonds between the hydroxyl group of E molecule and carbonyl group of PVP monomer unit in the mixture. Due to complex formation in the PVP–E mixture there may be breaking of linear structure of E molecules. Above 20 wt% PVP concentration in PVP–E mixture, the anomalous variation in relaxation time confirms that the breaking of homogeneous structure of E molecules with the addition of more carbonyl groups in the mixture is not uniform. At higher PVP concentration, the H-bond formation may saturated but there is continuous breaking and reforming of H-bonds due to reorientation of segments of PVP chain and also due to the switching of homogeneous structure of ethyl alcohol. The comparable τ value of PVP–E mixtures with the τ value of homogeneous structure of E molecules shows that besides the complex formation, the different size homogeneous structure of E molecules also exists in the mixture. The complex formation between E molecules and monomer unit of PVP chain results in a high degree of the orientation of the chain of E molecules which produces the crosslinking in the coiled PVP chain due to which there is also decrease in static dielectric constant ε_0. Although there is H-bond formation between the carbonyl and hydroxyl groups in the PVP–E mixture but the homogeneous linear chain structure of ethyl alcohol molecules exists in the mixture due to the high self association ability of E molecules which is confirmed by large value of Kirkwood correlation factor ($g \sim 3.1$) [29,33].

Feldstein et al. [19] studied the stoichiometry of PVP–PEG400 mixtures by FTIR spectroscopy, DSC, and optical micro interference and confirmed that over a wide interval of the reagent concentration, no more than 28 poly(ethylene glycol) macromolecules bearing 56 hydroxyl groups were involved in complex formation per 100 units of PVP, i.e. in hydroxyl group rich PVP–PEG mixtures 44% of PVP repeat units remain either intact or loosely bound within a wide mixture composition range. Similarly, in case of PVP–E mixtures, all PVP repeat units cannot form H-bonds with hydroxyl groups in the hydroxyl group rich solution and hence there is existence of linear homogeneous structure of E molecules which contributed in the dielectric relaxation processes. The chain ends hydroxyl groups of PEG molecules bridges the coiled PVP chain through complex formation resulting the super structure molecular network of PVP–PEG mixture [19]. In the same fashion, the linear structure of self associated E molecules also linkage the coiled structure of the long PVP chain in dynamic equilibrium as shown in Fig. 1.

The free energy of activation ΔF_τ of the dielectric relaxation process is found nearly 4 kcal mol^{-1} for ethyl alcohol and PVP–E mixtures (Table 2). This value is in agreement with the activation energy for the breakage of a hydrogen bond. This suggests that the formation and deformation of H-bonds between the carbonyl groups and hydroxyl groups occurs repeatedly in dynamic state equilibrium as shown in Fig. 1. From the observed τ and ΔF_τ values it can be concluded that in the PVP–E mixture, two types of cooperative domains (CDs) take place due to the transient structure of PVP chain and also due to the breaking of the some homogeneous structure of ethyl alcohol molecules. $\mathrm{CD_E}$ which includes the ethyl alcohol molecules that form the H-bonds only with ethyl alcohol molecules, and, $\mathrm{CD_{PVP-E}}$ which includes the ethyl alcohol molecules which interact directly with the PVP, and also the ethyl alcohol molecules which move cooperatively with the ethyl alcohol molecules interact directly with PVP. Similar type of the formation of CDs has also been suggested by Shinyashiki and Yagihara [17] in PVP–water mixtures and by Rohmann and Stockhausen [32] in PVP–pyrrolidone mixtures using the observed values of relaxation times at microwave frequencies. In the PVP–E mixture it can be assumed that due to reorientation of the chain segments in the applied alternating electric field, there is the breaking of loosely bound H-bonds between carbonyl and hydroxyl groups and at the same time the carbonyl group of other repeat unit of PVP chain reforms the new hydrogen bonds with ethyl alcohol in dynamic equilibrium.

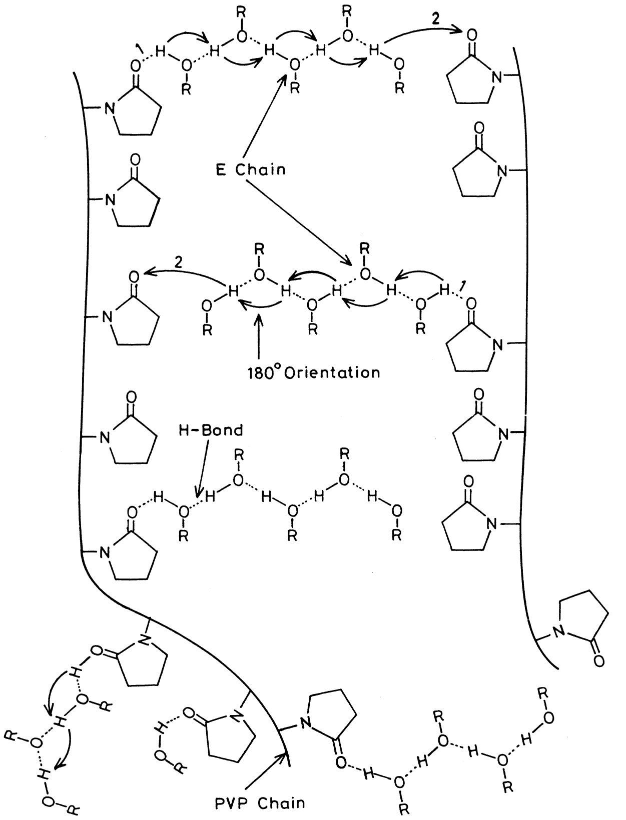

Fig. 1. Schematic diagram of the proposed structure of a complex between high-molecular-mass PVP and homogeneous short-chain of E, with the 180° orientation of hydroxyl groups in the E chain and the transition of PVP–E complex from position 1 to position 2.

In case of PVP–E mixtures, the viscosity of the mixture increases appreciably with the increase in PVP concentration. But it seems that the τ value of PVP–E mixture is practically independent of the mixture viscosity because its value does not follow the variation in the viscosity. The viscosity independent τ value of the PVA–water mixtures [13] and PVP–PEG mixtures [34] has also been confirmed by earlier workers. The anomalous variation in τ of PVP–E mixture at higher concentration confirms that there is monotonous variation in the H-bonded structures of homogenous and heterogeneous clusters with concentration variation, which may be due to the random coiling of the long PVP chain during the solvation in ethyl alcohol solvent.

3.2. PVP–E mixtures in benzene solution

Before interpretation of the values of τ_0, τ_1 and τ_2 of PVP–E mixtures in dilute solution of benzene, it is appropriate to report the earlier work on the relaxation studies of primary alcohols in dilute solution of non-polar solvent and also in pure liquid state. Earlier, Crossley et al. [35,36] extensively studied the series of primary alcohols in their pure liquid state and also with concentration variation in dilute solutions of non-polar solvent over wide frequency range at 25 °C. Three relaxation times were evaluated for the conformation primary alcohols. The high frequency process corresponding to rotation of the hydroxyl group about its C–O bond, the intermediate process is related to reorientational of motion of small multimer species, while the low-frequency process (switch-over mechanism) involves the hydrogen-bonded structure of some considerable size (principal relaxation process). Up to 0.1 mole fraction of solute, the dielectric absorption in primary alcohol were resolved only into two dispersion regions characterized by the rotation of –OH group and reorientation of small range multimer because in very dilute solution of non-polar solvent, the long chain polymeric structure of primary alcohol do not exist. Further, they have also observed that the high frequency process is independent of the solute concentration while the intermediate and low frequency relaxation processes lengthen with the increase in the concentration of solute due to increase in the range of intermolecular correlation. Mandal et al. [37] studied the switch-over mechanism in the principal relaxation process of primary alcohols in inert, weakly interacting and strongly hydrogen bonding solvents over the concentration range 0.3–1.0 mole fraction of solute in which the principal relaxation exist, with temperature variation in the frequency range 10^6–10^9 Hz by evaluating the enthalpy of activation and considering the earlier findings. The switch-over mechanism is also proposed by Higasi and co-workers [38] for alcohols. In this mechanism, due to breaking of O–H….H bond at the end of the alcohol polymeric chain; this group then rotates through 180° and the switch occurs cooperatively all along the multimer chain.

In the present study, the evaluated values of τ_1 and τ_2 of ethyl alcohol at 10.1 GHz in very dilute solutions of benzene can be assigned to the reorientational motion of small multimer species and to the rotation of –OH group around C–O bonds, respectively. The existence of short range multimers of ethyl alcohol molecules in very dilute solutions of non-polar solvent has already been confirmed by the earlier evaluated value of Kirkwood correlation factor [33]. The average relaxation time τ_0 of PVP–E mixture in dilute solution of benzene increases with the increase in concentration of PVP [Table 2]. The increase in concentration of PVP in PVP–E mixture, the density of H-bond formation between carbonyl group and hydroxyl groups increases due to which steric hindrance to the reorientation of ethyl alcohol molecules also increases and hence there is increase in the value of τ_0.

In the binary mixture of PVP–E, the observed τ_1 value can be ascribed to the combined effect of the reorientation of the small size homogeneous cluster of ethyl alcohol molecules and also the reorientation of the monomer unit of flexible long chain PVP molecules in dilute solution. In general τ_1 depends on the size of the reorientating segment and the intra- and intermolecular interactions [10]. The significant increase in τ_1 value with the increase in PVP concentration in PVP–E mixtures may be probably due to the increase in size of homogeneous species of ethyl alcohol molecules. The increase in size of linear multimer of ethyl alcohol may be explained on the following hypothesis. When the PVP–E mixture is added to benzene solvent, there is an elongation of the heterogeneous cooperation domain (CD_{PVP-E}). During elongation of the heterogeneous cluster, the unassociated ethyl alcohol molecules align with each other resulting in an increase in the length of self-associated ethyl alcohol molecules to remain in complex form with the extended chain of PVP molecules in dynamic equilibrium. This hypothesis is also supported by the phase separation observed in PVP–E mixtures above 50 wt% of PVP in the mixture in dilute solution of benzene. With increasing PVP concentration, the chain of ethyl alcohol molecules increases to bridge the elongated structure of PVP but above 50 wt% PVP concentration in PVP–E mixture there is dissociation of the hydroxyl and carbonyl group complexes resulting the phase separation in dilute solution of benzene at higher PVP concentration. Earlier [16] in case of PVP–PEG200 mixture, the increase in τ_1 was also observed with the increase in concentration of PVP in benzene solutions but the phase separation occurred above 30 wt% of PVP in the mixture in dilute solution. This is due to the large size of the PEG200 molecules and comparatively less density of complexes formed between ends hydroxyl group of PEG and carbonyl group of monomer unit of PVP.

The relaxation time τ_2 which arises from internal rotation of polar groups of the molecules in PVP–E mixture is found independent of the concentration of the constituents in the mixture. Further the value of τ_2 of PVP–E mixture is found equal to the τ_2 value of ethyl alcohol in dilute solution of benzene. The equal τ_2 value of ethyl alcohol and PVP–E mixtures confirms that there is rotation of –OH group of ethyl alcohol molecules about the C–O bond in dynamic equilibrium as suggested by Higasi and co-workers [38] in a switch-over type mechanism in alcohols. The τ_2 value of ethyl alcohol and PVP–E mixture is found in good agreement with the τ_2 value of the rotation of –OH group around C–O bond reported by Crossley et al. [35,36] for primary alcohol over whole concentration range in non-polar solvent. In case of PVP–PEG mixtures in benzene solution [16], the τ_2 value varies in the range 8–11 ps. The higher value of τ_2 shows the hindered rotation of PEG chain ends hydroxyl groups in PVP–PEG mixtures. This study confirms that the rotation of –OH group in dilute solution and also in PVP–E mixtures is independent of the PVP concentration but the –OH rotation phenomena is governed by the switch-over mechanism in the correlated chain of alcohol molecules. The free energy of activation ΔF_{τ_0} for ethyl alcohol and PVP–E mixtures in dilute solutions of benzene is found much lower than that the free energy of these system in their pure state which confirms that the molecular dynamics in dilute solution of non-polar solvent is less hindered.

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