Chain length effect on dynamical structure of poly(vinyl pyrrolidone)–polar solvent mixtures in dilute solution of dioxane studied by microwave dielectric relaxation measurement

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Abstract. Dielectric relaxation study of the binary mixtures of poly(vinyl pyrrolidone) (PVP) (Mw = 24000, 40000 and 360000 g mol^{-1}) with ethyl alcohol (EA) and poly(ethylene glycol)s (PEGs) (Mw = 200 and 400 g mol^{-1}) in dilute solutions of dioxane were carried out at 10.1 GHz and 35°C. The relaxation time of PVP–EA mixtures was interpreted by the consideration of a wait-and-switch model in the local structure of self-associated ethyl alcohol molecules and also the PVP chain length as a geometric constraint for the reorientational motion of ethyl alcohol molecules. The formation of complexes and effect of PVP chain length on the molecular dynamics, chain flexibility and stretching of PEG molecules in PVP–PEG mixtures were explored from the comparative values of dielectric relaxation time. Further, relaxation time values in dioxane and benzene solvent confirm the viscosity independent molecular dynamics in PVP–EA mixtures but the values vary significantly with the non-polar solvent environment.

Keywords. Poly(vinyl pyrrolidone); polar solvents; binary mixtures; dielectric relaxation time; molecular dynamics; solvent effect.

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1. Introduction

Compared to low molecular weight compounds, synthetic polymeric materials are very complex and can have an even larger number of conformations in solutions [1]. The conformation of the polar solvents and their molecular dynamics in polymer matrix are the most important and challenging problems in liquid state physics. The molecular size dependence of dielectric properties for two-component system shows various characteristic properties, which have been the subject of a large number of investigations [2–14].

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In this study, authors made an attempt to explore the effect of PVP chain length and concentration on the dynamics of EA (monohydric molecule), PEG200 and PEG400 (dihydric molecules) in quasi-isolated state of dioxane solvent by microwave dielectric relaxation measurements. This study is interesting because the molecules of EA, PEG200 and PEG400 have equal values of relaxation time τ_0 in their pure liquid state besides their different values of static dielectric constant ε_0 and Kirkwood correlation factor g [7,12]. Recently, Feldstein and coworkers [15–17] extensively studied the complex formation between carbonyl groups of PVP monomer units and hydroxyl groups of polar solvents using Fourier transform infra red (FTIR) spectroscopy and differential scanning calorimetry (DSC) measurements to confirm the molecular structure and dynamics of PVP chain segments and the polar solvent in the PVP matrix for their special use in transdermal drug delivery system (TDDS). Adhesive, transport, reservoir and biological properties of polymeric composites constitute a general basis for their applications as TDDS. Such diverse requirements are difficult to combine in a single system. Molecular structure of a polymer matrix, especially PVP–PEG has been recognized to govern its physical properties and control ultimately the TDDS pharmaceutical performance. Adhesion and diffusivity are interrelated through molecular structure of a polymer, and hence the conformation of the dynamics of polymer composite is an important parameter for its use in TDDS. The findings of Feldstein *et al* [15–17] on the PVP–PEG blends forced the authors to investigate the dynamics of polar solvents in PVP matrix of different molecular weights with concentration variation in quasi-isolated state, because the dynamics of the system governs the release of the specific drug loaded in the system.

2. Experimental

2.1 *Materials*

Poly(vinyl pyrrolidone) (PVP) of average molecular weight Mw = 40000 g mol^{-1} was obtained from Loba Chemie, India and PVP of Mw = 24000 and 360000 g mol^{-1} were purchased from S.D. Fine Chem, India. Ethyl alcohol (EA), poly(ethylene glycol) (PEG) of average molecular weight Mw = 200 and 400 g mol^{-1} and 1,4-dioxane were purchased from Merck, India.

The binary mixtures of different molecular weight PVP with EA, PEG200 and PEG400 of varying concentrations were prepared by adding different wt% PVP in the weight of liquid EA, PEG200 and PEG400 at room temperature. The viscosity of PVP–EA samples increases heavily with increase in molecular weight and concentration of PVP. Due to the poor solubility of PVP360000 in PEG200 and PEG400 at room temperature, these binary systems were not studied.

2.2 *Dielectric measurements*

The dielectric permittivity ε' and loss ε'' of the PVP–polar solvent binary mixtures in dioxane solutions at 10.1 GHz were determined using the short-circuited wave

guide method [14]. The static dielectric constant ε_0 at 1 MHz was measured using heterodyne beat method. High frequency limiting permittivity ε_∞ was taken as the square of refractive index n_D, which was measured by Abbe refractometer. All measurements were made at $35 \pm 0.5°$C.

2.3 *Analysis of data*

It has been observed that $\varepsilon_0, \varepsilon', \varepsilon''$ and ε_∞ are linear functions of the weight fraction of solute w_2 (polar solvent or PVP–polar solvent mixture) in dilute solutions of dioxane solvent. Linear slopes a_0, a', a'' and a_∞ corresponding to $\varepsilon_0, \varepsilon', \varepsilon''$ and ε_∞ vs. w_2 of the solute were used for the evaluation of different dielectric parameters. Distribution parameter α, and average relaxation time τ_0 were calculated using Higasi's [18] equations proposed for single frequency measurements in the dispersion region with solute concentration variation in non-polar solvent. The dipole moment μ of individual polar molecules in dilute solutions of dioxane were determined using Higasi's equation [19]. The values of specific dipole moment μ_{sp} of PVP and PEG molecules were determined by the relation $\mu_{sp} = [\mu^2/n]^{1/2}$, where n is the number of monomer units in the polymer chain.

3. Results and discussion

The observed τ_0 and α values of PVP24000, PVP40000 and PVP360000 are 1376 ps 0.77, 1270 ps 0.75, and 476 ps 0.70, respectively in dilute solutions of dioxane. The decrease in τ_0 with increase in PVP chainlength suggests that there is large random increase in chain coiling and flexibility with the increase in molecular size of PVP molecules. Further, the decrease in the size of reorientating segments with increase in PVP chain length cannot be ruled out for the comparative decrease in values of τ_0 for higher size PVP molecules.

Figure 1 shows the dielectric relaxation time τ_0 of PVP–EA, PVP–PEG200 and PVP–PEG400 mixtures at different PVP wt. fraction w_{PVP} in dilute solutions of dioxane at $35°$C. The observed τ_0 values can be assigned to the reorientation relaxation time of the polar solvent molecules, because at microwave frequency there is larger possibility of the dynamics of small size molecules. In the case of PVP–EA mixtures (figure 1a), comparatively small variations in τ_0 values suggest that the dynamics of EA molecules in their linear chain type self-associated structure [7,8,10] is less affected at lower PVP concentration and also by the variation in PVP molecular chain length in dilute solutions of dioxane. The anomalous increase in τ_0 values of PVP24000–EA and PVP40000–EA mixtures at higher PVP concentration confirms the increase in hindrance to the molecular reorientation of the EA molecules, which is also influenced by the PVP chain length. The dynamics of EA molecules in their homogeneous structures (Kirkwood correlation factor $g = 3.1$) in pure liquid state occur due to cooperative molecular switching (according to a wait-and-switch model) [7,8,20] all along the EA chain, resulting in the breaking and reforming of hydrogen bonds. The complex formations between short chain linear polymeric structures of EA molecules and coiled chain structure of PVP
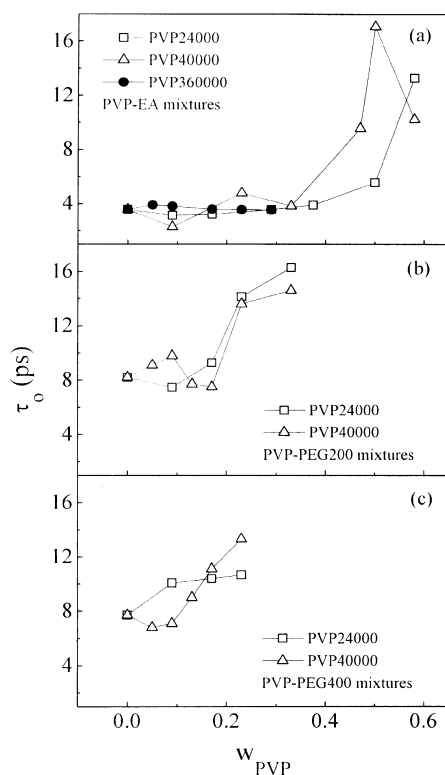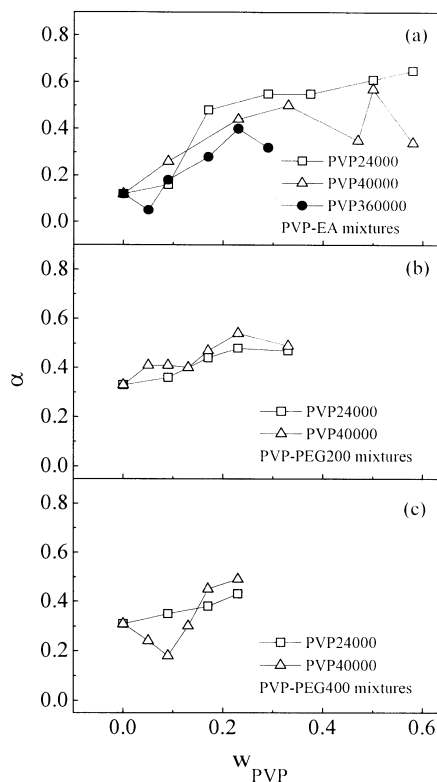
Figure 1. Plots of τ_0 vs. w_{PVP}.

Figure 2. Plots of α vs. w_{PVP}.

in PVP40000–EA mixtures were established by dielectric relaxation spectroscopy (DRS) [7,8]. The dilution of these mixtures in dioxane solvent unfolds the PVP–EA structures, which changes the dynamics of EA molecules at higher values of w_{PVP} in quasi-isolated state.

The viscosities of the prepared PVP–EA mixtures increase significantly with the increase in PVP concentration and also with the increase in PVP chain length at the same PVP concentration. But in the case of PVP–EA mixtures, nearly equal τ_0 values at lower PVP concentration confirm that the molecular dynamics is independent of the mixture viscosity in dioxane solvent. The viscosity independent τ_0 values were also confirmed in pure liquid state PVP–EA mixtures [7].

Earlier, dielectric relaxation spectroscopy [10,11] and FTIR measurements [17] confirmed the formation of supermolecular structure in PVP–PEG mixtures due to cross-link complexation between end hydroxyl groups of the PEG chain and the carbonyl groups of folded PVP chain in dynamic equilibrium. Figure 1b shows that the τ_0 values of PVP24000–PEG200 and PVP40000–PEG200 mixtures increase anomalously with increase in PVP concentration and chainlength in dilute solutions of dioxane. Comparative τ_0 values of PVP40000–PEG200 and PVP40000–PEG400 mixtures (figures 1b and 1c) show that the increase in PEG chain length and chain flexibility influence the molecular dynamics of low molecular weight PEG molecules
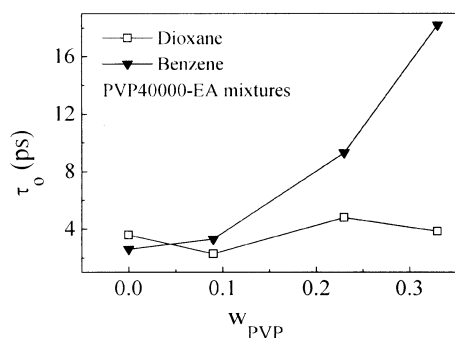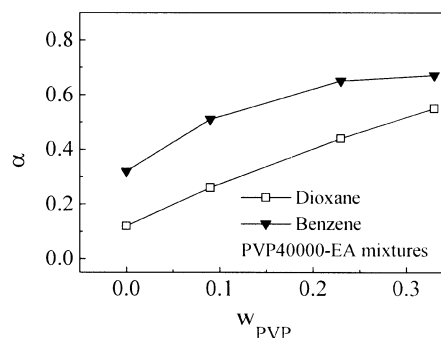
Figure 3. Plots of τ_0 vs. w_{PVP}.

Figure 4. Plots of α vs. w_{PVP}.

in the presence of PVP matrix in dilute solutions, which is similar to their dynamics in pure PVP–PEG mixtures [10]. Further, the PVP concentration dependent anomalous behaviour of τ_0 values of PVP–PEGs also suggests that the dynamics of PEGs is independent of their viscosity. Furthermore, the effect of self-association strength $g = 1.99$ and 1.82 of PEG200 and PEG400, respectively, on their molecular dynamics in PVP matrix in quasi-isolated state of dioxane solvent cannot be ignored, although pure PEG molecules have nearly equal τ_0 value (PEG200 $\tau_0 = 116.5$ ps; PEG400 $\tau_0 = 115.1$ ps) in their pure liquid state [21].

The value of distribution parameter α is the measure of the distribution of relaxation processes in PVP–polar solvent mixtures in dilute solutions. The observed non-zero α values (figure 2) of the studied mixtures also support the fact that besides the polar solvent reorientation, there is large contribution of the PVP chain flexibility and its dynamics to the relaxation processes. Figure 2 shows that, in most of the studied binary mixtures the α value increases anomalously with the increase in PVP weight fraction (w_{PVP}). This confirms the anomalous variation in PVP segmental motion in dilute solutions of dioxane with increase in the PVP concentration, which may be due to the change in complexation density in the mixtures. Further, it seems that the PVP chain length also affects the PVP segmental motion, because the α values of PVP molecules reduce from 0.77 to 0.70 with the increase in PVP chain length of the studied different molecular weight PVP molecules.

The observed values of specific dipole moment of different molecular weight PVP molecules in dioxane are equal ($\mu_{sp} \approx 3$ D), which is the characteristic behaviour of high molecular weight homologous polar polymers. Further, higher μ_{sp} value of PVP in comparison to the μ_{sp} value of PEG molecules (PEG200 $\mu_{sp} = 1.73$ D; PEG400 $\mu_{sp} = 1.32$ D), is due to the higher group moment value of carbonyl group of PVP monomer unit as compared to the group moment value of the chain end hydroxyl group of PEG molecules [13].

Figure 3 shows the comparative τ_0 values of PVP40000–EA mixtures in dioxane and benzene [12] solvents. It is found that the variation in τ_0 values in dioxane solvent up to $w_{PVP} = 0.33$ is small but the τ_0 values in benzene solvent increases with increase in PVP concentration. These results confirm that the solvent environment also influences the molecular dynamics of EA molecules in PVP matrix at

quasi-isolated state. From the comparative τ_0 values in benzene and dioxane, it seems that the weak interactions of dioxane solvent with the heterogeneous structures of PVP–EA system try to maintain favourable conditions for the reorientation of EA molecules at low concentration of PVP. Figure 4 shows the comparative α values of PVP40000–EA mixtures in benzene and dioxane. The comparative higher α values confirm the higher segmental mobility in PVP chain in benzene solvent. It is also expected, because the weak polar behaviour of dioxane influences the interactions between PVP and EA molecules as compared to their interaction in benzene solvent.

4. Conclusions

The reorientation of EA molecules in the PVP matrix in quasi-isolated state of dioxane solvent is independent of the PVP chain lengths at low PVP concentration. In PVP–PEG mixtures, the reorientations of PEG molecules are affected by the PVP chain length and also by the PVP concentration in dilute solutions of dioxane. The study of polymer–solvent interactions and polar solvent dynamics in different chain length PVP matrix is useful to understand the rate of release of specific drug loaded in the polymer matrix, because the release of drug depends on the molecular dynamics in polymer matrix. Further, the confirmation of the dynamics of PEG200 and PEG400 in PVP matrix has special interest, because the molecular sizes of drugs, namely aminostigmine, isosorbide dinitrate, glyceryl trinitrate, silabolin, propranolol etc. are usually in the molecular range of low molecular weight PEGs.

Acknowledgments

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