Study of solvent effect on microwave dielectric relaxation and molecular dynamics in PVP-PEG mixtures

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1 Introduction

The dielectric relaxation of poly(vinyl pyrrolidone) (PVP) (Mw=40000 g mol⁻¹) and poly(ethylene glycol) (PEG) (Mw = 200 and 400 g mol⁻¹) and their binary mixtures in dilute solutions of dioxone has been studied performed at 10.1 GHz and 35°C. The average relaxation time τ₀, relaxation time corresponding to segmental motion τₛ, and group rotations τₒ, distribution parameter α and free energy of activation ΔFₒ of these mixtures has been determined. These results have been compared with the values of relaxation times obtained earlier in benzene solutions to explore the effect of solvent environment on molecular dynamics. The values of α for PVP-PEG200 and PVP-PEG400 were found in the range of 0.18 - 0.75. The anomalous variation in the values of τ₀ and τₛ of these binary systems has been studied by considering the stretching effect in PEG molecular chain length in dilute solutions and the number of hydrogen bonding between carbonyl groups of PVP monomer units and terminal hydroxyl groups of PEGs in complex heterogeneous network. Further, in both benzene and dioxane solvents the τₒ values of PVP-PEGs mixtures are found to be nearly equal. This shows that group rotation is independent of the nature of solvation medium and attributed to the rotation of PEG chain ends –OH groups about the C-O bond in dynamic equilibrium. The relaxation times of PVP-PEGs in dilute solutions are found to be independent of the mixtures and solvent viscosity. The variations in dipole moment μ values of PEGs molecules in different solvents were explored by incorporating the solute-solvent interactions in hydrogen-bonding non-polar solvents.

[Keywords: Dielectric relaxation, Molecular dynamics, Poly(vinyl pyrrolidone), Poly(ethylene glycol)]
IPC Code: G01R 2200

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1 Introduction

The behaviour of binary mixtures of polar polymers under varying conditions of composition attracted a considerable interest because it helped in formulating adequate models of liquid relaxation. The synthetic polymers such as, poly(vinyl pyrrolidone) (PVP), poly(ethylene glycol) (PEG), poly(propylene glycol) (PPG), poly(vinyl alcohol) (PVA) etc. have a wide range of pharmaceutical, biological and technological applications. The PVP-PEGs binary mixtures exhibit properties not inherent in the parent polymers in particular high elasticity and high stickiness with the ability to form strong adhesive joints with a variety of substances i.e. glasses, metals, rocks, polymeric films, rubbers, human skin and other biological tissues. Due to adhesive, transport, reservoir and biological properties of PVP-PEG mixtures; at present these are found increasing applications in medicine as universal diffusion matrices for the controlled transdermal delivery of drugs having various structures, physico-chemical properties, and therapeutic activities. The main functional properties of these matrices are the controlled rate of release of the dissolved drugs, which are determined by the diffusion mobility of macro-molecular segments and the adhesion to human skin. The physical properties of polymeric materials are eventually determined by their molecular and supermolecular structures. The microwave dielectric relaxation studies of the associating molecules and their mixtures in non-polar solvents confirm the steric hindrance to the internal rotation due to hydrogen bonding and give information about the effect of solvent environment on these rotations. Molecular dynamics at microwave frequencies is characterized by the observed values of τₜ, τₛ, α and ΔFₒ. In the present work, the experiments were conducted at 10.1 GHz, because the dielectric loss peak of the polymers in the dilute solutions of non-polar solvent occurs around 10 GHz.

PVP at room temperature readily dissolves in an excess amount of liquid PEG and form true transparent solutions. The solubility of PVP in PEG is related to the formation of hydrogen bonds between carbonyl groups of the PVP units and terminal hydroxyl groups of the short chains PEGs molecules as sketched in Fig. 1. Both the terminal hydroxyl groups of PEG molecules are capable of forming the
hydrogen bonds with PVP units. The PEG behaves as a cross linking agent in the PVP-PEGs super molecular matrix. In case of binary mixtures of associating polymers, both theoretical and experimental efforts have been done in the last few years to confirm the solute-solvent interactions. Several theoretical equations were also developed to predict the competition between inter- and intramolecular hydrogen bonding in the polymers mixtures and the ability of the solute to bond the polymer intermolecularly.

Earlier, an extensive microwave relaxation study of poly(ethylene glycols) with increasing molecular chain length had been carried out in dilute solutions of non-polar solvents and also in pure liquid state. Further microwave dielectric relaxation study of PVP-ethanol in pure liquid state and in benzene solutions was also explored to confirm the formation of homogeneous and heterogeneous cooperative domains and their dynamics in the complex molecular network. In this work, the dielectric relaxation processes in PVP-PEGs mixtures in dilute solutions of dioxane at 10.1 GHz have been examined to understand the effect of the solvent environment on the molecular dynamics. A comparative study of PVP-PEGs mixtures in two different solvents i.e., benzene and dioxane, has been performed in order to explore the influence of solvation medium on their relaxation times.

2 Experimental Details
2.1 Materials
Poly(vinyl pyrrolidone) (PVP) of molecular weight 40,000 g mol⁻¹ of LR grade was purchased from Loba-Chemie, India. Poly(ethylene glycol) of molecular weight 200 g mol⁻¹ and 400 g mol⁻¹ (PEG200 and PEG400) of LR

![Schematic diagram of the proposed structure of a complex between high-molecular-mass PVP and short-chain PEG](image-url)
grade were obtained from S.D. Fine Chem., India. Dioxane of spectroscopic grade was obtained from Merck India and used as a solvent.

The binary mixtures of PVP-PEG200 and PVP-PEG400 of varying concentrations were prepared by mixing 5, 10, 15, 20, 30, 50 and 70 wt% PVP and 5, 10, 15, 20, 30 and 50 wt% PVP in the weight of liquid PEG200 and PEG400, respectively, at room temperature. The binary mixtures were allowed approximately for 2 days to dissolve PVP completely in the liquid PEGs. For dielectric measurements, five dilute solutions of varying concentrations of each mixture as a solute were made in dioxane solvent.

2.2 Dielectric measurements

The dielectric constant $\varepsilon'$ and dielectric loss $\varepsilon''$ at 10.1 GHz were determined using the short-circuited waveguide method proposed by Heston et al. This method is the highly accurate for the measurement of $\varepsilon'$ and $\varepsilon''$ of polar mixtures in dilute solutions of non-polar solvent at very low concentrations. The static dielectric constant $\varepsilon_0$ was determined by heterodyne beat method at 1 MHz. High frequency limiting value of permittivity $\varepsilon_\infty$ was taken as the square of the refractive index $n_\infty$, which was measured with Abbe’s refractometer. All measurements were made at 35 ± 0.5°C.

2.3 Data analysis

It has been observed that $\varepsilon_0$, $\varepsilon'$, $\varepsilon''$ and $\varepsilon\infty$ are linear functions of weight fractions of the PVP-PEGs binary mixtures in dioxane solvent. The linear slopes $a_0$, $a'$, $a''$ and $a\infty$ corresponding to $\varepsilon_0$, $\varepsilon'$, $\varepsilon''$ and $\varepsilon\infty$ versus weight fractions of the solute mixtures in dilute solutions of dioxane are recorded in Table 1. The linear slopes were used to evaluate the average relaxation time $\tau_\alpha$, relaxation time corresponding to segmental motion $\tau_\alpha$, group rotations $\tau_\beta$ and distribution parameter $\alpha$ using Higasi’s equations of dilute solutions described in detail elsewhere. The dielectric free energy of activation $\Delta F_t$ was evaluated using the Eyring’s formula. The ratios R of the hydroxyl groups of PEG to the carbonyl groups of PVP monomer units were also determined using the weights of PVP and PEG in the PVP-PEG mixtures, prepared for the dielectric measurements. The evaluated values of R, $\varepsilon_\alpha$, $\alpha$, $\tau_\alpha$, $\tau_\beta$, and $\Delta F_t$ are recorded in Table 2. The molecular dipole moment $\mu$ of PVP and PEGs have been calculated using Higasi’s equation. The values of $\mu$ in dioxane and earlier evaluated values of $\mu$ in benzene and carbon tetrachloride are recorded in Table 3 for the comparison. Further, the values of Kirkwood correlation factor $g$, which are the measure of the extent of intermolecular hydrogen bonding and average relaxation time $\tau_\alpha$ of PEGs molecules in their pure liquid states and in dilute solutions are also recorded in Table 4 for their comparison.

### Table 1—Values of the slopes of $\varepsilon_\alpha$, $\varepsilon'$, $\varepsilon''$ and $\varepsilon\infty$ versus wt fractions of PVP-PEG mixture in dilute solutions of benzene and dioxane at 10.1 GHz and 35°C

<table>
<thead>
<tr>
<th>PVP wt%</th>
<th>$a_0$</th>
<th>$a'$</th>
<th>$a''$</th>
<th>$a\infty$</th>
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<tbody>
<tr>
<td>PEG200</td>
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<td></td>
<td></td>
<td></td>
</tr>
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<td>1.19</td>
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<tr>
<td>PEG400</td>
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<td>10.00</td>
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<td>0.28</td>
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<td>2.63</td>
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*Ref No. 21*
Table 2– Microwave dielectric relaxation times, distribution parameter and free energy of activation of PEGs and PVP-PEGs mixtures in dilute solutions of benzene and dioxane at 10.1 GHz and 35°C

<table>
<thead>
<tr>
<th>Polymer</th>
<th>wt %</th>
<th>α (ps)</th>
<th>τ (_r) (ps)</th>
<th>τ (_f) (ps)</th>
<th>ΔF (kcal mol(^{-1}))</th>
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<tbody>
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<tr>
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<td>0.75</td>
<td>1270.0</td>
<td>162.0</td>
<td>4.8</td>
</tr>
</tbody>
</table>

*Ref No. 21

Table 3– Values of degree of polymerization \( n \) and dipole moment \( \mu \) in different solvents at 35°C

<table>
<thead>
<tr>
<th>Polymer</th>
<th>( n )</th>
<th>( \mu ) (D)</th>
<th>( \mu _\text{deg} ) (D)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Benzene*</td>
<td>Dioxane</td>
</tr>
<tr>
<td>PEG200</td>
<td>4.1</td>
<td>3.94</td>
<td>3.49</td>
</tr>
<tr>
<td>PEG400</td>
<td>8.7</td>
<td>4.72</td>
<td>3.89</td>
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<tr>
<td>PVP</td>
<td>358</td>
<td>57.12</td>
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</table>

*Ref No. 21

Table 4– Value of Kirkwood correlation factor \( g \) and average relaxation time \( \tau \_r \) at 35°C in pure liquid state

<table>
<thead>
<tr>
<th>Polymer</th>
<th>( g )</th>
<th>( \tau _r ) (ps)</th>
<th>( \tau _f ) (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Benzene</td>
<td>Dioxane</td>
</tr>
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<td>PEG200</td>
<td>1.99</td>
<td>116.5</td>
<td>52.0</td>
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<tr>
<td>PVP</td>
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<td>1270.0</td>
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</tr>
</tbody>
</table>

*molecules in comparison to the PEG200 molecules compensated the hindrance to the rotation of the molecules as a whole and hence the observed values of \( \tau \_r \) of PEG200 and PEG400 were found to be nearly the same in their pure liquid state (Table 4).

3.2 Dipole moment

Table 3 shows the \( \mu \) values of PEG200 and PEG400 molecules in benzene, carbon tetrachloride and dioxane...
solvents. The dipole moment of PVP is determined in dioxane only because it is insoluble in benzene and carbon tetrachloride. The comparative \( \mu \) values suggest that the structure of PEG molecules varies significantly in different solvents. Carbon tetrachloride is non-H-bonding solvent while the \( \pi \)-electrons of benzene and dioxane can interact with the protons of the solute. Therefore, it is expected that the dipole moment of PEG molecules in benzene and dioxane should be higher than that in carbon tetrachloride. Table 3 shows that the \( \mu \) values of PEG200 are found to be significantly higher in benzene and dioxane in comparison to the \( \mu \) value in carbon tetrachloride. But in case of PEG400 molecules, the observed values of \( \mu \) in benzene are higher than the \( \mu \) values in carbon tetrachloride, while it is lower in dioxane, which is interesting. These comparative \( \mu \) values suggest that the overall molecular structure of PEGs with increasing degree of polymerization in dioxane solvent varies significantly in comparison to its structure in benzene and carbon tetrachloride solvent. The high \( \mu \) value in benzene in comparison to the \( \mu \) value in carbon tetrachloride (6) is also observed for poly(propylene glycol). The specific dipole moment \( \mu_p = (\mu/\eta) \) of PEGs molecules decreases with the increase in degree of polymerization \( n \) in all these solvents (Table 3). The decrease in \( \mu_p \) is because of the increase in chain coiling of the molecules in dilute solutions of the non-polar solvents. The \( \mu \) value of PVP40000 in dioxane is found to be 57.12D. The high \( \mu \) value of PVP molecules is expected due to its larger molecular size. In case of PVP, the value of \( \mu_p =3.05 \) suggests that the chain coiling of PVP molecules is less in comparison to the chain coiling in PEG molecules in dioxane solvent which may be because of the presence of pyrrolidone ring in the side of monomer units of PVP molecules.

### 3.3 Molecular dynamics of individual polymers in non-polar solvents

The different observed values of \( \tau_p \) of PEGs in benzene, dioxane and carbon tetrachloride (Table 4) confirm that the molecular dynamics in dilute solutions of non-polar solvents is highly influenced by the solvent environment. It is found that the \( \tau_p \) values of PEGs in dioxane are smaller in comparison to the \( \tau_p \) values in benzene and carbon tetrachloride solvent which suggest that the hindrance to the reorientation of the molecule as a whole decreases in dioxane solvent. Dioxane itself is a good proton acceptor and it takes up the proton from the solute, thereby reducing the strength of intermolecular hydrogen bonding and hence there is an increase in the freedom of the molecules in quasi-isolated state. The greater increase in chain coiling of PEG200 in dioxane cannot be ruled out for lower \( \tau_p \) values. The higher value of \( \tau_p \) of these molecules in carbon tetrachloride is due to the higher chain rigidity in bulky environment. In benzene, dioxane and carbon tetrachloride, \( \tau_p \) values of PEGs decrease with increase in molecular size, which is due to the increase in chain coiling and also due to decrease in the intermolecular interactions. The viscosity of benzene, dioxane and carbon tetrachloride are 0.58, 0.987 and 0.89 cp, respectively at 35°C. Although the viscosity of dioxane is higher but the observed low values in this solvent confirm that the average relaxation time is independent of the solvent viscosity and it is governed by the solute-solvent interactions and the molecular chain coiling. The \( \tau_p \) values of PVP molecules were found to be very high in comparison to the \( \tau_p \) values of PEGs molecules in dioxane. It is expected because of the large size and random coiling nature of the PVP chain.

### 3.4 Molecular dynamics in PVP-PEGs mixtures in non-polar solvent

As confirmed by \( \gamma \) values, the molecules of PEGs form multimers with the parallel ordering of the dipoles in their pure liquid state. When the randomly coiled solid PVP is added in the liquid PEG, due to formation of complexes between carbonyl groups of PVP monomer units and chain ends hydroxyl group of PEG molecules, supermolecular structure is formed as shown in Fig. 1. This is confirmed earlier by FTIR and DSC studies and the same structure is used for the interpretation of dielectric relaxation times in benzene solvent. Although the ratio of hydroxyl groups to the carbonyl groups (R = OH/C=O) decreases with the increase in PVP concentration but all the prepared mixtures are rich from hydroxyl groups (Table 2).

In PVP-PEG mixtures Feldstein et al. also confirmed that only 44% carbonyl groups of PVP chain forms the complexes with terminal hydroxyl groups of PEG molecules. Therefore, in PVP-PEGs mixture, there is a large number of uncomplexed PEGs molecules and their value decreases with the increase in PVP concentration. In PVP-PEGs mixtures two types of cooperative domains (CDs) take place due to the transient structure of PVP chain and also due to breaking of homogeneous structure of PEG molecules. CD\text{PVP}\text{PEG}, which includes the self associated PEG molecules, and CD\text{PVP}\text{PEG}, which includes the PEG molecules those interact directly with the carbonyl groups of the monomer units of PVP chain. In benzene, only PEGs is soluble, while in dioxane both PVP and PEGs are soluble. When PVP dissolved in PEG is added in very small quantity in benzene and dioxane to prepare the dilute solutions, the non-polar solvent molecules penetrate into the inter-segmental space. Due to which, the segments of PVP-PEG supermolecular structure unfold and get solvated resulting into different molecular species (CDs). The dynamics of these species also vary because of the different behaviour of the molecular dynamics of individual polymer molecules in these solvents.
3.4.1 Overall dynamics of the PEG molecules

The $\tau_i$ values of PVP-PEG200 mixtures in benzene solvent increase with an increase in the PVP concentration but these values are lower than the $\tau_i$ values of PEG200 which suggest that there is a large probability of the rotation of PEG molecule as a whole. The increase in $\tau_i$ values confirms that there is an increase in complex formation and also the gradual elongation of PVP-PEG200 complex network in dilute solutions of benzene due to which there may be expansion in the chain length of PEG200 and hence there is increase in $\tau_i$ values\textsuperscript{39}. The PVP-PEG200 mixtures are studied up to 30 wt% of PVP. Above this concentration, the phase separation is observed in dilute solutions of benzene.

In dioxane, the observed $\tau_i$ values of PVP-PEG200 mixtures are found to be nearly equal to the $\tau_i$ value of PEG200 up to 20 wt% PVP concentration. Above 20 wt% PVP concentration, the observed $\tau_i$ values of these mixtures are significantly higher than the $\tau_i$ of PEG200. Further, there is a slight increase in $\tau_i$ at higher PVP concentration as depicted in Fig. 2. These $\tau_i$ values can be assigned to the rotation of PEG200 molecules. Further, these values also suggest that the molecular dynamics of PEG200 molecules above 20 wt% of PVP concentration in the PVP-PEG200 binary mixtures changes abruptly which may be due to the formation of different types of cooperative domains of PEGs complexed with PVP.

In case of PVP-PEG400 mixtures, the $\tau_i$ values are higher than the $\tau_i$ values of PEG400 in benzene (Table 2 and Fig. 2). The anomalous variation in $\tau_i$ with an increase in PVP concentration shows that in benzene, the molecular dynamics of PEG400 molecules vary in opposite manner in comparison to the dynamics of PEG200 molecules in PVP-PEG200 in benzene solvent\textsuperscript{39}. Fig. 2 also shows that in case of PVP-PEG400 mixtures, $\tau_i$ values also vary anomalously with the concentration of PVP in dioxane, but these values are lower than the $\tau_i$ values in benzene solvent. At 50 wt% concentration of PVP, the observed value of $\tau_i$ in dioxane is found to be very high which shows that the hindrance to molecular reorientation increases greatly at higher concentration. However, the viscosity of PVP-PEGs mixtures increases heavily with increasing PVP concentration in the mixture, but the observed comparative values of $\tau_i$ confirm that the molecular dynamics in these mixtures is independent of the solution viscosity. This is in agreement with the results of Stockhausen and Abd-El-Rehim\textsuperscript{40} who confirmed that the relaxation time of PVP24000-PEG200 mixtures is independent of their viscosity.

3.4.2 Segmental motion

The values of distribution parameter $\alpha$ obtained for PEGs, PVP and PVP-PEGs binary mixtures in dilute solutions of benzene and dioxane are found in the range 0.18 - 0.75 (Table 2). A large value of $\alpha$ suggests that there is a significant contribution of segmental motion and group rotation to the relaxation processes in these systems. Earlier, large values of $\alpha$ of associating polymers and their mixtures were also observed by several workers\textsuperscript{41,42,43} in dilute solutions of non-polar solvents.

In PVP-PEG200 mixtures, it is found that the $\tau_i$ values corresponding to segmental motion is higher for individual polymer in comparison to the $\tau_i$ values of binary mixtures in benzene solutions (Table 2). PVP concentration dependent $\tau_i$ values are also depicted in Fig. 2. These values confirmed that the segmental motion increases in PVP-PEG200 mixtures, which may be due to an increase in the flexibility of the PVP-PEG200 supermolecular network in dynamic equilibrium\textsuperscript{44}. But in case of PVP-PEG400, the $\tau_i$ values are higher than that of $\tau_i$ values of PEG400 in benzene which is due to less flexibility in PEG400 in binary mixtures\textsuperscript{44}. In dioxane, the $\tau_i$ values of PEGs molecules are lower than the $\tau_i$ values of PVP-PEGs binary mixtures. This suggests...
that dioxane accepted more protons from the -OH groups and thereby reducing the formation of intermolecular hydrogen bonding. Due to this, there is a decrease in the hindrance to the segmental motion of PEGs molecules.

Fig. 2 shows that at lower concentration of PVP, the $\tau_1$ values are of the order of $\tau_1$ of PEG200 but at higher concentration these values are larger. The observed values show that the flexibility of molecular chain in PVP-PEG400 mixtures reduces at higher concentrations in dioxane. The $\tau_2$ values of PVP in dioxane are much higher than the $\tau_1$ values of PEGs molecules which also shows that there is higher rigidity in the segmental motion of PVP molecules which may be due to the presence of side pyrrolidone ring in the PVP chain monomer units.

3.4.3 Group rotations

The observed $\tau_2$ values corresponding to group rotations of PEGs and PVP-PEGs mixtures may be assigned to the rotation of PEG chain ends hydroxyl groups around the C-O bonds in dynamic equilibrium and also the rotation of pyrrolidone ring of PVP monomer units. The evaluated $\tau_2$ values of PEG200, PEG400 and PVP-PEGs mixtures in dilute solutions of benzene and dioxane are found to be almost equal. This suggests that the group rotations are unaffected by the solvent viscosity and the constituents of binary mixtures. The $\tau_2$ values of PVP in dioxane may be assigned to the rotation of the pyrrolidone ring of PVP monomer units.

The dielectric relaxation free energy of activation $\Delta F$ for these binary mixtures is found in the range $2.30 - 3.56$ kcal mol$^{-1}$. These values are in agreement with the activation energy needed for the breakage of hydrogen bonds in dilute solutions of non-polar solvents. Further, these values suggest that the molecular dynamics in PVP-PEGs networks is in dynamic equilibrium due to continuous breaking and reforming of hydrogen bonds.

4 Conclusions

From the comparative systematic microwave dielectric relaxation study of PVP-PEGs mixtures with varying chain length of the PEG molecules, it is inferred that the molecular dynamics in these systems is governed by the complex formation between carbonyl groups and hydroxyl groups in the PVP-PEGs matrix and the molecular chain coiling. Further, the molecular dynamics is also influenced by the concentration of the PVP and chain length of the PEG molecules. Environment of the different non-polar solvents significantly changes the dynamics of the reorientation of the molecule as a whole and segmental motion. In dilute solutions of PVP-PEGs mixtures, there is reorientation of PEG molecules as a whole and these may be either uncomplexed PEGs molecules or the complexed PEGs molecules with PVP in dynamic equilibrium. The viscosity of the solution has no effect on the molecular dynamics in these binary systems.

References