

Dielectric Behavior and Molecular Dynamics of Polyvinylpyrrolidone in Aqueous Solutions: Structural and Thermodynamic Characteristics

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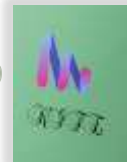
Abstract

This paper discusses the dielectric relaxation properties of water-soluble polyvinylpyrrolidone (PVP) solutions using time-domain reflectometry in the GHz region. It identifies low-frequency relaxation associated with PVP molecule alignment and high-frequency relaxation linked to bulk water dynamics. The study examines the effects of concentration and temperature on relaxation times, dipole moments, and molecular interactions. The findings highlight weak dipolar alignment and increasing solute-solute interactions at higher concentrations. The research provides insights into hydration dynamics and the entropy changes during relaxation, emphasizing the role of PVP's structure and interactions with water.

Keywords: Polyvinylpyrrolidone (PVP), Reflectometry, Dipole moments

1. Introduction

Solvent molecular dynamics and micro-Brownian motion of polymer chains impact the physical and chemical characteristics of polymer solutions. Because of these dynamics, polymer solutions are a great way to study molecular motions, which are associated with biopolymers' useful characteristics. Closely packed atoms of nitrogen (N), oxygen (O), carbon (C), and hydrogen (H) form the monomer units of polyvinylpyrrolidone (PVP), an amorphous polymer with an asymmetrical distribution of electrical charges. Through hydrogen bonding, PVP forms complexes with a wide variety of molecules, including hydroxyl groups in solvents including water, alcohols, ethylene glycol oligomers, and glycerol. These interactions are greatly influenced by the carbonyl group found in PVP. Researching the water structure surrounding a coiled polymer is a breeze with PVP, a highly water-soluble polymer that is both flexible and randomly coiled. Such non-electrolytic solutions can be easily analyzed using dielectric measurements. Polyvinylpyrrolidone (PVP), a water-soluble polymer, has garnered significant attention in various scientific fields due to its versatile physicochemical properties, biocompatibility, and wide-ranging applications. Its molecular structure, composed of highly polar carbonyl groups, facilitates extensive hydrogen bonding with water molecules, making it an excellent candidate for studying polymer-solvent interactions. The dynamic behavior of PVP in aqueous solutions is primarily influenced by its dielectric properties, which provide insights into molecular interactions, hydration dynamics, and structural organization. Dielectric spectroscopy, as a non-invasive and highly sensitive analytical tool, enables the exploration of these phenomena by investigating the material's response to an applied electric field across a broad frequency range. Such studies are vital for understanding the molecular motions, relaxation processes, and dipolar alignment in polymer solutions. The significance of PVP extends beyond its chemical versatility. Its applications in pharmaceuticals, cosmetics, food technology, and biomedical engineering are primarily driven by its solubility, film-forming ability, and stability in aqueous environments. These characteristics make it a crucial material for drug delivery systems, wound dressings, and other therapeutic formulations. Understanding the dielectric behavior of PVP in water not only enhances the theoretical knowledge of polymer dynamics but also provides practical insights for optimizing its applications. Factors such as temperature, concentration, and molecular weight significantly influence the polymer's dielectric relaxation, affecting its intermolecular and solute-solvent interactions. Dielectric studies of PVP solutions reveal two primary relaxation processes: high-frequency relaxation attributed to bulk water dynamics and low-frequency relaxation arising from polymer rotational motions. These processes are indicative of the intricate interplay between PVP molecules and water, where hydration shells play a critical role. The temperature-dependent



dielectric properties shed light on the thermal stability and mobility of PVP chains, while concentration-dependent studies elucidate the transition from solute-solvent interactions to solute-solute interactions at higher polymer concentrations. Additionally, the thermodynamic parameters derived from dielectric measurements, such as activation free energy, entropy, and enthalpy, provide a deeper understanding of the molecular reorientation and interaction mechanisms within the system. Exploring the dielectric behavior of PVP in aqueous solutions is a promising avenue for advancing material science, particularly in understanding the hydration dynamics and structural adaptability of polymers. By bridging experimental observations with theoretical models, such studies contribute to the broader field of polymer physics, offering a foundation for developing innovative applications in biopolymer technology and beyond. This research delves into the dielectric properties and molecular dynamics of aqueous PVP solutions, aiming to elucidate their structural and thermodynamic characteristics across varying concentrations and temperatures.

2. Experimental

2.1 Materials

The polyvinylpyrrolidone (PVP K-30) was purchased from Sigma Aldrich. Its average molecular weight is 40,000 g/mol. We didn't purify the substance any more before using it.

Measurements of Dielectric

Pure liquid PVP solutions had their dielectric permittivity (ϵ') and dielectric loss (ϵ'') tested with time-domain reflectometry. The measurements were carried out using tried and true methods and techniques outlined in earlier research, covering a temperature range of 298.15 K to 283.15 K.

3. Results and Discussion

The dielectric properties of PVP-water mixtures were studied at temperatures ranging from 298.15 K to 283.15 K. An average molecular weight of about 40,000 g/mol was observed in the polymer that was utilized. The findings show that the dielectric function's real and imaginary components are frequency dependent, as seen in Figure 1. These results demonstrate that the investigated temperature range is characterized by the dynamic interactions of PVP with water molecules.

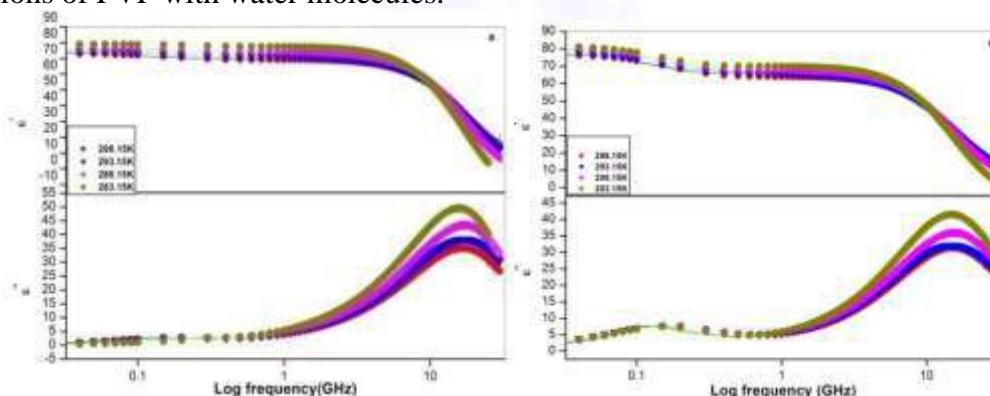


Figure 1. Variation of Complex Permittivity Spectra of Polyvinylpyrrolidone K-30 solution with frequency at different temperatures. Dielectric permittivity (ϵ') and dielectric loss (ϵ'') as a function of frequency (GHz) (Static Permittivity Spectra fig (a): 1.67×10^{-04} C(M) fig(e): 8.34×10^{-04} C(M))

Figure 1 shows that there are two separate relaxation peaks in the dielectric relaxation spectra of the PVP-water combination. Free water molecules' rotating motion is associated with the main relaxation process, while PVP molecules' rotational dynamics in the water medium is responsible for the secondary relaxation process. During these procedures, the solvent-polymer interactions are brought to light. Various relaxation types are examined using a sum of Havriliak-Negami (HN) equations or variations thereof, including the Debye (D), Cole-Cole (CC), and Cole-Davidson (CD) equations. Here is the dielectric function in its generalized form:



$$\varepsilon^*(\nu) = \sum_{j=1}^n \frac{\Delta\varepsilon_j}{[1 + (i2\pi\nu\tau_j)^{\beta_j}]^{\alpha_j}} + \varepsilon_{\infty} \quad (1)$$

$$\varepsilon^*(\nu) = \frac{\Delta\varepsilon_1}{1 + i2\pi\nu\tau_1} + \frac{\Delta\varepsilon_2}{1 + i2\pi\nu\tau_2} + \varepsilon_{\infty} \quad (2)$$

Static Dielectric constant (s): The static dielectric constant (s) is a fundamental parameter in dielectric spectroscopy, representing the material's ability to polarize in response to an applied electric field in the absence of any time-dependent variations. In the context of polyvinylpyrrolidone (PVP) solutions, it provides critical insights into the solute-solvent interactions and the structural organization of the polymer chains in an aqueous environment. For PVP solutions, the static dielectric constant is influenced by both temperature and polymer concentration. At low concentrations, water molecules form a hydration shell around PVP molecules, contributing to a relatively high dielectric constant due to strong dipole-dipole interactions. As the concentration increases, PVP molecules come into closer proximity, leading to enhanced solute-solute interactions and partial disruption of the hydration shell. This results in a decrease in the dielectric constant, indicating a shift in the dominant interaction dynamics from solute-solvent to solute-solute. Temperature also plays a crucial role in determining the static dielectric constant. At lower temperatures, reduced thermal motion allows for more stable hydrogen bonding and alignment of dipoles, leading to higher dielectric constant values. Conversely, at elevated temperatures, increased thermal agitation disrupts hydrogen bonds, resulting in a decrease in the static dielectric constant. In PVP-water mixtures, the low-frequency dielectric relaxation intensity ($\Delta\varepsilon_1(T)$) is directly linked to the effective dipole alignment of PVP molecules. The static dielectric constant at low frequencies reflects the cooperative polarization effects of the polymer molecules, which are influenced by their concentration-dependent alignment. At high frequencies, the static dielectric constant is associated with the relaxation of bulk-like water molecules. This high-frequency behavior highlights the role of PVP as a modulator of water dynamics, with the dielectric constant decreasing as the cooperative relaxation of water diminishes at higher solute concentrations. The static dielectric constant thus serves as a quantitative indicator of the complex interplay between PVP molecules and water, capturing the effects of polymer concentration, temperature, and hydration dynamics on the overall dielectric response of the system.

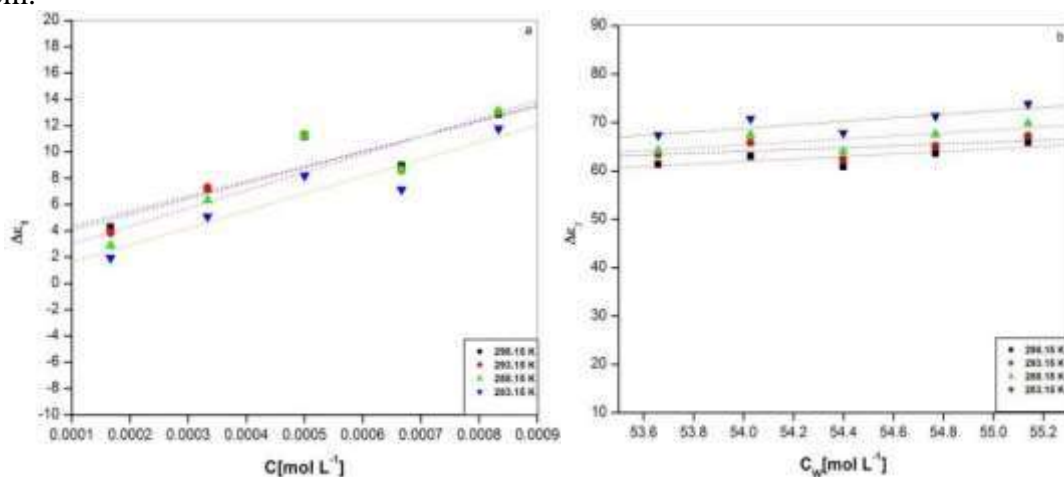
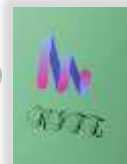


Figure 2. Dielectric relaxation strength of low frequency and high frequency processes

The relaxation process in the low frequency domain is primarily caused by a rise in the effective dipole-dipole antiparallel alignment of PVP molecules, as indicated by the fact that the low frequency dielectric relaxation intensity $\Delta\varepsilon_1(T)$ grows as the PVP concentration increases. At low Chapter V concentrations, water molecules completely round each PVP



molecule. The correlation factor g_1 decreases with increasing concentration, suggesting significant evidence of antiparallel dipole alignment, as shown in Dielectric Relaxation Studies of Aqueous Polyvinyl Pyrrolidone concentrations, which shield the contact between PVP molecules. Decreases in temperature cause $\Delta\epsilon_1(T)$ to decrease in value. There is a linear relationship between the concentration

dependence of the high frequency relaxation strength $\Delta\epsilon_2$ (c) and the cooperative relaxation of bulk-like water happening in the same frequency range as pure water, as seen at all measured temperatures. This suggests that PVP molecules include water and may be related to the relaxation period (τ_2) of high-frequency processes at larger concentrations of the solute. The rotation of "bulk-like" water molecules, which is clearly caused by the prevailing high-frequency dispersion and strong water-water contact, could also be to blame.

Relaxation time (τ_i): The relaxation time (τ_i) is a critical parameter in dielectric spectroscopy, representing the time scale over which dipoles within a material reorient themselves in response to an alternating electric field. For polyvinylpyrrolidone (PVP) solutions, the relaxation time provides valuable insights into the dynamics of solute-solvent interactions, the structural organization of PVP molecules, and the mobility of water molecules in the system. In PVP-water systems, two distinct relaxation processes are typically observed: low-frequency relaxation (τ_1) and high-frequency relaxation (τ_2). The low-frequency relaxation time (τ_1) is associated with the rotational dynamics of PVP molecules in the aqueous medium, while the high-frequency relaxation time (τ_2) corresponds to the rotational motion of bulk-like water molecules.

Low-Frequency Relaxation (τ_1): At low concentrations of PVP, water molecules form stable hydration shells around the polymer chains, allowing for relatively unhindered rotational dynamics of PVP dipoles. However, as the concentration of PVP increases, these hydration shells are disrupted, and solute-solute interactions become more prominent. This leads to a monotonic increase in τ_1 , reflecting reduced mobility of PVP molecules due to steric hindrance and stronger intermolecular interactions. Temperature also influences τ_1 . At lower temperatures, reduced thermal energy enhances hydrogen bonding and restricts the reorientational motion of PVP dipoles, resulting in longer relaxation times. As the temperature increases, thermal agitation weakens these interactions, allowing for faster reorientation and shorter τ_1 values.

High-Frequency Relaxation (τ_2): The high-frequency relaxation process is dominated by the dynamics of bulk-like water molecules, which are less influenced by the presence of PVP. At higher concentrations of PVP, τ_2 increases slightly due to the disruption of water-water interactions and the formation of a more heterogeneous environment caused by PVP molecules. This indicates a slower reorientation of water dipoles in the vicinity of the polymer chains. Temperature plays a similar role in high-frequency relaxation. At lower temperatures, the mobility of water molecules is reduced due to stronger hydrogen bonding, leading to higher τ_2 values. As the temperature rises, the increased thermal motion disrupts these interactions, resulting in shorter relaxation times.

Key Observations:

- ✚ At low concentrations, τ_1 remains relatively constant due to well-maintained hydration layers around PVP molecules.
- ✚ As PVP concentration increases beyond a critical threshold, τ_1 exhibits a marked increase, reflecting enhanced polymer-polymer interactions and restricted mobility.
- ✚ τ_2 values show less variation with concentration but are influenced by temperature, reflecting the dynamic interplay of water-water and water-PVP interactions.

The relaxation times, therefore, provide a detailed understanding of the molecular dynamics within PVP-water systems, highlighting the concentration-dependent transition from solute-solvent to solute-solute dominance and the temperature-induced modulation of dipole reorientation behavior. These findings are instrumental in characterizing the dielectric properties and structural dynamics of PVP in aqueous environments.

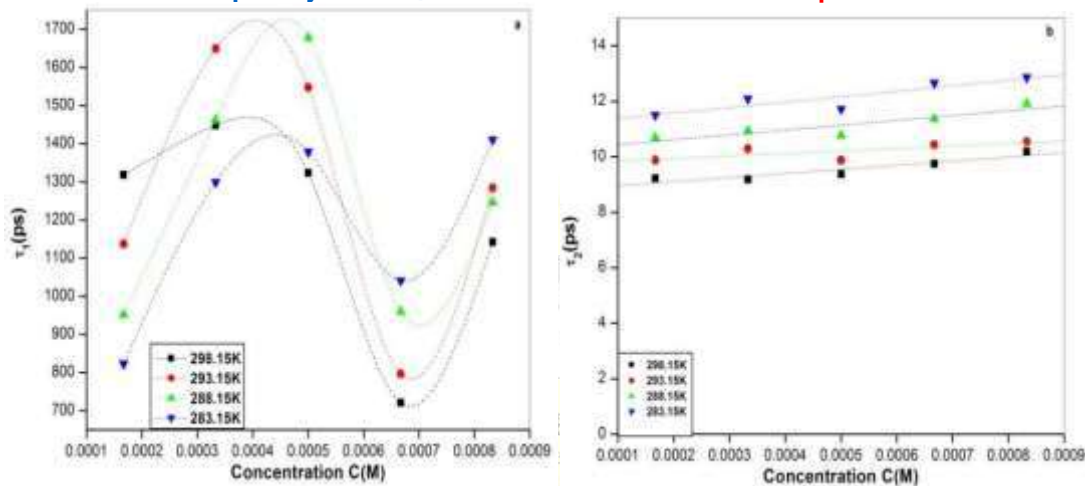


Figure 3. Dielectric Relaxation times τ_1 (ps) and τ_2 (ps) Vs Concentration CPVP
Relaxation Dynamics at Low and High Frequencies

Separate patterns for relaxation at low and high frequencies are shown by the examination of the PVP-water system's dielectric relaxation periods. As the concentration of the solute increases, the low-frequency relaxation time (τ_1) stays relatively constant up to a critical value of 0.000333 molar. When this concentration is exceeded, τ_1 shows a monotonic change. Due to the reorientational motion of its hydrogen-bonded linear polymeric structure, pure water has a high value of τ_1 . As the temperature drops, the dielectric relaxation time (τ_2) for the high-frequency relaxation process goes up. It can be inferred from this pattern that the rotational dynamics of PVP molecules in water are reduced at lower temperatures. The molecular interactions between water and PVP are responsible for the discrepancy in relaxation times (~9 ps) between pure water and all concentrations at ambient temperature. The steric barrier that results from these interactions makes it harder for water molecules to freely reorient themselves.

Dipole Moment (μ)

In order to examine the PVP-water system's dipole-dipole interactions and orientational correlations, the Cavell equation—an expansion of the Onsager equation—is employed. The relationship between the dielectric strength ($\Delta\epsilon_j$) and the effective dipole moment ($\mu_{eff,j}$) in multimer systems is as follows:

$$\Delta\epsilon_j = \frac{\epsilon_s}{3(\epsilon_s + (1 - \epsilon_s)A_j)} \frac{N_A k_B T \epsilon_0 \mu_{eff,j}^2}{(1 - \alpha_j f_j)^2 C_j} \quad (3)$$

Here:

- ϵ_s : Static permittivity.
- N_A : Avogadro's number.
- k_B : Boltzmann constant.
- ϵ_0 : Vacuum permittivity.
- A_j : Shape parameter of the reaction field, accounting for the geometry of relaxing particles.
- f_j : Cavity field factor.
- α_j : Molecular polarizability.
- T : Temperature.

The effective dipole moment ($\mu_{eff,j}$) is connected to the gas-phase dipole moment ($\mu_{0,j}$) through the correlation factor (g_j):

$$\mu_{eff,j}^2 = g_j \mu_{0,j}^2 \quad (4)$$

The correlation factor g_j indicates the alignment tendencies of dipoles:

- $g_j=1$: No orientational correlation between dipoles.



- $g_1 < 1$: Antiparallel alignment of dipoles.
- $g_1 > 1$: Parallel alignment of dipoles.

Assumptions and Calculations

The low-frequency relaxation process is predicated on the assumption that the polarizability (α_L) and reaction field factor (f_L) are concentration (c) independent. After that, we can say that the effective dipole moment is:

$$\hat{\mu} = \frac{\mu_{\text{eff},L}}{(1 - \alpha_L f_L)} = \frac{\sqrt{g_L} \mu_{0,L}}{(1 - \alpha_L f_L)} \quad (5)$$

The values of A_j and f_j were obtained from previously published works for this study. The assumption was made that the water molecules had a spherical geometry with a radius of 0.1425 nm and a partial derivative of $1/3A_j = 3.1$. The values of μ_{eff} and σ_{eff} were determined using Equation (5). With antiparallel alignment being the dominant factor in reducing the effective dipole moment in the PVP-water system, these results demonstrate the orientational correlations between dipoles and their dependence on molecular interactions and concentration.

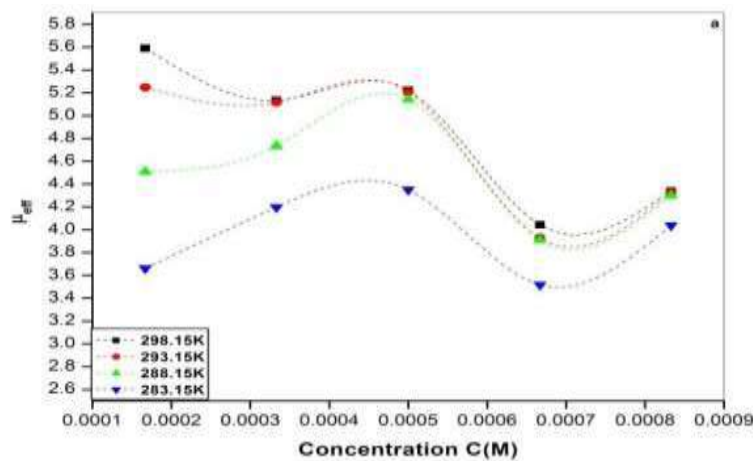


Figure 4. Dipole moment μ_{eff} using cavells equation

Kirkwood correlation factor (g_1):

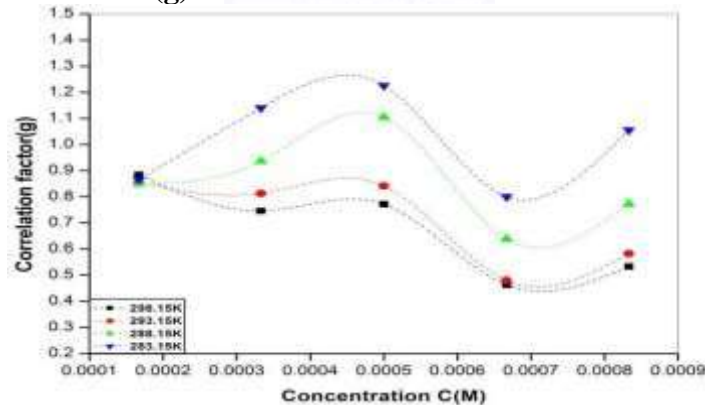


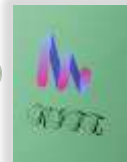
Figure 5. Correlation factor (g_1) as a function of concentration at different temperatures.

Correlation Factor (g_1)

The correlation factor (g_1) was estimated using the following relationship in order to further analyze the magnitude of antiparallel dipole alignment:

$$\frac{\hat{\mu}(C_{\text{max}})}{\hat{\mu}(C \rightarrow 0)} \approx \frac{g_1^{1/2}(C_{\text{max}})}{g_1^{1/2}(C \rightarrow 0)} = g_1^{1/2} \quad (6)$$

Here: $g_1(C \rightarrow 0) = 1$, as at infinite dilution, there is no correlation between PVP molecules. C_{max} represents the highest concentration used for PVP in the study.



At the maximum concentration, the values of g_1 were determined. At all concentrations and temperatures except 298.15 K, the low-frequency relaxation process had a g_1 value lower than 1. This shows that, at higher concentrations, the antiparallel dipole alignment causes a decrease in correlation between the molecules of the solute.

4. Conclusion

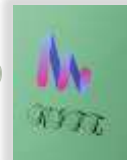
Using dielectric spectroscopy in the GHz region, this research offers a comprehensive molecular analysis of aqueous PVP at different concentrations. Both low-frequency relaxation (τ_γ) and high-frequency relaxation (τ_γ) are shown by the dielectric spectra. The results show that the dynamics and interactions in aqueous PVP systems can be well captured by dielectric relaxation spectroscopy (DRS). In the concentration range that was studied, the study shows that the dipolar alignment tendency is weak. The hydration layer surrounding PVP molecules becomes less robust at increasing solute concentrations, leading to an increase in solute-solute interactions. The process of β -relaxation results in negative molar entropy due to the release of free energy in the range of 5.00-5.30 kcal/mol caused by these interactions. At the highest concentration measured, the maximum negative entropy was noted, which sheds light on how PVP-water mixtures behave under different conditions.

5. Recommendations of the Study

- ✓ Consider using lower concentrations of PVP to maintain strong hydration shells and enhance solute-solvent interactions for applications requiring high molecular mobility.
- ✓ Maintain specific temperature ranges to control dipole reorientation and molecular interactions, particularly in temperature-sensitive industrial and biomedical applications.
- ✓ Leverage the observed hydration dynamics in designing drug delivery systems or hydrogels, where precise control of water-polymer interactions is crucial.
- ✓ Utilize the study's insights into static dielectric constants and relaxation processes to engineer stable PVP-based materials for dielectric and electronic applications.
- ✓ Modify environmental conditions, such as temperature and polymer concentration, to achieve desired relaxation times for targeted applications in biophysics and polymer science.
- ✓ Employ knowledge of enthalpy, entropy, and free energy variations to fine-tune PVP solutions for optimal performance in chemical and pharmaceutical formulations.

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