

Refractometric study of polymers and their blends in solution

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Measurement of refractive index (n_D) of poly(vinyl pyrrolidone) (PVP), poly(vinyl alcohol) (PVA) and poly(ethylene glycol) (PEG) in solution at 298 K is presented here. PVP has been investigated in nine different polar solvents including liquid PEG200 and PEG400, whereas PVA, PEG, and PVP+PVA and PVP+PEG blend have been investigated in water solution. High frequency limiting dielectric constant (ϵ_∞) has been taken as the square of the measured refractive index ($\epsilon_\infty = n_D^2$). It is observed that the concentration dependent ϵ_∞ values of these systems exhibit linear behaviour. The ϵ_∞ values of the pure polymers have been determined from the measured ϵ_∞ values of their polymeric solutions. The effect of molecular weight of the polymers on the electronic polarization is discussed by considering comparative ϵ_∞ values of different molecular weight polymers. Results reveal that these polymers and their blends have high solubility in the used solvents, which is mainly due to the polymer-solvent hydrogen bond interactions.

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Conformation changes originating in polymers and their blends due to various interactions with solvent and their effect on molecular dynamics have been the subject of large number of dielectricians¹⁻⁹. Polymer blends are physical mixtures of structurally different polymers that interact mainly through hydrogen bonds and dipolar bonding between the polar groups, to provide the tailor-made properties different from those of the constituent polymers^{4,5,10}. The properties of the blends depend on the degree of compatibility or miscibility of polymers at molecular level^{10,11}.

Poly(vinyl pyrrolidone) (PVP), poly(vinyl alcohol) (PVA), poly(ethylene glycol) (PEG), and their blends have many pharmaceutical, biomedical and technological applications¹⁰⁻¹³. The ionic conduction relaxation, polymer segmental mobility, polymer-solvent interaction and their hindrance to the solvent molecular reorientation motion in the blends of these

polymers with different polar solvents have been extensively investigated using broadband dielectric spectroscopy^{5-9,11,14-19}. In case of polymer blends, viscometric and refractometric techniques are efficient and simplest methods for the study of polymer-solvent or polymer-polymer miscibility²⁰⁻²³. It has been confirmed that the behaviour of viscosity and refractive index with blend composition is linear for miscible (compatible) blends and non-linear for semi-immiscible (semi compatible), or immiscible (incompatible) blends.

Measurement of the refractive index (n_D) in and near the visible region gives the high frequency limiting dielectric constant ($\epsilon_\infty = n_D^2$), which is due to electronic polarizability of the liquids and mainly arises from the displacement of electrons of a molecule in an applied field²⁴⁻²⁷. Refractive indices are usually measured for the sodium-doublet (i.e., n_D) but are dependent on the frequency of incident light.

The refractometric study (high frequency limiting dielectric constant) of the solutions of PVP, PVA and PEG, and their blends in polar solvents (two-phase and three-phase polymeric systems), for the conformation of concentration dependent macro-molecular electronic polarizability in solution, and its dependence on the solvent environment and the polymer molecular weight are reported here.

Experimental

PVP of average molecular weight 40000 g mol⁻¹, PVA of average molecular weight 14000 and 77000 g mol⁻¹, and PEG of average molecular weight 200, 400 and 4000 g mol⁻¹ of laboratory grade were obtained from Loba Chemie, India. The AR grade samples of ethyl alcohol (EA), ethylene glycol (EG), diethylene glycol (DEG), glycerol (Gly), dimethyl sulphoxide (DMSO), dimethyl formamide (DMF) and double-distilled water (W) were used as solvent.

The binary mixtures of the polymer powder sample in polar solvent, i.e. PVP+W, PVP+EA, PVP+EG, PVP+DEG, PVP+PEG200, PVP+PEG400, PVP+Gly, PVP+DMSO and PVP+DMF; PVA+W and PEG+W at different weight fraction of polymer (w_p) were prepared by adding accurate weight of polymer in known weight of the liquid solvent. The value of w_p was evaluated by the relation $w_p = W_p / (W_p + W_s)$, W_p

being the weight of the polymer, and W_s the weight of polar solvent in the polymeric solution or blend. The maximum polymer weight fraction concentration in different solvents was used until the solution turned turbid. In case of liquid polymer, i.e. PEG200 and PEG400, the polymer+water mixtures were prepared over the entire concentration range.

The ternary mixtures of the blend of PVP+PEG200 with 30 wt% PVP concentration were prepared over the entire weight fraction range of the polymer blend in water, ethyl alcohol and 1,4-dioxane (Dx) solvents. Further, the mixture of PVA+W with 15 wt% PVP concentration and PVP+W with 15 wt% PVA concentration were made by volume mixing over the entire concentration range. All mixtures were prepared at room temperature.

The refractive index (n_D) of the solutions of the polymer and their blends were measured at sodium doublet light with an Abbe's refractometer at 298 K. The temperature was controlled by Thermo-Haake DC10 controller with the accuracy of ± 0.01 K. The measurement accuracy of the n_D was $\pm 0.02\%$. The high frequency limiting dielectric constant ϵ_∞ was taken as the square of the refractive index, i.e. $\epsilon_\infty = n_D^2$.

Results and discussion

PVP was investigated in nine different polar solvents including liquid PEG200 and PEG400, whereas PVA and PEG were investigated in water solution. Figure 1 shows the plots of ϵ_∞ against weight fraction (w_p) of PVP, PVA and PEG in polar solvents. It has been found that the ϵ_∞ values of these polymer solutions have linear behaviour against w_p , which can be represented by the relation:

$$\epsilon_\infty = \epsilon_{\infty S} + \delta w_p \quad \dots(1)$$

where ϵ_∞ and $\epsilon_{\infty S}$ are the values of high frequency limiting dielectric constant of polymer solution and pure solvent, respectively, and δ is the increment/decrement factor to the high frequency limiting dielectric constant of the polymeric solution. The evaluated δ values of the polymer solutions are recorded in Table 1. The linear relationship of ϵ_∞ versus w_p confirms that their is uniform variation in the electronic polarization with change in polymer concentration in the solution. Further, the extrapolated ϵ_∞ values at $w_p = 1$ for pure PVP in the different polar solvents have nearly equal magnitude (Fig. 1c). The

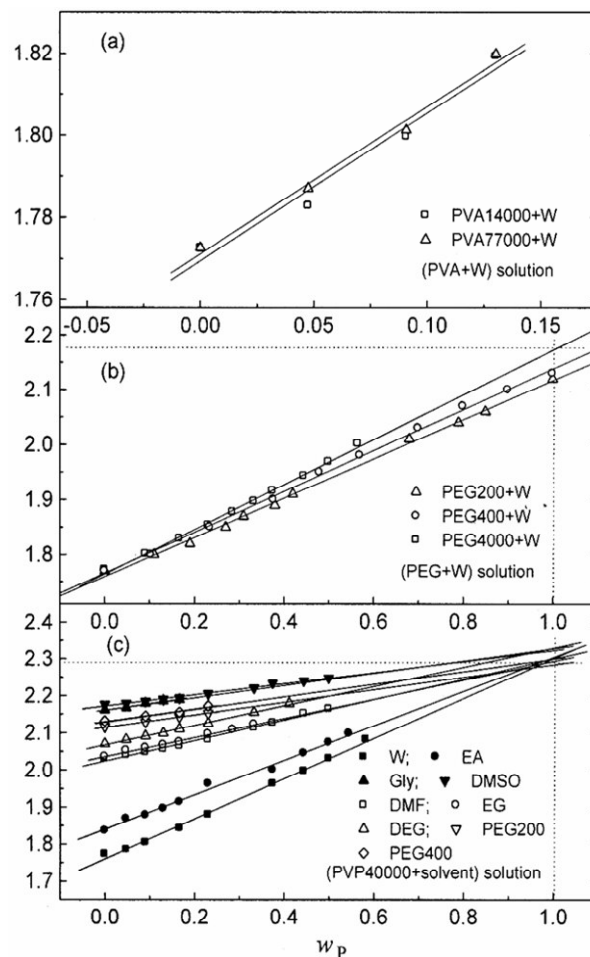


Fig. 1 — Polymer weight fraction (w_p) dependence of the high frequency limiting dielectric constant (ϵ_∞) of polymer solutions. Lines are linear fit of the data. The values of the slopes of the lines, δ (increment factor) are listed in Table 1.

Table 1 — Values of increment/decrement factor δ for the polymer solution and the solutions of polymer blends at 298 K

Polymer solution	δ	Polymer solution	δ
PVP40000+W	0.54	PEG200+W	0.357
PVP40000+EA	0.45	PEG400+W	0.372
PVP40000+Gly	0.23	PEG4000+W	0.407
PVP40000+DMSO	0.17	PVA14000+W	0.358
PVP40000+DMF	0.28	PVA77000+W	0.357
PVP40000+EG	0.26	(PVP+PEG200)+W	-0.393
PVP40000+DEG	0.24	(PVP+PEG200)+EA	-0.319
PVP40000+PEG200	0.20	(PVP+PEG200)+Dx	-0.139
PVP40000+PEG400	0.17	(PVP+W) + (PVA+W)	0.003

average of these ϵ_∞ values at $w_p = 1$ for the pure PVP is ~ 2.3 . The extrapolated values of the high frequency limiting dielectric constant of PEG4000 and PVA were found ~ 2.17 , and ~ 2.14 , respectively from Figs 1a and 1b. Further, the ϵ_∞ values of PVA and PEG are nearly equal and these values are lower than

the ϵ_∞ value of PVP. It is expected due to the higher group moment of the carbonyl group of PVP monomer units as compared to the hydroxyl group moment value of PVA and PEG molecules. Furthermore, the nearly equal ϵ_∞ values of PVA14000 and PVA77000 in water solutions (Fig. 1a) suggest that these values are independent of the polymer molecular weight. Figure 1b shows that the extrapolated ϵ_∞ value of PEG4000 is higher than the measured ϵ_∞ values of liquid PEG200 and PEG400. These ϵ_∞ values of PEG samples slightly increase with increase of the PEG molecular weight.

The PVP+PEG200 blend with 30 wt% PVP concentration in dilute solutions of water, ethyl alcohol and 1,4-dioxane solvent also shows linear relationship between the ϵ_∞ values with the weight fraction concentration of solvent w_s (Fig. 2). The linear behaviour of ϵ_∞ versus w_s confirms that the electronic polarization of the PVP+PEG blend changes uniformly with the variation of the solvent concentration and depends on the type of solvent. The values of decrement factor δ of the PVP+PEG blend solutions are in the order $W > EA > Dx$, which is according to the polar behaviour of these solvents. The evaluated δ values of these three-phase polymers blends in solutions are given in Table 1.

Figure 3 shows the variation in ϵ_∞ values of the mixtures of the solutions of PVP+W with 15 wt% PVP concentration and PVA+W with 15 wt% PVA concentration over the entire volume mixture concentration range (ϕ_A) of PVP+W. It is observed that the ϵ_∞ value of the polymeric blends is reduced little in PVA+W rich solution, whereas it increases slightly in PVP+W rich solution from the ideal behaviour of the aqueous polymer mixtures. This variation of ϵ_∞ values shows the existence of electronic interaction between the liquid phases of PVP+W and PVA+W systems, which is also confirmed from their low frequency dielectric dispersion¹¹. In case of the mixtures of small size polar molecules, the simple mole-fraction mixture law is used to evaluate the values of excess parameter²⁵⁻²⁷, which confirms that the change in electronic polarization is caused by molecular interaction. But in case of polymer solutions, because of complexity the simple mixture law cannot be applied and therefore the interpretation is made from their comparative ϵ_∞ values.

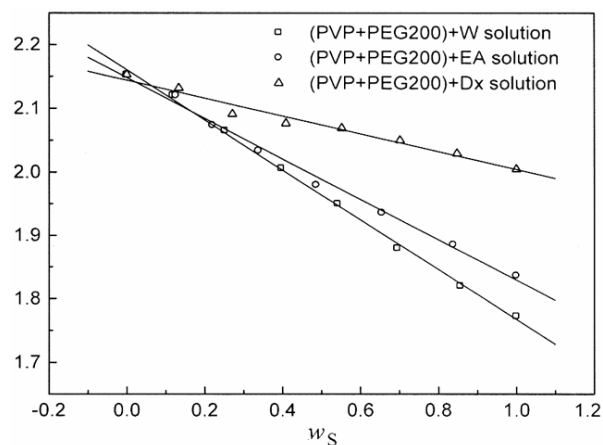


Fig. 2 — Solvent weight fraction (w_s) dependence of the high frequency limiting dielectric constant (ϵ_∞) of the PVP+PEG blend with 30 wt% PVP concentration in the solutions of water, ethyl alcohol and dioxane over the entire concentration range. Lines are linear fit of the data. The values of the slopes of the lines, δ (decrement factor) are listed in Table 1.

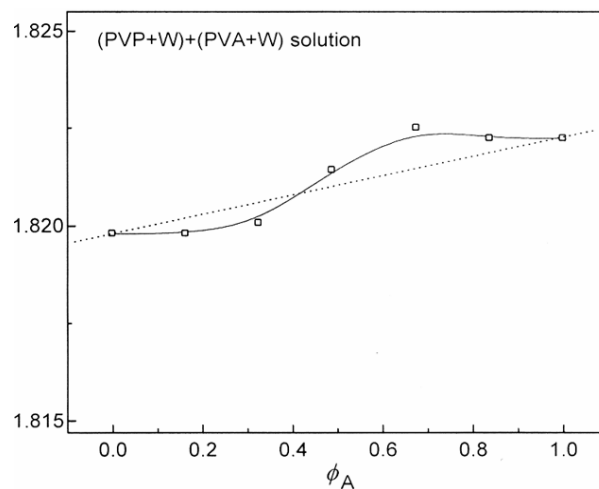


Fig. 3 — Polymer blends volume fraction (ϕ_A) dependence of the high frequency limiting dielectric constant (ϵ_∞) of the mixtures of PVP+W with 15 wt% PVP and PVA+W with 15 wt% PVA over the entire concentration range. Continuous line is the fourth order non-linear fit of the data.

The concentration dependent linear behaviour of high frequency limiting dielectric constant values show that the magnitude of electronic polarizability of PVP, PVA and PEG, and their blends changes systematically with the change of polymer concentration in solution or blend concentration in different solvents, which may be due to the miscible behaviour of these systems. The miscibility is mainly due to H-bond interactions between the polymer and the solvent, and also between polymer-polymer

molecules in the polar solvent environment. Thus, refractometric measurement technique is suitable for the estimation of the refractive index values of powder polymer from their solution data. These findings may help to confirm the effect of breaking and reforming of polymer-solvent H-bonding on the electronic polarization with wide temperature variation.

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