

Low-frequency dielectric response and chain dynamics study of poly(vinyl pyrrolidone)–poly(ethylene glycol) coexisting two-phase polymeric blends

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The dielectric response of various concentration poly(vinyl pyrrolidone)-poly(ethylene glycol) (PVP-PEG) blends with change in polymer chain-length and their different volume mixtures over the entire concentration range were investigated in the frequency range 20 Hz-1 MHz at 25°C. The complex dielectric constant $\epsilon^*(\omega)$, complex electric modulus $M^*(\omega)$, complex impedance $Z^*(\omega)$, and a.c. conductivity data were used for the confirmation of the electrode polarization effect, ionic conduction and the micro-Brownian motion of the PVP chain (*m*-process) in the PVP-PEG blends. All the blends show the dielectric dispersion corresponding to the PVP segmental motion in the upper experimental frequency range whereas in the lower frequency side of the spectra has dielectric dispersion is due to ionic conduction and electrode polarization. The different volume mixtures of some of the different chain-length PVP-PEG blends also shows the polymer chain-length and concentration dependence *m*-process. All the blends show the d.c. conductivity behaviour in the lower frequency region, which is little affected by the blends composition. The appearance of two separate arcs in the complex impedance plane plots confirms the contribution of nickel-plated cobalt electrodes polarization effect to the values of complex dielectric constant of the PVP-PEG blends in the lower frequency range up to 500 Hz.

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Non-toxic synthetic polymer blends have significant pharmaceutical usages, particularly in transdermal drug delivery system (TDDS)^{1,2}. For TDDS, the non-toxic polymers blend matrix requires the reservoir, adhesive and transport properties. Adhesive and diffusivity are interrelated through molecular structure of polymers blend, and hence the conformation of the dynamics of such blend is an important parameter for their use as TDDS¹⁻³. Dielectric dispersion spectroscopy⁴⁻⁶ has proved to be a very powerful tool in investigating the chain dynamics of polymer blends in liquid state.

In last one decade, the PVP-PEG blends, which possess most of the TDDS properties, have been the subject of a large number of investigations²⁻⁶. Feldstein and coworkers^{2,3,7,8} extensively investigated the complex formation between the carbonyl groups of PVP monomer units and the hydroxyl groups of PEG, and their dynamics by using Fourier Transform Infra Red (FTIR) spectroscopy and differential scanning calorimetry (DSC) measurements in reference to the use of PVP-PEG blends in TDDS. Several^{4-6,9-12} attempts were also made to explore the hindrance to the dynamics of PEG molecules due to H-bond formation in the PVP-PEG blends by

dielectric measurements in the microwave frequency region where the dielectric dispersion occurs due to reorientation motion of the comparatively small size polar molecules. However, not much has been done in the frequency region 20 Hz-1 MHz on the PVP-PEG blends at room temperature where the interference between ionic conduction, electrode polarization and polymer chain segmental relaxations may be the largest¹³⁻¹⁶. Besides the other properties the ionic conduction of the polymeric blend also influences the TDDS properties, and hence the low frequency dielectric dispersion study of the PVP-PEG blends is needed to understand better about the electrical behaviour and chain dynamics of these systems. Further, the low-frequency dielectric study of the PVP-PEG blends will also help to gain insight about the dielectric behaviour of these blends based solution grown films for their various technological and industrial applications.

The present paper reports the detailed dielectric behaviour of different molecular weight PVP-PEG blends of different concentration in the frequency range 20 Hz-1 MHz at 25°C. This study has the main objectives (i) to confirm the dielectric dispersion process corresponding to PVP segmental motion (the micro-Brownian motion) within the frequency range 20 Hz-1 MHz, (ii) to explore the effect of PVP and

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PEG chain length and their concentrations on the PVP segmental motion of the PVP-PEG two-phase polymeric blends, and (iii) to see the ionic conduction behaviour and electrode polarization effect in the PVP-PEG blends.

Experimental Procedure

Materials

The poly(vinyl pyrrolidone)s of average molecular weight 24000 g mol⁻¹ (PVP24000) and 40000 g mol⁻¹ (PVP40000) of Laboratory grade were obtained from S. D. Fine Chem. India, and Loba Chemie India, respectively. The poly(ethylene glycol) of average molecular weight 200 g mol⁻¹ (PEG200) and 400 g mol⁻¹ (PEG400) were obtained from Loba Chemie, India. PVP-PEG blends of different molecular weight polymers were prepared by adding 20 wt% and 30 wt% PVP in the weight of PEG. These different molecular weight polymer blends were mixed at volume ratio, i.e., 20:80; 40:60; 60:40 and 80:20, over the entire concentration range for the dielectric characterization of the two-phase polymeric blends.

Measurements

An Agilent 4284A Precision LCR Meter and a four terminal nickel-plated cobalt electrode dielectric cell Agilent 16452A Liquid Test Fixture were used for the capacitance and resistance measurement in the frequency range 20 Hz-1 MHz. The capacitances and parallel resistance of the liquid dielectric test fixture, without and with samples, were measured in order to compensate for a short. The test fixture correction coefficient was also considered to cancel the effect of stray capacitance during the evaluation of the complex dielectric constant values of the PVP-PEG blends. All measurements were made at 25°C and the temperature was controlled by Thermo-Haake DC10 controller up to ± 0.01°C.

Results and Discussion

The complex dielectric constant ε*(ω) is determined from the relation¹⁷

$$\epsilon^*(\omega) = \epsilon_0 \left[\epsilon_\infty + \frac{\alpha \epsilon_0 C_p}{\epsilon_0 C_0} - j \frac{1}{\omega C_0 R_p} \right] \dots (1)$$

where angular frequency ω = 2πf, C₀ and C_p are the capacitances of the free space and with sample, respectively, R_p is the equivalent parallel resistance of the cell with sample, and α is the correction coefficient of the cell. The maximum error in the

measured values of ε' and ε'' is ± 0.5%, which is checked by repetition of some measurements.

Figures 1 and 2 show the plots of the real part of dielectric constant ε', and dielectric loss ε'', against frequency f, at 25°C. The broadband values of complex dielectric permittivity ε*(ω) over the frequency range 20 Hz-20 GHz for polymer solutions in polar solvent can be well described by a sum of three relaxation processes with the contribution of d.c. conductivity, σ_{dc}, by the equation^{4,5}

$$\epsilon^*(\omega) = \epsilon_\infty + \Delta\epsilon_l^*(\omega) + \Delta\epsilon_m^*(\omega) + \Delta\epsilon_h^*(\omega) - j(\sigma_{dc}/\omega\epsilon_0) \dots (2)$$

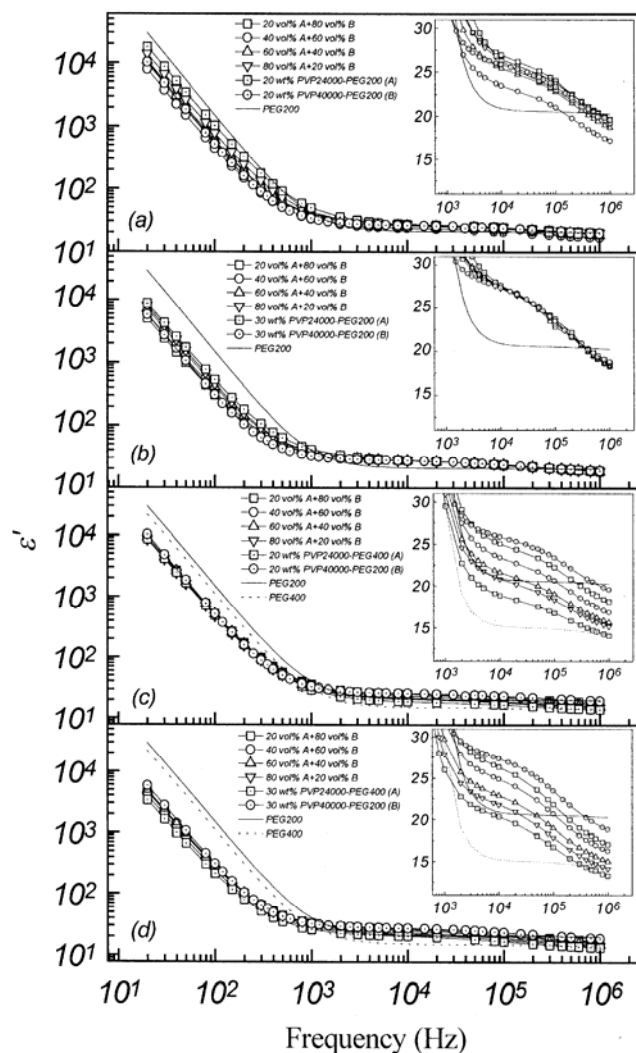


Fig. 1 — Plots of the real part of dielectric constant ε' versus frequency f, of PEG200, PEG400 and different chain-length PVP-PEG blends and their different volume mixtures (coexisting phases) at 25°C. The insets show the dielectric constant around m-process.

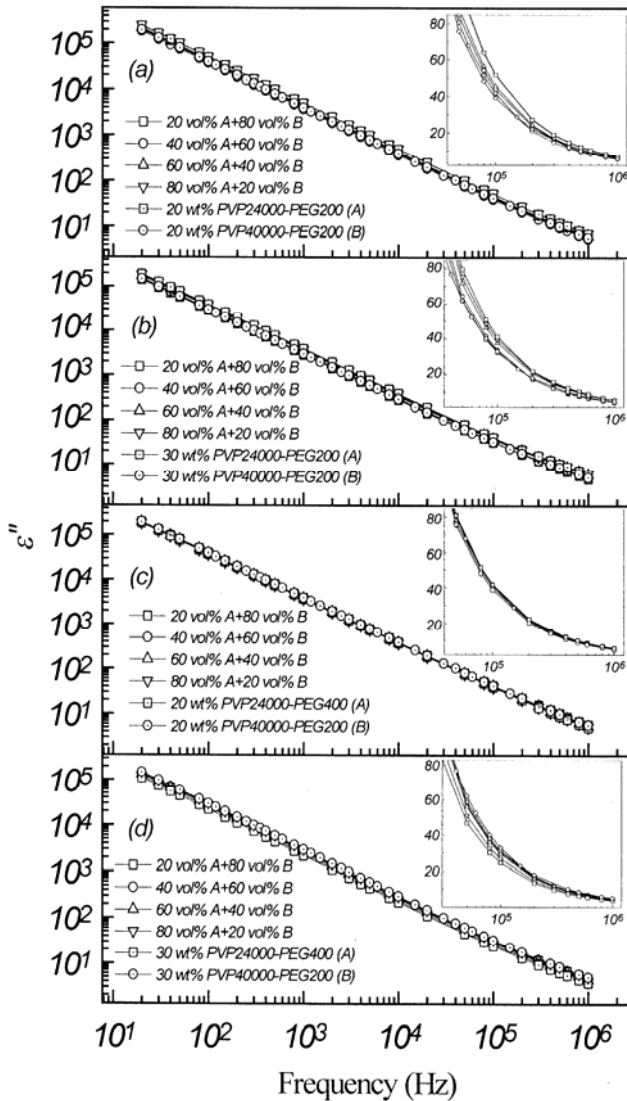


Fig. 2 — Plots of the dielectric loss ϵ'' , versus frequency f_i , of different chain-length PVP-PEG blends and their different volume mixtures (coexisting phases) at 25°C. The insets show the dielectric loss around m -process.

where ϵ_0 is the dielectric constant in vacuum, ϵ_∞ is the high frequency limiting dielectric constant, $\Delta\epsilon$ is the dielectric relaxation strength, and the subscripts l , m , and h denote the low, middle and high-frequency processes, respectively.

The low-frequency process is caused by the electrode polarization. When an electric field is applied to the materials, due to the long-range drift of ions and barrier layer formation on the electrode surface results the large values of dielectric constant and loss^{4,5,13-16}. The loss peak of the l -process was outside the low-frequency limit of our experiment (it is below 20 Hz) and only its high-frequency tail was observed (Figs 1 and 2). The response corresponding

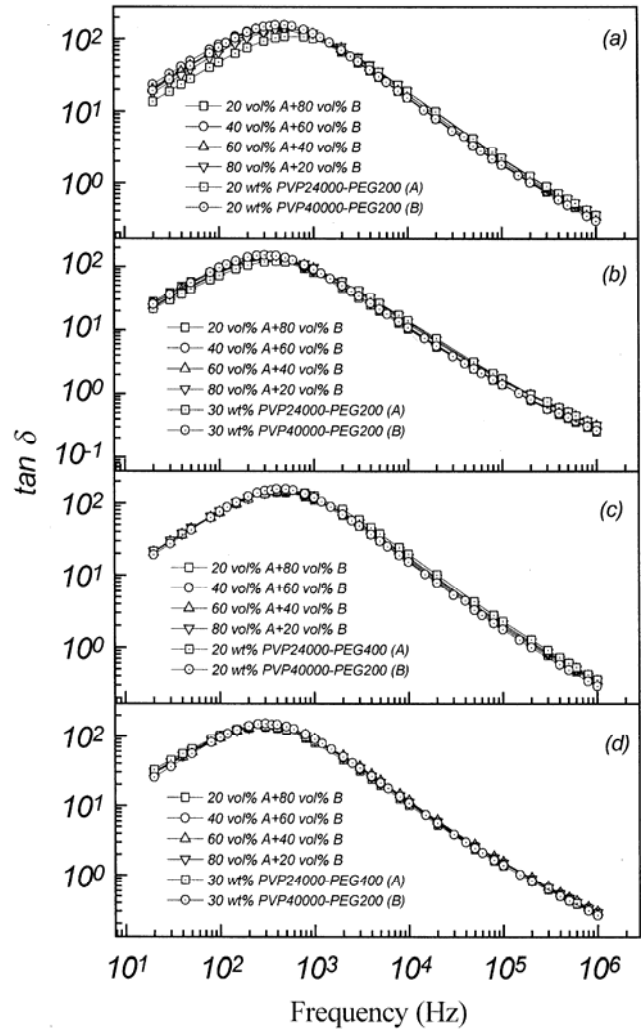


Fig. 3 — Plots of loss tangent $\tan\delta$, versus frequency f_i , of different chain-length PVP-PEG blends and their different volume mixtures (coexisting phases) at 25°C.

to m -process was found in the frequency range 10^3 - 10^6 Hz of the dielectric dispersion spectrum. The h -process is corresponding to the reorientation motion of small size molecules, which occurs in the microwave frequency range. The comparative variation in the values of ϵ' , ϵ'' and σ_{ac} of these PVP-PEG blends were used to explore the interactions in the blends of different volume concentration mixtures. Figure 3 shows the loss tangent $\tan\delta = \epsilon''/\epsilon'$ values at different frequencies of the studied blends.

The real part of ac conductivity, σ_{ac} is obtained from the relation

$$\sigma_{ac}(\omega) = \omega\epsilon_0\epsilon'' \quad \dots (3)$$

Figure 4 shows the variation of the σ_{ac} against frequency.

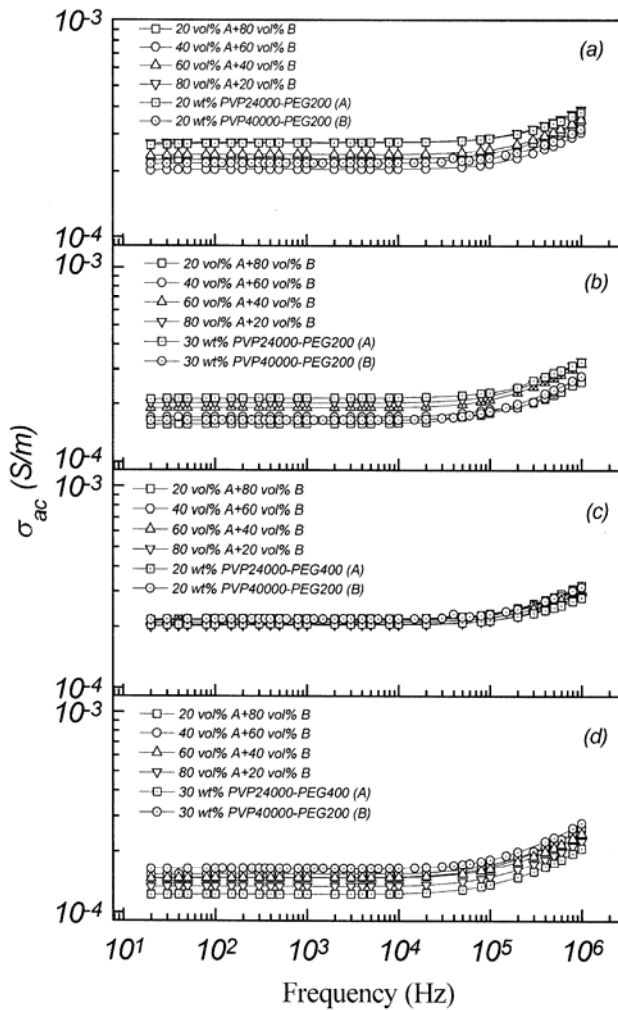


Fig. 4 — Plots of ac conductivity, σ_{ac} , versus frequency f , of different chain-length PVP-PEG blends and their different volume mixtures (coexisting phases) at 25°C.

Considering the charges as the independent variable, conductivity relaxation effects can be well analyzed within the modulus formalism in terms of a dimensionless quantity, M^* . By analogy to mechanical relaxation, the ‘electric modulus’ M^* is obtained from the relation^{13-16,18,19}

$$M^*(\omega) = \frac{1}{\epsilon^*(\omega)} = M\epsilon' + jM\epsilon''$$

$$= \frac{\epsilon'\epsilon''}{\epsilon'^2 + \epsilon''^2} + j \frac{\epsilon'\epsilon''}{\epsilon'^2 + \epsilon''^2} \quad (4)$$

The main advantage of this formalism is that space charge effects often do not mask the features of the spectra; since highly capacitance phenomena are suppressed in the $M''(f)$ plots. Figures 5 and 6 shows the variation of M' and M'' versus f of the PVP-PEG blends. The M'' spectra of these materials have the

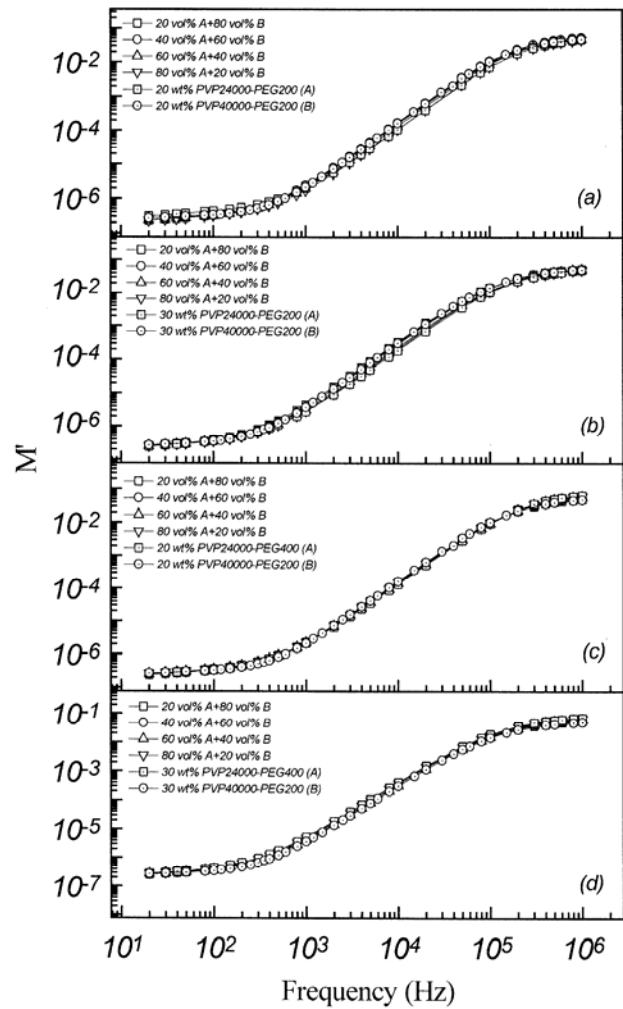


Fig. 5 — Plots of M' , versus frequency f , of different chain-length PVP-PEG blends and their different volume mixtures (coexisting phases) at 25°C.

peaks in the upper region of the experimental frequency range, which are related to the ionic conductivity relaxation, in which both charge carrier transport and reorientation may contribute to the electric field relaxation^{13,14}.

The complex impedance formalism $Z^* = 1/Y^*$ is commonly used to separate the bulk dielectric and the electrode surface phenomena²⁰. A common feature of dielectrics with dc conductivity is a discontinuity at electrode/dielectric interface, which has different polarization properties than the bulk dielectric. The complex impedance of the material was evaluated by the following relation

$$Z^*(\omega) = Z\epsilon' - jZ\epsilon'' = \frac{1}{Y^*(\omega)}$$

$$= \frac{R_p}{1 + (\omega C_p R_p)^2} - \frac{j\omega C_p R_p^2}{1 + (\omega C_p R_p)^2} \quad \dots (5)$$

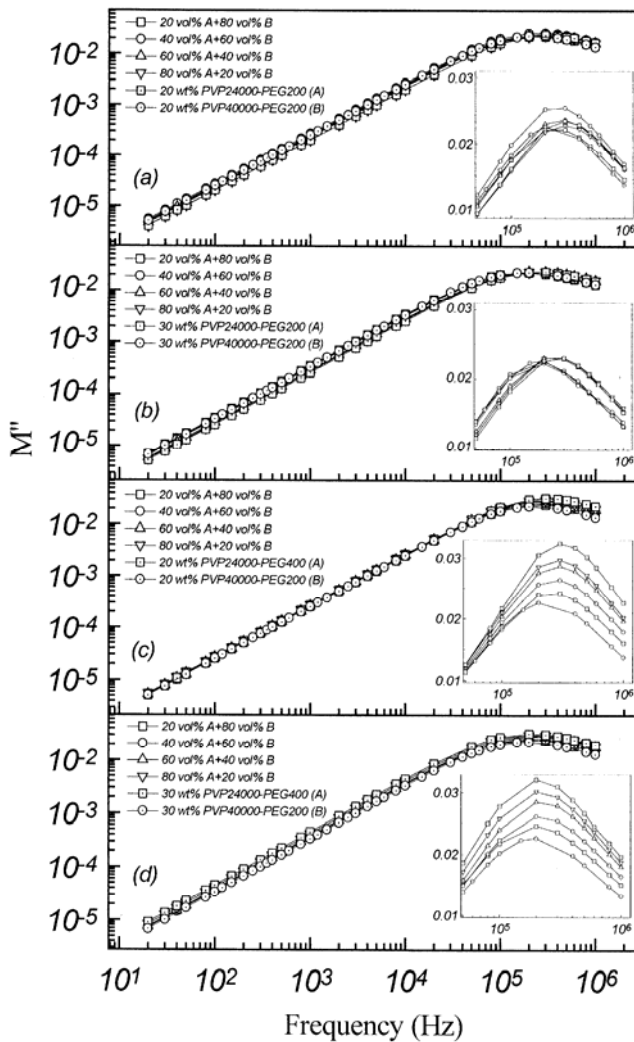


Fig. 6 — Plots of M'' , versus frequency f , of different chain-length PVP-PEG blends and their different volume mixtures (coexisting phases) at 25°C. The insets show the electric modulus loss around the loss peak.

Figure 7 shows the complex impedance plane plots (Z'' versus Z') of the PVP-PEG blends, in which frequency of experimental points increases on going from right to left side of the arcs.

Complex dielectric behaviour

Figures 1 and 2 show the response of ϵ' and ϵ'' values of the PVP-PEG blends in the frequency range 20 Hz-1 MHz. The insets of Figs 1 and 2 show the dielectric dispersion of the PVP-PEG blends around the micro-Brownian motion of the PVP chain (m -process) in the upper frequency region. The large increase in ϵ' and ϵ'' values with decrease in frequency in the lower side of our experimental frequency range is mainly due to the ionic conduction and electrode polarization effects (l -process)^{4,5,13-16}.

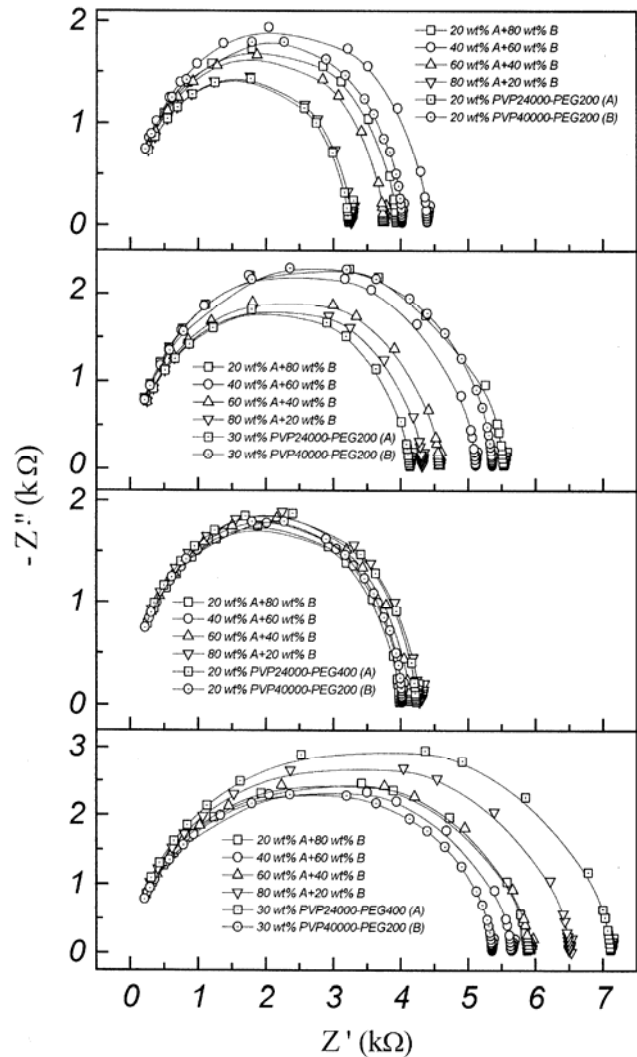


Fig. 7 — Complex plane plots of Z'' versus Z' , of different chain-length PVP-PEG blends and their different volume mixtures (coexisting phases) at 25°C.

We are interested here only to explore the effect of polymers chain-length and concentration of the PVP-PEG blends on the m -process.

The frequency dependent ϵ' values of PEG200 and PEG400 in the upper experimental frequency range, i.e., above 10^4 Hz were found constants (see insets of Fig. 1), which confirms that there is no m -process of the pure PEGs in the upper frequency range of the present study, and these values are corresponding to their static dielectric constant (for PEG200, $\epsilon_0 = 20.26$; and PEG400, $\epsilon_0 = 14.27$ at 25°C)²¹. But all the PVP-PEG blends shows the dispersion in the ϵ' and ϵ'' values in the frequency range 10^4 - 10^6 , and hence these dielectric dispersions are only corresponding to the segmental motion of the randomly coiled PVP chain in the H-bonded heterogeneous complex cross-

linked super molecular structure of the PVP-PEG blends as proposed earlier by Feldstein *et al.*²². Therefore, we are using the comparative study of the *m*-process in the dielectric dispersions of the PVP-PEG blends, to gain a better understanding about the effect of these polymers chain-length, and the polymers concentrations on the dynamics of the PVP chain segmental motion.

First, we consider the PVP chain-length effect on the *m*-process of PVP24000-PEG200 and PVP40000-PEG200 blends of equal wt% PVP concentration. From insets of Fig. 1a and 1b; it seems that the *m*-process in these blends is almost independent of the PVP chain-length, because the ϵ' values above 10^4 Hz are nearly same. But Figs 1a and 1b shows that the *m*-process dynamics is influenced by the PVP concentration in the blend. Further, the ϵ' dispersion plots of different volume mixtures of coexisting PVP-PEG blends having different PVP chain-length at 20 wt% PVP concentration depends on the volume concentration of the mixture constituents, which is more pronounced at the 40:60 volume ratio of PVP24000-PEG200 and PVP40000-PEG200 blend, respectively (see inset of Fig. 1a). But in case of 30 wt% PVP concentration, the mixtures of PVP24000-PEG200 and PVP40000-PEG200 blends of different volume concentration shows, almost equal ϵ' values in their dispersion plots (Fig. 1b), which confirms that the *m*-process dynamics is independent of volume mixing ratio of different PVP chain-length PVP-PEG blends at 30 wt% PVP concentration, which is not the case at 20 wt% PVP.

Now we consider the ϵ' dispersion plots (Figs 1c and 1d) of PVP-PEG blends having different chain-length of PVP and also PEG molecules with the variation of PVP concentration. The significant changes in the *m*-process were found with the change in the PEG chain-length and also with the PVP wt% concentration in these PVP-PEG blends. The change in ϵ' dispersion is expected because of the low value of static dielectric constant of the PEG400 as compared to the static dielectric constant value of the PEG200. Further the different concentration volume mixtures of the PVP24000-PEG400 and PVP40000-PEG200 blends show the monotonous lowering in the ϵ' dispersion plots with increase of the PVP24000-PEG400 blend volume concentration in the volume concentration of the PVP40000-PEG200 blend. The observed monotonous and symmetrical ϵ' dispersion plots confirms that the *m*-process dynamics in the mixtures of different volume concentration blends

retains their characteristic segmental dynamical behaviour in the polymeric two-phase systems. The $\tan\delta$ versus f plots (Fig. 3) show the peak values in the frequency range 200 Hz-500 Hz, which is little affected by the concentration and type of the mixed blends, and have value nearly 100.

All the a.c. conductivity plots (Fig. 4) of the PVP-PEG blends have plateaus of σ_{ac} at lower frequencies, i.e., frequency independent value of conductivity, which corresponds to d.c. conductivity. Above 10^4 Hz these blends a.c. conductivity increases with the increase in frequency, which is corresponding to the ionic conductivity relaxation. Further some blends also show little change in conductivity values with the change in polymers chain-length and the PVP concentration in the blends.

Electric modulus behaviour

The frequency dependent real part of the electric modulus M' , and loss M'' of the PVP-PEG blends have the dispersion in the 20 Hz-1 MHz frequency range (Figs 5 and 6). Almost overlapped dispersion plots were found for the studied different chain-length and concentration PVP-PEG blends. Further in the 200-500 kHz range, these blends have the peak in M'' values, which is corresponding to the ionic conduction relaxation, because the a.c. conductivity also shows the dispersion in the same frequency range. The average ionic conductivity relaxation time $\tau_c = 1/2\pi f_p$, where f_p is the M'' peak frequency, is found about 0.45 μ s for these blends. The insets of Fig. 6 show the enlarged view of the region around M'' peaks. The comparative insets curves indicates that there is more enhancement in M'' peak amplitude of the coexisting phases of PVP-PEG blends having different chain-length PEG as compared as compared to the different chain-length PVP. This may be because of the difference in chain flexibility of PEG200 and PEG400, which also affects their H-bonded structure with PVP. Furthermore, the M'' peak frequency (f_p) values of these blends are exactly three order higher than the corresponding $\tan\delta$ peak frequency values, which is also found for the other polymers blend^{15,16}.

Complex impedance behaviour

The appearance of two separate arcs in the complex impedance plane plots (Z'' versus Z') of the PVP-PEG blends (Fig. 7) confirms that in the lower frequency region dielectric response is corrupted by the electrode polarization effect. In all these impedance

plots the frequency of the experimental points increases on going from right to left side of the arcs. The higher frequency arcs are corresponding to the PVP-PEG sample response (bulk effect), and the lower frequency arcs are corresponding to the electrode surface polarization effect. In these arcs, the frequency corresponding to the minimum Z'' value separates the bulk effect and the surface effect. These frequency values are in the range 200-500 Hz, which are exactly equal to the frequency values observed from the $\tan\delta$ peak values of the PVP-PEG blends. This observation confirms that the $\tan\delta$ peaks frequencies are also corresponding to the separation of the blends bulk effect properties and the electrode surface polarization effect. Further, the negligible change in the frequency range corresponding to the electrode surface polarization effect confirms that the electrode surface barrier layers arises due to the adsorption²³ of one or more layers of the PVP-PEG blends are almost independent of the polymer chain-length and the concentration of the blends constituents. Furthermore, from the impedance plots (Fig. 7), it can also be seen that the d.c. resistance, R_{dc} of the PVP-PEG blends (the extrapolated intercept value on the real impedance axis of the common point of the arcs²⁴) depends on the polymers chain-length, and also vary with the PVP concentration in the blends and the volume concentration of the constituents of the blends in the coexisting phases.

Conclusions

The PVP-PEG blends have the dielectric dispersion corresponding to the micro-Brownian motion of the PVP chain above 10^4 Hz, whereas the lower frequency range dispersion in these blends occurs due to ionic conduction and electrode polarization effects. The m -process of the dielectric dispersion of these blends is influenced by the PEG chain-length and also by the PVP wt% concentration but little affected by the PVP chain-length. The systematic change in dielectric dispersion plots of the different volume concentration coexisting phases of the blends of different chain-length PVP and PEG blends confirms that the individual blend retains their H-bonded heterogeneous complex structures properties in the mixtures of coexisting phases. The electrode polarization effect contributed to the complex dielectric constant values for the frequencies lower than 500 Hz for the nickel-plated cobalt electrodes, which is found almost independent of the

blends constituents concentration and the polymer chain-length.

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