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Dielectric dispersion study of coexisting phases of aqueous polymeric solution: Poly(vinyl alcohol) + poly(vinyl pyrrolidone) two-phase systems

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Abstract

The complex dielectric constant $\varepsilon^*(\omega) = \varepsilon' - j\varepsilon''$, electric modulus $M^*(\omega) = M' + jM''$, impedance $Z^*(\omega) = Z' - jZ''$ and ac conductivity dispersion behaviour of 5, 10 and 15 wt% concentration aqueous solutions of poly(vinyl alcohol) (PVA) (14 000 and 77 000 g mol^{-1}) and poly(vinyl pyrrolidone) (PVP) (24 000, 40 000 and 360 000 g mol^{-1}) and their binary mixtures were investigated in the frequency range 20 Hz to 1 MHz at 25 °C. Analysis of dielectric constant values confirms that hydrophilic effect of PVA in aqueous solution increases the real part of dielectric constant ε', whereas for aqueous PVP solutions the hydrophobic effect masks the hydrophilic effect, which reduces ε' values below 10 kHz. Low-frequency dielectric constant of these aqueous polymeric systems is sensitive to ionic conduction and electrode polarization. The monotonous change in various electrical properties with change in volume percentage of mixture constituents indicates that individual aqueous polymer system retains their own electrical properties in the aqueous two-phase polymeric system.

Keywords: Aqueous polymeric two-phase system; Dielectric behaviour; Electrical conductivity

1. Introduction

Interactions and dynamics of polymer–polar solvent mixture are one of the most important problems in liquid state physics. Among synthetic polymers, poly(vinyl alcohol) (PVA) and poly(vinyl pyrrolidone) (PVP) are the most important pharmaceutical polymers and have a wide range of biochemical, medical and technological applications [1,2]. These are non-toxic and amorphous polymers, which are water soluble, and have a randomly coiled and highly flexible chain behaviour in solutions. Aqueous solutions of PVA and PVP are widely used for the preparation of membranes and films of different dopants for biomedical and technological applications [1–9]. The structure of the film formed from the aqueous polymeric solutions with different additives strongly depends on the structure of solution and casting condition. Therefore, in view of the current wide interest on the aqueous polymeric grown films, it is required to investigate a comparative electrical behaviour of the aqueous solutions of the PVA, PVP and PVA + PVP blends over a wide range of compositions.

The solubility of the solid PVA and PVP in water is due to some kind of interactions between the molecules of water and the monomer units of the polymer chain. In these systems, the polymer molecules act on the surrounding water due to the H-bond accepting ability of their polar groups (the hydrophilic effect) and by the ability of their inert groups to promote the water structure around them (the hydrophobic effect). These two effects interfere with each other leading to destructive or, may be under certain conditions, to cooperative interaction. The hydrophilic and hydrophobic effects strongly depend on the steric arrangement of the respective groups and on the particular size and shape of the solute (polymer) molecule [10–14]. PVA is a highly hydrophilic polymer, which shows the strong H-bond interaction between the hydroxyl group of PVA monomer units and the water molecules, whereas the PVP has strong hydrophobic behaviour in aqueous solution and has comparatively less

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hydrophilic effect due to the formation of H-bond complexes between the carbonyl group of PVP monomer units and the water molecules [11–14]. These effects can disturb the water structure in aqueous PVA + PVP solutions.

Literature survey confirms that several attempts [10–20] have been made to explore the hydration properties and water structure by dielectric measurements on aqueous PVA and PVP solutions, and also in other hydroxyl groups containing polar solvents in the microwave frequency region, where the dielectric dispersion occurs due to reorientational motion of the small-size polar solvent molecules. However, not much has been done in the frequency region 10 Hz to 1 MHz, where the interference between conduction, electrode polarization and structural relaxations may be the largest. The detailed electrical properties of aqueous polymeric solutions in the frequency range 10 Hz to 1 MHz is needed because the aqueous polymeric solutions grown doped and undoped films are in general electrically characterized in this frequency range for their different technological applications [2–9]. Further, the electrical properties of such films are governed by the nature of the polymer–solvent interactions in the solutions.

This paper presents a comparative study of dielectric dispersion of aqueous PVA, aqueous PVP, and their aqueous coexisting phases with concentration variation in the frequency range 20 Hz to 1 MHz at 25 °C. This study aims to explore the effect of the polymer chain length and concentration on their dielectric properties in aqueous PVA + PVP coexisting phases by analyzing the experimental values of complex dielectric constant $\varepsilon^*(\omega)$, ac electrical conductivity $\sigma_{ac}(\omega)$, complex electric modulus $M^*(\omega)$, and complex impedance $Z^*(\omega)$ over the frequency range 20 Hz to 1 MHz.

2. Experimental

2.1. Materials

Table 1 shows the polymers used in the measurements. Double distilled water was used for the preparation of aqueous polymeric solutions. Aqueous solutions of 5, 10 and 15 wt% PVA (PVA14000 and PVA77000) and of PVP (PVP24000 and PVP40000) were prepared for their dielectric characterization. Only 5 wt% concentration of aqueous solution of PVP360000 was prepared because above this concentration the solution turned turbid due to high viscosity. The equal weight concentration aqueous solution of PVA14000 and aqueous solution of PVP (PVP24000, PVP40000, PVP360000) was mixed at four volume percentages, i.e. 80:20, 60:40, 40:60, and 20:80, respectively, at room temperature for the preparation of coexisting aqueous polymeric two-phase systems. Similarly, equal weight concentration aqueous solution of PVA77000 and PVP40000 was mixed at five volume percentages, i.e. 84:16, 67:33, 50:50, 33:67, and 16:84, respectively, for dielectric study of coexisting aqueous polymeric two-phase systems.

2.2. Measurements

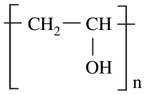
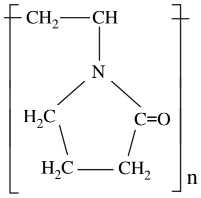
An Agilent 4284A Precision LCR Meter and a four terminal nickel-plated cobalt parallel plate electrodes' dielectric cell Agilent 16452A Liquid Test Fixture were used for the capacitance and resistance measurements in the frequency range 20 Hz to 1 MHz. The capacitances and parallel resistance of the 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 complex dielectric constant values. All measurements were made at 25 °C and the temperature was controlled by Thermo-Haake DC10 controller to ±0.01 °C.

3. Results

The complex dielectric constant $\varepsilon^*(\omega)$ is obtained from the relation [21]:

$$\varepsilon^*(\omega) = \varepsilon' - j\varepsilon'' = \alpha\left(\frac{C_P}{C_o} - j\frac{1}{\omega C_o R_P}\right) \tag{1}$$

Table 1
Polymers used in the measurements

Polymer and formula	Abbreviation name	Average molecular weight (g mol^{-1})	Number of monomer units	Manufacturer supplier	Grade
Poly(vinyl alcohol)	PVA	14 000	318	S.D. Fine Chem, India	Laboratory
		77 000	1750	Loba Chemie, India	Laboratory
Poly(vinyl pyrrolidone)	PVP	24 000	216	S.D. Fine Chem, India	Laboratory
		40 000	360	Loba Chemie, India	Laboratory
		360 000	3241	S.D. Fine Chem, India	Laboratory

where $\omega = 2\pi f$ is the angular frequency, C_o and C_P are the capacitances of the free space and with sample, respectively, and R_P is the equivalent parallel resistance of the cell with sample, and α is the correction coefficient of the cell.

Figs. 1–3 show the concentration dependence spectra of the real part of dielectric constant ε', dielectric loss ε'', loss tangent ($\tan\delta = \varepsilon''/\varepsilon'$) and real part of ac conductivity $\sigma_{ac}(\omega) = \omega\varepsilon_o\varepsilon''$ of aqueous PVA14000, aqueous PVP40000 and aqueous PVA14000 + PVP40000 two-phase systems at 25 °C. The spectra of ε', ε'', $\tan\delta$, and σ_{ac} of aqueous PVA14000 + PVP360000 coexisting phases are shown in Fig. 6. Similar concentration dependence spectra were also obtained in the aqueous PVA14000 + PVP24000 and aqueous PVA77000 + PVP40000 coexisting polymer phases in the same frequency range. The broadband values of complex dielectric constant $\varepsilon^*(\omega)$ for polymer–polar solvent mixture can be well described by a sum of three relaxation processes with the contribution of dc conductivity, σ_{dc}, by the equation [20]:

$$\varepsilon^*(\omega) = \varepsilon_\infty + \varepsilon_l^*(\omega) + \varepsilon_m^*(\omega) + \varepsilon_h^*(\omega) - j(\sigma_{dc}/\omega\varepsilon_o) \tag{2}$$

where ε_o (8.854×10^{-12} F/m) is the dielectric constant of the vacuum, ε_∞ is the limiting high-frequency dielectric constant, and the subscripts l, m, and h denote the low, middle, and high-frequency processes, respectively.

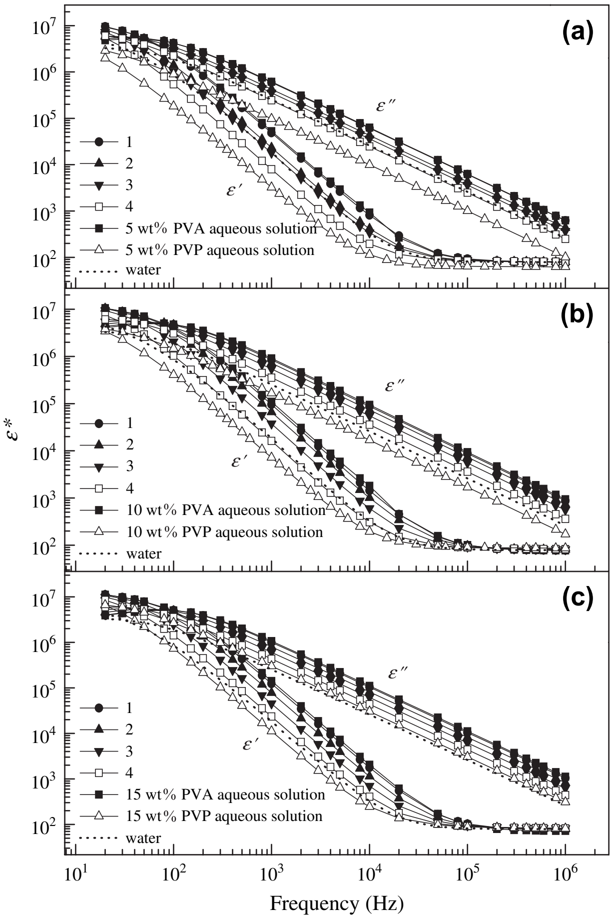


Fig. 1. Frequency dependence of real part of dielectric constant ε' and dielectric loss ε'' of water, aqueous PVA14000, aqueous PVP40000 solutions, and coexisting aqueous PVA14000 + PVP40000 two-phase systems at volume percentage ratios (1) 80:20, (2) 60:40, (3) 40:60, and (4) 20:80.

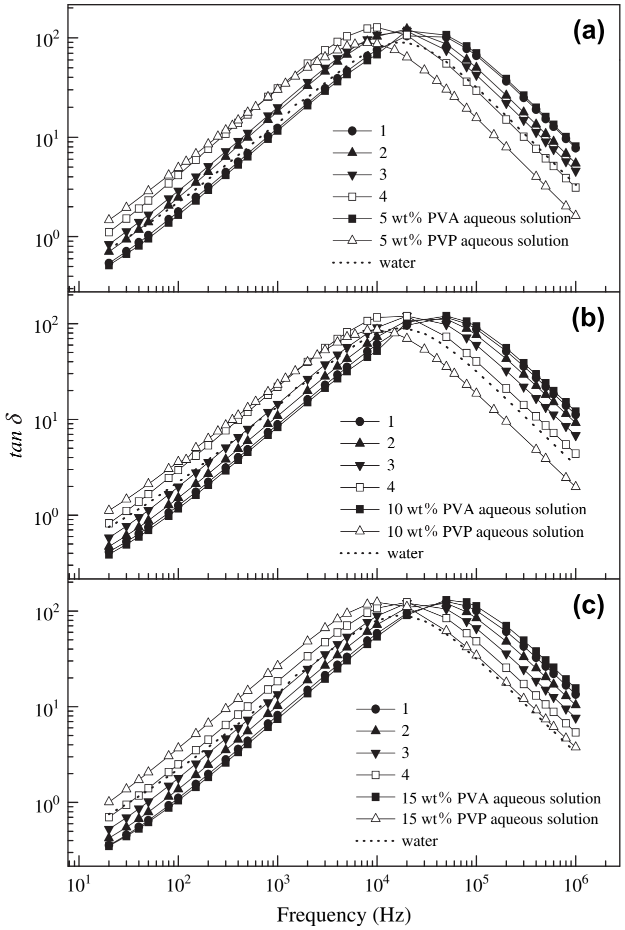


Fig. 2. Frequency dependence of loss tangent $\tan\delta$ of water, aqueous PVA14000, aqueous PVP40000 solutions, and coexisting aqueous PVA-14000 + PVP40000 two-phase systems at volume percentage ratios (1) 80:20, (2) 60:40, (3) 40:60, and (4) 20:80.

The low-frequency process in polar solutions is caused by the electrode polarization. When an electric field is applied to the materials, the long-range drift of ions and barrier layer formation on the electrode surface result large values of dielectric constant and loss [22–29]. We are concerned only in the l-process in the present study. The comparative variation in the observed dielectric parameter values of ε', ε'' and σ_{ac} of the aqueous PVA + PVP coexisting two-phase systems was used to explore the electrode polarization and ionic conduction in these systems.

The $\varepsilon^*(\omega) = \varepsilon' - j\varepsilon''$ is a meaningful quantity under the condition that in the experiment the electric field is an independent variable and the charge is the dependent one. Considering the charges as the independent variable, conductivity relaxation effects can be suitably analyzed within the modulus formalism in terms of a dimensionless quantity M^*. Analogous to mechanical relaxation, the 'electric modulus' M^* is obtained from the relation [22]:

$$M^*(\omega) = \frac{1}{\varepsilon^*(\omega)} = M' + jM'' = \frac{\varepsilon'}{\varepsilon'^2 + \varepsilon''^2} + j\frac{\varepsilon''}{\varepsilon'^2 + \varepsilon''^2} \tag{3}$$

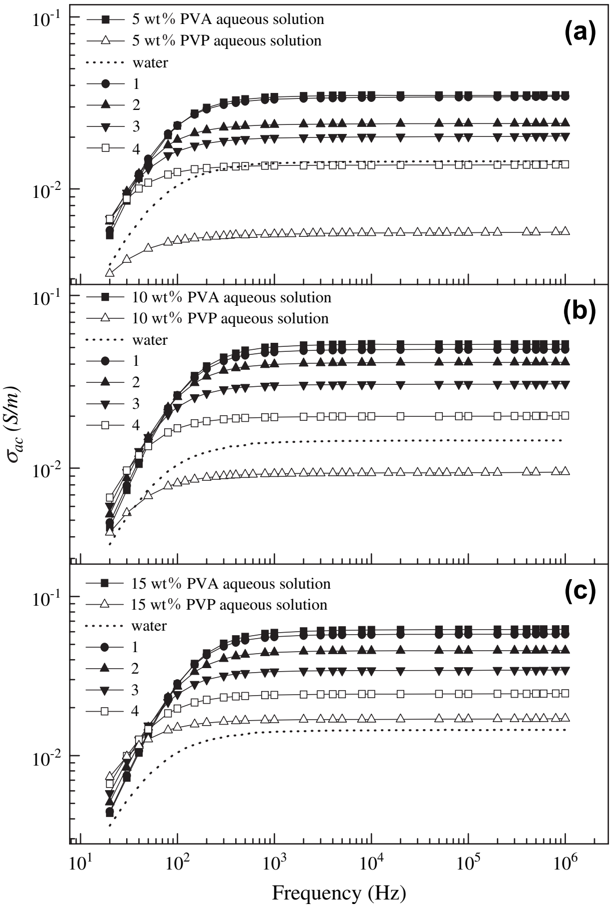


Fig. 3. Frequency dependence of ac conductivity σ_{ac} of water, aqueous PVA14000, aqueous PVP40000 solutions, and coexisting aqueous PVA-14000 + PVP40000 two-phase systems at volume percentage ratios (1) 80:20, (2) 60:40, (3) 40:60, and (4) 20:80.

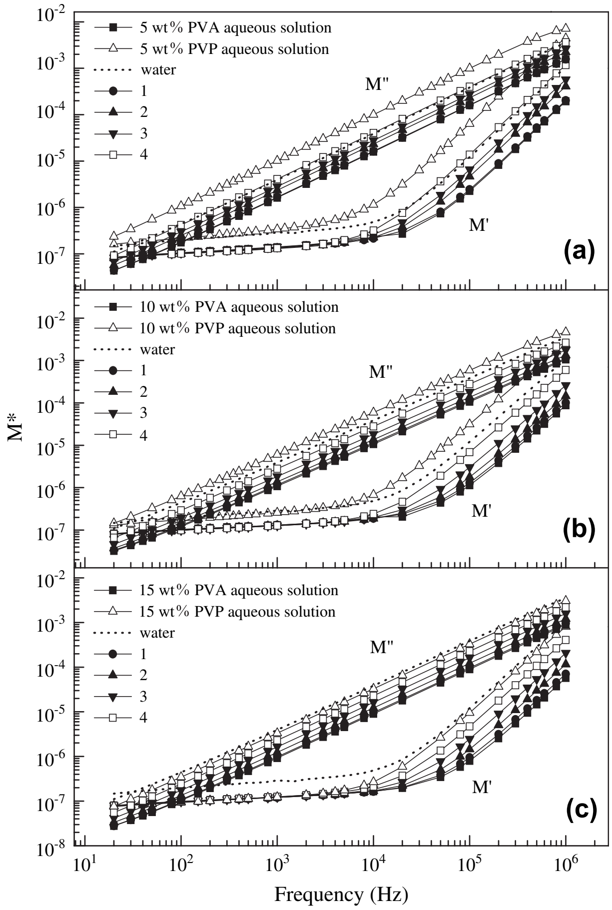


Fig. 4. Frequency dependence of real part of electric modulus M' and loss M'' of water, aqueous PVA14000, aqueous PVP40000 solutions, and coexisting aqueous PVA14000 + PVP40000 two-phase systems at volume percentage ratios (1) 80:20, (2) 60:40, (3) 40:60, and (4) 20:80.

The main advantage of this formalism is that the space charge effects often do not mask the features of the spectra, owing to the suppression of high capacitance phenomena in $M''(f)$ spectra. In ac dielectric relaxation spectroscopy measurements, the electric field, $E^*(\omega)$, or electric displacement vector, $D^*(\omega)$, may be considered as an independent variable. Therefore, the formalisms of $\varepsilon^*(\omega)$ and $M^*(\omega)$ are equivalent. Transformation from one to another may emphasize and therefore help to resolve particular aspects of the relaxation process. Figs. 4 and 6 show the M' and M'' versus f spectra of the studied aqueous PVA14000 + PVP40000 and aqueous PVA14000 + PVP360000 two-phase coexisting systems. Similar $M^*(\omega)$ spectra were also obtained for other different molecular weight aqueous PVA and PVP coexisting phases. In the M'' spectra, peak corresponding to the ionic conductivity relaxation is not observed in the 20 Hz to 1 MHz range, in which both charge carrier transport and polymer segmental reorientation may contribute to the electric field relaxation [29–31].

Beside the ε^* and M^*, analysis of dielectric relaxation spectroscopic data within the complex impedance formalism $Z^* = 1/Y^*$, where Y^* is the complex admittance, is commonly used to separate the bulk and the surface phenomena [23]. A common feature of dielectrics with dc conductivity is a discontinuity at electrode/dielectric interface, which has different polarization properties than the bulk of the dielectric. Usually complex impedance plane plots (Z'' versus Z') are used to separate the bulk and the surface phenomena. The electrode polarization is a highly capacitive phenomenon and is therefore characterized by large relaxation times than the polarization mechanisms in bulk. This fact usually results in the appearance of two separate arcs of semicircles in the Z'' versus Z' complex plane plots. The complex impedance of the material was evaluated by the relation:

$$Z^*(\omega) = Z' - jZ'' = \frac{1}{Y^*(\omega)} = \frac{1}{1/R_P + j\omega C_P} = \frac{R_P}{1+(\omega C_P R_P)^2} - j\frac{\omega C_P R_P^2}{1+(\omega C_P R_P)^2} \quad (4)$$

Figs. 5 and 7 show the complex impedance plane plots of the aqueous PVA14000 + PVP40000 and aqueous PVA-14000 + PVP360000 two-phase systems, respectively. Similar plots were also obtained in the other molecular weight aqueous PVA and PVP coexisting phases. All these plots have two separate arcs. The frequency value, which separates the

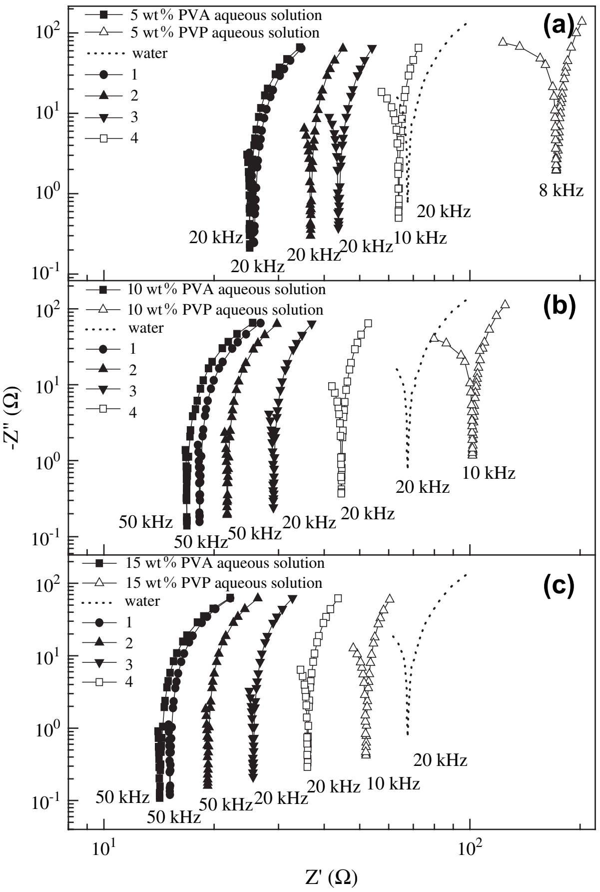


Fig. 5. Plots of Z'' versus Z' of water, aqueous PVA14000, aqueous PVP40000 solutions, and coexisting aqueous PVA14000 + PVP40000 two-phase systems at volume percentage ratios (1) 80:20, (2) 60:40, (3) 40:60, and (4) 20:80.

electrode polarization effect and the ionic conduction effect, was determined by using the frequency corresponding to the Z'' minimum value in the plots and same has also been shown in their respective plots.

4. Discussion

4.1. Complex dielectric constant

Figs. 1 and 6 show the frequency dependent ε' and ε'' values of water, different molecular weight aqueous PVA and aqueous PVP solutions, and coexisting aqueous PVA + PVP two-phase systems of different volume percentage mixture. For all the aqueous polymeric solutions, values of ε' and ε'' decrease with increase in frequency from 20 Hz to 1 MHz. The high values of ε' and ε'' in the lower-frequency side confirm the contribution of ionic conduction and electrode polarization phenomenon in these solutions [20,23–30].

4.1.1. Aqueous polymeric single-phase system

The frequency dependent ε' values of aqueous PVA system are higher than the ε' values of pure water (dotted plots), whereas aqueous PVP system has comparatively lower ε' values (Figs. 1 and 6). It is because of the higher strength of hydrophilic effect of aqueous PVA system, i.e. the strong H-bond interactions between the hydroxyl groups of PVA monomer units and water molecules [10,14,16], which orients the PVA chain segments for increase in net polarization. The hydroxyl group of PVA is capable of both accepting and donating binding protons that promote the water interaction with large number of PVA monomer units as compared to the PVP–water interactions, which may also result in the high ε' values of the aqueous PVA systems as compared to the ε' values of aqueous PVP systems. The lower ε' values of aqueous PVP system as compared to the frequency dependent ε' values of pure water confirm that the strong hydrophobic effect of PVP in aqueous solution [16] dominates its hydrophilic effect (interactions between carbonyl groups of the PVP monomer units and water molecules). Further, the decrease in ε' values due to differently oriented segments of randomly coiled flexible PVP chain in aqueous solution cannot be ruled out.

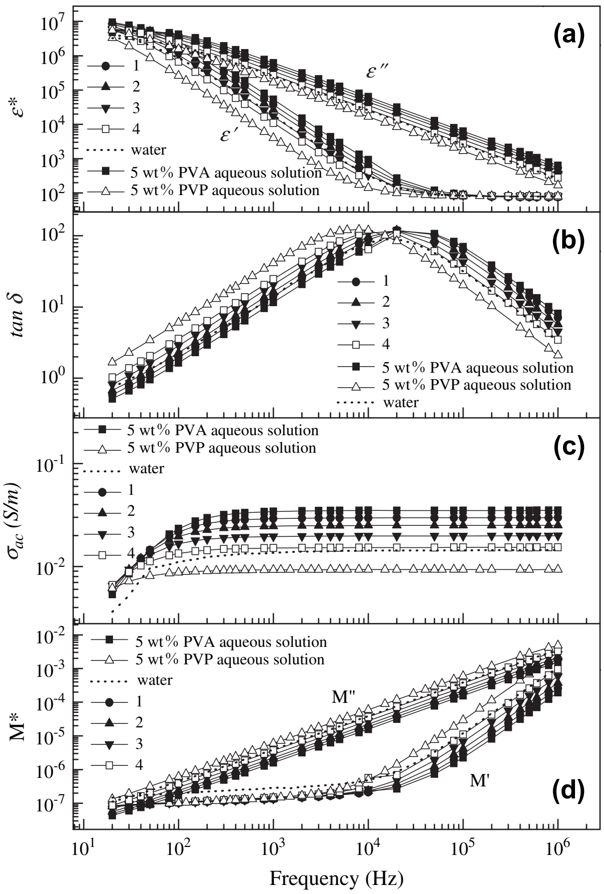


Fig. 6. Frequency dependence of real part of dielectric constant ε', dielectric loss ε'', loss tangent tan δ, ac conductivity σ_{ac} and real part of electric modulus M' and loss M'' of water, aqueous PVA14000, aqueous PVP360000 solutions, and coexisting aqueous PVA14000 + PVP360000 two-phase systems at volume percentage ratios (1) 80:20, (2) 60:40, (3) 40:60, and (4) 20:80.

The comparative ε' values of aqueous PVP and water also show that the difference in the frequency dependent ε' values reduces with the increase in PVP concentration (Fig. 1). This may be due to the decrease in the strength of hydrophobic effect and simultaneous increase in hydrophilic effect in aqueous PVP solutions with increase in PVP concentration up to 15 wt% PVP. In case of aqueous PVA solution, there is small increase in the frequency dependent ε' values with increase in PVA concentration, which confirms strengthening in the hydrophilic effect. Fig. 1 shows that the ε'' values also vary with the increase in PVP concentration in water. Further, the increase in concentration of PVA increases the frequency dependent ε'' values as compared to the ε'' values of pure water.

From the comparative study of frequency dependent ε' and ε'' values of aqueous PVP and PVA systems of different molecular weights, it is observed that the ε' values are more or less independent of the PVP molecular weight, whereas both ε' and ε'' gradually increases with the increase of PVA molecular weight.

4.1.2. Aqueous polymeric two-phase system

In case of 40:60 vol% mixture ratio of aqueous 5 wt% PVA14000 + aqueous 5 wt% PVP40000 two-phase system, the frequency dependent ε' values were found nearly equal to the ε' values of pure water (Fig. 1a). Further, the PVA rich mixtures have higher ε' values, whereas the PVP rich mixtures show the lower ε' values as compared to the frequency dependent ε' values of water. From these observations it can be concluded that around equal volume mixture concentration of the solution, the net enhancement in polarization is zero. This may be due to neutralization of the PVA hydrophilic effect contribution in polarization by the PVP hydrophobic effect in water solution. Similar behaviour was also found at 40:60 vol% mixture ratio of aqueous 5 wt% PVA14000 + aqueous 5 wt% PVP24000 system, aqueous 5 wt% PVA-77000 + aqueous 5 wt% PVP40000, and aqueous 5 wt% PVA-14000 + aqueous 5 wt% PVP360000 systems (Fig. 6a).

The significant shift in the frequency dependent ε' values of aqueous 10 wt% PVA + aqueous 10 wt% PVP system, and aqueous 15 wt% PVA + aqueous 15 wt% PVP system, (Fig. 1b and c) toward the ε' values of aqueous PVP solutions shows that the PVA hydrophilic effect masks the PVP hydrophobic effect at these concentrations. Further, the comparative ε'' values of the aqueous PVA + aqueous PVP systems show that the trend in change of the frequency dependent ε'' values is identical in all the systems but their magnitude is affected by the polymer concentration and also by the polymer molecular size. The monotonous change of the ε' and ε'' values with change in the volume concentration of the mixture constituents of the aqueous PVA + aqueous PVP mixtures confirms that the dielectric spectroscopy can be applied for the *in situ* monitoring of the dielectric constant of these film forming two-phase aqueous polymeric solutions.

Figs. 2 and 6b, show the frequency dependent tan δ ($\varepsilon''/\varepsilon'$) values of water, aqueous PVA14000, aqueous PVP40000 systems, and their volume mixtures. All spectra have the tan δ peak, which is in the frequency range 5–50 kHz. The aqueous PVA system has tan δ peak at high frequency, whereas aqueous PVP system has tan δ peak at comparatively low frequency, and in between these the tan δ peak frequencies of aqueous PVA + aqueous PVP two-phase systems were observed.

The value of electrode polarization relaxation time τ_{EP}, which involves charging/discharging of double layer capacitance formed on the electrode surfaces, was determined by the relation $\tau_{EP} = 1/2\pi f_{EP}$, where f_{EP} is the tan δ peak frequency [29–31]. Fig. 6 shows that the f_{EP} value is closely related to the frequency where the ε' values have strong upturn. The exact location of f_{EP} is determined by fitting the data to the Origin® non-linear curve fitting tool. The τ_{EP} values of aqueous PVA14000 + aqueous PVP40000 and aqueous PVA14000 + aqueous PVP360000 systems of various volume ratios are shown in Table 2. These values show that the electrode polarization relaxation time of these blends depends on the polymers' concentration in their aqueous solution two-phase system.

Figs. 3 and 6c show the ac conductivity of the aqueous single-phase and two-phase polymeric systems. In polymeric aqueous solutions, the segmental motion of the polymer host is essential for ionic conduction [32]. The conductivity plots (Fig. 3) of different volume percentage mixtures of aqueous PVA14000 + aqueous PVP40000 show that the ionic conductivity increases with the increase in concentration of PVA in water. The viscosity of aqueous PVA solutions is much higher than the viscosity of aqueous PVP solutions at equal concentration and it increases with increase in polymer concentration in water. The increase in conductivity with increase in PVA concentration in water suggests that the conductivity values of aqueous polymeric systems are independent of their viscosity. These coexisting aqueous polymeric systems (Fig. 3) show the increase in conductivity with the increase in volume percentage of PVA in two-phase mixture, which is maximum for aqueous PVA system. The comparative conductivity values of aqueous PVA, aqueous PVP and aqueous PVA + aqueous PVP systems confirm that the PVA segmental motion is much higher than the PVP segmental motion in their aqueous solutions, which mainly governs their ionic conductivity. The frequency independent conductivity values in the frequency

Table 2
Values of electrode polarization relaxation time, τ_{EP}, of the aqueous PVA14000 + PVP40000 and aqueous PVA14000 + PVP360000 two-phase systems at 25 °C

Vol% ratio PVA:PVP	τ_{EP} (μs)	Vol% ratio PVA:PVP	τ_{EP} (μs)
5 wt% aqueous PVA14000 + PVP40000		10 wt% aqueous PVA14000 + PVP40000	
100:0	7.96	100:0	3.18
80:20	7.96	80:20	3.18
60:40	7.96	60:40	3.18
40:60	7.96	40:60	7.96
20:80	15.92	20:80	7.96
0:100	19.89	0:100	15.92
Water	7.96	Water	7.96
15 wt% aqueous PVA14000 + PVP40000		5 wt% aqueous PVA14000 + PVP360000	
100:0	3.18	100:0	7.96
80:20	3.18	80:20	7.96
60:40	3.18	60:40	7.96
40:60	7.96	40:60	7.96
20:80	7.96	20:80	7.96
0:100	15.92	0:100	19.89
Water	7.96	Water	7.96

range 100 Hz to 1 MHz confirm the dc conduction behaviour of these systems.

Further from Fig. 3, it is found that the conductivity values of aqueous 5 and 10 wt% PVP40000 solutions are lower than the frequency dependent conductivity values of pure water. But the conductivity of 15 wt% PVP aqueous solutions is higher than the water conductivity. These results indicate that the chain segmental mobility of higher molecular weight PVP at lower concentration in aqueous solution is comparatively low, which increases at higher concentrations. Further the systematic change in conductivity of aqueous PVA + aqueous PVP two-phase systems with change in their volume concentration indicates that the aqueous single-phase PVA/PVP systems retain their individual segmental mobility behaviour in coexisting phases.

4.2. Electric modulus formalism

Figs. 4 and 6d show the variation of M' and M'' versus f for water, aqueous PVA14000, aqueous PVP40000 and aqueous PVP360000 systems, and their mixtures at 25 °C. The variations in M' values up to 10 kHz of these systems are negligible, but above 10 kHz the M' values increase with the increase in frequency, and have different plots corresponding to each volume mixture of these aqueous polymeric two-phase systems. Further, the comparative examination of these plots confirms that the polymer molecular weight and concentration in aqueous solutions affect the frequency dependent values of M' and M''. The M'' values of all these aqueous systems increase linearly with the increase in frequency. It seems that for these aqueous polymeric systems the peak value of M'' is above our experimental higher frequency limit, i.e. 1 MHz. Therefore, it is not possible to evaluate the values of ionic conductivity relaxation time, τ_σ, in these systems, which is estimated earlier in other aqueous polymeric systems [23,25,27] in the same frequency range using the relation $\tau_\sigma = 1/2\pi f_\sigma$, where f_σ is the frequency corresponding to the M'' peak value.

4.3. Complex impedance formalism

In Figs. 5 and 7, the impedance values of water, aqueous PVA14000, aqueous PVP40000, aqueous PVP360000 and aqueous PVA + aqueous PVP systems were plotted as the complex plane plots ($\log Z''(f)$ against $\log Z'(f)$) in order to isolate the desired bulk sample response from the portion, which is corrupted by electrode polarization effect. In all these impedance plots the frequency of the experimental points increases on going from right to left side on the arcs. The appearance of the two separate arcs in the impedance plots corresponds to the bulk effect (the high-frequency arc) and the surface polarization effect (the low-frequency arc), respectively. The frequency value corresponding to Z'' minimum value (indicated in respective plots) separates the bulk effect and the surface effect [23–29]. These frequencies are in the range 10–50 kHz, which vary with the polymer molecular weight and also with the volume concentration in the aqueous polymeric two-phase systems.

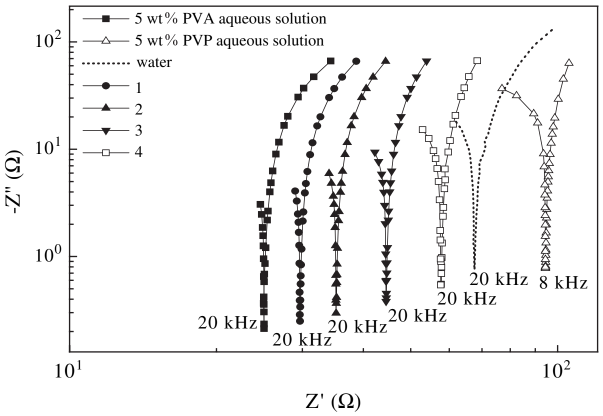


Fig. 7. Plots of Z'' versus Z' of water, aqueous PVA14000, aqueous PVP360000 solutions, and coexisting aqueous PVA14000 + PVP360000 two-phase systems at volume percentage ratios (1) 80:20, (2) 60:40, (3) 40:60, and (4) 20:80.

The dc bulk resistance, R_{dc}, can be estimated by extrapolating the section of the arc corresponding to the bulk phenomena to the low-frequency side in the complex impedance plots [33]. The intercept on the real axis Z' is considered as the R_{dc} of the aqueous polymeric solutions. From Figs. 5 and 7, it seems that the R_{dc} values decrease with the increase of PVA concentration of equal weight percentage PVA/PVP in aqueous two-phase systems. Further, the value of R_{dc} increases with the increase in weight percentage of PVA in the aqueous PVA + PVP two-phase system. This observation confirms that the addition of PVA in water increases the dc conductance, G_{dc} ($1/R_{dc}$). Further, it is also found that the higher molecular weight PVP aqueous system of 5 and 10 wt% PVP concentrations reduces the solution conductance, whereas the 15 wt% PVP aqueous solution increases the solution conductance as compared to the conductance value of the water.

5. Conclusion

The hydrophilic effect of aqueous PVA enhances the value of real part of dielectric constant ε', whereas the hydrophobic effect of aqueous PVP reduces the ε' values as compared to the frequency dependent ε' values of water over the frequency range of 20 Hz to 100 kHz. The ε' values vary monotonously with the change in the volume percentage of the constituent of the equal weight concentration aqueous PVA + aqueous PVP system, and also with the molecular weight of PVA/PVP.

The formation of hydrogen bonds between the water molecules and the hydroxyl groups of PVA monomer units facilitates the PVA chain segmental motion, which enhances the ionic conductivity. The formation of H bonds between the carbonyl groups of PVP monomer units and water molecules contributes to the ionic conduction, but adversely affected by the hydrophobic effect of higher molecular weight PVP. The coexisting aqueous PVA + aqueous PVP two-phase system has monotonous change in the ionic conduction behaviour with the change in polymer molecular weight and volume concentration in the mixture.

The electric modulus formalism and the impedance formalism confirm the contribution of ionic conduction and surface effect in the low-frequency values of complex dielectric constant of the studied single-phase and two-phase aqueous polymeric (PVA/PVP) systems. The surface effect for the nickel-plated cobalt electrodes in these aqueous polymeric systems occurs below 50 kHz. The electrode polarization relaxation of these aqueous systems occurs in the range from ~3 μs to ~20 μs. The comparative dielectric properties of the aqueous PVA + aqueous PVP solutions confirm that the required volume ratio of these aqueous two-phase polymeric solution can be mentioned by the dielectric measurement for the grown of the *in situ* aqueous polymeric films of different technological applications.

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