Flow and Conductance Behaviour of Poly (Ethylene Oxide) in the Presence of Some Inorganic Salts

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Summary:Different solution properties like viscosities, conductance, surface tension and light scattering of poly(ethylene oxide) dissolved in water, in the absence as well as presence of some salts like LiCl, NaCl and KCl have been studied over a wide range of polymer concentration. The data so obtained are analyzed and correlated/discussed in the light of conformational changes with the change in ionic strength and ionic size of the electrolytes used. From the initial data of conductance, the limiting conductance and other related parameters have been obtained. From these results, the degree of association (α_a), association constant (k_a) of the polymer and effect of different parameters upon these are discussed. From the results, we can conclude that degree of association and association constant of polyelectrolytes can also be estimated through conductance measurement.

Introduction

Polyelectrolytes possess a number of novel and versatile properties due to their electrostatic characteristics nature in solution and hence gaining extensive interest. Out of these, poly(ethylene oxide), PEO, has been much investigated as it is one of the few polymers which are soluble in water as well as organic solvents and that it has potential applications in high energy density batteries [1-5] and electronic devices [6-7]. Aside from battery technology, understanding solute-solvent interactions is of fundamental interest and importance which can be investigated in way as well. For example the controlled introduction of salts (electrolytes) in to solvents is used to study the solvent property like structural behaviour of water has been extensively studied using this approach [8]. However, most of the work carried out up to now is mixing of electrolytes with melted Poly(ethylene oxide) or its co-polymers and measuring of their mechanical properties [9-17]. Though it is important to investigate the polymers and their interactions with the electrolytes in solution form but it is almost neglected due to one or the other reason. Realizing this important aspect, some authors [18-22] have reported the solution properties of different water soluble polymers, where as others [23-24] tried to give some theoretical background about these polymers to explain their flow properties with reference to electrical charges and succeeded up to some extent. Their emphasize was on the role of charge/charge density and solvent density on viscosity of polyelectrolytes in the presence of some ions.

However, an important property of polymer solutions (keeping in view their applications), like conductance is neglected, though it is easy to measure and can provides a number of important information, such as degree of association of polymers, electric charge density, adsorption of ions on polymer molecules and type of adsorption taking place at the polymers and variation in the polymer-electrolytes interactions etc. In this respect we can find only two references [25-26] in which the authors have investigated PEO in methanol with reference to effect of addition of electrolyte concentration on polymer conductance. Keeping in view these facts, we have investigated PEO in pure water and in the presence of different electrolytes such as LiCl, NaCl and KCl, having a constant concentration of 5×10^{-5} mole/liter, with reference to its viscosity, conductance, surface tension and light scattering measurements as a function of polymer concentration. The results so obtained have been discussed in terms of conformational changes, selective adsorption of electrolytes on polymers and variation in extent of association of polymers with the change in ionic strength, ionic size and polymer concentration.

Results and Discussion

The intrinsic viscosity of PEO measured in the absence as well as presence of different electrolytes i.e. LiCl, NaCl, and KCl is plotted in Fig.1. The figure shows that the intrinsic viscosity of PEO decreases with temperature for all the solvent

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systems. It is to be noted that, the intrinsic viscosity of polymer is high in salt solutions as compared to pure water. The figure further shows that the viscosity remains almost constant up to about 40°C, when it is measure in water or LiCl solution. However, after this temperature, it decreases sharply with the increase in temperature. In case of NaCl and KCl, the viscosity decreases regularly with the increase in temperature. This phenomenon ean be explained in term of solvent quality/variation in rigidity of polymer molecules etc, which varies with temperature. This concludes that the quality of solvent deteriorates quickly in case of water and LiCl whereas the effect is less in case of NaCl or KCl. The order of intrinsic viscosity at a particular temperature is noted to be:

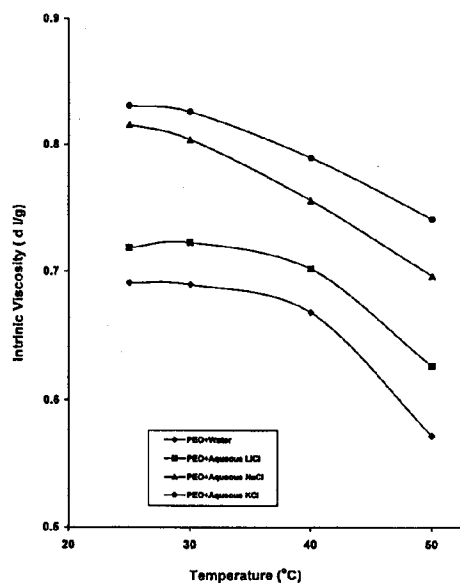Water < Aqueous LiCl < Aqueous NaCl < Aqueous KCl

Fig. 1: Variation in intrinsic viscosity of poly (ethylene oxide), dissolved in different solvent systems, as a function of temperature.

This variation in the viscosity of PEO for different solvent system is due to the fact the added electrolytes, get adsorbed on the polymer molecules, create a charge on them and the polymer molecules repel each other, resulting a change in conformational properties of the polymer [25]. However, the extent

of adsorption is different for different electrolytes. Due to the reason, the quality of the solvent and conformational properties of the polymer vary from salt to salt. The increasing order of viscosity also support the explanation stated above i.e KCl solution is better solvent than all the others used. The flow activation energy of PEO dissolved in different solvent systems was calculated by plotting log [η] versus 1/T (using Arrhenious equation (see Fig.2)). It can be noted that the plots are linear except for the values obtained in water and in LiCl solution measured at 50 °C. The results obtained are reported in Table 1. It can be noted that activation energy varies in the following order,

H_2O > Aqueous LiCl > Aqueous NaCl > Aqueous KCl
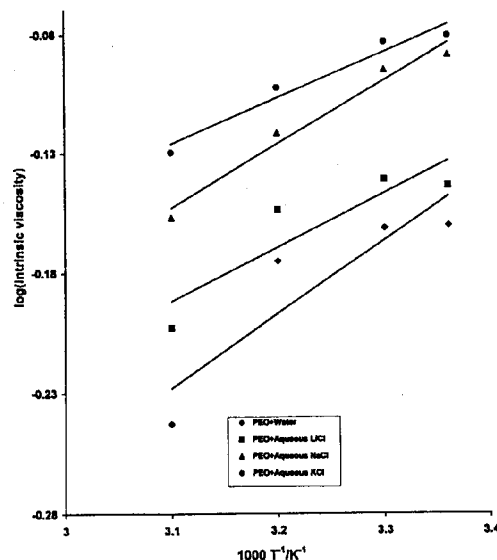

Fig. 2: Variation in log(intrinsic viscosity) of poly (ethylene oxide), dissolved in different solvent systems, as a function of reciprocal of temperature.

Table-1:Activation energy of PEO in different solvent systems.

Solvents	Activation Energy (J. mole[-1])
Water	9185
Aqueous LiCl	7684
Aqueous NaCl	5823
Aqueous KCl	4377

The decrease in activation energy with increase in ionic size is due to improvement in solvent

quality, conformational changes [27-29] of the polymer molecules and due to the adsorption of the electrolytes on polymer or complexation with polymer as explained earlier. Further the extent of complexation with Li^+ is weaker than Na^+ and K^+ ion and hence the order of decrease in activation energy from water system to aqueous KCl system is consistent with the observations made by others [30-31].

The conductance of polymer measured in different solvent systems is plotted versus concentration of polymer in Fig. 3. The results show that the conductance first increases with concentration of polymer and then levels off. This is due to the fact that PEO is a weak electrolyte, so the increase in concentration increases the polymer- polymer interactions and results in an increase in polymer molecules association. This association of polymer molecules results in a decrease in number of charge carriers and hence conductance. The data further show that the conductance obtained for a polymer concentration equal to 0.25g/dl for different solvent systems is in the order of

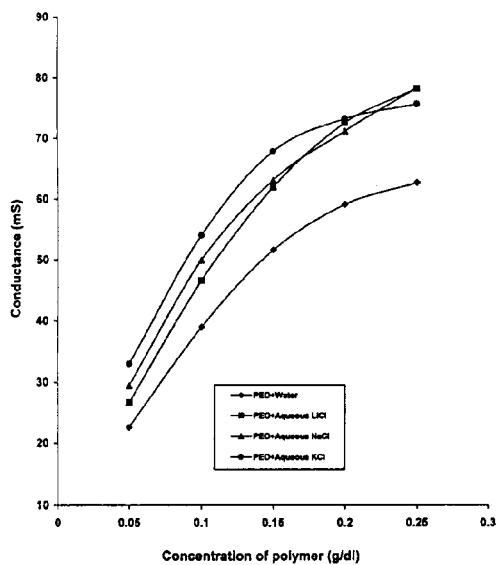H_2O < Aqueous LiCl < Aqueous NaCl < Aqueous KCl

Fig. 3: Dependence of conductance of poly (ethylene oxide), dissolved in different solvent systems, on its concentration.

which is according to expectations. Since the flow activation energy and association of polymer

molecules is lowest in aqueous KCl system, hence should show highest conductance if all the other parameters are the same.

The equivalent conductance has also been plotted versus concentration of polymer in Fig. .4. It can be noted that the equivalent conductance decreases with concentration of polymer as is expected in case of weak electrolytes [32]. Similarly the equivalent conductance at infinite dilution (Λ_0) of PEO in different solvent systems, determined through extrapolation method, show the order of variation of Λ_0 as

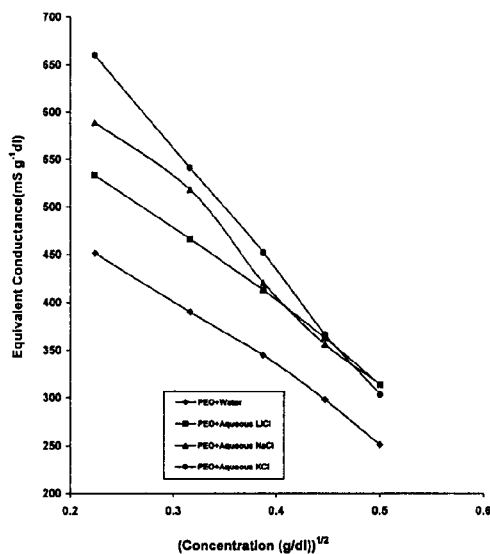H_2O < Aqueous LiCl < Aqueous NaCl < Aqueous KCl.

Fig. 4: Illustration of equivalent conductance of poly (ethylene oxide), dissolved in different solvent system, as a function of its concentration.

The reasons for such type of trends seems to be not due to the fact that the extent of bond/ complex formation/adsorption is in the order of Li^+ > Na^+ > K^+. Due to the reason the K^+ will move faster than Li^+ and hence show the conductance in the stated order.

Further the conductance is directly proportional to ionic mobility, which in a way is directly proportional to charge of molecules/ion and applied electric field and inversely proportional to dielectric

constant of the media and ionic size. Since the ionic size remains constant, the conductance should only depend upon the amount of charge on molecules/ ions. This means, when electrolytes are added to polymer solution the charge is created on the polymer due to adsorption/complexation phenomenon and the polymer behaves as a charged particle and helps in conducting the electricity. These charged particles increase with the increase in concentration of polymer and hence the conductance. It is a known fact that the conductance of Aqueous NaCl > Aqueous KCl >Aqueous LiCl > H_2O, hence we conclude that the difference in expected and observed trend is due to adsorption of ions over the polymer. When the polymer concentration is further increased the association among the molecules will step in and hence the number of free molecules will be less than the expected value, resulting in decrease in conductance or leveling off. It is to be noted that the data obtained in different electrolytes show a cross over behaviour. This phenomenon can be explained in terms of variations in extent of association of polymer molecules with the variations in polymer concentration for different electrolytes.

From the above explained phenomenon, we expect that the degree of association 'α_a' of the polymer can be estimated from the conductance variation of solution with concentration of polymer, as in case of surfactants [33]. For the purpose the following equation was used which is in analogy with the poor electrolytes theory for dilute systems.

$$\alpha_a = 1 - \Lambda_c / \Lambda_0$$

where Λ_c and Λ_0 represent the equivalent conductance at dilution 'c ' and infinite dilution, respectively. The results obtained are plotted in Fig. 5, the figure shows that the value of α_a increases with concentration of polymer which is according to expected trend of polyelectrolytes. This means that the polymer molecules associate with each other up to some extent in dilute solution, and extent of this association increases with the increase in polymer concentration. However, the extent of association, in addition to other parameters, strongly depends upon the quality of the solvent [34-37]. It is noted that α_a of PEO in aqueous media increases with concentration of polymer and that the order of it for a particular concentration is

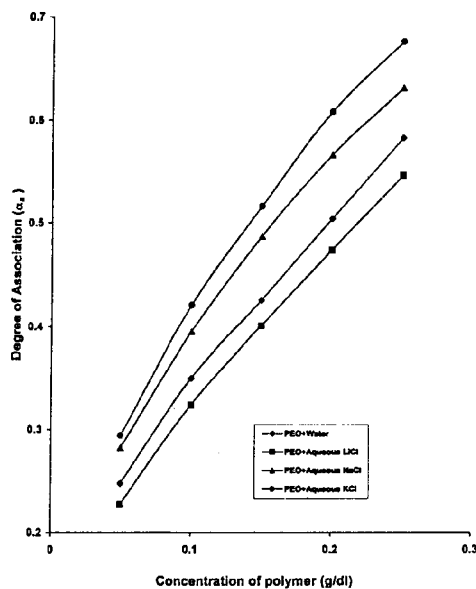Aqueous LiCl < H_2O < Aqueous NaCl < Aqueous KCl.

Fig. 5: Dependence of degree of association of poly (ethylene oxide), dissolved in different solvent systems, on its concentration.

which is as per our expectations and shows that KCl solution is better solvent than others.

Further the difference in degree of association for different solvent system can be explained in term of bond strength between polymer and salt added. For example Li^+ has weak bonding as compared to K^+ and Na^+ [38-39] and hence aqueous solution of LiCl behave as a poor solvent. Therefore, we conclude that aqueous solution of LiCl behave as poorer solvent for PEO as compared to aqueous NaCl and KCl.

Similarly the association constant (K_a) of polymer in different solvent system has also been determined by the following equation,

$$K_a = \alpha_a / ((1 - \alpha_a)^2 C)$$

Which was obtained by considering the system at simple dynamic equilibrium. K_a obtained in this way is plotted versus concentration in Fig-6. The results show the same trend as in case of degree of association and the difference in association constant of PEO in difference solvent systems can also be explained in term of complex formation of alkali metals ions with polymer in solution. The phenomenon of degree of association/complexation of polyelectrolytes in different solvent system is further
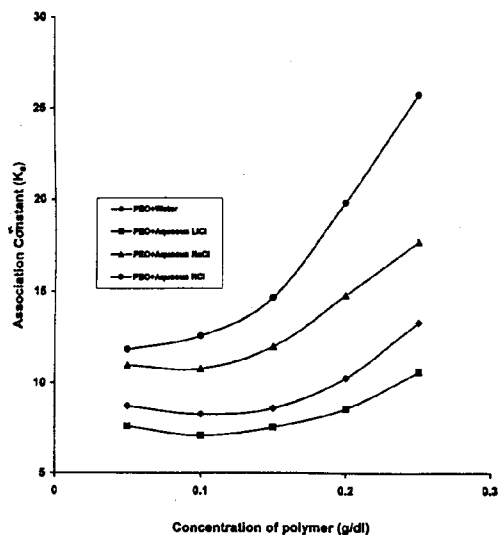
Fig. 6: Dependence of association constant of poly (ethylene oxide), dissolved in different solvent systems, on its concentration.

confirmed by CMC data, obtained by surface tension and light scattering measurements.

The CMC obtained for PEO in difference solvent system is in the following order.

Water < Aqueous. LiCl < Aqueous: NaCl < Aqueous: KCl

The order of CMC support the conclusion already drawn by us that is aqueous KCl is better solvent than the all used. Similarly the results obtained by the light scattering (R_θ) measurement also show a similar trend. From these observations, we conclude that aqueous KCl proved to be a good solvent as compared to other solvents investigated by us.

Experimental

Material

Poly (ethylene oxide) used, during this investigation, was having mass average molecular weight 100,000 g/mole and provided by Riedal-be-Hanhn CO. Solvent used for the purpose was de-ionized water. The electrolytes used to observe their effect on intrinsic viscosity, conductivity, cmc (critical micelles concentration) and light scattering parameter, R_θ, were lithium chloride, sodium chloride and potassium chloride. These chemicals were

supplied by E.Merck, Germany, all were of analytical purity grade and used as such.

Sample Preparation

The polymer concentration used for viscosity and conductance measurement was in the range of 0.05-0.25 g/dl, whereas for surface tension and light scattering measurement the concentration range selected was very dilute. To get a solution of required polymer concentration, a higher amount of polymer than required was first dissolved in water and then the required concentration was obtained through dilution method. The polymer solutions were filtered through Millipore filter paper before use to reduce the impurities which may present in the form of gels etc. To observe the effect of addition of metallic ions, the solvent (deionized water) was replaced by 5×10^{-5} M aqueous solution of LiCl, NaCl and KCl. The concentration of electrolytes was kept constant throughout the measurement.

Viscometry

The viscosity of all polymer solutions was measured both in pure water and in different electrolyte solutions, while the temperature was varied from 20-55 ^{0}C. The viscometer used during the measurements was Ostwald-Fenske type. The measurements were made in a thermostat, manufactured by F.G Bode and Co-Laboratory equipment Hamburg, Germany through which the temperature was kept constant up to ± 0.01 ^{0}C

The intrinsic viscosity was obtained using both Huggins's and Kraemer's equation.

$$\eta_{sp}/C = [\eta] + K^- [\eta]^2 C \qquad \text{Huggins's equation}$$

$$\ln \eta_r/C = [\eta] + K^{--} [\eta]^2 C \qquad \text{Kraemer's equation}$$

Where [η], η_{sp}/C, ln η_r/C, K^- and K^- is the intrinsic viscosity, reduced viscosity, inherent viscosity, Huggins's constant and Kraemer's constant respectively.

Conductometry

The conductance of all the prepared solutions was measured at 30 ^{0}C and at one atmospheric pressure using conductometer, Model No.931611 type HI 8820 Hanna Instrument Co. having automatic temperature compensation arrangement. The instrument was first standardized and then the conductance

was measured. The specific conductance was then calculated by the following equation,

$$L_s = L \cdot l/a$$

Where,

L_s= specific conductance of solutions

L= observed conductance of solutions

l= distance between the electrodes

a= area of cross section of electrodes.

For a given cell both l and a are constant, hence the ratio l/a is known as cell constant and is represented by K. Hence the equation becomes

$$L_s = L \cdot K$$

Then from specific conductance the equivalent conductance was calculated.

Surface Tension Measurement

The surface tension of the polymer solution made in water as well as in aqueous electrolytes solution was measured, at 25 °C using Landa digital tensiometer. From these data the critical micelles concentration of polymer was determined.

Light Scattering Measurements

Light scattering measurements were made using Brice Phoenix light scattering photometer. The measurements were made at temperature 25°C.

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