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***Solutions of Neutralized Poly-(acrylic acid) in Mixtures
Water-Ethanol***

It is well known that generally polyelectrolytes dissolve better when charged than in the uncharged state. The best known example for this is the minimum of the solubility of many proteins at the isoelectric point. The opposite was observed in solutions of poly-(acrylic acid) (PAA) in water-ethanol mixtures and is reported herewith.

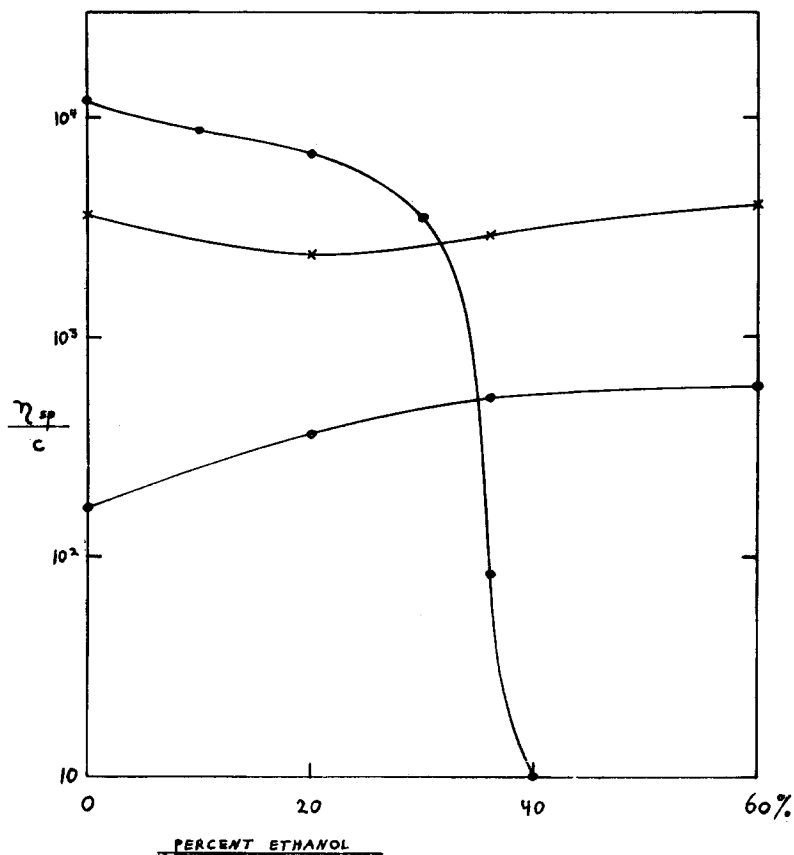


Fig. 1. The reduced specific viscosity of poly-(acrylic acid) ($c = 5.7 \times 10^{-4}$ g./cc.) in Water-ethanol mixtures (volume percentage) at 30°C.: O in 0.2N hydrochloric acid; X with no addend; ● fully neutralized with sodium hydroxide.

The reduced specific viscosity of PAA at various water-ethanol mixtures, up to 60% ethanol, was measured (a) in the unionized state (addition of 0.2*N* hydrochloric acid); (b) in the state of self ionization and (c) in the fully neutralized state (by sodium hydroxide). The measurements were carried out at 30.0°C. in an Ostwald-Fenske viscometer in which the time of flow of water at 30° is about 300 sec. The results are summarized in Figure 1.

In the unionized state PAA is soluble in all water-ethanol mixtures as observed previously.¹ The fact that the addition of hydrochloric acid decreases the reduced specific viscosity indicates that without an addend the PAA molecule is partially ionized in all water-ethanol mixtures and hence more expanded than in the presence of hydrochloric acid. The still higher reduced specific viscosity of the fully neutralized molecule indicates an even more expanded coil (below 36% ethanol) as expected. Surprisingly the reduced specific viscosity of the neutralized form in mixtures that contain 36% ethanol or more, is less than even that of the uncharged molecule. At 40% or more the reduced specific viscosity is practically zero. Besides, these solutions are definitely turbid. This turbidity disappears upon addition of acid and reappears upon addition of alkali. In other words, *fully ionized PAA is insoluble in 40% ethanol, whereas unionized PAA is soluble.*

It was also observed that fully neutralized PAA is precipitated from water by acetone and by methyl alcohol, and that these precipitates, too, dissolve on acidification. Polymethacrylic acid, when fully neutralized, is also precipitated from water by ethanol (about 50%) and redissolved by acid. It is remarkable that the effect of acetone, ethanol, and methanol on the fully ionized polyacids is the same as on the respective polyamides,^{1,2} whereas the effect on the unionized polyacids is quite different. (The charged polyacids as well as the polyamides are precipitated by those addends, the uncharged polyacids dissolve better at a high percentage of ethanol.) The fully neutralized PAA in 40% ethanol dissolved on heating and reprecipitates when the solution is allowed to cool to room temperature.

The behavior of PAA in 36% ethanol is similar to that of Poly-(aspartic acid) in water-dioxane mixtures³ in which the intrinsic viscosity is reduced upon increase of pH. This decrease has been explained by a transition of the molecule from helical form to random coil. This explanation cannot be applied to PAA. Fuoss and Strauss⁴ found that poly-(vinyl pyridine) in 91% ethanol has a higher intrinsic viscosity than poly-(vinyl pyridonium bromide) and ascribed this to increase triplet formation between two pyridonium groups and one bromide ion with decreasing dielectric constant. It is quite reasonable that the same applies to PAA solutions so that the following tentative explanation may be offered: With increasing percentage of ethanol the diminishing of the dielectric constant enhances the formation of the dielectric constant enhances the formation of ion triplets consisting of two carboxylic groups and one sodium ion. Because of the stiffness of the fully neutralized polyacid the triplets involve carboxyl groups of different molecules so that insoluble aggregates are formed. The uncharged and the partially charged molecule is flexible enough to satisfy any bonding internally and no aggregates are formed.

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