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The Effect of Urea on the Viscosity of Polymer Aqueous Solutions

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The effect of urea on the behavior of such hydrocolloids as proteins, synthetic polymers, and micelles of amphiphilic compounds in the water phase has been studied by several investigators. We will here report our experimental results on the change in the viscosity of the aqueous solutions of polyvinylpyrrolidone and sodium polystyrenesulfonate upon the addition of urea.

Experimental

Two kinds of polyvinylpyrrolidone (PVP), K-30 and K-90, with molecular weights of 4×10^4 and 9×10^5 respectively, were purchased from the Tokyo Kasei Kogyo Co. Sodium polystyrenesulfonate (NaPSS) was prepared by the neutralization of polystyrenesulfonic acid with a sodium hydroxide solution. Polystyrenesulfonic acid was prepared by the sulfonation of polystyrene (molecular weight 2.0×10^5) with concentrated sulfuric acid in the presence of silver sulfate, and it was purified by successive dialysis.¹⁾ The degree of sulfonation was found to be 0.73. The urea was a reagent-grade product of the Koso Chemical Co. The 1,3-dimethylurea was an E. P.-grade product of the Tokyo Kasei Kogyo Co.; it was recrystallized from a chloroform-ether mixture.

The viscosity measurements were carried out with Ostwald viscometers with an outflow time for water of about 90 sec and with a total volume of 5 ml in a water bath at $25 \pm 0.02^\circ\text{C}$.

Results and Discussion

It was found that the change in the reduced viscosities of PVP upon the addition of urea and

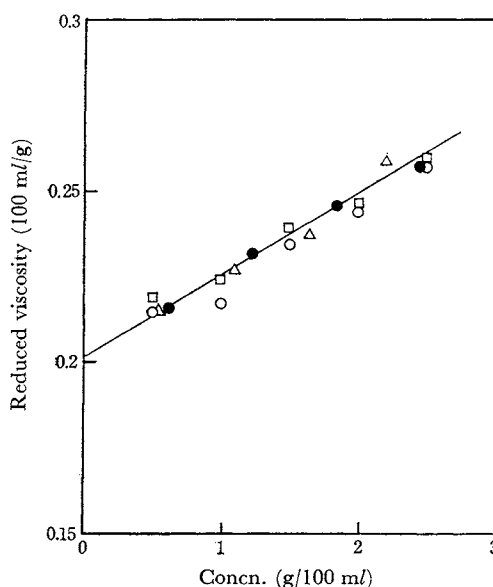


Fig. 1. Reduced viscosity of PVP, K-30, as a function of concentration in g per 100 ml; ● in water, ○ in 2M urea, □ in 4M urea, △ in 6M urea.

1,3-dimethylurea was very small, as is indicated in Figs. 1 and 2. Jirgenson²⁾ has reported that the reduced viscosities of PVP were reduced by the addition of urea and guanidine hydrochloride, whereas Klotz and Russell³⁾ have shown that urea had very little effect on the reduced viscosities of

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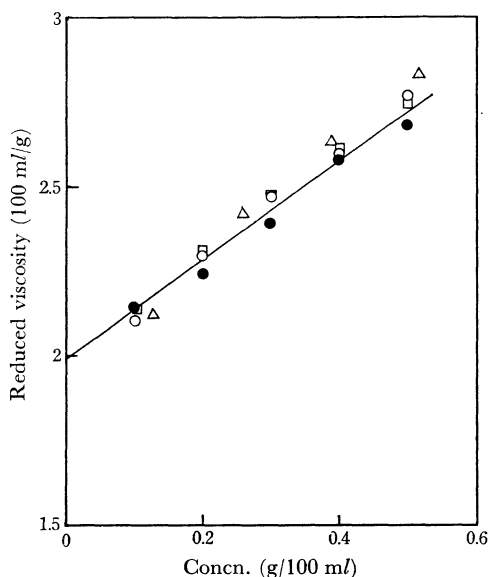


Fig. 2. Reduced viscosity of PVP, K-90, as a function of concentration in g per 100 ml; ● in water, ○ in 2M urea, □ in 2M 1,3-dimethylurea, △ in 4M urea.

PVP. Our results are in agreement with those of Klotz and Russell.³⁾

Several different results regarding the change in the viscosity of other water-soluble polymers upon the addition of urea have been reported. Urea did not affect the reduced viscosities of polyacrylamide;⁴⁾ this behavior is similar to that of PVP discussed in this paper. Urea addition increased the reduced viscosities of polyvinyl-alcohol,⁵⁻⁷⁾ polyethylene glycol,⁸⁾ and un-ionized polyacrylic acid in hydrochloric acid.⁴⁾ Urea addition decreased the reduced viscosities of un-ionized polymethacrylic acid in hydrochloric acid.⁴⁾

Urea, a well-known protein denaturant, is believed to behave as a structure breaker of water,⁹⁻¹¹⁾

although a contrary opinion has also been reported.¹²⁾ Klotz¹³⁾ proposed the idea that the modification of water structure by the addition of urea can change the conformation and behavior of macromolecules, markedly different even in their primary structure, in a similar way. However, the experimental results reported in this paper as well as in the literature suggest the existence of some kinds of specificity¹⁴⁾ in the interaction of polymers with urea.

The reduced viscosities of NaPSS were greatly diminished by the addition of urea, as is shown in Fig. 3. NaPSS belongs to a strongly-ionized polyelectrolyte. The depression of ionization seems to be improbable, because the dielectric constant of aqueous urea solutions is slightly higher than that of pure water. Iso¹⁵⁾ obtained results showing a decrease in the reduced viscosities of sodium polyacrylate in the presence of urea. The decrease in the viscosity of strongly-ionized polyelectrolytes by the addition of urea seems to be a common feature, although the mechanism is still unknown.

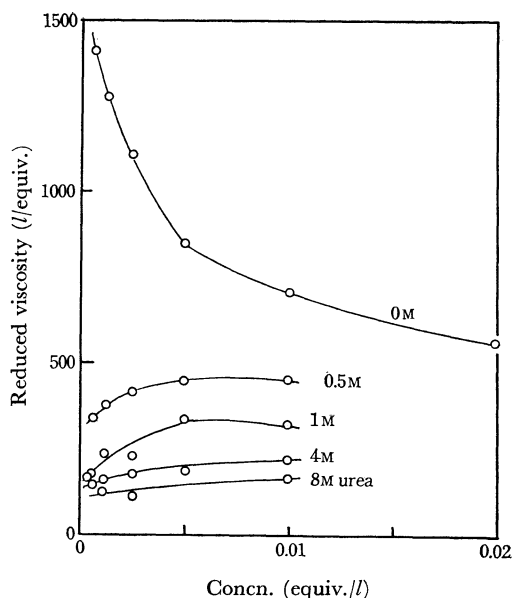


Fig. 3. Reduced viscosity of NaPSS as a function of concentration in equiv. per liter.

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