Decrease in Intrinsic Viscosity of Polyvinylpyrrolidone in the Presence of Sodium Chondroitin Sulfate or Sodium Carboxymethylcellulose in an Aqueous Solution

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Intrinsic viscosity and cloud point of an aqueous solution of polyvinylpyrrolidone (PVP) were measured as a function of the concentration of another added polymer, sodium carboxymethylcellulose (NaCMC) or sodium chondroitin sulfate (Na_2Chs). The intrinsic viscosity of PVP decreased with increase in the concentration of NaCMC or Na_2Chs owing to the volume effect of the polymer coils. The intrinsic viscosity of NaCMC or Na_2Chs decreased more remarkably in the presence of PVP K-90 (M.W. = 1.19×10^6) than in the presence of PVP K-30 (M.W. = 4.20×10^4) because the volume effect of polymer coils of PVP K-90 was stronger than that in the case of PVP K-30. The cloud point of an aqueous solution of PVP decreased with increase in the concentration of another added polymer (Na_2Chs or NaCMC) and inorganic salt (Na_2CO_3) because the polymer coils of PVP shrank and the affinity of PVP for water decreased with increase in the concentrations of these additives.

Keywords polyvinylpyrrolidone; sodium chondroitin sulfate; sodium carboxymethylcellulose; intrinsic viscosity; cloud point; incompatibility

Incompatibility between polymers has been observed when two or more polymers, such as dextran–polyvinylpyrrolidone,[2)] gelatin–polyvinylpyrrolidone,[3)] gelatin–acacia,[4)] gelatin–acacia–polyethylene glycol,[4)] or gelatin–sodium carboxymethylcellulose,[5)] are dissolved in water. In these aqueous solutions, the turbidity increases and phase separation proceeds, resulting in coacervate formation.

On the other hand, a block copolymer composed of hydrophobic and hydrophilic segments forms hydrophobic and hydrophilic microdomains (*i.e.*, microphase separation) through intra- and intermolecular interaction in the water phase. It has been reported, for example, that block copolymers such as poly(ethylene oxide–propylene oxide) and poly(*N*-vinylpyrrolidone–styrene) form micelles by aggregation of the hydrophobic segments, and that these copolymers solubilize the aromatic benzene more selectively than the aliphatic hexane into the micelle core from a mixture of solubilizates.[6)]

In contrast with the phase separation quoted above, certain polymers form intermolecular complexes in the water phase. Polycations bind polyanions through the electrostatic attractive force, resulting in the formation of a polyelectrolyte complex. Glycol chitosan and polyvinyl sulfate form such a water-insoluble complex in the presence or absence of [2-(dimethylamino)ethyl] dextran hydrochloride.[7)] On the other hand, polyacrylic acid and polyoxyethylene form a water-soluble complex by virtue of the hydrogen bonding between sequences of carboxylic groups of the polyacid and polyether sequences.[8)] Recently physicochemical studies on polymer–polymer interaction have become important to understand the miscibility of polymers, the competitive and/or preferential adsorption of polymers on the suspended particles,[9)] and the affinity of biopolymers for the surface of synthetic biomedical materials.[10,11)]

In the present paper, solution properties of a mixture of polyvinylpyrrolidone (PVP) and sodium chondroitin sulfate (Na_2Chs) or sodium carboxymethylcellulose (NaCMC) are discussed on the basis of the intrinsic viscosity of the polymers and the cloud point of the solution. These polymers are typical dispersing agents for pharmaceutical and industrial suspensions.[12)] It is, therefore, important to characterize the aqueous solution of a mixture of these polymers to provide a basis for the understanding of competitive adsorption and dispersing/flocculating effects.

Experimental

Materials PVP K-90 and PVP K-30 were purchased from Nakarai Chemicals, Ltd. These samples were dialyzed in Visking cellulose tubing against distilled water to remove low-molecular impurities. The viscosity-average molecular weight, M, of PVP, thus prepared, was determined as 119×10^4 for PVP K-90 and 4.20×10^4 for PVP K-30 from the intrinsic viscosity, $[\eta]$, at 30°C in distilled water by means of the following equation,[13)]

$$[\eta] = 3.93 \times 10^{-4} M^{0.59} \qquad (1)$$

Na_2Chs was of the C-type, *i.e.*, sodium chondroitin-6-sulfate, kindly provided by Kaken Yakukako Co., Ltd. NaCMC was purchased from Wako Pure Chemical Industries, Ltd. The viscosity-average molecular weight, M, of Na_2Chs was estimated as 5.66×10^4 from the intrinsic viscosity in 0.15 M phosphate buffer (pH 7.0) containing 0.2 M NaCl at 25 °C by means of the equation,[14)]

$$[\eta] = 3.1 \times 10^{-4} M^{0.79} \qquad (2)$$

That of NaCMC was determined as 14.1×10^4 from the intrinsic viscosity in 0.01 M NaCl at 25 °C, according to the equation,[15)]

$$[\eta] = 6.46 \times 10^{-6} M^{1.20} \qquad (3)$$

The pH of the solution of each polymer at 1 g/dl (30 °C) was in the range of 6.0—6.5.

Methods The measurement of the solution viscosity was made by a Ubbelohde-type viscometer at 30 °C. The intrinsic viscosity, $[\eta]$, of a polymer (A) in an aqueous solution of another polymer (B) was obtained by the extrapolation of the reduced viscosity to infinite dilution with an aqueous solution of a constant concentration of the polymer (B), regarding an aqueous solution of the polymer (B) as a solvent for the polymer (A). The combinations of the polymers (A) and (B) were PVP–Na_2Chs, PVP–NaCMC, Na_2Chs–PVP, and NaCMC–PVP in the present paper.

Cloud point of the solution was measured as follows. Sample solution (10 ml), containing PVP K-90, sodium carbonate, and Na_2Chs (or NaCMC) in a test tube, was heated or cooled gradually at a rate of 1 °C/min with gentle stirring in a water bath. The clear solution became turbid and separated into two phases above a certain temperature when it was heated, while the turbid solution became clear and transparent again below a certain temperature when it was cooled. Both temperatures coincided with each other within the range of experimental error (less than ±1 °C). The average of the above two temperatures was regarded as the cloud point of the system.[16)]

Results and Discussion

Intrinsic viscosity, $[\eta]$, of PVP K-90 and PVP K-30 is shown in Fig. 1 as a function of the concentration of Na_2Chs or NaCMC. The decrease in $[\eta]$ was more conspicuous in the presence of NaCMC than in the presence of Na_2Chs. Intrinsic viscosity of Na_2Chs and NaCMC is shown in Fig. 2 as a function of the concentration of added PVP K-90 or PVP K-30. The figure shows that the decrease was more remarkable in the presence of PVP K-90 than in the presence of PVP K-30 when compared at a given weight concentration of PVP.

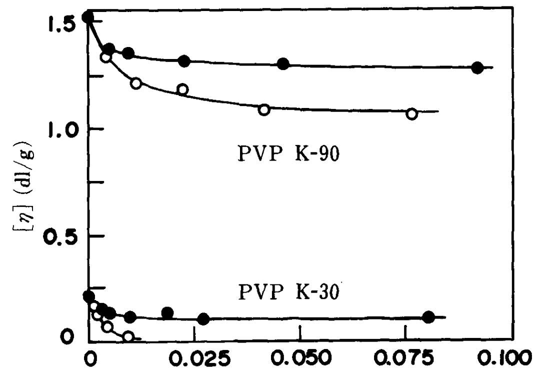

Fig. 1. Decrease in Intrinsic Viscosity of PVP in the Presence of Na_2Chs or NaCMC

●, Na_2Chs; ○, NaCMC.

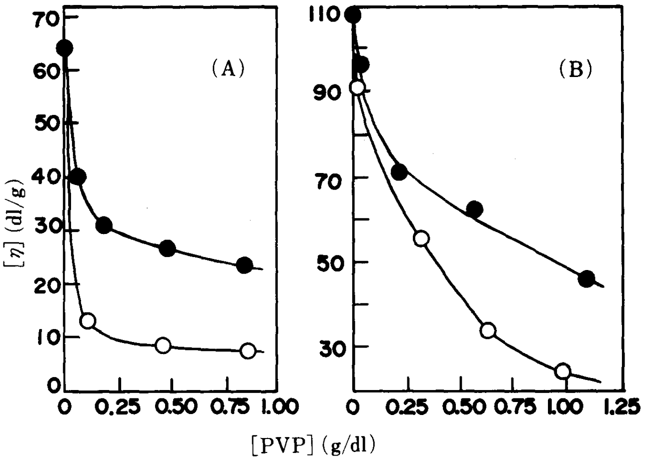

Fig. 2. Decrease in Intrinsic Viscosity in the Presence of PVP

(A): intrinsic viscosity of Na_2Chs *vs.* [PVP]. (B): intrinsic viscosity of NaCMC *vs.* [PVP]. ●, PVP K-30; ○, PVP K-90.

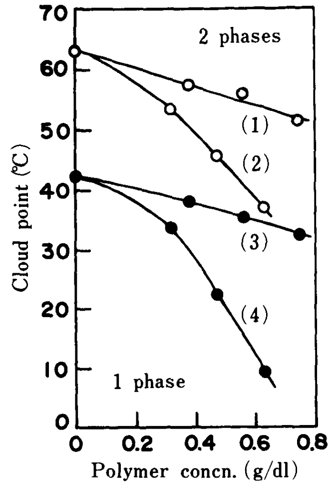

Fig. 3. Cloud Point of an Aqueous Solution of a Mixture of PVP–Na_2CO_3–Na_2Chs or NaCMC

○, $[Na_2CO_3]=0.360$ M, [PVP K-90]$=0.754$ g/dl; ●, $[Na_2CO_3]=0.450$ M, [PVP K-90]$=0.565$ g/dl; curves (1) and (3): cloud point *vs.* $[Na_2Chs]$; curves (2) and (4): cloud point *vs.* [NaCMC]. Above the cloud point the solution separates into two phases, while below the cloud point the solution is transparent and monophasic.

The cloud point of an aqueous solution of a mixture of PVP K-90, another polymer (NaCMC or Na_2Chs), and Na_2CO_3 was measured at various concentrations of NaCMC or Na_2Chs, where the concentration of PVP K-90 and Na_2CO_3 were kept constant. Typical results are shown in Fig. 3. The effect of NaCMC was stronger than that of Na_2Chs.

The size of the polymer coil, *i.e.*, $[\eta]$, became smaller in the presence of another polymer (Figs. 1 and 2) owing to the fact that the latter polymer occupies space into which the former polymer could have expanded. As the result of the coil shrinking and the concomitant dehydration of the polymer chain of PVP,[16] the cloud point of an aqueous solution of a mixture of PVP and Na_2CO_3 decreased with increase in the concentration of the other polymer, NaCMC or Na_2Chs. However, an aqueous solution of Na_2Chs or NaCMC did not separate into two phases even in the presence of Na_2CO_3 in the range of temperature examined because these polymers are more hydrophilic than PVP.

According to Fig. 2, the effect of PVP on the intrinsic viscosities of NaCMC and Na_2Chs is more remarkable in PVP K-90 than in PVP K-30. This effect can be explained in terms of the volume effect of polymer coils of PVP, because the polymer coils of PVP K-90 occupy more space than those of PVP K-30 when compared at the same weight concentration.[17] The difference in the effects of Na_2Chs and NaCMC on the intrinsic viscosity and the cloud point of PVP (Figs. 1 and 3) might be also explained mainly in terms of the volume effect of the polymer coils in a similar manner to that mentioned above, because the molecular weight and the intrinsic viscosity of NaCMC are bigger than those of Na_2Chs.

References and Notes

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