Lyotropic Liquid Crystalline Solutions of Hydroxypropyl Cellulose in Water: Effect of Salts on the Turbidity and Viscometric Behavior

SHINICHI SUTO, WATARU NISHIBORI, KAZUHISA KUDO,
and MIKIO KARASAWA, *Department of Polymer Chemistry,
Faculty of Engineering, Yamagata University, Jonan 4-3-16,
Yonezawa, Yamagata, 992, Japan*

Synopsis

Effect of addition of salt on the viscometric behavior of the dilute or concentrated aqueous solution of hydroxypropyl cellulose (HPC) was determined by means of an Ubbelohde or a cone-plate viscometer. That effect on the turbidity of the dilute system was also determined. As salts, NaCl, LiCl, and thiourea were chosen. The turbidity and viscometric behavior for the dilute system, and the viscometric behavior for the concentrated system were greatly affected by salt type and concentration. With increasing NaCl or LiCl concentration, the cloud point decreased, $[\eta]$ showed a maximum, Huggins' constant k' showed a minimum, and the shear viscosity for concentrated isotropic solutions showed a maximum. The 45 wt % solution with no salt showed a viscometric behavior which was characteristic of lyotropic liquid crystals; however, with increasing NaCl concentration, a critical temperature at which the shear viscosity showed a maximum with respect to temperature shifted to lower temperature. This behavior was due to an increase in the turbidity, not due to a phase transformation. On the other hand, an addition of thiourea did not affect so greatly the turbidity and viscometric behavior as an addition of NaCl or LiCl did. We speculated different actions of NaCl and thiourea.

INTRODUCTION

The research reported on this paper forms part of an ongoing study of the rheological properties of cellulosic liquid crystals.[1-6] Hydroxypropyl cellulose (HPC) forms a lyotropic liquid crystal in a great many solvents.[7] The viscometric behavior of liquid crystalline solutions of HPC in water was different from that of HPC in organic solvents.[2] This was because, as temperature decreased, the phase transformation from isotropic to anisotropic phases occurred in common organic solvents, whereas in water the phase transformation from isotropic to gel phases or white suspension did.[8-10] The HPC/water system is a typical one which has a lower critical solution temperature (LCST)[11-13] and above ca. 40°C HPC solutions become turbid and exhibit precipitation in the entire range of concentration.[12] Therefore, it is expected that the interaction between HPC–HPC or HPC–water (for example, hydrogen bonding) plays an important role in the phase transformation for the HPC/water system. That interaction may be controlled by addition of salts and be dependent on the type of salts.

Journal of Applied Polymer Science, Vol. 37, 737–749 (1989)

CCC 0021-8995/89/030737-13$04.00

In this paper, the temperature dependence of the shear viscosity for the concentrated aqueous salt solutions of HPC was determined by means of cone-plate type viscometer at a constant shear rate of 1 s^{-1}, and the effect of salts on the viscometric behavior was investigated. The viscometric and turbid behavior of the dilute system was also determined. We used NaCl, LiCl, and thiourea as salt.

EXPERIMENTAL

Samples

Commercial reagent grade hydroxypropyl cellulose (HPC, Tokyo Kasei Kogyo, Ltd.) was the same as one used in our previous investigations. [2-5] The weight-average molecular weight $\overline{M}_w$ determined by GPC in THF was 11.7×10^4 and the ratio $\overline{M}_w/\overline{M}_n$ was 2.11. The molar substitution of HPC was 4.25 which was determined from NMR.[14] HPC powder was dried *in vacuo* at 60°C for about 24 h. NaCl, LiCl (Kanto Chemical Ltd.), and thiourea (Wako Pure Chemical Ind., Ltd.) were commercial reagent grade and were used without any purification. Distilled deionized water (hereafter water) prepared in our laboratory was used.

Preparation of Dilute Solutions

HPC was so hygroscopic,[15] and the following precaution was taken to reduce the possible effect of adsorbed water on the dilute solution properties. The previously dried HPC in a glass flasco (the weight has been known) was roughly weighted and then HPC in the flasco was again vacuum-dried at 60°C for 24 h. After drying, the flasco was stoppered as soon as possible, the flasco containing HPC was accurately weighted again, and the net weight of dried HPC could be determined. After a given amount of water containing salt was added to the flasco. The sample solution was stored in the dark for 24 h for swelling HPC. Then, the solution (ca. 0.5 g/dL) was stirred for 12 h to ensure homogeneity. The other concentrations of the solutions were prepared by dilution of the mother solution (ca. 0.5 g/dL) in a volumetric flasco. The concentration range of salts is 0–15 g/dL for NaCl, 0–5 g/dL for LiCl, and 0–10 g/dL for thiourea.

Preparation of Concentrated Solutions

Procedure and precaution were the same as those for the dilute solutions except for storing in a refrigerator (ca. 7°C) for about 2 months. HPC concentration range was 35–50 wt %. Salt concentration range was the same as that for the dilute solutions.

Turbidimetry

A double-beam spectrophotometer UV-200S (Shimazu Seisakusho Ltd.) was used for the measurements of the cloud point T_c of the dilute solutions. The sample solution at given concentrations in a cell was heated slowly (< 0.5°C/min) by circulating water through a cell holder. A thermometer was used to measure the temperature of the circulating water to within ± 0.1°C. A decrease in transmittance at a 500 nm wavelength was used to determine the onset of precipitation. The critical temperature was taken as T_c, at which the precipitation was first observed. This precipitation process was reversible with temperature; however, two slightly different critical temperatures were observed depending on whether the solution was heated or cooled. In this study, T_c on heating was taken.

Viscometry

Dilute Solution

Viscosity measurements were carried out at 35 ± 0.02°C with a Ubbelohde dilution viscometer. The flow time for each concentration was averaged from five to six measurements of which reproducibility was better than 0.2%. The kinetic energy correction was ignored because the flow time for the water/salt was greater than 100 s. The intrinsic viscosity $[\eta]$ and Huggins' constant k' were determined graphically using the Huggins' equation.

Concentrated Solution

A cone-plate type viscometer was used to measure the shear viscosity at shear rate of 1 s^{-1} and at given temperatures. The details of the measurement have been described elsewhere.[2,4] It must be emphasized that the solution is allowed to rest at least 45 min before starting measurements at a given temperature.

RESULTS AND DISCUSSION

Dilute Aqueous Salt Solutions of HPC

Figure 1 shows the cloud point T_c of HPC solution without salts as a function of HPC concentration. T_c decreased with HPC concentration. This behavior was similar to that reported by Tagawa et al.[13] Above the higher concentration range than our experimental one, T_c seemed by visual appearance to decrease gradually with HPC concentration and become to be around 40°C in the concentration region that has been reported by Uematsu et al.[8] and Werbowyj and Gray.[9]

Figure 2 shows the effect of a salt concentration on T_c at a HPC concentration of 1.0 g/dL. T_c for the solutions with NaCl and LiCl decreased with NaCl and LiCl concentration, whereas T_c for the solutions with thiourea behaved in the opposite manner: T_c slightly increased with thiourea concentration.

Figure 3 shows the intrinsic viscosity $[\eta]$ as a function of salt concentration. For NaCl and LiCl, $[\eta]$ (relative to pure water) first increased with increasing salt concentration, but then passed through maximum and decreased with further increase of salt concentration, whereas for thiourea $[\eta]$ decreased slightly with salt concentration. In our HPC concentration range, the solution with 0.5 g/dL NaCl became turbid, and $[\eta]$ could not be determined.

Figure 4 shows the dependence of Huggins' constant k' on salt concentration. k' for NaCl and LiCl exhibited a minimum with respect to salt concentration, whereas k' for thiourea slightly increased with salt concentration or

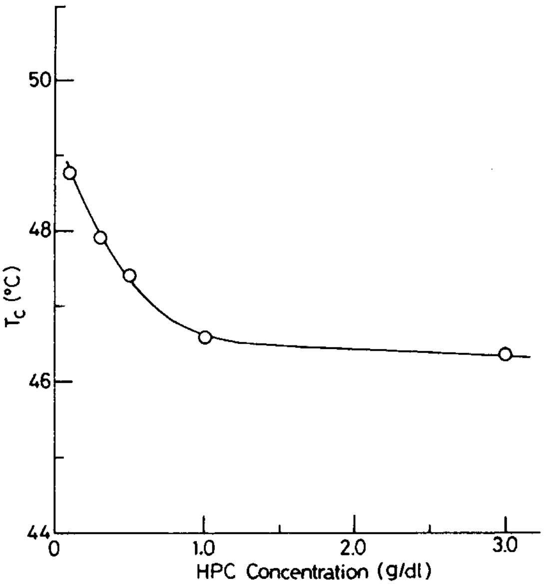


Fig. 1. Dependence of cloud point T_c on HPC concentration for HPC/water system.

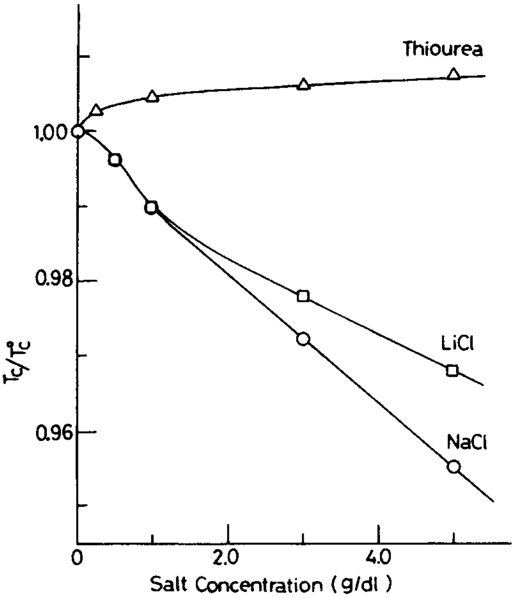


Fig. 2. Dependence of cloud point T_c on salt concentration for HPC/water/salt system; HPC concentration 1.0 g/dL. Salt: (○) NaCl; (△) thiourea; (□) LiCl. T_c^0 is T_c for HPC/water system: 46.5°C.

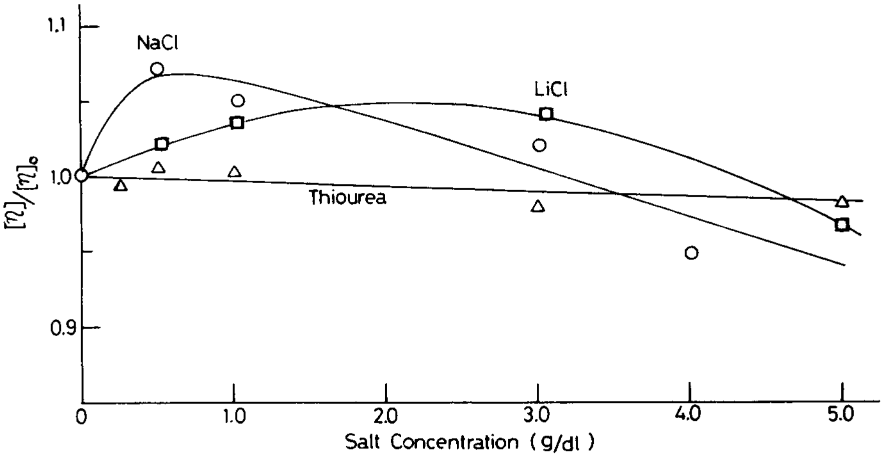


Fig. 3. Dependence of intrinsic viscosity $[\eta]$ on salt concentration for HPC/water/salt system at 35°C. Salt: (○) NaCl; (△) thiourea; (□) LiCl. $[\eta]_0$ is $[\eta]$ for HPC/water system: 0.7747 (dL/g).

was independent of salt concentration. Generally k' can be taken as a measure of the interaction between polymer molecules. Therefore, when a molecule extends or solvation occurs, k' decreases.[16]

Figures 2, 3, and 4 show that the role of NaCl or LiCl is quite different from that of thiourea. Some investigators[17-20] have been reported the effects of salt on T_c and $[\eta]$ of various nonionic polymers in aqueous media; NaCl and LiCl have been known as a water-structure maker and thiourea as a water-structure breaker. Here we speculate on the origin of the behavior shown in Figures 2, 3, and 4. Bergman and Sundelof[12] showed that water is a good solvent for HPC at 25° and θ-solvent at about 41°C. Therefore, at 35°C water is still a good solvent for HPC: then HPC molecules prefer to be surrounded by solvent molecules rather than its own molecules. HPC molecules are hydrated in water, and the hydrated HPC molecule is intrahydrogen bonded (interhydrogen bonding may also be possible, but not dominant in a good solvent). When

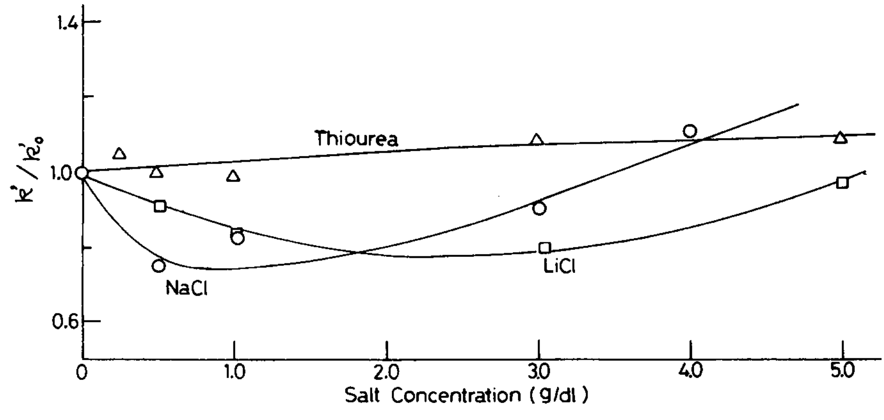


Fig. 4. Dependence of Huggings' constant k' on salt concentration for HPC/water/salt system at 35°C. Salt: (○) NaCl; (△) thiourea; (□) LiCl. k'_0 is k' for HPC/water system: 0.8038.

a very small amount of NaCl or LiCl is added to the solution, that salt acts as the water-structure maker: NaCl or LiCl induces the degree of water–water hydrogen bonding and relatively reduces the degree of water–HPC molecule hydrogen bonding. Therefore, with a small amount of NaCl or LiCl, HPC molecules become naked (less hydrated) in water and are somewhat extended because of breaking intrahydrogen bonding; however, HPC molecules are still wormlike.

The viscometric and turbid behavior qualitatively supports our speculation; the variation in $[\eta]$ implies that a hydrodynamic size of HPC molecules first increases and a decrease in k' also indicates the extention of HPC molecules. When the amount of NaCl or LiCl exceeds a critical one, the situations in solution are changed; association of wormlike chains tends to occur. Here we distinguish between the association and an aggregation as follows: The association is defined as a reversible process and leads to an equilibrium state, whereas the aggregation is done as an irreversible process and leads to a metastable state.[21] That association, for example, interhydrogen bonding, is side-by-side type; therefore, the apparent aspect ratio of HPC molecules decreases and the decrease in $[\eta]$ results. The remarkable decrease in T_c supports the association of HPC molecules. Consequently, we speculate, the addition of or LiCl has a two-step effect: First, HPC molecules are extended; next, HPC molecules are associated.

On the other hand, when thiourea is added to the aqueous solutions of HPC, thiourea, which acts as the water-structure breaker, reduces, the degree of water–water hydrogen bonding. Therefore, no conformational change of HPC molecules in water occurs, just water-structure surrounding HPC molecules changes and the hydration of HPC molecules may be induced somewhat. Guven and Elton[22] suggested that thiourea breaks the hydrogen bonding between poly(vinyl pyrrolidone) (PVP) molecules in water. The action of thiourea for HPC/water system seems to be different from that for PVP/water system.[22]

Viscometric Behavior for Concentrated Aqueous Salt Solutions of HPC

NaCl System

Figures 5(a), (b), and (c) show the shear viscosity as a function of temperature at given salt concentrations for the 35, 45, and 50 wt % solutions, respectively. For the 35 wt % solution the shear viscosity decreased monotonically with temperature, and this was general behavior for isotropic solutions. The behavior for the solutions with 0.5 and 1.0 g/dL NaCl followed a similar trend to that for the solution with no salt; however, over the salt concentration of 3.0 g/dL, the temperature dependence of the viscosity was changed. The shear viscosity for the 45 wt % solutions showed a maximum and/or a minimum at critical temperatures T_{max} and T_{min}, respectively. The viscosity for the nonsalt solutions shown in Figures 5(b) and (c) was typical of lyotropic liquid crystalline solutions and was associated with the phase transformation,[8-10] not with the precipitation because T_c for the concentrated

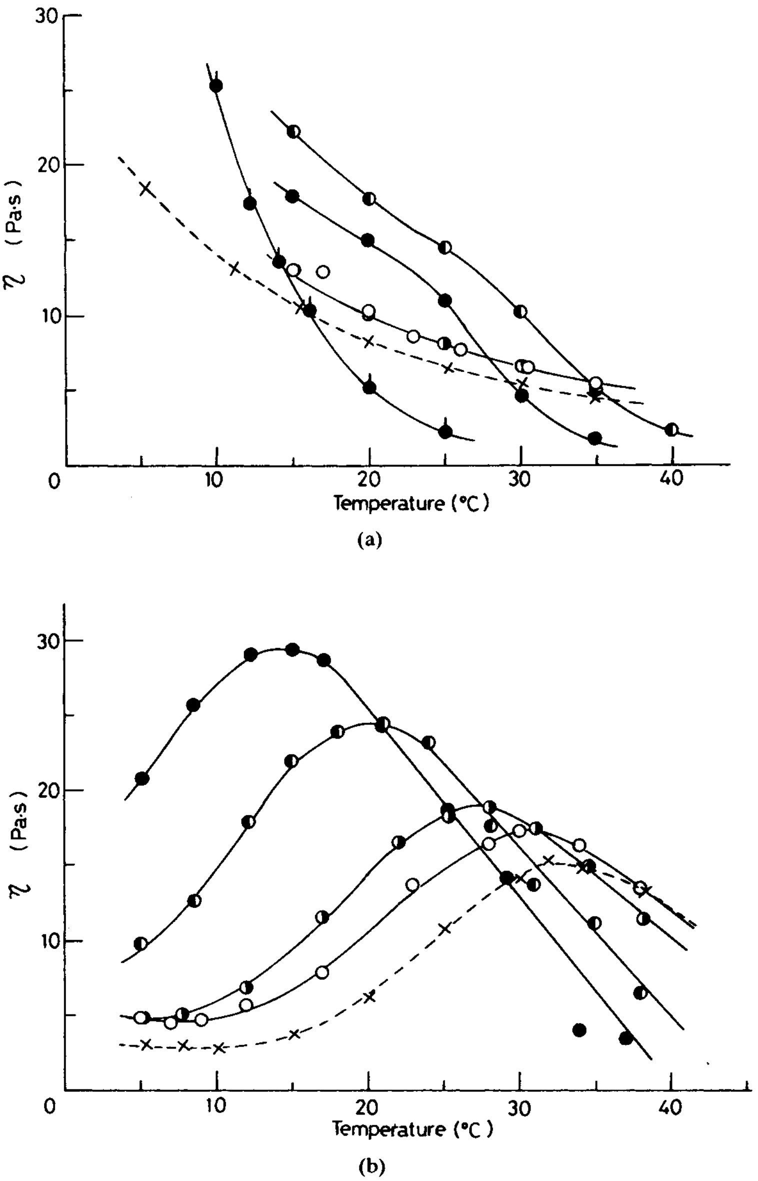


Fig. 5. Dependence of shear viscosity on temperature for HPC/water/NaCl system at given NaCl concentrations. (a) HPC concentration 35 wt %; NaCl concentration: (×) 0; (○) 0.5; (◑) 1.0; (◐) 3.0; (●) 5.0; (♦) 10.0 g/dL. (b) HPC concentration 45 wt %; NaCl concentration (g/dL): (×) 0; (○) 0.5; (◑) 1.0; (◐) 3.0; (●) 5.0; (♦) 10.0 (c) HPC concentration 50 wt %; NaCl concentration (g/dL): (×) 0; (○) 0.5; (◑) 1.0.

HPC/water system was ca. 38°C by visual observation. Our findings clearly showed that there existed a biphasic region for given concentrations. This was consistent with the phase diagram reported by Uematsu et al.,[8] but was not with that reported by Werbowyj and Gray[9] and Navard et al.[10] who have not shown the biphasic region. This difference between us and them may be due

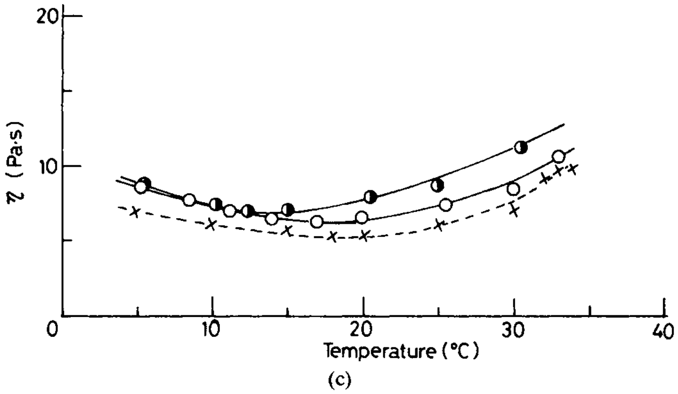


Fig. 5. (*Continued from the previous page.*)

to the different manner to investigate the phase diagram of HPC/water system.

The most striking feature of Figure 5 was that T_{max} decreased with NaCl concentration for the 45 wt % solution. The shift in T_{max} to lower temperature with salt concentration resembles that with decreasing HPC concentration previously reported by us.[2, 4] However, the origin of those behavior was quite different; for the salt concentration dependence, the viscosity maximum contributed to an increase in turbidity or gelation (salting-out effect), whereas for the HPC concentration dependence, the viscosity maximum was done to the phase transformation from biphasic to isotropic phases. The qualitative evidence for the salting-out effect noted above was that: although the 45 wt % solution with 5 g/dL NaCl was just slightly turbid in a refrigerator (ca. 7°C), the turbidity of the same solution increased at room temperature; even in the refrigerator, the 45 wt % solution with 10 g/dL NaCl was obviously turbid and the 45 wt % solution with 15 g/dL NaCl looked like white gum. Furthermore, Klug[11] has already reported the viscometric behavior of HPC/water system with respect to temperature: the introduction of small amount of ionic substitution into HPC at suitable pH results in the behavior similar to that shown in Figure 5, due to gelation. In this way, the effect of NaCl on the viscometric behavior of liquid crystalline solutions could be explained on the basis of the salting-out effect. The effect of LiCl on the phase diagram of aqueous HPC solution was reported in a paper published during the preparation of this manuscript: The formation of gel becomes easier with LiCl.[23] The result also supports our speculation noted above. It is necessary to note that the viscosity method adopted by us may not be an ideal one for the construction of the phase diagram of HPC/water system.

The effect of the salt concentration on the shear viscosity was dependent on the HPC concentration. The shear viscosity at given HPC concentration is plotted against temperature at the salt concentration of 0.5 g/dL in Figure 6. At other salt concentrations (1.0 and 3.0 g/dL), the behavior was similar to that in Figure 6. The critical temperatures T_{max} and T_{min} increased with HPC concentration. This result was similar to that for the solutions with no salt. As we have noted above, the behavior at a higher temperature that about 30°C in Figure 6 was not general for the isotropic solutions. Compared with each curve

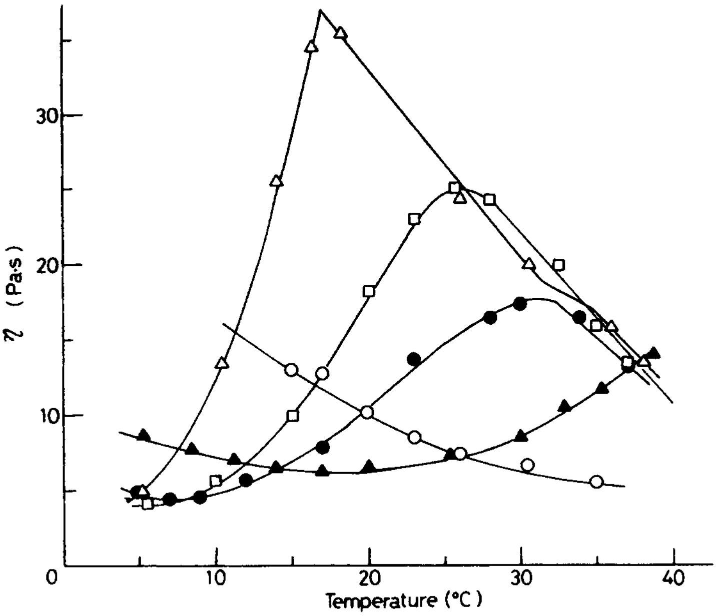


Fig. 6. Dependence of shear viscosity on temperature for HPC/water/NaCl system at given HPC concentrations. NaCl concentration 0.5 g/dL; HPC concentration (wt %): (○) 35; (△) 40; (□) 43; (●) 45; (▲) 50.

at a given temperature above each T_{max}, the viscosity for higher HPC concentration solution should be higher than that for relatively lower HPC concentration solution because at that temperature range the solutions are isotropic. However, above ca. 35°C the viscosity for the 45 wt % solution was not higher than those for the 40 and 43 wt % solutions. Therefore, it is apparent that each solution is not isotropic, but is suspension with gel or is turbid.

The shear viscosity is plotted as a function of the salt concentration at given temperatures in Figures 7(a) and (b) for the 35 and 45 wt % solutions, respectively. The shear viscosity for the 35 wt % solution exhibited a maximum with respect to salt concentration at every temperature. For the 45 wt % solution, the effect of salt concentration was dependent on temperature: At relatively lower temperatures the viscosity increased; however, at relatively higher temperatures, the viscosity showed a maximum, similar to the behavior of the 35 wt % solution.

As noted in the dilute solution section above, the dependence of the shear viscosity on the salt concentration can be correlated with the alteration in the degree of water–water hydrogen bonding: (1) For the isotropic solutions (at lower concentration than C_a or higher temperature than T_{max}) with an addition of NaCl, first HPC molecules extend somewhat due to decreasing intrahydrogen bonding, then the viscosity increases; with a further addition of NaCl, beyond a critical NaCl concentration (ca. 3.0 g/dL for the 35 wt % solution), the increase in the turbibity results in a decrease in the viscosity.[24] Consequently, the viscosity for the isotropic solutions shows a maximum with respect to NaCl concentration. (2) For the biphasic solutions, however, the

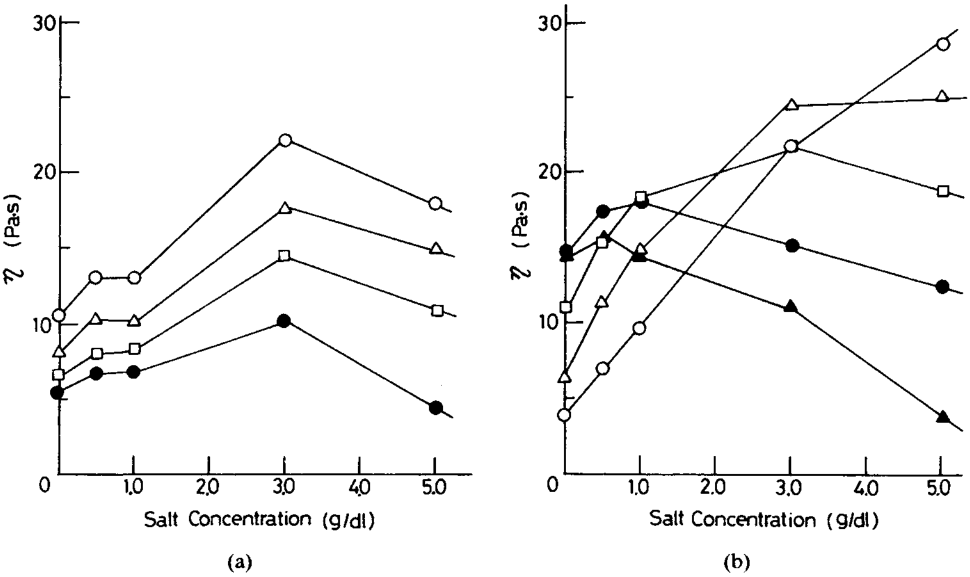


Fig. 7. Dependence of shear viscosity on NaCl concentration for HPC/water/NaCl system at given temperatures. (a) HPC concentration 35 wt %; temperature (°C): (○) 15; (△) 20; (□) 25; (●) 30. (b) HPC concentration 45 wt %; temperature (°C): (○) 15; (△) 20; (□) 25; (●) 30; (▲) 35.

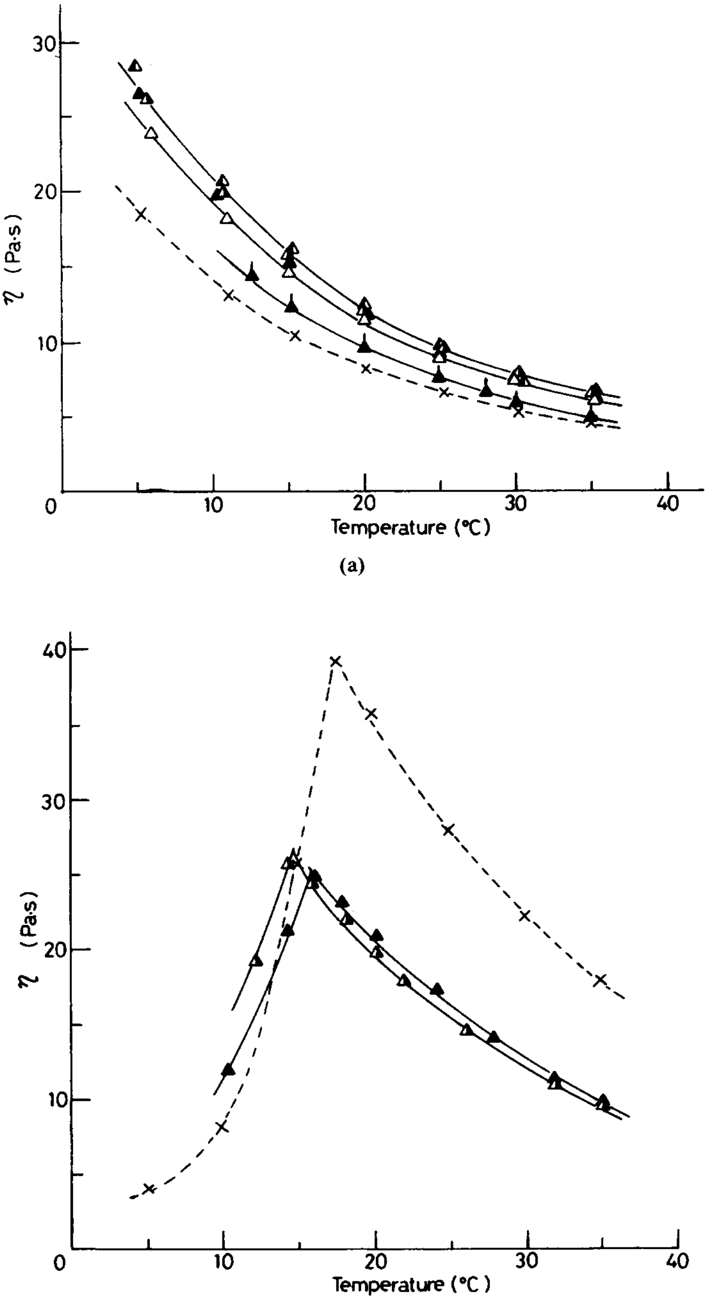
rate of isotropizaton in the anisotropic matrix increases with salt concentration, and a change of composition in the biphasic solution dominates the viscometric behavior rather than the conformational change in HPC molecules; then the viscosity increases with salt concentration.

In this paper, there were no data on the viscometric behavior of the concentrated solutions with LiCl. However, the viscometric behavior for that system seems to be similar to that for the system with NaCl.

Thiourea System

Figures 8(a), (b), and (c) show the temperature dependence of the shear viscosity at given salt concentrations for the 35, 40, and 45 wt % solutions, respectively. For the 35 wt % solution, the shear viscosity decreased with temperature, irrespective of whether the solution contained salt or not. For the 40 wt % solution, the viscosity exhibited a maximum. For the 45 wt % solution, the viscosity showed a minimum (ca. 10°C) and a maximum (32°C). This temperature dependence of the viscosity was similar to that for the NaCl system; however, there was a different point between the 45 wt % solutions with NaCl and thiourea [compare Figs. 8(c) and 5(b)]; T_{min} and T_{max} were independent of salt concentration for the thiourea system whereas for the NaCl system T_{max} decreased and T_{min} seemed to decrease with salt concentration. This difference was due to the different origin of the viscosity maximum; the viscosity maximum for the NaCl system was attributed to the increase in turbidity, whereas the maximum for the thiourea system was done to the phase transformation.

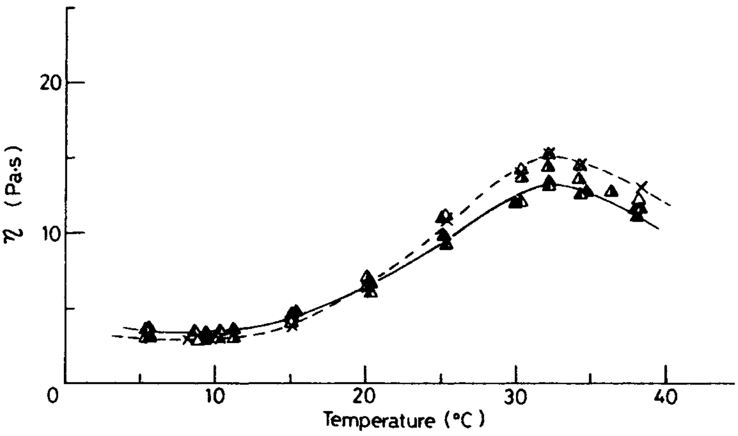
The effect of thiourea concentration on the shear viscosity for the 35 wt % solution was the same as that for the NaCl system; in the entire range of



(a)

(b)

Fig. 8. Dependence of shear viscosity on temperature for HPC/water/thiourea system at given thiourea concentration. (a) HPC concentration 35 wt %; thiourea concentration (g/dL): (×) 0; (△) 0.25; (△) 1.0; (△) 3.0; (▲) 5.0; (▲) 10.0. (b) HPC concentration 40 wt %; thiourea concentration (g/dL); (×) 0: (▲) 1.0; (▲) 5.0. (c) HPC concentration 45 wt %; thiourea concentration (g/dL): (×) 0; (△) 0.25; (▲) 1.0; (▲) 3.0; (▲) 5.0.



(c)

Fig. 8. *(Continued from the previous page.)*

temperature the viscosity showed a maximum with respect to salt concentration. In the case of the 45 wt % solution, the viscosity did not depend on the salt concentration or slightly increased with salt concentration at a relatively lower temperature (around T_{min}); however, as the temperature increased, a decrease in the viscosity with salt concentration became clear. The viscometric behavior for the 40 wt % solution was similar to that for the 45 wt % solution. Our finding suggests that the shear viscosity in the biphasic region decreases with thiourea.

The phase transformation for the HPC solutions with thiourea was independent of thiourea concentation. This supports our speculation noted above that thiourea cannot change the conformation of HPC molecules in water, but change only the water structure surrounding HPC molecules.

Finally we need to note the following: As Werbowyj and Gray[9] pointed out, T_c for liquid crystalline solutions was very difficult to determine quantitatively by means of optical methods; therefore, T_{max} could not be corresponded quantitatively to T_c for the 40 and 45 wt % solutions with NaCl, but could be done qualitatively.

CONCLUSIONS

The turbidity and viscometric behavior for the aqueous dilute solutions of HPC were greatly affected by salt type and concentration. With increasing NaCl or LiCl, T_c decreased, $[\eta]$ showed a maximum, and the Huggins' constant showed a minimum. The shear viscosity for the concentrated isotropic solutions showed a maximum with respect to NaCl concentration. On the other hand, the addition of thiourea did not affect so strongly the turbidity and viscometric behavior as the addition of NaCl or LiCl did. We speculate that the difference between the solutions with NaCl or LiCl and thiourea is due to the alteration of the degree of water–water hydrogen bonding. NaCl or LiCl acts as a water-structure maker. The salt affects the conformation of HPC molecules in two steps: In the first step, HPC molecules extend due to breaking intrahydrogen bonding; in the next step, the association of HPC molecules occurs. On the other hand, thiourea acts as a water-structure breaker and changes the water structure surrounding HPC molecules; the hydration of HPC molecules may be induced somewhat. Therefore, no conformational change of HPC molecules in water occurs. The shear viscosity for the liquid crystalline solutions with NaCl and thiourea showed a minimum and/or a maximum with respect to temperature, but the origin of the maximum for the solution with NaCl was different from that for the solution with thiourea: The former is due to the increase in turbidity, and the latter is due to the phase transformation.

The authors are grateful to Mr. O. Takatsu for assistance with part of the experimental work.

References

1. S. Suto, *J. Polym. Sci., Polym. Phys. Ed.*, **22**, 637 (1984).
2. S. Suto, K. Obara, and M. Karasawa, *Kobunshi Ronbunshu*, **43**, 231 (1986).
3. S. Suto, R. Ito, and M. Karasawa, *Sen-i Gakkaishi*, **42**, T-317 (1986).
4. S. Suto, K. Obara, S. Nishitani, and M. Karasawa, *J. Polym. Sci., Polym. Phys. Ed.*, **24**, 1849 (1986).
5. S. Suto, M. Ohshiro, R. Ito, and M. Karasawa, *Polymer*, **28**, 23 (1987).
6. S. Suto, M. Ohshiro, W. Nishibori, H. Tomita, and M. Karasawa, *J. Appl. Polym. Sci.*, **35**, 407 (1988).
7. D. G. Gray, *J. Appl. Polym. Sci., Appl. Polym. Symp.*, **37**, 179 (1983).
8. H. Toriumi, K. Miyasaka, and I. Uematsu, *Rep. Prog. Polym. Phys. Jpn.*, **22**, 31 (1979).
9. R. S. Werbowyj and D. G. Gray, *Macromolecules*, **13**, 69 (1980).
10. P. Navard, J. M. Haudin, S. Dayan, and P. Sixou, *J. Apply. Polym. Sci., Appl. Polym. Symp.*, **37**, 211 (1983).
11. E. D. Klug, *J. Polym. Sci., C*, **36**, 491 (1971).
12. R. Bergman and L.-O. Sundelof, *Eur. Polym. J.*, **13**, 881 (1977).
13. T. Tagawa, S. Yamashita, and K. Furusawa, *Kobunshi Ronbunshu*, **40**, 273 (1983).
14. F. F-L. Ho, R. R. Kohler, and G. A. Ward, *Anal. Chem.*, **44**, 178 (1972).
15. S. Suto, M. Kudo, and M. Karasawa, *J. Appl. Polym. Sci.*, **31**, 1327 (1986).
16. M. Bohdanecky and J. Kovar, *Viscosity of Polymer Solutions*, Elsevier, Amsterdam, 1982, p. 177.
17. S. Saito, *J. Polym. Sci., A-1*, **7**, 1789 (1969).
18. M. Ataman, *Colloid Polym. Sci.*, **265**, 19 (1987).
19. E. Bianchi, G. Conio, and A. Ciferri, *J. Phys. Chem.*, **71**, 4563 (1967).
20. H. S. Frank and J. Franks, *J. Chem. Phys.*, **48**, 4746 (1968).
21. H.-G. Elias, *Int. J. Polym. Mater.*, **4**, 209 (1976).
22. O. Guven and E. Eltan, *Makromol. Chem.*, **182**, 3129 (1981).
23. M. J. Seurin and P. Sixou, *Eur. Polym. J.*, **23**, 77 (1987).
24. S. Nagura, S. Nakamura, and Y. Onda, *Kobunshi Ronbunshu*, **38**, 133 (1981).

Received June 12, 1987
Accepted January 28, 1988