

Salt Addition Effects on Mesophase Structure and Optical Properties of Aqueous Hydroxypropyl Cellulose Solutions

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ABSTRACT: The effects of addition of neutral salts on the cholesteric mesophase structure and optical properties of aqueous solutions of hydroxypropyl cellulose (HPC) were investigated by spectrophotometry and an NMR technique with D₂O as solvent. In the measurements of selective light-reflection spectra, the wavelength of maximal reflectance and therefore the cholesteric helical pitch (*P*), too, varied systematically with a change in strength of a so-called “chaotropic” effect of the additive salts; *i.e.*, their effectiveness in increasing *P* was pronounced in the order of Cl⁻ < Br⁻ < NO₃⁻ < I⁻ < SCN⁻ and Cs⁺ < K⁺ < Na⁺ < Ca²⁺ < Li⁺ ≤ Mg²⁺ < Al³⁺, when compared in a series of salts with a common sort of cation or anion. An LCST-type of phase separation behavior of the HPC/water system was also affected by the coexistence of salt ions; the cloud point shifted either down or up in almost the same manner as that found in the salt-sort dependence of the cholesteric periodicity. In the deuteron NMR study, a frequency width of the quadrupolar splitting, detected as a measure of the molecular orientation development within the mesophase, was found to be less affected by the salt addition. It is suggested that the hydrophobic bond-disrupting or promoting activity of the salts added could regulate subtly a conformational state of the cellulosic polymer, to induce a marked change in cholesteric twisting power without disturbing the orientational ordering in each of the pseudonematic layers.

KEY WORDS Hydroxypropyl Cellulose / Liquid Crystal / Salt Addition / Chaotropic Effect / Cholesteric Pitch / Cloud Point /

Cellulosic polymers possess inherently the semi-rigidity and chirality in the carbohydrate backbone, and therefore, they are capable of forming a cholesteric type of mesophase in a condensed fluid state.^{1–4} The mesomorphic solutions or melts are often colored due to selective reflection of visible light, originating from the supramolecular helical periodicity. The pitch and rotatory sense (handedness) in the cholesteric helical structure are changeable depending on the chemical nature and content of substituents on the anhydroglucose unit, the sort of solvents used, temperature, and so on. Hydroxypropyl cellulose (HPC) investigated in the present work is the most familiar liquid-crystalline cellulose ether. The explicit formation of a cholesteric mesophase of cellulose was first reported for the concentrated aqueous solutions of this ether derivative.^{5,6} There have been a number of studies concerned with mesomorphic characterization and structural and physical properties of this polymer for its individual solutions in many solvents. Among them, several reports have dealt with some effects of addition of neutral salts into concentrated HPC solutions in water^{7,8} or in a few organic solvents⁹ and demonstrated, for instance, that

the mesomorphic behavior and rheological properties of the solutions are much affected by the coexistence of a small amount of the additives. The systematization and explanation of the effectiveness of the additive salts are still unsatisfactory, however.

Recently, the authors have communicated briefly that the selective light reflection of liquid-crystalline aqueous HPC/salt solutions is controllable externally by the action of a relatively weak electric field, possibly owing to electrophoretic migration of the coexistent salt ions as perturbant of the cholesteric ordering.¹⁰ In the present paper, we characterize the phase behavior of the HPC/salt/water system in detail by spectrophotometry and NMR measurements, and a further insight into the electrical control of the optical properties of this lyotropic system will be provided in a subsequent paper.¹¹

EXPERIMENTAL

Preparation of Samples

The HPC powder used was a commercially available sample (Scientific Polymer Products, Inc.); the

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nominal molecular weight was 60000. On the basis of GPC measurements using a column calibrated with polystyrene standards, the weight-average and number-average molar masses of this HPC sample were estimated as $M_w = 15.7 \times 10^4$ and $M_n = 5.3 \times 10^4$, respectively. The DS (degree of substitution) and MS (molar substitution indicating the average number of introduced hydroxypropyl groups per anhydroglucose residue) were determined as 1.8 and 3.3, respectively, by ^{13}C NMR spectroscopy based on the peak assignments described in a literature.¹²

Distilled water and reagent-grade salts were used directly to prepare concentrated HPC solutions. The solutions were made by mixing weighed HPC and water containing an appropriate amount of salt in glass vials over a period of 4 weeks, with the aid of repeated centrifugation to accelerate the dissolution of HPC. The vials were usually stored in a refrigerator (4°C) before use. Throughout this work, the polymer concentration is denoted by wt% of HPC in each solution, and the salt concentration is designated in terms of a usual molarity (M) with respect to only the aqueous solvent. However, commercial salts of divalent or trivalent metallic cations were obtained usually in a form of hydrate crystal, and therefore their aqueous solutions as HPC solvent were prepared through precise determination of the cation concentration by chelometric titration with ethylene diamine tetraacetic acid.

Measurements

Selective light-reflection of liquid crystals was examined by visual observations, and the quantitative measurements of reflection band were conducted with a UV-visible spectrometer (Hitachi U-2000) equipped with a thermo-regulated cell-holder. The samples were usually sealed in form of a thin layer of solution between parallel glass plates separated by a Teflon spacer 200 μm thick, and then allowed to equilibrate for at least 12 h prior to the measurement. An LCST-type phase separation behavior of HPC solutions were also examined in the same apparatus. Apparent light-absorbance as a measure of turbidity was recorded as a function of temperature, with an appropriate wavelength at which no selective reflection of the sample took place. The cloud point T_c was estimated from the onset of a marked deviation in the optical turbidity vs. temperature plot. Circular dichroism (CD) spectra were measured with a Jasco J-720 spectropolarimeter for selected liquid-crystalline samples sandwiched between parallel glass plates, to determine the handedness of the cholesteric helical structure. Refractive index measurements were carried out by using an Abbé refractometer with a rotatable polarizer mounted over the eyepiece.

The jacket of the prism cell was maintained at a desired temperature of 5–35°C by circulation of ethylene glycol/water from a thermo-regulated bath.

^2H NMR spectra were recorded on a JEOL JNM-EX-400 spectrometer operating at 61.4 MHz. Liquid-crystalline samples for the measurement were prepared in a 4 mm ϕ NMR tube by mixing powdered HPC with a Li salt/ D_2O solution, which took usually more than 1 month. The resultant polymer solutions were stored in a refrigerator until used.

RESULTS AND DISCUSSION

A scheme indicating the phase behavior and visual appearance of the HPC/water system appears to be well established.⁶ In accordance with the general trend, the present HPC solutions in water were completely anisotropic and colored at polymer concentrations of *ca.* 50–70 wt%, which is attributed to the selective reflection of visible light due to the cholesteric twisted structure. When an inorganic salt is existent in the solvent, the appearance of the liquid crystals varied in a wide range of spectrum, depending on the sort and amount of the additive. For example, a 62.5 wt% HPC/water solution was greenish in normal water at room temperature ($\sim 20^\circ\text{C}$), whereas the coexistence of LiI caused a change of the reflection color to orange through yellow as the salt concentration was increased from 0.1 M to 0.5 M. Further increase in the salt concentration to 2.0 M allowed the HPC solution to become uncolored, *via* reddish at 1.0 M. The addition of other salts, *e.g.*, LiCl, KI, and KCl to the 62.5 wt% polymer solution rendered the originally greenish appearance to be, respectively, bluish, almost unchanged, and heavily whitened, when compared at the same salt concentration of 0.5 M. A more quantitative and systematic examination of such a salt-addition effect was conducted by UV-visible spectrophotometry coupled with refractometry.

Figure 1 displays light-reflection spectra obtained at 20°C for two series of aqueous HPC liquid crystals which contain a lithium salt or nitrate one, both compared at a fixed concentration of polymer (62.5 wt%) and that of salt (0.5 M). Figure 1a demonstrates clearly the effect of lithium salts on the selective reflection phenomenon of the HPC liquid crystals. In comparison with the situation of the salt-free sample giving a reflection band centered at *ca.* 520 nm, the wavelength (λ_M) of maximal reflectance shifts to the blue side when lithium chloride or bromide is present in the solvent. Contrary to this, the respective additions of thiocyanate, iodide, and nitrate of lithium result in a red shift in λ_M . A similar comparison between a nitrate-

containing samples is illustrated in Figure 1b. We find here an order, $\text{KNO}_3 < \text{NaNO}_3 < (\text{no salt}) < \text{Ca}(\text{NO}_3)_2 < \text{LiNO}_3 \leq \text{Mg}(\text{NO}_3)_2 < \text{Al}(\text{NO}_3)_3$, with respect to their coexistent effect in changing the location of a re-

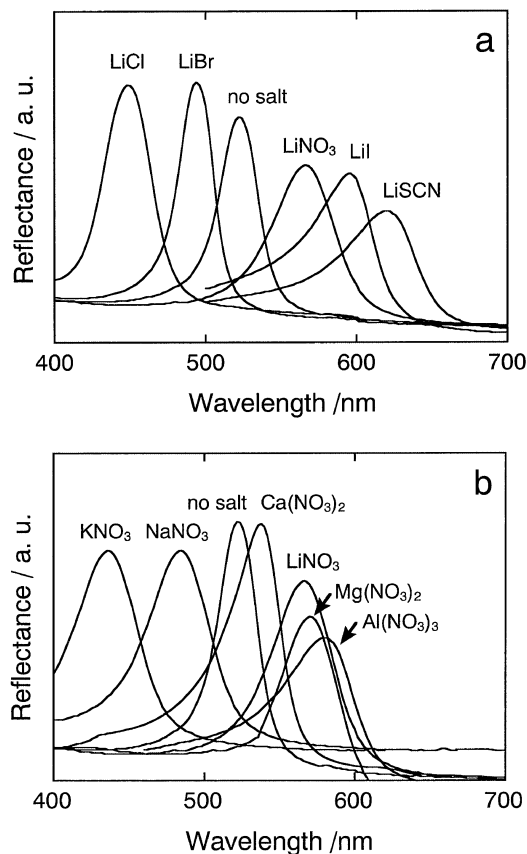
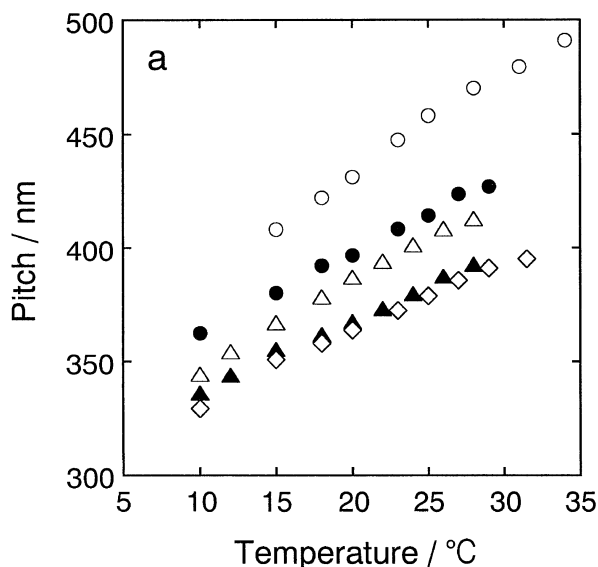


Figure 1. Selective light-reflection spectra at 20°C for liquid-crystalline HPC/salt/water systems (polym. conc., 62.5 wt%; salt conc., 0.5 M): (a) lithium salt-containing series; (b) nitrate salt-containing series.



flection spectral band; the central position moves to the side of longer wavelength according to this order of salt employment. In the comparison of cation sort, however, caution should be exercised, since the additions of the nitrates of multivalent metallic cations results in a NO_3^- concentration higher than that in the use of a uni-univalent type, the anion NO_3^- having of a weak nature of chaotropicity to act a structure breaker in the aqueous cellulosic polymer solutions (see below).

As is known well,¹³ the wavelength λ_M can be related to the cholesteric pitch (P) by the de Vries equation, $\lambda_M = \bar{n} \cdot P$, where \bar{n} is an average refractive index of the mesophase. By the combined use of the data of refractive indices and that of selective reflection spectra, both obtained at different temperatures, a variation manner of the cholesteric pitch was estimated as a function of temperature and salt concentration for the respective liquid-crystalline systems composed of HPC and an aqueous salt solvent. Examples of the results are shown in Figure 2 for two systems containing lithium thiocyanate (Figure 2a) or lithium chloride (Figure 2b), both prepared at the same polymer concentration of 62.5 wt%. From the data we can readily see the mutually opposite effects of the two salts in varying the pitch with increasing concentration, *i.e.*, the progressive increase and decrease in P with LiSCN and LiCl concentrations, respectively. Irrespective of the difference in sort of the coexistent salts, the cholesteric pitch appears to increase approximately linearly with increasing temperature in the measurement range. In the data for the HPC/LiCl/water system, however, it is observed that there seems to exist a certain point at which the temperature dependence of the pitch changes

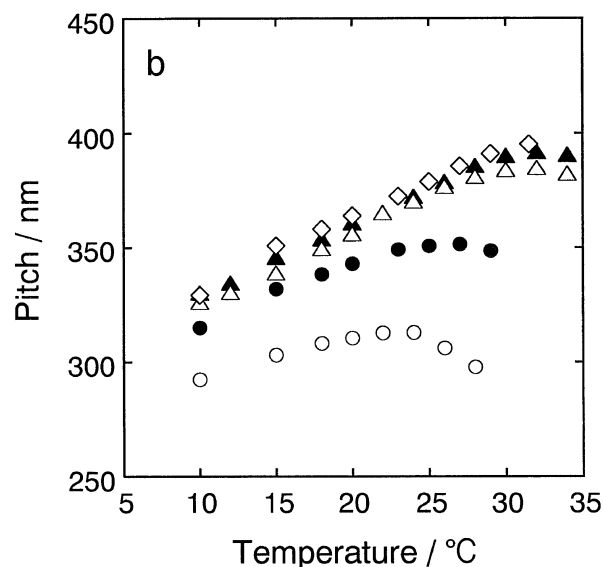


Figure 2. Cholesteric pitch (P) vs. temperature plots for HPC/salt/water systems (polym. conc., 62.5 wt%): (a) LiSCN-containing series; (b) LiCl-containing series. Salt concentration: \diamond , 0 M (no salt); \blacktriangle , 0.005 M; \triangle , 0.05 M; \bullet , 0.2 M; \circ , 0.5 M.

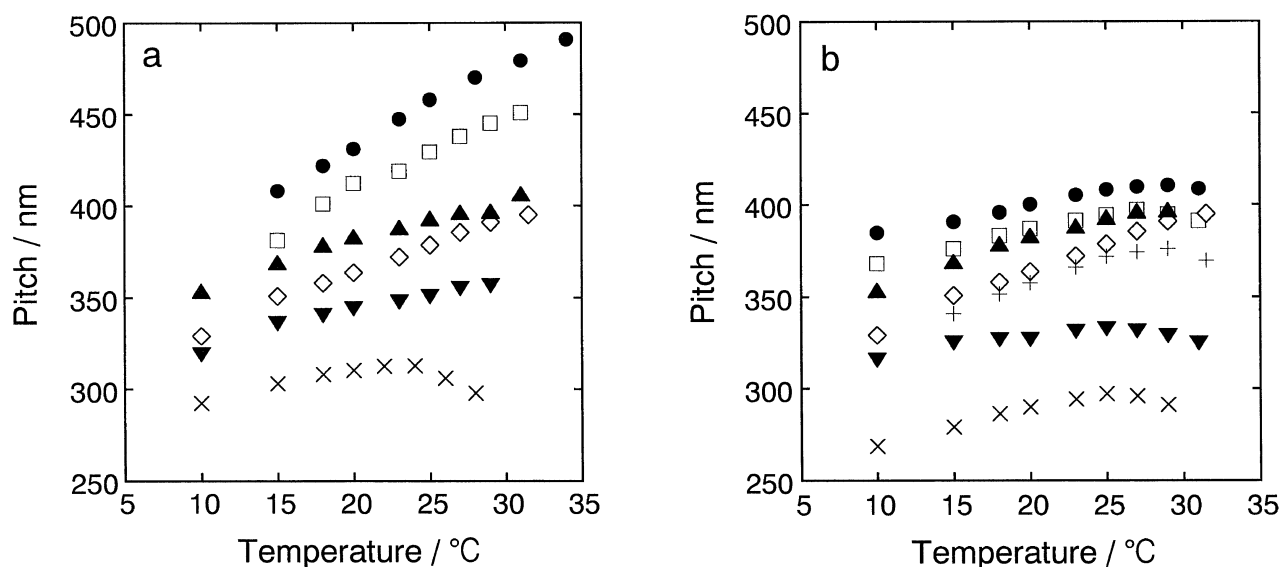


Figure 3. Temperature dependence of cholesteric pitch for aqueous HPC liquid crystals containing a series of (a) lithium salts or (b) metallic nitrates, compared at concentrations of 62.5 wt% HPC and 0.5 M salt. Anion sort in (a): ●, SCN^- ; □, I^- ; ▲, NO_3^- ; ◆, no salt; ▼, Br^- ; ×, Cl^- . Cation sort in (b): ●, Al^{3+} ; □, Mg^{2+} ; ▲, Li^+ ; ◆, no salt; +, Ca^{2+} ; ▼, Na^+ ; ×, K^+ .

from positive to negative, the point shifting to lower temperatures as the salt concentration increases. Actually, this phenomenon was noted more clearly for 55 wt% polymer solutions of the same ternary system, and even for some of 55 wt% samples containing LiSCN. Such a transition to a negative temperature dependence of the cholesteric pitch may be ascribed to a possible phase separation upon heating (see below) which is attended by the decrease in pitch due to the increase in equilibrium HPC concentration.¹⁴

Figure 3 compiles the data of the temperature dependence of the cholesteric pitch for aqueous HPC liquid crystals containing a series of lithium salts or metallic nitrates, compared at the same polymer and salt concentrations. The increase in pitch with elevating temperature is observed for all the systems, as a general property of the aqueous HPC mesophase, except for a slight negative deviation perceived above 25°C for one sample containing Cl^- and those containing the respective metallic cations as an NO_3^- partner. Concerning the salt-sort dependence of the periodicity parameter, it is apparent that anions and cations can both affect P , according to a certain rule satisfying the following orders in effectiveness: $\text{Cl}^- < \text{Br}^- < \text{NO}_3^- < \text{I}^- < \text{SCN}^-$ and $\text{K}^+ < \text{Na}^+ < \text{Ca}^{2+} < \text{Li}^+ \leq \text{Mg}^{2+} < \text{Al}^{3+}$. The respective rank order agrees very closely with that of a so-called chaotropic ion effect,^{15–17} with a minor exception in location of the multivalent cations relative to that of Li^+ . This effect is known originally as a measure of the relative strength of ions in denaturing protein structures or in inhibiting protein precipitation in aqueous solutions. However, highly chaotropic ions may be restricted to some of anions such as SCN^- and I^- , employed often

as constituent of salting-in agents.¹⁷ These anions may act as water-structure breakers and disrupt hydrophobic assemblage of nonpolar substances (usually non-polar side-groups in solute molecules) to increase their solubility in water. In contrast to this, Cl^- and Br^- may be rather water-structure makers and behave as salting-out agents to enhance the hydrophobic interaction of the substances in water. Regarding the cations of alkaline metals listed above, most of them appear to have fairly intense antichaotropicity in the present cellulosic solutions; however, it should be noted that the ranking series in their effectiveness would not necessarily reflect the order of ion effects on structuring of water molecules themselves.¹⁶

Figure 4 shows a scheme representing the relative strength of increasing or decreasing the cholesteric periodicity in aqueous HPC solutions, estimated for co-existent salt-ions through a quantitative comparison between the data of reflective spectra obtained by using various combinations of cation and anion sorts, which gave rise to different colorations of the liquid crystals. The effectiveness of a given salt in altering the cholesteric pitch and therefore λ_M , too,¹⁸ was reasonably taken to be approximately the algebraic sum of the respective effects of its constituent ions. In the case where a mixed solvent containing plural salts was employed, the effects of the individual perturbants on P and λ_M were again almost algebraically additive; *i.e.*, an HPC liquid crystal containing equimolar amounts of two different salts gave a reflection-peak maximum at a wavelength just intermediate between the corresponding spectral positions observed for two samples which contained separately double the molar quantity of the

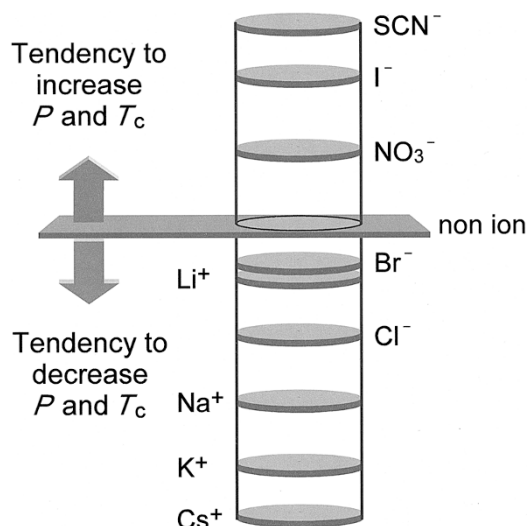


Figure 4. Schematic representation of an order of the effects of various ions on the cholesteric periodicity and phase separation behavior in aqueous HPC solutions. The total effectiveness of an added salt in altering the cholesteric pitch (P) and cloud point (T_c) of the solutions is, approximately, determined by the algebraic sum of the respective effects of its constituent cation and anion.

respective salts.

The ranking in Figure 4 is restricted to ions constituting uni-univalent type of inorganic salts. Concerning multivalent ions, it is not so easy to precisely evaluate their effectiveness in the same manner as that for univalent ions; because there is an essential difference in the so-called 'ionic strength' as electrolyte between uni-divalent or uni-trivalent salt solutions and those containing the same concentration of uni-univalent species as that in the former. An order $\text{Ca}^{2+} < \text{Li}^+ \leq \text{Mg}^{2+} < \text{Al}^{3+}$, estimated based on the data of the cholesteric pitch, would be applicable solely to the case in which the comparison is made at a fixed concentration of their salts with a common counter ion. Instead of such metallic salts, a series of guanidinium (Gu) salts, some of which are often utilized as denaturants for proteins, were employed as an additive to the HPC liquid crystals. The addition led to the observation of a somewhat longer cholesteric periodicity, rather than the case using the corresponding aqueous Li-salt solvent. Therefore the univalent, but nonmetallic cation Gu^+ may be ranked at a potential level higher than that of Li^+ and, possibly, even above the nonion level in the scheme given in Figure 4.

In supplementary CD measurements for the salt-containing systems, all the samples tested showed a negative signal of circular reflectivity, indicating that the cholesteric sense, *i.e.*, the handedness of the supramolecular helical arrangement remained right-handed as it was in the absence of any salt. Thus the salt-addition was confirmed to affect simply the ampli-

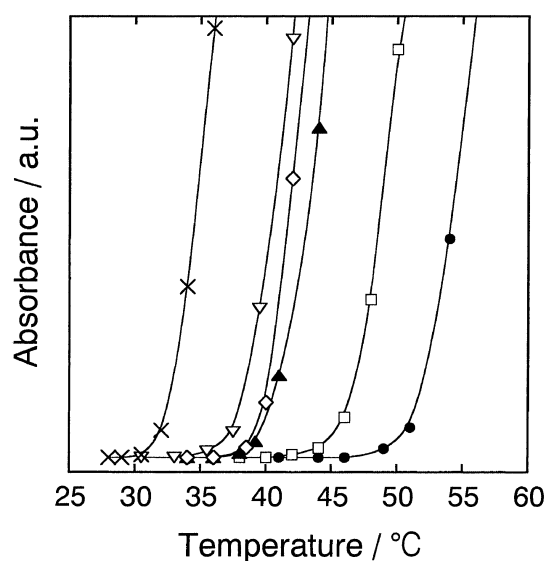


Figure 5. Variation of apparent light-absorbance (at 700 nm) as a function of temperature for aqueous HPC solutions containing a series of lithium salts, compared at concentrations of 40 wt% HPC and 0.5 M salt. Anion sort: ●, SCN^- ; □, I^- ; ▲, NO_3^- ; ◇, no salt; ▽, Br^- ; ×, Cl^- .

tude of P , as long as the solution retains the state of cholesteric monophasic.

It is already known^{6,7,14,19} that the HPC/water binary system phase-separates to give a lower critical solution temperature (LCST) and visually becomes turbid on heating. The addition of neutral salts also affects seriously this phase separation behavior. Figure 5 illustrates the variation of an apparent light-absorbance as a measure of turbidity with increasing temperature for each of 40 wt% HPC solutions with a series of Li-salt aqueous solvents, all the samples assuming an optically isotropic monophasic at room temperature ($\sim 20^\circ\text{C}$). A so-called cloud point T_c , defined here as the onset temperature at which turbidity is developed sharply on heating, is situated at *ca.* 39°C for the salt-free solution. As is evident in the figure, however, the T_c is shifted by the 0.5 M additions of Li-salts, either down or up depending on the sort of the associated anions.

Figure 6 summarizes the T_c -shifting effects with respective concentrations of lithium salts and metallic nitrates, compared at a 62.5 wt% HPC concentration eliciting a clear cholesteric ordering in the solution. It can be seen from the data that the relative magnitudes and directions of the effects of these additives upon T_c are very similar to those of the salts in altering the pitch of the cholesteric helical structure. The rule of additivity with respect to the total effect of salt mixtures as well as that of a salt-constituent ion pair on the pitch was also mostly applicable to the T_c alteration. Thus appropriate combinations of cation and anion sorts can give occasion to desired visual appearances, in both coloration

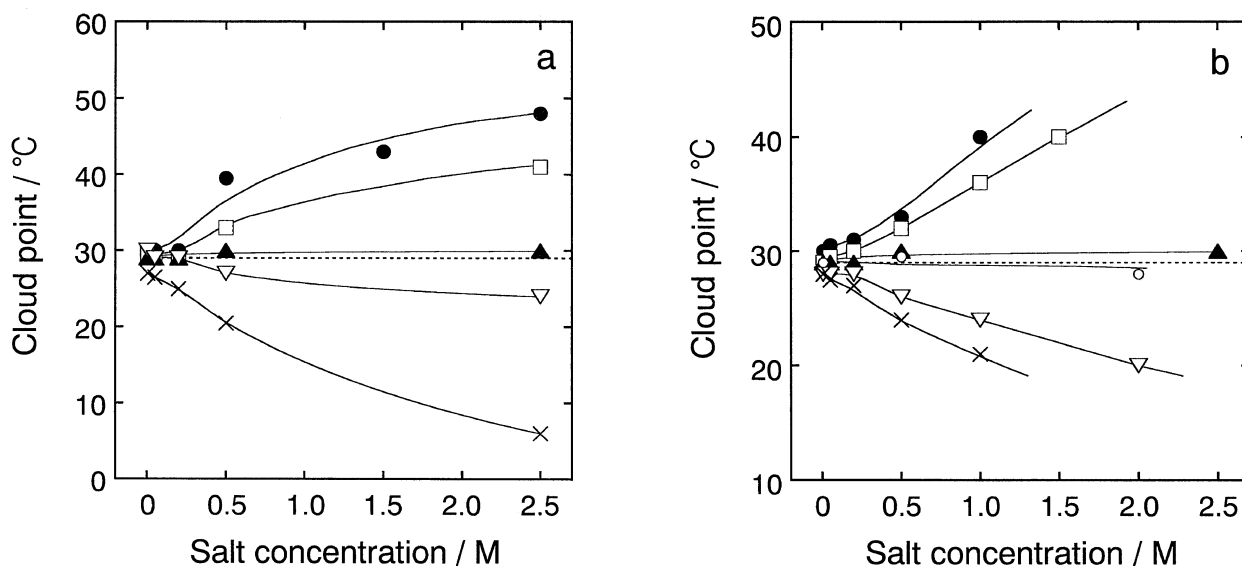


Figure 6. Cloud points as a function of salt concentration for aqueous HPC liquid crystals containing a series of (a) lithium salts or (b) metallic nitrates, compared at a polymer concentration of 62.5 wt%. Anion sort in (a): ●, SCN⁻; □, I⁻; ▲, NO₃⁻; ---, no salt; ▽, Br⁻; ×, Cl⁻. Cation sort in (b): ●, Al³⁺; □, Mg²⁺; ▲, Li⁺; ---, no salt; ○, Ca²⁺; ▽, Na⁺; ×, K⁺.

and optical turbidity, for the aqueous HPC liquid crystals at constant temperature and polymer concentration. According to the scheme shown in Figure 4, it is expected that cesium chloride should be the most potent T_c -depressant and lithium thiocyanate could exhibit the most effective action in raising T_c in the uni-univalent type of inorganic salts used in the present study. This is in fact what was observed. In Figure 6b, it can be assumed for Al(NO₃)₃- and Mg(NO₃)₂-added HPC solutions that a moderately T_c -elevating effect of the nitrate anion would more than offset the T_c -depressing potential of the metallic cations, resulting in a net increase in T_c with increasing salt concentrations. The nitrates of lithium and calcium appear to be generally weak T_c -shifters; the effect of LiNO₃ in elevating T_c was quite deficient, and Ca(NO₃)₂ was rather incapacitated to shift the point (see Figure 6b).

In Figure 7, the cloud points are plotted as a function of polymer concentration for aqueous HPC solutions, each containing one of lithium salts or metallic nitrates at a concentration of 0.5 M. Phase diagrams of the respective salt-added solutions are made clearer by the plotting. Concerning the phase diagram of the binary system of HPC and water, a detailed study has been accomplished by Fortin and Charlet.¹⁴ A point of great significance found in their study is that the phase separation of cholesteric liquid crystals takes place at lower temperatures than that of isotropic solutions. For the present HPC liquid-crystalline solutions in normal water, the data of $T_c = 23^\circ\text{C}$ (at 50 wt%), 25°C (at 55 wt%), and 29°C (at 62.5 wt%) were obtained, actually assuming rather smaller values compared with *ca.* 39°C for the isotropic samples of ≤ 40 wt% HPC (see Fig-

ure 7a). The less stability of the cholesteric mesophases upon heating may be interpreted as due to a conformational change of HPC accompanying the isotropic to anisotropic transition; *viz.*, the polymer chains would display a more hydrophobic surface to the solvent in cholesteric phases than in isotropic solutions.¹⁴ However, this thought does not necessarily come into conflict with the possibility^{4,20} of a helical or twisted conformation in dilute solution of liquid-crystalline cellulosic polymers.

As can readily be recognized at sight of the data in Figure 7, the additive salts solely lower or raise the LCST-type phase boundary of the salt-free HPC solutions. The anion-sort dependence of the parallel shift is generally more conspicuous in displacement than the corresponding cation-sort dependence. Thus, phenomenologically, the observed effects of the salt-ions on T_c reflect an equilibrium shift depending on whether their coexistence promotes or inhibits association of the solute molecules, in other words, whether the solvation of them is destabilized or stabilized by the salt employed, beyond the infinitely dilute salt level. Of importance for the HPC/salt/water systems is the finding of the same order of activity of ions in influencing the mutually different physicochemical phenomena, *i.e.*, the phase separation behavior and the cholesteric helical periodicity (at temperatures below T_c). Taking into account the similarity to the salting effects on the denaturation and precipitation of proteins in water,^{16,17} it would be reasonable to attribute the salt effects on T_c and P observed here, primarily to alterations in the strength of hydrophobic interactions in which the alkyl side chains of the cellulosic polymer participate. Then,

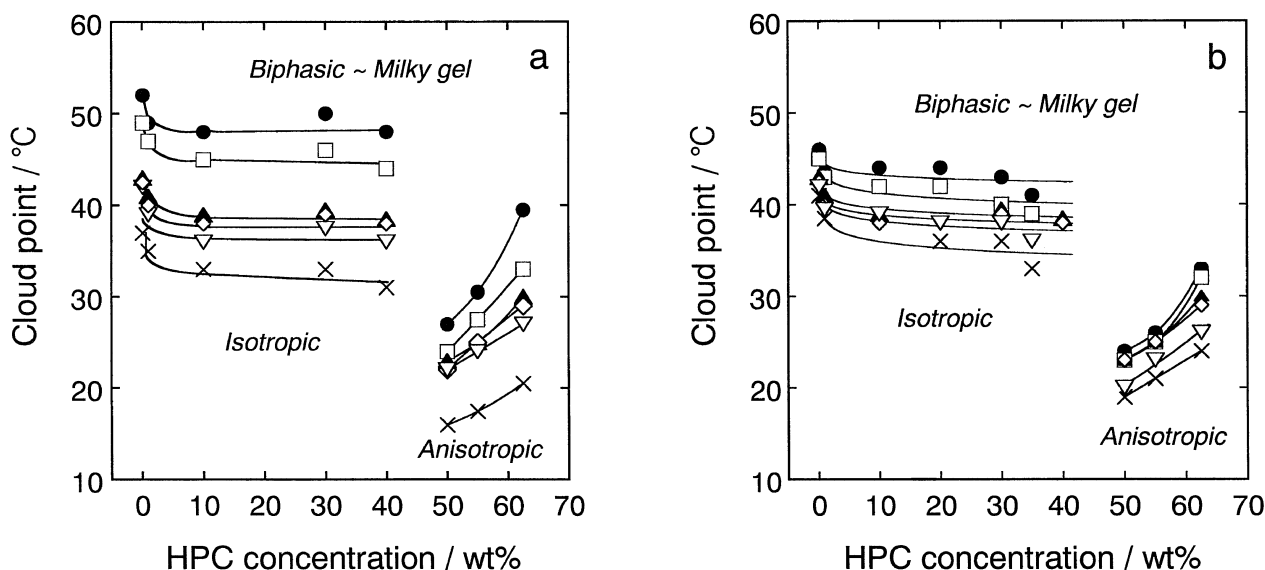


Figure 7. Cloud points vs. polymer concentration, representing the respective phase diagrams of aqueous HPC solutions containing a series of (a) lithium salts or (b) metallic nitrates, compared at a salt concentration of 0.5 M. Anion sort in (a): ●, SCN^- ; □, I^- ; ▲, NO_3^- ; ◇, no salt; ▽, Br^- ; ×, Cl^- . Cation sort in (b): ●, Al^{3+} ; □, Mg^{2+} ; ▲, Li^+ ; ◇, no salt; ▽, Na^+ ; ×, K^+ .

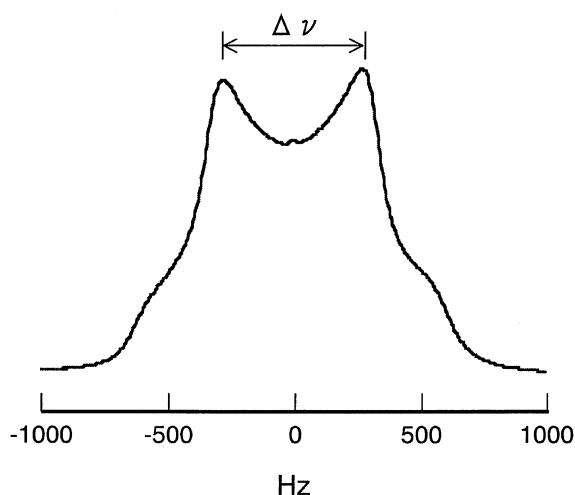


Figure 8. A typical powder pattern of ^2H NMR spectrum obtained for an HPC(70 wt%)/LiCl(0.5 M)/ D_2O sample at 20°C . $\Delta\nu$ indicates the quadrupolar splitting.

it seems also natural to assume that the salt perturbants, having potent hydrophobic bond-disrupting or promoting activity, should affect significantly the polymer conformation itself. In relation to this, an interesting result was obtained in a deuteron NMR measurement.

Molecules possessing a deuterium nucleus give a symmetrically split ^2H NMR spectrum in the state of mesomorphic assemblage.²¹ The spectrum often provides us some useful structural informations such as an orientational order in the mesophase. In the present study, we measured deuterium spectra for liquid-crystalline solutions of HPC in D_2O containing a lithium salt; where the solvent D_2O may also be regarded as a local orientational probe within the aqueous cellulosic mesophase.^{6,22} Figure 8 shows an example

of ^2H NMR spectra obtained for the HPC/Li salt/ D_2O systems, demonstrating a typical powder pattern²¹ with a doublet splitting of the quadrupolar line. This spectral shape is observed when the liquid-crystalline sample has a totally random orientation distribution of uniaxially ordered microdomains. In such a case, the quadrupole splitting $\Delta\nu$, defined as the peak-to-peak separation of frequency, can be related to the order parameter S of a deuterium bond vector (O-D here), in the following way²¹

$$\Delta\nu = \frac{3}{4} \frac{e^2 q Q}{h} S$$

where $e^2 q Q/h$ is the quadrupolar coupling constant.

In Figure 9, $\Delta\nu$ values measured for liquid crystals of HPC/LiSCN/ D_2O and HPC/LiCl/ D_2O are plotted as a function of polymer concentration, together with the corresponding data for the samples containing no salt. Definitely, the increase of $\Delta\nu$ with HPC concentration observed for any of the three series reflects an enhancement of the orientational ordering along a so-called nematic director within the mesophase, although the degree of orientation of the low molecular solvent may be taken to be much smaller than that of the macromolecular backbone itself. The $\Delta\nu$ vs. concentration curves tend to be somewhat concave, suggesting an acceleration of the orientation of D_2O along the HPC chains and/or a possible increase of the persistent length of the semi-flexible polymer chains with concentration.²³ Of great interest is the result that the salt-free values of $\Delta\nu$ are not appreciably affected by the salt addition which gave rise to the drastic changes in cholesteric pitch. It follows that the inorganic salts employed vary

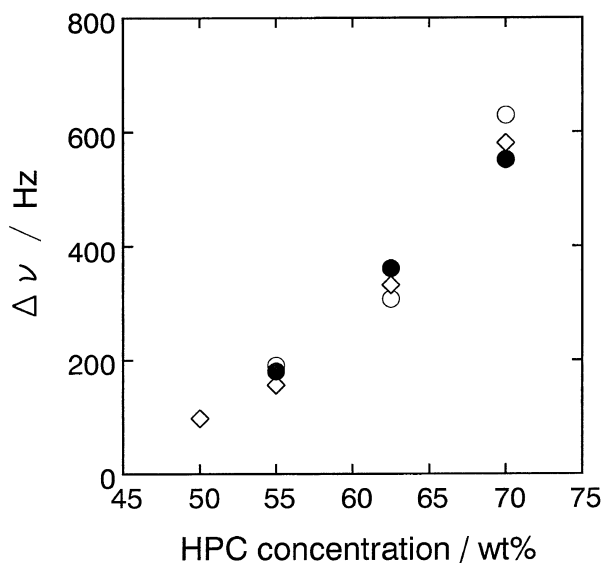


Figure 9. Variation of the quadrupolar splitting $\Delta\nu$ as a function of polymer concentration for HPC/Li salt/D₂O systems at 20°C. Additive salt: ○, 0.5 M LiSCN; ◇, no salt; ●, 0.5 M LiCl.

the cholesteric twisting property without disturbing the molecular orientation in each of pseudonematic layers constituting the HPC mesophase. If the observed salt-sort dependence of the cholesteric pitch is ascribed simply to an effective change in solute polymer fraction, we should observe an explicit parallel-shift of the salt-free data of $\Delta\nu$ vs. concentration plots in Figure 9, upward (*i.e.*, to the side of lower concentrations) and downward (*i.e.*, to the side of higher concentrations) for the LiCl and LiSCN additions, respectively. It would be more plausible to assume that the additive salts affect directly a molecular conformational factor, possibly involved in determining the cholesteric twisting power emerging between adjacent pseudonematic layers.

There is a cholesteric model²⁴ based on the steric interaction between a pair of helical or spirally threaded rods aligned in mutually adjacent nematic planes, in which the pair of rods approach closely in the minimum distance to yield a small twist angle between the two layers; whereupon the angle should be variable with the amplitude of their screw thread. Supposing that a similar model is applicable to the present system of aqueous HPC cholesterics by replacing the stiff rod by a more flexible but twisted molecule; then, the change in helical periodicity of the mesophase under coexistence of different salts may be readily interpreted as due to a change of the molecular twisting itself, originating from a certain rearrangement of the side-chains attainable by virtue of a potent hydrophobic bond-disrupting or promoting activity of the employed salt. However, the applicability is still conjectural, although there are several pieces of evidence^{4,20,25} suggesting some helical or twisted conformations of liquid-crystalline cellu-

lose derivatives.

CONCLUSION

As has been demonstrated clearly in this study, the cholesteric mesophase structure and LCST-type phase separation behavior, and ensuing optical characteristics of concentrated aqueous HPC solutions are seriously affected by addition of neutral salts with a universal dependence on the sort of the constituent ions. Through the systematic examination by spectrophotometry, it turned out that the cholesteric periodicity parameter P as well as the cloud point T_c of the solutions increases with increasing strength of a so-called chaotropic effect of additive salts, this effect being pronounced in the order of $\text{Cl}^- < \text{Br}^- < \text{NO}_3^- < \text{I}^- < \text{SCN}^-$ and $\text{Cs}^+ < \text{K}^+ < \text{Na}^+ < \text{Ca}^{2+} < \text{Li}^+ \leq \text{Mg}^{2+} < \text{Al}^{3+}$ in the present cellulosic solutions, when compared in a series of salts with a common sort of cation or anion. The total effectiveness of a given salt in altering P and T_c was approximately determinable in terms of an algebraic addition of the respective effects of the constituent ions.

In the deuteron NMR measurement for HPC liquid crystals with D₂O as solvent, the quadrupolar splitting $\Delta\nu$, observed as a variable reflecting the degree of molecular orientation development in the mesophase, was insensitive to the salt additions. It may be inferred that the additive salts would be able to alter a conformational state of the cellulosic polymer subtly, so as to induce a marked change in cholesteric twisting power without disturbing the molecular orientational order in the pseudonematic layers.

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