Electrooptical Behavior of Liquid-Crystalline (Hydroxypropyl)cellulose/Inorganic Salt Aqueous Solutions

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Received September 24, 2002; Revised Manuscript Received November 25, 2002

ABSTRACT: The selective light reflection and turbidimetric property of concentrated aqueous solutions of (hydroxypropyl)cellulose (HPC), originating from their cholesteric mesophase structure and LCST-type phase behavior, respectively, are much affected by coexistence of inorganic salts therein. This is ascribed to a strong dependence of both cholesteric helical pitch (P) and cloud point (T_c) of the aqueous cellulosic solutions on the sort and concentration of the additive salts. By virtue of electrophoretic motility of the coexistent salt ions as P and/or T_c shifter, the dynamic variation in cholesteric coloration and/or optical turbidity of the HPC solutions was realized under the action of a relatively weak electromotive force to electrodes in contact with their layered sample. It was reasonably taken that the electrical stimulation allowed the ion particles to migrate and localize in this lyotropic system, resulting in occurrence of a certain degree of gradient in magnitude of P and/or T_c in response to the uneven ionic distribution. To make clearer the mechanism of the novel electrooptical function, discussion took into consideration a storage effect of electric charge in the solution samples, detectable as a remaining potential difference after cessation of the application of the electric field.

Introduction

A cellulose ether derivative, (hydroxypropyl)cellulose (HPC), would have some degree of semirigidity and a chiral nature in the molecular structure. It is therefore capable of forming a cholesteric type of liquid-crystalline phase in concentrated solutions.[1−5] The liquid crystals often colored due to selective reflection of visible light, originating from the supramolecular helical arrangement. HPC solutions in water are already known to exhibit such a typical cholesteric character at polymer concentrations of ca. 50−70 wt %.[1,6] The aqueous solutions also show a phase diagram with the lower critical solution temperature (LCST) usually located at <45 °C.[1,7,8]

Recently, we reported on the aqueous HPC lyotropic system that the optical characteristics, occasioned by the cholesteric mesophase structure and LCST-type phase behavior, are much affected by addition of an adequate amount of neutral salts.[9] For instance, when lithium chloride is dissolved in the liquid-crystalline system, the wavelength (λ_M) of maximal light reflectance and the cloud point (T_c) shift, respectively, to the blue side and to the lower temperature side. In contrast to this, the coexistence of lithium thiocyanate results in a red shift in λ_M and an elevation in T_c. In both cases, the higher the salt concentration, the greater is the extent of the λ_M and T_c shifts. From quantitative measurements by UV−visible spectrophotometry, the λ_M and T_c, and therefore the cholesteric helical pitch (P) and phase separation temperature, were found to vary systematically with a change in strength of a so-called "chaotropic" effect[10] of the ions constituting the additive salts. This effect became pronounced, e.g., in the order of $Cl^- < Br^- < NO_3^- < I^- < SCN^-$ and the order of $Cs^+ < K^+ < Na^+ < Ca^{2+} < Li^+ \leq Mg^{2+} < Al^{3+} < Gu^+$ (guanidinium ion), when compared in a series of salts with a common sort of cation or anion, where Cl^-, Br^-, and most alkali-metal cations were antichaotropic for the aqueous cellulosic solutions. The degree and directional sense of the effectiveness of a given salt in altering the optical parameters were determined by the algebraic sum of the respective effects of its constituent ions, and thus the coloration and turbidity of the aqueous HPC lyotropic system could be controlled desiably by selecting the combination of cation and anion species.

In parallel with the static investigation of phase behavior for the relevant system, we have made a novel attempt to control the selective light reflection from the cholesteric HPC mesophase by electrical stimulation. In general, it is not so easy to manipulate the mesomorphic structure and property of a main-chain type of liquid-crystalline polymers in such an external nonmechanical way, due to their lesser sensitivity to an electric field of a practical magnitude. In the case of the salt-containing HPC/water system, however, it may be more successful to realize the "dynamic" control by application of relatively weak electric field. If an appropriate electric potential difference is applied to the liquid crystal loaded between a pair of electrodes, the salt-constituent cation and anion particles will migrate with time, more or less, toward the negative and positive sides, respectively. In consequence, there should occur some degree of gradient in concentration of the salt ions in the lyotropic system. This would also give rise to a synchronous fluctuation of the cholesteric ordering, resulting in the gradation of reflection color from the originally unified one. On the basis of the concept, a few results have been reported in a preliminary communication.[11] In the present paper, further insight is provided into the dynamic variation not only in cholesteric coloration but also in optical clarity of the aqueous HPC/salt system

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10.1021/ma021522x CCC: $25.00

under the action of an electric field, in connection with the design of a new type of electrooptical device utilizing natural polysaccharides.

Experimental Section

Throughout this work, the polymer concentration is denoted by weight percent of HPC in each solution, and the salt concentration is designated in terms of a usual molarity (M) with respect to the aqueous solvent.

The HPC used here is a commercially available sample (Scientific Polymer Products, Inc.), the same as that described in the preceding paper:[9] nominal molecular weight, 60 000; weight-average and number-average molar masses, $M_w = 15.7 \times 10^4$ and $M_n = 5.3 \times 10^4$, respectively (from GPC measurements); degree of side-group substitution, DS = 1.8 and MS = 3.2 (from ^{13}C NMR measurements), where DS and MS denote an average number of substituted hydroxyls and that of introduced hydroxypropyl groups, respectively, per anhydroglucose residue. Neutral salts were all reagent-grade chemical and used without further purification.

Aqueous HPC solutions were prepared at polymer concentrations ranging from 30 to 62.5 wt %, by mixing weighed amounts of dried HPC powder and distilled water containing a salt at 0.5 M in a glass vial over a period of 4 weeks. During this period, the vials were usually stored in a refrigerator at 4 °C; however, they were sometimes turned upside down in a centrifuge for the purpose of accelerating the dissolution of HPC.

For electrooptical examinations, two types of sample cells were devised, termed H (horizontal) type and V (vertical) type. The H-type cell was made up of slide glasses, two platinum (Pt) or carbon plates as a pair of inert electrodes and spacers, and a sealing Teflon spacer. In the arrangement, each sample was sealed in a layer of solution between parallel slide glasses spaced by a pair of electrodes of 500 μm thickness, so that the sectional planes of the twinning Pt or carbon plates were apart face to face at a distance of 7.5−15 mm on both sides of the layered solution. In the V type, each solution sample was sealed between an ITO (indium tin oxide)-coated glass plate and a carbon sheet, the electrode pair being spaced by a Teflon film 200 μm thick. An electric generator, Multifunction Synthesizer 1946 (NF Electric Instruments Inc.), was used to electrify the sample-charged cells. The electromotive force applied was usually 4.0−4.5 V on the H-type cell and 3.0−9.0 V on the V-type one. All the electrification experiments were carried out at room temperature (~22 °C). In some cases using the H-type cell, after cessation of the application of the electric field, the time-course of a possible electric discharge was followed by measuring the variation of a potential difference remaining in the electrified samples. A digital multimeter TR6846 (Advantest Co.) was employed for this purpose.

Results and Discussion

Observations of Dynamic Coloration Changes. A result of the electrification experiment with an H-type cell is shown in Figure 1 for an HPC (62.5 wt %)/LiNO$_3$ (0.5 M)/water system. In this example, Pt plates were used as a pair of electrodes so as to be 15 mm apart from each other, and the potential difference applied between them was 4.0 V. In the initial stage free of the electric field, the liquid-crystalline solution was uniformly colored bright green (Figure 1a). With an elapse of time, this cholesteric coloration varied as follows: About 60 min after imposing the electric potential, the sample exhibited yellowish and bluish hues in the vicinity of the positive and negative plates, respectively, as demonstrated in Figure 1b. When another 60 min had passed, the reflective colors of the cholesteric liquid crystal ranged from light orange-yellow on the positive side through green in the central part to blue-violet in the neighborhood of the negative electrode (Figure 1c). Further continuous electrification resulted in gradual expansion of the light orange and blue-violet regions toward the negative and positive sides, respectively, attended by the occurrence of a hazy, pale violet or uncolored zone in the vicinity of the negative electrode (Figure 1d). After more than ca. 150 min elapsed in the total time of electrification, however, the coloration of the lyotropic system hardly changed with time in the visual observation. In the course of the process of color changing, an attempt was made to discontinue the supply of electricity, by opening the direct circuit to cut off a connection of the sample cell with the electric generator; then, the state of cholesteric coloration at that time was maintained almost intact for at least 1 week. If the circuit was closed with a leading wire immediately after the separation from the generator, the color gradation became somewhat loosen in several hours, and ultimately, the sandwiched sample regained almost the original unified color within 2−3 days.

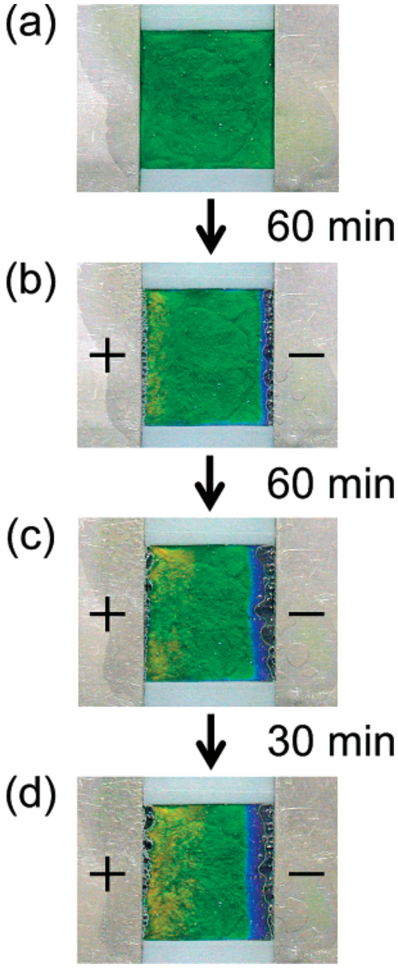

Figure 1. Variation in cholesteric reflection color of an HPC/LiNO$_3$/water system at 22 °C with an elapse of time (polymer concentration, 62.5 wt %; salt concentration, 0.5 M). The liquid crystalline sample was loaded in an H-type cell with a pair of Pt electrodes and subjected to the action of an electric field of 4.0 V/15 mm: (a) initial quiescent state; (b) sample after 60 min; (c) sample after 120 min; (d) sample after 150 min.

Similar experiments were conducted by altering the distance (L) between Pt electrodes and the imposed electromotive force (E_i). As a result, it was confirmed that the change in coloration with time became more rapid as E_i was raised and L was decreased; i.e., the speed of the coloring process was approximately proportional to the electric field strength E_i/L within the limits of the measurements for a given lyotropic system.

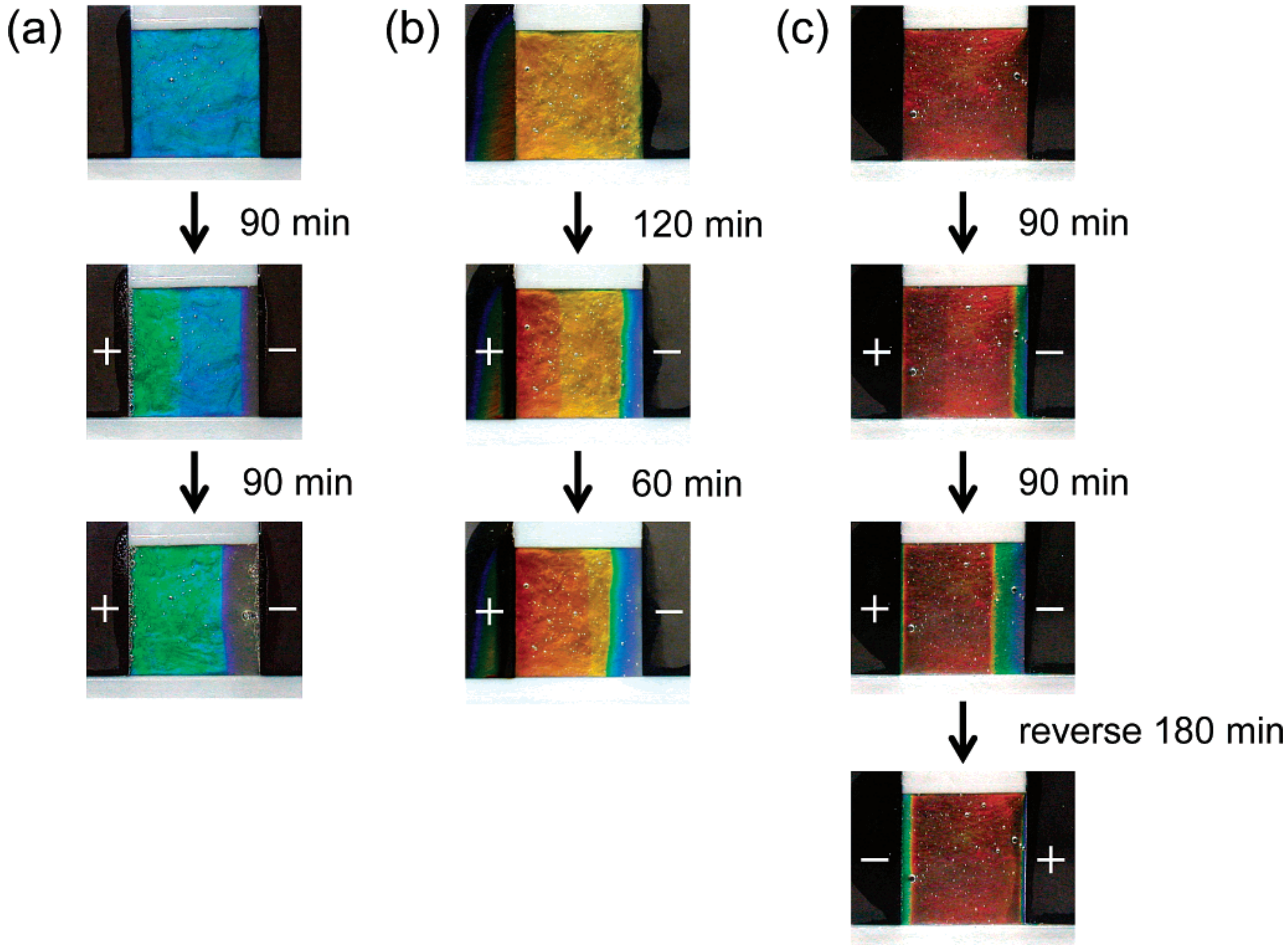

Figure 2. Time course of the cholesteric colorations of 62.5 wt % HPC liquid crystals in water, each solution containing a 0.5 M salt: (a) $NaNO_3$; (b) LiI; (c) LiSCN. The observation was made at 23 °C for the respective samples loaded in an H-type cell with a pair of carbon electrodes, under application of an electric field of 4.5 V/15 mm.

However, caution should be exercised to the following observation: When the field strength exceeded ca. 4.0 V/cm, air bubbles present in the viscous solution were liable to heavily disturb the regular formation of reflection color bands, and more seriously, evolution of hydrogen gas from the negative Pt plate became manifest in the course of electrification.

The H_2 generation is evidently due to electrolysis of water containing ionized salts. The degree of hydrogen evolving, in general, depends on the sort of the electrode materials used, each showing an intrinsic hydrogen overvoltage.[12] The overvoltage observed for metals belonging to the platinum group is relatively low, and it is therefore plausible that the use of Pt plates as electrodes for the present system resulted in occurrence of abundant hydrogen bubbles under the action of >4.0 V/cm. An alternative facile way to make the bubbling less effective was adoption of carbon plates, giving a comparatively high hydrogen overvoltage. For instance, hydrogen bubbles hardly occurred over a time period of at least 3 h in the use of carbon electrodes under an electric field strength of <5.5 V/cm. Parts a−c of Figure 2 show a result of the electrification experiment with a pair of carbon electrodes for three liquid-crystalline samples containing 0.5 M sodium nitrate, lithium iodide, and lithium thiocyanate, respectively, all prepared at an HPC concentration of 62.5 wt %. The condition of the electric-field application was $E_i = 4.5$ V and $L = 15$ mm.

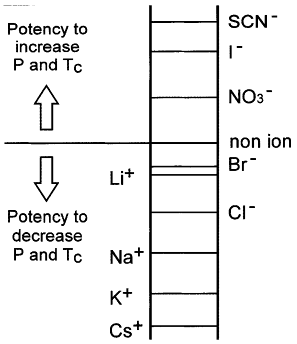

Figure 3. Schematic representation of a rank order of the relative effectiveness of different ions in altering the cholesteric pitch (P) and cloud point (T_c) of aqueous HPC solutions, quoted from ref 9 in a rearranged style.

As shown in the top of the respective figures, the $NaNO_3$-containing system imparts an indigo blue in the initial state, while the other two containing LiI or LiSCN assume orange and red colors, respectively. Thus, the addition of inorganic salts to the aqueous HPC liquid crystal, which exhibited a greenish appearance in the salt-free state at 62.5 wt %, causes a change of the reflection color, according to a rule of additivety with respect to the effectiveness of the salt-constituent ions in altering the cholesteric pitch (P) and therefore the wavelength of maximal reflectance (λ_M), too. Figure 3 illustrates a scheme to rank the relative potency of representative ions in increasing or decreasing the cholesteric pitch of the present lyotropic mesophase, which was constructed through comparison between many reflection spectra data obtained by using various combinations of cation and anion species.[9] The initial cholesteric colorations of the above three samples can readily be understood qualitatively from the ranking positions of the salt ions incorporated thereinto. In the previous example of lithium nitrate addition (Figure 1a), the effect of NO_3^- to increase P and that of Li^+ to decrease P should be canceled out, resulting in the observation of almost the same greenish hue as in the salt-free situation.

Voltage application to the three samples laid between carbon electrodes resulted in formation of a clear array of color bands; e.g., after a lapse of 120−180 min, the $NaNO_3$-coexistent system displayed color regions of bright green, dark green, blue, and pale violet, and an additional colorless zone (but slightly clouded) (Figure 2a), and the LiI-coexistent system was covered with an entire spectrum of reflection colors ranging from red to violet (Figure 2b). When the polarity of the pair of electrodes was reversed in mid-course of the electrification, the samples substantially recovered their original uniform color with the passage of almost the same time as consumed until the exchange, as demonstrated for the LiSCN-coexistent system (Figure 2c). These findings of dynamic coloration change indicate formation of a gradient in magnitude of the cholesteric pitch in the liquid-crystalline HPC solutions, possibly coming from an ionic uneven distribution generated by the external electric field.

As has been described in the preceding paper,[9] the salting effect on the helical periodicity in the aqueous HPC cholesterics may be attributed primarily to alteration in strength of the hydrophobic interaction in which the alkyl side chains of the cellulose derivative participate. Highly chaotropic anions such as SCN^- and I^- act as water-structure breakers and disrupt hydrophobic assemblage of nonpolar substances (usually side groups in solute macromolecules) to increase their solubility in water. In contrast, Cl^- and Br^- are instead structure formers in aqueous solutions and behave as salting-out agents to enhance the hydrophobic interaction of the substances. Alkali-metal cations listed in Figure 3 have also potent hydrophobic bond-promoting activity in the present cellulosic solutions. Suppose that the cholesteric structure of the cellulose derivative is made up of closely stacked layers, each occupied with uniaxially oriented molecular threads having a twisted or helical habit;[13,14] then, the salt-sort dependence of the cholesteric pitch can be interpreted as due to a change in degree of the molecular twisting itself, originating from a rearrangement of the side chains induced by the action of the employed salt. Actually, it has been suggested by a deuteron NMR measurement[9] that the salt ions added would be able to regulate subtly a conformational state of the cellulosic polymer, to give rise to a marked change in cholesteric twisting power without disturbing the molecular orientational order in each of the pseudonematic layers.

When an electric potential difference is applied to an aqueous salt-containing HPC liquid crystal loaded between a pair of electrodes, the constituent cation and anion particles will be localized with time on the negative and positive sides, respectively, due to their electrophoretic migrations; generally, however, the rate of migration would be mutually different between them. Thus, it follows that some degree of gradient in concentration of the salt ions occurrs in the lyotropic system. In response to this change in ionic environment, the cholesteric helical pitch of the HPC mesophase should also fluctuate synchronously, which results in the gradation in reflection color instead of the originally unified one. In a case where the coexistent salt is composed of a pair of alkali cation/chaotropic anion, as in the above examples, a display of colors with longer wavelengths is available at the positive electrode side and conversely a display of colors with shorter wavelengths is available at the negative electrode side, both being compared with the coloring situation in which no electric field is applied.

As is already stated above, there was a case where an electrolytic reaction was noticed, especially explicit in the use of Pt electrodes under a fairly high strength of electric field. In that case, we ascertained occurrence of a position-dependent pH shift for the sample rendered colorful by the electrification. However, it can be assumed that the pH gradient is not the primary factor inducing the dynamic coloring process, judging from the following result of a control test: A series of 62.5 wt % HPC liquid crystals were prepared at pH = 1−12.5, for example, with HNO_3 and LiOH. All the samples imparted a greenish hue visually, and the λ_M in their respective reflection spectra was located in the range 510−550 nm at 18 °C. At both ends of the pH range, however, the existence of an alkali cation and that of a nitric or halide anion were rather non-negligible, the cholesteric pitch being variable according to the sort of the acid or base employed for the pH adjustment.

Observations of Dynamic Turbidity Changes. As is well-known,[1,8] HPC solutions in water phase separate and visually become turbid on heating; i.e., the system shows an LCST-type phase diagram. A so-called cloud point T_c, conventionally defined as an onset temperature at which the optical density rises sharply on heating, is situated around 40 °C for isotropic HPC/water solutions and rather lowered for higher HPC concentrations leading to the mesophase formation.[8] This phase separation behavior of the aqueous HPC solutions would also be affected by the addition of salt ions into the solutions, depending on the species and concentration of the employed additive. Actually, the relative magnitudes and directions of the effects of the additives upon T_c were ascertained to be quite similar to those of the corresponding effects on the cholesteric helical pitch.[9]

In the electrification experiment conducted for salt-containing liquid crystals of HPC, it was often observed that an opaque colorless zone developed with time on the negative side of the sample (e.g., see Figure 2b (bottom)). This may be ascribed to a lowering of T_c to less than ∼20 °C (room temperature) which was regionally induced by concentration of the constituent cations as a T_c-depressant on the negative side.

Some of the HPC liquid crystals containing a highly antichaotropic cation/anion pair, e.g., KCl or CsCl (see Figure 3), were colorless and already opaque in the quiescent state free of electric supply, when viewed at room temperature and at polymer and salt concentrations of 62.5 wt % and 0.5 M, respectively. Under the electrified state in an H-type cell, those samples displayed a colored zone in the neighborhood of the positive electrode along with a further increase in turbidity on the negative side. This observation is also readily

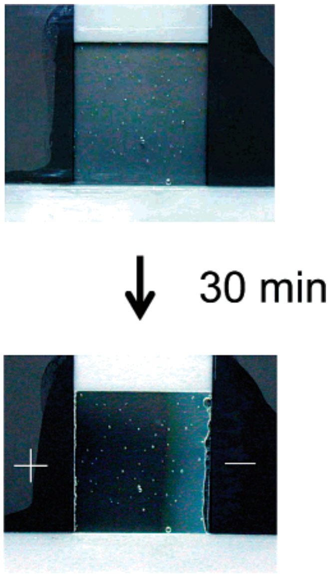

Figure 4. Photographs of a 40 wt % HPC/water solution containing 0.5 M cesium chloride at 23 °C, demonstrating a variation in the optical turbidity with time caused by the action of an electric field of 4.0 V/15 mm.

understandable in a similar way as mentioned above, as a result of fluctuation of the ionic environment caused by electrical stimulation. If such a lyotropic system containing a potent depressor of T_c is employed at an adequate HPC concentration of <45 wt %, the isotropic sample may be expected to alter solely its optical clarity under electrification, without showing iridescence. This is in fact what was observed, as demonstrated in Figure 4 for an HPC (40 wt %)/CsCl (0.5 M)/water isotropic system.

According to the ranking scheme shown in Figure 3, cesium chloride should exhibit the most effective action in depressing T_c to this cellulosic system in the conventional uniunivalent type of inorganic salts employed in the present work. Therefore, the salted HPC solution was hazy in the initial stage, although the cloud point of a salt-free sample with the same polymer concentration was ca. 39 °C. Following application of an electric field (4.0 V/15 mm), a negative-side area of the CsCl-containing sample became fairly turbid, while the opposite side gained a transparency, as seen in Figure 4, reflecting the regional depression and elevation of T_c. A similar dynamic change in optical turbidity was observable for KCl-containing and LiCl-containing isotropic solutions; however, their original appearances were of lower haziness, and it took a somewhat longer time to perceive a clouded area spreading out on the negative side, when compared with the HPC/CsCl aqueous system under the same conditions of solute concentrations and of electric supply. The observations of such a preferential increase in opacity at the negative electrode side indicate that the electrophoretic mobilities of the alkali-metal cations are higher than that of the halide anion in the present polymer medium.

In the above experiments where the H-type cell was used, the gradation in coloration and/or optical turbidity of the lyotropic system took place in a direction perpendicular to the view axis. In the other type of cell for electrification, arranged as a V-type with ITO/carbon electrodes, such a gradation should be made parallel to the visual direction, whereupon, for example, a transition from transparency to opacity, and vice versa, may be attainable over the whole plane of the sample cell. An example of electrification using this type is shown in Figure 5 for an HPC (30 wt %)/LiCl (0.5 M)/water

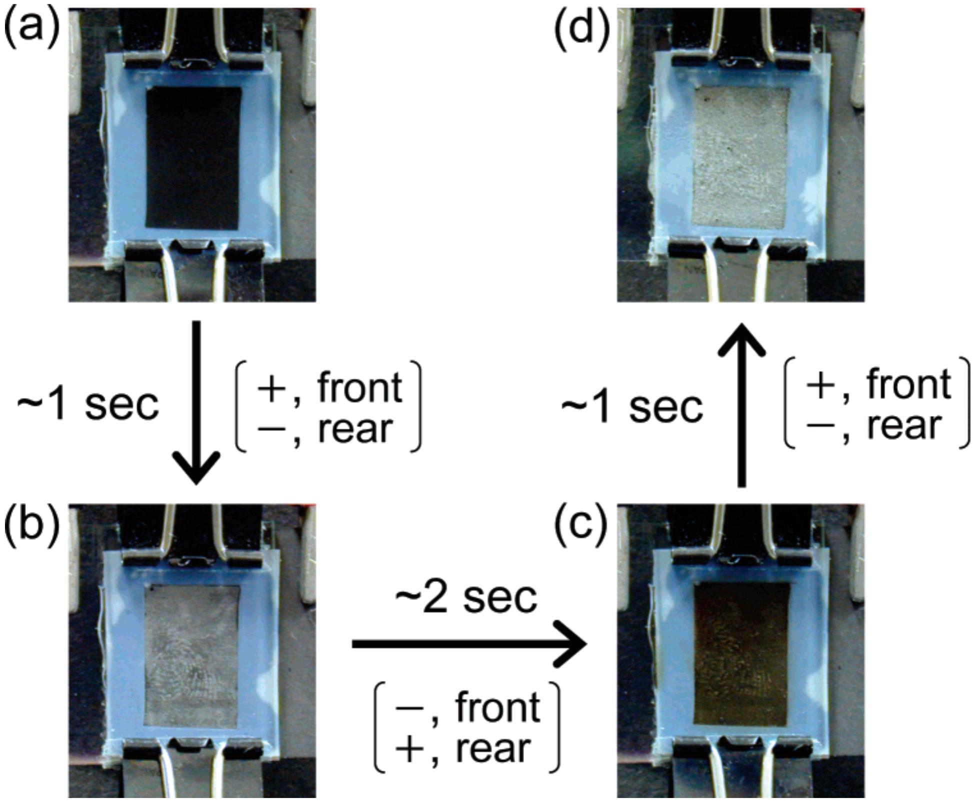

Figure 5. Photographs of an HPC (30 wt %)/LiCl (0.5 M)/water system interposed in a V-type cell with a pair of ITO (front)/carbon (rear) electrodes, demonstrating a rapid transition between the state of transparency and that of opacity realized at 23 °C by the action of an electric field of 4.5 V/0.2 mm. See text for discussion of parts a−d.

system. The isotropic solution was interposed between an ITO glass (front) and a carbon sheet (rear), 0.2 mm apart (Figure 5a). The potential difference applied between the electrodes was 4.5 V.

On imposing the voltage, the sample lost transparency in a second, as expected, over the whole field of view (Figure 5b). Following this, the polarity of the pair of electrodes was reversed; then the sample recovered the original transparency within a few seconds (Figure 5c). The opacity generated in the first step can be attributed to concentration of lithium ions as a T_c-depressor on the side of the negative carbon electrode. The subsequent observation of clarity indicates that the ions retraced their migrating way to cancel the induced localization, so that the T_c in the vicinity of the carbon plate rose to almost the initial level. After this recovery, further electrification with reexchanging the polarity led to a rapid increase in opacity once again (Figure 5d) and, hereafter, a few additional cycles were reproducible.

The reversible control of opacity/clarity over the whole plane of the sample cell was also accomplished for HPC solutions (30−40 wt %) with other salt additives (e.g., KCl and $NaNO_3$). As a matter of course, lowering of the electric field strength led to a slower rate of the conversion. In the above electrification cycle, however, special care should be taken to the following point: ITO is not inert but liable to generate an electrochemical reduction, and therefore, it could not endure either a prolonged use or a higher field strength, when operated as a negative electrode in the V-type cell.

A similar electrical experiment with the V-type cell was carried out for cholesteric solutions composed of HPC/lithium salt/water. When an electric field (4.5−6.0 V/0.2 mm) was applied between the electrodes, usually the sample loaded therein was covered with cloud simultaneously with loss of the original hue. A change of tint that was expected to occur due to a possible superposition of different color layers was not clearly observed. Most likely the alkali cation localized more rapidly to form a thin layer of lower T_c at the negative site. It was also difficult to realize a rapid recovery of the initial colored state by reversing the polarity of the electrodes, presumably due to an effect of inertia originating from a higher viscosity of the liquid-crystalline solutions.

Effect of Charge Storage in the Lyotropic System. In a series of electrooptical experiments, the concentrated HPC/salt solutions used may be taken, essentially, as a viscous electrolytic medium of electrically high resistance. Unlike the case of common electrolyte solutions showing much lower resistance and viscosity, an electric potential gradient would prevail all over the medium in the direction of one side of the electrodes from the other during electrification; however, it may be admitted that a steeper gradient arises in contact with the respective electrode faces due to formation of a so-called electrical double layer.[15] Even after the supply of electricity is stopped, the internal potential generated until then would be retained, so that the sample cell should behave like a condenser. The storage effect may be interpreted as due to the electrophoretic migration of salt ions, driven by an electrostatic force of attraction between the ions and the corresponding electrodes, not as due to the polarization via orientation of dipoles as in conventional insulators.

Figure 6 shows a result of a potentiometry carried out for LiCl-containing solutions of 40, 55, and 62.5 wt % HPC. Before the measurement, each sample was electrified continually for ∼180 min under a field strength of 4.5 V/15 mm in the H-type cell equipped with Pt electrodes. The time course of a potential change followed after cessation of the respective electrifications is plotted in the figure. Here it should be noted that there was a loss time of ∼1 min to set up the circuit in which a potentiometer (digital multimeter) was inserted, after the original circuit was once broken by separating from the electric source.

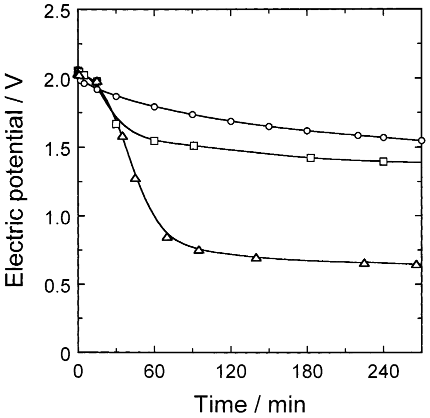

Figure 6. Electric potential change followed with an elapse of time for HPC/LiCl(0.5 M)/water solutions, after cessation of the application of an electric field of 4.5 V/15 mm for 180 min at 22 °C. HPC concentration: (○) 62.5 wt %; (□) 55 wt %; (△) 40 wt %.

As is evident from the plots, an electric discharge was observed in any of the three examples. The samples gave a value of ca. 2.05 V as an initial potential difference, regardless of HPC concentration. At the beginning stage of the respective measurements, however, there was a possibility of undetecting a process of very rapid potential decay to quench a steep gradient of the double layer in the close vicinity of each electrode. In the anisotropic solutions of 62.5 and 55 wt % HPC, the electric potential decreased gradually with the passage of time, while, in the isotropic one of 40 wt %, the potential decrease was comparatively rapid before 1 h passed, and then it became gradual. Even after a few hours elapsed, an appreciable quantity of electric charge appeared to be still stored in the respective systems, as is inferable from the presented data. Over this time period, colored arrays in the anisotropic samples and a turbid zone in the isotropic one were also reserved with a sparing relaxation. A higher level of residual potential observed with an increase in HPC concentration may be ascribed to a slower diffusion of salt ions dispersed in the medium of higher viscosity. In a continued process of discharging, it took 2−3 days for the salted samples to assume eventually a uniformly colored or transparent state.

The process of electric discharge was then compared between liquid-crystalline samples of 62.5 wt % HPC, each containing one of lithium salts at 0.5 M. The result is shown in Figure 7. We can readily see a difference in the extent of retention of the electric potential between the salted samples; e.g., at a 180 min lapse, a LiSCN-containing liquid crystal retains 1.23 V, lower by 0.40 V than the corresponding potential in the LiCl-containing one (the same as a sample shown in Figure 6). In an alternative measurement with an ammeter under the same situation, an electric current of less than few microamperes was on the respective closed circuits. The much lower magnitude of current reflects the higher resistance of the viscous cellulosic solutions.

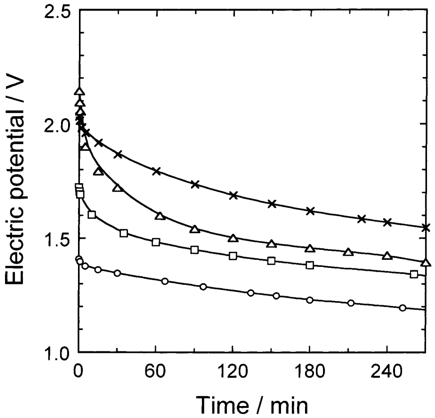

Figure 7. Electric potential change with time for aqueous HPC liquid crystals containing a series of lithium salts, compared at concentrations of 62.5 wt % HPC and 0.5 M salt. The condition of the measurements is the same as that applied to the examples shown in Figure 6. Anion species employed: (○) SCN^-; (□) I^-; (△) NO_3^-; (×) Cl^-.

Of particular interest in Figure 7 is the finding of the order of the activity of the four species of anions affecting the retention of the internal potential of the salted HPC cholesterics; viz., the order of Cl^-, NO_3^-, I^-, and SCN^- is just in accordance with that of the effectiveness of the ions in loosening the cholesteric twisting power. Visually, a slight rapid degradation of an array of different colors was perceived for the LiSCN-containing liquid crystal in comparison with the others, when the samples were allowed to stand continuously under discharging conditions. The highly chaotropic anion would lower the viscosity of the concentrated cellulosic solution to some degree, which acts as an advantage for diffusion of the ion particle itself in the medium, when compared with the existence of other anions with a lesser chaotropicity. Actually, the dependence of the viscosity on the anion species has recently been well confirmed in a rheo-optical study[16] dealing with shear deformation of salt-added liquid crystals of HPC.

Conclusion

Dynamic variations in the cholesteric coloration and optical turbidity of concentrated HPC solutions in salted water can be realized under the action of a relatively weak electric field, as has been demonstrated with two types of sample cells devised to interpose and electrify the solutions. The novel electrooptical property of this lyotropic system is due to the specific characteristics of the cellulosic polymer, i.e., the sensitive dependence of the cholesteric helical periodicity and of the LCST-type phase diagram on the species and concentration of the coexistent salt ions. The time-evolving gradation in color and/or turbidity observed during electrification is due to formation of an uneven distribution in salt concentration, which may be interpreted as an effect of the electrophoretic migration of ion particles as P and T_c-shifters in the viscous cellulosic medium. Even after the supply of electricity is stopped, the resulting ionic distribution does not appear to quickly disappear; actually, visual appearances of the electrified samples were mostly preserved for more than 1 week (but in an open circuit). The view is also supported by the observations of the time course of a residual potential difference for the samples being under discharge.

Acknowledgment. The authors wish to acknowledge Drs. T. Watanabe and H. Usui of Tokyo University of Agriculture and Technology, for their useful discussions. This work was partially financed by a Grant-in-Aid for Scientific Research on Priority Areas (A) (No. 11167219 to Y.N.) from the Ministry of Education, Culture, Sports, Science, and Technology, Japan.

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MA021522X