Helical aggregate formation of cholate salts in poly(N-vinyl-2-pyrrolidinone) gel and its effect on conductivity enhancement

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Abstract

The polymer gels (cross-linked poly(N-vinyl-2-pyrrolidinone) (c-PVP) containing sodium deoxycholate (NaDC) or sodium taurodeoxycholate (NaTDC), and N-methyl-2-pyrrolidinone (NMP) were prepared by radical polymerization using 2,2-dimethoxy-2-phenylacetophenone as a photoinitiator. Conductivity of the gels were measured as a function of temperature and cholate salt concentration. NaDC and NaTDC molecules in the c-PVP films formed aggregates above a concentration of $\sim 2 \times 10^{-2}$ mol kg^{-1} (per kg of gel) and $(8-9) \times 10^{-2}$ mol kg^{-1}, respectively. The conductivity of the NaDC/c-PVP gel increased from 7.73×10^{-8} to 2.88×10^{-6} S cm^{-1} with the formation of NaDC aggregates in the gel. The conductivity of the NaTDC/c-PVP gel also increased from 5.30×10^{-9} to 6.33×10^{-7} S cm^{-1}. Furthermore, the induced circular dichroism measurements of the surfactant gels containing bilirubin as a probe dye suggested that structure of aggregates in the gel is a helical structure. The conductivity jump is induced by an increase in number of charge carriers produced by increased dissociation of cholate salt molecules and formation of helical aggregates in the gel. © 1997 Elsevier Science S.A.

Keywords. Conductivity, Gel, Cholate salts, Aggregation, Electrolytes

1. Introduction

Polymer gel electrolytes containing organic co-solvents have been used in various electrochemical devices, such as batteries and display devices [1–6]. Interactions of electrolyte salts with itself, polymer, and co-solvent are important factors which determine the conductivity and other properties of the gel electrolytes. The design of the polymer matrix and the electrolyte salt based on this idea are very important parameters to prepare high conducting polymer electrolytes. However, the design of the electrolyte salt has been rarely investigated. We think that the surfactant is one of the candidates for such interactive electrolyte salts. Furthermore, the aggregation behavior of surfactants in solutions containing polymer has been studied to elucidate specific interactions between surfactant molecules and polymer chains [7]. Dissolved polymer affects the aggregation number of a micelle, the critical micelle formation concentration (CMC), and other physical properties of the solution. We have reported the preparation of polymer gel films containing surfactant as

the electrolyte salt and their properties, especially the conductivity enhancement by aggregate formation in the gel [8–10]. In those reports we observed the aggregate formation of sodium deoxycholate (NaDC) playing the key role in conductivity enhancement. In this paper we report the aggregation structure of NaDC or sodium taurodeoxycholate (NaTDC) in the gel being estimated by induced circular dichroism (CD) measurements for bilirubin (BR) in the cholate salt/c-PVP gels and the effect of the aggregate formation on conductivity.

2. Experimental

2.1. Materials

Monomer (N-vinyl-2-pyrrolidinone) and solvent (N-methyl-2-pyrrolidinone, NMP) were purchased from Ishizu and used as received. Surfactants (sodium deoxycholate (NaDC) (Ishizu) and sodium taurodeoxycholate (NaTDC, Fluka)) (Fig. 1) were also purchased and used without further purification.

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Sodium deoxycholate (NaDC)
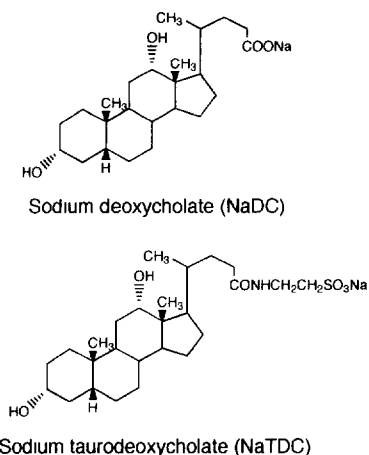
Sodium taurodeoxycholate (NaTDC)

Fig. 1. Structure of sodium deoxycholate (NaDC) and sodium taurodeoxycholate (NaTDC)

2.2. Preparation of polymer gel film containing surfactant

The detail preparation of a polymer gel film containing surfactant was described in our previous papers [8–10]. A mixture of N-vinyl-2-pyrrolidinone (0.01 mol), N-methyl-2-pyrrolidinone (0.005 mol), N,N'-methylenebisacrylamide (3×10^{-4} mol) as a cross-linking reagent, and 2,2-dimethoxy-2-phenylacetophenone (5×10^{-5} mol) as an initiator was prepared. Between 1.48×10^{-8} and 4×10^{-4} mol of surfactant was also added to the solution. The solution was irradiated by a UV lamp and polymerized for 1 h at room temperature (20 to 25 °C). Gel films containing Eosin Y or BR as a probe (spectral change method, 5×10^{-7} mol, CD measurements 2×10^{-8} mol) were similarly prepared and used for some measurements. Unless specified otherwise, all gel films had the same composition except for the surfactant content. The surfactant content is cited as molal concentration of surfactant, for example, the surfactant concentration of the gel presented as 0.1 mol kg^{-1} means that the gel contains 0.1 mol of surfactant per 1 kg of gel.

2.3. Measurements

UV/visible spectra of the solution and the gel containing dye were measured with a Shimadzu UV-2200 spectrophotometer at room temperature (20 to 25 °C). CD spectra were recorded on a JASCO J-20 spectropolarimeter by flushing with dry nitrogen during the experiments.

2.4. Conductivity measurements of gel films

The conductivity of the gel film was measured with a two-probe method after the gel film was sandwiched between two stainless-steel plates and set in the thermostat chamber. All measurements used an a.c. impedance system (HZ-1AC, Hokuto Denko).

3. Results and discussion

3.1. Aggregation behavior of sodium deoxycholate and sodium taurodeoxycholate in the polymer gel

Cholate salts such as NaDC, NaTDC form aggregates (micelle or higher ordered structure) in aqueous solutions [11–15]. However, their aggregation behavior in organic solutions or organo gels has not been investigated. We checked the formation of aggregates of NaDC or NaTDC in N-methyl-2-pyrrolidinone (NMP) or cross-linked poly-(N-vinyl-2-pyrrolidinone) (c-PVP) gel by spectral change method. Fig. 2 show the relationship between the molal concentration of NaDC or NaTDC and the wavelength of maximum absorbance for Eosin Y in the c-PVP gel. The peak of Eosin Y in the c-PVP film without surfactant was 540–542 nm. In the c-PVP film containing NaDC the peak shifted to shorter wavelength with increase in concentration. The blue shift for Eosin Y from 540 nm to 531 nm was observed in the NaDC concentration range from 2×10^{-2} to 1×10^{-1} mol kg^{-1}. Hirano [16,17] reported that the electronic bands of Eosin Y are shifted by dispersion force and/or hydrogen bond interaction between Eosin Y and the solvent. Thus, the blue shift of the peak for Eosin Y in the surfactant solution is induced by a change in the environment around the Eosin Y molecules. At low surfactant concentration the Eosin Y is dispersed homogeneously in the c-PVP gel. At high surfactant concentrations (over the critical aggregate formation concentration) the Eosin Y molecules are incorporated into the aggregates of surfactant and surrounded by the surfactant molecules. Therefore, formation of molecular assemblies of NaDC in c-PVP film is suggested.

Peak shift for Eosin Y was also observed in the c-PVP gel containing NaTDC. The peak shifted to longer wavelength with an increase in concentration of NaTDC. The red shift for Eosin Y from 542 to 546 nm was observed in the NaTDC concentration range from 3×10^{-2} to 3×10^{-1} mol kg^{-1}. The red shift suggests that the formation of aggregates in the gel and main interaction between Eosin Y and NaTDC is dispersion force interaction [16,17].

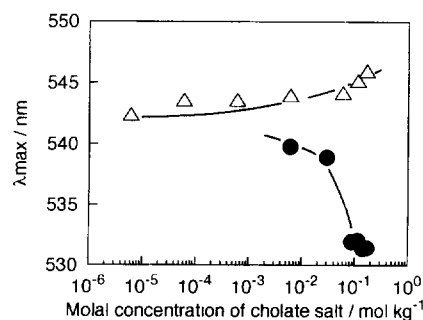NaDC or NaTDC molecules in aqueous solution form a polymer-like aggregation (helical complex) [11–15]. Inter-

Fig. 2. Variation of λ_{max} of eosin Y with molal concentration of cholate salt. (●) sodium deoxycholate (NaDC), (△) sodium taurodeoxycholate (NaTDC) in cross-linked poly(N-vinyl-2-pyrrolidinone) (c-PVP) gel.
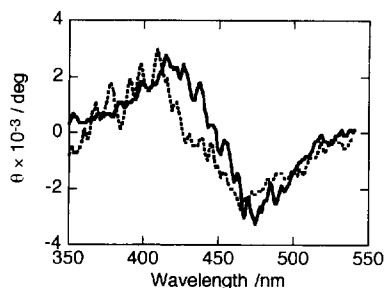
Fig. 3. Circular dichroism spectra of bilirubin in (————) NaDC/c-PVP gel and (- - -) in NaDC/NMP solution. Molal concentration of NaDC is 1 14×10⁻¹ mol kg⁻¹ in gel and 9.51 × 10⁻² mol kg⁻¹ in solution.

actions between the helical complex and dye have been investigated by means of CD measurements [13–15]. In the paper, BR was used as a probe dye and the relationships between the induced Cotton effect of BR and helical structure of cholate salts was reported. We applied this method to our organo gel system. Fig. 3 shows the CD spectra of NaDC/c-PVP and NaDC/NMP solution containing BR as a probe. The concentration of NaDC is enough high to form aggregates in the systems. As shown in Fig. 3, a bisignate Cotton effect was observed in the NMP solution and the c-PVP gel containing NaDC. This suggests that the aggregate structure in the solution and the gel is chiral helical one.

Fig. 4 shows the CD spectra of NaTDC/c-PVP and NaTDC/NMP solution containing BR as a probe. A bisignate Cotton effect was observed in the NaTDC/c-PVP gel, however, not observed in the NaTDC/c-PVP solution. Polymer chain may play the important role in the formation of the helical aggregates of NaTDC in the NMP system, However, the detailed mechanism of formation of those aggregates in the gel is not clear from this study.

3.2. Conductivity versus concentration of NaDC or NaTDC in polymer gel film

The conductivity of NaDC/c-PVP and NaTDC/c-PVP gel was measured by the a.c. impedance technique. Fig. 5 shows the relationships between the NaDC or NaTDC concentration and the conductivity (at 20 °C) for the systems. At low cholate salt concentrations, the conductivity of the gels increased linearly with an increase in molal concentration of
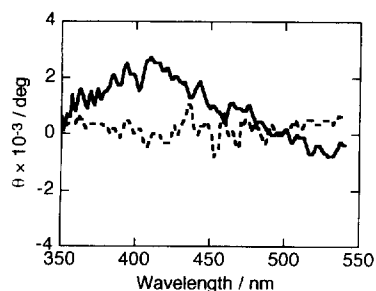

Fig. 4. Circular dichroism spectra of bilirubin in (————) NaTDC/c-PVP gel and (- - -) NaTDC/NMP solution. Molal concentration of NaTDC is 1.13×10⁻¹ mol kg⁻¹ in gel and 9.76 × 10⁻² mol kg⁻¹ in solution.
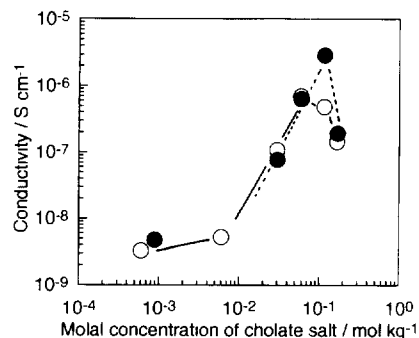

Fig. 5. Variation of conductivity at 20 °C with molar concentration of cholate salts in c-PVP gel: (●) NaDC/c-PVP gel, and (○) NaTDC/c-PVP gel.

cholate salt. Above $\sim 3 \times 10^{-2}$ mol kg⁻¹, the conductivity of the NaDC/c-PVP gel increased dramatically (from 7.73×10^{-8} S cm⁻¹ to 2.88×10^{-6} S cm⁻¹, a factor of 37). The conductivity of the NaTDC/c-PVP gel increased in a similar manner as of the NaDC/c-PVP gel. Above $\sim 1 \times 10^{-2}$ mol kg⁻¹, the conductivity increased from 5.30×10^{-9} to 6.33×10^{-7} S cm⁻¹, a factor of 119. This cholate salt concentration suggests that the increase in conductivity is based on the formation of aggregates in the gel. However, the conductivity decreases with a further increase in concentration above 0.1 mol kg⁻¹, possibly because of the formation of triple ions of NaDC or NaTDC and the resultant decrease in number of charge carriers.

To estimate the activation energy of conduction and the number of charge carriers in the gel, the temperature dependence of conductivity for the cholate salt/c-PVP gel was measured. The relationships between $1/T$ and the logarithm of the conductivity for gels with various content of salts show an almost linear dependence. The apparent activation energy, E_a, and frequency constant, A, of the gel and the solution systems are estimated based on an Arrhenius-like relationship and listed in Table 1.

The value of A was 2.4×10^1 S cm⁻¹ at 8.9×10^{-4} mol kg⁻¹ (before aggregate formation) and 6.3×10^6 S cm⁻¹ at 3.0×10^{-2} mol kg⁻¹ (after aggregate formation) in the NaDC/c-PVP gel [9] and 6.9×10^3 S cm⁻¹ at 6.0×10^{-5} mol kg⁻¹ (before aggregate formation) and 1.5×10^7 S cm⁻¹ at 3.0×10^{-2} mol kg⁻¹ (after aggregate formation) in the NaTDC/c-PVP gel. The A value in the gels increased after the aggregate formation. The conductivity, σ, is usually as

Table 1
Frequency constant and activation energy of cholate salt/c-PVP gels

Samples	Molal concentration (mol kg⁻¹)	Frequency constant (S cm⁻¹)	Activation energy (kJ mol⁻¹)
NaDC/c-PVP	8.9×10^{-4}	2.4×10^1	55.2
	3.0×10^{-2}	6.3×10^6	77.9
	1.3×10^{-1}	4.6×10^6	68.5
NaTDC/c-PVP	6.0×10^{-5}	6.9×10^3	142
	3.0×10^{-2}	1.5×10^7	182
	5.8×10^{-2}	1.6×10^8	188

$$\sigma = \Sigma n_i e_i \mu_i$$

(i = anion, cation, and other charge carriers) (1)

where n_i is the numbers of charge carrier, e_i is the charges of the carrier (in this case $e_{anion} = e_{cation} = 1$), and μ_i is the mobility of the carrier. The microviscosity of the gel affects the mobility of the ions and chemical species in the gel and can be estimated by fluorescence depolarization measurement, whereby changes in mobility of the dye in the gel are detected. Thus, the mobility of the co-existing ion can be also estimated. The results reported in our previous paper [9] indicated that the change in gel microviscosity, i.e., the change in mobility of charge carriers in the gel was not observed in the NaDC/c-PVP gel film.

The frequency factor, A, proportional to the number of charge carriers, increased after the aggregate formation as shown in Table 1, implying that the conductivity enhancement is caused by an increase in number of charge carriers in the gel. The mechanism of the increase in number of charge carriers is considered below. The presence of polymer in the system affects the increase in conductivity. Cholate salt molecules form aggregates along the polymer chains with interaction between cholate salts and PVP polymer chains, such as hydrogen bond, hydrophobic interaction. The aggregation of cholate salt molecules brings about their dissociation into cations and anions. Thus, the number of carriers in the gel increases, and the conductivity of the gel also increases over the critical aggregate formation concentration of NaDC or NaTDC. However, the detailed mechanism of the enhancement of dissociation is not clarified; we believe that the specific environment formed by cross-linked polymer chains is closely related to the mechanism. Helical aggregate structure produced in the gels may also affect the ionic conducting behavior in the polymer gel. The large size aggregates may behave as flexible spacers between polymer chains in the gels and accelerate the local movement of the polymer chains.

The conductivity enhancement of polymeric solid electrolytes should be assisted by a choice of the electrolyte salt based on its interaction with the polymer matrix, such as hydrogen bonding or hydrophobic interaction.

References

[1] M. Armand, Adv. Mater., 2 (1990) 278–286.
[2] P.G. Bruce and C A. Vincent, J. Chem. Soc., Faraday Trans., 89 (1993) 3187–3203
[3] F M Gray, Solid Polymer Electrolytes, Fundamentals and Technological Applications, VCH, Weinheim, 1991.
[4] O. Bohnke, C. Rousselot, P.A. Gillet and C. Truche, J. Electrochem. Soc., 139 (1992) 1862–1865.
[5] R. Xue, H Huang, M. Menetrier and L. Chen, J. Power Sources, 43–44 (1993) 431–438.
[6] M. Alamgir and K.M. Abraham, J. Electrochem. Soc., 140 (1993) 96–97.
[7] E.D. Goddard and K.P. Ananthapadmanabhan (eds.), Interactions of Surfactants with Polymers and Proteins, CRC Press, Boca Raton, FL, 1993.
[8] H. Tsutsumi, S. Hamamoto, M. Morita and Y. Matsuda, J. Polym. Sci.: Part A. Polym. Chem., 31 (1993) 2883–2886
[9] H Tsutsumi and H Doi, J. Electrochem. Soc., 142 (1995) 4215–4218.
[10] H. Tsutsumi, H Doi and T. Oishi, Electrochim. Acta, 41 (1996) 345–347.
[11] A. Rich and D.M. Blow, Nature, 182 (1958) 423–426.
[12] D.M. Blow and A. Rich, J. Am. Chem. Soc., 82 (1960) 3566–3571.
[13] A.R. Campanelli, S C. De Sanctis, E. Chiessi, M. D'Alagni, E. Giglio and L. Scaramuzza, J. Phys. Chem., 93 (1989) 1536–1542.
[14] M. D'Alagni, M. Delfini, L. Galantini and E Giglio, J. Phys. Chem., 96 (1992) 10520–10528.
[15] M. D'Alagni, A.A. D'Archivio, E. Giglio and L. Scaramuzza, J. Phys. Chem, 98 (1994) 343–353.
[16] K. Hirano, Nippon Kagaku Kaishi, (1978), 481–488.
[17] K. Hirano, Nippon Kagaku Kaishi, (1980), 675–680.