ELSEVIER

Polymer 43 (2002) 2255–2260

polymer

www.elsevier.com/locate/polymer

Formation of amphiphilic complexes of cationic polyelectrolyte carrying pendant saccharide residue with anionic surfactants

Tomoyuki Itaya*

Laboratory of Chemistry, Department of General Education, Nagano National College of Technology, Nagano 381-8550, Japan

Received 31 August 2001; received in revised form 6 December 2001; accepted 17 December 2001

Abstract

The formation of amphiphilic complexes of poly(allylammonium chloride) carrying pendant maltose residue (PAAHCl-Mal) with sodium alkylsulfonates (sodium octanesulfonate (NaOcS), sodium dodecanesulfonate (NaDoS), sodium hexadecanesulfonate (NaHeDeS)) in aqueous solution was studied by means of turbidimetry, fluorescence spectroscopy using pyrene, ^{1}H NMR and viscometry. In contrast to the complex of PAAHCl homopolymer with NaDoS, which precipitated at the ratio of the concentration of DoS to the concentration of ammonium group in the polymer, $[\text{DoS}]/[\text{NH}_3^+] = 0.01$, the complexes of PAAHCl-Mal(14) containing 14 mol% maltose residue with NaDoS are water-soluble over the whole range of compositions of the mixture, including the electroneutralized condition, $[\text{DoS}]/[\text{NH}_3^+] = 1$. In the mixture of PAAHCl-Mal(14) and NaDoS at $[\text{DoS}]/[\text{NH}_3^+] = 1$, the ratio ($I_3/I_1$) of the intensities of third and first vibrational bands of pyrene was 0.83, indicating that the complexation of PAAHCl-Mal(14) with NaDoS gives rise to a hydrophobic domain. In addition to these results, from ^{1}H NMR and viscosity measurements of the PAAHCl-Mal(14) and NaDoS system, it seems that these species form a micelle like aggregate with a hydrophobic core from the surfactants bound to the polymer and a hydrophilic outer shell from the maltose residues. Moreover, the effects of content of maltose residue in the polymer and alkyl chain length of surfactant on the complexation of PAAHCl-Mal with alkylsulfonates are discussed. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Sugar-containing polycation; Anionic surfactant; Polyelectrolyte–surfactant aggregate

1. Introduction

Polymer–surfactant complexes formed between polyions and oppositely charged ionic surfactants are a subject of intensive investigations [1–3]. The complexes have a hydrophobic domain from clusters of surfactant bound to the polymer chain, and the hydrophobic domain can be utilized as reaction field involving solubilization [4–6]. However, stoichiometric complexes that contain equivalent amounts of the charged polyion units and surfactant counterions are water-insoluble. Owing to this, the application of polyelectrolyte–surfactant complexes in aqueous media is rather limited.

A novel family of polymer–surfactant complexes formed by poly(ethyleneoxide)-*graft*-poly(ethyleneimine) and alkyl sulfates has recently been reported [7]. These systems are water-soluble and can form a microphase composed of the surfactant alkyl chains surrounded by a shell from poly(ethyleneoxide) segments. On the other hand, linear polymers containing carbohydrate residues which are covalently linked to the backbone represent an important class of macromolecules and have found broad applications [8–14]. If a polyelectrolyte carrying pendant carbohydrate residue were mixed with oppositely charged ionic surfactant in water, the resulted novel amphiphilic polyelectrolyte–surfactant complex would be expected to possess water-solubility. In addition, the amphiphilic polyelectrolyte–surfactant complex may be utilized as material for separator and solubilization.

The present study aims to construct a water-soluble amphiphilic structure by combining hydrophobic domain formed from the surfactants bound to polyelectrolyte and hydrophilic saccharide residues. We chose poly(allylammonium chloride) (PAAHCl) as the polyelectrolyte, because the polymer has a side chain containing primary amino group and is convertible to various functional polymers by chemical modification [15–17]. In this study, the complexation behavior of PAAHCl carrying pendant maltose residue (PAAHCl-Mal) and sodium alkylsulfonates in aqueous solution was investigated by means of turbidimetry,

---

* Tel./fax: +81-26-295-7028.
E-mail address: itaya@ge.nagano-nct.ac.jp (T. Itaya).

PII: S0032-3861(02)00023-X

fluorescence spectroscopy using pyrene, ^{1}H NMR and viscometry.

2. Experimental section

2.1. Materials

PAAHCl was supplied by Nitto Boseki Co. Ltd. It was purified by reprecipitation with methanol containing 0.5 M HCl. The weight-molecular weight was determined by light scattering to be 1.0×10^5 in 0.2 M NaCl solution [18]. PAAHCl with pendant maltose residue (PAAHCl-Mal) was accomplished by reacting amino groups on poly(allylamine) with maltoselactone [19]. A formamide solution (40 ml) of PAAHCl (1.0 g) containing NaOH equimolar to ammonium group in the polymer was added to a formamide solution (10 ml) of maltoselactone at two different molar ratios of maltoselactone to amino group in the poly(allylamine) (1:5 and 1:2). The reaction mixture was stirred for 10 h at 40 °C under nitrogen atmosphere, and was dialyzed against water, and then the solution was concentrated. The resulted product precipitated by the addition of methanol containing HCl and the polymer was dried in vacuo. The ^{1}H NMR spectra of two polymers exhibit the presence of an amide group (8.40 ppm), indicating the successful reaction of poly(allylamine) with maltoselactone. In addition, from ^{1}H NMR spectra in D_2O at 80 °C, the content of maltose residue in the polymers was determined to be 6 and 14 mol%, respectively. Fig. 1 shows the chemical structure of the polymers, which are coded as PAAHCl-Mal(x), where x represents the mol% content of maltose residue in the polymers. The molecular weights of PAAHCl-Mal(6) and PAAHCl-Mal(14) estimated from viscometric measurements in aqueous 0.050 M NaCl solution using the relation $[\eta] = 2.40 \times 10^{-3}\ \mathrm{M}^{0.975}$, which has brought forward for PAAHCl in aqueous 0.050 M NaCl solution [20], are approximately 9.2×10^4 and 8.5×10^4, respectively.

The anionic surfactants, sodium hexadecanesulfonate (NaHeDeS), sodium dodecanesulfonate (NaDoS), and sodium octanesulfonate (NaOcS) were obtained from Tokyo Kasei Co. Ltd and were used without further purification. Pyrene (Tokyo Kasei) was purified by recrystallization from ethanol. Deionized and distilled water was used as the solvent.

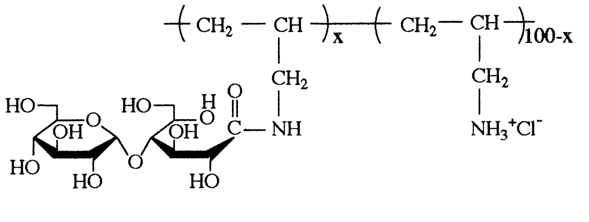


Fig. 1. Chemical structure of PAAHCl-Mal.

2.2. Measurements

The turbidity measurements were carried out using a Shimadzu UV-260 spectrophotometer at 450 nm after equilibration of the sample solutions. Steady-state fluorescence spectra were recorded on a Shimazu RF-5000 spectrofluorometer. Pyrene used as the fluorescent probe was excited at 325 nm. The sample solutions were prepared by adding known amounts of pyrene in acetone to empty vials. After acetone evaporation, measured amounts of polymer and surfactant solutions were added to the vials. The pyrene concentration in the final solution was 1×10^{-6} M. ^{1}H NMR spectra were measured at 400 MHz on a JEOL EX-400 spectrometer at 27 °C in D_2O. The chemical shifts were given in ppm relative to the external tetramethylsilane standard. Viscosity was measured at 30 °C with a modified Ubbelhode capillary viscometer.

3. Results and discussion

3.1. Complexation of PAAHCl-Mal with NaDoS

Fluorescence probe techniques using pyrene have been performed to detect the occurrence of polymer/surfactant interactions and to characterize the polymer/surfactant aggregates [21–24]. The pyrene is known to show the well-characterized long-lived excited state, the sensitivity of vibrational fine structure shifts to microenvironment polarity, and the propensity for forming excimers [25,26]. The ratio of the third to the first vibrational bands (I_3/I_1) in the fluorescence spectra of pyrene reflects the polarity in local media where pyrene exists, i.e. I_3/I_1 ratio being larger in less polar media [27]. The fluorescence spectrum of pyrene in water was not influenced by the addition of PAAHCl-Mal(14) ($[\mathrm{NH}^{3+}] = 1.00 \times 10^{-2}$ M). The I_3/I_1 ratio was 0.54 for both water and aqueous PAAHCl-Mal(14) systems. On the other hand, the fluorescence intensity and the I_3/I_1 ratio of pyrene in aqueous PAAHCl-Mal(14) solution ($[\mathrm{NH}^{3+}] = 1.00 \times 10^{-2}$ M) increased by the addition of NaDoS. The I_3/I_1 ratios for the PAAHCl-Mal(14)–NaDoS (1.00×10^{-4} M) and PAAHCl-Mal(14)–NaDoS (1.00×10^{-2} M) systems are estimated to be 0.76 and 0.83, respectively. This observation indicates that the pyrene molecule is localized in a less polar environment. In addition, in the PAAHCl-Mal(14)–NaDoS (1.00×10^{-4} M) system, the excimer fluorescence of pyrene was also observed. Therefore, the interaction between PAAHCl-Mal(14) and NaDoS provides a hydrophobic region to guest pyrene.

Turbidity and the I_3/I_1 ratio for the PAAHCl-Mal(14)–NaDoS and PAAHCl–NaDoS systems are plotted as a function of NaDoS concentration in Fig. 2. The interaction between polyions and oppositely charged surfactants is characterized by a ‘critical association concentration’ (cac). Above the cac, pyrene incorporates into the nonpolar

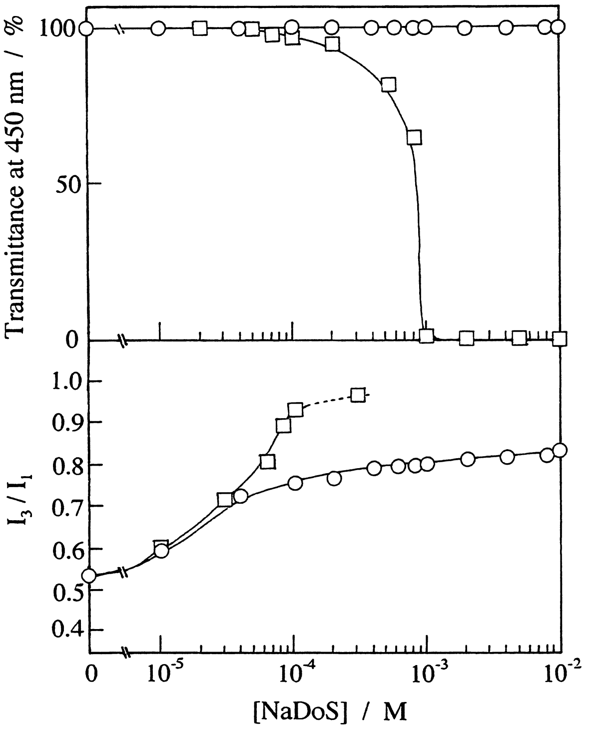


Fig. 2. Plots of the transmittance and the I_3/I_1 ratio of the intensities of the third and first vibrational bands for pyrene (1.00×10^{-6} M) of the PAAHCl-Mal(14) ($[NH_3^+] = 1.00 \times 10^{-2}$ M)–NaDoS (○) and PAAHCl homopolymer ($[NH_3^+] = 1.00 \times 10^{-2}$ M)–NaDoS (□) systems as a function of NaDoS concentration.

microphase formed by the surfactant alkyl groups, leading to the increase in the I_3/I_1 ratio. Generally, it has been reported that the aggregate of polyion with surfactant is formed at concentrations one or two orders less than the critical micelle concentration (c.m.c.) of the corresponding surfactant [22]. The cac value for the PAAHCl-Mal–NaDoS system was practically the same as that for the PAAHCl homopolymer–NaDoS system. In both systems, the aggregation between the polymers and NaDoS begins to occur approximately at $[\text{NaDoS}] = 1.00 \times 10^{-5}$ M, which is about three orders lower than the c.m.c. (8×10^{-3} M) of NaDoS itself. Thus, it seems that this aggregation is assisted by stronger electrostatic forces and more cooperative hydrophobic effects among bound surfactant anions [24].

The I_3/I_1 ratio of the PAAHCl-Mal(14)–NaDoS mixture is lower than that of the PAAHCl–NaDoS mixture. This suggests that the hydrophobic domain of the PAAHCl-Mal(14)–NaDoS complex is loose compared to that of the PAAHCl–NaDoS complex due to the separation of positive charges on the polymer backbone by the introduction of maltose residues.

As shown in Fig. 2, addition of NaDoS to PAAHCl-Mal(14) in water exhibits a different solution turbidity behavior than that for the solution of PAAHCl homopolymer and NaDoS. Upon addition of increasing amounts of NaDoS to the solution of PAAHCl, we observed an increase in the turbidity of the solutions above very low NaDoS concentrations. For example, the onset of turbidity was observed for an aqueous PAAHCl solution ($[NH^{3+}] = 1.00 \times 10^{-2}$ M) at approximately $[\text{NaDoS}] = 1.00 \times 10^{-4}$ M. Further addition of NaDoS to the PAAHCl solution results in the formation of precipitates. This type of behavior is well-known for addition of an oppositely charged surfactant to an aqueous solution of polyelectrolyte [28,29]. On the other hand, the complexes of PAAHCl-Mal(14) with NaDoS are water-soluble over the whole range of compositions of the mixture, including the electronuetralized condition ($[\text{NaDoS}] = 1.00 \times 10^{-2}$ M). It seems that the acquisition of water-solubility of the complexes between PAAHCl-Mal(14) and NaDoS is caused by the introduction of hydrophilic maltose residues into PAAHCl.

3.2. Effect of maltose residue content in the polymer on the complexation between PAAHCl-Mal and NaDoS

Fig. 3 shows the effect of maltose residue content in the polymer on the I_3/I_1 and I_E/I_M ratios for the mixtures of PAAHCl-Mal and NaDoS. The I_E/I_M ratio as well as the I_3/I_1 ratio were used as a measure of the interaction between PAAHCl-Mal and NaDoS. The I_E/I_M ratio first increases and reaches a maximum, and then decreases in all systems. The increase in the I_E/I_M ratio is explained by

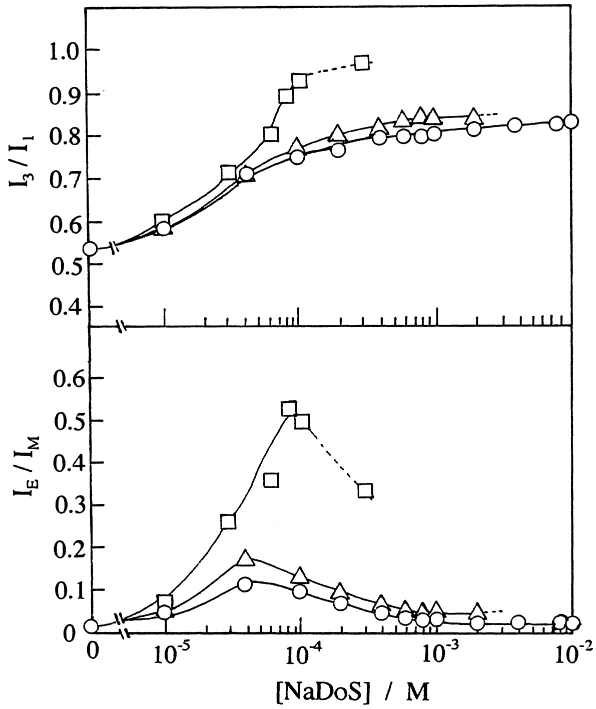


Fig. 3. Effect of substitution of maltose residue in the PAAHCl-Mal on the I_3/I_1 ratio and I_E/I_M ratio for pyrene (1.00×10^{-6} M) in aqueous PAAHCl-Mal ($[NH_3^+] = 1.00 \times 10^{-2}$ M) solution as a function of NaDoS concentration. I_M and I_E are the fluorescence intensity at 374 and 480 nm, respectively. (□); the PAAHCl–NaDoS system, (△); the PAAHCl-Mal(6)–NaDoS system, (○); the PAAHCl-Mal(14)–NaDoS system.

the incorporation of pyrene molecules into a hydrophobic domain of the complex of PAAHCl-Mal with NaDoS and the close proximity of pyrene pairs. The decrease in the I_E/I_M ratio at higher concentrations of NaDoS appears to suggest the separation of pyrene pairs, which is accomplished by the enlargement of hydrophobic domain of the polyion–surfactant complexes.

In the PAAHCl-Mal(6)–NaDoS system, the turbidity was observed at $[\text{NaDoS}] > 3.00 \times 10^{-3}$ M. On the contrary, the complexes of PAAHCl-Mal(14) with NaDoS are water-soluble over the whole range of composition of the mixture. This solubility behavior was reproducible on repeated runs. Although the author does not have the data for polymers with more than 14 mol% maltose residue, the balance between hydrophilic maltose residues and the hydrophobicity of added surfactant seems to be important to form water-soluble amphiphilic complex with hydrophobic domain.

3.3. Effect of alkyl chain length of surfactant on the complexation between PAAHCl-Mal and alkylsulfonates

Effect of the alkyl chain length of surfactant on the complexation between PAAHCl-Mal(14) and sodium alkylsulfonates is shown in Fig. 4, where the I_3/I_1 and I_E/I_M ratios were plotted as a function of the surfactant concentration. The data show that the complexation is dependent on the alkyl chain length, i.e. the cac of PAAHCl-Mal(14) with alkylsulfonates decreased with increasing the alkyl chain length. In the PAAHCl-Mal(14)–NaOcS system, the change of the I_E/I_M ratio was not observed almost. In addition, the I_3/I_1 ratio of the PAAHCl-Mal(14)–NaOcS system was lower than that of PAAHCl-Mal(14)–NaDoS and PAAHCl-Mal(14)–NaHeDeS systems in the all range of the surfactant concentration examined. These results indicate that the combination of PAAHCl-Mal(14) with NaOcS could not form an effective hydrophobic domain. On the other hand, PAAHCl-Mal(14) ($[\text{NH}_3^+] = 1.00 \times 10^{-2}$ M) precipitated at $[\text{NaHeDeS}] = 1.00 \times 10^{-3}$ M, suggesting that the hydrophobicity of HeDeS is superior to the hydrophilicity of PAAHCl-Mal(14). Taking into account the balance between hydrophilicity of maltose residues and hydrophobicity of surfactant, the combination of PAAHCl-Mal(14) with NaDoS is suitable for our purpose of this study, which is to construct a water-soluble amphiphilic complex.

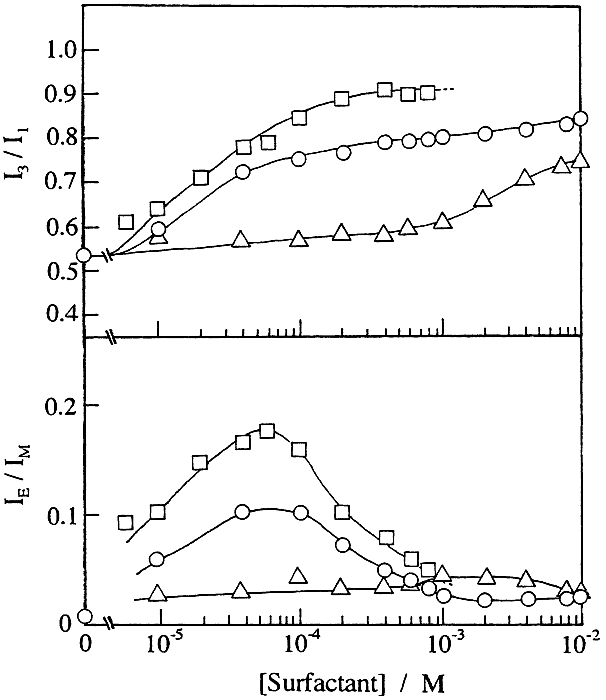


Fig. 4. Effect of alkyl chain length of the surfactant on the I_3/I_1 ratio and the I_E/I_M ratio of the intensities of the excimer and monomer band for pyrene (1.00×10^{-6} M) in aqueous PAAHCl-Mal(14) ($[\text{NH}_3^+] = 1.00 \times 10^{-2}$ M) solution as a function of surfactant concentration. (□); the PAAHCl-Mal(14)–NaHeDeS system, (○); the PAAHCl-Mal(14)–NaDoS system, (△); the PAAHCl-Mal(14)–NaOcS system.

3.4. Structure of the complex composed of PAAHCl-Mal and NaDoS

We performed the ^{1}H NMR and viscosity measurements of the PAAHCl-Mal(14) and NaDoS mixture in order to clarify the structure of complex between PAAHCl-Mal and NaDoS. ^{1}H NMR spectroscopy and viscosity measurements provide qualitative information on the motional restrictions owing to the aggregation of the hydrophobic residues and on the conformation of polymer chain, respectively [30,31].

Fig. 5 compares the ^{1}H NMR spectra of NaDoS, PAAHCl-Mal(14), and the mixture of PAAHCl-Mal(14) and NaDoS in D_2O. In Fig. 5(a), all signals of NaDoS can be observed with sharp. Upon the complexation of PAAHCl-Mal with NaDoS, the mobility of DoS clearly decreases, as can be observed in a broadening of the corresponding NMR signals for the mixture of PAAHCl-Mal and NaDoS (Fig. 5(c)). The signals of polymer main and side chains for PAAHCl-Mal(14) also seem to become broadening upon the complexation, but the signals of maltose residue were not almost affected by the complexation. These are supported the integral ratio of maltose residue (i), polymer side chain (h), and methylene group (b) at 1.8 ppm of NaDoS is 1:0.64:0.65 (theoretical ratio is 1:1.10:0.94) for the PAAHCl-Mal(14)–NaDoS system. Thus, from these results, it seems likely that the hydrophobic surfactant alkyl chains are densely packed in the complex, and that the hydrophilic maltose residues are expose to bulk water phase.

Fig. 6 shows the variation of the reduced viscosity of PAAHCl-Mal(14) as a function of NaDoS concentration. The drastic decrease in viscosity was observed by the addition of NaDoS. The addition of equivalent amounts of NaDoS (1.00×10^{-3} M) was reduced to one over 15th its

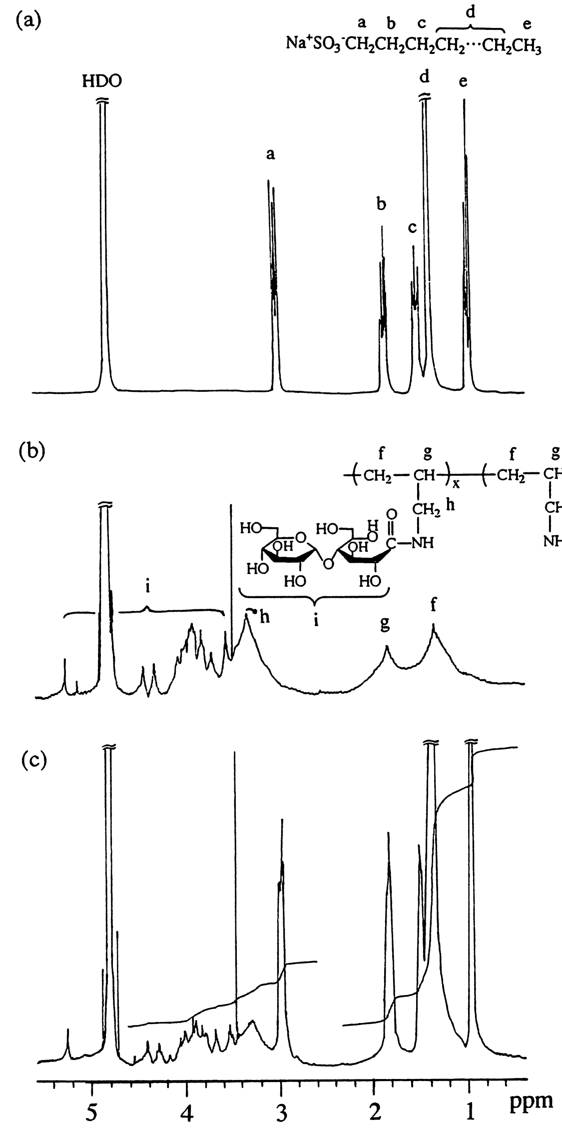


Fig. 5. ^{1}H NMR spectra (in D_2O) of NaDoS (1.00×10^{-2} M) (a), PAAHCl-Mal(14) ($[NH_3^+] = 1.00 \times 10^{-2}$ M) (b) and the PAAHCl-Mal(14) ($[NH_3^+] = 1.00 \times 10^{-2}$ M) and NaDoS (1.00×10^{-2} M) mixture (c).

initial viscosity of PAAHCl-Mal(14) in pure water. This result indicates that the complex between PAAHCl-Mal(14) and NaDoS takes a compact conformation. The decrease in viscosity of PAAHCl-Mal(14) upon addition of NaDoS is attributed to a coiling of the initially more extended polymer chain due to the hydrophobic interaction of the surfactants bound to the polycation [31].

Taking into considerations the results of turbidimetry, fluorescence spectra using pyrene, ^{1}H NMR and viscometry, it seems reasonable to assume that PAAHCl-Mal(14) and NaDoS form a micelle like aggregate with both a hydrophobic core from the surfactants bound to the polycation and a hydrophilic shell from the maltose residues (Scheme 1). This amphiphilic structure causes the complex to be water-soluble. The application of the complex to drug and gene delivery systems is underway.

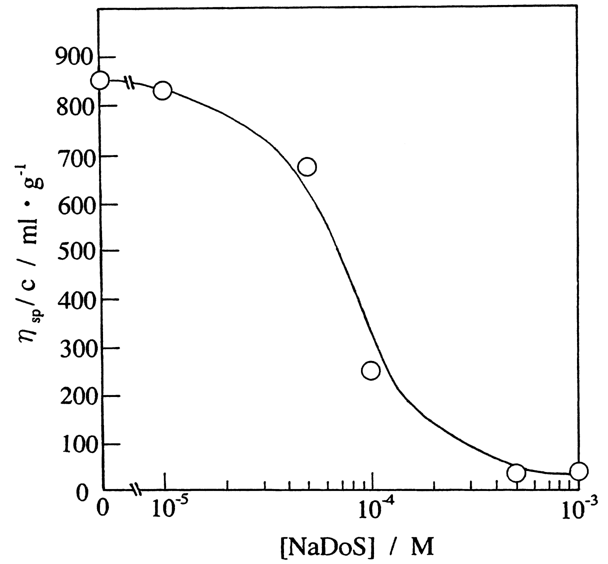
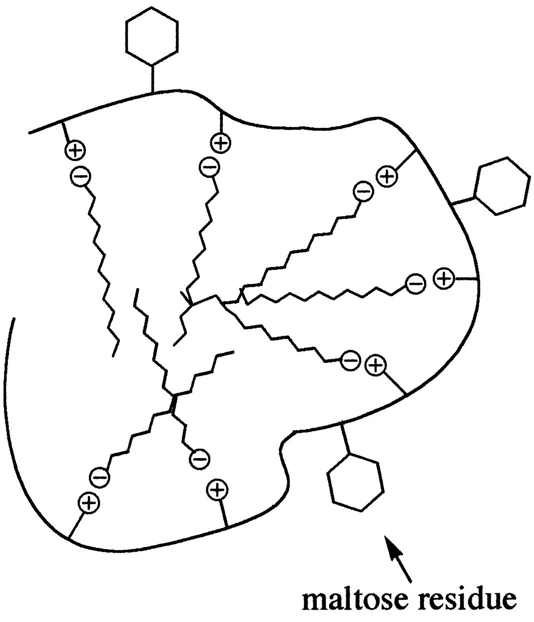


Fig. 6. Variation of reduced viscosity of PAAHCl-Mal(14) (1.58×10^{-4} g ml^{-1} ($[NH_3^+] = 1.00 \times 10^{-3}$ M)) as a function of NaDoS concentration.

4. Conclusions

The polycations (PAAHCl-Mal) carrying pendant maltose residue were prepared by the reaction of poly(allylamine) with maltoselactone. The complexation between PAAHCl-Mal and alkylsulfonates is influenced by the content of maltose residue in PAAHCl-Mal and the alkyl chain length of alkylsulfonates. The complex composed of PAAHCl-Mal(14) containing 14 mol% maltose residue and sodium dodecylsulfonate (NaDoS) was water-soluble in



Scheme 1. Schematic illustration of the aggregate of PAAHCl-Mal(14) with NaDoS.

all mixed proportions. For the complex of PAAHCl-Mal(14) with NaDoS, a micelle like aggregate with a hydrophobic core from the surfactants bound to the polycation and a hydrophilic outer shell from the maltose residues was proposed as a model. This amphiphilic structure will contribute to utilizing as a material for separation and solubilization.

References

[1] Goddard ED. Colloid Surf 1986;19:255.

[2] Chen L, Yu S, Kagami Y, Going J, Osada Y. Macromolecules 1998;31:787.

[3] Zhou S, Chu B. Adv Mater 2000;12:545.

[4] Hayakawa K, Oyama T, Maeda T, Satake I, Sato M, Kwak JCT. Langmuir 1988;4:481.

[5] Hayakawa K, Shinohara S, Sasawaki S, Satake I, Kwak JCT. Bull Chem Soc Jpn 1995;68:2179.

[6] Hayakawa K, Nakano I, Satake I. Langmuir 1996;12:269.

[7] Bronich TK, Cherry T, Vinogradov SV, Eisenberg A, Kabanov VA, Kabanov AV. Langmuir 1998;14:6101.

[8] Kobayashi K, Sumitomo H, Ina Y. Polym J 1985;17:567.

[9] Kobayashi K, Sumitomo H, Kobayashi A, Akaike T. J Macromol Sci Chem 1988;A25:655.

[10] Aoi K, Itoh K, Okada M. Macromolecules 1995;28:5391.

[11] Mann DA, Kanai M, Maly DJ, Kiessling LL. J Am Chem Soc 1998;120:10575.

[12] Qiu Y, Zhang T, Ruegsegger M, Marchant RE. Macromolecules 1998;31:165.

[13] Holland NB, Qiu Y, Ruegsegger M, Marchant RE. Nature 1998;392:799.

[14] Miyazaki M, Torigoe K, Esumi K. Langmuir 2000;16:1522.

[15] Kobayashi S, Tokunoh M, Saegusa T, Masino F. Macromolecules 1985;18:2357.

[16] Yonetake K, Seo T, Iijima T. J Polym Sci, Polym Phys 1990;28:303.

[17] Hollas M, Chung MA, Adams J. J Phys Chem B 1998;102:2947.

[18] Itaya T, Ochiai H, Ueda K, Imamura A. Macromolecules 1993;26:6021.

[19] Zhang T, Marchant RE. Macromolecules 1994;27:7302.

[20] Ochiai H, Handa M, Matsumoto H, Moriga T, Murakami I. Makromol Chem 1985;186:2547.

[21] Abuin EB, Scaiano JC. J Am Chem Soc 1984;106:6274.

[22] Chu D, Thomas JK. J Am Chem Soc 1986;108:6270.

[23] Benrraou M, Zana R, Varoqui R, Peferkorn E. J Phys Chem 1992;96:1468.

[24] Itaya T, Ochai H, Ueda K, Imamura A. Polymer 1994;35:2004.

[25] Chandar P, Somansundarn P, Turro NJ. Macromolecules 1988;21:950.

[26] Feigon J, Leupin W, Denny WA, Kearns DR. Biochemistry 1983;22:598.

[27] Kalyanasundaram K, Thomasa JK. J Am Chem Soc 1976;99:2039.

[28] Saito SV. Kolloid Z 1955;143:66.

[29] Goddard ED, Hannan RB. J Colloid Interface Sci 1976;55:73.

[30] Seki M, Morishima Y, Kamachi M. Macromolecules 1992;25:6540.

[31] Herslof A, Sundelof L, Edsman K. J Phys Chem 1992;96:2345.