

Micellization Behavior of an Amphiphilic Statistical Copolymer in Water-Methanol Mixtures

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Sedimentation equilibrium measurements were made on an amphiphilic statistical copolymer p(AMPS/C6) made of sodium 2-(acrylamido)-2-methylpropane-sulfonate (AMPS) and *n*-hexyl methacrylate (C6), dissolved in water-methanol mixtures with 0.2 M LiClO₄ and different methanol contents over a wide polymer concentration range. The experimental results were analyzed in terms of a micellar solution theory for amphiphilic polyelectrolytes to estimate the aggregation number *m* of the micelle and the internal free energy change Δ_m/m (per polymer chain) due to micellization. Both *m* and Δ_m/m decreased with increasing the methanol content in the solvent. In addition, dynamic light scattering for the same copolymer system indicated that p(AMPS/C6) formed a uni-core star-like micelle in water-methanol mixture with the methanol mole fractions of 0 and 0.06.

KEY WORDS: Micelle / Amphiphilic Polymer / Statistical Copolymer / Sedimentation Equilibrium / Dynamic Light Scattering /

Amphiphilic copolymers form micelles in aqueous media due to the strong hydrophobic interaction among the polymer chains.¹ The micellization is important for their applications to the rheology modifier, emulsifier, drug delivery system, and so on,^{2–4} because the micellization changes remarkably their solution properties. In the practical applications for those purposes, their aqueous solutions are often mixed with various additives, *e.g.*, low molar mass organic compounds, salts, surfactants, and other polymers. Those additives can modify the micellization behavior of the polymers in aqueous media by interacting with the hydrophobic or hydrophilic moieties of the copolymer chain, so that it is essentially important to understand the effect of additives on the micellization behavior in aqueous solutions of amphiphilic copolymers.

Recently, Hashidzume *et al.*⁵ investigated the micellar structure of an amphiphilic statistical copolymer p(AMPS/C6), made of sodium 2-(acrylamido)-2-methylpropane-sulfonate (AMPS) and *n*-hexyl methacrylate (C6), in aqueous salt solution. The copolymer aggregation number *m* of the micelle and the number of hydrophobic cores per micelle depended on the copolymer molecular weight and hydrophobic monomer content. Furthermore, their hydrodynamic radius data indicated that the copolymer formed a uni-core star-like micelle at low copolymer molecular weights.

Afterward, Nojima *et al.*⁶ refined the data analysis for the p(AMPS/C6) micelle in aqueous salt solution by taking into account the association-dissociation equilibrium in the micellar solution. Using a micellar solution theory for amphiphilic polyelectrolytes, they estimated more precise *m* for the p(AMPS/C6) micelle in aqueous salt solution.

In the present study, we have made sedimentation equilibrium and dynamic light scattering measurements on p(AMPS/C6) dissolved in water-methanol mixtures with 0.2 M LiClO₄ and different methanol mole fraction x_{methanol} . Applying the micellar

solution theory, we have estimated *m* and also the internal free energy change Δ_m/m due to micellization as functions of the methanol content, from the sedimentation equilibrium data. On the other hand, we have analyzed the dynamic light scattering results to elucidate the micellar structure in aqueous and aqueous methanol solutions. It was found that the micellization behavior of p(AMPS/C6) was very sensitive to the addition of small amount of methanol, which weakened the hydrophobic interaction among hexyl groups on copolymer chains.

EXPERIMENTAL

p(AMPS/C6) Sample and Test Solutions

A statistical copolymer sample of p(AMPS/C6) was obtained by the reversible addition-fragmentation chain transfer (RAFT) polymerization,^{7–9} as reported previously.⁵ The sample was purified by reprecipitation and dialysis, and then freeze-dried from aqueous solution.

The weight-average molecular weight M_w , the ratio M_z/M_w of the *z*-average molecular weight to M_w , and the second virial coefficient A_2 of the copolymer sample obtained were determined in methanol with 0.2 M LiClO₄ at 25 °C by sedimentation equilibrium (*cf.* below). The mole fraction *x* of the hydrophobic monomer units in the copolymer sample was estimated by ¹H NMR using D₂O as the solvent at 30 °C.⁵ All the results are listed in Table I. The M_z/M_w value indicates a narrow molecular weight distribution of the sample prepared by the RAFT polymerization.

Water, methanol, and their mixtures with different compositions all of which contained 0.2 M LiClO₄ were used as solvents. The freeze-dry sample of p(AMPS/C6) was directly dissolved in those solvents. In what follows, the solvent composition is expressed in terms of the mole fraction x_{methanol} of methanol in the solvent.

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Table I. Molecular characteristics of copolymers in methanol with 0.2M LiClO₄

sample	$M_w/10^4$ ^{a)}	M_z/M_w ^{a)}	χ ^{b)}	$A_2/10^{-3}$ mol cm ³ g ⁻² ^{a)}
p(AMPS/C6)	1.69	1.17	0.15	1.00

The above data were determined by a) sedimentation equilibrium or b) ¹H NMR.

Measurements

Sedimentation equilibrium measurements on p(AMPS/C6) solutions with different x_{methanol} were performed at 25.0 °C using an Optima XL-I type ultracentrifuge (Beckman-Coulter) equipped with a Rayleigh interference optical system with a 675 nm light emitting from a diode laser. The concentration distribution in the solution under the centrifugal field was determined by the interferometry using the specific refractive index increment $(\partial n/\partial c)_\mu$ at constant solvent chemical potential.

The apparent molecular weight M_{app} was calculated from^{10,11}

$$M_{\text{app}}^{-1} = \frac{\omega^2(r_b^2 - r_a^2)c_0(\partial\rho/\partial c)_\mu}{2RT(c_b - c_a)}$$

where r_b and r_a are the distance from the center of revolution to the cell bottom and meniscus, respectively, c_b and c_a are polymer mass concentrations at r_b and r_a respectively, ω is the angular velocity, c_0 is concentration of solution before centrifugation, and $(\partial\rho/\partial c)_\mu$ is the specific density increment at constant solvent chemical potential; RT is the gas constant multiplied by the absolute temperature. In dilute methanol solutions where p(AMPS/C6) is molecularly dispersed,⁵ the equation $M_{\text{app}}^{-1} = 1/M_w + 2A_2\bar{c}$ holds where $\bar{c} = (c_a + c_b)/2$, and we can estimate M_w and A_2 .¹² Using the established procedure, we can also estimate M_z/M_w from sedimentation equilibrium data for dilute solutions.¹³

Values of $(\partial n/\partial c)_\mu$ and $(\partial\rho/\partial c)_\mu$ of p(AMPS/C6) at different x_{methanol} were measured using solutions dialyzed against their solvents at 25 °C for a week. A modified Schulz-Cantow type differential refractometer (Shimadzu) and a DMA5000 densitometer (Anton Paar) were used for refractometry and densitometry. The results summarize in Table II. The partial specific volume \bar{v} of p(AMPS/C6) at each x_{methanol} , calculated from $\bar{v} = [1 - (\partial\rho/\partial c)_\mu]/\rho_0$ (ρ_0 : the solvent density) is also listed in Table II.

Dynamic light scattering measurements for copolymer solutions at $x_{\text{methanol}} = 0$ and 0.06 were performed using an ALV/DLS/SLS-5000 light scattering system equipped by an ALV-5000 multiple τ digital correlator at 25 °C. Vertically polarized light with the wavelength λ_0 of 532 nm emitted from

Table II. Values of $(\partial n/\partial c)_\mu$ and $(\partial\rho/\partial c)_\mu$ for p(AMPS/C6) in methanol-water mixtures at 25 °C

x_{methanol}	0	0.06	0.13	0.31	1
$\partial n/\partial c$ (675 nm)/g ⁻¹ cm ³	0.128	0.142	0.147	0.146	0.146
$\partial\rho/\partial c$	0.211	0.320	0.334	0.403	0.599
\bar{v} /cm ³ g ⁻¹	0.782	0.684	0.682	0.637	0.499

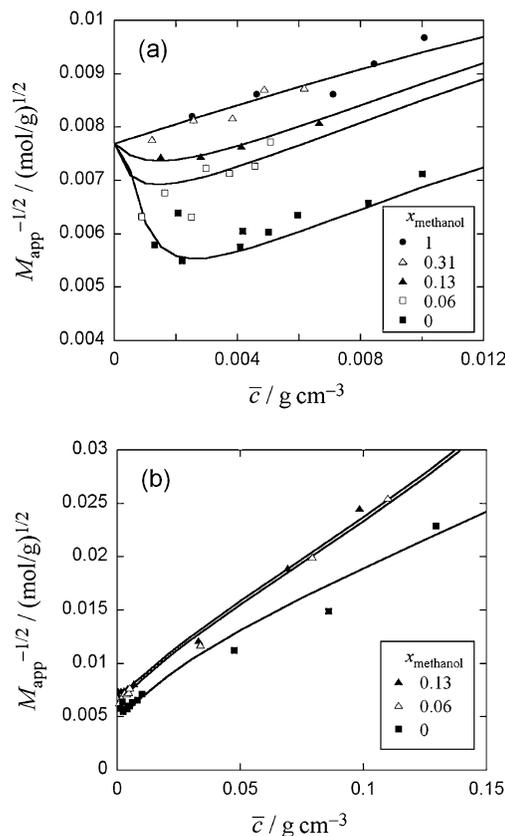


Figure 1. Concentration dependence of the apparent molecular weight M_{app} obtained by sedimentation equilibrium for the amphiphilic statistical copolymer p(AMPS/C6) dissolved in water-methanol mixtures with 0.2M LiClO₄ and different methanol mole fraction x_{methanol} . (a) Data in a dilute region; (b) data in a wide concentration range; Curves: the micellar solution theory for amphiphilic polyelectrolytes (see the text) to determine the aggregation number m and the internal free energy change $\Delta m/m$ due to the micellization.

a Nd:YAG laser was used as an incident light, and the scattered light was measured with no analyzer. Test solutions for light scattering measurements were optically purified by filtration through a 0.8 μm membrane filter, followed by a 3 h centrifugation at 9000 rpm prior to measurements. The intensity autocorrelation function obtained by dynamic light scattering was analyzed by a CONTIN program to estimate the spectrum $A(\tau, k)$ of the relaxation time τ in the logarithmic scale at each scattering angle or the magnitude of the scattering vector k .

RESULTS

Figure 1 shows plots of $M_{\text{app}}^{-1/2}$ vs. \bar{c} obtained by sedimentation equilibrium for p(AMPS/C6) in water-methanol mixtures with 0.2M LiClO₄. In Panel a showing a dilute region, data points at $x_{\text{methanol}} = 1$ (filled circles) almost follow the straight line, from which we have determined M_w and A_2 , already shown in Table I. With decreasing x_{methanol} , data points shift downward at $x_{\text{methanol}} < 0.31$, indicating the micellization of p(AMPS/C6) chains. Although data points at $x_{\text{methanol}} = 0$ (filled squares) slightly scatter, they seem to obey a curve

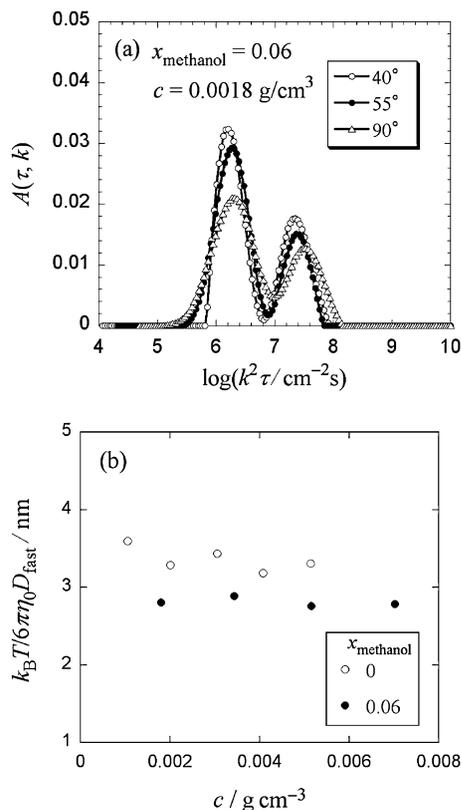


Figure 2. (a) Relaxation time spectra $A(\tau, k)$ obtained by dynamic light scattering for a p(AMPS/C6) solution with $x_{\text{methanol}} = 0.06$ and $c = 0.0018 \text{ g/cm}^3$ at three different scattering angles; (b) Concentration dependence of the diffusion coefficient (of the fast relaxation component) for p(AMPS/C6) dissolved in water-methanol mixtures with 0.2 M LiClO_4 at $x_{\text{methanol}} = 0$ and 0.06 .

convex downward. In Panel b of a wider concentration range, $M_{\text{app}}^{-1/2}$ monotonically increases with \bar{c} . Even at $\bar{c} > 0.1 \text{ g/cm}^3$, solution viscosities were still low and gelation was not observed for all solutions examined.

Figure 2a illustrates examples of the relaxation time spectra $A(\tau, k)$ obtained by dynamic light scattering ($x_{\text{methanol}} = 0.06$ and $c = 0.018 \text{ g/cm}^3$). The spectra are bimodal, being similar to those reported previously for other p(AMPS/C6) samples in 0.1 M aqueous sodium chloride,⁵ and indicating the existence of two scattering components with fast and slow relaxation times. Most of solutions with $x_{\text{methanol}} = 0$ and 0.06 exhibited similar bimodal $A(\tau, k)$.

The mutual diffusion coefficient D_{fast} of the fast relaxation component was estimated by $D_{\text{fast}} = \lim_{k \rightarrow 0} k^{-2} \sum_{\tau \in \text{fast}} \tau^{-1} A(\tau, k)$.¹⁴ Figure 2b shows the results of D_{fast} for solutions with $x_{\text{methanol}} = 0$ and 0.06 , where k_B is the Boltzmann constant, η_0 is the solvent viscosity coefficient, and $k_B T / (6\pi\eta_0 D_{\text{fast}})$ corresponds to the apparent hydrodynamic radius. It can be seen that $k_B T / (6\pi\eta_0 D_{\text{fast}})$ is a slowly decreasing function of c at $x_{\text{methanol}} = 0$, but almost independent of c at $x_{\text{methanol}} = 0.06$.

On the other hand, we may estimate (the upper bound of) the weight fraction w_{slow} of the slow relaxation component in dilute solution using the approximated equation¹⁴

$$w_{\text{slow}} M_{\text{slow}} \approx M_{\text{app}} \lim_{k \rightarrow 0} \left[\frac{\sum_{\tau \in \text{slow}} A(\tau, k)}{\sum_{\tau \in \text{all}} A(\tau, k)} \right]$$

Here M_{slow} is the molar mass of the slow relaxation component, the lower bound of which may be estimated from the hydrodynamic radius of the slow relaxation component (obtained from $A(\tau, k)$ of the component) in the procedure applied in the previous study.⁵ The upper bound of w_{slow} obtained by the above method was less than 0.5% both at $x_{\text{methanol}} = 0$ and 0.06 . Therefore, although the slow relaxation component was detectable by light scattering due to its very high scattering power, it may not affect sedimentation equilibrium results. At present, we have no information about the origin of the coexistence of a tiny amount of large aggregates.

DISCUSSION

Theoretical Basis

In previous publications,^{5,6} we have already demonstrated that p(AMPS/C6) forms a uni-core micelle in aqueous media if the molecular weight is low enough. We here adopt the same uni-core micelle model for our p(AMPS/C6) sample; the suitability of the model will be checked in the following.

For star-like micelles, the internal free energy change Δ_m/m (per polymer chain) due to micellization is written as¹⁵

$$\Delta_m/m = (-\delta m + \sigma m^2 + 4\pi R_c^2 \gamma)/m \quad (1)$$

where m is the aggregation number, δ is the free energy gain when a hydrophobic moiety of a polymer chain enters in the micelle core from the solvent, σ is the free energy due to interaction between two coronal chains of the micelle, and the third term is the interfacial free energy of the micelle core (R_c : the radius of the micellar core; γ : the interfacial tension). The optimum aggregation number is equal to $(4\pi R_c^2 \gamma / \sigma)^{1/2}$, and in what follows, we consider the monodisperse micellar solution with this optimum aggregation number.

Under the micellization equilibrium, the association constant K_m is determined by the equilibrium condition $\mu_m = m\mu_1$, where μ_m and μ_1 are the chemical potentials of m -mer and unimer, respectively. Thus, we need chemical potential expressions applicable over a wide polymer concentration range. Here, we use the single-contact approximation to the micellar system, and apply Sato *et al.*'s expression¹¹ of μ_m given by

$$\frac{\mu_m}{k_B T} = \frac{\mu_m^\circ}{k_B T} + \ln C_m + F'_5(\phi) + m M_1 \tilde{F}(\phi) \quad (2)$$

where, μ_m° and C_m are the standard chemical potential (or the internal free energy) and the molar concentration of m -mer, respectively, M_1 is the molecular weight of unimer, and $F'_5(\phi)$ and $\tilde{F}(\phi)$ are known functions of the total volume fraction ϕ of the polymer; $F'_5(\phi)$ necessary in what follows is defined by

$$F'_5 \equiv \frac{5\phi - 3\phi^2}{3(1 - \phi)^2} - \ln(1 - \phi) \quad (3)$$

(We have neglected an attractive interaction term of the chain end.¹¹) The chemical potential of unimer μ_1 can be calculated by eq 2 with $m = 1$. The above expression of μ_m was originally derived on the basis of the scaled particle theory for polydisperse wormlike spherocylinders, and may be a good approximation to polymer systems with lower molar mass and lower degree of branching.

Applying this μ_m to the equilibrium condition, we have the following equation

$$K_m \equiv \frac{C_m}{C_1^m} = \frac{(1 - w_1)/m}{w_1^m(1000c/M_1)^{m-1}} \quad (4)$$

$$= \exp[-\Delta_m - (m - 1)F'_5(\phi)]$$

Here, w_1 is the weight fraction in the total polymer, $M_1 = 1.69 \times 10^4$ in our system, and $\Delta_m \equiv (\mu_m^\circ - m\mu_1^\circ)/k_B T$ is the internal free energy change due to micellization being identical with that given in eq 1 except for a constant term. For given m , Δ_m , c , and ϕ , we can calculate w_1 from the above equation.

Sato *et al.*¹¹ also formulated the apparent molecular weight M_{app} obtained by sedimentation equilibrium, which is written as

$$M_{\text{app}}^{-1} = M_w^{-1} + 2(\Gamma_{2,0} + A_{2,w})c \quad (5)$$

where M_w is the weight-average molar mass, $\Gamma_{2,0}$ is the apparent second virial coefficient for the hard-core potential, and $A_{2,w}$ is the second virial coefficient with respect to the electrostatic and hydrophobic interactions. (The original paper dealt with the quantity $Z(r)$, which can be identified with M_{app}^{-1} in a good approximation.) The coefficient $\Gamma_{2,0}$ is calculated by

$$\Gamma_{2,0} = \frac{\pi d^2 N_A}{4M_L} \left[\frac{F_6}{dM_L} + \frac{F_2}{M_w} + \frac{F_7}{M_n} \right. \quad (6)$$

$$\left. - \left(\frac{1}{M_n} - \frac{1}{M_w} \right) F_2 (1 + \phi F_2) \right]$$

where d are M_L are the hard-core diameter and the molar mass per unit contour length of the polymer chain, respectively, M_n is the number average molar mass, and N_A is the Avogadro constant. The functions F_2 , F_6 , and F_7 are defined by

$$F_2 \equiv \frac{8 - 7\phi + 3\phi^2}{3(1 - \phi)^3}, \quad (7)$$

$$F_6 \equiv 2 \frac{1 + \phi}{(1 - \phi)^4},$$

$$F_7 \equiv \frac{2}{3} \left[\frac{4 + \phi + \phi^2}{(1 - \phi)^4} \right]$$

The volume fraction of the total polymer can be calculated by $\phi = \pi d^2 N_A c / 4M_L$, while the average molar masses by $M_w/M_1 = w_1 + (1 - w_1)m$ and $M_1/M_n = w_1 + (1 - w_1)m^{-1}$. It is noted that the equality between M_{app}^{-1} and the reciprocal of the osmotic compressibility $(RT)^{-1} \partial \Pi / \partial c$ does not strictly hold for multicomponent polymer solutions.

On the other hand, $A_{2,w}$ for amphiphilic copolymers may be calculated by

$$A_{2,w} = \frac{N_A}{2\bar{M}_0^2} [(1 - x)^2 \beta_{\text{el}} + x^2 \beta_v] \quad (8)$$

where \bar{M}_0 is the average monomer molar mass, x is the content of hydrophobic monomer unit, and β_{el} and β_v are the binary cluster integrals with respect to the electrostatic and hydrophobic interactions, respectively. The theory of polyelectrolytes^{16,17} provides us the following equation of β_{el}

$$\beta_{\text{el}} = \frac{2h^2}{\kappa} R(y) \quad (9)$$

Here, h is the contour length per monomer unit, κ is the reciprocal of the Debye screening length, and $y \equiv 2\pi v_{\text{eff}}^2 Q e^{-\kappa d} / \kappa$ with the effective charge density v_{eff} and the Bjerrum length Q . In this study, v_{eff} was calculated based on the Philip-Wooding theory¹⁸ for charged cylinder model. The function $R(y)$ is given in ref 16. Taking into account the contribution of counter ions of the copolymer to the ionic strength, we calculate κ by

$$\kappa^2 = 8\pi Q N_A \left(\frac{C_s}{1000} + \frac{1 - x}{2\bar{M}_0} c \right) \quad (10)$$

The mutual diffusion coefficient D_{fast} in micellar solutions at finite concentrations may be written as^{15,19}

$$\frac{k_B T}{6\pi\eta_0 D_{\text{fast}}} = \frac{M_{\text{app}}(1 + k'_H c/c^*)}{M_w(1 - \bar{v}c)} R_H \quad (11)$$

where \bar{v} is the polymer partial specific volume, k'_H is the strength of the intermolecular hydrodynamic interaction (corresponding to the Huggins coefficient for the polymer solution viscosity), c^* is the overlap concentration, and R_H is the average hydrodynamic radius given by

$$\frac{R_H}{M_w} = \left[\frac{w_1 M_1}{R_{H,1}} + \frac{(1 - w_1)m M_1}{g_{H,m} R_{H,m}(\text{linear})} \right]^{-1} \quad (12)$$

Here, $R_{H,1}$ and $R_{H,m}$ (linear) are the hydrodynamic radii of the linear chains with the molar masses of M_1 and mM_1 , respectively, and $g_{H,m}$ is the g -factor with respect to the hydrodynamic radius for the m -mer, depending on the branching architecture. The overlap concentration c^* may be calculated by¹⁵

$$c^* = 3M_w / 4\pi N_A R_H^3 \quad (13)$$

Analysis of Experimental Results

Using the above theoretical expressions, we analyze our experimental M_{app} and D_{fast} results for p(AMPS/C6) solutions. To calculate M_{app} as a function of c , we need the following parameters: m , Δ_m , d , M_L , h , v_{eff} , and β_v . Among them, we have $h = 0.25$ nm for vinyl polymers,²⁰ and $M_L = \bar{M}_0/h = 835$ nm⁻¹. The effective charge density v_{eff} can be calculated from the linear charge density [$= (1 - x)/h = 3.4$ nm⁻¹] and d .¹⁸ Thus the remaining unknown parameters are m , Δ_m , d , and β_v .

At $x_{\text{methanol}} = 1$ and 0.31, where the micelle is not formed, M_{app} is determined only by d and β_v . If d is calculated from the experimental partial specific volume \bar{v} (*cf.* Table II) by $d = (4\bar{v}M_L/\pi N_A)^{1/2}$, we can fit eq 5 to the M_{app} data at $x_{\text{methanol}} = 1$ and 0.31 with $\beta_v = -0.3$ nm³. Even at

Table III. Values of parameters determined from M_{app} data

x_{methanol}	d/nm	β_v/nm^3	m	Δ_m/m
0	1.17	-0.8	4	-6.87
0.06	1.5	-0.3	2	-4.35
0.13	1.5	-0.3	2	-3.80
0.31 & 1	0.96	-0.3	—	—

$x_{\text{methanol}} = 0$ where micelle is formed, M_{app} in a concentrated region is little dependent on m and Δ_m , so that we can similarly determine values of d and β_v by fitting high concentration M_{app} data. Values of m and Δ_m were determined afterward by fitting lower concentration M_{app} data.

At $x_{\text{methanol}} = 0.06$ and 0.13, we had to choose d values larger than those estimated from \bar{v} to fit eq 5 to high concentration data of M_{app} . This may have something to do with the solvation of methanol to the p(AMPS/C6) chain. Here, we assumed that β_v at $x_{\text{methanol}} = 0.06$ and 0.13 is equal to that at $x_{\text{methanol}} = 1$ and 0.31, and determined d to fit eq 5 to M_{app} data at high c . Values of m and Δ_m were determined from M_{app} data at low c .

As shown by solid curves in Figure 1, we can satisfactorily fit the theoretical curve to experimental data at every x_{methanol} . Values of d , β_v , m , and Δ_m/m used in the fittings are listed in Table III. The aggregation number m is 4 at $x_{\text{methanol}} = 0$, but reduces to 2 at $x_{\text{methanol}} = 0.06$ and 0.13, and micellization does not take place at $x_{\text{methanol}} > 0.3$. Furthermore, Δ_m/m (the free energy change per polymer chain due to micellization) increases with increasing x_{methanol} . Destabilization of the micelle by addition of methanol arises from diminishing the hydrophobic interaction. From the same reason, we can expect an increase of the repulsion among coronal chains and then of σ (the interaction free energy between two coronal chains) in eq 1 as x_{methanol} increases, which may lead the reduction of the optimum aggregation number $[= (4\pi R_c^2 \gamma / \sigma)^{1/2}]$.

The diffusion coefficient D_{fast} for the micellar solution is calculated by eqs 11–13, which include $R_{\text{H},1}$, $R_{\text{H},m}$ (linear), $g_{\text{H},m}$, and k'_{H} . In general, the hydrodynamic radius R_{H} of linear polymers has a power-law dependence on the degree of polymerization N_0 : $R_{\text{H}} = K'_{\text{H}} N_0^{a_{\text{H}}}$ with two parameters K'_{H} and a_{H} characteristic to the polymer-solvent system. The N_0 dependence of R_{H} of p(AMPS/C6) with $x = 0.15$ at $x_{\text{methanol}} = 0$ and 0.06 should be similar to that for the AMPS homopolymer in aqueous solution,⁵ but due to the hydrophobic interaction among hexyl groups within the chain the solvent quality may be more or less reduced. We have used K'_{H} ($= 0.22$ nm) and a_{H} ($= 0.58$) values of the AMPS homopolymers in 0.5 M aqueous NaCl which may be a slightly poorer solvent than 0.2 M aqueous LiClO₄.²¹

If hydrophobes near one of p(AMPS/C6) chain ends are incorporated into the core, our uni-core micelle of the m -mer can be regarded as an m -arm star polymer. On the other hand, when hydrophobes in the middle portion of the chain are included into the core, the uni-core micelle should be a $2m$ -arm star polymer. It is known that the g -factor of the f -arm star polymer with respect to the hydrodynamic radius is given by²²

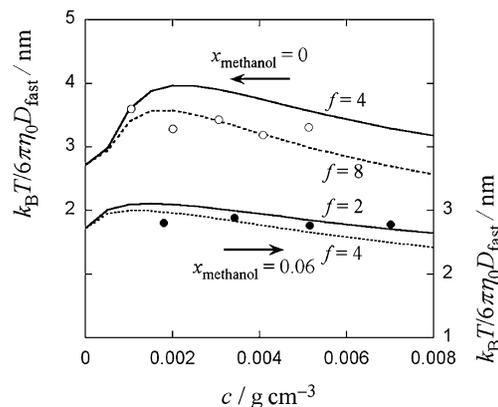


Figure 3. Comparison of experimental data of the diffusion coefficient for p(AMPS/C6) micelles at $x_{\text{methanol}} = 0$ and 0.06 with the theory for the f -arm star-like micelle.

$$g_{\text{H},m} = \frac{f^{1/4}}{[2 - f + \sqrt{2}(f - 1)]^{1/2}} \frac{1 - 0.068 - 0.0075(f - 1)}{1 - 0.068} \quad (14)$$

Finally, linear flexible homopolymers in good solvents take values of 4–7 for the strength k'_{H} of the intermolecular hydrodynamic interaction.¹⁵ Choosing $k'_{\text{H}} = 8$ which is slightly larger than those for linear polymers, we obtain solid and dashed curves in Figure 3. Here, the solid and dashed curves correspond to theoretical values for $f = m$ and $2m$, respectively. Experimental data points at both $x_{\text{methanol}} = 0$ and 0.06 are between the solid and dashed curves. This demonstrates that the micelle of p(AMPS/C6) is star-like and its hydrophobic core consists of hexyl groups attaching to random positions of the copolymer chain.

Comparison with the Corresponding Low-Molar Mass Amphiphile

Recently, Ruso *et al.*²³ investigated the micellization behavior of n -hexyltrimethylammonium bromide (C6TAB) in aqueous 0.2–0.7 M NaBr, of which hydrophobic moiety is the same as p(AMPS/C6). The aggregation number reported for C6TAB (3–4) is close to our aggregation number of p(AMPS/C6) chains in aqueous LiClO₄, but C6TAB forms the micelle only at high concentrations (0.4–0.6 M of C6TAB). For p(AMPS/C6), the micelle is formed at concentration as low as 0.002 g/cm³, which corresponds to 10⁻³ M of the hexyl group. The remarkable stabilization of the p(AMPS/C6) micelle may be owing to (1) hexyl groups are concentrated within the copolymer chain domain and (2) the charged sulphate group is apart from the hexyl group. Although the aggregation number of p(AMPS/C6) chains is four, the core of the copolymer micelle may consist of hexyl groups more than four, which can stabilize the copolymer micelle more.

Since the p(AMPS/C6) micelle is star-like, not all hexyl groups attaching to the copolymer chain are incorporated into the hydrophobic core. The high critical aggregation concentration for C6TAB indicates that hydrophobicity of the hexyl group is not so strong that the hexyl group is completely helped exposing to aqueous medium.

CONCLUSION

We have investigated the micellization equilibrium of the statistical copolymer p(AMPS/C6) in water, methanol, and their mixtures. In aqueous 0.2 M LiClO₄, p(AMPS/C6) forms a uni-core star-like tetramer, and both stability and aggregation number of the micelle sharply decrease by addition of methanol which reduces the hydrophobic interaction among hexyl groups attaching to copolymer chains. The micellization equilibrium and also micellar conformation were successfully described by the proposed theory.

Received: September 20, 2008

Accepted: November 20, 2008

Published: January 15, 2009

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