

Micellization of Amphiphilic Random Copolymers in Mixtures of Water and Methanol

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Introduction

Amphiphilic polyelectrolytes which comprise a number of hydrophobic and hydrophilic monomer units in the same chain can form in aqueous media various macromolecular assemblies of which structure and stability are determined by the balance between electrostatic (repulsive) and hydrophobic (attractive) interactions. Recently, Hashidzume et al.^[1] studied amphiphilic random copolymers of sodium 2-(acrylamido)-2-methylpropanesulfonate and hexyl methacrylate by light scattering and fluorescence, and found this copolymer (p(AMPS/C6); see Chart 1) exists as micelles with uni-core or multi-cores in aqueous media.

Micellization of amphiphilic polyelectrolytes may be affected by organic solvents added to the aqueous solution, because the organic solvents can reduce the hydrophobic interaction and also may change the structure of the hydrophobic core in the micelle. In the present study, we have investigated the association-dissociation equilibrium of p(AMPS/C6) in mixtures of water and methanol. It is known that p(AMPS/C6) is molecularly dispersed in methanol, so that the hydrophobic interaction among hexyl groups in the copolymer is considerably reduced in methanol. Thus, the methanol content in the solvent may be able to control the equilibrium of the amphiphilic copolymer.

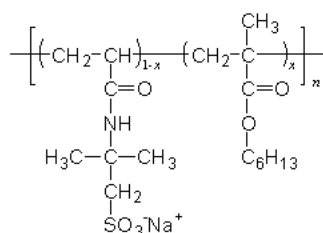


Chart 1. Chemical structure for p(AMPS/C6)

Experimental

Sample. A random copolymer p(AMPS/C6) sample was synthesized by reversible addition-fragmentation chain transfer (RAFT) polymerization. The mole fraction x of C6 was estimated to be 0.15 in D₂O at 30°C by ¹H-NMR.

Sedimentation equilibrium. Sedimentation equilibrium measurements for p(AMPS/C6) in mixtures of water and methanol containing 0.2M LiClO₄ were performed at 25°C using a Beckman-Coulter Optima XL-I ultracentrifuge, equipped with a Rayleigh interferometer with a 675nm light emitting from a diode laser. The apparent molecular weight M_{app} was determined in the standard procedure. The specific refractive index increment and specific density increment necessary to calculate M_{app} were determined for dialyzed solutions of p(AMPS/C6) with each solvent composition. The ratio of the z-average to weight average molecular weight of the copolymer sample was also determined by sedimentation equilibrium in methanol with 0.2M LiClO₄ to be 1.17, which indicates the molecular weight distribution of the sample is considerably narrow.

Fluorescence measurements. Steady-state and time-resolved fluorescence measurements were made for pyrene solubilized aqueous solutions of p(AMPS/C6) with 0.2M LiClO₄. Steady-state fluorescence spectra recorded on a Hitachi F-4500 fluorescence spectrometer indicated that hydrophobic cores are formed in aqueous p(AMPS/C6) solutions. Fluorescence decay data collected on a HORIBA NAES 550 system were analyzed by the Infelta-Tachiya equation to estimate the average number n_c of the hydrophobic cores per micelle.

Results

Figure 1 shows the concentration c dependencies of $M_{\text{app}}^{-1/2}$ for the p(AMPS/C6) sample in mixtures of water and methanol of different methanol contents x_M (the mole fraction of methanol) with 0.2 M LiClO₄. The extrapolation of the data points in methanol ($x_M = 1$; filled circles) to the zero c provides the weight average molecular weight of the sample ($= 1.69 \times 10^4$). With decreasing x_M , $M_{\text{app}}^{-1/2}$ does not change at $x_M > 0.31$, and then decreases at every c , indicating the micellization of p(AMPS/C6) at $x_M < 0.31$, with strengthening the hydrophobic interaction. However, at $x_M = 0$ (unfilled circles) the concentration dependence of $M_{\text{app}}^{-1/2}$ exhibits upswing at low c . This is indication of the dissociation of the micelle at lowering c .

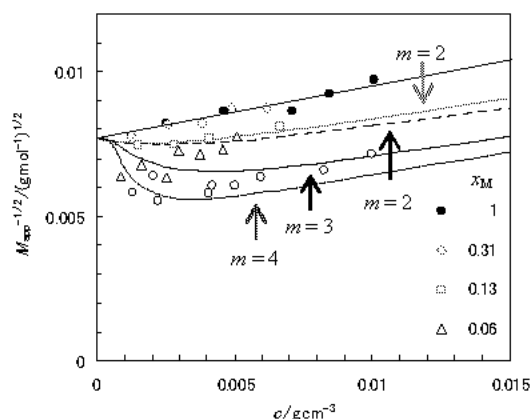
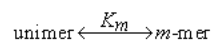


Figure 1. Plots of $M_{\text{app}}^{-1/2}$ vs c for p(AMPS/C6) in mixtures of water and methanol with different x_M .

Discussion

We have considered the following association-dissociation equilibrium:



where K_m is the association constant. The weight fraction w_1 of the unimer can be calculated by the equation $1 - w_1 = mK_m w_1^m \times (1000c/M_1)^{m-1}$ where M_1 is the molecular weight of the unimer ($= 1.69 \times 10^4$). Then M_{app} is calculated by

$$M_{\text{app}}^{-1} = [w_1 + (1 - w_1)m]^{-1} M_1^{-1} + 2(\Gamma_{2,0} + A_{2,w})c \quad (1)$$

where $\Gamma_{2,0}$ 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 plus hydrophobic interactions. The average number n_c of the hydrophobic core per micelle can be also calculated from w_1 on the assumption that the unimer and m -mer possess no and one hydrophobic core, respectively.

The above theory contains two adjustable parameters, K_m and $A_{2,w}$. They can be determined from experimental M_{app} at high concentrations as well as n_c . Such data were obtained for aqueous solutions of p(AMPS/C6) with $x_M = 0$. The solid blue curve in Figure 1 indicate theoretical values at $x_M = 0$ calculated by eq 1 assuming $m = 4$ and using K_m and $A_{2,w}$ values such determined. The agreement between the theory and experiment is reasonably good. Although data of M_{app} at high concentrations and n_c have not been obtained for the mixed solvent systems with $x_M = 0.06$ and 0.13, we have calculated M_{app} choosing reasonable values of K_m and $A_{2,w}$. As demonstrated by the green curve, the experimental results for $x_M = 0.13$ are favorably compared with theoretical values calculated by eq 1 for $m = 2$. The experimental data for $x_M = 0.06$ are located between the theoretical curves for $m = 3$ and 2. It can be seen that the aggregation number m of the p(AMPS/C6) micelle decreases with increasing the methanol content.

References

- [1] Hashidzume, A.; Kawaguchi, A.; Tagawa, A.; Hyoda, K.; Sato, T. *Macromolecules* **2006**, *39*, 1135.