Enthalpy-Entropy Compensation in Aggregation of Poly(styrene-*co*-sodium methacrylate) Ionomers in Aqueous Solution

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Summary: Spectroscopic methods were employed to evaluate the thermodynamics of aggregates formation of P(S-*co*-MANa) in aqueous solution containing a trace of DMF(0.2 mol%) using pyrene as an optical probe. The mol %s of methacrylate unit in poly(styrene-*co*-sodium methacrylate)[P(S-*co*-MANa)] were 3.6, 5.0, 6.2 and 9.4. Measurements were made at a series of temperatures in the range 10–80 °C. Based on the temperature dependence of the critical aggregation concentration (CAC) and by the use of van't Hoff equation, thermodynamic parameters were calculated. At low temperature the aggregation is accomplished by a large positive entropy change and a small negative enthalpy changes. As the temperature increases, the magnitude of entropy change becomes smaller and the enthalpy change is more exothermic. Moreover, the changes in enthalpy and entropy compensate each other for all samples we have studied, and the compensation temperature was ~320 K.

Keywords: CAC; poly(styrene-*co*-sodium methacrylate); solution; spectroscopic methods; thermodynamic parameters

Introduction

The aggregates formation of amphiphiles above a critical concentration is an important solution property evaluating the thermodynamics of the process that can provide insight into the principles of governing aggregates formation. Thermodynamic quantities of aggregates formation can be derived from either the temperature dependence of the critical aggregates concentration (CAC) or from the direct measurement of the enthalpy by microcalorimetry.[1] Light scattering is known to be one of the most powerful methods for the determination of the CAC. However, scattering techniques are able to detect the onset of aggregation only if the CAC occurs in a concentration region where this technique is sensitive. For randomly co-polymerized poly(styrene-*co*-sodium methacrylate) [P(S-co-MANa)] in aqueous media we have studied in this work, this is not the case (CAC~10^{-6} g/mL.[2] To determine the thermodynamic parameters, we utilized fluorescence spectroscopic methods, which is known as a powerful tools for the investigation of micellar aggregates properties.[3]

The thermodynamics of aggregates formation can be evaluated data from the temperature dependence of the CAC by the use of van't Hoff equation. By the mass action model and pseudo-phase model, and neglecting low weight terms, thermodynamic parameters can be expressed as follows,[1,4]

$$\Delta G^o = RT \ln X_{CAC} \quad (1)$$

$$\Delta H^o = -RT^2 \left[\frac{d \ln X_{CAC}}{dT}\right] \quad (2)$$

Where ΔG° and ΔH° are standard molar Gibbs free energy and molar enthalpy of

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aggregates formation, and X_{CAC} is the mole fraction of the P(S-co-MANa) in aqueous solution at the CAC. With ΔG^o and ΔH^o, ΔS^o can be obtained.

In the present study, to determine the thermodynamics of aggregation process, the CAC values of P(S-*co*-MANa) with various content of ionic groups in aqueous solution containing 0.2 mol% DMF were measured using pyrene as an optical probe. The mol %s of methacrylate unit in P(S-*co*-MANa) were 3.6, 5.0, 6.2 and 9.4. Measurements were made at a series of temperatures in the range 10–80 °C.

Experimental Part

Preparation of P(S-x-MANa) Solutions

Poly(styrene-*co*-methacrylic acid) random copolymers with various content of methacylic acids were synthesized by ionic polymerization and hydrolyzed as reported in the literature.[5] The copolymers in the acid form (MW = ca. 300,000) were neutralized (100%) in benzene/methanol (9/1 v/v) by adding a predetermined amount of methanolic NaOH. The solutions were freeze-dried and further dried under vacuum at 130 °C for 1 day. To prepare aqueous dispersion, the ionomer was dissolved in DMF. The initial ionomer concentration in DMF was 2.0×10^{-2} g/mL and the solution diluted to different concentrations before it was added into an excessive amount of doubly distilled deionized water. After the addition of water, probe pyrene dissolved in DMF was incorporated. The solutions were allowed to stand at room temperature for at least 12 hours before the measurements. The final concentrations of the dispersion were in the range of $5.0 \times 10^{-9} \sim 2.0 \times 10^{-4}$ g/mL. The final mole percentages of DMF to water were kept at 0.2(~1/99 v/v) and the concentration of pyrene estimated from the absorption spectrum was $\sim 3 \times 10^{-6}$ M.

Measurements

Steady-state fluorescence and absorption were measured using an Aminco-Bowman Luminescence Spectrometer and a Cary 3(Varian Co.), respectively. Measurements were made at a series of temperatures in the range 10–80 °C. Excitation wavelength was 320/340 nm for emission, and the detection wavelength was 392 nm for excitation spectra. The data treatments, such as the smoothing (Savitzky-Golay method) of absorption spectra, the deconvolution of the excitation spectra, and the non-linear fitting, were performed with Microcal Origin software (OriginLab Co.).

Results and Discussion

The absorption, excitation and emission spectra of pyrene in various concentrations of P(S-*x*-MANa) ($5 \times 10^{-9} \sim 2 \times 10^{-4}$ g/mL) solutions at the temperature range 10–80 °C were observed. Figure 1 shows the absorption (A) and excitation (B) spectra of pyrene in ionomer solutions at various temperatures.

Above CAC, as the temperature increases, the absorption and excitation peak intensity of pyrene at 340 nm decreases rapidly, while that of at 333 nm increases. In addition, absorption spectra show an isosbestic point denoted as (*) in Figure 1(a). Unlike absorption, excitation spectra depend on the absorbance and the quantum yield. Because of quantum yield excitation spectra do not show an isosbestic point. The peaks at 333 nm and 340 nm are characteristics of pyrene in an aqueous media and in a hydrophobic environment, respectively.[a] The intensity ratio of the first vibrational band to the third band, I_1/I_3, in the emission spectrum of pyrene also changed (spectra are not shown here). The I_1/I_3 ratios of pyrene serve as a measure of the polarity of the microenvironment of the pyrene, but the ratios depend on the excitation wavelength. It has been reported that the concentration dependence of the area ratios A_{340}/A_{333} (or intensity ratios I_{340}/I_{333}) obtained from the decon-

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[a] The absorbance of pyrene at low P[S-*co*-MANa] concentration is small and signal to noise ratios are too low to determine CACs.

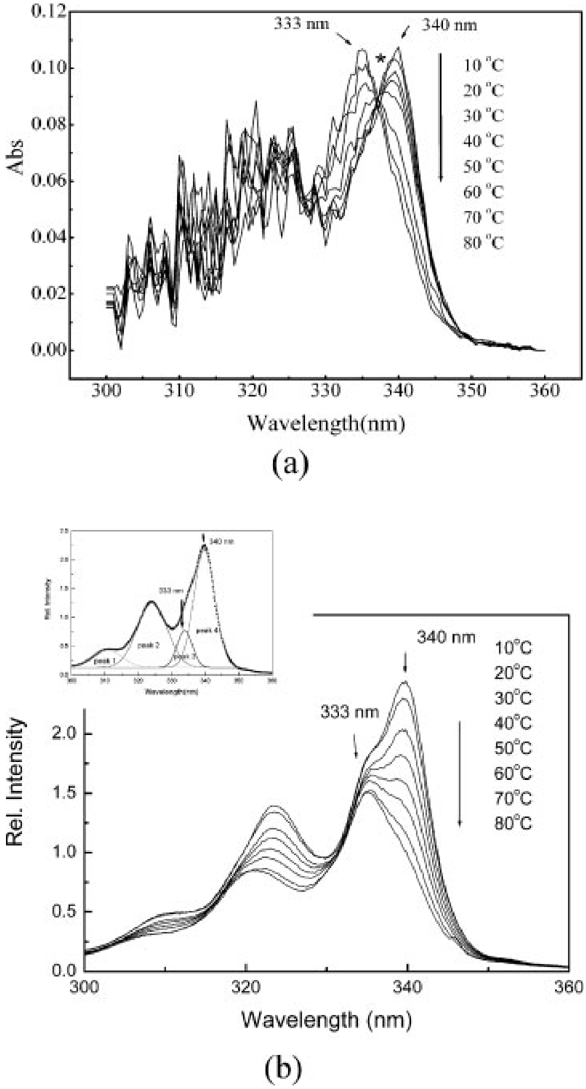

Figure 1.

Absorption (a) and excitation (b) ($\lambda_{em} = 392$ nm) spectra of pyrene in 2×10^{-5} g/mL of P(S-6.2-MANa) in aqueous media at various temperatures. Pyrene concentration was 3×10^{-6} M. The inset shows deconvoluted excitation spectrum of pyrene at 20 °C.

voluted excitation spectra is more sensitive to the aggregation behavior of the polymer than that of the emission spectra.[6] Therefore, excitation spectra were used for the determination of the apparent CAC values. It is worthy of note that the change in the fluorescence signal can be influenced not only by the aggregation of ionomers but also by the partitioning of the pyrene between an aqueous and a hydrophobic environment. At the early stage of the aggregation process, however, a very small amount of aggregates are presented in a solution that contains an excess amount of probe pyrene. For that reason, as soon as aggregates are formed, pyrene must dissolve into hydrophobic interior of the aggregates regardless of the magnitude of the partition coefficient of pyrene. Therefore the observed CAC, judging from the

Table 1.
Thermodynamic parameters of the aggregates formation (error < 15%).

T/K	Content of Ionic groups/mol%											
	3.6			5.0			6.2			9.4		
	ΔG^{o}[a)]	ΔH^{o}	ΔS^{o}	ΔG^{o}	ΔH^{o}	ΔS^{o}	ΔG^{o}	ΔH^{o}	ΔS^{o}	ΔG^{o}	ΔH^{o}	ΔS^{o}
283	−51.7	−5.6	163	−51.2	−5.7	161	−51.7	−1.0	179	−51.0	−21.0	108
293	−53.5	−9.6	150	−52.3	−9.2	147	−53.4	−7.3	158	−53.2	−22.2	106
303	−54.3	−14.1	133	−53.8	−13.2	134	−55.2	−14.3	135	−53.8	−23.5	100
313	−56.0	−19.1	118	−54.9	−17.7	119	−56.7	−22.3	110	−54.7	−24.7	95.8
323	−56.9	−24.7	99.8	−56.2	−22.6	104	−57.0	−31.2	79.7	−55.9	−26.0	95.2
333	−58.2	−30.9	82.1	−57.2	−28.1	84.7	−57.4	−41.1	49.0	−56.9	−27.2	89.2
343	−58.4	−37.6	60.4	−57.6	−34.1	68.5	−58.2	−52.0	18.1	−57.5	−28.5	84.6
353	−60.1	−45.1	42.5	−58.0	−40.7	49.0	−58.6	−64.0	15.3	−59.2	−29.8	83.4

[a)] Units are $kJmol^{-1}$ for ΔG^{o} and ΔH^{o}, and $Jmol^{-1}\ K^{-1}$ for ΔS^{o}.

concentration where the A_{340}/A_{333} value starts to increase rapidly, represents the onset of the aggregation well.

Based on the temperature dependence of the observed CACs and the use of van't Hoff equation, thermodynamic parameters of aggregates formation can be obtained. Since the obtained *ln* X_{CAC}*vs* T plots were not linear, to evaluate the ΔH^{o} we used polynomial form of *ln* X_{CAC} with temperature.[1,7–9]

$$\ln X_{CAC} = a + bT + cT^{2} \tag{3}$$

Where, a, b and c are polynomial constants, which were obtained by polynomial fitting. Thermodynamic parameters were calculated from the equations (1–3), and the results are summarized in Table 1.

At low temperature the aggregation process is accomplished by a large positive entropy change for all samples and a small negative enthalpy changes except in 9.4 mol%. As the temperature increases, the magnitude of entropy change becomes smaller and the enthalpy change becomes more exothermic, which is normally observed for the self-association of amphiphiles leading to micelle formation.[7,10] Moreover, the changes in enthalpy and entropy compensate each other for all samples we've studied, and the compensation temperature was ~320 K (shown in Figure 2).

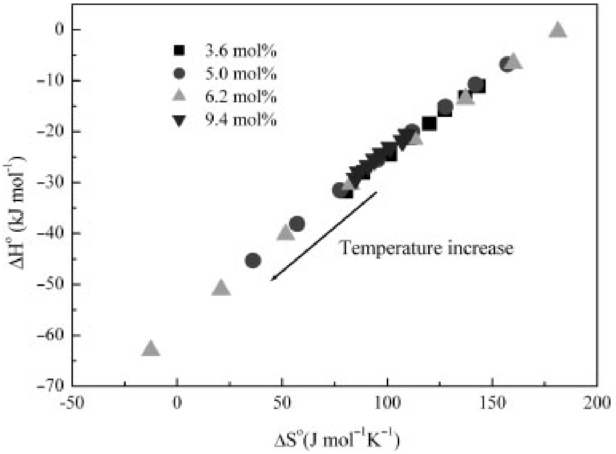

Figure 2.
Enthalpy changes of the aggregates formation versus entropy changes at various temperatures for P(S-x-MANa) in aqueous solution.

It is usually accepted that the positive entropy change is unique to water for surfactant in aqueous solution.[4] The entropy change of the aggregation process is made up of two parts: a large positive part due to removal of water from around the hydrophobic parts(positive enthalpy change), and a smaller negative part due to transfer of the hydrophobic domain into the hydrophobic interior and form aggregates(negative enthalpy change). At room temperature the major driving forces for aggregates formation are due to a large gain in entropy when water molecules in hydration shells around the hydrophobic parts of the monomeric ionomers are released during the aggregation process. Since the former water structure part is not major part in aqueous solution at high temperature,[10] it can not be the general driving force for aggregation. Rather it is the second part that must be the usual driving force, for which ΔH^o is negative also. It is worthy of note that the solvent (water) we've used in this work contains 0.2 mol% of DMF. We can not rule out the role of DMF in the aggregation process. Further investigations are needed for the details.

Conclusions

Based on the temperature dependence of CAC, thermodynamic parameters of the P(S-co-MANa) aggregates formation in aqueous solution were calculated. At low temperature the aggregation is accomplished by a large positive entropy change and a small negative enthalpy changes. As the temperature increases, the magnitude of entropy change becomes smaller and the enthalpy change becomes more exothermic. Moreover, the changes in enthalpy and entropy compensate each other for all samples we have studied. These behaviors are normally observed for the self-association of amphiphiles leading to micelle formation.

Acknowledgements: This work was supported by fund from Chosun University (2002).

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