

Temperature-Dependent Solubilization of PEO-PPO-PEO Block Copolymers and Their Application for Extraction Trace Organics from Aqueous Solutions

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Abstract—The effect of temperature on naphthalene solubilization in aqueous PEO-PPO-PEO block copolymer solutions has been investigated. Increasing temperature would enhance the apparent solubility of naphthalene in aqueous PEO-PPO-PEO block copolymer solutions. The pseudo-phase model was employed to calculate thermodynamic parameters for naphthalene solubilization in aqueous PEO-PPO-PEO block copolymer solutions.

Key words: PEO-PPO-PEO Block Copolymers, Temperature, Solubilization, Extraction

INTRODUCTION

It has long been recognized that hydrophobic solutes can be incorporated into aqueous surfactant aggregates known as micelles, which increases the aqueous solubility of solutes by orders of magnitude. The solubilization property of micelles makes it attractive for a variety of practical applications, such as drug delivery and separation processes. Using an aqueous micellar solutions to extract trace organics has considerable environmental and economic advantages over organic solvent extraction and activated carbon adsorption, which provides more flexible mediums to reclaim the solutes [Hurter and Hatton, 1992; Paterson et al., 1999]. One of the most important steps in micellar extraction technique is to separate micelles from aqueous solutions. Several approaches for separating the micelles from solutions have been proposed, such as ultrafiltration and membrane extraction. Large PEO-PPO-PEO block copolymer surfactants have been elected [Hurter and Hatton, 1992], because these surfactants may be retained more effectively than the normal low molecular weight surfactants in membrane extraction process.

Poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) (PEO-PPO-PEO) block copolymers, commercially available as Poloxamers or Pluronic, are high molecular weight nonionic surfactants. The amphiphilic character of the block copolymers leads to self-assembly behavior resembling that of the low molecular weight surfactants. It is generally accepted that the micelle is spherical shaped, with a dense core consisting mainly of PPO and a hydrated PEO swollen corona [Alexandridis et al., 1994a, b]. It is well known that varying temperature can alter the hydrophobic/hydrophilic property of PEO-PPO-PEO block copolymers in aqueous solutions. However, no more attention is paid to the effect of temperature on solubilization. The purpose of this work is to explore the effect of temperature on solubilization property of PEO-PPO-PEO block copolymers and its application for extraction trace organics from aqueous solutions.

EXPERIMENTAL SECTION

1. Materials

PEO-PPO-PEO block copolymers were obtained from BASF Corp., and used without further purification. The Pluronic block copolymers are listed in Table 1 where their trade names, molar weights, percentages of PPO (PPO wt%), and general formulas are given. Aqueous Pluronic block copolymer solutions were prepared by dissolving block copolymers in distilled water with gentle agitation, and then stored in a refrigerator. Naphthalene (analysis grade, >99.0%) was purchased from Beijing Chemical Factory and methanol (chromatogram grade, >99.5%) was obtained from Tianjing Siyou Biomedical Technology Corp.; those materials were also used as received.

2. Experimental Methods

2-1. Surface Tension

The ring method was employed for measuring the surface tension of Pluronic block copolymer solutions by using an automatic tensiometer. All glassware was cleaned with chromate acid, and then thoroughly rinsed with distilled water before use. The platinum ring was washed with acetone, rinsed in distilled water, and flamed until red-hot before each measurement.

2-2. Solubilization Experiment

The concentration-absorbance calibration curve of naphthalene in 1 : 1 (v/v) methanol/water solution was established by using a Perkin-Elmer Lambda 3B UV-vis spectrophotometer. The solubilization experiment was carried out as follows: 50 mL conical vials were filled with 15 mL aqueous Pluronic solutions (10 g/L), and a few solid naphthalene crystals were placed in the solutions. The vials were sealed with glass plugs and placed in a temperature-controlled shaker, and then shaken at 100 rpm. Equilibrium was reached in 5 h; 0.5 mL solutions were taken out and diluted with 0.5 mL methanol. The absorbance of the 1 : 1 (v/v) methanol/water solution was measured, and the concentrations of naphthalene in aqueous copolymer solutions were calculated.

2-3. Alginate Hydrogel Encapsulating Pluronic Block Copolymers

The stock aqueous solutions of PEO-PPO-PEO block copolymers (2 wt%) were prepared. Sodium alginate was added to the sur-

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factant solutions and stirred to make a 5 wt% mixtures. A 2 wt% calcium chloride solution was also made with the stock surfactant solution as the solvent. The drops of Pluronic block copolymer/alginate mixture were added to the calcium chloride solution by using a syringe. The drops began to gel immediately and were left in the cross-linking solution for at least 2 h to ensure complete gelation. After gelation, the beads were washed repeatedly to remove ungelated alginate and non-encapsulated block copolymers. The diameter of hydrogel beads is about 2-3 mm.

RESULTS AND DISCUSSION

1. Surface Activity of PEO-PPO-PEO Block Copolymers

The surface tension measurements for aqueous Pluronic P123 solutions at two temperatures, 22 and 30 °C, as a function of concentration are presented in Fig. 1. At low concentration the surface tension is decreased with increasing concentration until a plateau is reached; the copolymer concentration at the inflection corresponds to critical micellization concentration (CMC). After CMC, the block copolymer forms micelles in aqueous solutions, and the surface tension values remain almost constant with a further increase of copolymer concentration. Increasing temperature would decrease the surface tension for the block copolymer solution at same concentration and the CMC values. The CMC of Pluronic P123 is 0.4 g/L at 22 °C, and 0.04 g/L at 30 °C (the CMC values are denoted in Fig. 1). The CMC values of studied Pluronic block copolymers at 22 and 30 °C are given in Table 1. For copolymers with the same PPO/

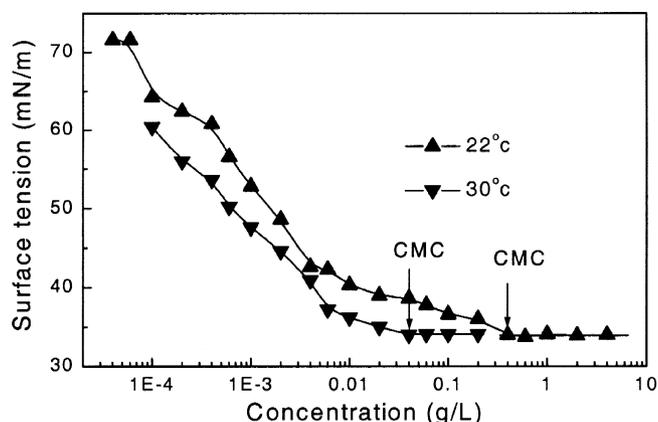


Fig. 1. The surface tension of aqueous Pluronic block copolymer P123 solutions as a function of concentration at 22 °C and 30 °C; the arrows indicate the CMC values.

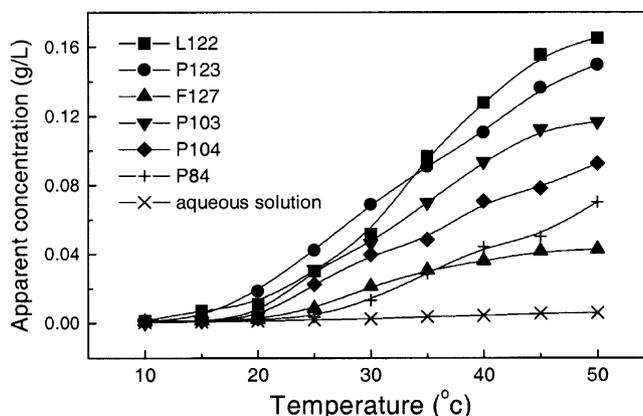


Fig. 2. The temperature dependence of the apparent concentrations of naphthalene in aqueous Pluronic block copolymer solutions; the concentration of block copolymers in water is 10 g/L.

PEO ratio, Pluronic block copolymer of higher molecular weight forms micelle at lower concentration and temperature. For copolymers with the same hydrophobic segment and varying hydrophilic segment, Pluronic block copolymer of higher PPO/PEO ratio has lower CMC [Alexandridis et al., 1994a, b]. The interpretation of solubilization relies upon the PEO-PPO-PEO block copolymer forming micelles.

2. Temperature-Dependent Solubilization

The hydrophobic cores of micelles can accommodate a certain amount of lipophilic organic compound as a solubilize. The apparent concentrations of naphthalene in 10 g/L aqueous Pluronic copolymer solutions as a function of temperature are presented in Fig. 2. The apparent solubility of naphthalene in water is slightly increased with an increase of temperature, but dramatically increased in aqueous Pluronic block copolymer solutions. The temperature denoted by a sharp increase in the apparent solubility is critical micellization temperature (CMT) (more accurate CMT values have been reported by Alexandridis et al., 1994a, b). Above CMT, the block copolymers form micelles in aqueous solution. The increase of naphthalene solubility demonstrates that the affinity between the solute and the micelles increases with an increase of temperature. The influence of various Pluronic block copolymers upon enhanced solubility can also be observed in Fig. 2. The most effective block copolymer surfactant for enhancing naphthalene solubility is Pluronic P123 at temperature below 35 °C. When the temperature is above 35 °C, however, naphthalene solubility using Pluronic L122 is highest. Pluronic P123 and L122 possess fairly large PPO blocks and

Table 1. Composition and critical micelle concentration (CMC) of PEO-PPO-PEO block copolymers

| Block copolymer | Molar weight | PPO wt% | General formula | CMC (g/L) | |
|-----------------|--------------|---------|--|-----------|-------|
| | | | | 22 °C | 30 °C |
| P84 | 4200 | 60 | (EO) ₁₉ (PO) ₄₃ (EO) ₁₉ | 40 | 1 |
| P104 | 5900 | 60 | (EO) ₂₇ (PO) ₆₁ (EO) ₂₇ | 10 | 0.44 |
| P103 | 4950 | 70 | (EO) ₁₇ (PO) ₆₀ (EO) ₁₇ | 1 | 0.1 |
| F127 | 12600 | 30 | (EO) ₁₀₀ (PO) ₆₅ (EO) ₁₀₀ | 10 | 0.6 |
| P123 | 5750 | 70 | (EO) ₁₉ (PO) ₆₉ (EO) ₁₉ | 0.4 | 0.04 |
| L122 | 5000 | 80 | (EO) ₁₂ (PO) ₆₇ (EO) ₁₂ | 0.06 | 0.01 |

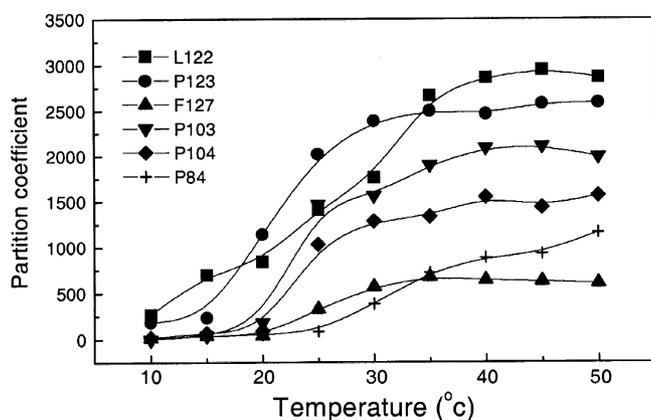


Fig. 3. The temperature dependence of the micelle/water partition coefficients of naphthalene in aqueous Pluronic block copolymer solutions; the concentration of block copolymers in water is 10 g/L.

small PEO blocks, which would produce more hydrophobic micro-environment (micellar cores) that is more favorable for naphthalene incorporation.

3. Temperature-Dependent Partition Coefficient

Fig. 3 shows the relationship between the micelle/water partition coefficient of naphthalene, K_{mw} , and the temperature, where

$$K_{mw} = c_m^s / c_w^s \quad (1)$$

c_m^s and c_w^s are the concentrations of naphthalene in the micelles (based on total polymer mass) and in the water, respectively. The c_m^s is obtained by subtracting the concentration of naphthalene in water from its total concentration in aqueous Pluronic block copolymer solutions. The partition coefficients begin to increase markedly when the temperature is above CMT. However, no durative increase of partition coefficients can be found when the temperature is about higher than 35 °C, which level off at higher temperatures.

The partition coefficients have relation to the property of Pluronic block copolymers. The partition coefficients are smaller at lower temperatures, which means that PEO-PPO-PEO block copolymers do not form aggregation, and no hydrophobic microenvironment is formed. The partition coefficients change markedly in the temperature range from 20 °C to 35 °C, which are related to micellar formation and the structural change of micelles. The higher the partition coefficient, the more hydrophobic microenvironment would be formed by PEO-PPO-PEO block copolymer. The results of solubilization are consistent with that of small angle neutron scattering [Goldmints et al., 1999]. The water content of micellar cores decreases with increasing temperature in the transition region, with a corresponding increase in the micelle aggregation number. The presence of naphthalene in the micellar cores also has a significant effect on the structure of micelles. Gadelle has suggested that solubilization initially takes place through a replacement process in which water is displaced from the micellar cores [Gadelle et al., 1995]. At higher temperatures, no evident change of partition coefficients means the property of micelles is not influenced by temperature.

4. Thermodynamics of Solubilization

To calculate thermodynamic parameters, a simple pseudo-phase model is employed. In this model, the micelles are described as a

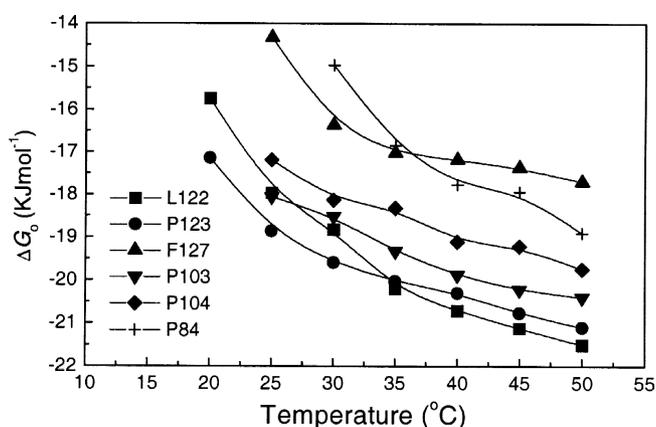


Fig. 4. The temperature dependence of solubilization free energy of naphthalene in Pluronic block copolymer aqueous solutions; the concentration of block copolymers in water is 10 g/L.

separate phase. The standard free energy change (ΔG°) for transferring 1 mole solute from the solvent to the micellar phase can be given as

$$\Delta G^\circ = -RT \ln K_{mw} \quad (2)$$

where R is the molar gas constant, and T is the absolute temperature. The thermodynamic parameters for solubilization of naphthalene in 10 g/L aqueous Pluronic block copolymer solutions as a function of temperature are shown in Fig. 4. Since micellar aggregates in water do not form at lower temperatures, the ΔG° values are only given at temperature above CMT. Spontaneous solubilization of naphthalene in aqueous Pluronic block copolymer solutions is manifested by the negative ΔG° values. Increasing temperature would make ΔG° values more negative, which suggests appreciable changes in the micellar structure. At same temperature, it can be seen in Fig. 4 that the absolute value of ΔG° is bigger for the more hydrophobic Pluronic block copolymer. Naphthalene prefers to solubilize in more hydrophobic micelles.

5. Extraction Trace Organics from Aqueous Solutions

Alginate hydrogel is one of the most widely used carriers for the immobilization of microbial cells. Since the high molecular weight makes PEO-PPO-PEO block copolymer unimer have lower diffusion coefficient, and the diameter of PEO-PPO-PEO micelles is bigger than the pore size of hydrogel, a stable micelle/hydrogel mixture can be obtained [Calvert et al., 1994]. At room temperature, 22 °C, 5 mL hydrogel beads were put into 20 mL saturated naphthalene solution; the naphthalene was extracted by hydrogel. The extraction rate (E) is defined as

$$E = \frac{(C_0 V - C_t V)}{C_0 V} \times 100\% \quad (3)$$

where C_0 is concentration of naphthalene in aqueous solution at initial time, C_t is concentration of naphthalene in aqueous solution at t time; V is the volume of saturated naphthalene solution. The extraction process reaches equilibrium in 2 h [Su and Liu, 2000]. The extraction rates of hydrogel at 2 h are shown in Fig. 5. It is seen in Fig. 5 that the extraction capacity of hydrogel is enhanced dramatically by encapsulating Pluronic block copolymers. The hydrogel

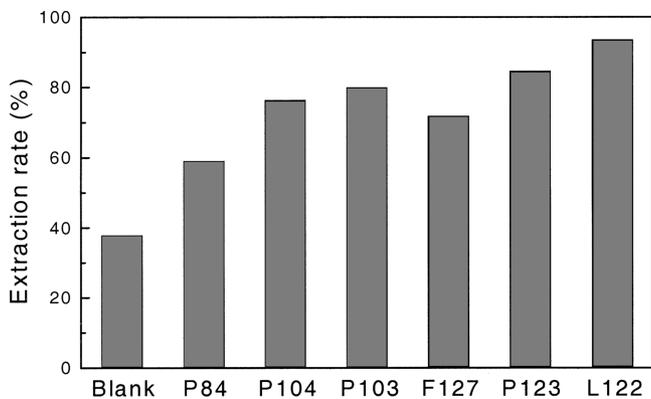


Fig. 5. The extraction rates of hydrogel at 22 °C; the hydrogel was composed of 5 wt% alginate gel and 2 wt% Pluronic copolymer.

encapsulating Pluronic L122 has the largest capacity to extract naphthalene, which is the most hydrophobic copolymer among the studied PEO-PPO-PEO block copolymers. The alginate hydrogel can be reused through a process of dryness, reverse-extraction and regeneration [Su and Liu, 2000].

CONCLUSIONS

Increasing temperature would enhance the apparent solubility of naphthalene in aqueous PEO-PPO-PEO block copolymer solutions. In certain temperature regions, the micelle/water partition coefficients of naphthalene were increased with increasing temperature. However, the partition coefficients of naphthalene leveled off at the higher temperature. The negative values of the solubilization free energy for naphthalene indicated that the solubilization process is spontaneous. When PEO-PPO-PEO block copolymers were encapsulated with sodium alginate hydrogel, the hydrogel had stronger capacity to extract trace organics from aqueous solutions.

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