

Study of the Micellization Behavior of Pluronic L64 in Different Salt Solution by FTIR Spectroscopy

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Abstract: The micellization behavior of a poly (ethylene oxide)–poly (propylene oxide)–poly (ethylene oxide) (PEO–PPO–PEO) triblock copolymer (Pluronic L64: EO₁₃PO₃₀EO₁₃) in the presence of various alkali halide salts (NaF, NaCl, NaBr, NaI) was studied by Fourier transform infrared spectroscopy. The CMT of Pluronic L64 in salt aqueous solution decrease with the increase of the salt concentration, and the anion effect for sodium halide follows the sequence: F⁻>Cl⁻>Br⁻>I⁻. The wavenumber shifts of the bands at 1100, 1373, and 2980 are investigated as a function of temperature, which are assigned to the C-O stretching mode for aliphatic ether, methyl deformation mode and the antisymmetric C-H stretching vibration of methyl groups, respectively, and the salt effect on the phase transition of the Pluronic L64 in aqueous solution is suggested.

Introduction

Polyethylene oxide-polypropylene oxide-polyethylene oxide (PEO-PPO-PEO) triblock copolymers are typical nonionic polymeric surfactants with potential applications in the pharmaceutical, textile and detergent industries¹⁻⁴. These triblock copolymers possess symmetrical structure (EO)_x(PO)_y(EO)_x where x and y denote the number of ethylene oxide and propylene oxide monomers per block and are commercially available in a range of x and y values under the trade names like pluronics (BASF), synperonics (ICI), poloxamers or generic name like EPE polyols⁵.

Pluronic form micelles in aqueous solutions composed of a core of PPO blocks and an outer shell consisting of PEO end blocks and water. Strongly concentration- and temperature-dependent micellization has been observed for various Pluronic differing in molecular characteristics⁶⁻¹³. The phase behavior of block copolymer in water and in salt solutions have been extensively studied¹⁴⁻²⁰.

It has been observed that the added salt exerts a strong influence on the solution behavior of these block copolymers. Paschalis Alexandridis¹³ et al. have found that the presence of LiCl, KCl, NaCl, and NaBr decreased both CMT and CP (in the order Cl⁻ > Br⁻ and Na⁺ > K⁺ > Li⁺), whereas addition of NaSCN and urea resulted in a CMT and CP increase (in the order NaSCN > urea). NaI appeared to be an intermediate case as it decreased the CMT but increased the CP. P.R. Desai et al.²¹ have examined the micellization of F127 (EO₉₉PO₆₅EO₉₉, MOL.WT.PPO=1750, %PEO=70) in aqueous solution in the presence of various additives (i.e. sodium chloride, urea and sodium dodecyl sulfate (SDS)) by cloud point, surface tension, dye spectral change, sound velocity, viscosity and dynamic light scattering measurements over the temperature range 25-50°C). But more detail information about salt effect on Pluronic micellization is needed, and the mechanism of the salt effect on the phase transition of the block copolymer is not clear.

Fourier transform infrared (FTIR) spectroscopy is sensitive to any molecular structural changes, so it has been extensively used to study the conformation of hydrocarbon chains in the normal low molecular weight surfactant micelles in aqueous solutions. It has been applied to study the temperature-dependent micellization of Pluronic in aqueous solutions and in salt aqueous solution^{22, 23, 24}. It is evident that drastic changes of the infrared spectra of the polymers occur over a given temperature interval, with small changes before and after.

The starting temperature of the interval can be taken as the CMT. The purpose of this work is to further study detail information about the different salt effects on the temperature-dependent micellization of PEO-PPO-PEO block copolymers in aqueous solutions using FTIR spectroscopy, and give the mechanism of the salt effect on the phase transition of the block copolymer.

Materials and Methods

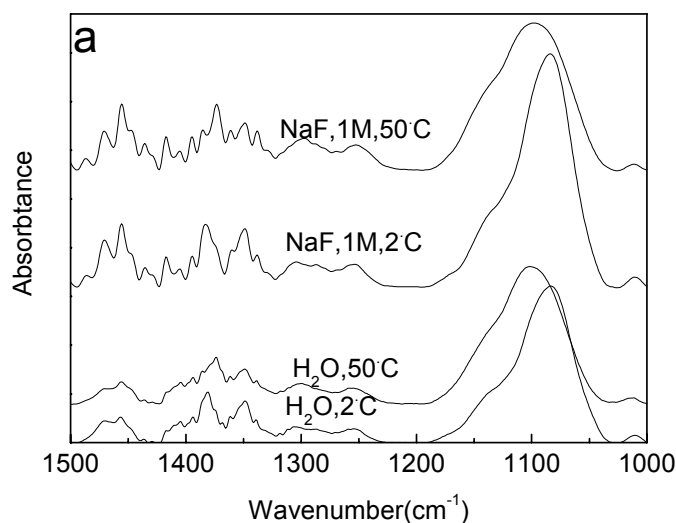
Materials. PEO-PPO-PEO block copolymers Pluronic L64 was donated by BASF Corp. and used as received. The copolymer has a nominal molecular weight of 2900 and approximately 40wt% PEO and can thus be represented by the formula $\text{EO}_{13}\text{PO}_{30}\text{EO}_{13}$. The various salts used were of analytical grade or better, while the water was triple-distilled.

Fourier transform infrared (FTIR). FTIR spectra were recorded on a Bruker Vector 22 FTIR spectrometer with a resolution of 2 cm^{-1} using a DTGS (deuteriotriglycine sulfate) detector. The temperature of the sample was measured by a thermocouple inserted into a stainless steel block containing the sample cell. This system was comprised of a Graseby-Specac temperature cell (P/N 21525), and the temperature measurement was accurate to $0.1\text{ }^{\circ}\text{C}$. The equilibration time for each measurement was 1 min. FTIR spectra of all samples were recorded from 2°C to $50\text{ }^{\circ}\text{C}$ by scanning 64 times and using a BaF₂ cell. The OPUS spectroscopic software was used for data handling.

Results and Discussion

The Assignments of FTIR Bands of Pluronic L64

The FTIR spectra of the 10wt% Pluronic L64 in aqueous solution and in 1M NaF aqueous solution at different temperature are shown in Figure 1. It is shown that the band shapes of the infrared spectra of the Pluronic L64 in aqueous solution and in NaF aqueous solution are similar, but they are different at different temperature. The bands at 1100, 1373, and 2980 are assigned to the C-O stretching mode for aliphatic ether, methyl deformation mode and the antisymmetric C-H stretching vibration of methyl groups, respectively^{25, 26}.



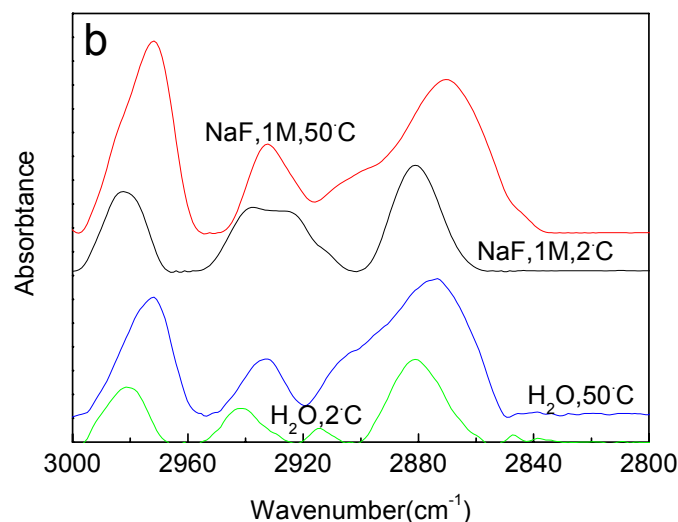


Figure 1. FTIR spectra of Pluronic L64 in aqueous solution and in 1M NaF aqueous solution at a concentration of 10wt% at 2°C and 50°C (a) in the range from 1000-1500 cm^{-1} . (b) in the range from 2800-3000 cm^{-1} .

The Salt Effects on the Temperature-Dependent Micellization of Pluronic L64 in Salt Solution.

Wavenumber shift of the C-O-C stretching vibration band, the CH_3 symmetric deformation band, and the antisymmetric C-H stretching vibration of methyl groups of Pluronic L64 in different concentration of NaCl solutions with the increase of the temperature is plotted.

The CMT of 10 wt% Pluronic L64 aqueous solution moved to lower temperature when salt is added, the more NaCl added, the lower the CMT of 10 wt% Pluronic L 64 aqueous solution. The CMT of 10 wt% Pluronic L64 in aqueous solution, 0.5M NaCl solution, 1M NaCl solution, 1.25M NaCl solution, and 1.5M NaCl solution is 22.5°C, 20.5°C, 16°C, 14°C, and 2°C(or even more lower) respectively.

Wavenumber shift of the C-O-C stretching vibration band, the CH_3 symmetric deformation band, and the antisymmetric C-H stretching vibration of methyl groups of Pluronic L64 in different salt solutions with the increase of the temperature is plotted. It can be seen that the CMT of 10 wt% Pluronic L 64 in water, 1M NaF, 1M NaCl, 1M NaBr and 1 M NaI are 8.5°C, 12.5°C, 16°C, and 26°C. So all salts studied could decrease the CMT of the Pluronic L64. The effect of anion on CMT follows the sequence: $\text{F}^- > \text{Cl}^- > \text{Br}^- > \text{I}^-$.

The band of the C-O stretching mode for aliphatic ether shifts abruptly to higher frequency at CMT, which may result from the split of the hydrogen band between the ether oxygen atom and the water molecular. When the salt is added, the water molecular around the inorganic salt ion is polarized, so there is competition between the oxide of the aliphatic ether and the inorganic salt ion, and it accelerates the dehydration of PPO and the CMT become lower. With the increase of the anion radius, the polarize ability of the ion become stronger, and the change of the CMT is more pronounced. The band of the methyl deformation mode shifts abruptly to lower frequencies at CMT, which may means the decrease of the force between the ether oxygen atom and the water molecular and the increase in the intermolecular interation of the PO chains. The band of the antisymmetric C-H stretching vibration of methyl groups shifts abruptly to lower frequencies at CMT too, which is quite possibly due to the increase in the gauche conformer of the PO chains from the unimer phase to the micellar phase. With the increase of the anion radius of the salt, the shift of wavenumber occurred at a lower temperature. This indicates the addition of salts accelerate the change of the PO chains.

Conclusions

The systematically micellization behavior of Pluronic L64 (EO₁₃PO₃₀EO₁₃) in aqueous solutions and salt solutions is studied by FTIR spectroscopy.

To get the phase transition information, the change of wavenumber of the C-O-C stretching vibration band, the CH₃ symmetric deformation band, and the antisymmetric C-H stretching vibration of methyl groups of Pluronic L64 in t aqueous solutions of different concentration, in NaCl solutions of different concentration, and in different salt solutions of 10wt% with the increase of the temperature are plotted. The CMT is defined as the temperature at which the wavenumber shifts abruptly. The addition of salts distinctly decreases the CMT of the Pluronic L64 aqueous solution, and the CMT become lower as the concentration of the aqueous solution become larger. The anion effect for sodium halide follows the sequence: F⁻>Cl⁻>Br⁻>I⁻. When the salts are added, the water molecular around the inorganic salt ion is polarized, which accelerates the dehydration of PO and EO blocks, and thus the CMT of the Pluronic L64 becomes lower.

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