



Energetics of poloxamer micellization at normal and high pressures

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ABSTRACT

Micellization of a poloxamer P105 in diluted aqueous solutions was first investigated by means of high-sensitivity differential scanning calorimetry at different pressures up to ~160 MPa. The temperature dependence of partial heat capacity of the poloxamer clearly indicates that the unimers have the random coil conformation while the micelles are built of a “dry” PO core and hydrated EO shell. Independently of the polymer concentration, the micellization temperature increases upon increasing pressure while the enthalpy decreases. Based on these dependences, the micellization increments of the partial volume $\Delta_t v$ as well as the coefficients of thermal volume expansion and compressibility, $\Delta_t \alpha$ and $\Delta_t \chi$, of the poloxamer were calculated. They prove that the dehydration of PO hydrophobic blocks makes the main contribution to the micellization energetics. We demonstrate that poloxamer micelles are formed *via* a nucleation stage of unimer dimerization followed by consecutive energetically favored attachment of unimers to the dimer and further to the growing micelle.

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1. Introduction

Poloxamers, water-soluble PEO-PPO-PEO triblock copolymers, are widespread commercially available non-ionic macromolecular surfactants. Variations in the composition and molecular weight of these polymers upon synthesis enables production of macromolecules with optimal properties in accordance to technologic requirements for a desired target polymer [1].

In diluted aqueous solutions poloxamers exist as unimers at low temperatures. Upon heating they self-associate into micelles [2]. The micelle core mainly consists of PPO blocks [3–5]. An increase in the content of PPO block in a poloxamer leads to a decrease in the critical micelle concentration.

According to DSC data [2,4,6–14], the micellization enthalpy of poloxamers is rather high ($\sim 60 \text{ J g}^{-1}$). Typically, the transition temperature decreases upon increase in the poloxamer concentration. A model of cooperative micellization was proposed for the analysis of the calorimetric data [6,13,15]. According to this model the micellization process follows “all-or-none” scheme:



where n is a number of primary particles (unimers) in the micelle. The n value was determined as a ratio of the van't Hoff enthalpy to the calorimetric one. Importantly, such estimates for n ranged from 2 to 10, while the experimental values of the micelle aggregation number were of order of several tens. To eliminate this contradiction a consecutive mechanism of micellization was proposed [13] that implies that at the initial stage small micelles are formed. This is the stage that is registered calorimetrically. The second stage of the transition includes a progressive athermal association of small micelles upon further increase in temperature. However, this assumption seems to be doubtful since in accordance with the Le Chatelier-Braun principle heating should not affect an athermal process.

A discrepancy between the cooperative micellization model and experimental data manifests itself in a well-known phenomenon that the experimental excess heat capacity function is much broader than the theoretic one. Hvidt et al. [16,17] have suggested that such discrepancy reflects the molecular weight and compositional heterogeneity of the copolymers. Indeed, among the copolymers they detected a fraction of low-molecular impurities unable to form micelles. However, elimination of these impurities did not affect the transition temperature and width but increases

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the transition enthalpy by about 10%. The fractionation of poloxamers by the content of PPO blocks was more effective. Relatively narrow poloxamer fractions with different average content of PPO blocks (from 35 to 50 per primary chain) were isolated. They differed substantially by the transition temperature but had close values of enthalpy and width. Upon increasing average content of the PPO blocks within the above given range the transition temperature decreased by 10 °C. However, the transition width of the isolated fractions was only two times less than that of the initial copolymer. Analysis of these data in terms of the cooperative association model revealed that the theoretic value of the association degree was of 3 for the non-fractionated polymer and of 5–8 for its fractions while the experimental value of this parameter amounted to 30. Thus, we can conclude that the composition heterogeneity of poloxamers is not a key factor responsible for the diffuse character of the micellization transition.

Meilleur et al. [18] measured the partial heat capacity for a set of poloxamers within the concentration range of 0.1–10% at temperatures 5, 25, and 45 °C. Under conditions where primary chains (unimers) or micelles dominate, the partial heat capacity does not depend on the copolymer concentration. Herewith the partial heat capacity of micelles is lower than that of unimers. In the transition area the concentration dependence of the partial heat capacity passes, as a rule, through a maximum that reflects obviously a shift of the micellization equilibrium.

Pressure is another thermodynamic variable which is important for the analysis of mechanisms of self-association of amphiphilic copolymers in water. Pressure effects on micellization of block copolymers including poloxamers in aqueous solutions have been mainly investigated by structural methods such as DLS [19,20] and SANS [19,21–25]. Most of structural measurements have been carried out at high polymer concentrations (of about 20–50%) and have focused on identification of variety of micellar structures and phases as well as transformations between these phases [20–22]. Less is known about the pressure effects on the unimer-micelle transition mechanism of poloxamers in diluted solutions [24,25]. Upon increasing pressure up to about 150–200 MPa, the micellization temperature was shown to increase for poloxamers P85 [22,25], F88 [21], F108 and F127 [22], block copolymers poly(2-ethoxyethoxyethyl vinyl ether)-block-poly(2-hydroxyethyl vinyl ether) [24] and poly[2-(2-ethoxy) ethoxyethyl vinyl ether]-block-poly(2-methoxyethyl vinyl ether) [19,23]. The micelle volume fraction increased with decreasing pressure [22]. Density measurements revealed an increase in the apparent partial volume of poloxamer P94 related to its micellization [26]. Consequently, application of increasing hydrostatic pressure would shift the unimer-micelle equilibrium in the poloxamer solution towards unimers. In fact, a decreased stability of the poloxamer F88 micelles caused by a pressure of 6.3 MPa could be compensated by a temperature increase of 1 °C [21]. Thus, temperature and pressure could have similar effects on the micellar solution: an increase in temperature corresponds to a decrease in pressure [21]. Such a coherence of the temperature and pressure effects was presumed to be a consequence of crucial dehydration changes, affecting mainly PO units, as a result of the micellization [26]. However, to prove this hypothesis direct thermodynamic measurements of the transition temperature and enthalpy changes upon pressure variations are required. These parameters could be derived from calorimetric measurements of micellization at different pressures. Until now, no pressure dependent calorimetric data have been obtained for poloxamers or related amphiphilic block copolymers in aqueous solutions.

In summary, despite the large number of DSC studies on the micellization of poloxamers no calorimetric data for dilute solutions of these copolymers have been obtained until now. There are

no reliable data on partial heat capacity of poloxamers and its change as a result of the micellization transition. The mechanism of micellization still remains an open question. The “all-or-none” model does not seem to be adequate in this case since it leads to a clear underestimation of the average number of primary chains in micelle (about three against experimental value of several tens). Pressure effects on the micellization of poloxamers have been investigated only from the structural points of view. For rigorous thermodynamic analysis of these effects calorimetric data on the micellization energetics at high pressures are necessary.

In the present work we investigated the micellization of a poloxamer P105 in diluted aqueous solutions using high-sensitivity differential scanning calorimetry at normal and high pressure up to ~160 MPa. The poloxamer P105 is one of the typical examples of PEO-PPO-PEO triblock copolymers. Its molecular weight is equal to 6.5 kDa and it is composed of 56 units of PO and 37×2 units of EO [2]. The copolymer P105 micelle represents a sphere of a diameter ~80 nm which involves a hydrophobic core of the diameter ~46 nm and a hydrophilic shell [27]. These dimensions demonstrate a slight temperature dependence. On the other hand, the aggregation degree of the P105 micelles increases notably with increasing temperature. Within temperature range from 30 to 60 °C it raises from 50 to 80. Here we report calorimetric parameters of the P105 micellization at normal and high pressures and discuss congruous mechanisms of this transition.

2. Experimental

Poloxamer P105 (Synperonic PE/P-105, “Croda”, UK) was used without additional purification.

The poloxamer was dissolved by weight in deionized Milli-Q water for no less than 12 h at 4 °C. Poloxamer solutions of concentrations 2.5 mg mL⁻¹ and 0.5–20 mg mL⁻¹ were used, respectively, for densitometric and calorimetric measurements at normal pressure. Calorimetric measurements at high pressures were carried out with the poloxamer solutions of concentrations 5–15 mg mL⁻¹.

Densitometric measurements were performed with a vibration densitometer AD-1 (NPO “Biopribor”, Pushchino, Russia) at temperature of 18.0 °C. The instrument was calibrated by air and deionized Milli-Q water. The poloxamer solutions were degassed for 15–20 min under vacuum prior to measurements. Density of a poloxamer solution of concentration 2.5 mg mL⁻¹ was equal to $\rho = 0.99893$ g cm⁻³ which resulted in a value of the partial specific volume of the poloxamer $\bar{v} = 0.868$ cm³ g⁻¹. The absolute error in the partial specific volume determination was no more than $\pm 2 \times 10^{-3}$ cm³ g⁻¹.

Calorimetric measurements were carried out with a differential adiabatic scanning microcalorimeter DASM-4A (NPO “Biopribor”, Pushchino, Russia) at normal pressure and with a high pressure differential scanning calorimeter “SCAL-3HP” [28] (Institute of Protein Research, Pushchino, Russia) at different pressures up to ~160 MPa. The heating rate was of 1 K min⁻¹ in both cases. Experimental thermograms were converted to the temperature dependences of partial specific heat capacity of the poloxamer using its partial specific volume [29], and then to the excess heat capacity functions $c_p^E(T)$ by means of a proprietary computer program “Nairta-2” (A.N. Nesmeyanov Institute of Organoelement Compounds). The transition baseline in the latter calculations was constructed as a progressive curve as described in Ref. [30]. Thermodynamic parameters of micellization were determined at normal and high pressures. These are the transition temperature T_t as a temperature of the maximum of the excess heat capacity function $c_p^E(T)$, the midpoint transition temperature $T_{0.5}$, the transition enthalpy $\Delta_t h$ as an area under the curve $c_p^E(T)$ and the

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