Journal of Engineering Physics and Thermophysics, Vol. 79, No. 3, 2006

HEAT AND MASS TRANSFER IN DISPERSIVE MEDIA

THERMOPHYSICAL AND ACOUSTIC PROPERTIES OF AQUEOUS SOLUTIONS OF THE PLURONIC PE6400 COPOLYMER

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UDC 678.76

Experimental results of investigations of the specific heat and the velocity of sound in aqueous solutions of the Pluronic PE6400 copolymer have been presented. Phase transitions, phase states, and possible physical mechanisms of the effects have been discussed based on these results.

Poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) (PEO–PPO–PEO) water-soluble copolymers are commercially available nonion macromolecular surfactants. The commercial name of these surfactants is Pluronic (BASF made).

As compared to the widespread surfactants, a distinctive feature of these compounds is that their critical micelle concentration (CMC) and surface activity are strongly dependent on temperature. The CMC of block copolymers may shift by several orders of magnitude within a small temperature interval. For systems of commercial use, the shifts mainly occur in the temperature range 293–323 K. Consequently, these systems cannot be used efficiently without reliable data on the CMC and the critical micelle temperature (CMT). It has been established that the CMT and the CMC are significantly different due to a possible difference in the procedures used in sensitivity [1–5]. Simultaneous use of the adiabatic-calorimetry and acoustics methods is known [6, 7] to be quite efficient in such investigations. Therefore, this work seeks to investigate the temperature dependence of the specific heat at constant pressure $C_p(T)$ and the velocity of sound $u(T)$ of the least understood copolymer, Pluronic PE6400.

Materials and Procedure. The PEO_{13}–PPO_{30}–PEO_{13} copolymer under study is produced by the BASF Chemical Concern and has the trade name Pluronic PE6400. Freshly prepared deionized 2–18% aqueous solutions were used for measurements.

Measurements of the temperature dependence of the specific heat $C_p(T)$ in such systems for the most part were carried out using differential scanning calorimetry. As is well known, the necessity of using the solution under study and a reference solution close in thermal characteristics in calorimetric cells is one substantial drawback of the differential-scanning-calorimetry method. Therefore, we used the "direct" method implying that $C_p(T)$ was investigated by a vacuum-adiabatic calorimeter with discrete heat supply on a universal, low-temperature, thermophysical reference setup. Based on the measurements of the specific heat of reference samples, it has been established that the confidence error in determining C_p (in the temperature range 273–373 K) amounts to 0.1%.

The absorption and the velocity of ultrasound in the frequency range 0.1–20 MHz were measured by the resonator method. This method [8, 9], based on the use of the parameters of standing sound waves in a cylindrical resonator, enables one to determine the velocity and relative attenuation of sound in a liquid from the frequency and width of the characteristic resonance peaks. The cell temperature was monitored and measured accurate to 0.03 K.

Experimental Results on the Specific Heat. Typical $C_p(T)$ curves for the aqueous solutions of Pluronic PE6400 are presented in Fig. 1. The presence of a sharp $C_p(T)$ minimum is found in these systems at temperatures

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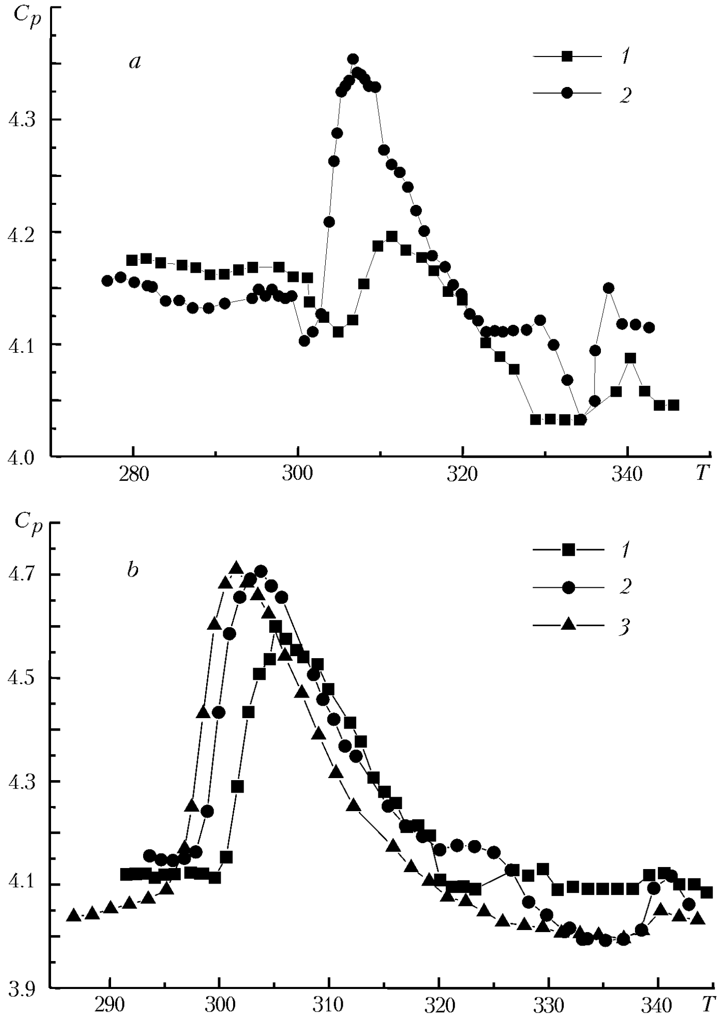

Fig. 1. Temperature dependence of the specific heat of PE6400 for different concentrations of the polymer in water: a) 1) 2 and 2) 6%; b) 1) 10, 2) 14, and 3) 18%. C_p, J/(g·K); T, K.

TABLE 1. Characteristic Temperatures of the PE6400–Water System

N, %	T_{in}, K	T_{m}, K	ΔT, K
2	33.4	38.231	7.93
6	29.621	33.523	18.066
10	26.409	31.942	19.523
14	22.583	30.603	24.337
18	20.352	28.372	27.296

below room temperature, which is inconsistent with the available experimental data on differential scanning calorimetry in such solutions [3]. We have established that such effects are only observed in sharp (of more than 1 deg/min) cooling of the solutions below 283 K; the temperature of the minimum is determined by the cooling rate.

A sharp growth in the specific heat with a characteristic maximum typical of the phase transition of the first kind is observed at temperatures above room temperature. A pronounced "mean-temperature" peak of specific heat shows the micelle formation of the copolymer, i.e., the occurrence of a thermal transition in the process of micellization corresponds to the polymer CMT; the CMT is virtually linearly dependent on concentration (see Table 1). Although the phase transition of micellization is of cooperative-type, the phase-transition width (ΔT) is fairly large

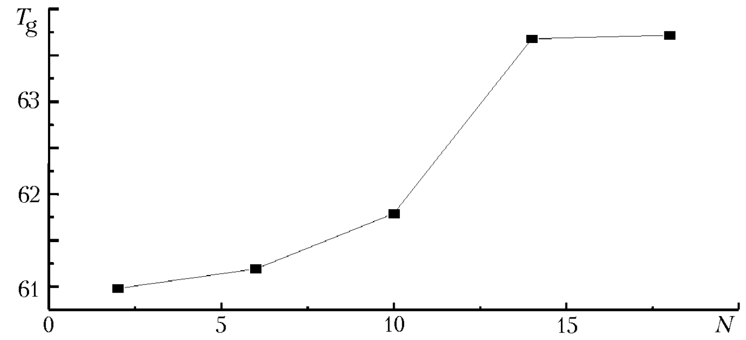

Fig. 2. Dependence of T_g on the concentration of PE6400. T_g, K; N, %.

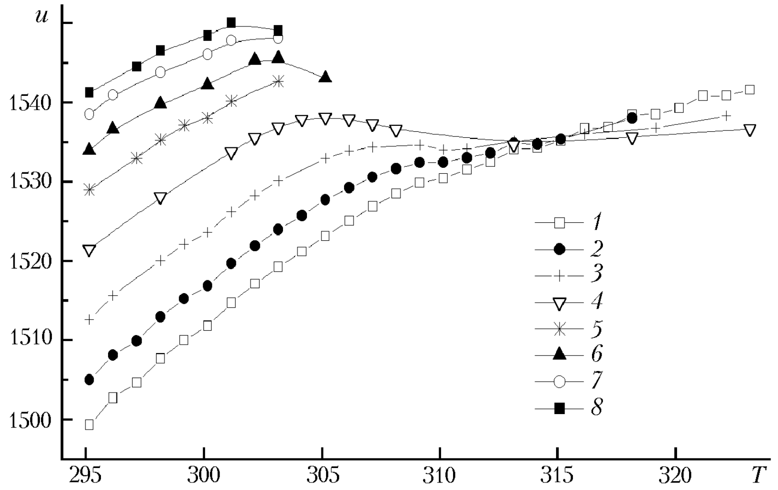

Fig. 3. Temperature dependence of the velocity of sound for different concentrations of the copolymer in the solution: 1) 1, 2) 3, 3) 4.3, 4) 6, 5) 6.5, 6) 8, 7) 9, and 8) 10%. u, m/sec; T, K.

(~7–27 K) and is also substantially determined by the polymer concentration. This is due [4] to the temperature dependence of the number of monomers in equilibrium with micelles and to the polydispersity inherent in polymers. Conceivably, the pronounced width of the peak of specific heat (ΔT) [6] might be due to the fact that copolymers show different distributions of molecular weights and are not "pure" compounds and "fusion" peaks become broad in the presence of impurities.

Also, we observe weak specific-heat peaks caused by the same phase transitions of the first kind at temperatures above 320 K; the transition heats are several times lower than those in micelle formation. The characteristic temperature of these transitions (T_g) for low concentrations is exponential in character, reaching saturation for higher concentrations (Fig. 2). This is conceivably because of the following factor. From an analysis of the method of obtaining data on solid spheres [5], it has become known that micelle formation falls within the framework of the behavior of a regular phase transition where the CMT is determined from the PPO concentration, whereas the crystallization (gelation) temperature is dependent on the total concentration of the copolymer [8]. The micelle concentration increased linearly with temperature until saturation was reached (where the entire polymer was associated into micelles), or the volume density of micelles was so high that the macromolecules were "blocked" into the crystal structure of a solid sphere. In the temperature range 330–343 K, the micelle shape changed from a spherical one to that of a prolate ellipsoid, which led to a decrease in micellar interactions and caused an opaque suspension to form.

Experimental Results on the Velocity of Sound. The velocity of sound was measured in copolymer solutions with 2–10 wt.% at temperatures of 293 to 323 K. As is seen in Fig. 3, the velocity of sound departs from the characteristic behavior at low temperatures in a certain temperature interval. The values of the transition temperatures are presented in Fig. 4. The velocity of sound sharply changes for high copolymer concentrations and has a minimum

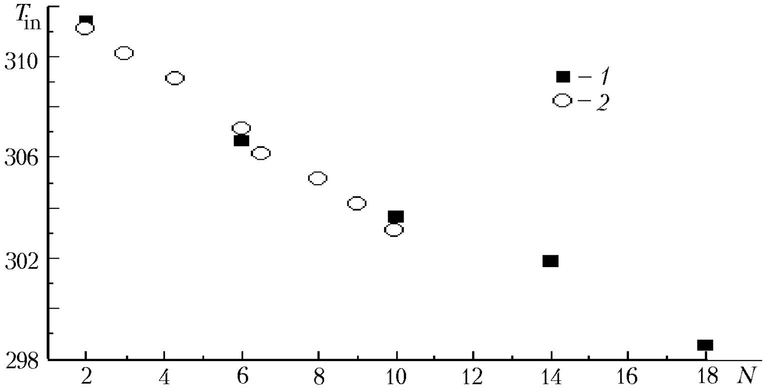

Fig. 4. Dependence of the transition temperature on the concentration, obtained by determination of the specific heat (1) and the velocity of sound (2). *T*, K; *N*, %.

for the solutions containing more than 4% of the copolymer. For copolymer concentrations higher than 6.5%, the velocity of sound was measured to 303 K, since the half-width of the resonant peaks was large at high temperatures and affected the width of the neighboring resonances, which reduced measurement accuracy.

It is well known that the velocity of sound is dependent on the number of particles in the solution, since the formation of aggregates of a nonionic surfactant containing PEO–PPO segments is enhanced with increase in the temperature, and the sharp change in the velocity of sound reflects the increase in particles due to self-organization, which is confirmed by experiments with the use of other methods [10–16]. However, on the other hand, at high (above 313 K) temperatures, the velocity of sound has close values for low and high concentrations: for high concentrations, there is a large number of aggregates and the interaction between them is dominant, which leads to a decrease in the number of aggregates and in the velocity of sound. The existence of the minimum of the velocity of sound is brought about by the formation of micelle-copolymer monomers in it. This assumption is confirmed by the results of measurements of the specific heat in the solution. Figure 4 gives the values of the transition temperatures obtained by determination of the specific heat and the velocity of sound. The results are in good agreement throughout the range of the copolymer concentrations in the solution. The temperature behavior of the specific heat and the velocity of sound confirms the dehydration of the block copolymer with increase in the temperature, which causes the monomers to interact and the micellelike aggregates with a hydrophobic nucleus to form.

Discussion of the Results. Above we have shown the presence of the phase state of the studied solutions characterized as a supercooled system [17]; the capacity for supercooling was only observed for concentrations of 2 and 6%. Such effects were presumably attributed to a certain conformation rearrangement of macromolecules in the solution. It is well known that the amphiphilicity of block copolymers assumes the presence of a set of more or less favorable conformation states for a macromolecule. According to the evaluation available in the literature, the size of a molecularly dispersed macromolecule is approximately 1 nm. This size is inconsistent with the extended spiral of a macrochain with a molecular weight of about 2900. Clearly, this evaluation is true of the effective diameter of a statistically streamlined coil. If it is allowed that these macromolecules do not interact at low temperatures, from the viewpoint of thermodynamic stability, the middle hydrophobic block inside the macromolecular coil can be one of the most stable conformations, which makes the interaction with water much weaker. The hydration of PEO blocks increases with temperature, which leads to a growth in macromolecular coils. This process continues to a certain temperature, when the solubility of a PEO block significantly differs from the solubility of a PPO block. A spontaneous rearrangement of the solution microstructure, accompanied by a change in the conformation, results; thereafter, the process of association through spontaneous connection of hydrophobic blocks together begins.

Taking into account the results of these investigations, we can say that micelle animers and "micellar aggregates" coexist in the solution in the Pluronic PE6400–water system; the relative proportions of each kind of aggregate are strongly dependent on the copolymer temperature and concentration.

When the concentration and temperatures of the copolymer are below the CMC–CMT limit, there are free polymers (animers) in the solution; above this limit, we have equilibrium between the micelles and animers. Phase diagrams of certain (PE6400-like) PEO–PPO–PEO copolymers in water were reported later by Wanka et al. [12, 16]. These authors observed the animer, micellar, cubic (gel), hexagonal, and lamellar phases; their location was dependent on the composition relation of PPO/PEO copolymers. The copolymers with a small PEO hydrophilic block usually formed a hexagonal phase as the first liquid-crystalline mesophase. Lyotropic phases showed a thermotropic behavior: reversible transitions between different phases occurred with growth in the temperature for a constant copolymer concentration.

The "dissolved substance–solvent" [1, 2] or "dissolved substance–dissolved substance" interactions [4] are also proposed for interpretation of the mechanism of "molecular levels" due to the temperature dependence observed in the micelle formation of PEO–PPO–PEO copolymers in water (we note that the hydrophobic effect described above is based on the "solvent–solvent" interactions). Lobry et al. [4] made an attempt at reproducing the negative entropy and enthalpy in the water–PEO mixture and the phase diagram of the water–PEO system and assumed the existence of a zone with an increased structurization of water around the PEO chain. The phase equilibrium occurring at high temperatures was related to the destruction of zones with enhanced water structurization. It is stated in [4] that, when PPO is added to water, a hydration shell with an enhanced water structure is developed, too, but at the same time, the methyl groups determine the presence of steric hindrances and the aqueous structure is weak and leads to phase separation. Wanka et al. [16] predicted the water–PEO phase diagram, using the Flory–Huggins theory and allowing that each segment of the PEO chain can exist in two forms: one is polar and with a low energy and a low statistical weight, whereas the other is less polar or nonpolar and with higher energy and statistical weight. Polar conformations dominate at low temperatures, so that the "dissolved substance–solvent" interactions become favorable; at the same time, the class of nonpolar states is increasingly more preferable at high temperatures, whereas the "dissolved substance–solvent" interaction is less favorable [16]. A model for prediction of the behavior of the solution of block-copolymer micelles has been developed in [1–4]. It includes Karlstrom's ideas for taking account of the conformation distribution in PEO and PPO; the predictions of the model are consistent with experiment, which confirms the suitability of the model of a polar–nonpolar state for explaining of the influence of temperature on the behavior of PEO and PPO solutions.

The investigation results show that the Pluronic PE6400 systems, just as other analogous copolymers, have a fairly wide variation of the CMC and the CMT, which is significant in commercial use as compared to the traditional surfactants. Thus, PEO–PPO–PEO block copolymers are an important class of surfactants. They can find wide industrial use in such processes as the production of detergents, the stabilization of disperse systems, foaming, emulsification, and lubrication, and in pharmaceuticals (stabilization of medicines and monitoring in cleaning and covering burn-induced wounds), in biotechnology (protection of microorganisms against mechanical injury), and in separation of substances (dissolution of organic matter in aqueous solutions). Furthermore, these copolymers can be used as a base for cosmetics, ink, etc.

The investigations were carried out within the framework of the State Programs for Basic Research Works of the Republic of Uzbekistan and the OTAN (RIG 981193, Brussels, Belgium) and Volkswagenstiftung (Hannover, Germany) international grants.

NOTATION

C_p, specific heat at constant pressure, J/(g·K); N, concentration of the polymer in water, %; T, absolute temperature, K; T_g, characteristic temperature of the peak of specific heat at $T \geq 330$ K (critical gelation temperature), K; T_m, temperature of the maximum of specific heat in the region of micelle formation, K; T_in, critical micelle temperature (beginning of the rise of the specific-heat curve), K; $u(T)$, temperature dependence of the velocity of sound, m/sec. Subscripts: g, gelation; m, maximum; in, initial.

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