

Micellar medium structure of the cetyltrimethylammonium – oxyethylated polyethylenimine – water system

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We have used several experimental methods including viscosity and surface tension measurements as well as small angle neutron scattering method for the investigation of the associations in the cetyltrimethylammonium bromide – oxyethylated polyethylenimine – water ternary system. It is shown that in this system cetyltrimethylammonium bromide micelles coexist with molecular or polymer-colloidal complexes formed by cetyltrimethylammonium bromide monomers adsorbed on the polymer.

1. THEORY

We have shown previously [1] that the mixed micelles are formed in the cetyltrimethylammonium bromide (CTAB) – polyethylenimine (PEI 30000) – water system. The system exhibits catalytic activity in decomposition of toxic phosphoric acids. Its catalysis efficiency and micelle geometric features are sensitive to the PEI concentration. Therefore, the molecular conformation and aggregation structure of the solutions containing CTAB and polymers of various structure and molecular weight is important.

In this report we present the results of our investigations for the CTAB – OPEI 50000 – water ternary system. OPEI denotes the oxyethylated polyethylenimine. This modification of PEI by ethoxy group is of relatively simple structure. Several experimental methods including viscosity and surface tension measurements as well as small angle neutron scattering (SANS) were employed. The system properties were studied for various concentrations of OPEI.

The viscosity measurements were performed for water solution (pH = 9.02) with concentration of OPEI varied from $7 \cdot 10^{-4}$ to $3 \cdot 10^{-2}$ mole/l. OPEI dissolves well in water and exhibits buffer properties. The vanishing reduced viscosity (ratio of the specific viscosity η_{sp} and the OPEI concentration C) with increasing concentration of the polymer (Fig. 1) is characteristic of a polyelectrolyte system.

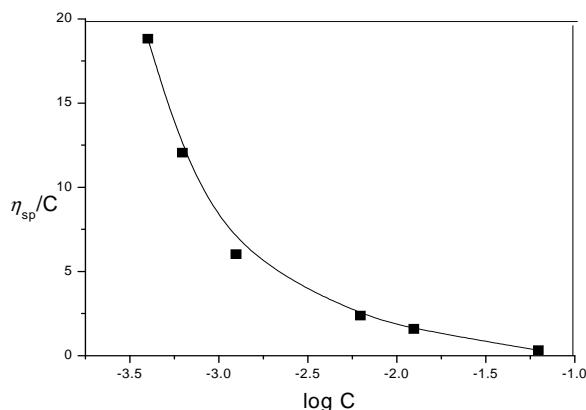


Fig. 1. The reduced viscosity vs the concentration of OPEI in water

The behavior can be explained in terms of the changing conformation of polymer macromolecules. The increase in OPEI concentration results in polymer tubes formation and yields the reduction of viscosity. The reduction of the PEI concentrations is accompanied by untwisting the macromolecular tubes. The polymer conformation is then linear and the size of the macromolecules increases. This effect produces enhancement of the reduced viscosity (polyelectrolyte effect).

The tensiometric measurements were performed using De Nuy method. The surface tension dependence on the surfactant concentration for four different contents of OPEI ($C_{\text{OPEI}} = 0, 7 \cdot 10^{-4}, 7 \cdot 10^{-3}$ and $2 \cdot 10^{-2}$ mole/l) was determined. The marked decrease of the surface tension with increasing concentration of surfactant proves the formation of micelles in the system studied. We found that the critical micelle concentration (CMC) of CTAB decreases substantially with addition of the OPEI and is approximately ten times lower than for the CTAB – water system.

Tab. 1. The C_{CMC} , correlation length (L), and the specific volume of scattering units in the CTAB – OPEI – water system

C_{CTAB} mole/l	C_{OPEI} mole/l	$C_{CMC} \times 10^4$ mole/l	$\Delta\phi$	L nm
0.00500	0.0	6.50 ± 0.24	$1.72 \cdot 10^{-3}$	$4.8 \pm .4$
0.00585	$7 \cdot 10^{-4}$	1.43 ± 0.25	$1.72 \cdot 10^{-3}$	$4.8 \pm .4$
0.00585	$7 \cdot 10^{-3}$	0.90 ± 0.07	$1.96 \cdot 10^{-3}$	$5.1 \pm .4$
0.00585	$2 \cdot 10^{-2}$	0.35 ± 0.01	$2.41 \cdot 10^{-3}$	$5.2 \pm ..4$

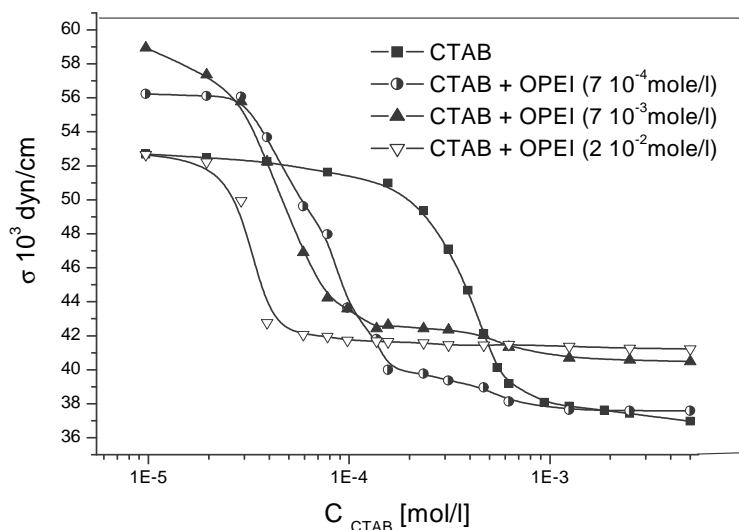


Fig 2. The dependences of surface tension upon the C_{CTAB} for the CTAB-OPEI-water system

With increasing the OPEI concentration the region is reached where polymer exists in the form of molecular tubes ($2.00 \cdot 10^{-2}$ mole/l). In effect (Fig. 2) a significant reduction of C_{CMC} (to $3.50 \cdot 10^{-5}$ mole/l) occurs. This feature indicates the formation of mixed associative structure. It suggests that OPEI makes the formation of the micelles easier.

In order to obtain more detailed information on the aggregation structure of the system the small angle neutron scattering (SANS) technique was applied. Due to its versatility the SANS is widely used in studies of crystals, alloys, surface layers, liquids, polymers, biological macromolecules and micelles [2]. Small angle scattering (of X-rays or neutrons) is almost the only source of direct information on the structure of colloidal systems containing objects of

linear dimension within the region of $10^{-10} - 10^{-8}$ m [3]. The result of a SANS experiment is a scattering curve representing the dependence of the scattered neutron intensity upon the scattering vector q . That intensity is proportional to the product of the form factor and the structure factor [3]. Form factor depends on the shape of the single scattering object (e.g. micelle). The structure factor describes the correlation between positions of scattering objects.

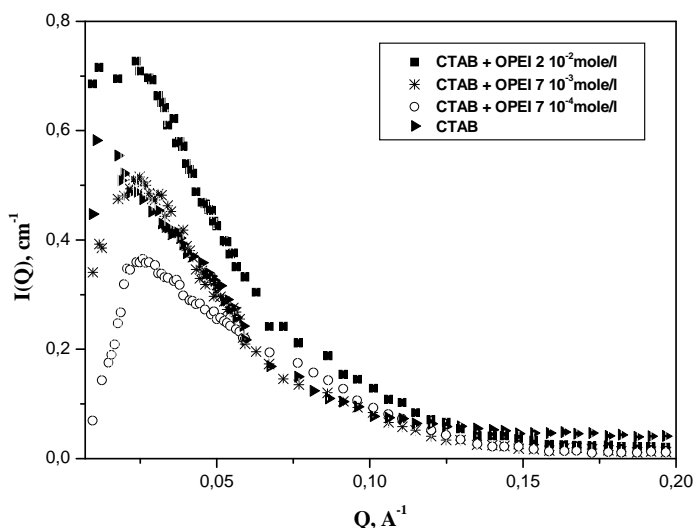


Fig. 3. The neutron scattering intensity vs scattering vector for various water solutions of CTAB and OPEI

Our SANS investigations were carried out with the time-of-flight SANS spectrometer at JINR Dubna, Russia. The measurements were performed for four samples with different content of OPEI (0 , $7 \cdot 10^{-4}$; $7 \cdot 10^{-3}$; $2 \cdot 10^{-2}$ mole/l) in the colloidal system CTAB – OPEI – water (Fig. 3). The position q_m of the maximum observed on the scattering curves $I(q)$ changes only slightly with concentration as a result of interaction between the charged aggregates (CTAB-OPEI). The average distance between those aggregates can be estimated as $2\pi/q_m \approx 26$ nm from the position of that maximum.

The intensity I of scattered neutrons depends on the concentration of OPEI. For very low concentration ($7 \cdot 10^{-4}$ mole/l) of OPEI the intensity is reduced in comparison to that observed for the CTAB – water system. This is due to the reduction of the micelle concentration in the solution. At higher concentrations of OPEI the neutron intensity increases due to enhanced micelle concentration.

The concentration and size of micelles can be estimated using so-called Porod's invariant

$$Q = \int_0^{\infty} I(q) q^2 dq = 2\pi^2 \Delta\rho^2 n V_p$$

where n is the number of scattering particles in unit of a volume, V_p – the volume of particle, $\Delta\rho$ – the scattering density contrast. The value of the invariant is proportional to the volumetric content φ of the scattering phase (micelles) in the solution. The correlation length (\sim average chord length) L can be estimated according to

$$L = \frac{\pi}{Q} \int_0^{\infty} I(q) q dq$$

The change of the volumetric fraction φ_m in respect to the OPEI free solution was determined assuming that the scattering contrast density does not change with addition of OPEI molecules.

The estimated values of the correlation length L and the change in the volumetric fraction of the scattering phase $\Delta\varphi$ for various OPEI contents are given in Table 1.

The small addition of OPEI ($7 \cdot 10^{-4}$ mole/l) does not change the volumetric fraction of the scattering phase (micelles) in the solution (Fig.4). The reduction of micelle concentration may be due to the sorption of CTAB molecules on the polymer yielding the observed reduction of the scattering intensity. In that case the CTAB micelles and molecular complexes OPEI-CTAB coexist in the system. Since the position of the maximum of scattering curves has not changed substantially the distance between micelles has not changed.

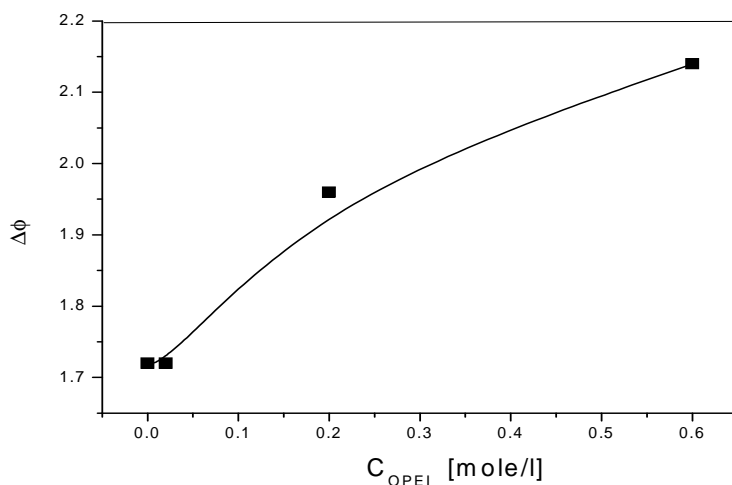


Fig. 4. Dependence of the volumetric fraction of the scattering phase on the OPEI concentration

Further increase of OPEI concentration leads to significant enhancement of the scattering phase volumetric fraction $\Delta\phi$. This feature can be explained by assumption that the polymer wraps around the tubes of the micelle size. The wrapped tubes yield the same contribution to the scattering as micelles.

The presented results indicate that in the CTAB – OPEI – water system the CTAB micelles coexist with molecular or polymer-colloidal complexes formed by CTAB monomers adsorbed on the polymer added to the solution.

2. REFERENCES

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CURRICULUM VITAE



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