Colloidal properties of polymerizable counterion surfmers solutions based on alkylamino 2-acrylamido-2-methylpropanesulfonates in different solvents

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ABSTRACT

Three polymerizable surfactants (surfmers) bearing 2-acrylamido-2-methylpropanesulfonic acid (AMPS) as polymerizable group in the counterion have been designed, synthesized, and their micelle-forming properties have been investigated in different solvents. Solutions of dodecylammonium (DDA-AMPS), cetylammonium (CA-AMPS), and cetyltrimethylammonium (CTA-AMPS) 2-acrylamido-2-methylpropanesulfonates were studied in water, water–dioxane mixtures in a whole range of components ratios, and xylene. The solutions were investigated by capillary and rotational viscometry, conductometry, and small-angle neutron scattering; aggregates adsorbed from the solutions on as-split mica were studied by atomic force microscopy (AFM). The surfmers follow general regularities of surfactant behavior in aqueous solutions. Decrease in polarity of the media with an increase in dioxane content in water–dioxane mixtures leads to disappearance of direct micelles. At low water content (below 5%) the surfmers form reverse micelles in the mixtures. The surfmers form reverse micelles in low polarity solvents, such as xylene, which should affect the polymerization results.

1. Introduction

Polymerization of monomers, capable of structural self-organization (liquid crystalline, micellar, etc.), is a very fast-developing branch of science at the boundary of macromolecular and colloid chemistry and physics.[1,2] Correlation of colloidal properties of surface active monomers with polymerization process and the resultant properties of the polymers is an important subject in relation to preparation of novel structured materials.

Polymerizable surfactants (surfmers) are functional compounds combining surface activity and polymerizability, they are usually characterized as common surfactants. Insertion of polymerizable group in a surfactant molecule results in formation of surfmers. The polymerizable group can be either covalently bound to a surfactant molecule locating in its tail (T-type) or head (H-type), or it can be located in a counterion being bound to the surfactant molecule ionically (‘counterion surfmers’). Location of polymerizable group strongly affects the polymerization rate and structure and morphology of resulting product.[3]

‘Counterion surfmers’ are of considerable interest because they form polyelectrolyte–surfactant complexes (PSC) as a result of their polymerization. In this case, a polymerizable counterion forms a polyelectrolyte macromolecule. The surfactant molecules are bound to ionic groups of this macromolecule. PSC attract significant interest because of their scientific and practical importance.[4,5] The matter is that they are capable to form self-organized nanostructures and well-structured nanoparticles.[6,7]

Polymerization of counterion surfmers is a very convenient method for preparation of stoichiometric PSC.[8] It ensures stoichiometry precisely; in addition, it does not produce excess ions. In a sense, it is similar to Carothers invention of ‘nylon salt’ for nylon preparation with stoichiometric ratio of dicarboxylic acid and diamine.[9]

Publications on structure forming properties of counterion surfmers and their polymerization are widely presented in scientific literature. Most of them deal with surfmers, which polymerize in aqueous media without precipitation of the product and retention of initial structure of the solution. Thus, Pileni et al. have reported colloidal properties of cetyltrimethylammonium methacrylate in direct micelles in aqueous solutions.[10] The micelles retained their shape after polymer formation.[11] The reaction mixture remained
transparent, no precipitation occurred. The authors have not studied molecular weight of the product.

Walker et al. have published a set of papers dealing with the synthesis and structural studies of three surfmers with 4-vinyl-benzoate counterion.[12–14] These surfactants form cylindrically shaped micelles in aqueous solutions due to the hydrotropic nature of the counterion.[8] Water-soluble cylindrically shaped nanoparticles have been formed as a result of the polymerization. The authors reported rather high molecular weights of the products ($M_w$ of the core polyelectrolyte is up to $4 \times 10^5$).

Sanderson has reported investigation of the phases formed by dodecylammonium acrylate, the structure formed by the monomers was fixed during the polymerization.[15,16]

In all these publications,[10–16] the authors used rather weak carboxylic acids as polymerizable counterions for cationic surfactants and performed the polymerization in aqueous media. Structure-forming properties and polymerization of counterion surfmers in organic media have been investigated far less.

Probably, weakness of the polyelectrolytes determines solubility of the resulting complexes with surfactants in water. PSC consisting of strong acid polyelectrolyte (e.g. polystyrenesulfonic acid or AMPS) and cationic surfactant are water-insoluble as a rule.[17] Generally, they are prepared by direct mixing of polysulfonic acid and cationic surfactant in water. Such complexes are of intense interest as organosoluble, nanostructured materials.[17] We have not found any publication dealing with the colloidal properties of surfmers containing strong sulfonic acid as polymerizable counterion.

Only few examples have been described of polymerization of counterion surfmers with strong sulfonic acid counterion in low-polarity organics. This kind of polymerization is investigated far less. Surfer with AMPS counterion and diestearyldimethylammonium surfactant was mentioned in patent.[18] Its polymerization under ultrasonic treatment results in formation of PSC particles of 82 nm size proposed for hair cosmetics compositions. No colloidal properties of the surfmer solutions were presented.

Cavicchi et al. described RAFT polymerization of trioctylammonium $p$-styrenesulfonate in benzene.[19] Later they have reported RAFT polymerization of N,N-dimethyloctadecylammonium $p$-styrenesulfonate in chlorobenzene and the study of gelation of resulting PSC in low-polarity organic solvents.[20] In both cases polymerization proceeded in molecular dispersed solutions. Micellar-forming properties of the monomers have not been discussed.

All the publications,[10–18] except the works of Cavicchi, dealt with formation and polymerization of colloid solutions in water. Micelle formation of the surfmers in organic solvents has not been investigated at all.

Bilibin et al. have published some results concerning polymerization of DDA-AMPS, CA-AMPS, and CTA-AMPS in water, water–dioxane mixtures and low-polarity organic solvents.[21,22] The polymerization of these surfmers in micellar aqueous solutions and water–dioxane mixtures occurs with precipitation of insoluble PSC. Polymerization in low-polarity solvents (xylene, tetrachloromethane) results in the formation of tough organogels.[22] These publications contain insufficient information concerning colloidal properties of the micellar solutions of the surfmers designed for the polymerization in different solvents. In the present paper, we fill up this gap in our knowledge.

Preliminary results on micelle forming properties and polymerization of DDA-AMPS in aqueous solutions and water–dioxane mixtures have been published in [21] and [23]. The present paper deals with detailed comparative study of micelle forming properties of three surfmers with 2-acrylamido-2-methylpropanesulfonic acid as a polymerizable counterion in a wide range of solvents and solvent systems. These results are of interest not only in studying of influence of structure of initial solution on a structure and properties of a product of polymerization, but also represent independent interest because colloidal properties of these and similar surfmers have been studied insufficiently. These results are of fundamental importance as reference data, especially in colloid and organic chemistry.

For the studying of micelle and structure forming properties of the surfmers in different solvent systems, we have used a set of methods: conductometry, capillary and rotational viscometry, atomic force microscopy (AFM), small-angle neutron, and dynamic light scattering.

### 2. Experimental

#### 2.1. Materials and instruments

##### 2.1.1. Materials

Dodecylamine (DDA), cetylamine (CA), cetyltrimethylammonium bromide (CTAB), and 2-acrylamido-2-methylpropanesulfonic acid of 99% purity were purchased from Aldrich.

Freshly distilled and deionized water with conductivity less than 2 μS/cm was used for all experiments and preparations.

Organic solvents were purified according to standard methods of purification.[24]

Conductometry was performed at 25 and 60 °C by ‘Expert-002’ conductometer (Economics-Expert Ltd, Russia) with a filler-type sensor (measurement range 0.01–1999 μS/cm).

Ubbelohde viscometer (capillary diameter 0.22 mm) was used for viscosity measuring of the surfmers solutions in water and organic solvents.
Steady-shear rotational experiments were taken on a Physica MCR 301 (Anton Paar, Austria) rheometer equipped with double-gap coaxial cylinder measuring cell DG 26.7. 

\(^1\)H NMR spectra were recorded by Bruker DPX and Bruker Avance spectrometers at 300 or 400 MHz in D$_2$O, CDCl$_3$ and DMSO-d$_6$.

AFM was performed by Veeco Nanoscope V instrument in Tapping mode with RTESP probes. Samples for AFM were prepared by adsorption from sessile drop. A drop of a solution was put onto as-split mica, exposed for 20–40 s, rinsed with pure solvent to remove an excess of a solution, and dried. Recrystallization from acetone was used for final purification.

SANS (small-angle neutron scattering) was recorded with diffractometer ‘Membrane-2’ (FSBE ‘PINP’) in D$_2$O solutions (20 °C, thickness of the solution layer dS = 5 mm) in a range of imparted impulses (scattering vectors) $q = (4\pi/\lambda) \sin (\theta/2) = 0.04–1.6$ nm$^{-1}$ (neutrons wave length $\lambda = 0.3$ nm, $\Delta\lambda/\lambda = 0.25$, $\theta$ – scattering angle).

2.2. Preparation of DDA-AMPS surfmer

The surfmer DDA-AMPS was prepared by mixing of equimolar amounts of DDA and AMPS in methylene chloride (0.015 mol of each reagent in 100 ml of methylene chloride). AMPS does not dissolve in methylene chloride, but it dissolves while the reaction proceeds. In 20 min after dissolution, the salt precipitated. The mixture was heated to dissolution of the precipitate and then cooled. Crystals of DDA-AMPS were collected by filtration and dried. Recrystallization from acetone was used for final purification.

Chemical composition and structure of the prepared surfmers were confirmed by elemental analysis and \(^1\)H NMR.

DDA-AMPS: Yield 98%, $T_m = 61–63$ °C

\(^1\)H-NMR (CDCl$_3$): $\delta$/ppm; 7.45 (3H, s), 6.20(2H, dd), 5.55(1H, d), 3.20(2H, s), 2.90(2H, m), 1.65(2H, q), 1.55(6H, s),1.25(19H, m), 0.85(3H, t).

\(^1\)H-NMR (D$_2$O): $\delta$/ppm; 6.05(2H, dd), 5.55(1H, d), 3.35(2H, s), 2.85(2H, m), 1.65(2H, q), 1.35(6H, s),1.20(19H, m), 0.75(3H, t).

Elemental analysis
Calculated for C$_{23}$H$_{54}$N$_2$S: %: C 60.85; H 11.65; N 6.27; Found %: C 60.85; H 11.65; N 6.27.

CTA-AMPS was prepared from AMPS and cetyltrimethylammonium hydroxide, which was obtained by passing of cetyltrimethylammonium bromide solution in methanol through anion-exchange column loaded with Amberlite IRA-410 in hydroxide form.

CTA-AMPS: Yield 91%, $T_m = 63–65$ °C

\(^1\)H-NMR (DMSO): $\delta$/ppm; 8.45 (1H, s), 6.00(2H, dd), 5.50(1H, d), 3.25(2H, m), 3.05(9H, s), 2.65(2H, s), 1.65(2H, m), 1.45(6H, s), 1.25(26H, m), 0.85(3H, t).

Elemental analysis
Calculated for C$_{26}$H$_{54}$N$_2$O$_4$S: %: C 63.63; H 11.09; N 5.71; Found, %: C 62.85; H 11.15; N5.50.

3. Results and discussion

In the present work, we have performed synthesis and studying of micelle-forming properties of several novel polymerizable surfactants bearing a polymerizable group in the counterion – DDA-AMPS, CA-AMPS, and CTA-AMPS (Scheme 1). They were designed in order to estimate contributions of hydrophobic and electrostatic interactions in their micelle-forming properties, specificity of their polymerization as well as peculiarities of the PSCs formation during polymerization in different solvents. DDA-AMPS and CA-AMPS are identical in the nature of their ionic groups, but differ in hydrophobicity, whereas CA-AMPS and CTA-AMPS are similar in hydrophobicity, but differ in the nature of the ionic groups.

We have investigated behavior of the surfmers in different solvent systems – water, mixtures of dioxane and water in a wide range of the components ratio, p-xylene, chlorinated hydrocarbons. Dioxane–water mixtures were chosen as basic solvent system for this study because they cover a wide range of solvent dielectric permittivity (2.2–80 at 20 °C). Their chemical properties do not depend considerably on the components ratio. A decrease in dielectric permittivity with increase in dioxane content in the mixture leads to a decrease in the contribution of hydrophobicity in structure-forming properties of the surfactants and gives reason to the formation of reverse micelles (Scheme 1).

Water–dioxane solvent mixtures with respect to surfactant micelle formation have been studied insufficiently. Anand et al. studied formation of mixed micelles of sodium dodecyl sulfate (SDS) + Triton X-100 and dodecyltrimethylammonium bromide (DTAB) + Triton X-100 in water–dioxane mixtures.[25]

We have studied micelle formation of the surfmers in aqueous solutions by viscometry and conductometry, and small-angle neutron scattering (SANS) methods. In
The slope in the pre-micellar region is greater than that in the post-micellar region for direct micelles. The CMC is identified by the intersection point of conductivity plots. The ratio between the slopes above CMC to that in the concentration region below CMC gives the degree of the counterion dissociation, $\alpha$. Degree of the counterion binding to the micelles is $\beta = 1-\alpha$.\[26\]

Figure 1(A) and (B) represents conductivity dependence on concentration in aqueous solutions of the surfmers. The values of CMC and $\beta$ determined with conductivity measurements at various temperatures for the surfmers are given in Table 1. It should be noted that these $\beta$ values cover the concentration range just above CMC. They can take other values at higher concentrations.

Results given in Table 1 for AMPS surfactants correlate well with literature data for surfactants bearing methacrylate, propanesulfonate, and bromide anions. Analysis of the table data gives reason to a number of definite conclusions.

Firstly, CMC as it must, correlated with the hydrophobicity of surfactant – the higher the hydrophobicity is, the lower CMC (1.1 × 10^{-2} mol/L DDA-AMPS (C12) > 1.5 × 10^{-3} mol/L CA-AMPS (C16) > 8.8 × 10^{-4} mol/L CTA-AMPS (C19)). It should be noted that for CA-AMPS CMC was measured at 60 °C.

In addition, we have investigated aggregation behavior of the surfmers in dioxane–water mixed solvents using conductometry measurements.

Critical micelle concentration (CMC) is the most important structure-forming characteristic of ionic surfactants. All added amounts of a surfactant form micelles above this concentration. Above CMC, spherical micelles exist in solution together with single molecules of surfactant. Further increase in concentration leads to formation of cylindrical micelles and more complex structures. We have determined CMC of the surfmers in different water-containing solvent systems by viscometry and conductometry methods. These methods are rather simple and give reliable results. In addition, we have studied aggregation behavior of the surfmers in low-polarity solvents by a viscometry and conductometry method.

3.1. Investigation of water–dioxane solutions of the surfmers conductometry

Conductometry is a very reliable and convenient method for the determination of CMC.

Specific conductivity of surfactant solutions in polar solvents correlates linearly to the surfactant concentration in both the pre-micellar and in the post-micellar regions.

Scheme 1. Chemical structures of polymerizable surfmers and reaction scheme for monomers and polymers. (1) monomer synthesis by direct reaction of AMPS with corresponding amine in CH2Cl2 (in the case of CTA-AMPS cetyltrimethylammonium hydroxide was used). (2) polymerization at appropriate conditions.
We have performed conductivity measurements of DDA-AMPS solutions in water–dioxane mixed solvents in order to determine influence of decrease in polarity of the solvent media on aggregation properties of the surfmers. Figure 1(B–D) represents plots of conductivity dependence on concentration for DDA-AMPS solutions in mixed systems containing 80, 20, and 5% of water. The slope of the straight line in pre-micellar region for a water-enriched system is greater than the slope in the post-micellar region (Figure 1(B)), which is typical for formation of direct micelles. The slope for solutions containing 20% water does not change in whole range of the concentrations (Figure 1(C)). The degree of counterion binding to micelles $\beta$ increases with an increase in primary charge of the micelle. [29] This suggests that CTA-AMPS micelles ($\beta = 0.47$) are the smallest ones and their aggregation number is the lowest as compared to other surfmers ($\beta = 0.59$ and 0.61).

Secondly, the nature of the counterion does not substantially affect CMC (compare DDA-AMPS and DDA-methacrylate as well as CTA-AMPS and CTAB). The degree of counterion binding to micelles $\beta$ increases with an increase in primary charge of the micelle. [29] This suggests that CTA-AMPS micelles ($\beta = 0.47$) are the smallest ones and their aggregation number is the lowest as compared to other surfmers ($\beta = 0.59$ and 0.61).

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Table 1. CMC and degree of counterion binding to micelles ($\beta$) of the surfmers measured in water.

| Surfactant        | CMC, mol/L | $\beta$ | Temperature (°C) |
|-------------------|------------|---------|------------------|
| DDA-AMPS          | $1.1 \times 10^{-2}$ | 0.61    | 25               |
| DDA-methacrylate* | $1.0 \times 10^{-2}$ | 0.85    | 25 [15]          |
| DDA-propanesulfonate* | $9.5 \times 10^{-3}$ | 0.61    | 25 [27]          |
| CA-AMPS           | $1.5 \times 10^{-4}$ | 0.59    | 60               |
| CTA-AMPS          | $8.8 \times 10^{-4}$ | 0.47    | 25               |
| CTAB*             | $9.2 \times 10^{-4}$ | 0.77    | 25 [28]          |

*The literature data are given for comparison of CMC values.
Solutions of DDA-AMPS and CTA-AMPS in water were studied at 25 °C. At low concentrations of the monomers, values of dynamic viscosity are close to the viscosity of water. Plots for DDA-AMPS and CTA-AMPS do not change their slope with an increase in concentration up to concentration 0.40 mol/L. The viscosity increases slowly with increasing concentration. The lines on the figure 3 are theoretical lines according to Einstein’s equation for dilute solution of sphere-like objects (including spherical and short cylindrical micelles) with concentration up to 10 vol. %

\[\eta = \eta_{\text{solvent}} (1 + 2.5\phi)\]

where \(\phi\) – volume fraction of the objects, \(\eta_{\text{solvent}}\) – viscosity of pure solvent at studied temperature.[33,34]

The dependence of viscosity of the monomers solutions are fitted by the theoretical line at low concentrations and become higher with increasing concentration, but not sufficiently, hence we may conclude, that at the concentrations studied the DDA-AMPS and CTA-AMPS form low anisometry micelles, i.e. spherical or short cylindrical ones.

The CA-AMPS solutions were studied at 60 °C. At low concentrations the viscosity is equal to that of water (Figure 1(D)) is lower than that at higher concentrations for solutions containing 5% of water. It should be noted that absolute value of specific conductivity of solutions containing 5% of water is three orders of magnitude less than that of pure water solutions.

This can be attributed to formation of reverse micelles, which was confirmed indirectly by AFM experiments (see below).

Similar conductivity–concentration dependence was observed by Peukert et al. [30] who studied the conductivity of AOT (sodium bis(2-ethylhexyl) sulfosuccinate) solutions in hexadecane. The authors observed noticeable increase in conductivity for higher AOT concentrations, which they refer to formation of ‘macroions’ – charged reverse micelles as charge carriers.

### 3.2. Viscometry measurements

Viscometry measurements were performed using capillary viscometer and rotational rheometer. Generally, viscometry method is much less applicable for CMC determination than conductometry, but it makes it possible to detect structural transitions of higher orders associated with change of micelles shape, which cannot be identified by conductometry.

Graphically, the values of CMC were obtained from the point of intersection of two straight lines in the reduced viscosity–concentration plots as it was done by conductivity method.

CMC was determined for DDA-AMPS in water at 25 and 60 °C (Figure 2).

Each break in the curve corresponds to some structural transition of the solution. Curve 1 displays two breaks formed by intersections of linear segments. The first break (at \(C = 16\) mmol/L) can be referred to CMC, its value coincides with that determined by conductometry. The second break can be referred to a transition of higher order. Its nature is discussed in the section 3.3.

It was impossible to identify CMC for CA-AMPS and CTA-AMPS by means of capillary viscometry because flow times of their solutions in water in the range of CMC are too close to the flow time of the pure solvent.

The dynamic viscosity of aqueous solutions of the monomers was measured by steady-state experiments. For all of the samples studied, the viscosity did not depend on shear rate, i.e. the samples exhibit the Newtonian behavior that is typically for dilute solutions of spherical and short cylindrical micelles of surfactant. [31,32]. The values of Newtonian viscosity of the surfmers were plotted as a function of the concentrations of the monomers (Figure 3).
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in micellar structures. Figure 5 shows that the specific surface area of the interface of the phases $A(c)$ (counting on gross concentration of the surfactant) increases from the minimal observed value $0.9 \times 10^3$ m$^2$/g ($C = 13$ mmol/L) to limiting value $1.4 \times 10^3$ m$^2$/g at concentration of the surfactant $C \geq 50$ mmol/L with increase in concentration. Therefore, there is a redistribution of molecules of the surfactant between not aggregated solution and micelles in this concentration range. At concentration $50$ mmol/L the saturation is reached with constant concentration of non-aggregated solution and constant aggregation number of micelles.

Thus, formation of the first spherical micelles in the solution occurs at $C = 10$ mmol/L. At $C = 50$ mmol/L constant concentration of non-aggregated surfactant and constant aggregation number of micelles are reached. Complete transformation of the system to ensemble of micelles occurs at the concentration of the surfactant about $50$ mmol/L. As follows from the reduced viscosity–concentration curve of DDA-AMPS solution (Figure 2), the structure of the solution changes at $C = 51$ mmol/L, (0.47 mPa-s). But the rise of the viscosity with increasing concentration is more pronounced. The values become higher even than those for others monomers solutions at $25$ °C. The sharp increase in the viscosity of CA-AMPS solutions above concentration $0.17$ mol/L indicates long cylindrical micelles.[14,35]

Both capillary and rotational measurements give no grounds to assume the formation of anisometric micelles of DDA-AMPS and CTA-AMPS in concentration range up to $0.40$ mol/L. At the same time a plot of variation of reduced viscosity of DDA-AMPS with concentration displays intersections of straight lines at $C_2 = 51$ mmol/L (25 °C) or $89$ mmol/L (60 °C) well above CMC. We will try to explain the nature of this transition hypothetically with small-angle neutron scattering data.

3.3. Small-angle neutron scattering

It was established in the experiments on neutron scattering, that the transmission of neutron flux of $T(c)$ decreases with growth of concentration of AMPS-DDA in D$_2$O, from $C = 5.1$ mmol/L to $0.26$ mol/L that is caused by increase in a number of hydrogen atoms in the system, causing additional absorption.

Comparison of pulse dependences of scattering intensity (Figure 4(A)) displays a gain of scattering and qualitative change of a mode of scattering intensity with growth of concentration of the surfactant. Dependence of position of the peak on concentration of $q_{\text{max}}$ ($C$) (Figure 4(B)) reveals the break at $C_1 = 10$ mmol/L. Almost no shifts of the peak were observed below this break. Power dependence of $q_{\text{max}} \sim c^{0.28}$ appears at higher concentrations. The width of the peak decreases which indicates an ordering of the system with the concentration growth. The position of the peak doesn’t depend on concentration with a growth of a scattering intensity, which means that the increase in number of molecules of the surfactant in the solution doesn’t lead to a change of a scale of the structure though it can be condensed and scatter more strongly. Transition to power dependence of $q_{\text{max}} \sim c^{1/3}$ indicates the established process of formation of supramolecular structures. The increase in concentration leads only to formation of new particles approximately the same size and weight.

Thus, formation of aggregates really takes place at concentration of DDA-AMPS of $10$ mmol/L (10.5 mmol/L according to a conductometry), and this concentration can be correlated to CMC for the surfactant.

The mode of scattering intensity at high impulses of $q \geq 1$ nm$^{-1} > q_{\text{max}}$ corresponds to the scattering on sharp borders of the particles. It means that a separation of phases at nanodimensional level in solution, really occurs, as a result of assembly of molecules of surfactants in micellar structures. Figure 5 shows that the specific surface area of the interface of the phases $A(c)$ (counting on gross concentration of the surfactant) increases from the minimal observed value $0.9 \times 10^3$ m$^2$/g ($C = 13$ mmol/L) to limiting value $1.4 \times 10^3$ m$^2$/g at the content of the surfactant $C \geq 50$ mmol/L with increase in concentration. Therefore, there is a redistribution of molecules of the surfactant between not aggregated solution and micelles in this concentration range. At concentration $50$ mmol/L the saturation is reached with constant concentration of not aggregated solution and micelles.

Thus, formation of the first spherical micelles in the solution occurs at $C = 10$ mmol/L. At $C = 50$ mmol/L constant concentration of non-aggregated surfactant and constant aggregation number of micelles are reached.
Conductivity measurement in non-polar xylene is rather complicated due to infinitesimal conductivity values. We have estimated possibility of reverse micelle formation of CA-AMPS by indirect methods of viscometry and AFM. Reduced viscosity-concentration variation curve (Figure 7(B)) displays a break at concentration 0.15 mol/L. We assume formation of reverse micelles above this concentration. This assumption is confirmed indirectly by AFM image (Figure 7(A)) of the aggregates adsorbed from the solution at as-split mica.

One more indirect confirmation of the micelle formation is very high polymerization rate, which is typical for micellar polymerization.[22]

3.5. AFM investigation of the aggregates adsorbed on mica surface

AFM is a powerful instrument for studying the relief of flat surfaces and shape of objects adsorbed on these surfaces at the nanometer scale.[37] It provides a 3D profile of the surface on a nanoscale, by measuring forces between a sharp probe (<10 nm) and surface at a very short distance (0.2–10 nm probe-sample separation).[38]

We have studied AFM images of the micelles adsorbed on as-split mica surface.

Figure 8 displays images of micelles of DDA-AMPS (Figure 8(A)), CA-AMPS (Figure 8(B)), and CTA-AMPS (Figure 8(C)) adsorbed from aqueous solutions on the surface of as-split mica.

Pieces adsorbed from DDA-AMPS aqueous solutions form flattened sphere-like aggregates with average height about 5 nm and 10–20 nm in diameter. Adsorption from water solutions of CA-AMPS results in formation of similar sphere-like aggregates and anisometric aggregates with cross-section nearly equal to the diameter of the spherical particles. CTA-AMPS forms small spherical particles, an average height is about 1 nm. This correlates with the lower degree of counterion binding to micelles of the surfmer (Table 1).

The next AFM experiment dealt with study of aggregates of DDA-AMPS on as-split mica from water–dioxane solution with different water content – 80, 20, and 5%. It has been shown earlier that the conductivity–concentration plot exhibits positive break for water-enriched solutions, straight line for solutions with water content 15–20%, and negative break for solutions with water content below 10%. We suggested formation of direct micelles in water-enriched solutions, no micelle formation in range 18–20% water, and formation of reverse micelles in low water-content solutions.

Figure 9 confirms the assumption indirectly.

The solution with 80% of water (Figure 9(A)) contains many rather large particles. Figure 9(B) displays very small,
images can be observed for DDA-AMPS solution in pure dioxane.

The number and size of the particles adsorbed from the solution in the mixture with 5% water (Figure 9(C)) increase and become similar to that in water and 80% water–dioxane mixture. Very similar images can be observed for DDA-AMPS solution in pure dioxane.

All these results indicate that the surfmers are subject to the general laws of behavior of surfactants, namely CMC of the three surfmers observes a
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Weakening of the electrostatic attraction force between the CTA-AMPS micelle and counterion leads to decrease in both micelle size and counterion binding degree. This assumption is confirmed indirectly by the behavior of the surfmers in the polymerization.[22]

4. Conclusion

Main micelle-forming properties (CMC, shape, size, counterion binding degree) of three surfmers with 2-acrylamido-2-methylpropanesulfonate polymerizable counterion have been studied by a set of methods, together quite sufficient to unambiguously establish the parameters of micellization in water and other media (conductometry, viscometry, AFM, SANS). The measurements were performed in water and water–dioxane mixtures in wide range of composition and in non-polar xylene. Formation of reverse micelles was suggested for water–dioxane solvent mixtures with low water content and in xylene solutions. The results obtained by different methods correlate each other and correspond to literature data.[22]

These results correspond very well to the results obtained by the polymerization of these surfmers.[22]
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References
[1] Polymerization in organized media. Paleoesc CM, editor. Philadelphia, PA: Gordon and Breach Science Publishers S. A.; 1992. p. 454.
[2] Hentze HP, Kaler EW. Polymerization of and within self-organized media. Curr. Opin. Colloid Interface Sci. 2003;8:164–178.
[3] Moroi Y. Micelles: theoretical and applied aspects. New York, NY: Plenum Press; 1992.
[4] Bain CD, Claesson PM, Langevin D, et al. Complexes of surfactants with oppositely charged polymers at surfaces and in bulk. Adv. Colloid Interface Sci. 2010;155:32–49.
[5] Kwak JCT. Polymer-surfactant systems. Surfactant Science Series, Vol. 77. New York, NY: Marcel Dekker; 1998.
[6] Hentze HP. Polyelectrolyte–surfactant complex nanoparticles. In: Contescu CI, Putyera K, editors. Dekker encyclopedia of nanoscience and nanotechnology. 2nd ed, Vol. 5, p. 3403–3408 LLC, Boca Raton, FL: CRC Press, Taylor & Francis Group; 2009.
[7] Faul CFJ, Antonietti M. Ionic self-assembly: facile synthesis of supramolecular materials. Adv. Mater. 2003;15:673–683.
[8] Kuntz DM, Walker LM. Solution behavior of rod-like polyelectrolyte–surfactant aggregates polymerized from wormlike micelles. J. Phys. Chem. B. 2007;111:6417–6424.
[9] Carothers W. U.S. Patent 2,130,947. 1938.
[10] Lerebours B, Perly B, Pileni MP. Polymerization of cetyltrimethylammonium metacrylate in micellar solution. Chem. Phys. Lett. 1988;147:503–508.
[11] Lerebours B, Perly B, Pileni MP. Polymerization of cetyltrimethylammonium metacrylate in direct micelles. Prog. Colloid Polym. Sci. 1989;79:239–243.
[12] Biggs S, Kline SR, Walker LM. The adsorption of polymerized rod-like micelles at the solid-liquid interfaces. Langmuir. 2004;20:1085–1094.
[13] Gerber MJ, Kline RS, Walker LM. Characterization of rod-like aggregates generated from a cationic surfactant and a polymerizable counterion. Langmuir. 2004;20:8510–8516.
[14] Gerber MJ, Walker LM. Controlling dimensions of polymerized micelles: micelle template versus reaction conditions. Langmuir. 2006;22:941–948.
[15] Hartmann PC, Dieudonné P, Sanderson RD. Self-assembly and influence of the organic counterion in the ternary systems dodecylamine/acrylic acid/water and dodecylamine/methacrylic acid/water. J. Colloid Interface Sci. 2005;284:289–297.
[16] Hartmann PC, Sanderson RD. Templating polymerization of dodecylammonium surfactant with polymerizable (meth) acrylate counterion. Macromol. Symp. 2005;225:229–237.
[17] Antonietti M, Conrad J, Thuenemann A. Polyelectrolyte-surfactant complexes: a new type of solid, mesomorphous material. Macromolecules. 1994;27:6007–6011.
[18] Miyake M, Toda H, Yasu M. US patent 4885159 A. 1989.
[19] Liu Y, Pollock KL, Cavicchi KA. Synthesis of poly(triethyleneglycol methyl ether methacrylate)–dodecylamine acetate complexes with poly(methyl methacrylate) and poly(4-vinylpyridine) as hydrophilic blocks. J. Appl. Polym. Sci. 2006;99:6834–6842.
[20] Liu Y, Lloyd A, Guzman G, et al. Polyelectrolyte–surfactant complexes as thermoreversible organogelators. Macromolecules. 2011;44:8622–8630.
[21] Bilibin AY, Sukhanova TM, Matuschkin NI, et al. Polymerization of dodecylammonium2-acrylamido-2-methylpropanesulfonate in solvents with different dielectric constants and study of the resulting ionic complexes. Macromol. Symp. 2012;317:160–168.
[22] Bilibin AY, Shcherbinina TM, Kondratenko YA, et al. Micellar polymerization of alkylammonium 2-acrylamido-2-methylpropanesulfonates in solvents of different polarity and properties of resulting polyelectrolyte-surfactant complexes. Colloid Polym. Sci. 2015;293:1215–1225.
[23] Zorin IM, Shcherbinina TM, Mel’nikov AB, et al. A study of polyelectrolym ammonium acrylamido-2-methylpropanesulfonate association in aqueous solutions. Colloid J. 2014;76:314–318.
[24] Riddick JK, Burger WB, Sakanoine TK. Organic solvents: Physical properties and purification. 4th ed, Vol. 2. New York, NY: Willey Interscience Publication/John Willey and Sons; 1986.
[25] Anand K, Yadav OP, Singh PP. Surfactant-surfactant interactions in their binary mixtures in the mixed solvent 1,4-dioxane + H2O. Colloids Surf. A. 1993;75:21–24.
[26] Dominguez A, Fernandez A, Gonzalez N, et al. Determination of critical micelle concentration of some surfactants by three techniques. J. Chem. Educ. 1974;51:1227–1231.
[27] Sugihara G, Arakawa Y, Tanaka K, et al. Micelle formation and counterion binding of dodecylammonium alkanesulfonates in water at different temperatures. J. Colloid Interface Sci. 1995;170:399–406.
[28] Nazir N, Ahanger MS, Akbar A. Micellization of cationic surfactant cetyltrimethylammonium bromide in mixed water-alcohol media. J. Dispersion Sci. Technol. 2009;30:51–55.
[29] Rusanov AI. Micellization in surfactant solutions. Cambridge: Taylor and Francis group/Harwood Academic; 1997.
[30] Schmidt J, Pignizit R, Peschka D, et al. Conductivity in nonpolar media: experimental and numerical studies on sodium AOT–hexadecane, lecithin–hexadecane and aluminum(III)–2,5-diisopropylsalicylate–hexadecane systems. J. Colloid Interface Sci. 2012;386:240–251.
[31] Molchanov VS, Shashkina YA, Philippova OE, et al. Viscoelastic properties of aqueous anionic surfactant (potassium oleate) solutions. Colloid J. 2005;67:606–609.
[32] Molchanov VS, Philippova OE. Effect of concentration and temperature on viscoelastic properties of aqueous potassium oleate solutions. Colloid J. 2009;71:239–245.
[33] Einstein A. Eine neue Bestimmung der Molekül
dimensionen [A new determination of molecular
dimensions]. Ann. Phys. 1906;324:289–306.
[34] Einstein A. Berichtigung zu meiner Arbeit. Eine neue
Bestimmung der Molekül dimensionen [Correction for my
work: a new determination of molecular dimensions]. Ann.
Phys. 1911;339:591–592.
[35] Nagarajan R, Shah KM, Hammond S. Viscometric detection
of sphere to cylinder transition and polydispersity in
aqueous micellar solutions. Colloids Surf. 1982;4:147–162.
[36] Syergun DI. Determination of the regulation parameter
in direct-transform method using perceptual criteria. J.
Appl. Crystallogr. 1992;25:495–503.
[37] Manne S. Visualizing self-assembly: force microscopy of
ionic surfactant aggregates at solid-liquid interface. Prog.
Colloid Polym. Sci. 1997;103:226–233.
[38] Butt H-J, Cappella B, Kappl M. Force measurements with
the atomic force microscope: technique, interpretation
and applications. Surf. Sci. Rep. 2005;59:1–152.
[39] Aue DH, Webb HM, Bowers MT. A thermodynamic analysis
of solvation effects on the basicities of alkylamines. An
electrostatic analysis of substituent effects. J. Am. Chem.
Soc. 1976;98:318–329.