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Mendeleev Commun., 2014, **24**, 185–186
Mendeleev Communications

Adsorption characteristics of *N'*-undecylenamidopropyl-*N''*-trimethylammonium methyl sulfate at the air–water interface

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DOI: 10.1016/j.mencom.2014.04.022

The dynamic surface tension and adsorption properties of the aqueous solutions of *N'*-undecylenamidopropyl-*N''*-trimethylammonium methyl sulfate, an eco-friendly cationic surfactant, were evaluated by a maximum bubble pressure method at various life times.

The use of eco-friendly polyfunctional surfactants from renewable resources is of considerable current interest.[1,2]

The derivatives of castor (*Ricinus communis*) seed oil are particularly beneficial among such 'green' surfactants. Undecylenic acid is formed upon the thermal destruction of castor oil at ~400 °C, and undecylenic and ricinoleic derivatives serve as hydrophobic building blocks for the synthesis of surfactants and special intermediates.[3–5] The hydrocarbon tail of this quaternary cationic surfactant has a double bond in the terminal chain position, which broadens its antimicrobial and antiseborrheic properties and also provides a possibility to (co)polymerize it or to introduce functional groups.[3–6]

Here, we report the results of a dynamic adsorption study of the cationic surfactant *N'*-undecylenamidopropyl-*N''*-trimethylammonium methyl sulfate (UATMS),[†] a derivative of undecylenic acid.

The surface tension (ST) of surfactant solutions was measured with a BPA-1 tensiometer (Sinterface Technologies, Germany) using a maximum bubble pressure method at life times of 10 ms to 5–10 min.[7,8] Static surface tensions of aqueous UATMS solutions were obtained by extrapolation to an infinitely large life time from the plots of ST *vs.* the inverse square root of surface age t_{age}. The ST isotherm shown in Figure 1 validates the colloid-chemical purity of UATMS. The absence of a minimum from the ST–log *C* isotherm indicates the lack of surface-active impurities in this surfactant.[9] The data are consistent with the results of single ST measurements by the pendant drop method, whereas the du Nouy ring method gives too little ST values owing to cationic nature of the surfactant and poor wetting of the platinum ring. The isotherm was used for calculating adsorption characteristics for this surfactant (Table 1).

Table 1 Adsorption characteristics of UATMS at 25 °C.

CMC, mM	γ_{CMC}/mN m^{-1}	Γ_{m}/mol m^{-2}	*s*/nm^2 per molecule	δ/nm
38±2	41.8	2.14×10^{-6}	0.78	0.83

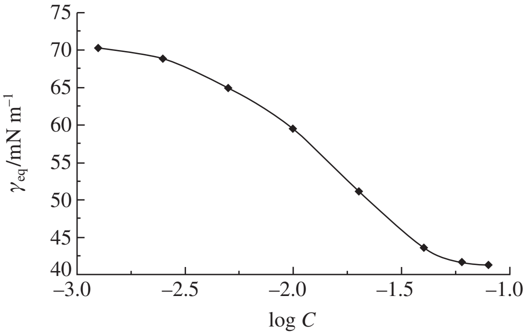

Figure 1 The surface tension–log *C* isotherm for UATMS (25 °C).

Figure 2 shows the experimentally measured dynamic surface tension of sub-micellar (up to 20 mM), slightly above critical micelle concentration (CMC) (40 mM) and micellar (60 and 80 mM) solutions of UATMS. The measured ST values fit well to curves calculated based on the assumption that an adsorption layer behaves as a nonideal two-dimensional gas. The ST is adequately described by the equation[10]

$$\gamma = \gamma_{\text{eq}} + s_{\gamma}/(a_{\gamma} + t_{\text{age}}^{1/2}).$$

Essentially diffusion-limited regime for the UATMS adsorption is substantiated, along with data shown in Figure 2, by the facts that (i) ST at various concentrations is a simple function of $t_{\text{age}}^{1/2}$ [the graph is not linear, but linear, when plotted as $\gamma = f(t_{\text{age}}^{-1/2})$] and (ii) the diffusion coefficient is essentially constant below CMC [$D \approx (1–3)\times10^{-10}$ m^2 s^{-1}]. The succeeding gradual lowering *D* above CMC (~6×10^{-11} m^2 s^{-1} at 40 mM and 2.5×10^{-11} m^2 s^{-1} at 60 mM)

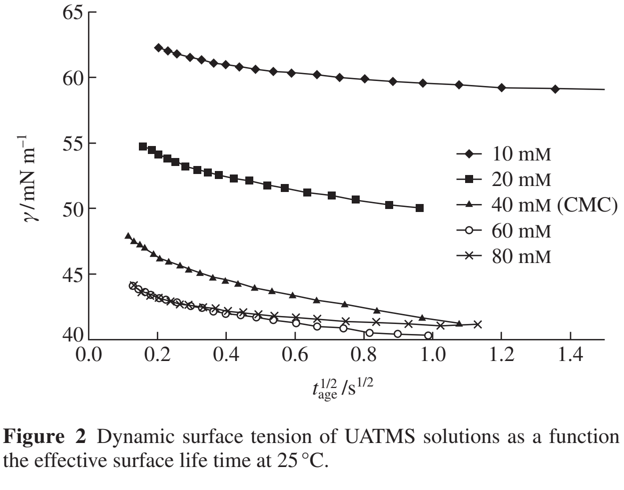

Figure 2 Dynamic surface tension of UATMS solutions as a function of the effective surface life time at 25 °C.

[†] UATMS used in this work was prepared from commercial Rewocid® UTM 185 (Evonik Goldschmidt GmbH)[6] by vacuum drying followed by recrystallization from methanol and drying in a desiccator over P_2O_5. Aqueous UATMS solutions were prepared by the repeated dilution of a stock micellar solution using double-distilled water with surface tension (ST) $\gamma \geqslant 72.0$ mN m^{-1} at 25 °C.

is due to much slower diffusivity of UATMS micelles in comparison with the monomeric surfactant. Thus, the diffusion coefficient for monomeric UATMS is of the same order of magnitude as $D = (5\text{–}8)\times10^{-10}$ m^2 s^{-1} for cationic dodecyltrimethylammonium bromide/chloride[10–13] having a comparable length of the molecule and a more compact polar group.

Strictly speaking, both concepts of diffusion-limited adsorption kinetics and mixed (diffusion, desorption and adsorption barrier) kinetics are essentially theoretical and only indicate, which process is rate-determining under certain conditions.

Figure 1 shows that the CMC of UATMS does not match the definite concentration and corresponds to the concentration range within 38±2 mM. Owing to the terminal ethylene group, the surface tension of an aqueous UATMS solution at CMC (41.8 mN m^{-1}) is high as compared with that of aliphatic-chain surfactants such as dodecyltrimethylammonium bromide.

The calculated saturation adsorption of UATMS is attained at $C \approx 285$ mM, which is higher than its CMC by about one order of magnitude. It seems unusual that the adsorption layer of UATMS at CMC is far from saturation and its hydrocarbon chains arrange randomly, presumably retaining contact with water in wide concentration ranges.

The surface excess concentration Γ_m, area per molecule s, and thickness of the adsorbed layer of UATMS are given in Table 1. The data were derived from the semilogarithmic plot using the Gibbs equation for 1:1 ionic surfactants with coefficient 2 in the denominator.[14] Molecules of the surfactant are arranged horizontally at the air–water interface in a wide range of bulk concentrations due to the terminal double bond. The following conclusions can be suggested: (i) the dynamic surface tension γ shows linear dependence with $t^{-1/2}$ revealing essentially diffusion-controlled regime of UATMS adsorption and the fast dissolution of its micelles;[7,8] (ii) UATMS does not effectively diminish the surface tension in comparison with conventional surfactants; (iii) it has small saturation adsorption Γ_m and small calculated thickness $\delta = 0.83$ nm of the adsorption layer (Table 1); and (iv) small saturation adsorption within the concentrations studied may serve reason of the simple diffusion-limited behavior. Rather high values of CMC and s also reveal the low-cooperative aggregation of UATMS.

This work was supported by the Ministry of Education and Science of the Russian Federation (grant no. 1B-2-325, 2012). We are grateful to Professor V. D. Sobolev (Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences) for performing a part of ST measurements.

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Received: 25th November 2013; Com. 13/4251