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P. Baglioni^a, C.M.C. Gambi^{b,*}, R. Giordano^c, P. Lo Nostro^a, J. Teixeira^d

^a*Dept. of Chemistry, Univ. of Florence, v. G. Capponi 9, I-50121 Florence*

^b*Dept. of Physics, Univ. of Florence and INFN, l.E.Fermi 2, I-50125 Florence*

^c*Dept. of Physics, Univ. of Messina and INFN, Salita Sperone 31, I-98010S, Agata, Italy*

^d*Lab. Léon Brillouin, CEN-CNRS-Saclay, 91191 Gif sur Yvette Cédex, France*



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P. Baglioni^a, C.M.C. Gambi^{b,*}, R. Giordano^c, P. Lo Nostro^a, J. Teixeira^d

^aDept. of Chemistry, Univ. of Florence, v. G. Capponi 9, I-50121 Florence

^bDept. of Physics, Univ. of Florence and INFN, I.E. Fermi 2, I-50125 Florence

^cDept. of Physics, Univ. of Messina and INFN, Salita Sperone 31, I-98010S, Agata, Italy

^dLab. Léon Brillouin, CEN-CNRS-Saclay, 91191 Gif sur Yvette Cédex, France

Abstract

Micellar solutions of the nonionic surfactant octyl-18-crown-6, formed of an alkyl chain and a polar head able to complex the potassium ion, K^+ , have been studied by SANS as a function of the surfactant concentration with and without salt addition (potassium chloride).

Keywords: Small-angle neutron scattering; Micelles; Nonionic surfactant

Crown ethers are cyclic oligoethers with an outstanding ability to complex cations and to behave as ionophores capable of transporting cations across lipophilic barriers. The attachment of a lipophilic long-chain alkyl group to a crown ether [1] can convert the latter into a crown ether surfactant capable of forming micelles or more complex structures in water, in a way similar to classical nonionic surfactants. The behavior of such micellar systems upon addition of a metal cation, which can be complexed by the polar head group of the alkylcrown ether surfactant, are of interest because of the possibility of producing micelles in which the surface charge is controlled simply by changing the mole ratio between the complexed metal ion and the surfactant [2,3]. As a result, the solution properties of aqueous solutions of crown ether surfactants are expected to respond differently to the addition of alkali metal salts than conventional nonionic polyoxyethylene long-chain alcohol surfactants (C_nE_j). This study reports preliminary results on a novel surfactant, the octyl-18-crown-6 ether ($C_8\phi_6$) represented in Fig. 1, obtained

by cyclization of the ethylene oxide polar head group of the parent surfactant C_8E_6 , able to complex selectively potassium ions. $C_8\phi_6$ was synthesized and purified according to [1]. D_2O was from Aldrich, KCl from Fluka (purity > 99%). By surface tension measurements at room temperature, the critical micelle concentration (cmc) of $C_8\phi_6$ in water is 0.037 M and in D_2O is 0.038 M. For KCl addition to the solution ($KCl/C_8\phi_6 = 0.4$ molar ratio), the cmc varies to 0.063 M in water and to 0.056 M in D_2O . The value 0.037 is higher than the value (~ 0.010) of the parent linear surfactant [4]. This is surprising since, in the linear surfactant C_8E_6 , an OH group is present which should increase the solubility, and therefore the cmc of the surfactant. This result can be explained by considering that the polar head group of the cyclized $C_8\phi_6$ is quite large and probably the steric effects are predominant. The solvent effect (H_2O-D_2O) on the cmc is similar to common linear polyoxyethylene nonionic surfactant. On the contrary to linear polyoxyethylene surfactants, salt addition increases the cmc, suggesting that the K^+ ion is complexed by the polar head group of the $C_8\phi_6$. The SANS experiments were performed at the spectrometer PAXE (Lab. Léon

* Corresponding author.

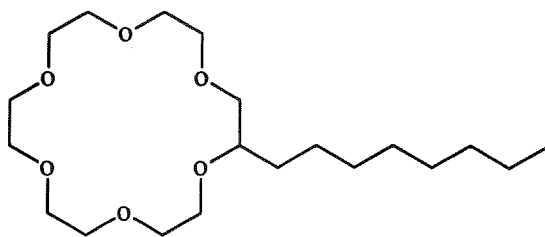


Fig. 1. $C_8\phi_6$ molecule of chemical formula $C_{20}H_{40}O_6$.

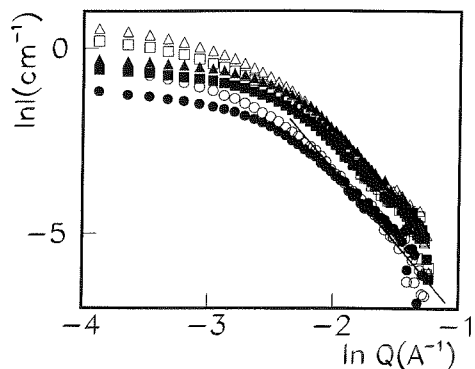


Fig. 2. $I(Q)$ in double logarithmic scale (natural logarithm) for aqueous micellar solutions of $C_8\phi_6$. $C = 5\%$ without salt (circles) and with salt (full points). $C = 9\%$ without salt (open squares) and with salt (full squares). $C = 13\%$ without salt (open triangles) and with salt (full triangles). The solvent contribution and the background (which represents the incoherent contribution of the hydrogen atoms of the sample and any other incoherent part) have been subtracted in order to detect the Porod region at high Q . In the figure is reported a straight line with slope of -4 to which all the curves are parallel at high Q values.

Brillouin, Saclay) with a sample-detector distance of 2.5 m and incident neutron wavelength of 5 Å. Collimation was achieved by two slits of 12 and 7 mm placed 2.5 m apart. The overall momentum resolution was 10%, mainly imposed by the mechanical selector monochromator. Fig 2 shows the SANS spectra of 5%, 9% and 13%(w/w) $C_8\phi_6$ aqueous micellar solutions at $T = (20 \pm 0.1)^\circ\text{C}$ with and without KCl in molar ratio salt/surfactant = 0.4. For each $C_8\phi_6$ concentration, C (w/w of surfactant over total), salt addition to the micellar solution produces a decrease of the $I(Q)$ value. Moreover $I(Q)$ increases as C increases. Thus, we expect that the shape and size of the micelles as well as the interactions between

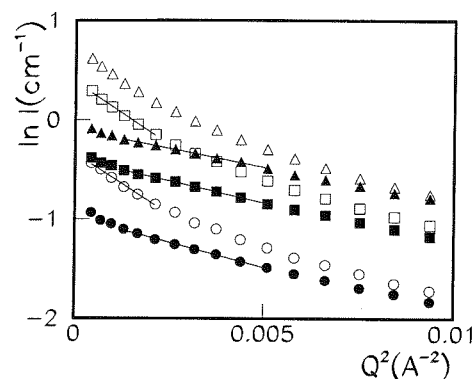


Fig. 3. Guinier plots of the curves of Fig. 2 (the symbols are the same as in Fig. 2). The solid lines represent the fitted straight lines to the data points. The trend is linear in the low Q region ($QR < 1$) except for the unsalted sample with $C = 13\%$. The values of the particle radius are: $21 \pm 1 \text{ \AA}$ for the salted samples and $35 \pm 1 \text{ \AA}$ for the samples at $C = 5\%$ and 9% without salt.

micelles, change as a function of the surfactant and salt concentrations. Since the coherent part of the signal is very similar, the continuous medium in which the micelles are dispersed is similar for the salted and the salt-free samples. All the curves follow the Porod law [5] at high Q , as detailed in the caption of Fig. 2. This supports that a well-defined interface is present in the system studied. For a system composed of monodispersed noninteracting particles (in micellar systems such condition is better realized close to the cmc), the asymptotic behavior at low Q of the $I(Q)$ follows the Guinier relationship and the size of the micelles can be calculated [5]. In Fig. 3, a Guinier plot is shown for all the curves. For each concentration, except 13% without salt, the samples are diluted enough to follow the Guinier relationship. The radius of the micelles can be found. It is 21 Å for salt free and 35 Å for salted samples, in the dilute region. A deeper analysis of the SANS data is in progress.

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