Final Draft
of the original manuscript:

Petrenko, V.I.; Avdeev, M.V.; Haramus, V.M.; Bulavin, L.A.; Kopcansky, P.:
**Impact of polyethylene glycol on aqueous micellar solutions of
sodium oleate studied by small-angle neutron scattering**

IMPACT OF POLYETHYLENE GLYCOL ON AQUEOUS MICELLAR SOLUTIONS OF SODIUM OLEATE STUDIED BY SMALL-ANGLE NEUTRON SCATTERING

V.I.Petrenko[1,2,*], M.V.Avdeev[1], V.M.Garamus[3], L.A.Bulavin[2], P.Kopcansky[4]

[1]Joint Institute for Nuclear Research, Dubna, Russia
[2]Kyiv Taras Shevchenko National University, Kyiv, Ukraine
[3]Helmholtz-Zentrum Geesthacht: Centre for Materials and Coastal Research, Geesthacht, Germany
[4]Institute of Experimental Physics SAS, Kosice, Slovakia

*CORRESPONDING AUTHOR: Viktor I. Petrenko, Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research, Joliot-Curie 6, 141980 Dubna, Moscow Reg., Russia. Tel: 007 496 21 64 988. Fax: 007 496 21 65 484. e-mail: vip@nf.jinr.ru.

ABSTRACT

The structure and interaction parameters of micelles in solutions of anionic surfactant sodium oleate (SO) in deuterated water were studied by small-angle neutron scattering. The effect of addition of polymer, polyethylene glycol (PEG), on micelle solutions was investigated. The dependences of the micelle aggregation number, degree of ionization, axial ratio, average size, charge, inverse screening length, surface potential on the surfactant concentration with and without PEG in the solutions were obtained and analyzed. A change in the power-law type behaviour of the aggregation number on the SO concentration was observed at 2 wt. % of PEG in the surfactant/polymer mixtures. The screening effect with respect to the micelle interaction took place on addition of a large amount of PEG (about 10 wt. % in the mixture). The obtained results are particularly important for understanding the structure reorganization effect on addition of biocompatible PEG to water-based magnetic fluids stabilized by SO.

Keywords: sodium oleate; polyethylene glycol; micelle formation; small-angle neutron scattering; polar magnetic fluids

1. Introduction

Mixed polymer-surfactant systems are of current interest for both academic and industrial research. This is because the interactions of such molecules often produce cooperative effects on the physicochemical properties and alter rheological properties and stability of colloidal systems. Thus, it was shown [1] that the interaction between polymer, surfactant, and colloidal particles can lead to

three distinct scenarios depending on the sequence of adsorption of the polymer and surfactant on the colloidal interface. Polymers and surfactants are widely used in various combinations in cosmetic, medicinal and pharmaceutical products. The introduction of a polymer into the structure of various surfactant-containing interfaces can either remove the surfactant from the surface or, vice versa, enhance its adsorption, thus making it possible to control the interfacial properties in complex systems.

Sodium oleate (SO), $CH_3(CH_2)_7CH=CH(CH_2)_7COONa$, is a widely used anionic surfactant as a dispersant, surface modifier and collector in mineral processing. In particular, it was successfully applied in the synthesis of stable colloidal solutions of nanocrystalline particles including detonation nanodiamond particles [2]; monodisperse nanocrystals of many transition metal oxides in ultra-large quantities [3]; carbonate particles [4]. It was probed as a drug carrier itself [5]. There is a well-proven technique to produce aqueous suspensions of magnetic nanoparticles coated with SO layers [6-9] known as magnetic fluids. Recently, it was shown [10;11] that the biocompatibility of SO-stabilized magnetic fluids can be improved through the introduction in their structure of a biocompatible water-soluble polymer, polyethylene glycol (PEG), $H(OCH_2-CH_2)_nOH$. Nowadays, PEG is used in a great number of applications including the coating of colloidal particles of various origins due to its good biocompatibility [12-14]. At the same time, the mentioned modification of magnetic fluids is accompanied by several structural effects relating to the different types of aggregation in these systems [8;15]. One of them concerns micelles of non-adsorbed SO molecules formed in the bulk of magnetic fluids.

Here, we are concerned with the interaction of PEG with SO micelles in water under the conditions characteristic for the previously studied magnetic fluids [8]. Specifically, we investigated aqueous micelle solutions of SO in a concentration range of 1 - 8.5 wt. % and analyzed the changes in the structural characteristics of the micelles and their interaction after the addition of PEG (M_w = 1000 g/mol) up to 10 wt. % content in the final mixture. For this purpose, small-angle neutron scattering (SANS) was used. The solutions were prepared on the basis of heavy water, D_2O, usually used to enhance the scattering contrast between hydrogen-containing organic molecules and solvent and to reduce the incoherent scattering background by hydrogen/deuterium substitution in the solvent. As regards SO aqueous solutions, the given work to some extent compensates for the lack of information on the structure and interaction of SO micelles in addition to the numerous experimental studies concerning surface tension, conductivity, Raman scattering, molar volume, osmotic pressure, surface partitioning, and transport numbers [e.g., 16-21]. The previous SANS applications to the neat aqueous solutions of PEG in a wide range of molecular masses showed [22;23] that the polymer matches well the structure of Gaussian coils in solutions. It should be noted that in some approaches the analogous SANS data from diluted PEG solutions were

interpreted in terms of the flat packed PEG aggregates [24]. The coils start to interact with each other significantly at the polymer concentration of above 3 vol. %. In concentrated solutions the polymer coils associate into rather extended formations with the size of above 30 nm [23].

2. Experimental

Sodium oleate (c.p., Merck) was dissolved in d-water (99.9%, Sigma–Aldrich) with the mass fraction in the interval of 1-8.5% (0.036-0.302 mol/l). Various amounts of SO and PEG, average molecular mass Mw = 1000 g/mol (mol. wt. 950-1050) (Sigma-Aldrich), were dissolved in d-water to obtain aqueous SO solutions with PEG (up to 10 wt. % of polymer in the final mixture). The studied concentration range for SO significantly exceeded its critical micelle concentration (cmc) in water (0.5-2 mmol/l) reported previously [19-21;16], thus ensuring the formation of micelles in the solutions under investigation.

SANS experiments were performed at the SANS-1 diffractometer at the steady-state reactor of the former GKSS Research Centre (at present, Helmholtz-Zentrum Geesthacht), Geesthacht, Germany. The differential cross-section per sample volume (hereafter referred to as scattered intensity) was obtained as a function of the scattering vector module, $q = (4\pi/\lambda)\sin(\theta/2)$, where λ is the incident neutron wavelength and θ is the scattering angle. The fixed wavelength of 0.81 nm (monochromatization $\Delta\lambda/\lambda = 10\%$) and a series of sample-detector distances within an interval of 0.7–9.7 m (detector size 55×55 cm^2) were used to cover the q-interval of 0.06–2 nm^{-1}. SANS measurements were performed at physiological temperature of 37 °C taking into account a particular interest in using SO and PEG in biocompatible ferrofluids. The calibration with 1-mm water sample was performed after the corrections for background, buffer (D$_2$O) and empty cuvette were made in a standard way [25]. At large sample-detector distances (>4.5 m) the calibration patterns were obtained by recalculating the curves for H$_2$O at a sample-detector distance of 1.8 m with the corresponding distance coefficients.

3. Results and discussion

The obtained experimental SANS curves for the SO micelle solutions without and with addition of PEG are compared in Fig.1. The peak in the experimental SANS curves at $q < 1$ nm^{-1} corresponds to the interaction between micelles. For the neat SO solutions (Fig.1a), its position shifts to a larger q-value when increasing the surfactant concentration, which points to a decrease in the characteristic micelle-micelle distance in the solution. For the mixed SO/PEG solutions (Fig.1b) a similar shift of the micelle interaction peak towards higher q-values takes place together with some changes in its width as well as the variations of the forward scattered intensity, which is proportional to isothermal solution compressibility. It should be noted that the scattering from the

neat PEG solutions is negligibly small compared to the observed scattering from micelles (Fig.1c). For better visualization of the PEG effect on the SO micelles the scattering curves for the same SO concentration and varied PEG content are collected in Fig.1c, which clearly demonstrates that the addition of PEG can affect both the position and width of the micelle interaction peak.

Assuming that micelles are monodisperse spheres, the scattered intensity can be written in the standard form as:

$$I(q) = n(\Delta\rho)^2 V^2 F^2(q) S(q), \tag{1}$$

where n is the number particle density; $\Delta\rho = \rho - \rho_s$ is the contrast, the difference between the scattering length densities of the particle, ρ, and solvent, ρ_s; V is the micelle volume; $F^2(q)$ is the squared form-factor of a single particle (defined in such a way that $F^2(0) = 1$); and $S(q)$ is the structure-factor describing the interaction between micelles. For non-spherical micelles the well-known decoupling approximation [26;27], which assumes that there is no correlation between the position and size/orientation of the particles, can be used where

$$I(q) = n(\Delta\rho)^2 < |F(q)|^2 > (1 + \beta(q)[S(q)-1]). \tag{2}$$

Here, $\beta(q) = |<F(q)>|^2 / <|F(q)|^2>$ is a q-dependent anisotropy factor where the brackets $<\dots>$ denote the averaging over all possible micelle orientations. To describe the micelle interaction peak, for which the $S(q)$ function is responsible, we apply the rescaled mean spherical approximation for dilute charged colloidal dispersions developed by Hansen and Hayter [28]. Since the studied micelles consist of ionic surfactant molecules, the screened Coulomb potential is used in the model:

$$U(r) = \pi\varepsilon_0\varepsilon D^2 \Psi_0^2 \frac{e^{-(r-D)/k_d}}{r}, \text{ for } r > D, \tag{6}$$

where $\varepsilon_0 = 8.85\cdot10^{-12}$ F/m is the vacuum permittivity; $\varepsilon = 78.5$ is the dielectric constant of the solvent medium (water); D is the particle diameter; $\psi_0 = z/[\varepsilon_0\varepsilon D_0(2+k_dD_0)]$ is the surface potential, which is related to the charge on the micelle, z; k_d is the Debye-Huckel inverse screening length. In addition, the resolution function of the SANS setup with the pin-hole geometry [29] is taken into account when calculating the model curves.

The resulting model fits are shown as solid lines in Fig.1. The varied parameters are the aggregation number (N_{agg}), degree of ionization (α), axial ratio (γ) and residual background. They

are used for calculating the average size ($D_0=(3V/4\pi)^{1/3}$, V is the volume of a micelle) and charge (z) of the micelles, as well as the inverse screening length (k_d) and surface potential (ψ_0). Both types of the resulting parameters for the aqueous SO solutions without and with addition of PEG are presented in Table 1 and Table 2, respectively.

For the neat SO solutions one can see that the micelle axial ratio grows with the surfactant concentration within the interval of 1.5 - 2.68 thus naturally showing a transition towards elongated (rod-like) particles. This is accompanied by an increase in the mean micelle size from $D_0=6.28$ nm up to $D_0=8.45$ nm. The obtained fractional charge of the micelles (below 0.15) is in agreement with the well-known fact that in micellar systems of ionic surfactants only a fraction of about 0.15 of counterions are dissociated; the rest of them are effectively bound to the micellar surface [30].

In the case of the addition of the polymer to the micelle solutions one can see that the aggregation number of the micelles significantly decreases; at the same time, other micelle parameters are varied in different ways depending on the PEG concentration. The analysis of the changes in the micelle parameters as a function of the SO concentration without and with PEG is given in Figs. 2. Thus, for the neat SO solutions, one can see (Fig.2*a*) that the corresponding dependence for the aggregation number has a breaking point between two close-to-linear parts in a double logarithmic scale, which can be associated with the mentioned transition from spherical to rod-like micelles. For higher surfactant concentrations it was found that $N_{agg} \sim \varphi^{0.5}$. This dependence is typical for elongated micelle systems [31;32]. Again, an expected decrease both in the degree of micelle ionization and in the calculated surface potential is observed with increasing surfactant concentration (Fig.2*b,d*). Recently, similar results were obtained [33] for another ionic surfactant (dodecylbenzene sulfonic acid) which is widely used for stabilization of aqueous magnetic fluids [34;35]. Surprisingly, one can observe a slight increase in the charge per micelle at the smallest concentrations of SO (Fig. 2c), which requires further investigation.

The decrease in the micelle aggregation number value as well as the change in the power law dependence of the aggregation number versus surfactant concentration are clearly seen in Fig.2a for the same values of the added PEG (about 2.5 wt. %) in various SO solutions. Other micelles parameters (degree of micelle ionization, charge per micelle and surface potential) keep constant or just slightly decrease with increasing SO concentration (Fig.2 b, c, d). It should be mentioned that the well-known tendency of SO to form soaps at near-neutral pH is of little significance in the studied natural solutions of SO (pH~10) [17].

The most pronounced effect of the presence of PEG on the SO micelles is observed for the micelle aggregation number, which significantly decreases with the addition of PEG as compared to the neat SO solutions and does not change much with the growth of the PEG concentration (Table 2). Other parameters vary sharply with the PEG concentration (Table 2). Thus, the degree of micelle

ionization, charge per micelle and surface potential show an increase on the small addition of the polymer of about 2 wt. % and a decrease at the PEG concentration of about 10 wt. %. Recently, similar results were obtained [36] for the mixtures of non-ionic surfactants with PEG showing the reduction of the micelle aggregation number on addition of the PEG additive and some kind of changes in the micelle structure at the constant value of surfactant and varied polymer content in the systems. A reasonable explanation for this effect is some adsorption of free surfactant on the PEG coils, which unbalances the ratio between the SO molecules in a free state and in micelles.

The effective decrease in the micelle-micelle distance (as it follows from the shift of the interaction maximum towards larger q-values) on addition of PEG can be connected with a possible decrease in cmc, which could result in an increase in the micelle concentration. However, this is highly unlikely if one takes into account the studied SO concentration range, which exceeds cmc in the neat SO solutions by at least two orders of magnitude. Also it is well known [37-41;19] that cmc shows only slight changes in the mixed surfactant-polymer solutions. So, the discussed change in the scattering is related to some kind of attraction between the micelles, which depends on the PEG content in a complex way as it follows from the significant variations in the maximum position and the width of the interaction peak (the corresponding changes of the interaction parameters can be followed in Table 2). At small PEG concentrations, the most probable candidate for the attraction mechanism is depletion forces [42] between small polymer coils and comparatively large colloidal micelles. At high PEG concentrations it is reasonable to assume that the polymer adsorbs on the micelle surface or in other words micelles are wrapped by some part of the polymer. The corresponding model was proposed by Cabane [37] for certain stoichiometric compositions surfactant/polymer/water when investigating polyethylene oxide (PEO) polymer in water on addition of sodium dodecyl sulphate (SDS) by NMR. It was estimated that only 10% of the PEO monomer units are adsorbed directly on the micellar surface. Later Gao and co-authors concluded [43] that their own results of the NMR paramagnetic relaxation method clearly indicate that the degree of solubilization of PEO in the SDS micelles is significantly higher than the Cabane's value. It was suggested that only a small fraction of polyethylene oxide is located in the micelle electric double layer and it was also concluded that the nature of the interaction between PEO and SDS is dependent on the PEO molecular weight [43]. Here, this principally explains the change in the micelle-micelle interaction with increasing PEG concentration in the micelle solution, namely, the polymer shape is perturbed as it becomes structured around the surfactant micelles and some screening of Coulomb potential occurs due to a "polymer layer" around the charged micelles.

The obtained results are consistent with the analysis of the interaction of PEG with SO-coated magnetite nanoparticles in water-based magnetic fluids [8], where the structure reorganization of the particle aggregates at sufficiently high PEG content was explained by the formation of the

"polymer layer" around colloidal particles as a result of partial replacement of SO with PEG on the surface of magnetite.

4. Conclusion

To summarize, the SO micelle structure and interaction parameters were obtained as a function of the surfactant concentration in solution without and with addition of PEG by analyzing SANS curves. It was demonstrated that the neat SO aqueous solutions (D_2O) show a typical behaviour for solutions of ionic surfactants and are characterized by the transition from spherical to rod-like micelles at about 2% mass fraction of SO. A significant impact of PEG on the structure and interaction of SO micelles was observed. The corresponding effects concern a decrease in the micelle aggregation number and complicated sensitivity of other parameters of micelle structure and interaction to the PEG presence in the solution. The decrease in the micelle repulsion at high PEG concentration (about 10 wt. % in the mixture) is explained by partial screening of the electrical charge due to some effective PEG coating of SO micelles.

References

1. J. Philip, G. Gnanaprakash, T. Jayakumar, P. Kalyanasundaram, B. Raj, Three distinct scenarios under polymer, surfactant and colloidal interaction, Macromol. 36 (2003) 9230-9236.

2. X. Xu, Zh. Yu, Y. Zhu, B. Wang, Effect of sodium oleate adsorption on the colloidal stability and zeta potential of detonation synthesized diamond particles in aqueous solutions, Diamond & Related Materials 14 (2005) 206-212.

3. J. Park, K. An, Y. Hwang et al. Ultra-large-scale syntheses of monodisperse nanocrystals, Nature materials 3 (2004) 891-895.

4. Y. Sheng, B. Zhou, C. Wang, X. Zhao, Y. Deng, Z. Wang, In situ preparation of hydrophobic CaCO3 in the presence of sodium oleate, Applied Surface Science 253 (2006) 1983-1987.

5. S.H. Choi, T.G. Park, Hydrophobic ion pair formation between leuprolide and sodium oleate for sustained release from biodegradable polymeric microspheres, Int. J. Pharm. 203 (2000) 193-202.

6. A. Hajdu, E. Tombacz, E. Illes et al. Magnetite nanoparticles stabilized under physiological conditions for biomedical application, Prog. Colloid Polym. Sci. 135 (2008) 29-37.

7. A. Vorobiev, J. Major, H. Dosch, G. Gordeev, D. Orlova, Magnetic field dependent ordering in ferrofluids at SiO2 interfaces, Phys. Rev. Lett. 93 (2004) 267203.

8. M.V. Avdeev, A.V. Feoktystov, P. Kopcansky et al. Structure of water-based ferrofluids with sodium oleate and polyethylene glycol stabilization by small-angle neutron scattering: contrast-variation experiments, J. Appl. Cryst. 43 (2010) 959-969.

9. A.L. Kholmetskii, S.A. Vorobyova, A.I. Lesnikovich, V.V. Mushinskii, N.S. Sobal, A novel route for the preparation of magnetic fluids, Materials Letters 59(16) (2005) 1993-1996.

10. R.Y. Hong, Z.Q. Ren, Y.P. Han, et al. Rheological properties of water-based Fe3O4 ferrofluids, Chem. Eng. Sci. 62 (2007) 5912-5924.

11. N. Tomasovicova, M. Koneracka, P. Kopcansky, M. Timko, V. Zavisova, Infrared study of biocompatible magnetic nanoparticles, Meas. Sci. Rev. 6 (2006) 32-35.

12. A. Angelova, B. Angelov, M. Drechsler, et al. Protein entrapment in PEGylated lipid nanoparticles, Int. J. Pharmaceutics 454 (2013), 625-632.

13. A. Gabizon, H. Shmeeda, A.T. Horowitz, S. Zalipsky, Tumor cell targeting of liposome-entrapped drugs with phospholipid-anchored folic acid–PEG conjugates, Adv. Drug Delivery Rev. 56 (2004) 1177-1192.

14. Y. Zhang, N. Kohler, M. Zhang, Surface modification of superparamagnetic magnetite nanoparticles and their intracellular uptake, Biomaterials 23 (2002) 1553-1561.

15. V. Závišová, M. Koneracká, M. Múčková et al. Magnetic fluid poly(ethylene glycol) with moderate anticancer activity, J. Magn. Magn. Mater. 323 (2011) 1408-1412.

16. N. Mahieu, D. Canet, J.M. Cases, J.C. Boubel, Micellization of sodium oleate in D2O as probed by proton longitudinal magnetic relaxation and self-diffusion measurements, J. Phys. Chem. 95 (1991) 1844-1846.

17. K. Theander, R.J. Pugh, The Influence of pH and temperature on the equilibrium and dynamic surface tension of aqueous solutions of sodium oleate. J. Coll. Inter. Sci. 239 (2001) 209-216.

18. P.T.T. Wong, H.H. Mantsch, Temperature-induced phase transition and structural changes in micellar solutions of sodium oleate observed by Raman scattering, J. Phys. Chem. 87 (1983) 2436-2443.

19. X. Xin, G. Xu, Y. Wang, H. Mao, Z. Zhang, Interaction between star-like block copolymer and sodium oleate in aqueous solutions, European Polymer Journal 44 (2008) 3246-3255.

20. A. Hildebrand, P. Garidel, R. Neubert, A. Blume, Thermodynamics of demicellization of mixed micelles composed of sodium oleate and bile salts, Langmuir 20 (2004) 320-328.

21. N.E. Kadi, F. Martins, D. Clausse, P.C. Schulz, Critical micelle concentrations of aqueous hexadecytrimethylammonium bromide-sodium oleate mixtures, Colloid Polym. Sci. 281 (2003) 353-362.

22. G. Lancz, M.V. Avdeev, V.I. Petrenko et al. SANS study of poly(ethylene glycol) solutions in D_2O, Acta Physica Polonica A 118(5) (2010) 980-982.

23. V. Petrenko, L. Bulavin, M. Avdeev et al. Structure and interaction of poly(ethylene glycol) in aqueous solutions. Small-angle neutron scattering data. Macromol. Symp. 335 (2014) 20-23.

24. K.A. Rubinson, S. Krueger, Poly(ethylene glycol)s 2000–8000 in water may be planar: A small-angle neutron scattering (SANS) structure study, Polymer 50 (2009) 4852-4858.

25. G.D. Wignall, F.S. Bates, Absolute calibration of small-angle neutron scattering data, J. Appl. Cryst. 20 (1987) 28-40.

26. M. Kotlarchyk, S.H. Chen, Analysis of small angle neutron scattering spectra from polydisperse interacting colloids, J. Chem. Phys. 79 (1983) 2461-2469.

27. J. Kalus, H. Hoffmann, K. Ibel, Small-angle neutron scattering on shear-induced micellar structures, Colloid Polym. Sci. 267 (1989) 818-824.

28. J.P. Hansen, J.B. Hayter, A rescaled MSA structure factor for dilute charged colloidal dispersions, Mol. Phys. 46 (1982) 651-656.

29. J.S. Pedersen, D. Posselt, K. Mortensen, Analytical treatment of the resolution function for small-angle scattering, J. Appl. Cryst. 23 (1990) 321-333.

30. L.A. Bulavin, V.M. Garamus, T.V. Karmazina et al. Measurements of structural and electrostatis parameters and surface tension of micelles of an ionic surfactant versus

concentration, ionic strength of solution and temperature by small-angle neutron scattering, Col. Surf. A 131 (1998) 137-144.

31. M.E. Cates, S.J. Candau, Statics and dynamics of worm-like surfactant micelles, J. Phys.: Condens. Matter 2 (1990) 6869-6892.

32. S. Puvvadat, D. Blankschtein, Thermodynamic description of micellization, phase behavior, and phase separation of aqueous solutions of surfactant mixtures, J. Phys. Chem. 96 (1992) 5567-5579.

33. V.I. Petrenko, M.V. Avdeev, V.M. Garamus et al. Micelle formation in aqueous solutions of dodecylbenzene sulfonic acid studied by small-angle neutron scattering, Col. Surf. A 369 (2010) 160–164

34. V.I. Petrenko, V.L. Aksenov, M.V. Avdeev et al. Analysis of the structure of aqueous ferrofluids by the small-angle neutron scattering method, Physics of the Solid State 52(5) (2010) 974-978.

35. M. Balasoiu, M.V. Avdeev, V.L. Aksenov et al. Structural organization of water-based ferrofluids with sterical stabilization as revealed by SANS, J. Mag. Mag. Mater. 300 (2006) e225-e228.

36. R.K. Mahajan, J. Chawla, K.K. Vohra, V.K. Aswal, Small-angle neutron scattering study of structural aspects of nonionic surfactants (tween 20 and tween 80) in the presence of polyethylene glycols and triblock polymers, J. Appl. Pol. Sci. 117 (2010) 3038-3046.

37. B.J. Cabane, Structure of some polymer-detergent aggregates in water, Phys. Chem. 81 (1977) 1639-1645.

38. J. Xiao, F. Liu, V.M. Garamus et al. Insights into the interactions among surfactin, betaines, and pam: surface tension, small-angle neutron scattering, and small-angle x-ray scattering study, Langmuir 30(12) (2014) 3363-3372.

39. D.J.F. Taylor, R.K. Thomas, J. Penfold, Polymer/surfactant interactions at the air/water interface, Adv. Coll. Interface Science 132 (2007) 69-110.

40. E.D. Goddard, Polymer-surfactant interaction part I. uncharged water-soluble polymers and charged surfactants, Colloids and Surfaces 19 (1986) 255-300.

41. E.D. Goddard, Polymer/surfactant interaction: interfacial aspects. J. Coll. Inter. Sci. 256 (2002) 228-235.

42. Y. Mao, M.E. Cates, H.N.W. Lekkerkerker, Depletion force in colloidal systems, Physica A: Statistical Mechanics and its Applications, 222(1-4) (1995) 10-24.

43. Zh. Gao, R.E. Wasylishen, J.C.T. Kwak, Distribution equilibrium of poly(ethy1ene oxide) in sodium dodecyl sulfate micellar solutions: an nmr paramagnetic relaxation study, J. Phys. Chem. 95 (1991) 462-467.
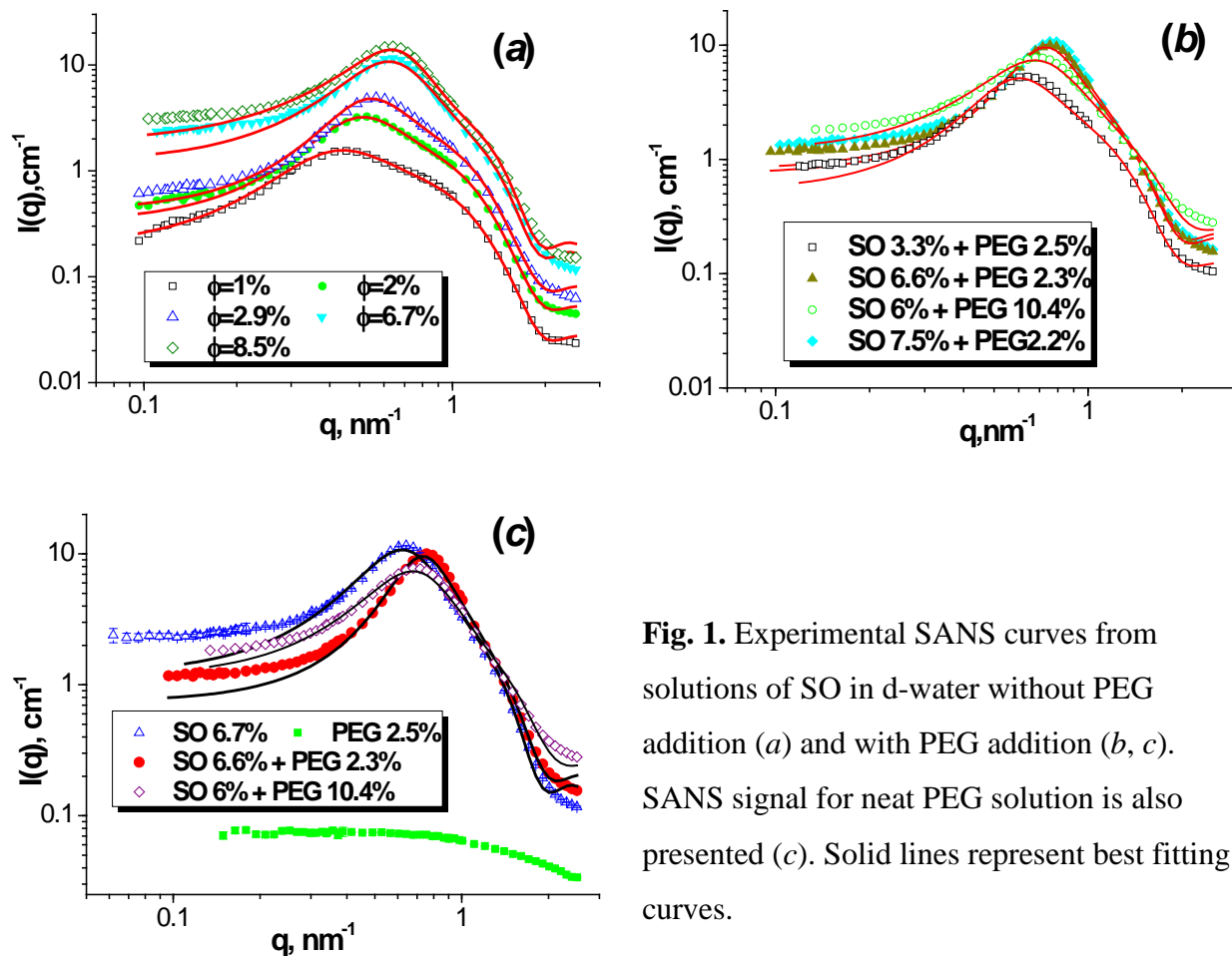
Fig. 1. Experimental SANS curves from solutions of SO in d-water without PEG addition (*a*) and with PEG addition (*b*, *c*). SANS signal for neat PEG solution is also presented (*c*). Solid lines represent best fitting curves.
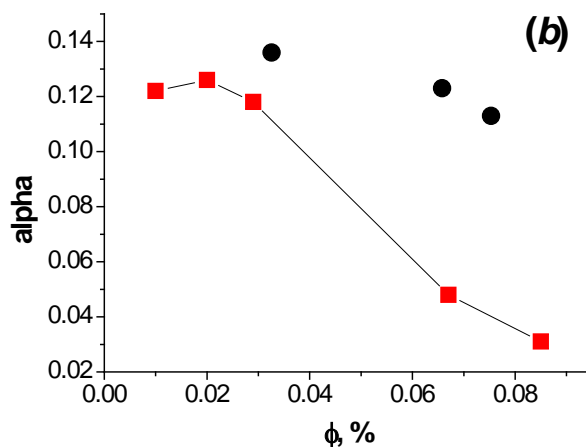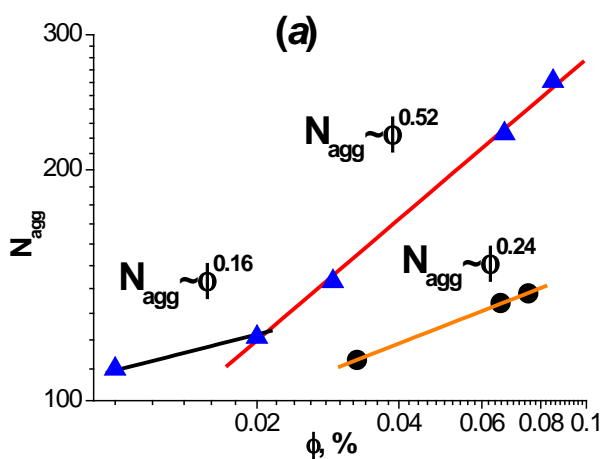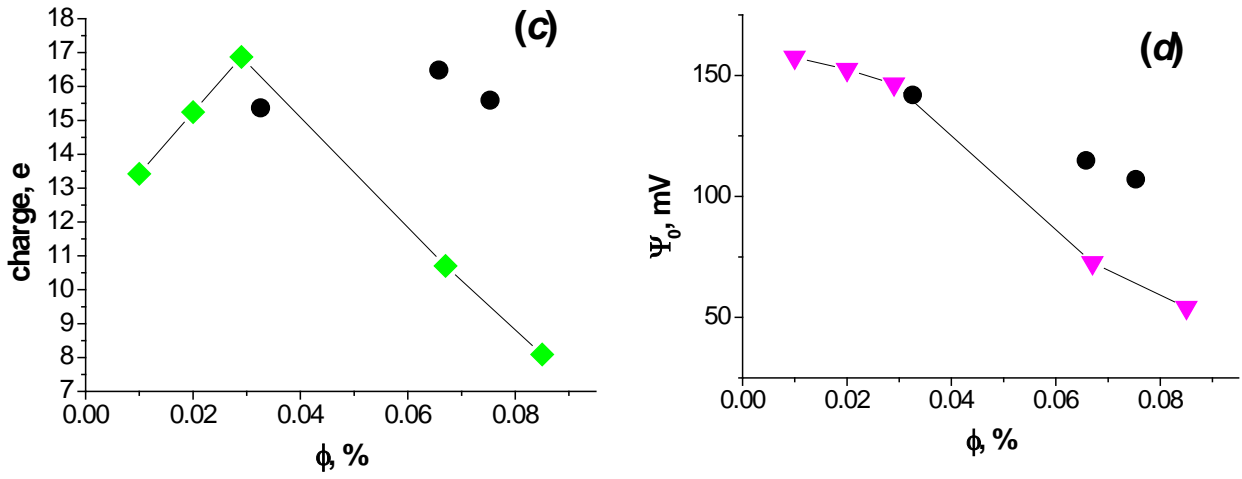
Fig. 2. Dependence of micelle parameters vs. mass fraction of SO in solutions without and with 2.5 wt. % PEG (black circles): aggregation number (*a*), degree of ionization (*b*), charge per micelle (*c*) and surface potential (*d*). Experimental errors do not exceed the size of the points.

Table 1. Derived from SANS data parameters of SO micelles including micelle aggregation number, N_{agg}; degree of ionization, α; axial ratio, γ; average size, D_0; charge, z; inverse screening length, k_d; surface potential, ψ_0. Errors are determined by the last indicated digits.

φ, SO mass fraction	N_{agg}	A	γ	D_0, nm	z, e	k_d, nm^{-1}	Ψ_0, mV
0.01	110	0.122	1.5	6.28	13.42	0.178	158
0.02	121	0.126	1.61	6.48	15.25	0.239	152
0.029	143	0.118	1.69	6.85	16.87	0.273	146
0.067	223	0.048	2.27	8	10.70	0.28	73
0.085	261	0.031	2.68	8.45	8.09	0.245	54

Table 2. Derived from SANS data micelles parameters (including micelle aggregation number, N_{agg}; degree of ionization, α; axial ratio, γ; average size, D_0; charge, z; inverse screening length, k_d; surface potential, ψ_0) for mixed aqueous SO+PEG solutions with corresponding SO and PEG mass fraction together with estimated Polymer/Micelles Ratio$\approx N_{agg} \frac{\varphi PEG * \mu SO}{\varphi SO * \mu PEG}$ Errors are determined by the last indicated digits.

φ_{SO}	φ_{PEG}	Ratio	N_{agg}	α	γ	D_0, Nm	z, e	k_d, nm^{-1}	Ψ_0, mV
0.033	0.025	26	113	0.136	1.6	6.32	15.37	0.307	142
0.066	0.023	14	134	0.123	1.66	6.71	16.48	0.435	115
0.075	0.022	12	138	0.113	1.68	6.78	15.59	0.434	107

| 0.06 | 0.104 | 73 | 141 | 0.073 | 2.45 | 6.86 | 10.29 | 0.318 | 83 |