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On the impact of surfactant type on the structure of aqueous ferrofluids

ON THE IMPACT OF SURFACTANT KIND ON THE STRUCTURE OF AQUEOUS FERROFLUIDS

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ABSTRACT

The impact of surfactant kind on the structure organization of aqueous ferrofluids was considered basing on the data of small-angle neutron scattering (SANS). Thus, the aggregates of different size and type were observed when stabilizing magnetic nanoparticles (MNPs) of magnetite in heavy water by sodium oleate (SO) or dodecylbenzene sulphonic acid (DBSA) which, according to the surface tension measurements, show significantly different critical micelle concentrations. The found aggregate difference was related to the behaviour of surfactant molecules in aqueous solutions including the structure and interaction parameters of micelles (micelle aggregation number, fractional charge, charge per micelle and surface potential, etc.) derived from the SANS analysis.

Keywords: aqueous ferrofluids, nanoparticle aggregation, sodium oleate, dodecylbenzene sulfonic acid, micelle formation, small-angle neutron scattering

1. **Introduction**

Ferrofluids (FFs) or magnetic fluids are suspensions of magnetic nanoparticles with characteristic size at the level of 10 nm. The structure investigations of ferrofluids are motivated by both the fundamental and applied interests [1-3]. Despite a wide range of solvents used as liquid carriers in these systems, still the controllable synthesis of highly stable aqueous ferrofluids under close-to-neutral conditions is still a problem. The direct way for this purpose is the so-called sterical repulsion when magnetic nanoparticles (MNPs) are coated in solutions by surfactant layer/layers to decrease strong attraction (magnetic dipole-dipole and van der Waals interactions) between MNPs by increasing the mean particle-particle distance and thus preventing the aggregation in the FFs. In practice, the structure and aggregation stability of such systems are often determined by the surfactant kind and its amount in ferrofluids.

Thus, for FFs with non-polar carriers a single coating layer of different non-saturated and saturated mono-carboxylic acids [4,5] around magnetite MNPs can be used to provide high aggregation stability of the systems. At the same time, the stabilization efficiency and the size distribution functions for MNPs depend on the surfactant kind [6]. The correlation between the efficiency of surfactant used for stabilization and the structure of non-polar FFs was revealed in the systems with surfactant excess [7-9]. The structure analysis in both cases was done by applying small-angle neutron scattering (SANS) for the systems based on either fully deuterated or close to the full deuteration solvents to achieve sufficient contrasts for the different components of FFs.

For polar ferrofluids including aqueous FFs the excess of surfactants is necessary to form the second layer of surfactant molecules on the MNP surface to provide the so-called double layer stabilization. Again, in this case the surfactant kind and its amount in FFs affect the ferrofluid structure and stability, which was concluded in the previous SANS studies of the possibilities for various surfactants to stabilize aqueous FFs [10].

The aim of the given work was to study the structure of aqueous ferrofluids stabilized by two kinds of surfactants using SANS method and find out a correlation between the behavior of surfactants in solutions and the final structure of water-based FFs. After the critical micelle concentrations were determined in the surface tension measurement the micelle formation of surfactants molecules in aqueous solutions with and without MNPs is analyzed using the parameters derived from the scattering curves.

2. Experimental

The preparation of aqueous ferrofluids was based on the co-precipitation reaction to produce nanomagnetite and subsequent addition of surfactant solutions, namely the solutions of dodecylbenzene sulfonic acid (DBSA) and sodium oleate (SO). The ferrofluids studied were

synthesized at the Center for Fundamental and Advanced Technical Research, Romanian Academy-Timisoara Branch, Timisoara, Romania, and at the Institute of Experimental Physics, Slovak Academy of Sciences, Kosice, Slovakia in accordance with the quite similar procedures described in [11] and [12] correspondingly. The FFs with the SO stabilization were prepared directly in D_2O; in the case of the DBSA stabilization the initial FFs based on H_2O was diluted (1:4) by D_2O, so that the relative concentration of heavy water in the final fluids was 80 vol. %, which made it possible to achieve sufficient contrast for the surfactant in the SANS experiment.

In SANS experiments with pure surfactant solutions DBSA, $CH_3(CH_2)_{11}C_6H_4SO_3H$, and SO, $CH_3(CH_2)_7CH=CH(CH_2)_7COONa$, were dissolved in D_2O within a wide concentration interval of 1-15 vol. %.

SANS experiments were performed at two small-angle scattering instruments including Yellow Submarine at the steady-state reactor (Budapest Neutron Centre, Hungary) and YuMO at the IBR-2 pulsed reactor (JINR, Dubna, Russia) operating in time-of-flight regime. The isotropic 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. SANS measurements were performed at RT. The fixed wavelength of 0.488 nm and sample-detector distances of 1.1 and 5.2 m (detector size 0.64 m) were used at the Yellow Submarine diffractometer. The calibration on 1-mm water sample was made after the standard corrections for background, buffer (pure D_2O) and empty cell [13]. On the YuMO small-angle spectrometer a two-detector set-up with ring wire detectors was used. The neutron wavelength range was 0.05-0.8 nm. The measured scattering curves were corrected for the background scattering from buffer solutions and the absolute calibration of the scattered intensity was made according to a special procedure using vanadium standard [14].

The critical micelle concentration (*cmc*) of DBSA and SO in water was determined from the surface tension measurements performed with the Krüss Tensiometer K20 using the ring method. DBSA and SO were dissolved in bi-distilled water (Millipore) with several concentrations within the range of 10^{-5}-10^{-3} vol. fraction. Surface tension was determined at RT by recording ten data points per one concentration.

3. Results and discussion

The experimental SANS curves for the two aqueous FFs stabilized by DBSA and SO are presented in Fig. 1. Since the studied FFs are based on heavy water (scattering length density SLD = $6.4\cdot10^{10}$ cm^{-2})), a scattering contribution from hydrogen-containing components (SLD ~ $0\cdot10^{10}$ cm^{-2}) is significant due to a high contrast between d-buffer and h-inhomogeneities. Therefore, broad bands in the curves around $q \sim 0.7$ nm^{-1} are attributed to the scattering from the

surfactants which form a stabilizing shell around magnetite particles, as well as micelles in the solutions. It is clearly seen that the SANS curves for the studied FFs have different behavior at the small q-values. The scattering from the aqueous FF stabilized by SO corresponds to the scattering from compact particles, which is reflected in the existence of the so-called Guinier regime (the corresponding Guinier plot is given in Fig. 1) at lowest q-values with the radius of gyration, $Rg = 17$ nm. This value is larger than that expected for separated particles, so there is some fraction of compact and structurally stable aggregates in the SO stabilized FF. In the aqueous FF with the DBSA stabilization the scattering from significantly larger aggregates is observed. This is concluded from the power-law behavior of the scattering, $I(q) \sim q^{-2.4}$, at low q-values, which indicates now a fractal-type organization of the aggregates with the mass fractal dimension, $D = 2.4$. The Guinier regime is not resolved in the initial parts of the curves for these aggregates, which means that the aggregate size, $D > 120$ nm (the estimate is derived from the minimum measured q-value in accordance with the rule $D \sim 2\pi/q$), is beyond the instrumental limit. The observations are in full agreement with the previous SANS studies of similar aqueous FFs with the double layer sterical stabilization [12,15].
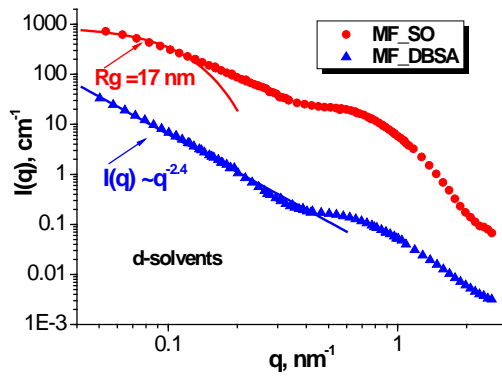

Fig. 1. Experimental SANS curves for aqueous ferrofluids stabilized by the double layer of SO (red circle) in D_2O and DBSA (blue triangle) in the aqueous solution with 80 vol. % of D_2O. Solid lines represent the Guinier function and power-law behavior of scattered intensity.

The experimental values of the surface tension, $\sigma(\varphi)$, against the logarithm of the concentration (φ, vol. fraction) are plotted in Fig.2 for the DBSA and SO aqueous solutions. This dependence has a typical shape for micelle formation solutions described well by the expression:

$$\sigma(c) = -A \, (\ln(cmc) - \ln(c)) \, g(c) + \sigma_o, \tag{1}$$

$$\text{with } g(c) = \begin{cases} 1 \text{ for } c \leq cmc \\ 0 \text{ for } c > cmc \end{cases},$$

where σ_o is the surface tension at surfactant concentrations higher than cmc and $A = \partial\sigma/\partial\ln(c)$ (a slope in the double logarithmic scale) corresponds to an alteration in the surface tension as a function of the natural logarithm of the surfactant concentration, c. A large difference in the mentioned above parameters was observed for the DBSA ($cmc = 1.21 \pm 0.01 \cdot 10^{-2}$ vol. %, $A = 9.4 \pm 0.2$ mN/m and $\sigma_o = 33.3 \pm 0.2$ mN/m) and SO ($cmc = 3.38 \pm 0.01 \cdot 10^{-2}$ vol. %, $A = 4.07 \pm 0.02$ mN/m and $\sigma_o = 24.7 \pm 0.1$ mN/m) aqueous solutions. Thus, the cmc-value for SO is three times higher than in the DBSA case. It should be mentioned that the cmc-value for DBSA is comparable with that previously obtained by similar method [16]. To the best of our knowledge cmc for SO solutions were obtained only by other methods but our value is again comparable with that reported previously [17-19].
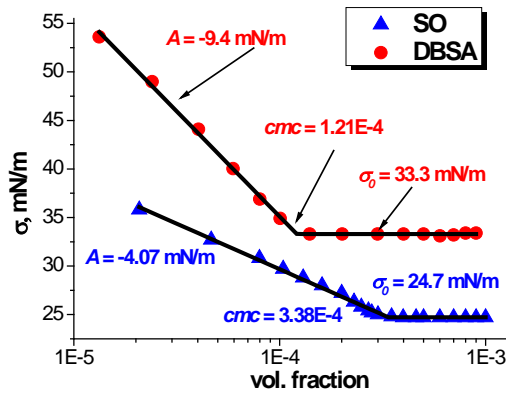

Fig. 2. Determination of the critical micelle concentration by surface tension vs DBSA (red circles) and SO (blue triangles) volume fraction (concentration). Solid line shows approximation according to (1).

The obtained experimental SANS curves from micellar solutions of DBSA and SO in heavy water are given in Fig.3 a and b, respectively. The peaks in the curves at $q < 1$ nm^{-1} correspond to the scattering structure-factor and reflect the interaction between micelles. The position of the interference maximum ($q \sim 2\pi/R_{int}$, where R_{int} is the radius of interaction) shifts to a larger q-value with an increase in the surfactant concentration, which points to a decrease in the characteristic inter-micellar distances in the solution. Similar behavior for DBSA and SO solutions were previously described [16,20] and correspond to charge micelles solutions.

The results of simultaneous fits of the micelle form-factor and structure factor are shown as solid lines in Fig.3. Spherical and non-spherical (ellipsoidal) form-factors were used to model the shape of micelles. For non-spherical micelles the well-known decoupling approximation [21,22], which assumes that there is no correlation between position and size/orientation of particles was applied. To model the structure factor we used the rescaled mean spherical approximation for dilute charged colloidal dispersions developed by Hansen and Hayter [23]. Since the studied micelles consist of ionic surfactant molecules, the screened Coulomb potential was used in the model. The varied parameters included the aggregation number (N_{agg}), degree of ionization (α), axial ratio (γ) and residual background. They were used for calculating the average size ($D_{0=}=(3V/4\pi)^{1/3}$, where 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). The resulting parameters for the aqueous SO solutions are collected in Table 1. They show quite good agreement with our data for mixed solutions of SO with polyethylene glycol [20] in the overlapped concentration range. The structure parameters for DBSA micelles (not shown) coincide within the errors with the previous data [16].
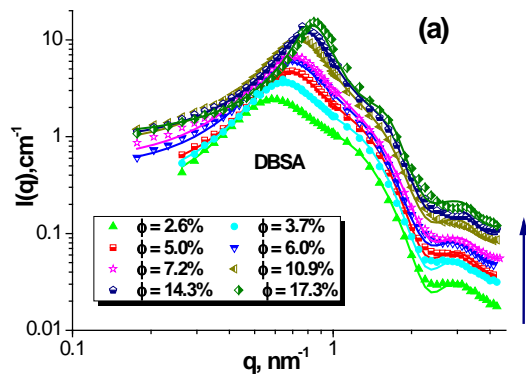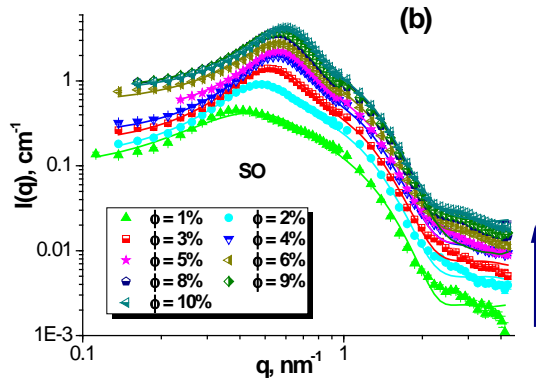
Fig. 3. Experimental SANS curves from solutions of DBSA (a) and SO (b) in heavy water with various surfactant content. Arrow shows the concentration growth. Solid lines represent best fitting curves.

For the SO solutions one can see that the micelle axial ratio grows with the surfactant concentration within the interval of 2.7 - 5.6, thus naturally showing a transition towards elongated particles. This is accompanied by an increase in the mean micelle size from $D_0 = 5.2$ nm up to $D_0 = 8.6$ nm. The obtained fractional charge of the micelles (about and 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 counter-ions are dissociated; the rest of them are effectively bound to the micellar surface [24]. In Fig.4 the comparison of the obtained micelle parameters for DBSA and SO is presented. It can be seen that in both cases we have similar tendencies regarding the dependences of the aggregation number and degree of ionization vs surfactant concentration but the absolute values are slightly different. In the case of the SO micelles, the aggregation number is higher and the surfactant concentration at which one can see the change in the power-law type behaviour of the aggregation number is shifted to smaller values (fig.4a). These differences in the behaviour of the SO and DBSA micelles can be related to different structures of surfactant molecules. Thus, despite very close overall lengths of both surfactants, the polar head group is more complicated in the DBSA molecule.

Table 1. Derived from SANS data the 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.

vol. fraction, %	N_{agg}	α	γ	D_0, nm	Z, e	k_d, nm^{-1}	Ψ_0, mV
1	81	0.15	2.7	5.2	9.87	0.192	189

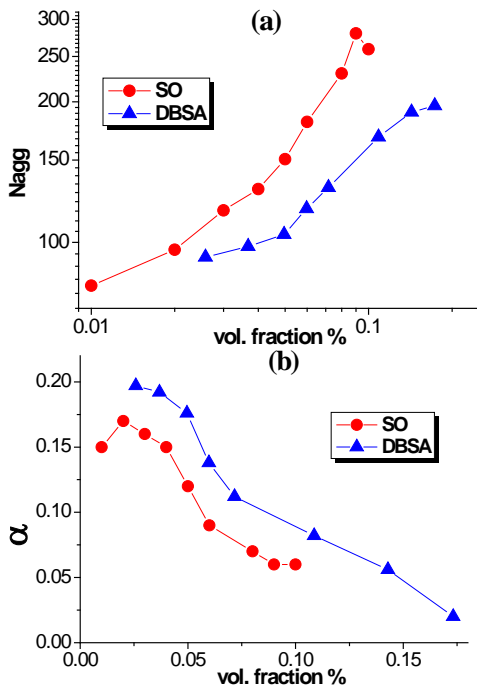| 2	96	0.17	2.8	6.0	16.39	0.251	157
3	117	0.16	3.1	6.4	18.72	0.298	136
4	130	0.15	3	6.6	19.5	0.317	125
5	151	0.12	4.6	7.0	18.08	0.329	100
6	181	0.09	4.9	7.4	16.29	0.309	85
8	230	0.07	4.9	8.1	16.1	0.322	69
9	280	0.06	5.6	8.6	16.8	0.301	67
10	259	0.06	4.7	8.4	15.55	0.333	60

Fig. 4. Aggregation number (*a*) and degree of ionization (*b*) for micelles of DBSA (blue triangles) and SO (red circles) vs. volume fraction of surfactant.

From the comparison of the behaviour of the aqueous micellar solutions of DBSA and SO with the structure characteristics of aqueous FF one can see a distinct correlation between the number of monomers of surfactants molecules (*cmc*-value) and MNPs structure in ferrofluids, namely the higher *cmc* the less aggregated FF. From the structural viewpoint, the FF stabilized

by DBSA is very similar to the FF with PEG modification when large branched fractal-like aggregates were observed at addition of some amount of PEG into solutions [12]. For both ferrofluids the power- law behaviour at small q-values is observed together with a distinct contribution from surfactants (stabilizing shell around magnetite particles and micelles in the solution). This is a strong indication that not only the number of free surfactant molecules in the solutions but also the surfactant-MNPs and surfactant-solvent interactions affects the stabilization mechanism in FFs.

4. Conclusion

To summarize, various structure organizations of aqueous (D_2O) ferrofluids stabilized by SO and DBSA is detected in SANS experiments. While comparatively small and compact MNPs aggregates are observed in the case of the SO stabilization, large and developed fractal type aggregates are revealed in water-based FF with the DBSA stabilization. DBSA and SO micelle structure and interaction parameters are obtained as a function of the surfactant concentration in aqueous (D_2O) solutions. The determined dependences can be used in the study of complex systems with DBSA and SO where potential presence of micelles takes a strong effect on the properties and synthesis of such systems. In particularly, the micelle size is comparable with the size of surfactant aggregates in water-based ferrofluids with the double layer stabilization. Finally, the behaviour of the surfactants in aqueous solutions correlates with their stabilizing properties in ferrofluids.

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