
NEUTRON INVESTIGATIONS OF THE INTERACTION OF SURFACTANT MOLECULES IN NON-POLAR SOLVENT

V.I. PETRENKO^{1,2}, L.A. BULAVIN¹, M.V. AVDEEV², V.L. AKSENOV^{2,3},
L. ROSTA⁴

UDC 539.6
© 2008

¹Taras Shevchenko Kyiv National University, Faculty of Physics
(2/1, Academician Glushkov Ave., Kyiv 03127, Ukraine),

²Joint Institute for Nuclear Research
(6, Joliot-Curie Str., Dubna 141980, Russia; e-mail: vip@nf.jinr.ru),

³Russian Research Center "Kurchatov Institute"
(1, Academician Kurchatov Sq., Moscow 123182, Russia),

⁴Institute for Solid State Physics and Optics
(29-33, Konkol-Tege Str., Budapest, Hungary)

Behavior of non-saturated (oleic acid) and saturated (stearic and myristic acids) monocarboxylic acids in a non-polar organic solvent (deuterated benzene) is studied by means of small-angle neutron scattering (SANS). Values of the second virial coefficient and the volumes of molecules of the acids are obtained from experimental data and compared. Oleic and myristic acids are found to be solvated in benzene rather similarly and display a weak attractive interaction in addition to the steric repulsion. But molecules of stearic acid display a very strong attractive interaction, which results in the formation of big aggregates for volume fractions of the acid higher than 6%. The results obtained explain some peculiarities of the different stabilization properties of these acids in ferrofluids.

1. Introduction

Oleic acid (OA) is non-saturated monocarboxylic acid, a classical stabilizing agent used in the fabrication of ferrofluids on the basis of non-polar solvents [1]. The high stabilization efficiency of OA is related to its non-saturated bond, which leads to the bend of ($\approx 120^\circ$ [2]) in the middle of a molecule. This conclusion follows from the fact that a linear saturated analog of oleic acid, stearic acid (SA), has a rather low stabilization efficiency as for the production of magnetic liquid systems. Despite the fact that the first ferrofluid was produced in the middle of the 1960s, this problem known in the literature as "the puzzle of stearic acid" [3] is unsolved till now.

Recently, it was shown [4] that shorter saturated myristic acid (MA) reveals better stabilization properties as compared with SA, but the size and the dispersion of magnetic particles stabilized by MA are significantly less than those in the case of the stabilization with OA at the same thickness of a stabilizing shell. Thus, the efficiency of the stabilization of acids on the fabrication of ferrofluids was related to elastic properties of the layers of a surfactant near magnetite which define the distribution function over sizes of magnetic particles in a ferrofluid. The comprehension and the more profound explanation of this effect require a systematic study of the interaction of molecules of the acids in the bulk of a solvent and on the surface.

The purpose of the present work is the comparison of the interaction of molecules of oleic, stearic, and myristic acids in benzene on the basis of the SANS data. In order to form a significant contrast between molecules of a surfactant and a solvent, we used deuterated benzene, which also decreases the incoherent background from a solvent. We analyzed the experimental data within the well-known approach [5] to the study of properties of small molecules in the bulk of a solvent by the method of SANS with the purpose to obtain the information about the structural parameters of molecules of a surfactant and the character of their interaction.

2. Experiment

Pure OA, SA, and MA were given by the Center of Fundamental and Advanced Technical Research, Timisoara Branch of Romanian Academy of Sciences. Oleic, stearic, and myristic acids were dissolved with the help of ultrasound after their addition to deuterated benzene. Solutions of OA, MA, and SA in benzene were obtained in the range of concentrations 5–35, 3–25, and 2–7%, respectively. An increase in the concentration of myristic or stearic acid above the indicated values leads to both a sharp increase in the solution viscosity and the formation of a new gel-like phase which is related, probably, to the transition into the liquid-crystal state well-known in the thermodynamics of tough rod-like polymers.

The experiments on SANS were executed on the SANS “Yellow Submarine” at the Budapest Neutron Center. A fixed wavelength of neutrons ($\lambda = 0.386$ nm) and the sample-detector distances 1.3 and 5.6 m were used to obtain the scattering curves in the interval of scattering vectors $q = (0.1 \div 4)$ nm⁻¹. The measurements were performed at a fixed temperature of 25 °C. The calibration of detectors was carried out with the help of a 1-mm water specimen [6] with regard for the correction for the background, buffer, and an empty cuvette.

For the processing of experimental curves, we used the approach described in [5, 7].

The scattering intensity for a system of monodispersed particles which are in a homogeneous medium looks generally as

$$I(q) = n(B_x - \rho_x v)^2 \langle |F(q)|^2 \rangle S(q), \quad (1)$$

where n – the number of particles per unit volume of a solution; $B_x = \sum_i b_i$ – the sum of coherent scattering lengths taken over the whole particle; ρ_s – an analogous sum referred to the unit volume of a solvent (the scattering length density); v – the volume occupied by one molecule of a dissolved substance; $\langle |F(q)|^2 \rangle$ – the square of the form-factor of one molecule which is averaged over all possible orientations of a particle (by definition, $F(0) = 1$), and $S(q)$ – the structural factor which describes the interference of the scattering between various particles in a solution and depends on the concentration and the temperature. At the infinite dilution or in the absence of the interaction, $S(q) = 1$.

For a system of particles present in a solvent, the structural factor can be represented as follows [8]:

$$S(q) = 1 + (\Phi/v) \int (g(r) - 1) (\sin(gr)/(gr)) dV. \quad (2)$$

Here, $g(r)$ – the binary radial distribution function, r – the distance between particles, and Φ – volume fraction of the solute.

With the help of the second virial coefficient B , we carried out the analysis of the behavior of molecules in a solution. As known, the sign of this coefficient indicates the repulsion ($B < 0$) or attraction ($B > 0$) between molecules, and its value testifies the interaction intensity. We used the dimensionless analog [9] of the second virial coefficient which does not depend on the molecular mass and the size of particles, but only on the interaction potential between molecules, and is related to the binary radial distribution function by the formula

$$B = (1/v) \int (g(r) - 1) dV. \quad (3)$$

We determined the coefficient B by analyzing the concentration dependence of the scattering intensity $I(0)$ at the zero angle

$$I(0)/\Phi = \text{const}(1 + B\Phi), \quad (4)$$

where const – a constant including the Avogadro number, density, mole mass, scattering length of a dissolved substance, and density of a solvent.

In the approximation of the coherent scattering intensity at small values of q , we used the Guinier formula which determines the effective sizes of molecules or aggregates formed by molecules:

$$I(q) = I(0) \exp(-(qR_g)^2/3). \quad (5)$$

The values of R_g and $I(0)$ were obtained from the q -region satisfying the condition $qR_g < 1$ with regard for the incoherent background.

3. Results and Discussion

The experimental SANS curves for oleic and myristic acids are presented in Fig. 1. The scattering intensity normed on the concentration reveals a negative value of the second virial coefficient for both solutions of acids (Fig. 2), which testifies the repulsion between molecules of an acid in the system. However, the values of this coefficient $B = -2.2$ (for OA) and $B = -2.0$ (for MA)

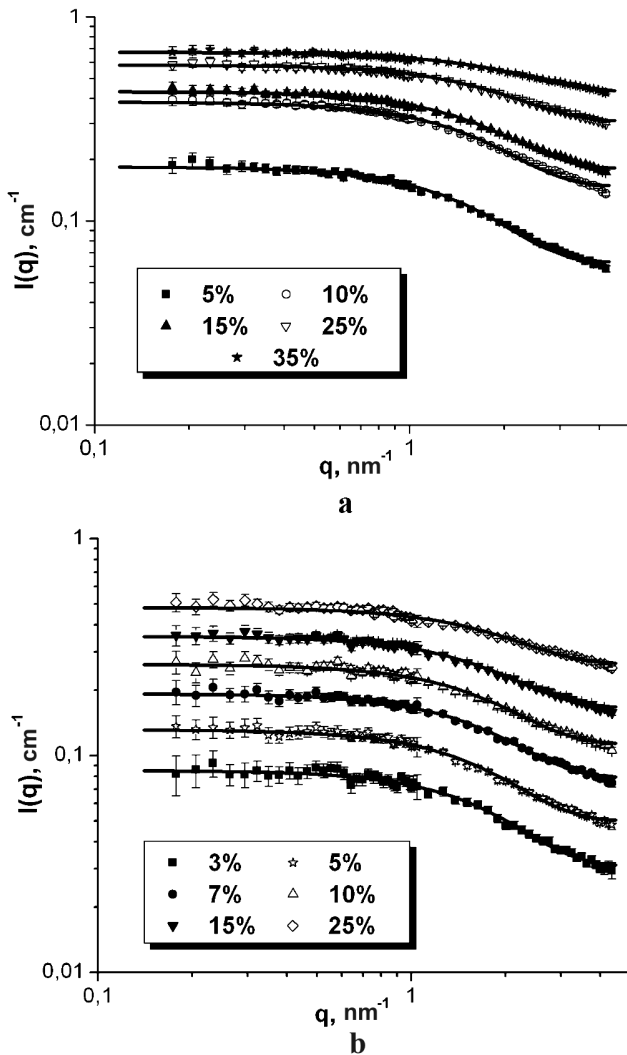


Fig. 1. Experimental SANS curves for the solutions of oleic (a) and myristic (b) acids in deuterated benzene for various concentrations. Solid lines – the Guinier approximation of curves according to Eq. (5)

are significantly greater than $B = -8$, which corresponds to the interaction potential of hard spheres [7]. This observation indicates that the attraction plays a rather significant role in the pairwise potential describing the interaction between molecules of the acid, despite the domination of steric repulsion. The value of the virial coefficient of the same order was given in works [7] and [10] for aqueous and nonaqueous solutions of tetramethylurea. The repulsion between molecules of a surfactant in the solution is also indicated by the negative slope (Fig. 3) of the dependence of the gyration radius on the concentration.

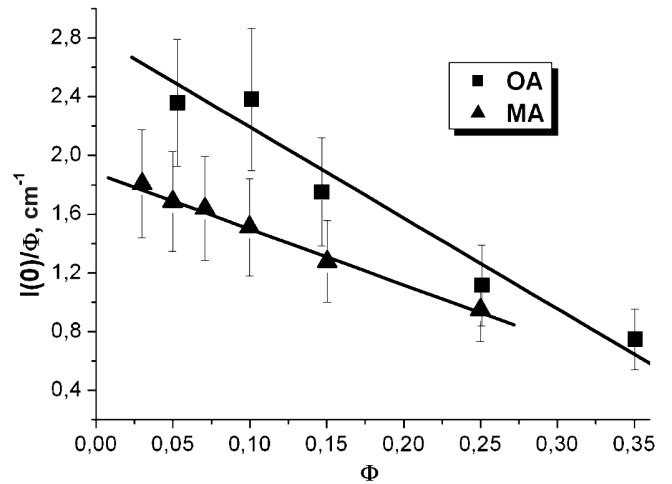


Fig. 2. Scattering intensity of neutrons at the zero angle normed on the volume fraction of molecules of oleic (squares) and myristic (triangles) acids in benzene versus the bulk share of an acid. Solid lines correspond to the linear approximation according to Eq. (4)

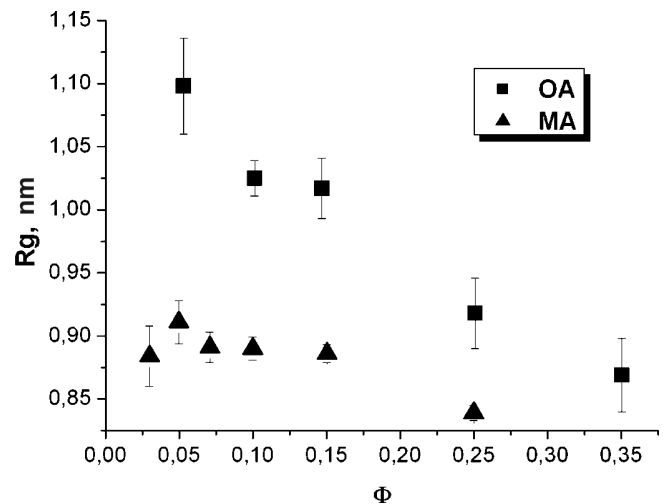


Fig. 3. Gyration radius of molecules of oleic (squares) and myristic (triangles) acids in deuterated benzene versus the volume fraction of an acid. The negative slope of curves testifies to the repulsion of molecules in the system

The scattering curves for stearic acid are shown in Fig. 4. As seen, their behavior differs essentially from those for solutions of oleic and myristic acids. For the range of concentrations $\Phi = 0.02 \div 0.05$, the Guinier approximation demonstrates the growth with increase in both the scattering intensity normed on the concentration at the zero angle and the gyration radius (Fig. 5) as compared with two other acids. The value of the second virial dimensionless coefficient $B = +4$ was

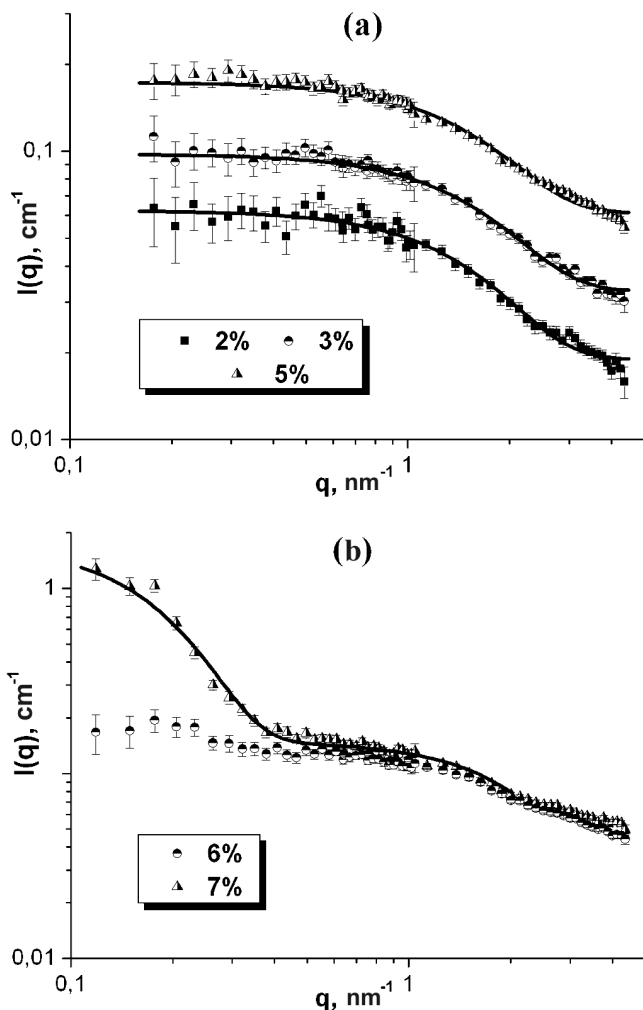


Fig. 4. Experimental SANS curves for the solutions of stearic acid in deuterated benzene for various concentrations of the acid: 2, 3, 5% (a), and 6, 7 % (b). Solid lines – the Guinier approximation of curves according to Eq. (5). For (b), we used the Guinier function with the following gyration radii: $R_{g2} \approx 5.8$ nm and $R_{g1} \approx 1.1$ nm

determined by using the data for three above-indicated values of concentrations. To clarify the character of the interaction between molecules of a dissolved acid, the concentration dependence of the gyration radius is more informative as compared with the scattering intensity at the zero angle [7]. A positive value of the coefficient B indicates the effective attraction between molecules of

Parameters obtained from the analysis of experimental data

Acids	$V_{VDW}, \text{\AA}^3$	$V_{exp}, \text{\AA}^3$	V_{VDW}/V_{exp}	B	$R_{g0}, \text{\AA}$
OA	300	699 ± 53	2.23	- 2.2	11.0 ± 0.3
SA	300	644 ± 75	2.15	+ 4.0	9.0 ± 1.0
MA	233	522 ± 48	2.24	- 2.0	9.3 ± 9.3

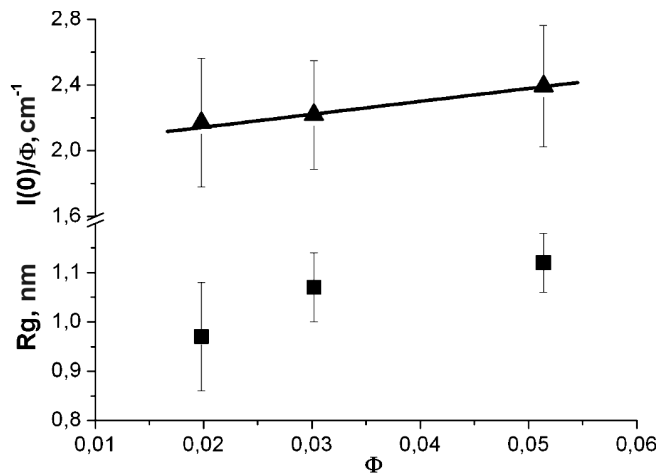


Fig. 5. Scattering intensity of neutrons at the zero angle normed on the volume fraction of the solute (triangles) and the gyration radii (squares) for various concentrations of stearic acid in benzene. The solid line corresponds to the linear approximation according to Eq. (4)

stearic acid in the solution, which is confirmed also by the dependence of the inertia radius on the concentration.

For concentrations Φ more than 5%, the attraction leads to the aggregation of molecules of SA, which causes a deviation from the Guinier law in the region of the smallest values of the scattering vector. At $\Phi = 0.07$, the signal from these aggregates becomes quite significant, and this allows us to estimate their size which is equal to about 10 nm.

All values of the parameters determined from the experiments are presented in the Table.

On the processing of experimental data, we determined the volumes of molecules of the acids in benzene (V_{exp}). The comparison of the volumes obtained experimentally with those given by the van der Waals theory (V_{VDW}) gave $V_{exp}/V_{VDW} \sim 2.2$ for all three acids. This means that the interaction of the acids with the solvent is the same. Assuming the cylindrical form of molecules, we can estimate the effective radius of the cross-section of a molecule. We got that $R_{VDW} \sim 2 \text{\AA}$ for the volume in the van-der-Waals theory and $R_{exp} \sim 3 \text{\AA}$ for the molecule volume according to the SANS data. Such a difference of the radius obtained from experiments and the theoretical value was expected. In our opinion, this is explained by the fact that a neutron interacts with the nuclei of atoms; therefore, the effective radius of a molecule obtained from experiments differs from its van der Waals analog (calculated from the electron distribution) approximately by the van-der-Waals radius of a

hydrogen atom of the solvent which is in contact with the surface of a molecule.

The results obtained by us indicate the quite similar behavior of molecules of oleic and myristic acids in benzene from the viewpoint of the second virial coefficient. The attraction between molecules of an acid, which was revealed by the analysis of experimental data, is not related to the nematic interaction, but, most probably, it happens due to the interaction of the solvent with a dissolved substance. By comparing the values of the second virial coefficient for OA and MA, we may conclude that the attraction between molecules of myristic acid is somewhat greater than that between molecules of oleic acid. The different stabilization properties of a surfactant is related, obviously, to different arrangements of molecules on the absorbing surface. A similar behavior of OA and MA explains the good miscibility of these acids in the bulk of a solvent [11], which is essential for the production of ferrofluids with a mixture of surfactants [12].

It is worth noting that the attraction decreases significantly the concentration corresponding to the transition from the isotropic phase into the nematic one; therefore, the transition of stearic acid into the liquid-crystal phase can be an important factor changing the stability of magnetic liquid systems.

4. Conclusions

The analysis of the SANS curves for solutions of free molecules of surfactants allows us to conclude that there is no basic difference in the behaviors of non-saturated oleic acid and short saturated myristic acid. Whereas the steric repulsion dominates for molecules of both acids, we have found that a significant attraction is characteristic of the system as a result of the interaction of molecules of a solvent with molecules of a dissolved substance. At the same time, the behavior of molecules of stearic acid in benzene is essentially different. For stearic acid in benzene, the interaction of the solvent with the dissolved substance causes the effective attraction between molecules of the acid. At the bulk share of stearic acid in the solution $\Phi > 0.06$, a considerable amount of aggregates is formed. The discovered attraction between molecules shifts the transition point into the liquid-crystal state to the side of small concentrations, which is observed, indeed, in the case of stearic acid. Worse stabilization properties of molecules of stearic acid revealed in the production of ferrofluids can be related, in our opinion, to the formation of aggregates in organic non-polar solutions.

We thank our colleagues from the Center of Fundamental and Advanced Technical Research, Timisoara Branch of Romanian Academy of Sciences for the specimens courteously given for studies.

1. R.E. Rozenweig, *Ferrohydrodynamics* (Cambridge Univ. Press, Cambridge, 1985).
2. S. Abrahamson and I. Ryderstedt-Nahringbauer, *Acta Crystallogr.* **15**, 1261 (1962).
3. R. Tadmor, R.E. Rozenweig, and J. Frey, *Langmuir* **16**, 9117 (2000).
4. M.V. Avdeev, D. Bica, and L. Vekas, *Journ. Magn. Magn. Mat.* **311**, 6 (2007).
5. G. Jancso, L. Cser, T. Grosz, and Yu.M. Ostanevich, *Pure and Appl. Chem.* **66**, 515 (1994).
6. B. Jacrot, *Rep. Prog. Phys.* **39**, 911 (1976).
7. V.Yu. Bezzabotnov, L. Cser, T. Grosz *et al.*, *Journ. Phys. Chem.* **96**, 976 (1992).
8. D. Frenkel, R.J. Vos, C.G. de Kruif, and A. Vrij, *Journ. Phys. Chem.* **84**, 4625 (1986).
9. F. Bonnete and D. Vivares, *Acta Cryst. D* **58**, 1571 (2002).
10. L. Cser, G. Jancso, Gy. Kali, and P. Jovari, *Journ. Phys. Chem.* **102**, 2313 (1998).
11. N.L. Gershfeld, *Ann. Rev. Phys. Chem.* **27**, 349 (1976).
12. D. Bica, L. Vekas, M.V. Avdeev *et al.*, *Journ. Magn. Magn. Mat.* **311**, 17 (2007).
13. A.G. Ramazanov, V.I. Yashkova, O.V. Balmasova *et al.*, *Rus. Chem. Bul.* **55**, 666 (2006).
14. A.G. Ramazanov, V.V. Korolev, and E.V. Ivanov, *Rus. Journ. Phys. Chem.* **81**, 560 (2007).

Received 31.01.08.

Translated from Ukrainian by V.V. Kukhtin

НЕЙТРОННІ ДОСЛІДЖЕННЯ ВЗАЄМОДІЇ МОЛЕКУЛ ПОВЕРХНЕВО-АКТИВНИХ РІЧОВИН В НЕПОЛЯРНОМУ РОЗЧИННИКУ

В.І. Петренко, Л.А. Булавін, М.В. Авдєєв, В.Л. Аксьонов, Л. Рошта

Резюме

Методом малокутового розсіяння нейтронів (МКРН) досліджено поведінку ненасиченої олеїнової та насичених стеаринової та міристинової монокарбоксильних кислот в органічному неполярному розчиннику (дейтерований бензол). З експериментальних даних знайдено та порівняно між собою значення другого віріального коефіцієнта та об'єми молекул кислот. Показано, що олеїнова та міристинова кислоти однаково сольватовані в бензолі, а між молекулами цих кислот відбувається незначне притягання на додаток до стеричного відштовхування. Разом з тим між молекулами стеаринової кислоти відбувається досить сильне притягання, що приводить до утворення великих агрегатів за об'ємної частки кислоти в розчині, більшої за 6%. Отримані результати пояснюють особливості стабілізаційних характеристик даних кислот у випадку ферофлюїдів.