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Small-angle neutron scattering (SANS) determination of the volume occupied by a single water molecule in the inverted micellar systems AOT + X(H,D)₂O + C₁₀D₂₂ by internal contrast variation technique

N. GORSKI and Y.M. OSTANEVICH

Laboratory of Neutron Physics, Joint Institute for Nuclear Research, 141980 Dubna, Moscow Reg., Russia

abstract: we performed the small-angle neutron scattering measurements on the AOT + X(H,D)₂O + C₁₀D₂₂ reverse micellar solution over a wide range of water molar ratios $X = 3 - 40$. We determined the match - point b_c , the aggregation numbers N , the radii of the spherical water nuclei r_w , the area per head group of surfactant a_0 and the volumes of single water molecules in micelles v_w . In detail we obtained $v_w = 143 \text{ \AA}^3$ for $X = 3$, $v_w = 53 \text{ \AA}^3$ for $X = 7$, $v_w = 45 \text{ \AA}^3$ for $X = 14$, $v_w = 31 \text{ \AA}^3$ for $X = 20$ and $v_w = 27 \text{ \AA}^3$ for $X = 40$. All these data show that with increasing water nucleus size the volume per water molecule decreases and reaches the volume of the water molecule in bulk at $X \geq 20$.

1. INTRODUCTION

The question of the nature of water in small volumes is of course of great interest and general importance in the field of reverse micelles, in particular. In fact the physical properties of reverse micelles are strongly affected by water and the study of the nature of water in the interior of a water pool is of key interest for the understanding of the behavior of a reverse micellar system [1-6]. In our publication [7] we previously reported on the specific volume per water molecule in the system AOT + X D₂O + benzene, which was estimated to be $v_w = 98 \text{ \AA}^3$ for $X=4.3$ and $v_w = 51 \text{ \AA}^3$ for $X = 8.6$ (X , molar ratio for water to AOT). These values are much higher than the volume of a water molecule in the bulk state ($30 \text{ \AA}^3$). The system AOT+X D₂O+benzene was restricted in the water content by a value of $X = 10$ at normal temperature. This ratio reaches a value of $X=100$ in the case of decane as the solvent. If the remarkable friability of inverted micelles, observed by us in benzene at the smallest water concentration, is realized in decane also, we get the possibility to follow the case of this interesting property at the water content increases.

2. EXPERIMENTAL

The surfactant AOT ((bis-2-ethylhexyl)sodium sulfosuccinate, Fluka, Schweiz) was dissolved in D-decane (99,8% C₁₀D₂₂, ZfI, Leipzig). The concentration of these dry stock solutions was 56.0-68.6 mM. The samples were prepared by adding the appropriate amounts of D₂O (99,8%, Isotop, Moscow) / H₂O mixtures to give systems with water to AOT ratios of $X = 3.1, 7, 14, 20$ and 40 . The SANS experiments were performed at the MURN-spectrometer located at the IBR-2 pulsed reactor (JINR, Dubna). This type of SANS spectrometers allows one to use nearly the whole of the thermal neutrons, which are monochromatized by the time-of-flight method. We used the wave length range from $0.7 \text{ \AA}$ to $10 \text{ \AA}$ with a time - averaged flux of thermal neutrons on the sample of about

$1.3 \cdot 10^7 \text{ cm}^{-2} \text{ sec}^{-1}$. The length of the scattering vector Q ranged from $0.01 \text{ \AA}^{-1}$ - $0.25 \text{ \AA}^{-1}$. The solutions were introduced into cylindrical optical quartz glass scattering cells of 1 mm useful thickness. The exposure of a sample took from 0.5 to 2 hours depending on the concentration of water. Pure D-decane was used for incoherent background subtraction. After being appropriately corrected, the scattering data were transformed into absolute scattering cross-sections per unit volume of a solution, $d\Sigma/d\Omega(Q)$ in $\text{cm}^{-1} \text{ ster}^{-1}$, by using the internal calibration standard of the MURN spectrometer, a simple metallic vanadium body. The systematical error of our absolute cross-section scale is expected to be less than 10 %.

3. THEORETICAL BACKGROUND

In our experiments we used the internal contrast variation method. Consequently we measured the small-angle scattering cross-section $d\Sigma/d\Omega(Q)$ as a function of the contrast $b - \varphi_s v$ by varying the neutron scattering length of the water nucleus only, using various $\text{D}_2\text{O} / \text{H}_2\text{O}$ mixtures.

According to the standard theory of a system of nearly spherical particles with low polydispersity in the case of a dilute solution (the interparticle structure factor $S(Q) = 1$) the scattering cross-section is given by

$$d\Sigma/d\Omega(Q) = n (b - \varphi_s v)^2 N^2 P(Q) \quad (1)$$

where n is the number density of micelles, φ_s is the mean scattering length density of the solvent, v is the solvent-excluded total volume per single AOT molecule and water per it $v = v_{\text{AOT}} + X v_w$, N is the mean aggregation number of micelles, $P(Q)$ is the particle structure factor normalized to $P(0) = 1$, b is the total neutron scattering length per single AOT molecule and water per it. By definition

$$\begin{aligned} b &= b_{\text{AOT}} + X [y b_D + (1 - y) b_H] \\ &= b_{\text{AOT}} + b_{\text{aq}} \end{aligned} \quad (2)$$

$y = n_D/n_D + n_H$ is the mole fraction of D_2O in the $\text{D}_2\text{O}/\text{H}_2\text{O}$ mixtures. b_{AOT} , b_D and b_H are the coherent scattering lengths of AOT, D_2O and H_2O molecules, respectively.

From Eq.(1) follows that the zero-angle cross-section square root $[d\Sigma/d\Omega(0)]^{1/2}$ is a linear function of b_{aq} , with the value of b_c given by the intercept of the line with b_{aq} axis.

$$[d\Sigma/d\Omega(0)]^{1/2} = n^{1/2} N (b_{\text{AOT}} - \varphi_s v) + n^{1/2} N b_{\text{aq}} \quad (3)$$

In this the match-point is $d\Sigma/d\Omega(0) = 0$ and from the value of b_c this obtained one can calculate $v = v_{\text{AOT}} + X v_w$ from the relation

$$\begin{aligned} \text{as } b_{\text{AOT}} + b_c - (v_{\text{AOT}} + X v_w) \varphi_s &= 0 \\ v_{\text{AOT}} + X v_w &= (b_{\text{AOT}} + b_c) / \varphi_s \end{aligned} \quad (4)$$

Furthermore, the slope of the line defined by Eq.(3) gives the quantity $k = n^{1/2} N$ thus providing a direct determination of the micellar aggregation number $N = k^2 / C_{\text{AOT}} N_a$, the number density of micelles $n = C_{\text{AOT}} N_a / N$, the volume of the water nucleus $v_w = v/n$, its radius $r_w^3 = 3 v_w / 4\pi$, its surface $S_w = 4\pi r_w^2$, the area per head group $a_0 = S_w / N$, the volume of a micelle $v_m = v N$ and its radius $r_m^3 = 3 v_m / 4\pi$. C_{AOT} , v , N_a are the concentration of surfactant AOT, the totale volume of water and the Avogadro number, respectively.

4. EXPERIMENTAL RESULTS

The parameters $d\Sigma/d\Omega(0)$ and R_g^2 were determined from the Guinier plot of $\ln [d\Sigma/d\Omega(Q)]$ vs. Q^2 . A semilogarithmic plot of the $d\Sigma/d\Omega(Q)$ data and a linear approximation allow one to find both the extrapolation to $Q^2 = 0$ $d\Sigma/d\Omega(0)$ and the slope of a straight line which, in turn, is connected with the squared radius of gyration R_g^2 of a micelle.

In Fig. 1 is shown the typical linear dependence of the square root of zero-angle cross-section $[d\Sigma/d\Omega(0)]^{1/2}$ on the coherent scattering length of water nucleus b_{aq} .

Fig. 1: The square root of the zero-angle cross section $d\Sigma/d\Omega(0)^{1/2}$ vs. the coherent scattering length of water core b_{aq} . AOT + 40 $(\text{H,D})_2\text{O}$ + $\text{C}_{10}\text{D}_{22}$

It is seen that linear approximation predicted by Eq.(3) is valid. Numerical values of both parameters in Eq.(3), the values of the coherent scattering lengths in the match-points b_c and the list of calculated values are presented in Tab.1. The volume of water was found as $v_w = (v - v_{AOT}) / X$. The volume of dry v_{AOT} was determined to be $667 \text{ \AA}^3$ [7].

Fig. 2: The volume v_w , occupied by a single water molecule vs. the molar ratio $X = [\text{H}_2\text{O}]/[\text{AOT}]$.

In Figs.2 and 3 are shown the volume, occupied by a single water molecule in the micelle v_w and the area of the water core per single AOT head group a_0 versus the molar ratio X in the AOT / X $(\text{H,D})_2\text{O}$ / $\text{C}_{10}\text{D}_{22}$ systems. The v_w data show that with increasing water nucleus size the volume per water molecule decreases from $v_w = 143 \text{ \AA}^3$ for $X = 3.1$ to $v_w = 27 \text{ \AA}^3$ for $X = 40$ and reaches accordingly the volume of the water molecule in bulk water at $X \geq 20$.

Tab.1: Characteristics of inverted micelles in the ternary system
AOT + X (H,D)₂O + C₁₀D₂₂

X	α $\text{cm}^{-1/2}$	$10^{-10}k$ $\text{cm}^{-3/2}$	$10^{12}b_o$ cm	N	ν $\text{\AA}^3$	r_w Å	r_H Å	$10^5 C_{AOT}$ Mol/ml
3.1	1.47	2.13	68.85	13	1108	6.5	15.0	5.96
7.4	2.65	4.17	63.36	39	1059	12.8	21.5	7.40
14.0	3.18	3.97	80.05	44	1279	16.2	23.8	5.96
20.0	4.80	5.92	81.16	104	1295	24.5	31.8	5.60
40.0	13.90	12.70	109.80	478	1730	51.4	58.2	5.60

Fig. 3: The area of the water core per single AOT head group a_o vs. the molar ratio $X = [\text{H}_2\text{O}]/[\text{AOT}]$.

5. CONCLUSION

This investigation has shown that the great volume effect of water molecule observed in a AOT + X D₂O + benzene reversed micellar system by small X exists also in AOT + X(H,D)₂O + C₁₀D₂₂ system. It is not a system specific.

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