SANS method study of surfactant mixture system TX-100+C16TAB in heavy water solutions

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Abstract. The mixture system of two classic surfactants cationic and non-ionic – C16TAB (hexadecyltrimethylammonium bromide)+TX-100(p-(1,1,3,3-tetramethyl) poly(oxyethylene) in heavy water solutions was investigated at temperatures 30º, 50º, 70º for compositions 1:1, 2:1, 3:1 by the small-angle neutron scattering(SANS) method on spectrometer ('YuMO') at the IBR-2 pulsed neutron source at FLNP, JINR in Dubna (Russia). Measurements have covered Q range from $7x10^{-3}$ to 0.4 $Å^{-1}$. The SANS measurements of aqueous solutions of nonionic / cationic surfactants have shown that the mixed micelles are formed [1-2]. From the measured dependence of the scattered intensity on the scattering angle, we derived the size, shape of micelles, aggregation number at various compositions and temperatures. The size of mixed micelle is a weak function of the mixing ratio between the two components.

1. Introduction

Currently, the structures and properties of mixed solutions formed by two surfactant types, especially by nonionic and ionic surfactants are extensively studied by experimental and theoretical methods, since properties of mixed systems are in many cases better than properties of individual components. Taking into account the fact nonionic surfactants tend to ideal mixing, it can be expected that large deviations from the ideal behavior should appear for mixtures with certain interactions between two surfactant types. Although the synergistic behavior of mixed surfactant systems has long been studied, acquisition of the data on the behavior of various surfactant molecule types in mixed solutions remains an urgent problem. The aim of this work is to study mixed systems of nonionic surfactant TX-100 with cationic surfactant by small angle neutron scattering (SANS) with the determination of the micelle shape and size. The SANS and small angle X - ray scattering are efficient methods for obtaining information on the structure of mixed micelles and are often used in practice. The critical micelle formation concentration (CMC) was also determined during the study by the surface tension method.

2. Experimental section

Materials

Triton X-100 nonionic classic surfactant (p-(1,1,3,3-tetramethyl) poly(oxyethylene) with CMC= $0.2x10^{-3}$M was obtained as a gift from JINR, Dubna, (Russia), C16TAB cationic classic surfactant (hexadecyltrimethylammonium bromide (CMC= 1 mM) were purchased from Fluka(99.9 %) and was used these substances without further purification. Heavy water D_2O (99.9%) was purchased in Prikladnaya Chimia" in St.Petersburg (Russia).

2.1. Measurement of CMC - surface tension method
Du Nouy ring method we used for measured the CMC of investigated solutions. The CMC values for TX-100+C16TAB+D_2O micellar solutions are presented in Table 1.

Table 1. Influence of temperature on CMC for mixed system TX-100-C_{16}TAB-D_2O for different compositions.

composition of mixture $C_{TX\text{-}100}$ / C_{CTAB}	$C_{CMC}\cdot 10^{-4}$,M		
	temperature		
	30°C	50°C	70°C
1 : 1	0,915	0,941	0,790
2 : 1	0,568	0,667	0,363
3 : 1	0,465	0,470	0,474

2.2. SANS measurements-small angle neutron scattering (SANS) method
The SANS spectra were measured using a YuMO diffractometer by the time of flight at the IBR-2 pulsed reactor (Joint Institute for Nuclear Research, Dubna, Russia). The specific features of this diffractometer were described in details previously [3]. Neutrons in the range of 0.7–10 A^{-1} were used. Solutions were poured into tightly closed quartz cells (Hellma) 2 mm thick. The temperature within cells (30°,50°,70° ± 0.5°C) was maintained constant during measurements using a thermostat. The measured differential scattering cross section was calibrated using a vanadium reference sample. Data pre-processing was performed using the SAS program [4]. For all samples, heavy water (D_2O) was used as a solvent to achieve good contrast conditions. The experimental results were processed using the PCG Software 2.01.02 program (Austria).

3. Results and discussion

Effect of nonionic surfactant TX-100 concentration on structure of micellar solutions in mixed [5-10] system (TX-100+C16TAB+D_2O) for different compositions and temperatures
The experiment was performed at temperatures of 30°C,50°C and 70°C for three mixed solutions: (i) nonionic surfactant TX-100 (c_1 = 0.022mol/l = 1.294%) in D_2O with cationic surfactant C16TAB concentrations c =0.022mol/l (ii) nonionic surfactant TX-100(c_2 = 0.044mol/l= 2.588%) in D_2O with cationic surfactant C16TAB for concentration c =0.022mol/l = 1.294%.; (iii) nonionic surfactant TX-100 (c_3 = 0.066mol/l= 2.588%) in D_2O with cationic surfactant C16TAB for concentration c =0.022mol/l = 1.294%. The effect of nonionic surfactant TX-100 on the structure of micellar solutions of mixed surfactants system TX-100+C16TAB+D_2O was studied by small angle neutron scattering as a function of composition and temperature (Figure 1). In Table 1 shown the compositions of investigated in experiment mixture systems.

Table 2. TX-100+C16TAB+D_2O (composition of solutions)

1:1	0.022mol/l(TX-100)+0.022mol/l(C16TAB)=1.294%+0.7289%=2%
2:1	0.044mol/l(TX-100)+0.022mol/l(C16TAB)=2.588%+0.7289%=3.4%
3:1	0.066mol/l(TX-100)+0.022mol/l(C16TAB)=3.882%+0.7289%=4.6%

IOP Conf. Series: Journal of Physics: Conf. Series **848** (2017) 012023 doi:10.1088/1742-6596/848/1/012023

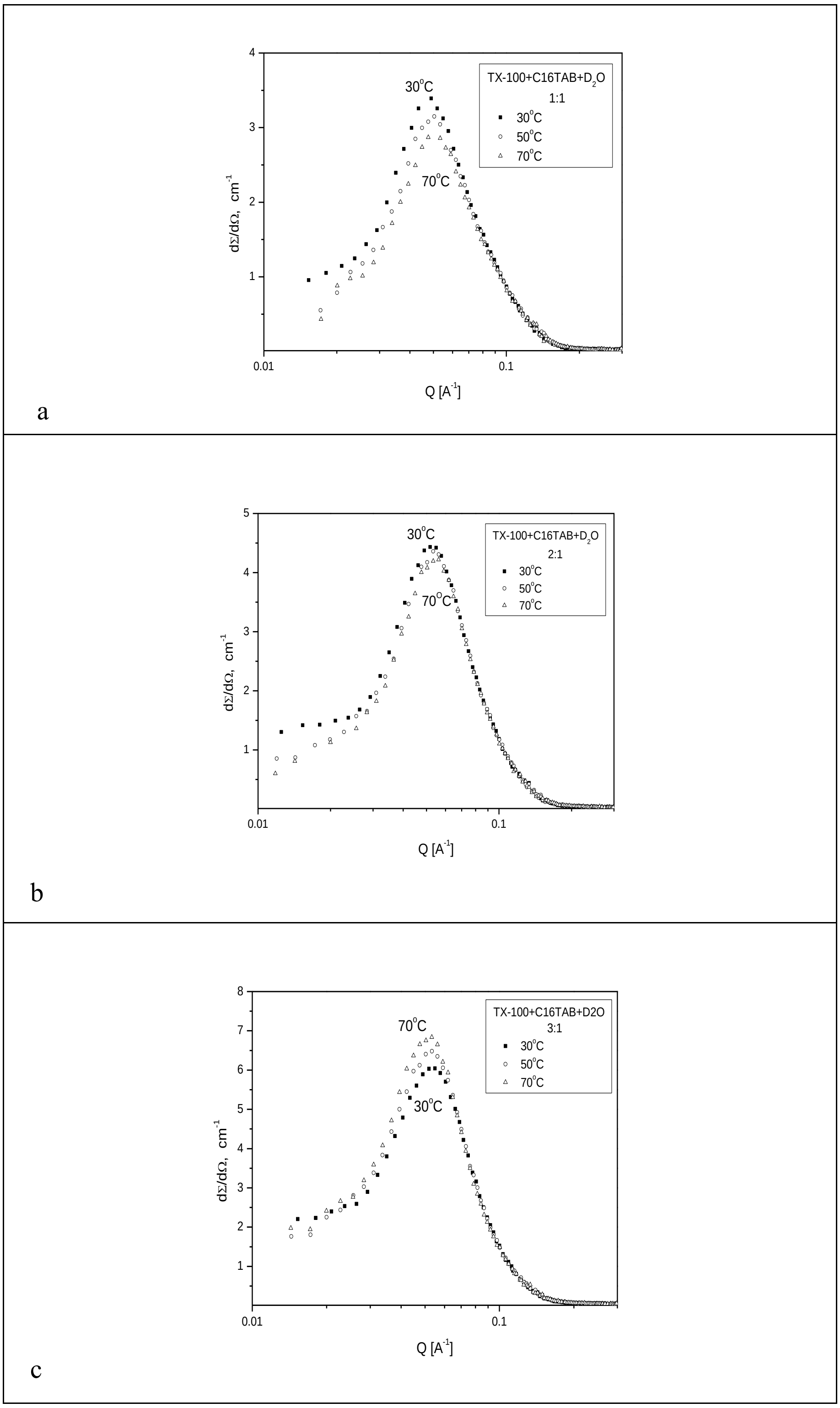

Figure 1. Intensity of neutron scattering vs scattering vector for mixture solution of TX-100 +C16TAB+D_2O for three various mix ratios 1:1(a),2:1(b),3:1(c) at temperatures 30ºC, 50ºC,70 º C.

Table 3. Average distance between micelles (d) and aggregation number (N_{agg}) in micellar solutions for mixture system TX-100+C16TAB+D_2O.

	average distance between micelles (1) aggregation number (2)					
composition	30°C		50°C		70°C	
	1	2	1	2	1	2
1:1	128.1 Å	72	124.5 Å	73	124.5 Å	77
2:1	121.2 Å	79	117.7 Å	80	117.8 Å	81
3:1	117.7 Å	74	117.8 Å	90	117.8 Å	107

The range of measured temperature was 30°C - 70 °C. The changes of the scattering curves were very small but tendencies for 1:1, 2:1 and 3:1 compositions of the mixed systems were opposite. In case of 1:1 composition the position of maximum curves for increases temperatures shifts to larger Q values for higher temperatures 50°C and 70°C and the maximum height decreases. The experimental curves for composition 2:1 shown that the position of the maximum is approximately the same at all three temperatures (slightly higher at 30 °C) but intensity of the scattering neutrons increases which points to the increasing micellar size. From these results the conclusion is that with increasing ratio between concentration of nonionic surfactant TX-100 and cationic C16TAB from 1:1 to 3:1 (increase the amount of non-ionic surfactant) the system changes properties from ionic like to nonionic like. In micellar solutions ionic like the micelles become smaller with increasing temperature but in nonionic like mixture system micelles increases in solutions.
The intensity of scattering neutrons for the mix ratio 3:1 is higher than for the mix ratios 1:1 and 2:1 and highest experimental curve is at temperature 70°C. The maximum of the scattering neutrons intensity increases with increase of temperature for mix ratio 3:1 and shift to the smaller Q value. The experimental results for CMC values for all investigated solutions shown that CMC changes with the composition of solutions. In mixed system solutions are mixed micelles. The intensity of scattering neutrons for the mix ratio 3:1 is higher than for the mix ratios 1:1 and 2:1 and highest experimental curve is at temperature 70°C. The maximum of the scattering neutrons intensity increases with increase of temperature for ratio 3:1 between concentrations. In Table 3 are the values of the average distance between micelles d and aggregation number N_{agg}.

Conclusions
The preliminary results obtained in this study can be summarized as follows. For all the studied aqueous solutions with constant amount of cationic surfactant C16TAB+D_2O (0.7289%) with additions of non-ionic surfactant TX-100, the existence of micelles was detected. It was found that spherical micelles were formed in mixed system TX-100+C16TAB+D_2O in all studied solutions. The aggregation number for the solutions with composition 1:1 is smaller at temperature 70°C than at 30°C. For mix ratio 2:1 the aggregation number was constant for all temperatures (30 °C,50 °C,70°C).
The aggregation number for mixed system with the highest concentration (3:1) increases with increase of temperature. The average distance between micelles in investigated micellar mixed systems at three different concentrations (at constant cationic C16TAB surfactant concentration) decreases with increasing concentration of the non-ionic TX-100 surfactant. There are only preliminary experimentally results and the next paper is ready for these mixed micellar solutions.

References
[1] Clint J 1975 *J. Chem.Soc. Faraday Trans.***1** 1327; Cantu L, Corti M, Degiorgio V, 1990 *J.Phys. Chem.* **94** 793
[2] Rathman J, Scamehorn J F, 1984 *J. Phys. Chem.* **88** 580
[3] Ostanievich Yu M 1988 *Makromol. Chem. Macromol. Symp*. **15** 91
[4] Solov'ev A G, Solov'eva T N, Stadnik A V, Islamov A Kh, Kuklin A I 2003 *Soobshch.*

Ob'edin. Inst. Yad. Issled. Dubna **86** 10
[5] Rajewska A, Mędrzycka K, Hallmann E 2014 *Physics of the Solid State* **56** 125
[6] Rajewska A, Mędrzycka K, Hallmann E 2007 *Kristallografiya* **52** 811
[7] Almgren M, Garamus V M 2005 *J. Chem. Phys.* **109** 11348
[8] Scamehorn J R, Schechter R S, Wade W H 1982 *J.Dispersion Sci. Technol*. **3** 261
[9] Puvvada S, Blankschtein D 1992 *J. Phys. Chem.* **96** 5567
[10] Zemb T, P. Charpin P 1985 *J. Phys. (Paris)* **46** 249