Journal of Saudi Chemical Society (2015) **19**, 423–428

King Saud University

Journal of Saudi Chemical Society

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ORIGINAL ARTICLE

Effect of presence of benzene ring in surfactant hydrophobic chain on the transformation towards one dimensional aggregate

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Received 9 April 2014; revised 15 May 2014; accepted 29 May 2014
Available online 10 June 2014

KEYWORDS

Wormlike micelles;
Critical intermolecular forces;
Surfactants;
Sodium dodecylbenzene-sulphonate;
Cetyltrimethylammonium bromide;
Supramolecular chemistry;
Thermodynamic properties

Abstract The formation of wormlike micelle and the following significant changes in rheological properties suffer misunderstanding from both theoretical and fundamental aspects. Recently, we have introduced a theory for interpreting such important phenomenon which is referred to as critical intermolecular forces (*CIF*). The theory has stated that the hydrophobic effect is the main factor for the formation of worm-like aggregates. Therefore, it seems interesting to check out the validity of this new physical insight through investigating the presence of benzene ring as less hydrophobic group in contrast to that of alkyl in surfactant tail. The mixture of anionic sodium dodecylbenzenesulphonate (*SDBS*) and cationic cetyltrimethylammonium bromide (*CTAB*) shows a high dynamic viscosity peak at the ratio of 80/20 of 3 wt.% *CTAB*/*SDBS* indicating the formation of wormlike micelles. The thermodynamic properties have been evaluated for this mixture exhibiting good agreement with the rheological changes. Interestingly, the results show the presence of benzene ring (in *SDBS*) causing a negative effect towards the formation of one dimensional aggregate in contrast to previous results which support the proposed *CIF* theory. The presence of nonionic surfactant *TritonX-100* in binary and ternary systems of *SDBS* and *CTAB* prohibits the formation of wormlike micelles.

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1. Introduction

Wormlike micelles are considered as one of the biggest sizes of supra-molecular structure that formed by self-assembled amphiphilic molecules [1]. The unique physical properties of such one dimensional structure guarantee significant industrial and commercial applications [1–3]. On the other side, there is a considerable lack in the theoretical background for interpretation of the transition phenomenon from three to one dimensional shape of aggregate together with the following sharp change in physical properties. Recently, we have investigated some of binary and ternary systems of mixed surfactants for the formation of wormlike micelles [4]. The mixture of anionic [sodium dodecyl sulphate (*SDS*)] and cationic [cetyltrimethylammonium bromide (*CTAB*)] surfactants exhibits a remarkable high viscosity peak at a weight ratio of 80/20 *CTAB*/*SDS*. No

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Peer review under responsibility of King Saud University.

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http://dx.doi.org/10.1016/j.jscs.2014.05.008
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wormlike micelles have been detected for binary mixtures of anionic- nonionic (*Triton-X 100*) nor for ternary mixtures of *SDS/CTAB/Triton-X 100* surfactants [4]. The achieved results from such explorations together with those of previously published [1–3,5–17] have guided us for proposing a theory which is referred to as critical intermolecular forces (*CIF*) for understanding such interesting phenomenon. According to the *CIF* theory [4], the transition process towards one dimensional shape of aggregate results from a combination of three main intermolecular forces: electrostatic interactions of head groups, dispersion forces between tail groups, and the excess of formed hydrogen bonds between water molecules due to hydrophobic effect (icebergs). It was found that the latter effect plays a major role in the formation of wormlike micelle, which has no significance in previous publications. Indeed, the *CIF* approach explains the transformation process from sphere to one-dimensional, as at specific concentrations of molecules, there are intermolecular interactions capable of creating a critical state that makes the transition towards wormlike micelle energetically favourable. This theory showed that the wormlike solution is more stable than that of three dimensional, but the main task that works against the transformation process is the entropy factor. It has been concluded that the suggested theory of *CIF* is considered as a helpful tool in understanding not only the transition state towards wormlike micelles together with the associated significant increase in solution viscosity, but also in helping researchers who are interested in exploring any kind of new wormlike systems [4]. Experimentally, the sudden change of surfactant solution making the viscosity give sharp peaks resulting from a jell-like state due to change in its composite can be considered as a function for the transformation towards one-dimensional micelles according to the images of Cryo-transmission electron microscopy [2–4]. Hence, it seems interesting to extend this work through the investigation of the effect of the presence of benzene ring in the hydrophobic chain because it is well-known that the π system which presents in benzene could have polar characteristics as not existing in alkyl chain. For instance, the dielectric constant of benzene at 20°C is 2.3 while for n-hexane is equal to 1.9. In other words, such job may provide a fresh opportunity to our previous suggestion as the hydrophobic effect is entirely responsible for the formation of worm-like micelles. In addition, the present study could also give general comments about the effect of the presence of benzene ring on the transformation phenomenon towards one dimensional shape.

In the present work, investigations were carried out for the formation of wormlike micelles for mixtures of anionic *SDBS* (sodium dodecylbenzenesulphonate)-cationic *CTAB*, anionic *SDBS*-nonionic Triton X-100, cationic *CTAB*-nonionic *Triton X-100* surfactants, and their ternary system of anionic (*SDBS*)-cationic (*CTAB*)-nonionic (*Triton X-100*) surfactants at different temperatures. Indeed, there are no such investigations mentioned in the literature. It should be noted that *SDBS* and *CTAB* are frequently used as vital surfactants for the successful preparation of functional nanomaterials of conducting polymers [18–20].

2. Experimental

The surfactants *SDBS* ($CH_3(CH_2)_{10}CH_2(C_6H_6)$–$SO_3^-Na^+$), *CTAB* ($CH_3(CH_2)_{14}CH_2N^+(CH_3)_3Br^-$) and *Triton X-100* ($CH_3C(CH_3)_2CH_2C(CH_3)_2C_6H_4(OCH_2CH_2-)_{10}OH$) were obtained in a high purification form from Aldrich and Fluka companies. Conductivity water was used for preparation of all solutions with specific conductance of 3–5 μS cm^{-1}. The water was freshly prepared through redistilling distilled water with the addition of little amounts of $KMnO_4$ and KOH.

3 wt.% solution of each surfactant is made to give concentrations of *0.08875*, *0.08486* and *0.0478 M* for *SDBS*, *CTAB* and *Triton X-100* respectively.

The dynamic viscosity (η) measurements were carried out using modified Ostwald apparatus as detailed in Ref. [4]. The conductivity measurements were determined, using WTW conductometer with an accuracy ± 0.01 μS cm^{-1}. To control the temperature of the above determined physical properties within ± 0.1 °C, water thermostated Hakke NK22 is used. All measurements are repeated for at least three times in order to check the reproducibility of the data.

The approximate thermodynamic functions for the transition process towards one-dimensional shape were estimated using the following suggested models of the *CIF* theory [4]. The standard Gibbs free energy (ΔG^o) was estimated using the following approximate relation [4]:

$$\Delta G^o \approx -RT\ln(\eta/2\times 10^{-3}) \tag{1}$$

where R is the gas constant, T is the absolute temperature and η is the observed dynamic viscosity. The approximate standard enthalpy (ΔH^o) was evaluated graphically using this model [4]:

$$\frac{d(\ln\eta/2\times 10^{-3})}{d(1/T)} \approx \frac{-\Delta H^o}{R} \tag{2}$$

The standard entropy (ΔS^o) was calculated using the following general thermodynamic relation:

$$\Delta S^o = \frac{\Delta H^o - \Delta G^o}{T} \tag{3}$$

while the activation energy of viscosity (E_a) has been determined according to the following model: [21]:

$$\eta \propto e^{E_a/RT} \tag{4}$$

3. Results and discussion

Indeed, any combination between the solution of high viscosity or a jell-like state due to the formation of wormlike micelle with that of high molecular polymer (whose chain length is fixed by a covalent bond) is considered as a big mistake. The main reason for this can be attributed to the fact that the high viscosity in wormlike solution is belonging to solvent molecules (H_2O) according to the *CIF* theory [4] while solution of polymers is resulted from the solute (polymer itself) in addition to other factors that mentioned briefly in Ref. [4]. Therefore, investigations concerning the effect of the presence of benzene ring towards the formation of wormlike micelles are quite necessary in order to verify the *CIF* theory. Thus, the anionic *SDBS* surfactant could be considered as a quite sufficient sample for this job in order to compare with the previously studied *SDS* as clearly illustrated in Scheme 1. Moreover, it is quite necessary to do this job at different temperatures because we are dealing with thermodynamically controlled living polymers and also in order to evaluate ΔH^o and ΔS^o parameters.

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