Colloid Polym Sci (2005) 283: 845–853
DOI 10.1007/s00396-004-1200-6

ORIGINAL CONTRIBUTIONS

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# Self aggregation of binary mixtures of sodium dodecyl sulfate and polyoxyethylene alkyl ethers in aqueous solution

Received: 14 June 2004
Accepted: 30 July 2004

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**Abstract** The mixed micelles of sodium dodecyl sulphate (SDS) with Brij35 and Brij 97 were studied separately by fluorescence measurement using pyrene as fluorescent probe. In the range of 0–1.0 mole fraction ($X$) of added SDS to Brij solutions, the cmc value of the mixed micelles varies from 0.085 to 8 mmol with Brij 35 and 0.04 to 8 mmol with Brij 97. The aggregation number also changes. A measure of the stability of mixed micelles is also presented. The interaction parameter $\beta_{12}$ and the chain–chain contribution parameter ($B_1$) are extracted from the analysis of the results. This parameter $B_1$ is related to the standard free energy change associated with the introduction of one ionic species into a nonionic micelle coupled with the release of one nonionic species from the micelle. The clouding behaviour of Brij 97 in the presence of SDS was investigated and the associated thermodynamic parameters of clouding were generated and discussed.

**Keywords** Anionic/nonionic surfactant · Critical micelle concentration · Interaction parameter · Mixed micelle · Aggregation number · Cloud point

## Introduction

The self-assemble property of surfactant molecules in water arises because of the presence of the hydrophobic groups in the surfactants. The majority of surfactants used in practice are not pure, but are mixtures of several surfactants. One important reason for this is that purification of the surfactant is very expensive. In addition the majority of important properties of a pure surfactant are inferior to those of a mixed surfactant system [1]. The association properties of mixed surfactants have been widely studied in recent years [2–7] because of their favourable effects in numerous technical applications [8–10]. The surfactant mixtures are useful in adjusting the required properties [10–12]. The properties of mixed surfactant solutions are much different from those of pure surfactant solutions. Micelles composed of mixtures of surfactants of similar structure are nearly ideal, i.e. ideal solution theory describes the thermodynamics of mixing in the micelle. But mixed micelles containing ionic, nonionic surfactants often show negative deviations from ideality [13, 14]. On the other hand, mixed micelles composed of mixtures of fluorocarbon and hydrocarbon surfactants exhibit positive deviations from ideality [15]. The mixed micellar system are also of great theoretical interest recently [4], since the structural properties of the mixed aggregates can become substantially different from those formed only by the individual surfactants [16]. Extensive studies [17–21] have been carried out on various mixed surfactant systems like ionic–ionic and ionic–nonionic. Mixed micelles of ionic with nonionic surfactants have been the topic of several investigations owing to their extended colloidal stability when compared with pure nonionic micellar systems [22–27]. An ionic surfactant generally forms small globular aggregates but may have the size increased upon addition of a nonionic surfactant. The larger size and stability of the mixed micelles would enhance the micellar property [28].

In this work, the mixed micelles formed by sodium dodecyl sulphate (SDS) with polyoxyethylene (23) lauryl ether (Brij 35) and polyoxyethylene(10)oleyl ether (Brij 97) were studied by fluorescence spectroscopy viscosity, density and cloud point measurements.

The cmc, aggregation number, partial specific volume, radius of the unhydrated micelles, and head group area were determined. The stability of mixed micelles has been analysed in terms of an interaction parameter $\beta_{12}$ [13].

## Experimental

### Materials

Sodium dodecyl sulphate from Merck (Germany); Brij 35 [$CH_3$ $(CH_2)_{11}O(OCH_2CH_2)_{23}H$] M.W. 1199.8 (E. Merck, Germany); Brij 97 [$CH_3CH{=}CH(CH_2)_{15}O$ $(OCH_2CH_2)_{10}H$], M.W. 709 (E. Merck, Germany) were used as received. The fluorescence probe pyrene from Sigma was purified by sublimation, followed by recrystallization from ethanol. Cetyl pyridinium chloride (CPCl) was used as quencher. All experiments were carried out with freshly prepared solutions.

### Density measurements

To determine the partial specific volume of mixed micelles in aqueous solution, we performed density measurements with an Anton-Paar DMA 5000 densimeter. The instrument has an accuracy of $1\times10^{-6}$ g cm$^{-3}$ and it was calibrated with air and water at 25 °C. The temperature was controlled within $\pm 0.001$ °C.

### Viscosity measurements

Viscosity measurements of SDS plus Brij 35 and SDS plus Brij 97 mixtures at various concentrations were measured using Cannon–Fenske viscometers and a viscosity bath (Koehler Instrument).

### Fluorescence measurements

A spex Fluoro Max-3 spectrofluorometer was used for all fluorescence measurements. The emission spectrum of pyrene was measured in the range 360–400 nm by exciting pyrene molecules at 340 nm. The concentration of pyrene used in the micellar solution was of the order of $10^{-6}$ M. The surfactant concentration was in the order ≅50 mM. The quencher, CPCl concentration was varied in the range 0.1–0.9 mM. The fluorescence spectra of pyrene at different quencher concentration were recorded. The quencher CPCl, is a surfactant itself and at low concentration much below its cmc, it virtually resides in the micelles of the major surfactant.

## Results and discussion

### Fluorescence

The ratio of fluorescence intensity of first ($I_1$) and third ($I_3$) vibronic peaks, $I_1/I_3$, in a monomeric pyrene fluorescence emission spectrum is known to be sensitive to the local environment of the probe. The variation of the intensity ratio for SDS plus Brij 35, was plotted against a concentration of surfactant mixture, and the break point indicates the cmc value of the mixture (Fig. 1). The cmc

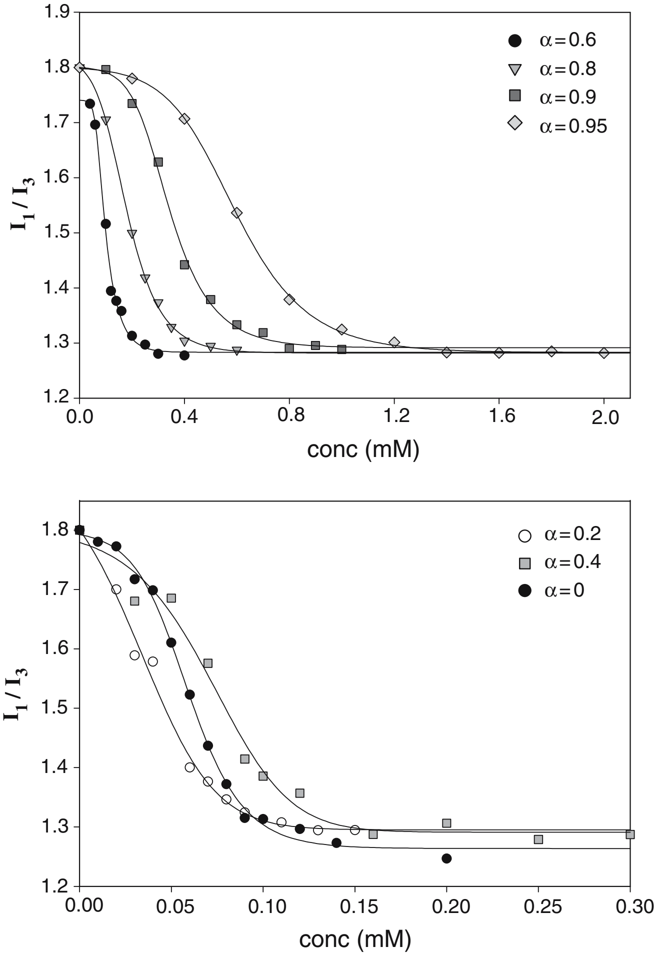

**Fig. 1** Determination of cmc from $I_1/I_3$ ratio of pyrene as a function of concentration of binary mixture at various bulk compositions ($\alpha$)

values for SDS with Brij 35 and Brij 97 are given in Table 1.

The determination of aggregation number ($N_{agg}$) by fluorescence quenching is the most frequently applied method [29]. An advantage with this method is that the aggregation number can be determined also when the micelles interact in solution. The micellar aggregation number ($N_{agg}$) was deduced from the equation

$$\ln\frac{I_0}{I} = \frac{[Q]N_{agg}}{([s] - \text{cmc})} \qquad (1)$$

where $[Q]$ and $[s]$ are the concentrations of quencher and total surfactant respectively [30, 31]. The $I_0$ and $I$ are the fluorescence intensities in the absence and presence of the quencher. The intensity of fluorescence of pyrene against wavelength as a function of quencher concentration is presented in Fig. 2.

The determined aggregation number values for the mixture of SDS-Brij 35 and SDS-Brij 97 are given in Table 2.

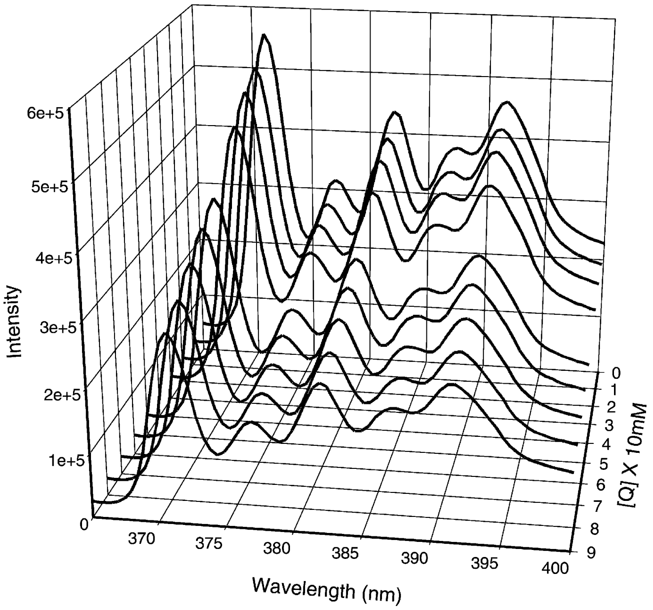

**Fig. 2** Pyrene fluorescence spectrum as a function of quencher concentration

## Surfactant–surfactant interaction

The cmc values for the mixed surfactant systems ($\text{cmc}_{cal}$) can be calculated theoretically for the mixed surfactant systems that behave ideally using Clint's [32] equation

$$\frac{1}{\text{cmc}_{cal}} = \frac{\alpha_1}{\text{cmc}_1} + \frac{\alpha_2}{\text{cmc}_2} \qquad (2)$$

where $\text{cmc}_1$, $\text{cmc}_2$ are the cmc of pure surfactants 1 and 2 and $\alpha_1$, $\alpha_2$ are the mole fraction values in the bulk respectively. The cmc values obtained experimentally ($\text{cmc}_{obs}$) are plotted as a function of mole fraction of SDS in Fig. 3a, b. The $\text{cmc}_{obs}$ values are lower than $\text{cmc}_{cal}$ values. This indicates that there are interactions between the constituent surfactants in the mixed micelles, which cause non-ideal behaviour. To investigate the nature of the interaction between the constituent surfactants in the mixed micelle, the interaction parameters, $\beta_{12}$ and $B_1$ were calculated using Rubingh [13] as well as Meada's theory [33], respectively. The $\beta_{12}$ values were calculated using the equation

$$\frac{(X_1)^2\ln(\alpha_1 C_{12}/X_1 C_1)}{(1 - X_1)^2\ln[(1 - \alpha_1)C_{12}/(1 - X_1)C_2]} = 1 \qquad (3)$$

$$\beta_{12} = \frac{\ln(\alpha_1 C_{12}/X_1 C_1)}{(1 - X_1)^2} \qquad (4)$$

where $X_1$ is the mole fraction of surfactant 1 in the mixed micelle. $C_{12}$ is the cmc of the binary systems and

**Table 1** Various physico-chemical parameters for SDS–Brij 35 and SDS–Brij 97

| System | $\alpha_{SDS}$ | Cmc (mM) | $X_{SDS}$ | $\beta$ | $\gamma_1$ | $\gamma_2$ | $B_o$ | $B_1$ | $B_2$ | $\Delta G_{mic}$ (J/mol) Maeda | $\Delta G_{mic}$ (J/mol) P.S. model |
|---|---|---|---|---|---|---|---|---|---|---|---|
| SDS and Brij 35 | 0 | 0.085 | | | | | | | | −33192 | −33189 |
| | 0.2 | 0.090 | 0.10 | −4.82 | 0.10 | 0.97 | −13.39 | −0.27 | 4.82 | −33130 | −33047 |
| | 0.4 | 0.13 | 0.08 | −3.08 | 0.09 | 0.98 | −13.39 | 1.47 | 3.08 | −32833 | −32194 |
| | 0.6 | 0.18 | 0.21 | −3.01 | 0.11 | 0.95 | −13.39 | 1.54 | 3.01 | −32076 | −31385 |
| | 0.8 | 0.36 | 0.17 | −2.37 | 0.14 | 0.92 | −13.39 | 2.18 | 2.37 | −32111 | −29590 |
| | 0.9 | 0.58 | 0.23 | −2.15 | 0.18 | 0.86 | −13.39 | 2.40 | 2.15 | −31526 | −28424 |
| | 0.95 | 0.99 | 0.30 | −1.95 | 0.24 | 0.77 | −13.39 | 2.59 | 1.95 | −30798 | −27104 |
| | 1.00 | 8.0 | | | | | | | | −21927 | −21924 |
| SDS and Brij 97 | 0 | 0.041 | | | | | | | | −35022 | −35020 |
| | 0.2 | 0.043 | 0.098 | −5.54 | 0.003 | 0.94 | −14.13 | −0.25 | 5.54 | −35165 | −34855 |
| | 0.4 | 0.045 | 0.18 | −6.51 | 0.010 | 0.77 | −14.13 | −1.23 | 6.51 | −35287 | −34445 |
| | 0.6 | 0.051 | 0.24 | −7.15 | 0.020 | 0.67 | −14.13 | −1.87 | 7.15 | −34887 | −34446 |
| | 0.8 | 0.075 | 0.30 | −7.40 | 0.040 | 0.50 | −14.13 | −2.12 | 7.40 | −35226 | −33499 |
| | 1.0 | 8.0 | | | | | | | | −21927 | −21924 |

**Table 2** Micellar composition, aggregation number, radius, and area of the head group of the dry mixed micelles

| System | $\alpha_{SDS}$ | $X_{SDS}$ | $N_{agg}$ | $M$_W (g/mol) | $v$ (cm$^3$/g) | $V_o$ ($10^{-20}$ cm$^3$) | $R_o$ (nm) | $a_o$ (Å$^2$) |
|---|---|---|---|---|---|---|---|---|
| SDS and Brij 35 | 0.0 | 0.0000 | 36 | 43640 | 0.8986 | 6.51 | 2.50 | 215 |
| | 0.2 | 0.1059 | 38 | 41982 | 0.8937 | 6.23 | 2.46 | 199 |
| | 0.4 | 0.0839 | 40 | 44384 | 0.8922 | 6.58 | 2.50 | 199 |
| | 0.6 | 0.2081 | 38 | 38107 | 0.8918 | 5.64 | 2.38 | 188 |
| | 0.8 | 0.1691 | 41 | 42580 | 0.8830 | 6.24 | 2.46 | 187 |
| | 1.0 | 1.0000 | 60 | 17292 | 0.8627 | 2.48 | 1.87 | 73 |
| SDS and Brij 97 | 0.0 | 0.0000 | 45 | 31551 | 0.9427 | 4.94 | 2.28 | 146 |
| | 0.2 | 0.0981 | 44 | 29515 | 0.9690 | 4.75 | 2.25 | 143 |
| | 0.4 | 0.1796 | 44 | 28126 | 0.9564 | 4.47 | 2.20 | 137 |
| | 0.6 | 0.2396 | 50 | 30108 | 0.9374 | 4.69 | 2.24 | 127 |
| | 0.8 | 0.2954 | 56 | 32806 | 0.9193 | 5.01 | 2.29 | 117 |
| | 1.0 | 1.0000 | 60 | 17292 | 0.9536 | 2.74 | 1.87 | 73 |

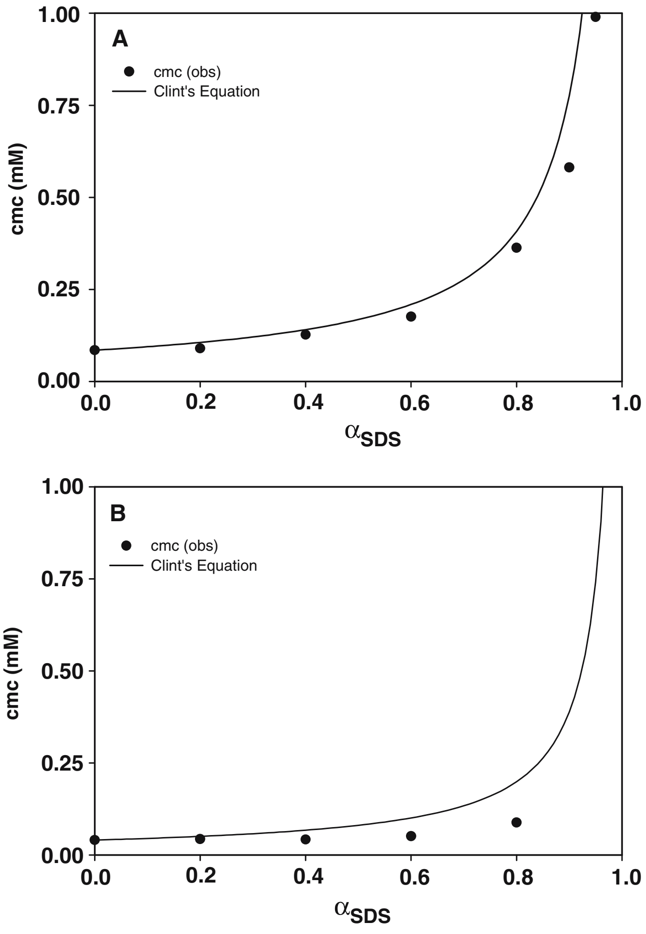

**Fig. 3** Plots of experimental and calculated (Clint's equation) cmc values determined for **a** SDS and Brij 35, **b** SDS and Brij 97

$C_1$ and $C_2$ are the cmc for pure surfactants 1 and 2 respectively. The $\beta_{12}$ values are presented in Table 1. This interaction parameter is related to the activity coefficients of the surfactants within the micelle by

$$\gamma_1 = \exp[\beta_{12}(1 - X_1)^2] \tag{5}$$

and

$$\gamma_2 = \exp[\beta_{12}X_1^2] \tag{6}$$

$\beta_{12}$ is an indication not only of the degree of interaction between the two surfactants but also accounts for the deviation from ideality. A negative value of $\beta_{12}$ implies an attractive interaction, the more negative the $\beta_{12}$ value the greater the attraction. It was found that for the Brij 97/SDS system $\beta_{12}$ value becomes more negative with increase in mole fraction of SDS in the system, whereas for the Brij 35/SDS system the $\beta_{12}$ value becomes less negative as the mole fraction of SDS in the system increases. The more negative $\beta_{12}$ value in Brij 97/SDS system indicates that the interaction between the two surfactants is more attractive in the mixed micelle than the self-interaction of two surfactants before mixing. However, the $\beta_{12}$ values become less negative as the concentration of SDS increases in mixed surfactant systems. Similar behaviour has been observed for the interaction parameter calculated using Maeda's approach [33] discussed later. Maeda [30] and Ruiz et al. [2, 4] have reported that both chain–chain and head group–head group interactions may operate in the mixed system. It is established that while $\beta_{12}$ value explains the head group–head group interactions, it does not encompass the chain–chain interactions between the hydrocarbon segments of the constituent surfactant molecules when the chains are of dissimilar lengths [33]. The stronger chain–chain interactions for Brij 97/SDS, compared to Brij 35/SDS may be attributed to dissimilar chain lengths in the former case. According to Maeda [33], as the chain lengths differ, there should be chain–chain interaction helping the stability of the mixed micelle. The interaction may be explained by the fact that some water molecules may be shared by different head groups as well as hydrophobic chains; thereby water molecules may act as some type of bridge between the molecules just below the water–micelle interface, result in an increased attractive interactions. The lower cmc values for these systems can be due to the decrease in ionic head group repulsions caused by the presence of non-ionic surfactant molecules between the SDS head groups. The larger decrease in cmc values for the SDS/Brij 97 system (Fig. 3b) is due to the decrease in ionic head group repulsion due to steric factor in the presence of Brij 97. Maeda [33] suggested another parameter $B_1$, in addition to $\beta_{12}$ that contributes to the stability of the mixed micelle. The free energy of micellization ($\Delta G_m$) as a function of the mole fraction of the ionic component in the mixed micelle is

$$\Delta G_m = RT(B_0 + B_1X_1 + B_2X_1^2) \tag{7}$$

where

$$B_0 = \ln C_1 \quad (C_1 \text{ is the cmc of nonionic surfactant}) \tag{8}$$

$$B_1 + B_2 = \ln\left(\frac{C_2}{C_1}\right) \tag{9}$$

$C_2$ is the cmc of ionic surfactant and

$$B_2 = -\beta_{12} \tag{10}$$

The calculated values of $B_0$, $B_1$ and $B_2$ are reported in Table 1. It is evident that the $\Delta G_m$ values calculated from phase separation [34] ($\Delta G_m = RT \ln$ cmc) and by Maeda's method [33] agree reasonably well. This indicates that the fraction of counter ions bound to the mixed micelle is probably negligible. The small difference may be attributed to increase in counter ion binding. $B_1$ values are found to depend on the composition of the system. The experimental mole fraction of SDS in the mixed micelle (Fig. 4a, b) are lower than that of stoichiometric mole fraction values. This suggests less transfer of SDS from the solution to the micellar phase and more dominance of Brij surfactants in the mixed micelle. Thus, the negative $\beta_{12}$ values are a result of reduction of electrostatic self-repulsion between SDS head groups due to the presence of Brij surfactants in the mixture. The activity coefficient values of the nonionic surfactant ($\gamma_2$) are higher compared to the ionic surfactant ($\gamma_1$), indicating that the nonionic surfactant in the mixed micelle is closer to its standard state [35, 36]. The excess Gibbs energy of mixing ($\Delta G_e^o$) values calculated employing the following equation [37, 38]

$$\Delta G_e^o = RT\sum_{i=1}^{2} X_i \ln \gamma_i \tag{11}$$

are plotted against the composition (Fig. 5a, b). The symmetrical plots of $\Delta G_e^o$ vs. micelle composition are in agreement with the regular solution theory's prediction.

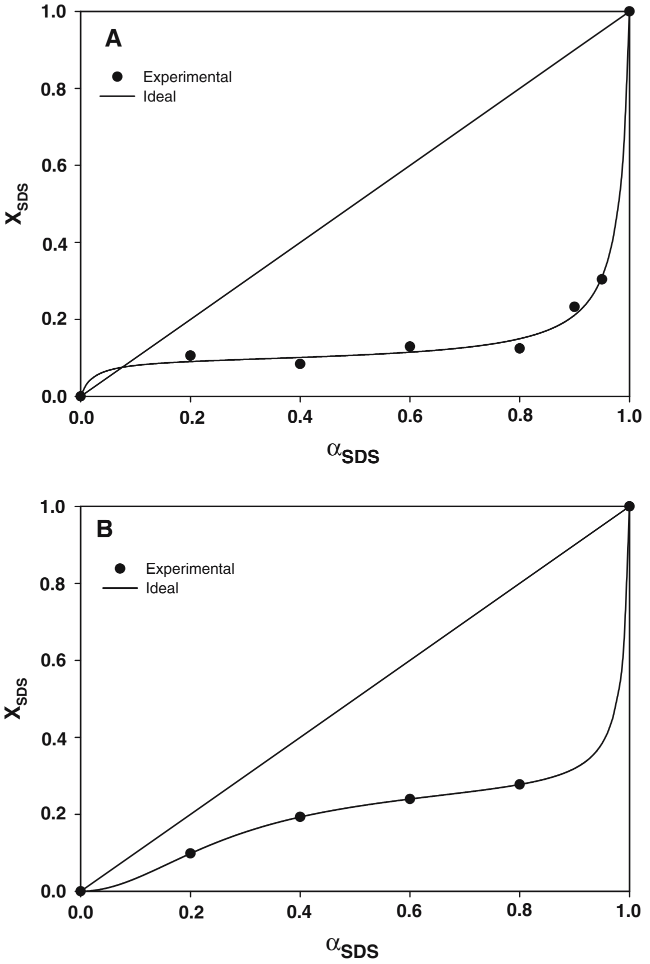

**Fig. 4** Mole fraction of SDS in the mixed micelle systems versus bulk composition for **a** SDS and Brij 35, **b** SDS and Brij 97

## Partial specific volumes

Partial specific volumes ($v$) of pure and binary mixtures of Brij 35 and Brij 97 with SDS were calculated using the following equation:

$$v = \frac{1}{\rho_W}\left[1 - \frac{d\rho}{dc}\right] \tag{12}$$

where $c$ is the concentration in g/ml and $\rho$ and $\rho_W$ are the densities of the sample and the water, respectively.

The unhydrated radius ($R_0$) of the mixed micelle was estimated as follows [37, 38]:

(a) The average molar mass ($M_W$) of the mixed micelles were obtained employing the following equation:

$$M_W = [XM_1 + (1-X)M_2]N_{agg} \tag{13}$$

where $N_{agg}$ is the aggregation number of the mixed micelle, $X$ is the mole fraction of SDS in the mixed micelle obtained from Rubingh's method and $M_1$, $M_2$ are molar masses of SDS and Brij respectively.

(b) Employing the average molar mass of the micelle, the dry micellar volume $V_0$ can be obtained by the relationship

$$V_0 = \frac{vM_W}{N} \tag{14}$$

where $N$ is the Avogadros number.

(c) The dry micellar radius ($R_0$) is then obtained assuming a spherical geometry for the micelle.

$$\text{i.e. } V_0 = \frac{4}{3}\pi R_0^3 \tag{15}$$

(d) The surface area of the dry micelle is then calculated assuming spherical shape employing the following equation

$$a_0 = \frac{4\pi R_0^2}{N_{agg}} \tag{16}$$

The area is found to lie between that of the two surfactants (Table 2).

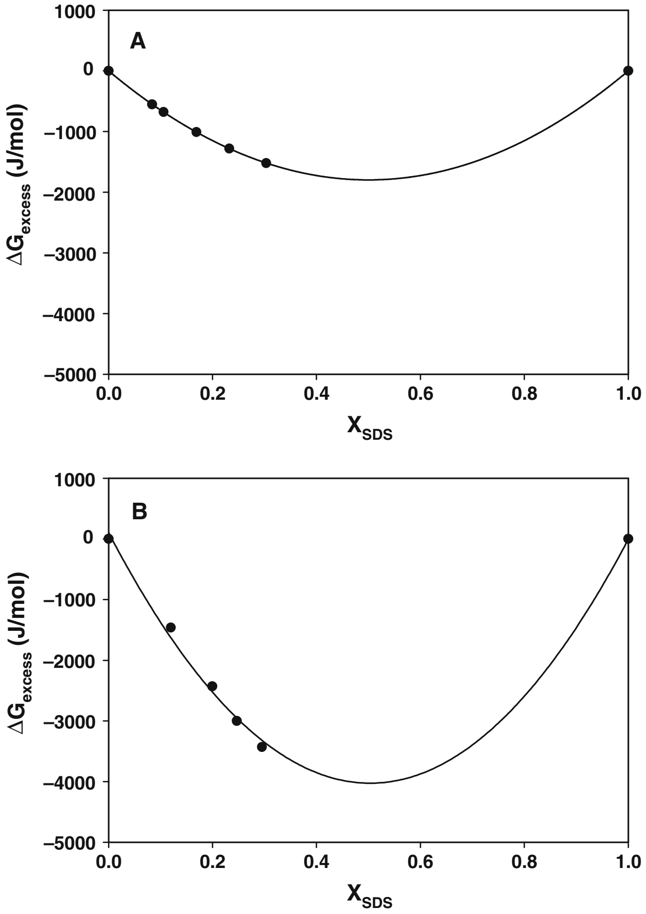

**Fig. 5** Excess Gibbs free energy of micellization versus mole fraction of SDS for **a** SDS and Brij 35, **b** SDS and Brij 97

Partial specific volumes of the mixed micelle vary very slightly as a function of $\alpha_{SDS}$ in these systems. Partial specific volume is a thermodynamic parameter sensitive to hydrophobic and hydrophilic interactions involving the solute and the solvent [37]. These results indicate that micellar hydration is thermodynamic and not hydrodynamic in nature. Hence, thermodynamic contributions to micellar hydration of the mixed micelles are very similar in nature.

## Viscosity

The variation of viscosity coefficient of the mixed micellar system with increase in mole fraction of SDS in the mixture has been shown in Fig. 6. For the Brij 35–SDS system the ideal and experimental values agree well. The viscosity coefficient decreases with increase in the mole fraction of SDS in the mixture. This may be due to the compact nature of the mixed micelle formed due to the same length of the hydrophobic chain of the components. But for the mixture of SDS with Brij 97 the experimental value differs from the ideal value. This is due to deviation from ideal behaviour of the mixture owing to the different chain length of the hydrophobic part of the components in the mixture.

## Clouding behaviour

The characteristic feature of nonionic surfactants is that a liquid–liquid phase separation occurs when the temperature is raised above a certain value. This phenom-

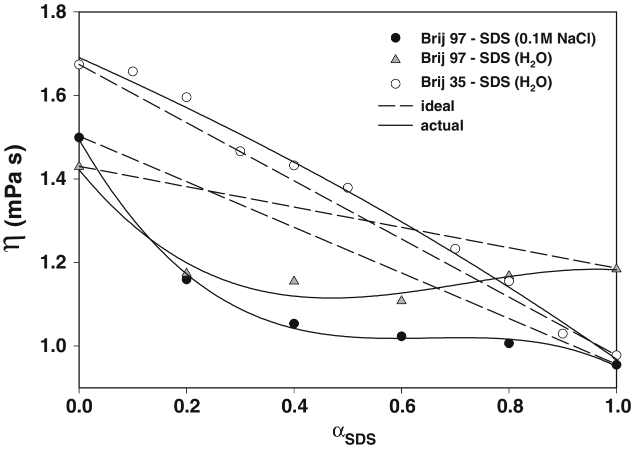

**Fig. 6** Viscosity of mixed micellar systems in aqueous medium for **a** SDS and Brij 35, **b** SDS and Brij 97

enon produces turbidity in the solution and that temperature at which the turbidity appears is known as cloud point (CP). The existence of CP depends on the hydropholic–lipophilic balance (HLB) value of a nonionic surfactant [36]. It is well-established that the phase separation is due to the reduction of the intermicellar repulsion as a result of dehydration of the oxyethylene groups with increasing temperature.

Addition of various additives is known to affect the CP temperature of nonionics [39–44]. In the present study, the effect of addition of SDS on the clouding behaviour of Brij 97 is investigated at various concentrations of Brij 97. In the absence of the additive, the CP values varied very slightly with the concentration of Brij 97. However, in the presence of small quantities of SDS, the CP values increase rapidly and the increase is more pronounced at lower concentrations of Brij 97 (Fig. 7). The function of the additive SDS as a CP inhibitor can be explained on the basis that the inclusion of the ionic surfactant into the nonionic micelle, imparts a charge to the mixed micelle thereby delaying the clouding due to electrostatic repulsions. Also, inclusion of SDS into the nonionic micelles will increase the hydration near the head group area via hydrogen bonding with water molecules, thereby increasing the CP.

Assuming CP as the point of phasing out of Brij 97, the Gibbs free energy of clouding ($\Delta G_c^{\circ}$) is calculated employing the following equation [45]:

$$\Delta G^{\mathrm{o}}_{\mathrm{c}} = RT \ln X_{\mathrm{c}} \qquad (17)$$

where $X_c$ is the mole fraction of the clouding agent. At a fixed concentration of SDS, different concentrations of Brij 97 produced different CP values. This enabled the calculation of $\Delta G_c^{\circ}$ as a function of temperature [46], and from a plot of $\mathrm{d}\left(\Delta G^{\mathrm{o}}_{\mathrm{c}}/T\right)/\mathrm{d}T$ vs. $T$, the values of $\Delta H_c^{\circ}$ were obtained (Fig. 8). The values of $\Delta S_c^{\circ}$ were calculated employing Gibbs–Helmoltz's equation. The thermodynamic values are presented in Table 3. In the present system both $\Delta H_c^{\circ}$ and $\Delta S_c^{\circ}$ values are positive and decrease with increasing [SDS] for a fixed value of clouding agent, indicating that the dehydration process along with the other endothermic processes such as: demixing, demicellization etc. are the dominating factors. The contribution of the exothermic aggregation process of clouding agent is relatively small.

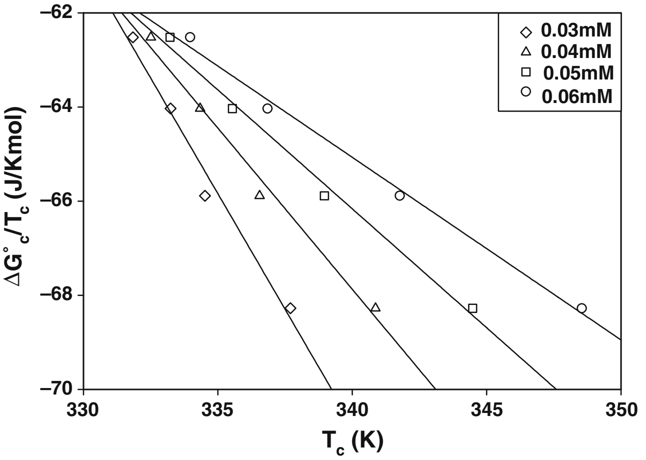

**Fig. 8** Plots of $\Delta G^{\mathrm{o}}_{\mathrm{c}}/T_{\mathrm{c}}$ vs. $T_{\mathrm{c}}$ at different SDS concentrations for the determination of $\Delta H^{\mathrm{o}}_{\mathrm{c}}$

For a large number of aqueous systems the entropy and enthalpy quantities are known to obey a linear relationship and this is known as enthalpy–entropy compensation effect. The compensation temperature ($T_{\mathrm{comp}}$) of 330.2 K is obtained from the plot of $\Delta H_c^{\circ}$ vs. $\Delta S_c^{\circ}$ (Fig. 9). This value is comparable to the average

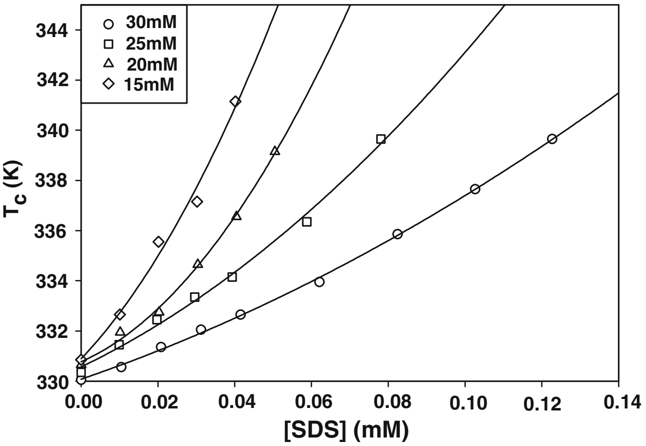

**Fig. 7** Clouding temperatures of varying concentrations of Brij 97 as a function of SDS concentration

**Table 3** Clouding temperatures and thermodynamic parameters of the clouding of Brij 97 in the presence of SDS

| [Brij 97] (mM) | [SDS] (mM) | $T_c$ (K) | $\Delta G^{\mathrm{o}}_{\mathrm{c}}$ (kJ/mol) | $\Delta H^{\mathrm{o}}_{\mathrm{c}}$ (kJ/mol) | $\Delta S^{\mathrm{o}}_{\mathrm{c}}$ (J/Kmol) |
|---|---|---|---|---|---|
| 30 | 0.03 | 331.8 | −20.7 | 108.2 | 389 |
| 25 | | 333.2 | −21.3 | 109.1 | 391 |
| 20 | | 334.5 | −22.0 | 110.0 | 395 |
| 15 | | 337.7 | −23.0 | 112.0 | 400 |
| 30 | 0.04 | 332.5 | −20.8 | 75.7 | 290 |
| 25 | | 334.3 | −21.4 | 76.6 | 293 |
| 20 | | 336.6 | −22.2 | 77.6 | 296 |
| 15 | | 340.9 | −23.3 | 79.6 | 302 |
| 30 | 0.05 | 333.2 | −20.8 | 56.1 | 231 |
| 25 | | 335.5 | −21.5 | 56.9 | 234 |
| 20 | | 339.0 | −22.3 | 58.1 | 237 |
| 15 | | 344.5 | −23.5 | 60.0 | 242 |
| 30 | 0.06 | 334.0 | −20.9 | 43.3 | 192 |
| 25 | | 336.8 | −21.6 | 44.0 | 194 |
| 20 | | 341.8 | −22.5 | 45.3 | 198 |
| 15 | | 348.5 | −23.8 | 47.1 | 204 |

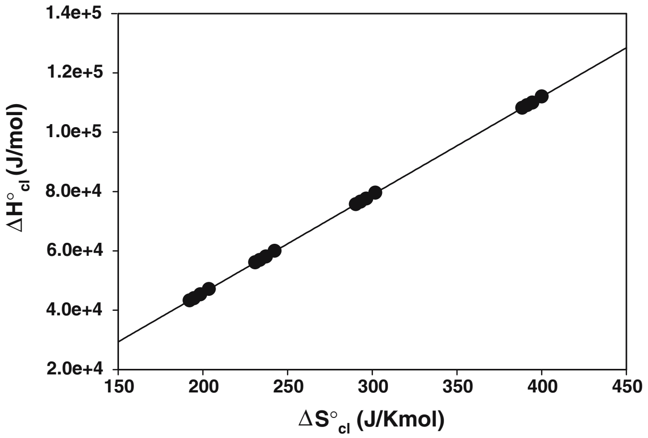

**Fig. 9** Enthalpy–entropy compensation plot

temperature of 334.2 K obtained by the following equation [47]:

$$T_{\text{ave}} = \left[\prod_{i}^{h} T_i\right]^{1/h} \tag{18}$$

where $T_i$ is the ith temperature of the total number $h$. The product of $T_{\text{comp}}$ and $\Delta S_c^{\text{o}}$ emerges to be equivalent to the non-useful part of the enthalpy of clouding. Compensation temperature in the micellization process may be regarded as the additional heat required in increasing the entropy change by a definite amount and may be treated as a measure of strength of surfactant–water interaction [48]. Higher value of $T_{\text{comp}}$ indicates more energy is required to induce release of a definite amount of water molecules resulting in a definite amount of entropy increase.

The compensation temperature of 330 K for Brij 97 + SDS system is slightly higher than 323 K for Brij 97 + alkanols systems [49]. Extending the above compensation temperature concept for the micellization process to the present system one can conclude that more energy is required to induce clouding of Brij 97 when SDS is an additive compared to the alkanols. This indicates that stronger surfactant/water interactions are present in the presence of SDS as an additive compared to alkanols.

## Conclusions

Micellar properties of mixed systems of SDS with Brij 35 and Brij 97 were investigated employing several physicochemical techniques. Analysis of the data employing the known theories of binary mixtures revealed that both nonionic surfactants interact synergistically with the anionic surfactant and the chain–chain interactions are stronger in the case of SDS–Brij 97.

Both nonionic surfactants interact attractively with SDS and the mixed micelles are mainly composed of the nonionic component. The activity coefficients of the nonionic components are closer to the standard state in the mixed micelle. The variations in the micellar aggregation number with the solution composition were attributed to the effects produced by the charged head group of the ionic surfactant in the mixed micelle. The clouding behaviour of Brij 97 is greatly influenced by the addition of even small quantities of SDS and the thermodynamic properties of clouding indicate that the dehydration process along with demixing and demicellization are the dominating factors.

**Acknowledgements** This research was supported by an operating grant to R.P. from (NSERC). S.C.B is grateful to the authorities of St. F.X. University for the James Chair visiting professorship, K.G. and A.V.B are grateful for the USRA award from NSERC (2003) and UCR award from St. F.X. University, respectively.

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