Journal of Colloid and Interface Science 378 (2012) 144–151

Contents lists available at SciVerse ScienceDirect

Journal of Colloid and Interface Science

www.elsevier.com/locate/jcis

Aggregation of sodium dodecylsulfate in aqueous nitric acid medium

Jahar Dey, Kochi Ismail *

Department of Chemistry, North-Eastern Hill University, Shillong 793 022, India

ARTICLE INFO

Article history:
Received 5 March 2012
Accepted 5 April 2012
Available online 13 April 2012

Keywords:
Sodium dodecylsulfate
Nitric acid
Conductivity
Critical micelle concentration
Competitive counterion binding
Nitration

ABSTRACT

Nitric acid medium is invariably used for nitration of organic molecules. Although surfactants are known to influence reaction rates, little is known about the aggregation behavior of surfactants in nitric acid medium. Micellization characteristics of sodium dodecylsulfate (SDS) in aqueous nitric acid are investigated in this work by using the conductance method. The critical micelle concentration (cmc) and the aggregation number were also determined by the surface tension and the steady-state fluorescence methods, respectively. This study reveals that in acidic medium SDS exhibits both normal and unusual conductivity behaviors. Equations developed on the basis of the mixed electrolyte model, Debye–Hückel–Onsager approach, and the pseudophase ion-exchange model successfully simulate the conductivity data. The exchange of sodium and hydrogen counterions at the micellar surface has no significant effect on the cmc of SDS. Acid concentration, surfactant concentration, and cmc control the competitive binding of sodium and hydrogen counterions. Analysis of conductivity data revealed hydrolysis of about 12% SDS when $[HNO_3] \geqslant 0.02$ mol dm^{-3}. Hydrolysis of SDS has been confirmed by nitrating some of the substituted phenols. It has been predicted that SDS + aqueous HNO_3 medium with $[HNO_3] \geqslant 0.02$ mol dm^{-3} may be used as a green medium for nitration.

1. Introduction

In the presence of the suitable solvent surfactants undergo aggregation that is greatly influenced by the solvent properties. The dependence of surfactant aggregation on solvent type and composition is nicely illustrated by the recent study of Seguin et al. [1]. They reported [1] that in a mixture of ethylene glycol and propylene glycol the aggregation of nonionic surfactants can be switched on or off by adjusting the relative amounts of the two glycols. Studies carried out on the aggregation behavior of surfactants by altering the quality of solvent can provide information of both fundamental and applied importance. One of the ways of varying solvent quality/property is by adding electrolytes or nonelectrolytes to the solvent of interest.

Nitric acid is invariably used for nitration of organic molecules, and surfactants are known to catalyze chemical reactions. Yet, surprisingly there is no report on micellization study of surfactants in nitric acid medium. The knowledge about the critical micelle concentration (cmc) and counterion binding behavior of surfactants in nitric acid medium will be useful to understand the effect of surfactants on nitration reactions. Therefore, in the present study we investigated the micellization characteristics of sodium dodecylsulfate (SDS) in aqueous nitric acid medium by using mainly the conductance method. Surface tension and fluorescence quenching methods have also been used to determine cmc and aggregation number, respectively.

2. Materials and methods

SDS (Fluka, ⩾99% assay), HNO_3 (Merck), pyrene (Fluka), and cetylpyridinium chloride (CPC; Aldrich, >99.0%) were used as received. All solutions were prepared in Millipore water. A stock solution of the acid was prepared after standardization of HNO_3. From this stock solution other solutions of HNO_3 of required concentrations were made by dilution. Every solution of HNO_3 having a particular concentration is divided into two portions (portions A and B). Using portion A as solvent, a stock solution of SDS was prepared, and this gives us SDS solution containing a particular amount of HNO_3 (solution C).

From portion B of the HNO_3 solution a known amount was taken in the sample tube, and the conductance values were measured at 1 kHz after each addition of aliquots of solution C by using a dip-type conductivity cell with platinized platinum electrodes and Wayne Kerr B905 Automatic Precision Bridge. For addition of solution C we used a Finn pipette. The cell constant of the conductivity cell was determined by using standard KCl solution. During conductance measurements, after each addition of solution C the sample tube was kept closed. The instrument (resolution = 0.01 nS and accuracy = 0.05%) has an averaging facility and each conductance reading corresponds to an average of 128 measurements taken in a time span of 36 s.

---

* Corresponding author. Address: Department of Chemistry, North-Eastern Hill University, NEHU Campus, Shillong 793 022, India. Fax: +91 364 2550486.

E-mail addresses: kismail@nehu.ac.in, kinehu@hotmail.com (K. Ismail).

0021-9797/$ - see front matter © 2012 Elsevier Inc. All rights reserved.
http://dx.doi.org/10.1016/j.jcis.2012.04.015

For surface tension measurements, from portion B of the HNO_3 solution a known amount was taken in the sample vessel of the K11 Krüss Tensiometer, and the surface tension values were measured by using the Wilhelmy plate method after each addition of aliquots of solution C. The Wilhelmy plate, before use, was cleaned thoroughly and then heated red hot in Bunsen flame.

Aggregation numbers were determined by making steady-state fluorescence measurements for which we used Hitachi F4500 FL spectrophotometer, Hellma quartz 10 mm fluorescence cell with Teflon lid, pyrene as the probe and CPC as the quencher. The concentration of pyrene was in the μM (M = mol dm^{-3}) range.

The temperature of the sample during conductance, surface tension and fluorescence measurements was maintained at 25 °C by using Haake DC 10 circulation bath.

3. Results and discussion

The experimental values of specific conductivity (κ) of SDS in aqueous HNO_3 medium are shown in Fig. 1. From Fig. 1 it is clear that the trend in the variation of κ with SDS concentration (c_s) in HNO_3 medium is dependent on the acid concentration (c_a). Generally, κ increases with increase in the concentration of ionic surfactant and κ data when plotted against surfactant concentration fall on two straight lines with the line in the premicellar concentration region having higher slope than that of the line in the micellar concentration region irrespective of the presence of single or mixed counterions in the surfactant solution (this we refer as the normal conductance behavior). As evident from Fig. 1, SDS exhibits the normal conductance behavior in 0.001M HNO_3 only. In 0.002M HNO_3, κ above the cmc (c_0) just begins to decrease and the decrease in κ becomes very prominent as the acid concentration increases further. Above 0.002M HNO_3, κ versus c_s plot passes through a maximum as well as minimum and thus SDS exhibits an unusual conductance behavior. The maximum in the plot corresponds to c_0. Such unusual conductance behavior of SDS was reported [2–4] in aqueous HCl medium also, but normal conductance behavior of SDS in aqueous HCl medium has not been reported. The present study therefore reveals that SDS can exhibit the normal conductance behavior even in the presence of an acid, provided the acid concentration is below a threshold value (c^*). The ratio c_0/c_a can also be taken as a criterion for observing normal conductance behavior in an acid medium. In the case of nitric acid, c^* = 0.002 M and $c_0/c_a > 3.4$.

3.1. Conductivity data analysis

Conductivity of ionic surfactant solutions is analyzed by using the mixed – electrolyte model (MEM) described elsewhere [5–8]. However, in the earlier studies [5–8] the MEM was applied to surfactant solutions containing single counterion only, whereas in the present study we could apply the MEM to surfactant solution containing mixed counterions (sodium and hydrogen) as well. In this model, a surfactant solution is treated as a mixed electrolyte system. The surfactant monomers and an equivalent number of counterions are considered to form electrolyte 1, and the ionic micelles along with the remaining counterions are considered to form electrolyte 2. The MEM uses the Debye–Hückel–Onsager (DHO) approach to account for the ion–ion interactions. For fitting the conductivity data to different equations (given in the following sections) and to obtain the best-fit values of micellization parameters, an iterative least-squares method of computation was used as described elsewhere [6].

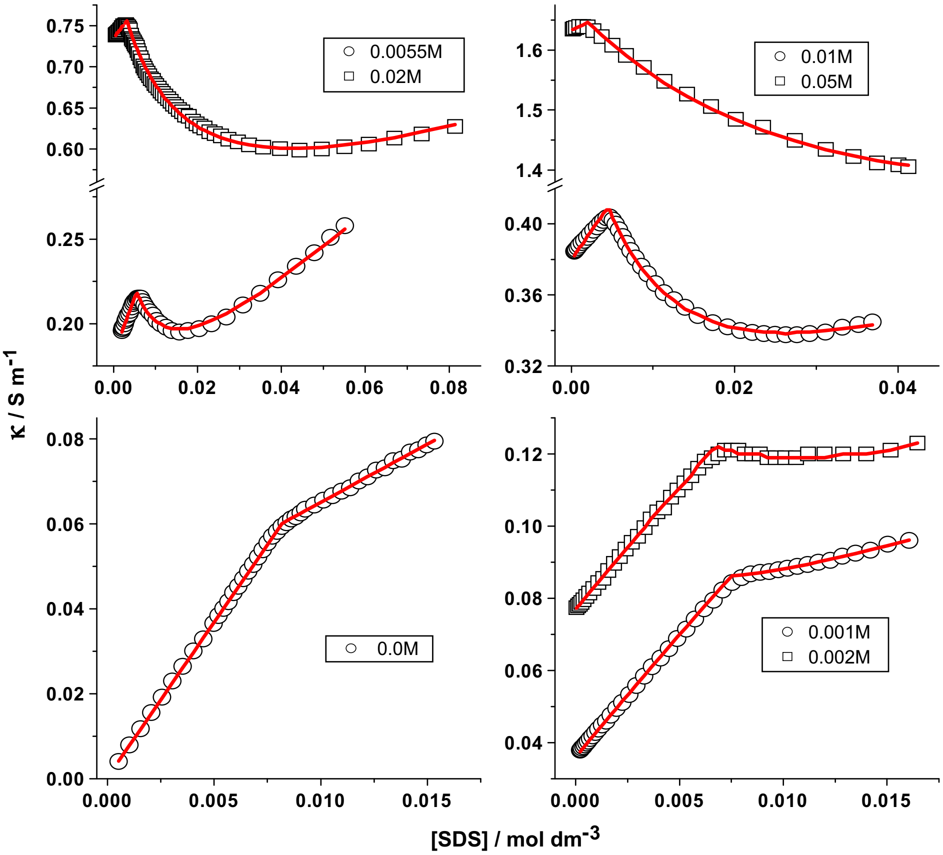

Fig. 1. Plots of κ versus SDS concentration in aqueous HNO_3 media at 25 °C. Numbers in the insets indicate concentration of HNO_3. The black symbols represent experimental data. Red lines represent calculated values of κ. (For interpretation of the references to color in this figure legend the reader is referred to the web version of this article.)

3.2. Conductance equations in the absence of HNO_3

On the basis of the MEM, κ of SDS solution in the absence of any added electrolyte is expressed (i) at $c_s < c_0$ as

$$\kappa = [\Lambda_1^0 - (A_1\Lambda_1^0 + B_1)I^{1/2}/(1 + B_0a_1)]c_s \tag{1}$$

and (ii) at $c_s \geqslant c_0$ as

$$\kappa = [\Lambda_1^0 - (A_1\Lambda_1^0 + B_1)I^{1/2}/(1 + B_0a_1)]c_0 + [\Lambda_n^0 - (A_n\Lambda_n^0 + B_n)I^{1/2}/(1 + B_0a_n)](c_s - c_0)(1 - \beta) \tag{2}$$

The ion-size parameters a_1 and a_n are evaluated from the relations $a_1 = r_{DS} + r_{Na}$ and $a_n = r_{mic} + r_{Na}$, where the r terms refer to the radii of dodecylsulfate ion (r_{DS}), sodium ion (r_{Na}), and dodecylsulfate micelle (r_{mic}). β is the total counterion binding constant equal to the ratio of the number of counterions (m) bound to the micelle to the aggregation number (n_a). Concentrations are given in moles per unit volume. Ionic strength of the solution is denoted by I. Expressions used to evaluate other terms in Eqs. (1) and (2) are

$$\Lambda_1^0 = \lambda_{DS}^0 + \lambda_{Na}^0 \tag{3}$$

$$\Lambda_n^0 = \lambda_{mic}^0 + \lambda_{Na}^0 \tag{4}$$

$$A_i = \frac{2.801 \times 10^6|z_+z_-|q}{(\varepsilon T)^{3/2}(1 + q^{1/2})} \tag{5}$$

$$B_i = \frac{41.25(|z_+| + |z_-|)}{\eta(\varepsilon T)^{1/2}} \tag{6}$$

$$q = \frac{(\lambda_+^0 + \lambda_-^0)|z_+z_-|}{(|z_+| + |z_-|)(|z_+|\lambda_-^0 + |z_-|\lambda_+^0)} \tag{7}$$

$$B_0 = \left[\frac{8\pi e^2 N_A I}{10^3\varepsilon k_B T}\right]^{1/2} \tag{8}$$

In the above equations, T is the absolute temperature, η is the viscosity of water, ε is the dielectric constant of water, k_B is the Boltzmann constant, N_A is the Avogadro number, and e is the charge on electron. λ_{DS}^0, λ_{Na}^0, λ_{mic}^0, λ_+^0 and λ_-^0 represent limiting equivalent conductances of dodecylsulfate ion, sodium ion, ionic micelle, cationic species with charge z_+, and anionic species with charge z_-, respectively. When $z_+ = z_- = 1$, $A_i = A_1$ in Eq. (5) and $B_i = B_1$ in Eq. (6). When $z_+ = 1$ and z_- (charge on the micelle) = $n_a(1 - \beta)$, $A_i = A_n$ in Eq. (5), and $B_i = B_n$ in Eq. (6). The value of q was 0.5 in A_1, but the value of q in A_n was obtained by putting $z_+ = 1$, $z_- = n_a(1 - \beta)$, $\lambda_+^0 = \lambda_{Na}^0$ and $\lambda_-^0 = \lambda_{mic}^0$ in Eq. (7). The value of λ_{mic}^0 was estimated from the expression [5,6]

$$\lambda_{mic}^0 = n_a^{2/3}(1 - \beta)\lambda_{DS}^0 \tag{9}$$

The values of λ_{Na}^0 and λ_{DS}^0 at 25 °C were taken from the literature [4–6] as 50.1 and 22.9 S cm^2 mol^{-1}, respectively.

3.3. Conductance equations in the presence of HNO_3

In the presence of acid, SDS is reported [9] to undergo hydrolysis. The hydrolysis reaction can be written as

$$C_{12}H_{25}SO_4^- + H_2O \xrightarrow{H^+} C_{12}H_{25}OH + HSO_4^- \tag{10}$$

Moreover, in the presence of HNO_3 the SDS micellar solution consists of sodium and hydrogen counterions and both these counterions tend to bind to the ionic micelle. Therefore, Eqs. (1) and (2) are to be modified for application in the presence of HNO_3. Denoting the degree of hydrolysis of dodecylsulfate ion by α_h, κ of SDS in aqueous HNO_3 medium can be represented in the submicellar concentration region ($c_s < c_0$) as

$$\kappa = \kappa_{HNO3} + \lambda_1 c_s \tag{11}$$

where

$$\lambda_1 = \Big\{[\lambda_{DS}^0 - (A_1\lambda_{DS}^0 + 0.5B_1)I^{1/2}/(1 + B_0a_1)](1 - \alpha_h) + [\lambda_{Na}^0 - (A_1\lambda_{Na}^0 + 0.5B_1)I^{1/2}/(1 + B_0a_1)] + [\lambda_{BS}^0 - (A_1\lambda_{BS}^0 + 0.5B_1)I^{1/2}/(1 + B_0a_2)]\alpha_h\Big\} \tag{12}$$

κ_{HNO3} is the specific conductivity of HNO_3 solution before adding the surfactant. The ion-size parameter $a_2 = r_{BS} + r_{Na}$, where r_{BS} is the radius of the bisulfate ion. λ_{BS}^0 is the limiting equivalent conductance of bisulfate ion. In the presence of HNO_3 the limiting equivalent conductance of the solution below c_0 (Λ_1^0) is given by the relation

$$\Lambda_1^0 = (1 - \alpha_h)\lambda_{DS}^0 + \alpha_h\lambda_{BS}^0 + \lambda_{Na}^0 \tag{13}$$

In the micellar region ($c_s \geqslant c_0$) κ of SDS solution in the presence of HNO_3 can be written as

$$\kappa = \kappa_{HNO3} + \lambda_1 c_0 + \lambda_2(c_s - c_0) \tag{14}$$

where

$$\lambda_2 = \Big\{[\lambda_{mic}^0 - (A_n\lambda_{mic}^0 + 0.5n_a(1 - \beta)B_1)I^{1/2}/(1 + B_0a_n)](1 - \beta) + [\lambda_{Na}^0 - (A_n\lambda_{Na}^0 + 0.5B_1)I^{1/2}/(1 + B_0a_n)](1 - \beta_{Na}) - [\lambda_H^0 - (A_n\lambda_H^0 + 0.5B_1)I^{1/2}/(1 + B_0a_n)]\beta_H\Big\} \tag{15}$$

λ_H^0 is the limiting equivalent conductance of hydrogen ion. In the presence of HNO_3 q required for calculating A_n was evaluated by substituting $z_+ = 1$, $z_- = n_a(1 - \beta)$, $\lambda_+^0 = \lambda_{SH}^0$ and $\lambda_-^0 = \lambda_{mic}^0$ in Eq. (7). λ_{SH}^0 is defined as

$$\lambda_{SH}^0 = (\beta_{Na}\lambda_{Na}^0 + \beta_H\lambda_H^0)/\beta \tag{16}$$

The values λ_{BS}^0 and λ_H^0 at 25 °C were taken from the literature [4,10] as 51.2 and 349.7 S cm^2 mol^{-1}, respectively.

In Eqs. (15) and (16), β_{Na} and β_H are the counterion binding constants for sodium and hydrogen ions, respectively, and the total counterion binding constant β is given by

$$\beta = \beta_{Na} + \beta_H \tag{17}$$

Due to the presence of mixed counterions a competitive binding of sodium and hydrogen ions to the SDS micelle occurs in the micellar solution. Equilibria exist between the bound (Na_b) and unbound (Na_{ub}) sodium ions as well as between the bound (H_b) and unbound (H_{ub}) hydrogen ions. By balancing the chemical potentials of the bound and unbound counterions as a thermodynamic requirement for equilibrium, the pseudophase ion-exchange (PIE) model [11–13] was developed, and according to this model we can write a counterion exchange equilibrium constant K_e as [11–13]

$$K_e = \frac{[H_b][Na_{ub}]}{[H_{ub}][Na_b]} \tag{18}$$

The different terms in Eq. (18) are defined as $H_b = \beta_H(c_s - c_0), Na_b = \beta_{Na}(c_s - c_0), H_{ub} = (c_a - H_b)$ and $Na_{ub} = (c_s - Na_b)$. Equation (18) can be rearranged to give a quadratic equation of the form

$$(c_s - c_0)(K_e - 1)\beta_H^2 - [c_s + K_ec_a + \beta(c_s - c_0)(K_e - 1)]\beta_H + \beta c_aK_e = 0 \tag{19}$$

3.4. Ionic strength of ionic surfactant solutions

Evaluating I of ionic surfactant solutions has been a problem. The problem arises due to unreasonably high increase in I that occurs when square of micellar charge is substituted in the expression for I. For example, if I calculated by including the contribution from ionic micelle is substituted in the DHO equation then molar conductance becomes even negative at surfactant concentrations sufficiently higher than cmc. Based on conductivity and freezing point depression data, McBain and Searles [14] first reported that the ionic strength principle does not apply to ionic micelles and showed that I of ionic micelles resemble that for a uni-univalent electrolyte. Pashley and Ninham [15] as well as Richetti and Kekicheff [16] measured double-layer forces between two molecularly smooth mica surfaces coated with adsorbed bilayers of cetyltrimethylammonium bromide (CTAB) and separated by an aqueous solution of CTAB. They reported [15,16] on the basis of the measured forces, which are related to the Debye length, that above the cmc micelles and their bound counterions do not contribute to I and hence to the Debye length. Similar observation regarding ionic micelles not contributing to I was also made by Marra and Hair [17] by using sodium dodecylsulfate and sodium polystyrene sulfonate instead of CTAB in the experiments for double-layer force measurement. During the analysis of small-angle neutron scattering data of micellar solutions also ionic micelles are considered not to make any contribution to I [18,19]. Shielding factor is sometimes used to reduce the contribution of ionic micelles to I. Burchfield and Woolley [20] derived equations for activity coefficients and osmotic coefficients of aqueous ionic surfactant solutions by treating these solutions as mixed electrolytes and reported that these equations become applicable to experimental data when shielding factor having values in the range 0.5–0.68 was used to shield the charge on the micelles. Jalšenjak [21] introduced a concentration-dependent shielding factor to assess the contribution of micelles to I of surfactant solution. Different values for shielding factor were also tested in the earlier studies [5,6] while analyzing the conductivity data of ionic surfactant solutions. In light of the above reports [5,6,14–21] we calculated I in the present study by using the expressions

$$I = c_s + c_a \quad \text{at } c_s < c_0 \tag{20a}$$

$$I = c_0 + c_a \quad \text{at } c_s \geqslant c_0 \tag{20b}$$

Using Eq. (20b) for I is equivalent to substituting zero for the shielding factor, which amounts to shielding completely the charge of ionic micelle and bound counterions. It may be noted that Eq. (20a) is used to compute I (below cmc) in Eqs. (1) and (12), whereas Eq. (20b) is used to compute I (above cmc) in Eqs. (2) and (15).

3.5. Ionic radius and ion-size parameter

To fit the κ data to Eqs. (1), (2), (11), and (14) we need to estimate the values of ion-size parameters a_1, a_n and a_2 for which we require the values of r_{DS}, r_{mic}, r_{Na} and r_{BS}. It may be noted that in the system under study, since there are two counterions, it is difficult to substitute a correct ion-size parameter in the ion–ion interaction term of DHO approach. Therefore, the ion-size parameters have been estimated ($a_1 = r_{\mathrm{DS}} + r_{\mathrm{Na}}$, $a_n = r_{\mathrm{mic}} + r_{\mathrm{Na}}$ and $a_2 = r_{\mathrm{BS}} + r_{\mathrm{Na}}$) by ignoring the size of hydrogen counterion.

Two approaches are used for quantifying the size of monomeric ion of any surfactant by assuming an equivalent-sphere concept. In the first approach [5,6,22,23] radius of the dodecylsulfate ion (DS) is estimated by using the Stokes–Einstein relation

$$r_i = \frac{z_i e F}{6\pi\eta\lambda_i^0} \tag{21}$$

F in Eq. (21) is the Faraday constant. It may be noted that DS has limiting ionic conductance = 22.9 S cm^2 mol^{-1} due to its actual geometry and not because of spherical shape. But by calculating r_{DS} from Eq. (21) we visualize that DS would have 22.9 S cm^2 mol^{-1} limiting ionic conductance if it is assigned an effective spherical radius = 4.02 Å. In the second approach the volume of the monomeric ion is evaluated using the Tanford equation [24], v (in Å^3) = 27.4 + 26.9n_c, where n_c is the number of carbon atoms in the monomer chain. This volume is then equated to the volume of a sphere having effective radius = $(3v/4\pi)^{1/3}$. For DS we get from this method v = 350.2 Å^3 and r_{DS} = 4.37 Å. In both the approaches DS is assigned an effective spherical radius so that it gives either the experimental λ^0_{DS} according to Eq. (21) or v according to the Tanford equation [24]. In this study we have used the first approach to estimate r_{DS} since the study is related to conductivity. Based on Eq. (21) the different ion sizes used for the conductivity data analysis are r_{Na} = 1.84 Å, r_{DS} = 4.02 Å and r_{BS} = 1.8 Å. The radius of the micelle is generally determined by considering it to be spherical and using the relation [5,6,25–29]

$$r_{\mathrm{mic}} = n_a^{1/3} r_{\mathrm{DS}} \tag{22}$$

Using the above values of the radii, ion-size parameters a_1, a_2 and a_n were evaluated.

The κ data of aqueous SDS solutions in the absence of HNO$_3$ were least-squares fitted to Eqs. (1) and (2) by iterating the values of c_0, n_a and β and the best-fit values of c_0, n_a and β obtained in this fashion are given in Table 1. In the presence of HNO$_3$, experimental values of κ in the submicellar region were first least-squares fitted to Eq. (11). The value of α_h was iterated for obtaining the best fit. Using this value of α_h the experimental values of κ in the micellar region ($c_s \geqslant c_0$) were least-squares fitted to Eq. (14) by iterating the values of c_0, K_e, n_a and β and by substituting the value of β_{H} determined by solving the quadratic Eq. (19). The best-fit values of α_h, c_0, K_e, n_a and β in the presence of HNO$_3$ are listed in Table 1. The values of κ of SDS in water (in the absence of HNO$_3$) and in aqueous HNO$_3$ solutions calculated from Eqs. (1), (2), (11), and (14) are shown in Fig. 1 (red lines) and they are in good agreement with the experimental values.

3.6. Critical micelle concentration

The best-fit values of cmc of SDS in aqueous HNO$_3$ solutions obtained from the κ data fitting are given in Table 1 and shown in Fig. 2. The cmc values of SDS in the presence of HNO$_3$ were also confirmed from surface tension (γ) measurements (Table 1 and Fig. 2). It may, however, be noted that in the presence of HNO$_3$ as shown in Eq. (10) some of the SDS molecules hydrolyze to form dodecanol thereby leading to loss of SDS. Therefore, overestimation of cmc of SDS in acid medium, particularly when the acid content is high, cannot be ruled out. By comparing (Fig. 2) the present cmc values with those reported [5,6,25] in other aqueous electrolyte solutions, it is noted that the cmc values of SDS in aqueous HNO$_3$ media, in spite of the presence of mixed counter ions, are not very much different from those in aqueous NaCl [5,6] or NaAc (sodium acetate) [25] solutions. Therefore, the effect of hydrogen ion binding to dodecylsulfate micelle on the cmc of SDS seems to be similar to that due to sodium ion binding. This observation is in conformity with the inference made by Bunton et al. [2] that dodecylsulfate micelle does not discriminate markedly between hydrogen and sodium counterions.

3.7. Aggregation number

The best-fit values of n_a of SDS in aqueous HNO$_3$ solutions obtained from the κ data fitting are given in Table 1. To ascertain the correctness of the n_a values, we determined n_a from the steady-state fluorescence quenching (SSFQ) method. The expression used in this method is of the form [25]

Table 1
Best-fit values of cmc, degree of hydrolysis, ion-exchange constant, counterion binding constant, and aggregation number of SDS in aqueous HNO_3 solutions at 25 °C obtained from conductivity data fitting with ion-size effect.

Parameters	Nitric acid concentration (mM)						
	0	1.00	2.00	5.50	10.0	20.0	50.0
cmc/mM	8.20	7.50	6.72	5.56	4.54	3.03	1.78
	(8.40)[c]	(8.26)[d]	(7.44)	(6.01)	(4.93)	(3.37)	(2.25)
K_e	–	0.74	0.75	0.87	0.87	0.73	1.51
α_h	–	0	0	0	0	0.12	0.12
β	0.700	0.719	0.746	0.692	0.751	0.760	0.601
β_H[a]	–	0.065	0.136	0.320	0.493	0.629	0.587
β_{Na}[a]	0.700	0.654	0.610	0.372	0.258	0.131	0.014
n_a	32	38	40	41	49	61	72
	(31)[e]	(40)	–	(44)	(51)	(68)	(69)
$10^2\ \kappa_{HNO3}$ ($S\ m^{-1}$)	0	3.6000	7.7000	18.180	38.000	73.480	163.32
σ[b] ($mS\ m^{-1}$)	0.28	0.47	0.44	1.39	1.56	1.52	1.49

[a] Values of β_H and β_{Na} given here are at the cmc.
[b] σ denotes standard deviation in κ.
[c] All values of cmc given in the parentheses are from surface tension measurements.
[d] This value of cmc from surface tension corresponds to $[HNO_3]$ = 0.90 mM.
[e] All values of n_a given in the parentheses are from fluorescence measurements.

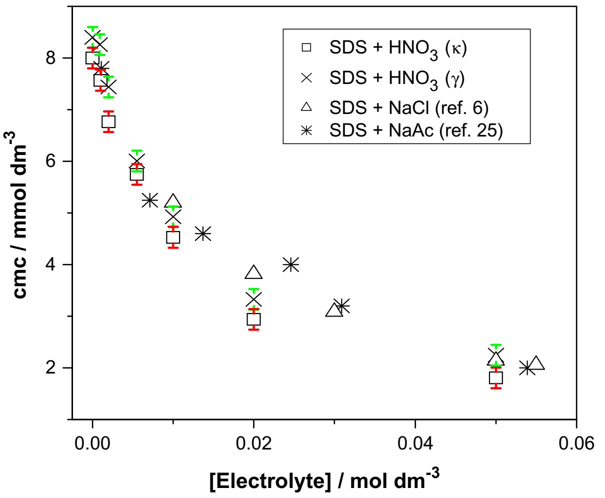

Fig. 2. Variation of cmc of SDS with the concentration of the added electrolyte (indicated in the inset). In HNO_3 (present data), κ and γ in the inset denote that cmc values are from specific conductivity and surface tension data, respectively. Errors in the measured cmc are shown by error bars (red: cmc from κ, green: cmc from γ). (For interpretation of the references to color in this figure legend the reader is referred to the web version of this article.)

$$\ln(I_0/I_Q) = \{n_a/(c_s - c_0)\}[Q] \tag{23}$$

I_0 and I_Q are the intensities of fluorescence emission (at 373 nm) of pyrene in the absence and presence of the quencher, respectively. [Q] denotes the concentration of CPC, the quencher. Representative emission spectra of pyrene in SDS + 5.50 mM HNO_3 medium at different CPC concentrations and the plots of $\ln(I_0/I_Q)$ versus [Q] at different c_a are shown in Figs. 3 and 4, respectively.

The values of n_a determined from this method at a fixed $c_s - c_0$ value (=0.45 mM) are listed in Table 1. Since the value of $c_s - c_0$ is kept very low during the fluorescence measurements, the measured values of n_a of the present study are considered as n_a at cmc. The reported values of n_a of SDS in the absence and presence of added salt are quite scattered [27–40]. Based on the values summarized by Bales and Almgren [27] and other reported [25,30,34] values, n_a of SDS near the cmc in the absence of electrolyte has values varying from 42 to 54. In the presence of electrolyte, some of the reported values of n_a of SDS are 50, 61, 67, 70, 87 and 80 in solutions of 0.018M SDS + 0.006M NaCl (25 °C) [25], 0.0042M SDS (=cmc) + 0.015M NaCl (25 °C) [29], 0.0033M SDS (=cmc) + 0.025M NaCl (25 °C) [29], 0.070M SDS + 0.050M NaCl (25 °C) [30], 0.05M SDS + 0.05M NaCl (30 °C) [32], and 0.009M SDS + 0.1M NaBr (40 °C) [34], respectively. Thus, the aggregation

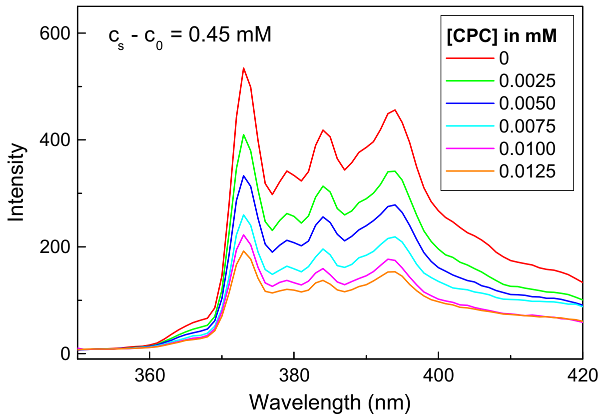

Fig. 3. Typical fluorescence emission spectra of pyrene at 25 °C in aqueous SDS + 5.50 mM HNO_3 medium at different quencher concentrations shown in the inset.

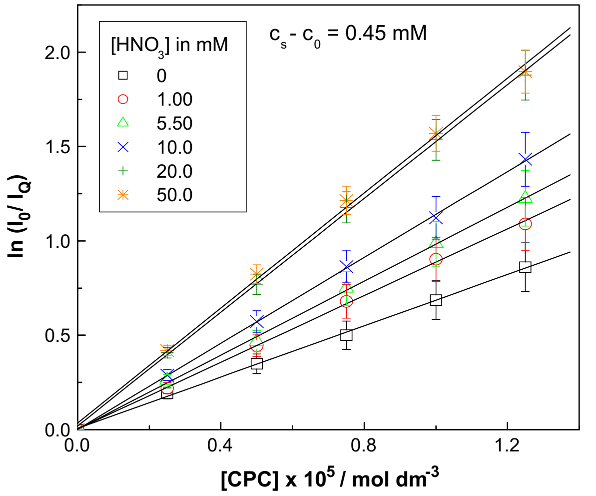

Fig. 4. Plots of $\ln(I_0/I_Q)$ versus quencher concentration at 25 °C in aqueous SDS + HNO_3 media at different acid concentrations shown in the inset. Errors in the measured intensity ratio are shown by error bars.

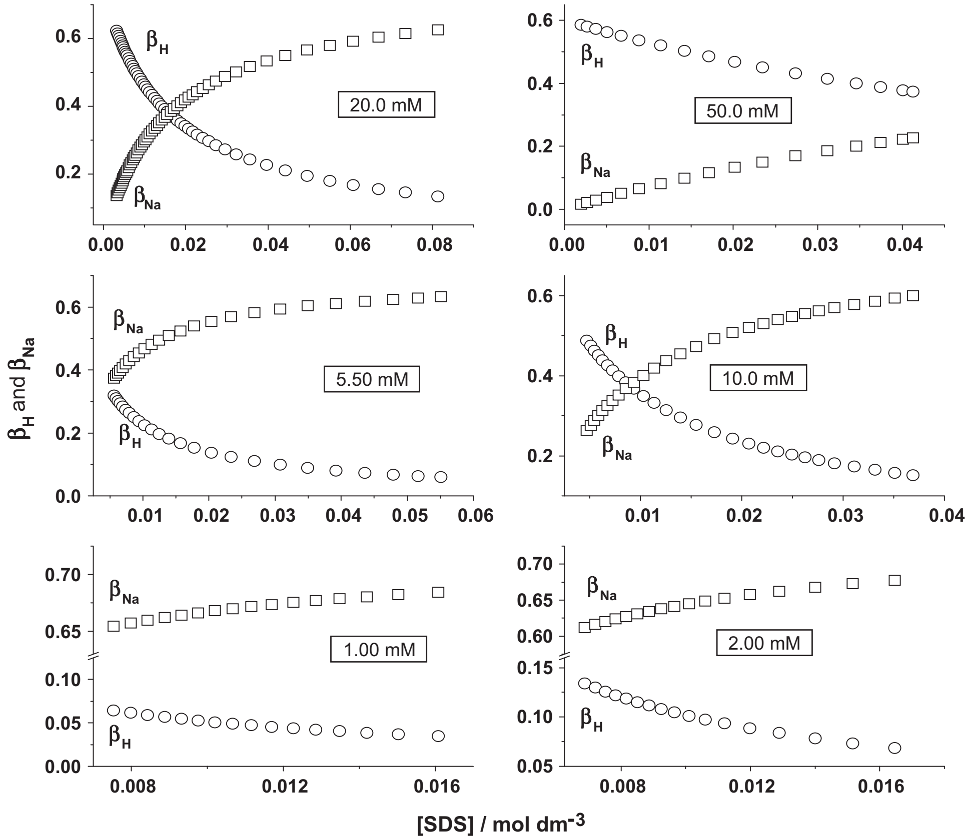

Fig. 5. Variation of β_H and β_{Na} with SDS concentration. The [HNO_3] in mol dm^{-3} are shown in the insets.

numbers of SDS + HNO_3 system determined in this study from the SSFQ measurements (Table 1) are within the range of reported values for SDS + NaCl/NaBr system. From Table 1 it is evident that the best-fit values of n_a obtained from the κ data fitting are in good agreement with the measured values of n_a.

3.8. Counterion binding constant

The values of β_H and β_{Na} as a function of SDS concentration computed from Eq. (19) during the fitting of κ data are shown in Fig. 5. From Fig. 5 it is clear that the value of β_H decreases with increase in SDS concentration, whereas β_{Na} has the opposite trend. Similar type of profiles for the variation of β_{Ca} (binding constant of calcium counterion) and β_{Na} with SDS concentration have been reported [41] very recently in aqueous solutions of SDS in the presence of $CaCl_2$. At higher concentrations of SDS sodium predominantly binds to the micelle irrespective of the HNO_3 concentration. On the other hand, near the cmc the acid concentration largely controls the competitive counterion binding. Based on Eq. (19) at the cmc we can write an expression for β_H as

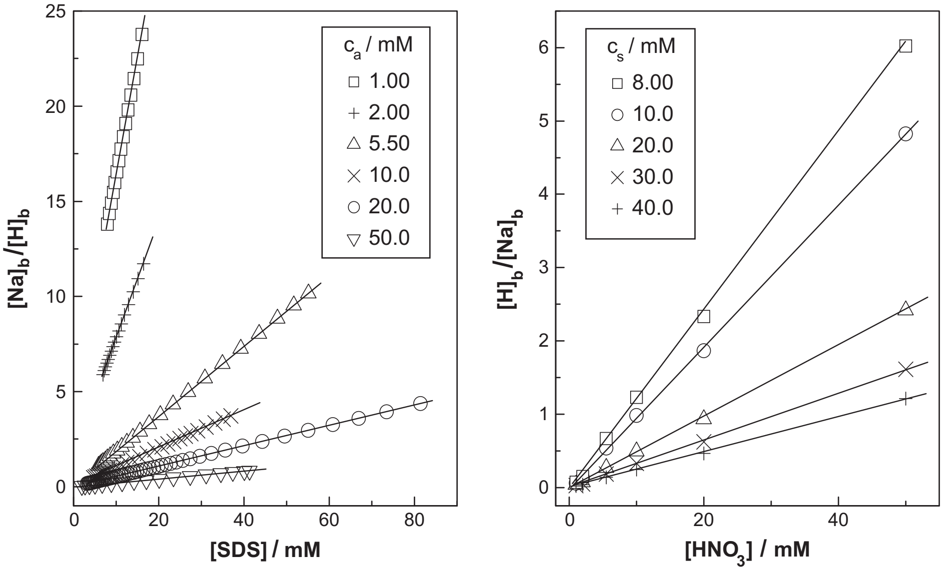

Fig. 6. Variation of [Na_b]/[H_b] with surfactant concentration and [H_b]/[Na_b] with acid concentration.

$$\beta_{H} = \beta K_e c_a/(K_e c_a + c_0) \tag{24}$$

The values of β_H and β_{Na} at the cmc determined from Eq. (24) are listed in Table 1. As evident from Table 1 and Fig. 5, the relative values of β_H and β_{Na} at the cmc differ depending upon the acid concentration. The different trends are as follows: (i) If $c_0 > c_a$ then $\beta_H < \beta_{Na}$ at $c_s \geqslant c_0$ and the plots of β_H and β_{Na} versus c_s are separated. (ii) If $c_0 \approx c_a$ then $\beta_H = \beta_{Na}$ at c_0 and $\beta_H < \beta_{Na}$ at $c_s > c_0$. (iii) If $c_0 < c_a$ then $\beta_H > \beta_{Na}$ at c_0 and the plots of β_H and β_{Na} versus c_s cross each other at a point where $c_s \approx K_e c_a$. Exchange between the two bound counterions starts at the cmc and it can be shown from Eq. (24) that $\beta_H/\beta_{Na} = K_e(c_a/c_0)$ at the cmc. Therefore, the ratio c_a/c_0 has a control over the relative values of β_H and β_{Na} as obvious from the above three trends.

The ion-exchange at the micellar interface is also assessed by evaluating $[Na_b]/[H_b]$, which is equal to β_{Na}/β_H. Fig. 6 shows linear increase in $[Na_b]/[H_b]$ with c_s at constant c_a and that of $[H_b]/[Na_b]$ with c_a at constant c_s. As the acid concentration increases the rate of increase in $[Na_b]/[H_b]$ with c_s decreases sharply. It is found that $[H_b] < [Na_b]$ when $c_a < c_s$, $[H_b] = [Na_b]$ when $c_a = c_s$, and $[H_b] > [Na_b]$ when $c_a > c_s$. Thus, the relative values of surfactant and acid concentrations in the solution determine the extent of ion-exchange of H^+ and Na^+ ions at the micellar interface. The dodecylsulfate micelle does not therefore show any ion specificity toward H^+ and Na^+ ions. Furthermore, the competitive binding of sodium and hydrogen ions to ionic micelle, which are counterions with large difference in their limiting ionic conductivity, is responsible for the unusual trend in the variation of κ with SDS concentration. The unusual behavior in κ can be explained in light of Eqs. (11) and (14). Below the cmc, κ increases with increasing SDS concentration in accordance with Eq. (11). Above the cmc, λ_2 term of Eq. (14) controls the dependence of κ on SDS concentration. The value of λ_2 can be either negative or positive depending upon the relative values of β_H and β_{Na}, which are determined by the concentrations of SDS and acid as evident from Fig. 5. Just above the cmc, λ_2 is negative and hence κ decreases with increasing SDS concentration. At sufficiently high concentrations of SDS, β_H becomes very low due to which λ_2 turns positive and κ starts increasing once again. Thus the value of λ_2 accounts for the occurrence of maximum and minimum in the plot of κ versus c_s.

3.9. Degree of hydrolysis

From the analysis of κ data in the manner explained above we found that hydrolysis of SDS is negligible below 0.02M HNO_3. In the presence of 0.02M and 0.05M HNO_3 about 12% of SDS undergoes hydrolysis. Hydrolysis of SDS in the presence of HNO_3 may generate nitronium ion as shown below

$$HSO_4^- \rightleftharpoons H^+ + SO_4^= \tag{25}$$

$$HNO_3 + H^+ \rightleftharpoons NO_2^+ + H_2O \tag{26}$$

This indicates that SDS solution in nitric acid with nitric acid concentration $\geqslant$0.02M may be used as a nitrating medium. To confirm this, we prepared a solution of p-nitrophenol (PNP) in aqueous SDS (c_s > cmc) solution and to this HNO_3 was added so that in the solution $[HNO_3] \geqslant 0.02M$. The reaction mixture was then stirred for about 30 min by maintaining the temperature at about 25 °C. The reaction was monitored by thin layer chromatography. On completion of the reaction, the product was extracted with diethyl ether and the organic layer was separated, dried over sodium sulfate and evaporated under vacuum. The product, dinitrophenol, was confirmed by IR and mass spectroscopy, and the yield was found to be 75–80%. The nitration of PNP did not take place in aqueous SDS solution containing less than 0.02M HNO_3 nor in neat dilute nitric acid medium ($[HNO_3] > 0.02$ M) without SDS. Thus nitration of PNP in turn confirms the hydrolysis of SDS in the presence of $[HNO_3] \geqslant 0.02M$ as expected from the conductance data analysis. Interestingly, this study reveals that aqueous SDS + HNO_3 solution with $[HNO_3] \geqslant 0.02M$ can be used as a very convenient soft medium for nitration.

4. Conclusions

This study has revealed that SDS in aqueous HNO_3 medium can exhibit both the normal and the unusual conductance behaviors. The normal conductance behavior of SDS in acid medium is observed only if $c_0/c_a > 3.4$, which was not reported from the earlier studies [2–4] in aqueous HCl medium. On the basis of the present results it can be predicted that solutions of ionic surfactant + electrolyte with foreign counterion would exhibit unusual conductance behavior (i) if the two counterions have large difference in their limiting ionic conductivity and undergo competitive binding to the ionic micelle and (ii) if $c_0/c_a < 3.4$. The relative values of the binding constants of the two counterions are controlled by c_a, c_s, and c_0. The exchange of sodium and hydrogen counterions at the micellar surface has no significant effect on the cmc of SDS implying that these two counterions are not markedly discriminated by the dodecylsulfate micelle.

This study provides a quantitative method for determining the cmc, aggregation number, and counterion binding constants from the conductivity data of ionic surfactant + electrolyte solutions no matter such solutions consist of mixed counterions and show normal or unusual conductance behavior.

Another very useful conclusion of this study is that SDS + aqueous HNO_3 medium with $[HNO_3] \geqslant 0.02M$ can be used as a green medium for nitration of organic molecules thereby envisaging potential application of this medium in organic synthesis.

Acknowledgments

The authors acknowledge the financial support received from the DST, New Delhi (Project No. SR/S1/PC-36/2006). JD acknowledges Senior Research Fellowship received from the CSIR, New Delhi.

References

[1] C. Seguin, J. Eastoe, R.K. Heenan, I. Grillo, Langmuir 23 (2007) 4199.
[2] C.A. Bunton, K. Ohmenzetter, L. Sepulveda, J. Phys. Chem. 81 (1977) 2000.
[3] A. Domínguez, A. Fernández, N. González, E. Iglesias, L. Montenegro, J. Chem. Educ. 74 (1997) 1227.
[4] R. Pazo-Llorente, C. Bravo-Diaz, E. Gonzalez-Romero, Langmuir 20 (2004) 2962.
[5] P.C. Shanks, E.I. Franses, J. Phys. Chem. 96 (1992) 1794.
[6] B.C. Paul, S.S. Islam, K. Ismail, J. Phys. Chem. B 102 (1998) 7807.
[7] K. Gunaseelan, I.M. Umlong, T. Mukhim, K. Ismail, Langmuir 19 (2003) 7276.
[8] S. Dev, K. Gunaseelan, K. Ismail, Langmuir 16 (2000) 6110.
[9] J.L. Kurz, J. Phys. Chem. 66 (1962) 2239.
[10] A.S. Quist, W.L. Marshall, J. Phys. Chem. 69 (1965) 2984.
[11] L.S. Romsted, J. Phys. Chem. 89 (1985) 5107.
[12] L.S. Romsted, J. Phys. Chem. 89 (1985) 5113.
[13] L.S. Romsted, D. Zanette, J. Phys. Chem. 92 (1988) 4690.
[14] J.W. McBain, J. Searles, J. Phys. Chem. 40 (1936) 493.
[15] R.M. Pashley, B.W. Ninham, J. Phys. Chem. 91 (1987) 2902.
[16] P. Richetti, P. Kekicheff, Phys. Rev. Lett. 68 (1992) 1951.
[17] J. Marra, M.L. Hair, J. Colloid Interface Sci. 128 (1989) 511.
[18] J. Haldar, V.K. Aswal, P.S. Goyal, S. Bhattacharya, J. Phys. Chem. B 105 (2001) 12803.
[19] J. Dey, J. Bhattacharjee, P.A. Hassan, V.K. Aswal, S. Das, K. Ismail, Langmuir 26 (2010) 15802.
[20] T.E. Burchfield, J. Phys. Chem. 88 (1984) 2149.
[21] N. Jalšenjak, J. Colloid Interface Sci. 293 (2006) 230.
[22] G.M. Roger, S. Durand-Vidal, O. Bernard, P. Turq, T.-M. Perger, M. Bester-Rogac, J. Phys. Chem. B 112 (2008) 16529.
[23] Y. Moroi, N. Yoshida, Langmuir 13 (1997) 3909.
[24] C. Tanford, The Hydrophobic Effect: Formation of Micelles and Biological Membranes, Wiley-Interscience, New York, 1973.
[25] I.M. Umlong, K. Ismail, Colloids Surf. A 299 (2007) 8.
[26] C.J. Drummond, F. Grieser, T.W. Healy, Chem. Phys. Lett. 140 (1987) 493.

[27] B.L. Bales, M. Almgren, J. Phys. Chem. 99 (1995) 15153.
[28] B.L. Bales, L. Messina, A. Vidal, M. Peric, O.R. Nascimento, J. Phys. Chem. B 102 (1998) 10347.
[29] E. Dutkiewicz, A. Jakubowska, Colloid Polym. Sci. 280 (2002) 1009.
[30] N.J. Turro, A. Yekta, J. Am. Chem. Soc. 100 (1978) 5951.
[31] V.Y. Bezzobotnov, S. Borbely, L. Cser, B. Farago, I.A. Gladkih, Y.M. Ostanevich, S. Vass, J. Phys. Chem. 92 (1988) 5738.
[32] F.H. Quina, P.M. Nassar, J.B.S. Bonilha, B.L. Bales, J. Phys. Chem. 99 (1995) 17028.
[33] B.L. Bales, J. Phys. Chem. B 105 (2001) 6798.
[34] M. Bergstrom, J.S. Pedersen, Phys. Chem. Chem. Phys. 1 (1999) 4437.
[35] D. Stigter, K.J. Mysels, J. Phys. Chem. 59 (1955) 45.
[36] R.G. Alargova, I.I. Kochijashky, M.L. Sierra, R. Zana, Langmuir 14 (1998) 5412.
[37] G. Garg, P.A. Hassan, V.K. Aswal, S.K. Kulshreshtha, J. Phys. Chem. B 109 (2005) 1340.
[38] G.G. War, F. Grieser, D.F. Evans, J. Chem. Soc. Faraday Trans. 1 (82) (1829) 1986.
[39] E.Y. Sheu, S.-H. Chen, J. Phys. Chem. 92 (1988) 4466.
[40] A. Siemiarczuk, W.R. Ware, Y.S. Liu, J. Phys. Chem. 97 (1993) 8082.
[41] A. Maneedaeng, K.J. Haller, B.P. Grady, A.E. Flood, J. Colloid Interface Sci. 356 (2011) 598.