RESEARCH ARTICLE

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Manipulation of Concentration-Conductivity Data of Sodium Dodecyl Sulphate and Sodium Dodecylbenzene Sulphonate in KCl Solution in Relation to Micellisation Parameters

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Abstract

The conductivity of sodium dodecyl sulphate (SDS) and sodium dodecylbenzenesulphonate (SDBS) has been studied in varying concentrations (0-5 mM) of aqueous KCl solution at 25°C. Data analysis was based on the conventional treatment of conductivity-concentration data, differential, and integration methods with the aim of knowing the best method. As expected, the conductivity increased with an increase in surfactant concentration; the plot of which showed a kink at critical micelle concentration, *cmc* (*i.e.* point of aggregation). The results showed no apparent relationship between the degree of counterion binding, β and [KCl]; and an inverse relationship between the *cmc* values and [KCl]. β was within 0.4-0.6 for SDS and 0.1-0.3 for SDBS. The *cmc* of SDS decreased from *ca*. 8 to 6 mM and that of SDBS from *ca*. 2 to 1 mM as the [KCl] increased from 0-5 mM. These values are in mutual agreement irrespective of the method used. It was confirmed that in the absence of KCl, values obtained from the integration method were more consistent with those reported in the literature; therefore this method is recommended as the best method for determination of micellisation parameters provided the process is followed by conductivity measurements.

Keywords: Aggregation; counterions; *cmc*; micellisation; surfactant.

1. Introduction

Surface active agents, also known as surfactants, are among the most important chemicals available to chemists. They are amphiphilic molecules possessing a long chain hydrocarbon 'tail' and a polar or an apolar 'head'. Based on the nature of head group, they have been classified as non-ionic, anionic, cationic and zwitter ionic surfactants. In aqueous systems, the tail is said to be hydrophobic as it 'dislikes' water while the head is said to be hydrophilic because it 'likes' water [1]. Surfactants are important component of many consumer products like motor oils, soaps, pharmaceuticals and foods. Surfactants are also used in oil recovery, chemical kinetics and biochemistry as membrane mimics [2, 3]. One outstanding property of surfactants is that at relatively high concentrations (> 10^{-4} M), they arrange themselves into organised molecular aggregates known as micelles. This phenomenon is driven by hydrophobic effect and opposed by electrostatic repulsions between the ionic head groups [4]. Counterions bind to surfactant monomer head groups in the micelles and screen the electrostatic repulsions between them. This favours the micellisation process and has a stabilising effect on the micelles. The concentration at which micelle formation occurs is known as the *cmc*. There are several structures of micelles. Normal spherical micelles are formed in aqueous solutions when the surfactant molecules orient themselves into spherical structures with their hydrophobic tails oriented towards the centre and their hydrophilic heads oriented towards the surrounding water. The opposite is true for reverse normal micelles in apolar solvents. When spherical micelles grow (*e.g*. by salt addition or increasing surfactant concentration), they become either disc-like or cylindrical when the aggregation number reaches a certain stage [1, 5, 6].

The *cmc* is a measurement that quantifies the ability of a surfactant to form micelles: the lower the *cmc*, the greater the ability of the surfactant to form micelles and vice versa. The *cmc* is obtained by measuring any surfactant solution property (*e.g*. density, speed of sound, light scattering intensity, light absorption, molar conductivity, etc.) as a function of surfactant concentration [7, 8]. The focus of this paper is on the conductometric method. This method is frequently used for the determination of the *cmc* of ionic surfactant because it is simple and accurate. It is based on the fact that under normal conditions, an ionic surfactant (below its *cmc*) is completely dissociated and there is a linear relationship between the molar conductivity, $\kappa$of the surfactant solution and its concentration as the surfactant monomers behave as normal electrolytes and thus obeying Kohlrausch's law (Eq. 1). Above the *cmc*, $\kappa$is constant and independent of surfactant concentration as micelles behave like weak electrolyte and Eq. 2 is obeyed. Eq. 2 shows that κ depends on the extent of dissociation of the free surfactant monomers and the conductivity of the micelles with the concentration of the former being equivalent to the *cmc*.

$$\kappa = (\lambda_{\text{cation}} + \lambda_{\text{anion}})[\text{surfactant}]' \quad (1)$$

$$\kappa = (\lambda_{\text{cation}} + \lambda_{\text{anion}})\text{cmc} + \lambda_{\text{cation}}\alpha[\text{surfactant}]'' + \lambda_{\text{micelle}}[\text{micelle}] \quad (2)$$

Where $\lambda_{\text{cation (anion)}}$, [surfactant]’, λ_{micelle}, [surfactant]’’, and α represent conductivity of the cation (anion), concentration of surfactant below *cmc*, conductivity of a micelle, fractional micellar ionisation, and degree of counterion dissociation respectively. A plot of molar conductivity of the surfactant *versus* the surfactant concentration gives a kink from which the *cmc* of the surfactant is obtained.

Despite the accuracy and simplicity of this method, it is very difficult to observe the break in the conductance-concentration curve for surfactants with small aggregation number and the *cmc* value determined is affected by a great uncertainty [9]. Several procedures have been proposed to circumvent this problem. A common approach is to plot the differential conductance against the concentration [10, 11]. García-Mateos *et al*. [12] have proposed a method which is based on transformation of the second derivative of the conductivity-concentration data to Gaussian approximation followed by two consecutive numerical integrations. A procedure which consists of the application of a Runge-Kutta numerical integration method and the Levenberg-Marquardt least-squares fitting algorithm has also been proposed [13]. In addition, LópezFontán and co-workers [14] have reported a statistical method, the local polynomial regression method, based on a nonparametric estimation of the regression function. This approach seems to be very accurate but, it requires a great knowledge of statistics and determination of other micellisation parameters like degree of counterion binding *β* from only *cmc* was not described.

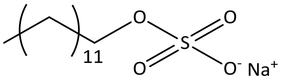
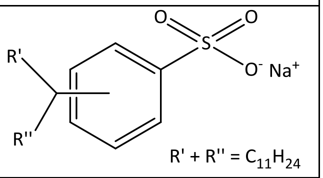
In this paper, the *cmc* and *β* of the surfactants in KCl solution would be determined from conductance-concentration data using the conventional, differentiation and integration methods so as to demonstrate how the *cmc* varies with these methods and then answer the question ‘which is the best method?’ that has appeared recently in some literature [9].

2. Experimental

2.1 Materials

SDS (~99% pure), SDBS (purity above 88%) and potassium chloride (purity ≥99.5%) were from Sigma-Aldrich, Acros Organics and BDH laboratory supplies, respectively and were used as received. Some physicochemical properties of these surfactants are given in Table 1. Water was passed through an Elga Prima reverse osmosis unit and then a Milli-Q reagent water system. The treated water has surface tension 71.7 mN m^{-1}, pH 7.93 and resistivity 18 MΩ cm.

Table 1: Some physicochemical properties (at 25ºC) of SDS and SDBS.

Property	SDS	SDBS
Chemical structure		
Molar mass/g mol^{-1}	288.37	348.48
Density/g cm^{-3}	1.01	1
Melting point/ºC	206	300
Refractive index (n_D)	1.461	1.478
Appearance	white or cream-coloured solid	cream-coloured solid
Odour	odourless	odourless

2.2 Method

The conductivity-concentration data were obtained from salt free solutions of the surfactants and in solutions containing 1-5 mM KCl. In the first case, stock SDS (20 mM) and SDBS (5 mM) solutions were prepared and diluted with water according to the procedure proposed by Jover *et al.* [15] to obtain other concentrations. The second case involved preparing similar surfactant solutions in the desired concentration of KCl solution and diluting with the same KCl solution to obtain other concentrations. This procedure kept the concentration of the salt effectively constant while that of the surfactant decreases. The conduction of surfactants in these solutions was obtained by subtracting that due to the KCl solution from that containing the contributions of both the surfactant and the salt. The conductivity of the various solutions was determined at constant temperature (25± 0.2ºC) by circulating water from a water bath (Grant GD 120) through a jacketed double-walled glass vessel holding the solution under study. The conductivity values were determined using a Jenway digital conductivity meter (model 4510) with Pt/Pt black electrodes after thorough mixing and temperature equilibrium at each dilution. The conductivity meter was calibrated with 10 mM KCl solution prior to the experiment. The uncertainty in conductivity measurements was estimated to be ± 0.5 µS cm^{-1}.

3. Results and Discussion

3.1 Conventional treatment of conductivity-concentration data

Because *cmc* is a 'phase transition' between two different regimes of a surfactant solution, the plot of conductivity *versus* concentration shows a linear behaviour with two different slopes as mentioned before. Usually, the intersection of the two straight lines below and above the *cmc* gives the *cmc* of the surfactant and the ratio of the slope of the postmicellar region to that of the premicellar region gives α from which β can be calculated [16, 17]. Figure 1 shows a plot of conductivity as a function of [SDS] and [SDBS] in varying concentrations of KCl. In the absence of KCl, the *cmc* values of SDS and SDBS are consistent with those reported by Capena *et al.* [9] and Tu *et al*. [18], respectively; using conductometric method at 25ºC. Figure 2 shows that the *cmc* of these surfactants, obtained from Figure 1, decreases with an increase in [KCl] as expected and that the *cmc* of SDS is higher than that of SDBS. These observations are due to the tendency of the hydrocarbon chains to remove themselves from water. There are two competing processes in the formation of micelles of ionic surfactants in aqueous systems as mentioned earlier on. The binding affinity of the counterion to the micelles, which depends on the magnitude of its charge and size [4, 19], has a positive influence on the micellisation process as shown in Figure 2. Note that Na^+ from the dissociation of the surfactants and K^+ furnished by KCl are counterions in these systems. Nevertheless, the former has little effect on the micelles as its concentration is relatively low compared to the latter with relatively high concentration. Because SDBS has a phenyl ring attached to the dodecyl group, its tail is more hydrophobic and has a higher tendency to remove itself from water than that of SDS containing only the dodecyl group. This structural difference and the behaviour of the hydrocarbon tails account for the observed difference in the *cmc* of these surfactants.

3.2 *cmc* from differential method

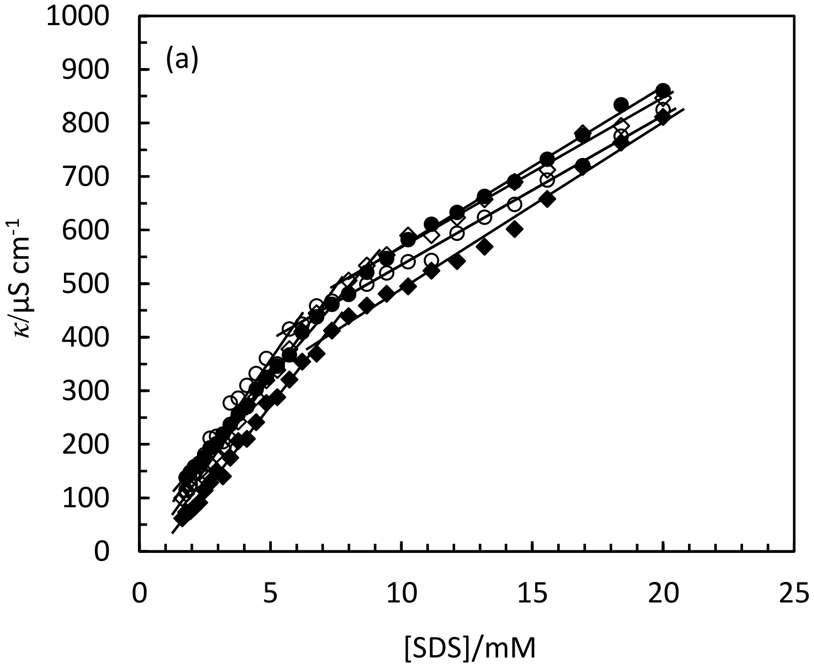
The general features of the first derivative of a typical conductivity-concentration plot have been detailed by Carpena *et al*. [9]. This derivative is of the sigmoidal type and can be sufficiently described using the Boltzmann type sigmoid, which can be expressed analytically as:

$$\left(\frac{d\kappa(c)}{dc}\right)_{TP} = \frac{S_1 - S_2}{1+\exp^{(c-c_0)/\Delta c}} + S_2 \qquad (3)$$

Where the left hand side term stands for the first derivative of conductivity-concentration plot at constant temperature and pressure, $S_1(S_2)$ stand for the asymptotic value for small (large) values of concentration (c), c_0 stands for the central point of the transition and Δc is the width of the transition.

As mentioned before, it is difficult to determine the *cmc* of surfactants with small aggregation number from their conductivity-concentration plot. SDBS, whose *cmc* is less than 2 mM, and some *n*-alkyltriphenylphosphoniumbromides are excellent examples. This behaviour is shown in Figure 1b for SDBS and the situation is worse as the *cmc* decreases with an increase in [KCl]. Plotting the differential conductivity as a function of concentration has proved to be one of the ways to surmount this difficulty. This kind of plot is shown in Figure 3 for SDS and SDBS. These curves consist of three regions: constant high *dκ/dc* values (at relatively low surfactant concentrations), sharp decrease in *dκ/dc* values (at moderately high surfactant concentrations) and constant low *dκ/dc* values (at relatively high surfactant concentrations). The midpoint of the second region represents the *cmc* of the surfactant. Clearly, *cmc* values can be extracted easily from

Figure 3 than from Figure 1. One general problem associated with this method is distortion of the experimental data in systems in which the micellisation process is rather gradual (*e.g.* *n*-alkyltriphenylphosphonium bromides [20]). This distortion often produces a large uncertainty in the micellisation parameters.



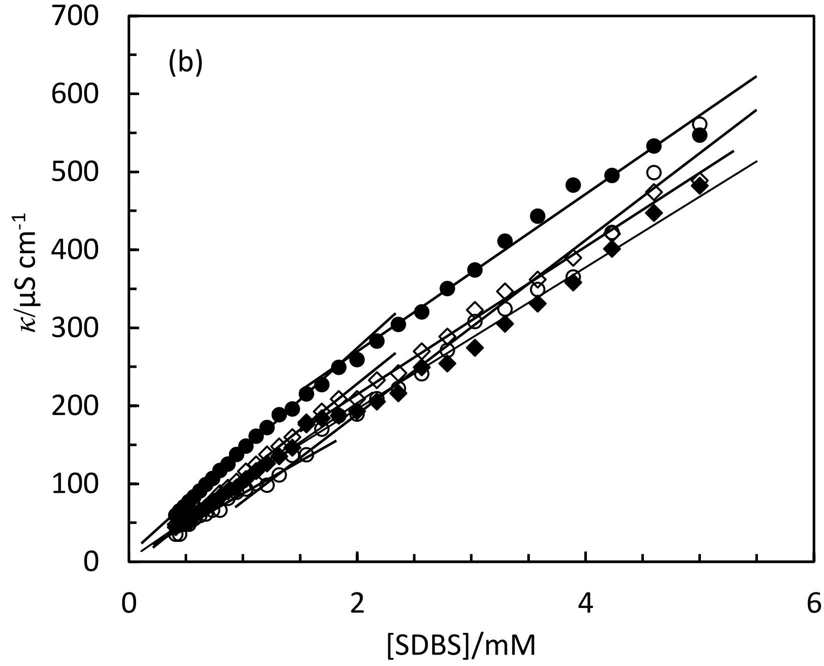


Figure 1: Experimental data of conductivity *versus* concentration of (a) SDS and (b) SDBS in varying concentrations of aqueous KCl solution at 25ºC: (●) 0, (◇) 1, (◆) 3 and (○) 5 mM.

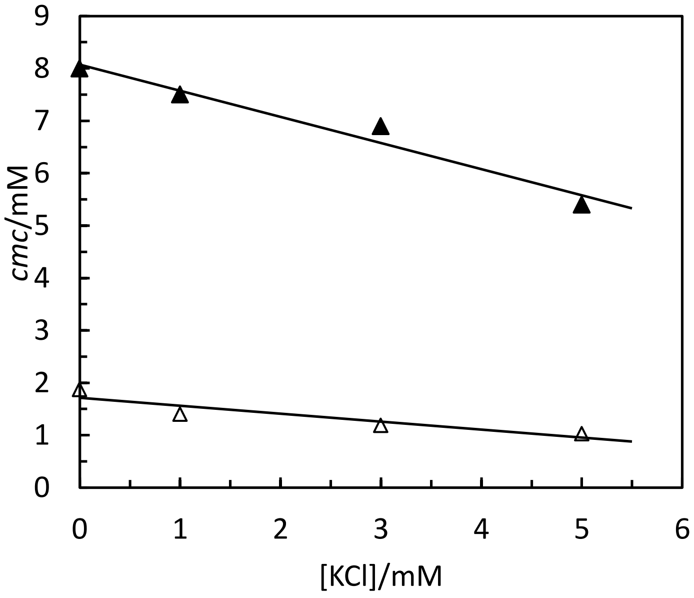


Figure 2: *cmc* (obtained from Figure 1) of SDS (▲) and SDBS (△) *versus* [KCl].

3.3 *cmc* from integration method

According to Carpena and co-workers [9], if the derivative of conductivity-concentration data behaves as a sigmoid; the original data should behave as the integral of the sigmoid. Based on this proposal, they integrated Eq. 3 to obtain Eq. 4.

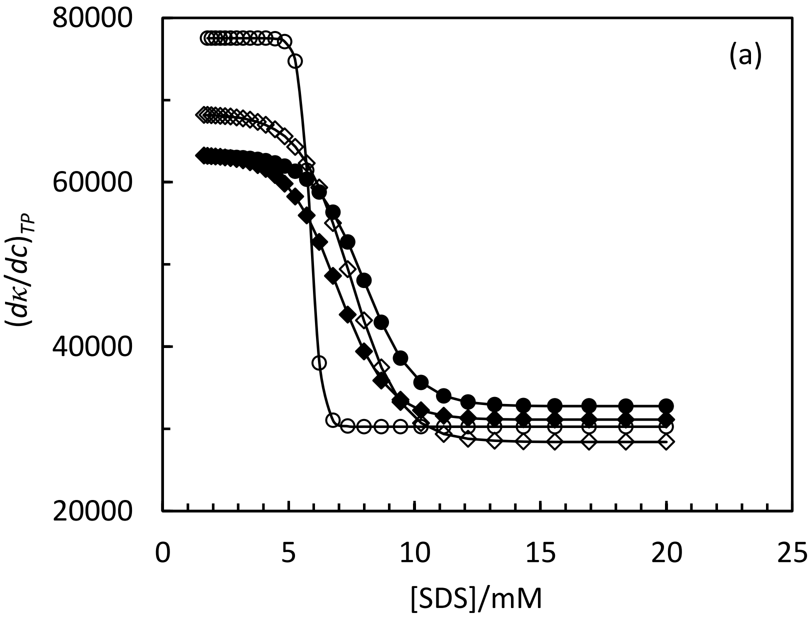
$$\kappa(c) = \kappa(c=0) + S_1 c + \Delta c(S_2 - S_1)\ln\left(\frac{1+\exp^{(c-c_0)/\Delta c}}{1+\exp^{-c_0/\Delta c}}\right) \tag{4}$$

All the symbols (Eq. 4) retain their usual meanings. A typical plot of conductivity *versus* surfactant concentration in varying concentrations of KCl based on this method is shown in Figure 4.

Figure 4 is very similar to Figure 1, suggesting that integration has little effect on the behaviour of the experimental data. Values of *cmc* and *β* for SDS and SDBS in varying [KCl] based on these methods are given in Table 2. *β* is 1-s_2/s_1, 1-S_2/S_1 or 1-A_2/A_1, for the conventional, differential and integration method, respectively. Where $s_{1(2)}$ and $A_{1(2)}$ are slopes of the premicellar (postmicellar) region. Two important pieces of information can be extracted from Table 2. Firstly, the *cmc* and *β* values obtained from these methods are in close agreement with each other. In the KCl free systems, the *cmc* values from the integration method are more consistent with values reported in surfactant encyclopaedia and other papers [5, 14, 21]. This suggests that even though the plot is similar to conventional conductivity-concentration plot, it provides accurate and reliable values of *cmc* and *β*. Secondly, *β* values of the surfactants are independent of [KCl] and are between 0.5-0.6 for SDS and 0.1-0.2 for SDBS. These values indicate that SDS head groups repair each other more than those of SDBS. This is another reason why the *cmc* of SDS is greater than that of SDBS.

4. Conclusion

All the methods have some advantages and drawbacks and provide similar results for *cmc* and *β*. Therefore, if there is an appropriate curvature and the break point is clear, any method is suitable for determination of these parameters. Because the values obtained from the integration method were more consistent with those reported in the literature, it is recommended as the best method for determination of micellisation parameters.



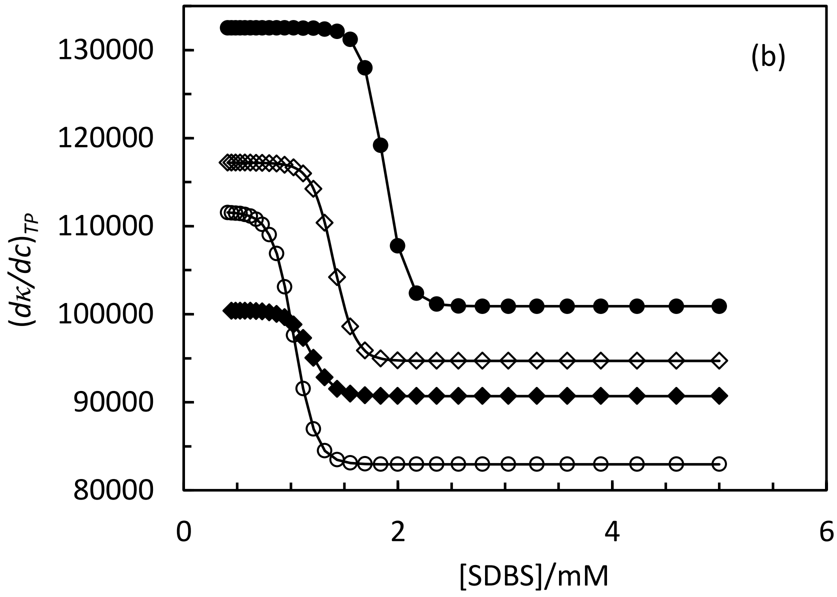
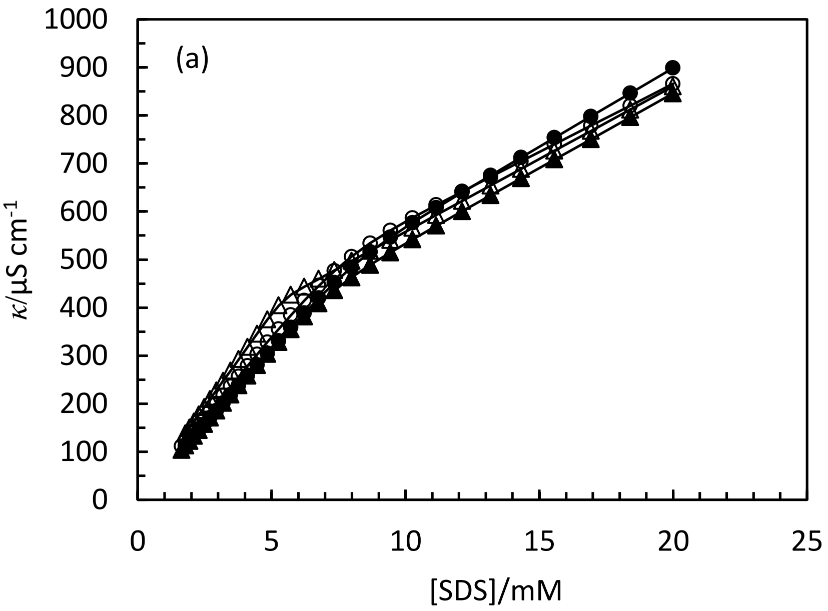


Figure 3: Differential conductivity *versus* concentration of (a) SDS and (b) SDBS in varying [KCl] at 25ºC: (●) 0, (◇) 1, (◆) 3 and (○) 5 mM.



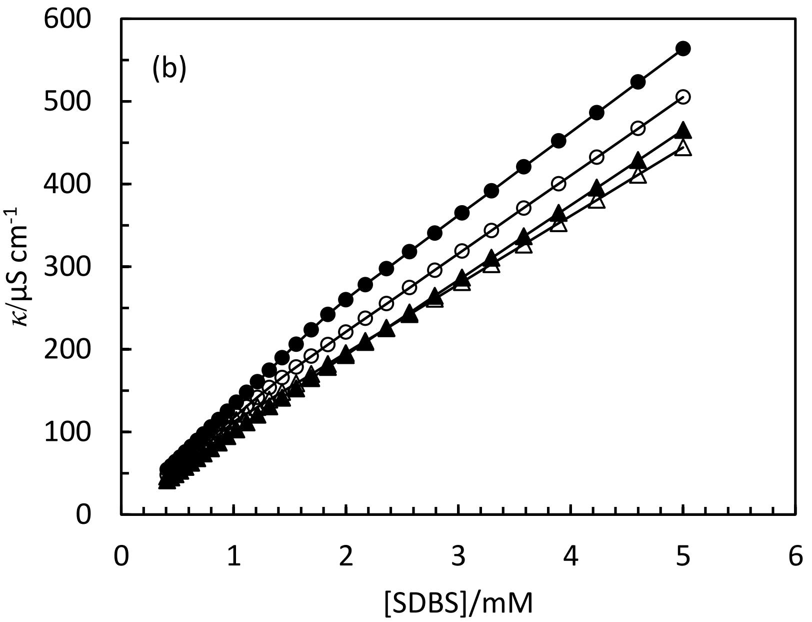


Figure 4: Integral conductivity *versus* concentration of (a) SDS and (b) SDBS in varying [KCl] at 25ºC: (●) 0, (○) 1, (▲) 3 and (△) 5 mM.

Table 2: *cmc* and *β* of SDS and SDBS in varying concentrations of KCl at 25ºC as obtained from different treatment of conductivity-concentration data.

		Conventional		**Differentiation**		**Integration**	
Surfactant	**[KCl]/mM**	***cmc*/mM**	***β***	***cmc*/mM**	***β***	***cmc*/mM**	***β***
SDS	0	8.00	0.483	8.00	0.481	8.20	0.446
	1	7.50	0.584	7.60	0.583	7.80	0.546
	3	6.90	0.509	7.00	0.508	7.50	0.470
	5	5.40	0.610	6.00	0.610	6.00	0.583
SDBS	0	1.87	0.238	1.80	0.238	2.00	0.234
	1	1.40	0.192	1.40	0.192	1.60	0.157
	3	1.19	0.097	1.25	0.096	1.25	0.183
	5	1.03	0.257	1.00	0.256	1.00	0.211

Competing Interests

The authors declare that they have no competing interests.

Authors' Contributions

AT developed the project and prepared the manuscript; SG and RA worked on the project.

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