Determination of Critical Micelle Concentration (*Cmc*) of Sodium Dodecyl Sulfate (SDS) and the Effect of Low Concentration of Pyrene on its *Cmc* Using ORIGIN Software

ASAD MUHAMMAD KHAN AND SYED SAKHAWAT SHAH*
Department of Chemistry Quaid-i-Azam University 45320 Islamabad, Pakistan.

(Received 21st May 2007, revised 16th August 2007)

Summary: Critical micelle concentration of sodium dodecyl sulfate (SDS) was determined using conductance and fluorescence method. Effect of low concentration of pyrene was checked on the *Cmc* of SDS conductometrically. The *Cmc* was determined from the data using two different methods. ORIGIN software shown up as a much better and easier way for the theoretical treatment of experimental data. It was observed that low concentration of pyrene has no effect on the *Cmc* of SDS.

Introduction

Surfactants constitute an important class of industrial chemicals widely used in almost every sector of modern industry [1]. Extensive interest in the self association phenomenon is evident in such wide ranging chemical and technological areas as organic and physical chemistry, pharmaceutical, petroleum and mineral processing, cosmetic and food science [2-4]. By their nature surfactants are amphiphilic molecules containing hydrophilic and a hydrophobic moiety. Based on their functional groups these are classified as anionic, cationic, zwitterionic and non-ionic surfactants. Gemini or dimeric surfactants are new types of amphiphilic compounds with hydrophobic chains connected by a spacer group [5]. A large group of polymers with amphiphilic structure shows surfactant's properties and hence are known as polymeric surfactants [1, 6-7].

Surfactant molecules orient themselves according to their schizophrenic molecular structure and hence they adsorb at the interfaces with the polar groups towards water and nonpolar groups towards nonaqueous phase. One of the fundamental properties of surfactants is their self-association into organized molecular structures such as micelles, vesicles, microemulsions, bilayers membranes and liquid crystals [8]. The simplest class of association colloids is the micelle i.e, clusters of surfactant's ions inside the bulk of the solvent. Micellization characteristics of a surfactant are understood by determining the values of its micellization parameters, such as critical micelle concentration (*Cmc*), aggregation number etc.

Micelles are the most prevalent aggregate structure in surfactant solutions and form over a narrow range of surfactant concentration called the critical micelle concentration, *Cmc*. Sodium dodecyl sulfate and its micellar properties have been under investigation over the years and a number of models have been reported [9-11]. There are many ways in which *Cmc* could be determined. The *Cmc* is the narrow concentration range over which amphiphilic or surfactant solutions show an abrupt change in a physical property such as electrical conductivity, surface tension, osmotic pressure, density, light scattering, or refractive index [11].

Micelle formation is usually explained by two models. One is mass action model in which a kind of equilibrium is considered between monomeric species and the micelles. The other is phase separation model in which micelles are thought to form new phase in the system above the *Cmc*. The mass action model is important because monomer micelle equilibrium leads to calculation of many important thermodynamic parameters. The monomer-micelle equilibrium can be written as

$$nS \leftrightarrow S_n \qquad (1)$$

Here n shows the number of monomer units present in the solution where S stands for any surfactant. S_n shows micelle formed from the surfactant monomers. The corresponding equilibrium is given by the equation

$$K_m = \frac{[S_n]}{[S]^n} \qquad (2)$$

*To whom all correspondence should be addressed.

Where K_m is the micellar equilibrium constant, [*S*] stands for the surfactant concentration and [S_n] indicates the micellar concentration of the surfactant, n is the number of monomers in the micelles i.e, the aggregation number. From equation 2 free energy change of micellization can be calculated using the equation

$$\Delta G_m = -RT \ln K_m = -RT \ln[S_n] + nRT \ln[S] \quad (3)$$

Where *R* is universal gas constant and *T* is the absolute temperature. The free energy change per mole of free surfactant is

$$\Delta G_m = -(\frac{RT}{n}) \ln[S_n] + RT \ln[S] \quad (4)$$

At or near the *Cmc* $[S] \approx [S_n]$ so that we can write the above equation in a form

$$\Delta G_m = -RT \ln Cmc \quad (5)$$

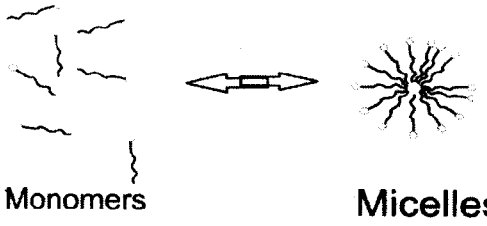
Where *Cmc* stands for critical micelle concentration of some particular surfactant. Similarly we can write

$$-\Delta H_m = RT^2 [d \ln \frac{Cmc}{dT}] \quad (6)$$

In the above equation 6, ΔH_m is the enthalpy change of micellization. It can be either positive or negative, depending on the nature of the process occurring inside the system. Usually micellization is entropy driven process and the enthalpy contribution is usually positive [12]. Entropy change can be calculated using the relationship:

$$-T\Delta S_m = \Delta G_m - \Delta H_m \quad (7)$$

As defined, micellization take place after certain concentration of surfactants is achieved inside the solvent system. As the concentration of monomers inside the system increase, there appears a tendency of these monomers to combine into an organized molecular assembly i.e., which micelle with hydrophilic head towards the water solvent and hydrophobic chains inside making an interior non polar environment as shown in the diagram below.



Since the process is very complex hence it becomes very difficult to pinpoint the concentration where it happens. That's why people are still trying to make an easy method available to determine this concentration which is very important in many of the biological phenomenon and of great industrial use. Critical micelle concentration (*Cmc*) is defined as the point corresponding to the maximum change in gradient in an ideal property-concentration against total concentration. In agreement with Phillips, the critical concentration is defined by

$$\left(\frac{d^3\kappa}{dc^3}\right) = 0 \quad (8)$$

Where κ denotes the conductivity and *c* the critical micelle concentration [13]. In the case of drugs and surfactants with low aggregation numbers, a conductivity/concentration curve shows a very slow variation. This slow change causes difficulties in obtaining precise *Cmc* values. Rodriguez *et. al.*, improved Williams and Phillips method to determine *cmc* of binary mixtures of surfactants. Mosquera *et. al.*, devised some complex algorithm using Runge- Kutta method for numerical integration combined with Levenberg – Maquardt least square fitting algorithm [2, 14-15].

In this work it was observed that Levenberg –Maquardt least square fitting algorithm can be applied for Guassian fitting of second derivative of the experimental data to get the values of *Cmc* [15].

The derivative is taken by averaging the slopes of two adjacent data points by using the given below

$$\frac{d\kappa}{dc} = \frac{1}{2}\left(\frac{\kappa_{i+1} - \kappa_i}{c_{i+1} - c_i} + \frac{\kappa_i - \kappa_{i-1}}{c_i - c_{i-1}}\right) \quad (9)$$

Which results in 1st order derivative data of specific conductivity with respect to concentration. In this equation κ and c are specific conductance ($\mu S\ cm^{-1}$) and concentration (mole dm^{-3}) respectively.

Similarly we can again apply the same formula to the data obtained for 1st derivative to get the vale of second derivative i.e., $\frac{d^2\kappa}{dc^2}$ or which can be written as κ'' or y''. The data obtained here can be fitted using Gaussian fit application of the software which is rather improved due to its integration with Levenberg –Maquardt non linear fitting which use reduction of χ^2 to get fit of the curve[16].

$$y = y_0 + \frac{A}{w\sqrt{\frac{\pi}{2}}} e^{\frac{-2(x-x_0)}{w^2}} \qquad 10)$$

The above equation is used in this program to fit the curve. Here y is dependent variable, x and x_0 are independent variables where x_0 represents mean value which is given by the centre of bell shaped Gaussian curve. Similarly w is the standard deviation. This can be compared to the equation given below used by other workers to make the Gaussian fitting curve of the 2nd derivative data.
The equation is as follows

$$\kappa'' = A\exp\left\{-\frac{(C - Cmc)^2}{2\delta^2}\right\} \qquad (11)$$

Here $A = \frac{A_g\beta}{\delta\sqrt{2\pi}}$ which is pre exponential factor and can be taken same as the one in equation 10. Similarly x and x_0 can be compared to C and Cmc respectively in equation 10 and 11, where C is the total surfactant concentration and Cmc is the critical micelle concentration. In the above equation y_0 is the offset value which can be set to 0 in this particular case which is obvious from equation 11. $2\delta^2$ is the standard deviation value in that equation. This can be compared to the w of equation 10 above.

The aim of the present study is to obtain precise critical concentrations at which the aggregation of SDS takes place. SDS, a well known surfactant with well recorded values of Cmc and other parameters in literature is used here to check the validity of the equation which is used in the ORIGIN. So this will help to make the method applicable for further studies and if any improvement can be done to the existing methods of determining Cmc.

Results and Discussion

The Cmc of pure SDS was determined using conventional conductivity measurement method. A break is observed in the value of conductivity of the micellar solution with the formation of the micelles. Micelle formation is a well known phenomenon but the measurement of exact value of the cmc has always been a subject of controversy. A lot of different models and complex algorithms are proposed to do the same [2, 13-15].

Here we used simple, easy to use software to determine the Cmc values of the systems. The inbuilt functions of ORIGIN 7 are deployed for these purposes and the values are compared to the one measured by the standard methods available in a variety of literature [2, 13-15].

Fig. 1 shows plot of different concentrations of pure SDS in water. The correlation value was higher then 0.99 for the two regressions and the Cmc value obtained was $9.5 \times 10^{-3}\ mol\ dm^{-3}$.

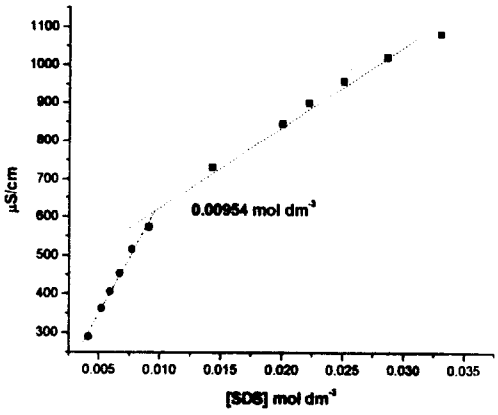


Fig. 1: Plot of conductivity versus varying concentrations of pure SDS. Least square fitting is applied here to the curve points.

The same values were checked by taking double differential of conductivity values with respect to concentration using ORIGIN inbuilt functions and the fitting it non linearly using nonlinear fitting tool of the software (Fig. 2). Gaussian distribution function was applied and minima was taken as the *cmc* value. The bell shaped line in the figure 2, 5 and 7 shows the Gaussian fit. The value obtained was 8.0×10^{-3} *mol* dm^{-3} which was in close agreement with the values reported in literature.

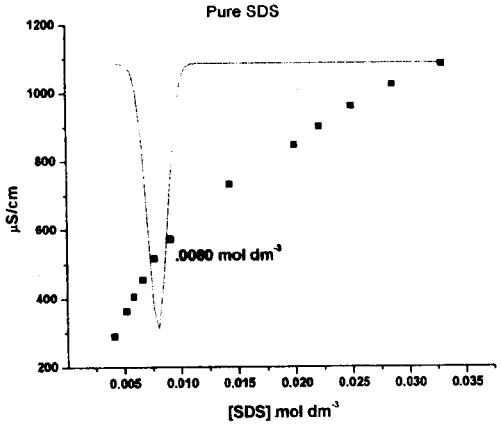


Fig. 2: Gaussian fit applied to the 2nd derivative of specific conductance values with respect to the varying concentration of pure SDS.

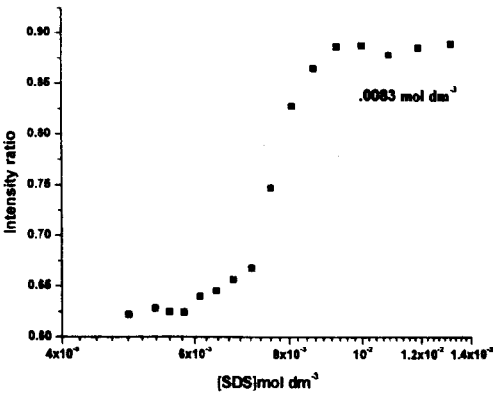


Fig. 3: Change in intensity ratio of 1st and 3rd vibronic bands of pyrene versus varying concentrations of SDS.

The value was counter-checked using fluorescence spectroscopy method which is very sensitive to micellar environment [17-18]. The value comes out to be 8.3×10^{-3} *mol* dm^{-3} (Fig. 3). It is assumed that this method give an upper limit of the micellization.

Usually the method followed, for the determination of *Cmc*, is based on the one suggested by Williams [2, 14-19]. Two lines are simply drawn before and after the break of the curve. Here it was determined applying linear fitting to the two linear portions separately and taking one point common by intelligent guessing (Fig. 1).

Using conductivity the effect of low concentration pyrene on the *Cmc* of SDS was checked because of the frequent use of pyrene for purpose of determination of *cmc* of different surfactants in fluorescence spectroscopy. There was no significant change in *cmc* and the values obtained lied in the range of pure SDS (Fig. 4-7). The two methods were applied and the values compared.

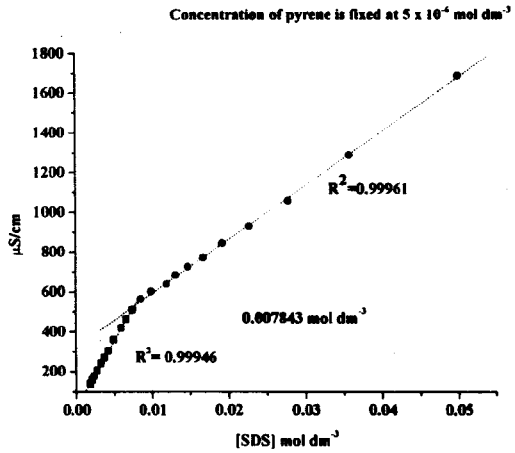


Fig. 4: Change in specific conductance values versus concentration of SDS in presence of 5×10^{-6}mol dm^{-3} pyrene.

From Fig. 4 it is clear that although the correlation value is in agreement to the values of data but the *cmc* value obtained is lesser than the one reported in many literature for *Cmc* of SDS. But when we applied the second derivative method (Fig. 5) using origin based iterations, we get a value of 8.3×10^{-3} *mol* dm^{-3} which is closer to the reported values which lies in the range of 8 to 8.3×10^{-3} *mol* dm^{-3}. This leads to the fact that second derivative method using ORIGIN gives more clear results and supports the assumption that

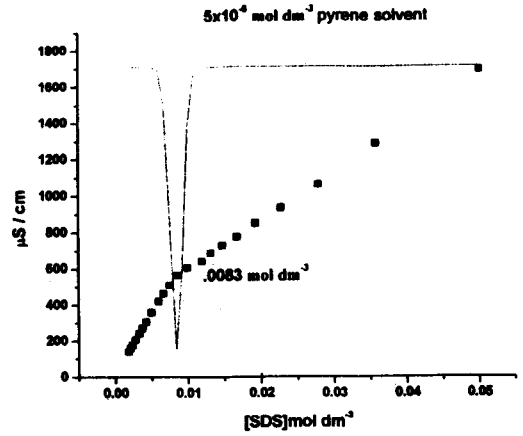


Fig. 5: Gaussian fit applied to the 2nd derivative of the same data as used in Fig. 4.

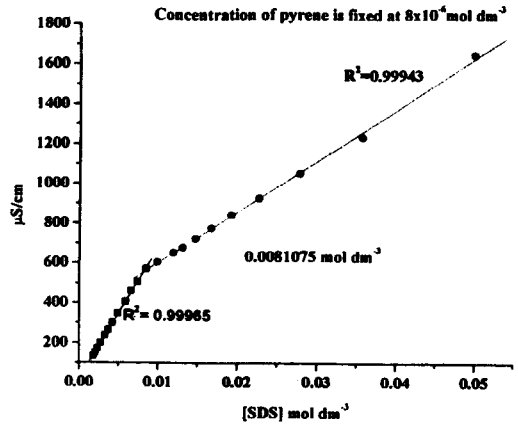


Fig. 6: Specific conductance of SDS in presence of $8x10^{-6}$ mol dm^{-3} pyrene versus different concentration of SDS

'able-1: Comparison of the results.obtained applying near regression and 2nd derivative to the onductivity data of pure SDS and in presence of low oncentrations of pyrene and the result from luorescence method.

ample information	10^3 *Cmc* using linear regression (mol dm^{-3})	10^3 *Cmc* using Gaussian fit of 2nd derivative (mol dm^{-3})	10^3 *Cmc* From the fluorescence method (mol dm^{-3})
ure SDS	9.4	8.0	8.3
DS with 5μM pyrene	7.8	8.3	
DS with 8μM pyrene	8.1	8.1	

low concentrations of pyrene have no effect on the *cmc* of the SDS and hence this can be generalized to the other surfactants.

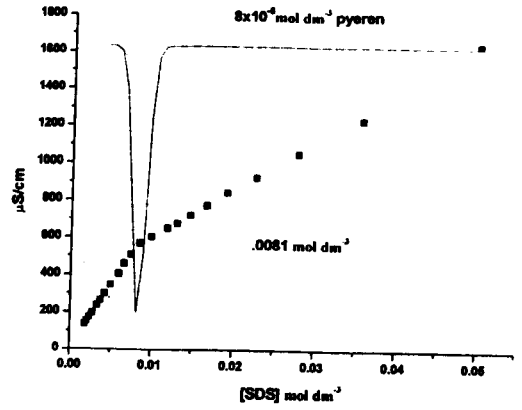


Fig. 7: Gaussian fit of the 2nd derivative of the specific conductance with respect to the concentration of SDS in presence of $8x10^{-6}$ mol dm^{-3} pyrene

In case of Fig. 6 the value obtained from simple least square fit data is also in fairly good agreement with the reported values. The same value is obtained using Gaussian fit method.

The results obtained clearly show that the values of *cmc* obtained using ORIGIN are in fairly good agreement with those quoted in different literature. If figures 1, 2 and 3 are compared then it is clear that there are more chances of error when we use classical method of determination of *cmc* even with the help of computer. Some times the high correlation value in the conductivity value may end in a falsified result. On the other hand the method incorporating the theory of Phillips, Williams and other scientist gives good results. The results are obtained from both methods are summarized in table 1. It can be clearly seen from the table that in all the three cases there seems to be a change in *cmc* when the data was treated using conventional linear regression method. Only in case of 8 micro molar pyrene the result from linear regression and the 2nd derivative method is same. It also shows low concentration of pyrene doesnot effect *Cmc* of SDS. So, *Cmc* determined using pyrene as a probe is as good as determined from the other methods. The higher concentrations of pyrene produce clouding before *Cmc* is reached and therefore are not suitable for fluorescence measurement of *Cmc*.

Experimental

SDS used was procured from fluka and was ≥ 99 % pure (lot No 1170075). The solutions

were prepared using deionized water which was first distilled using Water Still Apparatus Model IM-100 and after that it was passed through an ELGA B114 deionizer Reference number MANU30357. The conductivity of water was ≤ 1 μScm^{-1}.

Solutions were prepared by dilution method to avoid any possibility of error in solution making. The conductivity of solution was noted at a constant temperature using InoLab 720 Precision conductivity meter (WTW) with a cell constant value of 0.475 cm^{-1}. The temperature of the samples was maintained using standard water bath with accuracy of ± 0.1. The temperature was automatically checked by an inbuilt sensor inside the conductivity probe.

Steady State Fluorescence Spectroscopy was performed using a Perkin Elmer Luminescence spectrometer Model LS 55 (Serial Number 73135). The cell used for measuring fluorescence was of 10mm path length and was clear in all dimensions. The temperature of the solution was maintained by using an external circulator water bath to the jacketed cell of the instrument. The spectrum for the sample was noted after the temperature was set to the desired value.

For the preparation of the solutions for fluorescence measurements, Pyrene solution in water was used as solvent so that its concentration was kept constant and the concentration of the surfactant used was varied. The solutions prepared were usually incubated overnight.

References

1. J. Texter, J. H. Moore and N. D. Spencer, *Encyclopedia of Chemical Physics and Physical Chemistry,* Institute of Physics Publishing, Bristol and Phialdelphia, USA., 2285 (2001).
2. V. Mosquera, M. García and L. M. Varela, H. S. Nalwa, *Association colloids: Cmc a property to calculate., Handbook of Surfaces and Interfaces of Materials* Acacemic Press, New York, 401 (2001).
3. S. S. Shah, G. M. Laghari, K. Naeem and S. W. H. Shah, *Colloids Surf., A,* **143,** 111 (1998).
4. B. Naseem, A. Sabri, A. Hasan and S. S. Shah, *Colloids Surf., B,* **35,** 7 (2004).
5. U. S. Siddiqui, G. Ghosh and D. Kabir ud, *Langmuir,* **22,** 9874 (2006).
6. Y. Zhang and Y. M. Lam, *J. Nanosci. Nanotechnol.,* **6,** 3877 (2006).
7. E. Rotureau, M. Leonard, E. Marie, E. Dellacherie, T. A. Camesano and A. Durand, *Colloids Surf., A,* **288,** 131 (2006).
8. S. S. Shah, S. W. H. Shah and K. Naeem, P. Somasundaran and A. Hubbard, *Surfactant-Dye Aggregate, Encyclopedia of surface and colloid science,* Marcel Dekker, Inc, 6082 (2006).
9. S. S. Shah and A. Mahmood, *J. Surf Sci Tecnol.,* **1,** 87 (1985).
10. S. S. Shah, A. Saeed and Q. M. Sharif, *Colloids Surf., A,* **155,** 405 (1999).
11. S. S. Shah, N. U. Jamroz and Q. M. Sharif, *Colloids Surf., A,* **178,** 199 (2001).
12. D. Mayers, *Surfactants in Cosmetics,* Marcel Dekker, Inc., New York, 47 (1997).
13. J. N. Phillips, *Trans. Faraday Soc. ,* **51,** 561 (1955).
14. M. Perez-Rodriguez, G. Prieto, C. Rega, L. M. Varela, F. Sarmiento and V. Mosquera, *Langmuir,* **14,** 4422 (1998).
15. I. Garcia-Mateos, M. Mercedes Velazquez and L. J. Rodriguez, *Langmuir,* **6,** 1078 (1990).
16. A. Savitzky and M. J. E. Golay, *Analytical Chemistry,* **36,** 1627 (1964).
17. K. Kalyanasundaram and J. K. Thomas, *J. Am. Chem. Soc.,* **99,** 2039 (1976).
18. Nicholas J. Turro and A. Yekta, *J. Am. Chem. Soc.,* **100,** 5951 (1978).
19. D. F. Evans and H. Wennerstrom, *The colloidal domain : where physics, chemistry, biology, and technology meet,* VCH Publishers, New York, 6 (1994).