Micillization Of Linear Alkyl Benzene Sulphonate In Dilute Aqueous Solution Of Glycine

Corresponding Author

N.D.Kandpal
Physical Chemistry Laboratory, Chemistry Department
Kumaun University,S.S.J Campus, Almora–263601
(Uttarakhand) (INDIA)
Email: narain_datt@rediffmail.com

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Co-Authors

Ritu Sing, S.K.Joshi, Kiran Kandpal
Physical Chemistry Laboratory,Chemistry Department
Kumaun University, S.S.J Campus, Almora–263601
(Uttarakhand) (INDIA)
Email: dr.s.k.joshi.alm@gmail.com

ABSTRACT

The micellar properties of linear alkyl benzene sulphonate(LABS) have been studied conductometrically in presence of a glycine in aqueous solution. The plots of conductance versus surfactant concentration, at different glycine concentrations in water show interesting features of surfactant- glycine binding. The critical aggregation concentrations(CAC), glycine saturation points(GSP) and binding capacity have been determined. The results are interpreted in terms of glycine-surfactant complex/micelle formed in different concentration ranges. © 2007 Trade Science Inc. - INDIA

INTRODUCTION

The micellization behaviour of surfactants in the presence of additives is of considerable interest for both practical and theoretical investigations[1]. The determination of critical micelle concentration in presence of additives is used as guide to study the solute solvent and solute-solute interactions in aqueous surfactant solutions[2]. These studies aids in the interpretation of the catalytic activity of functionalised micelle for enzymatic sites[3] and is useful in studying the biological and medicinal mechanism of any system[4, 5]. The work has been done on elucidating the various factors related to structural, kinetic and thermodynamic behaviour of surfactants in presence of different additives[6-10]. It is believed that the principal driving force for binding between an ionic surfactant and additive species are electrostatic interactions and the process is similar to that of micellization of surfactant[11]. Therefore, changes in the nature of binding of the surfactant to the additive specie in solution are generally evaluated by the micellization studies.

The linear alkyl benzene sulphonate, LABS, is chosen as the surfactant here because at present it is the most commonly used surfactant for laundry products. It is industrially important due to its excellent biodegradable tendency[12].

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Conductance measurements have earlier been used to study the interaction between surfactants and amino acids. The micellization of sodium dodecyl sulphate and dodecyl trimethyl ammonium bromide have been reported in water in the presence of amino acids such as glycine, alanine, valine and methionine [13]. Ultrasonic, viscometric and volumetric studies have been utilized to analyse the interaction behaviour of bio-molecules, carbohydrate and amino acids in aqueous solutions[14]. We have already reported the physicochemical properties[15] of LABS in aqueous solution and its micellization in presence of an electrolyte[2]. Amino acids are considered to be strong "structure breakers" in aqueous solution due to the zwitterionic nature. Therefore it is appropriate to study the micellization of LABS in presence of glycine in aqueous solution. The data obtained in this study may be useful in understanding the biochemical processes and newer biodegradable conditions for LABS in the light of environmental protection.

EXPERIMENTAL

Materials and methods

Demonized water was distilled twice with a small quantity of alkaline potassium permanganate. Then, water was distilled[16] in a quick fit apparatus with sulphuric acid. The specific conductance of the distilled water prepared for the present study was of the order of $<2\times10^{-6}\ \Omega cm^{-1}$. The LABS used in the study were obtained in the laboratory by sulphonation of linear alkyl benzenes(1PCL, $C_{10}=$ $14 C_{11}=31$ $C_{12}=37$ $C_{13}=16$ and $C_{14}=1x_0$) having an average molecular weight of 343. Surface tension measurements were made on an aqueous solution of LABS prepared by dissolving an accurately weighed sample in distilled water. No surface tension minima were found which implies that no surface-active impurities exist in the studied LABS samples. The techniques employed for test of impurities was same as reported in literature[17] .

Conductance measurements: Conductance measurement, were carried out on a digital conduc tivity meter(systronics type 306) with a sensitivity of 0.1% and a dipping type conductivity cell with a platinised platinum electrode of cell constant 1.0. All the measurements were made at constant temperature using thermostatically controlled water bath (Tonco, Kanpur) capable of maintaining the temperature constant to $\pm 0.1^0C$

RESULTS AND DISCUSSION

Experimental values of the specific conductivity of aqueous glycine solutions with different concentrations of LABS at 311K are reported in TABLE 1.

The specific conductivity data is linearly related to the surfactant concentration with two break points. The first break in the plot of specific conductivity versus surfactant concentration indicates the critical aggregation concentration, CAC, of glycine surfactant. Where the formation of micelle like aggregates takes place in the presence of glycine. The second break point observed with the increase in surfactant in the plot corresponds to glycine saturation concentration, where co-existence of dynamic equilibrium of regular micelles and surfactant-saturated glycine occur. Such second transition point in the conductance versus surfactant concentration plot is also reported[18] as CMC of polymer surfactant complex or polymer saturation point. The behaviour of aqueous solutions of glycine surfactant somewhat similar to observed[19] aqueous polymer surfactant solution.

TABLE 1 :Specific conductivity of aqueous LABS in presence of glycine at 311 K

S. No.	10^4[LABS] (mol dm⁻)	Sp Conductance (ms) Glycine (mol dm⁻³)				
		0.04	0.08	0.12	0.16	0.20
1	2.0	0.029	0.019	0.035	0.032	0.030
2	8.0	0.157	0.134	0.147	0.124	0.120
3	10.0	0.204	0.166	0.189	0.152	0.152
4	15.0	0.300	0.251	0.257	0.229	0.226
5	20.0	0.360	0.280	0.280	0.250	0.245
6	25.0	0.465	0.317	0.315	0.283	0.283
7	30.0	0.541	0.381	0.408	0.334	0.333
8	35.0	0.534	0.437	0.473	0.383	0.384
9	45.0	0.705	0.571	0.600	0.503	0.503
10	55.0	0.872	0.700	0.745	0.622	0.612
11	65.0	1.00	0.833	0.923	0.724	0.728
12	75.0	1.17	0.970	1.06	0.837	0.822
13	85.0	1.33	1.10	1.20	0.917	0.920

TABLE 2 : Glycine saturation point, GSP, CAC and binding capacities of glycine – LABS at 311 K

S.No.	Glycine (mol dm⁻)	GSP (mmol)	CAC (mmol)	Binding capacity mmol LABS/ mol glycine
1	0.04	3.5	3.0	12.5
2	0.08	2.5	1.5	12.5
3	0.12	2.5	1.5	8.3
4	0.16	3.0	1.5	9.4
5	0.20	3.0	1.5	7.5

Our observation suggested that the glycine in water behave as zwitter ion having NH_3^+ and COO^- groups. The water molecules are attached to the ions by electrostatic forces and form a hydration network having two-dimensional co-operative domains. The assumption is in a good agreement with the results of investigation[20] that the glycine behaves as "structure breaker".

The structure of water is considered in terms of three dimensional hydrogen bonded "flickering cluster" which retain much of the ordered structure of ice[1] . When self-interactions of both surfactants and water molecules cannot be compensated by their mutual interactions, the surfactant molecule tends to associate in a systematic pattern with the formation of micelle or an aggregate.

In this process the polar and nonpolar part of surfactant monomer are involved in non-covalent interactions different in nature and independently influenced due to the presence of zwitter ion in contact with water. In aqueous glycine solution the surfactant exist in monomeric form at lower concentration. At critical aggregation concentration, CAC, the self interaction of both surfactant and water molecule can not compensated by their mutual interactions, the surfactant monomer tends to associate in a regular pattern forming glycine surfactant aggregate or micelle. The conductivity of LABS solution at each dilution taken in this study decreases with the increase in glycine concentration up to 0.08mol dm⁻³ which confirms the formation of aggregate/complex between glycine and surfactant.

In the conductance versus surfactant concentration plots with the increase in surfactant concentration in presence of glycine, the second transition known as CMC of glycine, surfactant complex or the glycine saturation points GSP is obtained. The values of CAC and GSP at different concentrations of glycine are given in TABLE 2.

From the values of GSP and CAC, it is possible to calculate the amount of LABS molecule bound to per mole of glycine. The calculated values of binding capacity at each concentration of glycine are given in TABLE 2. The maximum binding in this case is 12.5m mole per mole of glycine in the concentration range 0.04mol dm⁻³ to 0.08 m mol dm⁻³. The results show that the critical aggregation concentration is not changed with incrase in concentration of glycine but the values of critical saturation concentrations have been found to fall in the range 1.5m mol to 3.5m mol of LABS. This indicates that this concentration range of LABS is sensitive to glycine concentration.

It has been concluded that due to the initial electrostatic interactions LABS leads the formation of pre-micelle attached to the glycine in the concentration range 1.5m mol to 3.5m mol. Only a limited number of LABS - glycine aggregates can be bound through such electrostatic interactions. Above a certain concentration of surfactant a saturation point is reached beyond this concentration micellization of surfactant leads to a regular trend of micro domains. These results may be ascribed to the surfactant activity in the presence of particular additive/fillers/co-surfactant system of commercial importance.

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