

MICELLIZATION STUDIES OF DODECYL BENZENESULFONIC ACID AND ITS INTERACTION WITH POLYVINYLPIRROLIDONE

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Abstract Dodecyl benzenesulfonic acid (DBSA) surfactant was used in the present study to find the effect of concentration on its electrical conductance in solution from 293–323 K above and below the critical micelle concentration (CMC). The micellization parameters *i.e.* degree of counter ion binding (β), aggregation number (n) and number of counter ion micelle (m) were measured. The interaction of DBSA with polyvinylpyrrolidone (PVP) was also studied at 293 K through conductance and surface tension measurements. A number of important parameters *i.e.* critical aggregation concentration (CAC), Gibb's free energy (ΔG) and binding ratio (R) were determined and the effect of NaCl on the CAC and polymer saturation point (PSP) was also investigated.

Keywords: Micellization; PVP; Interaction; Dodecyl benzene sulfonic acid (DBSA).

INTRODUCTION

Surfactants are playing a major role in everyday life for their many applications in biology, chemistry and pharmacy. Micellization phenomenon is responsible for all such kind of activities by the surfactant. The surfactants have the ability to form micelles (aggregates) when surfactant concentration in aqueous solution exceeds critical micelle concentration (CMC)^[1]. Many physical and electrostatic models are presented in great deal^[2–4] but still many questions remain unresolved, micellization parameters *i.e.* the micellization constant kc , the micellization aggregation number n , and the number of counter ions per micelle m , are not easily determinable. A number of ionic surfactants especially sodium dodecyl sulfate (SDS) and their micelle formation has been extensively studied and their micellization parameters were discussed in detail^[5, 6]. Dodecyl benzenesulfonic acid (DBSA) is a very important commercial surfactant which is used in household cleaning purposes but its micellization parameters are not available. Surface tension of linear alkyl benzenesulfonates was discussed in terms of their technical uses by Wustneck^[7] and the interaction of mixed micelle containing dodecyl benzene sulfonate with polyvinylpyrrolidone are published^[8] but still a comprehensive study regarding micellization parameters of this surfactant is lacking. It is well known that anionic surfactants form complexes with water-soluble polymers such as poly vinylpyrrolidone (PVP)^[9–11], nonionic surfactants on the other hand are generally considered not to interact with neutral water-soluble polymer. Different mechanisms however, for complex formation has been proposed which are, hydrophobic interaction^[12] and electrostatic interactions^[13, 14]. The latter interaction has been attributed to the surfactant counter ions, forming pseudo-polycation by coordinating with polymers^[15, 16]. It is clear that the interaction that governs the complex formation is highly system dependent. The interaction between polymer (anionic) and ionic surfactants has been extensively studied especially with sodium dodecyl sulfate (SDS) and polyethylene oxide (PEO) and PVP^[15, 16]. Light scattering^[17, 18], surface tension measurements, ¹³C-NMR and ESR spectroscopy^[19] of these systems are given in detail.

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As it is clear that literature is extensively available for SDS and its interaction with polymers like PEO and PVP. There is not much reported on dodecylbenzenesulfonic acid surfactant and its interaction with polymers. This prompted us to look at the micellization of this commercial surfactant and its interaction with polymer PVP. The work on micellization on DBSA and its interaction with PVP is reported here.

EXPERIMENTAL

Materials and Methods

Surfactant used in this work was DBSA [$\text{CH}_3(\text{CH}_2)_{11}\text{C}_6\text{H}_4\text{SO}_3\text{H}$]. It was commercially available in the form of liquid and was used without any purification or pretreatment. PVP, (M_w ca. 44, 000) was obtained from BDH Poole Limited, England. It was kept in oven at 50°C for half an hour before use. All the solutions of PVP *i.e.* stocks and diluted, were prepared in deionized water which was twice distilled from KMnO_4 in Pyrex still.

Conductivity Study

Several techniques have been used to examine non-ionic water-soluble polymer surfactant aggregates formed in solution. Two general methods for measuring surface tension and specific conductance, originally described by Jones^[20] and Schwuger^[21] were used to investigate the behavior of solutions containing PVP and the surfactant. In the present work conductivities of all solutions were measured by M-20E conductivity meter (Ogawa Seiki, Japan) with CG-210 PL electrode type and cell constant 1.035×10 in water-jacketed flow dilution cell. The temperature of the measuring cell was controlled by a water thermostat. Conductivity cell was fitted with electrode, temperature sensor and magnetic stirrer.

A 7.6×10^{-2} mol/L solution of DBSA was prepared in doubly distilled water and placed with in the same water bath where conductivity cell was already available at a specific temperature. 60 mL of doubly distilled water was put in the conductivity cell and 3 mL of stock solution was added into it drop wise from a burette. This process was repeated and consecutive data were recorded till the total volume reached 135 mL. The specific conductance was recorded immediately in order to avoid the hydrolysis of the DBSA as much as possible.

For studying polymer-surfactant interactions the polymer-surfactant solutions were mixed in different ratios and their conductivities were measured at 293 K. Different concentrations of NaCl salt *i.e.* 10 mmol/L, 20 mmol/L, 30 mmol/L, 40 mmol/L, 50 mmol/L were added to polymer surfactant mixtures of different combinations and their effect on the conductivities was studied. Critical aggregation concentration (CAC) was determined by plotting conductance versus concentration.

Surface Tension Study

For studying polymer-surfactant interactions, surface tension measurements were carried out at 293 K by using a stalagmometer in double wall water flow dilution cell. The surface tension of different polymer surfactant mixtures was determined by drop counting method. Effect of various concentrations of NaCl salt on the CAC was also studied. The surface tension was plotted as a function of concentration.

RESULTS AND DISCUSSIONS

The specific conductance of DBSA changes with total surfactant concentration and with temperature. Increase in conductance becomes sharp in the pre-micellar region with respect to the surfactant concentration and is reduced at certain concentration which reflects the CMC. The values of CMC were obtained from the intersection of the two lines extended from the pre-micellar and micellar phase for all the temperatures and are plotted against temperature in Fig. 1. The CMC of DBSA increases slightly with increase of temperature, which may be attributed to the de-micellization process because of the disruption of the palisade layer of the micelles. The degree of counter ion binding (β) was calculated from the ratio of slopes of micellar and pre-micellar phase following Evans^[22]

$$\beta = S_2/S_1$$

where S_2 and S_1 are the slopes for micellar and pre-micellar phases, respectively. The values so obtained were taken to be Eq.^[23] as

$$\beta = m/n$$

where m is counter ion number and n is aggregation number.

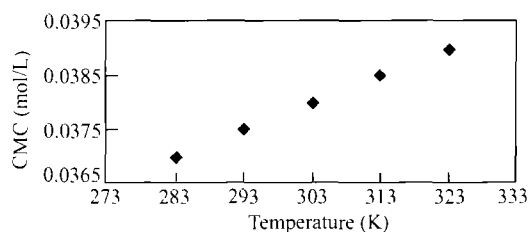


Fig. 1 Temperature dependence of critical micelle concentration.

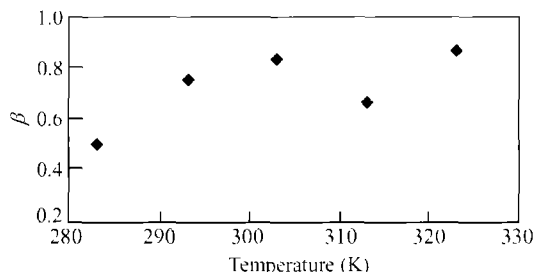


Fig. 2 Temperature dependence of counterion binding

β was found to be in the range of 0.50–0.87 *i.e.* ($0 < \beta \leq 1$). Counter ion binding of the surfactant is a peripheral phenomenon in which there exists equilibrium between bound counter ions with the free counter ion. β values generally increase with increase of temperature (see Table 1 and Fig. 2). This means that as the temperature increases the equilibrium is shifting toward more counter ion binding.

Table 1. Variation of micellization parameters (CMC, m , n , β) with temperature for dodecyl benzenesulfonic acid

Temperature (K)	CMC (mol/L)	m	n	$\beta = m/n$
283	0.0370	275.9	551.8	0.50
293	0.0375	396.8	554.1	0.75
303	0.0380	465.0	562.7	0.83
313	0.0385	384.7	577.1	0.67
323	0.0390	520.6	598.7	0.87

Aggregation number n was calculated for all the temperatures by using the following Eq.

$$n = (2.5229)l^3 \Delta d$$

where $\Delta d = d_2 - d_1$ and d_1 and d_2 are the densities of solvent and surfactant solutions, respectively, and l is the length of the hydrocarbon chain attached to the sulfonic acid group, which can be calculated from the Eq.:

$$l = 1.5 + 1.265n_c A^0$$

where n_c is the number of carbon atom attached to the hydrocarbon chain. The n values calculated for DBSA are higher than those available in the literatures for other surfactants^[24]. The reason is that DBSA has a longer hydrocarbon chain and can bind more molecules than other surfactants.

The specific conductance (K) for different concentrations of pure PVP in water at 293 K in the presence and absence of DBSA is plotted in Fig. 3. Figure 3(a) represents the conductance of pure PVP while Fig. 3(b) represent the conductance of PVP in the presence of various concentrations of DBSA. In the absence of surfactant the conductance linearly increases with concentration. The reason is that the number of mobile ions increases with concentration, which contributes to the total conductance, however, after it reaches some concentrations of PVP, the conductance becomes steady. This trend may due to the formation of polymer coil. This graph is used to illustrate the effect of surfactant addition on the conductance of polymer. Figure 3(b) shows the K values for a constant concentration PVP (9.9×10^{-2} mol/L) in the presence of various concentrations of DBSA in water at 293 K. The curve shows an inflection at certain concentration after which K

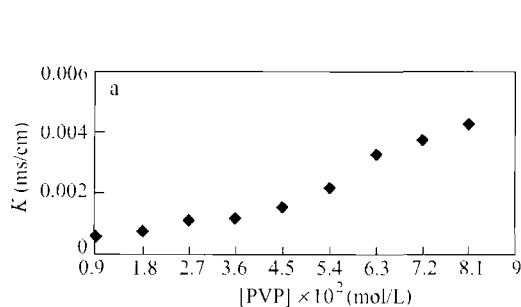


Fig. 3a Plot of conductance versus concn of pure polyvinylpyrrolidone

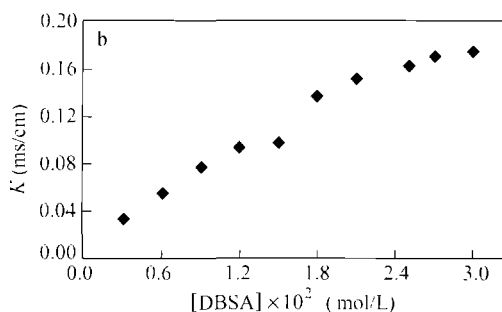


Fig. 3b Plot of conductance versus concn of DBSA at PVP = 0.099 mol/L

increases slowly with the increase of concentration of DBSA. The concentration at which this inflection occurs is called the critical aggregation concentration. In this plot at a constant PVP concentration of 9×10^{-2} mol/L, different concentrations of surfactant (in the range of 0.3×10^{-2} – 3.0×10^{-2} mol/L) were added. Upon the addition of surfactant the conductance increases much rapidly for some time but after that an inflection is observed at about 1.2×10^{-2} mol/L. This sharp inflection is the point at which the supposed aggregates are assumed to develop. A second inflection is also observed at about 2.4×10^{-2} mol/L and this point is called the polymer saturation point (PSP) at which most of the space is occupied by the polymer chains and there is no more vacancy available for the surfactant molecules to attach to the polymer chain. After this point, the addition of more DBSA will increase the conductance only and have no contribution towards the aggregate formation and remains in its original form in the mixture.

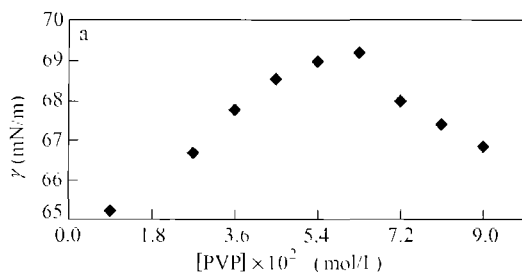


Fig. 4a Plot of surface tension versus concentration of pure polyvinylpyrrolidone

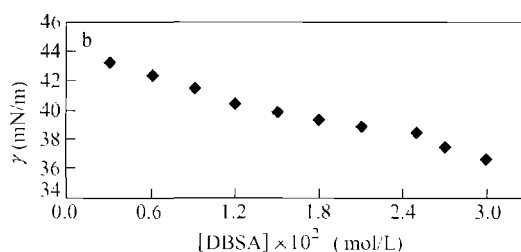


Fig. 4b Plot of surface tension versus concentration of DBSA at [PVP] = 0.099 mol/L

The surface tension (γ) for pure PVP and in the presence of different concentrations of DBSA is shown in Fig. 4(a). Figure 4(a) represents the surface tension of pure polymer PVP as a function of concentration. It could be observed that the surface tension of PVP increases with increase of concentration up to 6.3×10^{-2} mol/L, then it decreases, this decrease might possibly be due to the coiling of the polymer chain, which tends to reduce the surface tension. While Fig. 4(b) shows the γ of PVP in the presence of different concentrations (in the range of 0.3×10^{-2} – 3.0×10^{-2} mol/L) of DBSA. The curve obtained has inflections at certain points after which (γ) decreases slowly with increase of surfactant concentration. In this plot, at a constant PVP concentration of 9×10^{-2} mol/L, different concentrations of the surfactant were added. Upon the addition of surfactant, the surface tension decreases rapidly for some time but after that a inflection is observed at about 1.2×10^{-2} mol/L. This break is the CAC point at which the supposed aggregates are assumed to develop. A second inflection, the PSP is also observed at about 2.4×10^{-2} mol/L. The addition of DBSA to the polymer solution decreases the surface tension to about 20 mN/m, which is the property of a good surfactant. The CAC and PSP values obtained from both the conductance and surface tension measurements are in good agreement with each other, which shows the consistency of the two techniques.

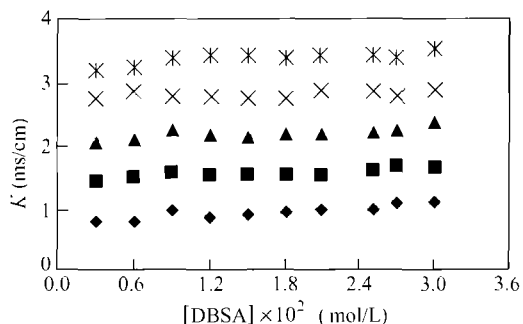


Fig. 5 Effect of NaCl on the conductance of PVP-DBSA system (PVP = 9.9×10^{-2} mol/L) at 293 K
 ◆ = 10 mmol/L, ■ = 20 mmol/L, ▲ = 30 mmol/L,
 × = 40 mmol/L, * = 50 mmol/L

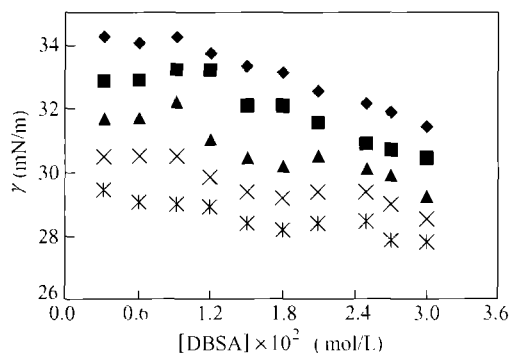


Fig. 6 Effect of NaCl on the surface tension of PVP-DBSA system (PVP = 2×10^{-2} mol/L) at 293 K
 ◆ = 10 mmol/L, ■ = 20 mmol/L, ▲ = 30 mmol/L,
 × = 40 mmol/L, * = 50 mmol/L

Figure 5 shows the specific conductance (K) values for polymer-surfactant system in the presence of various concentrations (10 mmol – 50 mmol) of the NaCl salt at fixed polymer concentration (9.9×10^{-2} mol/L). It could be observed that the conductance of the polymer-surfactant system increases linearly with the salt as the number of the mobile ions increases and they contribute to total conductance. However the CAC values are decreased upon the addition of the salt much obviously, afterward the effect of salt addition become less prominent and the CAC values decrease to about 0.9×10^{-2} mol/L. This trend is in close agreement with the values available in literature.

Figure 6 shows the surface tension (γ) values for polymer-surfactant system in the presence of various concentrations (10 mmol – 50 mmol) of the NaCl salt at fixed polymer concentration (9.9×10^{-2} mol/L). It could be observed that the surface tension of the polymer-surfactant system decreases linearly with the salt. However the CAC values decrease rapidly upon the addition of the salt, after which the effect of the salt addition becomes less prominent. The CAC values decrease to about 0.9×10^{-2} mol/L. This trend is in close agreement with the literature available. It has been reported that the addition of electrolytes increase the binding ratio of surfactant to polymer. Cabane and Duplessix^[25] reported an increasing binding ratio of SDS to PEO from 0.25, without salt, to 0.4 in the presence of NaBr. This increase is attributed to an extension of CAC-PSP range, mainly because the CAC markedly decreases indicating that association starts at much lower surfactant concentration. This behavior is similar to ionic micelle *i.e.* salts stabilize surfactant aggregates by effectively screening electrostatic interaction in micellar surface^[26]. This plot shows that up to 30 mmol/L addition of sodium chloride the CAC of the system decreases and after it again increases sharply. All earlier work believe that the CAC regularly decreases with the salt addition but in our system we found surprisingly that there is a threshold limit to the addition of salt after which it increases again.

Similarly the binding ratio R , which shows the number of surfactant molecules bind per chain of the polymer also linearly increases up to 30 mmol/L but after that it goes down again as the concentration increases. It seems that salt addition favors the aggregate formation up to certain limit and after that it adversely effects its formation. Probably, the charge on the alkali metal cation destabilizes the system in a way, which effects the aggregates formation. This fact can be further supported by the free energy (ΔG) values, which show the difference in Gibbs free energy when a surfactant molecule goes from micellar phase to an aggregation phase (calculated from equation $\Delta G = -RT \ln CAC/CMC$). The free energy values also increase up to 30 mmol/L, which favors the aggregate formation, and after that it decreases which is not favorable for aggregate formation. The justification for describing decrease in the CAC and CMC values is being due to the salt effect was made by Dubin and his co-workers^[27, 28] by suggesting a model for polymer-surfactant interactions in which the counter ion in the double layer coordinates with the non-ionic polymer to form a “pseudopolycation” which then complexes with the anionic micelles. In agreement with this postulated pseudopolycation formation, Sartori

et al.^[29] estimated the binding constant for PEO of several cations. In this contest the alkali metal cations creates a net positive potential at the surface and therefore, attracts a sulphate anion which acts as a nucleus for the development of micelle like aggregates. From this point of view, the increase in salt concentration leads to increasing positive potentials and, consequently, induces surfactant binding. The binding ratio “*R*” is the number of the surfactant molecule bound per chain of a polymer molecule and is calculated by the following formula

$$R = X_2 - CAC/c_p$$

where X_2 is a point at the surface tension curve where the surface tension of the mixture decreases sufficiently and c_p is the concentration of the polymer.

The *R* increases with increase of sodium chloride concentration up to 30 mmol/L and then decreases again. Table 2 shows the variation of *R* and ΔG values with sodium chloride concentration.

Table 2. Effect of sodium chloride on CAC, *R* and ΔG values of PVP and dodecylbenzenesulfonic acid system

NaCl (mmol/L)	CAC (mol/L)	<i>R</i> /monomer (Binding ratio per monomer)	ΔG (J/mol)
0	1.2×10^{-2}	0.1333	2775.7
10	0.9×10^{-2}	0.1666	3476.5
20	0.8×10^{-2}	0.1777	3763.4
30	0.7×10^{-2}	0.1888	4088.7
40	1.02×10^{-2}	0.1533	3171.6
50	1.1×10^{-2}	0.1444	2987.6

CMC = 0.0375 mol /L, $T = 293$ K, $c_p = 9 \times 10^{-2}$ mol/L, $X_2 = 2.4 \times 10^{-2}$ mol/ L

As far as the possibility of binding in this system is concerned, it can be attributed to the fact that both surfactant DBSA and carbonyl group of PVP ring have binding sites and has hydrogen-bonding capability.

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