Micellization of Dodecyl Benzenesulfonic Acid and its Interaction with Poly(Ethylene Oxide) Polymer

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Summary: The interaction between dodecyl benzene sulfonic acid (DBSA) with poly (ethylene oxide) (PEO) has been investigated at 293 K by conductance and surface tension measurements. The effect of concentration on the electrical conductance of DBSA in solution itself from 293-323 K above and below the Critical Micelle Concentration (CMC) was also studied. A number of important parameters i.e. critical aggregation concentration (CAC), Gibb's free energy (ΔG) and binding ratio (R) was also determined. The effect of NaCl on the CAC and Polymer saturation point (PSP) was also investigated. It was found that conductance of PEO increased with the introduction of DBSA.

Introduction

Surfactants are playing a major role in every day life with many applications in biology, chemistry and pharmaceuticals. Micellization phenomenon is responsible for all such kind of activities by the surfactant. The surfactants have the ability to form micelles (aggregates) when their concentration in aqueous solution exceeds critical micelle concentration (CMC) [1].

Many physical and electrostatic models are presented with great deal [2-4] but still many questions remain unresolved e.g., electrical conductivity of the micelle itself in aqueous solutions and 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 have been extensively studied and their micellization parameters discussed in detail [5, 6].

Dodecyl benzenesulfonic acid [CH_3 $(CH_2)_{11}C_6H_5SO_3H$] (DBSA) used in our homes for washing of clothes etc, is very useful commercial surfactant, but unfortunately very little attention has been given to this and there are very few literature reports available. The micellization parameters are not available for this surfactant. Surface tension of linear alkyl benzenesulfonate were discussed in terms of their technical use by Wustneck [7] and the interaction of mixed micelle containing dodecyl benzene sulfonate with poly(vinyl pyrrolidone) were also published [8] but still a comprehensive study regarding micellization parameters of this surfactant is lacking. It is known fact that many technical products include mixtures of both polymers and surfactants, so it is of interest to investigate the interaction between these components. Polymers are added to achieve different effects such as rheology control, surface modification and adsorption [9]. It is well known that anionic surfactants form complexes with water-soluble polymers such as poly-(vinylpyrrolidone) (PVP) [10, 11]. Nonionic surfactants on the other hand are generally considered not to interact with neutral water soluble polymer [9]. It is generally thought that anionic surfactants form micelle-like aggregates along the polymer chain. However, different mechanisms for this complex formation have 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 have been extensively studied especially with sodium dodecyl sulfate (SDS) and poly-(ethylene oxide) (PEO) and Poly (vinyl pyrrolidone) (PVP) [15, 16]. Light scattering [17, 18], surface tension measurements, C^{13} NMR and ESR

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spectroscopy [19] of these systems are given in detail.

Some recent reports showed the use of DBSA as dopant for the synthesis of polyaniline [22], preparation of oligopyrrole [23], in blends preparation [24] and in hydro gels [25]. Furthermore, literature is extensively available for SDS and its interaction with polymers like PEO and PVP. Very little is reported on dodecyl benzenesulfonic acid surfactant and its interaction with polymers. This prompted us to look at the micellization of this commercial surfactant and its interaction with PEO. The work with PVP is reported by our group [26] while the work on micellization on DBSA and its interaction with PEO is reported here.

Results and Discussion

The specific conductance (K) values for different PEO concentrations Cp in water at different temperatures are shown in Fig. 1.
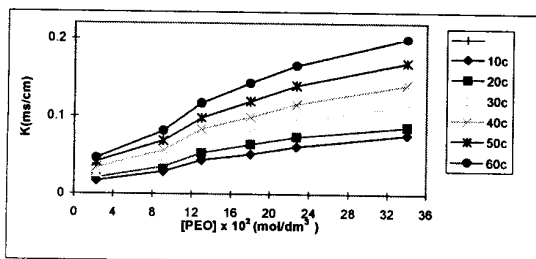

Fig. 1:   Conductance of PEO as a function of its concentration at different temperatures.

The plot shows that the conductance of the PEO linearly increases with increase in its concentration. This plot is used as reference to study the effect of surfactant dodecylbenzenesulfonic acid addition on the polymer PEO The (K) values for a constant PEO concentration $(22.7 \times 10^{-2}$ mol/l) in the presence of eight different concentrations of benzene sulfonic acid (in the range $0.6 \times 10^{-2} - 4.5 \times 10^{-2}$ mol/ l) are plotted in Fig. 2.

It was found that conductance of PEO increased with the introduction of DBSA. The curve obtained shows some break at certain concentration of the mixture. This concentration is called critical aggregation concentration (CAC) of the polymer
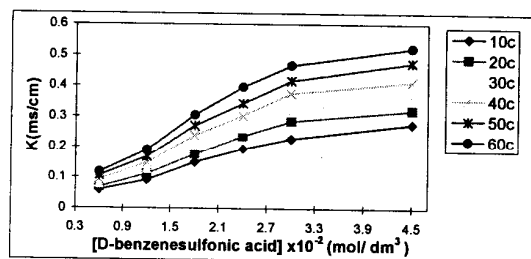

Fig. 2:   Conductance of PEO in the presence of various concentrations of DBSA.

surfactant mixture. For DBSA-PEO system the CAC point was noted to occur at 1.8×10^{-2} mol/ l. In our system like CMC, the CAC values are also not effected by the temperature changes. However the CAC value is lower than CMC, therefore we can say that PEO and DBSA interact strongly with each other. In presence of polymer a decrease in critical micelle concentration (CMC) is observed. It shows that in presence of polymer micelle formation is facilitated at lower concentration due to complex formation between polymer and surfactant. The specific conductance values (K) for a constant concentration of benzene sulfonic acid (i.e.3.0 $\times 10^{-2}$ mol/l) in the presence of eight different concentrations (in the range 2.2 $\times 10^{-2}$-34.0 $\times 10^{-2}$ mol/ l) of PEO are plotted in Fig. 3.
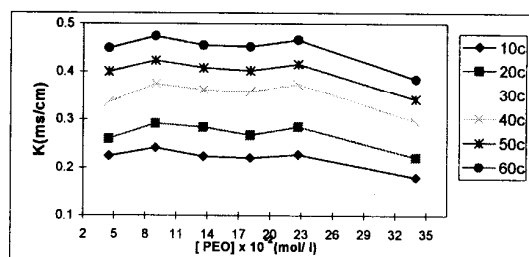

Fig. 3:   Conductance of DBSA in the presence of various concentrations of PEO.

It was found that the conductance decreases by the introduction of PEO, because the number of free molecules decreased which in turn decreased conductance.

For a simple polymer- surfactant system two break points were observed called here the critical aggregation concentration (CAC) and , polymer

saturation (PSP). The conductivity v/s [surfactant] plot usually exhibit three linear regions, below the CAC, between the CAC and the PSP, where micelle like aggregates are assumed to develop and above the PSP, where the co existence, in dynamic equilibrium, of polymer saturated by surfactant and regular aqueous micelles are postulated. At this CAC r (For the PEO-DBSA system the CAC was observed at 9 x10^{-2} mol/ l.) polymer is assumed to combine with surfactant molecules and to form these supposed aggregates. AT PSP the polymer chain is saturated and fully occupied by the surfactant molecule and no more vacancies are available for the surfactant molecules and thus it only serves to increase the conductance of the system constant.

Fig. 4 shows the specific conductance (K) values for the PEO and benzene sulfonic acid system in the presence of five different concentrations (10 mM, 20 mM, 30 mM, 40 mM, 50 mM) of the Sodium Chloride. The concentrations of the polymer and surfactant were kept constant ([PEO] = 13.5 x 10^{-2} mol/l) and [DBSA] = 1.8 x10^{-2} mol/ l) to study the effect of salt. It is found that the salt increases the conductance of the system very sharply. This is because the mobility of the ions increased due the addition of the salt. This curve has sharp break at certain points after which the effect of the salt becomes less pronounced and the conductance becomes constant.
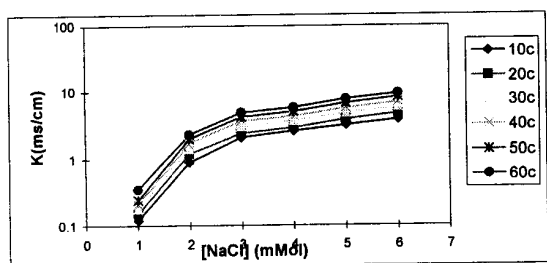

Fig. 4: Effect of salt on the conductance of PEO and DBSA system.

Fig. 5 shows the surface tension (γ) values for a constant concentration of PEO (22.7 x10^{-2} mol/ l) in the presence of eight different concentrations (in the range of 0.6 x10^{-2}-4.5 x10^{-2} mol/ l) of DBSA. It was found that surface tension of PEO decreased with the introduction of benzene sulfonic acid up to some extent after which the curve becomes smooth. The curve obtained having sharp breaks at certain

concentrations of the mixture (this is CAC). At this point a plateau like structure is produced, at which the surfactant is supposed to bind to the polymer chain to form polymer-surfactant complex. Dodecylbenzenesulfonic acid decreased the surface tension by about 27.07 m. N/m that is the property of a good surfactant. At this curve the CAC was observed at 1.8 x10^{-2} mol/ l, which aggress with the value obtained from conductance measurements. The ΔG which is associated with the binding interactions between polymer and surfactant and represents the difference in the Gibb's free energy of transfer from the aqueous phase to the miceller phase was calculated by the formula given in experimental section. The ΔG value was found out to be -9.90 cal/ K.mol at a temperature 283 K. Similarly the binding ratio R which is the number of surfactant molecule bound per chain of the polymer was calculated by the equation given (experimental section) The R-value calculated for PEO-DBSA system was 0.9/ monomer.
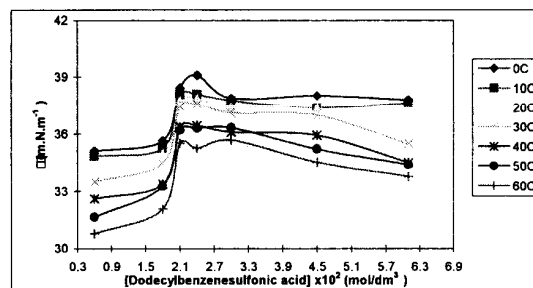

Fig. 5: Surface tension of PEO as a function of DBSA Concentration at different temperatures.

Fig. 6 shows the surface tension (γ) values for a constant concentration of benzenesulfonic acid (3.0 x10^{-2} mol/l) in presence of eight different concentrations (in the range of 2.2—34.0 x 10^{-2} mol/l) of PEO. At this curve the CAC break occurs at 9.0 x10^{-2} mol/l which is in close agreement with the value obtained from conductance measurements.

The Surface Tension (γ) values for the PEO and DBSA system in the presence of five different concentrations (10mM, 20mM, 30mM, 40mM, 50mM) of the Sodium Chloride salt are plotted in Fig. 7. The concentrations of the polymer and surfactant were kept constant ([PEO] =13.5x10^{-2} mol/l) and [DBSA] = 1.8 x10^{-2} mol/ l) to study the effect of NaCl. As for as the possibility of binding is

concerned, it can be attributed to the fact that both polymer and surfactant have binding sites and hydrogen binding capability.
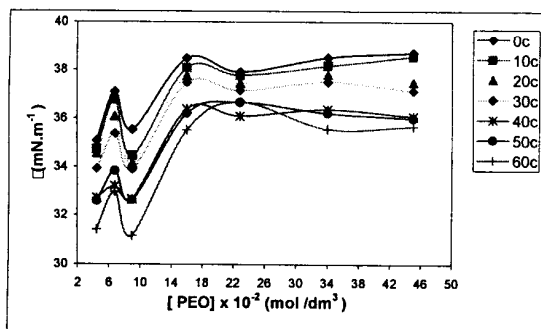

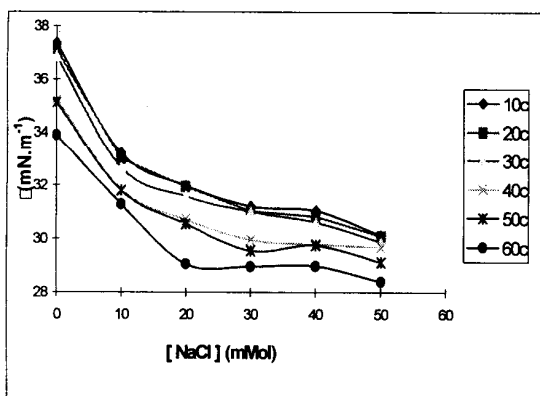Fig. 6: Surface tension of DBSA in the presence of various concentrations of PEO.

Fig. 7: Effect of salt on the surface tension of PEO and DBSA system.

Experimental

Materials and Methods

The surfactant used in this work was dodecyl benzene sulphonic acid (DBSA). [CH_3 $(CH_2)_{11}C_6H_5.SO_3H$]. It was commercially available in the market in the form of liquid and was used as such with out any purification or pretreatment.

Poly (ethylene oxide) (PEO) of molecular weight 100,000 was obtained from Aldrich Germany. The sample was in the form of white hygroscopic powder and was kept in oven at 50 $^\circ$C for half-hour before use.

Conductivity Study

Several techniques have been used to examine non-ionic water soluble polymer surfactant aggregates formed in solution. Two general methods surface tension and specific conductance, originally described by Jones [20] and Schwuger [21] were used to investigate the behavior of solutions containing PEO and surfactant. In present work conductivities of all solutions were measured by conductivity meter of Ogawa Seiki Japan M- 20E with electrode type C G- 210 PL and cell constant 1.035*10. The conductivities of solutions were measured at in water jacket flow dilution cell. The external temperature of the measuring cell was controlled by temperature regulated water bath. Conductivity cell was equipped with electrode, temperature sensor and magnetic stirrer.

Procedure

A 7.6 x 10^{-2} M solution of DBSA was prepared in doubly distilled water and maintained with in the same water bath where conductivity cell was already available at a specific temperature. 60 ml of doubly distilled water was taken in the conductivity cell and 3 ml of stock solution was added to it drop wise from the burette. This process was continued and stepwise data was recorded till the total volume of 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 *i.e.* 10 mM, 20 mM, 30 mM, 40 mm and 50 mM were added to polymer surfactant mixtures of different combinations and their effect on the conductivities was studied. CAC was determined by plotting conductance *v/s* concentration.

Surface Tension Study

For studying polymer-surfactant interactions Surface tension measurements were carried out at 293 K by using a stalagmometer in a double wall water flow dilution cell. The surface tension of different polymer surfactant mixtures was determined by counting the no of drops. Effect of various concentrations of NaCl salt on the CAC was also

studied. The surface tension was plotted as a function of concentration. Surface tension (γ) was determined by the using the formula

$$\gamma = \frac{N_{water} \times d_{polymer}}{N_{polymer} \times d_{water}} \times \gamma_{water}$$

where N_{water} = No. of drops of water,
$N_{polymer}$ = No of drops of polymer solution
d_{water} = Density of water
$d_{polymer}$ = density of polymer solution and
γ_{water} = Surface tension of water

CAC was determined by plotting conductance v/s concentration.

From the surface tension curve ΔG was also calculated, which is the difference in Gibb's free energy when a surfactant molecule goes from miceller phase to aggregation phase. The ΔG was determined by using the following formula.

$$\Delta G = - \frac{RT \ln CAC}{CMC}$$

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

$$R = X_2 \ CAC/ CP$$

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

Conclusions

A comprehensive study on interaction between PEO and DBSA was done using conductance and surface tension techniques. Conductance study on PEO-DBSA system showed the decrease in conductance of PEO with the introduction of DBSA. CAC was found to be at 1.8×10^{-2} mol/l which is not affected by temperature changes and it is situated below CMC showing strong interaction between the two. Addition of NaCl in the system increases conductance sharply. The surface tension studies on this system revealed a decrease in surface tension of about 27.0 m N/m showing DBSA

to be a good surfactant. There was good agreement between CAC values obtained by both conductance and surface tension studies. ΔG was found to be -9.90 Cal/Kmol at 283 K and the calculated value of binding ratio R (Number of surfactant molecules bound per chain of the polymer) was 0.9/monomer.

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