# Some Adsorption Characteristics of Sodium decyl and dodecyl Sulphates on the surface of Emulsifier-free Polymer Latex Particles

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بعض خصائص ادمصاص جزئيات ديسايل ودوديسايل كبريتات الصوديوم ( كمواد مستحلبة ) على سطح دقائق اللاتكس المحضرة بدون مادة مستحلبة

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تم في هذا البحث تعيين منحني الادمصاص لكل من المادتين المستحلبتين ، على سطح دقائق لاتكس البولي ستايرين المحضر بدون إضافة مادة مستحلبة، وذلك بتعيين تركيز المادة المستحلبة الموجود في حالة توازن مع تركيزها السطحي ( المدمص ) على سطح دقائق اللاتكس .

تم حساب التراكيز بعد إضافة المادة المستحلبة ( عند تراكيز أولية مختلفة ) وتركها في تماس مع اللاتكس ، في درجة حرارة ٣٣°م، الى حين حصول حالة التوازن ومن ثم فصل دقائق البوليمر بواسطة الطرد المركزي، وقياس التركيز بواسطة المطياف الضوئي بعد اضافة صبغة المثيلين الزرقاء واستخلاص المركب المعقد بواسطة مذيب عضوي .

ومن معرفة معدل قطر الجزئيات ( تم قياسه بواسطة جهاز التشتت الضوئي ) وحساب تركيز الجزيئات والمساحة السطحية الكلية، تم حساب المساحة السطحية الجزيئية للمركب المستحلب ( التي تشغلها جزيئة واحدة من المركب ) على سطح دقائق البوليمر، حيث وجد بأن جزيئة ديسايل كبريتات الصوديوم تشغل مساحة قدرها ٦٢ أنجستروم وتشغل جزيئة دوديسايل كبريتات الصوديوم مساحة قدرها ٣٧ أنجستروم بوجود ١و٠ مولاري من محلول كلوريد الصوديوم . في حين تشغل كل جزيئة منها مساحة سطحية محددة بمقدار ٥٩ و ٢٨ أنجستروم على التوالي ( المساحة السطحية المحددة هي المساحة التي تشغلها كل جزيئة من المادة المستحلبة على فرض أن جميع الجزيئات المضافة الى السطح يتم ادمصاصها ) .

تبين ايضا بأن وجود الالكتروليت يعمل على إزاحة المنحنيات نحو تراكيز توازن واطئة ويقلل من احتمالية حصول التحلل المائي الجزئي للمركبات المستحلبة .

**Key-words** : Sodium decyl and dodecyl sulphates.

# ABSTRACT

The adsorption characteristics of sodium decyl and dodecyl sulphates on polystyrene latex particles have been investigated.

The study involves the addition of known amounts of the surfactant to an emulsifier-free latex, allowed to equilibrate at 33°C, and separating the two phases by a high speed centrifugation. The remaining concentration of the emulsifier is complexed with a solution of methylene blue and extracted by an organic solvent . the absorption of the organic phase is then measured at 610 nm. The adsorption isotherm is determined from the concentration profile from which the amount of emulsifier adsorbed is calculated.

Knowing the average particle size, and consequently, number concentration of latex particles, allows the calculation of the moleculer area, $A_s$ of the emulsifier in the saturated monolayer at the interface. This was found to be as $62A^{o2}$ for the decyl sulphate and $37A^{o2}$ for dodecyl sulphate in the presence of 0.1 M NaCl. The limiting molecular area, $A_o$ were, respectively, 59 and 28 $A^{o2}$.

The presence of electrolyte displaces the isotherms to lower equilibrium concentrations and, greatly, reduces the extent of hydrolysis of the surfactants.

## Introduction

Surfactants play a key role in a wide variety of biological and technological processes . The underlining fundamental property of their various functions is the adsorption characteristics of their molecules at various interfaces [1]. Emulsion polymerization is one, among these important processes, in which it is important to control the emulsifier level sine too little may lead to instability ( coagulation ), while too much surfactant may lead to a secondary nucleation [2,3] . In both cases the amount and type of the adsorbed emulsifier is the key factor.

The kinetic treatment for most surfactant adsorption on polymer particles is based on the traditional Langmuir adsorption isotherm [4] expressed by the equation :

$$\frac{y}{y_m} = \frac{bC_e}{1+bCe} \quad \dots\dots\dots\dots (1)$$

Where $y$ = the amount of the adsorbate (mol cm$^{-2}$) in the adsorbed monolayer when the equilibrium concentration of the solute is $C_e$ .

$y_m$ = the amount of the adsorbate (mol cm$^{-2}$) in the completed monolayer (at the saturation point).

$b$ = a constant which is an exponential function of the free energy of adsorption, $\Delta G$

$$b = k_{exp} \frac{\Delta G}{RT} \quad \dots\dots\dots\dots (2)$$

Where k is a constant.

Equation(1) can be rearranged to give the equation :

$$\frac{C_e}{y} = \frac{1}{by_m} + \frac{C_e}{y_m} \quad \dots\dots\dots\dots\dots\dots (3)$$

From a plot of $\dfrac{C_e}{y}$ vs.$C_e$, the value of $y_m$ can be determined

from which the area occupied by one molecule of the adsorbate at saturation point can be calculated if the total surface area of the substrate is known.

The isotherm can be determined by the soap titration

technique of Maron et al.[5] which involves measuring the surface tension, or the conductivity of the diluted latex upon a gradual addition of a known concentration of the surfactant until the critical micelle concentration (CMC) is reached which indicates that the surface of the particles is saturated with the surfactant molecules. This method is easy and widely used but it suffers from uncertainities associated with the mechanism of adsorption during polymerization and its difference from the adsorption during titration; and also the possibility of desorption due to successive dilution. It is also well known (by experience) that it is difficult to obtain reliable results from titrating latices prepared with emulsifiers having high CMC values, even after introducing certain corrections (to account for volume fraction of the solids). This is mainly due to the high concentration of the free emulsifier in bulk solution, and the weak adsorption tendency of these emulsifiers.

To obviate these uncertainities, some investigations [6-8] have been recently performed to determine the characteristics of certain emulsifiers on emulsifier-free latices. These latices(stabilised by ionic-end groups from initiators) are also highly monodisperse with respect to particle size so that studies not be complicated by the effect of variations of particle size distributions between samples [7,9].

In this work the adsorption of two alkyl sulphates, sodium decyl(which has a relatively high CMC value) and sodium dodecyl sulphate(which has a moderate CMC value) have been investigated on an emulsifier-free polystyrene latex particles. Sodium dodecyl sulphate is widely used as a stabiliser in the preparation of many latex systems, and also in pharmaceuticals and cosmetics. Although several publications are available about its adsorption behaviour, no details are available about its adsorption characteristics on emulsifier-free latices. Sodium decyl sulphate is a less familiar emulsifier and rarely investigated although it is widely used in stabilising certain latex systems.

## EXPERIMENTAL
## Materials

Styrene monomer was a BDH product stabilized with t-butyl catechol. The inhibitor was removed by washing, successively, with 10% sodium hydroxide solution and deionized water, drying over calcium chloride for 24 hours, and vacuum distilled. The monomer was kept in a refrigerator until used.

Sodium decyl and dodecyl sulphates were specially pure BDH products which were further purified by extraction with petroleum ether and recrystallised from ethanol.

Methylene blue (ICI product) marketed as commercial zinc chloride double salt ,was purified by treatment with sodium carbonate solution, precipitated by dilute hydrochloric acid and recrystallised from methanol.

Potassium persulphate and sodium chloride were recrystallised from distilled water.

The extraction solvent was a 1 : 1 mixture of pure chloroform and ethyl acetate.

## Preparation of latex

The polystyrene latex, free of emulsifier, was prepared in a one-liter three-nicked flask fitted with double-surface condenser, mechanical stirrer and nitrogen inlet tube. Nitrogen was bubbled through the distilled water($470cm^3$) and styrene($50cm^3$), separately for about 30 minutes before mixing the two liquids in the reaction vessel. The vessel was placed in a water thermostat at 70°C. Potassium persulphate initiator (0.5 g dissolved in 30 $cm^3$ water) was added and stirring started. Polymerisation continued for 24 hours under an atmosphere of nitrogen and stirring at 350 rpm.

The latex was then filtered through a sintered-glass crucible. Two diluted samples were prepared and their average sizes were determined by measuring the angular distribution intensity of the scattered light by a light-scattering photometer( brice-phoenix).

## Adsorption

The adsorption of each emulsifier on polymer latex was carried out at 33°C in a water bath fixed at this temperature typical analysis was as follows.

1.0 $cm^3$ of the latex was placed into a clean thick-glass tube ( 5 tubes at each run with one blank). To each tube ,2.0 $cm^3$ of the emulsifier solution of a known concentration and

2.0 cm$^3$ of 0.1 M sodium chloride solution ,were added. The tubes were stoppered and placed in a water bath fixed at 33°C and left for one hour to achieve equilibrium between the adsorbed emulsifier and the free emulsifier in solution. The polymer was then separated by a high-speed centrifugation ( 22000 rpm ) at 33°C, in a temperature-controlled centrifuge.

1.0 cm$^3$ of the aqueous phase was then transferred to another tube to which 1.0 cm$^3$ of methylene blue solution and 0.5 cm$^3$ of 0.01 M hydrochloric acid, were added ( the acid was added to obviate hydrolysis of the dye, the pH was about 3.5 ). The colored complex was then extracted by a mixture of chloroform and ethyl acetate with the aid of a wrist-action shaker, and separated by centrifugation. The absorbance was then measured at 610 nm by means of a UV-visible spectrophotometer (spectronic-21 UV-D, Fisher) against a reference cell containing the solvent.

**Hydrolysis**

The acid-catalysed hydrolysis of the emulsifiers, in the presence and absence of electrolyte, was followed by means of a digital pH-meter (RL 150, Russel ). The pH was adjusted to within 0.01 by addition of dilute HCl.

**RESULTS**

**Total Surface Area (TSA)**

To calculate the amount of emulsifier adsorbed per unit area, y, the total surface area of the particles, present per unit volume of the latex under the conditions of adsorption, must be known. TSA is calculated from the number of particles per unit volume, which is in turn determined from the average particle diameter of the latex particles and the initial concentration of the monomer. Table-1 summaries the results of such calculations.

**Concentrations of the Adsorbed Surfactant**

**Table -1 : Calculation of the total surface area ( TSA ) and the concentration of latex particles.**

| Parmeter | Value and Unit |
|---|---|
| Average diameter of a single particle | 114 nm |
| Surface area of single particle ($4 \Pi r^2$)[a] | $4.049 \times 10^{-10}$ cm$^2$ |
| Volume of a single particle($4/3 P r3$) | $7.66 \times 10^{-16}$ cm$^3$ |
| Number of particles in the original latex | $1.095 \times 10^{14}$ cm$^{-3}$ |
| Number of particles in the diluted latex | $2.19 \times 10^{13}$ cm$^{-3}$ |
| TSA/cm$^3$ of latex | $8.867 \times 10^3$ cm$^2$ |

a )   r is the radius of the particle.

The concentration of surfactant remaining in the solution after adsorption i.e., the equilibrium concentration, $C_e$, was interpolated from a previously established calibration curve of absorbance vs. concentration.

The decrease in concentration due to adsorption, $C_{ads}$ (in mol dm$^{-3}$) is calculated :

$$C_{ads} = C_i - C_e \qquad \ldots\ldots\ldots\ldots\ldots \quad (4)$$

Where $C_i$ is the initially added concentration of the emulsifier.

The surface concentration, y (in mol cm$^{-2}$) corresponding to each initial concentration is calculated from the expression:

$$y = \frac{C_{ads}}{TSA} \times \frac{v}{1000} \qquad \ldots\ldots\ldots\ldots\ldots \quad (5)$$

Where v is volume (cm$^3$) of surfactant solution added to the latex sample at the onset of adsorption,

The adsorption is some times expressed by the number of moles of the emulsifier adsorbed per unit mass of the polymer, G , caclulated by the expression:

$$\Gamma(\text{mol/g}) = \frac{C_{ads}(\text{mol cm}^{-3})}{x_m \, \rho(\text{g cm}^{-3})} \qquad \ldots\ldots\ldots\ldots \quad (6)$$

Where $x_m$ = the mass fraction of monomer in the recipe used for the preparation of the latex (in the present work $x_m = 0.08$).

$\rho$ = density of the polymer (1.04 for polystyrene[10]).

Some selected values of G for both emulsifiers are given in table-2 together with their corresponding initial and equilibrium concentrations.

**Table -2 Some adsorption characteristics of sodium decyl and dodecyl sulphate. on the surface of polystyrene (emulsifier-free) latex particles at 33°C**

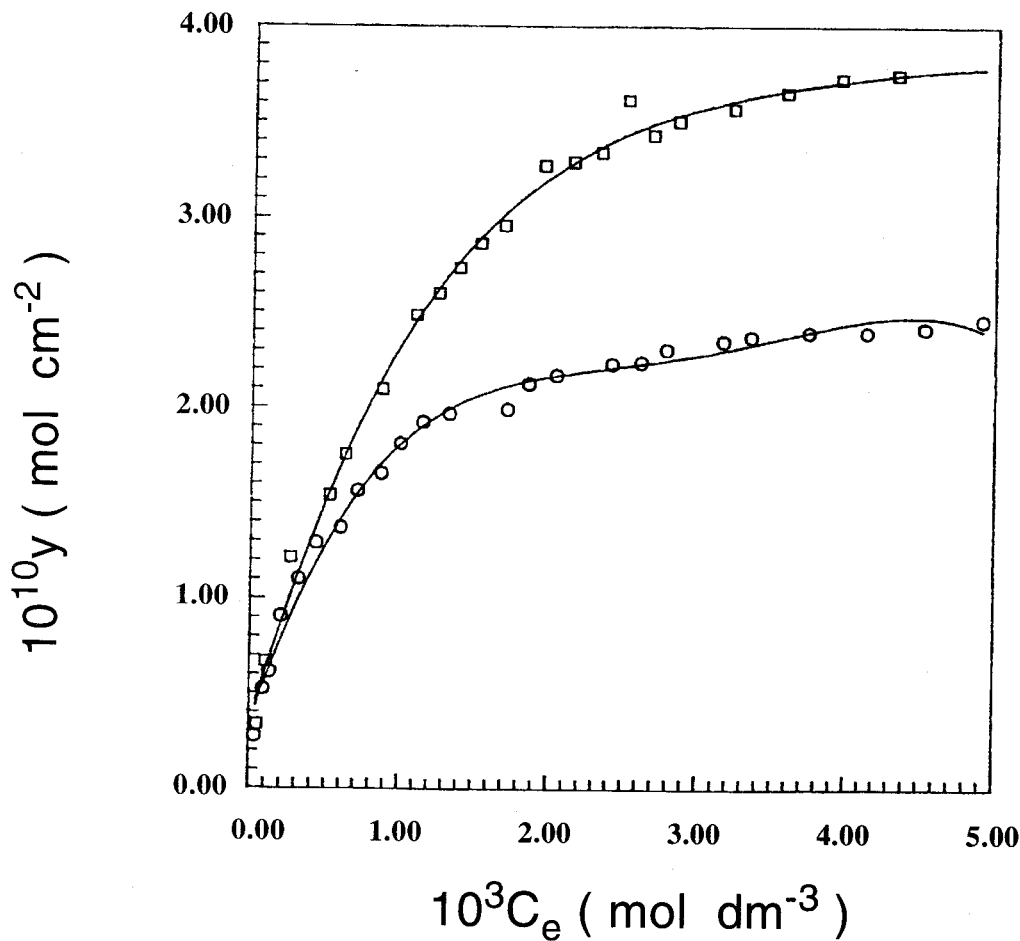| $10^3C_i$(mol dm$^{-3}$) | sodium decyl sulphate. | | Sodium dodecyl sulphate: | |
|---|---|---|---|---|
| | $10^3 C_e$(mol dm$^{-3}$) | $\Gamma$ (mol g$^{-1}$) | $10^3C_e$(mol dm$^{-3}$) | $\Gamma$ (mol g$^{-1}$) |
| 0.16 | 0.040 | 1.442 | ......... | ..... |
| 0.20 | ....... | ......... | 0.052 | 1.779 |
| 0.40 | 0.130 | 3.245 | 0.105 | 3.546 |
| 0.80 | 0.313 | 5.853 | 0.263 | 6.454 |
| 1.20 | 0.595 | 7.272 | 0.520 | 8.173 |
| 1.40 | 0.710 | 8.293 | 0.625 | 9.315 |
| 1.80 | 1.000 | 9.639 | 0.874 | 11.130 |
| 2.00 | 1.150 | 10.241 | ....... | ........ |
| 2.20 | 1.330 | 10.482 | 1.100 | 13.253 |
| 2.60 | 1.720 | 10.602 | 1.390 | 14.543 |
| 2.80 | 1.860 | 11.325 | 1.530 | 15.264 |
| 3.00 | 2.040 | 11.566 | 1.690 | 15.745 |
| 3.40 | 2.414 | 11.880 | 1.950 | 17.428 |
| 3.80 | 2.780 | 12.289 | 2.330 | 17.668 |
| 4.00 | 2.980 | 12.289 | 2.510 | 17.909 |
| 4.40 | 3.350 | 12.620 | 2.850 | 18.630 |
| 4.80 | 3.740 | 12.740 | 3.220 | 18.990 |
| 5.20 | ........ | ........ | 3.580 | 19.471 |
| 5.60 | 4.530 | 12.892 | 3.590 | 19.832 |
| 6.00 | 4.910 | 13.133 | 4.340 | 19.952 |

**Figure-1 :** Adsorption isotherms of sodium decyl sulphate (O), and sodium dodecyl sulphate (□ ),on polystyrene emulsifier-free latex at 33°C in the presence of 0.1 mol dm$^{-3}$ NaCl.

Figure-1 shows the adsorption isotherms plotted as y vs. Ce.

## Molecular Area in the Saturated Monolayer

Figure-2 represents the Langmuir plots (eq-3) from which the concentration of the surfactant adsorbed at the saturated monolayer ($y_m$) is calculated from the slope of the straight line. The value of the intercept can be used to calculate, b, of eq-3. The area (in $A^{o2}$), occupied by one molecule of emulsifier at the solid-liquid interface in the saturated monolayer, $A_s$, is calculated from the following expression.:

$$A_s = \frac{10^{16}}{y_m \cdot N_A} \qquad \qquad (5)$$

Where $N_A$ is the Avogadro's number.

The final results of $y_m$ and $A_s$ for both emulsifiers are summarised in table-3. This table also gives the ratio Ao/As where $A_o$ is the limiting molecular area corresponding to the area occupied by emulsifier molecule on the particle surface assuming all the emulsifier is adsorbed. $A_o$ is determined from the intercept of figure-3. This figure represents the variation of the molecular area ( during the adsorption ) with equilibrium concentration of each emulsifier. The above ratio is a measure of the relative degree of adsorption saturation. A highly saturated surface would be indicated by a ratio approaching a value of 1.0 (this point is further discussed in the next section).
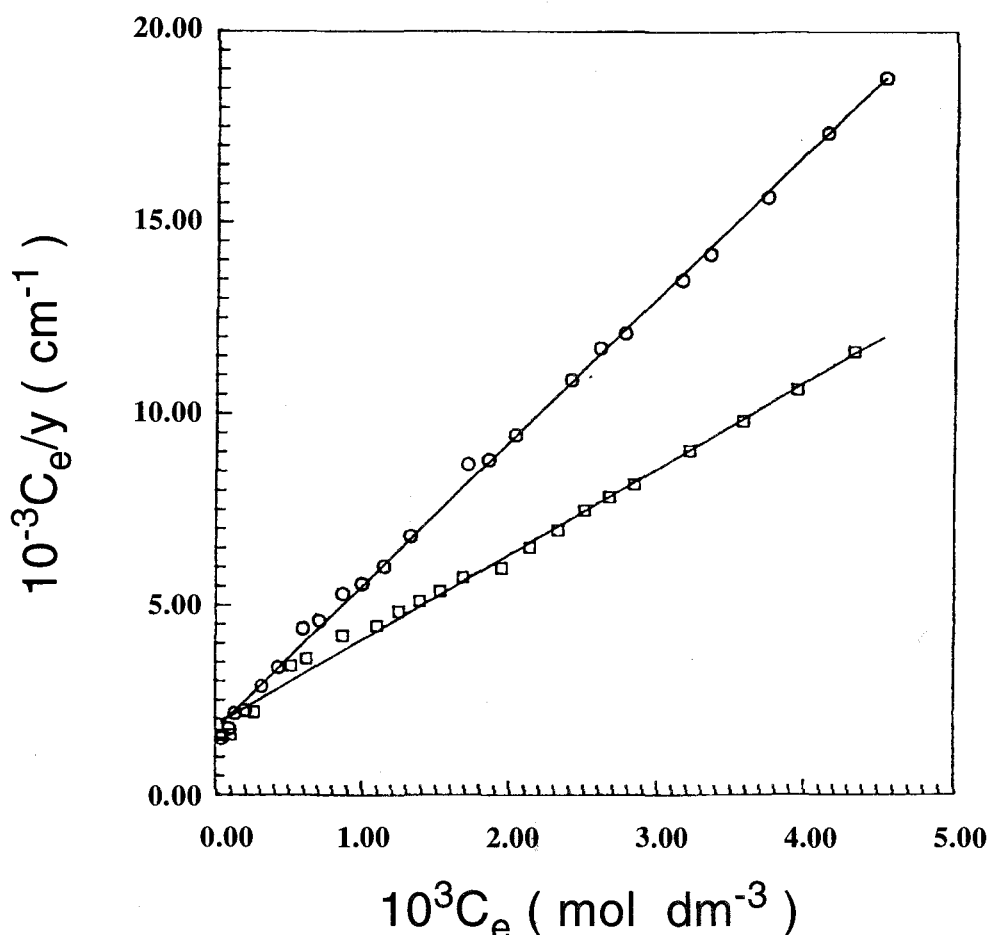
**Figure-2 :** Langmuir linear plots (eq.3), for the adsorption of sodium decyl sulphate (O), and sodium dodecyl sulphate ( □ ), at polystyrene latex/water interface at 33°C in the presence of 0.1 mol dm$^{-3}$ NaCl ( See table-3 for the numerical values of the slopes and intercepts ).

## Discussion : -

Figure- 1 shows that both emulsifiers have normal langmuir isotherm,which indicates a relatively low concentration at which saturation is achieved. Sodium dodecyl sulphate which has a lower CMC and a higher chain length adsorbs more strongly, its equilibrium concentration, at which saturation is achieved, is nearly the same as its CMC at the concentration of electrolyte used (0.1 M NaCI). The literature values of CMC in the presence and absence of electrolyte are 8 - 8.3 x 10$^{-3}$ mol dm$^{-3}$ in pure water and 1.5 x 10$^{-3}$ mol dm$^{-3}$ in a solution of 0.1 M NaCI ( 10,11 ) . The corresponding values for Sodium decyl sulphate are 33.0 x 10$^{-3}$ and 9.0 x 10$^{-3}$ mol dm$^{-3}$. It is evident from figure-1 that saturation of the particles surface by Sodium decyl sulphate is achieved at concentration much below its CMC which indicates less tendency for adsorption. This is also confirmed by the relatively high value of the ratio $A_0/A_s$ (tabel 3). This ratio is a characteristic of the degree of saturation but not ( as some

authors confuse ) the degree of filling of the adsorbed layer (density of packing of emulsifier molecules on the surface). A lower ratio may correspond to a more dense, stronger adsorbed molecules, and higher stability of the latex. The isotherm of Sodium decyl sulphate indicates that micellisation is not always a condition to achieve adsorption saturation especially for emulsifiers with high CMC.

The difference in the adsorption tendecy of the two emulsifiers ( reflected by the large difference in $A_s$ ) is mainly a result of the difference in the free energy change associated with the transfer of the methylene group, of the hydrocarbon part of the surfactant, from an aqueous environment to an oil-like environment on the surface of the polymer which is similar to the process of micellisation in which the methylene group is transferred to the more hydrophobic interior of the micelle. this change in free energy is reported (12) to be -1.1 KT per-CH$_2$- per molecule, where K is Boltzmann's contant.

**Table-3 : Adsorption Parameters Calculated from Figures 2 and 3[a].**

| Parameter | Sodium decyl sulphate | Sodium dodecyl sulphate |
|---|---|---|
| $10^{10}\, y_m$ ( mol cm$^{-2}$) | 2.66 | 4.47 |
| $10^{-6}$ (mol$^{-1}$ cm$^3$) | 2.17 | 1.22 |
| $A_o(A_o^2)$ b) | 59 | 28 |
| $A_s(A_o^2)$ | 62 | 37 |
| $A_o/A_s$ | 0.95 | 0.76 |

a) The slopes and intercepts of figuer-2 were:

for soduim decyl suphate:

slope $= 3.754 \times 10^9 \, cm^2 \, cm^{-1}$

intercept $= 1.730 \times 10^3 \, cm^{-1}$

for sodium dodecyl sulphate:

slope $= 2.239 \times 10^9 \, cm^2 \, mol^{-1}$

intercept $= 1.836 \, cm\text{-}1$

b) Interceptes of figure-3.

The choice of emulsifiers for many applications depend on their adsorption characteristics, Natural rubber latices, for example, are very often stabilised by adding approperiate amounts of certain ionic emulsifiers such as fatty acid soaps and alkyl sulphates ( 12, 13 ). The two important factors which govern the stability of any latex, stabilised by ionic emulsifiers, are the strength of adsorption and electrostatic repulsion between the adsorbed ions. The former increases with the chain length while the latter decreases. Abalance, between these two opposite effects, is to use an emulsifier in the middle of a homologous series.
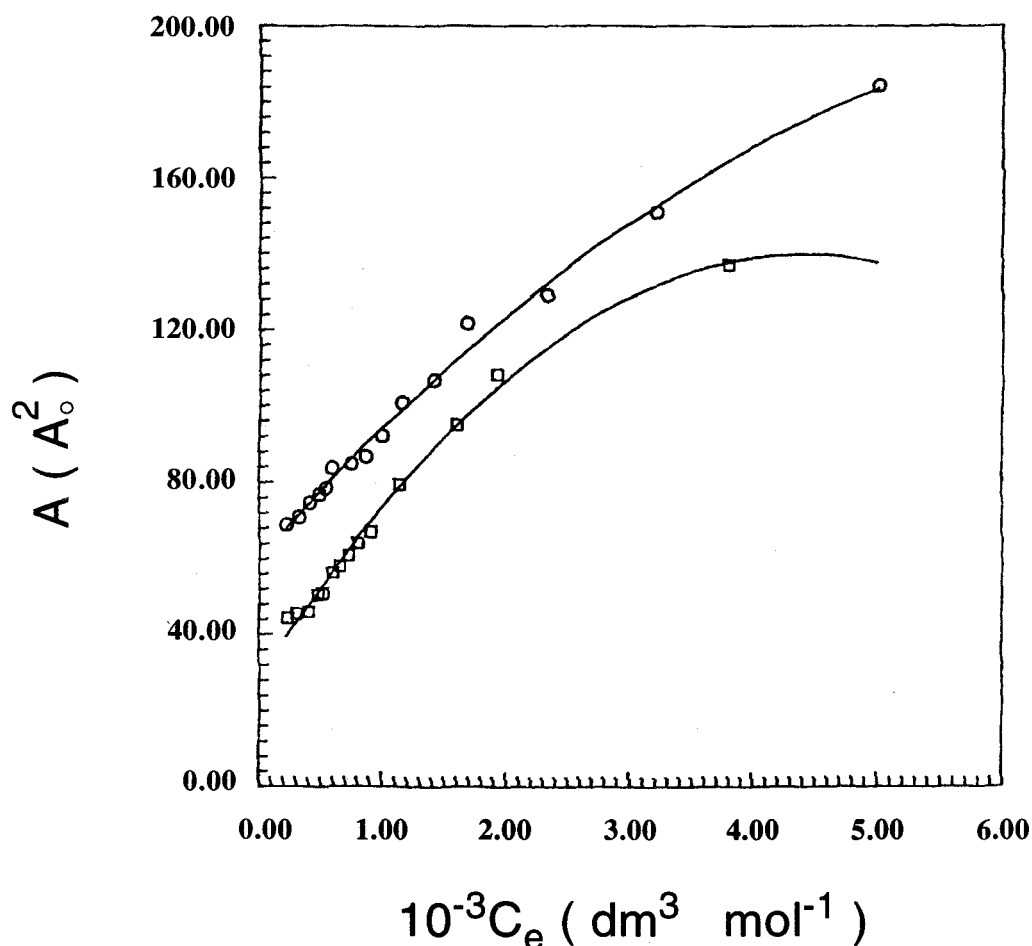


Figure-3 : Area per molecule versus $\dfrac{1}{Ce}$ for sodium decyl sulphate / polystyrene system (O) and sodium dodecyl sulphate / poly-styrene system ( □ ).

$$10^{-3}C_e \, ( \, dm^3 \quad mol^{-1} \, )$$

Sodium dodecyl sulphate seems to be a good choice since it satisfies both conditions reasonably well. It is, probably for this reason that this emulsifier is widely used to stabilise polymer latices and many other colloidal dispersions. In previous investigations (14 , 15) on the stability of polystyrene latices, potassium dodecanoate (12 carbon atoms fatty acid soap) was more effective than both the decanoate (10 carbon atoms) and the octadecanoate (18 carbon atoms) for the same reasons mentioned above .

### Hydrolysis and the Effects of Electrolyte

The problem of acid-catalysed hydrolysis of alkyl sulphates, to corresponding alcohols, may arise during the course of adsorption since the process was conducted in acidic medium (pH was abut 3.5 ), On the other hand, adsorption is probably very strong at pH < 4 due to the possible formation of hydrogen bonding between the protons and polar groups of the surfactant molecules ( 16 ).

However, the rate of hydrolysis is reduced to a great extent as the ionic strength is increased by addition of inorganic electorlyte. Electrolyte reduces the surface potential of the micelle, by increasing the strength of counter-ion binding, leading to a decrease in proton concentration at the micelle surface.

Figure-4 represents the data obtained by investigating the extent of hydrolysis of sodium dodecyl suphate at different levels of electrolyte. It is evident from the figure that hydrolysis is suppressed at the level of electrolyte ( 0.1 M ) used during the adsoption experiments and only little effect is produced . However, the results suggest that the pure emulsifier can hydrolyse significantly when left for some time in an acidic medium. Since this emulsifier is widely used as a sabiliser and a solubiliser for some drugs it is necessary to take into account these characteristics since hydrolysis may lead to a deterioration and spoilage of the acidic drug. Addition of little electrolyte may be useful if it does not produce any other effects.

No significant hydrolysis was detected in the case of sodium decyl sulphate even when its solutions were left to stand for several weeks. Moreover, for this emulsifier the adsorption saturation is achieved below its CMC and
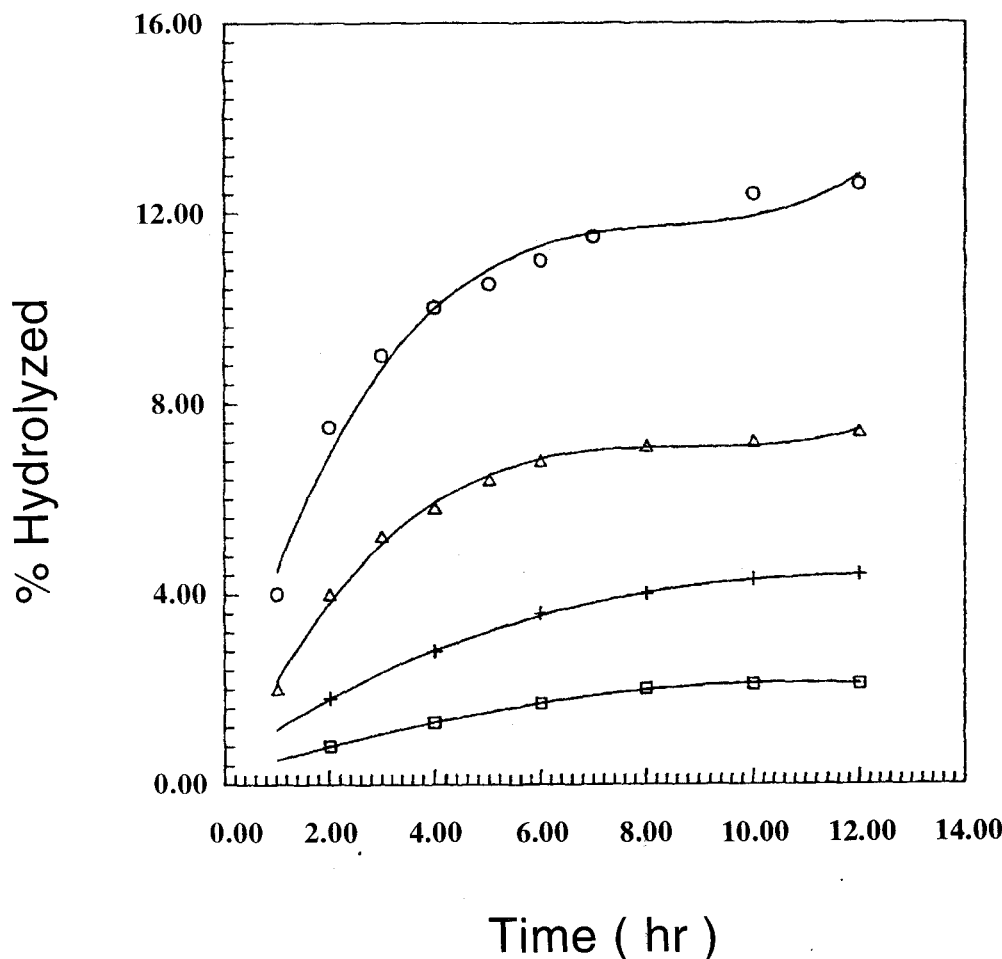


Figure-4 : Effect of electrolyte ( NaCI ) on the extent of hydrolysis of sodium dodecyl sulphate at 25 °C. The concentrations of NaCl : ( O ) 0.00 ( D ) 0.025, ( + ) 0.050 , and ( □) 0.100 mol dm .

therefore the hydrolysis effect is neglegible. The charge screening effect of electrolyte leads to a reduction in the electrostatic repulsion between latex particles; the result is an attractive interaction between particles, so that more soap can be adsorbed, with its molecules oriented tightly; on the surface of the particles. A consequence of this effect is a decrease in the molecular area, $A_s$ .

Some recent investigations (8, 17) of the adsorption of ionic emulsifiers on polymer latex particles show that low concentrations of electrolyte remove, or reduce the thickness of the hairy layer believed to be formed at the surface of polymer particles ( extending into solution due to electrostatic repulsion between the ionic groups ) with a thickness of about 7 nm. A consequence of the removal of this layer would be a decrease in the hydrodynamic radius of the latex particles, and consequently the total surface area. This is an anomalous behaviour since most investigations indicate an increase, rather than a decrese, in the size of latex particles caused by the presence of inorganic salt, mostly due to increase in the rate of coalescence of latex particles ( 18 - 21 ). In our recent investigation (22) electrolyte in the range 0.1 - 0.2 M produced only a little increase in the hydrodyanmic diameter of polystyrene latices, prepared by seeded emulsion polymerisation, using sodium dodecyl sulphate as emulsifier.

This probably support the hairy layer model since the concentration of electrolyte was relatively high so that the increasing effect of coalescence, on the size may have balanced the decreasing effffect of removing the hairy layer i.e, a possible decrease in hydrodnamic diameter would have been observed if the electrolyte concentrations were lower, although this is open to further experimental verification.

## Conclusion

Adsorption of surfactants on an emulsifier-free latex, provides a reliable method for the determination of adsorption isotherm and molecular area in the saturated adsorption layer.

The adsorption saturation of a high CMC emulsifier (such as sodium decyl sulfate) may be achieved before micellisation due to its weak adsorption tendency. Electrolyte reduces the extent of hydrolysis of the alkyl sulfates and tends to lower $A_s$, leading to an increase in the packing density of the emulsifiers molecules on the surface of polymer particles.

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