ADSORPTION OF LONG CHAIN ELECTROLYTES ON CARBONS

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Until recently little work has been done on the adsorption of long chain electrolytes such as surfactants on carbon surfaces (1-6). Since these compounds are invariably present in the industrial waste water, the problem has assumed considerable importance from the point of view of water pollution control. The present work describes some of the adsorption isotherms of surfactants on different types of carbons and attempts to explain the mechanism of adsorption of cationic and anionic surfactants.

The adsorption isotherms of cetyl trimethyl ammonium bromide (CTAB), a cationic surfactant, sodium dodecyl benzene sulphonate and sodium di-(2 ethyl hexyl) sulpho succinate (SDS), both anionic surfactants from their aqueous solutions on a series of sugar charcoals and several commercial grade carbon blacks were determined at 30°C in the concentration range 5×10^{-5} to 25×10^{-3}M. The results for CTAB and SDS on charcoals in the concentration range upto 2.5×10^{-3}M are shown in Figs 1 and 2. The adsorption tends to reach a limiting value after this concentration and therefore has been omitted in the figures. The distinctive feature of these isotherms is the existence of a pronounced maxima at a concentration of about 1.5×10^{-3}M for CTAB and 1.8×10^{-3} M for SDS.

The shape of the isotherm is independent of the nature of the carbon surface although the magnitude of adsorption is different for different carbons at each concentration. The adsorption of the anionic surfactant, SDS, increases with increase in the temperature of outgassing while that of CTAB decreases with increase in the temperature of outgass ing upto 800°C and increases thereafter. It appears that whereas the adsorption of an anionic surfactant onto a carbon surface is related inversely to the amount of associated oxygen, the adsorption of a cationic surfactant is related directly to the amount of associated oxygen.

Broadly speaking the isotherms could be split up into three parts: a gradual increase in adsorption with increasing concentration upto 1×10^{-3}M for CTAB and 1.25×10^{-3}M for SDS; a steep almost linear rise in adsorption with increasing concentration in the range $1 \times 10^{-3} - 1.8 \times 10^{-3}$M; and a symptotic fall at higher concentrations ultimately ending up towards a limiting value. The discontinuities in the curves and the occurrence of the maximum were verified by repeating the adsorption experiments. The duplicate values were found to be in good agreement indicating that these breakes are real.

It is interesting to correlate the adsorption isotherms with the formation of aggregates in solution i.e., with the critical miscelle concentration (cmc). The cmc was determined by the conductance measurements of the solutions of surfactants (7). The conductance - concentration curve shows a break at cmc.

It is seen that the break in the adsorption curve for all the surfactants agree very closely with the cmc. However, the maxima in the adsorption curve in each case occur at considerably higher concentrations. It is also evident that the characteristic break in the adsorption curve occurs almost at the same concentration irrespective of the nature of the carbon surface. This shows that the cause for it lies in the solution and not in the nature of the adsorbent surface.

Rates of Adsorption: The rates of adsorption were studied for time intervals varying between 30 minutes and 24 hrs. on several samples and several concentrations. The adsorption was rapid in the first few hours and was atleast 50 per cent complete within first 2 hrs. By the end of 12 hrs. the adsorption was almost complete. The rate of adsorption increased with increase in temperature.

Heats of Adsorption: The isosteric heats of adsorption for the adsorption of CTAB was determined from the adsorption isotherms at 30 and 40°C on a sample of carbon black. The shape of the isotherm was similar at the two temperatures. The heat of adsorption was of the order of 900 cals per mole indicating physical nature of the adsorption.

Influence of pH on adsorption: A few

experiments were carried out by controlling the pH of the surfactant solution by the addition of equal amounts of solutions of HCl or NaCl or NaOH of known strengths. Though the pH of the mixed solutions did not remain strictly constant over the whole ra range of concentrations for one experiment, the change was slight (0.1 - 0.4 pH units). It was found that the adsorption of CTAB decreases on increasing the pH of the solution.

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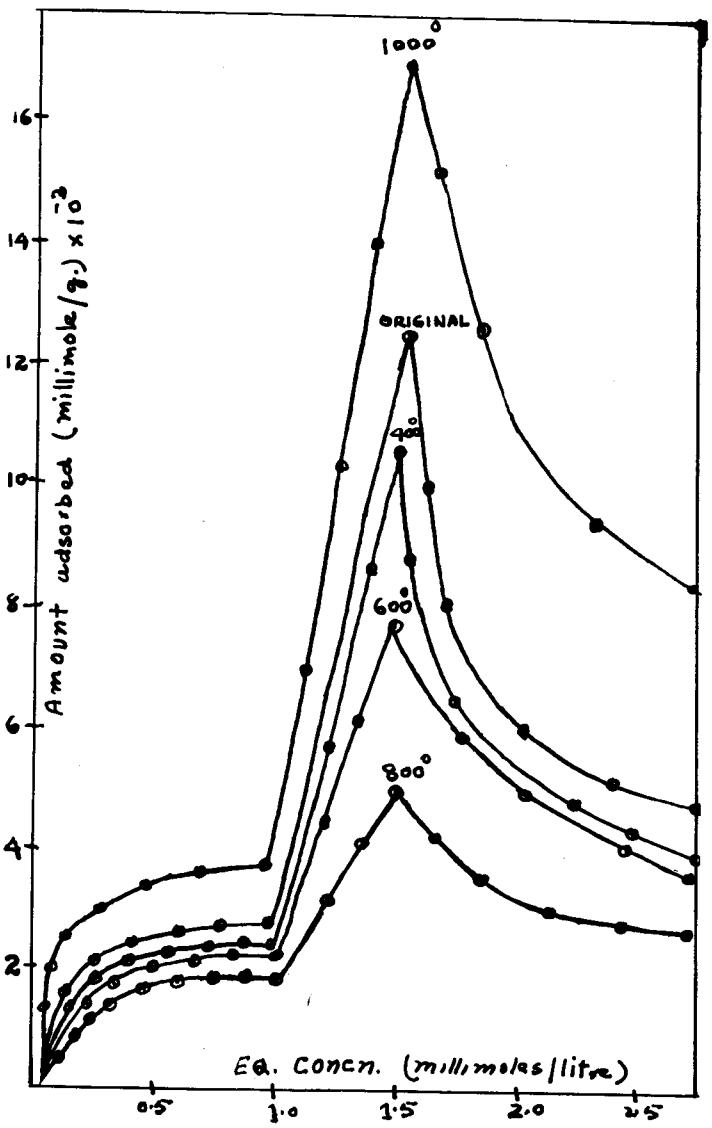

Fig. 1 Adsorption isotherms of CTAB on sugar charcoals outgassed at different temperatures.

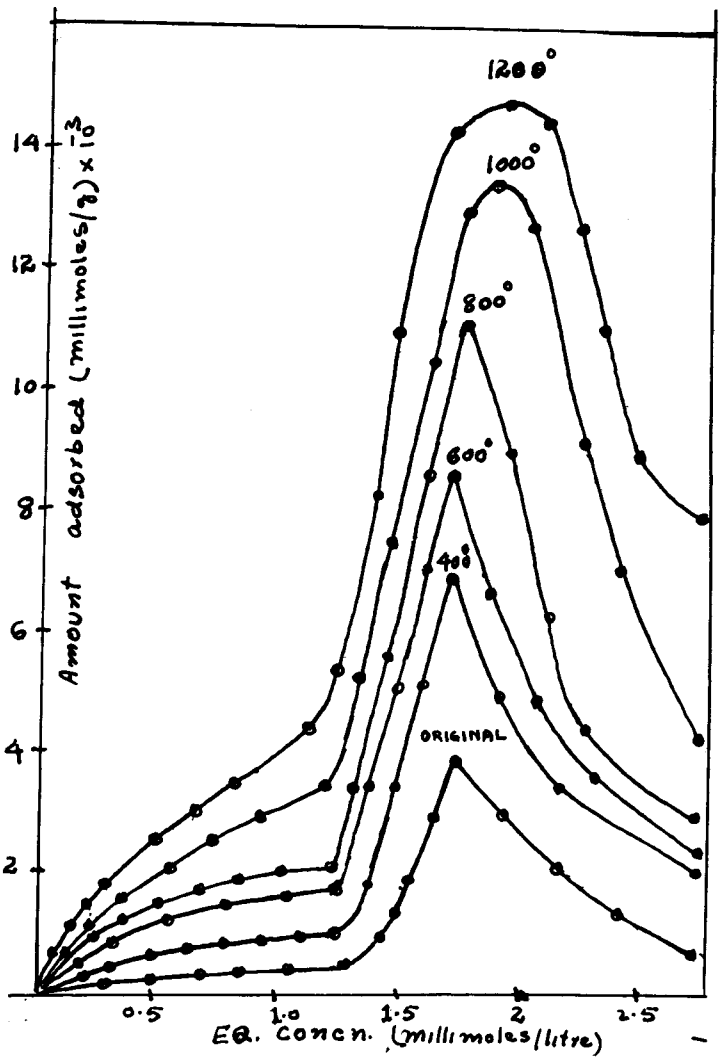

Fig.2 Adsorption isotherms of SDS on sugar charcoals outgassed at different temperatures.