

Adsorption of Cationic Surface Active Agents at Barium Sulphate/Solution Interface

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Adsorption of cationic surface active agents like dodecylpyridinium chloride, dodecylquinolinium bromide, dodecyltrimethylammonium chloride, tetradecylpyridinium bromide and cetylpyridinium chloride on barium sulphate suspensions at two temperatures has been studied in order to examine the effects of surface heterogeneity on the process and to assess the nature of binding. Free energies of adsorption calculated from Stern-Grahame equation have been compared with those obtained from thermodynamic considerations. Variation of the energies with coverage in the initial stages of adsorption is assigned to the surface heterogeneity and it is shown that free energies calculated from Stern-Grahame equation only qualitatively explain the behaviour of long chain ions when these approach the surface from solution. To get a quantitative idea of heterogeneity, adsorbate-adsorbate interaction and the nature of binding, an equation for isosteric heats has been derived for adsorption from solution. Variation of q^{st} and ${}^{\circ}\Delta\sigma\bar{S}$ with progressive adsorption is mainly due to the surface heterogeneity but with long chain ions having large head group or chain length of C_{16} or more, their accommodation problem on the surface and interaction between the chains of the adsorbing ions also contribute towards the relative magnitude of both quantities.

THE importance of the study of adsorption of long chain ions at solid-liquid interface increases many-fold particularly when the selected surface active agents can be used as collecting agents in ore beneficiation¹⁻⁵. The role of adsorption of long chain ions at solid-liquid interface has amply been discussed by Leja¹ on the basis of metal-monolayer interaction. He has classified them into two major groups, viz. (i) those which spread at air-water interface and (ii) those which do not. Reagents of the former group (long chain ionic surface active agents) give rise to two step adsorption isotherms²⁻⁶ the first step corresponding to the adsorption of monolayer and the second to the adsorption of other unilayer. The compounds of the latter group give rise to multilayer adsorption. Several attempts⁷⁻¹⁰ have been made to know the nature of adsorption and the mechanism of interaction of long chain ions at the solid-liquid interface, and most of the studies record S-shaped isotherms in the concentration range 10^{-6} to $10^{-2}M$, instead of two-step adsorption isotherms. However, Fuerstenau and coworkers¹¹⁻¹³ have shown that a break in the adsorption isotherms occurs at a low concentration region which according to them is due to the formation of 'hemi-micelles'. These authors^{11,13,14} have interpreted the results obtained both on adsorption and electrokinetic potentials on the basis of Stern-Grahame equation¹⁵.

The studies so far made give only a qualitative idea of the nature of the binding of the long chain ions at the solid-liquid interface, but fail to explain the effect of surface heterogeneity and fail to give a quantitative idea of the nature of binding in the early stages of adsorption and the adsorbate-

adsorbate interaction. The present study, therefore, is an attempt to obtain information about these aspects of interaction for the adsorption of cationic surface active agents at barium sulphate-solution interface.

Materials and Methods

Distilled water deionized by passing it through a column of mixed acid-base Biodeminerolit (BDH) ion exchange resin was redistilled before use (sp. conductivity 1×10^{-6} ohm⁻¹ cm⁻¹). It was used in the preparation of solutions and in washing precipitated barium sulphate.

Surface active agents were prepared in the laboratory from corresponding *n*-bromo or *n*-chloro-hydrocarbons and pyridine or quinoline (Eastman Kodak, USA). Dodecylpyridinium chloride (DPC) and dodecylquinolinium bromide (DQB) were prepared by the method described by Few *et al.*¹⁶.

Dodecyltrimethylammonium chloride (DTAC) — An excess of the alcoholic solution (10%) of trimethylamine was refluxed with 1-chlorododecane at 80-90°C for 16 hr. The resulting yellow solution was evaporated *in vacuo* to remove the excess amine. The residue set to a colourless mass at room temperature. This was repeatedly crystallized from ethanol-ethyl acetate in leafy crystal.

Tetradecylpyridinium bromide (TDPB) — 1-Bromotetradecane (10 g) was refluxed with pyridine (3.5 g) at 100-110° for 2 hr. The reaction mixture became solid on cooling. This was taken up in hot moist acetone (AR) and crystallized. Repeated crystallizations gave a snow white solid.

Cetylpyridinium chloride (CPC) — 1-Chlorohexadecane (12 g) was refluxed with pyridine (3.7 g) at

110° for 6 hr. On cooling the hard mass obtained was taken up in dry acetone (AR). After the first crystallization, the resulting mass was not very soluble in cold acetone. It was, therefore, recrystallized several times from hot moist acetone in long needles.

Determination of surface area—The following methods were used to have a relatively correct estimate of the surface area of BaSO₄ prepared in the laboratory.

Air permeametry (17) gave the surface area to be 0.15 m²/g while that obtained from photomicrography was 0.18 m²/gm. The specific surface area of the sample was also determined by BET method¹⁸ using krypton adsorption at liquid nitrogen temperature. At this temperature the area determined depends on the choice of p_0 . It should be the value of either saturation vapour pressure of solid krypton or of supercooled liquid gas¹⁹. The use of the latter improved the linearity of the BET plot. However, it was pointed out²⁰ that the mathematical nature of this equation is such that the calculated value of V_m is not greatly affected by the choice of p_0 , provided the numerical value of the parameter C is high ($C > 100$) and the difference may be partly allowed for by an adjustment of molecular cross-sectional area of the adsorbate molecule. Taking 19.5 Å² area of the krypton molecule²¹, the specific surface area was found to be 0.23 m²/g. Even if the area so determined is out by several per cent due to selection of p_0 , this error would not introduce any serious error in the calculations for an average value, i.e. 0.18 ± 0.02 m²/g has been used.

Determination of adsorption isotherm—Barium sulphate (0.4 g) was weighed in a series of thoroughly cleaned and steamed glass stoppered test tubes. Solution (10 ml each) of the surface active agents of known strength were added to each tube. These were placed in a thermostat maintained at a desired temperature for 48 hr in order to attain equilibrium. The tubes were intermittently shaken during this period. The supernatant liquid from each tube was decanted into clean, steamed dry test tubes and centrifuged. These solutions were then analysed by the method of Ottewill and Few²². Cationic surface active agents could then be estimated to 10⁻⁵M or even lower with an accuracy of $\pm 2\%$. The accuracy could be further improved by using 4 cm cell in a very low concentration range instead of 1 cm cell. The experiments were repeated at an interval of 10°.

Results

The experimental results are shown in Figs. 1-4. Isotherms in Figs. 1 and 2 correspond to low concentration region, showing the conventional plots and isotherms in Figs. 3 and 4 cover the whole concentration range as log-log plot. Adsorption isotherms at higher temperatures were similar in shape and show that adsorption decreases with the increase in temperature.

The shape of isotherms in these figures is similar and they give a comparative idea of adsorption of different surface active agents when chain length is increased from C₁₂ to C₁₆ and when head group

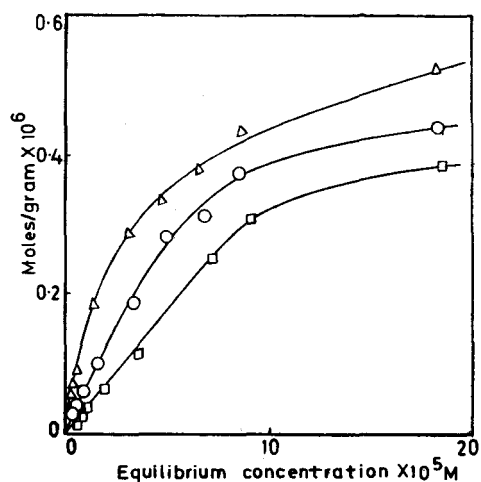


Fig. 1—Moles adsorbed per gram of BaSO₄ against equilibrium concentration of different surface active agents [(-Δ-) CPC; (-○-) TDPB; (-□-) DPB; temp. 293°K]

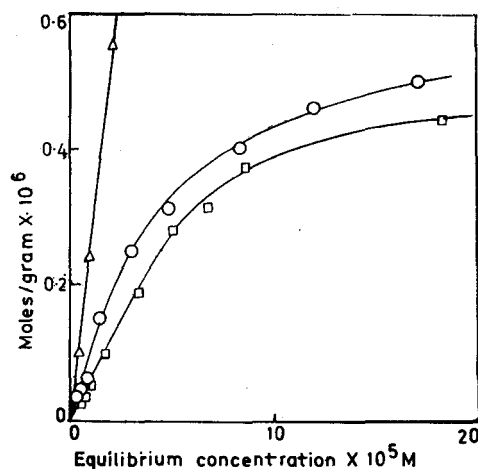


Fig. 2—Moles adsorbed per gram BaSO₄ against equilibrium concentration of different surface active agent [(-Δ-) DOB; (-○-) DPB; (-□-) DTAC; temp. 298°K]

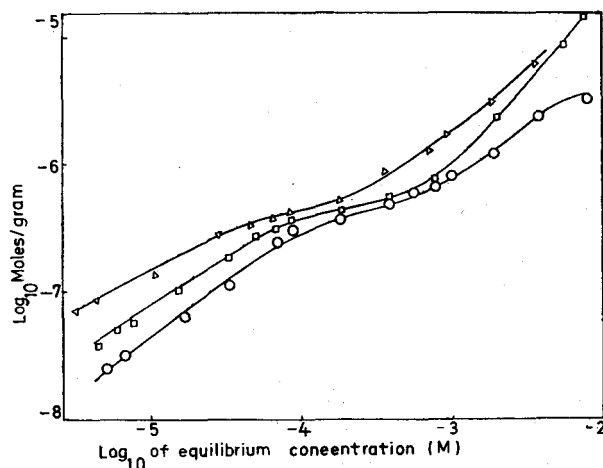


Fig. 3—Log moles adsorbed per gram of BaSO₄ against the log of the equilibrium concentration [(-Δ-) CPC; (-□-) DPB; (-○-) DPC; temp. 293°K]

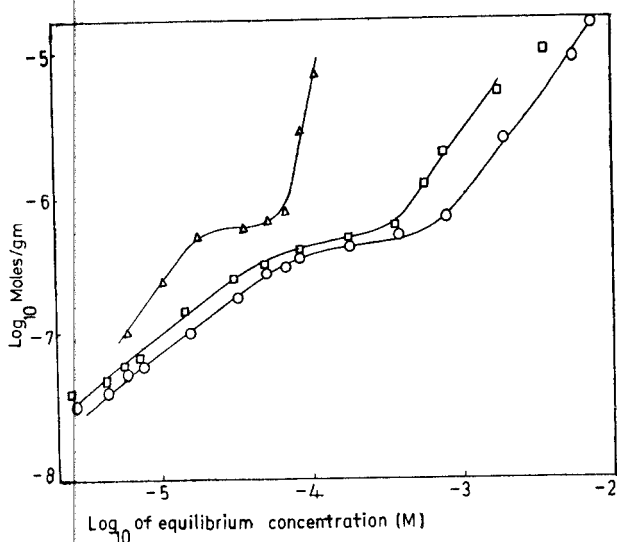


Fig. 4—Log moles adsorbed per gram of BaSO₄ against log of the equilibrium concentration [(-Δ-) DQB; (-□-) DPC; (-○-) DTAC; temp. 298° K]

size is increased from trimethylammonium to quolinium.

In the low concentration region, the steep gradients in adsorption isotherms indicate that barium sulphate has a high affinity for cationic surface agents. Obviously the exposed active sites attract oppositely charged surface active ions and their adsorption at these, therefore, be either due to forces similar to electrostatic in nature or of chemisorption type. Consequently polar head groups would point towards the surface with hydrocarbon chain floating in the bulk. This process would lead to the formation of thin or compact monolayer, depending on the hydrophilic-hydrophobic balance and on the anchorage of the head group of the surface active agent at the interface. When more of surface active ions are added, the isotherms first become concave towards the equilibrium concentration axis but at still higher concentration they shape themselves as convex to this axis. This is because, with increasing coverage, the high energy sites being occupied, the surface active ions are adsorbed at sites of lower energy causing the isotherm to become concave. At still higher coverages, the surface becomes hydrophilic²³ presumably due to amphipathatic adsorption of second unilayer of the surface active agent with polar groups oriented towards the aqueous solution and paraffin chain inwards, i.e. towards the surface. Such an adsorption would cause the isotherms to become convex to equilibrium concentration axis.

Discussion

The adsorption of ions from solution at solid-liquid interface can be followed using Stern's equation²⁴. Although Mukherjee proposed a similar equation^{24a} based on the electrostatic adsorption of counter ions, Stern's equation differs from that of Mukherjee's in many technical details.

$$n_i = N_i / [1 + \exp(\overline{\Delta G}^\circ / kT) / x_i] \quad \dots(1)$$

In Eq. (1) n_i is the number of ions adsorbed per cm² at the Stern plane, N_i the number of sites per

cm² available for adsorption, x_i the mole fraction of the ion i in the bulk and $\overline{\Delta G}^\circ$, the electrochemical free energy of adsorption. In deriving this equation Stern took recourse to the assumptions similar to those used by Langmuir, hence the limitation of the latter would be inherent in the derivation. Again the magnitude of the free energy would depend on the electrical potential difference between the adsorbed monolayer and the bulk and the specific adsorption potential and may be expressed as

$$\overline{\Delta G}^\circ = \Delta G^\circ + Ze\Psi\delta \quad \dots(2)$$

in which ΔG° being termed as specific adsorption potential and $\Psi\delta$, the Stern potential which in turn can be put as $(\Psi_1 - \Psi_B) \Psi_1$ and Ψ_B being the potentials at the monolayer and the bulk respectively. It is difficult to frame a suitable definition of Ψ_1 to give a meaning to separation shown in Eq. (2). Therefore, Eq. (2) is not useful for quantitative calculations although a qualitative idea of the adsorptive potential can be obtained if change in $\Psi\delta$ with progressive adsorption be estimated accurately. Experimentally these determinations are difficult. Attempts were made to use electrokinetic potential instead of $\Psi\delta$ in Eq. (2), assuming an equivalence between the two. This substitution would make the situation worse because of the uncertainty of the slipping plane. However, Grahame's equation¹⁵

$$n_i HP = 2r n_0 e^{W_{iHP} / kT} \quad \dots(3)$$

permits the calculation of $\overline{\Delta G}^\circ$ without using $\Psi\delta$ or ξ potential. The symbols used are defined as $n_i HP$ the number of counter ions per cm² specifically adsorbed at inner Helmholtz plane (iHP), n_0 , the number of ions per ml in the bulk, r the radius of unhydrated adsorbed ion and W_{iHP} , the work done in bringing ions from the bulk to iHP . In fact Eq. (3) is an improvement over that of Stern's equation (1), the limitation of the latter will also be associated with it. Eq. (3) can be modified to

$$\ln x/m = \ln \left[\frac{2rAC_0}{1000} \right] - \frac{\overline{\Delta G}^\circ}{RT} \quad \dots(4)$$

in which x/m is the amount of surface active agent adsorbed per gram, A the surface area in cm² per gram, C_0 , the equilibrium concentration in moles per litre, and $\overline{\Delta G}^\circ$, the change in electrochemical free energy of adsorption when one gram ion is brought to iHP from infinity. The equation permits the calculation of $\overline{\Delta G}^\circ$ with coverage provided r is known. This parameter has been calculated from the area of head group of pyridinium and quolinium ions²⁵ on the basis of assembled model. This is valid only when charged head group is adsorbed at the active site on the barium sulphate crystal. Even if there is an error in the values of r so calculated, it would only slightly affect the numerical values of $\overline{\Delta G}^\circ$ by a constant amount. Fig. 5 shows the variation of $\overline{\Delta G}^\circ$ with coverage. These curves are very similar to those obtained by Ball and Fuerstenau¹³. This data has been compared with surface free energy changes computed from the Eq. (22) derived from thermodynamic consideration. In these calculations the concentration of the surfactants and the

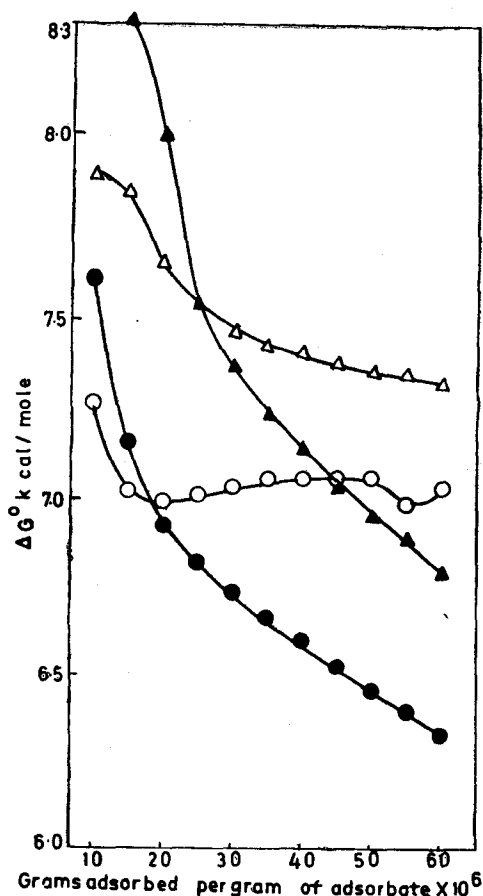


Fig. 5 — Variation of electrochemical free energy calculated (a) from Stern-Grahaime equation, (b) from Eq. (22) against the amount adsorbed per gram of adsorbent [(a) —△— DQB and —○— DPB; (b) —▲— DQB and —●— DPB]

temperatures used are the same as computed from Eqs. (18 and 19).

In the early stages of adsorption, the sharp fall in the values of $\Delta\bar{G}^\circ$ indicates the presence of sites of high energies at which surface active ions are adsorbed by some force similar to electrical in nature. Subsequently this fall becomes gradual in the case of DQB with increasing coverage while DPB shows no pattern. However, the results in both the cases suggest that the surface exposed is heterogeneous. But at corresponding coverages, the fall in values of surface free energy changes calculated from Eq. (22) are much steeper and regular in both the cases and clearly point out the difference between the two set of data though the adsorption of ions has been restricted up to the formation of monolayer only. Stern-Grahaime equation¹⁵ has its limitation for it was mainly developed to explain data at mercury-solution interface, the surface of mercury being treated as homogeneous with energy sites uniformly distributed over it. As such it can qualitatively explain the adsorption of long chain ion at the solid-liquid interface. In order to get a quantitative idea of the effect of surface heterogeneity, the nature of binding and adsorbent-adsorbate interaction, one will have to develop an

equation based on thermodynamic concept free from any restriction due to model consideration of the double layer.

Derivation of an expression for the heat of adsorption from solution phase — Adsorption from solutions phase on solids involves (i) solution phase α , (ii) solid phase and (iii) two-dimensional surface phase (σ) formed by the adsorption of long chain ions from aqueous phase. The equilibrium between the surface phase and the bulk phase can be expressed by Eq. (5)

$$\Delta\bar{\mu}_i^\sigma = \Delta\bar{\mu}_i^\alpha \quad \dots(5)$$

in which $\Delta\bar{\mu}_i^\sigma = \bar{\mu}_i^\sigma - \bar{\mu}_i^{\sigma^\circ}$ and $\Delta\bar{\mu}_i^\alpha = \bar{\mu}_i^\alpha - \bar{\mu}_i^{\alpha^\circ}$ and $\bar{\mu}_i^{\sigma^\circ}$ and $\bar{\mu}_i^{\alpha^\circ}$ are standard electrochemical potentials when ions of unit activity are transferred from the solution to surface phase and when activity coefficient of the same ions in solution is unity respectively.

Electrochemical potential of the ions in solution is the function of osmotic pressure, temperature and potential due to them in the bulk, i.e.

$$\bar{\mu}_i^\alpha = f(P, T, \phi^\alpha) \quad \dots(6)$$

and $\bar{\mu}_i^\sigma$ of the same species in the surface phase is also a function of surface coverage θ , besides P , T and ϕ^σ . It can be expressed as

$$\bar{\mu}_i^\sigma = f(P, T, \theta, \phi_i^\sigma) \quad \dots(7)$$

Deviating slightly from equilibrium defined by Eq. (5) and the system still remaining in equilibrium we have

$$d\bar{\mu}_i^\sigma = d\bar{\mu}_i^\alpha \quad \dots(8)$$

From Eqs. (6), (7) and (8) it can be shown that

$$\begin{aligned} \left(\frac{\partial\bar{\mu}_i^\alpha}{\partial P}\right)_{T, \phi^\alpha} dP + \left(\frac{\partial\bar{\mu}_i^\alpha}{\partial T}\right)_{P, \phi^\alpha} dT + \left(\frac{\partial\bar{\mu}_i^\alpha}{\partial \phi^\alpha}\right)_{T, P} d\phi^\alpha \\ = \left(\frac{\partial\bar{\mu}_i^\sigma}{\partial P}\right)_{T, \theta, \phi^\sigma} dP + \left(\frac{\partial\bar{\mu}_i^\sigma}{\partial T}\right)_{P, \theta, \phi^\sigma} dT + \left(\frac{\partial\bar{\mu}_i^\sigma}{\partial \theta}\right)_{P, T, \phi^\sigma} d\theta \\ + \left(\frac{\partial\bar{\mu}_i^\sigma}{\partial \phi^\sigma}\right)_{P, T, \theta} d\phi^\sigma \quad \dots(9) \end{aligned}$$

Rearranging and remembering that

$$\left(\frac{\partial\bar{\mu}_i}{\partial T}\right)_P = -S, \quad \left(\frac{\partial\bar{\mu}_i}{\partial T}\right)_T = V \quad \text{and} \quad \left(\frac{\partial\bar{\mu}_i}{\partial \phi}\right)_{P, T} = q$$

Eq. (9) at constant θ reduces to

$$dP(\bar{V}^\alpha - \bar{V}^\sigma) = dT(\bar{S}^\alpha - \bar{S}^\sigma) + [q^\sigma d\phi^\sigma - q^\alpha d\phi^\alpha] \quad \dots(10)$$

The last terms of Eq. (10) give the difference between work done in bringing ions from infinity to the surface phase and to the solution phase. The net work done may be put as ${}^\alpha\Delta\sigma q d\phi$. Considering the adsorption of the ions up to the formation of monolayer, the partial molar volume (\bar{V}^σ) of the adsorbed phase can be neglected in comparison with \bar{V}^α . Eq. (10) is then modified to

$$\left(\frac{dP}{dT}\right)_\theta = \frac{\bar{S}^\alpha - \bar{S}^\sigma}{\bar{V}^\alpha} + \frac{1}{\bar{V}^\alpha} \left[{}^\alpha\Delta\sigma q \left(\frac{d\phi}{dT}\right)_\theta \right] \quad \dots(11)$$

The term ${}^\alpha\Delta\sigma q (d\phi/dT)_\theta$ can be taken as change in entropy in analogy with the temperature coefficient of potential E of a chemical cell, i.e. $nF(dE/dT)_P$, when

ion i is transferred from the bulk to the surface phase. Hence Eq. (11) becomes

$$\left(\frac{dP}{dT}\right)_0 = \frac{\alpha \Delta^\sigma \bar{S}}{\bar{V}^\alpha} \quad \dots(12)$$

in which $\alpha \Delta^\sigma \bar{S} = \bar{S}^\alpha - \bar{S}^\sigma \sim \alpha d^\sigma S$. $\alpha d^\sigma S$ is dependent on the sign of $(d\phi/dT)_0$ and represents the molar differential entropy when one mole of ion is adsorbed relative to standard state defined above.

Again considering free energy changes for transference of the ions of unit activity from the bulk phase to the surface phase, keeping microscopic area of the interface constant and making use of Eq. (5), it can be shown that

$$\alpha \Delta^\sigma \bar{S} = \alpha \Delta^\sigma \bar{H}/T \quad \dots(13)$$

where $\alpha \Delta^\sigma \bar{H}$ denotes the heat evolved when ions of unit activity of the component passes from phase α to surface phase σ provided the process occurs at constant θ . Substituting the value of $\alpha \Delta^\sigma \bar{S}$ in Eq. (12), we get

$$\left(\frac{dP}{dT}\right)_0 = \alpha \Delta^\sigma \bar{H}/T \bar{V}^\alpha \quad \dots(14)$$

which is similar to Clausius-Clayperon equation. To determine $\alpha \Delta^\sigma \bar{H}$ experimentally, identified as isosteric heat of adsorption, Eq. (14) is simplified to

$$\left(\frac{d \ln P}{dT}\right)_0 = q^{st}/RT^2 \quad \dots(15)$$

Integrating Eq. (15) between two temperatures T_1 and T_2 and remembering the solutions are dilute, P being proportional to the concentration C , we get

$$q^{st} = \frac{2.303 R (\log C_2 - \log C_1) T_1 T_2}{T_2 - T_1} \quad \dots(16)$$

The values of q^{st} calculated from Eq. (16), depend considerably on the accuracy with which equilibrium concentrations (C_1 and C_2) are determined. It has been mentioned earlier that in the low concentration region, these can be estimated with an accuracy of 2% i.e. root mean square error of their ratio is of the order of $\pm 2.8\%$. Therefore

$$\ln (C_1/C_2)(1 \pm 0.028) \sim \ln(C_1/C_2) + 0.028$$

Eq. (16) then becomes

$$q^{st} = R[T_1 T_2 / (T_2 - T_1)] [\ln C_2 - \ln C_1] \pm R[T_1 T_2 / (T_2 - T_1)] \times 0.028 \quad \dots(17)$$

It follows, therefore, that factor $R[T_1 T_2 / (T_2 - T_1)]$ governs the accuracy in calculating q^{st} . Since T_1 and T_2 differ by 10° , the estimated error will be of the order of ± 500 cal per mole.

In view of the possible interaction between the hydrocarbon chains of different surface active agents at higher coverages, heats up to $\theta \approx 0.2$ were calculated and Fig. 7 shows the variation of q^{st} against the amount adsorbed per gram of adsorbent.

Since T_1 and T_2 differ by 10° , the values of q^{st} computed may be taken to represent both the isotherms. For a better approximation, the average

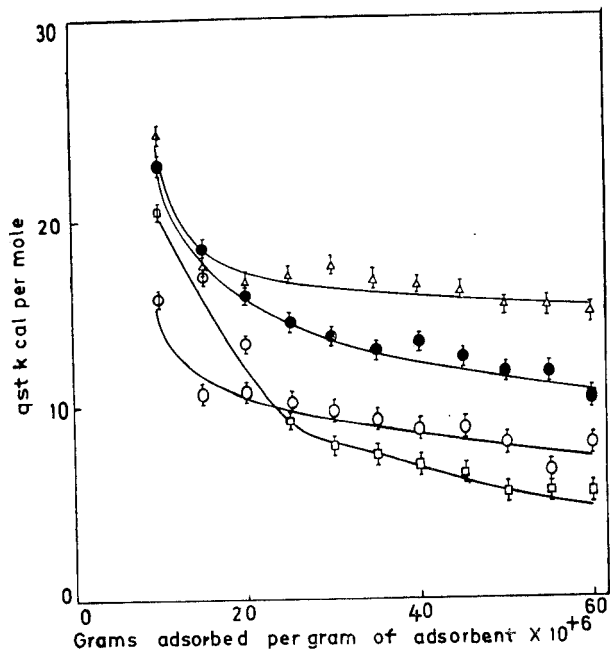


Fig. 6 — Variation of isosteric heat of adsorption of different surface active agents as a function of amount adsorbed per gram of BaSO_4 [(- Δ -) TDPB; (- \bullet -) DPC; experimental temperatures 293° and 305°K (- \square -) DQB; (- \circ -) DTAC; experimental temperatures 298° and 308°K]

temperature or concentration can be calculated²⁶ from Eqs. (18) and (19)

$$\frac{1}{T} = [1/T_1 + 1/T_2]/2 \quad \dots(18)$$

$$C = (C_1 - C_2) \quad \dots(19)$$

Dependence of isosteric heats on concentration — The variation of isosteric heats for different surface active agents with progressive coverage can be assigned to factors, viz. surface heterogeneity, adsorbate-adsorbate interaction and/or to the combined effect of both depending on their relative magnitude at a particular adsorption site.

The initial sharp fall in q^{st} due to the adsorption of different surface active agents shows the presence of high energy sites. The origin of these may be due to strong residual valence forces or due to forces arising out of crystal defects. The energy associated with them will also be dependent on the nature of the adsorbent and the particle size. Non-uniformity of this type gives rise to surface heterogeneity, as a result of which different degrees of interactions would occur between the adsorbate and adsorbent.

Surface active cations should, therefore, be preferentially adsorbed due to electrostatic attraction at sites of high energy with their head pointing towards the surface. Therefore, in the initial stages of adsorption high values of q^{st} are expected. When these sites are filled up, subsequent fall in q^{st} becomes gradual with increasing coverage. This adsorption pattern is followed by TDPB, DPC and DTAC. The effect of large head group, e.g. quolinium associated with C_{12} , is quite apparent. The gradient of the curve for this surfactant in the initial stages is much steeper than for pyridinium or trimethylammonium ions associated with the

same chain length. However, numerically, it seems that for the same fraction of the surface covered, DP^+ ions are more strongly adsorbed than DQ^+ ions. This apparent anomaly could be explained by taking into consideration the size of the ions as well as their accommodation on the surface. This aspect of the problem becomes clear by considering the variation of surface entropy with coverage, discussed in the sequel.

It is difficult to assess the contribution of adsorbate-adsorbate interaction from the data on q^{st} . If this factor outweighs the heterogeneity factor, q^{st} coverage curve should show a minimum²⁶. A situation of this kind may arise if one is working with surface active agents with chain length C_{16} or more or with large head group. In these cases, the possibility of interaction between adsorbing molecules even at low coverage becomes much more.

Surface entropy and its dependence on coverage — Surface entropy for the system can be represented by

$${}^a\Delta\sigma\bar{S} = \Delta\bar{S}^\sigma \text{ (configurational)} + \Delta\bar{S}^\sigma \text{ (thermal)}$$

The contribution of $\Delta\bar{S}^\sigma$ (configurational) should play an important role in governing ${}^a\Delta\sigma\bar{S}$, for it takes into account the possible arrangement of adsorbate molecules or ions on the surface. Changes in rotational and vibrational entropies, if any, of the adsorbing ions are incorporated in the term $\Delta\bar{S}^\sigma$ (thermal). The contribution of the latter when adsorbing ions are long chain ions and adsorb on ionogenic surface to entropy change is difficult to assess. Again separate estimation of changes in configurational entropies in the case also seems to be difficult. However, ${}^a\Delta\sigma\bar{S}$ can be calculated from Eq. (20). Free energy change for the adsorbed phase is given by

$${}^a\Delta\sigma\bar{C} = {}^a\Delta\sigma\bar{H} - T{}^a\Delta\sigma\bar{S} \quad \dots(20)$$

Terms involved in Eq. (20) have been defined earlier. Numerically²⁷

$$q^{st} = - {}^a\Delta\sigma\bar{H} \quad \dots(21)$$

and

$${}^a\Delta\sigma\bar{G} = 2.303 RT \log C \quad \dots(22)$$

in which C is the equilibrium concentration and T , the absolute temperature given by Eqs. (18) and (19) respectively.

In calculations, activities for ions should have been used. However, this approximation will not introduce any serious error because equilibrium concentrations substituted in Eq. (22) were of the order of $10^{-6}M$. Variation of ${}^a\Delta\sigma\bar{S}$ for different surface active agents versus amount adsorbed per gram of adsorbent is shown in Fig. 7.

Barium sulphate-solution system is constituted of the bulk phases, the interface and the oriented water molecular layers, if any, near the surface. Therefore, such a system would present a surface statistically with the same disorder arising due to dissociating surface groups or uneven distribution of adsorbing sites or exposition of a particular crystal face or due to the combined effects of these factors. Long chain ions when added to the system, will

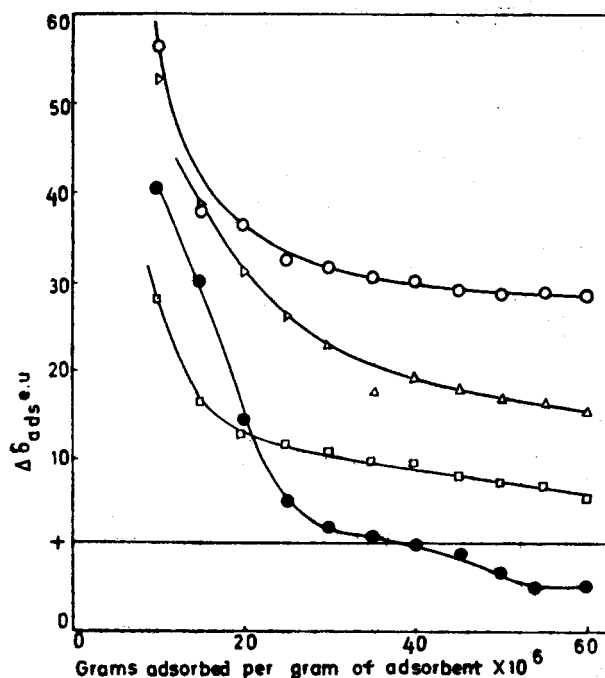


Fig. 7 — Variation of surface entropy of different surface active agent as a function of amount adsorbed per gram of adsorbent [(—△—) TDPB; (—●—) DPB; (—□—) DTAC and (—○—) DQB]

cause a change in surface entropy depending on their accommodation capability on the surface and on the hydrophobic-hydrophilic balance. To tilt the balance, the chain length has been increased from C_{12} to C_{14} with same pyridinium group and the head group size from trimethylammonium to quinolinium having same chain length, C_{12} .

The addition of surface active agents in increasing doses affects the environmental conditions around the barium sulphate particles responsible for the changes in surface entropies with coverage (Fig. 7). It may be noted that for the same amount of different surfactants adsorbed (per gram) the effect on surface entropies is different though the surface area exposed was the same in each case. It seems the process depends only on the nature and size of the adsorbing ions.

A sharp fall in ${}^a\Delta\sigma\bar{S}$ at low coverages for DTAC, DQB, DPC and TDPB, again shows that the surface exposed is heterogeneous. The variation of surface entropies even when the coverage does not exceed ~ 0.2 , indicate that Langmuir adsorption equation is not applicable to the data though a linear relationship exists between ${}^a\Delta\sigma\bar{S}$ and ${}^a\Delta\sigma\bar{H}$ for DPC, TDPB and DTAC up to corresponding to $\sim 3 \times 10^{-5}$ g per gram of adsorbent. The scatter of points (see Fig. 8) for pyridinium ions both for DPC and TDPB is such that a single straight line can be drawn having a slope of 3×10^{-3} . The theoretical values for the slopes are 3.36×10^{-3} (298°) and 3.30×10^{-3} ($302.9^\circ K$). The two sets are comparable and it can be said that the relationship between both the quantities shows more or less an ideal behaviour up to the coverages indicated.

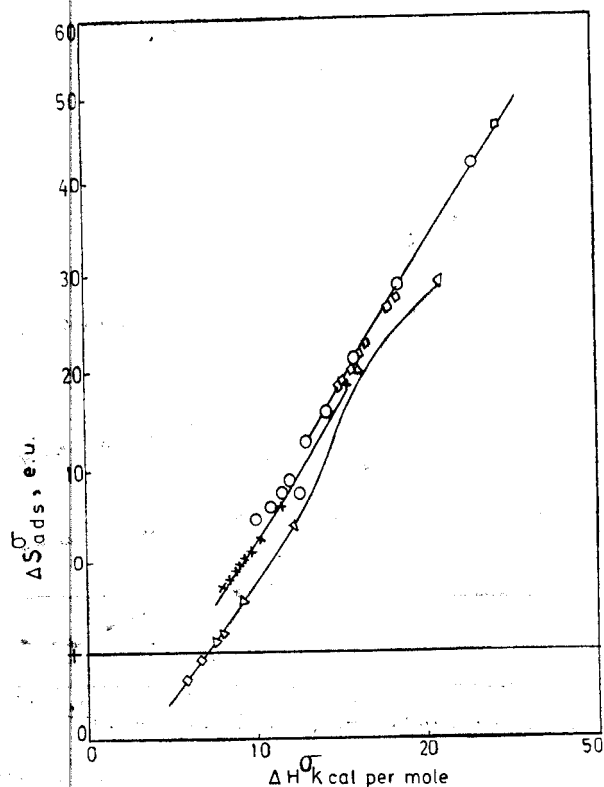


Fig. 8 — Variations of $^{\circ}\Delta S^{\circ}_{ads}$ with $^{\circ}\Delta H^{\circ}_{ads}$ for different surface active agent [(—□—) TDPB; (—○—) DPC; (—△—) DQB; (—×—) DTAC; temp. 305°K.]

Like entropy versus coverage curve, $^{\circ}\Delta S^{\circ}$ versus $^{\circ}\Delta H^{\circ}$ curve for DQB follows a pattern completely different from those of other surface active agents. Such a behaviour may be due to the accommodation problem of adsorbed large quinolinium group side by side and the interaction between the adjacent molecules on the surface. A combined effect of the two leads to a situation at which $^{\circ}\Delta S^{\circ}$ may end to zero and it does so at $\sim 4 \times 10^{-5}$ g of adsorbate. Further increase in its concentration causes $^{\circ}\Delta S^{\circ}$ to become positive. The effect of increasing chain length with the same head group should also show a similar effect for it not only increases the hydrophobic character but also the possibility of amphipathic interaction between hydrocarbon chains. The interaction of this type could be felt in the case of compounds having chain length C_{16} or more. The increase in chain length from C_{12} to C_{14} does not increase hydrophobicity to such an extent as to effect entropies as in the case of DQB. From the changes in entropies one can infer that TDPB is more strongly adsorbed than DPC, as was expected.

It can be concluded from the variation of $^{\circ}\Delta S^{\circ}$ with progressive adsorption for different surface active agents, the adsorbing surface is heterogeneous otherwise numerical values of $^{\circ}\Delta S^{\circ}$ would have been the same for each surfactant had the Langmuir postulate of equi-energy sites been valid for the system. For coverages corresponding to 4×10^{-5} g of adsorbate (DQB), the surface is practically covered

reducing the surface disorder to a minimum. Further adsorption of the same ion reverse the so-called order to increasing disorder, a case where interaction between adsorbing ions is strongly felt. The change in sign of $^{\circ}\Delta S^{\circ}$ further suggests the formation of second layer before the first one is completed. The other extreme case should be with surface active agents having C_{16} chain or more. The variation of $^{\circ}\Delta S^{\circ}$ with the amount adsorbed for other surfactant should follow a course intermediate between the two extremes.

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