

in the region 2900–3000 cm^{-1} the shape of the spectrum depends only on the nature of the alkyl radical. For a given radical, the spectra are identical both qualitatively and quantitatively. The assumption that the mutual effect of alkyl radicals and aromatic nuclei is weak is thus confirmed.

The intensity of the band at 2965 cm^{-1} is proportional to the number of methyl groups present. For example, for a normal radical, with one CH_3 group $E = 100$ units, while for a *t*-amyl radical $E = 300$ units. The same holds for the band at 2930 cm^{-1} , the intensity of which is directly proportional to the number of CH_2 groups. Thus for the *t*-amyl radical $E = 70$ –80 units, while for *n*-butyl $E = 220$ units. In order to obtain these quantitative data it was necessary to take into account the mutual overlapping of the absorption bands; this was done by assuming that the bands were symmetrical²¹. In some cases, in Figs. 1 and 2, the individual peaks are shown by dotted lines. We did not apply the usual correction for finite slit-width to the calculated intensities, since under our conditions (2900–3000 cm^{-1} , slit-width 0.13 mm) the correction would be negligible – the intensities would change by only 1.5–2%.

Radicals whose structure was in doubt were investigated further by the usual spectroscopic methods^{18,22}. Thus the spectrum of isoamylbenzene was studied in the skeletal CC -vibration region. The absence of absorption near 1250 cm^{-1} showed that there was no quaternary carbon atom in the molecule.

The rules discussed above apply also to the *para*-disubstituted aromatic compounds (Fig. 2); the intensities of the absorption bands are correspondingly doubled.

SUMMARY

A study of the infra-red spectra in the CH -vibration region has shown that it is possible to determine the structure of the alkyl radical in a compound of type Ar-R , where Ar is phenyl, diphenyl, or naphthyl and R is a C_3 – C_8 alkyl group.

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Received 17th September 1958

A STUDY OF THE ADSORPTION OF ALKYL HYDROGEN SULPHATE ANIONS ON THE MERCURY ELECTRODE AND THE EFFECT OF THE ANIONS ON THE KINETICS OF THE ELECTRODE PROCESSES

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Many organic compounds can be adsorbed at the interface between a metal and an electrolyte solution, and it has been shown¹ that this adsorption reduces the interfacial tension at a mercury/solution interface. The amount of neutral organic substance adsorbed depends on the potential difference between surface and solution, and at high surface charges the organic molecules are desorbed from the mercury surface. In this case sudden breaks are observed on the electrocapillary curves, which can be correlated with capacity peaks on curves relating differential capacity to potential, and which are connected with a sharp variation in capacity of the double layer in a narrow potential range.

A theory of desorption of organic molecules from an electrode surface at high surface charges has been given by Frumkin²; desorption-capacity peaks were first detected experimentally by Proskurnin and Frumkin³.

In the potential region of adsorption of surface-active materials there is a sudden decrease in the double-layer capacity to a value of ~ 4 –5 $\mu\text{F}/\text{cm}^2$ and lower, but for surfaces with both high positive and high negative charges, the differential-capacity curves approximate to those obtained for a solution containing no surface-active material.

Much work has already been done by the differential-capacity method on the formation of adsorbed layers, and also on the kinetics of the adsorption process for organic substances on an electrode surface^{4–12}. This question has been dealt with in detail by Frumkin and Melik-Gaikazyan⁶. By studying the frequency dependence of differential capacity in the region of desorption peaks for solutions containing normal saturated alcohols, Melik-Gaikazyan showed, on the basis of Frumkin's theory, that the slow step in the adsorption process of these alcohols appeared to be the diffusion of the alcohol molecules to the mercury surface. He observed multimolecular-layer formation on the mercury electrode surface for solutions of *n*-octyl and *n*-hexyl alcohols⁷. This multilayer formation is accompanied by an even greater reduction in capacity (to 0.9 $\mu\text{F}/\text{cm}^2$), the minimum becoming more pronounced as the electrolyte concentration is reduced; conversely, it becomes less marked on addition of polyvalent cations to the solution.

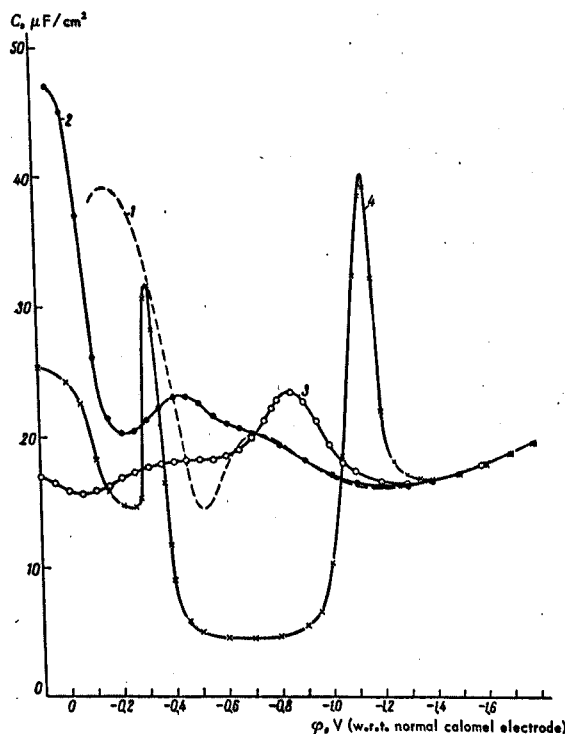


Fig. 1. Differential-capacity curves at 400 c/s and 25° in solutions of: 1) 0.01 N Na_2SO_4 ; 2) 0.01 N Na_2SO_4 + 10^{-3} N $\text{C}_6\text{H}_{13}\text{OSO}_3\text{Na}$; 3) 0.01 N Na_2SO_4 + 10^{-3} N $\text{C}_9\text{H}_{19}\text{OSO}_3\text{Na}$; 4) 0.01 N Na_2SO_4 + 10^{-3} N $\text{C}_{12}\text{H}_{25}\text{OSO}_3\text{Na}$.

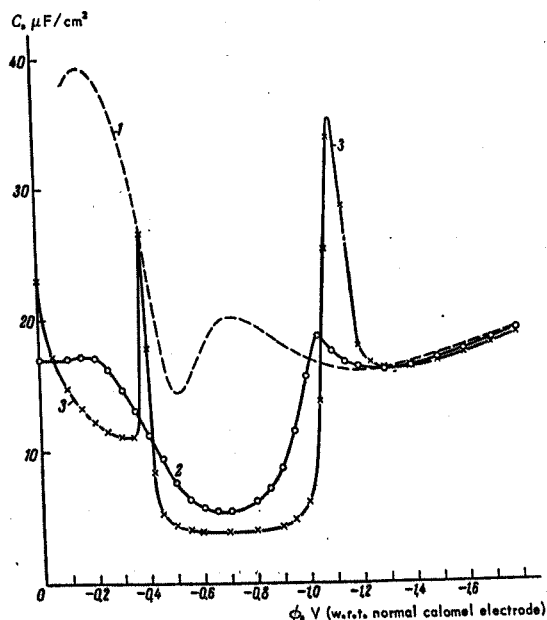


Fig. 2. Differential-capacity curves at 400 c/s and 25° in solutions of: 1) 0.01 N Na_2SO_4 ; 2) 0.01 N Na_2SO_4 + 10^{-4} N $\text{C}_{12}\text{H}_{25}\text{OSO}_3\text{Na}$; 3) 0.01 N Na_2SO_4 + 10^{-4} N $\text{C}_{14}\text{H}_{29}\text{OSO}_3\text{Na}$.

Large organic cations, such as $[(\text{C}_4\text{H}_9)_4\text{N}]^+$, behave analogously to neutral molecules, but are desorbed from a negatively charged surface at higher negative potentials than the neutral molecules¹³.

For solid electrodes in the presence of organic substances peaks are observed on the curves for differential capacity against potential. However, according to Kheifets and Krasikov⁸ desorption of organic substances from solid surfaces is not complete, as in the case of mercury, some of the adsorbed molecules remaining on the surface.

EXPERIMENTAL

Methods

In this paper the adsorption of alkyl hydrogen sulphate anions (having 6, 9, 12, 14, 16, and 18 carbon atoms*) on a mercury electrode has been studied by the differential-capacity method. The other salts used were recrystallised twice and ignited.

The apparatus for measuring the differential capacity resembled that described in the literature^{5,6}. The dropping-mercury electrode was surrounded by platinum cylinders to obtain uniform polarisation. From data on the relation between differential capacity and time, we showed that the time of formation of an adsorption layer was fairly short for short carbon chains, and we were able to effect a change in capacity 30 sec after the formation of a fresh mercury surface. The capacity ceased to vary after 60 sec for additions of $\text{C}_{16}\text{H}_{33}\text{OSO}_3\text{Na}$, and after 180 sec for $\text{C}_{18}\text{H}_{37}\text{OSO}_3\text{Na}$. The differential-capacity values given in this paper for the presence of these sulphonates were measured $1\frac{1}{2}$ and 5 min after the formation of a clean mercury surface.

A normal calomel electrode was used as a reference electrode and all changes in potential are expressed relative to this standard. Experiments were carried out at $25^\circ \pm 0.1^\circ$ except for one series which was carried out at $30^\circ \pm 0.1^\circ$ to increase the solubility of the alkylsulphonate.

Variation in Differential Capacity**

Fig. 1 shows the differential-capacity curves for a pure 0.01 N sodium sulphate solution (broken line), and for the same solution with millinormal additions of the sodium salts of hexyl, nonyl, and dodecyl hydrogen sulphates. For a positively charged mercury electrode even in the case of sodium hexyl sulphate a marked adsorption of $\text{C}_6\text{H}_{13}\text{OSO}_3^-$ anions is observed, which results in the disappearance of the minimum (associated with diffusion of the double layer in the vicinity of zero charge) and in a reduction of the differential capacity at $\phi = -0.2$ from $39.2 \mu\text{F}/\text{cm}^2$ (for 0.01 N Na_2SO_4) to $20.2 \mu\text{F}/\text{cm}^2$ (for 0.01 N Na_2SO_4 + 10^{-3} N $\text{C}_6\text{H}_{13}\text{OSO}_3\text{Na}$). At higher positive potentials the capacity curve rises sharply indicating the anionic character of the adsorption of the $\text{C}_6\text{H}_{13}\text{OSO}_3^-$ species. At $\phi = -0.45$ there is a

* The sodium alkyl sulphates were kindly put at our disposal by Prof. Bertsch, Director of the Institute of Organic Chemistry at the Berlin Academy of Sciences.

** After this paper had been submitted for publication, work by Eda was published [K. Eda, J. Chem. Soc. Japan, 80, 343, 347, 349, 708 (1959)], containing the data for the differential capacity of solutions containing the following sodium alkyl sulphates: $\text{C}_6\text{H}_{13}\text{OSO}_3\text{Na}$, $\text{C}_{10}\text{H}_{21}\text{OSO}_3\text{Na}$, $\text{C}_{12}\text{H}_{25}\text{OSO}_3\text{Na}$, and $\text{C}_{14}\text{H}_{29}\text{OSO}_3\text{Na}$.

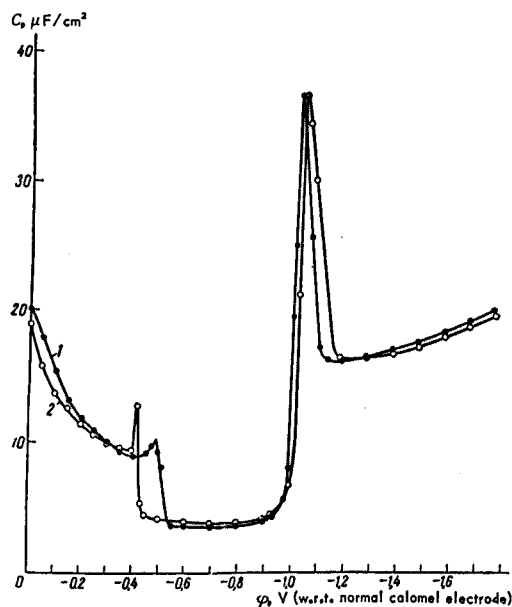


Fig. 3. Differential-capacity curves at 400 c/s and 25° in solutions of: 1) 0.01N Na_2SO_4 + sat. $\text{C}_{18}\text{H}_{37}\text{OSO}_3\text{Na}$; 2) 0.01N Na_2SO_4 + sat. $\text{C}_{16}\text{H}_{33}\text{OSO}_3\text{Na}$.

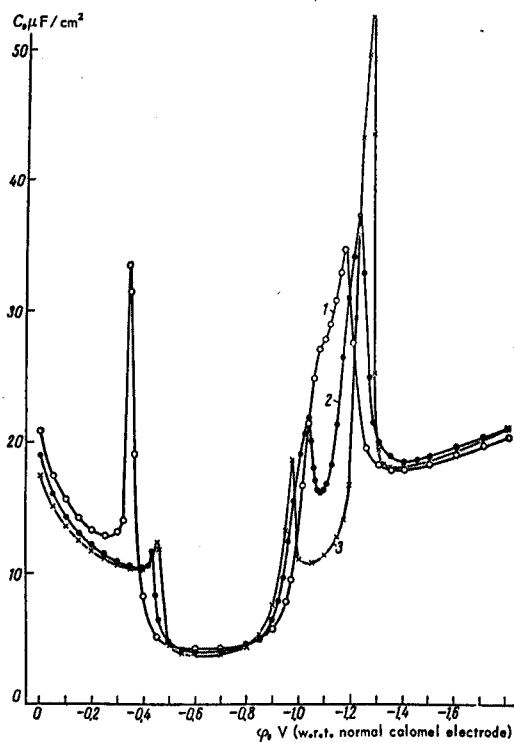


Fig. 4. Differential-capacity curves at 400 c/s and 25° in solutions of: 1) 0.1N Na_2SO_4 + 10^{-3} N $\text{C}_{12}\text{H}_{25}\text{OSO}_3\text{Na}$; 2) 0.25N Na_2SO_4 + 10^{-3} N $\text{C}_{12}\text{H}_{25}\text{OSO}_3\text{Na}$; 3) 1N Na_2SO_4 + 10^{-3} N $\text{C}_{12}\text{H}_{25}\text{OSO}_3\text{Na}$.

maximum, evidently connected with the desorption of $\text{C}_6\text{H}_{13}\text{OSO}_3^-$ anions when the mercury surface becomes negatively charged. Analogous desorption maxima near the point of zero charge on differential-capacity curves were observed by Miller and Grahame⁹ for polybasic-acid anions, the structural unit being $\text{NHCH}(\text{CH}_2\text{CH}_2\text{COOH})\text{CO}$, i.e. with a relatively small number of carbon atoms (equal to 5) per unit negative charge. For the addition of sodium nonyl sulphate (curve 3) adsorption of $\text{C}_9\text{H}_{19}\text{OSO}_3^-$ anions is observed over a wider potential range and the maximum capacity, associated with desorption from the mercury surface of nonyl sulphate anions, occurs at $\varphi = -0.85$. Also characteristic is the decrease in capacity to $15.5 \mu\text{F}/\text{cm}^2$ during adsorption of $\text{C}_9\text{H}_{19}\text{OSO}_3^-$ anions, linked with the increased number of carbon atoms in the adsorbed anion. On passing to a 10^{-3} N addition of $\text{C}_{12}\text{H}_{25}\text{OSO}_3\text{Na}$ the character of the adsorption changes sharply and Fig. 1 (curve 4) shows that the differential-capacity curve has two distinct peaks. The cathodic peak at $\varphi = -1.14$ appears to be a desorption peak for the surface-active anions, since at higher negative potentials the capacity curve approximates to that for a pure 0.01N sodium sulphate solution. But the anodic peak at $\varphi = -0.31$ cannot be associated with adsorption of $\text{C}_{12}\text{H}_{25}\text{OSO}_3^-$ anions, since at higher positive potentials the capacity curve is much lower than the curve for a pure 0.01N Na_2SO_4 solution. This would indicate that dodecyl sulphate anions were already adsorbed at $\varphi = 0.1$, which is not surprising in view of the negative charge of the adsorbed species. This peak can therefore be associated with a change in the nature of adsorption of the $\text{C}_{12}\text{H}_{25}\text{OSO}_3^-$ anions

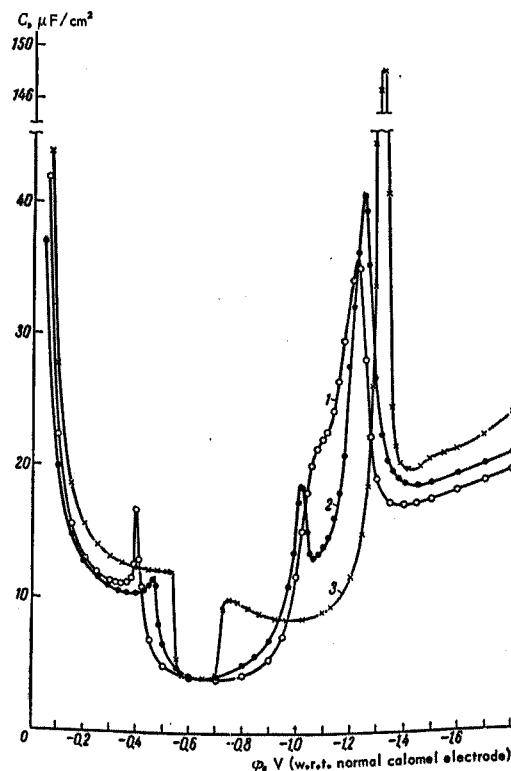


Fig. 5. Differential-capacity curves at 400 c/s and 30° in solutions of: 1) 0.5N LiCl + 10^{-3} N $\text{C}_{12}\text{H}_{25}\text{OSO}_3\text{Na}$; 2) 0.5N NaCl + 10^{-3} N $\text{C}_{12}\text{H}_{25}\text{OSO}_3\text{Na}$; 3) 0.5N CsCl + 10^{-3} N $\text{C}_{12}\text{H}_{25}\text{OSO}_3\text{Na}$.

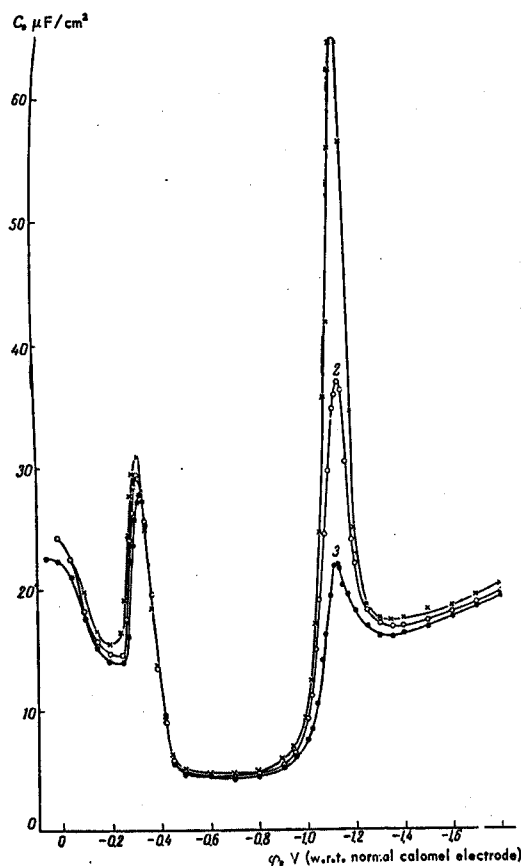


Fig. 6. Differential-capacity curves in solution of $0.01\text{ N Na}_2\text{SO}_4 + 10^{-3}\text{ N C}_{12}\text{H}_{25}\text{OSO}_3\text{Na}$ at 25° and frequencies of: 1) 20 c/s; 2) 400 c/s; 3) 10 000 c/s.

on the mercury-electrode surface. Curve 2 (Fig. 2) shows that this change in the character of adsorption on passing to a more positively charged surface is not accompanied by capacity peaks for $\text{C}_{12}\text{H}_{25}\text{OSO}_3^-$ anions for a lower concentration of the alkyl sulphate; the differential capacity goes smoothly from 17.1 to $5.3\text{ }\mu\text{F}/\text{cm}^2$ in the potential range -0.2 to -0.65 . Curve 3 (for $0.01\text{ N Na}_2\text{SO}_4 + 10^{-4}\text{ N C}_{14}\text{H}_{29}\text{OSO}_3^-$. Na) shows that an increase in the number of carbon atoms in the alkyl sulphate anion results in a marked increase in the amount of $\text{C}_{14}\text{H}_{29}\text{OSO}_3^-$ adsorbed compared to $\text{C}_{12}\text{H}_{25}\text{OSO}_3^-$. The differential-capacity curve for $0.01\text{ N Na}_2\text{SO}_4 + 10^{-4}\text{ N C}_{14}\text{H}_{29}\text{OSO}_3\text{Na}$ is thus very similar to that for $0.01\text{ N Na}_2\text{SO}_4 + 10^{-3}\text{ N C}_{12}\text{H}_{25}\text{OSO}_3\text{Na}$ (Fig. 1), having a distinct capacity peak at $\phi = -0.38$ associated with a change in the nature of the adsorption.

We also obtained the differential capacity-curves for saturated solutions of sodium hexadecyl and octadecyl sulphates in a base solution of $0.01\text{ N Na}_2\text{SO}_4$. The results (Fig. 3) show that the decrease in the potential range where adsorption of alkyl sulphate anions is observed is accompanied by a sharp reduction in capacity on passing from $\text{C}_{14}\text{H}_{29}\text{OSO}_3^-$ to $\text{C}_{18}\text{H}_{37}\text{OSO}_3^-$, which is probably connected with the sharp decrease in solubility of the alkyl sulphates with increasing length of carbon chain. At the same time the

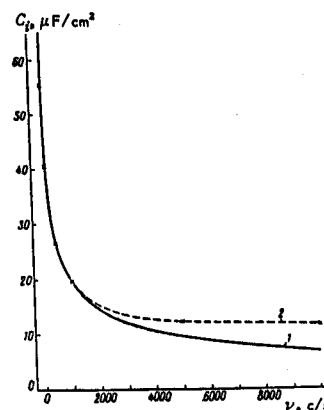


Fig. 7. Dependence of additional capacity on frequency for the cathodic peak in a solution of $0.01\text{ N Na}_2\text{SO}_4 + 10^{-3}\text{ N C}_{12}\text{H}_{25}\text{OSO}_3\text{Na}$; 1) calculated according to the theory of diffusion retardation; 2) experimental data.

minimum capacity also decreases, reaching a value of $3.5\text{ }\mu\text{F}/\text{cm}^2$ for $\text{C}_{18}\text{H}_{37}\text{OSO}_3\text{Na}$ (Fig. 3).

The differential-capacity curves for millinormal solutions of $\text{C}_{12}\text{H}_{25}\text{OSO}_3\text{Na}$ in 0.1 , 0.25 , and $1\text{ N Na}_2\text{SO}_4$ solutions are given in Fig. 4. In $0.1\text{ N Na}_2\text{SO}_4$ the cathodic desorption peak for $\text{C}_{12}\text{H}_{25}\text{OSO}_3^-$ is already noticeably expanded (cf. Fig. 1) and has an obvious kink at $\phi = -1.08$, and at higher Na_2SO_4 concentrations it is fully split into two peaks. With increasing concentration of base solution the right-hand peak increases and is displaced towards negative potentials, but the left-hand one decreases and is displaced towards positive potentials.

In $1\text{ N Na}_2\text{SO}_4$ the difference between the two peaks reaches 290 mV . Conversely, in $0.01\text{ N Na}_2\text{SO}_4$ the peaks coalesce into one complex peak. Increasing concentration of the base electrolyte also leads to a considerable shift of the anodic peak towards negative potentials. Thus an increase in the concentration of the base solution leads to an increase in the normal potential range where adsorption of $\text{C}_{12}\text{H}_{25}\text{OSO}_3^-$ on the mercury is observed, and to a decrease in the potential range where adsorption of these anions reduces the capacity of the electrical double layer to $\sim 4\text{ }\mu\text{F}/\text{cm}^2$. It should also be noted that for the same alkyl sulphate concentration (10^{-3} N) increasing the concentration of base solution from 0.01 N to 1 N decreases the minimum capacity from 4.4 to $3.6\text{ }\mu\text{F}/\text{cm}^2$. Differential capacities for $10^{-3}\text{ N C}_{12}\text{H}_{25}\text{OSO}_3\text{Na}$ in 0.5 N solutions of LiCl , NaCl , and CsCl^* were also measured (Fig. 5) and showed that the cationic radii of the base solutions strongly influenced the form of the curves. The nature of the changes induced on the curves on passing from LiCl to CsCl is analogous to the previous case of increasing concentration of Na_2SO_4 . With increasing cationic radius the cathodic desorption peak separates into two peaks, the right-hand one increasing (to $148\text{ }\mu\text{F}/\text{cm}^2$ for 0.5 N CsCl) and being displaced to more negative potentials. Further, the normal potential range, where adsorption of $\text{C}_{12}\text{H}_{25}\text{OSO}_3^-$ occurs, is increased on

* Potassium dodecyl sulphate is much less soluble in water than the corresponding Li , Na , Rb , and Cs salts and consequently no differential capacity values could be obtained for $10^{-3}\text{ N C}_{12}\text{H}_{25}\text{OSO}_3\text{Na}$ in 0.5 N KCl .

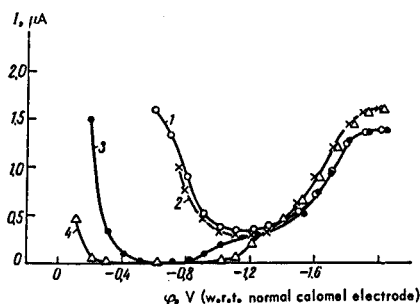


Fig. 8. Polarisation curves for solutions of: 1) $10^{-3} N K_2S_2O_8$; 2) $10^{-3} N K_2S_2O_8 + 10^{-3} N Na_2SO_4$; 3) $10^{-3} N K_2S_2O_8 + 10^{-4} N C_{12}H_{25}OSO_3Na$; 4) $10^{-3} N K_2S_2O_8 + 10^{-3} N C_{12}H_{25}OSO_3Na$.

passing from Li^+ to Cs^+ , and the potential range, where adsorption of alkyl sulphate anions is accompanied by minimum capacity, is sharply decreased.

DISCUSSION

It is of interest that, under certain conditions, peaks appear on the differential-capacity curves, which are not linked with desorption of alkyl sulphate anions from the mercury surface. Such a peak was clearly observed for a solution of $10^{-3} N C_{12}H_{25}OSO_3Na + 10^{-2} N Na_2SO_4$ at $\phi = -0.31$ (Fig. 1); the change in the nature of adsorption of the alkyl sulphate anions can be associated either with multimolecular adsorption of these anions, or with reorientation of the adsorbed species in the electrical double layer, or with the formation on the mercury surface of a micellar film, analogous to films formed on the surface of soap solutions¹⁴.

Micelle formation on the surface of aqueous solutions of aliphatic sodium alkyl sulphates has been established experimentally¹⁵, micelle formation being observed at an aqueous sodium alkyl sulphate solution n-heptane interface. One of the authors¹⁵ also obtained similar results for the aqueous solution/air interface (unpublished work). The critical concentration c_c for micelle formation, determined by different methods at 25° is $8.1 \times 10^{-3} N$ for a pure solution of $C_{12}H_{25}OSO_3Na$,¹⁶ but addition of an indifferent electrolyte noticeably decreases c_c due to the "salting out" effect. Betts and Pethica¹⁷ give c_c for a $C_{12}H_{25}OSO_3Na + 0.1 N NaCl$ solution at 22° as $1.36 \times 10^{-3} N$. Association of ions or micelle formation can also occur¹⁸ for concentrations of surface-active material less than c_c . All these results make it very probable that under certain conditions a micellar film forms on the mercury electrode/aqueous alkyl sulphate solution interface. The data contained in Fig. 5, apparently confirm this assumption, since, according to the literature, soaps which have the same aliphatic-acid anion but different cations, can differ basically in their properties¹⁴.

The capacity peaks which are not connected with complete desorption may be due to multimolecular adsorption of alkyl sulphate anions. This is supported by the data on $10^{-3} N$ sodium dodecyl sulphate solutions containing high concentrations of indifferent electrolytes (0.5 and 1 N) (see Figs. 4 and 5). There is a minimum-capacity region between two peaks, neither of which can be associated with

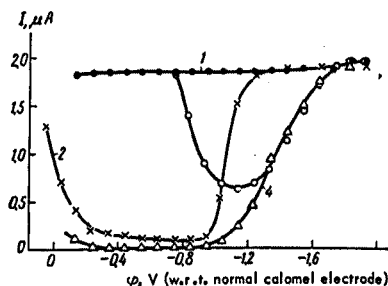


Fig. 9. Polarisation curves for solutions of: 1) $10^{-3} N K_2S_2O_8 + 1 N Na_2SO_4$; 2) $10^{-3} N K_2S_2O_8 + 1 N Na_2SO_4 + 10^{-3} N C_{12}H_{25}OSO_3Na$; 3) $10^{-3} N K_2S_2O_8 + 0.01 N Na_2SO_4$; 4) $10^{-3} N K_2S_2O_8 + 0.01 N Na_2SO_4 + 10^{-3} N C_{12}H_{25}OSO_3Na$.

complete desorption of the surface active material, and it is quite probable that they could be linked with the desorption of multilayers with increasing surface charge, the right-hand cathodic peak corresponding to desorption of the monolayer. When the concentration of indifferent-electrolyte is decreased, the surface charge decreases and the region of multilayer adsorption expands, thus causing the two cathodic peaks to approach each other until for a solution of $0.01 N Na_2SO_4 + 10^{-3} N C_{12}H_{25}OSO_3Na$ they finally combine to give one peak, indicating complete desorption. However, our minimum-capacity values ($\sim 4 \mu F/cm^2$) are very near to those obtained by Melik-Gaikazyan for monomolecular adsorption of n-hexyl and n-octyl alcohols; for multimolecular layers of these alcohols the capacity decreases from 2 to $0.9 \mu F/cm^2$.⁷ Further, we observed a decrease in minimum capacity with increasing concentration of indifferent electrolyte which contradicts the assumption of multilayer formation, since in the case of the aliphatic alcohols the reverse relation between minimum capacity and concentration of indifferent electrolyte is observed?

To elucidate the nature of these peaks we measured the differential capacities for a solution of $0.01 N Na_2SO_4 + 10^{-3} \times N C_{12}H_{25}OSO_3Na$ at the following a.c. frequencies: 20, 100, 400, 1000, 5000, and 10000 c/s. Fig. 6 containing data for 20, 400, and 10000 c/s, shows how much more the cathodic desorption peak depends on the frequency than the anodic peak, the former decreasing from 64.7 to $21.9 \mu F/cm^2$ on passing from 20 to 10000 c/s and the latter from 30.8 to $27.7 \mu F/cm^2$. Such a marked difference suggests that these peaks are connected with different processes on the surface of the mercury electrode.

Frumkin and Melik-Gaikazyan⁸ showed that experimental values for the additional capacity C_i plotted against a.c. frequency fitted well on a theoretical curve calculated on the assumption that diffusion of the organic substances to the mercury surface is the slow step in the adsorption process. We used analogous calculations for our work. According to this paper⁸ C_i can be calculated from the relation

$$C_i = C_0 \frac{a\sqrt{\nu} + 2}{(a\sqrt{\nu} + 1)^2 + 1}, \quad (1)$$

where C_0 is the additional capacity at zero frequency ($\nu = 0$) and

$$a = 2 \sqrt{\frac{\pi}{D}} \left(\frac{\partial \Gamma}{\partial c} \right)_s,$$

where D is the diffusion coefficient.

If the slow step in the adsorption process is diffusion, $(\partial I/\partial c)_\omega$ and consequently a should not depend on the frequency. We determined C_0 by extrapolation of the experimental data to zero frequency and a from Eqn. (1) at low frequencies, when the values of C_l are sufficiently great for errors in their determination to be a minimum.

The continuous curve (Fig. 7) shows the calculated dependence [from Eqn. (1)] of C_l on frequency for the cathodic desorption peak in a solution of $0.01 N Na_2SO_4 + 10^{-3} N C_{12}H_{25}OSO_3Na$, and the broken line represents the experimental values. At frequencies up to 1000 c/s the experimental points agree well with the theoretical curve, but above this the experimental frequency dependence is noticeably less than that required by theory. The experimental frequency dependence of the anodic capacity peak cannot be explained either by a slow diffusion step or by a slow adsorption process, indicating that this peak does not arise because of multilayer adsorption (associated in turn with diffusion of alkyl sulphate anions to the mercury surface), but because of some other process which occurs more rapidly on the mercury surface.

One such process could be the reorientation of the adsorbed $C_{12}H_{25}OSO_3^-$ ions in the electrical double layer, possibly with the formation of a micellar film, providing that this process can occur in the narrow potential range. The minimum-capacity region would then correspond to adsorption of alkyl sulphate anions with the carbon chains directed to the mercury surface. The decrease of this region on increasing the concentration of base solution (Fig. 4), and also on passing from LiCl to CsCl (Fig. 5) is easily explained as being due to the forcing out of the organic chain from the double layer, and this process will have greater effect the higher the charge on the mercury-electrode surface.

The divergence of experimental and theoretical values at frequencies greater than 1000 c/s indicates the more complex nature of the cathodic desorption peak for $C_{12}H_{25}OSO_3^-$ anions compared to the analogous case of the aliphatic alcohols⁸. This conclusion is confirmed by the occurrence of the split cathodic peak with increasing concentration of indifferent electrolyte (Fig. 4). If the assumption of multilayer adsorption is rejected, the left-hand cathodic peak on the differential-capacity curve can be explained as due to the breaking down of the surface micellar film, which is very probably formed at high concentrations of base solution. We may conclude, that although the most probable reason for the change in the nature of adsorption of alkyl sulphate anions on the surface of the mercury electrode seems to be the formation, under certain conditions, of a micellar film, the complex adsorption mechanism of these anions needs further investigation.

The Influence of Added Sodium Alkyl Sulphates on the Electrolytic Reduction of Anions

Adsorption of organic compounds can exert a strong influence on the course of electrochemical processes. In this paper we investigated polarographically the influence of the sodium alkyl sulphates listed above on the kinetics of the reduction of persulphate anions at the dropping mercury electrode. All the salts investigated retard this reduction. Figs. 8 and 9 show the polarisation curves for the reduction of potassium persulphate in the pure solution and also with additions of sodium dodecyl sulphate. With increasing negative polarisation the reaction ceases to be retarded, and the curves for the addition of alkyl sulphate coin-

cide with those for the pure solution. The potential at which this occurs usually corresponds to the desorption potential determined from the differential-capacity curves, but absolute correspondence of these potentials cannot be expected, since in the case of the electrolytic reduction of $S_2O_8^{2-}$ the time of formation of the adsorption layer is much less (5-6 sec instead of 30 sec). The more intimate changes in the structure of the double layer in the presence of added alkyl sulphate, which are indicated by the capacity peaks and linked with a change in the nature of the adsorption of alkyl sulphate anions, do not affect the kinetics of electrolytic reduction of persulphate anions. The effectiveness of added alkyl sulphates increases with increasing concentration (Figs. 8 and 9) and also with increasing carbon chain length.

A similar retardation by sodium alkyl sulphates is also observed in the electrolytic reduction of $PtCl_4^{2-}$ anions. In conclusion we would like to express our thanks to Academician A. N. Frumkin for his advice and attention.

We would also like to thank Prof. Bertsch, Director of the Institute of Organic Chemistry, Berlin Academy of Sciences, for supplying us with very pure sodium alkyl sulphates.

SUMMARY

1. The adsorption of alkyl sulphate anions (having 6, 9, 12, 14, 16, and 18 carbon atoms) on the mercury electrode has been studied. It has been shown that the anions desorb from the mercury surface at negative potentials, the process being accompanied by peaks on the differential-capacity curves.
2. Under certain conditions capacity peaks may be observed for sodium alkyl sulphate solutions, not associated with desorption of the surface active anions, but with a change in the nature of their adsorption on the mercury surface. Suggestions have been put forward as to the possible mechanisms of change of the double layer with change in the nature of the adsorption of alkyl sulphate ions.
3. All the alkyl sulphate anions investigated retard the electrolytic reduction of the $S_2O_8^{2-}$ anion over the entire range of potentials of their adsorption. The more intimate changes in the structure of the double layer in the presence of alkyl sulphate anions do not affect the kinetics of the electrolytic reduction of persulphate anions.

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Received 2nd October 1958

THE SIMILARITY METHOD IN MASS TRANSFER STUDIES

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Mass transfer by diffusion or thermal diffusion is often the principal mechanism of various processes, such as evaporation, and mixing and separation of gases. The kinetics of diffusion mass transfer govern partly or wholly the rate of chemical processes occurring in the intermediate or diffusion ranges. Study of thermal diffusion in gases provides information on intermolecular forces. Thermal diffusion is used in industry to separate gas mixtures. For these reasons diffusion and thermal diffusion have been the subjects of numerous experimental and theoretical investigations. These problems are considered here from the viewpoint of similarity of molecular processes.

Similarity of Molecular Transfer Processes

Conditions for the similarity of macroscopic transfer processes are now known in such detail that similarity methods are used in everyday practice. Molecular transfer processes present a different picture; Fourier, Newton, and Fick equations, employed in calculations, cannot be used for the derivation of similarity conditions for molecular transfer. This is so because the transfer coefficients are not constant but depend on temperature and pressure, generally in an unknown manner. Therefore the usual similarity analysis, consisting in finding the invariance conditions of the equations is here inapplicable. Other ways of analysing similarity conditions for molecular processes must therefore be sought. Usmanov's approach¹ is here briefly outlined.

Transfer processes are irreversible. In order to describe the state of a system in which such processes occur we shall break it up into several elementary macroscopic

subsystems. Provided gradients of the parameters are not excessive, the state of each subsystem can at any instant be described by specific values of the parameters. The state of a subsystem may be described by using the concept of a phase space characterised by a certain probability density distribution depending on the coordinates and molecular momenta:

$$\rho = \rho(q_i, p_i), \quad i = 1, 2, \dots, n. \quad (1)$$

The index i will from now on be omitted so as to simplify the notation.

The mean value of any function of the coordinates and molecular momenta of a subsystem is given by

$$\overline{f(q, p)} = \int f(q, p) \rho(q, p) dq dp, \quad (2)$$

where $f(q, p)$ is the value of a certain function of the coordinates and molecular momenta of the subsystem corresponding to a given microstate, and $\overline{f(q, p)}$ is the value of the same function taken as a mean for all possible microstates of the subsystem.

Let us consider two geometrically similar subsystems comprising equal numbers of molecules with the same number of degrees of freedom. These conditions must be obeyed if the corresponding phase spaces are to have the same number of dimensions. Let the states of the subsystems be then similar when

$$\frac{f'(q, p)}{f''(q, p)} = C_f, \quad \frac{\overline{f'(q, p)}}{\overline{f''(q, p)}} = C_f. \quad (3)$$

Furthermore we must have

$$\frac{\rho'(q, p)}{\rho''(q, p)} = C_\rho, \quad \frac{\overline{\rho'(q, p)}}{\overline{\rho''(q, p)}} = C_\rho, \quad (4)$$

since the probability density distribution is a function of the coordinates and molecular momenta and may therefore be regarded as a special form of the arbitrary function $f(q, p)$.

Using Eqn. (2), condition (3) for the mean values of $f(q, p)$ may be written down as

$$\frac{\overline{f'(q, p)}}{\overline{f''(q, p)}} = \frac{\int f'(q, p) \rho'(q, p) dq dp}{\int f''(q, p) \rho''(q, p) dq dp} = C_f. \quad (5)$$

On the basis of Eqns. (3) and (4) we can replace here functions of the first subsystem by analogous functions of the second subsystem. Since the elements of the phase volumes of these subsystems are equal we obtain

$$\frac{\overline{f'(q, p)}}{\overline{f''(q, p)}} = C_f C_\rho \frac{\int f''(q, p) \rho''(q, p) dq dp}{\int f''(q, p) \rho''(q, p) dq dp} = C_f, \quad (6)$$

whence it follows that the similarity constant for probability density distribution can only have one value $C_\rho = 1$; this is equivalent to the condition $\rho(q, p) = \text{idem}$ or, taking into account Eqn. (3), $\rho(q, p) = \text{idem}$.

This similarity condition is necessary but not sufficient. It does not contain any requirements with regard to uniqueness conditions which, we think, should take into account the properties of molecules and could be established by generalising experimental evidence.

As the subsystem changes the phase point moves along a certain trajectory. When the subsystem forms part of a system in equilibrium, the phase-point trajectory is confined to a thin layer adjoining the constant-energy surface, but leaves this layer when the system is not in equilibrium. Since the phase point moves in a varying field of probability distribution density and since probability density is a parameter which determines the similarity of molecular processes, the relative velocity of motion of the phase point