

# ADSORPTION-DESORPTION PROCESSES AT METAL SOLUTION INTERFACE A TENSAMMETRIC STUDY\*

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The role of various factors such as concentration and constitution of surface active agents,  $pH$ , anions of the electrolyte, frequency of alternating voltage and stirring in the adsorption-desorption processes at mercury solution interface are discussed on the basis of experimental results. Adsorption is primarily caused by squeezing type of forces and additionally by  $\Pi$  electron overlap and coulomb forces. Desorption results due to orientation of water dipoles at charged interfaces and specific adsorption of ions. Desorption of simple organic molecules appears to take place at the same surface charge density on either side of the electrocapillary zero.

## INTRODUCTION

Investigation of the adsorption of surface active substances can roughly be divided under two heads : (a) studies dealing with the equilibrium properties of the double layer and mechanism of adsorption-desorption processes and (b) dealing with the effect of adsorption on electrode reactions.

Studies of adsorption phenomena have been mainly conducted at mercury electrodes for obvious reasons of the ease of purification of the metals and reproducibility of the surface. A further advantage with mercury is that a wide range of potentials can be examined without interference from faradaic processes. These inferences for such a study can possibly be extrapolated to other metal electrodes (Antropov 1960).

The method of studying adsorption phenomena using the capillary electrometer, initiated by Gouy (1903), has been fully extended by Frumkin and Damaskin (1962) and many others.

A more accurate technique for the investigation of the adsorption processes which also helps in understanding the kinetics of the adsorption phenomena is the a.c. bridge technique, adopted first by Proskurnin and Frumkin (1935). The relevant literature, interpretation and implications of capacity measurement can be found in the publications of Frumkin and Damaskin (1962).

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A method which does not yield the phase characteristics essential for understanding the kinetics of the adsorption process but is useful for a rapid and extensive investigation is the method of tensammetry. Doss and co-workers (1959) in India and Bauer and co-workers (1960) in Australia have used this method both as an analytical tool and for the study of adsorption at mercury solution interface.

### EXPERIMENTAL

The method consists of superimposing a small alternating voltage of 30 mV (r.m.s.) over the polarizing potential and measuring the alternating current ( $i$ ) passing through the cell. If  $R_x$  and  $C_x$  are the resistance and capacity forming the impedance of the cell and are assumed to be in series

$$i = \frac{\Delta\phi}{\sqrt{R_x^2 + \frac{1}{C_x^2\omega^2}}} = \frac{\omega\Delta\phi C_x}{\sqrt{R_x^2 C_x^2 \omega^2 + 1}}$$

In the absence of any faradaic process  $C_x$  is the double layer capacity and if  $R_x^2 C_x^2 \omega^2 \ll 1$ , 'i' will be measure of the capacity. The i-V curves will be similar to C-V curves.

The electrical circuit adopted with a dropping mercury electrode is shown in Fig. 1. With a hanging mercury drop electrode, this circuit is modified as in Fig. 2. With a stationary electrode, it is necessary to remove traces of impurities present in the electrolytes. This was possible by passing the electrolytes through a column of specially prepared activated charcoal. Activated charcoal was heated to 500° for 24 h. in an atmosphere of nitrogen, washed repeatedly with pure hydrochloric acid and then with pure water. The charcoal was dried and packed in glass columns over similarly treated glass wool.

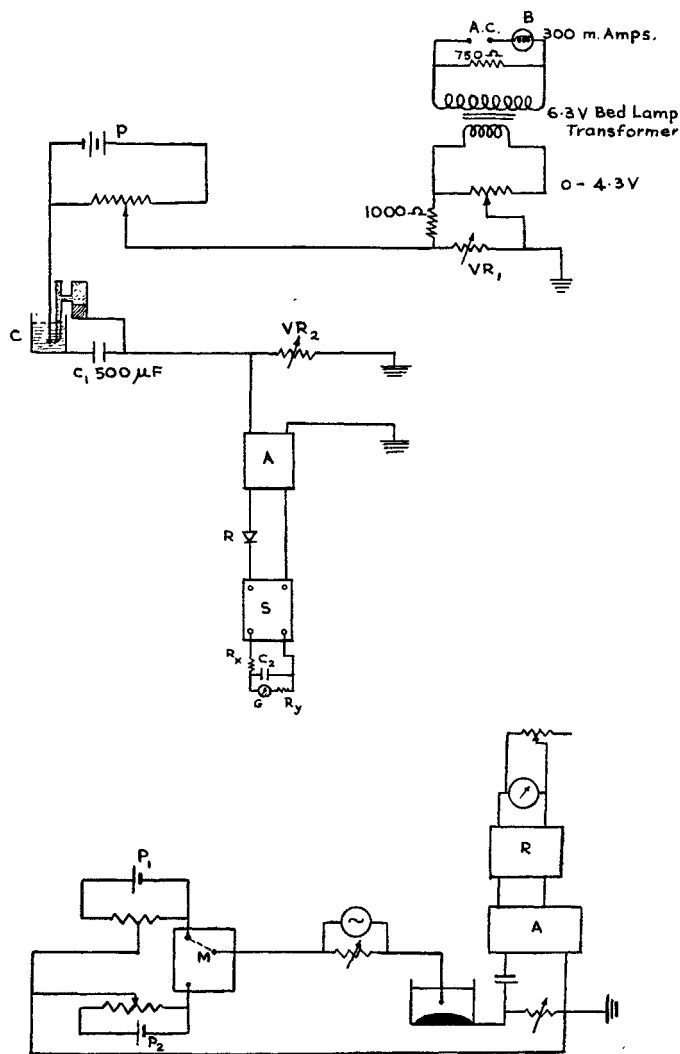
As an additional improvement the circuit was modified so that the hanging drop was maintained at a potential of -1.6 V when no impurities are expected to be adsorbed, then switched to the desired potentials and the current flowing was recorded as a function of time.

The chemicals used were of analytical grade. Benzene was tested for traces of thiophene and used when found free of thiophene. A pure sample of lauryl sulphate was supplied by Messrs. Marchon & Co. to whom thanks are due for the same.

### RESULTS

Some of the results of the investigation have been published previously (Narayan and Venkatesan 1961; Narayan 1962). Additional results presented are summarized in Tables 1-4 and Figs. 3-7. The behaviour of the aromatic

hydrocarbons and lauryl sulphate were investigated both with the d.m.e. and h.m.d.e.



FIGS. 1 and 2. Circuits adopted for the dropping mercury electrode and the hanging drop electrode respectively. *P*—Potentiometer, *A*—Amplifier, *R*—Rectifier, *S*—Shunt, *G*—Galvanometer, *C*<sub>1</sub> and *C*<sub>2</sub>—Condensers.

The important features are:

1. The tensammetric curves obtained with the organic substances in solution generally lie well below that obtained with the pure electrolyte alone, over a wide range of potentials. The depression in current is maximum near about the potential of the electrocapillary maximum (e.c.m.). However,

with thiourea in solution, capacity values are larger than those obtained with the pure electrolyte.

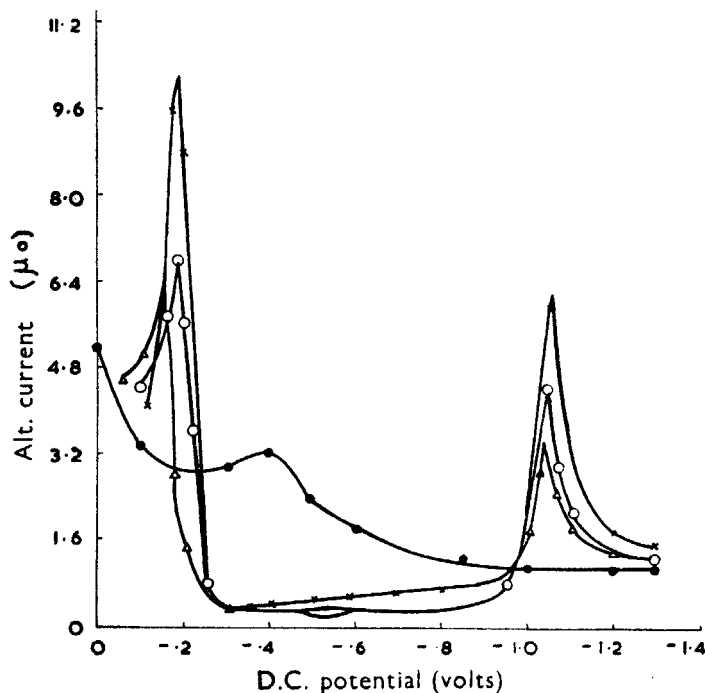


FIG. 3. Tensammetric study of hydrocarbons in 0.1 *M* KCl (d.m.e.). Frequency 50 *c/s*. 0.1 *M* KCl, ×, o, Δ solutions saturated with benzene, toluene and *m*-xylene respectively.

2. Two peaks on either side of the potential of the e.c.m. are generally obtained for the aromatic hydrocarbons in most electrolytes. Such peaks are not obtained with thiourea and derivatives (Narayan and Venkatesan 1961). With phloroglucinol in solution the peaks at cathodic polarization potentials are obtained only in alkaline media (Narayan 1962).

3. The peak potentials are nearly the same on the cathodic side while the anodic peak potential is dependent on the anion of the electrolyte.

4. With lauryl sulphate in solution, the peak obtained on the anodic side is small, sharp and lies below the curve of the supporting electrolyte. The current again rises to higher values on further anodic polarization.

5. With a large concentration of lauryl sulphate (0.015 per cent lauryl sulphate in 0.1 *M* Na<sub>2</sub>SO<sub>4</sub>) an additional small peak makes its appearance at negative potentials, preceding the large cathodic peaks. Even at the lower concentrations (0.008 per cent) the current at the peak potentials does not increase linearly but tends to form a hump.

## DISCUSSION

The view that depression in double layer capacity on the tensammetric current is a consequence of adsorption of a surface active agent has generally been accepted.

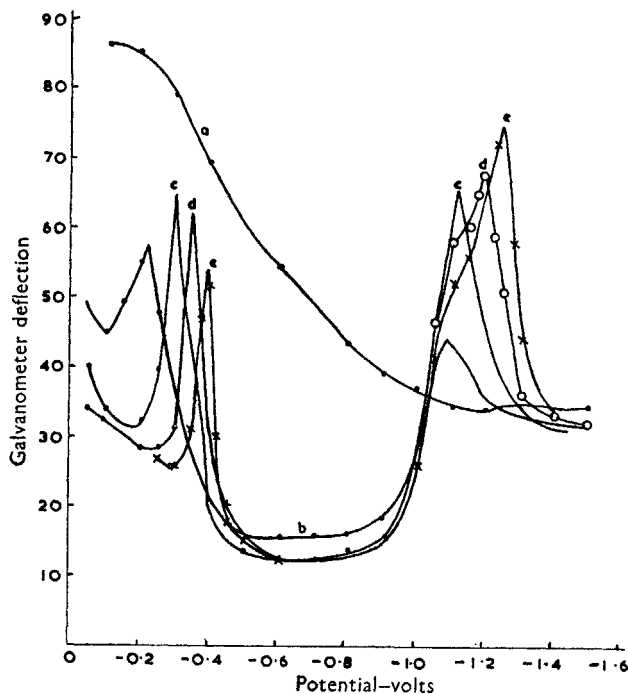


Fig. 4. Tensammetric study of sodium lauryl sulphate in  $0.1 M Na_2SO_4$  (d.m.e.), Frequency 50 c/s. *a* -  $0.1 M Na_2SO_4$ ; *b* to *e* correspond respectively to 0.002 per cent, 0.004 per cent, 0.008 per cent, 0.012 per cent lauryl sulphate in  $0.1 M Na_2SO_4$ .

The adsorption of an organic substance is limited to a range of potentials on either side of the potential of zero charge. At larger positive or negative polarizations, the surfactant is desorbed. The desorption is generally indicated by a sudden increase in the capacity or the tensammetric current, leading to the formation of peak. In some cases only humps instead of peaks are obtained.

It is our view that of the forces responsible for adsorption by:

1. Squeezing type of forces, exerted generally in aqueous or associated solvents,
  2. Coulomb forces, to be considered when surfactants with charged end groups are absorbed,
  3. Influence of metal— $\pi$  electron overlap, and
  4. Forces of chemisorptive nature,
- the first is the primary cause of adsorption.

The squeezing type of forces are mainly exhibited in aqueous solutions. The hydrophobic groups of the organic molecules are in a state of high energy and hence of instability and are squeezed out of the network of hydrogen bonds to the metal solution interface where they accumulate and are suitably

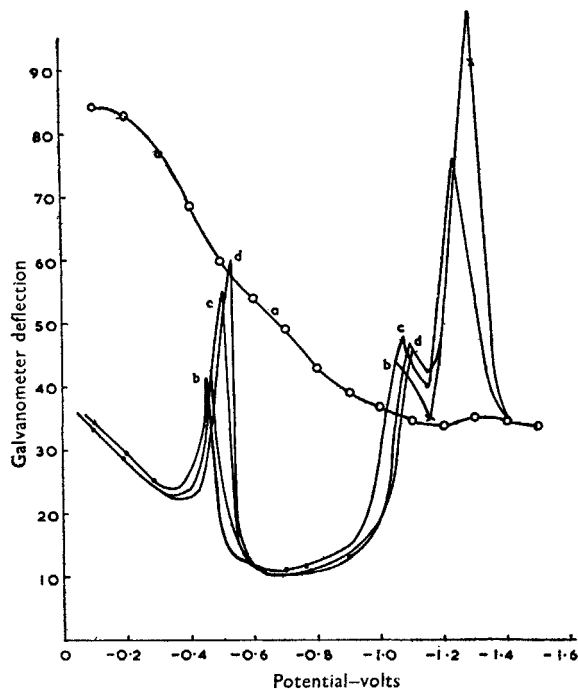


FIG. 5. Tensammetric study of sodium lauryl sulphate in  $0.1 M Na_2SO_4$  (d.m.e.), frequency 50 c/s. *a*.  $0.1 M Na_2SO_4$ ; *b* to *d* correspond respectively to 0.015 per cent, 0.035 per cent, 0.06 per cent lauryl sulphate in  $0.1 M Na_2SO_4$ .

oriented. The squeezing type of forces have been mainly credited for adsorption of organic compounds at solution-air interface with the polar end groups oriented towards the aqueous medium. Grahame and Miller (1957) had pointed out that the adsorption of ions like  $NO_3$  with unsymmetrical structure can be attributed to such forces.

We also observe that sodium lauryl sulphate, an anionic surfactant, is desorbed on the cathodic side almost at the same potential as the neutral aromatic hydrocarbon ( $-1.0 V$ ). The anionic sulphosuccinate manoxol OT is desorbed at a still higher negative potential of  $-1.3 V$ . The squeezing type of forces thus appear to overwhelm the electrical repulsion forces and stabilize adsorption.

Electrical interaction influences adsorption brought about by other factors. An anionic surfactant would be adsorbed over a large range of potentials on a positively charged metal surface and the reverse would be

true for a cationic surfactant. With neutral substances like benzene we observe two desorption peaks at potentials on either side of the electrocapillary maximum. With the anionic surfactant the cathodic desorption is sharply defined. The anodic desorption peak probably lies at potentials more positive than o.v.

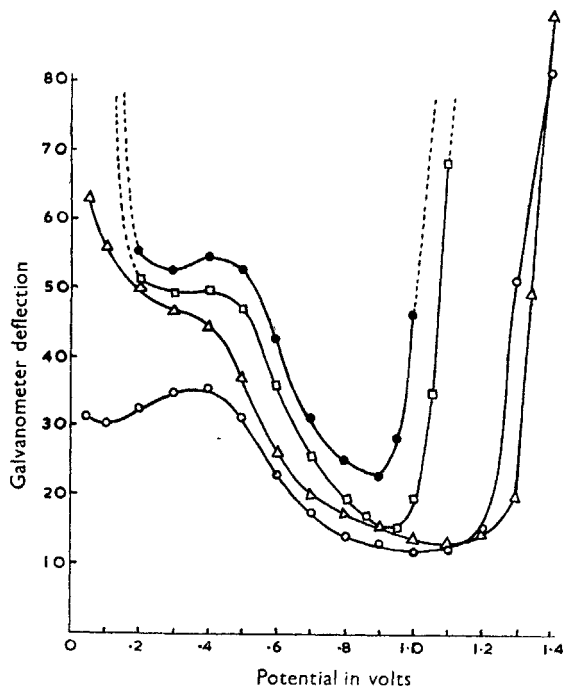
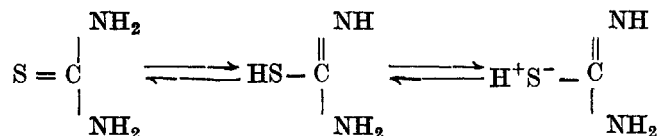


FIG. 6. Tensammetric study of thiourea and S-methyl thiuronium sulphate in 0.1 *M* HClO<sub>4</sub>.

- Δ — 0.1 *M* HClO<sub>4</sub>.  
 □, ● — 0.1 and 0.5 per cent thiourea in 0.1 *M* HClO<sub>4</sub>.  
 ○ — 0.1 per cent S-methyl derivative in 0.1 *M* HClO<sub>4</sub>.

It is to be pointed out that the capacity values obtained in the presence of thiourea are actually larger than for the pure electrolyte. Parsons (1961) had also drawn attention to the studies of Frumkin regarding the similarity of electrocapillary curves of thiourea and other specifically adsorbed anions and suggested this as due to the constant orientation of thiourea with its negative end towards the mercury even at negative values of the charge on the metal.

An explanation which involves a tautomeric shift in the thiourea molecule and further ionization in the adsorbed state is as follows:



This substance can thus be adsorbed in the anionic form and cause an increased capacitance as other specifically adsorbed anions. The ionization may possibly be restricted to within the double layer. Such a mechanism also explains lowering of the hydrogen overvoltage by thiourea. The molecule

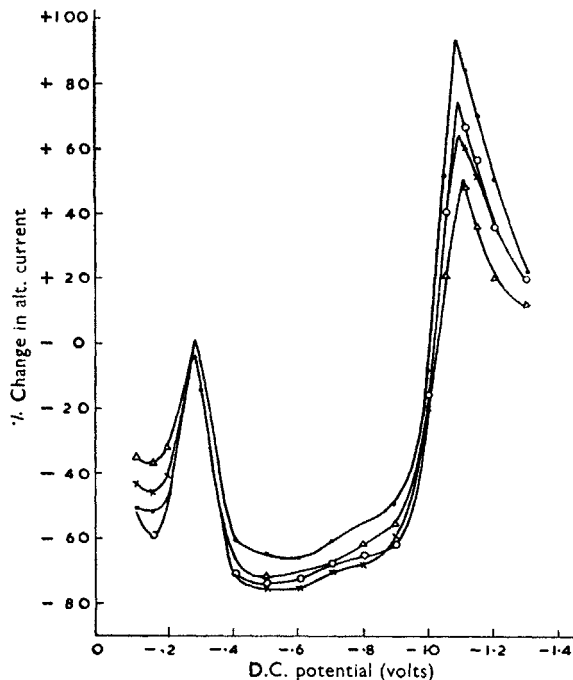


Fig. 7. Effect of frequency of alternating voltage on desorption peaks (d.m.e.).  
0.008 per cent lauryl sulphate in 0.1 M  $\text{Na}_2\text{SO}_4$ .  
50 c/s.  $\circ$  100 c/s.  $\times$  200 c/s.  $\triangle$  500 c/s.

may act as a bridge for the easy transfer of hydrogen atoms or ions to the metal. Further the steep rise in the current on the anodic side (o.v. vs. s.c.e.) with thiourea and monosubstituted thiourea can be attributed to the oxidation of the SH group (Edsberg 1954; Zuman, Mariosule and Federonko 1956; Jenovsky 1956). In the S-methyl derivative, substitution by the  $\text{CH}_3$  group on the S atom may hinder the tautomeric step or may shift the anodic oxidation potential and hence the steep rise is absent in the curve. Similarly with the disubstituted derivatives, as one hydrogen atom each of the two  $\text{NH}_2$  groups are substituted by aromatic groups, this tautomerism may be expected to be absent or not appreciable. Steric effects of the substituent phenyl groups have also to be taken into consideration. These groups will not only increase the thickness of the layer but also may prevent the close approach of sulphur atom to the mercury surface.

The increased capacitance resulting from specific adsorption of anions can be accounted for in terms of an 'anti-capacitance'. This is a capacitance



corresponding to the specifically adsorbed ions forming the inner Helmholtz plane, which is in series with the other capacitances of the outer Helmholtz and Gouy plane. However, the introduction, although in series of this capacitance, actually increases the total capacity and hence the term 'anti-capacitance'. The expression for the total capacitance derived in a simple manner is similar to the one derived by Devanathan and is

$$\frac{1}{C} = \frac{1}{C_{m-1}} + \frac{1}{C_{1-2}} + \frac{1}{C_{2-s}} + \left\{ \frac{1}{C_{1-2}} + \frac{1}{C_{2-s}} \right\} \frac{dq_1}{dq}$$

The fourth term is the anticapacitance term and is a negative quantity,  $C_{m-1}$ ,  $C_{1-2}$ ,  $C_{1-s}$  are respectively the capacitance magnitudes of the inner Helmholtz, outer Helmholtz and Gouy planes. Further implications and details are being published separately (Narayan 1962).

### DESORPTION

Desorption of the surfactants results from two forces:

1. The tendency for ions of the supporting electrolyte to be specifically adsorbed, and
2. The strong tendency for water dipoles to orient themselves at highly charged interfaces.

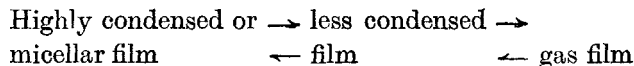
The oriented water layer forms the Helmholtz double layer and this orientation displaces the adsorbed molecules present in this part of the double layer. Further the competition from specifically adsorbable anion helps in making the desorption process complete. The desorption potential on the cathodic side is practically the same in all electrolytes except perchloric acid. If adsorption of ions causing desorption refers to the hydrated ions accumulating in the Gouy plane, this is almost equivalent to a water layer replacing the organic substance. The orientation of water dipoles due to electric field would be least at the point of zero charge and hence adsorption of organic molecules would be maximum at this potential although it has been shown that the adsorption is maximum at more negative potential (*e.g.* Devanathan). As the potential is made more anodic or cathodic, the orientation of water dipoles would increase and desorption of the organic molecule would take place due to displacement by these molecules and/or due to breaking up of the lateral bands between organic molecules in the adsorbed state.

As adsorption is indicated by a depression in the differential capacity or the alternating current in the present studies, desorption is indicated by a sharp rise in the current reaching a maximum and then falling sharply to the value in the supporting electrolyte. The peak potential is the desorption potential and is a characteristic of the substance adsorbed. The height of the peak depends upon a number of factors to be discussed.

With lauryl sulphate, in addition to the large cathodic desorption peak, we observe a sharp small peak on the anodic side at a concentration of the lauryl sulphate exceeding 0.002 per cent and a further small peak on the cathodic side when the concentration exceeds 0.015 per cent in sodium sulphate. These latter peaks have been obtained also in sodium perchlorate solutions. At this high concentration, precipitation takes place in potassium salts.

The process of actual desorption may be considered to be a phase transition from a liquid or condensed film to the gaseous film. This transition is expected to take place quickly over a small range of potentials. With increasing adsorption molecules accumulate at the interface and are oriented appropriately till a complete monolayer is formed. Further adsorption requires either the formation of multi-molecular layers or a further condensation of the adsorption film with consequent reorientations. An increased activation or concentration of the molecules may even lead to micelle formation as in the case of lauryl sulphate (Frumkin and Damaskin 1962). All these changes would be indicated by sharp changes in the differential capacity. With xylene and resorcinol in solution, a small hump is observed in the curves at about the potentials of large adsorption, probably for the same reasons.

In general, we may consider the adsorption-desorption processes to undergo successive stages of equilibrium as follows:



The first of these equilibria is indicated by a small sharp change in the capacity while the latter is indicated by a large sharp change in the capacity, the sharpness depending on the rate of transition.

Desorption of thiourea derivatives, of resorcinol and of phloroglucinol probably takes place gradually over a range of potentials. Hence only humps and not peaks are obtained in these cases. With thiourea derivatives, since adsorption involves the interaction of the functional group 'S' with the mercury surface, a slow desorption is understandable. In addition, the capacity peaks may not be sharp and marked since the differential capacity actually increases to a small extent on adsorption of thiourea.

#### INFLUENCE OF VARIOUS FACTORS ON THE ADSORPTION-DESORPTION PROCESSES

The desorption potential  $V_p$  is characteristic of the surfactant and varies with a number of factors such as concentration of the substance,  $pH$  of the medium, anions of the supporting electrolyte substituent groups on the nucleus, etc.

The desorption potential-concentration relation was shown to be logarithmic and this relation follows easily from the application of the absolute theory of rate processes. It was shown previously (Narayan 1962) that

desorption takes place for the condition  $\theta = \frac{1}{2}$  when  $\theta$  is the fraction of surface covered and 'x' is a statistical factor that accounts for mutual interactions of the adsorbed species. 'x' is characteristic of the adsorbed species and independent of bulk concentrations. Lateral repulsion effects would diminish the life of a molecule in the adsorbed state while attractive forces would lengthen the life in the adsorbed state. The variation in desorption potential  $V_p$  is given by the relation  $\frac{dV_p}{d \ln c} = \frac{KT}{h_3 \epsilon^0}$  where  $\epsilon^0$  is the energy of adsorption at the potential of e.c.m.\* Qualitatively speaking, the anodic and cathodic potentials are shifted respectively to more positive and negative values with increasing concentration. When one considers a charged surfactant, it is likely that the potential of zero charge itself may be shifted. Frumkin's derivation of the  $V_p$  concentration relationship includes a term for the latter factor.

The extent of adsorption and hence the extent of depression of the current increases with increasing concentration to a constant value when presumably saturation of the surface takes place.

The effect of substituent polar groups on the adsorption-desorption processes is seen from Tables 1-2. Toluene and xylene are desorbed earlier than benzene on the cathodic side while a higher positive polarization is required before they are desorbed on the anodic side. Introduction of a methyl group with its inductive effect may increase the negativity of the ring at the points of adsorption and hence cause an earlier desorption from negatively charged surface, and similarly shift the anodic desorption potential to a more positive value. However, the introduction of another methyl group in the ortho or meta positions influences to a smaller extent on the cathodic side. Alternatively electronmetal overlap may be affected by the introduction of the methyl groups. The extent of adsorption remains unaffected. The study of *p*-xylene with zero dipole moment will be of help in understanding these effects. With the thiourea derivatives the position of the halogen atoms exerts no influence.

The role of the anion of the electrolyte is more complicated. The extent of adsorption itself is unaffected. The cathodic desorption potentials also are nearly the same in all the electrolytes except with benzene in perchloric acid. Considering the three aromatic hydrocarbons we observe that the anodic desorption potential shifts to increasingly positive values in the order of  $\text{ClO}_4^-$ ;  $\text{NO}_3^-$ ;  $\text{Cl}^-$  and  $\text{SO}_4^-$  ions. With benzene in solution, the desorption potential on the cathodic side corresponds to a surface charge density of about -12

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\* The assumption made in the derivation that the energy of adsorption is linearly dependent on the potential has been objected to, as this will not yield double peaked capacity curves (*private communication*), see Frumkin and Damaskin (1962) also. It is felt that the other models suggested in this connection are also not satisfactory and this subject is under more detailed study.

TABLE I  
*Influence of different electrolytes on the adsorption-desorption behaviour of benzene*

Electrolyte	Potential (volts) of maximum adsorption		Percentage decrease in current		Desorption potential (volts)		Percentage increase in current	
	d.m.e.	h.m.d.e.	d.m.e.	h.m.d.e.	d.m.e.	h.m.d.e.	d.m.e.	h.m.d.e.
0.1 M KCl	-0.6	-0.6 to -0.7	77	67	(a) -0.18 (b) -1.18	-0.17	200	70
0.1 M KNO <sub>3</sub>	-0.6	-0.7 to -0.8	68	74	(a) -0.25 (b) -1.16	-0.3	200	170
0.1 M Na <sub>2</sub> SO <sub>4</sub>	-0.5	-0.7 to -0.8	68	72	(a) -0.16 (b) -1.15	-0.16	220	140
0.1 M NaClO <sub>4</sub>	-0.6	—	82	—	(a) -0.3 (b) -1.15	-1.15	11	87
0.1 M HClO <sub>4</sub>	-0.6	-0.9 to -1.1	58	65	(a) -0.36 (b) -1.22	-0.6	220	160
							41	*
							225	100

\* Anodic desorption peak not observed.

TABLE II  
*Influence of different electrolytes on the adsorption-desorption behaviour of toluene and m-xylene at the dropping mercury electrode*

Electrolyte	Potential (volts) of maximum adsorption		Percentage decrease in current		Desorption potential (volts)		Percentage increase in current	
	Toluene	m-xylene	Toluene	m-xylene	Toluene	m-xylene	Toluene	m-xylene
0.1 M KCL	-0.6	-0.5*	80	80	(a) -0.18 (b) -1.04	-0.16	170	150
0.1 M KNO <sub>3</sub>	-0.5	-0.4*	70	75	(a) -0.2 (b) -1.1	-1.03	280	200
0.1 M Na <sub>2</sub> SO <sub>4</sub>	-0.5	-0.5*	66	68	(a) -0.1 (b) -1.08	-1.05	70	77
0.1 M NaClO <sub>4</sub>	-0.6	-0.6	82	78	(a) -0.25 (b) -1.025	-0.05	174	155
0.1 M HClO <sub>4</sub>	—	-0.5*	—	70	(a) — (b) —	-1.04	230	140
						-0.1	5	†
						-1.025	200	120
						-0.26	—	10
						-1.1	—	160

\* Fluctuations of the current are observed.

† Desorption peaks not obtained.

micro coulombs as calculated from the differential capacity curves of the pure electrolytes. Similarly on the anodic side, the desorption potentials in potassium chloride and sodium sulphate correspond to 12 micro coulombs  $\text{cm}^{-2}$ . With potassium nitrate it is less than 8 micro coulombs  $\text{cm}^{-2}$ . The desorption potentials of the lauryl sulphate at the lower concentrations in the various media on the cathodic side are nearly the same. The behaviour in perchlorate and nitrate media is difficult to explain. From the capacity-potential curves given by Grahame, we observe that the capacity rises steeply in KCl,  $\text{KNO}_3$ ,  $\text{KClO}_4$  and gradually in  $\text{Na}_2\text{SO}_4$ . Further, the fall in capacity in the region of the 'hump' starts earlier with  $\text{KNO}_3$  than with KCl. The humps are also more pronounced in  $\text{KNO}_3$  and  $\text{NaClO}_4$  than in KCl. There definitely appears to be some relation between the potentials corresponding to the formation of the hump, of desorption and of drop-time effects (Narayan, Venkatesan and Doss 1961) previously observed by this author. Devanathan had stressed on the importance of the minimum in the capacity curves of various electrolytes. This minimum is obtained at 13 micro coulombs and probably corresponds to a layer of completely oriented water dipoles. The charge density, rather the desorption potential, is the important factor and this incidentally also brings out the role of anions.

The rise in the differential capacity or the tensammetric current at the peak potential is the consequence of rapid fluctuations in the integral capacity of the double layer, under the pulsating field. Such changes are particularly large when the surface active substances are desorbed. As an extreme case, we may consider at the desorption potential a dynamic equilibrium on the solution side of the double layer (Helmholtz layer) between two extreme states: a completely ionic state in the absence of adsorption and a completely non-ionic state when adsorption is large.

The height of the peak would thus largely depend on the sharpness of desorption. The desorption rate can be expected to be somewhat greater with the dropping mercury electrode than the hanging mercury drop electrode. We observe from Table I that the peak heights of benzene are larger at the dropping mercury electrode.

Electrocapillary phoretic movements reported by Doss and Venkatesan (1959) can enhance the peak currents by increasing the rate of renewal of the mercury surface. In this connection the effect of stirring on the adsorption-desorption process was studied. If an oxygen-free supporting electrolyte is stirred carefully so that the dropping mercury electrode is not mechanically affected, the current potential variations are essentially the same as in unstirred solutions. At a higher rate of stirring which causes a premature shearing off of the drop, the current fluctuates and is larger, particularly on the cathodic side than in unstirred solution. With a surface active substance in solution the extent of adsorption is unaffected by stirring.

With increasing concentration of the surfactant the height of the desorption peak also increases initially and then remains constant or decreases. We observe such variations with lauryl sulphate and phloroglucinol in alkaline media. With increasing concentration, the desorption potential is shifted generally in the direction of increasing charge density, assuming the potential of zero charge not being affected. It is difficult to understand why the peak height does not proportionately increase at the higher concentration.

A marked effect of  $pH$  on the desorption potential and on peak height is observed with phloroglucinol in solution. In alkaline media, the desorption rate becomes larger with phloroglucinol as indicated by increasing height of the peaks. It is to be inferred that the species adsorbed under these conditions contain negatively charged end groups and hence desorption is not only sharp but also involves the removal of a layer of negatively charged ions to be replaced by positive ions. The negatively charged species are the products of ionization of the parent molecules. The peak current at  $pH$  8 is small while it is large and constant beyond  $pH$  9. The dissociation constant for phloroglucinol is  $4.5 \times 10^{-10}$  while those of resorcinol are  $7.11 \times 10^{11}$  and  $4.78 \times 15^{-12}$  (Doss and Venkatesan 1959). Further, phloroglucinol can exist in the quinonoid form (Heilbron and Burnbury 1953) and hence the adsorption film formed can be different from that of resorcinol. The desorption potential of phloroglucinol is made more positive with increasing  $pH$ , desorption taking place earlier probably as a result of increasing negative charge of the adsorption layer.

The peak heights decrease in the series benzene, toluene and xylene, although the extent of adsorption is practically the same for all these substances. The reduction in peak heights is much larger at the cathodic desorption potentials than at the anodic desorption potentials. Considering the cathodic desorption peaks an explanation that offers itself is that the adsorption-desorption process becomes more sluggish with the introduction of methyl groups involving increased molecular weights, different modes of orientation and desorption at a lower negative surface charge density.

On the anodic side the desorption potentials, particularly in  $KNO_3$ ,  $NaClO_4$  and  $Na_2SO_4$ , are increasingly more positive for xylene and toluene than for benzene. Hence the reduction in peak heights due to other reasons are partly compensated for by the increase in peak heights due to desorption at a higher positive surface charge density.

The influence of frequency on the adsorption-desorption processes has also been investigated. As seen from the figures, frequencies up to 500 c/s have a small effect on the extent of depression of the current. The height of the desorption peaks, however, rapidly decreases with increasing frequency. The processes at the cathode desorption potential is thus inferred to be slow, and the rate-controlling process is probably diffusion of the adsorbable species

from and to the bulk. Accommodation into the double layer involves displacement of specifically adsorbed ions, oriented water dipoles and coulombic repulsion by ions already adsorbed and reorientation of the adsorbed species. These latter processes may contribute to the activation barrier for adsorption (Lorenz and Mockel 1956, 1958).

The anodic peak heights of lauryl sulphate on the other hand are unaffected by the frequency increase. The processes causing this peak hence must be rapid. As suggested earlier, the transitions involved are mostly restricted to the adsorption layer, involving only reorientations. As practically no diffusion step is to be considered, the transitions can be fast. Further the equilibrium involves only two otherwise identical states except for the modes of orientation, and hence the integral capacity changes are small. This anodic peak, however rapid the transition, will be sharp but small.

#### TIME REQUIRED FOR ADSORPTION EQUILIBRIUM

The present investigations reveal that the adsorption equilibrium is reached quite quickly. With a dropping mercury electrode of drop-time 5 sec, the maximum depression in current due to adsorption is seen to be nearly 80 per cent. Under the same experimental conditions, when a faster dropping mercury electrode with drop-time of about 2.5 sec is used, the depression in current is only 65-70 per cent. With a hanging mercury drop electrode also, the depression in current is 82 per cent. The work of Laitinen and Mosier (1958) indicates that adsorption equilibrium in the cases they studied is attained within 10 sec. Tables III and IV represent some typical results obtained in the present investigations with the hanging drop electrode. Current magnitudes in terms of galvanometer deflections are recorded as a function of time after switching to the polarizing potential.

From these results we may conclude, allowing for the response of the galvanometer, etc., that with an appreciable concentration of the surfactants under study the adsorption equilibrium is reached within 10 sec at a stationary electrode and probably earlier with a dropping mercury electrode. Alternatively, we can infer that adsorption takes place in two stages—the first occurring very quickly followed by a slower increase in adsorption. The process of adsorption could gradually slow down, particularly for surfactants with ionized end group as was pointed out by Doss (1940). After the adsorption of a few ions further adsorption will involve activation to overcome the potential barrier caused by repulsion from similar electrical charges.

#### CONCLUSIONS

1. The tensammetric method is a simple technique for extensive investigations of the adsorption-desorption processes.



TABLE III  
Galvanometer deflection at  $x$  sec after switching on

d.c. vs. s.c.e.	5 sec	10 sec	15 sec	30 sec	60 sec
-0.1 V	125	135	135	135	134
-0.2	140	150	150	150	..
-0.225	145	160	162	162	162
-0.250	155	162	162	162	160
-0.300	91	93	93	93.5	..
-0.4	50	32	29	28.5	28.5
-0.5	34	24	21.5	21.5	21.5
-0.6	30	22	20	20	20
-0.7	30	23	20.5	20	20
-0.8	34	24	22	21.5	21.5
-0.9	40	29	27	27	27
-1.0	72	88	90	92	93*
-1.025	114	130	136	136	..
-1.05	135	160	160	162*	..
-1.1	116	120	119	117	118*
-1.15	93	93	91	89	..
-1.2	75	76.5	76.5	76.5	..
-1.3	65.5	65.5	65.5	65.5	..
-1.4	63.5	63.5	63.5	63.5	..

Solution 0.1 M  $\text{KNO}_3$  saturated with toluene a.c. 30 mV r.m.s. 50 c/s. drop area 0.079  $\text{cm}^2$ .

\* Fluctuation in current.

TABLE IV  
Galvanometer deflection at  $x$  sec after switching on

d.c. vs. s.c.e.	5 sec	10 sec	15 sec	30 sec	60 sec
-0.1 V	48	46	45	44	—
-0.2	43	39	38	38	—
-0.25	44	40	39	39	—
-0.30	77	76	75	76*	—
-0.35	50	52	54	55	—
-0.4	30	22.5	22	22	—
-0.5	24	16	15	15	15
-0.6	21	15	13	13	13
-0.7	20	14	13.5	13	13
-0.8	24	16	14	13.5	13.5
-0.9	22	16.5	15	15	—
-1.0	40	33	31	29	28
-1.05	63	64	63	63.5*	—
-1.125	86	94	96	96*	—
-1.20	64	68	68	68	—
-1.3	48	48	48	48	—

Solution -0.004% lauryl sulphate in 0.1 M  $\text{NaClO}_4$  a.c. = 30 mV (r.m.s.) 50 c/s. Drop area -0.079  $\text{cm}^2$ .

\* Small current fluctuations are observed.

2. Desorption of organic substances are mainly caused by the strong tendency of water dipoles to orient at charged interfaces and competition from specifically adsorbable ions, the charge density being the important parameter.

3. Phase transitions in the adsorption film are indicated as peaks in the i-V curves.

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