

## ADSORPTION PARAMETERS OF STRONGLY ADSORBABLE TETRAALKYLAMMONIUM CATIONS ON MERCURY OBTAINED BY THE CAPILLARY ELECTROMETER

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The adsorption of tetrapropyl- and tetrabutylammonium cations in 0.1N-HClO<sub>4</sub> and 0.1N-H<sub>2</sub>SO<sub>4</sub> has been studied using capillary electrometer with a reasonable accuracy. Some experimental difficulties encountered in electrocapillary measurements are discussed. On  $q^m$  (charge density) vs  $E$  curves one point of intersection was found implying the existence of a single potential and a single charge density of maximum adsorption. A well defined potential and corresponding charge density of maximum adsorption was found. The  $\Gamma_m$ -values (maximum surface excesses) obtained experimentally were compared with theoretical values. In perchlorate solutions Esin and Markov coefficients were calculated.

In a series of previous papers (for review see<sup>1,2</sup>) the influence of strongly adsorbable surfactants (SAS) the adsorption of which was diffusion controlled on various electrode reactions using d.c. polarography was studied. From the form of  $i-t$  curves in d.c. polarography some information on the adsorption could be obtained and in many cases the maximum surface excess could be determined. For a better understanding of the inhibition or acceleration effect of these SAS on electrode reactions complementary adsorption measurements using direct methods are very important. A special attention was paid to the application of capillary electrometer for these studies.

The problem of faulty measurements with the capillary electrometer especially at potentials more positive than is the potential of the zero charge (pzc) was reported for pure dilute electrolytes (<0.1M) several times and an interesting approach to understanding of this behaviour is given in papers<sup>3,4</sup>. In our studies this effect had a minor importance. A still more peculiar behaviour is encountered in presence of highly adsorbable surfactants, *e.g.* extremely large time effects to reach adsorption equilibrium, deterioration of properties of the capillary with time, hysteresis, sticking of the meniscus<sup>5,6</sup> *etc.* As will be shown in case of highly adsorbable surfactants the surface tension values can be obtained with reasonable reproducibility and accuracy. This applies to tetrapropyl- and tetrabutylammonium cations and the obtained results are given in the present paper. However, no reproducible results could be obtained for tribenzylammonium cation which was used very often in our previous papers as a very strong inhibitor. Although the adsorption of tetraalkylammonium cations on mercury has been known for many years and was described in several papers (ref.<sup>7-11</sup>) the results are prevalingly of a qualitative nature or were not treated in detail.

Concerning the technique used for these studies capillary electrometer measurements were carried out predominantly for pure tetraalkylammonium at higher concentrations ( $>0.01\text{M}$ ). The interfacial tension at the mercury-solution interface showed a higher lowering in presence of iodide than in chloride solutions of  $0.1\text{M}$  tetrapropylammonium cations<sup>8,9</sup>. A thorough study of electrocapillary curves for iodide salt of tetramethyl- up to tetrabutylammonium cations is given by Devanathan and Fernando<sup>10</sup>. Due to the co-adsorption of iodide a very complicated shift of the pzc was observed. The relative surface excess  $\Gamma_+$  and  $\Gamma_-$  of the cation or the anion respectively, were determined from obtained surface tension values as function of the charge densities  $q^m$  of the mercury electrode. The electrocapillary curves of tetrapropylammonium iodide were measured in the concentration range  $0.01-0.25\text{M}$  and those of tetrabutylammonium iodide for two concentrations  $0.03$  and  $0.06\text{M}$ .

From differential capacity measurements<sup>11</sup> in the series of tetraalkylammonium cations the increase in the adsorptivity with the increase of the number of carbon atoms was found and the simultaneous adsorption of surface active anions at relatively negative potentials was demonstrated. The adsorption behaviour of the tetrabutylammonium cation<sup>12</sup> obtained from differential capacity measurements was interpreted by means of the Frumkin's theory of adsorption<sup>13</sup>.

In the recent paper<sup>14</sup> a comparison of the adsorption of the tetrapropyl- and tetrabutylammonium cation in sulfate solutions at the interface water-mercury and water-air was given and the corresponding interpretation of the difference in obtained values was presented. The results at mercury interface in the mentioned paper<sup>14</sup> were obtained using capillary electrometer and differential capacity measurements. However, neither electrocapillary curves, nor the reproducibility and other problems related to this kind of measurement were discussed.

## EXPERIMENTAL

Interfacial tension at the mercury interface was measured using capillary electrometer after Gouy in the modification made in the Electrochemical Institute of the Academy of Science USSR.\* The position of the meniscus of mercury in the conical capillary of the inner diameter  $25-30\ \mu$  was kept  $80\ \mu$  from the tip of the capillary, and observed at  $30\times$  magnification. When the position of the upper meniscus in the tube was read at the attached scale using a magnifying glass the precision in surface tension values was about  $\pm 0.15$  dyn. The cathetometer KM6 (made in USSR) placed in the distance  $75\ \text{cm}$  allowed the readings of the height of mercury column with the precision  $\pm 0.01\ \text{mm}$  which corresponds to  $\pm 0.01\ \text{dyn cm}^{-1}$ . However, the reproducibility even in a supporting electrolyte alone is lower, of about  $0.1-0.2\ \text{dyn cm}^{-1}$ . Practically the same reproducibility was found if surfactants of "a medium" adsorptivity as *e.g.* pyridine or of a lower adsorbability as *e.g.* hexafluoropropanol were studied.

The capillary "wear" effect described in the literature (*e.g.*<sup>3</sup>) in electrolyte solutions manifested itself by a gradual lowering of the surface tension at potentials more positive than pzc when repeating measurements with a new capillary. After several runs of measurements the values of surface tension were well reproducible even at positive potentials. The position of pzc and  $\gamma$ -values at more negative potentials than pzc were very well reproducible. As far as the proper function of the capillary was not deteriorated by some accidental factors the value of maximum surface tension in electrolyte solution was constant even within several months.

\* We express our thanks to the Electrochemical Institute of the Academy of Science, USSR for supply of drawings of the mechanical part of the instrument.

During electrocapillary measurements of tetrapropyl- (TPA) and tetrabutylammonium (TBA) cations in 0.1N-H<sub>2</sub>SO<sub>4</sub> and 0.1M-HClO<sub>4</sub> several difficulties were encountered especially with TBA. Both substances are strongly adsorbable at mercury electrode causing a substantial lowering of the surface tension even at concentrations 10<sup>-4</sup>M and lower. At such low concentrations sometimes several hours were necessary to obtain time-independent values of surface tension  $\gamma$ . When following the time dependence of  $\gamma$  usually a relatively large lowering was observed at the beginning, however, it took a long time to reach the limiting value. In case of the tetrapropylammonium cation at low concentration (10<sup>-4</sup>M) and for potentials more negative than -0.8 V (s.c.e.) a sudden decrease of the adsorption effect in comparison with mean average values obtained in smoothly running series of experiments was sometimes observed. After cleaning the capillary with 0.1N sulfuric acid a normal  $\gamma$ -lowering was again achieved. At higher concentrations of TPA the measurements proceeded smoothly. The measurements with TBA brought more difficulties than in the preceding case. Quite often the capillary worked properly and the whole concentration set of electrocapillary curves showed a regular decrease in  $\gamma$ -values with concentration and potential. After several runs the properties of the capillary were deteriorated in such a way that the surface tension returned to the values corresponding to that of the supporting electrolyte alone. The cleaning of such a capillary using dil. sulfuric acid, conc. nitric or hydrochloric acid, ethanol, acetone did not bring the expected result. Only the standing in a mixture of dichromate and sulfuric acid for several hours returned the capillary to the proper functioning. As a tentative explanation it is assumed that a preferential adsorption of the surfactant occurs on a layer of surfactant firmly attached to the wall of the capillary.

In the case of tribenzylammonium cation for concentrations smaller than 10<sup>-3</sup>M in 0.1N-H<sub>2</sub>SO<sub>4</sub> no regular shape of the electrocapillary curves could be obtained. The position of the meniscus in the capillary at a constant potential moved almost periodically upwards and downwards. Hence  $\gamma$ -values oscillated between the value of the supporting electrolyte and the value which should be expected for the given concentration of surfactant, especially at potentials more negative than pzc. At the concentration of tribenzylamine  $\approx 10^{-3}$ M which corresponds almost to its maximum solubility in water smooth  $\gamma$ -E curves using a capillary electrometer were obtained, however, the reproducibility was low,  $\pm 2$  dyn cm<sup>-1</sup>. Hence for extremely highly adsorbable substances the capillary electrometer is not applicable. For such substances the drop-time technique or even better the differential capacity measurements are to be preferred. When the dropping electrode is used it must be conical. Usual cylindrical capillary is not suitable since after a certain time the solution enters into the capillary and the drop-time is changed in an irreproducible way (for more detail see<sup>15</sup>). With drop-time technique the  $\gamma$ -E curves of tribenzylamine in water and water-ethanol mixture were relatively well reproducible and the results will be published elsewhere. The precision using the drop-time techniques is lower than with the capillary electrometer if the latter works properly.

Nevertheless for TPA and TBA in solutions used in previous inhibition studies<sup>1,2</sup> i.e. 0.1M-HClO<sub>4</sub> and 0.1N-H<sub>2</sub>SO<sub>4</sub> series of  $\gamma$ -E plots for various concentrations could be selected which were reasonably reproducible. The precision for higher concentration was  $\pm 0.2$  dyn cm<sup>-1</sup>, for lower concentrations somewhat less,  $\pm 1$  dyn cm<sup>-1</sup>. Those experiments at which one of some difficulties in functioning of the capillary electrometer mentioned above appeared were omitted. The obtained  $\gamma$ -values were plotted vs potential in a big scale, and the smoothed values were fed to a Hewlett-Packard calculator Model 9820A to obtain charge density  $q^m$  using the Chebyshev polynomials for  $n$  3 to 8. The obtained  $q^m$  values in 0.1M-HClO<sub>4</sub> for  $n = 6$  agreed within  $\pm 0.2$   $\mu$ C with  $q^m$ -values obtained by integration of differential capacities<sup>16</sup> measured by Payne.\*

\* We are very much indebted to Dr R. Payne for his kind supply of unpublished data.

Hence the most  $\gamma$ - $E$  values were processed using  $n = 6$ . The graphical derivation yielded also good results. The values of the surface excess  $\Gamma$  were determined from the  $\gamma$ - $\log c$  dependence ( $c$  is the concentration of SAS) by graphical derivation or by using spline function program for Hewlett-Packard calculator.

Solutions were prepared using water redistilled from alkaline permanganate. The corresponding concentrated acids were of analytical grade. In both acids perchlorate salts of tetrapropyl- or tetrabutylammonium cation respectively were added to ensure exactly the same concentration of the surface active cation. Perchlorate salts can be obtained in a very pure form. As it will follow from experimental results the perchlorate anion of the added surface active cation influences to certain extent the  $\gamma$ -values in sulfuric acid at positive potentials due to its specific adsorption. When the sulfate salt of TBA was used this effect was not observed. Solutions were deaerated by passing a stream of pure nitrogen. A separated saturated calomel electrode was used as reference electrode.

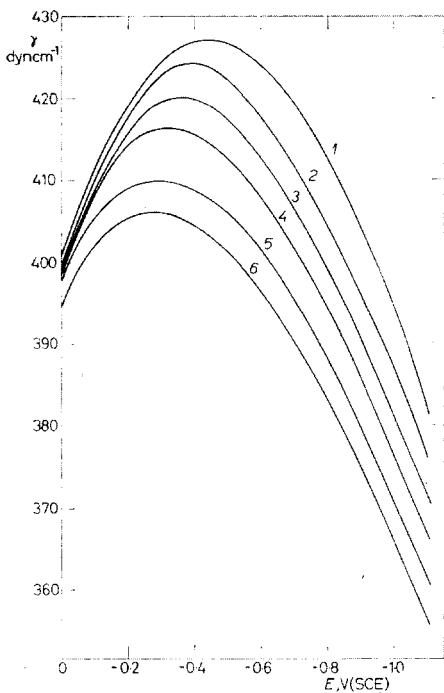


FIG. 1

Electrocapillary Curves of  $\text{TPAClO}_4$  in  $0.1\text{N-HClO}_4$

1  $0.1\text{N-HClO}_4$ ; conc. of  $\text{TPAClO}_4$ :  $2 \cdot 10^{-4}\text{M}$ ; 3  $3 \cdot 10^{-4}\text{M}$ ; 4  $1 \cdot 10^{-3}\text{M}$ ; 5  $3 \cdot 10^{-3}\text{M}$ ; 6  $7.15 \cdot 10^{-3}\text{M}$ .

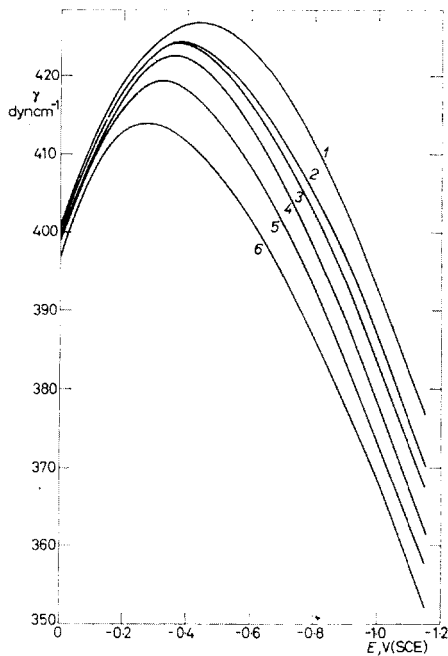


FIG. 2

Electrocapillary Curves of  $\text{TPAClO}_4$  in  $0.1\text{N-H}_2\text{SO}_4$

1  $0.1\text{N-H}_2\text{SO}_4$ ; conc. of  $\text{TPAClO}_4$ :  $2 \cdot 10^{-4}\text{M}$ ; 3  $3 \cdot 10^{-4}\text{M}$ ; 4  $1 \cdot 10^{-3}\text{M}$ ; 5  $3 \cdot 10^{-3}\text{M}$ ; 6  $9 \cdot 10^{-3}\text{M}$ .

## RESULTS AND DISCUSSION

The smoothed curves of the plot of surface tension  $\gamma$  vs potential ( $\gamma$ - $E$ -curves) obtained by means of capillary electrometer for tetrapropylammonium perchlorate in given acids are shown on Figs 1 and 2 and for tetrabutylammonium perchlorate on Figs 3 and 4. From these figures it follows that the lowering of the surface tension in presence of tetrabutylammonium cations is greater than with tetrapropylammonium cations. With both cations the adsorption activity is higher in perchloric than in sulfuric acid. For reasons indicated in the experimental part the perchlorate salts of tetralkylammonium cations were used. In perchlorate solutions containing TPA- $\text{ClO}_4$  the lowering of surface tension at positive potentials is smaller (Fig. 1) than in the presence of TBA- $\text{ClO}_4$  (Fig. 3). In sulfuric acid the tetrapropylammonium perchlorate exerts a quite small adsorption effect in the most positive part of the

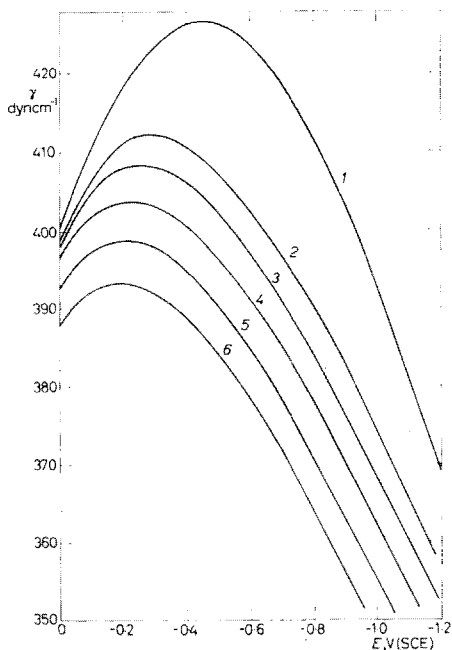


FIG. 3

Electrocapillary Curves of  $\text{TBAClO}_4$  in  $0.1\text{N-HClO}_4$

1  $0.1\text{N-HClO}_4$ ; conc. of  $\text{TBAClO}_4$ : 2  $3 \cdot 10^{-5}\text{M}$ ; 3  $1 \cdot 10^{-4}\text{M}$ ; 4  $3 \cdot 10^{-4}\text{M}$ ; 5  $1 \cdot 10^{-3}\text{M}$ ; 6  $3 \cdot 10^{-3}\text{M}$ .

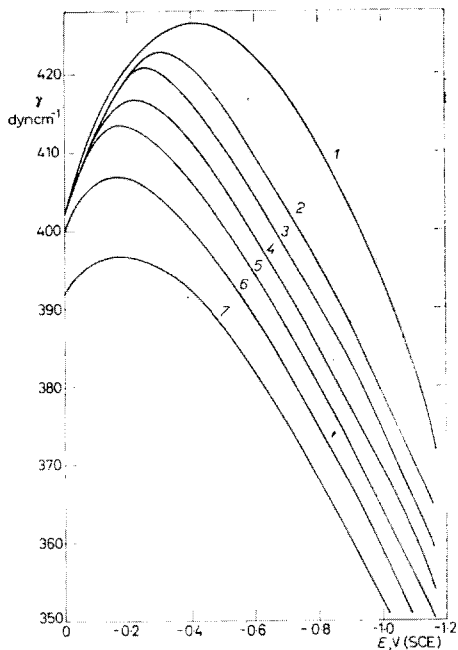


FIG. 4

Electrocapillary Curves of  $\text{TBAClO}_4$  in  $0.1\text{N-H}_2\text{SO}_4$

1  $0.1\text{N-H}_2\text{SO}_4$ ; conc. of  $\text{TBAClO}_4$ : 2  $3 \cdot 10^{-5}\text{M}$ ; 3  $1 \cdot 10^{-4}\text{M}$ ; 4  $3 \cdot 10^{-4}\text{M}$ ; 5  $1 \cdot 10^{-3}\text{M}$ ; 6  $3 \cdot 10^{-3}\text{M}$ ; 7  $9 \cdot 10^{-3}\text{M}$ .

electrocapillary curve and the  $\gamma$ -values are very near to those of pure sulfuric acid (Fig. 2).

TBA-ClO<sub>4</sub> in 0.1N-H<sub>2</sub>SO<sub>4</sub> up to the concentration of about  $3 \cdot 10^{-3}$ M lowers the surface tension at low potential values to a small extent whereas at the concentration approaching  $10^{-2}$ M a substantial lowering of surface tension at positive potentials is observed (Fig. 4 curve 7). Hence it follows that perchlorate anions which are also specifically adsorbed at the mercury interface, although to a smaller extent than halides, increase the adsorption of surface active cations at very positive potentials. If sulfate salts of these cations were applied in sulfuric acid this effect was not practically observed showing that sulfates in comparison with perchlorates are practically electrocapillary inactive.

Electrocapillary curves with a predominant adsorption of cations can be described by the known thermodynamic equation

$$-d\gamma = q^m dE + \Gamma_+ d\mu_+ \quad (1)$$

Here  $\gamma$  is surface tension,  $q^m$  charge density at the surface of mercury,  $E$  potential of the electrode with respect to the anion of reference electrode,  $\Gamma_+$  relative surface excess of the corresponding tetralkylammonium cation and  $\mu_+$  its chemical potential in the bulk of the solution. With respect

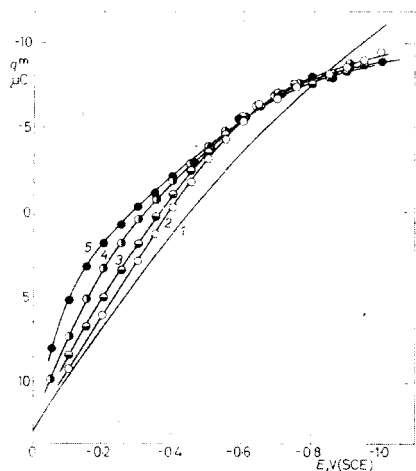


FIG. 5

$q^m$  vs  $E$  Curves of TPAClO<sub>4</sub> in 0.1N-HClO<sub>4</sub>  
 1 0.1N-HClO<sub>4</sub>; conc. of TPAClO<sub>4</sub>: 2  
 $10^{-4}$ M; 3  $3 \cdot 10^{-4}$ M; 4  $1 \cdot 10^{-3}$ M; 5  $3 \cdot 10^{-3}$ M.

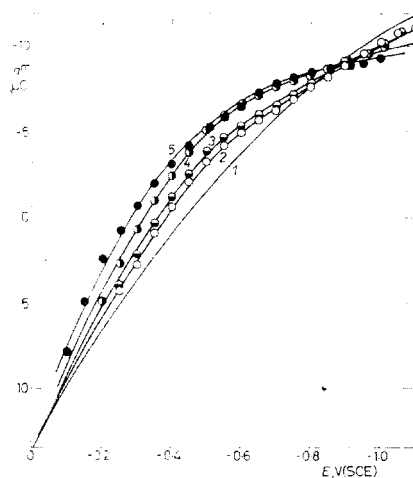


FIG. 6

$q^m$  vs  $E$  Curves of TPAClO<sub>4</sub> in 0.1N-H<sub>2</sub>SO<sub>4</sub>  
 1 0.1N-H<sub>2</sub>SO<sub>4</sub>; conc. of TPAClO<sub>4</sub>: 2  
 $1.5 \cdot 10^{-4}$ M; 3  $3 \cdot 10^{-4}$ M; 4  $3 \cdot 10^{-3}$ M; 5  
 $9 \cdot 10^{-3}$ M.

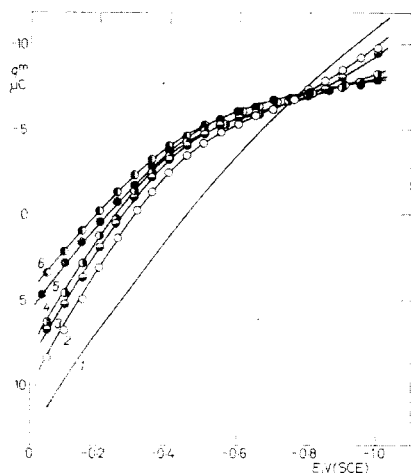


FIG. 7

$q^m$  vs  $E$  Curves of  $\text{TBAClO}_4$  in  $0.1\text{N-HClO}_4$   
 1  $0.1\text{N-HClO}_4$ ; conc. of  $\text{TBAClO}_4$ : 2  
 $3 \cdot 10^{-5}\text{M}$ ; 3  $1 \cdot 10^{-4}\text{M}$ ; 4  $3 \cdot 10^{-4}\text{M}$ ; 5  $1 \cdot$   
 $10^{-3}\text{M}$ ; 6  $3 \cdot 10^{-3}\text{M}$ .

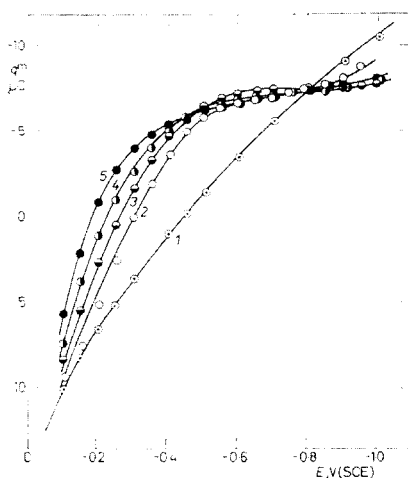


FIG. 8

$q^m$  vs  $E$  Curves of  $\text{TBAClO}_4$  in  $0.1\text{N-H}_2\text{SO}_4$   
 1  $0.1\text{N-H}_2\text{SO}_4$ ; conc. of  $\text{TBAClO}_4$ : 2  
 $3 \cdot 10^{-5}\text{M}$ ; 3  $1 \cdot 10^{-4}\text{M}$ ; 4  $3 \cdot 10^{-4}\text{M}$ ; 5  
 $1 \cdot 10^{-3}\text{M}$ .

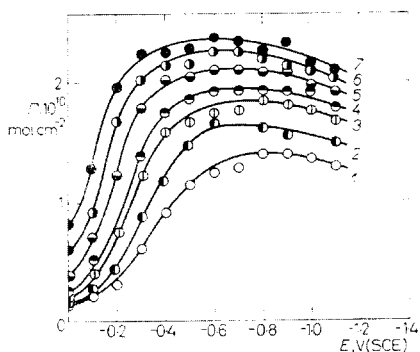


FIG. 9

Dependence of Surface Excess on Potential  
 for  $\text{TPAClO}_4$

Conc. of  $\text{TPAClO}_4$ : 1  $1 \cdot 10^{-4}\text{M}$ ; 2  $1.73 \cdot$   
 $10^{-4}\text{M}$ ; 3  $3 \cdot 10^{-4}\text{M}$ ; 4  $5.5 \cdot 10^{-4}\text{M}$ ; 5  
 $1 \cdot 10^{-3}\text{M}$ ; 6  $1.73 \cdot 10^{-3}\text{M}$ ; 7  $3 \cdot 10^{-3}\text{M}$ .

Dependence of Surface Excess on Potential  
 for  $\text{TBAClO}_4$ .

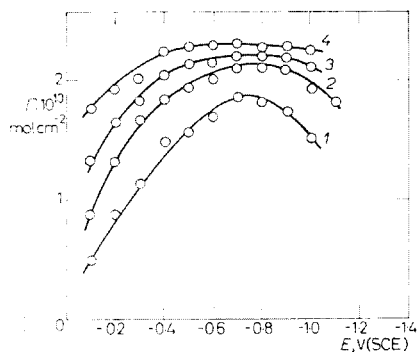


FIG. 10

Dependence of Surface Excess on Potential  
 for  $\text{TBAClO}_4$

Conc. of  $\text{TBAClO}_4$ : 1  $3 \cdot 10^{-5}\text{M}$ ; 2  $1 \cdot$   
 $10^{-4}\text{M}$ ; 3  $3 \cdot 10^{-4}\text{M}$ ; 4  $1 \cdot 10^{-3}\text{M}$ .

to the uncertainty of individual activity coefficients and with respect to small concentration ( $<10^{-2}M$ ) for evaluation of adsorption data concentrations instead of activities were used. Under this approximation the preceding equation can be written:

$$-dy = q^m dE + RT\Gamma d \ln c, \quad (2)$$

where subscripts were omitted and  $c$  is the concentration of tetrapropyl- and tetrabutylammonium salt, respectively.  $q^m$  values of the electrocapillary curve are given by the Lippmann equation

$$q^m = -(\partial\gamma/\partial E)_c. \quad (3)$$

The results of the numerical differentiation using Chebyshev polynomials are on Figs 5–8. On these Figures a point of intersection of the curves can be seen. From equations<sup>17,18</sup>

$$(\partial q^m/\partial \ln c)_E = RT(\partial\Gamma/\partial E)_c \quad (4)$$

and

$$(\partial E/\partial \ln c)_{q^m} = -RT(\partial\Gamma/\partial q^m)_c \quad (5)$$

it follows that a single value of charge density should exist at the maximum adsorption which is independent of concentration. For TPA the potential of intersection is  $-0.82$  V (SCE) and the corresponding charge density  $q^m = -7.7 \mu C.cm^{-2}$  in  $0.1N-HClO_4$ ; in  $0.1N-H_2SO_4$  the corresponding values are  $-0.85$  V and  $-8.7 \mu C.cm^{-2}$ , respectively. In the case of TBA the potential of intersection amounts

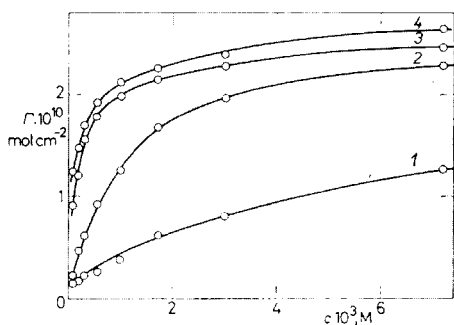


FIG. 11

Dependence of Surface Excess on Concentration for  $TPAClO_4$  in  $0.1M-HClO_4$

Potential: 1 0 V; 2  $-0.2$  V; 3  $-0.4$  V; 4  $-0.6$  V (SCE).

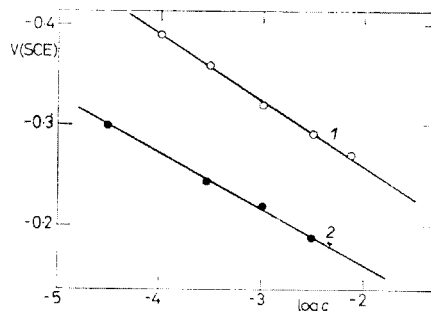


FIG. 12

Dependence of the Electrocapillary Maximum Potential (pzc) on Concentration

1  $TPAClO_4$  in  $0.1N-HClO_4$ ; 2  $TBAClO_4$  in  $0.1N-HClO_4$ .



to  $-0.78$  V and the charge density  $-7.0 \mu\text{C cm}^{-2}$  in  $0.1\text{N-HClO}_4$ ; in  $0.1\text{N-H}_2\text{SO}_4$  the potential is practically the same ( $-0.8$  V), the charge density of the intersection point being higher, *viz.*  $-7.7 \mu\text{C.cm}^{-2}$ .

Differentiation of the surface tension at constant potential with respect to  $\ln c$  yields the relative surface excess

$$\Gamma = -RT(\partial\gamma/\partial \ln c)_E.$$

The plot of  $\Gamma$  vs  $E$  for various concentrations of the surfactant is shown on Figs 9 and 10. The potential of the maximum adsorption can not be determined from these graphs with much precision, however, it is very near to  $-0.8$  V (SCE), in accordance with the previous plots. The precision in the evaluation of  $\Gamma$ -values is not sufficient to permit distinction between various adsorption isotherms. An attempt to visualize an experimental isotherm in the case of tetrapropylammonium cation is shown in Fig. 11. At more negative potentials for reasons mentioned in the experimental part it was not possible to determine the  $\Gamma$ -values at low concentration. This problem is still more difficult with tetrabutylammonium ions. In this case the lowest concentration ( $3 \cdot 10^{-5}\text{M}$  TBA) for which with difficulties and with lowered precision an electrocapillary curve could be obtained causes such a large lowering of the surface tension that the  $\Gamma$ -values corresponding to the rising portion of an adsorption isotherm cannot be evaluated. The maximum surface excess  $\Gamma_m$  can be determined with a good

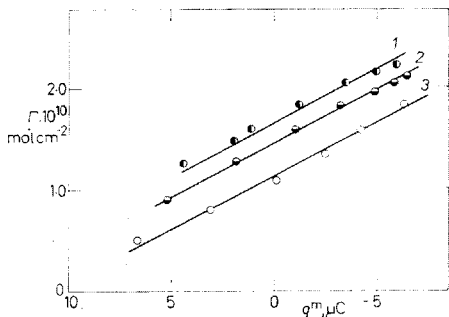


FIG. 13

$\Gamma$  vs  $q^m$  for Various Concentration of TBA.  $\text{ClO}_4$  in  $0.1\text{N-HClO}_4$

Conc. of  $\text{TBAClO}_4$ : 1  $3 \cdot 10^{-4}\text{M}$ ; 2  $1 \cdot 10^{-4}\text{M}$ ; 3  $3 \cdot 10^{-5}\text{M}$ .

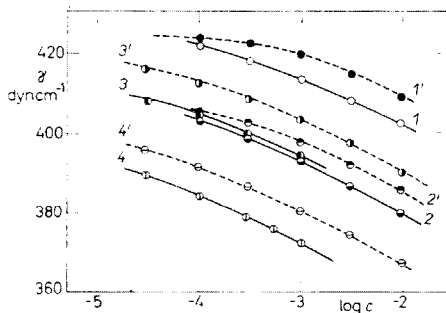


FIG. 14

$\gamma$  vs  $c$  of TPA and TBA at various Potentials (S.C.E.)

TPA,  $-0.45$  V: 1  $0.1\text{N-HClO}_4$ ; 1'  $0.1\text{N-H}_2\text{SO}_4$ . TPA,  $-0.80$  V: 2  $0.1\text{N-HClO}_4$ ; 2'  $0.1\text{N-H}_2\text{SO}_4$ . TBA,  $-0.45$  V: 3  $0.1\text{N-HClO}_4$ ; 3'  $0.1\text{N-H}_2\text{SO}_4$ . TBA,  $-0.80$  V: 4  $0.1\text{N-HClO}_4$ ; 4'  $0.1\text{N-H}_2\text{SO}_4$ .

accuracy. For tetrapropylammonium cation at pzc the maximum surface excess amounts to  $\Gamma_m \approx 2.4 \cdot 10^{-10} \text{ mol cm}^{-2}$  and for tetrabutylammonium its value attains  $\Gamma_m \approx 2.2 \cdot 10^{-10} \text{ mol cm}^{-2}$ . The value of  $\Gamma_m$  for TBA is in a good agreement with the value found from the inhibition on  $i-t$  curves in d. c. polarography and with the value given in paper<sup>14</sup>. For a closely packed film of TBA,  $\Gamma_m$  calculated from the geometrical model<sup>19</sup> ( $r = 4.94 \text{ \AA}$ ) agreed well with the experimental value. However, when inserting for the radius the value  $3.81 \text{ \AA}$  resulting from the scaled particle theory of the salt effect<sup>20</sup> the disagreement is quite large. This problem is still larger in case of TPA.  $\Gamma_m$  found experimentally is nearest to the calculated value for  $r = 4.5 \text{ \AA}$  (ref.<sup>19</sup>) yielding  $\Gamma_{m,\text{theor}} = 2.6 \cdot 10^{-10} \text{ mol cm}^{-2}$ , however, it deviates considerably for other values of  $r$  given in the literature<sup>20</sup>. Hence the conclusion whether also in case of TPA a close packed film is formed, is hampered by the uncertainty in  $r$ -values.

The shift of pzc with the concentration of surface active cations (Esin and Markov effect) should fulfill the equation (5) The dependence of the pzc *vs* concentration of both cations is on Fig. 12. The plot of  $\Gamma$  *vs*  $q^m$  is linear both for TPA and TBA and independent of concentration (Fig. 13). The comparison of results shows a very good agreement:

Surfactant	$\frac{1}{2.3RT} \left( \frac{\partial E}{\log c} \right)_{q^m=0} \cdot 10^5$	$\left( \frac{\partial \Gamma}{\partial q^m} \right)_c \cdot 10^5$
TPA	1.15	0.9
TBA	1.08	1.0

As it follows from previous results and as it can be seen clearly from Fig. 14 the adsorption effect in perchloric acid for TPA and TBA is always higher than in sulfuric acid. For the interpretation the explanation given in paper<sup>14</sup> could be accepted. The lowering of surface tension with the increase of the concentration of sulfate was explained<sup>14</sup> by the diminuation of mirror image forces for cations because of the positive charges induced by sulfate anions. Apparently in our case the induced positive charge of the electrode is higher in presence of sulfate than of perchlorate.

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