

ELECTROCAPILLARY MEASUREMENTS AT LOW CONCENTRATIONS OF SURFACTANTS: ADSORPTION OF TETRABUTYLMAMMONIUM CATION

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Using drop-time technique with long drop-times achieved by means of a spindle-type capillary with the combination of a interrupted convection the surface tension data of tetrabutylammonium perchlorate in $0\text{-}1\text{ mol l}^{-1}$ NaClO_4 in the concentration range $3\text{--}10^{-3}\text{ mol l}^{-1}$ down to $10^{-7}\text{ mol l}^{-1}$ could be measured. The corresponding adsorption parameters have been evaluated both from Langmuir (for $\Theta \leq 0\text{-}8$) and Frumkin isotherm. The maximum energy of adsorption amounts to $-48\text{-}1\text{ kJ mol}^{-1}$. The dependence of E vs $\log c$ (Yesin-Markov plot) carried out in the concentration range 10^{-7} to $10^{-3}\text{ mol l}^{-1}$ showed a S-shaped curve.

Although many papers¹⁻⁷ have been devoted to the adsorption studies of surfactants on the mercury-solution interface bringing important theoretical and experimental results some unsolved problems still remain. From experimental point of view many difficulties have been encountered in adsorption studies of strongly adsorbable surfactants but even in studies of substances of medium adsorptivity⁹. Both groups of this kind of substances can be approximately characterized⁹ in the following way: i) strong adsorption for which the coverage $\Theta \geq 0\text{-}5$ is attained at concentrations $c \leq 10^{-4}\text{ mol l}^{-1}$; ii) medium adsorption for which $\Theta \geq 0\text{-}5$ is attained at $10^{-4} < c \leq 10^{-1}\text{ mol l}^{-1}$.

As it follows from the literature^{1,5,8,9} the main problem with strongly adsorbable surfactants was to obtain reliable data corresponding to an adsorption equilibrium. This drawback seems to exist even with substances of medium adsorptivity⁹. One of the most complicating factors pertinent to all techniques is the diffusion rate of the surfactant to the polarized interface.

This effect is especially apparent if the polarized meniscus of the mercury is inside of a capillary having a very small diameter (e.g. 0.02 mm) as it is in measurements with capillary electrometer. At low concentrations of surfactants with strong adsorption extremely large times are necessary to reach adsorption equilibrium which may lead to a film formation even on the walls of the capillary, to the sticking of the meniscus and some further complications^{1,5,8-12} which may lower the precision and reproducibility of results.

Also the surface tension measurements using drop-time technique with ordinary capillaries in dilute solutions of surface active substances cannot be considered as equilibrium values. The purpose of this paper is to show the application of the new approach¹³⁻¹⁵ enabling to measure adsorption parameters at extremely low concentrations.

In searching for a suitable highly adsorbable and chemically well defined and stable surfactant many adsorption data of various tetraalkylammonium salts were already available^{8,16-19}. The interest in this class of substances is due to their application as supporting electrolytes in electrochemical measurements and to their inhibition effects^{5,20-22} on charge-transfer reactions especially when higher homologues are applied. In aqueous solutions the homologues of tetraalkylammonium salts starting from tetrapropylammonium cation can be considered as strongly adsorbable substances.

For the purpose of this study the tetrabutylammonium cation (TBA^+) added in the form of perchlorate ($TBAClO_4$) has been selected enabling us also to compare our measurements with literature data^{8,16,17} which are available for its higher concentrations. However, the aim of this work was to obtain adsorption data at extremely low concentration ($10^{-5} \text{ mol} \cdot \text{l}^{-1}$ down to $10^{-7} \text{ mol} \cdot \text{l}^{-1}$) using the method of the interrupted convection^{13,15} which was not previously possible.

EXPERIMENTAL

Using drop-time technique the surface tension of $TBAClO_4$ in $0.1 \text{ mol l}^{-1} NaClO_4$ was measured in the concentration range $3 \cdot 10^{-3} \text{ mol l}^{-1}$ down to $1 \cdot 10^{-7} \text{ mol l}^{-1}$. For concentration of $TBAClO_4$ $c \leq 3 \cdot 10^{-5} \text{ mol l}^{-1}$ the method of the interrupted convection was applied consisting in an intensive stirring of the solution during a certain period of the drop-time. The drop-times in the interval approx. 25 to 280 s have been chosen. A glass spindle-type capillary without polyethylene tip was used^{23,24}. In this case²³ the usual cylindrical capillary is enlarged towards the end in form of a spindle and then conically drawn out. The corresponding diameter of its orifice R has to be larger than the inner diameter r of the main cylindrical part. Using various values of r and R it is possible to change independently the out-flow velocity and the drop-time in a wide range. If one chooses e.g. the diameter of the main part 37 μm and the diameter of the orifice 170 μm at the height of mercury column about 0.40 m it is possible to achieve a slowly growing drop with the drop-time approaching c. 130 s. Also the drop-times of capillaries having 150–300 s are still very well reproducible with the precision of ± 0.02 s which corresponds to the deviation in surface tension γ to approx. $\pm 0.05 \text{ mN} \cdot \text{m}^{-1}$.

The cell is schematically described on Fig. 1. The capillary 1 giving very stable and reproducible drop-times was immersed in the measured solution 2 separated from the reference electrode 4. The solution after deaeration with nitrogen was thermostated at $25 \pm 0.15^\circ\text{C}$. The mixing of the solution in the vicinity of the capillary was carried out by the stream of nitrogen 5 and stopped by closing the stop-cock 6. The gas inlet was located near to the capillary in such a way as to ensure an intensive streaming in the vicinity of the drop. However, this streaming should not lead to a forced detachment of the drop. The suitable position of the gas inlet and the intensity of streaming has to be checked experimentally. As an indication of suitably chosen hydrodynamic condi-

tions the constancy of the drop-times in a pure solution of the supporting electrolyte both in quiet and stirred solution was taken.

A series of capillaries having appropriate drop-times (t_d) for achieving the adsorption values near to the equilibrium values depending on the concentration of $TBAClO_4$ have been selected (t_d at p.z.c.):

c_{TBAClO_4} , mol l^{-1}	3. 10^{-5} to 3. 10^{-3}	1. 10^{-5}	3. 10^{-6}	1. 10^{-6}	3. 10^{-7}	1. 10^{-7}
t_d , s	26	40	90	120	180	280

The indicated drop-time values were usually more than sufficient to ensure under given hydrodynamic conditions the achievement of equilibrium values. So *e.g.* using the drop-time 26 s and the stirring of the solution up to 2.5–3 s before the drop fall the surface tension of $10^{-5} M$ - $TBAClO_4$ could be measured. With the drop-time of 40 s for the given concentration under less strict hydrodynamic conditions the same equilibrium values are obtained. To check the independency of the results of the capillary some solutions were measured with still larger drop-times than that indicated as suitable in Table I for the given concentration or concentration range respectively. So *e.g.* for $1.10^{-6} M$ - $TBAClO_4$ the same surface tension was obtained with capillaries having drop-times 90, 130 or 170 s.

Since the proposed method is very sensitive to the traces of surface active impurities also the solution of the supporting electrolyte alone must be carefully prepared. The water after passing a ionex column was twice redistilled. Sodium perchlorate and $TBAClO_4$ (Fluka, Switzerland) were recrystallized. As reference electrode S.C.E. was used. The cell was cleaned with chromsulphuric mixture, several-times washed with redistilled water. At low concentration of surfactant $c \leq 10^{-5} M$ - $TBAClO_4$ the cell was repeatedly filled with the given solution to achieve an equilibrium concentration saturation. The same procedure was made with volumetric flasks.

The reproducibility of electrocapillary data was better than $\pm 0.25 \text{ mN} \cdot \text{m}^{-1}$. The data on figures are related to the value of the electrocapillary maximum $426.7 \text{ mN} \cdot \text{m}^{-1}$ as in some previous papers^{8,24} whereas the data in Table II to the value $425.6 \text{ mN} \cdot \text{m}^{-1}$ which corresponds to 25°C .

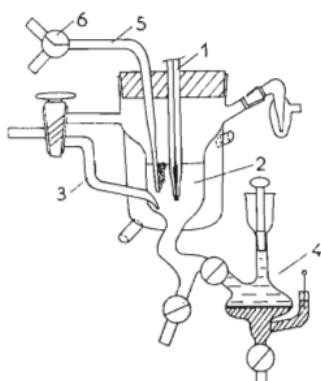


FIG. 1

Experimental cell (schematically). 1 capillary; 2 solution; 3 inert gas inlet; 4 S.C.E.; 5 and 6 inert gas inlet for stirring

RESULTS AND DISCUSSION

The surface tension-potential curves obtained by the modified drop-time technique are on Fig. 2 and their numerical values in Table I. As it can be seen from this figure the set of electrocapillary curves fills up the whole diagram whereas with capillary electrometer the γ -E curve for the lowest possible concentration to be measured corresponds to the curve 7 on Fig. 2.

The graphical derivation of the basic equation

$$-\mathrm{d}\gamma = q \mathrm{d}E + \Gamma \mathrm{d}\mu_+ \quad (1)$$

TABLE I

Surface tension data ($\mathrm{mN} \cdot \mathrm{m}^{-1}$) of tetrabutylammonium perchlorate (TBAClO_4) in 0.1M- NaClO_4 at 25°C (vs. S.C.E.)

-E, mV	Concentration of TBAClO_4 , mol. l^{-1}									
	0	$1 \cdot 10^{-7}$	$3 \cdot 10^{-7}$	$1 \cdot 10^{-6}$	$3 \cdot 10^{-6}$	$1 \cdot 10^{-5}$	$3 \cdot 10^{-5}$	$1 \cdot 10^{-4}$	$3 \cdot 10^{-4}$	$1 \cdot 10^{-3}$
0	396.9	396.9	396.9	396.9	396.9	396.9	396.9	396.4	395.5	392.2
50	402.0	402.0	402.0	402.0	402.0	402.0	402.0	401.5	400.1	395.0
100	406.9	406.9	406.9	406.9	406.9	406.9	406.9	405.9	503.3	397.0
150	411.3	411.3	411.3	411.3	411.3	411.3	411.3	409.3	404.7	398.1
200	415.3	415.3	415.3	415.3	415.3	415.2	414.3	410.7	405.2	398.3
250	418.9	418.9	418.9	418.9	418.9	418.3	415.9	410.9	404.9	397.9
300	421.6	421.6	421.6	421.6	420.9	419.6	416.1	410.2	403.9	396.9
350	423.7	423.7	423.7	423.7	422.2	419.6	415.2	408.9	402.3	395.5
400	425.0	—	424.9	424.3	422.1	418.4	413.7	406.9	400.3	393.6
450	425.6	—	425.1	423.9	420.9	416.7	411.5	404.6	398.0	391.4
500	425.3	425.0	424.3	422.6	418.9	414.5	409.1	402.3	395.5	389.0
550	424.4	423.9	422.9	420.5	416.5	412.0	401.3	399.4	392.7	386.3
600	422.9	422.3	420.9	418.1	413.9	409.3	403.4	396.5	389.7	383.4
650	421.5	420.3	418.5	415.4	411.0	406.2	400.3	393.3	386.7	380.4
700	418.5	417.6	415.7	412.5	407.8	403.0	397.0	389.9	383.3	377.1
750	415.7	414.5	412.5	409.1	404.5	399.5	393.5	386.7	379.9	373.8
800	412.1	411.1	409.1	405.7	401.0	395.9	390.0	383.1	376.5	370.3
850	408.1	407.1	405.1	401.9	397.3	392.0	386.1	379.3	373.0	366.9
900	403.7	402.7	400.9	397.9	393.3	387.9	382.2	375.5	369.3	363.3
950	398.9	398.1	396.3	392.9	389.1	383.9	378.2	371.8	365.7	360.1
1 000	393.9	393.1	391.3	388.5	384.7	379.9	374.1	367.3	362.0	—
1 050	388.3	387.5	386.1	383.3	379.9	375.3	369.9	363.9	—	—
1 100	382.3	381.7	380.5	378.1	374.9	370.9	365.7	—	—	—
1 150	376.5	376.5	375.1	—	—	—	—	—	—	—

yielded the charge density values q . Here Γ is the relative surface excess of the tetrabutylammonium cation, μ_+ chemical potential of the TBA^+ in the bulk which can be approximated at low concentrations

$$d\mu_+ = RT d \ln c. \quad (2)$$

The dependence of the charge density q on the potential for various concentrations of TBA^+ is on Fig. 3. The precision in the calculation of q values was better than $\pm 5 \text{ mC} \cdot \text{m}^{-2}$. The set of $q - E$ data covers a much larger concentration range of more than 4 orders of magnitude which was not possible in previous study⁸. It is again obvious that one intersection point corresponding to the potential of the maximum adsorption can be found at $E = E_{\max} = -0.77 \text{ V}$ (s.c.e.) consistently with the value -0.78 V from previous measurements⁸.

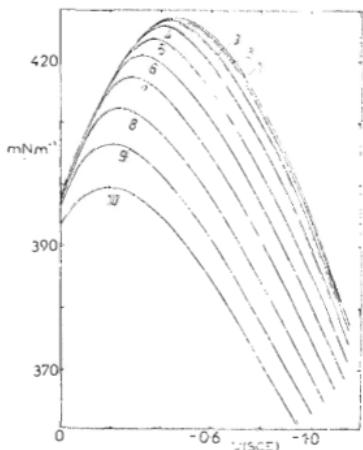


FIG. 2

Electrocapillary curves of tetrabutylammonium perchlorate in 0.1M-NaClO₄ *q vs E*. Conc. of TBAClO₄ mol/l⁻¹: 1 0; 2 1. 10⁻⁷; 3 3. . 10⁻⁷; 4 1. 10⁻⁶; 5 3. 10⁻⁶; 6 1. 10⁻⁵; 7 3. 10⁻⁵; 8 1. 10⁻⁴; 9 3. 10⁻⁴; 10 1. 10⁻³

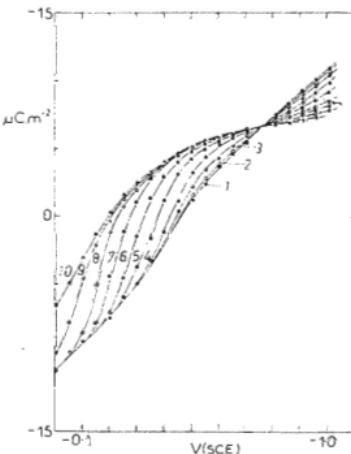


FIG. 3

Charge density *vs* potential ($10^4 q$ *vs E* curves) of TBAClO₄ in 0.1M-NaClO₄. Conc. of TBAClO₄, mol/l⁻¹: 1 0; 2 1. 10⁻⁷; 3 3. . 10⁻⁷; 4 1. 10⁻⁶; 5 3. 10⁻⁶; 6 1. 10⁻⁵; 7 3. 10⁻⁵; 8 1. 10⁻⁴; 9 3. 10⁻⁴; 10 1. 10⁻³

In further calculations of adsorption isotherms potential E was chosen as an electrical variable^{2,5,25} although equally well the charge density q ^{3,26,27} could be selected. The relative surface excess was determined by differentiation of the dependence $\gamma = -\log c$ (Fig. 4) in a usual way using the equation

$$\Gamma = - \frac{1}{2 \cdot 303 R T} \cdot \left(\frac{\partial \gamma}{\partial \log c} \right)_E . \quad (3)$$

The plot of Γ -values vs concentration of TBA^+ is on Fig. 5. For the analysis of the experimentally found $\Gamma - c$ plot both Langmuir and Frumkin isotherms were applied. From the Langmuir isotherm written in its linearized form

$$\frac{c}{\Gamma} = \frac{1}{\Gamma_m} \cdot c + \frac{1}{\Gamma_m \cdot \beta} \quad (4)$$

the maximum surface $\Gamma_m = (\Gamma_m)_L$ at $\Theta_L = 1$ and the adsorption coefficient $\beta = \beta_L$ (Table II and Fig. 6) were determined. The subscript L refers to Langmuir isotherm.

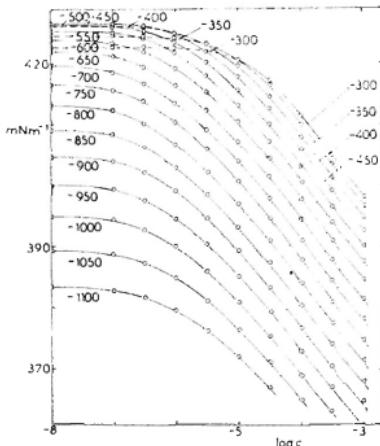


FIG. 4
 $\gamma - \log c$ plot of $TBAClO_4$ in $0 \cdot 1M\text{-NaClO}_4$ at various potentials E (in mV)

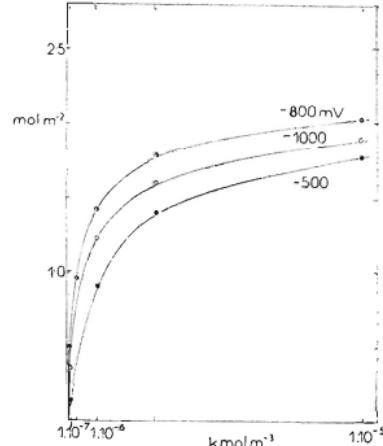


FIG. 5
 $10^6 \Gamma - c$ curves of $TBAClO_4$ in $0 \cdot 1M\text{-NaClO}_4$ at several potentials

The Frumkin isotherm in its linearized form can be written as

$$\ln \frac{\Theta}{(1 - \Theta)c} = \ln \beta + \frac{2a}{\Gamma_m} \cdot \Gamma, \quad (5)$$

where a is the interaction coefficient expressing the interactions of adsorbed particles. If the parameters $\Gamma_m = (\Gamma_m)_L$ and $\beta = \beta_L$ are taken from the Fig. 6 then the graphical representation according to Eq. (5) gives a line with $a = 0$. When inserting for Γ_m the experimental value $(\Gamma_m)_{exp}$ corresponding to the maximum slope of $\gamma - \log c$ plot on Fig. 4 into equation (5) the experimental results seem to be better described by Frumkin isotherm and $\beta = \beta_F$ and coefficient a can be determined (Fig. 7). Some deviations on the dependence $\ln \Theta/(1 - \Theta)c$ vs Γ from linearity namely in the region where $\Gamma \rightarrow (\Gamma_m)_{exp}$ are within limits of experimental error in the determination of surface excesses. The estimated values $\beta = \beta_F$ and a are in Table II.

The dependence of the free energy of adsorption $\overline{\Delta G}^0$ determined from equation²

$$\begin{aligned} \overline{\Delta G}^0 &= -RT \ln(\beta \cdot 55.5) = -RT \ln \beta + \overline{\Delta G}_0^0 \\ \overline{\Delta G}_0^0 &= -10.0 \text{ kJ} \cdot \text{mol}^{-1} \end{aligned} \quad (6)$$

at various potentials is given on Fig. 8. The difference in the values of $\overline{\Delta G}^0$ calculated from β_L or β_F -values at the same potential is rather small and does not exceed 5%. The free energy of adsorption depends on the potential according to equation

$$\overline{\Delta G}^0 = \overline{\Delta G}_{max}^0 + b(E - E_{max})^2, \quad (7)$$

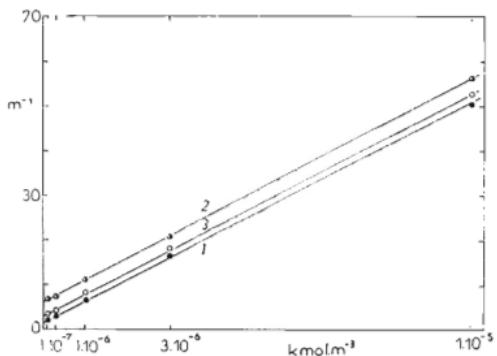


FIG. 6

Linearized Langmuir isotherm of TBAClO_4 in 0.1M-NaClO_4 ($c/\Gamma \cdot 10^{-2}$ vs C) 1 $E = -0.5 \text{ V}$; 2 $E = -0.8 \text{ V}$ and 3 $E = -1.0 \text{ V}$ (S.C.E.)

TABLE II
Adsorption parameters of TBA^+ in 0.1M- NaClO_4 ; $(\Gamma_m)_F \equiv \Gamma_m$ \exp

$-E, \text{mV}$	Langmuir				Frumkin			
	$10^{-6} \cdot \beta_L$ $\text{m}^3 \cdot \text{kmol}^{-1}$	$\ln \beta_L$	$-\overline{\Delta G_L^\circ}$ $\text{kJ} \cdot \text{mol}^{-1}$	$10^6 \cdot (\Gamma_m)_L$ $\text{mol} \cdot \text{m}^{-2}$	$10^{-6} \cdot \beta_F$ $\text{m}^3 \cdot \text{kmol}^{-1}$	$\ln \beta_F$	$-\overline{\Delta G_F^\circ}$ $\text{kJ} \cdot \text{mol}^{-1}$	a $10^6 \cdot (\Gamma_m)_F$ $\text{mol} \cdot \text{m}^{-2}$
500	0.81	13.60	3.7	2.0	0.81	13.61	3.7	0.48
600	1.62	14.30	5.4	1.97	2.15	14.58	6.1	0.82
700	2.60	14.77	6.6	1.96	3.65	15.11	7.4	1.02
800	3.14	14.96	7.1	1.96	5.03	15.43	8.2	1.07
900	2.68	14.80	6.7	1.97	3.61	15.10	7.4	0.81
1 000	1.79	14.40	5.7	2.0	2.55	14.75	6.6	0.63

where $\overline{\Delta G}_{\max}^0$ corresponds to the free energy at the potential of the maximum adsorption E_{\max} . However, the obtained curve does not have a fully parabolic form having b values slightly different for anodic (b_a) and cathodic (b_c) side respectively.

The corresponding values obtained from Langmuir and Frumkin isotherms are: $(\overline{\Delta G}_{\max}^0)_L = -47.0 \text{ kJ} \cdot \text{mol}^{-1}$, $(\overline{\Delta G}_{\max}^0)_F = -48.1 \text{ kJ} \cdot \text{mol}^{-1}$, $(b_a)_L = 44 \text{ kJ} \cdot \text{V}^{-2} \cdot \text{mol}^{-1}$, $(b_a)_F = 23.9 \text{ kJ} \cdot \text{V}^{-2} \cdot \text{mol}^{-1}$, $(b_a)_L = 23.9 \text{ kJ} \cdot \text{V}^{-2} \cdot \text{mol}^{-1}$ and $(b_c)_F = 42.4 \text{ kJ} \cdot \text{V}^{-2} \cdot \text{mol}^{-1}$.

The plot of q vs $RT\Gamma$ at a constant potential following from the known equation (8) (ref.²)

$$(\partial q / \partial \Gamma)_E = RT(\partial \ln \beta / \partial E) \quad (8)$$

given on Fig. 9 is linear for certain range of surface excesses. The departure from linearity shows that the condition for the congruence of adsorption isotherms is not fulfilled in the whole concentration range. The slope of the linear portion depends on the potential and for its change holds that for $E \geq E_{\max}$ is $(\partial q / \partial \Gamma)_E \geq 0$ in agreement with equations (6), (7) and (8).

The dependence of the interaction coefficient a on the potential is given (Table II). In the vicinity of $E = E_{\max}$ this plot can be described by a parabola, corresponding

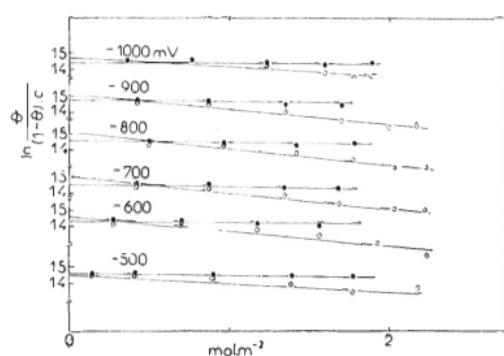


FIG. 7

Dependence of $\ln \Theta / (1 - \Theta) \cdot c$ vs $10^6 \Gamma$ of TBAClO_4 in 0.1M-NaClO_4 at various potentials. Values of interaction parameter a : $\bullet = 0$, $\circ \neq 0$

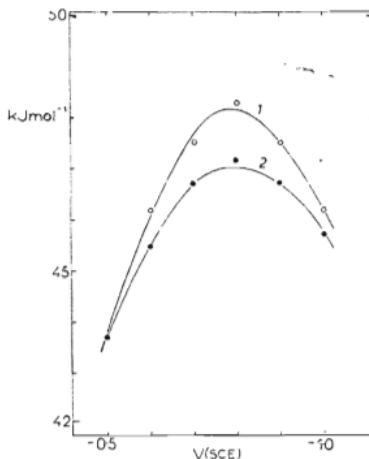


FIG. 8

Dependence of free energy of adsorption $\overline{\Delta G}^0$ of TBAClO_4 in 0.1M-NaClO_4 on the potential E . 1 for Frumkin isotherm; 2 for Langmuir isotherm

to the equation (9) (ref.²)

$$\frac{da}{dE} = (k - 1) \frac{q_0 + C'(E_N - E)}{RT\Gamma_m} \quad (9)$$

Here k is the constant, C' is the slope of a tangent to $q - E$ dependence at $\Theta = 1$ at $E = E_{\max}$, q_0 is the charge density of the pure supporting electrolyte at the given E and E_N is an intersection point of a tangent to the $q - E$ -curve at $\Theta = 1$ at the point $E = E_{\max}$ with the potential axis.

For the constant k follows from equation (9) and from the analysis of graphs on Fig. 3 and Fig. 10.

$$k = 1 + \frac{RT\Gamma_m}{C_0 - C'} \cdot \frac{d^2a}{dE^2} \doteq 1.48, \quad (10)$$

where $\Gamma_m = 2.37 \cdot 10^{-6} \text{ mol} \cdot \text{m}^{-2}$, $C' \approx 35 \text{ mF} \cdot \text{m}^{-2}$ and $C_0 \approx 200 \text{ mF} \cdot \text{m}^{-2}$ (slope of a tangent to the $q - E$ curves of the supporting electrolyte at $E = E_{\max}$).

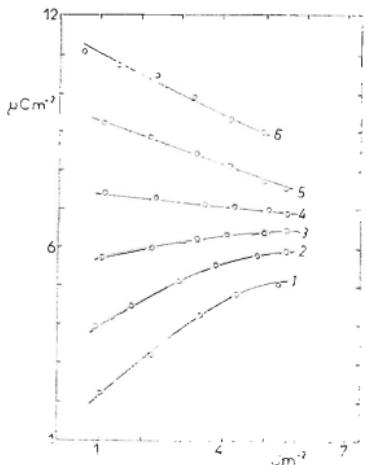


FIG. 9

Dependence of $-q \cdot 10^4$ vs. $10^4 \Gamma \cdot R \cdot T$ of TBAClO_4 in 0.1M-NaClO_4 at various potentials (V, s.c.e.): 1 - 0.5; 2 - 0.6; 3 - 0.7; 4 - 0.8; 5 - 0.9; 6 - 1.0

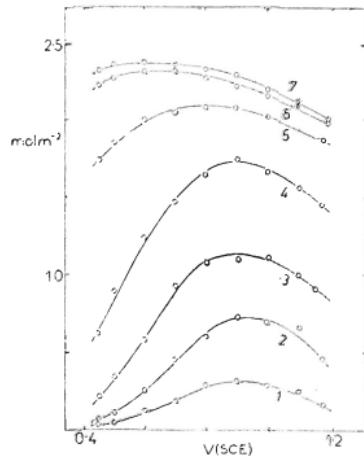


FIG. 10

Dependence of $10^6 \Gamma$ vs. $-E$ at various concentrations of TBAClO_4 in 0.1M-NaClO_4 . Conc. of TBAClO_4 (mol l^{-1}): 1 - $1 \cdot 10^{-7}$; $2.3 \cdot 10^{-7}$; $3.1 \cdot 10^{-6}$; $4.3 \cdot 10^{-6}$; $5.1 \cdot 10^{-5}$; $6.3 \cdot 10^{-5}$; 7 - $1 \cdot 10^{-4}$

The dependence and the numerical value from Eq. (10) is in a good agreement with results in ref.¹⁶ determined from differential capacitance data of tetrabutylammonium sulphate in Na_2SO_4 .

Also the dependence of Γ vs E (Fig. 10) supports the previous results. From this figure it follows that the Γ -values are approaching Γ_m with increasing concentration of tetrabutylammonium perchlorate. The position of the maximum on $\Gamma - E$ plots agrees with the position of the apex of the ΔG^0 vs E plot (Fig. 8) and with the position of the crossing point on $q - E$ curves.

The dependence of E vs $\log c$ at constant q (Yesin-Markov plot) made in this broad concentration range is S-shaped which can be approximated in a middle part by a straight line. The steepness of approximated straight lines depends on the charge density, the slope is equal zero at q -value corresponding $E = E_{\max}$. The value of $\partial E / \partial \log c$ at $q = 0$ amounts approx. 100 mV. The discussion of this dependence will be given in a next communication²⁸.

The fruitful discussion with Dr M. Heyrovský is highly appreciated.

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