SURFACE BEHAVIOUR OF TETRAPROPYLAMMONIUM CATION AT THE MERCURY/SOLUTION INTERFACE MEASURED BY USE OF CONTROLLED CONVECTIVE ADSORPTIVE ACCUMULATION

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Using drop time technique with long drop times and a controlled convection of the solution the surface tension data of Hg with tetrapropylammonium perchlorate in 0·1 mol l^{-1} $NaClO_4$ in the concentration range $4 . 10^{-6}$—$3 . 10^{-3}$ mol l^{-1} have been obtained. The corresponding adsorption parameters have been evaluated from the Frumkin isotherm both at constant potential E and at constant charge q. Both E and q could be chosen as an independent electrical variable. The maximum free adsorption energy amounts to approx. $-36·5$ kJ mol^{-1}. The congruence of adsorption isotherms with respect to E and with respect to q was very well fulfilled for the surface coverage $\Theta \leqq 0·6$—$0·7$.

The adsorption characteristics of many organic compounds at mercury-solution interface are described in the literature[1-5]. However, the study of highly adsorbable surfactants or surfactants of medium adsorptivity in very dilute solutions had not been practically carried out in the past due to the very slow mass transport rate[6,7] to the electrode surface. Recently, the use of intense convection for equilibrium adsorption measurements has been suggested[8] (like in voltammetry[9]) and adsorption data of tetrabutylammonium (TBA) cation in 0·1 mol l^{-1} $NaClO_4$ down to 10^{-7} mol l^{-1} have been reported[10]. The modified drop time technique of electrocapillary measurements has been found as a convenient method useful for this purpose.

In this paper tetrapropylammonium (TPA) cation has been selected as an example of a strongly adsorptive ion. Tetraalkylammonium salts are chemically stable and well defined surfactants. They have been applied as supporting electrolytes[11,14] in electrochemical measurements as well as effective inhibitors of charge-transfer reactions[11-13]. The aim of this work was, firstly, to obtain adsorption data at a sufficiently broad concentration range, especially at extremely low concentrations of TPA, using the method of the controlled convection and, secondly, to evaluate the isotherms with respect both to constant potential[1,7] and to constant charge[7,15]. Although these two kinds of approach are not contrasting in principle, there has been much discussion up to now about the proper model of the double layer in the presence of organic adsorbate[1–5,15–17]. The choice of $NaClO_4$ as base electrolyte enabled us to compare some obtained results with those for higher concentrations of TPA ClO_4, or for TBA ClO_4, published previously[18].

EXPERIMENTAL

Adsorption of TPA ClO_4 in aqueous 0·1 mol l^{-1} $NaClO_4$ on mercury electrode was studied by means of electrocapillary measurements. The usual drop time technique was used in the concentration range $1 . 10^{-4}$–$3 . 10^{-3}$ mol l^{-1}. For concentrations $4 . 10^{-6}$–$1 . 10^{-4}$ mol . . l^{-1} the controlled convection was applied consisting in an intense stirring of the measured solution during a certain period of the drop time. The experimental arrangement has been reported in more detail previously[8,10]. Glass spindle capillaries with various parameters were used, so that approximate drop times (t_d) for concentrations c (mol l^{-1}) $3 . 10^{-5}$–$3 . 10^{-3}$, $1 . 10^{-5}$ and $4 . 10^{-6}$ were gradually 25, 45 and 100 s, respectively. Spindle capillaries were prepared from cylindrical capillaries which were blown out and then drawn out in two steps so that the inner diameter decreased towards the end of the capillary. The regular circular shape of the orifice was checked by the microscope (enlargement 300-times) and showed no cracks. The stirring of the solution during the drop life was realized by bubbling nitrogen. Since the applied method is very sensitive to the traces of surface active impurities, the vessel was carefully cleaned with chromsulphuric mixture and washed several times with redistilled water. In case of $4 . 10^{-6}$ and $1 . 10^{-5}$ mol l^{-1} TPA ClO_4, the inner walls of the vessel were saturated by use of the measured solution before each electrocapillary measurement. All measurements were taken at 298·2 ± 0·2 K and solutions were deaerated with water-saturated nitrogen. Potentials were referred to a prepared saturated calomel electrode (S.C.E.) as a reference electrode.

The water for solutions was twice distilled after passing through an ionex column, TPA ClO_4 was prepared using TPA J, Ag_2O and $HClO_4$. Sodium perchlorate and TPA ClO_4 were recrystallized. The drop time was measured with a digital counter BM 520 (TESLA) and its mean deviation did not exceed ±0·03 s. The deviation of surface tension values was better than ±0·25 mN. m^{-1}. In case that the reproducibility had deteriorated, the capillary and the cell were repeatedly cleaned with chromsulphuric mixture. As a reference value for the evalution of electrocapillary data served the surface tension γ_m at electrocapillary maximum in 0·1 mol l^{-1} $NaClO_4$, taken as 425·6 mN/m.

RESULTS AND DISCUSSION

The set of electrocapillary γ–E curves is given in Fig. 1 and their numerical values are summarized in Table I. The adsorption effect occurs on the negative branch of the curves as expected. The set of γ–E curves fills up the whole area of the diagram down to the concentration $4 . 10^{-6}$ mol l^{-1} TPA ClO_4, which had not been previously possible[18]. But in comparison with TBA ClO_4 (ref.[12]) the depression of surface tension for corresponding concentrations is markedly smaller.

The surface charge density, *i.e.* q–E, curves were obtained by graphical as well as numerical differentiation of the electrocapillary curves, according to equation (*1*)

$$q = -(\partial\gamma/\partial E)_c . \qquad (1)$$

The q–E dependences in Fig. 2 exhibit intersection points at the potential E_{max} approx. −0·85 to −0·9 V (*vs* S.C.E.) and at the charge q_{max} between −80 to −90 mC m^{-2}. From the Gibbs–Lippmann equation[16]

$$\mathrm{d}\gamma = -q \, . \, \mathrm{d}E - \Gamma RT \mathrm{d} \ln c \,, \tag{2}$$

where Γ is the surface excess, it follows that

$$(\partial q / \partial \ln c)_{\mathrm{E}} = RT(\partial \Gamma / \partial E)_{\mathrm{c}} \tag{3}$$

and

$$(\partial E / \partial \ln c)_{\mathrm{q}} = -RT(\partial \Gamma / \partial q)_{\mathrm{c}} \, . \tag{4}$$

Hence the point of intersection q *vs* E with coordinates E_{max}, q_{max}, where q and E are independent of c, corresponds to the maximum surface excess. E_{max} and q_{max} slightly vary with concentration c, *viz.*, with amount of adsorption[2,7,16,19]. This fact is

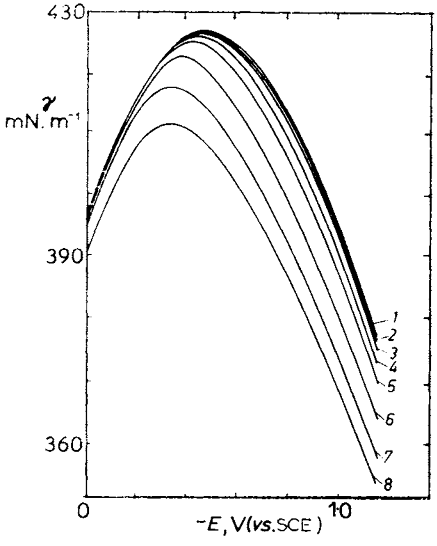

FIG. 1

Electrocapillary curves of tetrapropylammonium perchlorate TPA ClO_4 in 0·1 mol . l^{-1} $NaClO_4$. Conc. of TPA ClO_4 (mol l^{-1}): *1* 0; *2* 4 . 10^{-6}; *3* 1 . 10^{-5}; *4* 3 . 10^{-5}; *5* 1 . 10^{-4}; *6* 4 . 10^{-4}; *7* 1·35 . 10^{-3}; *8* 3 . . 10^{-3}

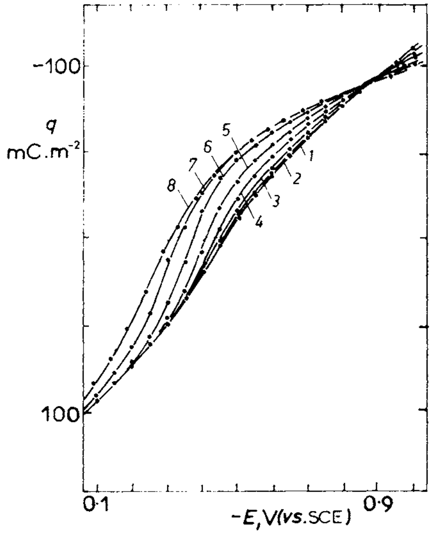

FIG. 2

Charge density *vs* potential (q–E curves) of TPA ClO_4 in 0·1 mol l^{-1} $NaClO_4$. Conc. of TPA ClO_4 (mol l^{-1}): *1* 0; *2* 4 . 10^{-6}; *3* 1 . 10^{-5}; *4* 3 . 10^{-5}; *5* 1 . 10^{-4}; *6* 4 . 10^{-4}; *7* 1·35 . 10^{-3}; *8* 3 . 10^{-3};

an indication of some complications in adsorption phenomena at higher surface excess.

First approximation tests for congruence of isotherms at constant potential and at constant charge have been made by superimposing the surface pressure π at constant potential (in Fig. 3) or the surface pressure Φ at constant charge (in Fig. 4) *vs* log c, at different potentials and charges by moving along the concentration axis[3]. The magnitudes π and Φ are defined by Eqs (5), (6)

$$\pi = \gamma_0 - \gamma \quad (E = \text{const}) \tag{5}$$

$$\Phi = \xi_0 - \xi = (\gamma_0 - \gamma) + q(E_0 - E) \quad (q = \text{const}) , \tag{6}$$

TABLE I

Surface tension data of tetrapropylammoniumperchlorate (TPA ClO_4) in 0·1 mol l^{-1} $NaClO_4$ at 25°C (*vs* S.C.E.)

	Concentration of TPA ClO_4 mol . l^{-1}							
$-E$, mV	0	$4{\cdot}05 \, . \, 10^{-6}$	$1 \, . \, 10^{-5}$	$3 \, . \, 10^{-5}$	$1 \, . \, 10^{-4}$	$4{\cdot}05 \, . \, 10^{-4}$	$1{\cdot}35 \, . \, 10^{-3}$	$3 \, . \, 10^{-3}$
0	396·7	396·7	396·7	396·7	396·7	396·0	395·1	390·7
50	402·0	402·0	402·0	402·0	402·0	401·4	400·2	395·7
100	406·8	406·8	406·8	406·8	406·8	406·2	404·9	400·2
150	411·4	411·4	411·4	411·4	411·4	410·6	409·2	404·2
200	415·1	415·1	415·1	415·1	415·1	414·4	412·8	407·5
250	418·4	418·4	418·4	418·4	418·4	417·7	415·3	410·0
300	421·3	421·2	421·2	421·2	420·9	420·2	416·5	411·3
350	423·5	423·5	423·5	423·3	422·9	421·5	416·7	411·2
400	425·2	425·1	425·0	424·6	424·0	421·5	415·9	410·3
450	425·6	425·5	425·3	424·9	423·8	420·2	414·3	408·6
500	425·4	425·2	424·9	424·1	422·6	418·1	412·1	406·4
550	424·5	424·2	423·8	422·7	420·8	415·6	409·3	403·8
600	423·1	422·6	422·1	420·7	418·4	412·7	406·2	400·8
650	421·2	420·6	419·9	418·2	415·5	409·6	402·9	397·6
700	418·8	418·1	417·2	415·1	412·3	406·0	399·4	394·2
750	415·7	415·0	414·1	411·8	408·7	402·3	395·7	390·5
800	412·3	411·3	410·4	407·9	405·0	398·2	391·5	386·5
850	408·3	407·4	406·4	403·8	400·7	393·9	387·1	382·4
900	404·0	403·2	402·1	399·5	396·2	389·5	382·8	378·0
950	399·2	398·5	397·4	394·8	391·5	384·8	378·0	373·7
1 000	394·2	393·3	392·2	389·8	386·4	379·9	373·2	368·7
1 050	388·6	387·7	386·9	384·4	381·2	374·8	368·3	363·8
1 100	382·4	381·8	381·0	378·7	375·4	369·5	363·1	358·6
1 150	376·0	375·5	374·9	373·0	369·9	364·2	358·0	353·6

where the subscript "0" refers to the solution in the absence of the adsorbate and ξ denotes the Parsons functions. Since the superimposability of $\pi - \log c[E]$ and $\Phi - \log c[q]$ seemed to be more or less possible, the horizontal shift has been ascribed to the difference $(\log B - \log B_{\max})$ or $(\log G - \log G_{\max})$ respectively, where B or G are adsorption coefficients at constant E or q and the subscript "max" refers to $E_{\max}$ or $q_{\max}$. Let us denote the horizontal shift $F(E)$ or $F'(q)$. It is related to the free energies of adsorption $\Delta\bar{G}_1^0$, $\Delta\bar{G}_2^0$ according to the equations (7), (8)

$$F(E) = \Delta \log c = (\log B - \log B_{\max}) = (\Delta\bar{G}^0_{1,\max} - \Delta\bar{G}^0_1)/2{\cdot}3\,.\,\boldsymbol{R}T\,[E] \qquad (7)$$

$$F'(q) = \Delta \log c = (\log G - \log G_{\max}) = (\Delta\bar{G}^0_{2,\max} - \Delta\bar{G}^0_2)/2{\cdot}3\,.\,\boldsymbol{R}T\,[q]\,. \qquad (8)$$

By plotting the shift $F(E)$ or $F'(q)$ in Fig. 5, as expressed by Eqs (7) and (8) as a function of $(E - E_{\max})^2$ or $(q - q_{\max})^2$, we have obtained curves somewhat deviated from the straight line. It means that instead of a linear dependence of $\Delta\bar{G}_1^0(\Delta\bar{G}_2^0)$ on $E(q)$, being usually expected in the case of ionic adsorption, rather a quadratic variation has occurred in our case. However, this fact is not surprising when taking into account that a linear variation in $\Delta\bar{G}^0$ is usually considered as a result of properties pertaining to the adsorbate, while a quadratic change in $\Delta\bar{G}^0$ is rather a consequence of the behaviour of the solvent.

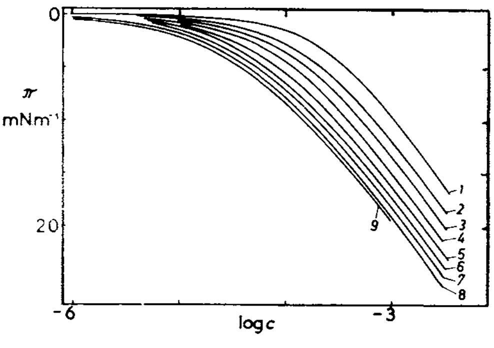

Fig. 3

Surface pressure π *vs* $\log c$ at constant potentials $-E$ (mV): *1* 450; *2* 500; *3* 550; *4* 600; *5* 650; *6* 700; *7* 750; *8* 800; *9* 850

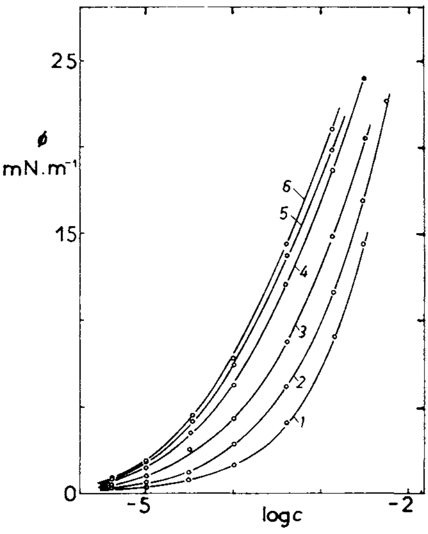

Fig. 4

Surface pressure Φ *vs* $\log c$ at constant charge $-q$ (mC m^{-2}): *1* 0; *2* 20; *3* 40; *4* 60; *5* 80; *6* 90

The relative surface excess at a constant E was determined by differentiation of the dependence $\gamma - \log c$ (Fig. 6) using (9), at various potentials between −0·45 to −1·15 V (*vs* S.C.E.).

$$\Gamma = -\frac{1}{2{\cdot}303\boldsymbol{RT}} \cdot \left(\frac{\partial \gamma}{\partial \log c}\right)_{\mathrm{E}} . \tag{9}$$

The maximum surface excess $(\Gamma_m)_E$ was obtained from the limiting slope of the γ *vs* $\log c$ plot. It coincides with $(\Gamma_m)_E$ determined from the extrapolation of the plot $1/\Gamma$ *vs* $1/c$ for $1/c \rightarrow 0$. Analogously

$$\Gamma = -\frac{1}{2{\cdot}303\boldsymbol{RT}} \cdot \left(\frac{\partial \Phi}{\partial \log c}\right)_{\mathrm{q}} . \tag{10}$$

The adsorption behaviour of TPA is graphically expressed in Fig. 7 and 8 in form of adsorption isotherms that are approximately fitting the Frumkin adsorption isotherm

$$\beta c = \frac{\Theta}{(1 - \Theta)} \exp\left(-2a\Theta\right), \tag{11}$$

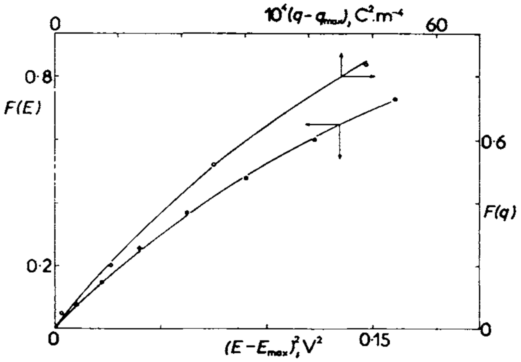

FIG. 5

The dependence of the shift $F(E)$, $F'(q) = \Delta \log c$ at constant π or Φ *vs* $(E - E_{max})^2$ or $(q - q_{max})^2$

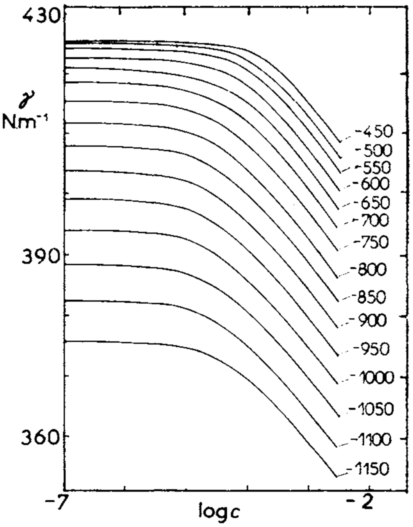

FIG. 6

γ-$\log c$ plot of TPA ClO_4 in 0·1 mol l^{-1} $NaClO_4$ at various potentials E (mV)

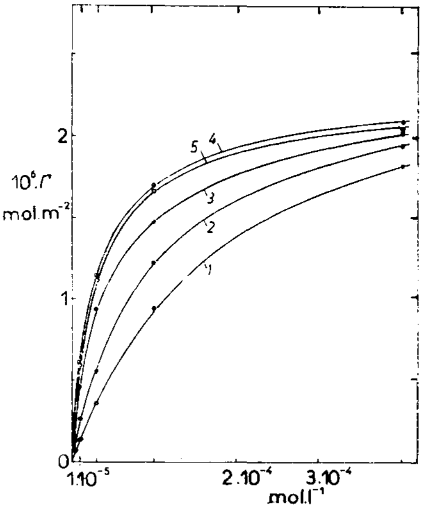

FIG. 7

Adsorption isotherms of TPA ClO_4 in 0·1 mol l^{-1} $NaClO_4$ at constant potentials $-E$ (mV): *1* 500; *2* 600; *3* 700; *4* 800; *5* 1 000

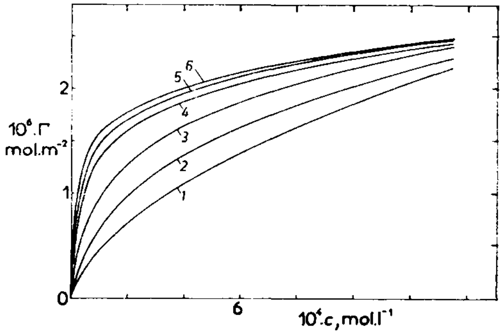

FIG. 8

Adsorption isotherms of TPA ClO_4 in 0·1 mol l^{-1} $NaClO_4$ at constant charges $-q$. (mC m^{-2}): *1* 0; *2* 20; *3* 40; *4* 60; *5* 80; *6* 90

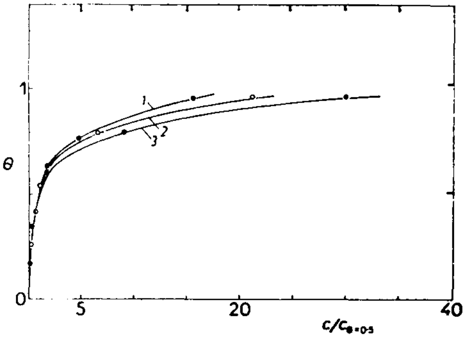

FIG. 9

The generalized dimensionless form of adsorption isotherms at various $-q$ (mC m^{-2}): *1* 60; *5* 80; *3* 90; Θ — the electrode surface coverage

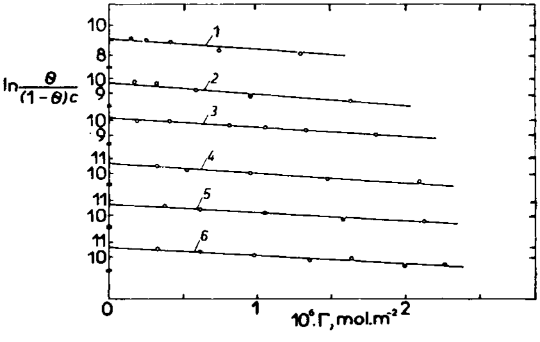

FIG. 10

Dependences of ln $[\Theta/(1 - \Theta)\,c]$ on Γ of TPA ClO_4 in 0·1 mol l^{-1} $NaClO_4$ at various charges $-q$ (mC m^{-2}): *1* 20; *2* 40; *3* 60; *4* 80; *5* 90; *6* 100 where Θ is the surface coverage, a the interaction coefficient and β the general symbol for the adsorption coefficient in previous paragraphs denoted B with respect to E or G with respect to q. The generalized dimensionless form of the adsorption isotherm drawn in Fig. 9 shows that the congruence of the isotherms with respect to q is (for given q's) strictly fulfilled only for $\Theta \leqq 0{\cdot}6-0{\cdot}7$.

The determination of the interaction coefficient was carried out graphically by use of the linearized form of the Frumkin isotherm (*11*) – see Fig. 10. Resulting straight

TABLE II

Adsorption parameters of TPA ClO_4 in 0·1 mol l^{-1} $NaClO_4$ at constant q or E, using the Frumkin adsorption isotherm. Average values of Γ_m (mol m^{-2}): $(\Gamma_m)_q = 2{\cdot}8 \cdot 10^{-6}$; $(\Gamma_m)_E = 2{\cdot}35 \cdot 10^{-6}$

$-q$ mC m^{-2}	ln G	$-\Delta\bar{G}^0$ kJ mol^{-1}	a	$-E$ V	ln β	$-\Delta\bar{G}^0$ kJ mol^{-1}	a
20	9·10	32·47	0·95	0·5	8·84	31·88	0
40	9·68	33·95	1·0	0·6	9·40	33·27	0·05
60	10·20	35·24	0·9	0·7	10·04	34·90	0·2
80	10·65	36·36	0·85	0·8	10·56	36·14	0·3
90	10·75	36·61	0·8	1·0	10·50	36·24	0·3
100	10·70	36·48	0·75				

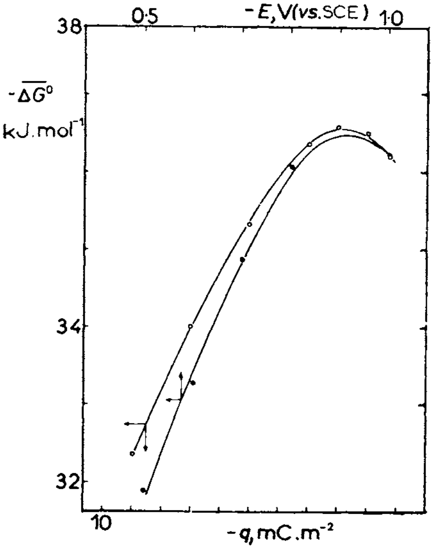

FIG. 11

Dependence of free energy of adsorption $\Delta\bar{G}^0$ of TPA ClO_4 in 0·1 mol l^{-1} $NaClO_4$ on the potential or charge, determined from adsorption isotherms at constant potential or charge (Figs 7 and 8) lines gave the values of a; the coefficient β was established as $\ln \beta = \ln [\Theta/(1 - \Theta) c]$ for $\Gamma = 0$. The positive sign of a can be interpreted as the evidence for weaker adsorbate–solvent interactions than 1/2 (adsorbate–adsorbate + solvent–solvent) interactions. The free energy of adsorption $\Delta\bar{G}^0$ was evaluated according to Eq. (*12*)

$$\beta = \frac{1}{55{\cdot}5} \exp\left(-\Delta\bar{G}^0/RT\right). \qquad (12)$$

All adsorption parameters are collected in Table II.

$\Delta\bar{G}^0$ meets a quadratic relationship (*13*)

$$\Delta\bar{G}^0 = \Delta\bar{G}^0_{\max} + b(X - X_{\max})^2 \qquad (13)$$

with parameters b and $\Delta\bar{G}^0_{\max}$. X denotes E or q, respectively. Two following relationships were obtained in our case

$$\Delta\bar{G}^0_2 = -36{\cdot}56 + 3{\cdot}1 \,.\, 10^{-3} \,.\, (q + 90)^2$$

$$\Delta\bar{G}^0_1 = -36{\cdot}50 + 10{\cdot}8 \,.\, (E + 0{\cdot}9)^2 \,.$$

The units are the following: $\Delta\bar{G}^0$, kJ mol^{-1}; q, mC m^{-2}; E, V. Both dependences are graphically expressed in Fig. 11. As is clear from Table II, the parameters a and Γ_m are to a certain extent potential or charge dependent, too. It correlates closely with deviations from the congruency of isotherms previously discussed. Γ *vs* E plot showed, among others, a slight shift of the maximum surface excess with the potential. For lowest concentrations, the maximum of bell-shaped curves lay at $E_{\max} \doteq \doteq -0{\cdot}9$ V.

The reported results, obtained from electrocapillary data with respect to constant potential or constant charge, showed that both these approaches could be chosen in principle, although some numerical differences in adsorption parameters (with respect to E or q) have appeared. The isotherm as described above in form (*11*) suggests in fact that one particle of the adsorbate displaces from the surface one pre-adsorbed solvent molecule. Its validity in our case can be explained by the displacement[3,7,16,20] of water clusters upon adsorption.

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