INTERFACIAL BEHAVIOUR OF INDOLECARBOXYLIC ACIDS AND STRUCTURAL PARAMETERS

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The adsorption at the mercury/aqueous solution interface of the 3-, 4-, 5-indolecarboxylic acids in their anionic form has been characterized. The thermodynamic analysis has shown that the process is mainly determined by the interaction of the planar aromatic system with the mercury surface and well described by a Frumkin type isotherm. From the experimental values of the electrosorption valency (γ_N) and using the model proposed by Schultze [*J. Electroanal. Chem.* *229*, 125 (1987)], a relation between the partial charge transfer (λ) and the repulsive Frumkin interaction parameter has been found. At last, the interfacial activity of the aromatic anions is also discussed on the basis of localized (charge densities) and delocalized (frontier MO energies) theoretical parameters.

Studies on organic electrosorption provide fundamental information useful to clear up the relation between the micro-structure of the double layer (in the presence of specific adsorption) and the macro properties of the electrochemical system directly measured. In particular, when the interfacial activity of aromatic compounds is investigated, reorientation processes and a sensitive partial charge transfer become relevant, also in relation to specific interactions between π electrons of the molecule and the electrode surface[1-3].

Owing to these molecular features which seem to drive the adsorption process, it appears sensible to look for a relationship between interfacial activity and structural parameters for these compounds, in the same way as it was suggested for the redox systems in term of Hammett–Taft equations[4].

So, the purpose of this study is to achieve detailed data on the adsorption of indolecarboxylic acids, to check the relation between experimental adsorption parameters (adsorption free energy, electrovalency, Frumkin interaction parameter) and derived experimental indexes (hindrance of the molecule on the surface, partial charge transfer coefficient) or purely calculated ones (net charges, frontier molecular orbital energies).

Some indications of the reliability of this approach have been already obtained for a series of aromatic N-substituted glycine derivatives[5,6], for benzensulfonamide derivatives and benzoic and *p*-aminobenzoic acids[7,8], all of them in anionic form.

Now, the three isomers (3, 4 and 5) of the indolecarboxylic acid are considered, in view of the fact that the presence of the heteroatom from one hand and the variable position of the carboxylic group on the other are effective on the electron richness of the whole aromatic system as well as on the net charge distribution within the molecular frame. Moreover, the presence of the carboxylic group greatly enhances the solubility in water, so that the condition close to the saturation coverage of the electrode can be attained.

EXPERIMENTAL

The 3-, 4-, and 5-indolecarboxylic acids are Aldrich Chem. Co. commercial products, 99%. Aqueous solutions with concentrations of surfactant in the range 10^{-4} to 10^{-2} mol l^{-1} and in the pH range 6 to 12 were examined and the results at pH 12 are discussed. 1M-$NaClO_4$ (Carlo Erba RPE) was used as base electrolyte and the pH was varied by adding highly concentrated NaOH (Carlo Erba RPE) and controlled before and after any analysis with a Beckmann Select Ion^c 5000 ion analyzer. The solutions were degased by purified nitrogen.

An AMEL Mod 471 multipolarograph was employed for ac phase selective polarographic measurements, with an ac signal amplitude of 20 mV peak-to-peak, 100 Hz fixed frequency and 1 mV/s potential scanning rate. All measurements were conducted in a jacketed cell, kept at (298 ± 0·2) K, consisting of a dropping mercury electrode (DME), drop time electronically controlled of 2 s, a large platinum sheet as a counter and a saturated calomel electrode (SCE) as reference.

The measured capacitances were tested using 1M- and 0·1M-KNO_3 solutions; it was found that all the value were always within 0·5% of the Hills and Payne data[9]. The drop time of 2 s ensures that the rate of growth of the mercury drop is sufficiently slow to warrant equilibrium conditions; in fact the time required to obtain equilibrium under diffusion-controlled adsorption, $t_e = 1{\cdot}85 \,.\, 10^6 \Gamma^2_{max}/C^2_{max}D$ (ref.[10]) for a diluted solution of 3-indolecarboxylic acid, as an example, results to be 0·5 s, $\Gamma_{max} = 2{\cdot}34 \,.\, 10^{-10}$ mol cm^{-2}, $C_{max} = 2 \,.\, 10^{-4}$ mol l^{-1} and $D = 5{\cdot}28 \,.\, 10^{-6}$ $cm^2 \,.\, s^{-1}$.

Impedance spectra recorded in the frequency range 50 Hz—3 kHz rule out the existence of any faradaic process and the absence of any relevant frequency dispersion of the capacitance was confirmed in the range of 70—1 000 Hz in the concentration range 10^{-4}—10^{-2} mol l^{-1}. These measurements were performed by means of a Solartron 1286 Electrochemical Interface and 1250 Frequency Response Analyzer, with an ac signal amplitude of 20 mV peak-to-peak; the cell was an AMEL 430 hanging drop mercury electrode (drop area 0·0217 cm^2) as working electrode, a platinum counter electrode and an $Ag/AgCl/KCl_{sat}$ as reference. However, all potential values are referred to the SCE scale with an accuracy ±5 mV.

Since capacitance versus potential curves at negative potentials are superimposable with that of the base electrolyte the double-back integration method was applied to the C vs E curves, to obtain γ (surface tension) versus potential curves[11], by means of an original program, TITAN, implemented on a 6310 Digital VAX.

Concentrations were used instead of activities in the calculation, since the ionic strength of the solution was almost constant (base electrolyte concentration at least 100 times that of the surfactant).

Quantum mechanical calculations were carried out by means of the MNDO method and the geometry of the COO^- group was fully optimized while the geometric parameters of the indole moiety were obtained from ref.[12].

RESULTS AND DISCUSSION

Differential capacitance vs potential curves for 3-, 4-, and 5-indolecarboxylic acids are reported for different concentrations at pH 12 in Figs 1–3. They show the typical features attributed in the literature to the specific interfacial activity of the aromatic moiety[13] when neutral and anionic organic compounds are concerned: a specific adsorption at positive electrode charges and desorption at increasing negative potentials; at pH 6 the general features of the adsorption are almost identical (pK_{COOH} = 5, for the 3-indolecarboxylic acid[14] thus at pH 12 the interfacial activity is due to the anionic molecular form of the compounds. In the following only the results obtained at pH 12 will be discussed.

The three indole derivatives are not reducible in the potential range examined ($-0{\cdot}2 \div -1{\cdot}6$ V vs SCE) and in fact the impedance analysis shows the typical pattern, in a Nyquist plot, due to a capacitance (double layer) in series with a resistance (bulk). In order to check the congruence of the adsorption isotherm with respect to the electrical variable, the values of π ($\pi = \gamma_{\text{base electrolyte}} - \gamma$) were plotted versus ln C at different potentials; these plots are superimposable by a simple translation along the x axis.

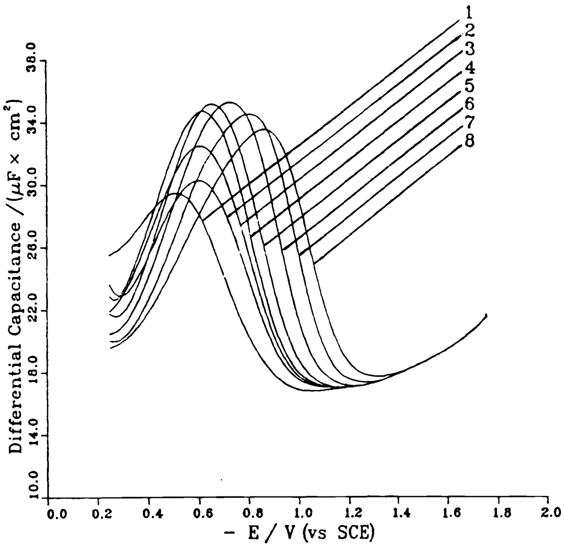

Fig. 1

Typical curves of differential capacitance vs potential for various concentrations (mol l^{-1}) of 3-indolecarboxylic acid in 1M-$NaClO_4$ + NaOH, pH 12: 1 0; 2 1 . 10^{-4}; 3 2 . 10^{-4}; 4 3 . 10^{-4}; 5 5 . 10^{-4}; 6 2 . 10^{-3}; 7 5 . 10^{-3}; 8 1 . 10^{-2}

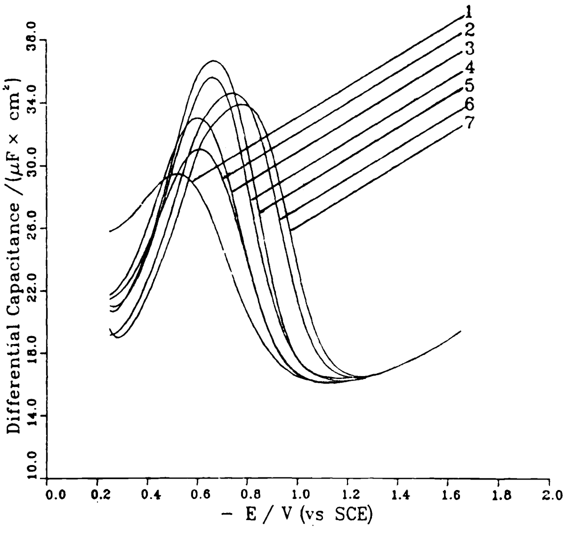

FIG. 2

Curves for 4-indolecarboxylic acid (other data see Fig. 1): **1** 0; **2** 1 . 10^{-4}; **3** 2 . 10^{-4}; **4** 7 . 10^{-4}; **5** 1 . 10^{-3}; **6** 7 . 10^{-3}; **7** 1 . 10^{-2}

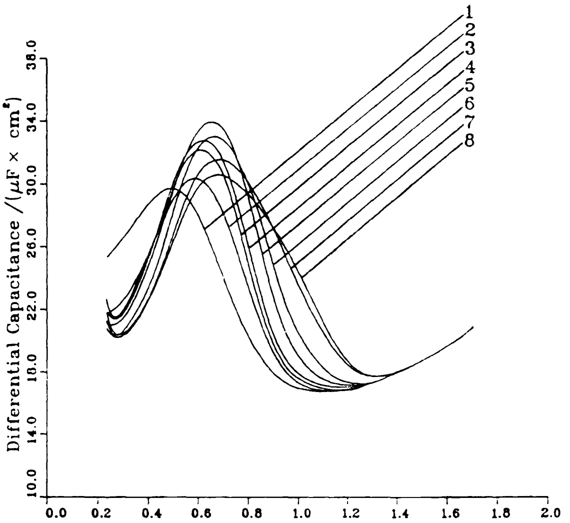

FIG. 3

Curves for 5-indolecarboxylic acid (other data see Fig. 1): **1** 0; **2** 1 . 10^{-4}; **3** 2 . 10^{-4}; **4** 3 . 10^{-4}; **5** 7 . 10^{-4}; **6** 1·5 . 10^{-3}; **7** 3 . 10^{-3}; **8** 4 . 10^{-3}

Furthermore, the charge density at fixed potential shows a good linear relationship with the surface concentration excess (Γ) in the range $-0{\cdot}4$ to $-1{\cdot}1$ V (see for example Fig. 4). This evidence allows us to conclude that the isoterm should be congruent with respect to the potential[15].

The values of Γ were obtained by differentiation of a third polynomial fit of the π plots and the maximum value $\Gamma_{\max}$ by interpolation of the final part of these curves[16]; the values of the surface coverage Θ were so calculated from the ratio $\Gamma/\Gamma_{\max}$.

The plots of $\ln[\Theta/(1-\Theta)C]$ vs Θ show a series of parallel straight lines (Fig. 5) and indicate that the adsorption process for the three isomers is well described by a Frumkin type isotherm, with a large and positive (repulsive) interaction factor (a), not dependent on potential; this finding is a general evidence for negatively charged adsorbed species, and excludes reorientation processes occurring at varying the potential (a constant).

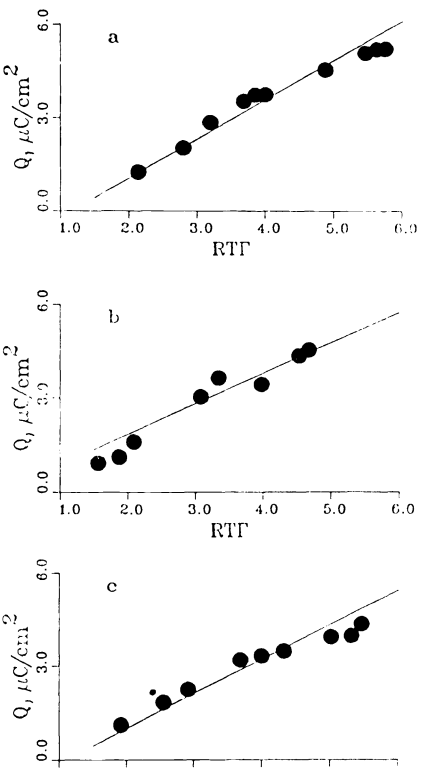

Fig. 4

Plot of the charge (Q) vs the surface concentration excess ($RT\Gamma$ units) at $E = -0{\cdot}500$ V vs SCE for the three indole derivatives: **a** 3-indolecarboxylic acid; **b** 4-indolecarboxylic acid; **c** 5-indolecarboxylic acid

The Gibbs adsorption free energies ($\Theta \to 0$) at different potentials have also been calculated and the main adsorption parameters for the three indole derivatives are reported in Table I, together with those regarding benzoate and *p*-benzoate anions, in some way structurally related to the compounds now in study.

Moreover, Table II shows some selected quantum mechanical structural parameters, the experimental values of γ_N (the electrosorption valency at −0·500 mV), and the calculated partial charge transfer coefficient, λ.

For the calculation of λ (flat adsorbed molecules), $\gamma_N = zg - \lambda(1 - g) - \nu K_{water}$, there is a general agreement on the value of the penetration factor, $g = 0{\cdot}2$, for sizeable inorganic and aromatic organic anions[2,17,18]; $\nu = 6$ is obtained from the

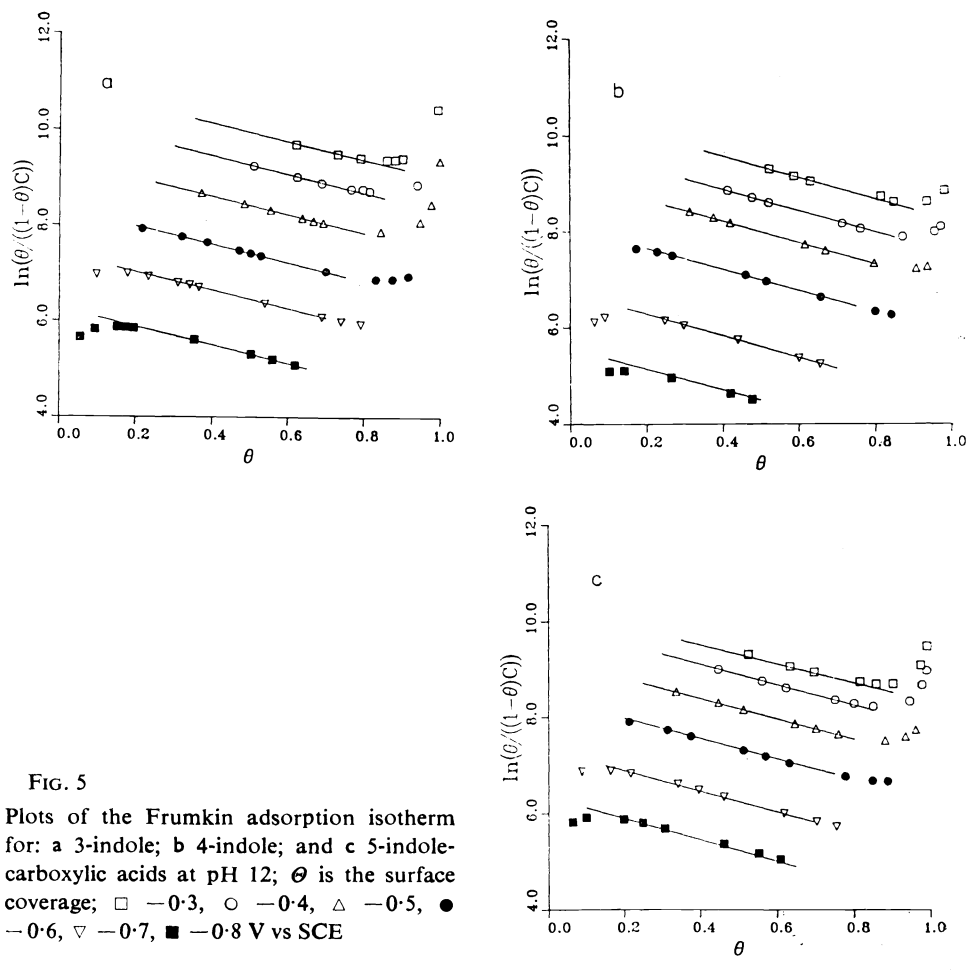

Fig. 5

Plots of the Frumkin adsorption isotherm for: a 3-indole; b 4-indole; and c 5-indolecarboxylic acids at pH 12; Θ is the surface coverage; □ −0·3, ○ −0·4, △ −0·5, ● −0·6, ▽ −0·7, ■ −0·8 V vs SCE experimental value of $\Gamma_{\max}$, taking the area of each water molecule about 0·12 nm^2 for 3- and 5-indolecarboxylic acids, while for the 4-indole derivative $v = 7$ is choosen;

TABLE I

Main adsorption parameters

	Compound	$\Gamma_{\max} \cdot 10^{-10}$ mol cm^{-2}	Area nm^2	a[a]	$-\Delta G^0_{\mathrm{ads}}$[b] kJ mol^{-1}
1	3-Indolecarboxylic acid	2·34	0·71	1·9	23·2
2	4-Indolecarboxylic acid	2·02	0·82	2·3	22·6
3	5-Indole carboxylic acid	2·3	0·72	2·1	22·9
4	Benzoic acid[c]	1·61	1·03	1·7	15·0
5	*p*-Aminobenzoic acid[c]	1·79	0·93	0·8	16·3

[a] Frumkin interaction factor calculated for the form of the isotherm used in ref.[22]; [b] adsorption free energy value at $E = -0{\cdot}500$ V (SCE), based on standard states for the adsorbate at unit molarity in solution and unit value of $\Theta/(1 - \Theta)$ on the surface; [c] ref.[23].

TABLE II

Electrosorption valency, partial charge transfer coefficient and quantum mechanical parameters (MNDO)

	Compound	γ_{N}[a]	λ	Q_{N}[b] e	Q_{H}[b] e	$Q_{\mathrm{C(COO^-)}}$[c] e MNDO	$\Delta E_{\mathrm{LUMO-HOMO}}$ eV	Q_π[d] e
1	3-Indole-carboxylic acid	−0·33	0·27	−0·2751	+0·1892	−0·6034	7·4790	6·2001
2	4-Indole-carboxylic acid	−0·25	0·19	−0·2719	+0·1899	−0·5911	7·7777	6·1416
3	5-Indole-carboxylic acid	−0·28	0·21	−0·2660	+0·1947	−0·5977	7·6259	6·1054
4	Benzoic acid	−0·25[e]	0·36[e]	—	—	−0·5997	8·2062	6·0005
5	*p*-Aminobenzoic acid	−0·30[e]	0·45[e]	—	—	−0·5995	8·0754	6·0432

[a] Obtained from the slopes of the lines in Fig. 4; [b] nitrogen and bound hydrogen net charges; [c] mean net charge referred to carboxylic oxygens; [d] π type charge density of benzenic carbon atoms; [e] ref.[19].

$K_w = -0{\cdot}015$ has the value in general assumed in these calculations[2] and $z = -1$; it is worth mentioning that the λ values for benzoate and *p*-amino benzoate anions have been independently calculated by Schultze on the basis of our previously published results[19]. Concerning the $\Gamma_{\max}$ values for the three isomers (Table I), they indicate a similar value of the area occupied per molecule on the electrode surface, corresponding to a planar arrangement of the aromatic moiety on the metal (from the CPK model $0{\cdot}7-0{\cdot}8\ \text{nm}^2$, while a perpendicular disposition would imply a calculated CPK area of about $0{\cdot}3\ \text{nm}^2$).

This is in accordance with the large and negative value of γ_N indicating the tendency of an anodic current flowing from the adsorbate to the metal typical of the planar interaction of aromatic compounds with the electrode[2]. Anyway, in this planar arrangement the three isomers show larger values of λ (Table II) when compared with those corresponding to the planar adsorption of neutral aromatic molecules[19], so that the presence of a substituent in the molecular frame bearing a negative charge (the COO^- group) can be regarded as inducing, for the whole molecule, a more relevant partial charge transfer, also in relation to the existence of partial negative charge on the nitrogen of the heterocycle (Table II).

Furthermore, a relationship between macroscopic and microscopic adsorption features is shown in Fig. 6: the higher the partial charge transfer the lower the value of the Frumkin interaction parameter, thus indicating that the partial flow of negative charge from the molecule to the metal lowers the repulsive interaction due to the remaining part of negative charge on adjacent adsorbed molecules. On the basis of this argument for the adsorption of neutral aromatic molecules (with a repulsive interaction parameter too) the opposite should happen and in fact this is the case clearly shown in ref.[19].

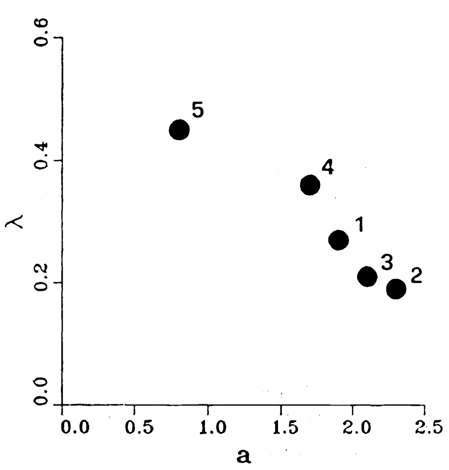

FIG. 6

Partial charge transfer (λ) vs Frumkin interaction parameter (a). Numbering of the compounds as in Table I

The attempt to attribute the origin of the observed repulsive interaction factor mainly to the negative charge localized only on the oxygen atoms (see Table II) has failed; on the other hand net charges on atoms are calculated for the isolated molecule, while λ is obtained on the basis of a model which tries to account for the whole interaction between the adsorbed molecule and the electrode, also involving the displacement of the solvent molecules.

Finally, the Gibbs adsorption energies (Table I) for the three isomers are almost the same, and higher in general with respect to those of other aromatic carboxylate anions like benzoate and *p*-aminobenzoate, N-benzoylglycinate ($\Delta G^0_{ads} = -20$ kJ . . mol^{-1})[5] and N-tosylglycinate ($\Delta G^0_{ads} = -16{\cdot}8$ kJ mol^{-1})[16]; no relation can be found (even if expected) between the λ value and the corresponding ΔG^0_{ads}, and this is not only due to the fact that the compounds are anions (the charge could play the main role in determining the energetic of the electrosorption instead of the partial charge transfer), because no clear relation of this type for neutral aromatic compounds is found either[19].

However, other calculated molecular descriptors are useful, almost on a qualitative ground, for assessing the weight of some structural features with regard to the electrosorption energetics. Thus, the reckoned values of the π charge density (Table II) show that to a higher availability of the delocalized π electrons corresponds an increased adsorption Gibbs energy; this fact together with the sign of the electrosorption valency and the λ value, indicates the leading role played by the aromatic moiety in the interfacial activity of planar adsorbed molecules.

Moreover, the rough trend between the ΔG^0_{ads} values and the difference in energy between the frontier MO's (ΔE_{L-H}), (Tables I and II), implies a high surface activity for the compounds with a low energy gap between the frontier MO's, as already reported for a series of neutral aromatics studied independently by Bockris[6].

This behaviour is justified within the model of "hard" and "soft" molecular interactions recently reviewed by Parr and Pearson[20,21], in which "soft" molecules (with low ΔE_{L-H}) are considered to be more reactive than "hard" ones (higher ΔE_{L-H}) if partial electron transfer or rearrangement are involved in the reactions.

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REFERENCES

1. Blomgren E., Bockris J. O' M., Jesch C.: J. Phys. Chem. *65*, 2000 (1961).
2. Rolle D., Schultze J. W.: Electrochim. Acta *31*, 991 (1986).
3. Damaskin B. B., Petri D. A., Batrakov V. V.: *Adsorption of Organic Compounds on Electrodes.* Plenum Press, New York 1971.
4. Zuman P.: *Substituents Effects in Organic Polarography.* Plenum Press, New York 1967.

5. Fontanesi C., Battistuzzi Gavioli G., Andreoli R., Benedetti L.: J. Electroanal. Chem. Interfacial Electrochem. *210*, 181 (1986).
6. Andreoli R., Barbieri A., Benedetti L., Fontanesi C., Battistuzzi Gavioli G.: J. Electroanal. Chem. Interfacial Electrochem. *251*, 201 (1988).
7. Benedetti L., Andreoli R.: Bioelectrochem. Bioenerg. *9*, 541 (1982).
8. Quartieri S., Andreoli R., Battistuzzi Gavioli G., Benedetti L.: Bioelectrochem. Bioenerg. *12*, 543 (1984).
9. Hills G. J., Payne R.: Trans. Faraday Soc. *61*, 316 (1965).
10. Koryta J.: Collect. Czech. Chem. Commun. *18*, 206 (1953).
11. Grahame P. G., Coffin E. M., Cummings J. P., Poth M. A.: J. Am. Chem. Soc. *74*, 1207 (1952).
12. Philips L. A., Levy D. H.: J. Chem. Phys. *83*, 1327 (1986).
13. Hills G. J., Schiffrin D. J., Salomon T.: J. Electroanal. Chem. Interfacial Electrochem. *41*, 41 (1973).
14. *Beilstein:* 4. Aufl., Band XXII, p. 65. Springer, Berlin 1935.
15. Parsons R.: J. Electroanal. Chem. Interfacial Electrochem. *8*, 93 (1964).
16. Andreoli R., Barbieri A., Benedetti L., Borghesani G., Battistuzzi Gavioli G.: Electrochim. Acta *32*, 325 (1987).
17. Schultze J. W., Vetter K. J.: J. Electroanal. Chem. Interfacial Electrochem. *44*, 63 (1973).
18. Grahame D. C., Parsons R.: J. Am. Chem. Soc. *83*, 1291 (1961).
19. Rolle D., Schultze J. W., J. Electroanal. Chem. Interfacial Electrochem. *229*, 141 (1987).
20. Parr R. G., Pearson R. G.: J. Am. Chem. Soc. *105*, 7512 (1983).
21. Pearson R. G.: Proc. Natl. Acad. Sci. U.S.A. *83*, 8440 (1986).
22. De Battisti A., Trasatti S.: J. Electroanal. Chem. Interfacial Electrochem. *48*, 213 (1973).
23. Andreoli R., Battistuzzi Gavioli G., Grandi G., Benedetti L.: J. Electroanal. Chem. Interfacial Electrochem. *157*, 369 (1983).