Double Layer Studies using Depolarizers as Probe — A Reassessment*

L. Gierst, E. Nicolas, and L. Tytgat-Vandenberghen

Faculté des Sciences, Université Libre de Bruxelles, Belgique 1050

The influence of the double layer on mercury electrodes has been assessed by examining a large number of depolarizers and supporting cations. Cross-analysis of the results shows that, besides the Frumkin mechanism, ion-pairing can be also a significant factor, either by increasing the local concentration of the depolarizer, or by enhancing its intrinsic electroactivity. These effects are correlated to various other types of behavior (electrolytes, colloids, exchangers) in terms of a common charge interaction model taking into account structural changes brought to the solvent.

INTRODUCTION

It is now fully recognized that the structure of the double layer is one of the cardinal factors which control the apparent rate constant of electrochemical reactions[1-5]. Many unexplained facts have been resolved satisfactorily** by taking into account that the overall composition of the solution may act indirectly upon electrode kinetics, by altering the interfacial structure. Polarization curves of unusual shape[7-9] are also very often quantitatively explained by the same argument.

The well-known Frumkin relation[10] which explicits the influence of the diffuse part of the double layer on electrode reactions involving electron transfer as rate-determining step, may be written under the form of the differential expression

$$\Delta \ln \frac{v_{E, \psi}}{k_E} = - (z_A \pm \alpha \, n_\alpha) \, f \, \Delta \, \psi_A \qquad (1)$$

where

$v_{E,\psi}$ is the »apparent« rate in cm. sec^{-1} measured at the potential E for a given ψ_A potential (the v values are easily calculated from the $i = f(E, t)$

* The present paper is the abridged version of a short series of didactic lectures presented at the first Summer School held in Cavtat in 1969. The major aim being to provide a compact review of an extensive field without entering too much into all the details, any non-essential data has been deliberately omitted. This auxiliary information can however be easily retrieved by resorting to the key references.

** A good example is afforded by the reduction of the chromate ion in alkaline medium[6], which gives apparent rate constants that increase by a factor well over 10^2 when the NaOH concentration is raised from 0.1 to 1.0 N^-. Close analysis of the data reveals that the reaction is in fact pH-independent, and that the observed effect is the indirect result of the concomitant increase of the ionic strength — which entails compression of the double layer atmosphere.

polarization curves, after the usual routine corrections for the back reaction and the mass transfer).

k_E is the corresponding »true« rate constant which would be observed at the same potential in absence of double layer

ψ_A is the diffuse layer ψ potential acting on the depolarizer particle A, when it reaches its reduction site.

z_A, α, n_α and f are respectively the electronic charge of A, the transfer coefficient, the number of electrons involved in the rate-determining step (usually 1), and the quantity F/RT. The signs $+$ and $-$ correspond respectively to oxidation and reduction processes.

Most of the conditions and problems associated with the validity of this equation have been stressed by the author himself. Among them: (1) no specific adsorption of A — which just »obeys« the potential-distance profile by adjusting its concentration (2) ψ_A may differ from ψ_δ , since planes of closest approach may not coincide for A and for the structure-determining support ion (δ plane) (3) α is not necessarily constant over the useful potential range (4) steric effects may be operative, *etc.* Despite these difficulties, and the approximate character of diffuse layer models[11-14], application of the Frumkin theory has been an overwhelming success. It allows indeed the determination of »true« rate constants which, even if the correction made is not absolutely exact, are far better than the experimental values (for example when one tries to assess the intrinsic electroactivity of a series of systems, in order to establish correlations with molecular structure). Besides, reaction rates can be selectively curbed — a factor may be exploited for improving separations in electroanalytical chemistry. More fundamentally, kinetic ψ effects afford unique information on both the mechanistics of electrode reactions, and the fine structure of the double-layer*.

For a given potential, ψ_δ (or ψ_A) may be controlled by various means

1) in absence of specific adsorption, simply by acting on the concentration of the supporting electrolyte[11]

2) by adsorbing tensioactive cations or anions

3) by adding organic surfactants, which modify the potential-distance profile by the way of their steric, dielectric and dipolar properties[15,16]

4) by altering the nature of the electrode itself (with reference to mercury the best method is to use amalgams, in order to affect as little as possible the intrinsic rate constant of the reaction).

As an illustration, Fig. 1. shows the role of these factors on the kinetics of the reduction of the trichloroacetate ion at the dropping mercury electrode.

The most common pitfalls, when one attempts to calculate ψ_δ potentials from changes in rate constants, are that the reactivity of the surface itself may be modified (by blocking or catalytic surfactants) or that the changing bulk composition may affect the reaction rate, by originating other chemical forms of the depolarizer having different intrinsic electroactivity.

---

* As an example of the sensitivity of the method, a variation of 5% in the rate constants of reduction for a divalent anion with $\alpha\,n_\alpha = 0.5$ corresponds to a $\Delta\psi$ of about 0.5 mV, which may be induced by as little as 0.1 μ Coulomb per cm² of specific adsorption — a value clearly well beyond the potentiality of the most precise electrocapillarity work.
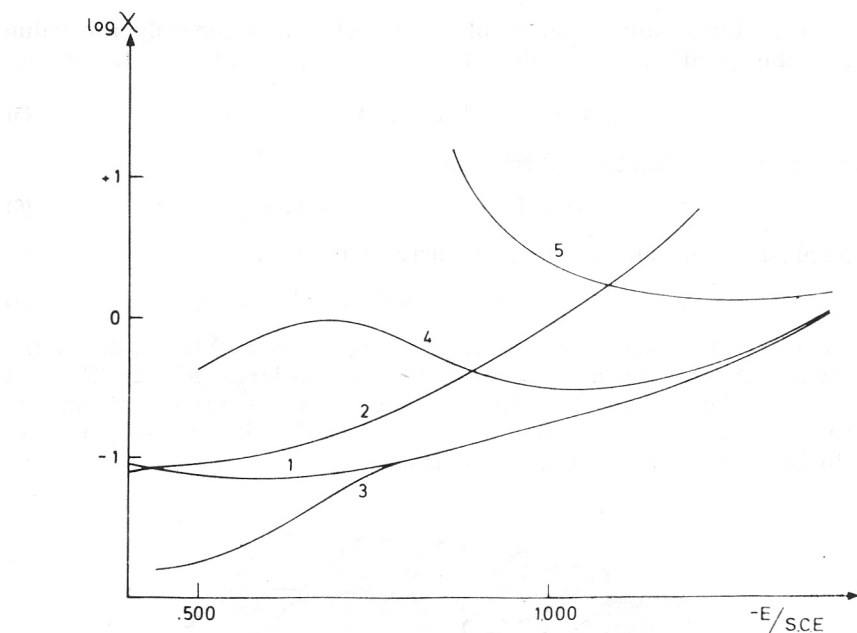
Fig. 1. Influence of the double layer on the polarographic reduction on D. M. E. of the trichloroacetate ion (χ is the Koutecky parameter, which is proportional to the apparent rate constant)
1. NaOH 0.1 N; 2. CsOH 0.1 N; 3. NaI 0.1 N; 4. NaClO$_4$ 0.1 N + 0.25 M thiourea; 5. NaOH 0.1 N + Thallium amalgam 7%.

More particularly, when ψ_δ is controlled by the concentration of a supporting electrolyte, there is a rather common situation for which *the assessment of the reaction path may be ambiguous*[2,17]. If the following conditions occur

a) the ions of the supporting electrolyte are not specifically adsorbed

b) ψ_δ potentials are sufficiently large ($\psi_\delta > 40$ mV) as to degenerate into a logarithmic function of the ionic strength at constant charge density[11,18]

c) z_A and ψ_δ have the same sign (repulsion effect).
it is then impossible to ascertain whether the reaction simply involves the bulk species A in its rate-determining electron-transfer step

$$A^{z_A} + n_\alpha \; \varepsilon \rightarrow \tag{2}$$

or whether association with the oppositely charged supporting ion occurs before the electron transfer proper

$$A^{z_A} + X^{z_X} \rightleftarrows AX^{(z_A + z_X)} \tag{3}$$

$$AX^{(z_A + z_X)} + n_\alpha \; \varepsilon \rightarrow \tag{4}$$

This ambiguity arises when the further following conditions occur

a) Equilibrium (3) is largely in favor of A^{z_A}

b) The apparent rate constant for (4) is much larger than for (2)

c) Reactions controlling (3) are fast as compared to (4) (otherwise kinetic currents will be detected)

Under such conditions, any variation of [X] affects simultaneously the value of ψ_δ and the position of equilibrium (3). As a result, for the direct discharge (2)

$$\Delta \ln v = - (z_A \pm \alpha n_\alpha) f \Delta\psi_A \tag{5}$$

while, for the »post-association« discharge

$$\Delta \ln v = - \Delta \ln [X^{z}x] - (z_A + z_X \pm \alpha n_\alpha) f \Delta\psi_{AX} \tag{6}$$

The two expressions (5) and (6) are obviously identical, if

$$\Delta\psi_A \simeq \Delta\psi_{AX} \simeq \Delta\psi_\delta \qquad \text{and} \qquad \Delta \ln [X^{z}x] = + z_X f \Delta\psi_\delta \tag{7}$$

which is actually the case if ψ_δ is large enough, *i. e.* not too close to the potential of nul charge, and at ionic strengths not too large (Fig. 2). The fact that the charge density of the electrode also depends somewhat on the concentration brings some deviation to the expected behavior — too small however to be exploited as a diagnostic test.
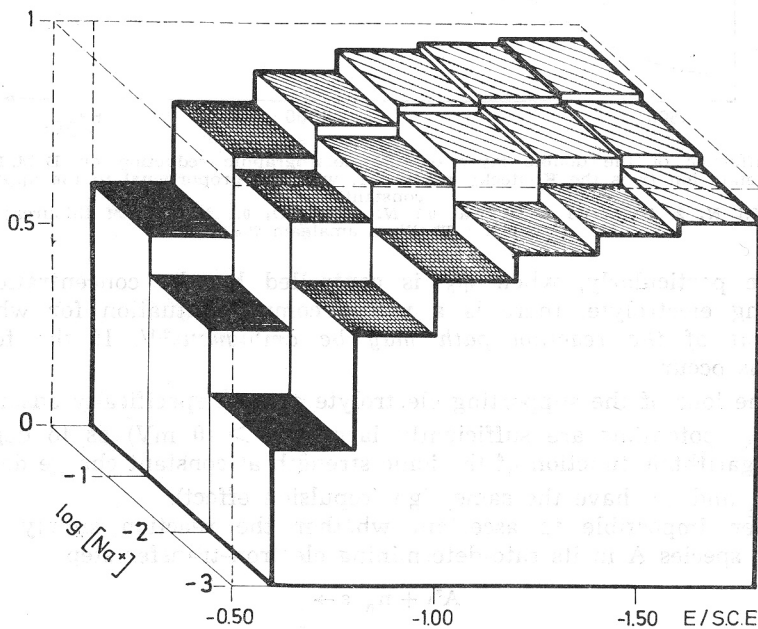

Fig. 2. »Apparent reaction order« of the ψ effect (vertical axis) in the case of the reduction of a mononegative anion, showing the upper region (dashed squares) where ambiguity arises between direct discharge and post-association discharge (discrete values are presented, in order to accentuate the three dimensional effect).

In order to eliminate the uncertainty, it is obviously better to maintain [X] constant, and to modify ψ_δ by any of the other methods listed above[2]. The major difficulty is that significant variations of ψ_δ are generally restricted to a rather narrow potential range over the point of zero charge (see Fig. 1 as an illustration), precisely where the ambiguity problem vanishes. In the particular case of the reduction of anions on negatively charged mercury, it should be much more convenient to use tensioactive cations of known

adsorbability, but new difficulties then arise: (a) quantitative data on the superficial excesses of cations are scarce and imprecise, since their specific adsorption is generally rather small (b) the extent of association is likely to vary with the nature of the cation[19] (c) some cations may act on the reaction mechanism itself, otherwise than through ion-pairing.

At least, the systematic and extensive study of the effect of cations of various adsorbability on a sufficient number of reactions, should help to recognize the *main kinetic factors* and to explain them in terms of suitable models. From the careful analysis of the various reaction patterns, and with the help of all *other available information about known phenomena involving ion-association,* deeper insight may be expected to be gained into the extent and the exact influence of ion-pairing on apparent rate contants. This pheno-menological approach may eventually provide a wealth of quantitative infor-mation, on one hand about the values of ψ_δ potentials and the extent of cation adsorption and, on the other, on the exact mechanism of the electro-reduction processes.

Essentially based on *the comparative examination of a large diversity of systems,* the present work accordingly aims at three distinct objectives (1) *a better understanding of the »composition« factor* in Electrochemistry, by (2) the definition of *the structure of the double-layer at negative electrode charge densities,* and by (3) *the elucidation of the processes involved together with the electron transfer itself.*

<div align="center">EXPERIMENTAL</div>

Reagents

Triply distilled water and doubly distilled mercury were used. The various supporting electrolytes were made from A. R. products (after recrystalization, when needed, and calcination each time it was possible). In the particular case of the pyrophosphate ion fresh solutions were prepared daily, to avoid appreciable hydro-lysis. It has been verified, for each supporting electrolyte, and after careful deoxygenation, that the residual current recorded at high sensitivity, was devoid of any waves or steps indicative of the presence of significative amounts of electroactive or adsorbable foreign species.

The depolarizers were generally determined according to standard procedures and used without further purification, at concentrations of the order of 10^{-3} N. Sodium chlorite was purified by following the procedure of Weiner[20].

Instrumentation

Most of the data presented have been derived from the analysis of instantaneous maximum current-time polarographic curves, obtained with a controlled drop-time of 4 sec. The experiments were carried out at $25^0 \pm 0.2^0$ C, in a conventional three-electrode cell, with a separate high-impedance circuit for the measurement of potentials. The I—E curves were recorded at slow scanning rates, with at least a hundred drops for the rising section of each wave.

Determination of Apparent Rate Constants

After verifying that the electrode reaction is first order and does not entail complications (like prior slow chemical steps, or autoinhibition by adsorption products) the waves were analyzed according to the classical Mejman-Koutecky theory[21], correcting for the back reaction when the process was not entirely irreversible. In the case of depolarizers which are only reduced at very negative potentials (NO_3^- , NO_2^- , ClO_2^-), the foot of the wave was analyzed from direct measurement of the current density at the drop time.

EXPERIMENTAL RESULTS — FACTS AND PRELIMINARY DISCUSSION

Scope

The following depolarizers have been studied under conditions (pH, ligand concentration, *etc.*) carefully selected in order to exclude any other rate-determining step than the electron transfer itself:

Cr^{3+}, Eu^{3+}, Ni^{2+}, Co^{2+}, H^+, IO_3^-, BrO_3^-, ClO_2^-, NO_2^-, NO_3^-, ReO_4^-,

CCl_3—COO^-, CrO_4^{2-}, $S_3O_6^{2-}$, $S_4O_6^{2-}$, $PtCl_4^{2-}$, periodate, uranylcarbonate, ura-nylpyrophosphate, tricarbonato-Co (III), trioxalato-Co (III)

Most of these depolarizers have been used in 1.0 and 0.1 N solutions of suitable salts of the following cations Me^{Z+}

$$Li^+, \quad Na^+, \quad K^+, \quad Cs^{+ \; 22}$$

$$Mg^{2+}, \quad Ca^{2+}, \quad Ba^{2+}, \quad La^{3+ \; 23}$$

$$NH_4^+, \quad NMe_4^+ \quad NEt_4^{+ \; 24}$$

For a few selected reactions, various aminium ions (NH_3Me^+, $NH_2Me_2^+$, $NHMe_3^+$, NH_3Et^+ *etc.*) have also been investigated[25].

It should be stressed that no systematic claim for rights of priority is laid, since a number of these systems have already been studied before the present study — but unfortunately under experimental conditions so variable that direct intercomparison is either imprecise or simply impossible.

RESULTS

The exposition and the discussion of the results can be considerably simplified if one takes into account, from the early beginning, the fact a few significative trends clearly emerge from the extensive intercomparison of the whole data.

1. Each *supporting cation* Me^{Z+} can be characterized by a set of two semi-quantitative coefficients (Fig. 3) which respectively grade (1) the extent of its specific adsorption (coefficient ϱ_A^+) and (2) its ability to act as a local proton source at the surface of the electrode (coefficient ϱ_H^+)

2. Amongst the *depolarizers,* the electroreduction of cations is not affected by ϱ_H^+, but only by ϱ_A^+ (in other words, they respond to the ψ-effect, but not to the superficial acidity). The behavior of anions is more diversified. Some act not very differently from the cations (ex: $S_4O_6^{2-}$, ReO_4^-, CCl_3—COO^-), while, for others, the apparent rate constants increase with ϱ_H^+, with various degrees in sensitivity (the reduction of iodate being the most enhanced — sometimes by about 6 orders of magnitude!)

3. A third empirical fact — which does not seem to be entirely fortuitous — is that anions very sensitive to ϱ_A^+ are generally rather little affected by ϱ_H^+, and vice-versa. The exact fundamental signification of these traits will be discussed in detail in the last section of the paper. It is worthwhile to draw attention on them at once, because they justify why the description of the results has been a priori divided into separate sections, dealing in succession with the influence of each of the two factors ϱ_A^+ and ϱ_H^+ before presenting a unified review of the whole phenomenology.
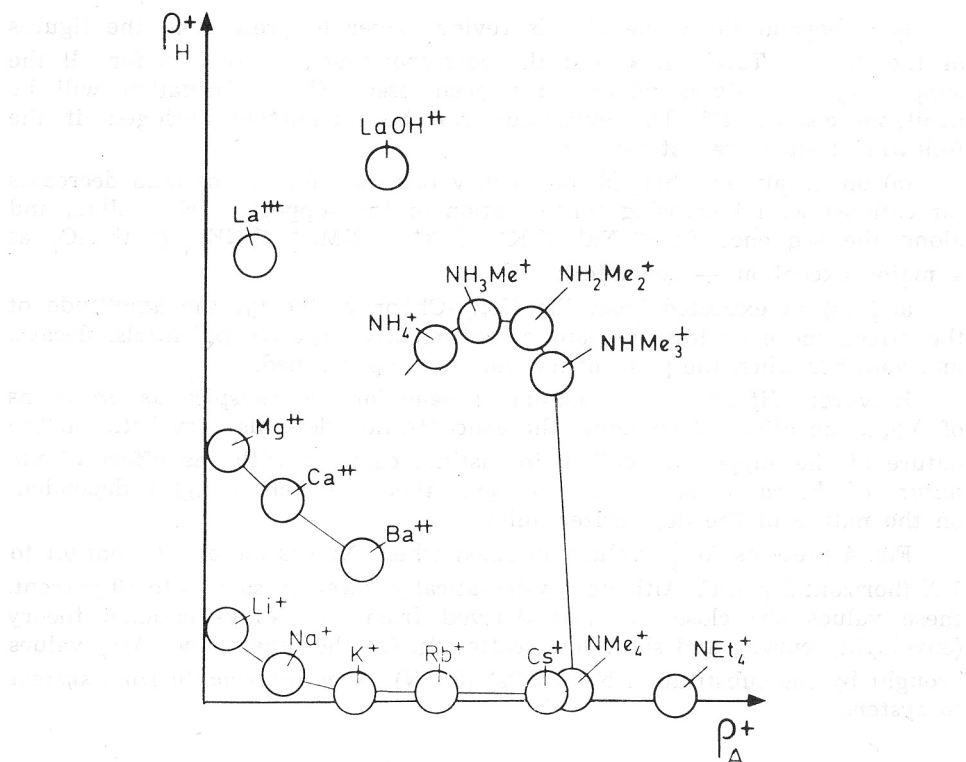
Fig. 3. Schematic qualitative diagram showing the behavior of various supporting cations, according to the extent of their specific adsorbability (ϱ_A^+), and their protogenic power (ϱ_A^+).

A. The Effect of the Specific Adsorption of the Supporting Cation

This effect can be observed at its best by resorting to cations with negligible acidic character. This condition is satisfied with Na^+, K^+, Cs^+, NMe_4^+ and NEt_4^+.

As indicated by the Frumkin relation, valid comparison must be based on the variation of apparent rate constants corrected by the $(z_A - \alpha n_\alpha) f$ factor.

By definition

$$\frac{\Delta \ln v}{(z_A - \alpha n_\alpha) f} = - \Delta \psi'_\delta \qquad (8)$$

represents the variation of the ψ_δ potential which should account for the observed effect, assuming *arbitrarily* that the Frumkin relation is perfectly obeyed.

$\Delta \psi'_\delta$ is accordingly a quantity which responds to any deviation from the theory, and which can be conveniently used for assessing the direction and the order of magnitude of the relative deviation between the various depolarizers under consideration.

It is beyond the scope of this review paper to present all the figures of the various Tafel plots, and the corresponding $\Delta\psi\,'_\delta$ values for all the supporting electrolytes which have been used. This information will be available elsewhere[26]. The exposition can be fortunately abridged, if the following trends are noticed:

(a) on negatively charged mercury, v increases for anions (and decreases for cations) with increasing concentration of the supporting electrolyte, and along the sequence $Li^+ < Na^+ < K^+ < Cs^+ \simeq NMe_4^+ < NEt_4^+$ (with IO_3^- as a major exception — see later);

and (b) as expected from the Gouy-Chapman theory, the amplitude of the effect, more or less constant at sufficiently negative potentials, decays, and vanishes when the point of nul charge is approached.

However, *differences in individual behavior are conspicuous.* In terms of $\Delta\psi'_\delta$, the effect of changing the concentration depends very little on the nature of the supporting cation, in distinct contrast with the effect of *the nature of the cation at constant concentration* — which is highly dependent on the nature of the depolarizer anion.

Fig. 4 presents $\Delta\psi\,'_\delta$ values obtained when (Na^+) is increased from 0.1 to 1 N (horizontal plane). Although systematically lower by some 5 to 10 percent, these values are close to those derived from the Gouy-Chapman theory (enveloping curve), and show low scattering. On the other hand, $\Delta\psi\,'_\delta$ values brought by the substitution $Na^+ \rightarrow Cs^+$ (0.1 N), *vary appreciably from system to system.*

Fig. 4. Intercomparison between the enhancement of the apparent rate constants for various systems (plotted along the potential axis) when 0.1 N Na^+ is replaced by 1.0 N Na^+ (horizontal plane) and by 0.1 N Cs^+ (vertical plane. Co (III) C = tricarbonato-Co (III), UPP = uranylpyrophosphate, Uperoxo = Uranylperoxodicarbonate, UC = Uranyltricarbonate.

Each depolarizer may be characterized (Table I) by the normalized selectivity coefficient

$$S_{Na^+, 0.1}^{Cs^+} = \Delta\psi'_{\delta} \left| {}^{Cs^+}_{Na^+ .01} \uparrow \middle/ \Delta\psi'_{\delta\,Na^+\,0.1}^{\quad 1} \uparrow \right|$$

which no more depends on any possible uncertainty on the quantity $(z_A - \alpha\,n_\alpha)$.

TABLE I

Caesium Effect on Various Electrode Reactions

Depolarizer	z_A	α	E/S. C. E.	$S_{Na^+}^{Cs^+} \Big|_{0.1} \uparrow$
Co^{2+}	$+2$	0.68	-1.30	0.75
H^+	$+1$	0.52	-1.56	0.92
IO_3^-	-1	0.96	-1.18	0.23
BrO_3^-	-1	0.88	-1.70	0.87
ClO_2^-	-1	0.37	-1.84	0.84
NO_3^-	-1	0.70	-1.76	0.95
NO_2^-	-1	0.72	-1.86	1.03
ReO_4^-	-1	0.72	-1.45	1.13
CCl_3-COO^-	-1	0.20	-1.20	1.33
$HCCl_2-COO^-$	-1	0.38	-1.60	1.60
CrO_4^{2-}	-2	0.60	-0.90	0.45
S_3O_6	-2	0.35	-1.60	1.53
$PtCl_4^{2-}$	-2	0.75	-1.50	1.73
$S_4O_6^{2-}$	-2	0.19	-1.10	1.30

(see text for caption)

In spite of the unavoidable differences in the potential range from system to system, it is obvious that most of the variations of $S_{Na^+, 0.1}^{Cs^+}$ can be traced back to *the nature of the depolarizer itself*. The same conclusion is reached if K^+, NMe_4^+, NEt_4^+ is substituted for Na^+ (with the notable exception of systems which can only be studied at very negative potentials, where tetraalkylammonium ions undergo desorption).

The hypothesis that increasing selectivity coefficients are related to the *growing extent of association* between the anion and the supporting cation is substantiated by the following arguments:

1. Selective ion-pairing could indeed increase the apparent rate constant, by providing an easier path for the reaction (see later).

2. The sequence of increasing selectivity for Cs^+ (and its parent cations) *parallels many other series which are held to reflect the extent of ion-pairing* (Table II).

TABLE II

Some Sequences Involving Interactions with Anions

1	2	3	4	5	6	7
	OH^-		OH^-	IO_3^-	IO_3^-	IO_3^-
F^-		Ac^-				
		IO_3^-	Ac^-			ClO_2^-
		OH^-	CN^-			
Cl^-		BrO_3^-	ClO_2^-	NO_2^-	BrO_3^-	BrO_3^-
		NO_2^-	BrO_3^-			NO_2^-
				BrO_3^-		
			NO_3^-			
Br^-	NO_3^-	NO_3^-	ClO_3^-	NO_3^-	NO_3^-	NO_3^-
	MnO_4^-				MnO_4^-	
I^-	ClO_3^-	SCN^-	SCN^-	MnO_4^-		
	SCN^-	ClO_4^-	ClO_4^-	ClO_3^-		ReO_4^-
				ClO_4^-		
				ReO_4^-		

1. anions common to all sequences
2. adsorption at the air-water interface[46]
3. selectivity for an anion exchanger (Dowex 2)[47]
4. coadsorption with tetraalkylammonium ions on negatively charged mercury[48]
5. distribution coefficient between water and chloroform, with the tetraphenylarsonium ion as extractant[49,50]
6. B coefficient of viscosity[34]
7. sequence found in this work

Close examination of these data leads to the conclusion that most of the large anions do associate appreciably with Cs^+ and with the other related cations, with resulting values substantially larger than the »real« $\Delta\psi_\delta$ ones. It is also probable that the intrinsic reducibility of the pair is somewhat »artificially« enhanced by the specific adsorption of the cationic partner. Taking into account these facts, it is possible to delineate the dashed area of Fig. (5) which gives the most probable error limits for the »true« ψ_δ (Cs^+ 0.1 N) potentials. Similar plots have been constructed for other cations at concentrations 0.1 and 1 N (Fig. 6a) — with only the reasonable hypothesis that ψ_δ values for Li^+ 0.1 N are not affected by specific adsorption and can be calculated from the Gouy-Chapman theory.

The reliability of the proposed ψ_δ values may be checked by two different ways.
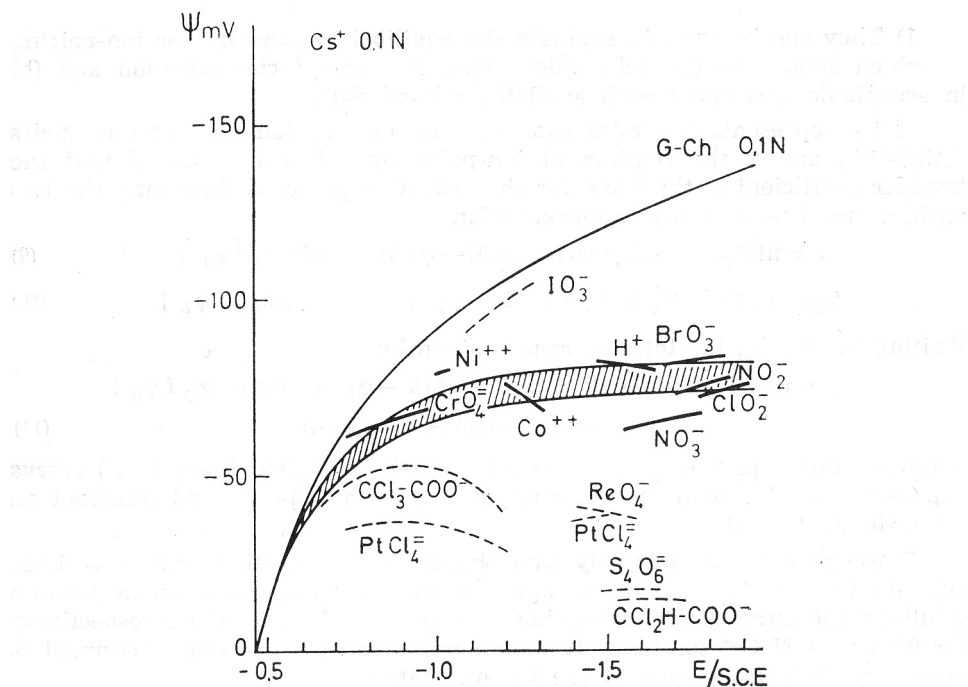
Fig. 5. Plot of the various ψ'_δ values for Cs+ 0.1 N. The dashed zone limits the probable »true« ψ_δ values.
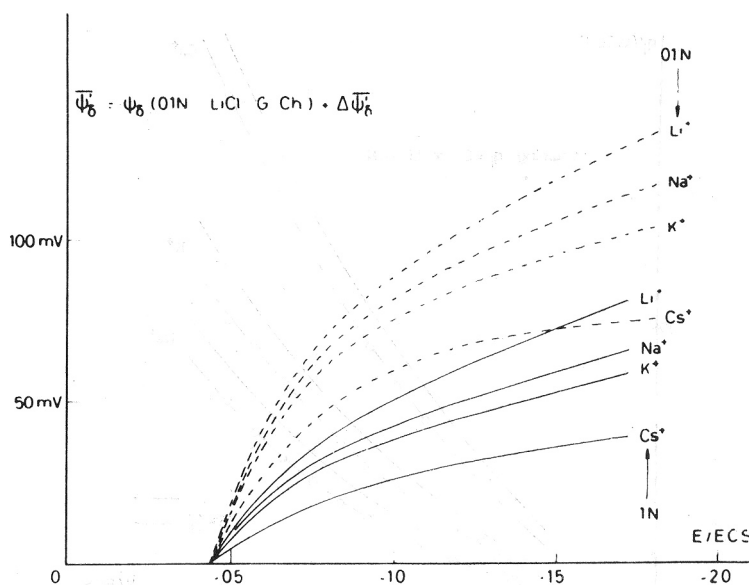

Fig. 6a. $\bar{\psi}'_\delta$ values for Li+, Na+, K+, Cs+ 0.1 and 1.0 N computed from the corresponding average experimental $\Delta\bar{\psi}'_\delta$, assuming that the $\psi_\delta = f(E)$ curve for Li+ 0.1 N can be calculated from the Gouy-Chapman theory.

1) They can be used to evaluate *the equilibrium constant* for ion-pairing — which should be (a) independent from the cation concentration and (b) in acceptable agreement with available related data.

If C_T represents the total concentration of free ions A^{z_A} and ion-pairs $AMe^{(z_A + z_{Me})}$, and x the fraction of ion-pairs, and if it is assumed that the transfer coefficient is the same for the reduction processes involving the two entities, one has, in a first approximation

$$i_A = nFC_T (1 - \varkappa) k_0 \exp [- \alpha f (E - \psi_\delta)] \cdot \exp [- z_A f \psi_\delta] \qquad (9)$$

$$i_{AMe} = nFC_T \varkappa k'_0 \exp [- \alpha f (E - \psi_\delta)] \cdot \exp [z_A + z_{Me}) f \psi_\delta] \qquad (10)$$

Writing $k'_0 = \beta k_0$, the total current is given by

$$i_T = i_A + i_{AMe} = nFC_T k_0 \cdot \exp [- \alpha f (E - \psi_\delta)] \cdot \exp [- Z_A f \psi_\delta]$$
$$[(1 - \varkappa) + \beta \varkappa \cdot \exp (- z_{Me} f \psi_\delta)] \qquad (11)$$

It follows that a plot of $i_T/nFC_T k_0 \exp [- \alpha f (E - \psi_\delta)] \exp [- z_A f \psi_\delta]$ *versus* $\exp (- z_{Me} f \psi_\delta)$ should yield a straight line with slope $\beta \varkappa$ and intercept on the ordinate $(1 - \varkappa)$.

These predictions are fairly well obeyed for the systems wich have been submitted to the test. As an example, for the trichloroacetate ion in caesium solutions, the association constant has been found to be 1.1 and 0.9 respectively for 0.1 and 1 N Cs^+ solutions. It should be noted however that agreement is poorer by 40% in the case of the tetrathionate ion.

2) From ψ'_δ, it is possible to calculate the corresponding *charge density of the diffuse part of the double layer.* By substracting it from the charge
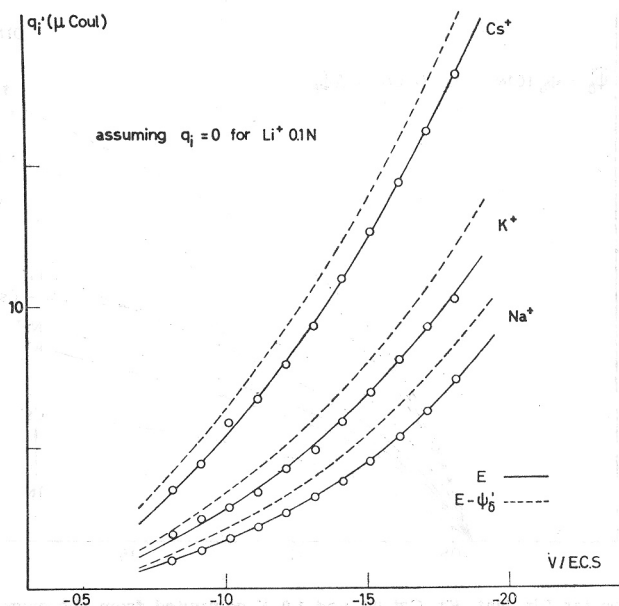
Fig. 6b. Corresponding values for the amount of specific adsorption (q_1 being assumed to be zero for Li^+ 0.1 N)

density of the electrode, the *amount of specific adsorption* q_i' may be evaluated (Fig. 6b), and the relevant *isotherms* may be constructed. It is only for Cs^+ that scanty related electrocapillarity data are available[27]. These data are not too conflicting.*

Plots of the amount of specific adsorption versus the total charge on mercury (Fig. 7) reveal that the isotherm curves for Na^+, K^+, and Cs^+ are
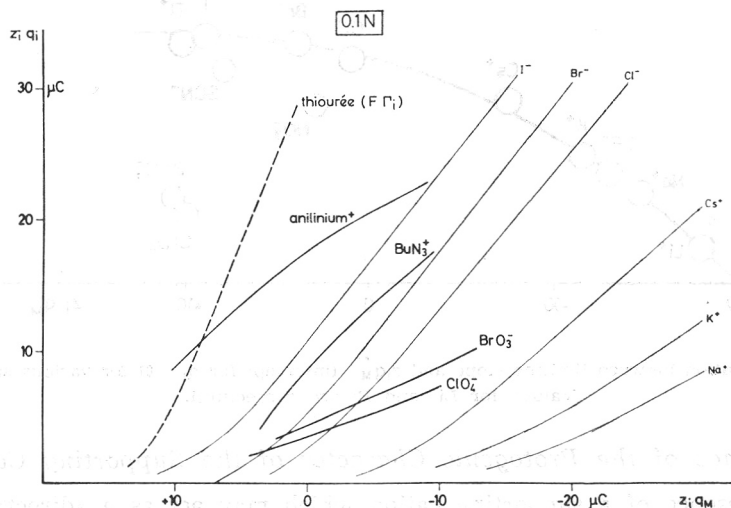

Fig. 7. Adsorption isotherms for 0.1 N Na^+, K^+ and Cs^+ (expressed by $z_i q_i'$ *vs.* $z_i q_M$ plots), compared with corresponding data for other surfactants.

not qualitatively different from that observed with Cl^-, Br^- and I^- (in marked contrast with the adsorption of large organic cations and oxygenated anions like ClO_4^-).

The slope dq_i'/dq_M of the upper parts of the curves (which are approaching linearity) can be correlated to their extrapolated intersect q_M' for $q_i' = 0$ (Fig. 8). Again halides and alkali metal ions do not behave very differently. Taking furthermore into account that dq_i'/dq_M and q_M' may be correlated to the corresponding ionic polarisabilities (which are also available for F^- and Li^+), it is possible to assign *hypothetical* values for the adsorption parameters of these latter ions (dotted circles of Fig. 8). Direct thermodynamic confirmation of these conjectural values is difficult, in view of the very limited adsorbability which can be expected.

---

* A very recent thermodynamic study of the adsorption of Cs^+ — published after these lectures were given —, leads to superficial excesses which are in excellent agreement with our values[28] — an a posteriori indication that the assignment of the ψ δ values was reasonably done.
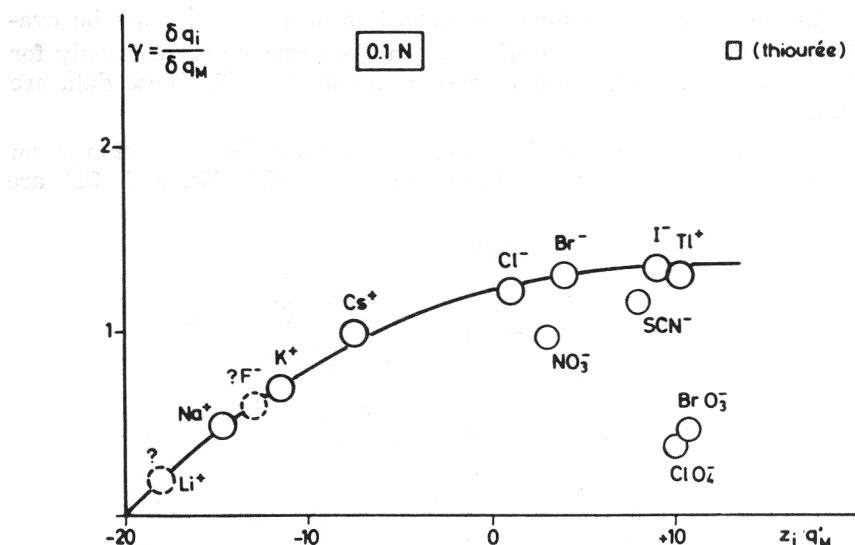
Fig. 8. Correlation between limiting slope and $z_1 q'_M$ (intercept for $q_i = 0$) for various surfactants.
Values for Li^+ and F^- are conjectural.

B. *Influence of the Protogenic Character of the Supporting Cation*

In presence of a supporting cation which may act as a »direct« proton donor (NH_4^+, $NH(CH_3)_3^+$ *etc.*), or which may act indirectly as such through the local hydrolysis of its own solvation water (Mg^{2+}, La^{3+}) it is observed that a number of electroreductions, which involve protons (or proton donors) in their stoichiometry, present markedly enhanced apparent rate constants, despite the fact that the conventional »bulk« or »average« pH is sufficiently high to render the reaction rate fully pH independent. A striking example of this phenomenon is afforded by the ammonium ion which, on the sole basis of its adsorbability (which is very close to that of the rubidium ion) should lead to the sequence $v_{K^+} < v_{NH_4^+} < v_{Cs^+}$ for any anion reduction. This is indeed very often the case, but for a number of anions, the apparent rate constants show positive deviations of variable amplitude (Fig. 9). It should be stressed that, within the same pH range (9—10), buffers other than NH_4^+/NH_3 give no detectable pH effect, as compared with sodium hydroxide solutions. (With the exception of the substituted ammonium ions still having at least one hydrogen left). That this effect is not specific to the ammonium ion is evident, since a similar behavior is displayed by cations with high peripheral field-strength, like Ca^{2+}, Mg^{2+} or La^{3+} (for the latter, it is known that the hydrolyzed form $LaOH^{2+}$ is still more active) (Figs. 10 and 11).

Experiments in which an additional inactive cation is added in order to gain information about the charge of the electroactive entity typically
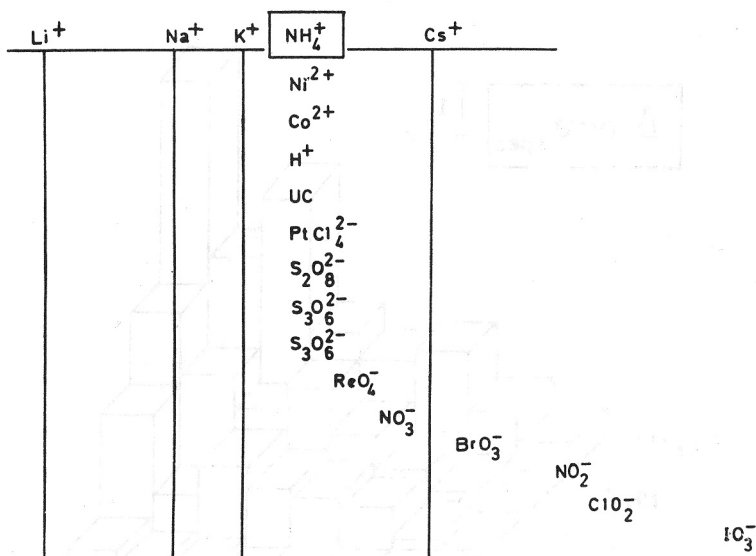
Li$^+$ Na$^+$ K$^+$ NH$_4^+$ Cs$^+$

Ni^{2+}

Co^{2+}

H$^+$

UC

PtCl$_4^{2-}$

S$_2$O$_8^{2-}$

S$_3$O$_6^{2-}$

S$_3$O$_6^{2-}$

ReO$_4^-$

NO$_3^-$

BrO$_3^-$

NO$_2^-$

ClO$_2^-$

IO$_3^-$

Fig. 9. Position of $v_{NH_4^+}$ in the sequence Li$^+$ Na$^+$ K$^+$ Cs$^+$, for various depolarizers.
(UC = uranyltricarbonate)

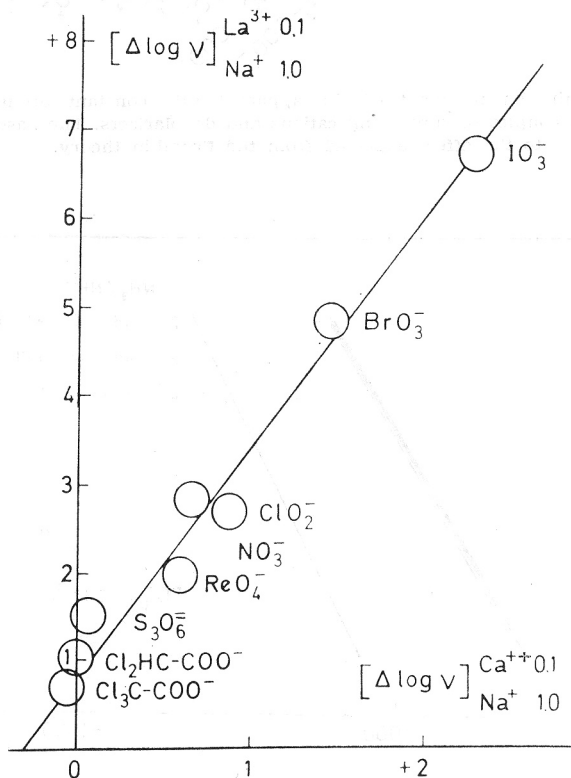$$\left[\Delta \log V\right]_{Na^+ \; 1.0}^{La^{3+} \; 0.1}$$

+8

7

6   IO$_3^-$

5   BrO$_3^-$

4

3   ClO$_2^-$

2   NO$_3^-$

ReO$_4^-$

S$_3$O$_6^=$

1   Cl$_2$HC-COO$^-$

Cl$_3$C-COO$^-$

$$\left[\Delta \log V\right]_{Na^+ \; 1.0}^{Ca^{++} \; 0.1}$$

0   1   +2

Fig. 10. Correlation between the enhancement of the apparent rate constants for various
depolarizers, brought by Ca^{2+} and La^{3+}.
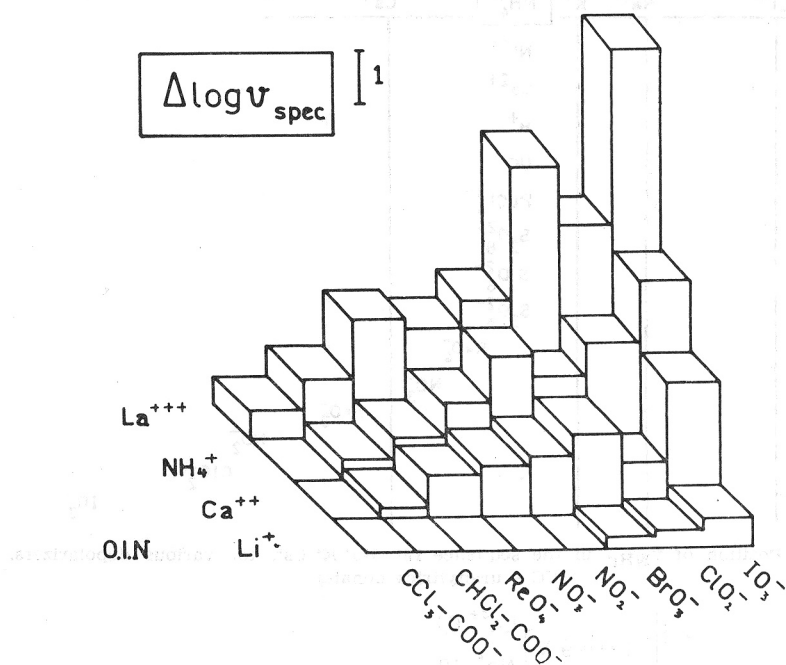
Fig. 11. Extent of the enhancement of the apparent rate constant brought by protogenic catalysis, for various couples of supporting cations and depolarizers. The base plane correspond to the effect expected from the Frumkin theory.
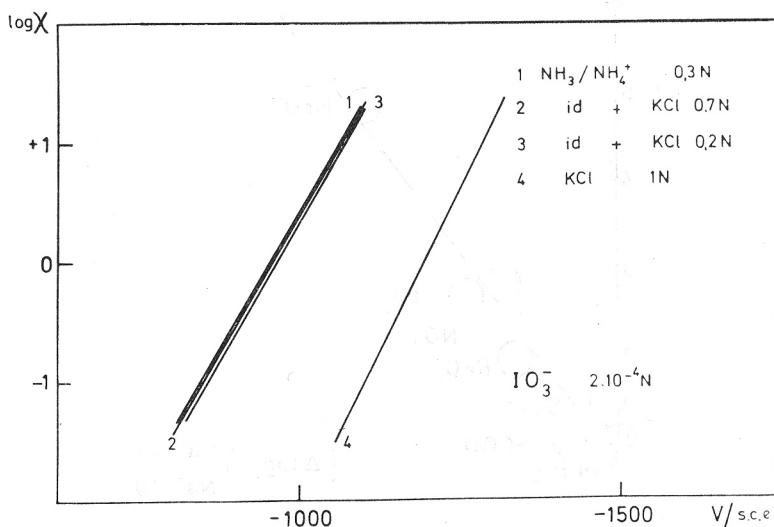
Fig. 12. Influence of the increase of the cationic strength (by addition of K⁺) on the Tafel plot for the reduction of iodate in presence of ammonium ions.
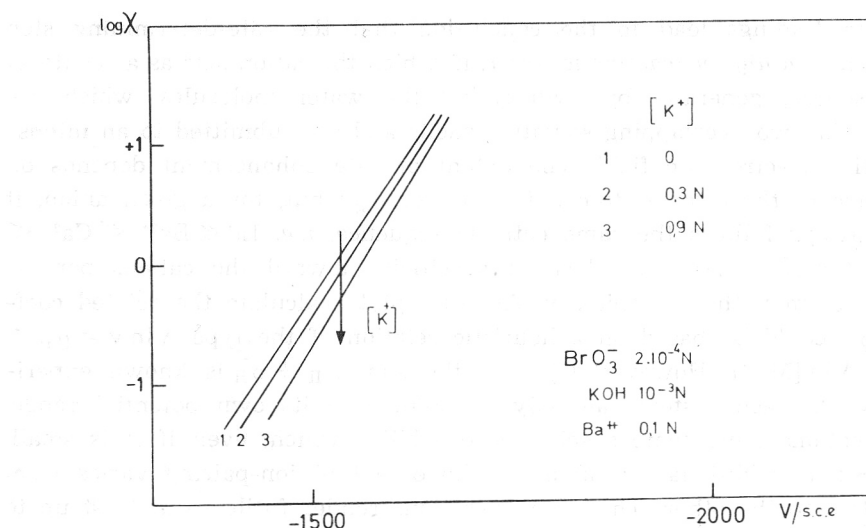
Fig. 13. Influence of the increase of the cationic strength (by addition of K⁺) on the Tafel plot for the reduction of bromate in presence of barium ions.

indicate that $z = 0$ in the case of ammonium acting on a mononegative anion (Fig. 12), and that $z \simeq +1$ when the protogenic cation is divalent (Fig. 13). Furthermore, when using mixtures of two monovalent cations of same ϱ_A^+ but different ϱ_H^+ at constant cationic strength, the rate constant is found to be first order with respect to the concentration of the protogenic cation (Fig. 14).
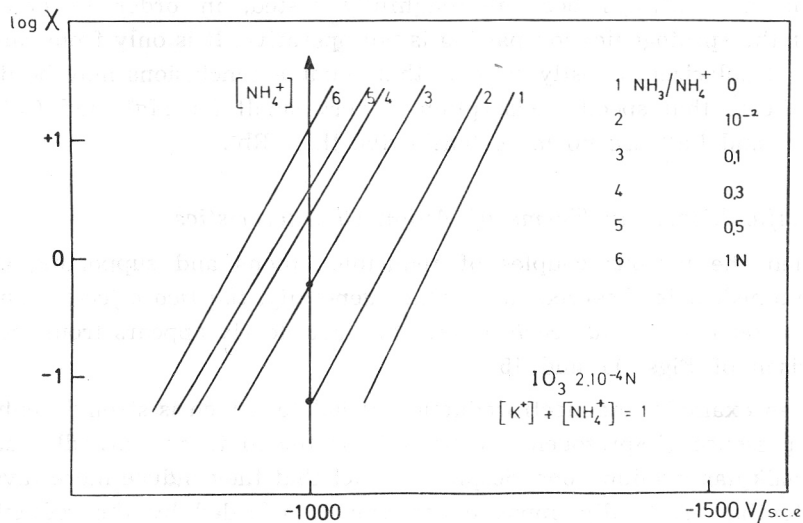
Fig. 14. Influence of the ammonium concentration on the Tafel plot for the reduction of iodate, at constant cationic strength.

These findings lead to the conclusion that the rate-determining step involves now *a highly reactive ion-pair,* in which the cation acts as a »contact« proton source, generally by hydrolyzing the water molecules, which are bridging the two overlapping solvation shells and are submitted to an intense dissociative electrostatic field. The extent of rate enhancement depends on *the nature of the electroactive anion,* (factor $\varrho_{\overline{H}}$) but, for a given anion, it nearly always follows the same cationic sequence, *i. e.* $Li^+ \ll Ba^{2+} < Ca^2 < < Mg^{2+} \ll NH_4^+ \ll La^{3+}$. This lack of specificity toward the cations permits to grade them without ambiguity. An attempt to calculate the related coefficient ϱ_{H}^+ could be based on a heuristic relation of the type $\Delta \ln v = \varrho_{H}^+ + + \varrho_{\overline{H}} + \Delta \ln [Me^{z+}]$. However, (1) only the sum $\varrho_{H}^+ + \varrho_{\overline{H}}$ is known experimentally, (2) each system can only be studied in its own potential range, (3) the cations have some specific adsorbability which, even if it is small, introduces an additional variable, (4) the extent of ion-pairing varies from one system to the other. These considerations render futile — at least up to now — the assignment of definite values to ϱ_{H}^+ (also for want of any suitable theory expressing the rate constants in terms of an accurate microscopic model for the ion-pair in its discharge-step configuration).

The occurrence of the »protogenic« mechanism can even be detected with Li^+, if $\varrho_{\overline{H}}$ is sufficiently large (it is the case for the iodate ion and, to a lesser extent, for the chromate ion). As a result, it can be dangerous to use the lithium ion as a reference cation for ψ_δ values — despite the fact that it is probably the best of any cation, in terms of absence of specific adsorption. More generally, information about ψ_δ potentials derived from the Frumkin equation must always been thoroughfully tested, in order to determine whether the »protogenic« ion-pairing is not operative. It is only from carefully selected depolarizers (mostly cations) that reliable conclusions may be drawn: they indicate that specific adsorption is very small for Mg^{2+} and Ca^{2+}, and that Ba^{2+} and La^{3+} are no more tensiactive than Rb^+.

C. Specific Effects in Terms of Anion Characteristics

When the various couples of reducible anions and supporting cations are examined, it is observed that, rather generally, *the two effects previously described tend to exclude each other.* This fact clearly appears from the close comparison of Figs. 11 and 15.

As an example, the electroreduction of iodate, which is strongly enhanced by the presence of »protogenic« cations, is on the contrary markedly retarded by tetraalkylammonium ions, despite the fact that they induce more favorable ψ_δ potentials. A totally opposite behavior is afforded by the reduction of the trichloroacetate ion, which is hardly affected at all high-field cations but, conversely, is abnormally enhanced by large organic cations.
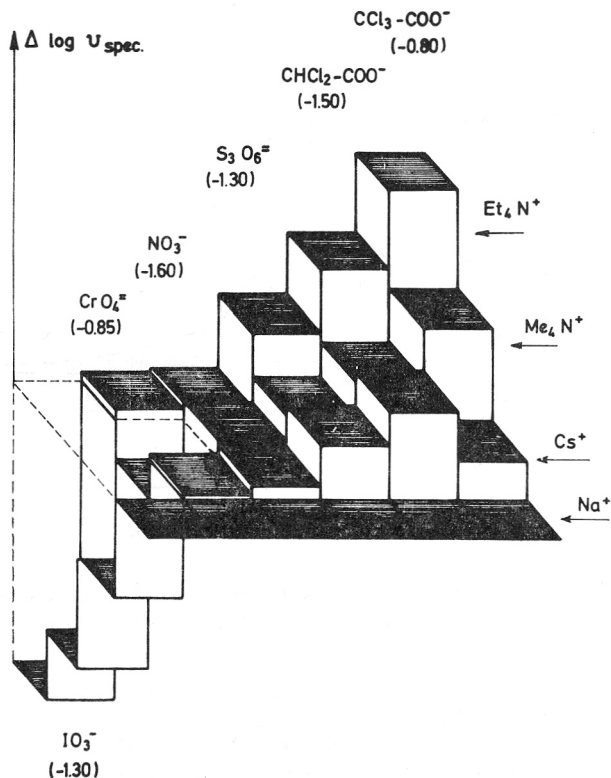
Fig. 15. Extent of variation of the apparent rate constant for various couples of supporting cations and depolarizers. The base plane correspond to the rate constants expected from the Frumkin theory. (iodate shows conspicious retardation in contrast with the enhancement observed for the other depolarizers).

GENERAL DISCUSSION

1. Before proposing a unified explanation for the various mechanisms which have been isolated, it is important to clarify first what are the essential factors which determine why a given behavior occurs or not, for a given composition. Under this respect, it is of interest to leave for a moment the field of electrode kinetics, and to reconsider the problem from a broader point of view, by examining the fundamental nature of attractive interactions between entities of opposite electronic charge.

1. a. The simplest case is that of *ion-ion interactions in aqueous solutions* (Fig. 16), for which it is now fully realized that there exist *two distinct types of situations*[29-32]: (a) the interaction between two ions developing both a high field strength, and for which the coupling arises essentially from charge-charge attraction and (b) the association between two bulky ions* (like

---

* The iodate ion presents a rather unique behavior: despite its large size, it acts very akin to the fluoride ion, as demonstrated by all known sequences (see Table II). This puzzling fact may be accounted for by recalling[33] that the $I = O$ bonding is weakened so much that the peripheral oxygen atoms are very labile and can be exchanged with water oxygen at a very high rate. The iodate ion is thus effectively a small ion, surrounded by highly structured solvent molecules.
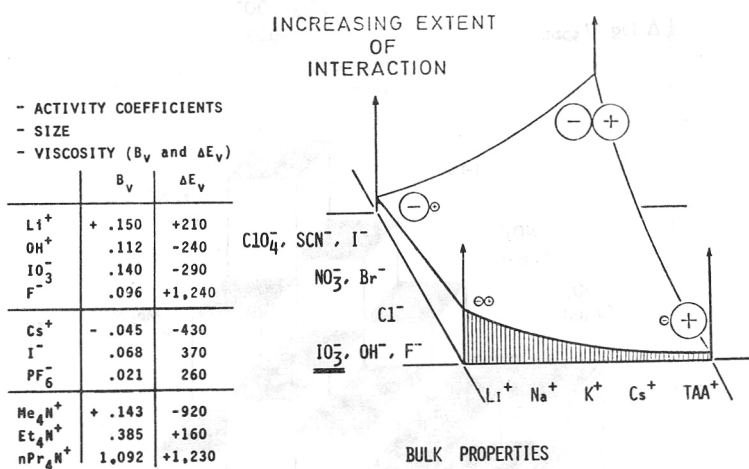
Fig. 16. Schematic diagram showing the extent of interaction between two ions of opposite sign, in function of their dimension.

ClO_4^- and NEt_4^+), which mostly results from the net decrease of the hydrophobic interactions with the solvent, which follows the shrinking of the total envelope area.

The existence of two distinct types of ion-ion interaction (which, for the sake of brevity, will be coined »charge-charge« and »cavity-cavity« pairings) supports the concept (originated by Gurney)[34], according to which attractive interaction between particles is observed when both exert the same type of structural action on their surrounding water molecules. As recently stressed (by Desnoyers et al.[35] in their paper about the influence of structural hydration interactions on the concentration dependence upon apparent molal volumes of alkali halides in water) the general rule which is at least implicitly assumed is that »two solutes will attract each other if their structural influences, or their tendencies to orient water molecules, are compatible with each other: conversely, an incompatibility in these structural influences or tendencies will result in repulsive forces«*.

1. b. A similar duality prevails when one of the two entities is no longer an ion but *an electrified interface* (excluding electrodes, which will be discussed in the next section) (Fig. 17). A recent striking example of this charge-charge interaction is afforded by colloidal rutile[38], which adsorbs preferentially high-field ions, more able than others to adjust their hydration shell to the highly-structured water molecules surrounding the particles. On the other hand, the increased affinity of a resin like Dowex 50 for large-sized cations,

---

* When relying on this rule to predict the extent of interaction in terms of »order-making« or »order-destroying« effects, as detected by individual ionic thermodynamic quantities like the B coefficients of viscosity, the heats of viscous flow, or the partial entropies, it should be emphasized that they are two distinct kinds of order-making processes: the first is the building of radial array of water molecules oriented by the ionic external field, the second is the stabilization of preexisting »flickering« clusters[36] (the »water structure enforcement« mechanism[37]) by large ions which are in fact *hydrophobic* by nature.
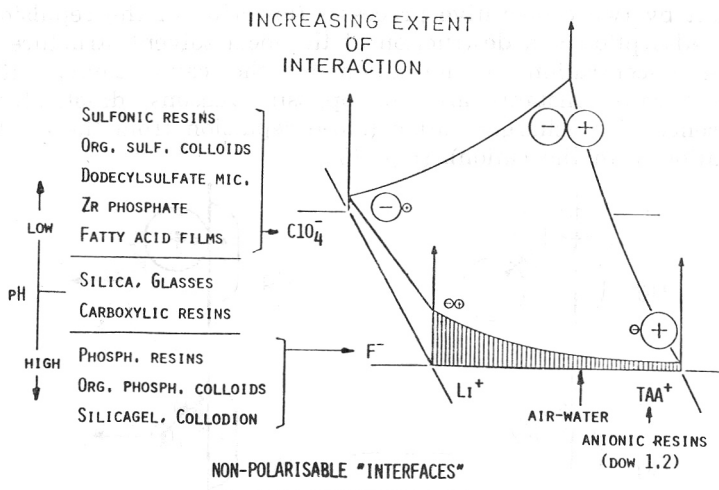
Fig. 17. Schematic diagram illustrating the extent of interaction between an ion and an interface of opposite charge.

and that of Dowex 2 for the corresponding anions are good examples of the »cavity-cavity« pairing, enhanced by the bulk water structure — which tends to squeeze both charged entities inside the same shared volume. The behavior of glasses depends on the pH[39].

1. c.   Information about *electrodes* is less abundant and remains mostly restricted to mercury (for which fortunately a very large amount of reliable quantitative data is available). Generally speaking, mercury acts as a »cavity« macro-ion, as reflected by the hydrophobic character of its surface, and, by the fact that it adsorbs selectively ions of the cavity-type like Cs^+, ClO_4^- ' NEt_4^+ etc. ... (neglecting here adsorptions which are induced by specific short range bonding forces). At very negative or positive charge densities, mercury can be expected to loose some of its »cavity« character, as it seems to appear from the lessenning of the adsorption increase for many hydrophobic ions (PF_6^-, ClO_4^-, tetraalkylammonium ions, among others).

When highly polar organic surfactants are adsorbed on mercury, their spontaneous tendency is to direct toward the metal their hydrophobic part while pointing the dipolar group (which is hydrophilic by virtue of its local field) on the solution side. In the particular case of surfactants related to pyridine and quinoline, compact films are easily built, with all the hydrated nitrogen groups facing the electrolyte solution[40]. This new surface presents now a »charge« character, and adsorbs Li^+ more than Cs^+, as demonstrated by the systematic reversal of the ψ sequence[41].

2. Most of the effects observed on »hydrated« mercury can be coherently explained on the basis of the Gurney concept by noting that:

(a) The extent of specific adsorption of cations on mercury parallels their »cavity« character.

(b) The electroreduction of »cavity« anions (like CCl_3—COO^-, perrhenate, tetrathionate, etc.) is abnormally sensitive to variations in the adsorbability of the supporting cation, simply because the latter enhances the apparent

rate constant by two cooperative processes (lowering of the repulsion barrier by specific adsorption and destruction of the local solvent structure — which favors over-concentration of the anion by the cavity-cavity interaction); the apparent rate constants are, for opposite reasons, drastically reduced in the presence of a »charge« cation (more repulsion from the electrode and less association with the cation). (Fig. 18.)
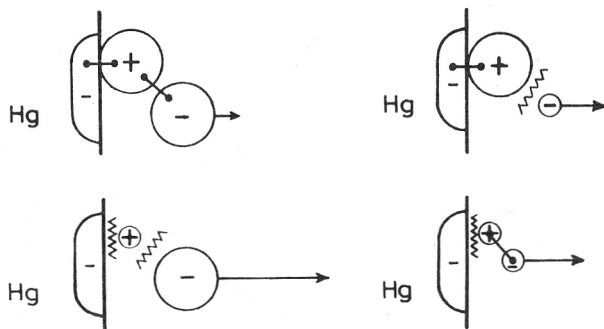

Fig. 18. Coupling of ψ_δ and pairing effects on the reduction of an anion on negatively charged mercury (the length of the arrow represents the extent of the total repulsion).

(c) on other hand, the reduction of »charge« anions (IO_3^-, ClO_2^-) is considerably less affected by the nature of the cation, since the ψ-effect and the extent of ion-pairing are now acting oppositely. This situation is of course drastically modified when the rate-determining step requires the participation of a protogenic cation.

3. The various aspects of the cation effect on anion reduction are schematically sketched in the diagram of Fig. 19. The horizontal square base
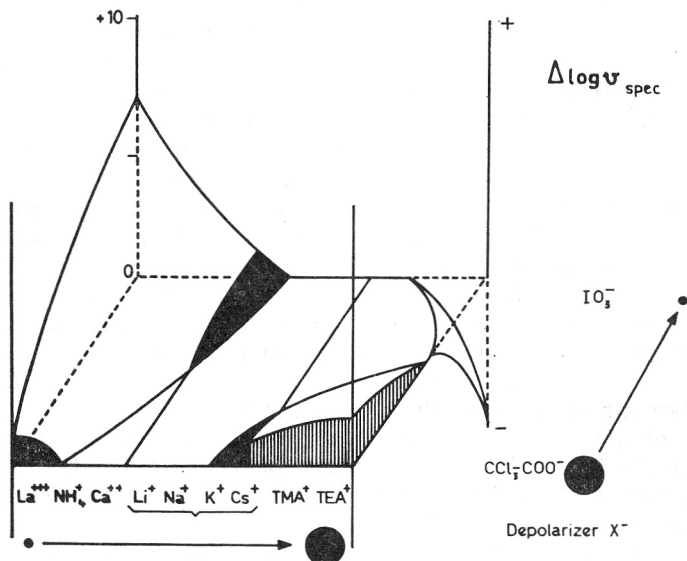

Fig. 19. Schematic diagram showing the extent of enhancement of the apparent rate constant (after correcting for the Frumkin contribution) for various pairs of depolarizers and supporting cations.

corresponds to the rate constants which should be observed if the kinetics would strictly obey the Frumkin theory. The two sloping regions correspond to enhancement of rate constants, respectively caused by »cavity-cavity« association (righ front corner) and by the »charge-charge« pairing, assisted by »protogenic« catalysis (left side). The similarity between this diagram and the preceeding ones shows conclusively that the mechanisms involved are basically the same in all cases.

CONCLUSION

The essential conclusion is that double layer effects on electrode kinetics can be satisfactorily explained by the Frumkin theory, *if suitable corrections take into account* (a) *the influence of the local ion-ion interactions and* (b) *the possible interference of protogenic catalysis.*

For *large-size anions,* it is in fact sufficient to measure one of the properties which are relevant to their »cavity« character (like the selectivity coefficient on an anion-exchange, see Table II), to be in a position of making reliable predictions about the way their reduction rate constants is actually affected by the double layer.

With respect to *anions which are affected by protogenic cations,* the question arises to know whether the enhancement in electro-activity could not also be promoted by using electrodes which are much more strongly hydrated, and which could accordingly play the role of the missing protogenic cation. Exploratory experiments indicate that the answer is positive[42]; the increase of the rate constants (referred to mercury) observed with platinum (which is strongly hydrated)[43] parallels that provoked by lanthanum ions adsorbed on mercury

$$IO_3^- > ClO_2^- > BrO_3^- > NO_2^- > NO_3^-$$

The problem of discriminating between direct discharge and »discharge-after-ion-pairing« appears to be reasonably settled in most of the cases. It should however be stressed that the ambiguity still subsists, when the cation does not display significant specific adsorption and does not induce protogenic catalysis. In that case, all the present information drawn from experiments using amalgams[2,44] or non-cationic surfactants (iodide, thiourea[45]) suggests that prior ion-pairing is not an important factor.

More fundamentally, the present work emphasizes the fact that the two divorced branches of Electrochemisty — which are respectively dealing with electrolyte solutions and electrodes — are much more interconnected that it can be supposed. After all, the diffuse part of the double layer is but a fraction of the solution, which is submitted by an externally — controlled electrostatic field not essentially different from the fields induced by its own ions — and very often much less intense.

Thanks are also due to my cardiologist, my psychiatrist, the entire staff of the University Hospital, and to my close relatives, for their attentive care, in these difficult days of a scientific life now condemned to be abridged very soon — perhaps for the sake of Mankind, by having permitted to avoid a second Sarajevo.

REFERENCES

1. A. N. F r u m k i n, *Trans. Faraday Soc.* **55** (1959) 156.
2. A. N. F r u m k i n, O. A. P e t r y, and N. V. N i k o l a e v a - F e d o r o v i c h, *Electrochim. Acta* **8** (1963) 177.
3. P. D e l a h a y, *Double-Layer and Electrode Kinetics,* Interscience, 1965.
4. L. G i e r s t, *Transactions of the Symposium on Electrode Processes,* Philadelphia 1959, p. 109 John Wiley & Sons, Inc., New York, 1961.
5. L. G i e r s t, L. V a n d e n b e r g h e n, E. N i c o l a s, and A. F r a b o n i, *J. Electrochem. Soc.* **113** (1966) 1025.
6. J. J. T o n d e u r, A. D o m b r e t, and L. G i e r s t, *J. Electroanal. Chem* **3** (1962) 225.
7. A. N. F r u m k i n and G. F l o r i a n o v i c h, *Doklady Akad. Nauk S. S. S. R.* **80** (1951) 907.
8. J. D a n d o y and L. G i e r s t, *J. Electroanal. Chem.* **2** (1961) 116.
9. L. G i e r s t and R. C o r n e l i s s e n, *Collection Czechoslov. Chem. Commun.* **25** (1960) 3004.
10. A. N. F r u m k i n, *Z. Phys. Chem.* **164 A** (1933) 121.
11. G. G o u y, *J. Phys.* (Paris) **9** (1910) 457; D. C h a p m a n, *Phil. Mag.* **25** (1913) 475.
12. C. A. B a r l o w and J. R. M c D o n a l d, in *Advances in Electrochemistry and Electrochemical Eng.,* ed. P. Delahay, Vol. 6, Interscience, 1967.
13. H. D. H u r w i t z, *J. Chem. Phys.* **48** (1968) 1541; also *Theoretical Considerations of the Double Layer* in *Electrosorption* ed. E. Gileadi, Plenum, New York, 1967.
14. S. L e v i n e, J. M i n g i n s, and G. M. B e l l s, *J. Electroanal. Chem.* **13** (1967) 280.
15. A. N. F r u m k i n and B. B. D a m a s k i n, Chapt. 3 in *Modern Aspects of Electrochemistry* Vol. 3 ed. Bockris, Butterworths, London, 1964.
16. B. E. C o n w a y, *Theory and Principles of Electrode Processes,* Ronald Press Co., New York, 1965.
17. W. H. R e i n m u t h, *Transaction of the Symposium on Electrode Processes,* Philadelphia 1959, p. 143, John Wiley & Sons, Inc., New York, 1961.
18. D. C. G r a h a m e, *Chem. Rev.* **41** (1947) 441.
19. C. W. D a v i e s, *Ion Association,* Butterworths, London, 1962.
20. R. W e i n e r, *Z. Elektrochem.* **52** (1948) 234.
21. J. K o u t e c k y, *Collection Czechoslov. Chem. Commun.* **18** (1953) 597.
22. L. T y t g a t - V a n d e n b e r g h e n, *Doct. Thesis,* 1969, U. Libre de Bruxelles.
23. E. N i c o l a s, *Doct. Thesis,* 1969, U. Libre de Bruxelles.
24. J. J. T o n d e u r, *Doct. Thesis,* 1962, U. Libre de Bruxelles.
25. A. F r a b o n i, *Doct. Thesis,* 1970, U. Libre de Bruxelles.
26. L. G i e r s t and all. to appear in *J. Electroanal. Chem.*
27. H. W r o b l o v a, Z. K o v a c, and J. O' M B o c k r i s, *Trans. Faraday Soc.* **61** (1965) 1523.
28. R. P a r s o n s and A. S t o c k t o n, *J. Electroanal. Chem.* **25** (1970) app. 10—12.
29. R. A. R o b i n s o n and R. H. S t o k e s, *Electrolyte Solutions,* Butterworths, London, 1959.
30. R. H. S t o k e s and R. A. R o b i n s o n, *J. Am. Chem. Soc.* **70** (1948) 1870.
31. S. L i n d e n b a u m, *J. Phys. Chem.* **72** (1968) 212.
32. H. S. F r a n k and R. L. R o b i n s o n, *J. Chem. Phys.* **8** (1940) 833.
33. E. N i g h t i n g a l e, *J. Phys. Chem.* **64** (1960) 162.
34. R. W. G u r n e y, *Ionic Processes in Solution,* Dover Publ., 1953.
35. J. E. D e s n o y e r s, M. A r e l, G. P e r r o n, and C. J o l i c o e u r, *J. Phys. Chem.* **73** (1969) 3346.
36. G. N e m e t h y and H. A. S h e r a g a, *J. Chem. Phys.* **36** (1962) 3382.
37. R. M. D i a m o n d, *J. Phys. Chem.* **67** (1963) 2513.
38. Y. G. B é r u b é and P. L. D e B r u y n, *J. Colloid. Sci.* **28** (1968) 92.
39. G. E i s e n m a n, *Ann. N.Y. Acad. Sciences* **148** (1968) 5.

40. L. Gierst and P. Herman, Z. Anal. Chem. 216 (1966) 238.
41. J. M. Chauvier, Mémoire de Licence, 1967, Université Libre de Bruxelles.
42. G. Quarin, Doct. Thesis (in prep.) Université Libre de Bruxelles.
43. J. W. Schultze, Ber. Bunsenges. Physik Chem. 73 (1969) 483.
44. M. L. Kervajan, Doct. Thesis (in prep.) U. of Paris.
45. N. Meurée, Doct. Thesis (in prep.) U. Libre de Bruxelles.
46. A. N. Frumkin, S. Reichstein, and R. Kulvarskaya, Kolloid. Z. 40 (1929) 9.
47. R. Kunin, Ion Exchange Resins, p. 62. J. Wiley & Sons, Inc., New York, 1963.
48. L. Gierst, J. Tondeur, and E. Nicolas, J. Electroanal. Chem. 10 (1965) 397.
49. R. Bock and G. M. Beilstein, Z. Anal. Chem. 44 (1963) 192.
50. R. Bock and J. Jainz, Fresenius Z. Anal. Chem 198 (1963) 315.
51. P. Gerard, Mémoire de Licence, 1969, U. Libre de Bruxelles.

IZVOD

Proučavanja dvosloja upotrebom depolarizatora — novi pogledi

L. Gierst, E. Nicolas i L. Tytgat Vandenberghen

Utjecaj strukture elektrokemijskog dvosloja na kinetiku elektrokemijskih re-akcija proučavan je upotrebom većeg broja različitih depolarizatora kao i kationa osnovnog elektrolita. Analizom rezultata vlastitih radova kao i podataka iz literature dolazi se do zaključka, da je, osim Frumkinovog mehanizma, stvaranje ionskih parova značajan faktor. Efekti opažani u kinetici elektrokemijskih reakcija usko su povezani s faktorima koji uvjetuju asocijacione pojave u elektrolitima, koagulaciju koloida, te izmjenu iona na ionskim izmjenjivačima. U nekim slučajevima hidra-tiziranih elektroda (prvenstveno platina, ali i živa u slučajevima specifične adsorp-cije) kao značajan efekt pojavljuje se i protogena kataliza. Živu u elektrodi možemo smatrati makro-ionom »šupljinskog« tipa, a rezultati mnogih istraživanja pokazuju, da je elektroredukcija »šupljinskih« iona (na pr. CCl_3—COO^-, perrenat, tetrationat) abnormalno osjetljiva na promjene adsorbabiliteta kationa osnovnog elektrolita. Na drugu ruku redukcija aniona »stvaraoca naboja« (JO_3^-, ClO_2^-) manje ovisi o vrsti kationa osnovnog elektrolita, zato što se efekti ψ-potencijala i stvaranja ionskih parova međusobno poništavaju.

FACULTÉ DES SCIENCES
UNIVERSITÉ LIBRE DE BRUXELLES
BRUXELLES, BELGIQUE