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Additivity of the *Hammett* Reaction Constants Ion Pairs Effect in the Polarographic Reduction of Nitrobenzene and 9,10-Anthraquinone Derivatives

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An attempt has been made to estimate the effect of the subsequent ion pairs formation on the value of the *Hammett* reaction constant measured polarographically. To this purpose, the reduction of *para*-substituted nitrobenzenes and 2-substituted 9,10-anthraquinones was studied at a dropping mercury electrode in N,N-dimethylformamide. The ion pairs reaction constant of substituted nitrobenzene radical anions with tetraethylammonium cations is equal to $-1.49\,V/\sigma$ unit. The corresponding reaction constant for the semiquinone—Li^+ series was estimated to be $-0.90\,V/\sigma$ unit. The method of calculation was based on the additivity rule within *Hammett's* treatment.

(Keywords: Hammett's reaction constant; Additivity rule; 9,10-Anthraquinone; Nitrobenzene; Polarography; Ion pairs formation)

Zur Additivität der Hammet'schen Reaktionskonstanten. Paar-Effekte bei der polarographischen Reduktion von Nitrobenzol und 9,10-Anthrachinonderivaten

Es wurde eine Abschätzung des Effekts der nachfolgenden Ionenpaarbildung auf den polarographisch bestimmten Wert der *Hammet'*schen Reaktionskonstanten versucht. Dazu wurde die Reduktion von *para*-substituierten Nitrobenzolen und 2-substituierten 9,10-Anthrachinonen an der tropfenden Quecksilberelektrode in N,N-Dimethylformamid untersucht. Die Ionenpaar-Reaktionskonstanten von substituierten Nitrobenzol-Radikalanionen mit Tetraethylammoniumkationen ist gleich $-1.49\,V/\sigma$-Einheiten. Die entsprechende Reaktionskonstante für die Semichinon-Li^+ Serie wurde mit $-0.9\,V/\sigma$-Einheiten abgeschätzt. Die Berechnungsmethode basiert auf der Additivitätsregel der *Hammet'*schen Reaktionskonstanten.

Introduction

In organic chemistry a number of empirical models has been emerged for describing relations between structure and reactivity. The most

intensively studied are those based on linear free energy relationships [1, 2] with the *Hammett* equation as the most prominent example. First attempts to correlate polarographic data with substituent constants σ were published in the early fifties, and then growing interest in electrochemical properties of organic substances led to numerous results which have been reviewed by *Zuman* [3, 4].

Generally, for reversible and irreversible electrochemical processes the change of the half-wave potential with respect to the value for the unsubstituted compound $(E_{1/2})_H$ to that of the *meta* or *para* substituted derivative $(E_{1/2})_X$ is given by

$$(E_{1/2})_X - (E_{1/2})_H = \rho\sigma \tag{1}$$

Obviously, Eqn. (1) may be applied when the half-wave potentials of the compounds are measured under exactly identical conditions and the mechanism of electrochemical reactions is identical for all depolarizers compared. The value of the reaction constant, ρ, proper for a given reaction series, depends usually on experimental conditions. The most important factors in non-aqueous electrochemistry are the properties of a solvent [5, 6] and the nature of supporting electrolyte. If the electroreduction is affected by sufficiently strong ion pairing interaction

$$R + e \rightleftharpoons R^{\cdot-} \qquad E^{\circ}_{1/2} \tag{2}$$

$$R^{\cdot-} + M^{+} \rightleftharpoons R^{\cdot-} \ldots M^{+} \qquad K_{as} \tag{3}$$

the overall reaction constant is described by an empirical formula [7]:

$$\rho' = \rho^{\circ} + (\mathrm{d}\mu/\mathrm{d}\sigma)\Phi \tag{4}$$

where ρ° stands for reaction constant of the process not influenced by ion association (Eqn. 2), μ is a constant parameter describing the sensitivity of a given radical anion $R^{\cdot-}$ toward ion pairs formation [8], whereas Φ denotes an ionic potential of the supporting electrolyte cation M^{+} (defined as the ratio of valency to the crystal radius).

Relation (4) should be considered as an example of the additivity rule within *Hammett*'s treatment: it may be proved that the term $\mathrm{d}\mu/\mathrm{d}\sigma$ is equivalent to the reaction constant of the association process (3) [9]. The purpose of the present investigations was to make a quantitative study on the possibility of separation of the *Hammett* reaction constants proper for the processes (2) and (3). The series of *para*-*X*-nitrobenzenes (*X* denotes —H, —Cl, —Br, —$COOCH_3$, —CN, —CH_3 and —OCH_3) and 2-*X*-9,10-anthraquinones [*X* stands for —H, —F, —Cl, —Br, —CH_3, —NH_2 and —$N(CH_3)_2$] were selected because their electrochemical properties in formally aprotic media are well known (for the mechanisms of electroreduction of nitrocompounds and quinones see reviewes [10] and [11], respectively). Our investigations were performed in N,N-dimethyl-

formamide (*DMF*) solutions; corresponding radical anions and ion pairs are stable under these conditions which facilitates discussion of the problem.

Experimental

Polarographic and cyclic voltammetric curves were registered with a Radelkis OH-105 apparatus (three electrode system). The working electrode was either a mercury drop electrode characterized by a drop time of 2.0 s (a drop timer was used throughout experiments) or a hanging mercury electrode [12] of 0.82 mm diameter. The counter electrode was constructed of cylindrical platinum gauze. An aqueous SCE was employed throughout all experiments and all potentials are referred to it. Electrical contact between the SCE and the solution investigated was made through the bridge with a *Luggin* capillary probe. The bridge solution was a solvent and electrolyte as in the polarographic vessel.

Commercial *DMF* was dried first with anhydrous K_2CO_3, later with CaH_2 and then stored over molecular sieves 4 Å type. The solvent was distilled at reduced pressure under argon atmosphere. Before each experiment the solvent was passed through a column of active alumina [13] (Woelm neutral, ICH Pharmaceuticals). Tetraethylammonium perchlorate was recrystallized from triply distilled water and dried *in vacuo* at 60 °C. $LiClO_4$ (AR-grade) was dried under argon atmosphere at 210 °C. Organic compounds were purified before use; their physicochemical characteristics were identical with literature values.

All solutions were deoxygenated with solvent presaturated dry argon. The concentrations of depolarizers and background electrolytes were 0.50 m*M* and 0.10 *M*, respectively. Experiments were run at 20 ± 0.1 °C.

Results and Discussion

Electrochemical behaviour of 9,10-anthraquinone and its derivatives was studied in the presence of two electrolytes: $(C_2H_5)_4NClO_4$ and $LiClO_4$, respectively. In the case of the nitrobenzene series only tetraethylammonium perchlorate was applied. Under these conditions all the compounds reduce at a dropping mercury electrode forming two cathodic waves (see also Refs. [10, 11] and corresponding references therein). The first waves, being an object of our interest, correspond to reversible one electron transfer. In all cases we have registered the cyclic voltammetric curves (scan rate 100 mV s^{-1}) with equal peak currents in the cathodic and anodic sweeps. The differences $E_{pa} - E_{pc}$ were 60 ± 3 mV; semilogarithmic analysis gives also $\Delta E/\Delta \log[i/(i_d - i)]$ values close to 60 mV/log unit. Measurements of the wave height as a function of depolarizer concentration (in the range 0.08 to 1.10 m*M*) and as a function of the square root of the mercury height indicated that limiting currents are controlled by diffusion.

The effect of supporting electrolyte concentration on the reduction processes was also examined. We have found that the half-wave potentials of all the members of the anthraquinone series are independent of the $(C_2H_5)_4NClO_4$ concentration, at least over the range 0.01 to 0.20 *M*. This

indicates that the waves are not affected by ion pairing phenomena. By contrast, addition of $LiClO_4$ shifts the half-wave potentials in a positive direction, showing ion pair formation (3) in the semiquinone-Li^+ systems. Let us add in this place that the equilibrium

$$(9,10\text{-anthraquinone})^{\overline{\cdot}} + Li^+ \rightleftharpoons (9,10\text{-anthraquinone})^{\overline{\cdot}} \ldots Li^+$$

in dimethylformamide solutions was quantitatively studied using the polarographic technique [14–16].

Table 1. *Substituent effects on the half-wave potential of the first reduction step of 9,10-anthraquinone in N,N-dimethylformamide solutions*

Substituent in 2 position	σ	$-E^{\circ}_{1/2}$ (V)[a]	$-E^{ipf}_{1/2}$ (V)[b]
$-NH_2$	−0.66	1.04	0.96
$-N(CH_3)_2$	−0.60	1.02	0.93
$-CH_3$	−0.17	0.92	0.89
—H	0.00	0.89	0.84
—F	0.06	0.86	0.80
—Cl	0.23	0.82	0.78
—Br	0.23	0.83	0.80

[a] Measured in the presence of 0.10 M $(C_2H_5)_4NClO_4$
[b] Determined in solutions containing 0.10 M $LiClO_4$ as background electrolyte

The situation is more complex for the cathodic reduction of nitrobenzene and its *p*-substituted derivatives: corresponding radical anions form ion pairs even with tetraethylammonium cations in *DMF* [17, 18]. Therefore the half-wave potentials measured in the presence of 0.1 M $(C_2H_5)_4NClO_4$ are now connected with electron transfer (2) and association processes (3). Let us note, however, that the ion pairs discussed in this paper are kinetically stable, i.e. they do not disappear under experimental conditions in any chemical reaction. Thus, it is clear that all $E_{1/2}$ values presented in Tables 1 and 2 may be considered as thermodynamic values.

These tables require some comments. First, for 2-substituted derivatives of 9,10-anthraquinone we have choosen the σ_{para} values as appropriate values of substituent constants, as it was anyway proposed in Ref. [19]. Second, the symbols $E^{\circ}_{1/2}$ and $E^{ipf}_{1/2}$ stand for the half-wave potentials in the absence and in the presence of ion pair formation, respectively. Thus, the half-wave potentials proper for members of the anthraquinone series in solutions containing $(C_2H_5)_4NClO_4$ can be directly used as $E^{\circ}_{1/2}$ values, whereas corresponding potentials determined in the presence of $LiClO_4$ can be treated as $E^{ipf}_{1/2}$ quantities.

In the case of *p*-substituted nitrobenzenes in *DMF* solutions containing 0.10 *M* tetraethylammonium perchlorate we have measured $E_{1/2}^{ipf}$ values, only. We are not able to determine corresponding $E_{1/2}^{\circ}$ values in direct experiments: even in the presence of tetra-*n*-hexylammonium iodide the half-wave potential of nitrobenzene was found to depend on the concentration of $(C_6H_{13})_4N^+$ ions. Consequently, we have calculated the $E_{1/2}^{\circ}$ potentials by studying the variation in half-wave potentials with solution compositions [20] as it was presented in Ref. [18].

Table 2. *Substituent effect on the half-wave potential of the first reduction step of nitrobenzene in N,N-dimethylformamide*

Substituent in *para* position	σ	$-E_{1/2}^{\circ}$ (V)[a]	$-E_{1/2}^{ipf}$ (V)[b]
—OCH_3	—0.27	1.39	1.27
—CH_3	—0.17	1.33	1.22
—H	0.00	1.18	1.10
—Cl	0.23	1.09	1.02
—Br	0.23	1.09	1.03
—$COOCH_3$	0.45	0.98	0.88
—CN	0.66	0.84	0.81

[a] Calculated by studying the variation in the half-wave potential with tetraethylammonium perchlorate concentration [18]
[b] Measured in the presence of 0.10 *M* $(C_2H_5)_4NClO_4$ as electrolyte

On the basis of the data tabulated in Tables 1 and 2 it is readily apparent that both $E_{1/2}^{\circ}$ and $E_{1/2}^{ipf}$ vary considerably with substituent constant σ. The potentials of the anthraquinone series display satisfactory correlations (Fig. 1) yielding

$$(E_{1/2}^{ipf})_X = 0.186\,\sigma - 0.833 \tag{5}$$

with a correlation coefficient of $r = 0.972$, and

$$(E_{1/2}^{\circ})_X = 0.238\,\sigma - 0.880 \tag{6}$$

with $r = 0.998$. Correlations are also observed for the nitrobenzene series (Fig. 2). Now we obtain

$$(E_{1/2}^{ipf})_X = 0.505\,\sigma - 1.130 \qquad r = 0.995 \tag{7}$$

and

$$(E_{1/2}^{\circ})_X = 0.591\,\sigma - 1.217 \qquad r = 0.995 \tag{8}$$

Thus, the change of supporting electrolyte influences the *Hammett* reaction constant, as it is anyway predicted by Eqn. (4). Let us analyse this finding in more details.

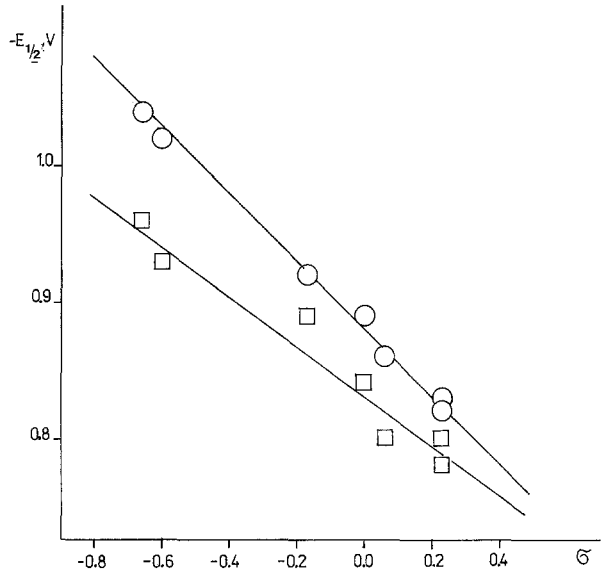

Fig. 1. Graph of the relationships of $E_{1/2}$ versus σ for the first reduction step of 2-substituted 9,10-anthraquinones in N,N-dimethylformamide. Supporting electrolytes: 0.10 M tetraethylammonium perchlorate (○) and 0.10 M lithium perchlorate (□), respectively

It is known [14] that $E_{1/2}^{ipf}$ potential determined for reversible one electron transfer affected by sufficiently strong ion pair formation (i.e. $K_{as}\, c_{M^+} \gg 1$) can be expressed by the rearranged *Nernst* equation

$$E_{1/2}^{ipf} = E_{1/2}^{\circ} + (RT/F) \times \ln(K_{as}\, c_{M^+}) \tag{9}$$

where c_{M^+} represents the concentration of supporting electrolyte cations (in our cases $c_{M^+} = 0.1\, M$, because both $(C_2H_5)_4NClO_4$ [21] as well as $LiClO_4$ [22] are not associated in *DMF* solutions). Thus, taking into account the substituent effect, the following expression can be written

$$(E_{1/2}^{ipf})_X - (E_{1/2}^{ipf})_H = (E_{1/2}^{\circ})_X - (E_{1/2}^{\circ})_H + \\ + (RT/F)\,[\ln(K_{as})_X - \ln(K_{as})_H] \tag{10}$$

But

$$(E_{1/2}^{ipf})_X - (E_{1/2}^{ipf})_H = \rho'\,\sigma \tag{11}$$

$$(E_{1/2}^{\circ})_X - (E_{1/2}^{\circ})_H = \rho^{\circ}\,\sigma \tag{12}$$

[cf. symbols used in Eqn. (4)] and, moreover, $\log K_{as}$ correlates linearly with σ [18] i.e.

$$\log(K_{as})_X - \log(K_{as})_H = \rho^{as}\,\sigma \tag{13}$$

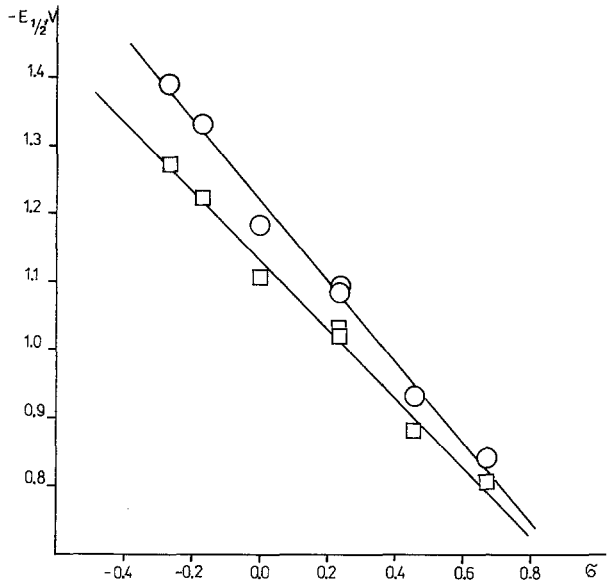

Fig. 2. Dependences of $E_{1/2}$ against σ for the first reduction step of *para* substituted nitrobenzenes in N,N-dimethylformamide. The points marked by □ correspond to the values determined in the presence of $0.10\,M$ tetraethylammonium perchlorate; the points signed by ○ have been calculated as reported in the text

Substituting (11), (12) and (13) into (10) one can obtain

$$\rho' = \rho^{\circ} + 0.058\,\rho^{as} \tag{14}$$

for the temperature 20 °C.

Relation (14) makes possible to calculate ρ^{as} values. Taking into account that for anthraquinone series $\rho' = 0.186$ V/σ unit and $\rho^{\circ} = 0.238$ V/σ unit [cf. Eqns. (5) and (6), respectively] we have obtained $\rho^{as} = -0.90$ V/σ unit. Since for substituted nitrobenzenes $\rho' = 0.505$ V/σ unit and $\rho^{\circ} = 0.591$ V/σ unit [Eqns. (7) and (8), respectively], the solution of equation (14) leads to the value of $\rho^{as} = -1.49$ V/σ unit.

Thus, for both the series under investigation ρ^{as} values are negative. This remark is fully comprehensible, because the ion pair formation (3) must be treated as an electrophilic process.

The results described above indicate that the additivity rule within the *Hammett* equation may yield valuable informations on the ion pairing reaction in organic electrochemistry. Let us add that these informations are rather difficult to obtain by other methods. There is, however, one question: does the method presented in this paper give *true* values of ρ^{as}? The answer is fully affirmative in the cases of strong ion pairing. For radical anions of nitrobenzene series in *DMF* $K_{as}\,c_{M^+} \gg 1$, and direct

correlation of $\log K_{as}$ against σ yields $\rho^{as} = -1.55\,\mathrm{V}/\sigma$ unit [18], i.e. the value comparable with the result obtained in this work. On the other hand, however, ρ^{as} estimated for the anthraquinone series can be treated as rough approximation only. The reason is obvious: for some radical anions of this series, particularly for those with substituents decreasing electron density at the position of functional group, the product $K_{as}\,c_{M^+}$ may be comparable to 1.

Finally, it should be pointed out that *Kargin* and *Ivanova* investigated earlier other aspects of the additivity rule within *Hammett*'s treatment in organic polarography. In the very interesting communication by these authors [23] an attempt was made to elucidate the effect of irreversible protonation on the *Hammett* reaction constant measured for substituted benzophenones in N,N-dimethylformamide.

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