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Author's review

Application of the LFER in Organic Electrochemistry: Interpretation of the Hammett Reaction Constant (ϱ) for Processes of Reversible Electroreduction in Aprotic Solvents

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The paper is an overview of the application of the concept of linear free energy relationships (LFER), most notably through the Hammett equation, to investigations of reversible organic electrochemical reactions in aprotic solvents. In sequence the following topics are covered: the effect of solvent properties on the equilibrium, ion pairing effects, the direct application of Hammett's equation on polarographic data, entropic and enthalpic contributions to substituent effects, and the quantum chemical interpretation of the reaction rate constant in aprotic media. The application of polarographic techniques is advocated as more sensitive and easier to interpret than the techniques of homogeneous kinetics.

In organic chemistry a number of empirical models for describing relations between structure and chemical and physico-chemical properties has emerged. The most successful and most intensively studied are those based on linear free energy relationships[1-3] (LFER), with the Hammett equation[4,5] as the most prominent example. Originally this equation was used only for the interpretation of substituent effects in chemical equilibrium and kinetics of meta- and para-substituted derivatives of benzene. In traditional form it reads

$$\lg K_x - \lg K_H = \varrho\,\sigma \tag{1}$$

where K_x and K_H stand for either equilibrium or rate constants for substituted and unsubstituted species, respectively. In the late'40 and later applications of eq (1) were extended to various physicochemical properties and to much more complex substituted systems than mentioned above[6].

Since Hammett's proposal, evidence has been accumulated demonstrating dependence of the reaction constant ϱ on solvents. This indicates the importance of environmental factors contributing to the transmission of substituent effects through the aromatic moiety; some of these factors will be discussed here.

In the past, several suggestions were made to elucidate the solvent influence on ϱ-values. Hammett himself[7] suggested the following approximate formulae where R is the gas constant, T is temperature, ε is the dielectric constant of the solvent and d is the distance from the substituent to the reaction site. B_1 and B_2 are constants, depending on purely electrostatic interactions between the reacting system and the medium, and susceptibility of the reaction to the changes in charge density at the reaction site, respectively. This relation has some validity but there are many exceptions[8]. Another approximate interpretation was given by Grunwald and Gutbezahl[9] who suggested a linear dependence of ϱ-values for the dissociation of aniline ions on the Y_o parameter of solvents[10]. Many other solvent parameters have subsequently been used in attempts to interpret the variation of reaction constant with solvent[11-16]. Evidently the reaction constant depends as well on a type of reaction: it is very interesting to note that electroreduction of substituted salicylaldehyde anils and electrooxidation of corresponding free radical anions in acetonitrile yields in considerably different ϱ-values[17].

Now let us consider applications of the Hammett equation in electroanalysis. First attempts at correlating polarographic data — as the most convenient experimental technique of measurements[18] — with substituent constants, σ, were published in the early 50-ties[19-23].

Then rapid development of the electroanalytical methods[18] and growing interest in electrochemical properties of organic substances led to numerous results, which then have been reviewed by Zuman[24] in the late'60-s. Initially electrochemical processes were studied in aqueous and in water-containing solutions, but to simplify the electrode reactions aprotic solvents began to be commonly used.

In general, the shift of the half wave potential, $\delta E_{1/2}$[25], with respect to the value of the unsubstituted compound, to that of the substituted molecule for a reversible system

$$\mathrm{Ox} + ne \underset{k_b}{\overset{k_f}{\rightleftarrows}} \mathrm{Red} \tag{3}$$

is given

$$\delta E_{1/2} = (E_{1/2})_x - (E_{1/2})_H = \frac{\Delta G_x^\circ - \Delta G_H^\circ}{nF} = \frac{\delta \Delta G^\circ}{nF} \tag{4}$$

(where F is the Faraday of charge).

In other words, the half-wave potential for this system is proportional to the logarithm of the equilibrium constant, $K = \frac{k_b}{k_f}$, of reaction (3).

For an irreversible system[18]

$$E_{1/2} = \frac{RT}{n_\alpha F} \ln 0.87\, k_f \sqrt{t_1 D^{-1}} \tag{5}$$

and, consequently,

$$\delta E_{1/2} = \frac{\Delta G_x^{\neq}}{\alpha_x (n_\alpha)_x F} - \frac{\Delta G_H^{\neq}}{\alpha_H (n_\alpha)_H F} \tag{6}$$

where t_1 is drop time, D is diffusion coefficient of depolarizer, α denotes transfer coefficient and n_α stands for the number of electrons transferred in the limiting potential step.

If $(n_\alpha)_X = (n_\alpha)_H$ and $\alpha_X = \alpha_H$ then:

$$\delta E_{1/2} = \Delta G^{\neq}_{X} - \Delta G^{\neq}_{H} = \delta \Delta G^{\neq} \tag{7}$$

Thus, the Hammett equation when applied to reversible as well as irreversible red-ox systems[26]

$$\delta E_{1/2} = \varrho \sigma \tag{8}$$

belongs to the family of LFER — equations[24]. The formal rate constant, k_f, involved in reaction (5) which is often looked upon as the rate constant of the surface heterogeneous process, may not be quantitatively completely equivalent to the rate constant of a homogeneous chemical reaction. It is impossible to predict theoretically whether the heterogeneous and homogeneous rate constants are affected by substituent in the same way. However thousands of reaction series fit eq. (8) well and hence support a conviction that heterogeneous rate constants in electrochemical reactions are influenced in a very similar way to the rate constant for homogeneous processes. Thus the half wave potentials can be treated as a measure of the reactivity of organic substances. For this reason electroanalytical techniques offer an important and powerful tool in extending our knowledge about reactivity of organic molecules.

The original Hammett equation has been modified and generalized by many workers[3,4]. An important step forward was made by Streitwieser[27] who extended it to polynuclear aromatic systems. Then this idea was associated with the Brown and Okamoto[28] substituent constants σ^+ and Eaborn's[29] rate constants for deteritriation of benzenoid hydrocarbons in trifluoroacetic acid leading to a new, more general, set of position constants[29,30]. This equation called the Hammett-Streitwieser equation has the same form as the original Hammett equation (1) with σ replaced by σ_r^+ : r denotes here a position in a polynuclear benzenoid hydrocarbon, whereas superscript + recalls connection of this scale of constants with the electrophilic reaction carried out to estimate them. By definition σ_r^+ describes the Brönsted basicity of position r of an aromatic hydrocarbon with benzene taken as reference. In principle the σ_r^+ scale is associated with localization energy[31], L_r^+, and the concept of generalized substituent[32,33]. The applicability of the Hammett-Streitwieser equation is very wide — as far as chemical and physicochemical properties of benzenoid hydrocarbons and their monosubstituted derivatives are concerned[30,34-37]. Due to the similarity of the basic ideas of the Hammett and the Hammett-Streitwieser equations, the interpretation of reaction constants is very similar to that described for Hammett's ϱ.

ELECTROREDUCTION OF ORGANIC COMPOUNDS IN APROTIC MEDIA

Electroreduction of organic compounds can be studied either in the absence of proton donors in formally aprotic solvents or in the presence of water or other Brönsted acids. Studies under these conditions offer some advantages both from the practical point of view (preparative electrosynthesis, electrochemical polymerization) and from certain theoretical aspects.

Most organic compounds in aprotic conditions are reduced electrochemically in two one-electron steps. The first step is, generally, not accompanied by a protonation antecedent or subsequent to the electron transfer. Therefore the half-wave potential of the first wave:

$$\mathrm{R}_{\mathrm{solv}} + \mathrm{e} \rightleftharpoons \mathrm{R}_{\mathrm{solv}}^{\cdot -}\,;\; E_{1/2}^{\circ} \tag{9}$$

is a direct measure of the difference between the standard free enthalpies of the parent molecule, R, and the radical anion formed (reagents in solvated form are marked by subscript solv). Radical anions, $\mathrm{R}^{\cdot -}$, and particularly dianions, R^{2-}, are strong Lewis bases which are even able to extract protons from residual water, or from other organic molecules, including the molecules of the compound that undergoes electroreduction. As a result, the overall processes involved in the second wave are frequently irreversible. Their investigation is rather difficult and successful in only a few cases[38] .For this reason the reaction

$$\mathrm{R}_{\mathrm{solv}}^{\cdot -} + \mathrm{e} \rightleftharpoons \mathrm{R}^{-2} \tag{10}$$

will not be considered here.

1. *The Effect of Solvent on Equilibrium (9)*

One of the major problems of organic electrochemistry is the description of the medium effect on the characteristics of electrochemical processes. From the theoretical viewpoint[40], the energetics of process (9) can be compared with the gas phase electron affinity, EA, of the depolarizer and with the difference in free solvation enthalpies of the reactant and the corresponding radical anion, $\Delta\Delta G^{0}_{\mathrm{solv}}$. The half -wave potential is given by

$$-FE_{1/2}^{\circ} = EA + (G_{\mathrm{el}}^{\circ})_{\mathrm{Hg}} + \Delta\,\Delta\, G^{0}_{\mathrm{solv}} \tag{11}$$

where $(G_{\mathrm{el}}^{\circ})_{\mathrm{Hg}}$ is the free enthalpy of the electron in an electrode. In practice it is not easy to estimate the real $\Delta\Delta G^{0}_{\mathrm{solv}}$ values, but the influence of solvent properties on redox potentials of organic compounds can be considered in terms of empirical equations based on LFER.

In general, the solvent effect on $\Delta\Delta G^{0}_{\mathrm{solv}}$ for charged species is composed of contributions due to non-specific electrostatic interactions, and specific interactions between solute and solvent treated as the Lewis acid and base. Thus, the Koppel and Palm[41] empirical equation in the following form can be used[42]:

$$\delta\, Q = \alpha\, A + \beta\, B + \gamma \frac{\varepsilon - 1}{2\,\varepsilon + 1} + \eta\, \frac{n^2 - 1}{n^2 + 2} + \mathrm{const} \tag{12}$$

where Q is the measured physicochemical property, whereas n stands for refractive index for a given solvent. However, most solvents applied in organic electrochemistry are those with large values of dielectric permittivity ($\varepsilon > 10$) and hence the non-specific contributions (dependent on $\frac{1}{\varepsilon}$ or $\frac{\varepsilon - 1}{2\varepsilon + 1}$) may be neglected[43]. In this case the application of the two-parameter equation describing solvent effect in terms of amphoteric Lewis acid-base properties of solvent[44,45] is particularly advantageous. This equation may be written in a general form as below

$$\delta\, E_{1/2} = \alpha\, \mathrm{A} + \beta\, \mathrm{B} + \mathrm{const} \tag{13}$$

where A and B stand for the Lewis acidity and basicity solvent parameters, respectively. For reaction series in which solute-solvent interactions are of one mechanism only (or predominantly) e. g. solutes chiefly interact as Lewis acids or bases, eq. (13) reduces to linear regression with solvent explanatory parameters B or A, respectively. Accordingly, the solvent effect on $E_{1/2}{}^0$ of one-electron, reversible electroreduction[46] values of quinones[48] and phenazines[49] (free radical anions are formed during electrochemical processes in solutions containing 0.1 M $(C_2H_5)_4NClO_4$) may be expressed by equation (14)

$$\delta E_{1/2}{}^{\circ} = \alpha\, AN + \text{const} \tag{14}$$

where AN is the acceptor number[50] i. e. the solvent parameter describing its Lewis acidity, while α defines the sensitivity of reaction (9) to the solvation effect.

Interpretation of eq. (14) is very simple based on the donor-acceptor concept for solvent-solute interaction[51]. Accordingly, the stronger a solvent as a Lewis acid, the stronger is the solvation of the radical anion, and hence, $E_{1/2}{}^0$ is shifted towards a more positive potential. It should be pointed out that similar linear correlations between the logarithm of standard rate constants of reversible electroreduction of *p*-dicyanobenzene and anthracene and AN were also obtained in a recent study[52].

Another situation arises in the case of electrooxidation of phenothiazine (PHN). As shown in ref.[49], the formal potential of the $PHN^{+\cdot}/PHN$ system measured voltammetrically in 9 solvents containing 0.1 M $NaClO_4$ is linearly dependent on solvent basicity, expressed by Gutmann's donor number[53], DN. In this case eq. (15) is fulfilled.

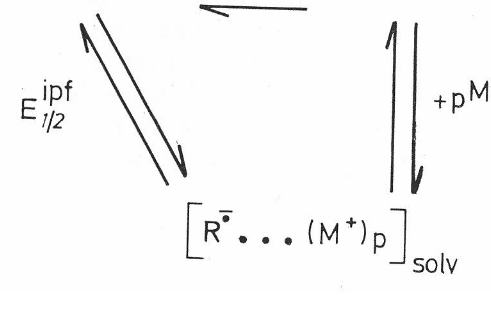
$$\delta E_{1/2}{}^{\circ} = \beta\, DN + \text{const} \tag{15}$$

Obviously, the reason is that the oxidized form (free radical cation, which is a Lewis acid) is much more strongly affected by interactions with solvent molecules than its parent molecule.

From a general point of view it should be noted here that in some redox systems the solvent has to be treated as a Lewis amphoteric species[42]. Such a situation has been described and discussed in the electrochemistry of parafuchsine[54], dibiphenylene-ethene[55] and diphenylpicrylhydrazyl[56]; in all these cases eq. (13) was successfully used to interpret experimental results.

2. *Ion Pair Effects*

In many cases reaction (9) is more complex and the electron transfer process is accompanied by ion association and should be described by a general scheme for the first step of polarographic reduction as (16)



(16)

where $E_{1/2}{}^{0}$ and $E_{1/2}^{\mathrm{ipf}}$ stand for half-wave potentials describing reversible reduction without ion pairing and followed by it, respectively, while M^+ denotes the cation of the supporting electrolyte. For reaction scheme (16) a modified Nernst formula may be written which describes a potential shift due to ion pairing processes:

$$\delta E_{1/2}^{\mathrm{ipf}} = E_{1/2}^{\mathrm{ipf}} - E_{1/2}^{0} = \frac{RT}{F}\ln\{1 + K_{\mathrm{as}}[\mathrm{M}^+] + K_{\mathrm{as}}{}^{\mathrm{T}}[\mathrm{M}^+]^2 + \dots\} \qquad (17)$$

where

$$K_{\mathrm{as}} = \frac{[\mathrm{R}^{\div}\dots\mathrm{M}^+]}{[\mathrm{R}^{\div}][\mathrm{M}^+]} \qquad (18)$$

and

$$K_{\mathrm{as}}{}^{\mathrm{T}} = \frac{[\mathrm{R}^{\div}][\mathrm{M}^+]^2}{[\mathrm{R}^{\div}\dots(\mathrm{M}^+)_2]} \qquad (18a)$$

If triple ions $\mathrm{R}^{\div}\dots(\mathrm{M}^+)_2$ are not formed and $\mathrm{K}_{\mathrm{as}}[\mathrm{M}^+] \gg 1$ eq. (17) is reduced to the form[57]

$$\delta E_{1/2}^{\mathrm{ipf}} = \frac{RT}{F}\ln\{K_{\mathrm{as}}[\mathrm{M}^+]\} \qquad (19)$$

If small amounts of water are present in aprotic solvents used in experiments, reaction scheme (16) may be still more complex. Even if the process remains reversible it is necessary to take into account the formation of separated ion pairs like e. g. $(\mathrm{R}^{\div}/\mathrm{H_2O}/\mathrm{M}^+)$[58]. These effects are, however, subtle and in most cases do not affect too much the observed $E_{1/2}$ — values. For another stoichiometry of ion association intervening in reaction (16) see ref.[59]

In the early paper of Holleck and Becher[60] the relation between $E_{1/1}^{\mathrm{ipf}}$ for a fixed depolarizer and the nature of the cations M^+ in a given solvent was observed. This reaction has subsequently been described quantitatively by the expression[61]

$$\delta E_{1/2}^{\mathrm{ipf}} - E_{1/2}^{\mathrm{ipf}} = E_{0}^{1/2} = \mu\,\Phi \qquad (20)$$

where μ is a regression coefficient (slope) while Φ stands for the ionic potential of the cation[62], defined as charge of the cation divided by its radius. When the experimental cation radius r is replaced by its corrected value $(r + x)$ following the Latimer, Pitzer and Slansky[63] modification of the Born theory of ion solvation, the fit of eq. (20) becomes considerably better[64]. This allows ns to conclude that a decisive factor in the medium effect described by eq. (20) is the solvation of the cation. The stronger Lewis acid it is (the higher its ionic potential) the greater is the free energy of solvation and the less favorable is the association between cations and radical anions[64]. On the other hand it is clear that eq. (20) belongs to the wide family of LFER equations: it relates changes in free energy of ion pairing, estimated by $\delta E_{1/2}^{\mathrm{ipf}}$ and the free energy of solvation of cations described by the Born-type approach (Φ — value). The value of the correlation term, x, can be approximately estimated by the empirical relation (21)[65]

$$(\mathrm{DN} - 9.7)\,(\mathrm{x} - 0.62) = 0.84 \qquad (21)$$

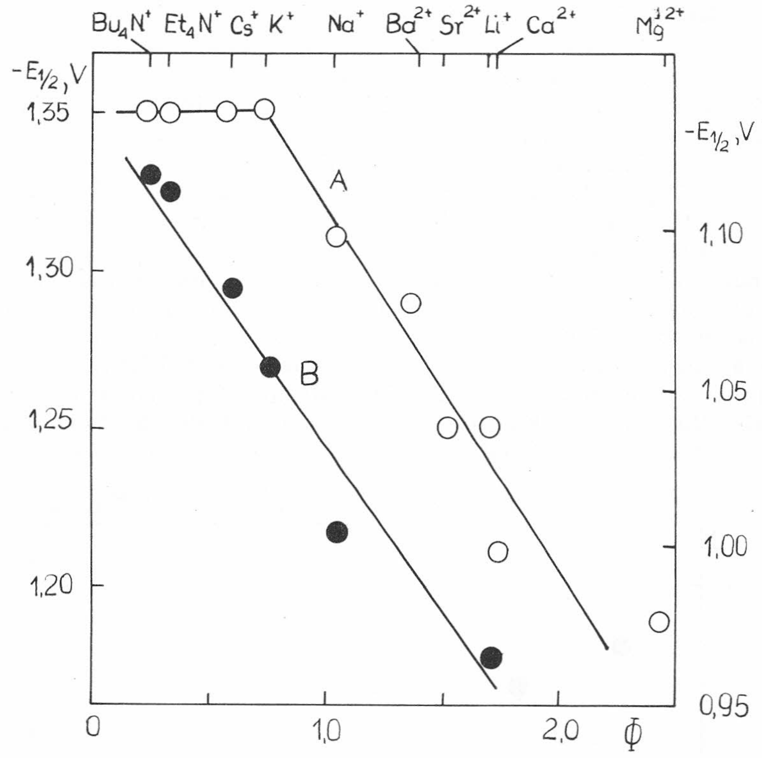


Figure 1. Variation in half-wave potential of 1 mM fluorenone (A) and 1 mM nitrobenzene (B) with ionic potential Φ of the supporting electrolyte cations in*N*,*N*-dimemethylformamide. Concentrations of electrolytes were 0.1 M and 0.05 M for the perchlorates of monovalent and divalent cations, respectively. A refers to the left, B — to the right-hand potential scale. Figure taken from ref. 61.

Figure 1. shows applications of eq. (20) to the first electroreduction step of nitrobenzene and fluorenone in *N*,*N*-dimethylformamide. As it can be seen, the half-wave potential of nitrobenzene, determined at constant metal ion concentration, is a linear function of Φ, which indicates that a nitrobenzene radical anion undergoes an ion pairing process even with tetraalkylammonium cations. Experiments with fluorenone give a plot with two linear sections. The first horizontal section (Φ smaller than 1) corresponds to the formation of free radical anions which do not form ion pairs with such large cations. For smaller counter ions a descending branch is observed, i. e. eq. (20) is followed.

Another factor influencing $E^{\text{ipf}}_{1/2}$ — values is directly due to solvent effects. In sufficiently polar solvents containing a given kind of cation, the medium effect on reversible electroreduction may be expected expressed by the empirical equation[66] (Figure 2).

$$\delta E^{\text{ipf}}_{1/2} = \beta \, \text{DN} + \text{const} \tag{22}$$

This relation shows that the stronger the solvent is a Lewis base, the stronger are the cation — solvent interactions and hence, the weaker the ion-pair formation. As a consequence, $\delta E^{\mathrm{ipf}}_{1/2}$ decreases and K_{ass} values calculated by use of eq. (17) diminish with and increasing value of DN[67]. Such formalism is correct because the free enthalpy of counter ion solvation is much more negative than that for the radical anion.

Obivously eqns (20) and (22) belong to the family of LFER equations. Regression coefficients in these equations, μ and β, are mutually interrelated with DN and Φ, respectively[66,68]. The higher the value of ionic potential, the lower (more negative) is the β-value. This simply means that in processes of electroreduction (16) the stronger Lewis acidic is the counter-cation the greater is the sensitivity of the solvent effect expressed here by β. In a similar way an increase of Lewis basicity of the solvent (DN) causes a decrease in sensitivity of reaction (16) to the ion-pairing effect. These interpretations are clearly illustrated by Figures 2 and 3. It should also be noted that in the case of electroreduction of substituted nitrobenzenes, μ correlates satisfacto-

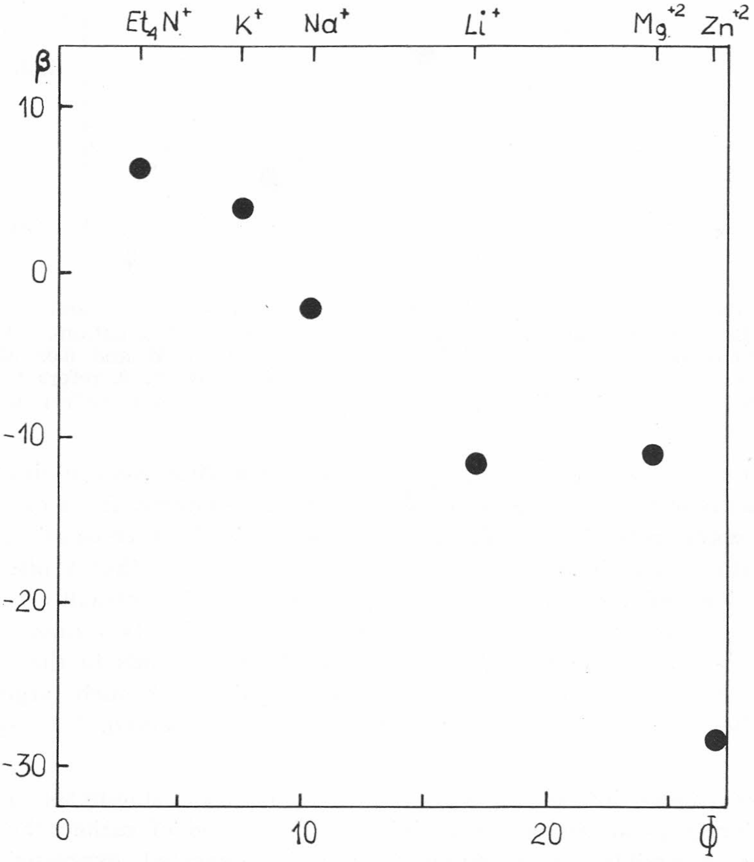


Figure 2. Plot of β-values (in mV/DN-unit) vs ionic potential Φ. Concentration of metal ions: 5 mM for K^+, Na^+ and Li^+ and 1 mM for Mg^{2+} and Zn^{2+}; original solutions 0.5 mM 1,2-naphthoquinone in 0.5 mM tetraethylammonium perchlorate. Figure taken from ref. 66.

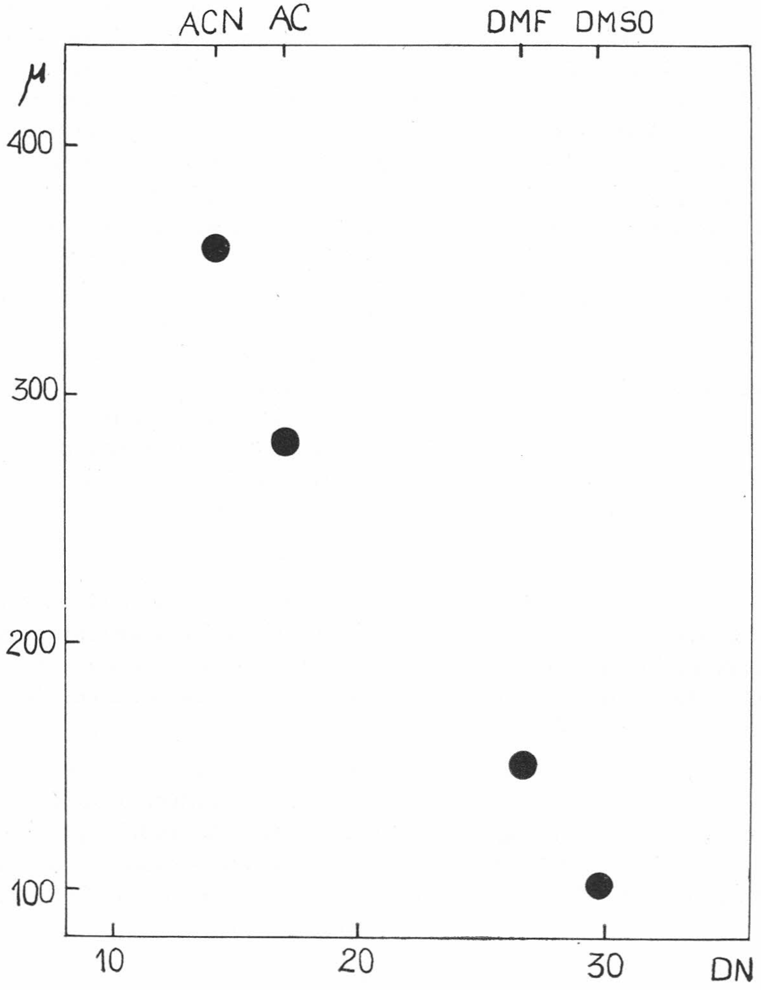


Figure 3. Plot of μ-values (in mV/Φ-unit) vs donor number DN. Concentrations as in Figure 2. ACN = acetonitrile, AC = acetone, DMF = *N,N*-dimethylformamide, DMSO = dimethylsulfoxide. Figure taken from ref. 66.

rily[69] with substituent constants σ_m and σ_p^0 and even better with hyperfine splitting constants at N-nuclei in the nitro group, since AN values express most of the medium effects present in the systems in question.

DIRECT APPLICATION OF THE HAMMETT EQUATION TO POLAROGRAPHIC DATA MEASURED IN APROTIC MEDIA

The applicability of the LFER principle to electrochemical reactions and the significance of scientific information obtained by its use leave no room for any doubt. As it was pointed out in a previous section the application of eq. (8) proved correct in many reaction series, but experiments were predodominantly carried out in protic conditions. With rare exceptions[60,70], no attempts have been made to correlate ϱ values with the fundamental characteristics of aprotic media, such as solvent properties and the kind of supporting electrolyte. This seems rather incomprehensible because as early as 1962 Holleck and Becher[60] demonstrated indirectly that for substituted nitrobenzenes in *N,N*-dimethylformamide and acetonitrile $E_{1/2}$ depends on both of these factors. Based on their results Zuman[70] found a linear correlation between half-wave potentials of the unsubstituted nitrobenzenes in solutions containing a given cation (Et_4N^+, Cs^+, Na^+ and Li^+) and the values of ϱ obtained for a series of substituted nitrobenzenes in the same supporting electrolyte. Then, growing interest in the ion pairing phenomena in organic electrochemistry led to a more quantitative description of experimental results. At the time, the influence of the supporting electrolyte cations on the ϱ constant was investigated in the case of the polarographic reduction of para-substituted nitrobenzenes and benzaldehydes in dimethylformamide solutions. It was found[71] that the formation of ion pairs between corresponding free radical anions and cations of the supporting electrolyte influences the value of the reaction constant according to the following formula

$$\varrho = \varrho^{\circ} + (d\mu/d\sigma)\,\Phi \tag{23}$$

where ϱ denotes the reaction constant in the presence of a given cation with which ion association occurs, ϱ° signifies the reaction constant measured in the absence of ion association, while μ and Φ are the parameters of eq. (20). The plot of the reaction constant ϱ versus Φ for *p*-substituted nitrobenzenes is presented in Figure 4.

Relation (23) was also used to compare the effects of supporting electrolyte cations on the reaction constant of para-substituted azobenzenes and their heterocyclic aza-analogs[72]. Its meaning may be simply justified on the basis of eqns (8) and (20). Formally, the reaction constant ϱ for the series conforming to both of these equations may be presented as follows:

$$\varrho = \frac{\mathrm{d}\,\delta\,E_{1/2}^{\mathrm{ipf}}}{\mathrm{d}\,\sigma} \tag{24}$$

After substituting eq. (20) in relation (24) we have[73]

$$\varrho = \frac{\mathrm{d}\,(E_{1/2}{}^{\circ} + \mu\,\Phi)}{\mathrm{d}\,\sigma} = \frac{\mathrm{d}\,E_{1/2}{}^{\circ}}{\mathrm{d}\,\sigma} + \frac{\mathrm{d}\,\mu}{\mathrm{d}\,\sigma}\,\Phi \tag{25}$$

which is obviously equivalent to eq. (23) since

$$\mathrm{d}\,E_{1/2}{}^{\circ}/\mathrm{d}\,\sigma = \varrho^{\circ} \tag{26}$$

As it was previously pointed out, μ describes the sensitivity of a given radical anion toward ion association effects. Therefore, it is dependent on the properties of the solvent used[67,69]. On the other hand, it is evident that the ϱ constant should also be influenced by the kind of solvent. For one electron reversible electroreduction of *m*-substituted nitrobenzenes such a dependence has actually been observed .The correlation of corresponding ϱ values with

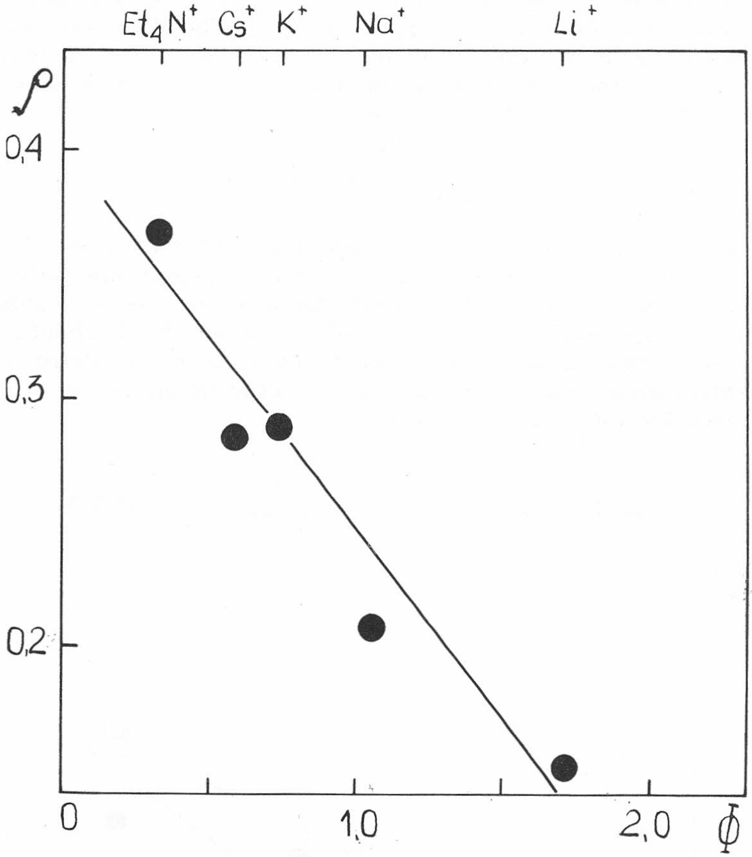


Figure 4. Plot of ϱ-values (in V/σ-unit) of p-substituted nitrobenzenes vs. ionic potential, Φ, of supporting electrolyte cations. Concentrations of depolarizers and cations were 1 mM and 0.1 M, respectively. Figure taken from ref. 71.

solvent parameters indicated that the Hammett reaction constant is linearly dependent on Gutmann's donicity, according to the empirical expression[75]

$$\varrho = \varrho^{\circ} + \frac{\mathrm{d}\,\beta}{\mathrm{d}\,\sigma}\mathrm{DN} \tag{27}$$

in which β is the coefficient of eq. (22). A similar relation has been observed for *p*-substituted azobenzenes[76], and, for the acidity of the —NH_2 group in para-substituted anilines measured in various solvents[15]. These kinds of intercorrelations are theoretically well known and are called iso-parameter relationships[77].

Figure 5. shows the dependence of Hammett's reaction constant for meta-substituted nitrobenzenes on Gutmann's donor number of solvent. Two linear plots are shown, corresponding to the values determined in solutions contaning $NaClO_4$ and $(C_2H_5)_4NClO_4$, respectively, as electrolytes. These plots

are well separated, as expected on the basis of eq. (20), and both the correlation lines fulfil satisfactorily expression (27). The discussion of eq. (27) on the basis of LFER is presented in ref. 75. A similar treatment may be also useful to describe the solvent effect on the value of reaction constant ϱ in the absence of ion pairing. In such cases[76]

$$\varrho = \varrho^{\circ} + \frac{d\,\alpha}{d\,\sigma} AN \tag{28}$$

where α is the coefficient of eq. (14). As it can be seen from Figure 6, ϱ values obtained for the series of quinones reduced polarographically in solutions containing 0.1 M $(C_2H_5)_4NClO_4$ (semiquinones are free i. e. unassociated radicals under experimental conditions) fulfil relation (28). It should be noted that the corresponding reaction constants have been calculated from the Hammett-Streitwieser equation, but their interpretation is very similar to that discussed for the original Hammett ϱ.

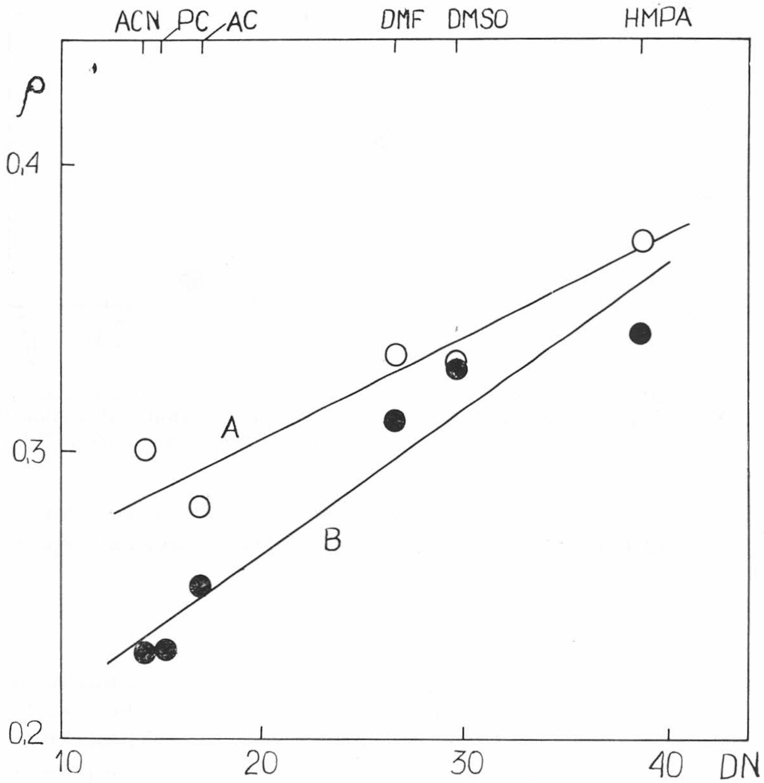


Figure 5. Plots of the reaction constant ϱ (in V/σ-unit) versus Gutmann's donor number for 1 mM m-substituted nitrobenzenes in various solvents. Supporting electrolytes: 0.1 M $(C_2H_5)_4NClO_4$ (A) and 0.1 M $NaClO_4$ (B). PC = propylene carbonate, HMPA = hexamethylphosphoramide; all remaining symbols as in Figure 3. Figure taken from ref. 77.

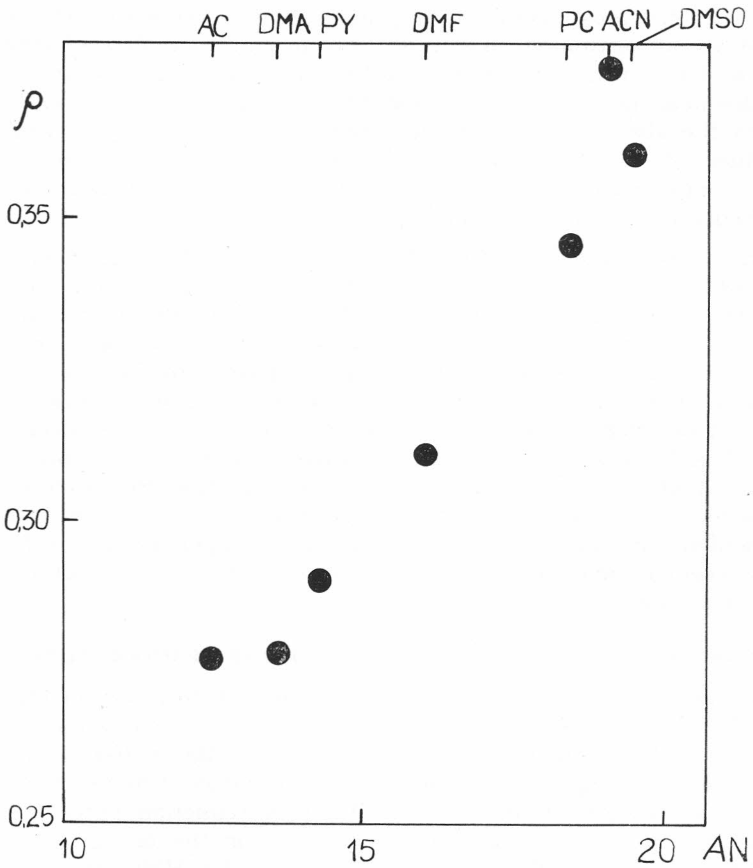


Figure 6. Dependence of ϱ-values (in V/σ-unit) from the Hammett-Streitwieser equation for the series of 0.5 mM quinones on acceptor number of solvents. Supporting electrolytes; 0.1 M $(C_2H_5)_4NClO_4$. PY = pyridine, DMA = N,N-dimethylacetamide, all remaining abbreviations as in Figs. 3 and 5. Figure taken from ref. 76.

THE ENTROPIC AND ENTHALPIC CONTRIBUTION TO SUBSTITUENT EFFECTS FOR THE ELECTROREDUCTION OF ORGANIC MOLECULES

The substituent effect on chemical reactivity usually described in terms of substituent constants may be, however, treated as composed of enthalpic and entropic contributions, described by σ_H and σ_S[78]; respectively. Applying these constants to the analysis of acid/base equilibrium data[78], as well as kinetic constants of ortho-, meta-, and para-substituted species treated together in a one reaction series[79] gave surprisingly good fit. When this treatment was applied to polarographic $E_{1/2}$ values measured in aprotic solvents, the results obtained were satisfactory as well[80]. The main conclusion drawn in this paper[81] was that in many cases e. g. electroreduction of substituted benzofurasons in acetonitrile[79], phenazine in DMF[82], the overall process is chiefly controlled by changes in entropy. The same finding was also observed

benzofurasons in acetonitrile[79], phenazine in DMF[82], the overall process is

in line[83] with the most recent studies on iso-kinetic temperature[84], which was described as an estimated blend of entropy and enhalpy changes in the changes of free energy, which is, usually indirectly measured in chemical or physicochemical measurements. It was clearly shown[83] that for reaction series, for which the absolute value of the isokinetic temperature is lower than the temperature of the experiment, the dominant contribution to free energy changes comes from $T \Delta S$-terms. This finding has important consequences in the theory of substituent effects[83].

It should be pointed out that the effect of the temperature on the values of reversible electrode potentials has been investigated to a very limited extent. The temperature dependence of the potentials proper for electroreduction of aromatic hydrocarbons in acetonitrile was found to vary in a manner predictable from the distribution of charges in free radical anions[85]. It was also demonstrated[86] that in the case of the electroreduction of substituted nitrobenzenes the entropy of the formation of radical anions is influenced both by steric and electronic effects of the alkyl substituents. The earlier work of Andrieux and Saveant indicated[87] that the entropy and enthalpy factors of successive electroreduction of aromatic dinitro compounds are dependent on the nature of solvent and supporting electrolyte cation. Parker's recent review[88] gives additional data on the entropy factor in electrochemical processes.

QUANTUM CHEMICAL INTERPRETATION OF THE REACTION CONSTANT

Quantum chemistry has several times been used to interpret the Hammett equation[89–91]. In the case of polarographic data for reversible electroreduction such an attempt was made[90,92] taking into account the well-known possibility of describing physicochemical properties of π-electron systems in terms of the simple HMO theory[27]. In the case of standard reduction potential (approximated by $E_{1/2}$-values) the appropriate quantity is the energy of the lowest vacant molecular orbital[93], E_{LVMO}, as estimated by HMO theory. Since, in general, reaction constant is defined by a simple derivative expression

$$\varrho = \frac{\mathrm{d}\,Q}{\mathrm{d}\,\sigma} \tag{29}$$

where Q is the measured property depending on the nature of the substituent, for our case one may write

$$\varrho = \frac{\mathrm{d}\,E_{\mathrm{LVMO}}}{\mathrm{d}\,\sigma} \tag{30}$$

In order to complete the quantum chemical description of ϱ, one must be able to interpret σ within the context of HMO theory. Such an interpretation was given[93] by relating σ to the so called Hückel effective inductive parameter. The definition of this parameter is based on the following assumptions: (i) changes in π-electron structure and energy caused by a substituent in a position para to the reaction centre can be described by a simple correction to the Coulomb integral of the carbon atom at the substituent position: that is, the Coulomb integral α_t becomes $\alpha_t + \mathrm{d}\,\alpha_t$ (ii) the corrections $\mathrm{d}\,\alpha_t$ depend linearly on the Hammett constants σ_p. The first of these assumptions was verified some time ago and is described by Streitweiser[27] as a method of interpreting the half-wave potentials of poly-methyl derivatives of naphthalene. The second was derived empirically from IR investigations of substituent effects on the carbonyl stretching frequency of 16 derivatives of anthraquinone[93]. It has been successfully applied to the interpretation of the polarographic and spectral properties of anthraquinones[93,94], the polarographic properties of substituted nitrobenzene, azobenzene, and azopyridine[95], and the NMR properties of substituted thiophenes[96].

From the above empirical considerations, one may replace $\mathrm{d}\,\sigma$ by the $\mathrm{d}\,\alpha_{\mathrm{t}}$ and equation (30) then reads as

$$\varrho_{\mathrm{HMO}} = \frac{\mathrm{d}\,E_{\mathrm{LVMO}}}{d\,\alpha_{\mathrm{t}}} \tag{31}$$

Furthermore, on the basis of the simple HMO perturbation theory, $\mathrm{d}E_{\mathrm{i}}/\mathrm{d}\alpha_{\mathrm{t}} = = C^{2}{}_{\mathrm{it,}}$ where $C_{\mathrm{i,t}}$ is the coefficient at the t-position for the i-th molecular orbital of the unsubstituted molecule. Thus, one may define ϱ_{HMO} in the case of a reversible electroreduction reaction as

$$\varrho_{\mathrm{HMO}} = C^{2}_{\mathrm{LVMO,\,t}} \tag{32}$$

According to the simple interpretation of the HMO model $C_{2}^{\mathrm{LVMO,\,t}}$ is the spin density at the t-position in the corresponding anion radical of the unsubstituted molecule. The spin density, in turn, is normally assumed to be proportional to the hyperfine splitting constant of the hydrogen atom at the same position as determined from the ESR spectrum[97]. Thus, the above analysis, points to the conclusion that ϱ_{HMO} is directly proportional to the hyperfine splitting constant of the hydrogen atom at the substituent position in the parent molecule.

The values of ϱ determined from the variation in half-wave potential with substituent for eight parent molecules are plotted in Figure 7 against $A_{\mathrm{H,t}}$, the hyperfine splitting constant at the substituent position. The correlation obtained may be considered satisfactory and is qualitative support of the model presented for ϱ.

CONCLUDING REMARKS

In conclusion, we wish to point out that polarography seems to be a very powerful technique in the field of LFER investigations. Measurements of the half-wave potentials are usually easy and fast procedures, often much faster than determination of rate or equilibrium constants. The elucidation of electrochemical processes is also usually simpler than the elucidation of the mechanism of a homogeneous reaction. The deviations from the mechanism operating in the whole series can sometimes be detected more easily in polarography than in homogeneous kinetics: one ought to compare the characteristics and slopes of registered waves. Generally these deviations can be caused by (i) steric effects for a given substance, (ii) specific effects of substituent in the given molecule and in the particular environment, as e. g. ortho--effects, field effects etc, which occur in a particular reaction series but which are not incorporated in the σ-substituent constant, and (iii) specific effects

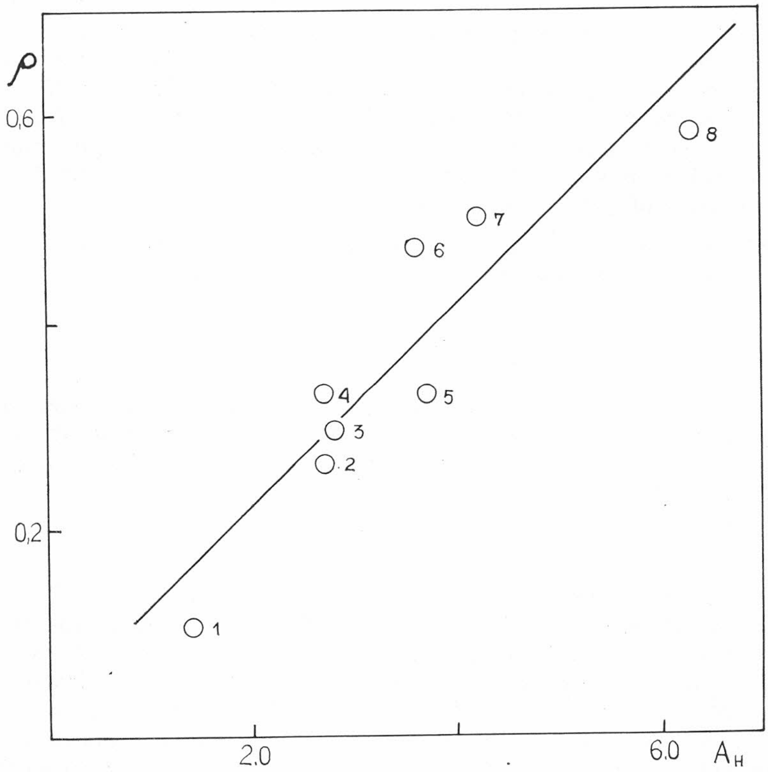


Figure 7. Plot of experimental Hammett reaction constant ϱ determined from polarographic data for reduction reactions against the e.s.r. hyperfine splitting constant for the proton at the substituent position in the parent molecule, $A_{H,t}$ for the following compounds: 1, stilbene; 2, α-substituted anthraquinone; 3, azobenzene; 4, β-substituted anthraquinone; 5, benzophenone; 6, nitrobenzene in acetonitrile; 7, nitrobenzenne in dimethylformamide; 8, benzaldehyde. Position t refers to para for all molecules except anthraquinone where it refers to α or β as noted. In all cases measurememts of $A_{H,t}$ and ϱ were carried out in the same solvent. A_H values are given in gauss (1 gauss = 10^{-4} T).

which may operate in polarographic measurements, such as adsorption phenomena. The identification of these effects is usually not difficult.

It seems proper to add that the accuracy of polarographic measurements is usually quits high and hence attempts to use these measurements for estimation »new« Hammett substituent constants[98,99]. Under common experimental conditions a difference of 0.01 V in half-wave potentials is well reproduced. Under carefully controlled conditions the precision of measurements increases even tenfold. This means that for $\varrho = 0.3$ V/σ-unit, the difference in substituent constants of 0.01 σ-units is significant, which is simply not attainable by non-electroanalytical methods. Polarographic ϱ-values are, as a rule, in the range of 0.1—0.6 V/σ-unit. It should be pointed out that ϱ-values determined from kinetics and equilibria of homogeneous reactions and those from polarographic measurements are on different scales. In order to transform the polarographic ϱ-values into the usual scale of magnitude for ϱ, the polarographic ϱ-values have to be multiplied by factor $nF/2.3\,RT = 16.91$ n, where the symbols have the same meaning as in eqns 4—6. For this reason, polarography seems to be a useful method for the determination of not only reaction constants but also of accurate values of substituent constants using properly chosen secondary standards. Even in those cases where very small differences in measured values are important, as e. g. in the proofs of hyperconjugation, polarography may be very serviceable.

In this account we have summarized some studies on the environmental effects affecting the value of the reaction constant. In our opinion, this is only the first step in more systhematic investigations in this field. We suggest in particular assume that the effect of temperature changes should be examined, since these changes influence the equilibria between different types of ion pairs (tight, solvent separated etc). Obviously, polarographic measurements in non-aqueous media are connected with difficulties involved in the changes of the potential of the reference electrode and in the problems with liquid-junction potentials. These difficulties, however, can be circumvented by measuring the changes in the difference $(E_{1/2})_x - (E_{1/2})_H$ and/or by an application of internal standards reducing the role of liquid junction effects.

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SAŽETAK

Primjena linearnih relacija slobodne energije u organskoj elektrokemiji. Interpretacija Hammettove reakcijske konstante na procese reverzibilne elektroredukcije u aprotičnim otapalima

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Dan je pregled primjena linearnih relacija slobodne energije, poglavito primjena Hammettove jednadžbe, na istraživanja reverzibilnih organskih elektrokemijskih reakcija u aprotičnim otapalima. U pregledu teorijskih i praktičkih rezultata posebno su izabrana slijedeća poglavlja: o utjecaju svojstava otapala na ravnoteže, o utjecaju stvaranja ionskih parova, o direktnoj primjeni Hammettove jednadžbe na polarografske podatke, o entropijskim i entalpijskim doprinosima supstituenata, te o kvantno-kemijskim interpretacijama reakcijskih konstanti u aprotičnim otapalima. Polarografskim tehnikama pridaje se posebno značenje u proučavanju organsko-kemijskih reakcija u aprotičnim otapalima stoga što su one osjetljivije i prikladnije za interpretaciju rezultata nego tehnike homogene reakcijske kinetike.