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Solvation Effects in the Electrochemistry of Diphenylpicrylhydrazyl

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The electrochemistry of diphenylpicrylhydrazyl (*DPPH*) was studied in nitromethane, nitrobenzene, benzonitrile, acetonitrile, acetone, methanol, ethanol, propanol-2, *N*,*N*-dimethylformamide, *N*,*N*-dimethylacetamide, and dimethylsulfoxide employing cyclic voltammetric technique. Reversible behaviour was observed for the systems $DPPH/DPPH^+$ and $DPPH/DPPH^-$ in all solvents on the platinum microelectrode. The variation of $\Delta E^{\text{form}} = (E^{\text{form}}_{\text{oxidation}} - E^{\text{form}}_{\text{reduction}})$ upon solvent can be well described by a complementary *Lewis* acid—base model for solvent—solute interactions: $\Delta E^{\text{form}} = -3.685\,DN - 4.537\,AN + 651.84$ with a correlation coefficient of $r = 0.991$ (E^{form} stands for formal potential whereas *DN* and *AN* are the donor number and the acceptor number). The solvent effect on the position of the spectral absorption of *DPPH* is also discussed; ν_{max} values show good linear regression with the π^*-parameter introduced by *Kamlet* and *Taft*.

(Keywords: Cyclic voltammetry; Diphenylpicrylhydrazyl; Solvent effects)

Lösungsmitteleffekte in der Elektrochemie von Diphenylpicrylhydrazyl

Das elektrochemische Verhalten von Diphenylpicrylhydrazyl (*DPPH*) wurde mittels cyclischer Voltametrie in Nitromethan, Nitrobenzol, Benzonitril, Acetonitril, Aceton, Methanol, Ethanol, 2-Propanol, *N*,*N*-Dimethylformamid, *N*,*N*-Dimethylacetamid und Dimethylsulfoxyd untersucht. Es wurde für die Systeme $DPPH/DPPH^+$ und $DPPH/DPPH^-$ an der Platinmikroelektrode in allen Lösungsmitteln reversibles Verhalten festgestellt. Der Lösungsmitteleinfluß auf $\Delta E^{\text{form}} = (E^{\text{form}}_{\text{Oxydation}} - E^{\text{form}}_{\text{Reduktion}})$ kann gut mit einem *Lewis*-Säure—Base-Modell für Lösungsmittel—gelöster Stoff beschrieben werden: $\Delta E^{\text{form}} = -3{,}685\,DN - 4{,}537\,AN + 651{,}84$ mit einem Korrelationskoeffizienten von $r = 0{,}991$ (E^{form} symbolisiert das formale Potential, *DN* und *AN* sind die Donor- bzw. Acceptor-Nummer). Lösungsmitteleffekte auf die Lage der UV-Absorptionsbanden von *DPPH* werden ebenfalls diskutiert, die ν_{max}-Werte zeigen eine gute lineare Regression mit den π^*-Parametern nach *Kamlet* und *Taft*.

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Introduction

Diphenylpicrylhydrazyl (*DPPH*), a stable free radical, is employed as a standard in e.s.r. technique. It is also a compound of profound interest in polymer chemistry and is often applied as an inhibitor and free radical trap.

Electrochemical properties of *DPPH* have been first studied by *Solon* and *Bard*[1]. The authors have found that both the anodic oxidation and the cathodic reduction are simple one-electron transfers in acetonitrile, methanol, ethanol, acetone, and dimethylsulfoxide. Quite identical results were obtained by *Iwakura* and *Tamura* in acetonitrile[2] as well as by *Funt* and *Gray* in tetrahydrofuran[3]. It can be seen from these papers that the separation between the reversible potentials of the oxidation and of the reduction is dependent on the nature of the solvent. This led us to an investigation of the solvent effect on the redox behavior of *DPPH* in a more quantitative way.

Materials and Methods

DPPH (Eastman Kodak Co.) was used as received. Tetraethylammonium perchlorate was recrystallized from triply distilled water and vacuum dried at 60 °C. All solvents applied were dried and purified by established procedures[4] immediately before use.

Cyclic voltammetric measurements were carried out in a three-electrode system using a Radelkis OH-105 apparatus. The working electrode was a platinum disc with geometrical area of 0.086 cm^2. It was pretreated before each set of experiments by rinsing with nitric acid and then distilled water, and then polished with an alumina slurry on felt. The counter electrode was constructed of cylindrical platinum gauze. An aqueous SCE was employed throughout experiments and all potentials are referred to it. Electrical contact between the SCE and the solution investigated was made through two-part salt bridge with a *Luggin* capilary probe. One branch of this bridge was filled with aqueous saturated KCl, whereas the second one contained the solvent and the electrolyte exactly as in the electrochemical cell. The concentrations of *DPPH* and supporting electrolyte were 0.5 m*M* and 0.1 *M*, respectively. Coulometric measurements (large scale electrolysis) were made by means of a *Radelkis* OH-404 apparatus.

A Specord uv-vis spectrophotometer (Zeiss, Jena) was used to record the optical spectra of *DPPH*. In these experiments the concentration of *DPPH* was changed within the range from $3 \cdot 10^{-5}$ to $2 \cdot 10^{-4}$ *M*. All solutions applied in electrochemical and spectrophotometric measurements were deaerated by pure argon. The experiments were performed at 25 ± 0.1 °C.

Results and Discussion

Much evidence on the interaction between *DPPH* and solvents has been accumulated in the literature[5–10]. Therefore, it was of interest to

Table 1. *Characteristics of the long-wavelength band in the optical spectrum of diphenylpicrylhydrazyl*

No.	Solvent	$\pi^{*\,a}$	$\nu \cdot 10^{-3}/\mathrm{cm}^{-1}$	$\log \varepsilon$
1	*n*-Hexane	—0.081	19.5	4.13
2	Cyclohexane	0.000	19.45	4.07
3	Diethyl ether	0.273	19.25	4.08
4	Carbon tetrachloride	0.294	19.16	4.12
5	Tetrachlorethylene	0.277	19.15	4.05
6	*p*-Xylene	0.426	19.1	3.97
7	Propanol-2	0.505	19.2	4.07
8	Ethanol	0.540	19.15	3.92
9	Methanol	0.586	19.15	3.96
10	Benzene	0.588	19.0	4.04
11	Acetone	0.683	19.0	3.96
12	Acetonitrile	0.713	18.8	3.98
13	Nitromethane	0.848	18.9	3.87
14	Pyridine	0.867	18.8	4.02
15	*N*,*N*-Dimethylformamide	0.875	18.75	4.02
16	*N*,*N*-Dimethylacetamide	0.882	18.9	4.08
17	Benzonitrile	0.904	18.8	3.84
18	Dimethylsulfoxide	1.000	18.75	4.04
19	Nitrobenzene	1.029	18.6	4.06
20	Formamide	1.118	18.65	4.04

[a] Solvent polarity parameter[12].

elucidate this problem before electrochemical experiments. To this purpose we have registered the visible π-π band of *DPPH* (for theoretical considerations see Ref.[11]) in 20 solvents differing markedly in their polarities and *Lewis* acid—base properties; some of these solvents were afterwards applied in voltammetric measurements. The results are collected in Table 1.

Fig. 1 presents the dependence between the wave-number of the band and the solvent polarity parameter, π^*, introduced by *Kamlet* and *Taft*[12]. Numerical calculations which were carried out using the least squares procedure indicated that equ. (1) correlates satisfactorily both these values. We have found that

$$\nu \cdot 10^{-3} = -0.711\,\pi^* + 19.44 \qquad (1)$$

with a correlation coefficient of $r = 0.956$, whereas the value of the *Fisher-Snedecor* test is $F = 90.6$. It can be seen from these values that the polar interactions are the most important in the *DPPH*—solvent systems. As a consequence, it stands to reason that the *Lewis* acid—base interactions between the molecules of *DPPH* and of a solvent are simply negligible (the percentage of the explanation of the dependence presented in Fig. 1 is $r^2 \times 100 = 91.4\%$).

Electrochemical experiments were carried out in 11 polar solvents. Registering cyclic voltammograms we have found that two reversible processes are observed in the anodic potential region. The electroreduction of —NO_2 groups[2] was not of interest to us, therefore we have not investigated the waves at negative potentials.

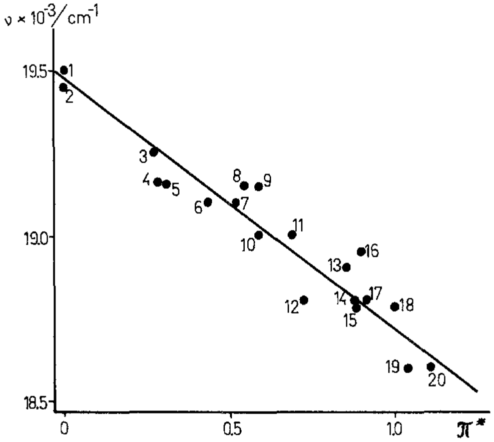

Fig. 1. Relationship between the wave-number of the visible absorption band of diphenylpicrylhydrazyl and the π^*-parameter of a solvent (for solvent numbers see Table 1)

Very similar shapes of cyclovoltammograms were registered for all solvents. Measurements of the peak heights as a function of *DPPH* concentration and as a function of sweep rate indicated that both the electroreduction and the electrooxidation are controlled by diffusion. Corresponding ($E_{pa} - E_{pc}$) values suggested that the electrochemical processes are connected with one-electron transfers.

The number of electrons participating in the oxidation and in the reduction of *DPPH* was also measured coulometrically. Large scale electrolysis, which was carried out on a platinum plate as a working electrode, confirmed one for the number of electrons for both electrochemical reactions in all the solvents under investigation. Essential characteristics of the cyclic voltammetric curves of *DPPH* are summarized in Table 2. It should be noted that all the potentials reported here were measured with accuracy of ± 5 mV.

Table 2. *Essential characteristics of the cyclic voltammetric curves of 0.5* m*M diphenylpicrylhydrazyl registered in solutions containing 0.1 M* $(C_2H_5)_4NClO_4$ *(sweep rate 100 mV s*$^{-1}$*)*

Solvent	*DN*[a]	*AN*[b]	*DPPH*$^+$/*DPPH* system			*DPPH*/*DPPH*$^-$ system		
			$E_{pc}-E_{pa}$ [mV]	i_{pc}/i_{pa}[c]	E_{ox}^{form}[d]	$E_{pa}-E_{pc}$ [mV]	i_{pa}/i_{pc}[c]	E_{red}^{form}[d]
Nitromethane	2.7	20.5	66	0.93	755	68	1.05	210
Nitrobenzene	4.4	14.8	65	1.0	790	68	1.03	225
Benzonitrile	11.9	15.5	63	0.94	810	66	1.0	260
Acetonitrile	14.1	18.9	62	0.95	730	65	1.03	215
Acetone	17.0	12.5	62	1.03	750	65	1.05	220
Methanol[e]	19	41.3	67	1.0	690	68	1.0	180
Ethanol[e]	20	37.1	65	1.0	715	68	1.0	195
Propanol-2[e]		33.5	65	1.0	695	66	1.07	160
N,*N*-dimethylformamide	26.6	16.0	62	0.92	805	60	1.0	325
N,*N*-dimethylacetamide	27.8	13.6	63	1.0	735	60	1.0	250
Dimethylsulfoxide	29.8	19.3	62	0.95	785	60	1.0	330

[a] *DN* = donor number[13].

[b] *AN* = acceptor number[14].

[c] i_{pc}/i_{pa} and i_{pa}/i_{pc} values were determined by the semi-empirical method of Ref.[15].

[d] E_{ox}^{form} and E_{red}^{form} values, in mV, were determined as $(E_{pc}-E_{pa})/2$ and $(E_{pa}-E_{pc})/2$, respectively.

[e] Cyclic voltammograms were registered in solutions containing saturated $(C_2H_5)_4NClO_4$.

It can be seen from these data that *DPPH* undergoes reversible one-electron reduction to form the anion $DPPH^-$ and one-electron oxidation to form the cation $DPPH^+$:

$$DPPH^+ \underset{E_{\mathrm{ox}}^{\mathrm{form}}}{\overset{-\mathrm{e}}{\leftrightharpoons}} DPPH \underset{E_{\mathrm{red}}^{\mathrm{form}}}{\overset{+\mathrm{e}}{\rightleftharpoons}} DPPH^- \qquad (2)$$

This is fully consistent with the results of previous papers[1–3].

The data listed in Table 2 indicate that the difference between the redox potentials of the oxidation and of the reduction of *DPPH* varies considerably with the nature of a solvent. Therefore it was of interest to study whether these differences can be correlated with solvent parameters. Plotting $\Delta E^{\mathrm{form}} = (E_{\mathrm{ox}}^{\mathrm{form}} - E_{\mathrm{red}}^{\mathrm{form}})$ values versus the dielectric permittivity gives no correlation. On the other hand, rather crude correlation between ΔE^{form} and *Gutmann*'s donor number[13], *DN*, has been found. In this case a corresponding correlation equation may be written in the form

$$\Delta E^{\mathrm{form}} = -3.40\, DN + 574.5 \qquad (3)$$

for all experimental points ($r = 0.929$ and $F = 14.7$), and

$$\Delta E^{\mathrm{form}} = -3.46\, DN + 573.7 \qquad (4)$$

with $r = 0.934$ and $F = 17.1$ when the values determined in alcoholic media are excluded.

The existence of the relationship presented in Fig. 2 indicates that the electron donating properties of the solvents are decisive in the solvation of the species participating in the system described by equ. (2). It is thus evident that the interaction of $DPPH^+$ with a solvent is most important. What is, however, the role of $DPPH^-$ solvation?

To solve this problem, we have employed a two parameter analysis[16] within the frame work of an extended *Lewis* type donor—acceptor concept[13, 17]. Similarly as in equs. (3) and (4), the donor number was used as a measure of the *Lewis* basicity, whereas the acceptor number[14], *AN*, was chosen as a measure of the *Lewis* acidity of the solvents. Indeed, the ΔE^{form} values were found to be related to both of these numbers, and corresponding planar regression can be described as

$$\Delta E^{\mathrm{form}} = -3.685\, DN - 4.537\, AN + 651.84 \qquad (5)$$

with a correlation coefficient of $R = 0.991$ and the *Fisher-Snedecor* test of $F = 70.8$. It should be pointed out that i) equ. (5) was obtained for ΔE^{form} values determined in formally aprotic media only, i.e. the values proper for alcoholic solutions were not taken into consideration (cf. text below), and ii) the values of *DN* and *AN* for aprotic solvents are not colinear and a correlation coefficient between them is $r = 0.184$.

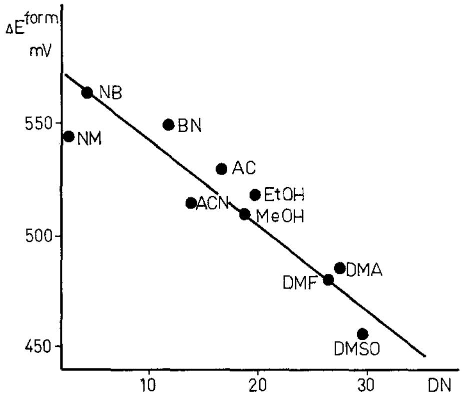

Fig. 2. Relationship between ΔE^{form} values of diphenylpicrylhydrazyl and the donor numbers of the solvents studied: *NM* nitromethane, *NB* nitrobenzene, *BN* benzonitrile, *ACN* acetonitrile, *AC* acetone, *Me*OH methanol, *Et*OH ethanol, *DMF N,N*-dimethylformamide, *DMA N,N*-dimethylacetamide, *DMSO* dimethylsulfoxide

Comparison of the correlation coefficients for equs. (4) and (5) shows an improvement in accuracy of the planar regression. Application of the *Fisher-Snedecor* test in a way proposed in Ref.[18] indicates that an addition of the second solvent parameter, *AN*, is significant at the 0.01 level. It is thus obvious that the donor term is the predominant contribution, but the acceptor term cannot be neglected in the description of the solvent effects on the ΔE^{form} values.

Numerical coefficients of equ. (5) describe the sensitivity of ΔE^{form} to change of the solvent nucleophilicity and electrophilicity, respectively. Since they are not at the same scale, we have calculated the percentage contributions of both these properties of a solvent to ΔE^{form}, similar to paper[16]. Accordingly, we have found that about 75% of the variation of ΔE^{form} upon solvent can be attributed to variations in the basicity parameter, whereas about 25% is connected with variations in the acidity parameter. This is fully consistent with the conclusions to be drawn from Fig. 2: electron donating solvation of $DPPH^+$ plays indeed a predominant role in the systems under investigation.

Finally, we have considered the possibility of an application of the two-parameter model to the all experimental points obtained in this study. As can be seen from equ. (6)

$$\Delta E^{\text{form}} = -3.406\, DN + 0.037\, AN + 573.75 \tag{6}$$

with $R = 0.924$ and $F = 11.6$, the correlation including the ΔE^{form} values determined in alcoholic solutions is much worse than the one described by equ. (5). Moreover, comparison of the correlation coefficients proper for equs. (3) and (6) indicates strongly that an addition of the second term to the linear regression (3) makes only matters worse. We suppose that this is connected with strong tendency of $DPPH^-$ toward hydrogen bonding with the alcohol molecules. However, such a suggestion was not experimentally verified and it needs much deeper studies involving spectroscopic techniques.

Based on the results presented in this work, it can be concluded that the donor—acceptor concept[13] is very useful to describe the problems of solvent—solute interaction in the electrochemistry of *DPPH*. This concept was previously applied to interpret some physicochemical properties of other organic compounds, principally in the electroreduction of quinones[16, 19] and dibiphenylene-ethene[20]. Thus, it seems to be justified to assume that the donor—acceptor approach[13] is generally attractive in the field of organic electrochemistry. Further investigations are in progress[21].

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