Substituent and solvent effects on the electrochemical properties of some iron(II) complexes with 1,10-phenanthroline

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The redox behaviour of the complex ions $[Fe(phen)_3]^{2+}$, $[Fe(TMPhen)_3]^{2+}$, and $[Fe(NO_2Phen)_3]^{2+}$ (where phen = 1,10-phenanthroline, TMPhen = 3,4,7,8-tetramethyl-1,10-phenanthroline, and NO_2Phen = 5-nitro-1,10-phenanthroline) was studied using cyclic voltammetry at a fixed platinum electrode in a series of nonaqueous solvents.

The obtained data of the half-wave potentials $E_{1/2}$ were used to compare the effect of substituents and solvents on the redox properties of the complex compounds under investigation. Substituent with a positive induction effect —CH_3 "facilitated" the oxidation process, while that with negative induction effect —NO_2 "impeded" it. An effect of solvents was observed only for the nitro derivative of the iron—phenanthroline complex and the measured value of $E_{1/2}$ was found to be approximately proportional to the acceptor number (AN) of the solvent.

Было изучено окислительно-восстановительное поведение комплексных ионов $[Fe(phen)_3]^{2+}$, $[Fe(TMPhen)_3]^{2+}$ и $[Fe(NO_2Phen)_3]^{2+}$ (где phen = 1,10-фенантролин, TMPhen = 3,4,7,8-тетраметил-1,10-фенантролин и NO_2Phen = 5-нитро-1,10-фенантролин) в ряду неводных растворителей при помощи циклической вольтамперометрии на неподвижном платиновом электроде.

Полученные данные потенциалов полуволн $E_{1/2}$ были использованы для сравнения эффектов заместителей и растворителей на окислительно-восстановительные свойства указанных комплексных соединений. Заместитель с положительным индукционным эффектом (CH_3) «облегчает» окислительный процесс; с отрицательным индукционным эффектом (NO_2) «препятствует» ему. Эффект растворителя был обнаружен только для нитропроизводного фенантролинового комплекса железа и полученные значения $E_{1/2}$ находятся в приблизительной пропорциональности акцепторному числу (AN) растворителя.

Electrochemical observations may be successfully used in studying the effect of substituents and solvents on the redox properties of dissolved compounds as far as the rate of the investigated electrode reaction is sufficiently high, so that in electrochemical sense the process appears to be "reversible".

Some years ago several phenanthroline complexes of iron and copper [1] were studied polarographically to determine the applicability of their half-wave potentials for evaluation of the liquid junction potentials. Kinetic studies of redox reactions done with phenanthroline complexes of iron [2] in nonaqueous solutions initiated the investigation of their redox behaviour by means of electrochemical methods. 1,10-Phenanthroline and its derivatives are largely used for determination of small amount of iron, copper, and other metals [3] forming with the respective ions intensively coloured complexes. Study of the electronic structure of tris-1,10-phenanthroline—iron(II) complex [4] showed that the intensive absorption band in the visible region belongs to the almost pure charge transfer from 3dπ AO of iron to the lowest vacant π MO of the ligand. The energy of the electron transfer from 3dπ AO of iron to the vacant π MO of the ligand depends mainly on the formal iron charge, or in other words, on the σ-electron distribution in the metal complex. Thus electron configuration and coordination structure considerably affect the properties of such complex ions. In order to determine the factors influencing the reactivity of phenanthroline complexes of Fe(II) the redox behaviour of these compounds was studied in dependence on the change of 1,10-phenanthroline substituents as well as that of solvents.

Experimental

The studied complex ions $[Fe(phen)_3]^{2+}$, $[Fe(TMPhen)_3]^{2+}$, and $[Fe(NO_2Phen)_3]^{2+}$ applied as perchlorates were prepared by the method given in [5].

Organic solvents were purified according to already published methods [6]. The water content was determined by the Karl Fischer method and in all cases it was lower than 10^{-4} M.

Tetrabutylammonium perchlorate (TBAP) in the concentration of 0.1 M was used as the supporting electrolyte. The concentration of the depolarizer was in the range of 10^{-4}—10^{-3} M. Solutions were prepared in the pure nitrogen atmosphere and before measuring they were deaerated by nitrogen saturated with vapours of the solvent in which measurements were to be done.

Voltammetric measurements were performed in a three-electrode arrangement with a polarographic analyzer, PAR 174 A. The working electrode was a platinum wire (area 0.021 cm^2) with a glass bead at its top. A saturated aqueous Ag/AgCl electrode was used as the reference electrode and the platinum wire was used as the auxiliary electrode. The reference electrode was separated from the measured solution by a specially for this case modified porous glass [7] being immersed in a solution of the solvent under investigation with the supporting electrolyte. This arrangement prevented contamination of the studied solution with water from the reference electrode.

Voltammograms were recorded at a rate of potential change $v = 50$ mV/s and the temperature 25°C by means of an Omnigraphic X – Y recorder, Series 2000.

Results

The data obtained by electrochemical oxidation of the complex ions $[Fe(phen)_3]^{2+}$, $[Fe(TMPhen)_3]^{2+}$, and $[Fe(NO_2Phen)_3]^{2+}$ in the nonaqueous solvents under investigation are listed in Table 1. They are expressed *vs.* $E_{1/2}$ of the redox pair ferricinium/ferrocene to eliminate the contribution of the liquid junction potential. Characteristic cyclic voltammograms of the above complex ions in one of the studied solvents (acetonitrile) are shown in Fig. 1. Rather positive half-wave potentials of the complex ions, especially with 5-nitro-1,10-phenanthroline and partly also with unsubstituted 1,10-phenanthroline limited the possibility of measuring these compounds in several solvents.

Table 1

Half-wave potentials of the redox systems $[Fe(phen)_3]^{3+}$—$[Fe(phen)_3]^{2+}$, $[Fe(TMPhen)_3]^{3+}$—$[Fe(TMPhen)_3]^{2+}$, and $[Fe(NO_2Phen)_3]^{3+}$—$[Fe(NO_2Phen)_3]^{2+}$ expressed *vs.* $E_{1/2}$ of the redox system ferricinium—ferrocene in some nonaqueous solvents

Solvent	$E_{1/2}$/V		
	$[Fe(phen)_3]^{3+}$— $[Fe(phen)_3]^{2+}$	$[Fe(TMPhen)_3]^{3+}$— $[Fe(TMPhen)_3]^{2+}$	$[Fe(NO_2Phen)_3]^{3+}$— $[Fe(NO_2Phen)_3]^{2+}$
NM	0.692	0.446	0.966
AN	0.669	0.448	0.893
PDC	0.681	0.455	0.890
AC	0.652	ls	0.827
DMF	0	0.427	0
NMeP	0.651	0.445	0
DMA	0	0.432	0
DMSO	0	0.445	0

0 — $E_{1/2}$ was not in electrochemically utilizable region of potentials of the given solvent; ls — low solubility.

NM — nitromethane, AN — acetonitrile, PDC — propanediol-1,2-carbonate, AC — acetone, DMF — *N,N'*-dimethylformamide, NMeP — *N*-methyl-2-pyrrolidone, DMA — *N,N'*-dimethylacetamide, DMSO — dimethyl sulfoxide.

The ratio between the cathodic and the anodic peak current $i_{p,c}/i_{p,a}$ was near to 1, indicating the absence of a following chemical reaction [8, 9]. An exception was shown by the voltammograms of $[Fe(NO_2Phen)_3]^{2+}$ ion in nitromethane and acetone, where this ratio was in the range of 0.81—0.84. This explains the fact that the half-wave potential of the above complex ion was close to the limit of the electrochemically usable region of the given solvents, so that the oxidation process

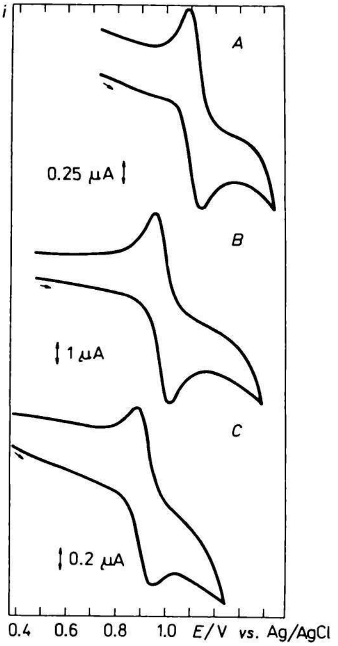

Fig. 1. Cyclic voltammograms of complexes $[Fe(NO_2Phen)_3]^{2+}$ (*A*), $[Fe(phen)_3]^{2+}$ (*B*), and $[Fe(TMPhen)_3]^{2+}$ (*C*) in acetonitrile.

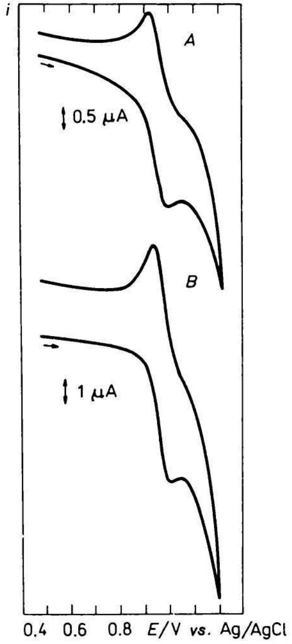

Fig. 2. Cyclic voltammograms of complex $[Fe(NO_2Phen)_3]^{2+}$ in nitromethane (*A*) and acetone (*B*).

could not be realized to such an extent at which the initial conditions for reduction (concentration of the depolarizer) were the same as for oxidation, *i.e.* the switching potential was not far enough from E_p (Fig. 2). In addition, the difference $E_{p,a} - E_{p,a/2}$ was about 60 mV indicating a one-electron diffusion-controlled oxidation.

Discussion

Change of substituent caused a marked change of the redox properties of the studied complex ions. Electron-donating groups (with +I effect) were found to "facilitate" the oxidation process, while electron-withdrawing group (with −I effect) showed the contrary influence. Compared with the unsubstituted phenanthroline complex ion $[Fe(phen)_3]^{2+}$ the half-wave potential of $[Fe(TMPhen)_3]^{2+}$ was more negative and that of $[Fe(NO_2Phen)_3]^{2+}$ was more positive.

The redox behaviour of the studied complex ions was investigated in different nonaqueous solvents in order to determine their influence on the redox properties of these compounds. As for complex ions with methylsubstituted and unsubstituted phenanthroline $E_{1/2}$ (Table 1) is almost independent of the chosen solvent. For the nitro derivative, on the contrary, the dependence of $E_{1/2}$ on the chosen solvent is apparent. With increasing acceptor property of the solvent (with its acceptor number AN) $E_{1/2}$ of $[\mathrm{Fe(NO_2Phen)_3}]^{2+}$ was shifted to more positive values (Table 2).

The change of the half-wave potential caused by change of the substituent and the solvent, respectively, with regard to the half-wave potential of the unsubstituted phenanthroline complex ion may be expressed by the sum of the two changes

$$\Delta E_{1/2} = (\Delta E_{1/2})_{\mathrm{R}} + (\Delta E_{1/2})_{\mathrm{S}} \qquad (1)$$

Table 2

Half-wave potentials of the redox system $[\mathrm{Fe(NO_2Phen)_3}]^{3+}$—$[\mathrm{Fe(NO_2Phen)_3}]^{2+}$ and the acceptor properties of the solvents (AN) [10] (expressed in ferrocene scale)

Solvent	$E_{1/2}$/V $[\mathrm{Fe(NO_2Phen)_3}]^{3+} - [\mathrm{Fe(NO_2Phen)_3}]^{2+}$	AN
NM	0.966	20.5
AN	0.893	18.9
PDC	0.890	18.3
AC	0.827	12.5

The symbol AN should not be confused with abbreviation used for the solvent acetonitrile.

$(\Delta E_{1/2})_{\mathrm{R}}$ and $(\Delta E_{1/2})_{\mathrm{s}}$ are contributions to the half-wave potential change caused by the substituent and the solvent, respectively. Since for $[\mathrm{Fe(TMPhen)_3}]^{2+}$ no dependence of $E_{1/2}$ on the solvent was observed, it may be supposed that the difference of

$$\Delta E_{1/2} = (\Delta E_{1/2})_{\mathrm{R}} \qquad (2)$$

and the observed change of the redox properties is due to the substituent influence only. In the case of $[\mathrm{Fe(NO_2Phen)_3}]^{2+}$, where the oxidation process showed also a certain dependence on the solvent, $\Delta E_{1/2}$ is given by superposition of both contributions (*1*).

The difference between the half-wave potentials of the individual complex ions is in agreement with the trend of the electron properties of the substituents (electron-donating and electron-withdrawing properties). This means that the oxidation of the Fe(II) complex ion with electron-donating substituent proceeds "easier" and it can be realized at less positive potentials than with an electron-withdrawing substituent.

The intensive absorption band in the visible region of the complexes under investigation was assigned to the electron transfer from 3dπ AO of iron to the vacant π MO of the ligand. It seems that the difference between the half-wave potentials of the complex ions is connected with the charge transfer [11, 12]. Namely, the central atom should have with the electron-withdrawing substituent a more positive partial charge and thus oxidation would proceed more "difficultly" causing a shift of $E_{1/2}$ to a more positive value than with unsubstituted ligands. Table 1 shows that the complex with the NO_2 group as substituent exhibits the most positive value of $E_{1/2}$.

Supposing that for the iron complexes studied the coordination sphere of the central atom remains unchanged during measurements (after the run of the redox process), the influence of the solvent is limited only to effects in the outer coordination sphere. The redox behaviour of the ions $[Fe(phen)_3]^{2+}$ and $[Fe(TMPhen)_3]^{2+}$ appeared to be almost independent of the solvent used. This result could also be suggested from the structure properties of the ions (bulky, little polarizable ions).

The observation that the redox behaviour of $[Fe(NO_2Phen)_3]^{2+}$ was influenced to a certain extent by the chosen solvent as well as the fact that a dependence of $E_{1/2}$ on the acceptor property of the solvent was found, is surprising. This phenomenon can be explained by an acid-base interaction of the complex with the solvent, caused by the presence of the NO_2 group as a substituent. Oxygen atoms of the nitro group appear as donors of the electron density and the solvent molecules as its acceptors. The donor properties of these oxygen atoms for the iron complex in a lower oxidation state are higher than for $[Fe(NO_2Phen)_3]^{3+}$, therefore the coordination of solvent molecules to this complex is a determining factor causing the observed dependence of $E_{1/2}$ on the acceptor properties of the solvent.

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