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Solvent Effects on the Redox Potential of Hexacyanoferrate(III)–Hexacyanoferrate(II)

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Dedicated to Professor Richard Kieffer on the occasion of his 70th birthday.

The redox behaviour of the system hexacyanoferrate(III)–hexacyanoferrate(II) has been studied by polarographic and voltammetric methods in the following solvents: N-methylpyrrolidinone, N,N-dimethylformamide, acetonitrile, dimethylsulfoxide, N,N-dimethylthioformamide,1,2-propanediolcarbonate,nitromethane, ethanol, methanol and water. The halfwave potentials of this reversible one-electron reduction have been measured against bisbiphenylchromium(I) iodide as a reference system, and the variation in the halfwavepotentials in these solvents has been explained as a function of coordinative interactions (the hexacyanoferrate ion being the donor and the solvent the acceptor). A semiquantitative order for the acceptor properties of the solvents has been derived.

Introduction

The redox behaviour of cations has already been studied in several solvents. In these studies a correlation has been shown between the donicity[1] as a measure of the donor properties of a solvent and the position of the halfwave potentials in several solvents.

No empirical quantity (analogous to the donicity) is presently available to characterize the acceptor properties of a solvent. The $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ couple was chosen as a model system to study the influence of acceptor properties of solvents on the redox behaviour of anions for the following reasons. This complex is symmetrically coordinated by the cyano ligands, with a strong bond between the ligands and the central metal ion which should exclude any exchange between the ligands and the solvent molecules. The reduction was found to be a reversible one-electron step in all the solvents studied. A shift of the halfwave potentials should therefore be a measure for the acceptor properties of the solvents:

$$\mathrm{Fe}\overset{\curvearrowright}{-}\mathrm{C}\overset{\curvearrowright}{\equiv}\mathrm{N}\rightarrow\mathrm{S}$$

Since alkali metal hexacyanoferrates are not soluble in the solvents studied, the tetraethylammonium salt was used.

Experimental

The tetraethylammonium hexacyanoferrate(III) was prepared according to Jaselskis and Diehl[2], except that it was not found necessary to saturate the water with HCN. The free acid was prepared by ion exchange of the potassium salt and neutralized with tetraethylammonium hydroxide, using a glass electrode system to monitor the pH. Most of this work has been done with the exclusion of light and under a nitrogen atmosphere. The dried product was recrystallized from acetonitrile and then dried again at 50° C and under a pressure of $< 5 \times 10^{-4}$ mm Hg. The product analysed as follows: Calc.: C 59.78, H 10.03, N 20.92, Fe 9.27%. Found: C 59.42, H 10.01, N 21.20, Fe 9.21% (the Fe content by means of complexometric titration).

The solvents were purified by standard techniques;[3] N,N-dimethylthioformamide was purified as described recently[4]. The water content was analyzed by the Karl Fischer method and was in any case below the detection limit of this method, *i.e.* below 10^{-4} mol H_2O/l of solvent. The polarograms were recorded on a Polariter PO-4 (Radiometer). All measurements were made with the three-electrode method employing a special operational amplifier which has been developed at our institute and which has an impedance of 10^{11} Ohm between the reference and the working electrode. The cyclic voltammetric measurements were made by means of a pulse polarograph UAP-4 and a potentiostat PRT 30-01 (Tacussel-SOLEA). The plots were recorded on a Hewlett–Packard 7044-A XY recorder. A commutator due to Kalousek and Rálek[5] was used to test the reversibility of the system.

The cell and the reference electrode have been described already[6]. Special care was taken in this arrangement to avoid any leakage of water from the reference electrode to the solution (contact being made through two specially prepared sintered glass discs)[7]. All measurements were made with strict exclusion of water. All solutions were prepared in a glove box and filled into gas-tight syringes. The needle tips of the syringes were sealed by a piece of silicone rubber and a silicone rubber septum was connected to the electrolytic cell. To fill the cell, the needle was pushed through both septa. To prevent changes in concentration caused by the evaporation of the solvent it was necessary to presaturate the nitrogen stream by bubbling it through an identical solution to that used in the electrolytic cell. All measurements were made at 25° C±0.02°. Unless indicated otherwise a $0.1M$ solution of tetraethylammonium perchlorate (TEAP) was used as a supporting electrolyte. The preparation of bisbiphenylchromium(I) iodide (BBCr(I) I) which served as an internal standard has been described[8].

Results

The reduction of $[Fe(CN)_6]^{3-}$ to $[Fe(CN)_6]^{4-}$ has been studied in the following solvents: N-methylpyrrolidinone (NMP), N,N-dimethylformamide (DMF), acetonitrile (AN), dimethylsulfoxide (DMSO), N,N-dimethylthioformamide (DMTF), 1,2-propanediolcarbonate (PDC), nitromethane (NM), ethanol (EtOH), methanol (MeOH) and water. The electrode reaction at the dropping mercury electrode was reversible with the exception of water, according to the logarithmic analysis of the polarograms and the form of the Kalousek diagrams. That the limiting current was controlled by diffusion was proven by a plot of the wave height as a function of the square root of the mercury height as well as by a plot of the wave height *versus* the concentration. It was found that both salts, $[Fe(CN)_6]^{3-}$ as well as $[Fe(CN)_6]^{4-}$ were soluble in all the solvents studied. The experimental halfwave potentials agree well within experimental error, with the standard redox potential for the system. Although the reduction in water could not be studied on the dropping mercury electrode, cyclic voltammetry on a stationary platinum electrode was used and a quasi-reversible behaviour of the system was observed. Separation of the cathodic and the anodic peaks was 0.111 V at a scan rate of 100 mV/sec. The potential difference corresponding to the half-distance between the cathodic and the anodic peaks was +0.17 V *vs.* aqueous Ag/AgCl electrode (satd. KCl). The concentration of $(Et_4N)_3Fe(CN)_6$ in this experiment was 2.17×10^{-3} M (Figure 1).

The halfwave potentials were measured with reference to the reduction of bisbiphenylchromium(I)/bisbiphenylchromium(0) in the same solvent. The technique of employing a reference ion[9, 10] as an internal standard makes it possible to avoid the diffusion potentials between the aqueous reference electrode and the non-aqueous electrolyte. In this work both bisbiphenylchromium(I)[11, 12] and ferrocene[10] have been used as reference ions. In DMTF oxidation of ferrocene occurred at a more positive potential than the oxidation of the solvent itself, and in many other cases the ferrocene wave was found to be more positive than the oxidation of mercury. On the other hand in some cases the reduction wave of BBCr(I) was too close to the reduction potential of the hexacyanoferrate(III) ion. The difference of the halfwave potentials of ferrocene and bisbiphenylchromium(I) has been studied by Gutmann and Duschek[13] and in several solvents a difference of 1.12 V±0.01 was reported.

The data presented in Table I have been checked again in this work. Exceptions were found in ethanol and in water. In ethanol a $0.1M$ solution of tetraethylammonium perchlorate could not be obtained; the value recorded has been extrapolated from PDC/EtOH mixtures and is thus subject to additional experi-

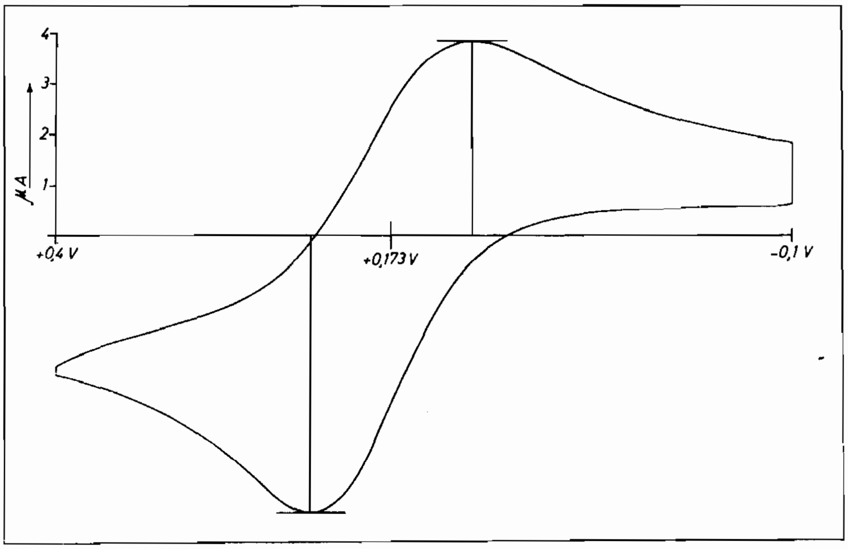

Figure 1. Cyclic voltammetry of a $2.17 \times 10^{-3} M$ solution of $(Et_4N)_3Fe(CN)_6$ on a stationary platinum electrode (scan rate: 100 m V/sec).

Table I. Difference of $E_{1/2}$ of Ferrocene and Bisbiphenylchromium(I) Iodide.

		DME[13]	RPE[13]
AN	1.12_7	1.13	1.13
DMSO	1.12_3	n.a.	1.12
DMTF	n.a.	–	–
NM	1.11_4	1.11	–
PDC	1.12_8	1.13	1.13
EtOH	1.18^a	–	–
MeOH	1.13_3	1.13	1.13
H_2O	–	0.97	–
DMF	–	–	1.13

[a] Extrapolated.

mental error. The reduction of BBCr(I) in water is complicated by adsorption phenomena of the oxidized as well as of the reduced form and furthermore the reduced form is insoluble in water. The halfwave potential for this reduction in water therefore cannot be used as a reference value[14] and thus the value employed has been extrapolated from water/MeOH mixtures[13]. Unfortunately, in water therefore the halfwave potential of BBCr(I) has to be considered as somewhat uncertain. In order to study the influence of the concentration of the supporting electrolyte on the difference of the halfwave potentials of ferrocene and BBCr(I) the TEAP concentration has been varied from 5×10^{-3} to greater than 0.1. The data reported in Table II, using nitromethane as the solvent show that within experimental error the difference between the $E_{1/2}$ values remains constant. The deviations at very low concentrations of the supporting electrolyte are probably due to a greater experimental error caused by migration currents.

With tetrabutylammonium perchlorate as a supporting electrolyte, no change in the difference of the halfwave potentials has been observed.

Table II. Difference of $E_{1/2}$ Ferrocene/Bisdiphenylchromium(I) Iodide as Function of the Concentration of the Supporting Electrolyte.

Conc. TEAP [mol/l]	$\Delta E_{1/2}$[V]
5×10^{-3}	1.12
2.31×10^{-2}	1.12
4.79×10^{-2}	1.11
8.39×10^{-2}	1.11
1.15×10^{-1}	1.11
1.37×10^{-1}	1.11
1.59×10^{-1}	1.11

Experimental data in the solvents studied have been summarized in Table III. It can be seen that the slope of the logarithmic analysis has, within the experimental error of ± 2 m V, the theoretical value of 59 m V for a reversible one electron reaction. This, together with the coulometric value of 1 for the electrode reaction indicates a reversible electrode process in all the solvents (except water). This has been confirmed with the Kalousek technique. A considerable shift of the $E_{1/2}$, depending on the nature of the solvent can be observed and this phenomenon will be discussed in detail later.

The diffusion currents allow an approximate check on Walden's rule:

$$\Lambda_\infty \eta = \text{const.}$$

The polarographically determined diffusion coefficients have been used in the Nernst equation to get a value for

$$D_\infty = \frac{RT}{nF^2}\Lambda_\infty$$

Although the diffusion coefficients obtained from the Ilkovič equation are subject to an experimental error of ± 10% and in any case are not exactly D_∞ values, it

Table III. Polarographic and Voltammetric Data of the Reduction $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ in Several Solvents.

Solvent	$E_{1/2}$ *vs.* BBCr(I) [V] $c_{TEAP} = 0.1$ mol/l	Log. Analysis [mV]	$D \times 10^6$ [cm^2sec^{-1}]	η_{25} [cP]	$\Lambda \eta$	ε
NMP	-0.35_2	59	1.64	1.66_6	0.10_3	32.0
DMF	-0.30_9	59	2.41	0.80_2	0.07_2	36.1
AN	-0.27_6	58	16.07	0.34_5	0.20_8	38.0
DMSO	-0.27_4	60	1.44	1.99_6	0.10_8	45.0
DMTF	-0.21_8	60	1.65	1.82_8	0.11_3	51.2
PDC	-0.17_3	59	1.77	2.51	0.16_7	69.0
NM	-0.07_1	60	6.05	0.62_0	0.14_1	35.9
EtOH	$+0.29_7{}^a$	60	2.50	1.07_8	0.10_1	24.3
MeOH	$+0.46_8$	61	7.01	0.54_7	0.14_4	32.6
H_2O	+0.95			0.89_{04}		78.5

[a] Extrapolated value from PDC/EtOH mixtures; value for an ethanolic solution, saturated with TEAP (1.34×10^{-2} mol/l): +0.344 V.

was of interest to find out what the Walden product would be in the solvents studied. The variation of the values for the Walden product shown in Table III has to be considered as reasonable under the circumstances indicated.

The variation of halfwave potentials in solvent mixtures is also of interest. We have selected four systems, namely PDC/EtOH, PDC/MeOH, PDC/water and AN/water for more detailed studies. The mixtures with PDC were always commenced with pure PDC, a stepwise addition of EtOH, MeOH and water respectively followed. The strong influence of the addition of another solvent on the $E_{1/2}$ is shown in Figure 2 and Figure 3. The measurements in the system PDC and water were carried out until saturation of PDC with water. It can be seen in Figure 2 that there is a shift in the $E_{1/2}$ to more positive values upon addition of either EtOH, MeOH or water. The shift is the stronger the more positive the $E_{1/2}$ in the pure solvent. This effect was also observed in the mixture of AN with water. The reduction in all solvent mixtures was found to be, as in the pure solvents, a reversible one. Acetone, ether, dioxane, tetrahydrofurane and dimethoxyethane could not be used as solvents since the tetraethylammonium hexacyanoferrate(III) was completely insoluble in them.

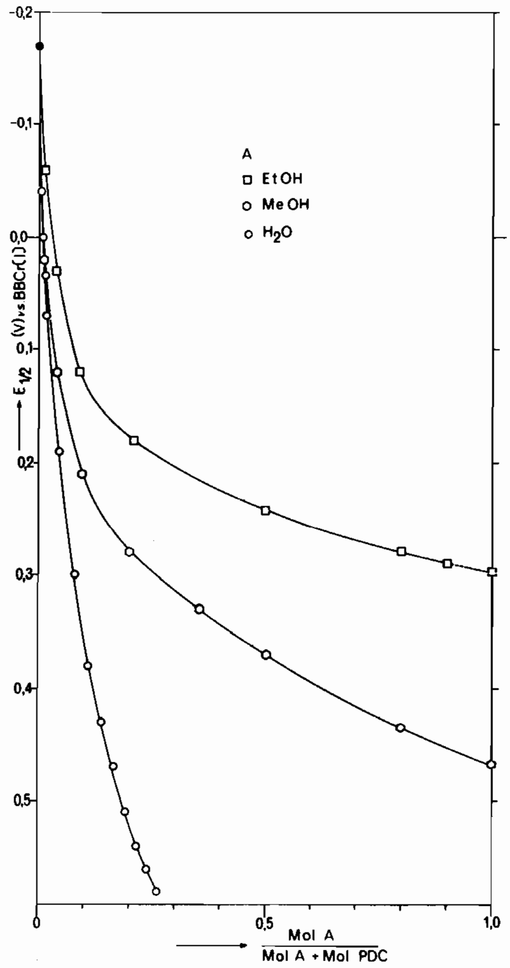

Figure 2. Halfwave potentials of the reduction of $(Et_4N)_3Fe(CN)_6$ as a function of the ratio mol solvent A to mol solvent A and mol propylenediolcarbonate (A: water, methanol, ethanol).

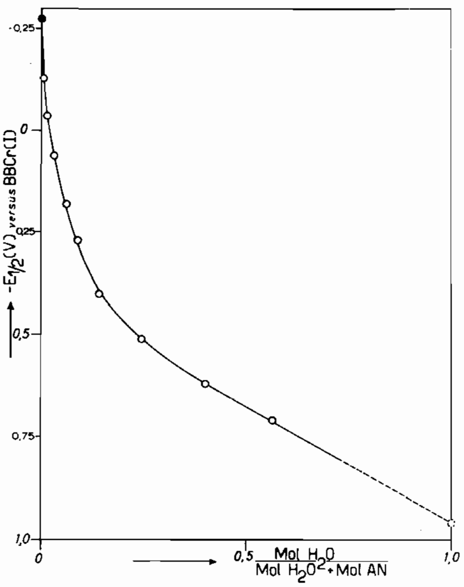

Figure 3. Halfwave potentials of the reduction of $(Et_4N)_3Fe(CN)_6$ as a function of the ratio mol water to mol acetonitrile and mol water.

Discussion

Among possible explanations for the shift of the $E_{1/2}$ in the various solvents we prefer the model of acceptor–donor interactions between the anionic species and the solvent molecules. The nitrogen atoms in both the trivalent iron and the divalent iron complex could in theory act as electron pair donors, although the donor properties of the N-atoms in the hexacyanoferrate(II) ion are much stronger than those of the hexacyanoferrate(III) ion. The Fe(II) is a much weaker electron acceptor than the trivalent iron and is furthermore a much stronger π-electron pair donor. The donor–acceptor interactions on the part of the *divalent* iron complex can therefore be considered as predominantly responsible for the observed effects. This assumption is supported by NMR, Raman and IR measurements on the crystals and in aqueous solutions. A very strong tendency of the hexacyanoferrate(II) to form hydrogen bonds has been observed[15–19], whereas no such bonds were observed with the hexacyanoferrate(III). Shriver has been able to prepare an addition compound of BF_3 with the $K_4Fe(CN)_6$[20] but no such compound could be prepared with $K_3Fe(CN)_6$. The system studied therefore consists of (i) an oxidized form of the depolarizer, the N atoms of which have only very weak donor properties and will not differentiate too much between the solvents, and (ii) a reduced form which contains N atoms with strong donor properties. The $[Fe(CN)_6]^{4-}$ anion will therefore be stabilized by interaction with the solvent, which in turn will lead to a shift of the $E_{1/2}$ to more positive values with increasing acceptor properties of a solvent.

The experimentally observed shift of $E_{1/2}$ is in good agreement with the stabilization rule for anions as formulated recently[1] and may be considered as an outer sphere effect of EPA ligands[21]. The experimental data obtained in the solvent mixtures also indicate that a model based on purely electrostatic principles will not suffice. This can readily be seen in the mixtures of PDC with EtOH, MeOH and water: PDC has a dielectric constant (ε) of 69; MeOH of 32.6; EtOH of 25.1 and water of 78.5. A monotonic change of ε in the solvent mixtures should therefore lead to a similar change of the halfwave potentials and what is more, the shift of the $E_{1/2}$ will have to be in *one* direction for MeOH and EtOH and in the *other* direction for water. The experimental data, however, show a shift in one direction only, namely to positive potentials in all the three mixtures. If it is accepted that the $E_{1/2}$ is influenced by the acceptor properties of the solvent, the $E_{1/2}$ values can be used to characterize the acceptor properties of the solvents in a qualitative and possibly even in a semiquantitative way.

It is also necessary, of course, to evaluate the influence of the supporting electrolyte since the cations of the supporting electrolyte can also act as acceptors. In several papers the interaction of the cation of the supporting electrolyte and the hexacyanoferrate has been described as ion-pair formation.[15,22–24] From this work, however, an interpretation of this interaction as a donor–acceptor interaction would seem to be preferable and we consider this as an example of outer sphere complex formation. Several experiments to study the influence of the supporting electrolyte on the $E_{1/2}$ have been carried out. The concentration of the TEAP has been varied from 5×10^{-3} to $0.1M$ keeping the concentration of the depolarizer at $10^{-4}M$. Only very minute shifts of the $E_{1/2}$ have been observed up to a concentration of *ca.* $10^{-2}M$ of TEAP. Measurements at lower concentrations of the supporting electrolyte, however, are not really valid since at very low concentrations migration currents are observed. Any influence of the supporting electrolyte would only be measurable at very low concentrations which is unfortunately outside the possibilities of polarographic techniques. We are therefore now engaged in potentiometric and spectrophotometric investigations to obtain information on the influence of the supporting electrolyte on the system $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$. The influence of various salts on the redox potential of the system $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ in water has been studied intensively by Hanania *et al.*[25].

Table IV shows a comparison of the $E_{1/2}$ values, the solvent activity coefficients of Parker *et al.*[26], the Z values of Kosower[27] and the E_T values of Dimroth and Reichardt[28] of different solvents. There is also a qualitative agreement with spectrophotometric data on the solvation of the vanadylacetylacetonate anion by the respective solvents[29,30]. Although the Z values based on the charge transfer transition energy of 1-ethyl-4-carbomethoxypyridinium iodide and the E_T values based on the charge transfer energy of a pyridinium phenolbetaine have been adopted as an empirical measure of the "polarity" of a solvent, the same order of solvents on the $E_{1/2}$ (hexacyanoferrate), solvent activity coefficient, E_T and Z scale is also observed. This leads to the conclusion that E_T and Z values predominantly represent the acceptor properties of a solvent. This would also explain the "abnormalities" of solvents such as DMF, DMSO, AN and acetone from the point of view of the "polarity"

Table IV. E_T, Z, Solvent Activity Coefficients and $E_{1/2}$ (hexacyanoferrate) of Various Solvents.

Solvent	E_T [kcal/mol][28]	Z [kcal/*Mol*][27]	Solvent Activity Coefficient (25° C)[26]	$E_{1/2}$
NMP			1.5	-0.35_2
DMF	43.8	68.5	0.9	-0.30_9
AN'	46.0	71.3	0.0	-0.27_6
DMSO	45.0	71.1	0.0	-0.27_4
DMTF	–	–	–	-0.21_8
PDC	46.6	–	–0.1	-0.17_3
NM	46.3	–	–2.3	-0.07_1
EtOH	51.9	79.6	–3.5	$+0.29_7{}^{+}$
MeOH	55.5	83.6	–4.4	$+0.46_8$
H_2O	63.1	94.6	–6.4	+0.95

[a] Extrapolated.

concept[27,28], since the acceptor properties of these solvents are modest compared with their donor properties. The solvent activity coefficient for the chloride ion obtained by means of an extrathermodynamic assumption should also reflect the acceptor properties of a solvent with regard to the chloride ion. The data for solvent activity coefficient in Table IV are based on AN as a reference solvent. Potentiometric measurements of the standard redox potential of the hexacyanoferrate system in several mixtures of water with aprotic and protic solvents show the same general trend[31,32]. Since the $E_{1/2}$ values are a measure of changes in the Gibb's Free Enthalpy, it would be of interest to obtain data on the corresponding changes in enthalpy.

In conclusion we express our hope that the halfwave potentials of the hexacyanoferrate system *vs.* bisbiphenylchromium(I)/bisbiphenylchromium(0) in various solvents will be useful as a semiquantitative measure of acceptor properties of solvents and may further stimulate research in this somewhat neglected field of coordinative interactions.

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