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Voltammetric Studies of Co(salen) and Ni(salen) in Nonaqueous Solvents at Pt Electrode*

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The electrochemical beahviour of the studied complexes in various solvents has been investigated at Pt electrodes. Both substances can be either oxidized or reduced to cation and anion respectively. Standard potentials and heterogeneous electron transfer rate constants were measured with cyclic voltammetry. The solvent effect on standard potentials of oxidation and reduction can be described using the donor-acceptor approach.

Introduction

A number of electrochemical studies of transition metals complexes with organic ligands have been reported [1–4]. Solvent effects on the redox potentials of complexes have been widely studied. Golding *et al.* [5] investigated the redox behaviour of iron(III) dithiocarbamates and discussed the variation in the half-wave potentials in acetone–water solutions. Gutmann, Gritzner and their coworkers have described the solvent effect on the half-wave potentials of tetraethylammonium hexacyanoferrate(III) [6] and hexacyanomanganate(III) [7], tris ethylenediamine cobalt(III) perchlorate [8] and tris(acetylacetonato)manganese(III) [9] by means of the donor-acceptor approach. Recently Ichimura and Kitagawa [10] reported linear correlations between redox properties of manganese(III), iron(III) and copper(II) 1-pyrrolidinecarbodithioate complexes and the solubility parameters of the solvents.

Salene complexes of transition metals attract considerable interest because of their physical and chemical (especially catalytic) properties [11].

The stoichiometry of most known salene complexes is M(salen) (Fig. 1) and there are some data about redox properties of these compounds.

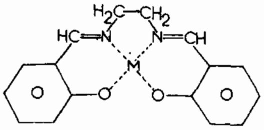

Fig. 1. Schematic representation of the structure of M(salen).

Electrochemical behaviour of Co(salen) is well known in dimethylformamide solutions [12–15]. It can be either oxidized or reduced to Co(salen)$^+$ and Co(salen)$^-$ respectively. It is also known that Ni(salen) can be reduced to Ni(salen)$^-$ in dimethylformamide and acetonitrile solutions [16, 17]. There exist some data about electrochemical properties of Cu [18, 19], Fe [20, 21] and V [22] salene complexes in dimethylformamide solutions, but virtually no data for corresponding compounds of other transition metals.

The aim of this work was a systematic study of both reduction and oxidation reactions in various solvents and an attempt to correlate the equilibrium potentials and rate constants of the electrochemical reactions with the parameters characterizing the properties of the solvents.

Experimental

Materials

Ni(salen) and Co(salen) were obtained as described in the ref. [23] and [24] respectively and purified by recrystallization from hot ethanol.

$(C_2H_5)_4NClO_4$-(TEAP) was prepared according to the procedure described in ref. [25], and recrystallized from thrice distilled water and dried at 60 °C under reduced pressure.

All solvents used (acetone-AC, acetonitrile-ACN, dimethylsulfoxide-DMSO, N-methylpyrrolidone(2)-

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*H_2salen is N,N'-bis(salicylidene)ethylenediamine.

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NMP, N,N-dimethylformamide-DMF, N,N-dimethylacetamide-DMA, propylene carbonate-PC and hexamethylphosphoracidtriamide-HMPT) were purified in a conventional manner [26].

Apparatus

The voltammetric curves were obtained using for low scan rates (up to 100 $mV{\cdot}s^{-1}$) a measuring system constructed from EP-20 potentiostat, EG-20 function generator (ELPAN-Poland) and TRP XY recorder (SEFRAM-France) or, for rapid scans (1–10 $V{\cdot}s^{-1}$), the OP-2 oscillopolarograph (TELPOD-Poland).

Measurements were performed in a conventional three-electrode cell. A bright-platinum plate with an active area of 0.093 cm^2 (as determined by electrochemical calibration with standard, aqueous solution of cadmium nitrate) was used as working electrode. The other electrodes were: a platinum wire as counter electrode and saturated aqueous calomel electrode (s.c.e.) with salt bridge (0.1 *M* KCl in aqueous solution) as reference electrode. The distance between working and counter electrodes was small (*ca.* 0.2 cm) to avoid large ohmic drops of potentials across the cell. The electrolyte resistance between these electrodes estimated for 0.1 *M* TEAP in DMF solution from impedance measurements was less than 100Ω.

All potentials cited in this paper were referred to internal reference redox system bisbiphenylchromium(I)/bisbiphenylchromium(0)/$BBCr^+$/BBCr [27], using for recalculation our own data from independent experiments.

Procedure

All measurements were carried out at 25 ± 0.5 °C. The solutions were deoxygenated with pure argon presaturated by bubbling through the solvent used. 0.1 *M* TEAP was used as supporting electrolyte. Two concentrations of metal complexes were employed: 1 and 2 mM.

Diffusion coefficients for both complexes were determined from current-voltage curves at potential scan rates 5–50 $mV{\cdot}s^{-1}$. Under these conditions the reversible behaviour was observed and diffusion coefficients could be calculated from the Randles and Ševčik equation [28] for one-electron process.

Standard heterogenous charge-transfer rate constants – k_s ($cm{\cdot}s^{-1}$) – were evaluated from the observed differences in cathodic and anodic peaks potentials (100–180 mV) on the cyclic voltammetric curves according to the relationship given by Nicholson [29]. A detailed discussion of the method as applied to determination of reaction rates of the order of k_s (0.01–0.4 $cm{\cdot}s^{-1}$) is given by Duś [30, 31]. In a few cases rate constants k_s and transfer coefficients were determined from differences in cathodic or anodic peaks and standard potentials (200–400 mV) using the Nicholson and Shain equation [32].

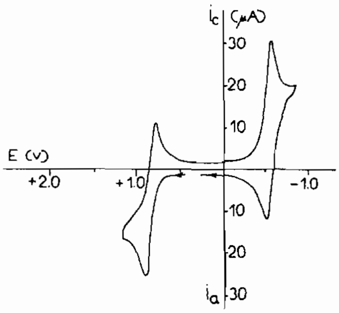

Fig. 2. Cyclic voltammogram of 2 mM Co(salen) in 0.1 *M* TEAP dimethylacetamide solution at Pt electrode (scan rate = 50 $mV{\cdot}s^{-1}$). Potentials *vs.* $BBCr^+$/BBCr.

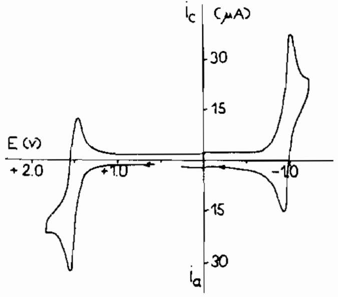

Fig. 3. Cyclic voltammogram of 2 mM Ni(salen) in 0.1 *M* TEAP dimethylacetamide solution at Pt electrode (scan rate = 50 $mV{\cdot}s^{-1}$). Potentials *vs.* $BBCr^+$/BBCr.

Results and Discussion

Co(salen) can be oxidized or reduced, in DMF solutions, to $Co(salen)^+$ and $Co(salen)^-$ respectively, as mentioned above. The same phenomena have been observed in all used solvents (see Fig. 2).

Ni(salen) can be reduced to $Ni(salen)^-$ in all studied solvents, as described in refs. [16, 17] for DMF and ACN solutions. In strongly basic solvents simple one-electron oxidation of Ni(salen) to $Ni(salen)^+$ can also be observed (Fig. 3).

In solvents which interact weakly with cations (ACN, AC and PC) the anodic process does not produce the reversible cyclic voltammetric system of peaks. The current of anodic process exceeds the theoretical value for one-electron diffusion limited current and is not reproducible during consequent sweeps. Evidently $Ni(salen)^+$ is not stable in these solvents and a different mechanism of electrooxidation is observed. These cases have not been studied in detail.

TABLE I. Effect of the Solvent on the Standard Potentials of Oxidation E_o^{ox} of Co(salen) and Ni(salen). Potentials *vs.* BBCr⁺/BBCr.

Solvent	DN	E_o^{ox}(Ni(salen))[a]	E_o^{ox}/(Co(salen))[a]
ACN	14.1	–	+0.930
PC	15.1	–	+1.013
AC	17.0	–	+1.000
DMF	26.6	+1.615	+0.813
NMP	27.3	+1.581	+0.815
DMA	27.8	+1.514	+0.900
DMSO	29.8	+1.525	+0.717
HMPT	38.8	+1.378	+0.728

[a] All potentials in volts (V).

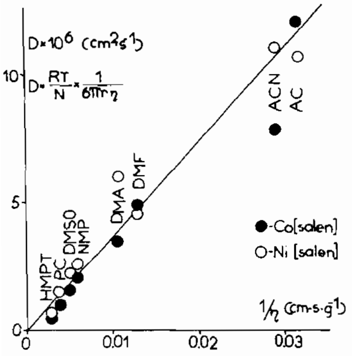

Fig. 4. Diffusion coefficients (D) of Ni(salen) and Co(salen) as function of the reciprocal of viscosity of the solvents (η). Solid line corresponds to the radius of molecule r = 5.87 A.

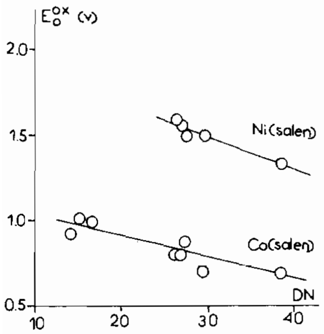

Fig. 5. Standard potentials of oxidation E_o^{ox} of Ni(salen) and Co(salen) as functions of donor numbers DN of the solvents. Potentials *vs.* BBCr⁺/BBCr.

TABLE II. Effect of the Solvent on the Standard Potentials of Reduction E_o^{red} of Co(salen) and Ni(salen). Potentials *vs.* BBCr⁺/BBCr.

Solvent	AN	E_o^{red}(Ni(salen))[a]	E_o^{red}(Co(salen))[a]
HMPT	10.6	−1.005	−0.622
AC	12.5	−0.995	−0.698
NMP	13.3	−0.908	−0.593
DMA	13.6	−0.988	−0.550
DMF	16.0	−0.843	−0.460
PC	18.3	−0.920	−0.535
ACN	18.9	−0.943	−0.520
DMSO	19.3	−0.800	−0.442

[a] All potentials in volts (V).

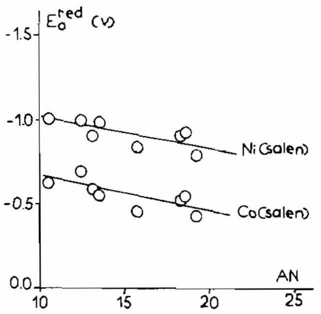

Fig. 6. Standard potentials of reduction E_o^{red} of Ni(salen) and Co(salen) as function of acceptor numbers AN of the solvents. Potentials *vs.* BBCr⁺/BBCr.

Diffusion coefficients of nickel and cobalt complexes with salene ligand are similar in most cases (see Fig. 4). For both complexes linear relationship of the diffusion coefficients (D) with the reciprocal of viscosity of the solvents (η) was found. These results were compatible with the assumption of one-electron oxidation and reduction processes in these solvents.

The standard potentials of the oxidation E_o^{ox} and the reduction E_o^{red} of the Co(salen) and Ni(salen) complexes were found to vary appreciably in different solvents. They are listed in the Tables I and II, together with the donor number DN and the acceptor number AN of the solvents.

We found approximately linear relationships between E_o^{red} and acceptor number, as well as between E_o^{ox} and donor number (*cf.* [15]). These correlations are shown on Figs. 5 and 6.

These results can be discussed on the basis of the donor-acceptor concept [33] for solvent–solute interactions between cation M(salen)⁺ or anion M(salen)⁻ and solvent molecules. The changes of E_o^{red} or E_o^{ox} with the changes of AN or DN indicate that the energies of solvation of cation M(salen)⁺ and anion M(salen)⁻ respectively are greater than those of neutral molecules M(salen).

TABLE III. Effect of the Solvent on the Standard Rate Constants of Electrode Processes of Ni(salen) and Co(salen).

Solvent	$k_s \times 10^2 (cm \cdot s^{-1})^a$			
	oxidation		reduction	
	Ni(salen)	Co(salen)	Ni(salen)	Co(salen)
AC	–	2.86	3.07	9.63
ACN	–	2.60	3.23	7.70
DMF	1.87	0.62	1.64	5.17
DMA	0.90	1.41	1.56	1.92
DMSO	0.34	0.95	1.22	1.30
NMP	0.43	0.44	0.55	0.51
PC	–	0.13	0.43	0.99
HMPT	0.02	0.13	0.40	0.45

[a] Values of the standard rate constants were estimated within an error (30–40%) having its origin in the error of measurement of potential (including the ohmic potential drop).

To check the possible influence of ion-pair formation the effect of concentration of supporting electrolyte on E_0^{red} and E_0^{ox} has been studied. Both Ni and Co complexes were studied in ACN and DMF solutions containing 0.05–0.5 *M* TEAP and no effect has been observed. Thus the deviations from straight lines presented on Figs. 5 and 6 could not be interpreted by interactions of molecules of complexes or corresponding ions with cation or anion of supporting electrolyte. It seems that these deviations are related only to rather crude approximations in the model of solvent–solute interactions using donor and acceptor numbers for quantitative interpretation.

The problem of increasing interest in the literature during recent years is the effect of the solvent on kinetics of electrode processes. Until now no simple correlation between standard rate constants and parameters characterizing the solvents has been found. This problem was recently discussed by Sahami and Weaver [34] with rather pessimistic conclusions. However there is one encouraging example – the results obtained by Elzanowska, Borkowska and Galus [35] on the electrode reaction Eu(III)/Eu(II) where the corrected rate constants, after subtracting the contribution of the reorganisation energy in the outher sphere (from the Marcus theory [36]), seems to correlate well with the donor numbers of the solvents.

It seemed interesting to compare the kinetics of the reactions M(salen)/M(salen)$^+$ and M(salen)/M(salen)$^-$ in various solvents. In many cases the reaction was found to be a rapid one, with the rate constant of the order of 10^{-2} $cm \cdot s^{-1}$. In other cases the reaction was slower, but rate constants were higher than 10^{-3} $cm \cdot s^{-1}$, except for oxidation of Ni(salen) in HMPT. They are listed in Table III.

No simple correlation with donor or acceptor numbers of the solvents could be found and the reaction rate could not be interpreted using simple Marcus theory. One regularity found was the same order in which rate constants change in each solvent for four reactions according to four subsequent columns in Table III (with two exceptions). There is also a second regularity. It follows from the comparison of Fig. 4 and Table III that the lower the viscosity of the solvent, the more rapid the electrode reaction.

However we can compare only uncorrected rate constants and doubt if the latter regularity is relevant. A serious disadvantage is that there are no data available which would enable the calculation of the potential drop in the diffuse double layer at the platinum electrode in the investigated solvents with 0.1 *M* TEAP. Thus the Frumkin [37] correction could not be introduced. Assuming that at the potentials of cathodic or anodic reactions the electrode charge is negative or positive respectively, the effect of the diffuse double layer (according to the Frumkin theory) should result in increase of the reaction rate with increasing electrolyte concentration, increasing with the electrode charge. Preliminary measurements indicate that the electrolyte concentration influences the reaction rate in the right direction. This problem is being studied in detail and will be the subject of a further paper.

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36 See *e.g.* ref. 28 p. 71.

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