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The Polarographic Behavior of Transition Metal Compounds in Dimethylsulfoxide and N,N-Dimethylformamide. III.* Vanadium and Chromium Compounds

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Polarographic investigations were carried out on vanadium(III) chloride, vanadium(V) oxoperchlorate and chromium(III) chloride in dimethylsulfoxide and N,N-dimethylformamide; the half-wave potentials (vs. aqueous saturated calomel electrode), the nature of the limiting currents, the temperature coefficients of the half-wave potentials and the wave heights, and the reversibility or irreversibility of the electrode processes were determined in 0.1 M *solutions of tetraethylammonium perchlorate at 25.0°. VCl_3 shows reversible V^{III}–V^{II} waves, V^{IV} is irreversibly reduced to V^{II}, and $CrCl_3$ exhibits a polarographic behavior corresponding to the stepwise reduction sequence Cr^{III}–Cr^{II}–Cr^0. The electrode mechanisms, the half-wave potentials in different solvents, analytical aspects and the influence of water have been discussed.*

Introduction

In aqueous solution vanadium(V) shows two waves corresponding to V^V–V^{IV}–V^{II},[1-3] vanadium(IV) one wave at about −1.3 V due to the reduction to V^{II},[2-5] and vanadium(III) is reduced to V^{II} at more positive potentials (−0.5 to −1.0 V);[2,5-7] no further reduction of V^{II} has been observed.[2,3,7-9] Catalytic effects of vanadium solutions have been studied recently.[10,11] Electrochemical work on V_2O_5 in melts has been reported,[12-14] but polarographic investigations in organic solvents have not yet been described.

The polarographic behavior of chromium(III) compounds is well known in aqueous solution:[15-22] normally two waves are found corresponding to Cr^{III}–Cr^{II}–Cr^0. Polarographic studies on chromium have been made both in salt melts[23-27] and in certain organic solvents.[28-44] π-complexes containing chromium in a low oxidation state have also been investigated.[28-32,39] The polarographic behavior of chromium(III) perchlorate has been described in ammonia solvents,[33-36] formamide,[37,38] acetonitrile,[40,41] benzonitrile,[42] phenylacetonitrile,[42] acrylonitrile,[42] propionitrile[42] and dimethylsulfoxide,[44] and the half-wave potentials of $CrCl_3.6H_2O$ have been reported in a number of solvents *vs.* an Ag/AgCl-reference electrode:[43] water, formamide, dimethylformamide, methanol, ethanol, propanol, iso-propanol, butanol, pentanol, and ethyleneglycol have been used. $Cr(ClO_4)_3.6H_2O$ gave two waves at −0.82 V and −1.56 V in 0.1 *M* $KClO_4$ in DMSO,[44] and $CrCl_3.6H_2O$ showed two waves at −0.29 V and −1.15 V in 0.2 *M* LiCl in DMF.[43]

The following experiments carried out under strictly anhydrous conditions are part of a programme of

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studies on transition metal compounds in dimethylsulfoxide (DMSO) and N,N-dimethylformamide (DMF).[45-51]

Experimental Section

A Polariter PO 4b from Radiometer, Copenhagen, was used and the capillaries were supplied by Sargent, Chicago (t=6–12 sec.). A Kalousek commutator, according to Ralek[52] and modified after Konrad,[53] was applied for direct reversibility tests. The water content was determined using the Karl-Fischer method by means of an automatic titrator TTT 1c from Radiometer.

An aqueous saturated calomel electrode was used as reference electrode.[54] The potential drop iR, caused by the high resistance of the diaphragm and the solution, was taken into account by direct compensation which was achieved by means of an iR-Compensator E 446 of Metrohm, Herisau, using a three-electrode circuit (platinum wire or platinum sheet as auxiliary electrode), and by measurements of the resistance with a Philips PR 9501 and of the current from the polarogram. Microcoulometric experiments[55] were carried out in order to determine the number of electrons involved in an electrode process. The methods used for the determination of the nature of the electrode reactions and of the limiting currents have been described.[48] In addition, the temperature coefficient of the half-wave potential was evaluated between 20° and 40°. The measurements were carried out at 25° in 0.1 *M* solutions of tetraethylammonium perchlorate (TEAP) in DMSO or DMF, unless otherwise stated. The purification of the solvents, the preparation of the supporting electrolyte[56] and of the solutions has been described.[45,47,49]

Vanadium(III) chloride was prepared by reacting vanadium(V) oxide with disulfur dichloride.[57] Analyses (V from V_2O_5, Cl potentiometrically) gave 32.1% V (32.4% V calc.) and 56.8% Cl (67.6% calc.). Vanadium(IV) chloride was obtained by chlorination of VCl_3,[58] but it reacted both with DMSO and DMF and could therefore not be used for polarographic purposes.

An aqueous solution of vanadium(IV) oxoperchlorate was obtained by reacting vanadium(IV) oxosulfate and barium perchlorate and filtering off the precipitate. This solution was added to an excess of DMSO or DMF; the blue crystals which separated were washed with ether and dried *in vacuo*.

Anal. Calcd. for $VO(ClO_4)_2.5DMSO$: ClO_4, 30.4; C, 18.35; H, 4.57; S, 24.4. Found: ClO_4, 31.0; C, 18.5; H, 4.6; S, 25.1.

Anal. Calcd. for $VO(ClO_4)_2.5DMF$: ClO_4, 31.5; C, 28.5; H, 5.55. Found: ClO_4, 32.3; C, 28.1; H, 5.4.

Anhydrous chromium(III) chloride was prepared by dehydration of $CrCl_3.6H_2O$ by means of $SOCl_2$;[59] the green solutions turned red-violet on heating.

Results

The numerical results are given in Table I and II.

(a) *Vanadium(III) chloride.* The two waves found in DMSO shifted to more negative potential values with increasing concentration: at c= 1.10 m*M* $E_{1/2}$ values are −0.77 and −0.86 V, respectively. The ratio of the wave heights does not change in the concentration range from 5×10^{-5} to 5×10^{-3} *M*, and the limiting currents are diffusion-controlled in this region. In DMF the limiting current of the full wave height is controlled by diffusion from 5×10^{-5} to 3×10^{-3} *M*. The ratio of the wave heights changes with concentration: 1.5:1 at c = 0.10 m*M* and 1:1.5 at c = 0.70 m*M* (Figure 1). The $E_{1/2}$ of the first wave shifts with increasing concentration to more negative values: −0.64 at c = 0.70 m*M*.

By comparing the full wave height of VCl_3 with those of K^+, Tl^+ and Pb^{2+}, a one-electron process is indicated in both DMSO and DMF. Traces of water or oxygen change the polarograms considerably: waves due to the reduction of VO^{2+} or HCl appear and if enough oxygen is present in the solution, the polarographic behavior characteristic of vanadyl(IV) compounds is observed.

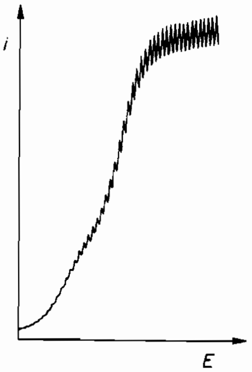

Figure 1. VCl_3 in DMF.

(b) *Vanadium(IV) oxoperchlorate.* The currents are diffusion-controlled in the range from 5×10^{-5} to 5×10^{-3} *M*. In DMSO traces of water shift the $E_{1/2}$ of the first wave to more positive values, but the limiting current does not change up to 4% of water. In DMF two further waves appear at −1.76 and −2.52 V, the

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Table I. Polarographic Data of Vanadium and Chromium Compounds in Dimethylsulfoxide

Compound	$E_{1/2}$ (V)	Temperature coefficient of $E_{1/2}$ (mV/°C)	Tomeš slope (V)	Slope of the log. analysis (V)	Temperature coefficient of i_D (%/°C)	Ratio of wave heights	Remarks
VCl_3	−0.74	1.4	−0.055	0.059	1.0	1 : 1	at c = 0.37 m*M*
	−0.84	1.6	−0.057	0.060	1.0		
$VO(ClO_4)_2.5DMSO$	−1.41	1.6	−0.10	0.108	1.4	3 : 1	
	−2.00	2.5	−0.22	0.241	0.2		
	−0.76	2.2	−0.055	0.060	1.1		
$CrCl_3$	−0.92	3.3	−0.080	0.082	1.9	2 : 1 : 3	at c = 0.25 m*M*
	−1.58	4.5	−0.15	0.160	1.2		

Table II. Polarographic Data of Vanadium and Chromium Compounds in N,N-Dimethylformamide

Compound	$E_{1/2}$ (V)	Temperature coefficient of $E_{1/2}$ (mV/°C)	Tomeš slope (V)	Slope of the log. analysis (V)	Temperature coefficient of i_D (%/°C)	Ratio of wave heights	Remarks
VCl_3	−0.62	1.8	−0.054	0.058	0.8	1 : 1	at c = 0.16 m*M*
	−0.76	1.3	−0.059	0.060	0.9		
$VO(ClO_4)_2.5DMF$	−1.40	0	−0.060	0.062	0.7		
	−0.735	1.9	−0.057	0.060	1.2		
$CrCl_3$	−0.915	2.1	−0.108	0.115	1.1	1 : 1 : 2	
	−1.54	1.6	−0.070	0.073	0.7		

full wave height of which does not exceed one quarter of the limiting current. The wave at −1.76 V is kinetically controlled by diffusion and by the rate of a chemical reaction; the wave at −2.52 V is due to a catalytic process. This can be seen from the $i-\sqrt{h}-$relationships and the high temperature coefficients of the limiting currents (3.0 and 4.0%/°C). The wave height of the most negative wave decreases with increasing mercury height and disappears finally. On addition of water (up to 2%) 4 waves appear −1.40, −1.76, −2.03 and −2.52 V.

From the comparison of the wave height with those of K^+, Tl^+ and Pb^{2+} the number of electrons involved in the electrode process is found to be two in both solvents.

(c) *Chromium(III) chloride.* The half-wave potentials of the first and second wave shift to more positive values with increasing concentration. In DMSO these two waves (Figure 2) are found at −0.74 and −0.94 V, respectively, at c = 1.10 m*M*. At c<0.5 m*M* a small wave appears at −2.09 V the wave height of which is independent of concentration and temperature. The temperature coefficient of the $E_{1/2}$ is 1.5 mV/°C.

Microcoulometric controlled potential electrolysis at −1.15 V indicates that n is about 1.5 for the sum of the two more positive waves. Addition of water up to 1% does not affect the polarograms; at higher water concentrations the half-wave potentials are shifted and the wave heights decreased: at 10% of water waves are found at −0.69, −0.89, −1.58 and 2.09 V. The ratio of the wave heights and the differences of $E_{3/4}$ and $E_{1/4}$ have not changed.

In DMF a maximum is found at −2.2 V. The microcoulometric determination of n at −1.15 V gave 1.4. If water is added, the maximum becomes higher but no other changes occur up to 0.5% of water. In both DMF and DMSO n was found to be 3 for the full wave height by comparison with those of K^+, Tl^+ and Pb^{2+}. Controlled potential electrolysis at −1.8 V in small volumes gave n = 1 for the sum of first and second wave and 3 for the whole limiting current. The limiting currents at −1.2 and −1.8 V are controlled by diffusion in the range from c = 5×10^{-5} to 5×10^{-3} *M*.

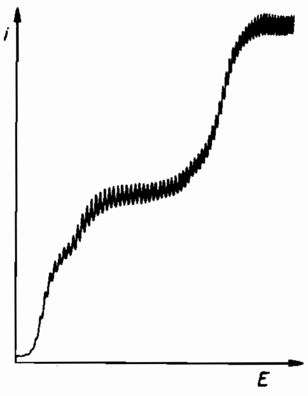

Figure 2. $CrCl_3$ in DMSO.

Discussion

The reduction of VCl_3 proceeds to the bivalent state only, since the standard potential of $V^{II}-V^{I}$ is extremely negative. The reduction steps to V^{II} occur reversibly at a potential close to the standard potential of $V^{III}-V^{II}$ in aqueous solution. The two waves might be due to the reduction of two different complexes: an unsymmetrical complex is reduced at a more positive potential than a symmetrical one provided that they have the same structure. The electrode processes occurring could be in analogy to aqueous solutions:

$$[V^{III}Cl_2S_4]^+ \overset{1e}{\rightleftharpoons} [V^{II}Cl_2S_4] \text{ and}$$

$$[V^{III}S_6]^{3+} \overset{1e}{\rightleftharpoons} [V^{II}S_6]^{2+}$$

The reduction $V^{III}-V^{II}$ occurs at a more positive potential than $V^{IV}-V^{II}$ in aqueous solution and the process V^{IV}–V^{III} is responsible for the high overvoltage. The reduction wave of VO^{2+} can be shifted to more positive potentials by hydrochloric acid, since the formation of chloro complexes and not only protonation of the VO^{2+} ion causes the decrease of the overvoltage.[60] The influence of DMSO- and DMF-complexes in this overvoltage is negligibly small.

$CrCl_3$ is reduced according to Cr^{III}–Cr^{II}–Cr^{0} in both solvents, and the first two waves correspond to the reduction to Cr^{II} as indicated by the microcoulometric experiments. The wave for the process Cr^{II}–Cr^{0} is found at similar potentials as in other solvents. The ratio of the wave heights, however, is not in agreement with the Cr^{III}–Cr^{II}–Cr^{0} process since it is 1:1 instead of 1:2. Different diffusion coefficients cannot be held responsible, since only Cr^{III} is diffusing to the electrode. It is unlikely that the two waves due to Cr^{III}–Cr^{II} correspond to the successive reductions of two solvate complexes as is assumed in the case of V^{III}–V^{II}, because the ratio of their heights does not change with depolarizer concentration. It is also known that $[CrCl_2(DMSO)_4]^+$ is the main species present in solutions of $CrCl_3$ in DMSO.[61]

The following reaction mechanism may be suggested:

$$\begin{tikzcd}
Cr_a^{III} \arrow[r, shift left, "1e"] & Cr^{II} \arrow[l, shift left] \arrow[r, "2e"] \arrow[d, "s"] & Cr^{0} & \\
 & Cr_b^{III} \arrow[r, "1e"] & Cr^{II} \arrow[r, "2e"] & Cr^{0}
\end{tikzcd}$$

Cr_b^{III} is formed from Cr^{II} by a chemical reaction and therefore the Cr^{III}–Cr^{II} process can be explained by assuming two different electroactive Cr^{III} species [Cr_a^{III} and Cr_b^{III} in the above scheme]. At more negative potentials the chemical reaction becomes negligible because of fast electrochemical reduction to Cr^{0}.

This mechanism would, however, require a limiting current which should at least partly be reaction rate controlled; furthermore the temperature coefficients of the wave heights are too small for an electrode process in which a chemical reaction should play a prominent role. The same consideration precludes an analogous reaction with traces of water or impurities or a disproportionation according to $3Cr^{II} \rightleftharpoons 2Cr^{III} + Cr^{0}$. It is assumed, however, that Cr^{II} reacts only with coordinated and not with uncoordinated solvent molecules and Cr_b^{III} exchanges the ligands slowly enough to avoid penetration of other solvent molecules into the coordination sphere under polarographic conditions. Thus no catalytic electrode process would take place and diffusion would be the rate-limiting step as has actually been found by experiment. This mechanism would also be in agreement with the results of microcoulometric experiments at −1.15 V, which gave too high values for n: in measurements over a long period of time the reactions $Cr^{II} \rightarrow Cr_b^{III}$ and the exchange of ligands have time to occur.

The reduction of Cr_a^{III} (probably $[CrCl_2S_4]^+$) occurs reversibly in both solvents, while Cr_b^{III} is reduced irreversibly at a slightly more negative potential.

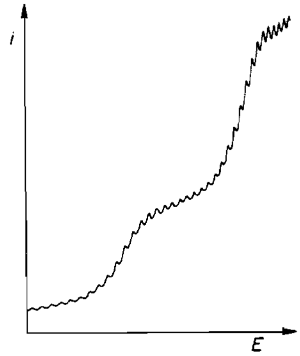

Figure 3. Simultaneous determination of VCl_3 and $VO(ClO_4)_2 \cdot 5DMSO$ in DMSO.

It has been pointed out recently[62] that the donor number of a solvent is a valuable criterion for its solvation properties; a relationship between donor number and polarographic $E_{1/2}$ has been detected.

This relationship is also confirmed by the present results: the half-wave potentials in DMSO and DMF are more negative than in water according to the donor number and not to the dielectric constant of these solvents (Table III and IV). Comparisons were made by using the rubidium scale.[62] Below (in italics type) are given the potentials *vs.* the $E_{1/2}$ of Rb.

Table III.

	Dielectric constant	Donor number
H_2O	81	18
DMSO	48.9	29.8
DMF	36.7	27.6

Table IV.

	$E_{1/2}$ in H_2O	$E_{1/2}$ in DMF	$E_{1/2}$ in DMSO	Electrode process
		−.062	−0.74	
		1.40	*1.29*	V^{III}–V^{II}
VCl_3	−0.51	−0.76	−0.84	
	1.61	*1.28*	*1.19*	
	−0.85	−1.40	−1.41	V^{IV}–V^{II}
VO^{2+}	*1.27*	*0.62*	*0.62*	
		−0.74	−0.76	
		1.28	*1.27*	Cr^{III}–Cr^{II}
$CrCl_3$	−0.81	−0.92	−0.92	
	1.31	*1.10*	*1.11*	
	−1.50	−1.54	−1.58	Cr^{II}–Cr^{0}
	0.62	*0.48*	*0.45*	

On account of the wide range of concentrations in which the Ilkovič-equation is valid, analytical applications are possible. V^{III} and VO^{2+} can be determined simultaneously (Figure 3), but strictly anhydrous and oxygen-free conditions are necessary. V^{III} can be separated from Cr^{III} or from Ti^{III}.[49] Ti^{III} and Cr^{III} can also be determined simultaneously in these solvents.

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