Electrochemistry of Vanadium–Salene Complexes in Dimethylformamide Solutions*

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Salene complexes of transition metals attract considerable interest because of their physical and chemical properties [1]. Most known vanadium–salene complexes have stoichiometry: VO(salen) [2] and V(salen)Cl$_2$ [3]. There are no data about redox properties of these compounds.

Electrochemical behaviour of Co(salen) is well known [4–7]. It can be either oxidized or reduced to Co(salen)$^+$ and Co(salen)$^-$ respectively. There exist some data about electrochemistry of Cu [8, 9], Ni [9, 10] and Fe [11] salene complexes and virtually no data for corresponding compounds of other transition metals.

Only one reduction wave was observed on polarograms of V(salen)Cl$_2$ in 0.1 M (C$_2$H$_5$)$_4$NClO$_4$ dimethylformamide solutions (Fig. 1).

Diffusion coefficients of vanadium and cobalt complexes with salene ligand are presumably very similar. This suggests that the reduction of V(IV) salene complex is a one-electron process (as it is in the case of Co(salen)) and V(III) compound is formed on electrode. Slope of the wave (E$_{1/4}$ – E$_{3/4}$) corresponds to the theoretical value for one-electron reversible process (58 and 56 mV respectively). The same results were observed during polarography of V(salen)(ClO$_4$)$_2$ in 0.1 M (C$_2$H$_5$)$_4$NClO$_4$ dimethylformamide solutions. Solutions of V(salen)(ClO$_4$)$_2$ have been obtained by mixing of V(salen)Cl$_2$ and AgClO$_4$ solutions (AgCl is formed instantaneously and quantitatively). E$_{1/2}$ of reductions waves of chloride and perchlorate complexes have this same value = –0.450 V *vs.* s.c.e.. These facts suggest that V(salen)Cl$_2$ and V(salen)(ClO$_4$)$_2$ are completely dissociated in dimethylformamide solutions and that V(salen)$^{+2}$ indeed is reduced on mercury electrode (eqn. 1):

$$V(salen)^{+2} + e \rightleftarrows V(salen)^+ \qquad (1)$$
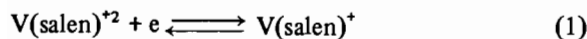
Reversibility of reaction (1) has been further supported by cyclic voltammetry on platinum electrode: E$_{pc}$ = –0.480 V *vs.* s.c.e., E$_{pa}$ – E$_{pc}$ = 56 mV and i$_{pa}$/i$_{pc}$ = 0.98 at scan rate V$_p$ = 50 mV/s. Cyclic voltammogram is shown on Fig. 1.

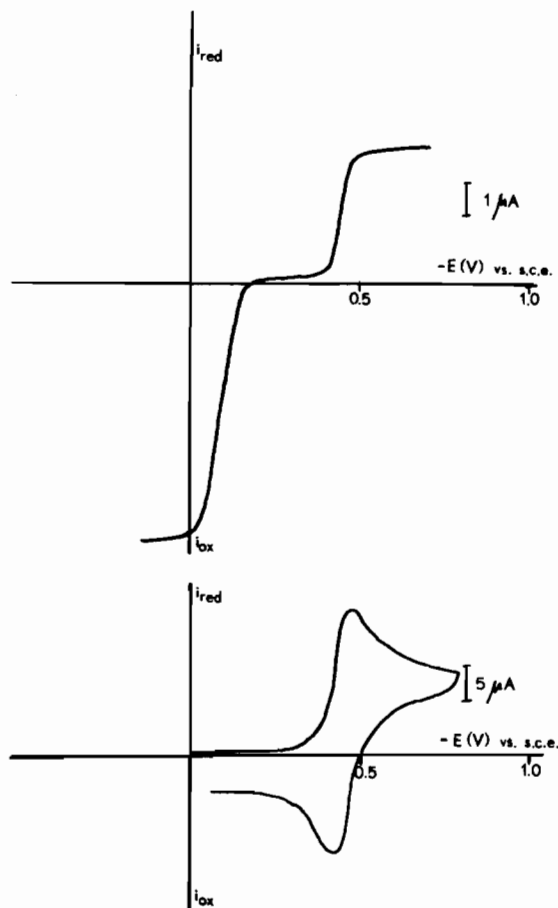
*H$_2$salen is N,N′-bis(salicylidene)ethylenediamine.

Fig. 1. Polarogram and cyclic voltammogram (Pt electrode, V$_p$ = 50 mV/s) of 1 mM V(salen)Cl$_2$ in 0.1 M (C$_2$H$_5$)$_4$NClO$_4$ dimethylformamide solutions (anodic wave on polarogram corresponds to oxidation of mercury in presence of Cl$^-$ ions).

Solutions of V(salen)Cl$_2$ and V(salen)(ClO$_4$)$_2$ in dimethylformamide are not stable. Their colours change from deep-blue to pale-green after about ten minutes and a new wave (at potentials about –1.3 V *vs.* s.c.e.) develops. This is accompanied by decrease of wave at –0.450 V *vs.* s.c.e. The products of this reaction have not been studied and their nature is unknown.

VO(salen) complex (in 0.1 M (C$_2$H$_5$)$_4$NClO$_4$ dimethylformamide solutions) is reduced at more negative potentials than V(salen)$^{+2}$ cation (see Fig. 2 and Table I). Value of limiting current and slope of wave (E$_{1/4}$ – E$_{3/4}$) = 54 mV corresponds to one-electron process.

VO(salen) (in 0.1 M (C$_2$H$_5$)$_4$NClO$_4$ dimethylformamide solutions) is also reduced on platinum electrode: E$_{pc}$ = –1.550 V *vs.* s.c.e. and E$_{pc/2}$ – E$_{pc}$ = 50 mV at V$_p$ = 50 mV/s (Fig. 2).
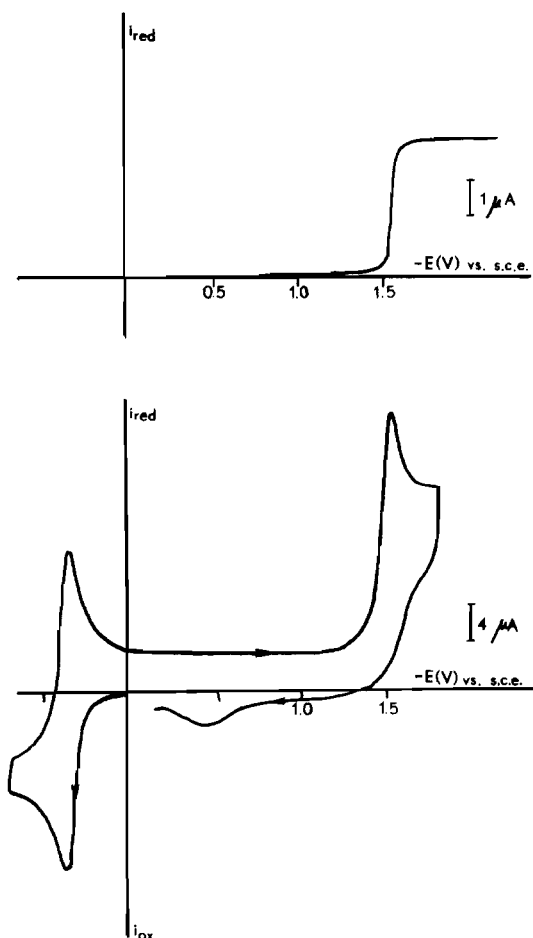
Fig. 2. Polarogram and cyclic voltammogram (Pt electrode, V_p = 50 mV/s) of 1 mM VO(salen) in 0.1 M $(C_2H_5)_4NClO_4$ dimethylformamide solutions.

Effect of scan rate V_p (in the range from 1 to 500 mV/s) on electroreduction of VO(salen) has also been studied. No anodic peak (in the region of -1.500 V *vs.* s.c.e.) was observed on cyclic voltammetry curve at all scan rates used. It suggests that the product of electroreduction of VO(salen) can be unstable. Potentials E_{pc} and $E_{pc/2}$ are shifted to more negative values when V_p is increasing.

$$\frac{\partial E_{pc}}{\partial logV_p} = -30 \text{ mV and } \frac{\partial E_{pc/2}}{\partial logV_p} = -28 \text{ mV}$$

Small anodic peaks at potential -0.420 V *vs.* s.c.e. (at the scan rates used) suggest that $V(salen)^{+2}$ is produced during electroreduction of VO(salen). No effect of concentration of depolaryzer (in the range from 10^{-4} to $2 \cdot 10^{-3}$ M) on potentials E_{pc} and $E_{pc/2}$ is observed in this case. These facts suggest that the process of electroreduction of VO(salen) is EC type [12]. Rate constant of the chemical reaction must be greater than 10 s^{-1}; no anodic peak corresponding to

reduction peak is observed at the scan rate = 500 mV/s [12].

In the case of electroreduction of VO(salen) the effect of cation of supporting electrolyte has also been studied and it is shown in Table I.

TABLE I. Effect of Supporting Electrolyte on Half-Wave Potentials of Reduction of VO(salen) on Dropping Mercury Electrode in Dimethylformamide Solutions $(c_d = 1 \text{ mM})$.

Supporting electrolyte	$E_{1/2}$ (V) *vs.* s.c.e.
0.1 M $(C_2H_5)_4NClO_4$	-1.555
0.1 M KClO$_4$	-1.537
0.1 M NaClO$_4$	-1.504
0.1 M LiClO$_4$	-1.475

Data from Table I suggest that cation M^+ of supporting electrolyte is one of the reagents in the reaction of electroreduction of VO(salen). It is known that VO^{+2} cation is reduced in water solutions and the product of electrolysis reacts further with H^+ forming V^{+3} ion [13]. The reaction of electroreduction of VO(salen) can be schematically described as follows:

$$VO(salen) + e \xrightarrow{\quad H^+ \quad} V(salen)^+ \qquad (2)$$
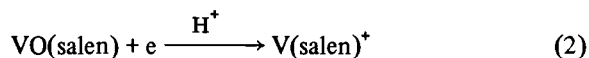
VO(salen) can be oxidized on platinum electrode in 0.1 M $(C_2H_5)_4NClO_4$ dimethylformamide solutions: E_{pa} = +0.380 V *vs.* s.c.e. This process is completely reversible: $E_{pa} - E_{pc}$ = 55 mV and i_{pc}/i_{pa} = 1.00 at V_p = 50 mV/s and can be described as:

$$VO(salen) - e \xrightleftharpoons{\quad\quad} VO(salen)^+ \qquad (3)$$

No reduction of V(salen)$^+$ is observed in dimethylformamide solutions. This fact suggests that low-oxidation states of vanadium (V(II), V(I) and V(0)) are not stabilised by salene ligand. This is a different behaviour in comparison to Co(I), Ni(I) and Fe(I) salene complexes.

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