

A POLAROGRAPHIC STUDY OF ANODIC PROCESSES IN ACETONITRILE: THE INFLUENCE OF CHLORIDE AND OF A MACROCYCLIC POLYETHER

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Received January 14th, 1975

In acetonitrile the chloride ion gives an anodic wave which corresponds to formation of a complex with mercury and is distorted by adsorption of the reaction product. In the presence of dibenzo-18-crown-6 the *I-E* curve of anodic dissolution of mercury is shifted to more negative potentials due to formation of a complex with Hg(I). The stability constant has the value $K_{\text{HgX}} = 1.36 \cdot 10^3$.

In recent years there is a growing interest in electrochemistry of non-aqueous solvents among the most important of which belongs acetonitrile. Besides other applications acetonitrile is an attractive solvent for polarographic investigations¹. The advantageous solvation conditions in acetonitrile result in a wider range of electrode potentials useful for polarography²⁻⁵. Acetonitrile has shown a good solvent for some organic species, particularly for macrocyclic ligands capable of complex formations with alkali metal and other cations⁶⁻⁸. Numerous communications^{2,9-12} were devoted to polarography of cations in acetonitrile. The influence of anions on reduction of cations¹¹ and on the potential of anodic dissolution of mercury¹² has also been studied. However there has been made no detailed study of the polarographic behaviour of anions in anodic processes.

The aim of the present study was twofold. First we attempted to elucidate the anodic behaviour of chlorides at the dropping mercury electrode. A similar study in aqueous solution was published by Vlček¹³. Besides this we were interested in the anodic processes of macrocyclic polyethers, particularly in the possibility of formation of the complex of dibenzo-18-crown-6 with ions of mercury.

EXPERIMENTAL

For experimental polarographic measurements a dropping mercury electrode in a three-electrode system and Polarograph OH-102 (Radelkis, Budapest, Hungary) with IR-compensation were used. The *I-t* curves were measured by means of an XY-recorder BAK 4T (Aritma, Prague ČSSR) and of a potentiostat working in the range ± 40 V and ± 250 mA which was

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made in this Institute. In this case a bent capillary after Smoler¹⁴ was used. We are much obliged to Dr K. Angelis for his help during these measurements. The reference electrode was a silver-silver chloride electrode in an acetonitrile solution saturated with tetrabutylammonium chloride¹⁵. As base electrolytes acetonitrile solutions of tetrabutylammonium chloride and perchlorate were used. Before use these salts were recrystallized and dried at 70°C. Dibenzo-18-crown-6 was kindly supplied by Dr J. Petránek and Dr O. Ryba, Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, who prepared it using the Pedersen method¹⁶.

RESULTS

Typical polarogrammes of chlorides in acetonitrile are shown in Fig. 1. The polarogramme at higher concentrations of Cl^- (curve 3) looks like composed of two waves the second of which starts rather sharply at the potential about 0.3 V. At more negative potentials a well developed limiting current appears with a plateau extending to the mercury dissolution current. The log plot of the first wave has the slope $dE/d \log [(I_d - I)/I]$ equal to 60 mV which shows that a reversible process takes place in that potential range. The cyclic-voltammetric curve recorded at the polarization speed 0.1 V/s has an analogous shape. The total limiting current is directly proportional to the chloride concentration in the range from 0.1 to 5 mM. The $E_{1/2} - \log c$ dependence for the first wave is linear with the slope about 60 mV in the concentration range from 0.1 to 2 mM. The $I-t$ curves were measured at various points of the polarographic curve. For the total limiting current the dependence $\log I - \log t$ has the slope between 0.17 and 0.22 which approximately corresponds to a diffusion controlled process. At less positive potentials corresponding to the foot of the second wave this dependence is no more linear and at time values about 0.5 s a discontinuity appears on the $I-t$ curve. The slope of $\log I - \log t$ plot changes from about 0.35 to 0.25.

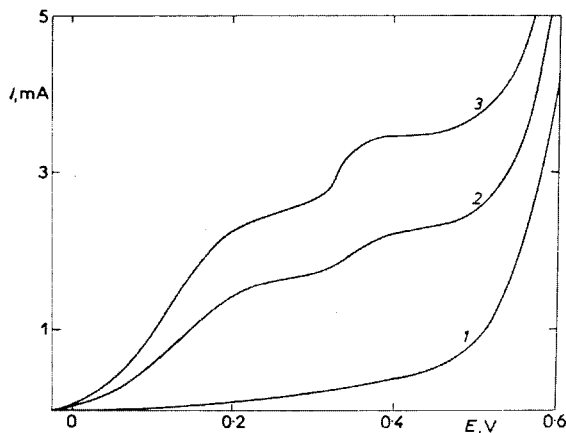


FIG. 1
Polarographic Curves Obtained
with DME in $2.5 \cdot 10^{-2} \text{M}$ Tetra-
butylammonium Perchlorate
Concentration of chloride: 1 0;
2 0.2 mM; 3 0.38 mM.

The second part of this work deals with the mercury complex of dibenzo-18-crown-6. The possibility of formation of such a complex has been already pointed out^{6,16-18}. The preceding work dealing with polarographic reduction of complexes of macrocyclic ligands was concerned only with complexes of alkali metal, ammonium and Tl(I) ions^{7,8,19,20}.

In the presence of dibenzo-18-crown-6 (further crown) the mercury dissolution potential is shifted to more negative values with increasing crown concentration. Assuming that the diffusion coefficients of the complex and of free mercury ions are approximately equal, further that only a small fraction of the crown is bound in the complex so that the crown concentration may be considered constant, then the polarographic current of mercury dissolution under influence of complex formation in the case of a reversible electrode reaction is given by equation

$$E = E_0 + (RT/zF) \ln \{I/[\kappa(1 + K_{MX}[X])]\}, \quad (1)$$

where I is the average current, K_{MX} the stability constant of the complex, $[X]$ the crown concentration, z the charge of the ion of mercury, κ the diffusion current constant. If E_1 is an electrode potential value in the absence of complex forming agent and E_2 at a concentration of complex forming agent $[X]$, both measured at the same current I then $\Delta E = E_2 - E_1$ is the shift of electrode potential due complex formation. From (1) we obtain

$$10^{-zF\Delta E/2.3RT} - 1 = K_{MX}[X]. \quad (2)$$

The divalent mercuric ion is much stronger solvated than the monovalent species so that its binding in the macrocyclic structure is less probable than Hg^+ . Thus, $z = 1$ being the most suitable choice we obtain, after inserting experimental values for ΔE and $[X]$ into Eq. (2), the average value of the stability constant $K_{MX} = 1.36 \cdot 10^3$. This quantity is near to the values for stability constants of the same crown with alkali metal ions⁶.

The assumption of complex formation of the crown with monovalent mercury ion is confirmed by the dependence of $\log I$ on E which is linear with a reciprocal slope of 58 mV (after a correction for ohmic potential drop). This correction has to be taken always into account with low permittivity solvents¹. The average value of the resistance of the electrolytic system was determined on the basis of the shift of the apparent halfwave potential of Tl^+ for two concentrations of this ion.

DISCUSSION

The first wave of chlorides in an acetonitrile electrolyte corresponds most probably to a reversible process of formation of a soluble mercury salt. The formation of the

second wave and, at the same time, of the change of the slope of the $\log I$ - $\log t$ dependence, is connected with the partial adsorption of this salt at more positive potentials. The particle adsorbed may be HgCl_3^- which is more stable in organic solvents¹².

Initially, we were also concerned with formation of crown complexes with monovalent copper ion which is stable in acetonitrile due to a specific solvation (or better to say coordination) effect in this solvent^{21,22}. However, this solvation effect is so strong that it prevents the Cu(I) ion from complexation with the crown.

The interaction of acetonitrile with mercury ions is weaker so that the existence of a 1 : 1 complex of Hg^+ with the crown is to be expected. The same may be concluded from the relationship of the crystallographic radius²³ of Hg^+ (0.125 nm) and the internal cavity of dibenzo-18-crown-6 (0.26 nm) (ref.²⁴).

The evaluation of the stability constant was based on the assumption that the crown does not form complexes with the cations of the base electrolyte due to the excessive radius of tetrabutylammonium ion in comparison with the cavity of the crown.

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