Electrochemical Reduction of Monovalent Cation Complexes of Macrocyclic Ionophores.
I. Crown Polyether Complexes

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Received September 14, 1977

The complex formation of alkali metals Na, K, Rb, Cs and of Tl(I) with cyclic polyethers ("crowns") and the stability of the complexes were studied in methanol and acetonitrile by the polarographic method. The influence of a number of members in the cycle and of substituents in the polyether ring on the stability of complexes was discussed. The character of the solvent was found to be an important factor in view of its ability to solvate the cation. In methanol where the alkali cations are solvated nearly as in water, the stability constants of sodium complexes are lower than those found in the present paper in acetonitrile. They are sometimes comparable or higher than the stability constants of cyclic polyethers with the potassium ion.

Introduction

In 1967 Pedersen [1] detected the ability of cyclic polyethers ("crowns") to form complexes with various cations, particularly of alkali metals. Since then these substances became a subject of many original papers as well as reviews (see, for example, [2–6]). These studies dealt with the stability constants of metal complexes of the crowns [7–13], with the kinetics of complex formation [14–17], with the structure of macrocyclic substances and their complexes (see, for example, [18–21]), with their role in the ion transport across artificial as well as biological membranes [22–24] and with the application of the selective complex formation to the design of ion-selective electrodes [25–30].

Polarographic methods of stability determination of crown complexes of alkali metal ions and monovalent thallium were used for the first time in this laboratory [8] (see also [9, 31–34]).

The aim of the present paper is to give a detailed survey of results obtained by means of this method in methanol and acetonitrile.

Experimental

Apparatus

Most of the measurements were carried out with the dropping mercury electrode with mechanically regulated drop-time in a three-electrode arrangement. The auxilliary electrode was a Pt-wire with a considerably larger surface than that of the DME. A silver–silver chloride reference electrode was placed either in 0.1 M tetramethylammonium chloride solution in methanol or in a saturated solution of the same salt in acetonitrile and connected to the electrolyzed solution by means of a capillary junction containing an asbestos fibre. However, in the majority of measurements in acetonitrile there was used a saturated aqueous calomel electrode with a bridge containing the base electrolyte of the electrolyzed solution. The base electrolyte was usually 0.025 M or 0.05 M tetrabutylammonium perchlorate. As polarographs the OH-102 and OH-105 instruments of Radelkis (Budapest, Hungary) were used.

The volume of the electrolyzed solution was 2 ml. Argon of high purity was used for removing oxygen from the investigated solution. It passed first a bubbler with the solvent in order to prevent concentration changes in the electrolyzed solution.

Chemicals

All cyclic polyethers were a gift of Dr. K. H. Frensdorff of Dow Chemical Co., Wilmington, Delaware, USA, with the exception of dicyclohexyl-18-crown-6, dibenzo-18-crown-6, 3,3'-dimethyldibenzo-18-crown-6, 3,3'-dimethyldibenzo-24-crown-8 and 3,3'-dimethyldibenzo-30-crown-10 which were kindly given to us by Dr. J. Petránek and Dr. O. Ryba of the Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, Prague.

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TABLE I. Stability Constants K_{MX} of Monovalent Ion Complexes with Cyclic Polyethers at 22 °C.

	lgK$_{MX}$					Notes
	Na$^+$	K$^+$	Rb$^+$	Cs$^+$	Tl$^+$	
Benzo-15-crown-5	4.55	3.40	2.90	3.10	5.20	a
	–	–	–	–	3.00	b
Dicyclohexyl-18-crown-6	–	6.60	5.40	5.10	7.40	a
	–	–	–	–	5.20	b
Benzo-18-crown-6	4.90	5.30	4.40	4.05	5.70	a
	–	5.20	–	–	4.60	b
Dibenzo-18-crown-6	5.00	4.70	3.70	3.50	4.90	a
	–	4.60	–	–	4.00	b
3.3-Dimethyldibenzo-18-crown-6	5.10	4.80	4.00	3.40	5.00	a
	–	5.00	–	–	3.80	b
Dibenzo-24-crown-8	4.00	3.70	3.40	3.80	4.80	a
	–	3.20	–	–	3.40	b
3.3-Dimethyldibenzo-24-crown-8	4.10	3.90	3.90	3.90	5.00	a
	–	3.50	–	–	3.30	b
Dibenzo-30-crown-10	3.60	4.70	4.70	3.50	5.60	a
	–	3.90	–	–	4.10	b
3.3-Dimethyldibenzo-3-crown-10	3.60	4.80	4.90	3.80	5.70	a
	–	4.70	4.65	–	4.20	b

[a] Base electrolyte 0.05 M tetrabutylammonium perchlorate in acetonitrile.   [b] Base electrolyte 0.025 M TBAP in methanol.
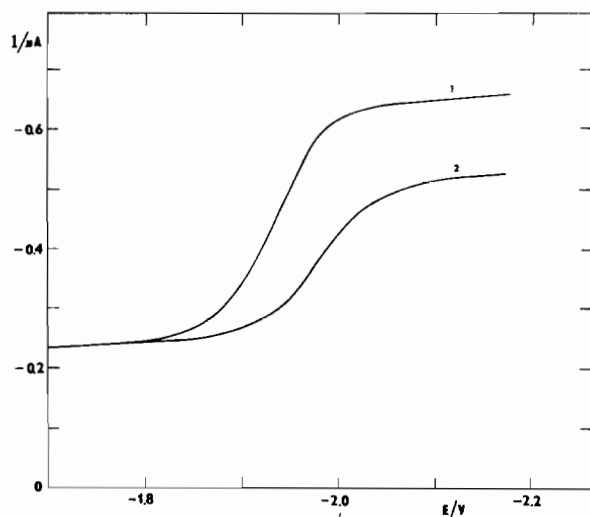

Figure 1. Curve 1: polarographic wave of 1.8 × 10^{-4} M KSCN; curve 2: polarographic wave of 1.4 × 10^{-4} M KSCN in the presence of 10^{-3} M dibenzo-24-crown-8. The base electrolyte was 0.05 M tetrabutylammonium perchlorate in acetonitrile, drop-time t_1 = 1 sec, t = 22 °C.

Perchlorates of Rb, Cs and Tl(I) were prepared in this laboratory while analytical grade NaClO$_4$ and KSCN were products of Lachema, Brno. A spectroscopically pure methanol UVASOL (Merck, Darmstadt) was used. Analytical grade acetonitrile (Lachema, Brno) was purified before use [36]. First it was boiled with aqueous KOH under reflux for several hours, then with aluminium oxide, then with

phosphorus pentoxide and fractionally distilled in a column with large reflux ratio and separation efficiency. In this way a rather pure acetonitrile was obtained which was examined polarographically as well as by means of UV spectra.

Terminology

The generic terms for cyclic polyethers were used such as introduced by Pedersen [1].

Results

In the polarographic investigation the significant quantity for the stability of the complex is the half-wave potential of the complex and of the free metal ion. The measure of the complex stability is the difference between the half-wave potential of the free metal ion and of the complex at a given concentration of ligand [35]. The half-wave potential of the polarographic wave of the complex is shifted to more negative potentials when the concentration of the ligand in solution is increased (Fig. 1). On the basis of plots of this type the stability constants were determined (Table I).

The reduction of monovalent thallium and of alkali metal ions with the exception of Cs$^+$ is characterized by a one-electron wave with the slope dE/dlog $(I_d - I)/I \approx 59$ mV. Here E is the potential of DME, I the average polarographic current and I_d the average limiting diffusion current. After addition of the cyclic polyether to the solution the slope is not

changed whereas the whole wave is shifted to more negative potentials [8, 9, 37]. This behaviour is significant for the fast charge transfer across the electrode interface resulting in the establishment of an equilibrium between the free and complexed metal ions in solution and metal atoms dissolved in the amalgam.

The slope for the reduction wave of the cesium ion in acetonitrile has the value of about 73 mV. Even in this case the slope is not changed after the addition of the complex forming agent. Under these conditions it is possible to determine the stability constant on the basis of the shift of the half-wave potential in dependence of ligand concentration [9, 35, 37]. For the study of the cesium ion the extremely short drop-time of 0.3 s was used.

The limiting currents of the cathodic waves of metal ions in the presence as well as in the absence of the crown ligands are controlled by diffusion either of the free metal ion (in the absence of ionophore) or of the complex (in an excess of ionophore). At the surface of the electrode the equilibrium between the complexed and the free metal ions is disturbed as a consequence of the electroreduction of the free metal ions and, thus, the complex dissociates into the free metal ions and the ligand molecules. In excess of cyclic polyether in solution the limiting current of the complex is lower than that of the free metal ions because of the lower diffusion coefficient of the former [9].

Discussion

The complexes of metal ions with macrocyclic ligands of the "crown" type are the so called "inclusion complexes" [6]. With the exception of the 30-membered ligand, which encircles the metal ion from all sides, the polyethers have in their complexes a planar conformation, *i.e.* with all oxygens situated on a single plane. A ring is formed around the cation by the ligand molecule which is able to coordinate, in a perpendicular direction to the ligand plane, one or two solvent or anion particles. Thus, the central cation is not screened-off from its surroundings by the macrocyclic ligand molecule [19]. This conformation is typical for ligands with 15–24 members which have been studied in the present paper. Their complexes show no particularly high selectivity. With respect to the ring size the stability of the complex depends on the ionic radius of the alkali metal cation. The 15-membered ring forms most stable complexes with sodium, the 18-membered ring with potassium and the 24-membered ring with cesium ions. This tendency is manifested in Table I.

However, if the stability alone is compared the sodium ions form more stable complexes with the 18-membered ring than with the 15-membered one. Here the effect of the number of binding sites may play a

role [6]. This assumption is based on the increase of stability of the sodium complex with 18-membered ligands with increasing number of benzene rings attached to the polyether cycle. The more benzene rings are bound to the polyether the smaller is the ring, so that the whole system has a more rigid structure [6].

The difference in stability of the complexes of sodium and potassium is rather low in acetonitrile (with the exception of dicyclohexyl-18-crown-6 and benzo-18-crown-6 for which the sodium ion is too small). These comparatively high values of the stability constants are obviously due to a relatively weaker solvation of sodium ions in acetonitrile than, for example, in methanol [38], where most of the constants were measured while in the case of potassium the solvation is about the same in the both solvents. Thus, in a final summation of all effects, the higher surface charge of the sodium ion and, therefore, the stronger dipole–ion bond of the ion with the ligand becomes important.

The methyl groups in the 3 position on benzene rings cause in most cases a certain increase of complex stability [7]. This not very conspicuous effect may be ascribed to the positive inductive effect of the methyl group.

The 30-membered cyclic polyether shows the highest selectivity for potassium and rubidium, forming the most stable complexes with these ions. In the complex the metal cation is perfectly wrapped with the ligand so that it is completely separated from the outer medium [19]. This kind of selectivity can be ascribed to the size of the cavity which is too large for the sodium ions, enabling thus its oscillations inside, and too small for the cesium ion which evokes by its size a tension in the cycle and a deformation of bond angles resulting in destabilization of the complex.

The thallium(I) ion has an exceptional position with respect to alkali metal ions. Its ionic radius is quite close to the potassium cation. However, the stability of its complexes is higher than that of potassium complexes. Obviously the Tl(I) ion is bound in the complex by an ion–dipole interaction with a covalent contribution [6]. The Tl(I) ion can be used as an indicator of the nature of binding sites in macrocyclic substances where the structure of the complex is unknown. If the stability constant of the complex of Tl(I) is higher than that of the potassium complex the binding sites are ether oxygens [39].

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