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STABILITY CONSTANTS OF BIS-CROWN ETHER - METAL ION COMPLEXES

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INTRODUCTION

Crown ether derivatives (macrocyclic polyethers) have been used as components in liquid membrane electrodes exhibiting potassium ion sensitivity (1). Nevertheless, the performance characteristics of such crown compound based electrodes, especially the selectivity data were found inferior to those of the antibiotic valinomycin based sensor (2).

Synthetic urethane linked bis-crown ether ligands were designed as ionophores for potassium ion-selective membranes at the Technical University of Budapest (3,4). The analytically important properties of these synthetic ligand based electrodes exceed the relevant characteristics of other macrocyclic polyether based sensors and are comparable with those of the valinomycin based electrode, the ion-selectivity of such sensors being advantageously affected not only by the ring size of the crown ethers and its substituents, but also by the chemical structure of the connecting chain.

It was found that bis-crown ether derivatives form 1:1 sandwich type complexes with most alkaline ions yielding a distinguished selectivity for potassium ions (5).

As known (6) there exists a close correlation between the stability constants of the inophore - cation complexes and the relevant potentiometric selectivity factors. Thus, the aim of our work, in this line, is to determine the stability constants of some bis-crown other ligands of different structures with various cations, in different media.

In the present study, potentiometric method, having a large dynamic concentration range has been used for following the complexation reaction and the experimental conditions were clarified in order to enable further studies.

EXPERIMENTAL

Materials

The bis-crown derivative (BME-15) has been synthetised according to the procedure described in ref. 3, having the formula shown in Fig. 1.

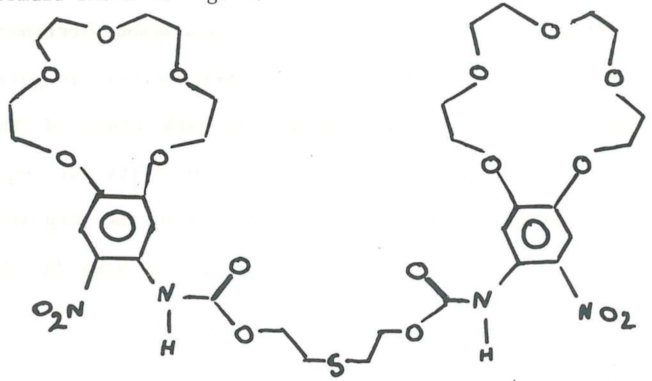

Fig. 1. Formula of the urethane linked 15-crown-5 bis-crown ether derivative (BME-15).

The other chemicals, e.g. KCl, NaCl and Li-Acetate, as well as the solvents, methanol and chloroform, were of analytical grade. Double quartz distilled water was used for the preparation of solutions.

Electrodes, Apparatus

Na-selective glass electrodes (Radelkis OP-Na-8204) and a double junction silver-silver chloride reference electrode were employed in the following arrangement

Ag,AgCl | KCl (aq.) 1 mol.dm^{-3} || Li Ac.(aq.) 1 mol.dm^{-3} || sample solution | Ion selective electrode

Before measurements, the ion selective electrodes were pretreated by overnight soaking in 10^{-1} mol.dm^{-3} solution of the appropriate primary ion, in increasingly concentrated methanol/chloroform: water mixture, during one week.

The e.m.f. measurements were carried out with a Radelkis OP-208 pH/mV meter.

EXPERIMENTAL PROCEDURE

For the determination of the stability constant values, the method suggested by Frensdorf (7) was employed by varying the ligand/metal ion ratio. Thus, 10^{-3} mol.dm^{-3} KCl and NaCl in 1:4 chloroform/methanol were titrated by adding 2.5 x 10^{-2} mol.dm^{-3} crown ether solution, in the same solvent, by a Hamilton syringe. The solvent mixture was selected as a result of high lipophilicity of the ligand.

The free metal ion concentration change was followed potentiometrically.

Readings were taken after 5 minutes of each addition. All concentration values C_M (total concentration of metal) and C_L (total concentration of ligand) were corrected for dilution.

The electrode response functions (e.m.f. vs log C_M) were checked before each titration, in the concentration range $5 \times 10^{-3} - 5 \cdot 10^{-5}$ mol.dm^{-3} and slope values s, were determined.

RESULTS AND DISCUSSION

As an example of the reliability of the results, the titration data of NaCl(A) and KCl(B) 10^{-3} mol.dm^{-3} with 2.5×10^{-2} mol.dm^{-3} ligand are shown in Fig. 2.

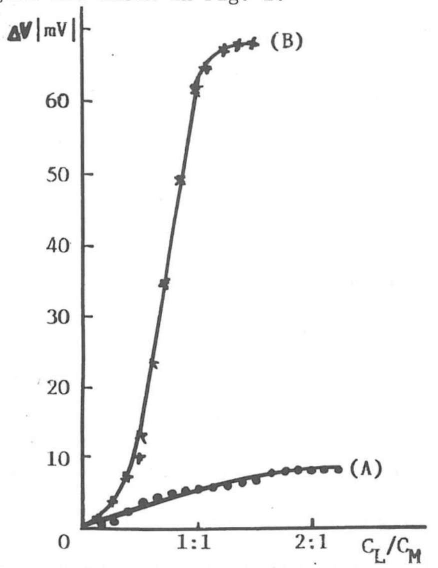

Fig. 2. Titration of NaCl(A) and KCl(B) 10^{-3} mol.dm^{-3} solutions with 2.5×10^{-5} mol.dm^{-3} BME 15 solution in chloroform/methanol 1:4.

Stability constant values were evaluated on the assumption of the formation of metal-ligand complexes of 1:1 stoichiometry (5). Thus it is

$$M + L \rightleftarrows ML$$
$$\text{(BME-15)} \quad \text{(BME-15-M)}$$

with the corresponding stability constant

$$K = \frac{|ML|}{|M|\ |L|}$$

where
$|L|$ is the free ligand concentration
$|M|$ is the free metal concentration
$|ML|$ is the complex concentration

Since the metal and the ligand concentration in the complex is

$$|ML| = C_M - |M|$$

while the free ligand concentration is

$$|L| = C_L - (C_M - |M|)$$

Then it is

$$K = \frac{C_M - |M|}{|M|\ (C_L - C_M + |M|)}$$

The free metal concentration was calculated from the ΔE values reported to that of the ligand free solution

$$|M| = \frac{C_M}{10^{\Delta E/S}}$$

TABLE 1 - Stability constant values of BME 15 - K complex

Total concentration $\|mol.dm^{-3}\|$ Metal (K)	Ligand	$\Delta V\|mV\|$	$\|K^+\|$	K'
9.52×10^{-4}	1.17×10^{-3}	66.8	1.84×10^{-5}	2.16×10^{5}
9.48×10^{-4}	1.28×10^{-3}	67	1.82×10^{-5}	1.46×10^{5}
9.43×10^{-4}	1.39×10^{-3}	67	1.80×10^{-5}	1.10×10^{5}
			Average	1.57×10^{5}

TABLE 2 - Stability constant values of BME 15 - Na complex

Total concentration $\|mol.dm^{-3}\|$ Metal(Na)	Ligand	$\Delta V\|mV\|$	$\|Na^+\|$	K'
9.52×10^{-4}	1.17×10^{-3}	5.7	7.30×10^{-4}	3.21×10^{2}
9.48×10^{-4}	1.28×10^{-3}	5.9	7.20×10^{-4}	3.01×10^{2}
9.43×10^{-4}	1.39×10^{-3}	7.4	6.68×10^{-4}	3.69×10^{2}
			Average	3.30×10^{2}

The ratio of the stability constants of the sodium and potassium complexes were in agreement with previously determined selectivity coefficients (4), $k^{pot.}_{K,Na} = \frac{K(Na)}{K(K)}$

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