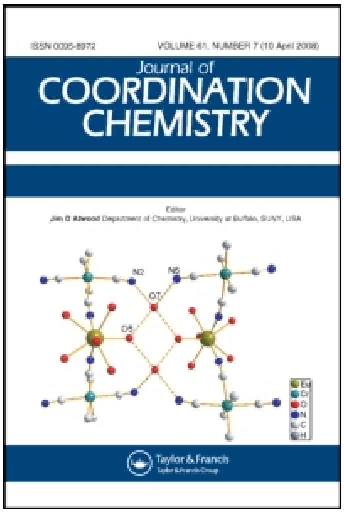

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THE STABILITY CONSTANTS OF SOME BENZO-15-CROWN-5 AND NAPHTHO-15-CROWN-5 DERIVATIVES

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The stability constants for the complexes of several benzo-15-crown-5 and naphtho-15-crown-5 derivatives containing various substituents in the aromatic ring have been determined in methanol. The potentiometric method with glass ion-selective electrodes has been employed. The stability constants have been compared to the selectivity coefficients ($\log k^{pot}_{K,Na}$) of membrane electrodes based on the mentioned compounds. No significant relationship has been stated.

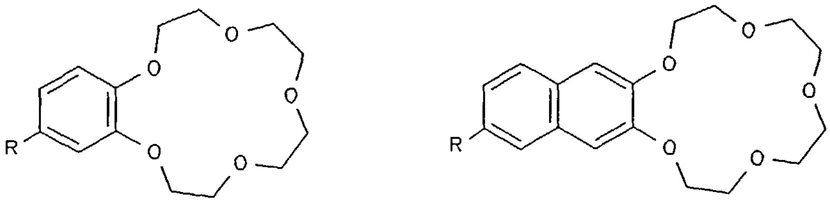
Keywords: Stability constants, crown ethers, potentiometry

1. INTRODUCTION

Introduction of lipophilic substituents into crown ethers or other ion carriers leads to a minimization of the carrier solubility in water and as a consequence increases the stability of the membrane ion-selective electrode due to a decrease of the washing out of the electroactive substance from the membrane. In our previous papers we have reported the results of investigations of the effect of substituents in aromatic macrocyclic polyethers on potassium ion-selective properties.[1,2] We have found that lipophilic substituted aromatic 15-crown-5 derivatives, used as the electroactive substance in an ion-selective electrode membrane, substantially increase the K,Na selectivity of the electrode. An explanation has been given suggesting increased participation of the 2:1 ligand to potassium ion complex in the distribution of potassium and sodium ions between the membrane and the aqueous solution. The present study was undertaken to find if the substituents also effect the stability constants of respective crown ethers.

2. EXPERIMENTAL

Macrocyclic polyethers (Figure 1), prepared by methods reported earlier,[2] have been purified by recrystallization or by column chromatography. An experimental procedure for the determination of stability constants was adopted from reference 3. The constants were determined in methanol by the potentiometric method with a sodium-selective electrode (manufactured by UMCS Lublin, Poland) and a potassium-selective electrode (a gift from Prof. W. Simon, ETH Zurich, Switzerland). An OP 08201 silver chloride electrode (Radelkis, Hungary) was used as reference electrode with a saturated NaCl solution in methanol as the internal solution. The measurements were conducted on a N517 pH-meter (Mera-Elwro, Poland) equipped with a V541 voltmeter allowing readings with an accuracy of 0.1 mV. Potassium chloride and



1 R = H

2 R = CH_3CO

3 R = $(CH_3)_3C$

4 R = $CH_3C(n\text{-}C_4H_9)_2$

5 R = $(CH_3)_2C(n\text{-}C_{12}H_{25})$

6 R = H

7 R = $(CH_3)_3C$

8 R = $CH_3C(n\text{-}C_4H_9)_2$

9 R = $(CH_3)_2C(n\text{-}C_{12}H_{25})$

FIGURE 1 Crown ethers used in this study.

sodium chloride methanolic solutions (concentration range 10^{-3}–2.10^{-4} M) were titrated with methanolic solutions of crown ethers (concentration approx. 0.01 M). The electrodes were calibrated in NaCl and KCl solutions in methanol in the $10^{-5}-10^{-2}$ M concentration range. They exhibited a linear dependence, a nernstian slope in the case of the potassium-selective electrode and an almost nernstian slope in the case of the sodium-selective electrode. The titrated solution was stirred and the experiments were conducted under argon. A steady reading was obtained after approx. 5 minutes from the addition of the titrant. The stability constants were calculated with the use of the programme CVEQUID.[4]

3. RESULTS AND DISCUSSION

The values of the stability constants and their standard deviations are given in Table I.

The stability constants of benzo-15-crown-5 complexes with sodium ions exhibit a similar Hammett relationship to that reported by Ungaro *et al.*[5] and Wu *et al.*[6]. No such relationship is found for the potassium complexes of benzo-15-crown-5 probably due to larger distances between the aromatic oxygen atoms and the cation in the 2:1 (crown to potassium) complex. Also no such relationship is found for the complexes of naphtho-15-crown-5 derivatives with sodium cations presumably due to the less aromatic character of the naphthalene ring and the larger distance of the substituents to the aromatic oxygen atoms. The $\log \beta_2$ values in the group of the naphtho-15-crown-5 derivatives and the group of benzo-15-crown-5 derivatives differ inconsiderably. The differences between the $\log K_1$ stability constants of complexes with sodium ions are even smaller. A higher $\log \beta_2$ stability constant for the complex of naphtho-15-crown-5 with potassium ions when compared to the analogous stability constant for benzo-15-crown-5 explains the higher selectivity of electrodes with naphtho-15-crown-5 in the membrane.

TABLE I

Stability constants determined in this study.

Compound	Na^+	K^+		
Derivatives of banzo-15-crown-5	$\log K_1$	$\log K_1$	$\log K_2$	$\log \beta_2$
1	2.78 (0.01)	2.73 (0.04)	3.40 (0.05)	6.13
2	2.31 (0.01)	2.83 (0.03)	3.02 (0.06)	5.85
3	2.78 (0.01)	2.53 (0.06)	3.66 (0.08)	6.19
4	2.81 (0.01)	3.05 (0.02)	3.32 (0.03)	6.37
5	2.86 (0.01)	3.06 (0.02)	3.17 (0.04)	6.23
Derivatives of naphtho-15-crown-5				
6	2.57 (0.01)	2.71 (0.04)	3.64 (0.05)	6.35
7	2.83 (0.01)	2.75 (0.07)	3.76 (0.09)	6.51
8	2.67 (0.01)	2.99 (0.03)	3.67 (0.04)	6.63
9	2.63 (0.02)	2.75 (0.04)	3.98 (0.04)	6.71

$K_1 = [CrM^+]/[Cr][M^+]$; $K_2 = [Cr_2M^+]/[Cr][CrM^+]$; $\beta_2 = [Cr_2M^+]/[Cr^2][M^+]$.

The differences between the stability constants respectively for sodium and potassium complexes of the aromatic 15-crown-5 derivatives are only small and they cannot explain the considerable differences in the log $k^{pot}_{K,Na}$ selectivity coefficients of electrodes with the compounds as electroactive substances (see references 1–2). The reported results confirm our earlier explanation of the effect of lipophilicity of aromatic 15-crown-5 derivatives on the selectivity of potassium-selective electrodes.

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