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Complex Forming and Extraction Properties of Oligo Benzo-Fused Crown Ethers

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Abstract. The complex forming properties with alkali metal and ammonium ions of a series of oligo benzo-condensed 18-crown-6 ethers **1–8** having a different gradation of lipophilicity and of molecular rigidity are investigated by voltammetry at the interface of two immiscible electrolyte solutions (ITIES) and by a liquid–liquid extraction technique. The experimental results obtained in the two phase system H_2O/nitrobenzene are discussed in relation to the structure of the crown and the cation type. The stability constants for the 1 : 1 complexes of Na^+, K^+, Rb^+, Cs^+ and NH_4^+ in nitrobenzene have been determined and compared with the extraction constants for the 1 : 1 complexes of Na^+ and K^+ and for the 1 : 1 and 1 : 2 complexes of Cs^+, showing the effect of oligo benzo condensation for the 18-crown-6 system.

Key words. Crown ethers, liquid–liquid extraction, voltammetry, stability constants.

1. Introduction

Liquid–liquid extraction is a very useful process for the separation and concentration of metal ions in solution. Application fields are analytical chemistry, the recovery of metals from primary and secondary sources, the removal of toxic species from waste water, and the preparation of high purity materials with defined properties [1].

For all these purposes, highly selective cation extractants are required [2]. In this nexus macrocyclic complexants such as crown ethers and their derivatives are very promising [3]. These and related host compounds are capable of forming stable complexes with different metal or organic cations and also with uncharged molecular organic guests [4]. High complex stabilities and selectivities for particular metal ions can be achieved by designed crown compounds [5] and their extraction efficiencies towards metal ions can be enhanced by attachment of lipophilic groups such as alkyl substituents [6]. On the other hand, benzo condensation in order to

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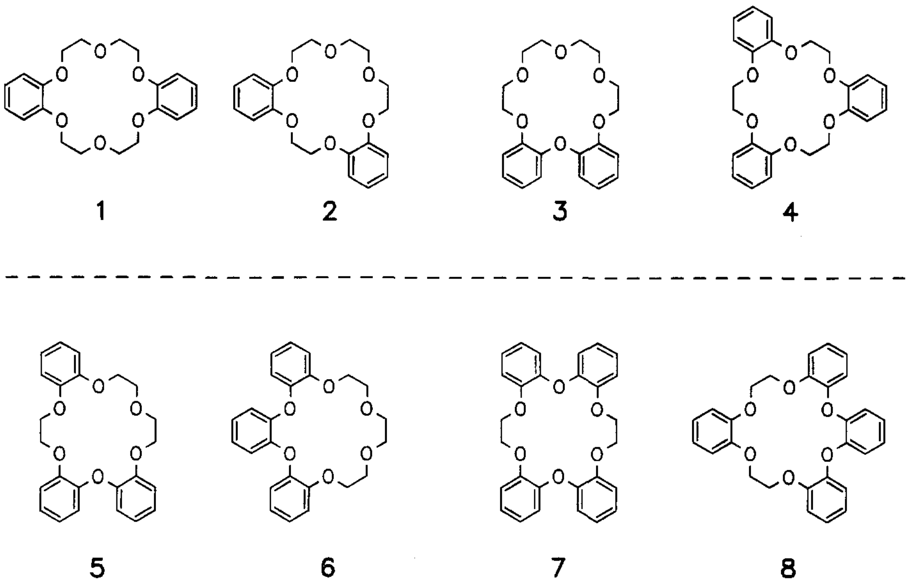

Fig. 1. Crown compounds investigated.

increase host lipophilicity and to enhance extraction efficiency has only scarcely been explored [3, 6]. However, there is a systematic series of oligo benzo-condensed 18-crown-6 ethers **1–8** (Figure 1) [7] which prompted us to undertake an extraction study. Some of these macrocycles have been tested preliminarily in respect of their carrier properties for alkali and alkaline earth metal ions in liquid membrane electrodes [7] and also complexation with protons [8] has been reported.

This paper describes cation transfer of Na^+, K^+, Rb^+, Cs^+ and NH_4^+ from water to a nitrobenzene phase assisted by the aforesaid benzo crowns **1–8**. Electrolysis at the interface of two immiscible electrolyte solutions (ITIES) [9] and solvent extraction techniques [10] have been applied. Stability constants of complexes formed in the non-aqueous phase have been determined from peak voltammograms [11].

2. Experimental

2.1. SYNTHESIS

Dibenzo-18-crown-6 (**1**) was obtained by the usual method [12]. Crown compounds **2–8** (Figure 1) have been prepared as described previously [7].

2.2. VOLTAMMETRY

The complex stability constants in nitrobenzene have been determined using voltammetry at the water/nitrobenzene interface from the peak potential of voltammograms [9, 11, 13].

In the presence of a complexing agent L in the organic phase the following equilibrium is established at the interface:

$$M^+_{(w)} \rightleftharpoons M^+_{(org)}; \qquad M^+_{(org)} + L_{(org)} \overset{K_1}{\rightleftharpoons} ML^+_{(org)} \tag{1}$$

The subscripts (org) and (w) denote the organic and aqueous phases, respectively. A four electrode system has been applied to compensate the IR drop in both phases between the reference electrodes RE_1 and RE_2. Single sweep voltammetry with a polarisation rate between 5 and 100 mV s^{-1} is used. The experiments were performed at room temperature of 23 ± 2°C with the help of potentiostat and pulse generator devices. The chlorides of the cations were used as supporting electrolytes in the aqueous phase (twice-distilled water).

The base electrolyte in the organic phase (nitrobenzene) was tetra-*n*-butylammonium tetraphenylborate (TBATPB). The desired amount of the crown compound [L] was added to the nitrobenzene phase.

Concentrations. $c_{MCl} = 1 \times 10^{-2}$ M, $c_{TBATPB} = 1 \times 10^{-2}$ M and $c_L = 1 \times 10^{-4}$–1×10^{-3} M/nitrobenzene.

2.3. EXTRACTION

The extraction studies were performed at 22 ± 1°C in mechanical shaking devices [10]. A H_2O/nitrobenzene solvent system was used for Na^+, K^+, Rb^+ and Cs^+. Furthermore, in the case of Na^+ comparison investigations were performed using $CHCl_3$ as diluent. The phase ratio $V_{(org)} : V_{(w)}$ was 1 : 1; the shaking time was 30 min (extraction equilibrium was achieved in each case). The metal concentration in both phases was determined by the γ-radiation measurement of ^{22}Na, ^{42}K and ^{137}Cs with a NaI(Tl) scintillation counter.

Concentrations. $c_{MNO_3} = 1 \times 10^{-4}$ M, $c_{HPic} = 5 \times 10^{-3}$ M and $c_L = 5 \times 10^{-4}$–1×10^{-2} M/organic diluent.

A liquid–liquid extraction equilibrium of a univalent metal ion with a crown ether is generally described [3] by Equation (2):

$$M^+_{(w)} + A^-_{(w)} + sL_{(org)} \overset{K_{ex}}{\rightleftharpoons} ML_sA_{(org)} \tag{2}$$

This equation is valid as it is in the case of $CHCl_3$ as diluent. In the case of nitrobenzene as diluent the dissociation of the extracted ML_sA complex in the organic phase must be taken into account as a result of the high dielectric constant of this solvent [14–16]. Therefore Danesi *et al.* discussed the equilibria (3) and (4) for the extraction reaction and the ion pair association in the organic phase, respectively, and determined the resulting constants [14]:

$$M^+_{(w)} + sL_{(org)} + A^-_{(w)} \overset{K_3}{\rightleftharpoons} ML^+_{s(org)} + A^-_{(org)} \tag{3}$$

$$ML^+_{s(org)} + A^-_{(org)} \overset{K_4}{\rightleftharpoons} ML_sA_{(org)} \tag{4}$$

The relatively small constant K_4 in nitrobenzene points to a low degree of association [14].

The relationship between Equations (2), (3) and (4) is given by $K_{ex} = K_3K_4$. From the experimental data obtained in this paper only the overall extraction constants K_{ex} have been determined. Moreover, using the corresponding data for K_4 published in [14] the constants K_3 for the investigated systems were also evaluated.

The distribution ratio $D_M = c_{M_{(org)}}/c_{M_{(w)}}$ of the metal M is used characterizing an extraction system. The number n and the composition of the extracted species and their extraction constants are determined by a least squares fit of Equation (5) using a modified Marquardt procedure [17] with K_{ex1} for $s = 1$ and K_{ex2} for $s = 2$,

$$\log D_M = \sum_{i=1}^{n} (\log K_{ex,i} + s_i \log c_{L_{(org)}} + \log c_{A^-_{(w)}}) \tag{5}$$

3. Results and Discussion

The potential-sweep voltammograms of the systems with Na^+ (see Figure 2 for crown compound **2**) and of some systems with K^+ have the shape of classical voltammograms obtained with mercury electrodes [9, 11]. The positive and negative current peaks appear on a votammogram in the presence of an ionophore at a low concentration. The dependence of the peak current on ionophore concentration and

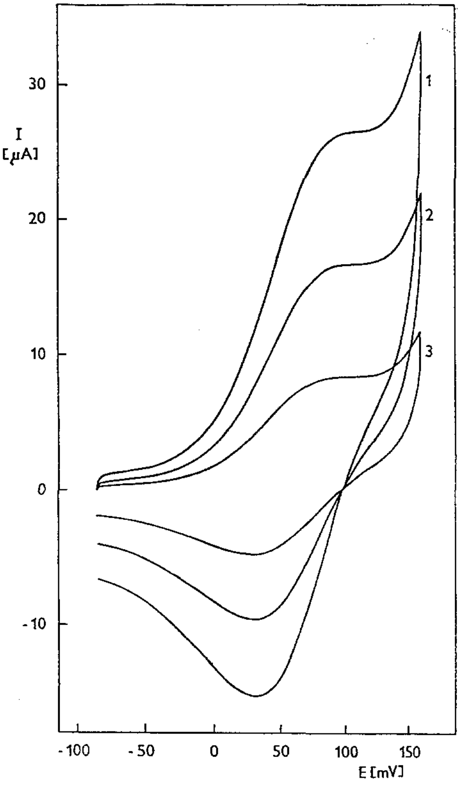

Fig. 2. Voltammograms of the transfer of sodium ions facilitated by crown **2**. Scan rate 45 mV s^{-1} (1), 18 mV s^{-1} (2), 4.5 mV s^{-1} (3) at the water/nitrobenzene interface.

on the square root of the polarisation rate is linear for the present crowns. It implies that the complex formation at the water/nitrobenzene interface is very fast. This fact is confirmed by the short time of equilibrium adjustment (< 1 min) during extraction.

The stability constants K_1 obtained by voltammetry are listed in Table I. Determination of the stability constants of complexes with K^+, Rb^+, Cs^+ and NH_4^+ is more complicated because of inaccuracy in the estimation of peak potentials. These ions have less positive standard transfer potentials in comparison with sodium which is caused by their larger hydrophobicity connected with their larger ionic radii. Peaks of these ions are shifted to the region in which the transfer of the TBA^+ ion already takes place and its current interferes with the negative waves of the complexes.

For the Na^+ complexes the temperature dependence of the stability constant has also been measured. The standard enthalpy and the standard entropy of complexation has been evaluated. The results are listed in Table II, showing that the standard

Table I. Extraction ($\log K_{ex}$ and $\log K_3$) and complex stability constants ($\log K_1$) of alkali and ammonium ions with crown ethers **1**–**8**.

cation		crown compound							
		1	**2**	**3**	**4**	**5**	**6**	**7**	**8**
Na^+	$\log K_{ex1}$	4.54	4.91	4.71	4.53	–	–	–	–
	$\log K_3$[a]	2.06	–	–	–	–	–	–	–
	$\log K_1$	6.9	6.3	7.0	6.4	6.1	6.2	4.7	5.2
K^+	$\log K_{ex1}$	6.37	6.25	6.19	5.29	5.24	–	3.97	3.94
	$\log K_3$[a]	3.58	–	–	–	–	–	–	–
	$\log L_1$	6.6	5.4	6.4	5.4	5.4	5.7	3.4	4.0
Rb^+	$\log K_{ex1}$	–	–	5.28	–	–	–	–	–
	$\log K_1$	5.5	4.1	5.8	3.9	4.5	4.6	3.4	3.8
Cs^+	$\log K_{ex1}$	5.19	–	5.43	4.15	4.71	5.28	–	4.12
	$\log K_3$[a]	2.61	–	–	–	–	–	–	–
	$\log K_{ex2}$	7.33	–	7.97	6.89	6.43	8.20	–	5.81
	$\log K_1$	4.5	2.7	4.0	3.3	3.6	3.7	2.5	3.0
NH_4^+	$\log K_1$	5.5	4.3	5.8	4.6	4.3	4.9	3.0	3.4

[a] These values are estimated using the data of K_4 from Danesi *et al.* [14].

Table II. The standard molar Gibbs energy, standard molar enthalpy and standard molar entropy of the transfer of sodium ion facilitated by the studied crown compounds

crown compound	ΔG kJ mol^{-1}	ΔH kJ mol^{-1}	ΔS J mol^{-1} K^{-1}
1	−39.1	−28.9	34
2	−36.2	−38.0	−7
3	−40.0	−41.4	−5
4	−39.0	−35.8	10
5	−34.7	−35.1	−1
6	−33.8	−41.4	−26
7	−26.8	–	–
8	−29.9	29.7	1

entropies of the symmetric polyethers **1** and **4** stand out from those of the asymmetric polyethers by being highly positive.

The overall extraction constants K_{ex} achieved with selected macrorings of the types **1–8** and the extraction constants of the dissociated ion pairs, K_3, for Na^+, K^+ and Cs^+ of **1** are summarized in Table I. It is worthy of note that the extraction constants for **1** are in good agreement with the previous results of Danesi *et al.* [14]. The $\log D - \log c_L$ diagrams for K^+, Na^+ and Cs^+, which illustrate the extraction efficiency of the investigated crown ethers clearly, are shown in Figures 3–5.

In the case of K^+ (Figure 3) a distinct trend can be recognized: (i) the best extractant is the symmetric dibenzo-18-crown-6 (**1**), the other dibenzo-18-crown-6-ethers (**2** and **3**) show a slightly lower extractability because they are somewhat more associated by structure with 18-crown-6 [6]; (ii) with increasing number of benzo groups the extraction constants and stability constants decrease obviously due to the reduced basicity of the aromatic ether oxygen and steric effects; (iii) if the same number of benzo condensation is present, such as in **4–6** or **7** and **8**, the most symmetric molecules (**4** and **7**) are always the best extractants, in accordance with the dibenzo crowns (**1–3**).

For the small Na^+ ion (Figure 4), hydration is more important than for K^+ (and Cs^+) contributing to the observed differences in extraction. Among the macrocycles studied, the best extractants of Na^+ are the dibenzo crown ethers **2** and **3** perhaps due to their flexible ring segments. Using $CHCl_3$ as solvent generally leads to a

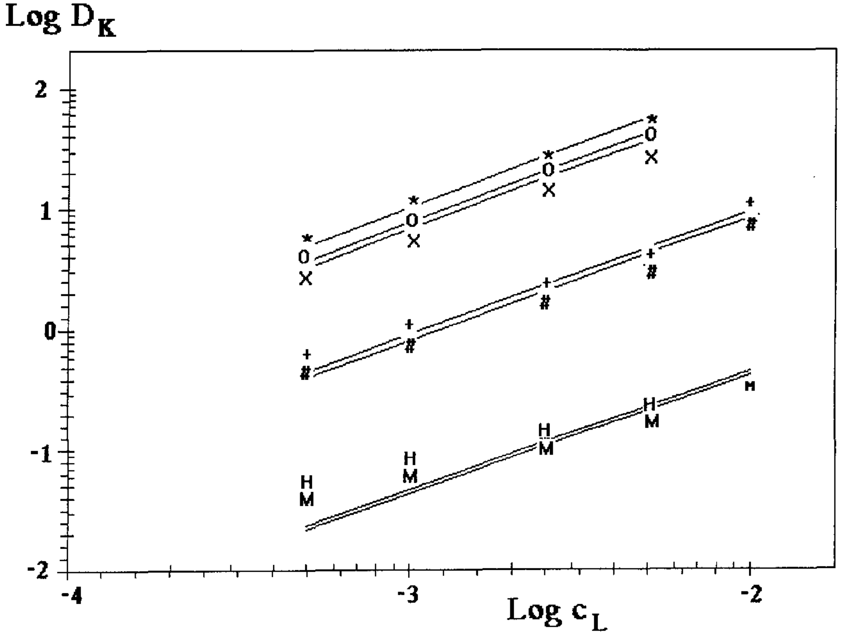

Fig. 3. Extraction of potassium picrate dependent on the extractant (crown) concentration with **1** (*); **2** (○); **3** (×); **4** (+); **5** (#); **7** (H); **8** (M) in nitrobenzene. Conditions see experimental; the points relate to the experimental data, the curves are calculated according to Equation (5).

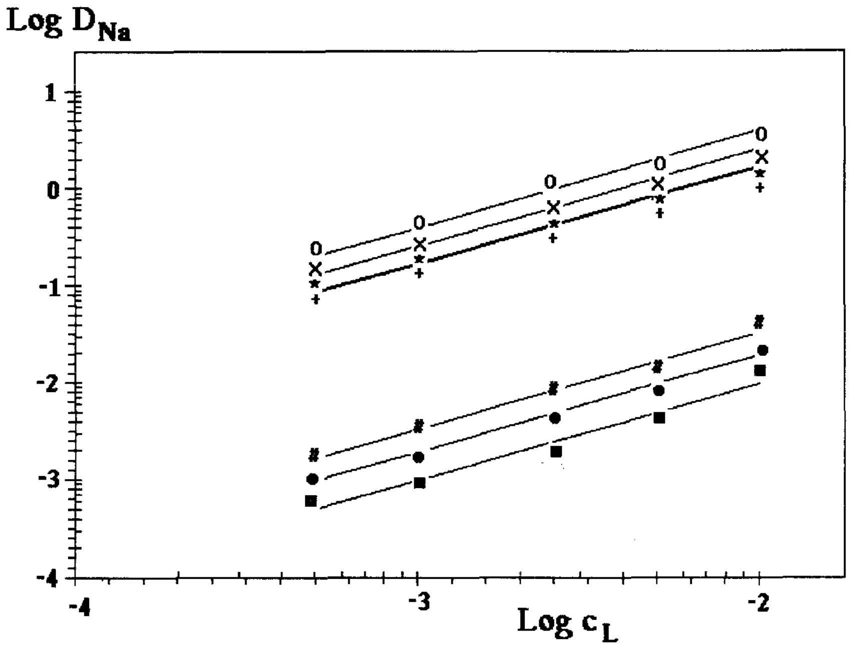

Fig. 4. Extraction of sodium picrate dependent on the extractant (crown) concentration with **1** (*); **2** (○); **3** (×); **4** (+) in nitrobenzene and **2** (●); **3** (#); **4** (■) in $CHCl_3$. Conditions see experimental; the points relate to the experimental data, the curves are calculated according to Equation (5).

strong decrease of extraction in comparison with nitrobenzene obviously caused by the different polarity of the diluents. It is interesting that the order of the extractability for **2** and **3** is changed.

In the case of Cs^+ (Figure 5), both 1 : 1 and 1 : 2 (metal : ligand) species were extracted into the organic phase. The best ligands for 1 : 2 sandwich complexation are the ethers of medium flexibility **3** and **6**. Remarkable differences in 1 : 1 and 1 : 2 complexation exist between the tribenzo crowns **4** and **5**. From the extraction constants of **4** and **5** it is obvious that the unsymmetric crown **5** shows weaker 1 : 1 and a stronger 1 : 2 complexation than the symmetric crown **4**. At low ligand concentrations only 1 : 1 complexes were found for all compounds (cf. voltammetry).

In summary, for the macrorings studied the following general gradation of extractabilities of Na^+, K^+ and Cs^+ picrates from water to nitrobenzene is shown: dibenzo > tribenzo > tetrabenzo crowns and symmetric > unsymmetric benzo crowns. The investigation also indicates that the potassium selectivity against Na^+ and Cs^+ is lower in **2**–**8** compared with **1**. However, the selectivity for Cs^+ against Na^+ is the highest with crown ether **3**, which has a high tendency to form sandwich complexes. A similar selectivity behavior is also deducible from a previous liquid membrane electrode study based on the given hosts [7].

Nevertheless, a comparison between the present complex stability constants determined by voltammetry and the extraction constants suggests no strict

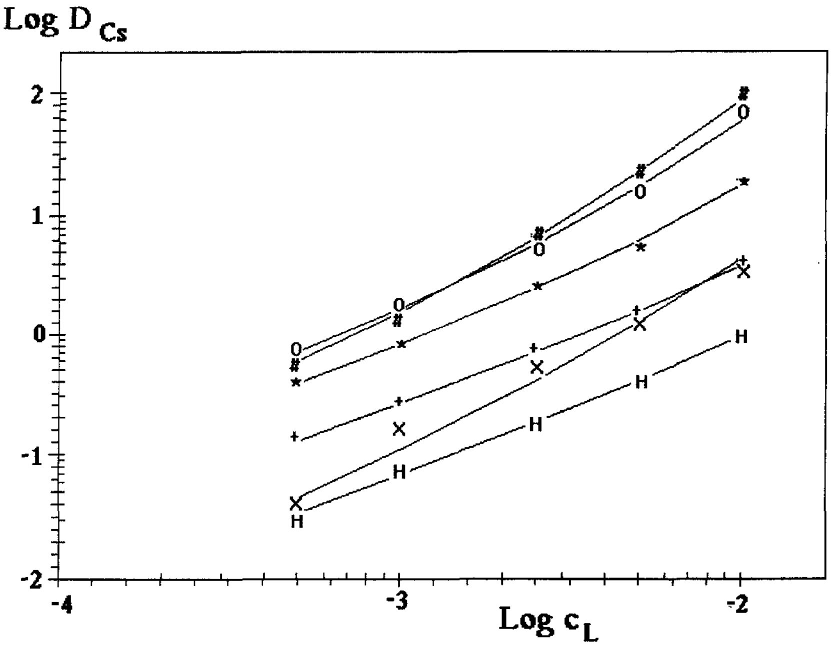

Fig. 5. Extraction of caesium picrate dependent on the extractant (crown) concentration with **1** (*); **3** (○); **4** (×); **5** (+); **6** (#); **8** (H) in nitrobenzene. Conditions see experimental; the points relate to the experimental data, the curves are calculated according to Equation (5).

proportionality (cf. [3]) which, however, is not surprising because of the different anions (picrate and chloride) and the different concentration ratios of extractant to metal ion used, although the solvent is the same.

Acknowledgement

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