Determination of Stability Constants of Complexes of Selected Amide Ionophores with Alkali Metal Cations

by M. Bocheñska[*] and I. Korczagin

Chemical Faculty, Technical University of Gdańsk, ul. Narutowicza 11/12, 80-952 Gdańsk, Poland
e-mail: marboch@ altis.chem.pg.gda.pl

Properties of four amide-type ionophores towards binding of alkali metal cations (K^+, Na^+, Li^+) have been established by determining the respective complex stability constants with the use of the liquid membrane ion-selective electrodes (ISEs).

Key words: ion selective electrodes, complexes, stability constants, alkali metal cations

New potentiometric procedures of determination of the complex stability constants were described recently [1–5]. Their advantages consist in that they use ion-selective electrodes as an analytical tool (so, only very small amount of the host compounds are required) and that the calculated values correspond to complexation, which occurs within the lipophilic electrode membrane. Therefore, these procedures are useful especially for characterizing highly lipophilic ionophores for potentiometric or optical liquid-membrane sensors. Moreover, these procedures allow to determine the stoichiometry and stability constants for complexes of different stoichiometry by varying the ionophore concentration in the membrane.

We report the complex stability constants of four synthesized by us [6,7] amide-type lithium ionophores (1–4 in Scheme 1) with Li^+, Na^+ and K^+, determined by using the DOS-PVC membranes and two different procedures [2,3]. Earlier research [7,8] proved that studied ionophores exhibit a high selectivity towards Li^+ cations and form complexes of 1:1 stoichiometry with alkali metal cations (Figure 1). The compounds 1 and 2 are highly lipophilic; the lipophilicity of ionophore 1 is log $P_{TLC} = 13.8$ [9].

We compare two experimental procedures with which β_{ML} values can be determined [2,3], differing in the membrane composition and approach to the measurements. In both procedures it is assumed that the membrane of ISE acts as a homogeneous organic phase in equilibrium with the aqueous sample solution. Furthermore, the concentration of the complexed ionophore is assumed to be equal to that of an ionic additive (tetrakis(4-chlorophenyl)borate) and the ionophores form complexes of the 1:1 stoichiometry.
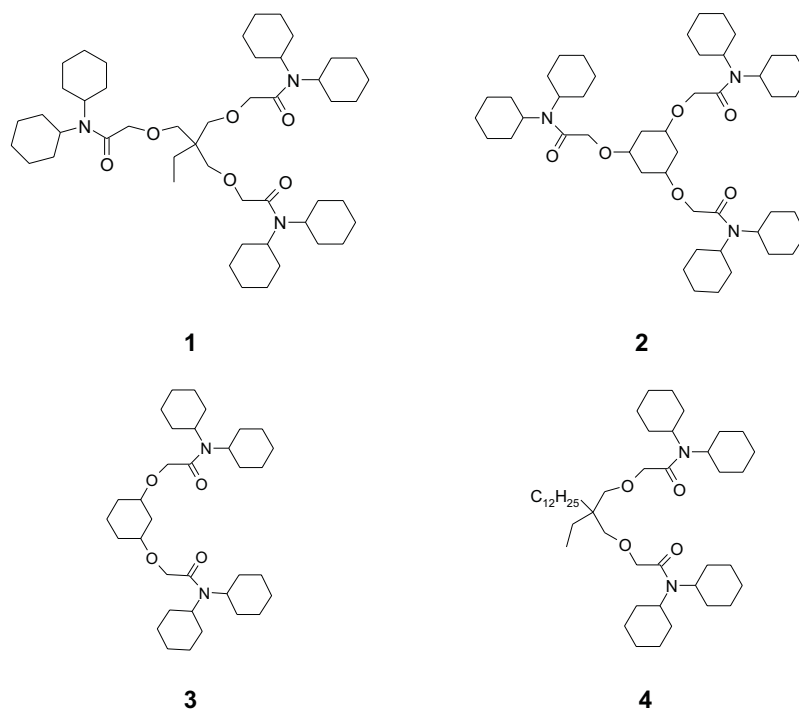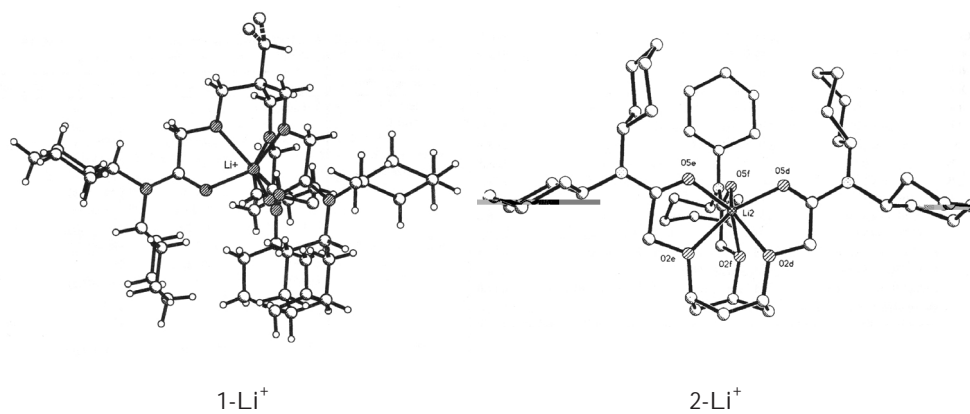
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[*] Author for correspondence.

1   **2**

3   **4**

Scheme 1. Structural formulae of the studied Li$^+$-ionophores.

1-Li$^+$ 2-Li$^+$

Figure 1. X-ray crystal structures of complexes of ionophores 1 and 2 with lithium cations [7,8].

The procedure I [2] compares potentiometric selectivity coefficients of the target cations with respect to that of tetramethylammonium cation for the ion exchanger in the absence of ionophore and the ionophore-containing ion-selective electrode membranes. Equation for the complex stability constant is:

$$\beta_{ML} = \frac{K^{pot}_{M,TMA}(EI)}{K^{pot}_{M,TMA}(L)[L_T - R_T]} \tag{1}$$

$K^{pot}_{M,TMA}(IE)$ and $K^{pot}_{M,TMA}(L)$ are the potentiometric selectivity coefficients for the ion exchanger and ionophore based electrode, respectively, L_T is a total concentration of ionophore and R_T is the total concentration of tetrakis(4-chlorophenyl)borate in the membrane. (1) is the simplified more general equation for monovalent cations that form 1:1 complexes.

In procedure II [3] measurements were also performed with two membranes of different composition, but one membrane contained H^+-selective highly lipophilic reference ionophore, ETH 2458 (Scheme 2) and anionic sites, while the other contains the same components and, additionally, the examined lipophilic Li-ionophore.
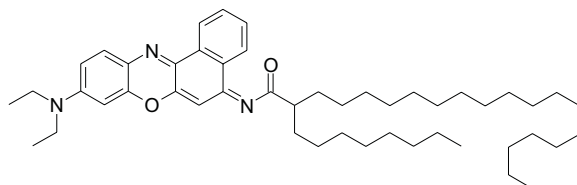
Scheme 2. Structural formula of the reference ionophore ETH 2458.

The chromoionophore, such as modified and lipophilized Nile Blue (ETH 2458), was selected on the basis of our earlier research on lithium optode in which similar, but slightly less lipophilic chromoionophore ETH 5294 was used [9]. The potential difference in the activity range of the cation interference of the H^+-selective membranes with and without the investigated ion carrier is used to calculate the effective complex stability constants. These are given by (2), valid for the 1:1 complexes and monovalent cations.

$$\ln \beta_{ML} = \frac{\Delta E_M \, F}{RT} - \ln (L_T - R_T) \tag{2}$$

ΔE_M is the potential difference between two described membranes, F, R and T have their usual meanings.

EXPERIMENTAL

1. Reagents. Poly(vinyl chloride) (PVC), bis(2-ethylhexyl) sebacate (DOS) and potassium tetrakis(4-chlorophenyl)borate (KTClPB) were from Fluka. Tetrahydrofuran (THF), from POCh, was freshly distilled before use. The ionophores were synthesized in our laboratory as described earlier [6–8]. Chromoionophore (ETH 2458) was kindly made available by Professor Erno Pretsch. All aqueous solutions were prepared with redistilled water (conductivity less than 2 μS/cm). The salts LiCl, NaCl, KCl (POCh) and tetramethylammonium chloride, (TMA)Cl, Fluka were of p.a. grade.

2. Preparation of membranes and measurements of the cell potential:

2.1. Procedure I. Membranes of *ca*. 0.1 mm thickness were prepared by pouring a solution of the membrane components (*ca*. 190 mg in total) in *ca*. 1.5 ml of THF into a glass ring (24 mm diameter) fixed on a glass plate. The ion-exchanger membrane contained KTClPB (5.4 mmol/kg), DOS plasticizer (126 mg) and PVC (60 mg). The membranes with an ionophore contained the same amount of KTClPB (4.8 to 5.3 mmol/kg), 57 to 60 wt % DOS and 25 to 27 wt % of PVC. The ionophore concentrations were: ionophore 1 – 26.19 mmol/kg, ionophore 2 – 27.21 mmol/kg, ionophore 3 – 26.43 mmol/kg and ionophore 4 – 26.46 mmol/kg. Disks of 7 mm diameter were cut from the membrane and glued with a THF-PVC slurry to a plasticized PVC tubing of the Ag/AgCl electrode. Three ISEs were prepared for each membrane composition. The inner electrolyte of all ISEs was 0.01 M KCl. All electrodes were conditioned in pure water for about 12 h. All measurements were carried out at room temperature (20°C) with cells of the type

Ag | AgCl | 1M KCl | 1M NH$_4$NO$_3$ | sample | | membrane | | 0.01M KCl | AgCl | Ag

All potentials were measured by using a Metrohm 654 digital voltmeter. Salt solutions used in experimental work were prepared by successive dilution of initial 5×10^{-2} mol/dm^3 stock solution. Activity coefficients were calculated by the Debye-Hueckel approximation [10]. For the ion-exchange membrane, values of the selectivity coefficient $K_{TMA,M}^{pot}$ were determined by the fix interference method (FIM) [11,12]. The initial solution was 10^{-2} (TMA)Cl and 2×10^{-3} mol/dm^3 in either LiCl, NaCl or KCl. The sample was diluted until further dilution resulted in no potential change, while concentration of the metal chloride was maintained constant. For the membranes containing ionophores 1 to 4, selectivity coefficients were determined by the separate solution method (SSM) [12].

2.2. Procedure II. Membranes were prepared in the same way as that described in Procedure I. The membrane with chromoionophore contained KTClPB (5.5 mmol/kg), DOS (121 mg), PVC (60 mg) and ETH 2458 (1.5 mg). The membranes with ionophore contained the same amount of KTClPB (5.2 to 5.5 mmol/kg), 55 to 60 wt % plasticizer (DOS), 27 to 30 wt % of PVC and ETH 2458 (1.5 mg). The ionophore concentrations were: ionophore 1 – 13.1 mmol/kg, ionophore 2 – 13.7 mmol/kg, ionophore 3 – 30.2 mmol/kg and ionophore 4 – 13.5 mmol/kg.

The electrodes were prepared in the same manner as that described in Procedure I. The inner electrolyte was 0.01 mol/dm^3 potassium chloride solution, buffer pH = 4 (1 mmol/dm^3 boric acid and 1 mmol/dm^3 citric acid). The ion-selective electrodes and reference electrodes were fabricated also in the same way. The sample buffered solution was 1 mmol/dm^3 boric acid, 1 mmol/dm^3 citric acid with 0.1 mol/dm^3 either LiCl, NaCl or KCl. It was titrated with either 1 mol/dm^3 LiOH, NaOH or KOH in order to increase pH of the sample. The pH was simultaneously monitored with a glass pH-electrode (type OSH 10-10 Metron).

RESULTS AND DISCUSSION

Complexation phenomena can be characterized by various parameters, however, the complex stoichiometry and complex stability constants seem to be most descriptive [13]. The possibility of determination of the ion-ionophore complex stability constant for the highly lipophilic ionophores, which do not dissolve well in polar organic solvents, is a great advantage of the described procedures. Procedure I seems to be more reliable, easier to perform and more general (provided that the studied ionophores do not interact with the TMA$^+$ reference cation). Procedure II, where two electrodes are compared, is likely to be biased, because the potential difference between those electrodes may depend not only on their composition but also on their characteristics. The complex stability constants, determined by using both procedures, are given in Table 1. The results clearly show higher β values of the Li$^+$ complexes than those of the Na$^+$ and K$^+$ complexes. Values determined by using both procedures confirm the general tendency in binding of alkali metal cations by studied ionophores. That is, ionophores with six coordinating sites (1 and 2) form more stable

complexes than ionophores with only four binding sites (3 and 4). Generally, slightly higher values of $\log\beta_{ML}$ were obtained by using Procedure II. The selectivity of the electrode depends on the ratio of complex stability constants, so the differences in stability constants of complexes of ionophore with corresponding ions are responsible for the membrane selectivity. The complex stability constant values for all studied ionophores 1–4 and sodium cation are very much alike, but the larger the difference between the values of $\log\beta_{LiL}$ and $\log\beta_{NaL}$ the better the selectivity of the electrode. The best Li^+ *vs*. Na^+ selectivity was found for 1, for which $\log K_{Li,Na}^{pot} = -2.4$ (FIM) or -2.1 (SSM).

Table 1. Complex stability constants determined using Procedures I and II.

Ionophore	Cation	$\text{Log}\beta_{ML}$	
	M^+	Procedure I	Procedure II
1	Li^+	6.7	7.4
	Na^+	4.5	5.1
	K^+	3.2	2.8
2	Li^+	6.4	7.7
	Na^+	4.7	5.6
	K^+	2.8	4.4
3	Li^+	5.9	5.8
	Na^+	4.3	4.2
	K^+	2.9	3.5
4	Li^+	5.9	7.0
	Na^+	4.1	5.2
	K^+	3.1	4.1

Recently, an improved procedure [5,14–16] was introduced, which utilizes a sandwich membrane. This procedure does not require the use of a reference ion in the sample or a second ionophore in the membrane. Stability constant of complex containing lithium cation and ionophore 1 determined by using the sandwich procedure equals to 7.4 with a membrane based on PVC-BBPA (bis(1-butylpentyl)adipate [16] or 8,24 if DOS was used as plasticizer [14]. These values are consistent [16] or higher [14] than those determined in the present study. Synthesized by us ligand 1, which can be used in electrodes of practical relevance, has been chosen for model studies of Li-ionophores.

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