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## Alkali-Metal and Alkaline-Earth Cation and Proton Selectivities of Dibenzo-14-crown-4 and Its Derivatives in Polymeric Membranes

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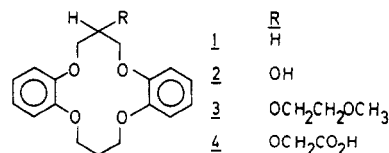
**The influence of attaching pendant groups with additional coordinating sites to dibenzo-14-crown-4 upon the response of solvent-polymeric membranes to alkali-metal and alkaline-earth cations and protons has been determined. Marked variation in cation selectivity is noted when  $-OH$ ,  $-OCH_2CH_2OCH_3$ , and  $-OCH_2CO_2H$  groups are attached to the central carbon of the three-carbon bridge in the ionophore.**

Electrically neutral macrocyclic polyethers (crown ethers) function as ionophores for alkali-metal and alkaline-earth cations. The metal ions are bound by the ethereal oxygens and the resulting complexes are usually highly stable and often significantly selective. These properties have been utilized in the development of cation-selective synthetic membranes (1-8). When incorporated into the matrix of solvent-polymeric membranes, lipophilic crown ethers act as ionophores and exhibit rather selective transport properties for alkali-metal and alkaline-earth metal cations (1-4, 6). One of the common methods used to determine the selectivity of the membrane toward a specific cation and, in turn, one of the potential uses of these membranes is emf measurement with an "ion-selective electrode" assembly (5, 7, 8). The selectivity of the membrane, which is estimated by  $K_j^{pot}$ , has been shown to be highly dependent on the selectivity of the incorporated ligands, as expressed by the complex stability constants of the ionophores with the cations.

Previously it was shown that the crown ether dibenzo-14-crown-4 (DB14C4, 1) is a selective complexing agent for  $Li^+$  (6) and is therefore a candidate for use in solvent extraction and membrane transport of  $Li^+$ . To probe the effect of attaching pendant functions which have additional coordination sites upon the cation selectivity of DB14C4 compounds, a

series of DB14C4 derivatives has been synthesized. This study is focused upon DB14C4 rather than 14-crown-4, which is also a selective ionophore for  $Li^+$  (9, 10). The DB14C4 system provides a rigid and well-defined macrocyclic conformation which is an ideal "base" for the square-pyramidal coordination that favors  $Li^+$  complexation (6, 11, 12). Hence with the DB14C4 system, conformational changes of the macrocyclic skeleton are minimized, which should enhance and sharpen the effects of pendant functional groups.

The cation selectivities of DB14C4 compounds toward alkali-metal and alkaline-earth cations and protons have been determined by the  $\Delta emf$  method, using an ion-selective cell assembly (4, 6, 8). We now report the results of cation selectivity measurements which have been performed on DB14C4 (1) and DB14C4 derivatives 2, 3, and 4.



### EXPERIMENTAL SECTION

**Synthesis.** Synthetic routes for 1-4 are summarized in Figure 1, whereas complete details for the preparation of 1, 2, and 4 are presented elsewhere (11, 13, 14).

*sym*-Dibenzo-14-crown-4-oxethyl methyl ether (3) was synthesized by the following procedure. After removal of the protecting mineral oil from sodium hydride (0.45 g, 19 mmol) by washing with pentane under nitrogen, dry tetrahydrofuran (200 mL) and 2 (2.0 g, 6.0 mmol) were added. The reaction mixture was stirred for 30 min at room temperature and 2-methoxyethyl bromide (1.8 g, 13 mmol) in 30 mL of THF was added dropwise during 1 h, after which the mixture was stirred 2 h at room temperature, refluxed for 2 h, and filtered. The filtrate was

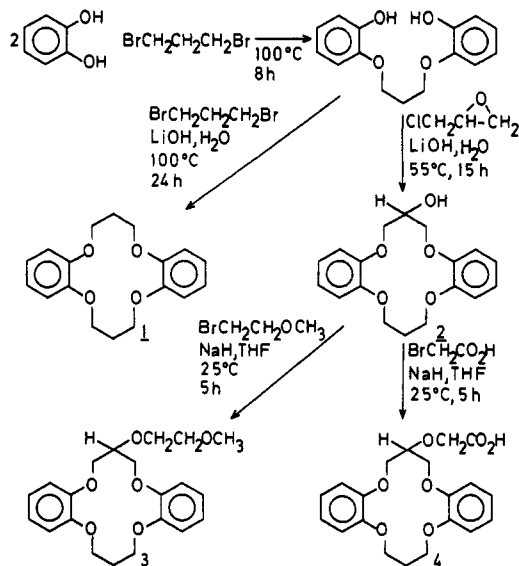


Figure 1. Synthetic routes to dibenzo-14-crown-4 and its derivatives.

Table I. Sensitivities of Crown-Based Polymeric Membrane Electrodes Containing Ionophores 1-4 for Ammonium Ion Standards

ionophore	range of linearity for aqueous $\text{NH}_4\text{Cl}$ solutions, M	slope <sup>a</sup>
1	$10^{-1}$ – $10^{-4}$	$41.7 \pm 0.9$
2	$10^{-1}$ – $10^{-4}$	$43.2 \pm 1.1$
3	$10^{-1}$ – $10^{-4}$	$42.8 \pm 1.2$
4	$10^{-1}$ – $10^{-8}$	$45.6 \pm 1.4$

<sup>a</sup> For plots of emf in mV vs  $\log [\text{NH}_4^+]$ , M.

evaporated in vacuo and the residue was dissolved in methylene chloride. The solution was washed with 1 N sodium hydroxide and water, dried over magnesium sulfate, and evaporated in vacuo. The residual oil was subjected to high vacuum at 100 °C to remove unreacted 2-methoxyethyl bromide, refluxed in pentane overnight, and placed in a refrigerator overnight. Crown ether 3 (2.20 g, 92% yield) was obtained as a white solid with mp 55–57 °C. IR (deposited film on sodium chloride plate): 1240, 1220, and 1110  $\text{cm}^{-1}$  (aryl and/or alkyl C–O).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  2.23 (q, 2 H), 3.37 (s, 3 H), 3.50–3.72 (m, 2 H), 3.72–4.00 (m, 9 H), 4.47 (m, 1 H), 6.91 (m, 8 H). Anal. Calcd for  $\text{C}_{21}\text{H}_{28}\text{O}_6$ : C, 67.38; H, 6.95. Found: C, 67.61; H, 6.82.

**Membrane Preparation and emf Measurement.** The solvent-polymeric membranes were prepared with 2 wt % of the crown ether, 33 wt % of poly(vinyl chloride) (PVC), and 65 wt % of the membrane solvent dioctyl sebacate (DOS). In a second set of experiments, the polymeric membranes were prepared in similar fashion but with the addition of 30 mol % of KTpCIPB relative to the weight of crown ether. The membrane preparation and the emf measurement technique have been described in detail elsewhere (3, 4, 6). Cells of the type  $\text{Hg}|\text{HgCl}_2|\text{KCl}(\text{satd})|\text{electrolyte bridge}|\text{sample solution}||\text{membrane}||\text{internal filling solution}, \text{AgCl}|\text{Ag}$  with double junction reference electrodes and Philips IS-560 electrode bodies for mounting the membranes were used. The internal filling solution was aqueous 0.010 M  $\text{NH}_4\text{Cl}$ . The separate solution technique (3, 4) and 0.10 M sample solutions were used to determine the selectivity factors, which are given by

$$\log K_{\text{NM}}^{\text{Pot}} = \frac{(\text{emf}_N - \text{emf}_M)Z_N F}{2.303RT} - \log a_m^{Z_N - Z_M} + \log a_N \quad (1)$$

where  $Z_N$  is the charge of reference ion,  $Z_M$  is the charge of interfering ion,  $\text{emf}_N$  is the emf of the cell assembly when the sample is a solution of the chloride of the interfering cation, and  $\text{emf}_M$  is the emf of the cell assembly when the sample is a solution of the chloride of the reference cation ( $\text{NH}_4^+$ ). The emf measurements were performed at 25 °C by using 0.10 M aqueous

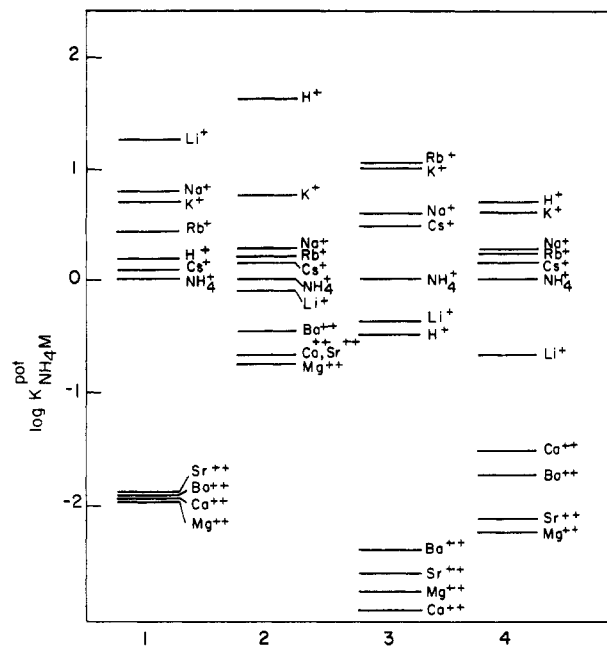


Figure 2. Selectivity factors  $\log K_{M_1, M_2}^{\text{pot}}$  for solvent polymeric membranes containing ionophores 1, 2, 3, and 4: reference,  $\text{NH}_4^+$  (M1); membrane composition, 2 wt % ionophore, 33 wt % PVC, 65 wt % DOS.

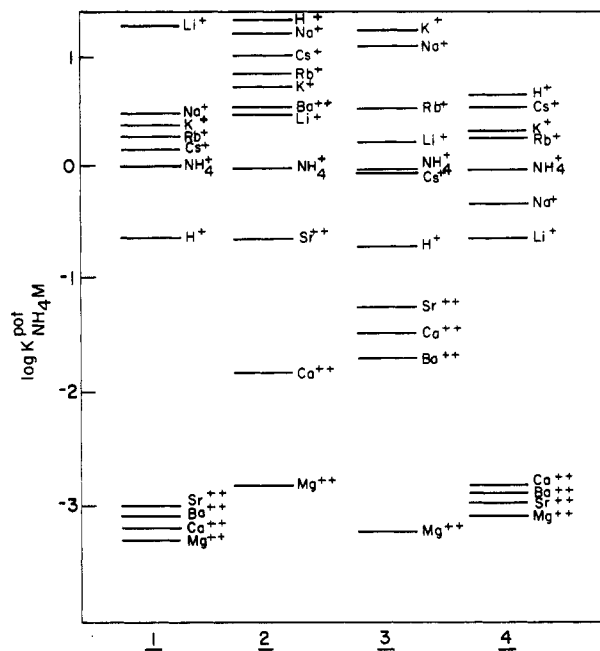


Figure 3. Selectivity factors  $\log K_{M_1, M_2}^{\text{pot}}$  for solvent polymeric membranes containing ionophores 1, 2, 3, and 4; reference,  $\text{NH}_4^+$  (M1); membrane composition, 2 wt % ionophore, 33 wt % PVC, 65 wt % DOS + incorporated lipophilic anionic sites (KTpCIPB).

solutions of the respective chlorides (4) and had a standard deviation of <0.1 mV for single determinations. Sensitivities of the crown-based electrodes containing ionophores 1–4 for lithium ion standards are given in Table I.

## RESULTS

The potentiometrically determined selectivity factors induced in solvent-polymeric membranes by the four DB14C4 compounds are presented in Figures 2 and 3. The selectivity factors, given as  $\log K_{M_1, M_2}^{\text{pot}}$  values, represent the membrane preference for cation M2 relative to cation M1, the reference cation. In this study, the reference cation was  $\text{NH}_4^+$  and the membrane solvent was dioctyl sebacate (DOS). In a second set of experiments, a similar system was used in which lipo-

philic anionic sites [potassium tetrakis(*p*-chlorophenyl)borate, KTpClPB] were incorporated into the synthetic membrane (Figure 3).

The results presented in Figures 2 and 3 can be summarized briefly as follows: [1] For the metal cations, the membrane containing 1 is selective for  $\text{Li}^+$ , the membrane containing 2 prefers  $\text{K}^+$  or  $\text{Na}^+$  (depending on the conditions), the membrane containing 3 prefers  $\text{Rb}^+$  or  $\text{K}^+$ , and the membrane containing 4 prefers  $\text{Cs}^+$  or  $\text{K}^+$ . [2] The membrane containing 1 prefers  $\text{Li}^+$  over all the other alkali-metal and alkaline-earth cations regardless of the membrane composition or the measurement conditions, whereas the selectivities of membranes containing 2, 3, or 4 are sensitive to both factors. [3] For membranes containing any of the four DB14C4 compounds, there is strong preference for monovalent cations over the divalent cations although to a lesser extent for membranes containing 2. [4] Proton uptake is significant for membranes containing compounds 2 or 4 (which possesses an ionizable group) and is much lower for membranes containing compounds 1 or 3. [5] Incorporation of lipophilic anionic sites (KTpClPB) in membranes containing 1 improves the selectivity toward  $\text{Li}^+$ . However for membranes containing 2–4, this type of membrane modification does not exhibit any clear effect on selectivity other than changing the apparent preferred cation.

## DISCUSSION

To be used as an ionophore, a compound should meet the following requirements: [1] The carrier molecule is composed of polar and nonpolar groups. [2] The carrier molecule is able to assume a stable conformation that provides a polar cavity, suitable for the uptake of a cation, and a nonpolar lipophilic exterior. [3] The polar groups in the cavity can be any polar atom that is capable of coordinating directly to the metal cation. Oxygen atoms are preferred for the alkali-metal and alkaline-earth cations and may be ether, hydroxyl, carbonyl, or carboxylate units. [4] The number of binding sites in the cavity is 4–12 with a lower coordination number for the smaller cations (e.g.  $\text{Li}^+$ ) and a higher coordination number for the larger cations (e.g.  $\text{Cs}^+$ ). [5] The molecular structure of the molecule and hence the geometry of the cavity binding sites are of central importance. High selectivities are achieved by locking the coordinating sites into a rigid arrangement around the cavity. The cation that best fits into the offered cavity is preferred. [6] Although relatively rigid (point 5 above), the ligand should be flexible enough to allow for a sufficiently rapid ion exchange. [7] To allow adequate stability and mobility in the membrane, the overall dimensions of the carrier molecule should be rather small but still compatible with high lipid solubility.

Compounds 1–4 appear to meet all these general requirements but differ considerably among themselves in the number of potential binding sites (point 4), in the arrangement and geometry of the "apparent cavity" (point 5), and in the overall polar character of the molecule (point 7). It is therefore not surprising that although all four derivatives are potentially good ionophores, they exhibit different selectivities toward the alkali-metal and alkaline-earth cations. Moreover, although the basic unit is DB14C4, the additional functional groups change completely the binding characteristic of the ligands. The crystal structure of the lithium complexes of 1 (12) and 4 (11) and the monohydrate complex of 2 (15) indicate that the DB14C4 units assume nearly identical conformations upon complexation with  $\text{H}_2\text{O}$  or  $\text{Li}^+$ . This suggests that the structure of the DB14C4 unit is identical in the complexes of all four compounds and is independent of environmental conditions and is also probably independent of the metal cation to be bound. This evidence for similar rigid and stable macrocyclic conformations in the DB14C4 unit indicates that

the macrocyclic ethereal oxygens form an identical geometrical arrangement in all four compounds and it is only the side arm functional groups that change the overall three-dimensional arrangement of the binding site (15).

The results of the membrane selectivity factor measurements for compounds 1–4 for the alkali-metal and alkaline-earth cations clearly demonstrate that compound 1 is a good and selective complexing agent for  $\text{Li}^+$ , whereas the derivatives 2–4 are poor complexing agents for  $\text{Li}^+$  relative to the other alkali-metal cations. Considering the crystal structures of the lithium complexes of 1 and 4 (11, 12) and the monohydrate complex of 2 (15) and on the basis of the examination of molecular models of all four compounds, we interpret the experimental selectivity results for compounds 1–4 as follows: [1] In stable complexes of  $\text{Li}^+$  with small macrocyclic polyether compounds,  $\text{Li}^+$  prefers pentacoordination, and especially the square-pyramidal geometry. [2] The DB14C4 macrocycle provides an ideal "base" for the square-pyramidal coordination, in which a direct interaction of the lithium cation and the four ethereal oxygens occurs. [3] The fifth (apical) coordination site in the DB14C4/ $\text{Li}^+$  complex is occupied by the counterion or a solvent molecule. [4] In derivative 2, the  $-\text{OH}$  group gives rise to proton binding probably because a monohydrate complex is formed which should strongly bind a proton. Also the encapsulated water molecule would hinder coordination of metal cations which explains the poor selectivity. [5] In derivatives 3 and 4, the additional side arm is too short to bring the functional group into a proper apical position for the preferred  $\text{Li}^+$  coordination. Moreover, these side arms are flexible enough to allow an "open" conformation in which the functional groups (the side arm ethereal oxygens and the carboxylate group) could participate in six- to eight-coordination binding of larger cations ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$  or  $\text{Cs}^+$ ). In these higher coordination complexes, the remaining binding sites are probably filled by counterions and/or solvent molecules. [6] The similar selectivities observed for crown ether alcohol 2 and crown ether carboxylic acid 4 indicate that the latter is functioning in its nonionized forms. [7] The reduced selectivities of compounds 2–4 toward any particular cation in certain conditions and the dependence of this selectivity on the membrane composition could be associated with the more "open" coordination assumed by these derivatives and the greater anion and solvent molecule participation in the coordination sphere. The macrocycle contribution (four binding sites) to the stability of the complex is reduced as the coordination number increases and when a monohydrate complex is formed. [8] The divalent cations are generally strongly rejected by all four compounds because of the special structural property of the DB14C4 frame whose "V"-shaped conformation allows direct or close contact with the counterion(s) only at one side of the complex (12). Divalent cations are disfavored, therefore, because of the lack of room for the charge balancing counterion(s) (especially if the counterions are monovalent (12)).

## CONCLUSIONS

For the design of more selective ionophores for  $\text{Li}^+$  to be incorporated in solvent-polymeric membranes, the following points are noted: [1] The DB14C4 frame (compound 1) appears to be a good starting structure. [2] To improve the selectivity of 1 toward  $\text{Li}^+$ , an internal fifth ligand should be added. [3] The side arms consisting of  $-\text{OH}$ ,  $-\text{OCH}_2\text{CH}_2\text{OCH}_3$ , or  $-\text{OCH}_2\text{COOH}$  are too short and the latter two are probably too flexible, which allows coordination of larger cations. [4] To eliminate competitive reactions with protons and formation of stable hydrate complexes, the ionophore should not contain functional groups which can participate in hydrogen bonding and in acid-base reactions (e.g.  $-\text{OH}$  and  $-\text{COOH}$ ). [5] From points 3 and 4, it appears that a longer and more rigid side

arm, carrying an etheral functionality, would be best for the lithium fifth coordination role.

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## Electrochemical Study of the Mechanism of Cadmium Extraction with Dithizone

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**A current-scanning polarographic study of extraction processes involving dithizone and its metal chelates using the ascending water electrode (AWE) has been conducted. Of the metals examined, Cd(II) gives a wave that arises from the transfer of an unusual, charged, mixed ligand complex species, Cd(OAc)Dz<sub>2</sub><sup>-</sup>. Other metal ions that form extractable dithizonates could be indirectly determined by their effect on the dithizonate wave.**

### INTRODUCTION

This represents a continuation of our electrochemical studies of the transfer processes associated with metal ion extractions utilizing the ascending water electrode (AWE) (1-7), which has proven to be a useful approach to the elucidation of the details of the chemistry of solvent extraction.

In this report, the behavior of diphenylthiocarbazonate (dithizone), a weak monobasic acid with an aqueous  $pK_a$  of 4.7 (8), a widely used extractant whose sulfur atom bonding site results in a fair degree of selectivity, is examined, and its mechanism of extraction of cadmium is elucidated in this paper.

### EXPERIMENTAL SECTION

The apparatus and procedures for current scan polarography at the AWE have been described earlier (2-8). The electrolytic cell used earlier was slightly modified in order to improve the stability of the organic reference electrode. The elimination of tetramethylammonium chloride, TMA<sup>+</sup>Cl<sup>-</sup>, from both aqueous and organic reference solutions (which contain 1 M LiCl and 0.01 M tetraheptylammonium tetraphenylborate, THA<sup>+</sup>TPB<sup>-</sup>, respectively) of the electrode resulted in stable readings for at least a month, whereas the earlier organic reference had to be replaced at least weekly. With the new arrangement, the potential of the organic reference electrode is largely determined by the charge

of the double layer, inasmuch as there is not a common ion transferring across the aqueous/organic interface. As no charge flows through the electrode, i.e., no charging or discharging occurs, the potential is reproducible. The net effect is a shift in the  $\Phi_0^*E$  of  $106 \pm 7$  mV in the positive direction, compared to the electrode containing TMA<sup>+</sup>Cl<sup>-</sup>.

The electrolyte used in the 1,2-dichloroethane (DCE) phase was 0.01 M THA<sup>+</sup>TPB<sup>-</sup>, prepared by mixing THA<sup>+</sup>Br<sup>-</sup> dissolved in DCE and aqueous Na<sup>+</sup>TPB<sup>-</sup> in stoichiometric proportions. Dithizone (Eastman Kodak Co.) was purified by recrystallization. 1,2-Dichloroethane (DCE) (Aldrich Chemical Co.) was used as received. All other reagents were analytical reagent grade.

### RESULTS AND DISCUSSION

When current scan polarography is carried out on a HDz-DCE solution containing 0.01 M THA<sup>+</sup>TPB<sup>-</sup> as supporting electrolyte in contact with 0.2 M sodium acetate aqueous solution, a well-defined cathodic wave is obtained (Figure 1). The features of this wave are as follows:

1. The limiting current of the cathodic wave is proportional to the initial concentration of HDz in DCE.
2. The limiting current is proportional to the square root of the height of the head of the aqueous reservoir.
3. The half wave potential shifts  $49.5 \text{ mV} \pm 2.0$  more positive per unit increase in pH in the range 6.4 to 10.7.
4. The logarithmic analysis shows the slope of  $59.3 \text{ mV} \pm 3.0$ .

These characteristics suggest that the diffusion-controlled cathodic wave represents the transfer of the dithizonate anion from aqueous to organic phase. This is quite analogous to the behavior of other acidic extractants (1-4).

When Cd ion is present in the aqueous solution, another cathodic wave having a more positive half-wave potential, which is completely distinct from the deprotonated wave, appears (Figure 2). The minimum pH of the appearance of the new wave is 5.4, which is lower than that for the depro-