Potassium-selectivities of Bis(benzo-15-crown-5) Derivatives Obtained from Cyclohexanedicarboxylic Acids

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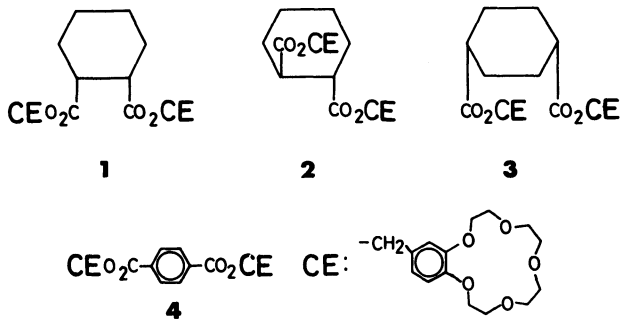
(Received November 25, 1982)

Synopsis. Several bis(benzo-15-crown-5) derivatives containing a cyclohexane or benzene ring in the bridge chain were synthesized as neutral carriers of coated-wire potassium-selective electrodes. The bis(benzocrown ether) derivative obtained from *cis*-1,2-cyclohexanedicarboxylic acid was found to be outstandingly potassium-selective.

Macrobicyclic polyethers containing benzo-15-crown-5 moieties at the end of a short bridge chain, which are commonly referred to as bis(benzo-15-crown-5) derivatives, have received considerable attention because of their attractive cation-binding properties.[1-5] They can form stable sandwich-type 2 : 1 crown ether ring to cation complexes with K^+ intramolecularly, which results in high K^+-selectivity of them on binding alkali and alkaline earth metal ions. Accordingly, some of the bis(benzo-15-crown-5) derivatives have turned out to be good neutral carriers for poly(vinyl chloride) (PVC) membrane K^+-selective electrodes,[6-8] although their K^+-selectivities depend more or less upon the configuration of bis(benzocrown ether) derivatives[7] and the length of the chain connecting two crown ether moieties.[6]

We would like to report here the K^+-selectivities of bis(benzo-15-crown-5) derivatives containing a cyclohexane or benzene ring in the bridge chain in the coated-wire type of K^+-selective electrodes based on them.



Experimental

Chemicals. Bis(benzo-15-crown-5) derivatives **1** through **4** were synthesized by the reaction of 4′-bromomethylbenzo-15-crown-5 with appropriate dicarboxylic acid potassium salts in acetonitrile, in a similar way to that reported previously.[9] The purification of them was performed by gel permeation chromatography. (**1**—**3**: colorless oil; **4**: colorless crystal, mp 100—102 °C) The plasticizer, *o*-nitrophenyl octyl ether (NPOE), was prepared in a usual manner,[10] and then purified by repeated distillation.

Electrode Construction. The coated-wire ion-selective electrodes were constructed using a silver wire, according to the procedure reported elsewhere.[11] The coating solution consists of 15 mg crown ether, 200 mg NPOE, 100 mg PVC, and 3 ml tetrahydrofuran. The external reference electrode was a standard calomel electrode with a 0.1 M (1 M = 1 mol/dm^3) NH_4NO_3 electrolyte bridge. No special conditioning of the ion-selective electrodes was performed before use.

Measurement. All of the emf measurements were made at 25±0.1 °C. Standard K^+ aqueous solutions for calibration plots were obtained by gradual dilution of 1 M KCl solution. Selectivity coefficients (k_{KM}) were determined by a mixed solution method, by taking a constant background of an interfering ion and varying K^+ concentration. The constant concentrations of Na^+, Rb^+, Cs^+, and NH_4^+ are 1×10^{-1}, 1×10^{-3}, 1×10^{-3}, and 1×10^{-2} M, respectively.

Results and Discussion

Three kinds of cyclohexanedicarboxylate-type bis(benzo-15-crown-5) derivatives **1**, **2**, and **3**, which are derived from *cis*-1,2-, *trans*-1,2-, and *cis*-1,4-cyclohexanedicarboxylic acids, respectively, were synthesized for the purpose of obtaining lipophilic and ion-selective neutral carriers for K^+-selective electrodes. Terephthalate-type bis(crown ether) derivative **4** was also prepared for comparison. The K^+-selectivities of the bis(benzo-15-crown-5) derivatives were elucidated by measuring the electrochemical selectivity of coated-wire ion-selective electrodes based on them, which can be easily made up owing to the simple construction.

The electrode properties are summarized in Table 1. The electrodes of bis(crown ether) derivatives **1** and **3** showed a linear response to K^+ activity in the range 10^{-4}—10^{-1} M, the slope of calibration plots being 55 and 58 mV per decade of activity change at 25 °C. The electrodes based on **2** and **4** exhibited a little poorer

Table 1. Electrode properties of coated-wire K^+-selective electrode based on bis(benzo-15-crown-5) derivatives **1** through **4**

Bis(crown ether)	Maximal[a] slope mV/decade	Range[b] pK	k_{KM} Na^+	Rb^+	Cs^+	NH_4^+
1	55	4—1	5×10^{-4}	5×10^{-2}	5×10^{-3}	2×10^{-1}
2	46	4—1	3×10^{-1}	1×10^{-1}	3×10^{-2}	1×10^{-2}
3	58	4—1	3×10^{-3}	2×10^{-1}	5×10^{-2}	3×10^{-1}
4	51	4—2	2×10^{-3}	3×10^{-1}	8×10^{-2}	5×10^{-2}

a) emf change in ten-time change of K^+ activity. b) pK = −log [K^+].

response than that of **1** and **3**.

It should be noted that bis(benzo-15-crown-5) derivatives **1**, **3**, and **4** are better in the K^+-selectivity over Na^+ than **2**. Particularly, the electrode of **1**, *cis*-cyclohexanedicarboxylate type of bis(benzo-15-crown-5) derivative, possesses an excellent k_{KNa} value, 5×10^{-4}. It has been reported previously that a *cis*-bis(benzo-15-crown-5) derivative obtained from maleic acid is easy to form sandwich-type complexes with K^+ intramolecularly, being rather K^+-selective compared to the corresponding *trans* isomer derived from fumaric acid.[3,7] This is also the case in these cyclohexanedicarboxylate type of bis(benzo-15-crown-5) derivatives. That is to say, the bis(benzo-15-crown-5) derivatives containing *cis* configuration, **1** and **3**, are much more K^+-selective than that containing *trans* configuration, **2**. Also, the k_{KNa} value for the electrode based on **1** is about one order of magnitude smaller than that of **3**, implying that the two crown ether moieties in the latter bis(benzo-15-crown-5) derivative are a little too far apart for the formation of the stable intramolecular sandwich-type K^+ complexes. The terephthalate unit of bis(crown ether) derivative **4** may be unfavorable again due to the rigidity of benzene ring.

Thus, the bis(benzo-15-crown-5) derivative obtained from *cis*-1,2-cyclohexanedicarboxylic acid is a highly K^+-selective neutral carrier for the ion-selective electrode. The response time of the electrode was within 10 s on measuring by an incremental method. In the stability and reproducibility of the emf reading, the electrode is similar to that based on the previous bis(benzo-15-crown-5) derivative.[11] Bis(benzo-15-crown-5) derivative **1** is surely superior to the previous ones[6,7] in the lipophilicity which is definitely required as the neutral carrier of the ion-selective electrodes, although they all seem to resemble in the K^+-selectivity.

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