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# Extraction of Alkali Metal Cations by Lipophilic Dibenzo-14-crown-4-carboxylic Acids

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# EXTRACTION OF ALKALI METAL CATIONS BY LIPOPHILIC DIBENZO-14-CROWN-4-CARBOXYLIC ACIDS

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## ABSTRACT

The extraction of alkali metal cations by the lipophilic crown ether, bis-*t*-octylbenzo-14-crown-4 (BOB14C4), three derivatives of BOB14C4 having pendant carboxylic acid sidearms, and a lipophilic carboxylic acid, 2-methyl-2-heptylnonanoic acid (HMHN) was studied by two-phase potentiometric titration and ion-chromatography. The lipophilic, ionizable crown ethers, BOB14C4-acetic acid (BOB14C4AA), BOB14C4-propanoic acid (BOB14C4PA), and BOB14C4-oxyacetic acid (BOB14C4OAA) extract cations efficiently from aqueous mixed alkali metal chloride solutions into 1-octanol by an ion-exchange mechanism in the range p[H] > 7, as does HMHN. The mode of attachment of the ionizable sidearm, via an ether linkage (BOB14C4OAA) versus a carbon linkage (BOB14C4AA and BOB14C4PA), has a significant effect on the cation selectivity and extraction efficiency of these extractants. BOB14C4 exhibits no p[H] dependent extraction behavior and has no significant effect on the extraction of alkali metal cations by HMHN in a mixture of these two compounds. Although BOB14C4AA and BOB14C4PA extract cations at lower p[H] than HMHN, all three compounds exhibit similar

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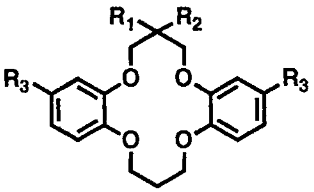
selectivity for $Li^+$ over $Na^+$, $K^+$, $Rb^+$, and $Cs^+$. A significant reversal in selectivity is observed with BOB14C4OAA, which extracts $Na^+$ and $K^+$ selectively over $Li^+$, $Rb^+$, and $Cs^+$ and at significanty lower p[H] than BOB14C4AA, BOB14C4PA, or HMHN. The unique behavior of BOB14C4OAA may be attributed to the presence of the ether linkage between the crown ether and the pendant carboxylic acid.

## INTRODUCTION

Crown ethers bearing ionizable sidearms have been shown to extract cations via an ion-exchange mechanism (1). While the recognition properties of the crown ether cavity are expected to contribute to the extraction selectivity of these compounds (2,3), the ionizable functionality can contribute ion-exchange selectivities of its own. In order to investigate how the ionizable sidearm and the macrocyclic cavity together affect the extraction properties of ionizable lariat ethers, we have been studying crown ether carboxylic acids (4) based on dibenzo-14-crown-4 (DB14C4), **1** (Figure 1), which has been shown to be a lithium-selective ionophore (5). We have focused on the series of lipophilic crown ether carboxylic acids **3-5**. Solid-state and solution structural studies (6-11) have shown that the orientation of the sidearm relative to the macrocyclic cavity in a series of DB14C4 lariat ethers depends strongly on the atom which connects the pendant carboxylic acid function to the crown ether; when the sidearm is connected via an oxygen atom (as in **5**) it is oriented towards the cavity (in a pseudo-axial position), whereas when the sidearm is attached through a carbon linkage (as in **3** and **4**), it adopts an orientation away from the cavity (pseudo-equatorial). Previous extraction studies on these and related compounds (**6** and **7**) have indicated lithium selectivity for compounds **3** (12,13) and **6** (3), while compound **7** extracted sodium more strongly than lithium (14). In order to investigate the factors that influence cation selectivity in crown ether carboxylic acids, we have performed competive extractions of alkali metal cations with **3-5** using a two-phase potentiometric titration method. We have compared the results of these extractions with those obtained using the organophilic acid, 2-methyl-2-heptylnonanoic acid (HMHN), the organophilic crown ether bis-*t*-



**1** $R_1 = R_2 = R_3 = H$
**2** $R_1 = H$, $R_2 = H$, $R_3 = $ -*t*-octyl
**3** $R_1 = -CH_2CO_2H$, $R_2 = H$, $R_3 = $ -*t*-octyl
**4** $R_1 = -CH_2CH_2CO_2H$, $R_2 = H$, $R_3 = $ -*t*-octyl
**5** $R_1 = -OCH_2CO_2H$, $R_2 = H$, $R_3 = $ -*t*-octyl
**6** $R_1 = -OCH_2CO_2H$, $R_2 = -C_{10}H_{21}$, $R_3 = H$
**7** $R_1 = -OCH(C_8H_{17})CO_2H$, $R_2 = R_3 = H$

*t*-octyl = $-C(CH_3)_2CH_2C(CH_3)_3$

FIGURE 1. Structures of dibenzo-14-crown-4 ethers.

octylbenzo-14-crown-4 (**2**) and a mixture of HMHN with **2** (called hereafter HMHN + **2**).

## EXPERIMENTAL

The extractants **2-5** were prepared by Friedel-Crafts alkylation of the corresponding dibenzo-14-crown-4 ethers (8) and purified as described previously (12). HMHN was prepared and purified as described previously (12). HPLC grade 1-octanol (Aldrich Chemical Co.) was used as obtained. Distilled water was passed through a Barnstead NANOPURE II water putification system and purged with a stream of $CO_2$-free argon gas before use. All aqueous solutions were maintained under an argon atmosphere and manipulated by syringe and/or cannula through rubber septa. All solutions for ion chromatography were stored in polypropylene bottles and vials. Alkali metal halide solutions were prepared from commercially available metal halide salts. Stock solutions of **4**, **5**, HMHN, and HMHN + **2** were prepared in 1-octanol and standardized by dilution of a measured aliquot in ethanol followed by titration with ethanolic NaOH. A stock solution of **2** in 1-octanol was used as prepared. The hydroxide-containing aqueous or ethanolic stock solutions were standardized against oven-dried KHP (NIST primary standard).

Two-phase titrations were performed at 25 °C using the technique described previously (12). The microsyringe and microburet were calibrated gravimetrically using doubly-distilled water. The p[H] was monitored using an Orion 8103 Ross double-junction combination electode. The electrodes were filled with 3.0 M NaCl. Titrations were performed with 2 mL of organic phase and 6 mL of aqueous phase (initial volumes). The organic phases consisted of 0.014 - 0.018 M HMHN, **2**, **4**, or **5** in 1-octanol. The mixture HMHN + **2** consisted of 0.015 M HMHN and 0.015 M **2**. Mixed-metal halide stock solutions were prepared at 0.040 M in each alkali metal chloride in 0.002 M aqueous HCl. The mixed-metal titrant solution was prepared at 0.040 M sodium hydroxide plus 0.040 M of each of the chloride salts of the other four alkali metals. Samples of the organic phases (10 to 50 µL) were removed periodically by syringe, diluted into 0.25 mL of toluene, and extracted once with 2.0-mL portions of 2 mM HCl for analysis by ion chromatography. Ion chromatography was performed on a Dionex 2020i Integrated Gradient Ion Chromatograph with conductivity detection. In all two-phase titrations, p[H] readings stabilized within several minutes of titrant additions, except in the vicinity of endpoints, at which point equilibrium was considered to have been established.

The titration data were treated essentially as described previously (12,13). Meter readings were converted to p[H] values (defined as the negative logarithm of the hydrogen ion molarity) by use of strong acid-strong base blank titrations and by the use of HCl internal standard in all titrations. No alkaline error was noted for the electrode. It has been shown (15) that BOB14C4AA (**3**) distributes negligibly from 1-octanol to 0.1 M NaOH ($[\mathrm{NaBOB14C4AA}]_{org}/[\mathrm{NaBOB14C4AA}]_{aq} > 5000$), that alkali metal halides are not extracted to any significant extent by **3** (13), and that negligible alkali metal hydroxide is extracted by the salt form of **3** (13). Assuming that **4** and **5** behave similarily, the equivalents of metal ions exchanged by **3** and **5** in the two-phase titrations may then be evaluated from the mass-balance relationship (12),

$$[\mathrm{MA}]_{org} = (V_{titr}/V_{org})[\mathrm{MOH}]_{titr} + (V_{aq}/V_{org})([\mathrm{H}^+] - K_w/[\mathrm{H}^+]) - (V_{aq,init}/V_{org})[\mathrm{HCl}]_{init} \qquad (1)$$

In eq. 1, $[MA]_{org}$ is the organic-phase molarity of lariat ether in the salt form, $V_{org}$ is the volume of the organic phase (assumed constant), $V_{aq,init}$ is the initial volume of the aqueous phase, $V_{titr}$ is the volume of alkali metal hydroxide (MOH) titrant added to the vessel, $V_{aq}$ is the total volume of the aqueous phase (equal to $V_{aq,init} + V_{titr}$), $[HCl]_{init}$ is the initial molarity of HCl in the aqueous phase, $[MOH]_{titr}$ is the molarity of MOH in the titrant, and $[H^+]$ is the equilibrium molarity of hydrogen ions. For these titrations, eq. 1 was corrected for the removal of small samples from the organic phase. No correction was made for the small volume changes of the two phases owing to the mutual solubility of octanol and water.

## RESULTS AND DISCUSSION

The corrected two-phase titration curves for the 1-octanol blank, HMHN, **2**, and HMHN + **2** are shown in Figure 2. The data for **2** and for the 1-octanol blank follow the titration curve expected for the neutralization of the strong-acid internal standard (HCl) by the strong-base titrant, indicating no weak-acid behavior for either of these reagents. The data for HMHN + **2** is superimposable on that for HMHN alone, indicating no enhancement of the acidity of HMHN by the addition of the crown ether **2**. From analysis of samples withdrawn from the organic phase during the titration, the organic-phase concentrations of the individual metal ions were determined. The organic-phase lithium and sodium concentrations for the two systems HMHN and HMHN + **2**, expressed as the loading ratio $[M]_{org}$ / $[HMHN]_{init}$ (where $[M]_{org}$ is the measured organic-phase concentration of $Li^+$ or $Na^+$ ions and $[HMHN]_{init}$ is the initial organic-phase concentration of HMHN), is given in Figure 3. The differences between the two systems are within experimental error and indicate that the carboxylic acid HMHN exhibits a modest selectivity for lithium, and that the $Li^+/Na^+$ selectivity is not altered by the addition of the crown ether **2**.

The corrected two-phase titration curves for the five systems, HMHN, HMHN + **2**, **3**, **4**, and **5**, are shown in Figure 4. Three different trends are evident. All three crown ether carboxylic acids act as stronger acids than either HMHN or HMHN + **2**. Whereas **3** and **4**, in which the

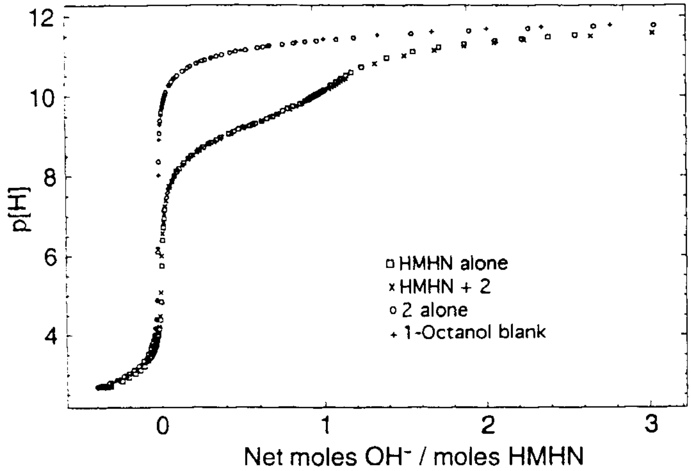


FIGURE 2. Two-phase potentiometric titrations of 1-octanol blank, HMHN, **2**, and HMHN + **2** at 25 °C. The aqueous phase (6 mL) consisted of 0.04 M LiCl, 0.04 M NaCl, 0.04 M KCl, 0.04 M RbCl, 0.04 M CsCl, and 0.002 M HCl. The organic phase (2 mL) initially consisted of pure 1-octranol, 0.0176 M HMHN, 0.0150 M **2**, or 0.0153 M HMHN + 0.0152 M **2**, respectively. Samples were withdrawn for analysis, and the mole ratio given on the x-axis was corrected for the withdrawal.

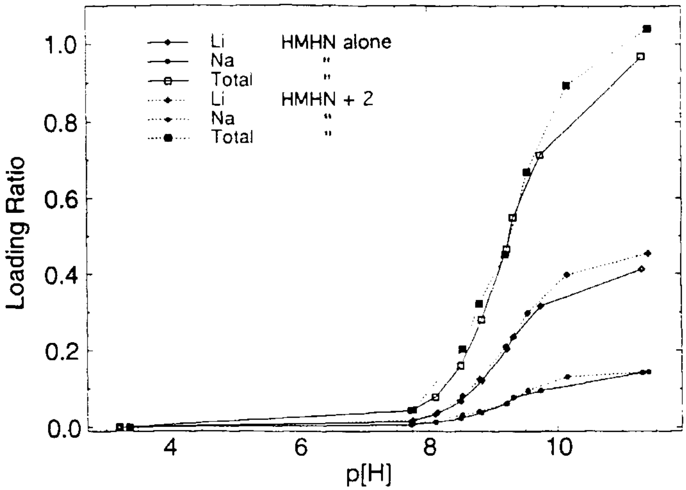


FIGURE 3. Ion-exchange loading of HMHN and HMHN + **2** with $Li^+$ and $Na^+$ as a function of p[H]. The loading ratio is expressed as $[M]_{org}/[HMHN]_{init}$ as defined in the text. The data were collected during the titrations depicted in Fig. 2.

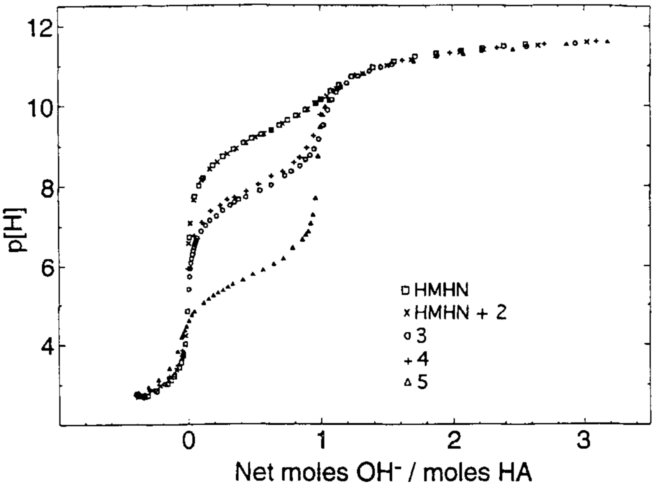


FIGURE 4. Two-phase potentiometric titrations of HMHN, HMHN + **2**, **3**, **4**, and **5** in 1-octanol at 25 °C. The aqueous-phase compositions were the same as in Fig. 2. The organic-phase compositions were 0.0176 M HMHN, 0.0153 M HMHN + 0.0152 M **2**, 0.0139 M **3**, 0.0142 M **4**, and 0.0139 M **5**.

carboxylic acid sidearm is attached though a carbon linkage, exhibit acidities approximately 1.2 - 1.3 pKa units below that of HMHN, **5**, which contains an ether linkage to the α-carbon of the carboxylic acid, acts as a stronger acid than HMHN by nearly 3.5 pKa units. Although the structures of the crown ether carboxylic acids differ significantly from that of HMHN, these results suggest that attachment of the carboxylic acid functionality to the crown ether has a significant effect on the apparent acidity of the carboxylic acid. The increase in acidity exhibited by **5** can be partially attributed to the inductive effects of the oxygen atom on the carbon α to the carboxylate group; however, the extent to which conformational effects and aggregation influence the apparent acidity of these crown ether carboxylic acids cannot be elucidated from these data.

The organic phase metal ion concentrations for all five alkali metals, as determined by analysis of samples withdrawn from the organic phase during the titrations and expressed as the loading ratios $[M]_{org}$ / $[HA]_{init}$

(where HA represents any of the organic acids), are given in Figure 5 for HMHN, **3**, **4**, and **5**. No significant p[H]-dependent effect on the selectivity of the metals extracted is observed for any of these systems. The three compounds, HMHN, **3** ,and **4**, exhibit similar selectivity for the extraction of lithium and little preference for any of the other four alkali metal cations. The extraction using **5**, however, displays a remarkably different pattern, with a significant selectivity for both sodium and potassium and little selectivity for the cations $Li^+$, $Rb^+$, and $Cs^+$. The reversal of extraction selectivity in **5**, as compared to HMHN, **3**, and **4**, may be attributed to the presence of the additional coordinating site provided by the ether oxygen linking the carboxylic acid sidearm to the macrocyclic ring. Previous studies have shown that this oxygen is optimally positioned to bind to a complexed sodium ion but does not bind directly to a coordinated lithium ion (5-8). These extraction results suggest that potassium also fits well into the cavity formed by the macrocyclic ring and the sidearm oxygen atom but that rubidium and cesium are poorly accommodated.

## CONCLUSION

Competitive extractions of alkali metal cations by a lipophilic carboxylic acid and by lipophilic crown ether carboxylic acids during two-phase potentiometic titration experiments have provided insights into the effect of crown ether structure on the extraction properties of ionizable lariat ethers. These results indicate that, although the dibenzo-14-crown-4 system is known to be selective for the extraction of lithium over the other four alkali metals, this property only slightly enhances the inherent lithium selectivity of the lipophilic carboxylic acid HMHN when a mixture of the two reagents is used. On the other hand, although the crown ether carboxylic acids **3** and **4** exhibit lithium selectivity similar to that of HMHN, attachment of the crown ether to a carboxylic acid increases the efficiency of the extraction, which is accompanied by an apparent decrease in the effective $pK_a$ of **3** and **4** relative to HMHN. This may suggest that while the crown ether provides a suitable coordinating environment for the

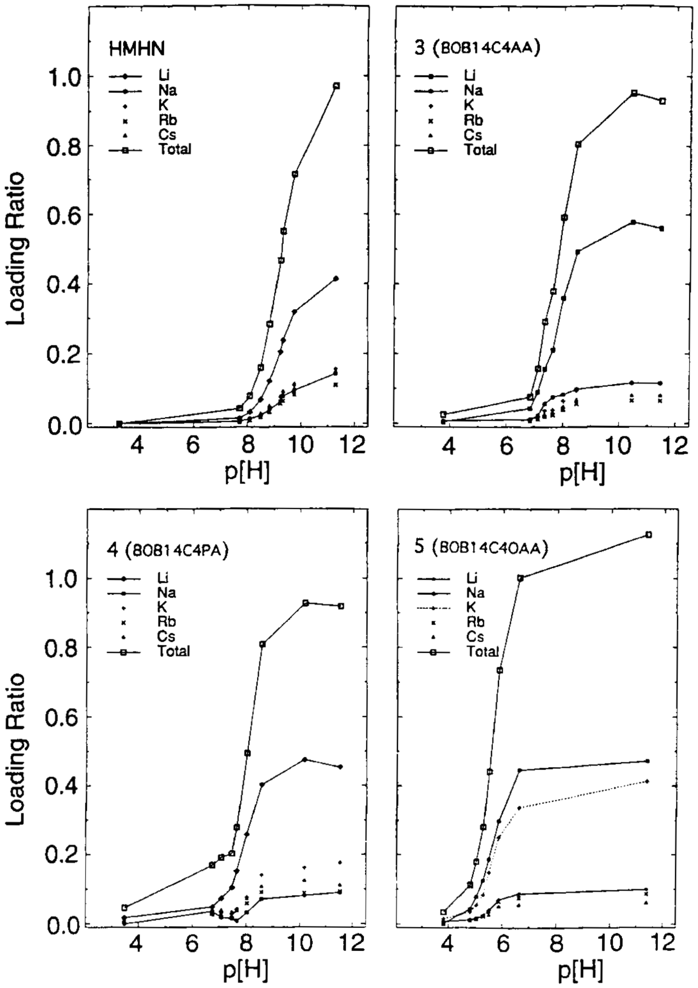


FIGURE 5. Ion-exchange loading of HMHN, **3**, **4**, and **5** with $Li^+$, $Na^+$, $K^+$, $Rb^+$ and $Cs^+$ as a function of p[H]. The loading ratio is expressed as $[M]_{org}/[HA]_{init}$. The data were collected during the titrations depicted in Fig. 3.

in the TRUEX solvent is most pronounced when the aqueous phase is 0.25M $Na_2CO_3$.

Based on these $N_{Di}$ values for Purex and TRUEX solvents, we can make three fairly general statements. First, $N_{Di}$ gives a measure of solvent quality with respect to its hydraulic performance in solvent extraction equipment. Second, the use of 0.25M $Na_2CO_3$ as the aqueous phase seems to be the most severe test of overall solvent performance. Third, the organic-continuous $N_{Di}$ values for solvents with chlorocarbon diluents are about twice those for solvents with NPH as the diluent.

## TRUEX-SREX Solvents

The TRUEX process for removing transuranic elements from nuclear waste solutions (10) is being combined with the SREX process for removing strontium (13) to create a new process, the TRUEX-SREX process (14). The combined TRUEX-SREX solvent contains the TRUEX extractant, CMPO, at a concentration of 0.2M; the SREX extractant, 4,4'(5)-di-t-butylcyclohexano-18-crown-6 (DtBuCH18C6, crown ether, or CE) at a concentration of 0.2M; and a modifier and diluent. Two modifiers considered for this solvent were 1.2M TBP and 1.2M diamyl amylphosphonate (DA[AP] or DAAP). The three diluents considered were Isopar L, Isopar M, and Norpar 12. Five of the solvent compositions evaluated are shown on Table 1 (the PS solvents), along with two TBP-in-nDD solvents (the T solvents) for comparison. The properties considered in the development of the solvent were (1) the ability of the solvent to be loaded with metal ions without the formation of a second organic phase, (2) a high flash point for process safety, and (3) the ability to work well in typical solvent extraction equipment such as a centrifugal contactor.

For a given number of carbon atoms, the normal paraffinic hydrocarbons (Norpar 12 and nDD) have higher flash points than the isoparaffinic hydrocarbons (Isopar L and Isopar M). However, even Isopar L, the solvent with the lowest flash point, 61°C, is well above the limit for a flammable liquid, 37.8°C (100°F), and is just above the limit for a Class II combustible liquid, 60°C (140°F). Once the extractants and modifiers are added to the diluent, the solvent flash point is increased with respect to that for the diluent alone (15).

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