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Alkylated Lariat Ethers as Solvent Extraction Reagents: Surveying the Extraction of Alkali Metals by Bis-*t*-octylbenzo-14-crown-4-acetic Acid by Use of Potentiometric Two-Phase Titration

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ALKYLATED LARIAT ETHERS AS SOLVENT EXTRACTION REAGENTS: SURVEYING THE EXTRACTION OF ALKALI METALS BY BIS-*t*-OCTYLBENZO-14-CROWN-4-ACETIC ACID BY USE OF POTENTIOMETRIC TWO-PHASE TITRATION

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ABSTRACT

Two-phase potentiometric titrimetry was used to survey the extraction of alkali metal cations from aqueous chloride solution by the lipophilic, ionizable lariat ether bis-(*t*-octylbenzo)-14-crown-4-acetic acid (BOB14C4AA) in *o*-xylene. Analysis of the data indicates that ion-exchange extraction by the crown-carboxylic acid at low loading (i.e., low conversion of BOB14C4AA to its salt form) is stronger for lithium ion than for the other alkali metals. Little or no selectivity occurs at high loadings. In comparison with the long-chain carboxylic acid 2-methyl-2-heptylnonanoic acid (HMHN), BOB14C4AA extracts lithium and sodium at significantly lower pH; in the loading range of 0.1 to 0.7, the pH shift is 1.4-1.8 pH units for sodium ion and 1.7-2.3 pH units for lithium ion. The titration data are interpreted in terms of aggregated organic-phase species. In the case of lithium extraction, clear evidence was found for a species in which neutral BOB14C4AA participates in the organic-phase complexation of the metal cation.

INTRODUCTION

The realization that macrocyclic polyethers can strongly and selectively complex certain metal cations (1) has led to intensive investigations of the complexation (2,3) and solvent-extraction properties of crown ethers (1,4,5). Since the extraction of metal cations by neutral complexants requires the cotransport of anions for charge compensation, the efficiency of cation extraction by crown ethers can be significantly influenced by the free energy of hydration of the aqueous anion (6). To level the matrix effects due to variation in the type and concentration of aqueous anions, the use of synergistic extraction systems where an organophilic acid is combined with a crown ether has been proposed (7-11). These systems provide both the coordination and cation-exchange requirements necessary to efficiently extract an aqueous-phase metal ion into an organic solvent without cotransport of the aqueous-phase anion.

Attachment of an ionizable functionality to a crown ether as a pendant arm provides not only the ion-exchange properties necessary to neutralize the charge on the complexed cation but also additional donor groups. Crown ethers containing carboxylic acid groups have been prepared in order to study the effect of the pendant functionality on the complexation properties of the macrocycle (12-14). The term "lariat ether" was proposed to describe crown ethers containing pendant ligating arms (15,16). The lariat structure allows for variation of the macrocycle size; number of coordination sites; the number, type and location of substituents; the type of ionizable functionality; and the preorganization of the different functional groups (17). Incorporation of the cation-exchange functionality into the macrocyclic molecule was shown to improve extraction of metal cations (18-20) and their transport across membranes (21,22). Extraction and thermodynamic studies have provided information on how substituents affect the relative strength of cation binding by macrocycles, and kinetic studies have provided insight into the mechanism of complex formation and decomplexation (2,23,24). Meanwhile, structural studies have allowed the determination of the specific interactions between the cation, the macrocycle, and the anion (24-27).

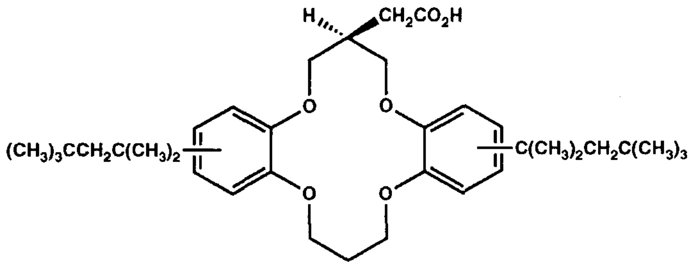
We have been investigating the effect of structural features on cation-anion interactions in ionizable lariat ethers. Our interest in this area stemmed from prior research by this group on synergistic extraction systems and correlations between solution and solid-state structures of crown ether-metal carboxylate (10,28,29) and crown ether-metal sulfonate (30-35) complexes. We were particularly interested in how the nature of the sidearm and the mode of attachment to the macrocycle influenced the binding of the ionizable functionality to the metal. Bartsch and coworkers had investigated the selective complexation and extraction of lithium cation by ionizable crown ethers (36,37) and reported an X-ray crystal structure of lithium dibenzo-14-crown-4-oxyacetate complex (38). We subsequently prepared a series of ionizable lariat ethers based on the small-ring macrocycle dibenzo-14-crown-4 (DB14C4) and studied the solid-state structures of lithium and sodium complexes by X-ray crystallography (39-42). All of these compounds differed from those studied by Bartsch in that they lacked any ether linkage in the pendant arm. We proposed that the presence of the ether linkage external to the macrocyclic ring would affect the relative complexation of different cations (39) and demonstrated that this ether linkage significantly influences both the conformation of the sidearm and the aggregation of the complexes in the solid state (40).

Recently, we modified the ionizable DB14C4 lariat ether (43) dibenzo-14-crown-4-acetic acid by Friedel-Crafts alkylation to prepare the lipophilic extractant, bis-(*t*-octylbenzo)-14-crown-4-acetic acid (BOB14C4AA) (Fig. 1). We have determined that this compound does not distribute measurably from *o*-xylene to 0.1 N NaOH ($[NaBOB]_{org}/[NaBOB]_{aq} > 5000$) (44) and have initiated studies to determine its extraction behavior toward alkali metal cations with the intent of augmenting our solid-state structural results with solution thermodynamic data. In this paper, we discuss the results of two-phase potentiometric titrations where an organic phase consisting of the extractant BOB14C4AA in *o*-xylene is contacted with an alkali metal chloride solution made increasingly alkaline by the addition of alkali metal hydroxide. Weak-acid titration curves for the cations Li^+, Na^+, Rb^+, and Cs^+ are interpreted in terms of extraction of the metal cation into the organic phase by ion exchange. Extraction by the lariat ether is compared to results obtained in parallel experiments in which Li^+ and Na^+ ions were extracted by the branched aliphatic carboxylic acid 2-methyl-2-heptylnonanoic acid (HMHN) (Fig. 1). The influence of the crown ether portion of the ionizable lariat is inferred from the difference between the two sets of titrations.

EXPERIMENTAL

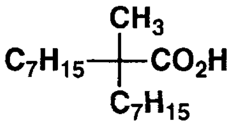
Materials

The extractant BOB14C4AA was prepared in our laboratory by the Friedel-Crafts alkylation of DB14C4AA and was purified by reverse-phase chromatography followed by recrystallization, first from ethanol, then from cyclohexane. HMHN was prepared by Aldrich Chemical Co. by Kock carboxylation of 8-methyl-8-pentadecanol and purified by repeated molecular distillation to obtain a pale yellow oil, bp



Bis-*t*-Octylbenzo-14-Crown-4-Acetic Acid

(BOB14C4AA)



$$C_7H_{15}-\underset{C_7H_{15}}{\overset{CH_3}{C}}-CO_2H$$

2-Methyl-2-Heptylnonanoic Acid

(HMHN)

FIGURE 1. Structures of bis-(*t*-octylbenzo)-14-crown-4 (top) and methylheptylnonanoic acid (bottom).

~70 °C (0.020 mm). The purity of these extractants was determined by titration for equivalent weight (HMHN - FW: 270.46, Found: 280.1, BOB14C4AA - FW: 582.84, Found: 583.5). Spectrophotometric grade *o*-xylene was used as obtained from Burdick and Jackson, Inc. Water was doubly distilled 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

TABLE 1. Two-Phase Titration Data

Cation	Extractant	$[\text{Extractant}]_{tot}$	$[OH^-]_{titrant}$	pK_w	$[HCl]_{vessel}$
Li^+	BOB14C4AA	0.0441	0.0943	13.704	0
Na^+	BOB14C4AA	0.0491	0.0986	13.745	0
Rb^+	BOB14C4AA	0.0484	0.1076	13.761	0
Cs^+	BOB14C4AA	0.0480	0.1037	13.764	0
Li^+	HMHN	0.0532	0.0943	13.704	4.0×10^{-4}
Na^+	HMHN	0.0532	0.0986	13.745	4.0×10^{-4}

septa. Alkali metal halide solutions were prepared at 0.20 M in water from commercially available metal halide salts. A stock 0.1 N lithium hydroxide solution was prepared by reaction of lithium metal (freshly cut in an inert atmosphere glove box) with cold water. Rubidium and cesium hydroxide solutions (0.1 N) were prepared from 50% w/w aqueous reagent (Alfa Inorganics) and standardized after passage through Amberlite IRA-400 anion exhange resin (hydroxide form). A standard 0.1 N sodium hydroxide solution was used as obtained from J. T. Baker, Inc.

Stock 50 mM solutions of BOB14C4AA and HMHN were prepared in *o*-xylene and standardized by dilution of a measured aliquot in 80% dioxane/water followed by titration with ethanolic NaOH. Titrant solutions were prepared at 0.10 M of alkali halide in 0.1 N aqueous alkali hydroxide and standardized against oven-dried KHP (NBS primary standard) on a Metrohm E536 automated titrator (Table 1). The microsyringe and microburet were calibrated gravimetrically using doubly distilled water.

Titration Procedure

Two-phase titrations were performed in an apparatus consisting of a water-jacketed conical flask fitted with a magnetic stir bar, Teflon cap, combination electrode, thermister, septum, and argon ports. Initially the vessel contained 1.00 mL of organic phase and 3.00 mL of 0.20 M alkali metal halide solution. In some of the experiments, HCl was added to the aqueous phase. The pH was measured using a glass combination electrode inserted into the aqueous (lower) phase. Titrant was added from a micrometer-driven syringe or microburet equipped with a microbore Teflon tube inserted through the rubber septum into the aqueous phase. After each addition of titrant, the mixture was stirred vigorously (aqueous continuous) until the aqueous pH reading stabilized, usually within 5 minutes. Stirring was then stopped and the pH measurement recorded after clear phase separation had occurred. Blank titrations where the organic phase consisted of pure *o*-xylene were run immediately prior to each extractive titration. The electrode response was standardized each day by the use of standard buffer solutions. The solutions were not pre-equilibrated with respect to the blank counter-phase; the mutual solubilities of the *o*-xylene/ water system are expected to be less than 0.1 wt% (45), therefore no correction for mixing was applied.

Treatment of Data

Conversion of the uncorrected pH meter readout ($pH_{uncorrected}$) to p[H] (defined as minus the logarithm of the actual hydrogen ion molarity) was made by use of the blank strong acid-strong base titration data. For the conversion, the concentration ionization constants of water (K_W) defined in eq.

1 for 0.2 M solutions of alkali metal chloride were obtained or

$$K_W = [H^+][OH^-] \qquad (1)$$

estimated from literature data (46) as summarized in Table 1. Endpoints of the blank titrations were determined from the first or second derivatives of the corresponding smoothed titration curves (cubic spline), giving the initial acid molarities of the titrands. For each blank titration, the known value of K_W and the known composition of the aqueous solution in the vessel at any point were used to construct linear calibration plots of $pH_{uncorrected}$ vs. p[H]. Electrode calibration parameters A_0 and A_1 were then determined by linear least squares fits according to

$$pH_{uncorrected} = A_1(p[H]) + A_0 \ , \qquad (2).$$

In the case of Na^+ ion extraction by BOB14C4AA, the electrode used exhibited an alkaline error in the range p[H] ≥ 10.66, requiring the quadratic term $A_2(p[H] - 10.66)^2$ to be added to the right side of eq. 2 for values of p[H] in this range. Slopes A_1 were found to lie in the range 0.98 - 1.02 in all cases.

From the determined calibration constants, corrected titration curves were constructed from the raw two-phase titration data for each of the alkali metals Li^+, Na^+, Rb^+, and Cs^+ using either BOB14C4AA or HMHN. Endpoints were determined from the curves using the second derivative of the data smoothed by a cubic spline. Over the course of the experiments, comparison of the weighed-in concentration of BOB14C4AA of the stock *o*-xylene solution with the concentration indicated by the endpoints of the two-phase titration curves suggested a gradual decrease in the molarity of BOB14C4AA in the stock solution (~10% in ca. 6 weeks). Since a fine white precipitate in the stock solution was observed to increase in quantity over the same time period, we used the experimental endpoints of the two-phase titration curves to establish the lariat ether concentrations $[BOB14C4AA]_{tot}$ in the stock for each titration as summarized in Table 1. No precipitate was observed in the case of HMHN, and the values of $[HMHN]_{tot}$ were thus taken from the standardization in homogeneous nonaqueous solution (vide supra). By use of these analytical concentrations of extractants in the *o*-xylene stocks, the volume scale of OH^- titrant added (in mL) in the two-phase titrations was converted to *n*, the equivalents of OH^- ion added per equivalent of extractant (HA) present initially in the organic phase.

The equivalents of metal ions exchanged by the organic-phase cation exchanger in the two-phase titrations were evaluated from the mass-balance relationship

$$V_{org}[HA]_{init} + V_{aq,init}[HCl]_{init} - V_{titr}[MOH]_{titr} = V_{org}\Sigma[HA] + V_{aq}([H^+] - [OH^-]) \ , \quad (3)$$

where 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 $V_{aq,init} + V_{titr}$), $[HA]_{init}$ is the initial organic-phase molarity of cation exchanger HA, $[HCl]_{init}$ is the initial molarity of HCl in the aqueous phase, $[MOH]_{titr}$ is the molarity of MOH in the titrant, $\Sigma[HA]$ is the analytical organic-phase molarity of unreacted HA at equilibrium (expressed as a sum of all aggregated forms), $[H^+]$ is the equilibrium molarity of hydrogen ions, and $[OH^-]$ is the equilibrium molarity of hydroxide ions. Equation 3 presupposes negligible distribution of HA to the aqueous phase; we have shown by UV absorption measurements that the two *t*-octyl substituents render the salt form NaA undetectable in 0.1 M NaOH in equilibrium with 0.01 M BOB14C4AA in *o*-xylene (44). Since $\Sigma[HA] = [HA]_{init} - \Sigma[MA]$, eq. 3 may be combined with eq. 1 and rearranged with cancellation of terms to give the molarity $\Sigma[\mathrm{MA}]$ of reacted organic-phase cation exchanger in all aggregated forms:

$$\Sigma[\mathrm{MA}] = (V_{\mathrm{titr}}/V_{\mathrm{org}})[\mathrm{MOH}]_{\mathrm{titr}} + (V_{\mathrm{aq}}/V_{\mathrm{org}})([\mathrm{H}^+] - K_{\mathrm{w}}/[\mathrm{H}^+]) - (V_{\mathrm{aq,init}}/V_{\mathrm{org}})[\mathrm{HCl}]_{\mathrm{init}} \quad (4).$$

By use of eq. 4, the loading ratio $\Sigma[\mathrm{MA}]/[\mathrm{HA}]_{\mathrm{init}}$ is obtained. It is important to recognize that the value $\Sigma[\mathrm{MA}]$ cannot be equated with the total organic-phase metal concentration $[\mathrm{M}]_{\mathrm{org}}$ because of the possibility of extraction of neutral salt MCl. Experiments are currently being conducted to investigate this possibility. Thus, in the present analysis we rigorously evaluate only that portion of alkali metal extraction that occurs by ion exchange.

RESULTS AND DISCUSSION

The corrected two-phase titration curves shown in Fig. 2 indicate detectable neutralization of the cation exchanger BOB14C4AA (HA) beginning in the range p[H] = 7.5 - 8.5 and reaching completion by p[H] = 11. Each curve exhibits a major plateau in the range p[H] = 9.0 - 10.5, and the final endpoints fall in the range 0.45 - 0.50 mL, corresponding to equivalent ratios *n* of 1, where *n* is the number of equivalents of OH^- ion added per equivalent of extractant (HA) present initially in the organic phase (Fig. 3). A minor plateau in the lower range p[H] = 7.5 - 9.0 is also exhibited in the Li^+ case, where the first apparent endpoint occurs at $n = 0.36$. Evidence for lesser plateaus may also be seen in the cases of Na^+, Rb^+, and Cs^+, where poorly defined inflections occur in the vicinity of $n = 0.1$.

An approximate comparison of the titration curves for all four metals given in Figs. 3 and 4 reveals significant differences in the strength of cation exchange of unmixed alkali

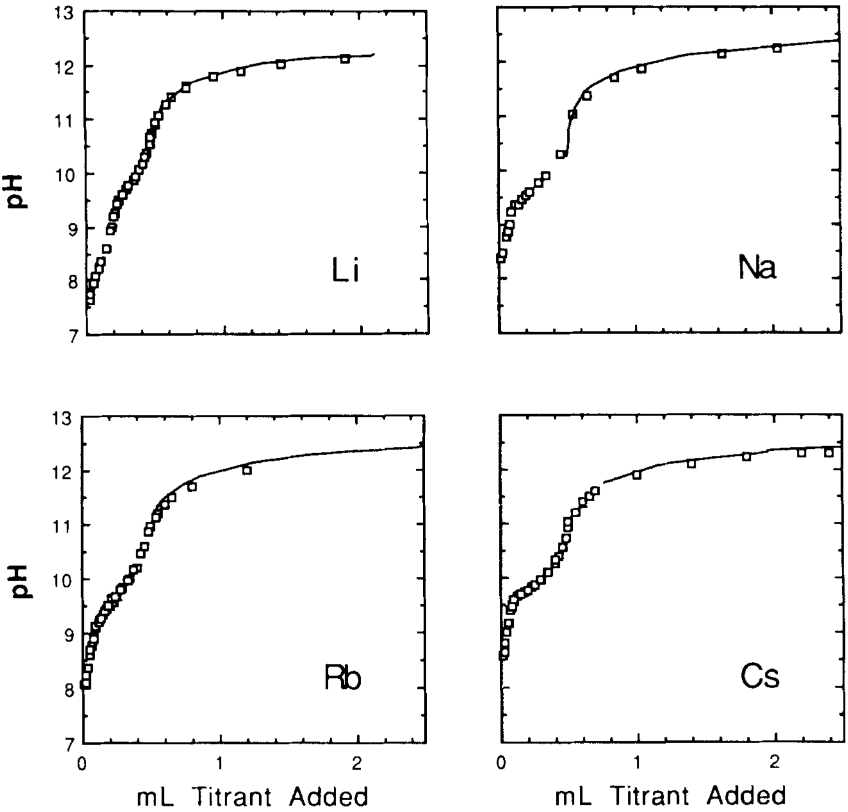


FIGURE 2. Two-phase potentiometric titrations of BOB14C4AA at 25 °C. By use of electrode calibration constants, the pH meter readouts in pH units were converted to p[H] and are shown here plotted as individual data points vs. mL of titrant added. For comparison, the solid lines correspond to blank curves displaced to the right an amount corresponding to the endpoints of each titration. The initial systems consisted of 1 mL solutions containing 0.044 - 0.049 M BOB14C4AA in o-xylene in contact with 3 mL of 0.2 M MCl (M = Li, Na, Rb, or Cs); no HCl was added to the initial aqueous solutions. The titrants consisted of 0.1 M MCl together with 0.094 - 0.108 M MOH. For Li, Rb, and Cs, the data shown include two runs which have been superimposed.

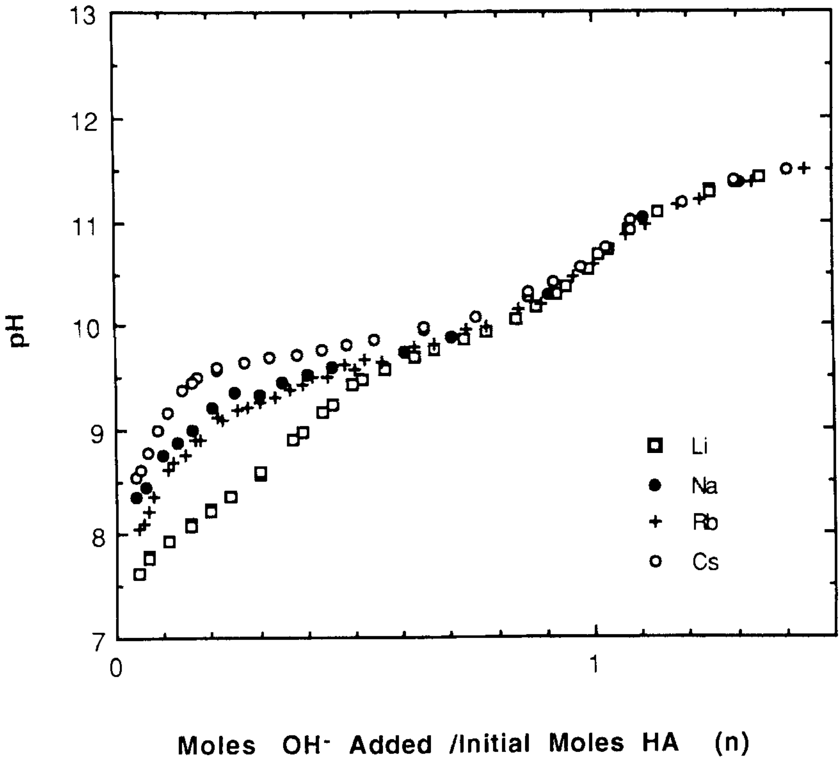


FIGURE 3. Normalized two-phase titrations of BOB14C4AA. The data of Fig. 3 have been replotted against *n*, the ratio of the moles of MOH added to the initial moles of BOB14C4AA (HA) present in the organic phase.

metal cations by BOB14C4AA. Quantitatively, this comparison assumes the equality of the activity coefficients of aqueous-phase ions in the four titrations at corresponding points and identical starting concentrations of all reagents. Though both assumptions must be regarded as approximations by reference to the literature (46) and to Table 1, respectively, these limitations do not preclude some general observations. As shown in Fig. 4, significant differences in the titration data as a

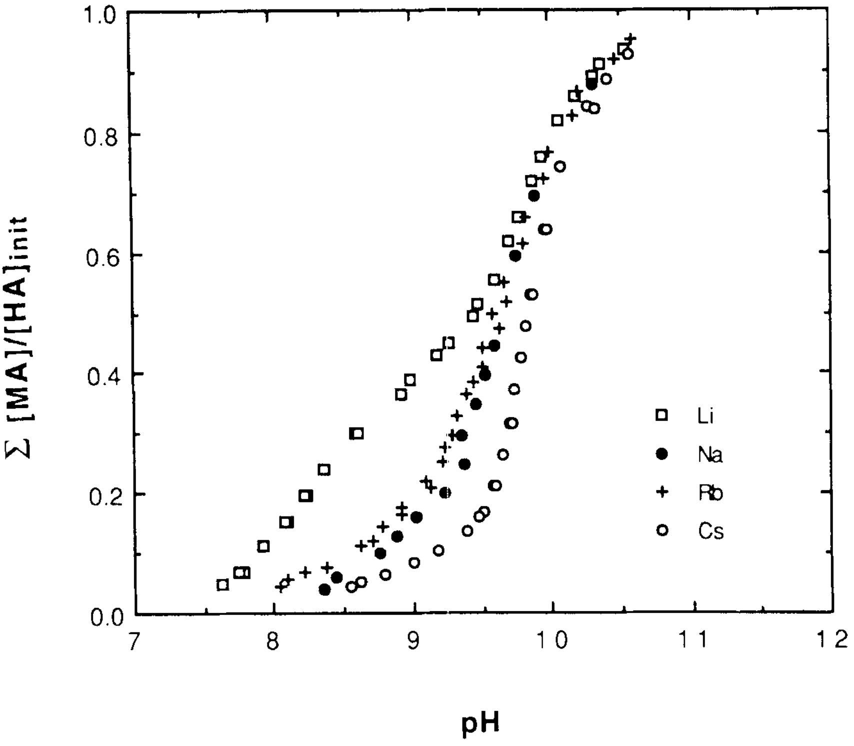


FIGURE 4. Ion-exchange loading of BOB14C4AA with Li^+, Na^+, Rb^+, and Cs^+ cations as a function of p[H]. From the data of Fig. 3, the organic-phase molarity of crown ether in the salt form (Σ[MA]) has been calculated and plotted as a ratio to the initial concentration ($[HA]_{init}$) of BOB14C4AA.

function of the equivalent ratio *n* may be observed only in the range $n < 0.5$, where the order of cation exchange is $Li^+ > Na^+ \sim Rb^+ > Cs^+$. At higher values of *n*, the curves gradually coalesce. Figure 4 expresses the same data in terms of the loading ratio $\Sigma[MA]/[HA]_{init}$ vs. p[H] by use of eq. 4. A clear preference for Li^+ cation may be seen at p[H] values less than 9.5, where the neutral lariat ether HA is in abundance.

All curves in Fig. 2 indicate slight extraction of MOH at values of n in the range $n > 1.0$. Here, the observed pH values consistently fall below the solid lines corresponding to the blank titration curves (no HA present) shifted to the right a distance $\Delta n = 1.0$. The magnitude of the effect is greatest for Rb^+ and Cs^+ ion extraction. In any case, the amount of extraction of MOH is relatively minor in comparison to the initial concentration of HA.

From the results shown in Figs. 2-4 it may be concluded that the participation of neutral HA in the alkali metal extraction complexes is important in obtaining Li^+ selectivity in this system. In particular, the inflection observed at $n = 0.36$ in the case of Li^+ (Fig. 3) implies the existence of species having the ratio of approximately 2 molecules of HA per ion pair MA. Extraction complexes containing neutral acid HA are, in fact, typical of carboxylic acid extraction systems at low loading (47, 48). In general, the cation exchange reaction of a univalent metal cation M^+ by HA may be written in terms of organic-phase aggregates:

$$a/b(\mathrm{HA})_b\ (\mathrm{org}) + m\mathrm{M}^+\ (\mathrm{aq}) \rightleftharpoons \mathrm{M}_m\mathrm{A}_a\mathrm{H}_{a-m}\ (\mathrm{org}) + m\mathrm{H}^+\ (\mathrm{aq})\ , \qquad (5)$$

where for convenience the state of hydration of the organic-phase species $(HA)_b$ and $M_mA_aH_{a-m}$ has been omitted. Although the dimerization of carboxylic acids in nonpolar diluents is well known (49), the ability of crown ethers to interact with organophilic acids and water via hydrogen bonding (30,50) may give the neutral lariat ether BOB14C4AA unique aggregation properties; no data are yet available on the aggregation of neutral carboxylic acid lariat ethers. On the other hand, a range of product species $M_mA_aH_{a-m}$ or alternately $(MA)_m(HA)_{a-m}$ typically exists depending on the degree of loading and the extractant concentration in systems employing carboxylic acid extractants. At low loading, typical values of the nuclearity m are 1 and 2; the latter value is especially characteristic of transition metal complexes (51). In the case of Na^+ extraction by a long-chain neo-carboxylic acid, distribution and other data were interpreted in terms of the complexes $(NaA)(HA)_2$ + $(NaA)(HA)_3$ (52). Since m is unknown in the extraction of Li^+ ion by BOB14C4AA, our present results point to a species having the stoichiometry $(LiA)_m(HA)_{2m}$.

At high loading, carboxylic acid extraction systems typically give large aggregates. Long-chain carboxylate salts are, in fact, known to form micelles or microemulsions (53). Since the lariat ether BOB14C4AA consists of a large hydrophobic region and a smaller hydrophilic region, formation of such structures in our alkali metal extraction systems seems possible and may explain the approximate coalescence of our titration curves (Figs. 3, 4) at high loading ($n > 0.5$). The case of Li^+ ion exchange here is unique in that the complex $(LiA)_m(HA)_{2m}$ formed at low loading has significantly greater stability than the species formed at high loading, giving rise to an identifiable inflection point. Modeling and spectroscopic studies are currently being conducted to more definitively identify the stoichiometries of our lariat ether extraction complexes.

Control titrations for Li^+ and Na^+ ion exchange with HMHN were performed to compare ion exchange by the crown ether carboxylic acid BOB14C4AA with ion exchange by a monofunctional carboxylic acid. The corrected titration curves are shown in Fig. 5; the loading curves are plotted together with the corresponding curves of BOB14C4AA in Fig. 6. As shown in Fig. 6, HMHN displays both weaker acidity toward Li^+ and Na^+ ion exchange and lower preference for Li^+ ion in comparison with BOB14C4AA; slight preference for Na^+ occurs

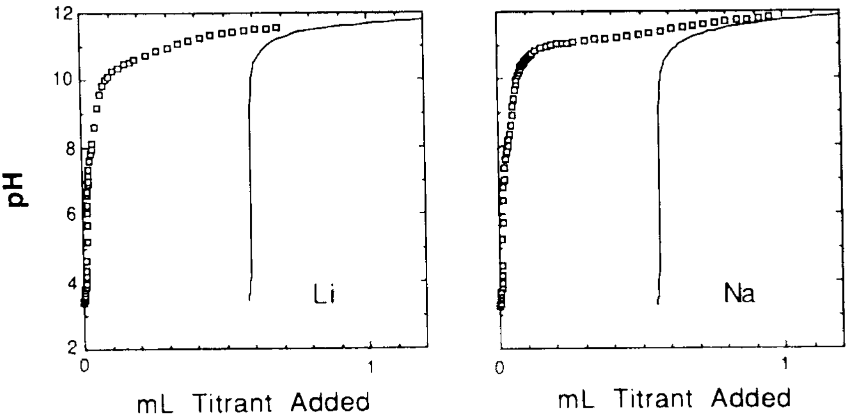


FIGURE 5. Two-phase potentiometric titrations of HMHN at 25 °C. By use of electrode calibration constants, the pH meter readouts (pH scale) were converted to p[H] values and are shown here plotted as individual data points vs. mL of titrant added. For comparison, the solid lines correspond to blank curves displaced to the right an amount corresponding to the endpoint of each titration. The initial systems consisted of 1 mL solutions containing 0.053 M HMHN in o-xylene in contact with 3 mL of 0.2 M MCl (M = Li or Na) plus 4.0 x 10^{-4} M HCl. The titrants consisted of 0.1 M MCl together with either 0.094 M LiOH or 0.099 M NaOH.

above p[H] = 11 for HMHN. However, it is clear that low loadings of HMHN occur in the p[H] range 7.5 - 10.0 with no apparent ion-exchange selectivity. Inflections in both Li^+ and Na^+ titration curves using HMHN occur at *n* = 0.07 (Fig. 5). In the loading range $\Sigma[MA]/[HA]_{init}$ = 0.1 - 0.8, the shifts in the p[H] curves for BOB14C4AA relative to HMHN are greater for Li^+ ion than for Na^+ ion. For Li^+ ion, the shifts are in the range 1.7-2.3 p[H] units, while for Na^+ ion, the shifts are in the range of 1.4-1.8 p[H] units.

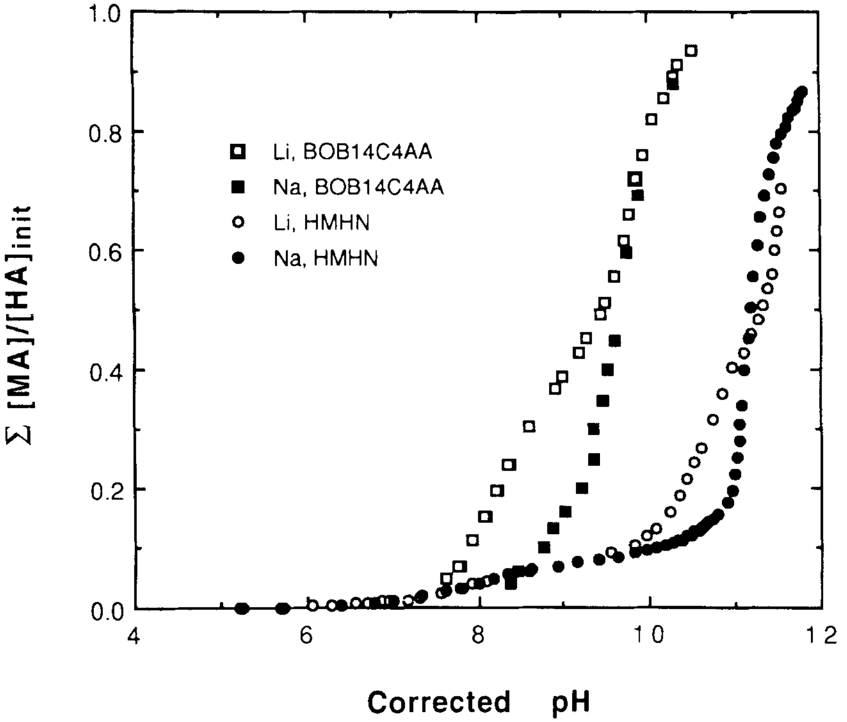


FIGURE 6. Ion-exchange loading of HMHN and BOB14C4AA with Li^+ and Na^+ cations as a function of p[H]. From the data of Fig. 5, the organic-phase molarity (Σ[MA]) of HMHN converted to the salt form has been calculated and plotted as a ratio to the initial concentration ($[HA]_{init}$) of HMHN, along with the data for Li^+ and Na^+ from Fig. 4.

CONCLUSION

Two-phase titration studies indicate that the lipophilic crown ether carboxylic acid bis-*t*-octylbenzo-14-crown-4-acetic acid extracts alkali metal cations from aqueous chloride solution by ion exchange. In the loading regime where the majority of the crown ether exists in the ionized form, little preference exists among the group of alkali metals tested. This is consistent with structural studies of lithium and sodium salts of DB14C4AA where the complexes adopt similar structures in which inter-molecular cation-anion interactions occur between carboxylate and crown-complexed cation. When excess neutral extractant is present, ion exchange for lithium occurs more strongly than for the other alkali metals. The nature of this phenomenon is not yet completely understood but probably involves aggregation and the formation of species containing both complex and neutral extractant molecules. Investigations are under way to better define the solution behavior of this extractant.

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