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Anion Effect on Selectivity in Crown Ether Extraction of Alkali Metal Cations

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For the solvent extraction of metal ions and their transport across liquid membranes by neutral ionophores,[1-3] concomitant transfer of one or more aqueous-phase anions into the organic medium is required for electroneutrality. The *efficiencies* of metal ion extraction and liquid membrane transport flux exhibit a pronounced inverse dependence on the solvation energy of the accompanying anion.[4-6] Scattered literature reports suggest that the *selectivity* of metal ion extraction and transport by neutral synthetic[7-11] and natural[12] ionophores may also be affected by anion variation.[13] To explore this possibility, we have determined the influence of anion variation in competitive alkali metal cation extractions from aqueous solutions into chloroform by *cis-syn-cis*-dicyclohexano-18-crown-6 (**1**).[14-16] This synthetic ionophore, which was separated from the commercially available isomer mixture by a reported method,[16] was chosen because of its high overall extraction efficiency, hydrophobicity, and relatively simple structure.

The anion effect in solvent extraction of alkali metal cations by **1** was assessed by extracting aqueous solutions of Li$^+$, Na$^+$, K$^+$, Rb$^+$, and Cs$^+$ (0.020 M in each) having a common anion with an equal volume of a 0.010 M chloroform solution of the crown ether. The series of aqueous-phase anions (bromide, iodide, nitrate, perchlorate, and thiocyanate) was chosen to include both hard (e.g., nitrate) and soft (e.g., thiocyanate) anions.[17] Back-extraction (stripping) of the extracted metal salts from the separated chloroform phase was accomplished by shaking with deionized water.[18] Alkali metal cation concentrations in the aqueous stripping solution were determined by ion chromatography. For each common anion, three independent competitive extraction experiments were conducted. Results are recorded in Table I.

Table I. Extraction Percentages for Competitive Solvent Extraction of Alkali Metal Cations from Aqueous Solution into Chloroform by *cis-syn-cis*-Dicyclohexano-18-crown-6[a,b]

	percent extracted			combined percent
anion	K$^+$	Rb$^+$	Cs$^+$	extracted
perchlorate	41.0 ± 0.5[c]	17.5 ± 0.2	4.1 ± 0.1	62.6 ± 0.7
iodide	16.5 ± 0.4	7.0 ± 0.2	2.1 ± 0.4	25.6 ± 0.9
thiocyanate	18.1 ± 0.5	6.0 ± 0.2	1.6 ± 0.1	25.7 ± 0.7
nitrate	3.99 ± 0.18	1.07 ± 0.06	0.25 ± 0.03	5.31 ± 0.25
bromide	0.58 ± 0.07	0.26 ± 0.02	0.16 ± 0.01	1.00 ± 0.08

[a] Based upon the crown ether concentration in the chloroform phase. [b] Extraction of Li$^+$ and Na$^+$ was not detectable. [c] Standard deviation from three independent extraction experiments.

Table II. Radii,[a] Hydration Enthalpies,[b] and Softness Parameters[c] for Selected Anions

anion	radius (nm)	$-\Delta H°_h$ (kJ/mol)	σ_x
perchlorate	0.240 ± 0.005	243	0.00
iodide	0.210 ± 0.008	297	0.40
thiocyanate	0.213 ± 0.010	310	0.84
nitrate	0.179 ± 0.006	329	−0.41
bromide	0.188 ± 0.006	337	0.10

[a] Calculated from thermochemical data.[19] [b] Calculated for $X^-_{(g)} \rightarrow X^-_{(aq)}$.[20] [c] Anion softness is a dimensionless quantity which is calculated from electron affinity and hydration enthalpy.[20]

The overall extraction efficiency decreases in the order: perchlorate > iodide, thiocyanate > nitrate > bromide. On the basis of the concentration of crown ether, the total extraction efficiency (last column in Table I) ranges from 63% for competitive extraction of the alkali metal perchlorates to only 1.0% loading for extraction of the alkali metal bromides. The combined percent extraction values only roughly correspond to the anion size[19] but correlate inversely with the anion hydration energy[20] (Table II). In aqueous media, the low surface charge density for a large anion creates a loosely packed anion hydration sphere which is more easily shed at the phase boundary during the extraction process than the densely packed hydration sphere of a small anion. In the organic medium, the reverse is true and larger anions are better solvated than smaller anions. Thus the observed anion effect on extraction *efficiency* is dependent upon the solvation energy of the anion in both phases. There appears to be no correlation between the extraction efficiency and the anion softness parameter[20] (Table II), which is calculated from both electron affinity and hydration enthalpy.

Now focusing attention upon *selectivity* for the competitive alkali metal cation extractions into chloroform by **1**, K$^+$ is the

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(18) Efficiency of the back-extraction step was assessed in a control study. Standard chloroform solutions of individual alkali metal perchlorates and nitrates were shaken with deionized water, and the metal ion concentrations in the aqueous stripping phase were determined by ion chromatography. The stripping experiments were conducted in triplicate for each metal salt complex. Stripping efficiencies (%) with standard deviations for perchlorates were Li$^+$, 95.0 ± 0.5; Na$^+$, 96.7 ± 0.5; K$^+$, 91.0 ± 1.6; Rb$^+$, 94.5 ± 2.7; Cs$^+$, 94.2 ± 1.5. Stripping efficiencies (%) for nitrates were Li$^+$, 98.0 ± 0.6; Na$^+$, 99.6 ± 0.9; K$^+$, 99.7 ± 1.6; Rb$^+$, 100.0 ± 2.9; Cs$^+$, 99.3 ± 2.1. Thus measured extraction efficiencies for the softer, more lipophilic anion systems, like perchlorate, will be very slightly lower than the actual extraction efficiencies due to incomplete stripping. For the hard anions like nitrate, stripping is quantitative.

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Table III. Influence of Anion upon Selectivity Factors[22,23] for Alkali Metal Cation Extraction from Aqueous Solution into Chloroform by *cis-syn-cis*-Dicyclohexano-18-crown-6

anion	f_{K^+/Rb^+}	f_{K^+/Cs^+}
nitrate	3.72 ± 0.04[a]	16.0 ± 2.0
thiocyanate	3.00 ± 0.01	11.2 ± 0.5
perchlorate	2.35 ± 0.01	10.1 ± 0.1
iodide	2.36 ± 0.02	7.9 ± 1.1
bromide	2.22 ± 0.08	3.5 ± 0.7

[a] Standard deviation from three independent extraction experiments.

best extracted alkali metal cation for all five anions (Table I). This would be predicted from the log K_s values for association of alkali metal cations with this crown ether in homogeneous media.[21] However, the selectivity factors[22] f_{K^+/Rb^+} and f_{K^+/Cs^+} vary appreciably for the different anions (Table III).[23] The extraction selectivity decreases in the order: nitrate > thiocyanate > perchlorate ≥ iodide > bromide. This selectivity ordering is completely different from the anion effect ordering on extraction efficiency (vide supra) and does not correlate with the anion radius, hydration enthalpy, or softness parameter (Table II). Thus the factors responsible for the anion effect on metal ion extraction efficiency and selectivity are shown to be different.

It is interesting to speculate on the influence of dimensional structure and specific binding sites in the anion upon selectivity. The availability of specific binding sites in the anion may produce significant changes in the structure of an ionophore–metal salt complex.[24-26] From the data in Table III, it is noted that lower selectivity is observed for spherical bromide and iodide ions, whereas nonspherical nitrate and thiocyanate ions, which have specific binding sites, produce higher selectivity.

We have clearly demonstrated that the *selectivity* of competitive metal ion extraction by a neutral, synthetic ionophore is significantly affected by anion identity. Further studies designed to elucidate the causative factors for this phenomenon are in progress.

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