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in Alkali Metal Extraction by Crown Ethers***

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ABSTRACT

Jean-Marie Lehn (Nobel laureate, 1987) suggested *ligand thickness* to be an important consideration in the design of host molecules for cation recognition. We have recently expanded the role of this simple ligand property by demonstrating a case in which ligand thickness contributes significantly to anion discrimination. It was found that in the extraction of sodium nitrate and perchlorate by a simple crown ether, bis(*t*-octylbenzo)-14-crown-4 (BOB14C4), the normal preference for perchlorate is almost completely lost when the complex cation has the "open-face sandwich" vs. the "sandwich" structure.

Keywords: Crown ether, anion effect, equilibrium modeling, sodium perchlorate, nitrate

INTRODUCTION

In this paper we address the fundamental question dealing with whether the structure of a crown ether and its complexes may influence the preference for a given co-anion in the extraction of salts of alkali metals. The converse question, namely whether the anion influences the preference of a crown ether for a given alkali metal cation, has been addressed by previous authors and answered in the affirmative.¹ One would thus expect that the properties of the crown-metal complex would have an effect on anion preference.

We were led to investigate this issue in the course of developing a process for the extraction of pertechnetate anion, TcO_4^- , from alkaline waste solutions by use of crown ethers.² The process, known as SRTALK (strontium and technetium extraction from alkaline solution), is depicted by the cycle shown in Fig. 1. As shown, the function of the crown ether involves complexation of the abundant Na^+ or K^+ cations in the waste, facilitating the transfer of the cation to the organic phase. Although any of the anions present in the waste represent potential co-anions in the net extraction process, the thermodynamically preferred co-anions are those having large radii and correspondingly low (more negative) Gibbs energies of hydration or, more exactly, Gibbs energies of partitioning to organic solvents.³ Even in the presence of an abundance of nitrate, nitrite,

hydroxide, carbonate, aluminate, and other anions in the waste, the large, poorly hydrated pertechnetate anion at trace concentrations can be efficiently extracted.

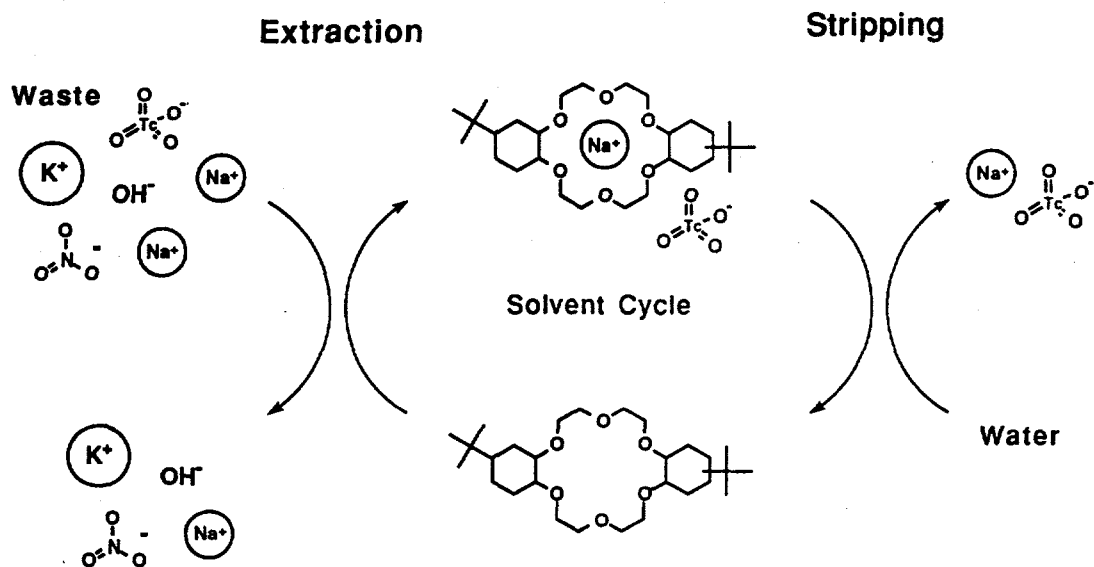
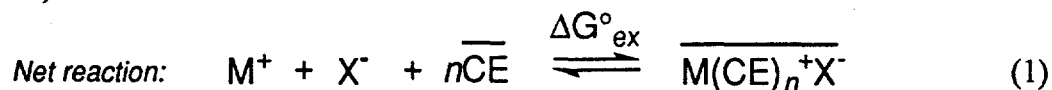


Figure 1. SRTALK process for separating pertechnetate from alkaline nitrate wastes.

From the practical issue of selecting an appropriate crown ether for this purpose arises the fundamental issue of how the crown ether structure can be tailored for the purpose of controlling anion selectivity. Although one may envisage many types of structural modifications to crown ethers that might influence anion interactions, one of the simplest properties of a crown ether in this regard relates to the degree to which it envelops the metal cation and prevents close contact between the cation and anion. In 1973, Jean-Marie Lehn examined the question of ligand thickness in connection with the selectivity of a host ligand for a given cation.⁴ Here, we examine this same property of ligand thickness, but in connection with co-anion selectivity. The example chosen for study is a simple system involving the small-cavity crown ether bis(*t*-octylbenzo)-14-crown-4 (BOB14C4) as an extractant for sodium nitrate and perchlorate salts into 1,2-dichloroethane (1,2-DCE). As will be discussed below, this particular system allows a direct assessment of the ligand-thickness effect by virtue of the formation of both 1:1 and 1:2 metal:crown complexes.

THEORY

Consider the extraction of a cation M^+ by a crown ether CE to form an ion pair consisting of the complex cation $M(CE)^+$ or $M(CE)_2^+$ and co-anion X^- (overbars indicate organic-phase species):



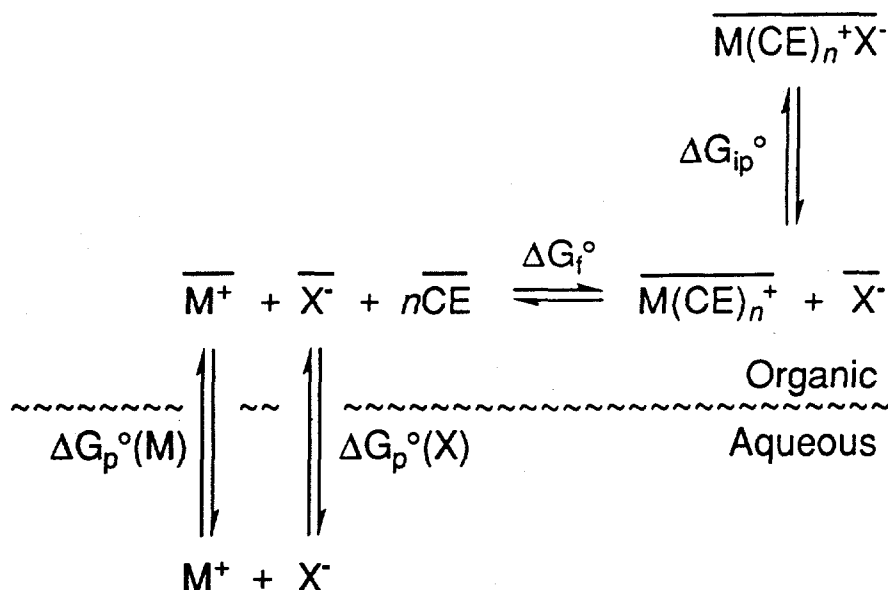


Figure 2. Component equilibria in the extraction of an alkali metal salt by a crown ether.

Component equilibria are defined in Fig. 2. These consist of partitioning of the free ions M^+ and X^- to the organic phase, formation of the complex in the organic phase, and ion pairing of the complex cation with the co-anion.^{5,6} The corresponding standard Gibbs energy changes comprise the net standard Gibbs energy change for the extraction process, and it may be seen that the ion-pairing term is the only term in which the crown structure and anion both have an effect:

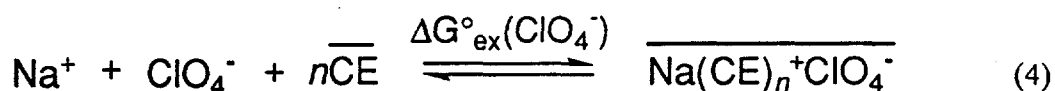
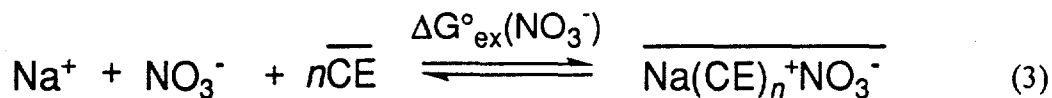
$$\Delta G^\circ_{\text{ex}} = \Delta G_p^\circ(M) + \Delta G_p^\circ(X) + \Delta G_f^\circ + \Delta G_{\text{ip}}^\circ \quad (2)$$

Dependent on anion

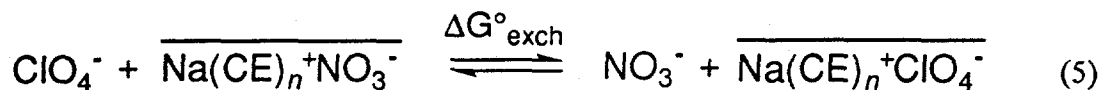
Dependent on crown structure



For extraction of sodium nitrate and perchlorate, the reactions may be written specifically:

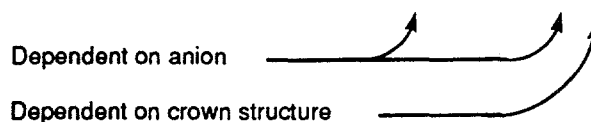


If nitrate and perchlorate are considered to be in competition, selectivity may be viewed in terms of anion exchange, obtained by subtraction of eq. 3 from eq. 4:



It may be seen that the standard Gibbs energy change of the resulting anion exchange is given by two terms, the ion-pairing term being the only one dependent on the crown ether:

$$\Delta\Delta G^{\circ}_{\text{exch}} = \Delta\Delta G^{\circ}_p(X) + \Delta\Delta G^{\circ}_{\text{ip}} \quad (6)$$



Equation 6 is the same expression used to evaluate the selectivity of anion exchange generally.³ Various levels of electrostatic theory may be used to estimate both $\Delta\Delta G^{\circ}_p(X)$ and $\Delta\Delta G^{\circ}_{\text{ip}}$ to the typical effect for the univalent case that for a large anion replacing a small anion, $\Delta\Delta G^{\circ}_p(X)$ is negative and dominant and $\Delta\Delta G^{\circ}_{\text{ip}}$ is a positive counter-effect. Because of the behavior of the first term, then, the larger the thermochemical radius of an anion is, the greater will be its tendency to exchange with another anion. At the same time, the ion-pairing term $\Delta\Delta G^{\circ}_{\text{ip}}$ becomes more positive, but since the first term dominates, the net effect still is higher selectivity toward the larger anion. However, as the cation radius becomes larger, the ion-pairing term for a given pair of anions becomes smaller and ultimately approaches zero. That is, for sufficiently large cationic radius, the contribution of ion pairing to selectivity becomes negligible, and selectivity toward the larger anion is maximized. Hence, the larger the radius of the cation is, the greater will be the selectivity toward the larger of a pair of anions up to a maximum plateau value. If the cation is a complex of a metal cation and one or more ligands, the thickness of the ligands determines the overall cationic radius and the corresponding selectivity in anion exchange. Ligands with greater thickness force the anion to lie at larger distance from the cationic charge, bringing about greater preference for larger anions.

EXPERIMENTAL

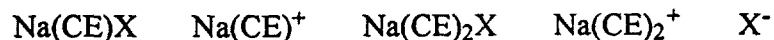
Extraction studies were performed by contacting solutions of BOB14C4 in 1,2-DCE with equal volumes of aqueous solutions of either NaNO_3 or NaClO_4 for 2 hours at 25 ± 1 °C by end-over-end rotation at 35 ± 5 RPM. Aqueous phases also contained ^{22}Na radiotracer, and distribution ratios were determined by gamma scintillation counting using a NaI detector. The following data sets were collected:

M NaNO_3	M BOB14C4	M NaClO_4	M BOB14C4
0.05 - 2.5	0.1	0.0001 - 5	0.1
0.5	0.005 - 0.2	0.001 - 2.5	0.01
2.5	0.005 - 0.2	0.1	0.0001 - 0.1
		0.005	0.00025 - 0.1

A total of 50 data points were subjected to equilibrium modeling using the program SXLSQI. As described elsewhere,^{6,7,8} the program employs Pitzer parameters and Hildebrand-Scott solubility parameters to respectively estimate the aqueous- and organic-phase activity coefficients. Values of $\log K$ corresponding to postulated equilibria thus refer to the condition of infinite dilution.

RESULTS AND DISCUSSION

Extraction experiments consisted of varying the concentration of either NaNO_3 or NaClO_4 while holding the concentration of BOB14C4 constant in 1,2-DCE, or holding the concentration of either NaNO_3 or NaClO_4 constant while varying the concentration of BOB14C4. By use of the program SXLSQI, the observed behavior was found to be consistent with the equilibrium scheme in Fig. 2, assuming the following set of species:



It was found possible to simultaneously fit the nitrate and perchlorate data sets in a single model. Although a complete presentation of the data and fitting results is beyond the scope of this paper, the model included the six sodium species Na(CE)NO_3 , Na(CE)ClO_4 , Na(CE)^+ , $\text{Na(CE)}_2\text{NO}_3$, $\text{Na(CE)}_2\text{ClO}_4$, and Na(CE)_2^+ . The nitrate and perchlorate data could be fit separately, but the two cationic complexes are common to both systems, making it preferable to fit all of the data together. Consistent with the somewhat polar nature of 1,2-DCE, it was necessary to assume the partial dissociation of the anion from the cationic complexes. The observation that two crown ether molecules could accommodate the metal cation follows reasonably from the small cavity size of the crown ether and the common tendency of the Na^+ cation to take on a coordination number of 8. In fact, it was possible to obtain crystals with the stoichiometries Na(DB14C4)ClO_4 and $[\text{Na(DB14C4)}_2]\text{ClO}_4 \cdot \text{CHCl}_3$ (DB14C4 = dibenzo-14-crown-4). The structures of these complexes as determined by X-ray crystallography⁹ entail an "open-face sandwich" structure with coordination to the metal by bidentate perchlorate in the first case and a "sandwich" structure with perchlorate unable to coordinate to the metal in the second case.

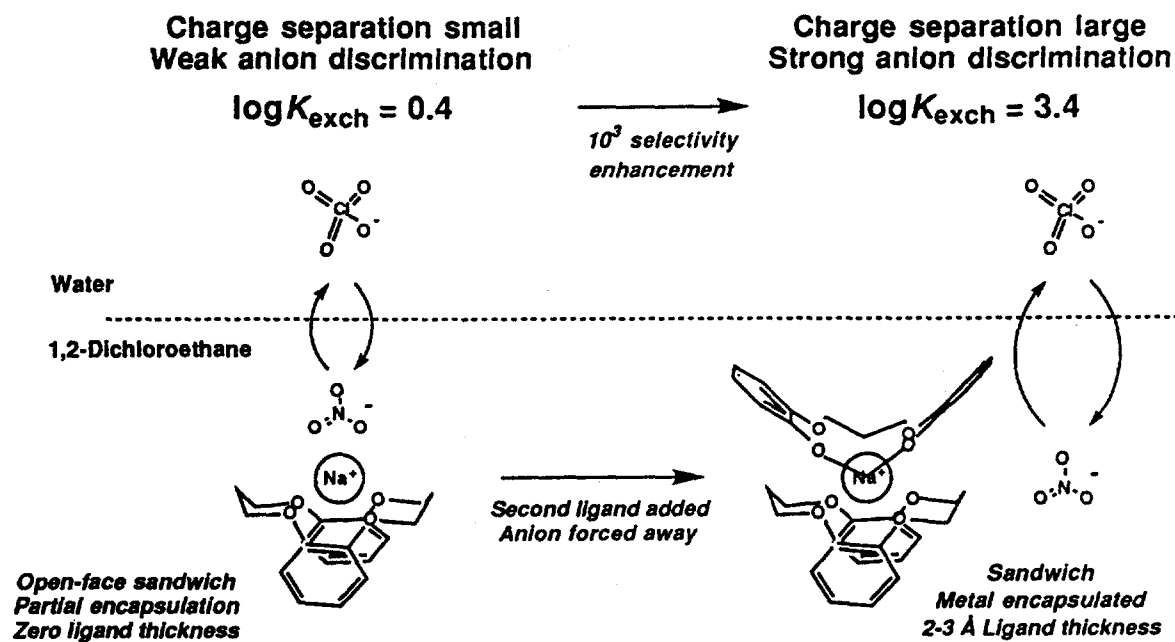


Figure 3. Scheme showing the effect of sandwich formation on anion selectivity, the extent of nitrate being displaced by the larger perchlorate.

From the obtained $\log K$ values, it was possible to evaluate the effect of sandwich formation on anion selectivity in this system. The results are summarized in part in Fig. 3. It may be seen that sandwich formation entails a dramatic effect on anion selectivity in the exchange process. Owing to the ability of the anion to approach closely to the Na^+ cation in the open-face sandwich complex, the ion pair with the smaller nitrate anion gains stability, almost negating the usual preference for perchlorate in anion-exchange. When the anion is forced away by sandwich formation, the selectivity toward perchlorate increases three orders of magnitude. The effect may be ascribed to ligand thickness, illustrating how this simple ligand property plays a key role in ion-pair extraction. This result has significance in its generality, via electrostatic principles, to other possible anion separations by ion-pair distribution processes. Further, this insight enables the design of improved extractants for anionic contaminants such as pertechnetate (TcO_4^-) found in radioactive wastes and groundwater.

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