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Solvent Extraction of Cesium by Substituted Crown Ethers

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ABSTRACT

The extraction of alkali metal nitrates by 18-crown-6, 21-crown-7, and 24-crown-8 ethers, bearing cyclohexano, benzo-, *t*-alkylbenzo, and furano- substituents, in 1,2-dichloroethane has been surveyed. Introduction of a furano substituent onto the macrocyclic ring of 18-crown-6 or 21-crown-7 ethers causes a significant reduction in both extraction efficiency and selectivity. Addition of an additional benzo group to dibenzo-21-crown-7, to give tribenzo-21-crown-7, decreases both extraction efficiency and selectivity, whereas addition of one or two additional benzo groups to dibenzo-24-crown-8 increases the extraction efficiency and selectivity for the larger ions Rb^+ and Cs^+ Detailed equilibrium modeling of the extraction by lipophilic 21-crown-7 ethers indicates that the addition of *t*-alkyl substituents onto the benzo groups has only a minor effect on the extraction of cesium nitrate by dibenzo-21-crown-7 ethers.

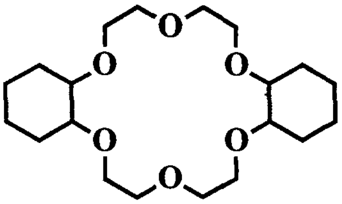
INTRODUCTION

The removal of cesium from radioactive wastes resulting from the reprocessing of nuclear fuels continues to be an important technological problem (Cecille, 1991). A variety of different separation methods have been studied, including solvent extraction, ion exchange, and precipitation (Schultz and Bray, 1987). Among the solvent extraction systems studied, the use of crown ethers as ion-selective complexants has received significant attention (Blasius, 1984; Gerow, 1979; Gerow, 1981; McDowell, 1992). As part of our continuing program to elucidate the physical and structural principles underlying efficiency and selectivity in solvent extraction (Chem.Div., 1993), we have surveyed the extraction of alkali metal nitrates by the series of large-ring crown ethers bearing cyclohexano and multiple aryl substituents, as shown in Figure 1. This study was undertaken to determine how substituent groups affect the selectivity and efficiency of cesium nitrate extraction by crown ethers. In addition, we have studied in detail the extraction of cesium nitrate by the three substituted dibenzo-21-crown-7 ethers **2b-d** and have developed a model to describe speciation in the organic phase using the computer program **SXLSQI** (Deng, submitted).

EXPERIMENTAL

Materials. The crown ethers **1a**, **1b**, **2a**, **3a**, and **3b** were purchased from commercial sources (Parish Chemical/Aldrich Chemical). The remaining crown ethers (**1c**, **2b-g**, and **3c-g**) were prepared as described elswhere (Deng, submitted). Dibenzo-18-crown-6 (**1b**) was recrystallized from dioxane. Dicyclohexano-21-crown-7 (**2e**) and dicyclohexano-24-crown-8 (**3c**) were purified by bulb-to-bulb distillation (180 °C @ 0.02 torr). Alkali metal nitrate salts were purchased as analytical reagents and dried at 110 °C for 3 days before use. 1,2-Dichloroethane (DCE) was of spectrophotometric grade. Distilled/de-ionized water was used for the all of the experiments.

Solvent Extraction. Equal volumes (0.5 mL each) of organic phase (0.025 M of crown ether) and aqueous phase (mixture of metal nitrate salts, MNO_3, each at 0.4 M where M = Li^+, Na^+, K^+, Rb^+, and Cs^+) were equilibrated by repeated inversion on a rotating device in a thermostatic air box at



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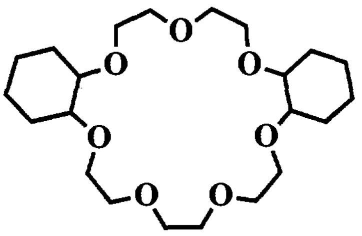

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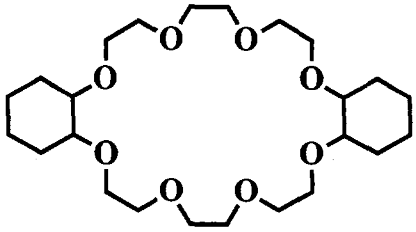

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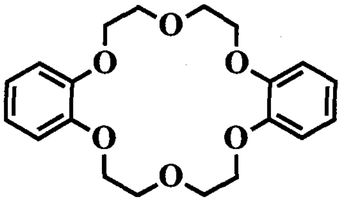

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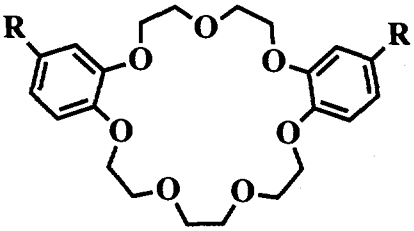

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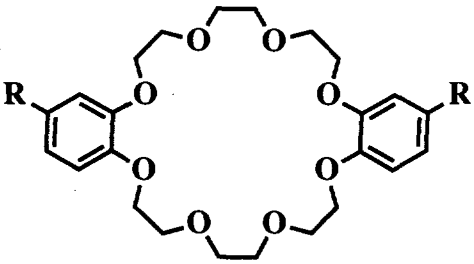
2c) R =*t*-butyl
2d) R =*t*-octyl



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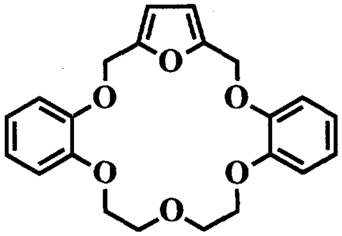

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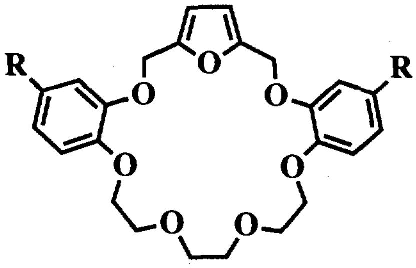

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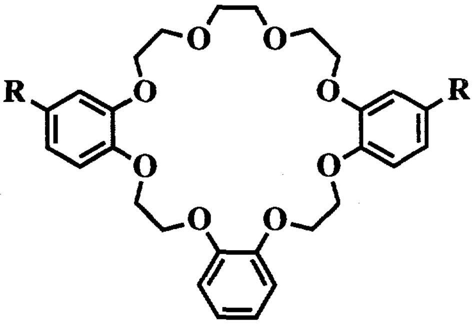
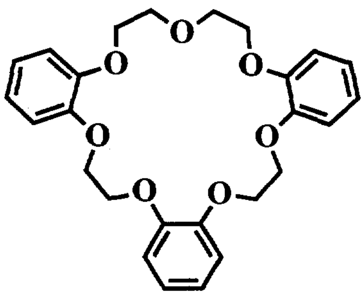


3c) R = H
3f) R = *t*-octyl



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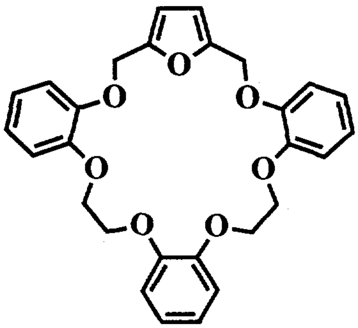

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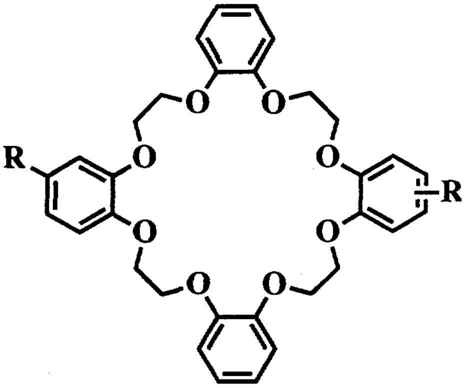

3d: R = H
3g: R = *t*-octyl

Figure 1. Structures of crown ethers.

25.0 °C (± 0.5 °C) for 2 to 15 hours; this procedure was determined previously to be sufficient to ensure equilibrium. The samples were centrifuged for 5 to 10 minutes. An aliquot of the organic phase (0.3 mL) was removed and contacted with 3.0 mL of water, following the same procedure as for the extraction. This back-extraction sample was centrifuged, and 2.0 mL of the aqueous phase was removed for analysis. A second back extraction showed that essentally all of the metal salts are removed from the sovent in the first back-extraction. The final metal ion concentrations in the organic phase were calculated on the basis of the first stripping results. Multiple (3 - 5) extraction runs were performed for each crown ether solution.

Metal cation analysis of aqueous solutions was performed on a Dionex 2020i ion chromatography system equipped with a autosampler, AI-450 workstation, and conductivity detector, using a Dionex IonPac CS12 cation exchange column with 0.02 m methanesulfonic acid as the eluent. Calculations were based on an average of three injections for each sample using the external standard method. Lower detection limits for Li^+, K^+, Rb^+ and Cs^+ were $[\mathrm{M}^+] \geq 3 \text{ x } 10^{-6}$; the lower limit for $[\mathrm{Na}^+] \geq 10^{-4}$ resulted from the high background of Na^+ in the controls. Acid-treated polypropylene vials and containers were used for both extraction and storage of aqueous solutions. All organic solutions were stored in Teflon® containers.

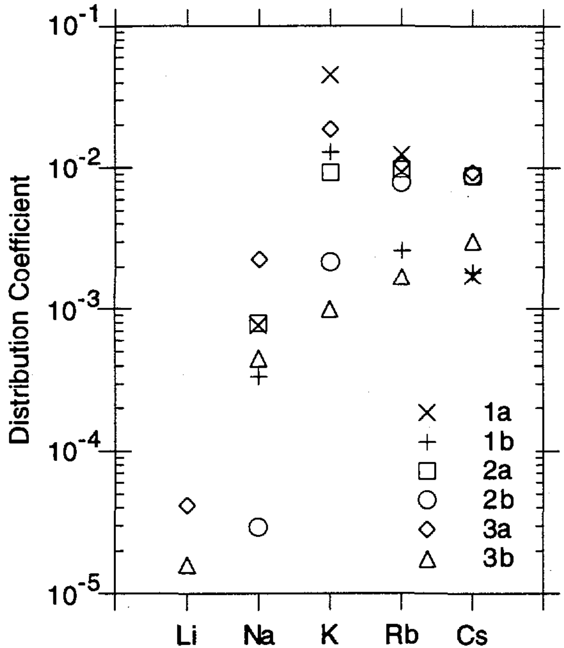

Figure 2. Extraction of alkali metal nitrates by dicyclohexano and dibenzo crown ethers in DCE. (Values for D_{Na} below 10^{-4} are approximate, see experimental.)

RESULTS AND DISCUSSION

The extraction of alkali metal nitrates by the commercially available dicyclohexano (**1a**, **2a** and **3a**) and dibenzo (**1b**, **2b** and **3b**) crown ethers in DCE is shown in Figure 2. These data are consistant with previous studies indicating that the 18C6 ethers **1a** and **1b** extract the intermediate sized K^+ ion most strongly while the dicyclohexano 21C7 (**2a**) and 24C8 (**3a**) ethers extract K^+, Rb^+, and Cs^+ ions similarly. Only the dibenzo-substituted 21C7 (**2b**) and 24C8 (**3b**) ethers exhibit a preference for the larger Rb^+ and Cs^+ ions. In general, the dibenzo crown ethers (**1b**, **2b**, and **3b**) extract more weakly than their dicyclohexano counterparts, reflecting the reduced basicity of the aryl ether oxygens in these macrocycles. In particular, **2b** exhibits notably weaker extraction of Na^+ ion, consistent with previous attributions of high cesium/sodium selectivity to this crown ether (Blasius, 1984).

In an effort to determine if improved cesium selectivity can be obtained by simple modification of the crown ether structure, we obtained data for the extraction of alkali metal nitrates by 21C7 and 24C8 ethers bearing multiple (2-4) benzo substituents (Figure 3) and by 18C6 and 21C7 ethers bearing furano substituents (Figure 4). Both benzo and furano substituents act as rigid spacer groups and reduce the electron-donating properties of the ether oxygens to which they are attached. The results shown in Figure 3 suggest that the effect of adding benzo substituents is most significant for the extraction of the larger Rb^+ and Cs^+ ions. In the case of the 21C7 ethers (Figure 3a), the addition of one benzo substituent to dibenzo-21-crown-7 (**2b** →**2f**) suppresses the extraction of Cs^+ ion by a factor of 4.0; thus, whereas **2b** extracts Rb^+ and Cs^+ ions similarly, **2f** exhibits Rb^+ selectivity. Conversely, the addition of benzo substituents to dibenzo-24-crown-8 (Fig 3b) increases the extraction of Cs^+ ion by a factor of 1.8 in going from **3b** to **3c** and by a factor of 4.2 in going from **3c** to **3d**. Consequently, **3d** is unique among the crown ethers in this study in that it exhibits selectivity for Cs^+ ion over all of the other alkali metal cations and it exhibits the largest D_{Cs}. The addition of furano groups to benzo crown ethers (Figure 4) significantly decreases the extraction of the larger cations (K^+, Rb^+, and Cs^+), consequently reducing the selectivity for these cations.

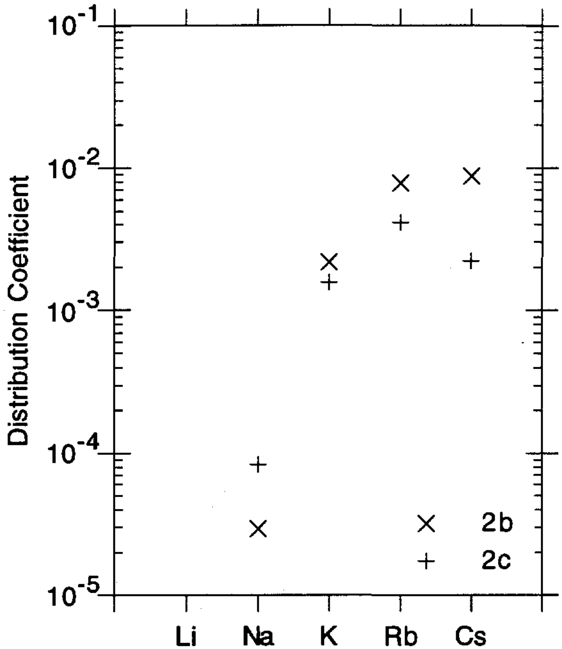

Figure 3a. Extraction of alkali metal nitrates by dibenzo- and tribenzo-21-crown-7 ethers. (Values for D_{Na} below 10^{-4} are approximate, see experimental.)

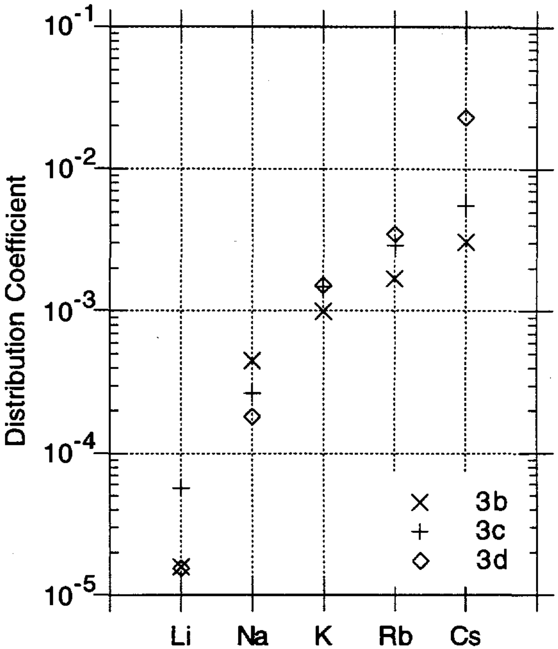

Figure 3b. Extraction of alkali metal nitrates by dibenzo-, tribenzo-, and tetrabenzo-24-crown-8 ethers.

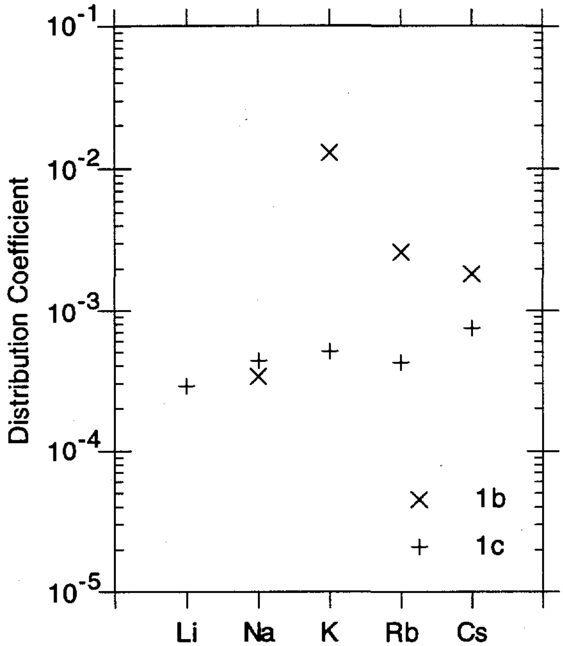

Figure 4a. Comparison of the extraction of alkali metal nitrates by dibenzo-18-crown-6 and furanodibenzo-18-crown-6.

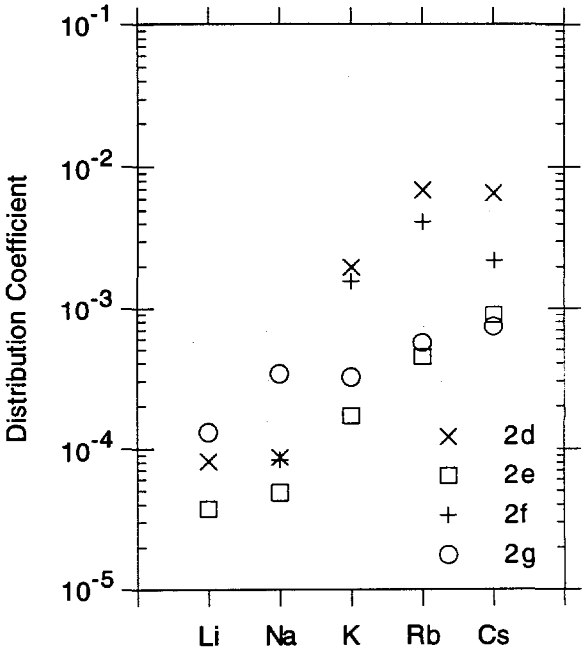

Figure 4b. Comparison of the extraction of alkali metal nitrates by benzo-21-crown-7 ethers and furano-substituted benzo-21-crown-7 ethers. (Values for D_{Na} below 10^{-4} are approximate, see experimental.)

Generally, benzo-substituted crown ethers exhibit low solubility in non-polar organic diluents; addition of alkyl substituents, particularly tertiary alkyl groups, increases both the solubility and lipophilicity of benzo crown ethers. The effect this type of substitution has on extraction properties has not yet been studied in detail by others. In Figure 5, we compare the extraction of alkali metal nitrates by benzo-crown ethers (**2b** and **3b**-**3d**) to that of their deriviatives bearing *t*-alkyl groups on the benzene rings (**2c**, **2d** and **3e**-**3g**).

For the series of 21C7 ethers, no significant differences are observed in the extraction of the larger cations K^+, Rb^+, and Cs^+ (vide infra). Increases in the extraction of the smaller Li^+ and Na^+ ions by the *t*-alkylbenzo crown ethers result in minor decreases in extraction selectivity. Similar trends were observed for the 24C8 ethers, except in the case of the tetrabenzo-24-crown-8 ethers **3d** and **3g**. The addition of *t*-octyl substituents to two of the four benzo groups of **3d** (to produce **3g**) appears to decrease the extraction of Cs^+ by a factor of 2, while increasing the extraction of K^+ and Rb^+ ions by a similar amount. The reasons for these unique observations are not well understood and suggest the need for further study.

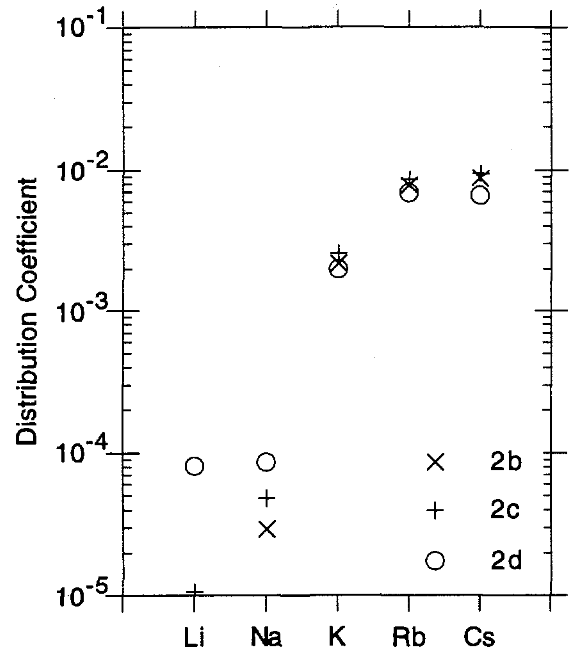

Figure 5a. Comparison of the extraction of alkali metal nitrates by benzo-21-crown-7 and *t*-alkylbenzo-21-crown-7 ethers. (Values for D_{Na} below 10^{-4} are approximate, see experimental.)

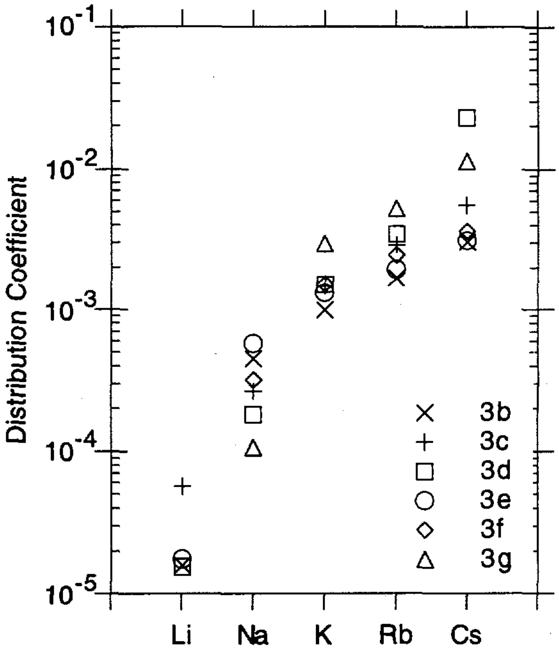

Figure 5b. Comparison of the extraction of alkali metal nitrates by benzo-24-crown-8 and *t*-alkylbenzo-24-crown-8 ethers

Finally, with the goal of relating crown ether structure to equilibrium constants for the formation of distinct extraction complexes, the extraction of cesium nitrate was determined over a range of conditions for four 21-crown-7 ethers in the partially ionizing diluent DCE at 25 °C. The crown ethers included **2a**-**2d**. Variation of aqueous cesium nitrate concentration up to 0.4 M and organic-phase crown ether concentration up to 0.025 M was modeled by the program ***SXLSQI*** (Deng, submitted). Formation of the species $CsBNO_3$ (B = crown ether) and partial dissociation to the ions $[CsB]^+$ and NO_3^- in the organic phase satisfactorily account for the observed behavior of the benzo-crown ethers. As shown in Table 1, differences in alkylation of the benzo groups give only minor differences in the extraction behavior. By contrast, **2a** exhibits much stronger extraction than the benzo crowns. On addition, **2a** entails behavior that can best be explained by formation of the higher complexes CsB_2NO_3 and $[CsB_2]^+$.

Table 1

Constants for the Extraction of $CsNO_3$ by 21-Crown-7 Ethers in 1,2-Dichloroethane at 25 °C.[a]

Crown Ether	$\log K_{ex}$ $CsBNO_3$	$\log K_{ex\pm}$ CsB^+	$\log K_{ex}$ CsB_2NO_3	$\log K_{ex\pm}$ CsB_2^+	R
2a	0.57(6)	-3.97(24)	1.6(3)	-1.59(6)	0.066
2b	0.12(2)	-4.71(6)			0.058
2c	0.15(2)	-4.97(12)			0.081
2d	0.05(3)	-4.31(5)			0.075

[a] In these experiments, $CsNO_3$ was the only aqueous salt present. R is the approximate standard relative error of the models compared with the data. **SXLSQI** corrects for the ionic activity by the Pitzer treatment for the aqueous phase and an extended Debye-Hückel equation for the organic phase. The Hildebrand-Scott treatment is employed for the nonideality of the neutral organic-phase species, although this was negligible in the present case.

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