



Analysis of Equilibria in the Extraction of Cesium Nitrate by Calix[4]arene-bis(*t*-Octylbenzo-Crown-6) in 1,2-Dichloroethane

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Abstract. The extraction of CsNO_3 by the highly lipophilic calixarene-crown ether calix[4]arene-bis(*t*-octylbenzo-crown-6) (CABOBC6) in 1,2-dichloroethane (1,2-DCE) at 25 °C has been shown to be consistent with the formation of both 1:1 and 2:1 metal:ligand species. Variation of the aqueous-phase CsNO_3 concentration up to 1.0 M and variation of the organic-phase calixarene concentration up to 0.10 M was modeled by the program SXLSQI. Formation of the organic-phase species CsBNO_3 (B = calixarene) was confirmed as well as the organic-phase dissociation products CsB^+ and NO_3^- . Good evidence for the 2:1 metal:ligand organic-phase species $\text{Cs}_2\text{B}(\text{NO}_3)_2$ was also found, although the dissociation of nitrate from this complex was not observed. Binding of the second Cs^+ cation by the ligand is approximately two orders of magnitude weaker than binding of the first Cs^+ cation. The logarithm of the apparent partition ratio ($\log P_B$) of the calixarene between water and 1,2-DCE was found by $^1\text{H-NMR}$ techniques to be > 5.1 .

Key words: Calixarene-crown ether, Cs^+ complexation, solvent extraction, SXLSQI, equilibrium constants, partition ratio, modeling.

1. Introduction

New cesium-selective extractants from the calix[4]arene-crown-6 family have recently been introduced by collaborating European investigators [1–15]. As shown in Figure 1, these compounds represent a hybrid of the calix[4]arene and crown ether families, in which one or two crown-6 fragments bridge the phenolic positions of the calix[4]arene in the 1,3-alternate conformation. The facing pairs of aromatic rings of the calixarene in this conformation form two cavities that are each preorganized for partial insertion of a Cs^+ ion. Crystal structures of model complexes with cesium salts [1, 10–13] have demonstrated a significant pi-interaction between these facing aromatic rings and the guest Cs^+ ion, which is also coordinated by the six ether oxygen atoms of the polyether chain. This unique structure leads to strongly enhanced selectivity and strength in the extraction of cesium [1, 7,

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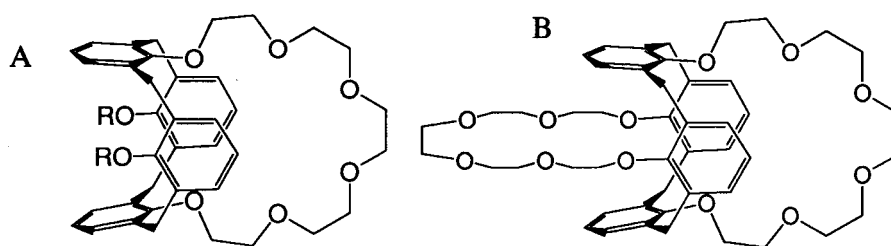


Figure 1. Examples of 1,3-alt-calix[4]arene-crown-6 compounds. A: monocrown calix[4]arene bearing two alkoxy substituents. B: calix[4]arene-bis(crown-6).

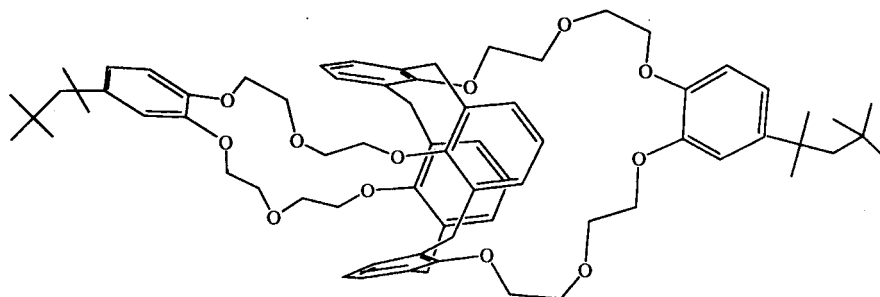


Figure 2. Lipophilic calixarene-crown derivative, calix[4]arene-bis(*t*-octylbenzo-crown-6), abbreviated CABOBC6.

10-15, 16]. By comparison to the most selective crown ethers, which give Cs/Na separation factors of “only” several hundred, the calix[4]arene-crown-6 family of compounds give Cs/Na separation factors exceeding 10^4 . Despite these highly favorable properties, members of the calix[4]arene-crown-6 family reported so far have hitherto not been adapted to practical solvent-extraction process applications. Needs that must be addressed for the specific application of cesium removal from nuclear waste include higher solubility of extractants in alkane diluents, improved selectivity over potassium, and improved stripping [16].

With regard to improving alkane solubility, our earlier results on dibenzo-21-crown-7 ethers showed that alkyl substitution of the benzo groups improves alkane solubility but does not strongly influence the cesium extraction behavior [17–20]. Therefore, a more lipophilic derivative of calix[4]arene-bis(benzo-crown-6) was prepared. This derivative, calix[4]arene-bis(*t*-octylbenzo-crown-6) (CABOBC6), shown in Figure 2 [21, 22], is likewise not expected to differ significantly from calix[4]arene-bis(benzo-crown-6) in the extraction of cesium. However, CABOBC6 is indeed much more soluble than the latter in modified or unmodified aliphatic diluents [22], allowing study of a member of the calix[4]arene-bis(crown-6) family in a nonpolar environment.

The problems associated with boosting Cs/K selectivity and stripping efficiency will require a more fundamental understanding of the equilibrium behavior of calix[4]arene-crown-6 extractants. Regarding CABOBC6 and other calix[4]arene-

bis(crown-6) compounds, an obvious issue concerns the importance of two Cs^+ ion binding sites in the same molecule. Namely, how does the binding of the first Cs^+ ion influence the binding of a second one? Initial results indicated only formation of 1 : 1 complexes [2–4, 6, 7, 15], but conductivity [8], NMR [12, 13], and electro-spray mass spectrometry [13] studies have later provided evidence for a less stable 2 : 1 metal : ligand species. These results have gained support from molecular dynamics calculations, in which such 2 : 1 complexes have been simulated [23]. However, the 2 : 1 species have not yet been observed in extraction. Another question concerns the role of the nitrate anion, including how tightly it is associated with the cesium-calixarene complex cation in the organic phase and ultimately whether this has an effect on Cs/K selectivity.

As a step toward addressing these fundamental issues, we present here the results of a study of the extraction of cesium nitrate with CABOBC6. For comparison with earlier results, we have chosen 1,2-dichloroethane (1,2-DCE) as the diluent. Although we do not consider 1,2-DCE to be a process-suitable diluent, it allows the strength of association of nitrate anion with the organic-phase cesium complex to be directly assessed from careful equilibrium measurements [17]. The only aqueous-phase salt examined here is CsNO_3 , which eliminates complications from competitive equilibria and allows a clear understanding of loading behavior. Nitrate is, of course, the most important co-anion in potential nuclear applications. In the experiments described herein, the dependencies of cesium extraction on aqueous-phase CsNO_3 and organic-phase CABOBC6 concentrations were precisely determined using ^{137}Cs tracer techniques. The results were then modeled with the program SXLSQI [17, 24, 25] to determine the organic-phase species and corresponding equilibrium constants.

2. Experimental

2.1. REAGENTS

Calix[4]arene-bis-(*t*-octylbenzo-crown-6) [CABOBC6] was prepared in our laboratory [21, 22]. The salt CsNO_3 (Aldrich Chemical, 99%) was dried at 110 °C for 1 day prior to use; purity was confirmed by use of a Dionex 500 ion chromatography system equipped with an IonPac CS12A cation-exchange column. The diluent 1,2-dichloroethane was purchased from EM Science as Omnisolve[®] reagent (99.91%) and used as received for extraction studies. The radiotracer ^{137}Cs was obtained as $^{137}\text{CsCl}$ in 1 M HCl from Amersham (Arlington Heights, IL) and converted to $^{137}\text{CsNO}_3$ in water by anion exchange. Amberlite[®] IRA-900 anion exchange resin in the nitrate form was washed and the eluent checked for metals by inductively coupled plasma optical emission spectroscopy (ICP-OES) prior to use. Conversion of the $^{137}\text{CsCl}$ tracer to the nitrate form was determined by washing the resin after conversion and quantifying the eluent by titration using the Mohr method for Cl^- ion. Distilled deionized water (resistivity $\geq 18.1 \text{ M}\Omega$) was used to prepare

all aqueous solutions. Chloroform-*d* (100 atom% listed isotopic purity) was purchased from Acros Chemical and passed through activated alumina to remove trace impurities and water.

2.2. METHODS

Solvent-extraction studies were performed on a small scale using 4-mL vials as extraction vessels. Equal volumes of aqueous and organic phases were contacted for one hour by gentle end-over-end rotation at a constant temperature of 25.0 ± 0.2 °C using a Glass-Col[®] laboratory rotator. A uniform contact time of one hour was used, though it was shown that equilibrium is reached within five minutes. All samples were centrifuged for three to five minutes to ensure complete phase separation. For Cs⁺ ion distribution measurements, an aliquot of each phase was taken and the activity of ¹³⁷Cs measured by gamma-counting techniques.

Two experiments were performed in which the initial CsNO₃ and calixarene concentrations were systematically varied. In the first experiment, the data set included initial variable CsNO₃ concentrations within the range of 0.001 to 1.00 M, while calixarene concentrations were kept constant at either 0.003 or 0.02 M. In the second experiment, the initial calixarene concentration was varied over a range from 1×10^{-5} to 0.10 M with constant CsNO₃ concentrations of 0.01 and 1.0 M.

The partitioning behavior of the calixarene was determined by contacting a solution of 0.01 M calixarene in distilled 1,2-DCE with aqueous CsNO₃ solutions at varying concentrations up to 0.1 M. Each aqueous phase was pre-saturated with 1,2-DCE. Each contact was made at an O:A ratio of 1:10 by vigorous hand shaking for 5 minutes. The aqueous phase was then separated and centrifuged in an RC-5 Sorvall centrifuge at 10,000 rpm for 30–40 minutes and a known volume contacted with an excess volume of distilled 1,2-DCE as described above. The solvent was removed by vacuum and the residue taken up in 1,2-DCE and transferred to 5-mm NMR tubes. The solvent was evaporated in the tube, and 0.75 mL of CDCl₃ containing 10^{-4} M mesitylene (Matheson Coleman and Bell, 99+%) was added as an internal integration standard. Except for the aqueous concentrations of CsNO₃ at 0.01 M and 0.1 M and water, the resulting spectra clearly showed only peaks characteristic of authentic CABOBC6 samples. The concentration of calixarene in each sample was measured by comparing the area of the singlet from the nine protons of the three methyl groups of mesitylene (2.277 ppm) with the area of the triplet from the four protons para to the oxygen atoms on the four arene rings of the calixarene frame (6.684 ppm).

2.3. INSTRUMENTAL ANALYSIS

The distribution of cesium from aqueous solutions of cesium nitrate to 1,2-DCE solutions of CABOBC6 was determined by gamma(γ)-counting techniques (¹³⁷Cs tracer) using a 3" NaI(Tl) crystal through-hole type detector (Packard Cobra

Quantum Model 5003). The extraction of CsNO_3 by 1,2-DCE alone was below the detection limits of this analysis (i.e., $D_{\text{Cs}} < 2 \times 10^{-5}$).

For the $^1\text{H-NMR}$ analyses, a Bruker MSL-400 spectrometer was used. All samples were run at a constant temperature of 300 K. $^1\text{H-NMR}$ spectra were obtained at 400.13 MHz using a spectral width of 3355.7 Hz over 16K data points. A relaxation delay (D_0) was set at 5 times the longest T_1 for peaks of both internal reference and calixarene that were integrated. Baseline corrections and integrals were repeated in triplicate, and the partition ratio P_B derived from each analysis was averaged to give an estimation of error. Precision ranged from 5–20%, increasing as the partition ratio increased. The detection limit for $^1\text{H-NMR}$ analysis was determined to be $\log P_B = 5.1$.

2.4. CALCULATIONS

The data were fit using the modeling program SXLSQI [17, 24, 25]. In the least-squares refinement of $\log K$ values corresponding to the formation of particular species (see next section), the program automatically takes into account nonideality effects of both organic- and aqueous-phase species. For organic-phase species, the Hildebrand–Scott [24, 26–28] and Debye–Hückel [17] treatments are respectively used for the neutral and electrostatic contributions to the organic-phase solute activity coefficients. The Pitzer treatment [24, 29] is used to calculate aqueous ionic activity coefficients. The program uses Masson coefficients [30] to convert the data from the molarity scale to the molality scale used in the Pitzer equations. Solubility parameters and molar volumes are also required by the program and are summarized in Table I. The goodness of fit for a particular model to the given data set is quantified by the *agreement factor* σ , defined according to the least-squares criterion as $\sigma = [\sum w_i (Y_i - Y_{c,i})^2 / (N_0 - N_p)]^{1/2}$ where Y_i is the i th experimentally observed quantity, $Y_{c,i}$ is the corresponding quantity calculated from the model being tested, w_i is the weighting factor defined as the reciprocal of the square of the estimated uncertainty of Y_i , N_0 is the number of observations, and N_p is the number of adjustable parameters (i.e., equilibrium constants). The uncertainty of Y_i was taken as $\pm 5\%$ of the mean of at least two determinations. In a systematic testing of equilibrium models, the best model is usually chosen as the one showing the minimum value of the agreement factor. The value of σ will approach unity when the error of fitting is equal to the estimated experimental error; values less than unity are interpreted as experimental precision being better than the estimated precision.

Table I. Parameters used in SXLSQI modeling.

Ion	Masson coefficients ^a		
	V_0 cm ³ mol ⁻¹	S_V^* cm ³ L ^{1/2} mol ^{-3/2}	
Cs ⁺	21.29	1.393	
NO ₃ ⁻	29.33	0.543	
Interaction	Pitzer parameters ^b		
	$\beta^{(0)}$	$\beta^{(1)}$	α
Cs ⁺ —NO ₃ ⁻	-0.0758	-0.0669	2.0
Species	Other parameters		
	V_0^c cm ³ mol ⁻¹	δ^e J ^{1/2} cm ^{-3/2}	
1,2-DCE	79.4	20.3 ^f	
CABOBC6	909.4 ^d	20.93 ^d	
Cs ⁺	21	14.0 ^g	
NO ₃ ⁻	29	25.8 ^g	

^a Masson coefficients allow the aqueous density to be estimated for molality-molarity interconversions. Values were taken from [30].

^b Pitzer parameters allow aqueous-phase ionic activity coefficients to be estimated. Values were taken from [29].

^c Molar volume of the species in the organic phase. Values for organic species were taken from [27] or estimated.^d Values for the inorganic ions were taken to be approximately equal to V_0 .

^d Estimated according to group contributions [27].

^e Hildebrand solubility parameters were used in estimation of the activity coefficients of organic-phase species. The solubility parameter of a complex was taken as the volume-weighted average of the solubility parameters of its constituents. For example, $\delta_{MB+} = (V_M \delta_M + V_B \delta_B) / (V_M + V_B)$ [28].

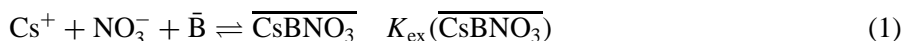
^f Taken from [27].

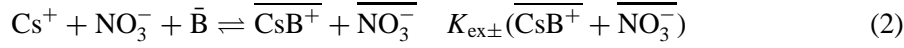
^g Taken from [28].

3. Results

3.1. EQUILIBRIUM EXPRESSIONS

By analogy to results on calix[4]arene-crown-6 compounds reported elsewhere [1, 6, 7, 11–15], the extraction of CsNO₃ by CABOBC6 can be expressed according to a 1 : 1 stoichiometry. Partial dissociation of nitrate may also be expected in 1,2-DCE [17, 31], and the corresponding equilibrium equations are given as





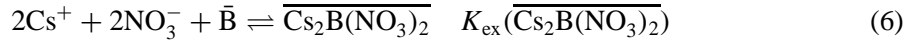
$$K_{\text{ex}}(\overline{\text{CsBNO}_3}) = \frac{\bar{y}_{\text{CsBNO}_3}[\overline{\text{CsBNO}_3}]}{y_{\text{Cs}}[\text{Cs}^+]y_{\text{NO}_3}[\text{NO}_3^-]\bar{y}_{\text{B}}[\bar{\text{B}}]} \quad (3)$$

$$K_{\text{ex}\pm}(\overline{\text{CsB}^+} + \overline{\text{NO}_3^-}) = \frac{\bar{y}_{\text{CsB}}[\overline{\text{CsB}^+}]\bar{y}_{\text{NO}_3}[\overline{\text{NO}_3^-}]}{y_{\text{Cs}}[\text{Cs}^+]y_{\text{NO}_3}[\text{NO}_3^-]\bar{y}_{\text{B}}[\bar{\text{B}}]} \quad (4)$$

In these equations, overbars indicate species in the organic phase, brackets indicate molarity, and y is the molar activity coefficient of a species as indicated by the subscript. The dissociation of the ion-pair species can then be expressed by the following:

$$K_{\text{diss}}(\overline{\text{CsBNO}_3}) = \frac{K_{\text{ex}\pm}(\overline{\text{CsB}^+} + \overline{\text{NO}_3^-})}{K_{\text{ex}}(\overline{\text{CsNO}_3})} \quad (5)$$

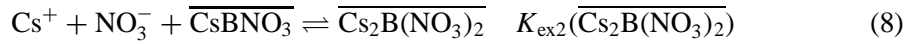
Although formation of 2 : 1 metal : ligand species in solution has not been observed previously for calix[4]arene-bis(crown-6) ethers in liquid-liquid extraction, the possible formation of the corresponding undissociated 2 : 1 species may also be written



where

$$K_{\text{ex}}(\overline{\text{Cs}_2\text{B}(\text{NO}_3)_2}) = \frac{\bar{y}_{\text{Cs}_2\text{B}}[\overline{\text{Cs}_2\text{B}(\text{NO}_3)_2}]}{y_{\text{Cs}}^2[\text{Cs}^+]^2y_{\text{NO}_3}^2[\text{NO}_3^-]^2\bar{y}_{\text{B}}[\bar{\text{B}}]} \quad (7)$$

In stepwise fashion, the extraction of the second CsNO_3 ion pair by the 1 : 1 complex may be expressed as follows:



where

$$K_{\text{ex}2} = \frac{K_{\text{ex}}(\overline{\text{Cs}_2\text{B}(\text{NO}_3)_2})}{K_{\text{ex}}(\overline{\text{CsBNO}_3})} \quad (9)$$

In principle, one may also consider formation of the anion-dissociated organic-phase dinuclear species $\overline{\text{Cs}_2\text{B}(\text{NO}_3)^+}$ and Cs_2B^{2+} , but no evidence was found that such species are significant relative to the neutral species $\overline{\text{Cs}_2\text{B}(\text{NO}_3)_2}$ under the experimental conditions employed (see below). Likewise, we found it unnecessary to consider species having more than one calixarene, although evidence for weak

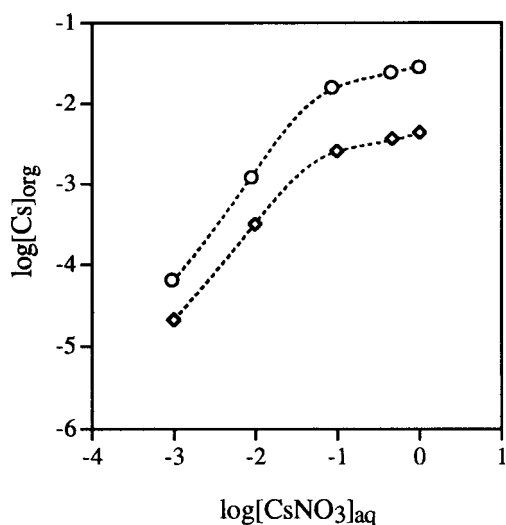


Figure 3. Comparison of calculated (dotted lines) and observed (symbols) equilibrium organic-phase cesium molarity as a function of equilibrium aqueous-phase cesium nitrate concentration. Initial organic-phase calixarene concentrations are equal to (\diamond) 0.003 M and (\circ) 0.02 M. Dotted lines were calculated assuming formation of the organic-phase species MBX, MB^+ , and M_2BX_2 (Model 2 in Table III).

formation of organic-phase cesium complexes having two crown ether ligands was noted previously [17].

An apparent partition ratio for the extractant is defined:

$$P_B = [\bar{B}]_{\text{total}}/[B]_{\text{total}} \quad (10)$$

Here, $[\bar{B}]_{\text{total}}$ and $[B]_{\text{total}}$ respectively include all organic- and aqueous-phase species containing B, including monomeric B, possible aggregates, and all complexes of the calixarene with cesium.

3.2. EXTRACTION RESULTS

The curves depicted in Figure 3 show loading or saturation of the calixarene exceeding 1:1 metal:ligand stoichiometry as $[CsNO_3]_{\text{aq}}$ exceeds 0.26 M. At $[CsNO_3]_{\text{aq}}$ equal to 1 M, the ratio of cesium in the organic phase to total calixarene equals 1.46 and 1.43 for 0.003 M and 0.02 M initial calixarene concentrations, respectively. In the $CsNO_3$ concentration range 0.001–0.01 M, nonintegral slopes of approximately 1.3 and 1.2 are observed corresponding respectively to 0.003 M and 0.02 M initial calixarene concentrations.

Figure 4 shows the dependence of the cesium concentration in the organic phase on the initial organic-phase calixarene concentration under both saturation and low-loading conditions. Slopes of 0.70 and 1.0 corresponding to initial aqueous-phase $CsNO_3$ concentrations of 0.01 and 1.0 M are apparent.

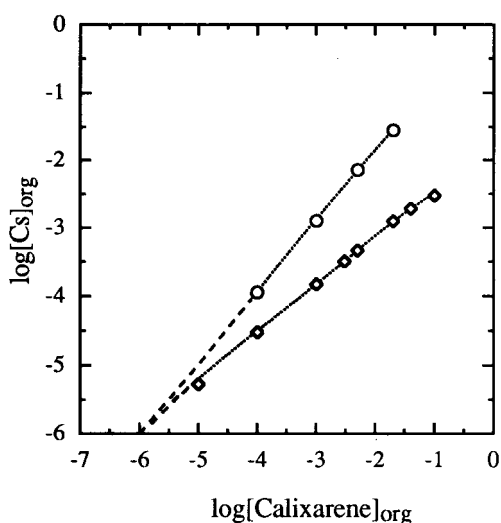


Figure 4. Comparison of calculated (dotted lines) and observed (symbols) equilibrium organic-phase cesium molarity as a function of initial organic-phase calixarene concentration. Initial aqueous-phase CsNO_3 concentrations are equal to (\diamond) 0.01 M and (\circ) 1.0 M. Dotted lines were calculated assuming formation of the organic-phase species MBX , MB^+ , and M_2BX_2 (Model 2 in Table III). Dashed portions of each line represent extrapolations of Model 2.

The slope analysis of a similar system involving substituted 21-crown-7 ethers in 1,2-DCE was discussed in detail for 1 : 1 metal:crown stoichiometries [17]. Even in that simple case, the complication due to partial ion-pair dissociation in the organic phase gives rise to non-linear and non-integral slope behavior in plots like those shown in Figures 3 and 4. For example, one expects to see an extractant dependence of less than unity (0.5–1.0) for a partially dissociated system, as may be observed in Figure 4 for the low-loading condition. In the present system, further complication due to probable 2 : 1 metal : ligand species arises, making a straightforward interpretation of slopes difficult. Hence, the results were modeled by computer using the program SXLSQI, as discussed in detail below.

A significant partitioning of such a lipophilic compound such as CABOBC6 to the aqueous phase was considered unlikely, and this expectation was verified by direct measurement. Partition ratios for the calixarene between 1,2-DCE and water or aqueous CsNO_3 solutions were determined by $^1\text{H-NMR}$ spectrometry and are reported in Table II. As expected, the results confirm that the calixarene is indeed highly lipophilic and may justifiably be neglected in further analysis of CsNO_3 extraction equilibria. However, some aspects of the data deserve brief comment. By reference to a recent review of crown ether partitioning [31], we may make a crude estimate of the lipophilicity of CABOBC6 by additive group-contribution methodology. Consider that the value of $\log P_B$ for the simple crown ether dibenzo-18-crown-6 between water and 1,2-DCE is 4.0 [32] and very roughly that each

Table II. Apparent partition ratios at 25 °C for calixarene distributing between aqueous CsNO₃ solutions and 1,2-dichloroethane.^a

CsNO ₃ (mol L ⁻¹)	log P_B
0	>5.1
1.0×10^{-6}	4.6
1.0×10^{-5}	4.7
1.0×10^{-4}	4.8
1.0×10^{-3}	5.1
1.0×10^{-2}	5.0
1.0×10^{-1}	>5.1

^a The calixarene was initially at 0.01 M in 1,2-DCE. Partition ratios were determined by ¹H NMR spectrometry (see Experimental section). Average precision was estimated to be ±0.2.

additional benzo group adds 2.0 and each aliphatic carbon adds 0.5 to the overall log P_B value. If one then rearranges these fragments and reconstructs CABOBC6, ignoring minor differences between aromatic and aliphatic ether oxygens and the mismatch of four hydrogen atoms, CABOBC6 is in principle expected to have an overall log P_B value on the order of 24! This is in line with the undetectability of CABOBC6 partitioning to water (i.e., log P_B > 5.1, Table II). The behavior of log P_B on addition of CsNO₃ to the aqueous phase, though, is problematic. Although the value of 4.6 for log P_B on addition of 1×10^{-6} M CsNO₃ to the aqueous phase might suggest strong binding of cesium ion in the aqueous phase by CABOBC6 [31], this would unreasonably require the aqueous binding constant to be at least 10^{25} to overcome the high lipophilicity of the ligand and would also lead one to expect, contrary to observation, that log P_B would continue to decrease on further addition of CsNO₃ (at least until salting-out effects became important at sufficiently high ionic strengths). At present, we offer no speculation on the origins of the observed behaviors and recognize the possibility that these measurements, at or near the limits of detection, may simply reflect an artifact such as entrainment. In any case, the aqueous concentrations of CABOBC6 are confirmed to be negligible and will be neglected from the modeling discussed below.

3.3. MODELING OF CsNO₃ EXTRACTION

Using the program SXLSQI, the consistency of the expected equilibrium processes described in Equations (1)–(9) with the data shown in Figures 3 and 4 may be tested. Based on the agreement of the various possible models with the

Table III. Trial models for CsNO₃ extraction.^a

Model	$\log K_{\text{ex}} = \log \frac{(\text{MBX})_{\text{o}}}{(\text{M})_{\text{a}}(\text{X})_{\text{a}}(\text{B})_{\text{o}}}$	$\log K_{\text{ex}\pm} = \log \frac{(\text{MB})_{\text{o}}(\text{X})_{\text{o}}}{(\text{M})_{\text{a}}(\text{X})_{\text{a}}(\text{B})_{\text{o}}}$	$\log K_{\text{ex}} = \log \frac{(\text{M}_2\text{BX}_2)_{\text{o}}}{(\text{M})_{\text{a}}^2(\text{X})_{\text{a}}^2(\text{B})_{\text{o}}}$	$\log K_{\text{ex}\pm} = \log \frac{(\text{M}_2\text{BX})_{\text{o}}(\text{X})_{\text{o}}}{(\text{M})_{\text{a}}^2(\text{X})_{\text{a}}^2(\text{B})_{\text{o}}}$	σ^{b}
1	2.78 ± 0.09	-0.94 ± 0.10			3.24
2	2.77 ± 0.02	-0.93 ± 0.02	3.54 ± 0.04		0.72
3	2.75 ± 0.05	-0.92 ± 0.05		0.23 ± 0.12	1.84
4	2.76 ± 0.03	-0.92 ± 0.03	3.39 ± 0.07	-0.4^{c}	0.97

^a In equilibrium expressions, M = Cs⁺, X = NO₃⁻, and B = calixarene; subscripts o and a respectively indicate organic and aqueous phase species. SXLSQI was used to fit the data shown in Figures 3 and 4 using parameters given in Table I. Model 2 is considered to be the best model.

^b SXLSQI agreement factor σ , as defined in the Experimental Section 2.4.

^c As discussed in the text, the value was fixed in the refinement of the other $\log K$ values based on Model 3 and is considered to be the maximum possible value of $\log K_{\text{ex}\pm}(\text{MB}^+ + \text{X}^-)$. When the value of $\log K_{\text{ex}\pm}(\text{MB}^+ + \text{X}^-)$ was allowed to refine, very low negative values were obtained, indicating rejection of this species.

data, one may determine the most likely species and their corresponding equilibrium constants. As discussed in the previous section, the obvious organic-phase cesium-containing species to test in order of complexity include CsBNO_3 , CsB^+ , $\text{Cs}_2\text{B}(\text{NO}_3)_2$, and $\text{Cs}_2\text{B}(\text{NO}_3)^+$. In the modeling procedure, combinations of these and possibly other species represent different hypothetical models, each of which is refined to find the best values of the equilibrium constants according to the least-squares criterion. The agreement factor σ (see Experimental Section 2.4) and systematic deviations between calculated and observed organic-phase cesium concentrations may then be examined for each refined model.

Results for four trial equilibrium models are summarized in Table III. Defined by Equations (1)–(5), Model 1 corresponds to the normal behavior of 1 : 1 complexation as described earlier [17]. However, the agreement factor for this model was no better than 3 times experimental error ($\sigma = 3.24$).

Since 1 : 1 stoichiometry was exceeded (Figure 3), it was reasonable to suppose that the second crown ring in the 1 : 1 organic-phase complex CsBNO_3 or CsB^+ was able to accommodate a Cs⁺ ion to give the 2 : 1 complex species $\text{Cs}_2\text{B}(\text{NO}_3)_2$ or $\text{Cs}_2\text{B}(\text{NO}_3)^+$. Agreement was indeed found to improve when either of these species were included to give Models 2 or 3. In Model 2, including $\text{Cs}_2\text{B}(\text{NO}_3)_2$, σ decreased markedly to less than unity ($\sigma = 0.72$). The good agreement of Model 2 (dotted lines) with the data may be seen in Figures 3 and 4. On the other hand, Model 3, including $\text{Cs}_2\text{B}(\text{NO}_3)^+$ as the only 2:1 complex, was inferior to Model 2. In the region of high loading in Figure 3, the calculated values of $[\text{Cs}]_{\text{org}}$ for Model 3 fell systematically below those of the observed data. In fact, when all four species were included together in a single model, $\text{Cs}_2\text{B}(\text{NO}_3)^+$ was rejected. That is, iteratively lower and lower $\log K_{\text{ex}\pm}$ values corresponding to $\text{Cs}_2\text{B}(\text{NO}_3)^+$ were obtained, and the model essentially converged with Model 2.

Although dissociation of NO_3^- ion from $\overline{\text{Cs}_2\text{B}(\text{NO}_3)_2}$ could not be detected in the modeling, it was possible to set an upper limit for the corresponding value of $\log K_{\text{ex}\pm}(\overline{\text{Cs}_2\text{B}(\text{NO}_3)^+})$. This was accomplished by refining models consisting of all four species, where the value of $\log K_{\text{ex}\pm}(\overline{\text{Cs}_2\text{B}(\text{NO}_3)^+})$ was fixed at trial values while refining the remaining three $\log K$ values. Since $\log K_{\text{ex}\pm}(\overline{\text{Cs}_2\text{B}(\text{NO}_3)^+})$ was rejected when allowed to refine, the model was thus forced to accept the trial fixed values, resulting in fits worse than Model 2. At a $\log K_{\text{ex}\pm}(\overline{\text{Cs}_2\text{B}(\text{NO}_3)^+})$ trial fixed value of -4.0 , the worsening was not noticeable (i.e., σ remained close to 0.72), but when trial fixed values of $\log K_{\text{ex}\pm}(\overline{\text{Cs}_2\text{B}(\text{NO}_3)^+})$ were gradually increased to an upper limit of -0.4 to give Model 4 (Table III), the overall value of σ increased to 0.97, and systematic deviation of the model from the data in the low-loading region of Figure 4 exceeded 20%.

4. Discussion

Model 2 was selected as the most probable representation of the predominant equilibria. An upper limit for $\log K_{\text{ex}\pm}(\overline{\text{Cs}_2\text{B}(\text{NO}_3)^+})$ is taken as -0.4 . As shown in Table III, the species CsBNO_3 , CsB^+ , and $\overline{\text{Cs}_2\text{B}(\text{NO}_3)_2}$ may be seen to be well determined in Model 2, as shown by the relatively low standard errors of the respective $\log K$ values. The agreement factor of 0.72 indicated a fit better than the estimated experimental error, suggesting that experimental error was actually $\pm 3.6\%$ (vs. $\pm 5\%$). It may also be noted that the $\log K$ values for the 1 : 1 species are practically unaffected by the choice of 2 : 1 species in the model, increasing confidence in their precise determination.

In general, literature evidence on Cs^+ ion binding by calix[4]arene-bis-crown-6 compounds provides support for the present model involving 1 : 1 and 2 : 1 metal : ligand species [2, 8, 12–15]. Evidence for the 1 : 1 species may be cited from previous equilibrium results on calix[4]arene-bis-crown-6 compounds in solution, both homogeneous [7, 8, 12, 13] and liquid-liquid extraction [4, 15]. Crystal structures now document 1 : 1 complexes of calix[4]arene-bis-crown-6 compounds with Cs^+ ion in the solid state [12]. Evidence for the formation of 2 : 1 complexes in homogeneous solution has also been presented [8, 12, 13]. Crystal structures of 2 : 1 species have been reported [10, 13], leaving little doubt as to the reasonableness of the species $\overline{\text{Cs}_2\text{B}(\text{NO}_3)_2}$ in our extraction model, though its formation in extraction has not been reported for any calix[4]arene-bis-crown-6 compound. The ability of univalent anions to dissociate from alkali metal complexes of crown ethers in polar organic diluents, including 1,2-DCE, is well documented [17, 31, 33].

Although 1 : 2 metal : ligand complexes have been suggested with certain crown ethers [17, 31] and with bis(isopropoxy)calix[4]arene-crown-6 [15], the importance of such species in the present system seems doubtful. In general, 1 : 2 species become increasingly favored as the ionic surface of the extracted cation becomes decreasingly subtended by the ligand [31]. That is, as the number of donor atoms decreases, the tendency for 1 : 2 metal : ligand complex formation increases.

The extreme case is sandwich formation. In the present case, crystal structures of calix[4]arene-bis-crown-6 complexes with CsNO_3 show complete encapsulation of the metal ion by the arene rings and oxygen atoms of the polyether chain and nitrate [10, 13]. Even with the anion dissociated, the resulting open coordination site would be sterically crowded for approach of another bulky CABOBC6 molecule. However, if we assume that the tendency toward 1 : 2 complex formation was at most comparable to that of DB21C7 [17], then the region of data most likely to be affected would be that of high CABOBC6 concentration and low Cs^+ ion extraction so that the predominant species is $\overline{\text{CsB}^+}$, the species most likely to interact with a second ligand molecule. Only one data point in Figure 3 meets this description, and it is well predicted by Model 2. Hence, we may estimate that the equilibrium constant for the stepwise addition of the second CABOBC6 to $\overline{\text{CsB}^+}$ is at most 10 (cf., ~ 25 for DB21C7 [17]). To detect such species (if they exist), one would therefore have to raise the CABOBC6 concentration to more than 0.1 M while keeping the organic-phase CsNO_3 concentration at or below 10^{-4} M.

Although their high selectivity toward Cs^+ ion earns the calix[4]arene-crown-6 family of compounds a special status, their high strength of binding is equally remarkable. Final refined equilibrium constants for cesium nitrate extraction by CABOBC6 are summarized in Table IV together with derived constants for dissociation of the anion (Equation (5)) and for complexation in 1,2-DCE (see below). For comparison, values from some previous studies on crown ethers have been included [17, 33, 35]. Although a direct comparison with other calixarene-crown compounds in Table IV would be desirable, unfortunately no comparable extraction results have been reported for the binding of Cs^+ ion by calixarene-crown compounds in 1,2-dichloroethane. It is evident by comparing the values of $\log K_{\text{ex}}(\overline{\text{CsBNO}_3})$ and $\log K_{\text{ex}\pm}(\overline{\text{CsB}^+ + \text{NO}_3^-})$ for CABOBC6 to the corresponding values of the 21-membered crown ethers that have been studied, that the calixarene offers superior extraction strength. In the formation of ion-paired 1 : 1 complexes $\overline{\text{CsBNO}_3}$, CABOBC6 extracts CsNO_3 ca. 2.7 orders of magnitude stronger than DB21C7 and its two alkylated derivatives. It may also be noted that the value of $\log K_{\text{diss}}$ is the least negative of all the 1 : 1 nitrate complexes, reflecting the good encapsulation of the Cs^+ cation by the ligand [17]. Thus, in the formation of anion-dissociated 1 : 1 complexes $\overline{\text{CsB}^+}$, CABOBC6 extracts CsNO_3 ca. 3.8 orders of magnitude stronger than DB21C7 and its two alkylated derivatives. It is therefore an interesting fact that the relative strength of CABOBC6, and presumably other calix[4]arene-bis(crown-6) compounds, vs. crown ethers is greatly enhanced when the anion is dissociated.

Under high-loading conditions, an important feature of CABOBC6 is the apparent ability to incorporate a second cesium into the complex via the second crown ether ring. The extraction of a second CsNO_3 by $\overline{\text{CsBNO}_3}$ to give $\overline{\text{Cs}_2\text{B}(\text{NO}_3)_2}$ may be expressed as in Equation (8). From the values of $\log K_{\text{ex}}(\overline{\text{CsBNO}_3})$ and $\log K_{\text{ex}}(\overline{\text{Cs}_2\text{B}(\text{NO}_3)_2})$ for CABOBC6 in Table IV, the logarithmic form of Equa-

Table IV. Equilibrium constants for extraction of CsNO₃ by crown compounds in 1,2-dichloroethane at 25 °C.^a

Cation ^b	Anion ^c	<i>m</i>	<i>b</i>	$\log K_{\text{ex}} = \log \frac{(M_m B_b X_m)_o}{(M)_a^m (X)_a^m (B)_o^b}$	$\log K_{\text{ex}\pm} = \log \frac{(M_m B_b X_{m-1})_o (X)_o}{(M)_a^m (X)_a^m (B)_o^b}$	$\log K_{\text{diss}} = \log \frac{(M_m B_b X_{m-1})_o (X)_o}{(M_m B_b X_m)_o}$	$\log K_f = \log \frac{(M B_b)_o}{(M)_o (B)_o^b}$
Cs(DB21C7) ⁺	NO ₃ ⁻	1	1	0.12 ^d	-4.7 ^d	-4.8	8.5
Cs(B(tBB)21C7) ⁺	NO ₃ ⁻	1	1	0.15 ^d	-5.0 ^d	-5.1	8.3
Cs(B(tOB)21C7) ⁺	NO ₃ ⁻	1	1	0.05 ^d	-4.3 ^d	-4.4	8.9
Cs(DC21C7) ⁺	NO ₃ ⁻	1	1	0.57 ^d	-4.0 ^d	-4.5	9.3
Cs(DC21C7) ₂ ⁺	NO ₃ ⁻	1	2	1.6 ^d	-1.6 ^d	-3.2	11.6
Cs(DB24C8) ⁺		1	1				8.5 ^e
Cs(DB30C10) ⁺		1	1				9.4 ^e
Cs(18C6) ⁺	PiCl ₂ ⁻	1	1	6.83 ^f	3.53 ^f	-3.30 ^f	10.2 ^f
Cs(CABOBC6) ⁺	NO ₃ ⁻	1	1	2.77 ± 0.02 ^g	-0.93 ± 0.02 ^g	-3.70 ± 0.03	12.3
Cs ₂ (CABOBC6)X ⁺	NO ₃ ⁻	2	1	3.54 ± 0.04 ^g	< -0.4 ^h	< -3.9	

^aParentheses in equilibrium quotients designate activities (or molarities at infinite dilution); o and a subscripts indicate respectively organic- and aqueous-phase species, and charges have been omitted. Unless otherwise noted, the following relations were used to derive the values listed in the table: $\log K_{\text{diss}} = \log K_{\text{ex}\pm} - \log K_{\text{ex}}$; $\log K_f = \log K_{\text{ex}\pm} + \Delta G_p^\circ(\text{Cs}^+)/2.303RT + \Delta G_p^\circ(\text{X}^-)/2.303RT$, where $\Delta G_p^\circ(\text{Cs}^+)$ and $\Delta G_p^\circ(\text{X}^-)$ are the Gibbs energies of partitioning of the indicated ions between water and 1,2-DCE (TATB assumption). For Cs⁺ and NO₃⁻ ions, values of ΔG_p° were taken as 41.7 [33] and 33.9 [34] kJ/mol, respectively. The reader is reminded that $\log K_{\text{diss}}$ and $\log K_f$ refer to water-saturated 1,2-DCE. Uncertainty in the listed $\log K_f$ values is estimated to be ±0.2.

^b DB21C7 is dibenzo-21-crown-7; B(tBB)21C7 is bis(*t*-butylbenzo)-21-crown-7; B(tOB)21C7 is bis(*t*-octylbenzo)-21-crown-7; DC21C7 is dicyclohexano-21-crown-7 (mixed isomers); DB24C8 is dibenzo-24-crown-8; DB30C10 is dibenzo-30-crown-10; and 18C6 is 18-crown-6.

^c PiCl₂⁻ = dichloropicrate (3,5-dichloro-2,4,6-trinitrophenol).

^d Ref. 17.

^e Ref. 33.

^f Ref. 35.

^g Determined in this work by SXLSQI modeling, Model 2 (Table III).

^h Upper limit set in Table III, Model 4 (see text).

tion (9) gives $\log K_{\text{ex}2} = 0.73$, showing that incorporation of the second CsNO_3 is approximately 2 orders of magnitude weaker than incorporation of the first CsNO_3 by the free calixarene ($\log K_{\text{ex}} = 2.77$). With regard to the known reluctance of calix[4]arene-bis-crown-6 ethers to form 2 : 1 metal : ligand complexes [2, 4, 6–8, 12, 15], negative allosteric effects [6] and electrostatic repulsion [12, 15] have been suggested as causative factors. The high degree of preorganization of the calix[4]arene framework for Cs^+ ion binding [8, 10–13], however, would tend to argue for the latter explanation as being dominant. With this in mind, it is not unreasonable for the dissociation of nitrate from the $\overline{\text{Cs}_2\text{B}(\text{NO}_3)_2}$ complex to be more unfavorable than dissociation of nitrate from $\overline{\text{CsBNO}_3}$, since in the former we would expect the reduced compensation of the $\text{Cs}^+ - \text{Cs}^+$ repulsion upon dissociation to destabilize Cs^+ ion binding. It would follow that $\log K_{\text{diss}}(\overline{\text{Cs}_2\text{B}(\text{NO}_3)_2}) < \log K_{\text{diss}}(\overline{\text{CsBNO}_3})$; noting that $\log K_{\text{diss}} = \log K_{\text{ex}\pm} - \log K_{\text{ex}}$, we may thus write $\log K_{\text{ex}\pm}(\overline{\text{Cs}_2\text{B}(\text{NO}_3)_2}) - \log K_{\text{ex}}(\overline{\text{Cs}_2\text{B}(\text{NO}_3)_2}) < \log K_{\text{diss}}(\overline{\text{CsBNO}_3})$. Taking values of $\log K_{\text{diss}}(\overline{\text{CsBNO}_3})$ and $\log K_{\text{ex}}(\overline{\text{Cs}_2\text{B}(\text{NO}_3)_2})$ from Table IV then gives $\log K_{\text{ex}\pm}(\overline{\text{Cs}_2\text{B}(\text{NO}_3)_2}) < -0.16$, which agrees with the experimental observation $\log K_{\text{ex}\pm}(\overline{\text{Cs}_2\text{B}(\text{NO}_3)_2}) < -0.4$ (Table IV).

To aid in making comparisons, conversion of $\log K_{\text{ex}\pm}$ values to complexation constants in homogeneous 1,2-DCE solution may be made by employing Gibbs energies of partitioning of nitrate [34] and cesium [33] ions from 1,2-DCE-saturated water (given by w(DCE)) to water-saturated 1,2-DCE (given by DCE(w)): $\Delta G_{\text{p}}^{\circ}(\text{NO}_3^-)_{\text{w(DCE)} \rightarrow \text{DCE(w)}} = 33.9$ kJ/mol and $\Delta G_{\text{p}}^{\circ}(\text{Cs}^+)_{\text{w(DCE)} \rightarrow \text{DCE(w)}} = 41.7$ kJ/mol (tetraphenylarsonium tetraphenylborate (TATB) assumption). Thus, the net process



is extremely unfavorable ($\Delta G_{\text{p}}^{\circ} = 76$ kJ/mol and $\log K_{\text{ex}\pm} = -13.2$), in agreement with the observed lack of extraction of cesium nitrate by the diluent [17]. Subtraction of Equation (11) from the extraction reaction



having equilibrium constant designated $\log K_{\text{ex}\pm}(\overline{\text{MB}_b^+} + \overline{\text{X}^-})_{\text{DCE(w)}}$ gives the homogeneous organic-phase reaction



having equilibrium constant designated $\log K_f(\overline{\text{MB}_b^+})_{\text{DCE(w)}}$. It may be seen that

$$\begin{aligned} \log K_f(\overline{\text{MB}_b^+})_{\text{DCE(w)}} &= \log K_{\text{ex}\pm}(\overline{\text{MB}_b^+} + \overline{\text{X}^-})_{\text{DCE(w)}} \\ &\quad + [\Delta G_{\text{p}}^{\circ}(\text{Cs}^+)_{\text{w(DCE)} \rightarrow \text{DCE(w)}} \\ &\quad + \Delta G_{\text{p}}^{\circ}(\text{NO}_3^-)_{\text{w(DCE)} \rightarrow \text{DCE(w)}}] / 2.303RT. \end{aligned} \quad (14)$$

From Table IV, values of $\log K_f$ may be seen to be large, in line with the poor solvation of the metal ion by 1,2-DCE saturated with water. The calixarene gives the strongest binding of Cs^+ ion over the crown ethers compared in Table IV. By comparison, the next strongest crown ether, 18-crown-6, is two orders of magnitude weaker; it is actually selective for K^+ ion [36]. The weakest crown ethers listed are 21- and 24-membered benzo crown ethers, which can form cavities approximately matched in size with Cs^+ ion and which exhibit modest selectivity for Cs^+ ion [18, 19]. All of the simple crown ethers have the disadvantage of high conformational mobility and generally must undergo significant reorganization upon extraction of metal ions [31]. Indeed they typically lack a cavity in the free state, and the donor atoms are exposed to the solvent. Among the unique properties of the calix[4]arene-crown-6 compounds that have been discussed [1–15], good pre-organization of the calix[4]arene framework fixed in the 1,3-alternate conformation and weak solvation of the binding site undoubtedly contribute to the unusually high strength of Cs^+ ion binding. Selectivity and speciation of CABOBC6 in binding of Cs^+ and K^+ ions competitively by calix[4]arene-bis-*t*-octylbenzo-crown-6) in various types of solvents will be discussed in a forthcoming paper.

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References

1. R. Ungaro, A. Casnati, F. Ugozzoli, A. Pochini, J.-F. Dozol, C. Hill, and H. Rouquette: *Angew. Chem. Int. Ed. Engl.* **33**, 1506 (1994).
2. Z. Asfari, S. Wenger, and J. Vicens: *J. Inclusion Phenom.* **19**, 137 (1994).
3. C. Hill, J.-F. Dozol, V. Lamare, H. Rouquette, S. Eymard, B. Tournois, J. Vicens, Z. Asfari, C. Bressot, R. Ungaro, and A. Casnati: *J. Inclusion Phenom. Mol. Recognit. Chem.* **19**, 399 (1994).
4. C. Hill, Ph. D. Thesis, Universite Louis Pasteur de Strasbourg, 1994.
5. A. Casnati, A. Pochini, R. Ungaro, F. Ugozzoli, F. Arnaud, S. Fanni, M.-J. Schwing, R. J. M. Egberink, F. de Jong, and D. N. Reinhoudt: *J. Am. Chem. Soc.* **117**, 2767 (1995).
6. Z. Asfari, C. Bressot, J. Vicens, C. Hill, J.-F. Dozol, H. Rouquette, S. Eymard, V. Lamare, and B. Tournois: *Anal. Chem.* **67**, 3133 (1995).
7. F. Arnaud-Neu, Z. Asfari, B. Souley, and J. Vicens: *New J. Chem.* **20**, 453 (1996).
8. Z. Asfari, M. Nierlich, P. Thuery, V. Lamare, J.-F. Dozol, M. Leroy, and J. Vicens: *Anales de Quimica Int. Ed.* **92**, 260 (1996).
9. M. Lauterbach and G. Wipff: in L. Echegoyen and A. E. Kaifer (eds.), *Physical Supramolecular Chemistry*, Kluwer Academic Publishers, the Netherlands, 1996, pp. 65–102.

10. P. Thuery, M. Nierlich, C. Bressot, V. Lamare, J.-F. Dozol, Z. Asfari, and J. Vicens: *J. Inclusion Phenom.* **23**, 305 (1996).
11. P. Thuery, M. Nierlich, Z. Asfari, and J. Vicens: *J. Inclusion Phenom. Chem.* **27**, 169 (1997).
12. Z. Asfari, C. Naumann, J. Vicens, M. Nierlich, P. Thuery, C. Bressot, V. Lamare, and J.-F. Dozol: *New J. Chem.* **20**, 1183 (1996).
13. P. Thuery, M. Nierlich, J. C. Bryan, V. Lamare, J.-F. Dozol, Z. Asfari, and J. Vicens: *J. Chem. Soc., Dalton Trans.*, 4191 (1997).
14. J.-F. Dozol, V. Bohmer, A. McKervey, F. Lopez Calahorra, D. Reinhoudt, M.-J. Schwing, R. Ungaro, and G. Wipff: *New Macrocyclic Extractants for Radioactive Waste Treatment: Ionizable Crown Ethers and Functionalized Calixarenes* Report EUR-17615, European Communities, Luxembourg, (1997).
15. J.-F. Dozol, N. Simon, V. Lamare, H. Rouquette, S. Eymard, B. Tournois, D. De Marc, and R. M. Macias: *Sep. Sci. Technol.* (in press).
16. T. J. Haverlock, P. V. Bonnesen, R. A. Sachleben, and B. A. Moyer: *Radiochim. Acta.* **76**, 103 (1997).
17. Y. Deng, R. A. Sachleben, and B. A. Moyer: *J. Chem. Soc., Faraday Trans.* **91**, 4215 (1995).
18. B. A. Moyer, Y. Deng, Y. Sun, and R. A. Sachleben: *Solvent Extr. Ion Exch.* **15**, 791 (1997).
19. R. A. Sachleben, Y. Deng, D. R. Bailey, and B. A. Moyer: *Solvent Extr. Ion Exch.* **14**, 995 (1996).
20. R. A. Sachleben, Y. Deng, and B. A. Moyer: *Sep. Sci. Technol.* **32**, 275 (1997).
21. R. A. Sachleben, P. V. Bonnesen, T. Descazeaud, T. J. Haverlock, A. Urvoas, and B. A. Moyer: *Solvent Extr. Ion Exch.* (in press).
22. B. A. Moyer, P. V. Bonnesen, R. A. Sachleben, and D. J. Presley: 'Solvent and Process for Extracting Cesium from Alkaline Waste Solutions', Application to the U.S. Patent and Trademarks Office, Sept. 8, 1998.
23. A. Varnek and G. Wipff: *J. Mol. Struct. (Theochem)* **363**, 67 (1996).
24. C. F. Baes, Jr., B. A. Moyer, G. N. Case, and F. I. Case: *Sep. Sci. Technol.* **25**, 1675 (1990).
25. C. F. Baes, Jr.: *SXLSQI, A Program for Modelling Solvent Extraction Systems*, Report ORNL/TM-13604, Oak Ridge National Laboratory, Oak Ridge, Tennessee, USA, Dec. 7, 1998.
26. E. J. Henley and J. D. Seader: *Equilibrium-Stage Separation Operation in Chemical Engineering*, John Wiley & Sons, New York (1981).
27. A. F. M. Barton: *CRC Handbook of Solubility Parameters and Other Cohesion Parameters*, CRC Press, Boca Raton, Florida (1991).
28. C. F. Baes, Jr. and B. A. Moyer: *J. Phys. Chem. B.* **101**, 6566 (1997).
29. K. S. Pitzer: in K. S. Pitzer (ed.), *Activity Coefficients in Electrolyte Solutions*, Chap. 3, CRC Press, Boca Raton, Florida, 1991.
30. F. J. Millero: in R. A. Horne (ed.), *Water and Aqueous Solutions*, Wiley-Interscience, New York, 1971, pp. 519–595.
31. B. A. Moyer: in G. W. Gokel, J. L. Atwood, J. E. D. Davies, D. D. MacNicol, F. Vögtle, and J.-M. Lehn (eds.), *Molecular Recognition: Receptors for Cationic Guests*, Comprehensive Supramolecular Chemistry, Pergamon, Elsevier, Oxford, 1996, pp. 377–416.
32. K. Kina, K. Shiraishi, and N. Ishibashi: *Bunseki Kagaku* **27**, 291 (1978).
33. I. M. Kolthoff, M. K. Chantooni, and W.-J. Wang: *J. Chem. Eng. Data* **38**, 556 (1993).
34. J. Czapkiewicz and B. Czapkiewicz-Tutaj: *J. Chem. Soc., Faraday Trans. 1* **76**, 1663 (1980).
35. Z. Samec and P. Papoff: *Anal. Chem.* **62**, 1010 (1990).
36. R. M. Izatt, K. Pawlak, J. S. Bradshaw, and R. L. Bruening: *Chem. Rev.* **91**, 1721 (1991).

