Anion Partitioning and Ion-Pairing Behavior of Anions in the Extraction of Cesium Salts by 4,5″-Bis(*tert*-octylbenzo)dibenzo-24-crown-8 in 1,2-Dichloroethane

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A systematic study of anion partitioning and ion pairing was performed for an extraction of individual cesium salts into 1,2-dichloroethane (1,2-DCE) using 4,5″-bis(*tert*-octylbenzo)dibenzo-24-crown-8 as the cesium receptor. Equilibrium constants corresponding to the extraction of ion pairs and dissociated ions, formation of the 1:1 cesium/crown complex (confirmed by electrospray mass spectrometry), and dissociation of the ion pairs in water-saturated 1,2-DCE at 25 °C were obtained from equilibrium modeling using the SXLSQI program. The standard Gibbs energy of partitioning between water and water-saturated 1,2-DCE was determined for picrate, permanganate, trifluoromethanesulfonate, methanesulfonate, trifluoroacetate, and acetate anions. The dissociation of the organic-phase complex ion pair [Cs(4,4″-bis(*tert*-octylbenzo)dibenzo-24-crown-8)]$^+$NO$_3^-$ observed in the extraction experiments was shown to be consistent with the dissociation constant determined independently by conductance measurements. As attributed to the large effective radius of the complex cation, the evident anion discrimination due to ion pairing in the 1,2-DCE phase was relatively small, by comparison only a tenth of the discrimination exhibited by the anion partitioning. Only chloride and picrate exhibit evidence for significantly greater-than-expected ion-pairing tendency. These results provide insight into the inclusion properties of the clefts formed by opposing arene rings of the crown ether upon encapsulation of the Cs$^+$ ion, whose weak anion recognition likely reflects the preferential inclusion of 1,2-DCE molecules in the clefts. Observed anion extraction selectivity in this system, which may be ascribed predominantly to solvent-induced Hofmeister bias selectivity toward large charge-diffuse anions, was nearly the same whether cesium salts were extracted as dissociated ions or ion pairs.

Introduction

The science of separating inorganic salts from aqueous matrices now commonly employs host–guest chemistry, which in many respects represents a paradigm shift in the way extraction and transport phenomena are approached generally.[1–3] One may study ion complexation, extraction, and transport within the host–guest paradigm[3] by use of cation receptors,[1b,4] anion receptors,[5] dual-host combinations of cation and anion receptors,[6] and ion-pair receptors.[6,7] For any of these approaches as applied to salt extraction and

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transport, the principle of electroneutrality requires moving equivalent cationic and anionic charges across phase interfaces. Hence, to understand the driving forces and comparative driving forces (i.e., selectivity) operating in such systems, one must investigate the extraction and transport of both ions of a salt. Historically, the host−guest paradigm in extraction and transport gained momentum with the introduction of cation receptors, especially the crown ethers. Thus, the main attention has thus been logically directed toward the design of novel cation receptors and understanding their properties in liquid−liquid systems. Despite the huge volume of information so far obtained on cation extraction and transport by neutral receptors, an equivalent understanding of the role of the anion lags far behind. However, anion effects have occasionally been observed.[1,8] It has become clear, for example, that the co-extracted anion can modulate cation selectivity and can even completely change the speciation in a given system.[9] Further, the strength of extraction of a given metal cation depends strongly on the nature of the anion, in effect providing a measure of anion selectivity, a theme of growing interest to us[3] and the major thrust of this report. In this regard, salt extraction is favored by use of large charge-diffuse anions, picrate being an example that was exploited in the infancy of research on crown ethers.[4b] Understood in terms of anion solvation,[10] this effect dominates liquid−liquid distribution behavior in the majority of ion-pair extraction and anion-exchange systems.[11] The ap-

parent selectivity in favor of charge-diffuse anions has been referred to as Hofmeister bias[3,12] by reference to the early ordering of anions noted by Hofmeister[13] in experiments on salting-out phenomena. It has proven very difficult to overcome the Hofmeister bias in liquid−liquid systems,[3,11] and examples of true deviations from this expected ordering by use of hydrogen-bond-donor receptors[12c,14] and solvation effects[10a] are rare. More generally, it is possible to attenuate the steepness of the bias by use of solvation effects[11] or hydrogen-bond receptors.[12]

Coulombic interactions contribute strongly to overall anion-binding energies[15] and are often exploited in the design of anion receptors,[5,16] as seen often in ammonium-, quaternary ammonium-, and guanidinium-based receptors. It follows that Coulombic interactions in the ion pairing that occurs between the cationic metal complex and the counteranion should contribute to the efficiency and selectivity of salt extraction and transport by crown ethers and other neutral cation receptors. Although such effects have long been assumed, no systematic study of the relationship between ion pairing and anion selectivity has been made in liquid−liquid systems. Preliminary results on this question showed that the normal solvent-induced preference for perchlorate vs nitrate anion on sodium extraction by dibenzo-14-crown-6 could be maintained or overcome depending on the structure of the cation−crown ether complex.[17] A host molecule only rarely saturates the cation's inner coordination sphere, and additional interactions of the ligand-bound cation with anions or solvent molecules often take place.[18] Thus, the stereoelectronic topography of the cation−host assembly may lead to specific effects on ion pairing and thereby impact the properties of the extraction system, possibly accounting for previous observations.[8]

An opportunity to systematically address the kinship between anion selectivity and ion pairing recently has arisen in our work on cesium salt extraction by the tetrabenzo-24-

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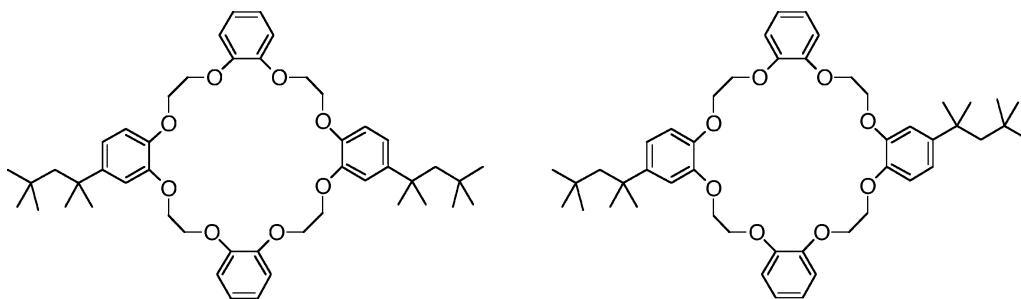
crown-8 (TB24C8) ligand and its alkyl-substituted derivatives.[19] Although it includes the guest Cs^+ ion within a boxlike cage of eight oxygen donor atoms, this host molecule still fails to completely saturate the Cs^+ inner coordination sphere, and two clefts formed by opposing pairs of benzo groups provide additional sites for auxiliary ligands. When 1,2-dichloroethane (1,2-DCE) was employed as the crystallization solvent, each cleft was found by X-ray crystallography to be occupied by a 1,2-DCE molecule coordinated to the Cs^+ ion in bidentate fashion through the chlorine atoms.[19a] It is remarkable that the nitrate counteranion is excluded from the Cs^+ coordination sphere in favor of a solvent molecule possessing only soft chlorine donor atoms. This finding was explained by the electronic complementarity between 1,2-DCE and the cleft, as the slightly electropositive hydrogen atoms of 1,2-DCE interact with the π-clouds of the opposing arene rings. Structural studies of the metal-free tetrabenzo-24-crown-8 solvated by 1,2-DCE supported this stereoelectronic complementarity.[20a] In the presence of this solvent, the ligand is forced to adopt a cagelike conformation, essentially identical to the Cs^+-binding conformation, so that the 1,2-DCE molecule resides in the cleft, forming C−H···O and C−H···π hydrogen bonds to the respective oxygen atoms and arene rings of the crown ether. In contrast, the unsolvated ligand exists in a relatively flat conformation and collapses in on itself.[19b,20b]

The present work was undertaken to systematically address the partitioning and ion-pairing behavior of a range of anions in the binding and extraction of Cs^+ion by a bisalkylated derivative of TB24C8 with enhanced solubility. It was of special interest to evaluate the potential effect of ion pairing in the organic phase on the anion selectivity. A previous study of the extraction behavior of the cesium nitrate and perchlorate by the ligands of the TB24C8 family into 1,2-DCE solvent demonstrated unusually small and nearly equal association constants for both salts in the organic phase.[19] The attenuated ion pairing and inability of the complexed cation to discriminate between these anions, despite their significant difference in size, suggested complete encapsulation of the Cs^+ ion by crown ether and 1,2-DCE molecules and exclusion of the anion from the Cs^+ inner coordination sphere. As a result, the solvent-induced anion selectivity in the liquid−liquid distribution systems remained unchanged whether the anions were ion-paired or not. This result raised the interesting question as to whether the clefts' preference for 1,2-DCE solvent molecules would persist over a wide range of inorganic and organic anions of different nature and size. The answer to this question has potentially broad

impact, since 1,2-DCE is a commonly used solvent in the areas of electrochemistry, solvent extraction, and physical solution chemistry, where it is considered as a noncoordinating solvent having weak hydrogen-bond donor and acceptor properties.[21] A means to study this effect lies in quantifying the ion-pairing equilibrium constant obtained from an equilibrium analysis of Cs^+ ion extraction employing 4,5″-bis(*tert*-octylbenzo)dibenzo-24-crown-8 host (Chart 1) in 1,2-DCE diluent. Preferential extraction and abnormally large ion pairing observed for a particular cesium salt would possibly indicate recognition of the corresponding anion by the ligand's cleft in preference to the 1,2-DCE molecule. Thorough equilibrium analysis would allow evaluation of the equilibrium constants of the extractive reactions leading to formation of the crown ether complex with cesium in the water-saturated 1,2-DCE. From the determined equilibrium constants, it would also be possible to determine the standard Gibbs energies of anion partitioning between water and water-saturated 1,2-DCE for a wide range of anions. It was also important to validate this approach by independent electrospray-ionization mass spectrometry and conductance measurements.

Experimental Section

Materials. All chemicals were used as supplied. 4,4″- and 4,5″-bis(*tert*-octylbenzo)dibenzo-24-crown-8 were prepared as described elsewhere.[19a,22] HPLC grade 1,2-DCE (Sigma-Aldrich) was purified by passage through activated alumina followed by distillation. The cesium acetate, chloride, nitrate, methanesulfonate, trifluoroacetate, and cesium permanganate (Aldrich, 99.9%) salts were dried at 110 °C for at least 48 h prior to use. The radiotracer ^{137}Cs was received as $^{137}CsCl$ in 1 M HCl (Amersham) and converted to a neutral aqueous solution of $^{137}CsNO_3$ by ion exchange, as described previously.[23] Aqueous solutions were prepared using distilled, deionized water.

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Cesium Thiocyanate Preparation. CsSCN salt was prepared by reaction between $Ba(SCN)_2$ and Cs_2CO_3 in water. $Ba(SCN)_2 \cdot 3H_2O$ (9.4 g, Aldrich) was dissolved in 50 mL of hot water and added at once to the near-boiling solution of 10.0 g of Cs_2CO_3 (Aldrich, 99.9%) in 400 mL of water under stirring. The white precipitate of $BaCO_3$ formed immediately. The suspension was cooled to room temperature and refrigerated overnight. The $BaCO_3$ precipitate was filtered out. The volume of supernatant was reduced to 50 mL, and 100 mL of isopropyl alcohol was added. The formed precipitate was filtered out. Solvent from the supernatant was removed in vacuo to give CsSCN crystalline product in 77% yield. The analysis of the product by inductively coupled argon plasma atomic emission spectrometry (ICAP-AES) and ion chromatography (IC) showed 0.09% of Ba^{2+} and $<0.05\%$ CO_3^{2-}, respectively.

Cesium Trifluoromethanesulfonate Preparation. $CsCF_3SO_3$ was prepared by the neutralization reaction between cesium hydroxide and trifluoromethanesulfonic acid. A solution of 20 mL of 50 wt % CsOH (Aldrich, 99.5%) was diluted to 100 mL with water. Neat CF_3SO_3H (Aldrich, 99 + %) was added in small portions under stirring and cooling in an ice−water bath until a pH of 5 was reached. Water was removed in vacuo. The product (in quantitative yield) was crystallized three times from 50% MeOH/water and analyzed for Cs^+ and $CF_3SO_3^-$ by IC to give 99.5% purity.

Cesium Picrate Preparation. CsPic was prepared by reaction between picric acid and Cs_2CO_3 in water. Cs_2CO_3 (9 g, Aldrich, 99.9%) was dissolved in water. Wet picric acid (21 g, Aldrich, ACS grade, contains 35% water) was added in small portions under stirring and gentle warming using hot water bath so that the pH of the reaction mixture was about 5. After the mixture cooled to room temperature, the yellow precipitate of CsPic was filtered out (*Caution: For safety reasons, it is important to keep the CsPic solid wet because it may contain picric acid.*) and washed with an excess of ethanol. CsPic was crystallized twice from water to give 14.8 g of product in 75% yield.

Liquid−Liquid Distribution Experiments. Aqueous phases contained variable concentrations of the cesium salts (CsX, where $X^- = Pic^-$, MnO_4^-, SCN^-, $CF_3SO_3^-$, $CF_3CO_2^-$, Cl^-, $CH_3SO_3^-$, or OAc^-) with a spike of ^{137}Cs tracer. The organic phases consisted of 10 mM 4,5″-bis(*tert*-octylbenzo)dibenzo-24-crown-8 in 1,2-DCE, except in the case of $CsCF_3SO_3$, wherein 1 mM crown ether was used. Equal volumes (0.5 mL each) of organic phase and aqueous phase were equilibrated in 2 mL cryogenic vials by repeated inversion on a Glass-Col laboratory rotator in a thermostated air box at 25 ± 0.2 °C for 2 h. Subsequently, the samples were centrifuged at 4000 rpm for 3 min. To determine the Cs^+ ion distribution ratio, a fraction of each phase was removed and the activity of ^{137}Cs measured by γ-radiometric techniques. Duplicate experiments were performed for every data point.

The cesium distribution from aqueous solutions to the 1,2-DCE phase was determined by γ-counting techniques (^{137}Cs tracer) using a 3″ NaI(Tl) crystal through-hole-type detector (Packard Cobra Quantum Model 5003). Cesium distribution ratios, D_{Cs}, defined as the ratio of total organic- and aqueous-phase cesium molarities, $[Cs]_{org}/[Cs]_{aq}$, were obtained directly as the ratio of background-corrected count rates per milliliter. For proper weighting of the data in SXLSQI modeling (see below), the experimental precision of D_{Cs} was estimated to be uniformly $\pm 5\%$ from a combination of replicate determinations, volumetric error, and counting precision. Because the same radiotracer concentration (i.e., spike) may be used even as the cesium concentration is varied widely, the value of D_{Cs} may be determined at the same level of precision for 8 or more orders of magnitude (i.e., $D = 10^{-4}-10^4$), limited finally by the radiometric detection limits. In control experiments, no extraction above background was observed for 1,2-DCE (without crown ether) equilibrated with aqueous CsX (where $X^- \neq Pic^-$) solutions under the experimental conditions employed. CsPic exhibited a weak extraction, giving $D_{Cs} = 1.5 \times 10^{-4}$. This value was used for the correction of the D_{Cs} value for CsPic measured in the presence of the crown ether (see below).

Conductance Experiments. Aqueous $CsNO_3$ solutions of different concentrations were equilibrated for 2 h with 10 mM 4,4″-bis(*tert*-octylbenzo)dibenzo-24-crown-8 solution in 1,2-DCE at 25 °C and a phase ratio of unity. (For reasons of compound availability, this was the only experiment that used the 4,4″ isomer of the crown ether. The isomer used, however, has no detectable effect on the ion-pairing and extraction behavior within our precision based on published equilibrium constants.[19a]) After being centrifuged at 3500 rpm for 3 min, the phases were separated, and 25 mL of the organic phase was placed in the conductance cell. Conductance measurements were performed in a conventional conductance cell with platinized electrodes of 15 mm diameter separated by a 7 mm gap. The cell was immersed in a temperature-controlled oil bath held at 25 °C. Determinations of conductance, κ, were made from 100 Hz to 300 kHz using a Wayne Kerr Multi Bridge 6425 (Wayne Kerr Electronics Ltd. West Sussex, UK). Ultimate conductance was extrapolated to infinite frequency. The cell constant was established to be 0.232 cm^{-1} from conductance measurements of potassium chloride solutions of known concentrations. The background conductance was measured to be 1.75×10^{-7} S cm^{-1} employing 10 mM 4,4″-bis(*tert*-octylbenzo)dibenzo-24-crown-8 solution in 1,2-DCE equilibrated with deionized water following the extraction protocol described above.

Positive Ion Mode Electrospray Ionization Mass Spectrometry (ES-MS). ES-MS experiments were performed on an API165 single-quadrupole mass spectrometer (MDS SCIEX, Concord, Ontario, Canada) using a TurboIonSpray source. Sample solutions were placed in plastic syringes and then continuously infused, using a syringe pump, through Telfon and PEEK transfer lines into the ion source. The transfer lines connected to a 3.5 cm long (100 μm i.d.) stainless steel capillary ES emitter electrode. The orifice (20 V) and ring electrode (200 V) in the atmospheric sampling interface were set to maximize signal and minimize fragmentation by collision-induced dissociation in this high-pressure ($\sim$1 Torr) region. The emitter electrode was held at 5.0 kV, placed 1.5 cm from the curtain gas (N_2) plate aperture (1.0 kV), and angled to spray across the aperture. Nitrogen was used for the sample nebulization. Full-scan mass spectra (m/z 100−2000) were obtained using a 0.1 m/z step size (2.5 ms dwell time). Data reported were determined from the sum of five scans.

To measure cesium ion concentration in the organic phase, extraction experiments were performed using a 1 mM solution of 4,5″-bis(*tert*-octylbenzo)dibenzo-24-crown-8 in 1,2-DCE according to the procedure described above. Aqueous phases were 10^{-5}, 3×10^{-5}, and 10^{-1} M $CsNO_3$ and 10^{-3} and 10^{-1} M CsCl. After the phases were separated, the organic phases were subjected to ES-MS analysis. To determine the cesium ion concentration in the 1,2-DCE phase, calibration standards were prepared by dissolving a measured amount of cesium tetraphenyl borate (CsTPB) salt in a 1 mM solution of 4,5″-bis(*tert*-octylbenzo)dibenzo-24-crown-8 in 1,2-DCE with subsequent dilution to obtain a series of solutions in the $3 \times 10^{-9}-3 \times 10^{-4}$ M concentration range.

Results

Liquid−Liquid Distribution Experiments. Liquid−liquid distribution experiments using 4,5″-bis(*tert*-octylben-
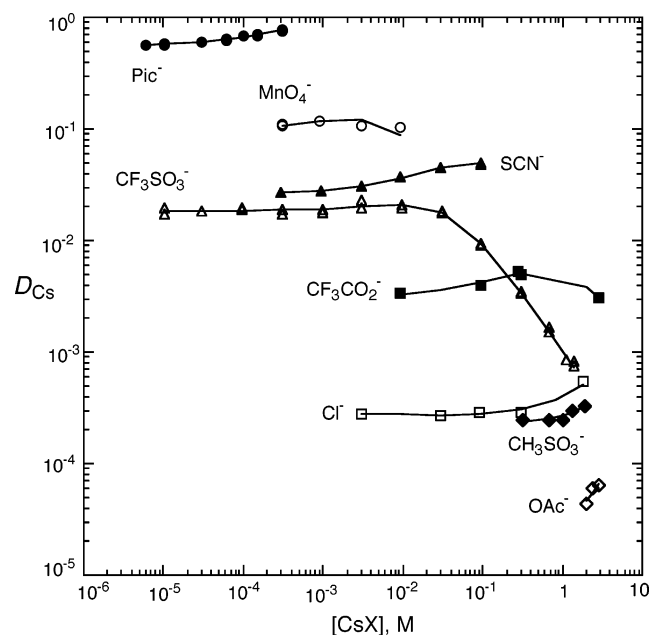
Figure 1. Comparison of calculated (solid line) and observed (symbols) cesium distribution ratios as a function of the equilibrium molarity of the specified aqueous cesium salt solution in contact with an equal volume of an organic phase consisting of 1 (for $CsCF_3SO_3^-$ only) or 10 mM (for all other salts) 4,5''-bis(*tert*-octylbenzo)dibenzo-24-crown-8 in 1,2-DCE at 25 °C. Data for nitrate and perchlorate were presented elsewhere.[19a]

zo)dibenzo-24-crown-8 to extract eight different cesium salts into 1,2-DCE were carried out to examine the anion effect on the cesium salt extraction. The Cs^+ ion distribution ratio ($D_{Cs} = [Cs]_{org}/[Cs]_{aq}$) was measured using a series of aqueous solutions with varying Cs^+ ion concentration for each cesium salt and 1,2-DCE phases containing a constant crown ether concentration of 1 or 10 mM. Observed extraction isotherms are shown in Figure 1. A detailed analysis of the shapes of the curves in similar systems as confirmed by equilibrium modeling using the SXLSQI program has been given earlier[19,23,24] and will not be repeated here. It may be seen that for each salt (except OAc^-) the value of D_{Cs} remains relatively unchanged over a range of low concentrations of Cs^+. This characteristic invariance of D_{Cs} is attributed to the extraction of cesium salts as dissociated ions. The onset of ion pairing is indicated by a rise in slope as the aqueous cesium salt concentration increases. When the crown ether extractant becomes saturated with cesium, values of D_{Cs} decrease as expected due to the decreased concentration of free crown ether. This effect was followed to complete loading in the case of $CsCF_3SO_3$, which exhibited the expected slope of -1 at the highest aqueous CsX concentration.

The cesium distribution ratios, D_{Cs}, were used as input to the solvent extraction modeling program SXLSQI[25] to obtain the equilibrium constants corresponding to the two dominant equilibrium reactions (eqs 1a and 2a in Table 1). In the fitting, nonideality effects were taken into account by use

of Pitzer parameters[26] for aqueous ions, the Hildebrand−Scott treatment[27] for non-ionic effects in the organic phase, and the Debye−Hückel treatment[26,28] for electrostatic effects in the organic phase. All constants are thus corrected to infinite dilution. The solubility parameter and molar volume of the crown ether were estimated from group contributions.[27] The program works with the experimental molarity concentration scale on input and output but converts molarity to molality internally using Masson coefficients[29] to facilitate use of the Pitzer treatment. The parameters used in the SXLSQI program are tabulated in available Supporting Information. The collected distribution data were fit assuming simultaneous formation of the CsB^+ and X^- ions and the ion-paired complexes [CsB]X in the organic phase (eqs 1a and 2a, respectively, Table 1). The logarithmic values of the corresponding extraction constants defined by eqs 1b and 2b are listed in Table 2. The extraction of CsPic was corrected for slight partitioning into 1,2-DCE described by the equilibrium reaction

$$Cs^+_{(aq)} + Pic^-_{(aq)} \rightleftharpoons Cs^+_{(org)} + Pic^-_{(org)}$$
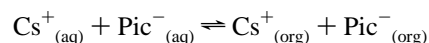
The corresponding log $K_{s\pm}$(CsPic) value was determined to be -7.7 ± 0.2. For other salts, simple ion partitioning from water into 1,2-DCE could be neglected as contributing significantly to the organic-phase concentration of cesium on the basis of the results of control distribution experiments using an organic phase containing no crown ether. Note, however, that the partitioning of the CsX salt to 1,2-DCE, though feeble, will be included necessarily in the stepwise thermochemical treatment described in the Discussion section.

From the tabulated values of log $K_{ex\pm}$ (Table 2), the homogeneous constant K_f corresponding to the formation of the complex cation [Cs(4,4''-bis(*tert*-octylbenzo)dibenzo-24-crown-8)]$^+$ (denoted as CsB^+ in the text below) in the water-saturated 1,2-DCE was derived using eq 1c. For this purpose, values of the standard Gibbs energy of anion partitioning between water and water-saturated 1,2-DCE, $\Delta G_p°(X^-)$, were taken from the literature for ClO_4^-, SCN^-, NO_3^-, and Cl^- (Table 2).[30] The value of $\Delta G°(Cs^+)$ was taken as 41.7 kJ mol^{-1} (TATB assumption) from Kolthoff et al.[31] The values of log K_f derived from the extraction constants obtained using CsSCN and CsCl salts in this work and CsClO$_4$ and CsNO$_3$ salts in our previous study[19a] (Table 2) were averaged. The averaging resulted in a log K_f value of 10.4 ± 0.1. This value was applied to eq 1c to obtain the unknown values of $\Delta G_p°(X^-)$ for the Pic$^-$, MnO$_4^-$, CF$_3$SO$_3^-$, CF$_3$CO$_2^-$, CH$_3$SO$_3^-$, and OAc$^-$ anions listed in Table 2.

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Table 1. Extractive Reactions Associated with Formation of the Organic-Phase Cesium Complex of 4,5″-Bis(*tert*-octylbenzo)dibenzo-24-crown-8[a]

extractive equilibrium process	eq no.	corresponding equilibrium constant	eq no.
$Cs^+_{(aq)} + X^-_{aq)} + B_{(org)} \rightleftharpoons CsB^+_{(org)} + X^-_{(org)}$	1a	$K_{ex\pm} = [CsB^+]_{org}^2 y_{\pm,org}^2/\{[B]_{org} y_B [Cs^+]_{aq}^2 y_{\pm,aq}^2\}$	1b
		$\log K_{ex\pm} = \log K_f - [\Delta G_p°(Cs^+) + \Delta G_p°(X^-)]/2.303RT$	1c
$Cs^+_{(aq)} + X^-_{(aq)} + B_{(org)} \rightleftharpoons CsBX_{(org)}$	2a	$K_{ex} = [CsBX]_{org} y_{CsBX}/\{[B]_{org} y_B [Cs^+]_{aq}^2 y_{\pm,aq}^2\}$	2b
		$\log K_{ex} = \log K_{ex\pm} - \Delta G_{ip}° / 2.303RT$	2c
$Cs^+_{(org)} + B_{(org)} \rightleftharpoons CsB^+_{(org)}$	3a	$K_f = [CsB^+]_{org} y_{\pm,org}/\{[B]_{org} y_B [Cs^+]_{aq} y_{\pm,aq}\}$	3b
$CsBX_{(org)} \rightleftharpoons CsB^+_{(org)} + X^-_{(org)}$	4a	$K_{diss} = [CsBX]_{org} y_{CsBX}/\{[CsB^+]_{org}[X^-]_{org} y_{\pm,org}^2\}$	4b
		$\log K_{diss} = \log K_{ex\pm} - \log K_{ex}$	4c
$X^-_{(org)} + ClO_4^-_{(aq)} \rightleftharpoons ClO_4^-_{(org)} + X^-_{(aq)}$	5a	$\log K_{exch\pm} = \log K_{ex\pm}(ClO_4^-) - \log K_{ex\pm}(X^-)$	5b
		$\log K_{exch\pm} = [\Delta G_p°(X^-) - \Delta G_p°(ClO_4^-)]/2.303RT$	5c
$CsBX_{(org)} + ClO_4^-_{(aq)} \rightleftharpoons CsBClO_{4\,(org)} + X^-_{(aq)}$	6a	$\log K_{exch} = \log K_{ex}(ClO_4^-) - \log K_{ex}(X^-)$	6b
		$\log K_{exch} = \log K_{exch\pm} + [\Delta G_{ip}°(X^-) - \Delta G_{ip}°(ClO_4^-)]/2.303RT$	6c

[a] In the chemical equilibria, B is the crown ether, X^- is an anion, and the phase is identified by subscript. Brackets in the expressions for the corresponding equilibrium constants K denote molarity, and y is the activity coefficient of the species indicated by subscript.

Conductance Experiments. The results of the conductance measurements were analyzed to determine the dissociation constant of the complex [Cs(4,4″-bis(*tert*-octylbenzo)-dibenzo-24-crown-8)]$^+$NO$_3^-$ salt in water-saturated 1,2-DCE.[32] The parameters applied in the treatment and obtained results are summarized in Table 3. The molar conductance Λ of the 1,2-DCE solutions of 4,4″-bis(*tert*-octylbenzo)-dibenzo-24-crown-8 contacted with aqueous CsNO$_3$ solutions of different concentrations was calculated from the measured background-corrected conductance, κ, of the corresponding solution. Total molar cesium concentrations, c, in 1,2-DCE were obtained by liquid−liquid distribution measurements using the ^{137}Cs tracer technique. The value of the limiting molar conductance Λ_0 of 48 ± 2 was determined from the intercept of the Fuoss and Kraus plot[32a] and used in the revised Fuoss−Onsager equation[32b] (eq 7) for an associated electrolyte for the determination of the degree of the [CsB]$^+$NO$_3^-$ ion-pair dissociation α:

$$\Lambda = \Lambda_0 - S(c\alpha)^{1/2} + Ec\alpha \log(c\alpha) +$$
$$Jc\alpha - K_a\Lambda\, c\alpha y_{\pm,org}^2 \quad (7)$$

where S, the Onsager limiting slope, and E are functions of Λ_0 and solvent dielectric constant and viscosity, which were approximated for water-saturated 1,2-DCE solvent at 25 °C as the corresponding values for pure 1,2-DCE, 10.4[33] and 0.782 mPa s,[34] respectively. The coefficient J is a function of Λ_0, solvent properties, and the ion diameter and was calculated as prescribed elsewhere.[32b] The ion diameter was set to an averaged value of the diameter of nitrate obtained from its thermochemical radius[37] and the diameter of the complexed cesium ion determined previously.[19a] The association constant K_a was calculated using eq 8 for each data point having α < 0.9:

$$K_a = (1 - \alpha) y_{CsBX}/\{c\alpha^2 y_{\pm,org}^2\} \quad (8)$$

Equation 8 was derived using $K_{diss} = 1/K_a$ and eq 4b (Table 1) taking into account that $[CsB^+]_{org} = [NO_3^-]_{org} = c\alpha$ and $[CsBNO_3]_{org} = c - c\alpha$. The mean molar activity coefficients

in 1,2-DCE were evaluated using the extended Debye−Hückel equation.[28] The activity coefficient of the associated ion pair y_{CsBX} was assumed to be unity. The value of log K_{diss} was determined to be −3.1 ± 0.2.

ES-MS Experiments. The ES-MS spectra of 1,2-DCE calibration solutions containing variable concentrations of CsTPB and a constant 1 mM concentration of 4,5″-bis(*tert*-octylbenzo)dibenzo-24-crown-8 gave a peak corresponding to the complex cation [Cs(4,5″-bis(*tert*-octylbenzo)dibenzo-24-crown-8)]$^+$ at *m/z* 901, in agreement with the predominant 1:1 complex stoichiometry found in the extraction study. An exceedingly low-abundance peak corresponding to the 1:2 complex stoichiometry, namely of [Cs(4,5″-bis(*tert*-octyl-benzo)dibenzo-24-crown-8)$_2$]$^+$, was observed for CsTPB solutions with concentration equal to or greater than 3×10^{-6} M. The peak at *m/z* 901 was used for calibration purposes. The intensity of this signal was found to be linearly dependent on the [Cs(4,5″-bis(*tert*-octylbenzo)dibenzo-24-crown-8)]$^+$ concentration in 1,2-DCE in the $3 \times 10^{-7}-3 \times 10^{-5}$ M range (Figure 2). The intensities of the peaks due to the [Cs(4,5″-bis(*tert*-octylbenzo)dibenzo-24-crown-8)]$^+$ complex cation in the organic phases equilibrated with aqueous CsNO$_3$ and CsCl solutions were plotted against their concentrations calculated using corresponding extraction constants (Table 2) employing the SXLSQI modeling program and compared with the calibration standards.

Discussion

Model. An ion-pair extraction of CsX salt from an aqueous solution into an organic phase containing a lipophilic macrocyclic neutral extractant, such as a crown ether, in 1,2-DCE or other water-immiscible diluent of moderately low dielectric constant can be treated thermodynamically in terms of three types of independent processes of interest, as depicted in Figure 3.[24,31] The stepwise equilibria consist of the partitioning of individual Cs$^+$ and X$^-$ ions between mutually saturated phases, formation of the complex cation CsB$^+$ (where B denotes a crown ether) in the organic phase,

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Table 2. Equilibrium Constants for Extractive Reactions Involving Cesium Complexes of 4,5″-Bis(t-octylbenzo)dibenzo-24-crown-8 in Water-Saturated 1,2-Dichloroethane[a]

anion	log K_{ex} = log $[(MBX)_o/(M)_a(X)_a(B)_o]$	log $K_{ex\pm}$ = log $[(MB)_o(X)_o/(M)_a(X)_a(B)_o]$	log K_{diss} = log $[(MB)_o(X)_o/(MXB)_o]$	log K_{diss}[b]	log K_f = log $[(MB)_o/(M)_o(B)_o]$	log $K_{exch\pm}$ = log $[(ClO_4)_a(X)_a/(X)_a(ClO_4)_a]$	log K_{exch} = log $[(MBClO_4)_o(X)_a/(MBX)_o(ClO_4)_a]$	σ[c]	$\Delta G°_p(X^-)$[d] lit[30]	$\Delta G°_p(X^-)$[d] this work[e]
ClO_4^-[f]	3.16 ± 0.03	0.104 ± 0.007	−3.26 ± 0.03	−3.01	10.4 ± 0.2				17.2	
Pic−	6.01 ± 0.04	2.45 ± 0.02	−3.56 ± 0.04	−2.88		−2.35 ± 0.02	−2.85 ± 0.05	1.06		3.7 ± 1.6
MnO_4^-	4.1 ± 0.2	0.96 ± 0.04	−3.1 ± 0.2	−3.02		−0.86 ± 0.04	−0.94 ± 0.2	1.45		12.2 ± 1.6
$CF_3SO_3^-$	2.4 ± 0.2	−0.50 ± 0.02	−2.9 ± 0.2	−2.93		0.60 ± 0.02	0.76 ± 0.2	1.25		20.5 ± 1.6
SCN−	1.88 ± 0.01	−1.191 ± 0.005	−3.07 ± 0.01	−3.08	10.6 ± 0.2	1.295 ± 0.009	1.28 ± 0.03	0.95	25.5	
NO_3^-[f]	0.30 ± 0.02	−2.88 ± 0.02	−3.18 ± 0.03	−3.11	10.4 ± 0.2	2.98 ± 0.02	2.86 ± 0.04		33.9	
$CF_3CO_2^-$	0.36 ± 0.03	−3.02 ± 0.02	−3.38 ± 0.04	−2.95		3.12 ± 0.02	2.80 ± 0.04	1.65		34.9 ± 1.6
Cl−[f]	−1.20 ± 0.04	−5.07 ± 0.03	−3.87 ± 0.05	−3.15	10.4 ± 0.2	5.17 ± 0.03	4.36 ± 0.05	1.12	46.4	
$CH_3SO_3^-$	−2.1 ± 0.1	−5.14 ± 0.06	−3.0 ± 0.1	−2.98		5.24 ± 0.06	5.3 ± 0.1	1.19		47.0 ± 1.6
OAc−	−3.7 ± 0.8	−7.0 ± 0.3	−3.3 ± 0.8	−3.20		7.1 ± 0.3	6.7 ± 0.8	1.90		57.6 ± 2.1

[a] Parentheses 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. Values of log K_{ex} and log $K_{ex\pm}$ were determined from the computer modeling (except for ClO_4^- and NO_3^-, which were taken from the literature as noted). Uncertainties shown are standard errors obtained directly from the fitting. Except as noted, all other log K values were derived from the determined values of log K_{ex} and log $K_{ex\pm}$, and precision error was propagated. [b] Dissociation constants of the complexes of 4,5″-bis(tert-octylbenzo)dibenzo-24-crown-8 with cesium salts were calculated using Fuoss's contact ion-pairing model[32] given by eq 2 for 1,2-DCE (ϵ = 10.4[33]). In the calculation, the cesium complex cation radius of 0.573 nm was used.[19a] The thermochemical radii for ClO_4^-, MnO_4^-, SCN−, NO_3^-, Cl−, and OAc− were taken from ref 37. The radii for Pic−, $CF_3SO_3^-$, $CF_3CO_2^-$, and $CH_3SO_3^-$ were obtained from molar volumes estimated based on the group-contribution method.[27] [c] 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 $\sigma = [\Sigma w_i(Y_i - Y_{c,i})^2/(N_o - N_p)]^{1/2}$, where Y_i is the ith experimentally observed quantity (i.e., D_{Cs}), $Y_{c,i}$ 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_o is the number of observations, and N_p is the number of adjustable parameters (i.e., log K values). 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. [d] All $\Delta G°_p(X^-)$ values are based on the tetraphenylarsonium tetraphenylborate (TATB) extrathermodynamic assumption.[37] [e] Uncertainties of the $\Delta G°_p(X^-)$ values were calculated in accord with eq 1c. The standard error for $\Delta G°_p(Cs^+)$ value was obtained from ref 31. [f] Log K values were taken from ref 19a.

and ion pairing between the organic complex cation CsB^+ and the co-extracted anion X^-. This particular scheme is convenient and instructive in that the stepwise equilibria are subject to independent observation and evaluation.

In this extraction model, formation of only the 1:1 cesium/crown ether complex was considered on the basis of our previous studies of cesium complexation by TB24C8 ligands both in solution and in the solid state.[19,20b] Other crown ethers have also been found to extract cesium salts into 1,2-DCE according to these same equilibria.[23,24] Partitioning of 4,5″-bis(tert-octylbenzo)dibenzo-24-crown-8 into the aqueous phase was neglected because of the high lipophilicity of this crown ether.[19a] For this reason, aqueous-phase complexation equilibria involving the crown ether, which have been explicitly treated by other authors,[35] could also be neglected.

A useful feature of an organic solvent of moderately low polarity like 1,2-DCE is that it tolerates the presence of both ion-paired and dissociated ions depending on the ionic strength of the organic phase. Thus, 1,2-DCE is most attractive for studying ion-pairing processes. Accordingly, fitting of experimental distribution data using the program SXLSQI provides a direct means of quantifying the simultaneous extraction of dissociated ions and ion pairs (eqs 1a and 2a) in terms of the corresponding values of log K_{ex} and log $K_{ex\pm}$ (eqs 1b and 2b). The difference of these two quantities gives the ion-pair dissociation constant log K_{diss} (eq 4c).

Under the conditions of low ionic strength in the 1,2-DCE phase, the dissociated ions CsB^+ and X^- are expected to be the predominant species, and CsX extraction (log $K_{ex\pm}$) involves only ion partitioning between water and water-saturated 1,2-DCE and the formation of the CsB^+ complex in the organic phase (eq 1c). It may be seen that the effect of the anion on the metal ion extraction by the crown ether is therefore given exclusively by the partitioning Gibbs energy term $\Delta G_p°(X^-)$. Thus, extraction efficiency will follow the well-known solvation-based Hofmeister bias favoring large charge-diffuse anions.[11]

An increase of the ionic strength in the 1,2-DCE phase leads to a condition wherein the organic-phase species are predominantly ion-paired, introducing an additional term dependent upon the nature of the anion, potentially leading to deviation from Hofmeister bias. Namely, the net extraction process (eq 2a) now also depends on the affinity between the complex cation CsB^+ and the anion as given by the ion-pairing energy term $\Delta G_{ip}°$ (eq 2c). The anion's ability to electrostatically interact with the cation primarily depends on its charge density in the order that can be described as "anti-Hofmeister," working in the opposite direction to that of anion partitioning, in effect the most hydrophobic anions being ion-paired the least. As can be rationalized simply by Fuoss's treatment,[36] the strength of this effect on anion selectivity will depend upon the radius of the cation. To

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(36) Fuoss, R. M. *J. Am. Chem. Soc.* **1958**, *80*, 5059.

Table 3. Conductance Parameters and Dissociation Constant of [Cs(4,4″-bis(*tert*-octylbenzo)dibenzo-24-crown-8)]$^+$NO$_3^-$ in Water-Saturated 1,2-DCE at 25 °C

[Cs]$_{org}$, mM^a	κ, S cm^{-1} ^{b}	Λ, S cm^{-1} mol^{-1} ^{c}	α^d	$y_{\pm,org}^e$	log K_{diss}^f
3.6	$(1.01 \pm 0.05) \times 10^{-4}$	28 ± 2	0.70 ± 0.04	0.280	-3.3 ± 0.1
1.53	$(4.6 \pm 0.2) \times 10^{-5}$	30 ± 2	0.80 ± 0.04	0.445	-3.0 ± 0.1
0.86	$(2.8 \pm 0.1) \times 10^{-5}$	33 ± 2	0.84 ± 0.04	0.536	-3.0 ± 0.1
0.43	$(1.59 \pm 0.08) \times 10^{-5}$	37 ± 2	0.91 ± 0.05	0.632	-2.8 ± 0.2
0.130	$(4.9 \pm 0.2) \times 10^{-6}$	38 ± 3	0.85 ± 0.05	0.779	-3.4 ± 0.4
0.039	$(1.9 \pm 0.2) \times 10^{-6}$	49 ± 4	0.97 ± 0.09	0.861	-3.0 ± 0.4
0.0038	$(1.8 \pm 0.2) \times 10^{-7}$	47 ± 4	0.98 ± 0.09	0.955	

^{a} Total molar cesium concentration in the 1,2-DCE phase as [CsB$^+$]$_{org}$ + [CsBNO$_3$]$_{org}$ obtained by liquid−liquid distribution measurements using the ^{137}Cs tracer technique at 25 °C and a phase ratio of unity. Aqueous phase: CsNO$_3$ of variable concentration. Organic phase: 10 mM 4,4″-bis(*tert*-octylbenzo)dibenzo-24-crown-8 in 1,2-DCE. The standard error was estimated to be ±5%. ^{b} Measured conductance of the solutions of 4,4″-bis(*tert*-octylbenzo)dibenzo-24-crown-8 in water-saturated 1,2-DCE loaded with CsNO$_3$. ^{c} The molar conductance of the corresponding 1,2-DCE solutions. ^{d} Degree of ion-pair dissociation. ^{e} The mean molar activity coefficients in 1,2-DCE estimated using the extended Debye−Hückel equation.[28] ^{f} The dissociation constant corresponds to equilibrium reaction 4a in Table 1.
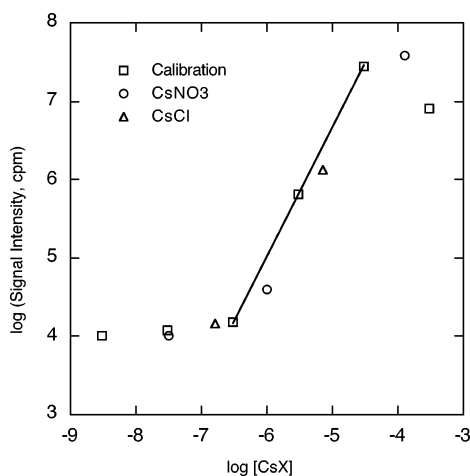

Figure 2. Dependence of the ES-MS signal intensity on the concentration of the [Cs(4,5″-bis(*tert*-octylbenzo)dibenzo-24-crown-8)]$^+$ complex cation ($m/z = 901$) in 1,2-DCE. The calibration curve was obtained using CsTPB solutions of variable concentration in 1 mM 4,5″-bis(*tert*-octylbenzo)-dibenzo-24-crown-8 in 1,2-DCE. Concentrations of CsNO$_3$ and CsCl in the extraction 1,2-DCE phase were calculated employing the SXLSQI modeling program. Extraction contacts were performed at 25 °C using an organic phase containing 1 mM crown ether in 1,2-DCE and aqueous phases containing 1×10^{-5}, 3×10^{-5}, and 1×10^{-1} M CsNO$_3$ or 1×10^{-3} and 1×10^{-1} M CsCl.
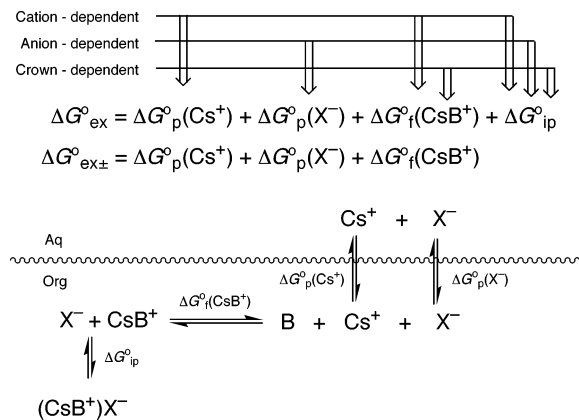

Figure 3. Stepwise equilibria in the extraction of a cesium salt by a crown ether.

illustrate the effect of cation size on the ion-pairing behavior, contact ion-pair association constants for perchlorate and chloride anions and a cation of the variable size were
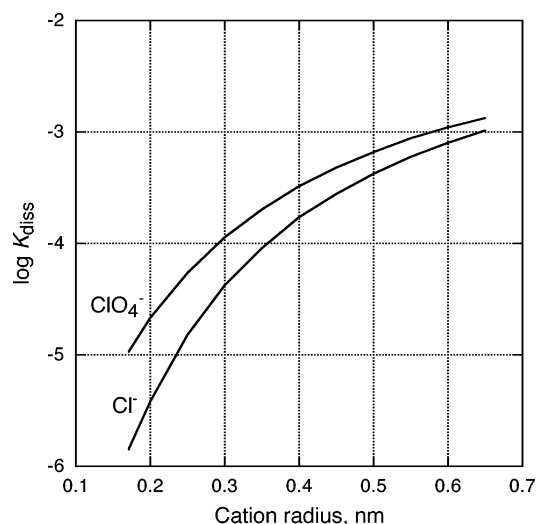

Figure 4. Dependence of the dissociation constants of hypothetical perchlorate and chloride salts on the cation radius calculated using Fuoss's contact ion-pairing model[36] for 1,2-DCE ($\epsilon = 10.4^{33}$).

estimated by Fuoss's equation:[36]

$$1/K_{diss} = K_A = 2.522a^3 \exp\left[\frac{56.05|Z_+Z_-|}{\epsilon a}\right] \qquad (9)$$

where a is the interionic distance in nm, ϵ is the relative permittivity, and Z is the ionic charge. Although a theoretical issue may be taken with the rigor of this expression, as regards the meaning of the parameter a, for instance, the simplicity of this model and the agreement in magnitude with observation (see below) nevertheless makes it useful for comparative purposes. The functional dependence of log K_{diss} on the cation radius is shown in Figure 4, where the smallest radius plotted (0.17 nm) corresponds to the size of the Cs$^+$ ion.[37] It may be observed that, as the size of the cation increases, ion pairing weakens and becomes essentially anion-independent within normal experimental error. Thus, whereas the naked Cs$^+$ cation would exhibit some anti-Hofmeister influence on anion selectivity, the inclusion of the Cs$^+$ ion by a host molecule would marginalize this influence by greatly increasing the effective cation radius. This expectation is a consequence of the ligand-thickness

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effect pointed out by Lehn.[38] In our previous study, the crystallographic radius of the complex cation [Cs(4,5′′-bis-(*tert*-octylbenzo)dibenzo-24-crown-8)·2(1,2-DCE)]$^+$ was estimated to be 0.573 nm,[19a] sufficiently large to demonstrate this effect (cf. estimated values of log K_{diss} in Table 2).

The selectivity of anion exchange may be viewed in terms of the hypothetical exchange processes given by the equilibrium reactions 5a and 6a, written for the dissociated and ion-paired ions, respectively. These equations take ClO_4^- as the reference anion, the corresponding constants log $K_{exch\pm}$ and log K_{exch} being given, respectively, by the differences log $K_{ex\pm}(ClO_4^-)$ − log $K_{ex\pm}(X^-)$ and log $K_{ex}(ClO_4^-)$ − log $K_{ex}(X^-)$ (eqs 5b and 6b). As may be seen from eq 5c, the exchange of dissociated anions depends exclusively on solvation effects and is independent of the metal ion and crown ether. Since $\Delta G_p°(X^-)$ increases as anion thermochemical radius decreases, the selectivity order correlates with anion hydrophobicity. For the ion-paired case, log K_{exch} can be expressed as log $K_{exch\pm}$ modified by the difference $\Delta G_{ip}°(X^-)$ − $\Delta G_{ip}°(ClO_4^-)$ (eq 6c). As noted above, the ion pairing tends to attenuate, normally not to reverse, the net bias favoring extraction of the large univalent anions.

Extraction Behavior. The extraction, conductance, and ES-MS results support the equilibrium model defined in Table 1 and Figure 3. Excellent agreement was observed between measured values of D_{Cs} and those calculated by the program SXLSQI, as may be seen visually in Figure 1, and the statistical agreement factors are accordingly close to unity (Table 2). In addition, the determined value of log $K_{s\pm}$-(CsPic), −7.7, is in reasonable agreement with the value −7.25 reported by Kikuchi et al.[39]

The conductance results confirm the existence of an equilibrium between free ions and their ion pairs. Independent determination of the log K_{diss} value, −3.1 ± 0.2 (Table 2), corresponding to the complex ion pair [Cs(4,4′′- bis(*tert*-octylbenzo)dibenzo-24-crown-8)]$^+$,NO_3^- via conductance measurements agrees well with the value −3.18 ± 0.03 previously obtained for the same extraction system by liquid−liquid distribution experiments.[19a] We caution that reported studies of extractions into 1,2-DCE, dichloromethane, and other diluents of moderate or moderately low dielectric constants occasionally fail to take proper account of ion-pair dissociation. Using Fuoss's equation, it may be easily shown that even chloroform, a popular diluent of low dielectric constant (4.8), will support significant ion-pair dissociation with of salts of univalent complex cations and large univalent anions (e.g., picrate). Previously reported conductance results[31] together with the present confirming results leave little doubt of the validity of the expectation of free ions in crown ether extraction systems.

Results from ES-MS experiments independently support the speciation model, indicating the formation of primarily 1:1 cesium−crown ether complexes in the 1,2-DCE phase,

as shown for the calibration with TPB$^-$ and extractions with Cl$^-$ and ClO$_4^-$. The concentration of this complex calculated using the distribution model was found to be in reasonable agreement with the ES-MS calibration curve (Figure 2). The calibration curve exhibits the typical preceding flat background region at low Cs concentration and a saturation effect at high Cs concentration.

Complex Formation. The four values of log K_f derived from the extraction constants obtained using CsSCN and CsCl salts in this work and CsClO$_4$ and CsNO$_3$ salts in our previous study (Table 2) agree, reflecting the expected independence of the complex stability constant on the nature of the counteranion. The observed value of 10.4 ± 0.1 is large, in line with the poor solvation ability of 1,2-DCE. Furthermore, as discussed previously,[19a] hosts of the TB24C8 family are among the strongest crown ether ligands for Cs$^+$ ion,[23] which is attributed in part to the relatively good preorganization of TB24C8 to bind the cesium ion. Molecular mechanics calculations previously showed that the cagelike binding conformation of TB24C8 is relatively weakly strained upon inclusion of a Cs$^+$ ion.[40] TB24C8 adopts this conformation when solvated by 1,2-DCE,[20a] suggesting that incorporation of the Cs$^+$ ion causes only minor modification of the crown ether cavity. Among simple crown ethers, which normally possess high conformational flexibility and suffer significant reorganizational strain upon complexation of metal ions, TB24C8 in 1,2-DCE represents a rare example of preorganization.

Anion Selectivity−Dissociated System. Observed values of the Cs$^+$ ion distribution ratio depend on the nature of the anion as predicted by Hofmeister bias (Figure 1). The corresponding log $K_{ex\pm}$ and log K_{ex} values obtained by SXLSQI modeling (Table 2) order the anions as follows. Pic$^-$ > MnO$_4^-$ > ClO$_4^-$ > CF$_3$SO$_3^-$ > SCN$^-$ > NO$_3^-$ > CF$_3$CO$_2^-$ > Cl$^-$ > CH$_3$SO$_3^-$ > OAc$^-$. Biased in favor of the large charge-diffuse anions, this extraction order very closely resembles the order of anion selectivity observed early in the study of crown ethers, specifically using dicyclohexano-18-crown-6 in 1,2-DCE.[8a] The efficiency of ion-pair extraction increases over a remarkably large range of anion hydrophobicity, cesium picrate being almost 10 orders of magnitude more extractable than cesium acetate.

The Hofmeister bias in this system can be quantitatively represented by plotting the obtained extraction constants log $K_{ex\pm}$ and log K_{ex} as a function of the standard Gibbs energies of anion partitioning. Equation 1c predicts a linear plot for log $K_{ex\pm}$ vs $\Delta G_p°(X^-)/2.303RT$ with a theoretical slope of −1. The obtained slope, −1.02 ± 0.03, for the four anions whose $\Delta G_p°(X^-)$ values were reported in the literature (ClO$_4^-$, SCN$^-$, NO$_3^-$, and Cl$^-$)[30] is in excellent agreement with the prediction, as can be seen in Figure 5 (solid squares). Because the literature $\Delta G_p°(X^-)$ values were obtained in extraction experiments with quaternary ammonium ions, the good agreement is mainly taken as a confirmation of the independence of the extraction constants on the nature of the cation (Figure 3).

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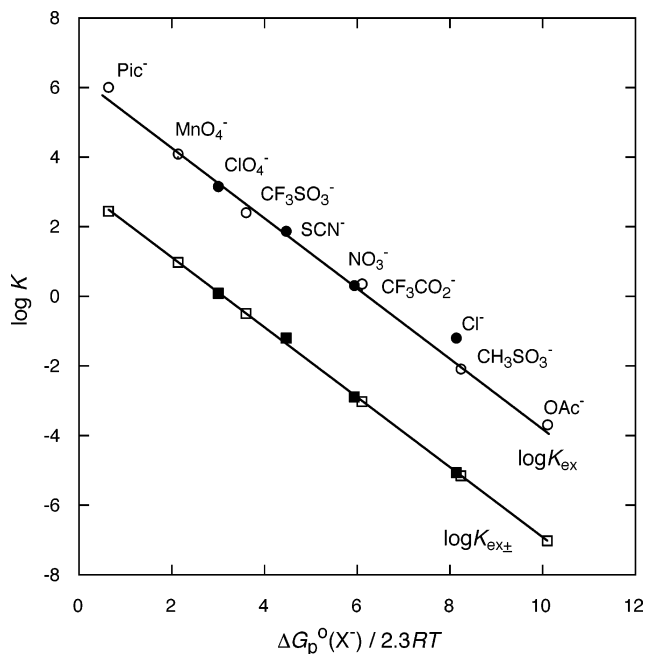
Figure 5. Dependence of the extraction constants for cesium salts on the standard Gibbs energy of anion partitioning between water and water-saturated 1,2-DCE at 25 °C. Log $K_{ex\pm}$ and log K_{ex} values are shown by squares and circles, respectively. The standard errors associated with log K values are given in Table 2. Solid and open symbols correspond to the $\Delta G_p°(X^-)$ values taken from ref 21 or determined in this work, respectively. Lines are unweighted linear least-squares fits through solid squares (slope = -1.02 ± 0.03, intercept = 3.2 ± 0.2) or through open and solid circles (slope = -0.97 ± 0.03, intercept = 6.1 ± 0.1, omitting Pic$^-$, Cl$^-$, and OAc$^-$).

Standard Gibbs Energies of Anion Partitioning. An important outcome of this work is the determination of $\Delta G_p°(X^-)$ values for the Pic$^-$, MnO$_4^-$, CF$_3$SO$_3^-$, CF$_3$CO$_2^-$, CH$_3$SO$_3^-$, and OAc$^-$ anions (Table 2). All values are positive, indicating unfavorable partitioning from water into 1,2-DCE, in agreement with the observed lack of detectable extraction of all cesium salts, except CsPic, by the diluent. The value, 3.7 ± 1.6 kJ mol^{-1}, for $\Delta G_p°(\text{Pic}^-)$ is in good agreement with the corresponding values reported in the literature: 2.2,[41] 5,[38] and 5.5 kJ mol^{-1}.[42]

Yoshida et al.[41] reported $\Delta G_p°(X^-)$ values between water and water-saturated 1,2-DCE for alkylsulfonate anions CH$_3$(CH$_2$)$_n$SO$_3^-$ (n = 5, 6, 7, or 8) determined electrochemically. These values correlated with our value of $\Delta G_p°(\text{CH}_3\text{SO}_3^-)$, as seen in Figure 6. A linear plot was obtained whose linear regression coefficients can be used for the estimation of the $\Delta G_p°\{\text{CH}_3(\text{CH}_2)_n\text{SO}_3^-\}$ values for intermediate n. The value $\Delta G_p°(\text{CH}_2)$, corresponding to the average contribution of each methylene group to partitioning is given as -3.28 ± 0.02 kJ mol^{-1}.

It may be observed for the highly hydrophilic acetate and methanesulfonate anions that substitution of the methyl by a trifluoromethyl group led to significantly increased extractability. Namely, the $\Delta G_p°(X^-)$ values decrease by 22.7 and 26.5 kJ mol^{-1}. This result is readily explained by the

increased size of the $-$CF$_3$ group together with its inductive electron-withdrawing effect, delocalizing the negative charge of the anion and reducing hydration.

Ion Pairing. Given the 10-orders-of-magnitude variation in the extractability of the univalent anions studied, ion pairing in this system evidently confers relatively minor discrimination, spanning only 1 order of magnitude. As shown in Table 2, the experimental values of log K_{diss} vary within and somewhat below the small predicted range -2.9 to -3.2. Accordingly, a linear relationship of log K_{ex} vs $\Delta G_p°(X^-)/2.303RT$ is evident in Figure 5, wherein an unweighted linear regression for all anions except Pic$^-$, Cl$^-$, and OAc$^-$ gives a slope of -0.99 ± 0.02. The two lines are thus essentially parallel, meaning that, on average, log K_{diss} is nearly constant, reflecting the expectations of the simple theory (Figure 4). Such dissociation behavior is therefore consistent with the formation of ligand-separated contact ion pairs in 1,2-DCE with large interionic distances determined mainly by the bulky cesium$-$crown complex. It may also be seen from Table 2 that the observed values of log K_{exch} and log $K_{exch\pm}$ for ion pairs and dissociated ions are nearly equal within observed standard deviations. It therefore appears likely that the previously observed supramolecular assembly with 1,2-DCE residing in the clefts[19] and an anion residing in the secondary coordination sphere of the Cs$^+$ ion tends to persist over the range of tested anions, with two possible exceptions (see below). A drawing of the tetrabenzo-24-crown-8 complex with CsNO$_3$ as taken from a crystal structure[19a] is shown in Figure 7. Recognizing that the dynamics in solution do not constrain the anion to a single position about the cation, the drawing serves as a model for how the excluded anion is limited to the secondary coordination sphere.

Given that ion pairing confers only a tenth of the magnitude of anion discrimination conferred by anion partitioning, the experimental range of log K_{diss} values (-2.9 to -3.87) and scatter about the upper line in Figure 5 still
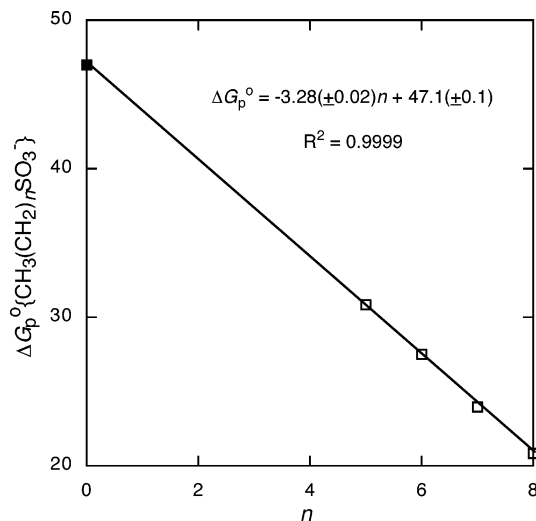

Figure 6. Dependence of the standard Gibbs energy of partitioning of alkylsulfonate anions between water and water-saturated 1,2-DCE at 25 °C. Open and solid symbols correspond to the $\Delta G_p°(X^-)$ values as taken from the literature[30] or as determined in this work (Table 2), respectively.

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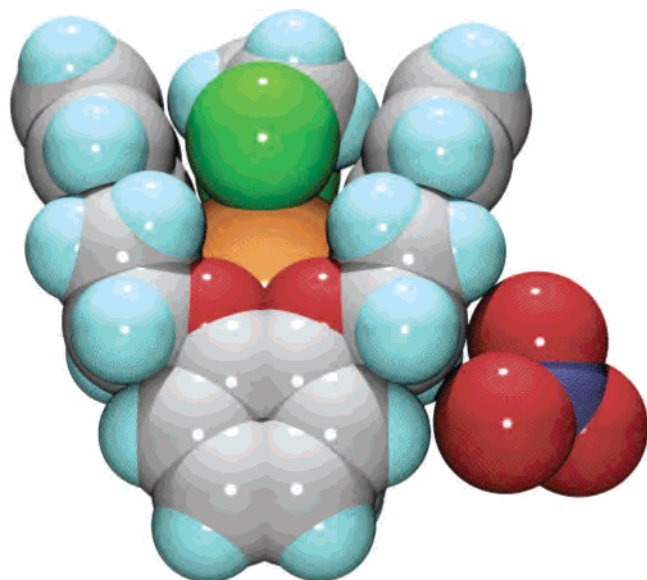(42) Wandlowski, T.; Marecek. V.; Samec, Z. *Electrochim. Acta* **1998**, *44*, 91.

Figure 7. Space-filling model of [Cs(tetrabenzo-24-crown-8)(1,2-DCE)$_2$]-(NO$_3$) as taken from ref 19a.

Table 4. Dissociation Constants of the 1:1 Cesium Complexes of Polyoxyethelene Compounds in Water-Saturated 1,2-DCE at 25 °C

salt	ligand	log K_{diss}	ref
CsPic	15-crown−5	−3.26	44
CsPic	18-crown−6	−4.09	34
		−4.81	45
		−4.15	46
CsPicCl$_2$[a]	18-crown−6	−3.3	31
CsPic	Benzo−18-crown−6	−4.30	46
CsPic	Dibenzo−18-crown−6	−4.39	47
CsPic	Dicyclohexano−18-crown−6[b]	−3.75	46
CsPic	DEO4[c]	−5.23	48
CsPic	DEO6[c]	−4.33	48
CsPic	DEO8[c]	−3.56	48
CsPic	Triton100 (EO9.6)[d]	−3.36	48
CsPic	Triton165 (EO16.8)[d]	−3.23	48
CsPic	Triton305 (EO31.0)[d]	−3.14	48
CsPic	Triton405 (EO42.8)[d]	−3.10	48
CsNO$_3$	dibenzo−21-crown−7	−4.8	48
CsNO$_3$	bis-*tert*-butylbenzo−21-crown−7	−5.1	24[b]
CsNO$_3$	bis-*tert*-octylbenzo−21-crown−7	−4.4	24[b]
CsNO$_3$	dicyclohexano−21-crown−7	−4.0	24[b]
CsNO$_3$	bis-tert-octylbenzo-crown−6-calix[4]arene	−3.70	23

[a] PicCl$_2^-$ is 3,5-dichloro-2,4,6-trinitrophenol. [b] Mixed isomers. [c] DEO$_n$ is C$_{12}$H$_{25}$(OCH$_2$CH$_2$)$_n$OH, where n = 4, 6, or 8. [d] Triton is a polydisperse polyoxyethelene alkylphenyl ether surfactant having a different average number of oxyethelene units (EOn).

indicate a degree of real discrimination. The disparate anions Pic$^-$ and Cl$^-$ stand out as having the lowest values of log K_{diss} (Table 2). Their log K_{diss} values are well determined, and both deviations are statistically significant on the basis of the Student *t*-distribution test.[43] Omitting OAc$^-$ as being too uncertain and using the seven remaining anions as a basis (ν = 7), the probabilities that Pic$^-$ and Cl$^-$ have an additional interaction are, respectively, 98.3% and 99.9%.

The exceptional nature of the anions Pic$^-$ and Cl$^-$ may also be seen by comparing the observed values of log K_{diss} with those estimated using eq 2 (see Table 2). Omitting the anions Pic$^-$ and Cl$^-$, the standard error of the deviation between the calculated and observed values of log K_{diss} is only ± 0.15, and this drops to ± 0.09 if CF$_3$CO$_2^-$ is further omitted. Thus, Pic$^-$ ($\Delta_{calc-obs}$ = 0.68) and Cl$^-$ ($\Delta_{calc-obs}$ = 0.72) clearly stand out. Possibly, CF$_3$CO$_2^-$ ($\Delta_{calc-obs}$ = 0.43) is also exceptional. Such exceptional cases could involve several possible interactions. These could include $\pi-\pi$ interactions (see below for Pic$^-$), partial insertion of the anion into the cleft, mediation of hydrogen bonds from water inserted into the cleft, or favorable C−H interactions. Further research is needed to elucidate such effects.

Examination of the various log K_{diss} values determined in this study and by others for extraction systems employing 1,2-DCE (Tables 2 and 4) provides additional insight. Most obvious is that a complex ion pair dissociates more easily as the number of donor atoms in the host molecule for the cation increases. For instance, the ion-pairing tendency of the picrate anion declines over 2 orders of magnitude as the

number of the oxyethylene units in open-chain ligands (podands) increases. This was explained by the elongation of the average interionic distance due to encapsulation of the Cs$^+$ ion by the host.[48] The explanation correlates with the present conclusion regarding encapsulation by TB24C8, and we may note that values of log K_{diss} observed in this work are relatively high and similar to those exhibited by cesium complexes of Triton podands with a large number of oxyethylene units.[48] The structure of the cesium complex with the podand DEO6 was proposed to be similar to that of cyclic 18-crown-6, which has the same number of donor atoms.[34] Both complexes exhibit similar ion-pairing constants. Another factor is associated with the nature of a substituent attached to a crown ether moiety. Within the 18-crown-6 and 21-crown-7 families, the benzo group is associated with somewhat greater ion-pairing tendency than the cyclohexano group. It is reasonable to explain the difference on the basis of the greater steric demands and electron-donating ability of the cyclohexano group.

As a final observation, ion pairing here exhibits a minor "picrate effect," which has been associated with a modification in extraction selectivity and has been attributed, based on interactions observed in the solid state,[49b] to a $\pi-\pi$ interaction between the picrate anion and arene ring of a benzocrown ether.[49] Although such an interaction between the picrate anion and the cesium complex of TB24C8 ligand certainly could account for the deviation of picrate in the present extraction system, its magnitude at best remains a perturbation on the overall solvation-based anion selectivity.

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Supporting Information Available: Table of parameters used in the SXLSQI modeling of the extraction data. This material is available free of charge via the Internet at http://pubs.acs.org.

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