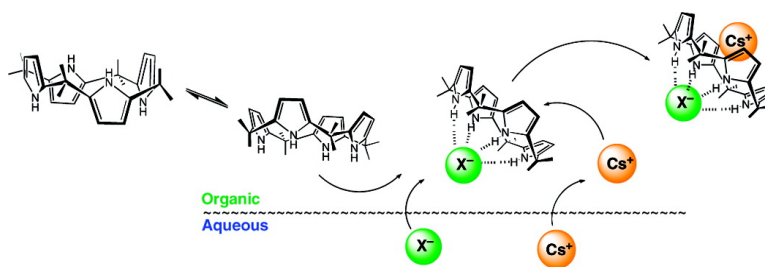


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J. Am. Chem. Soc., **2008**, 130 (12), 4129–4139 • DOI: 10.1021/ja7102179

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Calix[4]pyrrole: A New Ion-Pair Receptor As Demonstrated by Liquid–Liquid Extraction

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Abstract: Solvent-extraction studies provide confirming evidence that *meso*-octamethylcalix[4]pyrrole acts as an ion-pair receptor for cesium chloride and cesium bromide in nitrobenzene solution. The stoichiometry of the interaction under extraction conditions from water to nitrobenzene was determined from plots of the cesium distribution ratios vs cesium salt and receptor concentration, indicating the formation of an ion-paired 1:1:1 cesium:calix[4]pyrrole:halide complex. The extraction results were modeled to evaluate the equilibria inherent to the solvent-extraction system, with either chloride or bromide. The binding energy between the halide anion and the calix[4]pyrrole was found to be about 7 kJ/mol larger for cesium chloride than for the cesium bromide. The ion-pairing free energies between the calix[4]pyrrole–halide complex and the cesium cation are nearly the same within experimental uncertainty for either halide, consistent with a structural model in which the Cs⁺ cation resides in the calix bowl. These results are unexpected since nitrobenzene is a polar solvent that generally leads to dissociated complexes in the organic phase when used as a diluent in extraction studies of univalent ions. Control studies involving nitrate revealed no evidence of ion pairing for CsNO₃ under conditions identical to those where it is observed for CsCl and CsBr.

Introduction

As coordination chemistry has evolved from its traditional preoccupation with complexation of cations to a more comprehensive view that includes recognition of anions, it has become of interest to study systems that can effect the simultaneous binding of both cations and anions. This has provided an incentive to prepare and study so-called ditopic receptors, synthetic systems that for the most part incorporate individual cation- and anion-recognition sites within a single framework.¹

These multifunctional receptors are of inherent interest due to their potential ability to achieve higher levels of ion-recognition selectivity in a neutral complex that minimizes the effects of ion solvation. However, these systems are also important because they draw attention to the intriguing possibility that ion-pairing effects,² generally overlooked in the study of simple cation or anion receptors, may be playing a more important role than hitherto appreciated. Although suggested early on by Lehn,³ the importance of ion-pairing in regulating the recognition properties of synthetic receptors is underscored by the recent finding that the choice of counter cation affects the chloride anion binding behavior of two well-studied “simple” anion receptors, namely calix[4]pyrrole⁴ (*meso*-octamethylcalix[4]pyrrole; cf. Figure 1) and the open-chain heptapeptides of Gokel and co-workers.⁵ Ion-pairing effects have also been noted in solvent extraction-based separation,⁶ although not, to the best of our knowledge, where an anion-selective host is involved in a high-polarity solvent such as nitrobenzene. In this paper, we report equilibrium data confirming that calix[4]pyrrole, an easy-to-synthesize porphyrinogen analogue, acts as an ion-pair

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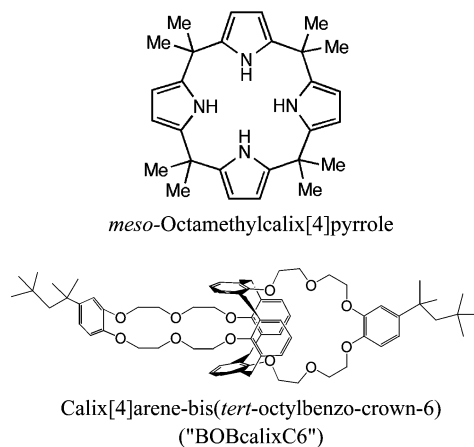


Figure 1. Compounds used in this study.

receptor for CsCl and CsBr, but not CsNO₃, under conditions of aqueous–nitrobenzene extraction.

meso-Octamethylcalix[4]pyrrole (“calix[4]pyrrole”; Figure 1) has been studied extensively in recent years as an easy-to-prepare anion receptor.^{7–11} Prompted by suggestive extraction behavior, we have recently found that this system acts as a ditopic receptor for certain salts, including CsCl and CsBr, in the solid state.⁷ Specifically, X-ray diffraction analyses of the CsCl and CsBr complexes revealed that the macrocycle adopts a cone conformation that allows for hydrogen-bonding interactions between the halide anion and the pyrrole NH protons while providing an electron-rich cavity that serves as a receptor for the cesium cation. Detailed ¹H NMR spectroscopic analyses provided qualitative support for the presence of weak, albeit significant, cesium cation receptor interactions in organic solution. These findings have led us to return to liquid–liquid extraction to determine whether calix[4]pyrrole functions as a ditopic receptor in cesium salt extraction and, if so, to quantify the equilibrium constants corresponding to the key thermochemical steps (see below).

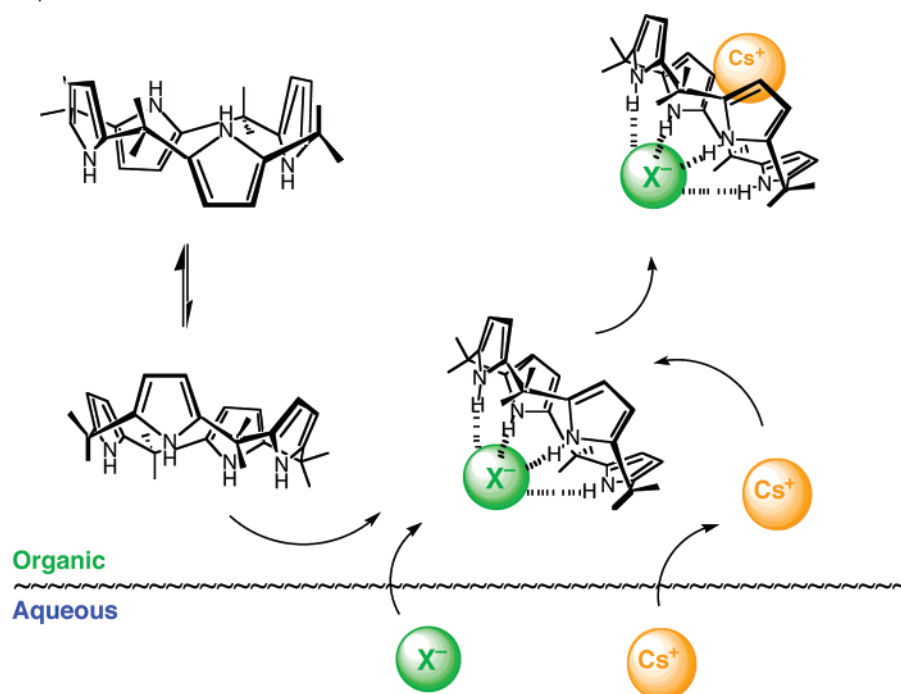
Previous experimental and computer modeling studies⁸ have been carried out on this calix[4]pyrrole system. On the basis of these studies, focused on anion recognition, we consider that a solvent-extraction process involving cesium salts, and particularly halide salts, may be described conveniently by three

thermochemical steps, as shown in Scheme 1. Each of these steps may be independently evaluated. First, the cation and anion partition from the aqueous phase into the organic phase. Second, the calix[4]pyrrole undergoes a conformational “flipping” so as to adopt the cone conformation that thereupon binds the halide. Third, the cesium cation binds within the bowl-like cavity that is created as the result of this conformational change. These steps, which could occur concurrently, are expected to allow the halide anion in question (Cl[−] or Br[−] in the present study) to be bound via pyrrole–NH hydrogen-bonding interactions and the Cs⁺ counter cation to be accommodated within the electron-rich cavity via a combination of π -cation and dipole interactions.

To test and evaluate the above model and to ascertain more generally whether calix[4]pyrrole was acting as a ditopic (i.e., ion-pair) receptor under conditions of solvent extraction, we decided to use a highly polar diluent, nitrobenzene, as the organic phase. This choice was made deliberately so as to reduce the effects of solvent-mediated receptor anion + counter cation ion-pairing, which might serve to mask the effect of concurrent anion + cation recognition and extraction. In the case of receptors that target only one ion, the nature of the complex (dissociated or ion-paired) is usually dictated by the polarity of the diluent (solvent or solvents) used to make up the organic phase. Specifically, diluents of high dielectric constant will lead, in the limit, to a fully dissociated system for univalent ions, wherein two charged entities, the receptor ion complex and the counter ion, are transferred into the organic phase as distinct species. Under conditions of low solvent polarity, however, effective ion-pairing may be encountered due to a strong electrostatic attraction between the receptor ion complex and the counter ion that is not disrupted extensively by the diluent. Thus, one of the hallmarks of an effective ditopic receptor would be an ability to extract paired cation–anion combinations into a range of organic phases, including ones of high polarity. Although a number of ditopic receptors have been reported in recent years,¹ to the best of our knowledge we are unaware of any synthetic receptor that can be used to effect ion-pair extraction of monovalent ions into highly polar organic phases, such as nitrobenzene. Nitrobenzene is a well-studied water-immiscible diluent of high net dielectric constant ($\epsilon = 34.6$) that, in our experience, stabilizes dissociated ions, including those formed from all monotopic receptor ion + counter ion combinations we have tested to date. Nonetheless, we have found that calix[4]pyrrole (cf. Figure 1) acts as an ion-pair receptor for CsCl and CsBr under conditions of aqueous–nitrobenzene extraction. Both the CsCl and CsBr extraction systems, where the ion-pairing effects were seen, were fully defined by detailed thermodynamic analyses. This has permitted quantification of all anion binding, ion-pair complexation, and extraction parameters. It has also provided insights into the structure of the receptor anion–cation complex that could not be inferred from simple correlations of receptor and salt concentration with extraction efficiency.

We also sought to find a cesium salt where the anion recognition was sufficiently weak that the calix[4]pyrrole would not adopt the cone conformation required for cesium cation complexation. Under these latter conditions, it was expected that calix[4]pyrrole would either show no effect on the extraction process or, at best, display behavior consistent with that of a monotopic anion receptor. Since both of these control scenarios

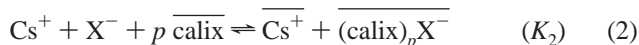
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Scheme 1. Proposed Steps in Cesium Salt Extraction

would give rise to extraction behavior characteristic of a fully dissociated extraction system, namely an independence of the extraction efficiency on salt concentration, they would stand in marked contrast to the case where calix[4]pyrrole is acting as a bona fide ditopic receptor. As detailed below, we found that CsNO₃ serves as the requisite control system when nitrobenzene is used as the diluent; in the presence of calix[4]pyrrole, this salt exhibits a complete independence of the extraction efficiency on the salt concentration. In contrast, the complexes of CsCl and CsBr were fully ion-paired in nitrobenzene, as demonstrated by the linear dependence of the extraction efficiency on both the salt and the calix[4]pyrrole concentrations.

Results and Discussion

Equilibrium Analysis. In the case of calix[4]pyrrole, two kinds of organic-phase complexes can be expected, depending on the extent of ion-pairing, according to the following two equilibria:



where X[−] = Cl[−], Br[−], or NO₃[−], calix represents the calix[4]pyrrole, and *p* represents the binding stoichiometry. Over bars indicate that species are present in the organic phase. In general, these complexes and the associated equilibria would be expected to reflect the nature of the counteranion and the polarity of the diluent, as noted above.

The first equilibrium (eq 1) corresponds to an extraction through ion-pairing, whereas the second equilibrium (eq 2) reflects an extraction via a dissociated system with the calix[4]pyrrole acting as the anion receptor. On the basis of previous findings,¹¹ a system controlled by eq 2 is expected for univalent ions when using a polar diluent, such as nitrobenzene.

Considering the associated system (eq 1) and assuming no other extracted form of Cs⁺, [Cs⁺]_{org} is equivalent to [Cs(X)(calix)_{*p*}]_{org}. Defining $D_{\text{Cs}} = [\text{Cs}^+]_{\text{org}}/[\text{Cs}^+]_{\text{aq}} = [\text{Cs(X)(calix)}_p]_{\text{org}}/[\text{Cs}^+]_{\text{aq}}$ and substituting into the standard expression for the extraction constant for eq 1, one obtains, upon rearrangement,

$$D_{\text{Cs}} = K_1 [\text{X}^-] \frac{\overline{[\text{calix}]^p}}{\gamma_{\text{Cs(X)(calix)}}} \quad (3)$$

For this purpose, the activity coefficients γ_{calix} and $\gamma_{\text{Cs(X)(calix)}}$ are assumed to be close to unity, a reasonable assumption considering the low calix[4]pyrrole concentration in the organic phase. Furthermore, if CsX is assumed to be the only electrolyte in the system, the following expression can be obtained:

$$\log(D_{\text{Cs}}) = \log(K_1) + \log(\gamma_{\text{Cs}}^2 [\text{Cs}^+] + p \log([\text{calix}]) + \log\left(\frac{\gamma_{\text{calix}}^p}{\gamma_{\text{Cs(X)(calix)}}}\right) \quad (4)$$

Slope analysis of plots of D_{Cs} vs [calix] (commonly in log–log scale) would allow determination of the calix[4]pyrrole stoichiometry (eqs 1 and 4). In addition, a plot of $\log(D_{\text{Cs}}/\gamma_{\text{Cs}})$ versus $\log(\gamma_{\text{Cs}}[\text{Cs}^+])$ according to eq 4 would show a slope of 1 in the case of extraction via an ion-pair mechanism.

If the extraction produces a dissociated system as defined by eq 2, assuming the electroneutrality of the organic phase and an appreciable concentration in this phase of only Cs⁺_(org) and (calix)_{*p*}X[−]_(org) as product species permits the following rearrangement of the standard extraction constant expression:

$$K_2 = D_{\text{Cs}} \frac{\overline{\gamma_{\text{Cs}}^{\text{org}} \gamma_{\text{X}}^{\text{org}} [\text{Cs}^+]}}{\gamma_{\text{Cs}}^{\text{aq}} \gamma_{\text{X}}^{\text{aq}} [\text{X}^-] [\text{calix}]^p} \quad (5)$$

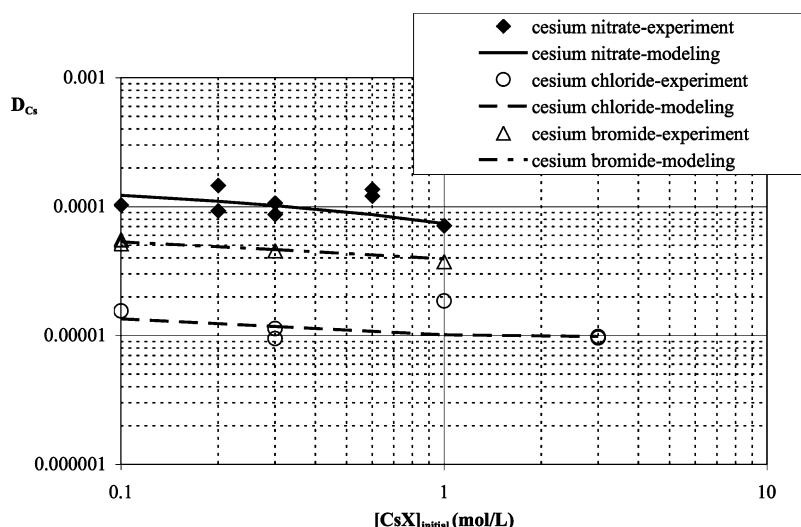


Figure 2. Extraction of cesium nitrate, cesium chloride, and cesium bromide by nitrobenzene. Experimental findings and modeling results. Organic (O) phase: nitrobenzene. Aqueous (A) phase: variable cesium nitrate, chloride, or bromide concentrations. O/A = 1; $T = 25$ °C.

Applying the concept of electroneutrality to the aqueous phase and assuming that the activity coefficients are close to unity, this equation becomes

$$K_2 = \frac{D_{\text{Cs}}^2}{[\text{calix}]^p} \Rightarrow \log(D_{\text{Cs}}) = \frac{1}{2}(\log(K_2) + p \log[\text{calix}]) \quad (6)$$

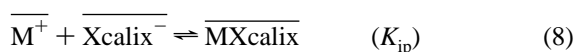
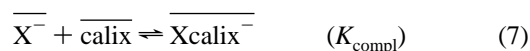
In the case of extraction as a dissociated system, eq 6 shows that the value of D_{Cs} is completely independent of the variable $[\text{Cs}^+]_{\text{aq}}$ when activity coefficients approach unity.

In summary, a simple slope analysis of various graphs permits one to obtain considerable insight into the system in question. For instance, given constant activity coefficients:

- A plot of $\log(D_{\text{Cs}})$ versus $\log([\text{CsX}])$ will generally give a straight line, the slope of which will allow one to determine the nature of the extraction process (i.e., slope = 1 and 0 for ion-pairing and dissociation, respectively).

- A plot of $\log(D_{\text{Cs}})$ versus $\log([\text{calix}])$ will give a straight line with a slope of p or $p/2$ for ion-pairing and dissociation processes, respectively, where p corresponds to the stoichiometric coefficient for the calix[4]pyrrole involved in the extraction system equilibrium.

Once the stoichiometry of extraction is determined through slope analysis, the associated thermodynamic values can be derived by modeling the cesium extraction process according to the equations presented above. Of particular interest are the equilibrium constants corresponding to halide anion complexation and ion-pairing with cesium. These values, referred to as K_{compl} and K_{ip} , respectively, are defined as follows:



A primary goal of this study was to determine both of these values for calix[4]pyrrole under a set of well-defined conditions. In point of fact, ion-pairing in the case of CsCl and CsBr proved so strong that K_{compl} could only be determined through indirect means, as discussed below.

Extraction by Nitrobenzene Alone. To determine the “background” due to the cesium salt partitioning between the aqueous phase and nitrobenzene, a series of control experiments was carried out; these involved separate extractions of cesium nitrate, cesium chloride, and cesium bromide using nitrobenzene in the absence of any added extractant. Figure 2 shows that, as expected for this polar diluent, nitrobenzene extracts cesium salts as dissociated ions (near independence of D_{Cs} on aqueous salt concentrations). Cesium distribution ratios also are very low, but this is expected and in agreement with the high free energies of partitioning for these ions (see Supporting Information, Table S1).

Extraction of Cesium Nitrate and Cesium Halide by Calix-[4]pyrrole in Nitrobenzene. 1. Cesium Nitrate. As explained in the Experimental Section (Supporting Information), a simple slope analysis allows the nature of the extraction system (dissociated ions vs ion-pairs) and its stoichiometry to be determined. The variation of the ratio D_{Cs} versus the cesium nitrate concentration in the aqueous phase (Figure 3) revealed that the ratio is essentially independent of the cesium nitrate concentration. (Note: The low values of D_{Cs} and the small amount of cesium transferred into the organic phase allow the cesium concentration in the aqueous phase at equilibrium to be approximated by the initial cesium nitrate concentration.) This independence is consistent with an extraction system that is dissociated according to eq 6. Considering the same equation and plotting $\log(D_{\text{Cs}})$ versus $\log[\text{calix[4]pyrrole}]$ gives a straight line, the slope of which is $p/2$, where p is the stoichiometric coefficient corresponding to the equilibrium of eq 2. The resulting plot is shown in Figure 4; since a slope of $1/2$ is seen, it is concluded that only one molecule of calix[4]pyrrole is involved per nitrate anion in the complex. This stoichiometry and the dissociated nature of the system meet the original assumptions and expectations for CsNO_3 , namely that with this salt, the calix[4]pyrrole does not act as an ion-pair receptor. This is not surprising since there is no evidence that nitrate anion binds strongly to the calix[4]pyrrole in organic media⁹ or can help organize it in the cone-like conformation that would favor Cs^+ binding.

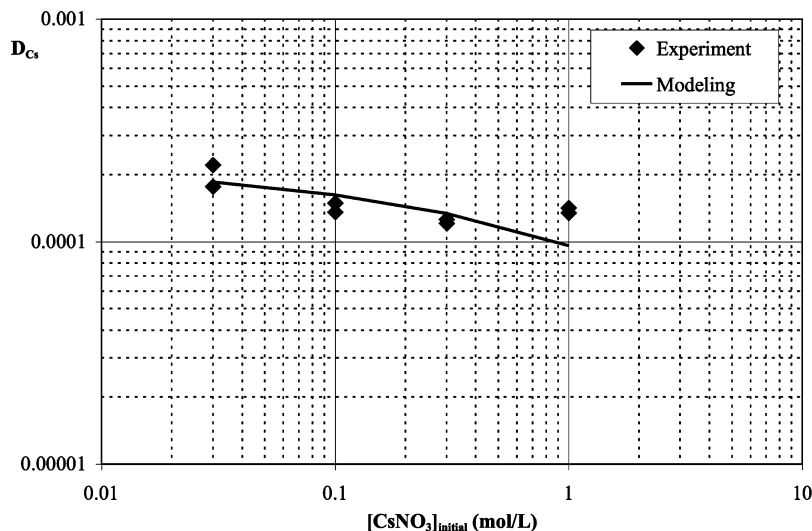


Figure 3. Extraction of cesium nitrate by calix[4]pyrrole. Experimental findings and modeling results. Organic phase: [calix[4]pyrrole] = 25 mM in nitrobenzene. Aqueous phase: variable cesium chloride concentrations. O/A = 1, $T = 25\text{ }^{\circ}\text{C}$.

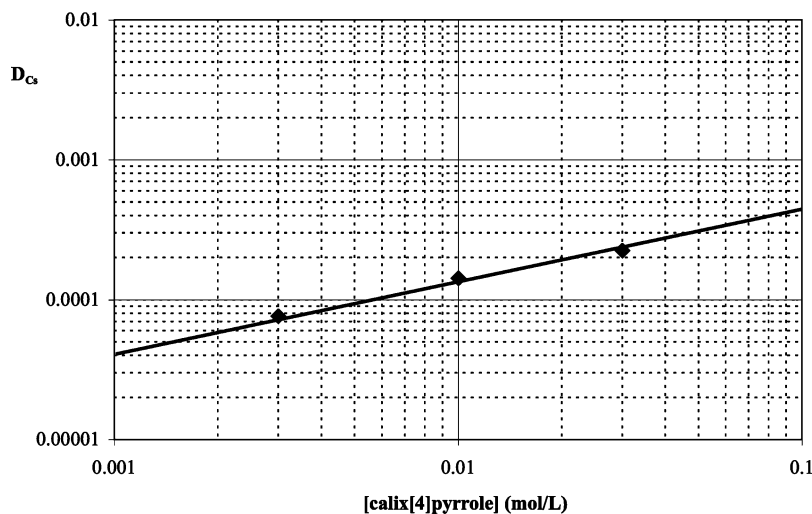


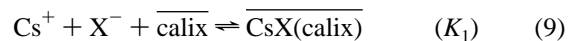
Figure 4. Extraction of cesium nitrate by calix[4]pyrrole. Organic phase: variable calix[4]pyrrole concentrations in nitrobenzene. Aqueous phase: $[\text{CsNO}_3] = 0.6\text{ M}$. O/A = 1, $T = 25\text{ }^{\circ}\text{C}$.

2. Cesium Halides. Experiments identical to those described above were run in the case of cesium chloride and cesium bromide. Again, D_{Cs} was plotted as a function of the cesium halide concentration in the aqueous phase, as well as against the concentration of calix[4]pyrrole in the organic phase.

The resulting slope analyses, shown in Figure 5, reveal that the cesium distribution ratios are dependent on the cesium halide concentration. Moreover, the slopes of these plots are close to one, especially at $[\text{CsX}] \geq 0.1\text{ M}$. Such a finding is thus fully consistent with the existence of an ion-pair complex between the calix[4]pyrrole and these two sets of salts.

However, before drawing definitive conclusions about the slopes in these plots, it is important to take into account the relevant activity coefficients. This was specifically done in the case of cesium bromide, as shown in Figure 6. Here, the cesium distribution ratio D_{Cs} is plotted versus the initial concentrations of cesium bromide in the aqueous phase, as well as versus the corresponding activities for comparison. The activity coefficients were calculated (see Supporting Information) using the specific ion interaction theory (SIT) or “extended Debye–Hückel theory”.¹²

The use of activity corrections in the chloride or bromide systems led to a significant difference in the overall shape of the curve. Subject to their use, the dependence of D_{Cs} on the salt concentration clearly exhibits a slope of one, providing strong evidence for the existence of an ion-pair interaction between the cesium cation and the anion/calix[4]pyrrole complex. Further support for this conclusion came from an experiment where the salt concentration was kept constant while the concentration of calix[4]pyrrole was allowed to vary. Figure 7 shows that plots of D_{Cs} vs concentration produced in this way also have a slope of one. On the basis of this slope analysis, we conclude that a 1:1:1 ion-pair of cesium:halide:calix[4]pyrrole is formed in the nitrobenzene phase (eq 9). This stoichiometry is consistent with the previous crystallographic results.⁷



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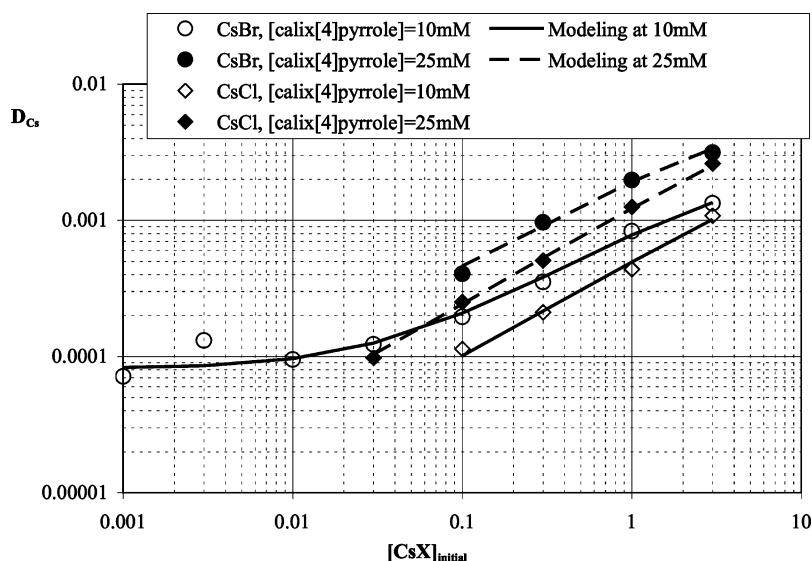


Figure 5. Extraction of cesium chloride or bromide by calix[4]pyrrole. Experimental findings and modeling results. Organic phase: [calix[4]pyrrole] = 10 or 25 mM in nitrobenzene. Aqueous phase: variable cesium chloride or cesium bromide concentrations. O/A = 1, $T = 25\text{ }^{\circ}\text{C}$.

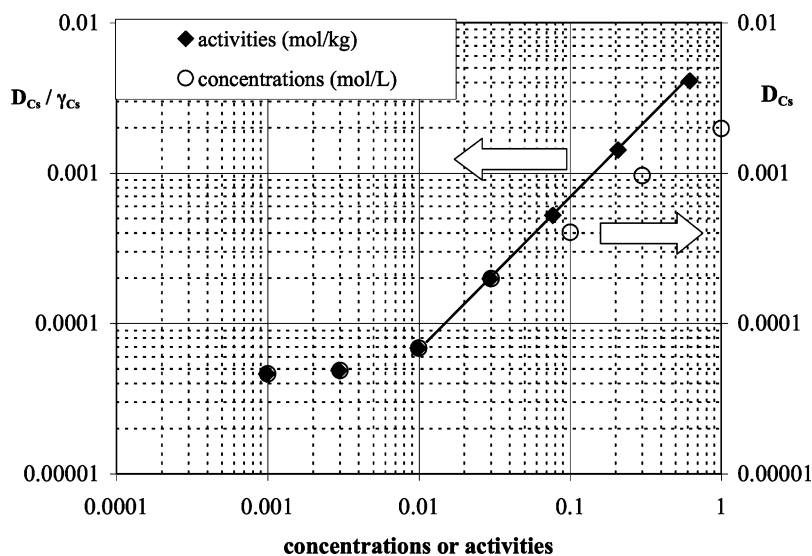


Figure 6. Extraction of cesium bromide by calix[4]pyrrole in nitrobenzene. Change in curve shape upon applying activity corrections. Organic phase: [calix[4]pyrrole] = 25 mM in nitrobenzene. Aqueous phase: variable cesium bromide concentrations. O/A = 1, $T = 25\text{ }^{\circ}\text{C}$.

Determination of the Thermodynamic Constants Governing the Dissociated System. While the slope analyses described above serve to define the stoichiometry of the extraction process in well-behaved systems, such as those comprised of calix[4]pyrrole and the three cesium salts considered in the present study, it is important to appreciate that they do not serve to define the thermodynamics of either the overall process or the individual binding events. Given the unusual nature of the ion-pairing observed in the case of CsCl and CsBr, and the paucity of systems that have been subject to this level of detailed analysis, it became of interest to map out the thermodynamics of binding in the case of these latter two salts.

In accord with Scheme 1, and appreciating the additive nature of the interactions involved, we thought it would prove easiest to calculate the equilibrium constant corresponding to formation of the ion-paired complex in nitrobenzene using a stepwise approach. With such considerations in mind, the plan was to determine first the formation constants corresponding to the complexation of the dissociated halide anion and the calix[4]-

pyrrole receptor in the organic phase. Following this, we would then derive those for the binding of the cesium cation to the negatively charged calix[4]pyrrole–halide anion complexes produced as the result of this first recognition process. In principle, the first of these stepwise contributions to the overall energetics associated with formation of the ion-pair complex could be determined at vanishingly low concentrations of cesium halide, since in this limit the salts in question would tend to exist as fully dissociated species in the organic phase. Unfortunately, conditions could not be found where this requirement is met. Specifically, it proved impossible to reduce the concentration of free cesium cation in the organic phase to a level low enough to preclude cation binding while concurrently providing anion concentrations sufficiently high to allow the desired calix[4]pyrrole–anion complexation equilibria to be measured accurately via direct means (including through data modeling). This is not surprising, given the very low D_{Cs} values that govern the CsCl and CsBr + calix[4]pyrrole aqueous–nitrobenzene extraction system.

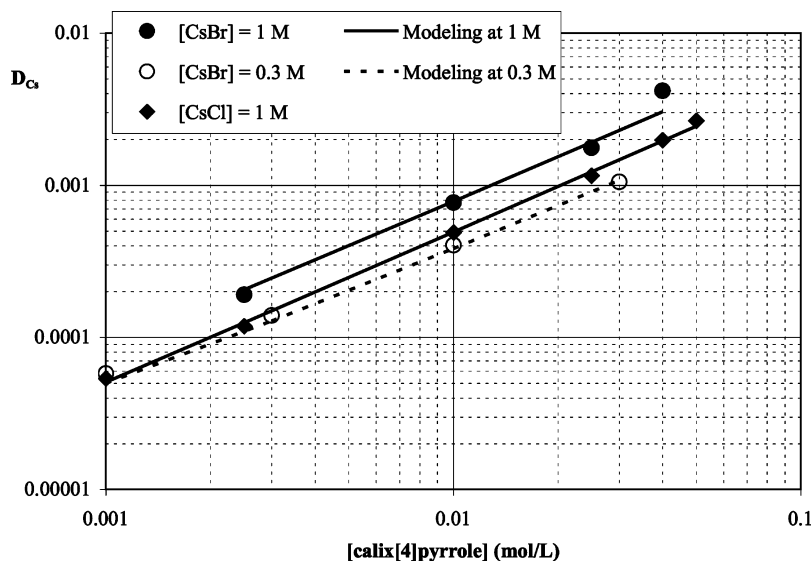


Figure 7. Extraction of cesium chloride or bromide by calix[4]pyrrole. Experimental findings and modeling results. Organic phase: variable calix[4]pyrrole concentrations in nitrobenzene. Aqueous phase: [CsCl] = 1 M, [CsBr] = 0.3 or 1 M. O/A = 1, $T = 25\text{ }^{\circ}\text{C}$.

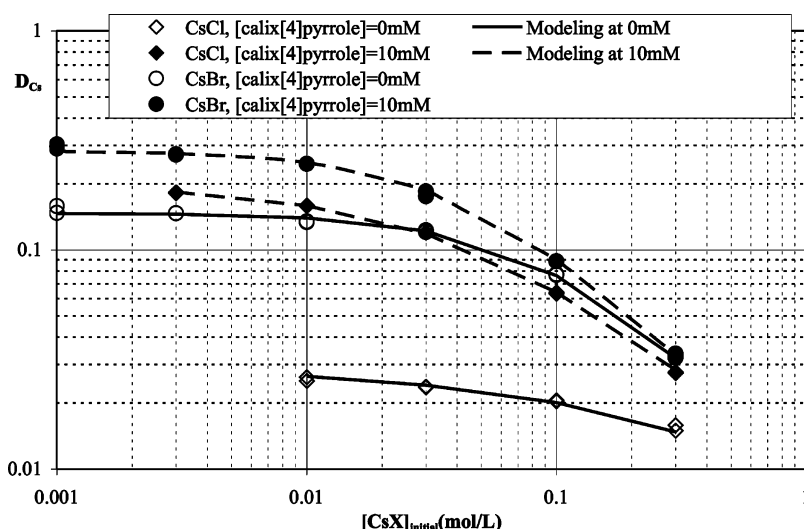


Figure 8. Extraction of cesium chloride or bromide by BOBcalixC6 and calix[4]pyrrole. Experimental findings and modeling results. Organic phase: [BOBcalixC6] = 10 mM, [calix[4]pyrrole] = 0 or 10 mM in nitrobenzene. Aqueous phase: variable cesium chloride or cesium bromide concentrations. O/A = 1; $T = 25\text{ }^{\circ}\text{C}$.

Given this challenge, an alternative approach was employed. It relies on the use of a cesium ligand to prevent ion-pairing and thereby increase the D_{Cs} values. This approach, which proved successful (vide infra), is predicated on the recognition that a strong cation receptor would act to complex the cesium in the organic phase and thus suppress ion-pairing over a wide range of salt concentrations. In our experience, one of the best receptors for the cesium cation in solvent extraction is the crown-strapped calixarene known as BOBcalixC6 (Figure 1).¹³

Figure 8 shows the results of these experiments in the case of cesium chloride and cesium bromide. As expected for a dissociated system, at low concentrations, the D_{Cs} values recorded in the presence of BOBcalixC6 were found to be independent of the salt concentration; this was true both in the

presence and in the absence of calix[4]pyrrole. Analysis of the data is described in the next section.

At higher concentrations, the cesium distribution ratio may be seen to decrease. The expected reason for the decrease is that, at high concentrations, the concentration of the cesium salt in the organic phase can exceed that of the initial calix[4]pyrrole extractant, making it and BOBcalixC6 unavailable for further extraction. The organic phase becomes saturated or “loaded” with cesium, which would give rise to a decrease in the D_{Cs} value, as seen by experiment (cf. Figure 8) and confirmed by equilibrium modeling (vide infra). Nevertheless, there remains a concern that, at higher concentrations, potential interactions between the free BOBcalixC6 and calix[4]pyrrole would be favored. In order to determine whether the interactions between BOBcalixC6 and calix[4]pyrrole were appreciable, a solution containing 10 mM of both receptors was made up in deuterated nitrobenzene. The use of deuterated nitrobenzene allowed the ^1H NMR spectrum to be recorded. It was found that the spectrum of the mixture was a perfect superposition of the

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Table 1. Comparison between the Partitioning Constants from the Literature and from the Computer Modeling for Cesium Nitrate, Cesium Chloride, and Cesium Bromide

system	$\Delta G_{\text{part}}^{\text{w-nitro}}$ (kJ mol ⁻¹) ^a	log $K_{s\pm}$ ^a	$\Delta G_{\text{part}}^{\text{w-nitro}}$ (kJ mol ⁻¹) ^b	log $K_{s\pm}$ ^b
CsNO ₃ /NB	42	-7.36	43.2 ± 0.4	-7.56 ± 0.07
CsCl/NB	53	-9.28	54.2 ± 0.5	-9.50 ± 0.09
CsBr/NB	47	-8.23	47.4 ± 0.1	-8.30 ± 0.02

^a Marcus, Y. *Ion properties*; Marcel Dekker: New York, 1997. ^b This work. NB = nitrobenzene.

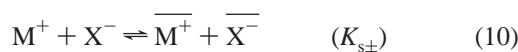
Table 2. Equilibrium Constant K_1 As Derived from the Model^a

system	log K_1
CsCl/calix[4]pyrrole	-0.80 ± 0.01
CsBr/calix[4]pyrrole	-0.58 ± 0.02

^a Data points used in the model are shown in Figures 5 and 7.

spectra for the individual components. This provides support for the notions that the interactions between BOBcalixC6 and calix[4]pyrrole in this solvent are not appreciable and that BOBcalixC6 could be used to prevent the cesium cation from binding to the calix[4]pyrrole-anion complex.

Modeling and Thermodynamic Data Sets. Data analysis and equilibrium-constant determinations were performed using the SXLSQI computer program.¹⁴ Parameters used in the modeling program to account for nonideality and volume effects are presented in Tables S4–S6. Computer modeling was performed in three stages. In the first stage, the extractions of cesium salts by nitrobenzene only were analyzed, with the goal of determining the partitioning constants and the free energies of transfer of the various salts between the aqueous phase and the organic nitrobenzene phase as shown below:



The values found experimentally were then compared to those available in the literature. Figure 2 shows the best fits obtained for the three cesium salts considered in this study. It reveals an approximate independence of the D_{Cs} value from the salt concentrations in the absence of calix[4]pyrrole and is thus consistent with the proposal that extractions occurring under these conditions involve fully dissociated species. The slight variation of D_{Cs} seen in the plots is quantitatively explained by activity effects. Likewise, the values in Table 1 serve to highlight the remarkable consistency between the partitioning constants from the literature and the refined fitting parameters calculated via the present computer modeling.

The second stage of the analysis was aimed at modeling the cesium distribution ratios produced by calix[4]pyrrole alone over the concentration regime where ion-pairing is prevalent, with the goal of calculating log K_1 (see eq 3). The modeling of the cesium chloride and the cesium bromide data is shown in Figures 7 and 8, which correspond to studies where the ligand and salt concentrations were varied, respectively. All plots demonstrate the excellent agreement between the observed and calculated data points. The refined formation constants obtained from the model, including K_1 , are given in Table 2.

Table 3. Equilibrium Constants K_3 and K_4 Obtained from the Model for the System Cs⁺–BOBcalix/X⁻–Calix[4]pyrrole and K_{compl} and K_2 Calculated from These Values^a

X ⁻	log K_3	log K_4	log K_{compl}	log K_2
Cl ⁻	-1.05 ± 0.01	2.61 ± 0.01	3.66 ± 0.02	-5.84 ± 0.11
Br ⁻	0.33 ± 0.01	2.76 ± 0.02	2.43 ± 0.03	-5.87 ± 0.05

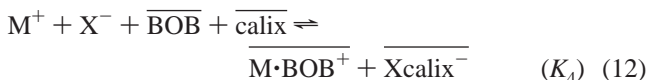
^a Data points used in the model are shown in Figure 8.

Table 4. Complexation Constant K_5 and K_{BOB} between BOBcalixC6 and Cesium Obtained from the Model and the Calculations, Respectively, for the CsCl and CsBr Salts^a

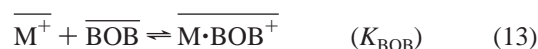
system	log K_{BOB}
Cs ⁺ –BOBcalix from Cl ⁻	8.23 ± 0.01
Cs ⁺ –BOBcalix from Br ⁻	8.57 ± 0.01

^a Data points used in the model are shown in Figure 8.

The last stage of the computer modeling involved calculating the formation constants, K_2 , according to eq 4. Here, as noted above, the use of BOBcalixC6 allows this key thermodynamic parameter to be derived in an indirect manner. According to the two equilibria of eqs 11 and 12, the constant K_2 may be determined from the ratio $K_4 K_{s\pm} / K_3$; this is because eq 4 is equivalent to eq 12 – eq 11 + eq 10; again, this assumes there are no interactions between BOBcalixC6 and calix[4]pyrrole and that BOBcalixC6 binds Cs⁺ much more strongly than calix[4]pyrrole.



The results obtained when BOBcalixC6 is used are shown in Figure 8, with the formation constants derived in this way being given in Table 3. These formation constants, in turn, can be used in order to derive the values of the complexation constants in nitrobenzene in the absence of ion-pairing (K_{BOB}) as follows:



This equation is derived from

$$K_{\text{BOB}} = \frac{K_3}{K_{s\pm}}$$

Table 4 summarizes the K_{BOB} values from the calculations using cesium chloride or bromide with, of course, the same value being expected in both cases. Thus, to the extent consistent results were seen, it would provide support for the validity of the model.

A congruence between the chloride and bromide cases was seen, with the corresponding values of K_{BOB} being reasonably close. These values were used to obtain the main equilibrium constants of interest, namely the halide–calix[4]pyrrole complexation constants, K_{compl} , and the ion-pairing constants, K_{ip} , defined by the equilibria summarized in eqs 1 and 2.

Considering eq 4 and the partitioning equilibrium (eq 10), the complexation constants can be calculated as the ratio, $K_{\text{compl}} = K_2 / K_{s\pm}$. However, as discussed previously, in order to determine K_2 directly, a very flat line, corresponding to a strong

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Table 5. Complexation Constants and Complexation Energies Obtained from Calculation

system ^a	log K_{compl}	K_{compl}	ΔG_{compl} (kJ mol ⁻¹)
calix[4]pyrrole-Cl ⁻	3.66 ± 0.02	4570 ± 209	-20.9 ± 0.1
calix[4]pyrrole-Br ⁻	2.43 ± 0.03	270 ± 18	-13.9 ± 0.2

^a The complexation constant was calculated from K_3 and K_4 .

Table 6. Ion-Pairing Constants and Ion-Pairing Energies Obtained from the Calculation

system ^a	log K_{ip}	$K_{\text{ip}} \times 10^{-5}$	ΔG_{ip} (kJ mol ⁻¹)
Cs ⁺ -calix[4]pyrrole/Cl ⁻	5.04 ± 0.12	(1.09 ± 0.30)	-28.8 ± 0.7
Cs ⁺ -calix[4]pyrrole/Br ⁻	5.25 ± 0.07	(1.93 ± 0.29)	-30.2 ± 0.6

^a The complexation constant was calculated from K_3 and K_4 and used to calculate K_2 .

dissociated system, is necessary at low concentrations. Since such a limiting scenario could not be achieved under the present experimental conditions, BOBcalixC6 was used. Recognizing that the complexation constant can be defined also as the ratio $K_{\text{compl}} = K_4/K_3$, the equilibrium K_2 can be calculated since $K_{\text{s}\pm}$ is known.

Thermodynamic Observations. Once the intermediate equilibrium constants, K_1 and K_2 , were calculated using the above computer modeling approach, both constants of interest, namely K_{compl} and K_{ip} , could be calculated using the following expressions:

$$K_{\text{compl}} = \frac{K_2}{K_{\text{s}\pm}} = \frac{K_4}{K_3} \quad \text{and} \quad K_{\text{ip}} = \frac{K_1}{K_2}$$

According to the values derived via this analysis, summarized in Tables 5 and 6, the chloride anion binds more strongly to calix[4]pyrrole than does the bromide anion. This result is in agreement with early solution phase analyses (carried out in dichloromethane).⁸ It is also consistent with the crystallographic data, which has established that the hydrogen bond distances between the four NH groups and the bound halide anion are shorter for chloride than bromide in the solid state ($d = 3.27$ – 3.32 and 3.45 – 3.52 Å for the relevant N \cdots Cl and N \cdots Br interactions, respectively).⁷ The ion-pairing constants are very high and nearly the same within experimental uncertainty. Tables 5 and 6 also list the complexation and ion-pairing energies. The value of the complexation energy reflects at least several energetic components, namely (1) the deformation energy corresponding to conversion of the calix[4]pyrrole from the 1,3-alternate conformation to the cone conformation, something that is expected to depend at least in part on the specific anion bound, and (2) the four hydrogen bond energies. Thus, the complexation energy directly relates to the overall binding energy of the halide-calix[4]pyrrole complex, with chloride and bromide displaying a difference of 7 kJ/mol in this solvent. While solubility considerations prevented an independent confirmation of these values by more direct means, as noted above, a number of previous studies, carried out in a range of solvents other than nitrobenzene, have served to confirm that chloride anion is bound far more strongly by calix[4]pyrrole than bromide

anion.^{8,9,15} In addition to these receptor-selective effects, the anion binding affinity can be attenuated by anion hydration in the nitrobenzene phase. The hydration numbers of Cl⁻ and Br⁻ in nitrobenzene are 4 and 2.1, respectively.¹⁶ Since this water of hydration presumably becomes partially lost upon anion complexation by calixpyrrole, the energetic cost is expected to be greater in the case of chloride than bromide, and the net effect is to attenuate any selectivity between Cl⁻ and Br⁻ that would be expected on the basis of anion binding affinities alone (i.e., $K_{\text{aCl}} > K_{\text{aBr}}$).

Conclusion

The most noteworthy finding to emerge from this study is that calix[4]pyrrole, a system well-appreciated for its anion binding capabilities,⁹ behaves as a ditopic ligand for cesium chloride and cesium bromide, forming a complex of 1:1:1 cesium:calix[4]pyrrole:halide stoichiometry, under conditions of aqueous-nitrobenzene solvent extraction. Such a finding, which is nearly unprecedented in the case of neutral extractants, occurs in spite of the high polarity of the organic phase (i.e., nitrobenzene). This ability to promote ion-pair formation appears, at least so far, to be limited to these two halide anions, as both qualitative and semiquantitative analyses of other cesium salts (e.g., CsNO₃) revealed behavior that was consistent with that of a fully dissociated extraction system.

Using experimental data and appropriate computer models, the thermodynamic constants and binding energies for various interactions of CsCl and CsBr could be determined. These analyses revealed, as expected, that the chloride anion is bound more strongly to *meso*-octamethylcalix[4]pyrrole than bromide. Specifically, a complexation energy roughly 7 kJ/mol higher was seen in the case of CsCl as compared to CsBr. The binding energy for the interaction of the cesium cation with the anionic complexes formed from these two salts was also determined and found to be nearly independent of the nature of the halide.

Depending on the size and the geometry of the extracted anion (e.g., halide vs nitrate), the calix[4]pyrrole is or is not able to complex the cesium cation and thus act as an ion-pair receptor. Such anion dependence has already been shown in the solid state, with the structures of various calix[4]pyrrole cesium cation anion complexes being found to differ considerably depending on the nature of the bound anion.⁷ In other words, cesium cation binding is seen only in those cases where the anion in question (e.g., Cl⁻ or Br⁻) is able to support formation of the so-called cone conformation of the calix[4]pyrrole.

It is not possible to determine the exact position of cesium in the ion-pair complex formed in nitrobenzene from CsCl or CsBr under the present solvent extraction conditions. However, by analogy to what is seen in the solid state, we think it is very likely that the cation lies in the bowl-shaped cavity of the calixpyrrole. In fact, the similarities in the ion-pairing formation constants for the chloride and bromide systems are most easily rationalized in terms of such an assumption as opposed to invoking other orientations, even ones where the bound anion and cesium counter cation might be in closer proximity.

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Additional evidence that actual coordination of Cs^+ ion in the bowl of the calixpyrrole is taking place lies in the unexpectedly large magnitude of the ion-pairing constants, $K_{\text{ip}} = 5.04 \times 10^5$ and 5.25×10^5 for $\text{Cs}(\text{calixpyrrole})^+$ with Cl^- and Br^- , respectively (Table 6). As a most conservative reference point, one might choose to compare these values of K_{ip} with those for the “naked” Cs^+ and halide ions in the water-saturated organic phase. Such values are not available in the literature, as the salts are too sparingly soluble and extraction is too feeble to achieve sufficient organic-phase concentrations of the ions for appreciable pairing. From the experiment shown in Figure 2, however, we estimate that ion-pairing could be detected if $K_{\text{ip}(\text{CsCl})} > 2 \times 10^4$ and $K_{\text{ip}(\text{CsBr})} > 4 \times 10^3$ for Cs^+ pairing with Cl^- and Br^- , respectively, if we assume the modeling could “see” $[\text{CsX}]_{\text{org}} > 0.2[\text{Cs}^+]_{\text{org}}$. On the other hand, calculation for dry nitrobenzene using the Fuoss theoretical ion-association treatment² predicts $K_{\text{ip}(\text{CsX})}$ values less than 100. Although literature on ion-pairing in nitrobenzene is scarce, one may compare with $K_{\text{ip}(\text{CsPicrate})} = 602\text{--}1510$ for the extraction of cesium picrate into nitrobenzene.¹⁷ It is known that complexed salts in polar solvents often behave as strong electrolytes,^{17,18} at least for cation complexation, in accord with the ligand-shielding effect.³ Indeed, we have seen in the extraction of Li^+ by a crown ether in 1-octanol that ion-pairing with Cl^- decreases from 1.3×10^4 for the free ions in the water-saturated 1-octanol to 5.4×10^3 for the complex with the anion.¹⁹ Given that the effective charge of the halide is reduced by the hydrogen bonding from the calixpyrrole, it thus seems likely that ion-pairing of the Cs^+ cation outside of the bowl of the calixpyrrole–halide complex is too weak to explain the high ion-pair association observed. It should be noted that the equilibrium analysis is indicative of $\text{Cl}^-(\text{calixpyrrole})\text{Cs}^+$ assembly formation. However, one can argue that, in this case, Cs^+ inclusion into the calixpyrrole cavity is driven not by electrostatic attraction to the bound anion (definition for ion-pairing process) but rather by favorable interactions with the electron-rich ligand cavity. Unfortunately, equilibrium analysis does not provide insight into the nature of the process. Rather, equilibrium analysis quantifies Cs^+ inclusion into the pre-organized calix-like “bowl” formed by the anion-binding calixpyrrole cavity. In this sense, formation of the $\text{Cl}^-(\text{calixpyrrole})\text{Cs}^+$ species could reflect the fact that Cs^+ coordination to the calixpyrrole bowl is more important in nitrobenzene than electrostatic ion-pairing effects, something that would manifest in terms of out-of-the cavity $\text{Cs}^+\text{--Cl}^-$ interactions leading to the generation of a contact ion-pair. This proposal is also supported by the finding that the D values depend on $[\text{CsCl}]$ over the entire concentration range, and a positive slope is observed even at very low CsCl concentrations in the organic phase (Figure 5), conditions under which contact ion-pair effects are not expected to be significant in the moderately polar solvent, nitrobenzene. Further, ion-pairing between the $\text{Cs}(\text{BOB})^+$ complexed cation and the test anions was not observed, even at high loading levels within the nitrobenzene phase. We thus infer that Cs^+ is bound

strongly to the anion-bound form of calixpyrrole via an effective combination of electronic and spatial complementarity. Moreover, since Cs^+ is only minimally hydrated in water-saturated nitrobenzene (hydration number of 0.4),¹⁶ there is little or no dehydration penalty to pay when it is bound within the calix like bowl.

In summary, we have demonstrated that, under appropriately chosen conditions, even a very simple macrocycle, such as the easy-to-prepare system *meso*-octamethylcalix[4]pyrrole, can act as both a cation (Cs^+) and an anion (Cl^- or Br^-) receptor, extracting such species concurrently into an organic phase as the result of ion-pairing effects. This finding has important implications in terms of the choice of systems that may be potentially considered as viable extractants for solvent-based separations systems. This is because, in the limit, very different properties might be expected for a neutral receptor that acts as a cation extractant or one that acts as an anion extractant vs a system that serves to facilitate the transfer of a salt from an aqueous to an organic phase to form a combined neutral receptor–cation–anion ensemble. A linear dependence of the extraction efficiency on both the salt and receptor concentrations would be expected in the case of paired anion–cation extraction. In contrast, an extraction efficiency independent from the salt concentration and increasing only with the square root of the receptor concentration is characteristic of a system where the receptor interacts exclusively with one ion and the counter ion is fully dissociated. These stark differences make the use of receptors, such as the calix[4]pyrrole described in this report, that favor the concurrent, paired extraction of both anions and cations (i.e., an overall neutral ensemble) more attractive for the simple reason that increasing the receptor concentration will produce an extraction efficiency that scales more strongly with concentration. Ion-pair extractant systems also offer practical advantages in terms of stripping, or removal of the extracted ions, where release after extraction is important, as discussed in greater detail elsewhere.²⁰

In a broader context, the present results are noteworthy because they underscore the fact that ion-pairing effects can be substantial, even in simple systems. In particular, the fact that ion-pairing effects are seen in the case of Cs^+ , a charge-diffuse cation that would be expected to interact strongly only with specifically tailored hosts, and in a solvent (nitrobenzene) that favors the formation of charge separated species, leads us to propose that they may be more prevalent in other milieus than hitherto considered, including in the all-important realm of biological anion and cation recognition. Efforts are therefore underway to explore the generality of the present findings and to test the extent to which hitherto unrecognized ion-pairing effects might be controlling the recognition characteristics of other “pure” cation or anion receptor systems.

Acknowledgment. The research at ORNL was sponsored by the Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences, U.S. Department of Energy, under contract DE-AC05-00OR22725 with Oak Ridge National Laboratory, managed and operated by UT-Battelle, LLC. The work at UT Austin was supported by the National Institutes of Health (grant no. GM 58907 to J.L.S.). We thank

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Mr. Dustin Gross of The University of Texas at Austin for providing the synthetic protocol used to prepare the calix[4]-pyrrole used in this study.

Supporting Information Available: General experimental section and Tables S1–S6, containing the following information: partitioning energies and constants for the partitioning between water and nitrobenzene for the different anions and cations used in this work, radii of alkali cations, specific ion

interaction theory parameters used to calculate activity coefficients, molecular weights of the constituents, Masson coefficients of the various ions present in the systems, organic solubility parameters (Hildebrand parameters) of the different organic components, and Pitzer parameters for the interactions between cations and anions. This material is available free of charge via the Internet at <http://pubs.acs.org>.

JA7102179