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Attenuation of Hofmeister bias in ion-pair extraction by a disulfonamide anion host used in strikingly effective synergistic combination with a calix-crown Cs^+ host

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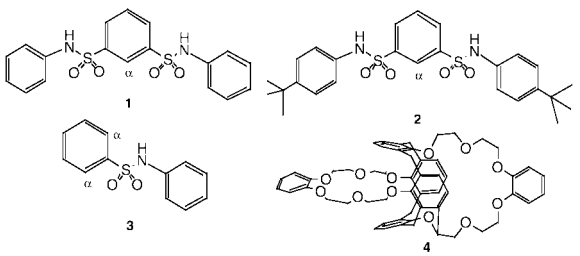
A calix-crown/disulfonamide dual-host combination in 1,2-dichloroethane exhibits markedly enhanced ion-pair extraction of caesium salts, with the observed synergism following an anti-Hofmeister order.

Ion-pair recognition and extraction by synthetic hosts is an area of intense interest. Design of early prototype ion receptors has mainly focused on cation complexation, the co-extracted anion selectivity being determined by non-specific solvation effects. Consequently, salt extractability generally increases in the direction of larger, more charge-diffuse anions, consistent with the well-known Hofmeister selectivity.[1] Hence arises the question as to the extent to which one may perturb this bias-type *vs*. recognition-type of selectivity.[2] This question has gained particular relevance in connection with the need to separate radiocaesium from nuclear waste,[3] where recent attention has been focusing on certain calix-crowns.[4] Although elegant heteroditopic hosts which are able to complex both the anion and the Cs cation have been reported,[5] the use of dual-host systems remains rare, despite their apparent simplicity and versatility.[6,7] We recently demonstrated that simple carboxamides enhance extraction of the $CsNO_3$ ion pair *via* binding of the co-extracted anion, when used together with a crown-ether cation host.[6a,b] These encouraging results prompted us to examine the question of anion selectivity in such systems.[6c] Herein, we report that synergism in the dual-host system involving disulfonamides **1** or **2** as anion hosts,[8] and the Cs^+ selective calix-crown **4** as cation host[4b] is strongly biased toward small anions, with remarkably uniform dependence on the standard Gibbs energies of partitioning for the anions OAc^-, Cl^-, Br^-, I^-, NO_3^- and ClO_4^-. In addition, this particular dual-host system is shown to be strikingly effective, generating the largest synergistic effects yet observed.

The anion-binding properties of disulfonamide **1**, the di(*tert*-butyl) disulfonamide **2**, and the monosulfonamide **3** (Scheme 1) were initially investigated in 1,2-dichloroethane-d_4 by ^{1}H NMR titrations of receptor solutions with ^{n}Bu$_4$NX salts (X = Cl^-, Br^-, I^-, OAc^-, NO_3^-, ClO_4^-). The observed large downfield chemical shift changes for the sulfonamide N–H protons, as well as for the α-C–H protons (Scheme 1) were analyzed *via* non-linear regression methods.[8a,9,10] The results confirm the observations of Crabtree and coworkers indicating a predominant 1:1 complex formation in CD_2Cl_2 for all anions plus a weaker 1:2 complexation mode for OAc^-, Cl^-, Br^- and NO_3^-.[8a] The association constants (Table 1) are generally higher for the more charge-dense Cl^- and OAc^- and much smaller for the large and more hydrophobic, NO_3^-, ClO_4^- and I^-. This general order is what one would expect for a strong non-specific hydrogen-bond receptor.[2,8a] It follows that synergistic enhancements on combining **1** or **2** with a cation receptor should also follow this general order.



Scheme 1 Ion receptors used in this study.

Table 1 Association constants K (M^{-1}) for the formation of 1:1 and 1:2 complexes of **1**, **2** and **3** with anions in 1,2-dichloroethane-d_4 at 295 K. Tetrabutylammonium salts were used as anion sources

Anion X^-		**1**	**2**	**3**
OAc^-	K_{11}	19 500 (± 1400)	13 500 (± 400)	750 (± 80)
	K_{12}	73 (± 1)	70 (± 1)	
Cl^-	K_{11}	50 000 (± 4000)	32 500 (± 2000)	410 (± 9)
	K_{12}	5.8 (± 0.2)	3.6 (± 0.1)	
Br^-	K_{11}	10 600 (± 500)	8 900 (± 600)	150 (± 5)
	K_{12}	1.7 (± 0.7)	1.2 (± 0.3)	
NO_3^-	K_{11}	4 300 (± 100)	1 800 (± 20)	55 (± 5)
	K_{12}	2 (± 0.2)	1.2 (± 0.7)	
I^-	K_{11}	1 400 (± 13)	690 (± 27)	19 (± 2.5)
ClO_4^-	K_{11}	81 (± 1)	48 (± 1)	< 3

The ^{137}Cs tracer distribution experiments were performed by methodology described earlier,[4b] using aqueous phases containing 0.10 M NaX (inextractable)[11] and 5×10^{-6} M CsX (X = Cl^-, Br^-, I^-, OAc^-, NO_3^-, ClO_4^-) and organic phases containing 0.010 M of calix[4]arene-bis(benzo-18-crown-6) **4** with 0.035 M of **1**, **2** or **3**. Based on previous results[4b] and ion-pairing theory,[12] these experimental conditions are expected to minimize ion-pairing and its role in anion selectivity. In particular, at the low maximum concentration of CsX that could be extracted, estimated ion-pairing in the organic phase would at most be 5%. Control experiments were also performed with organic phases containing (1) no sulfonamide, (2) no crown ether, and (3) solvent only. The results summarized in Table 2

Table 2 Caesium distribution ratios for calixarene **4** only (D_4) and for calixarene **4** plus sulfonamides **1**–**3** (D_{4+R}, R = **1**–**3**). Last column shows the synergistic factors observed for **1**, expressed as the ratio D_{4+1}/D_4[a]

Anion	D_4	D_{4+1}	D_{4+2}	D_{4+3}	D_{4+1}/D_4
OAc^-	0.471	291	62.3	1.45	618
Cl^-	0.357	42.2	11.8	0.88	118
Br^-	2.64	125	48.5	6.32	47.3
NO_3^-	8.44	180	73.0	17.0	21.3
I^-	77.6	644	284	113	8.3
ClO_4^-	850	1770	1070	1020	2.1

[a] D_1 is negligible in relation to D_4.

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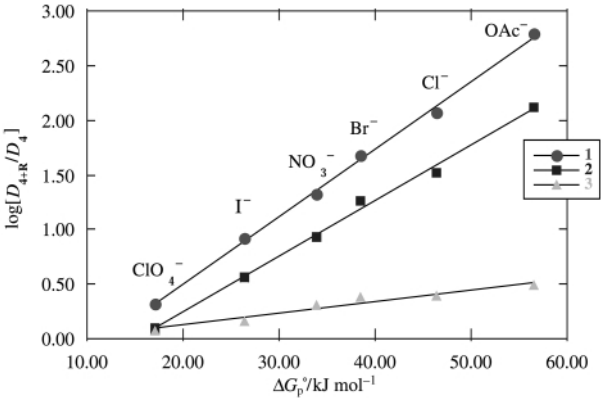

Fig. 1 Plot of the logarithm of the synergistic factor (D_{4+R}/D_4) for sulfonamides (**R** = **1**–**3**) *vs*. the standard Gibbs energy of partitioning $\Delta G°_p$ for various anions.

and Fig. 1 show that receptors **1** and **2** dramatically enhance Cs^+ ion extraction by the calix-crown. The synergism is stronger for the more charge-dense OAc^- and Cl^-, and weaker for the more hydrophobic I^- and ClO_4^-, as expected by the corresponding anion-receptor binding affinities. It is noteworthy that the extraction selectivity is higher for OAc^-, while K_{11} is higher for Cl^-, possibly reflecting a contribution of 1:2 complexation or anion-hydration effects.[13] For NO_3^- the observed synergism is in good agreement with data previously obtained using tetrabenzo-24-crown-8 as a cation receptor.[13] This observation implies weak if any ion-pairing effects and no significant role of the nature of the cation hosts.

One of the remarkable and unexpected aspects of this system is the excellent correlation between the synergistic effect and the standard Gibbs energy of anion partitioning $\Delta G_p°$.[11,14] Plotting the logarithm of the synergistic factor *vs*. $\Delta G_p°$ gave straight lines (Fig. 1) with a higher slope for the stronger anion receptor **1**. This correlation reveals that, whereas the bidentate nature of the disulfonamide receptor confers a strong interaction, the extraction enhancement is remarkably non-specific in breaking the simple bias-type dependence on anion size. Since the magnitude of enhancement reflects the strength of anion complexation in the organic phase,[7a,b] the strict correlation with $\Delta G_p°$ suggests that the anion receptor functions by non-specific solvation in a manner fundamentally resembling the partitioning process.

In conclusion, a potent disulfonamide anion receptor strongly synergizes the extraction of Cs salts when used together with a calix-crown cation host. The synergistic effects, as well as the anion binding affinities, are anti-Hofmeister, and thus these compounds and derivatives represent a new, valuable tool for tuning selectivity for anions in ion-pair extraction.

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