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New Calix[4]arene-monobenzo- and -dibenzo-crown-6 as Cesium Selective Ionophores in the Radioactive Waste Treatment: Synthesis, Complexation and Extraction Properties

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Abstract

Cesium possesses two long lived isotopes ^{135}Cs and ^{137}Cs and the first one has a very long (2.3×10^6 y) half life and is one of the most mobile nuclides in a repository. Calix[4]arene-crowns-6 in the *1,3-alternate* conformation are emerging as a new class of ionophores exhibiting a very high efficiency and selectivity in the complexation of cesium ion and its removal from highly acidic ([HNO_3] = 3–4 M) radioactive waste having also high sodium nitrate concentration ([$NaNO_3$] = 2–4 M). In order to improve both efficiency and cesium selectivity we have synthesised the novel calix[4]arene dibenzo-crowns-6 **1** and **2** and the calix[4]arene-monobenzocrown-6 **3** in *1,3-alternate* conformation and evaluated their complexation properties towards alkali metal cations in homogeneous solution and in two phase systems, together with their performance in radioactive waste treatment. All data confirm the higher Cs/Na selectivity of the *1,3-alternate* calix[4]crown-6 **1–3** containing aromatic rings in the polyether loop, in comparison to previously synthesised compounds of the same series.

Introduction

Crown ethers derived from calix[4]arenes [1] are actively investigated in supramolecular chemistry and separation science. Particularly interesting are the calix[4]arene-crowns-6 in *1,3-alternate* conformation which, together with the analogous biscrowns, [1] show remarkable selectivity in the complexation of cesium ion and, for this reason, are promising in the ^{135}Cesium removal from radioactive waste [2]. Previous studies, which include synthesis and X-ray crystal structure determination [3], solution thermodynamics [4], extraction and transport [4, 5], and molecular modeling [6, 7] have been concentrated on 1,3-dialkoxycalix[4]arene-crown-6 (e.g., **1**).

More recently, Molecular Dynamics (MD) simulations performed on calix[4]arene-monocrowns [8] and on calix[4]arene-biscrowns [9] and their alkali metal complexes, suggested that a possible way to enhance cation-binding and cesium/sodium selectivity in calix[4]arene-crown-6 in the *1,3-alternate* conformation was to incorporate aromatic rings in the crown ether loop. This prompted us [8, 10, 11] as well other authors active in the field [9, 12–19] to synthesise calix[4]arene mono- and biscrowns having aromatic rings in the crown. We report in this paper the full details for the synthesis, complexation and extraction properties of three new such compounds, belonging to the calix[4]arene monocrown-6 family.

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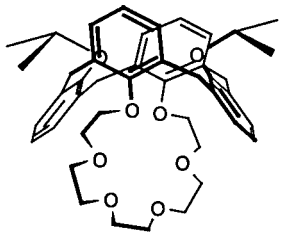
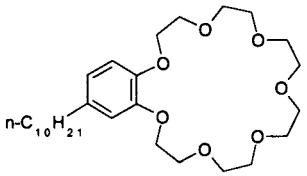
Results and discussion

Synthesis of the ligands

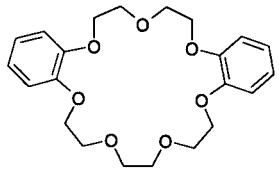
For the successful synthesis of calix[4]arene-dibenzo-crown-6 derivatives **1** and **2** it was required to have access to ditosylates **7** in large amounts. We have developed a novel route to **7** (Scheme 1), which exploits a useful and selective monoalkylation procedure of catechols **4** reported by Yamaguchi et al. [20]. Catechol **4a** or 3,5-di-*tert*-butylcatechol **4b** were reacted with ethylene carbonate in the presence of a catalytic amount of tetrabutyl ammonium iodide at 160 °C. Pure compounds **5a** and **5b** were isolated in 75 and 82% yields respectively. The structure of **5b** was unequivocally established through a two-dimensional NOESY experiment, which shows a strong NOE correlation between the OCH_2CH_2OH methylene group and H_6. No correlation was observed with H_4 or the *t*-butyl groups, thus ruling out the possible structural isomer, where the ethanol moiety is linked to the other catechol oxygen atom. Alkylation of compounds **5** (NaH, dry DMF) with ethylene glycol ditosylate,



(I)

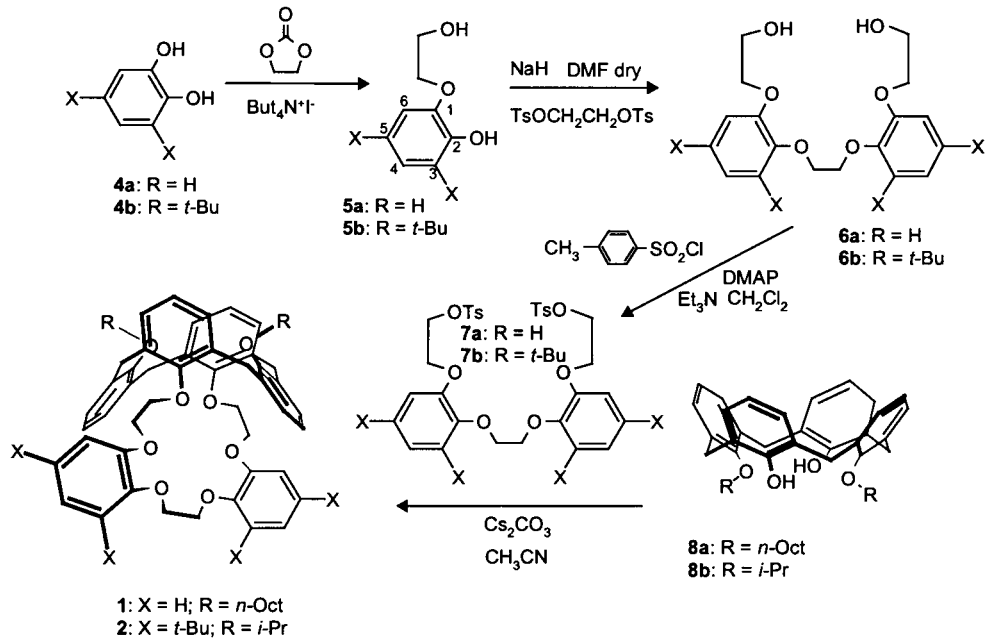


n-decylbenzo-21-crown-7 **(II)**



dibenzo-21-crown-7 **(III)**

Formulas 1.



Scheme 1.

afforded the glycols **6a** and **6b** in 81 and 27% yields, respectively. The low yield of compound **6b**, despite the stronger reaction conditions (higher temperature and excess of NaH) is to be ascribed to the reduced nucleophilicity of the 2-O^- group in compound **5b**, which is in *ortho* position to a bulky *tert*-butyl group. Ditosylates **7** was easily prepared by reaction of glycols **6** in dry CH_2Cl_2 with tosyl chloride and dimethylamino pyridine (DMAP).

For the synthesis of calix[4]arene-monobenzo-crown-6 **3** (Scheme 2) the ditosylate **13** which was synthesised through a protection-deprotection route was needed. The 4-*tert*-octyl catechol **9** was alkylated with monotosylated-monotritylated diethylene glycol **10** [21], then the trityl groups were removed and the glycol **12** esterified to the ditosylate **13** in 72% overall yield. Calix-benzo-crowns-6 **1–3** were then obtained in 68, 74 and 80% yields, respectively, starting from the proper ditosylate **7** (Scheme 1) or **13** (Scheme 2) and 1,3-dioctyloxy- (**8a**) or 1,3-di-*iso*-propoxy- (**8b**) calix[4]arenes, using the usual conditions which produce the calix[4]arene-crowns-6 in the *1,3-alternate* conformation [4]. The structure of compounds **1–3** was unambiguously established by ^1H and ^{13}C NMR spectroscopy. As expected for the *1,3-alternate* structure a signal for the $ArCH_2Ar$ methylene protons was observed at $\delta_H \cong 3.8$ ppm while the corresponding carbons give rise to a triplet at $\delta_C \cong 39$ ppm [22].

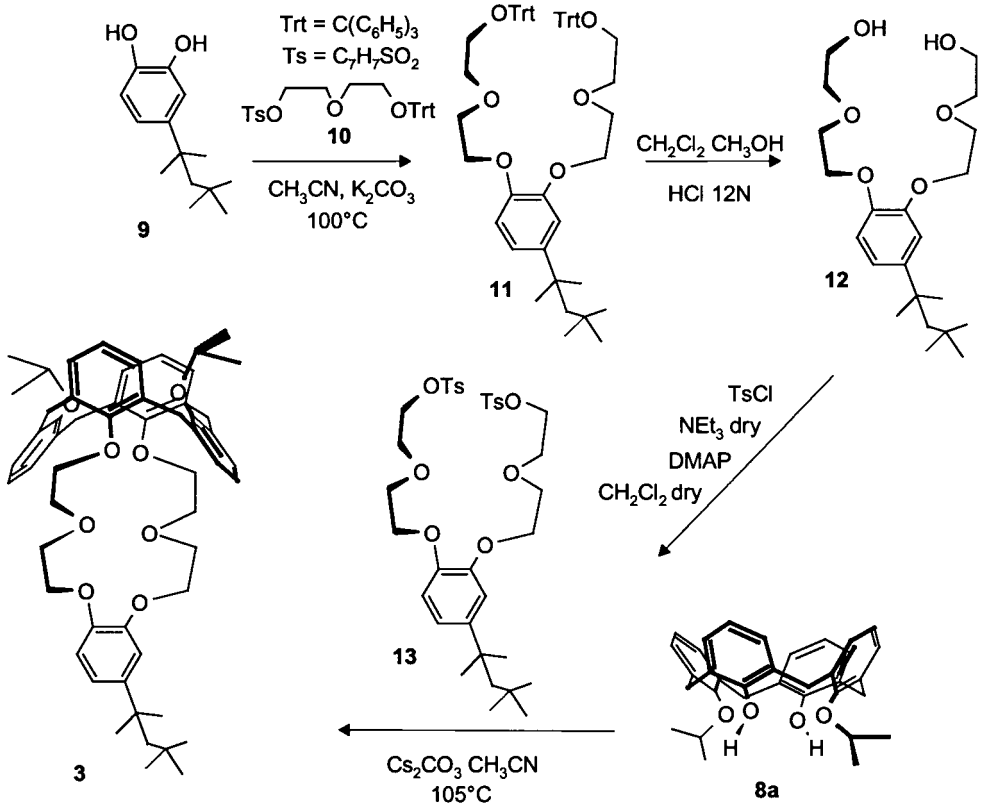
Table 1. Extraction percentages (%E) of alkali picrates from water into dichloromethane at 20 °C for 1,3-dialkoxycalix[4]arene-crowns-6

Ligand	Li^+	Na^+	K^+	Rb^+	Cs^+
I [4]	3.4	2.4	15.8	43.8	64.5
1	1.2	2.0	13.3	42.6	54.4
2	0.2	0.7	3.4	2.8	2.7
3	1.6	2.3	11.0	31.9	41.1

Extraction of metal picrates

In order to have a preliminary estimation of the binding properties of our new calix[4]arene-crown-6 derivatives **1–3** we determined the extraction percentages (E%) of alkali metal picrates from water to dichloromethane at 25 °C using Pedersen's procedure [23, 24].

The values reported in Table 1 indicate that, among these new derivatives, the calixdibenzo-crown-6 **1** is the most efficient in extraction of cesium ion followed by



Scheme 2.

Table 2. Cesium and sodium distribution coefficients and Cs/Na selectivity ($\alpha_{Cs/Na}$) for the extraction of nitrates from water to NPHE (T = 25 °C) by crown ethers.

Ligand	Single ion[a]			Competitive[b]
	D_{Na}	D_{Cs}	$\alpha_{Cs/Na}$	D_{Cs}
I	$<10^{-3}$	28.5	>28 500	18
1	$<10^{-3}$	31	>31 000	56
3	$<10^{-3}$	34	>34 000	45
DB21C7 (**II**)	1.2×10^{-3}	0.3	250	0.12

[a] $[MNO_3]_{aq} = 5 \times 10^{-4}$ M, $[HNO_3]_{aq} = 1$ M; $[Ligand]_{NPHE} = 1 \times 10^{-2}$ M.
[b] $[CsNO_3]_{aq} = 1 \times 10^{-6}$ M, $[NaNO_3]_{aq} = 4$ M, $[HNO_3]_{aq} = 1$ M; $[Ligand]_{NPHE} = 1 \times 10^{-2}$ M.

calix[4]arene-monobenzo-crown-6 **3** whereas the calix-di-t-butyldibenzocrown-6 **2** is unable to extract significantly alkali metal ions. The data show that compound **1** is slightly less efficient than the calix[4]arene-crown-6 **I**, in these conditions.

Extraction from simulated waste

The distribution coefficients D_M for cesium and sodium (Table 2) were determined by contacting an aqueous acidic solution ($[HNO_3]$ = 1 M) with solutions of different calix[4]arene crowns (10^{-2} M) in nitrophenyl hexyl ether (NPHE).

These results can be compared with those of 1,3-di-*iso*-propoxycalix[4]arene-crown-6 **I** and with one of the most efficient cesium selective crown ethers, such as *n*-decyl benzo 21-crown-7 (DB21C7 **II**). Interestingly, all calix-crowns are much more efficient and selective than DB21C7 **II**: this is due both to a D_{Cs}, that is two orders of magnitude higher than with **II**, and also to a very low extraction of sodium. D_{Na} is so low that only a higher limit could be estimated under these conditions ($D_{Na} < 10^{-3}$). Calix-benzo-crown-6 **1** and **3** are also slightly more selective than compound **I** thanks to their higher D_{Cs}. The remarkable efficiency of calixbenzo-crown-6 derivatives is also confirmed by the competitive extraction of cesium from acidic solutions containing large amounts of sodium ($[NaNO_3]$ = 4 M). Very high distribution coefficients are obtained (Table 2) with calix benzo-crown-6 (**3**) and especially with calix dibenzo-crown-6 (**1**).

Interestingly, the cesium distribution coefficients, much higher than that of dibenzo-21-crown-7 (**III**), strongly increase with the increase of the nitric acid concentration until a value of 2–3 M (Figure 1) and then rapidly decrease. The maximum of D_{Cs} is reached for a nitric acid concentration very close to that of fission products solutions. The presence of one (**3**) or two (**1**) benzene units on the crown bridge of the calixarene strongly enhances the distribution coefficients of cesium also in comparison with calix[4]arene-crown-6 **I** (Figure 1). In general, for nitric acid concentration lower than 2 M, the increase of nitrate ion (common ion effect) favours the extraction of cesium; however at higher acidity, H_3O^+ enters into competition with cesium ion, resulting in a decrease of D_{Cs}. Therefore the lower basicity of the catechol oxygens of **1** and **3** is responsible for the higher D_{Cs} under these conditions.

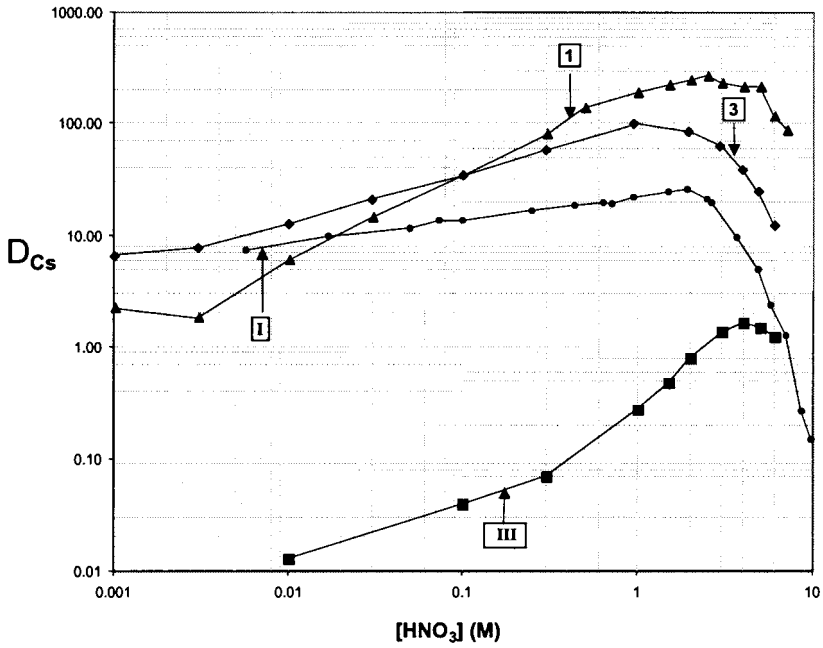


Figure 1. Extraction of cesium (D_{Cs}) from acidic media by calix[4]arene-crown-6 (**I**), calix[4]arene-benzocrowns-6 (**1** and **3**) and dibenzo-crown-7 (**III**).

Table 3. Association constants (Log K_a) for alkali metal picrate complexes of 1,3-dialkoxycalix[4]arene-crowns-6 in $CHCl_3$ saturated with water at 22 °C.[a]

Ligand	Log K_a				
	Na	K	Rb	Cs	$S_{(Cs/Na)}$
I [4]	5.2	6.4	7.9	8.8	4 000
1	<5	7.8	8.9	9.0	>10 000
2	<5	5.3	5.9	5.5	≈1
3	<5	7.0	7.0	8.0	<1 000

[a] Error <10%.

Table 4. Thermodynamic parameters for the complexation of alkali metal salts by ligand **1** in acetonitrile, at 25 °C.

Thermodynamic parameters	K^+	Rb^+	Cs^+
Log K_a	5.47	5.7	5.7
$-\Delta G°$ (kJ mol^{-1})	31.2	32.5	32.5
$-\Delta H°$ (kJ mol^{-1})	17.4	29	42
$T\Delta S°$ (kJ mol^{-1})	13.8	4	−10
$\Delta S°$ (J K^{-1} mol^{-1})	46	13	−34

Extraction studies

In order to better evaluate the binding properties of ligands **1–3** in comparison with the more classical di-iso-propoxy calix[4]arene-crown-6 **I** we also determined the association constants (Log K_a) with alkali picrates in chloroform, using Cram's method [25, 26] (Table 3) and, in the case of ligand **1**, determined the thermodynamic parameters (Table 4).

The data confirm the findings (Table 1) that the butylated calixdibenzocrown-6 **2** is a very poor ligand towards alkali metal ions, thus suggesting that the *tert*-butyl groups are strongly distorting the crown ether loop. Compared to **1**, compound **3** is less efficient in the binding of alkali metal ions by 1–2 orders of magnitude in these conditions. The reasons for such a decrease are not clear, but recently we have found that π-π stacking of the picrate ions with aromatic nuclei on the crown ether loop can influence the association constants in chloroform solution[11]. Compound **3**, bearing a bulky *tert*-octyl group on the benzo unit may lack of such extra-stabilisation. The dibenzo- (**1**) and the monobenzo (**3**) calix-crowns-6 exhibit a very low binding of sodium ion (Log K_a < 5) so that only a lower limit for the cesium/sodium selectivity could be estimated. The association constants of compound **1** and the more classical calixcrown **I** are comparable but the former is more selective for cesium ($S_{Cs/Na}$ > 10 000) than the latter ($S_{Cs/Na}$ = 4 000).

The thermodynamic parameters ($\Delta H°$ and $\Delta S°$) were determined in acetonitrile (Table 4) since compound **1** is not soluble enough in methanol. However the trend is similar to that previously observed for the di-*iso*-propoxycalix[4]arene-crown-6 (**I**) in methanol [4]. Complexation is enthalpically driven for all complexes and enthalphy increases from K^+ to Cs^+, concomitant with a decrease in entropy. This can be explained by a better size complementarity between the crown and Cs^+, resulting in loss of freedom, and by desolvation of the cations.

Conclusions

The extraction and complexation data for alkali metal ions reported in this paper confirm the expectation, based on molecular modeling and X-ray crystallography [8] that *1,3-alternate* calix[4]arene-crown-6, bearing one or two aromatic rings in the crown ether loop have a better Cs/Na

selectivity than more classical calix[4]arene-crowns-6 (e.g., **I**). This effect is even more evident in the extraction of simulated radioactive waste. The association constants of the mono- (**3**) and dibenzo- (**1**) calix[4]arene-crown-6 towards alkali metal cations are comparable to those of other calix[4]arene-crowns-6 in the *1,3-alternate* conformation. However if bulky *tert*-butyl groups are present on the aromatic nuclei (e.g., **2**) the complexation ability of the calix[4]crown drops dramatically, probably because these groups cause a distortion of the polyether ring from the optimal binding conformation. Calorimetric studies show that complexation is enthalpically driven and that the entropic contribution is unfavourable for the cesium complex, indicating a tight binding.

Experimental section

Most of the solvents and all reagents were obtained from commercial supplies and used without further purification. DMF was freshly distilled and stored over 4 Å molecular sieves while acetonitrile for synthesis was dried over 3 Å molecular sieves. Proton and carbon nuclear magnetic resonance spectra (^{1}H NMR and ^{13}C NMR) were recorded on a Bruker AC300 and Bruker AMX400 spectrometers of the Centro Interdipartimentale dell'Università di Parma. Chemical shifts are reported as δ values in ppm from tetramethylsilane (δ 0.0) as internal standard. Analytical thin-layer chromatography was carried out on silica gel plates (SiO_2, Merk 60 F_{254}). Mass spectra were performed with a FINNIGAN MAT SSQ 710 (Cl, CH_4). Melting points were obtained in a nitrogen-sealed capillary on an Electrothermal Apparatus.

Materials

1,1,3,3-tetramethylbutylcatechol (**9**) [27], diethylene glycol monotrityloxy monotosylate (**10**) [21], 25,27-dioctyloxycalix[4]arene (**8a**) [4] and 25,27-di-*iso*-propoxycalix[4]arene (**8b**) [4] were synthesised according to literature. *n*-Decylbenzo-21-crown-7 and dibenzo-21-crown-7 were synthesised by Chimie Plus (France) and Acros Organics (Belgium) respectively. Milli Q2 water was used to prepare solutions.

*Synthesis of 2-(2-hydroxyethoxy)phenol (**5a**) [20]*

A mixture of cathecol **4a** (22 g, 0.2 mol), ethylene carbonate (17.6 g, 0.2 mol), and tetrabutylammonium iodide (2.4 g, 6.5 mmol) was heated at 160 °C for about 1 h until evolution of CO_2 ceased. The mixture was purified by column chromatography (SiO_2, hexane/ethyl acetate:1/1), to afford a white solid. Crystallization of this solid from water gave pure compound (**5a**) (14.1 g, 75%); m.p. 100–101 °C; ^{1}H NMR ($CDCl_3$): δ 6.95–6.80 (m, 5H, ArOH and ArH), 4.13–4.10 (m, 2H, ArOCH_2), 4.0–3.97 (m, 3H, OCH_2CH_2OH); ^{13}C NMR ($CDCl_3$): δ 146.7, 146.3 (s, Ar), 122.7, 120.5, 116.0, 113.5 (d, Ar), 70.6 (t, ArOCH_2), 61.7 (t, CH_2OH); MS *m/z*: 138.5 (M^+). Anal. Calcd for $C_8H_{10}O_2$: C, 69.55; H, 7.30. Found: C, 69.43; H, 7.40.

*Synthesis of 2,4-bis(1,1-dimethyl)-6-(2-hydroxyethoxy)phenol (**5b**)*

A mixture of di-*tert*-butyl-catechol **4b** (20 g, 0.09 mol), ethylene carbonate (7.92 g, 0.09 mol) and $Bu_4N^+I^-$ (1.1 g, 0.003 mol) was melted at 160 °C under nitrogen atmosphere for 3 hours. After cooling, the resulting solid was treated with 150 mL of CH_2Cl_2 and 150 mL of 10% HCl. The organic phase was washed twice with water and the solvent distilled off. After crystallization with hexane, compound **5b** was obtained in 82% yield; m.p. 135–136 °C; ^{1}H NMR ($CDCl_3$): δ 6.95 (d, J = 2.2 Hz, 1H, ArH), 6.81 (d, J = 2.2 Hz, 1H, ArH), 6.4 (bs, 1H, ArOH), 4.16 (t, J = 2.1 Hz, 2H, OCH_2CH$_2$OH), 4.02 (t, J = 2.1 Hz, 2H, OCH$_2$CH_2OH), 1.41 (s, 9H, C(CH_3)$_3$), 2.65 (bs, 1H, CH$_2$OH), 1.29 (s, 9H, C(CH$_3$)$_3$); ^{13}C NMR ($CDCl_3$): δ 145.2, 142.6, 141.4, 135.2 (s, Ar), 116.6, 108.5 (d, Ar), 71.1 (t, ArOCH_2), 61.5 (t, CH_2OH), 34.9 (s, C(CH$_3$)$_3$), 31.6 (q, C(CH$_3$)$_3$), 29.4 (q, C(CH$_3$)$_3$); MS *m/z*: 266.3 (M^+). Anal. Calcd for $C_{16}H_{26}O_3$: C, 72.15; H, 9.83. Found: C, 72.03; H, 9.75.

*Synthesis of 1,2-bis[2-(2-hydroxyethoxy)phenoxy]ethane (**6a**)*

A mixture of (**5a**) (2 g, 13 mmol) and NaH (0.32 g, 13 mmol) in dry DMF (8 mL) was stirred at room temperature for 30 min. To this solution was added dropwise ethylene glycol ditosylate (2.4 g, 6.4 mmol) dissolved in dry DMF (25 mL) and the mixture was stirred at room temperature for 36 h. After removal of DMF *in vacuo*, the residue was dissolved in dichloromethane and washed with water (CAUTION!). The organic layer, dried over sodium sulfate, was evaporated. The pure product (**6a**) (1.71 g, 81%) was obtained by crystallization from ethanol/water (1/1); m.p. 75–77 °C; ^{1}H NMR ($CDCl_3$): δ 6.97–6.89 (m, 8H, ArH), 4.39 (s, 4H, ArOCH_2CH_2OAr), 4.34 (s, 2H, OH), 4.1 (t, J = 7 Hz, 4H, ArOCH_2CH$_2$OH), 3.87 (t, J = 7 Hz, 4H, ArOCH$_2$CH_2OH); ^{13}CNMR ($CDCl_3$): δ 148.7, 148.6 (s, Ar), 122.2, 121.7, 114.8, 114.2 (d, Ar), 71.6, 67.8 (t, ArOCH_2), 60.8 (t, CH_2OH); MS *m/z*: 334 (M^+). Anal. Calcd for $C_{18}H_{22}O_6$: C, 64.66; H, 6.63. Found: C, 64.58; H, 6.72.

*Synthesis of 1,2-bis[2,4-bis(1,1-dimethylethyl)-6-(2-hydroxyethoxy)phenoxy]ethane (**6b**)*

A sample of compound **5b** (15 g, 0.056 mol) was dissolved in 50 mL of dry DMF at 80 °C under nitrogen flux. To the stirred solution was added NaH (2.7 g, 0.11 mol) and after 30 minutes was slowly dropped a solution of ethylene glycol ditosylate (10.42 g, 0.028 mol) dissolved in 100 mL of DMF dry. The reaction was stirred at 160 °C for 12 hours. The solvent was removed under reduced pressure and the residue was extracted in 100 mL of CH_2Cl_2 and 100 mL of 10% HCl (CAUTION!). The organic layer was washed twice with (2 × 100 mL) 10% HCl and then the solvent distilled off. After crystallisation with 1:1 mixture of ethyl ether and hexane,

compound **3** was obtained in 27% yield; m.p. 127–128 °C; ^{1}H NMR ($CDCl_3$): δ 6.99 (d, J = 2.2 Hz, 2H, ArH), 6.86 (d, J = 2.2 Hz, 2H, ArH), 4.41 (s, 4H, OCH_2CH_2O), 4.14 (s, 4H, OCH_2CH_2OH), 3.87 (t, J = 4.4 Hz, 4H, OCH_2CH_2OH), 1.45 (s, 18H, $C(CH_3)_3$), 1.33 (s, 18H, $C(CH_3)_3$); ^{13}C NMR ($CDCl_3$): δ 151.5, 146.2, 144.6, 142.9 (s, Ar), 116.2, 109.4 (d, Ar), 71.7 (t, $ArOCH_2$), 70.5 (t, $ArOCH_2CH_2OH$), 61.2 (t, CH_2OH), 35.4 (s, $C(CH_3)_3$), 34.8 (s, $C(CH_3)_3$), 31.5 (q, $C(CH_3)_3$), 30.8 (q, $C(CH_3)_3$); MS *m/z*: 558.8 (M^+). Anal. Calcd for $C_{34}H_{54}O_6$: C, 73.09; H, 9.73. Found: C, 73.16; H, 9.65.

*Synthesis of 1,2-bis[2-(2-hydroxyethoxy)phenoxy]ethane, bis(p-toluenesulfonate) (***7a***)*

A mixture of compound **6a** (2 g, 5.9 mmol), triethylamine (1.7 ml, 12 mmol) in dichloromethane (32 mL) was cooled at 0 °C. To this solution tosyl chloride (2.3 g, 12 mmol) and 4-dimethylaminopyridine DMAP (7.3 mg, 0.06 mmol) were added. After 3 h, the mixture was extracted with 50 mL of 10% HCl. The organic layer was dried over sodium sulfate and evaporated under vacuo. The pure product (**7a**) (2.3 g, 85%) was obtained by crystallisation from methanol; m.p. 91–93 °C; ^{1}H NMR ($CDCl_3$): δ 7.75 (d, J = 8 Hz, 2H, TsH), 7.27 (d, J = 8 Hz, TsH), 6.86–6.81 (m, 8H, ArH), 4.34 (s, 4H, $ArOCH_2CH_2OAr$), 4.19–4.16 (m, 8H, $TsOCH_2CH_2O$), 2.39 (s, 6H, $TsCH_3$); ^{13}C NMR ($CDCl_3$): δ 151.2, 148.1, 146.3, 144.7 (s, Ar), 129.7, 127.8, (d, Ar), 122.6, 121.8, 116.4, 115.2 (d, Ar), 68.2, 67.9, 67.4 (t, $ArOCH_2$), 21.4 (q, CH_3). MS *m/z*: 642 (M^+). Anal. Calcd for $C_{32}H_{34}O_{10}S_2$: C, 59.80; H, 5.33. Found: C, 59.69; H, 5.38.

*Synthesis of 1,2-bis[2,4-bis(1,1-dimethylethyl)-6-(2-hydroxyethoxy)phenoxy]ethane, bis(p-toluene sulfonate) (***7b***)*

This compound was obtained starting from **6b** and using the same procedure as for **7a**. After crystallisation with hexane, compound **7b** was obtained in 70% yield; m.p. 139–140 °C; ^{1}H NMR ($CDCl_3$): δ 7.73 (d, J = 8.3 Hz, 4H, TsH), 7.20 (d, J = 8.3 Hz, 4H, TsH), 7.01 (d, J = 2.3 Hz, 2H, ArH), 6.79 (d, J = 2.3 Hz, 2H, ArH), 4.34 (t, J = 2.1 Hz, 4H, OCH_2CH_2Ots), 4.30 (s, 4H, OCH_2CH_2O), 4.21 (t, J = 2.1 Hz, 4H, OCH_2CH_2OTs), 2.34 (s, 6H, $TsCH_3$), 1.37 (s, 18H, $C(CH_3)_3$), 1.29 (s, 18H, $C(CH_3)_3$); ^{13}C NMR ($CDCl_3$): δ 151.0, 145.6, 144.7, 142.9 (s, ArH), 132.9 (s, Ar), 129.8, 127.8, 117.3, 111.6 (d, ArH), 71.3 (t, OCH_2CH_2O), 68.5 (t, OCH_2CH_2OTs), 67.1 (t, OCH_2CH_2OTs), 35.3 (s, $C(CH_3)_3$), 34.6 (s, $C(CH_3)_3$, 31.4 (q, $C(CH_3)_3$), 30.6 (q, $C(CH_3)_3$), 21.5 (q, $ArCH_3$); MS *m/z*: 866.5 (M^+). Anal. Calcd for $C_{48}H_{66}O_{10}S_2$: 66.49; H, 7.67. Found: C, 66.52; H, 7.52.

*Synthesis of 2-(2-[2-(2-trityloxyethoxy)-ethoxy]-4-(1,1,3,3-tetramethylbutyl)phenoxy)-ethoxy-trityloxy-1-ethane (***11***)*

A sample of 4-*tert*-octyl-catechol **9** (0.9 g, 4.0 mmol) was dissolved in 400 mL of dry acetonitrile at 100 °C under nitrogen atmosphere. Then compound **10** (4.48 g, 8.80 mmol) was added and the reaction was stirred for 2 days. After cooling, the solvent was distilled off and the residue extracted with 150 mL of CH_2Cl_2 and 150 mL of 1 N HCl; the organic layer was washed twice with water and the solvent removed under reduced pressure. The crude product was obtained (95%) as an oil; ^{1}H NMR ($CDCl_3$): δ 7.48 (dd, 12H, J = 15 Hz, J = 7.3 Hz, ArH), 7.28–7.18 (m, 18H, ArH), 6.98 (bs, 1H, ArH), 6.90 and 6.86 (d, J = 1.5 Hz, 2H, ArH), 4.20–4.14 (m, 4H, $ArOCH_2$), 3.83–3.78 (m, 4H, $ArOCH_2CH_2O$), 3.67–3.66 (m, 4H, $OCH_2CH_2OC_{19}H_{15}$), 3.27–3.23 (m, 4H, $OCH_2CH_2OC_{19}H_{15}$), 1.69 (s, 2H, $(CH_3)_3CCH_2C(CH_3)_2$), 1.33 (s, 6H, $(CH_3)_3CCH_2C(CH_3)_2$), 0.72 (s, 9H, $(CH_3)_3CCH_2C(CH_3)_2$); ^{13}C NMR ($CDCl_3$): δ 144.5 (s, ArH), 129.0, 127.9, 127.2 (d, Ar), 119.8, 115.3, 115.0 (d, Ar), 86.9 (s, $C(C_6H_5)_3$), 71.1, 70.3, 68.9, 63.7 (t, OCH_2CH_2O), 57.4 (t, $(CH_3)_3CCH_2C(CH_3)_2$), 38.5 (s, $(CH_3)_3CCH_2C(CH_3)_2$), 32.6 (s, $(CH_3)_3CCH_2C(CH_3)_2$), 32.0 (q, $(CH_3)_3CCH_2C(CH_3)_2$); MS *m/z*: 882.1 (M^+), 640.0 ($[M-(C_{19}H_{15}]^+$). Anal. Calcd for $C_{60}H_{66}O_6$: C, 81.59; H, 7.53. Found: C, 81.47; H, 7.41.

*Synthesis of 2-(2-[2-(2-hydroxy-ethoxy)-ethoxy]-4-(1,1,3,3-tetramethylbutyl)phenyloxy)-ethoxy-1-ethanol (***12***)*

A sample of crude compound **11** (4.7 g, 5.32 mmol) was dissolved at room temperature in 100 mL of CH_2Cl_2 and CH_3OH (1:1) and then 0.5 mL of 12N HCl were added. After 3 hours the reaction was cooled to 0 °C, 50 mL of 5% $KHCO_3$ solution were added slowly and the solution was stirred for 30 minutes. Then the solvent was distilled off under reduced pressure and the residue extracted with 100 mL of CH_2Cl_2 and 100 mL of 1 N HCl. The organic layer was washed twice with water and the solvent removed under reduced pressure; the crude product was purified on a silica gel column using CH_2Cl_2/MeOH 10:0.5 as eluent. The product was obtained as yellow oil in 80% yield; ^{1}H NMR ($CDCl_3$): δ 6.91 (dd, J = 8.1 Hz, J = 2.1 Hz, 2H, ArH), 6.79 (d, J = 8.1 Hz, 1H, ArH), 4.18-1.13 (m, 4H, $ArOCH_2CH_2O$), 3.91–3.87 (m, 4H, $ArOCH_2CH_2O$), 3.77–3.74 (m, 4H, $ArOCH_2CH_2O$), 3.70–3.66 (m, 8H, $ArOCH_2CH_2O$), 1.68 (s, 2H, $(CH_3)_3CCH_2C(CH_3)_2$), 1.33 (s, 6H, $(CH_3)_3CCH_2C(CH_3)_2$), 0.72 (s, 9H, $(CH_3)_3CCH_2C(CH_3)_2$); ^{13}C NMR ($CDCl_3$): δ 147.4, 144.6, 144.1 (s, Ar), 119.1, 112.9 (d, Ar), 72.7, 69.4, 68.8, 68.5, 61.6, 57.0 (t, OCH_2CH_2O), 39.1 (s, $(CH_3)_3CCH_2C(CH_3)_2$), 32.4 (s, $(CH_3)_3CCH_2C(CH_3)_2$), 31.7, 31.6 (q, $(CH_3)_3CCH_2C(CH_3)_2$); MS *m/z*: 398.5 (M^+). Anal. Calcd for $C_{22}H_{38}O_6$: C, 66.30; H, 9.61. Found: C, 66.15; H, 9.56.

*Synthesis of 2-(2-[2-(2-hydroxy-ethoxy)-ethoxy]-4-(1,1,3,3-tetramethylbutyl)phenyloxy)-ethoxy-1-ethanol, bis(p-toluenesulfonate) (***13***)*

Compound **12** (1.3 g, 3.3 mmol), was dissolved in dry CH_2Cl (75 mL) at room temperature and under nitrogen atmosphere. The stirred solution was cooled at 0 °C and tosyl chloride (1.89 g, 9.9 mmol), triethylamine dry (6 mL), and a catalytic amount of dimethylaminopyridine (DMAP)

were slowly added. After 12 hours the solvent was removed under reduced pressure and the residue was extracted with 100 mL of CH_2Cl_2 and 100 mL of 1 N HCl. The organic layer was washed twice with 100 mL of water and the solvent distilled off to give compound **13** (>95%) as oil; ^{1}H NMR ($CDCl_3$): δ 7.80 (dd, J = 9.0 Hz, J = 1.7 Hz, 4H, TsH), 7.30 (dd, J = 9.0 Hz, J = 1.7 Hz, 4H, TsH), 6.91 (s, 1H, ArH), 6.90 (dd, J = 8.1 Hz, J = 2.2 Hz, 2H, ArH), 6.77 (d, J = 8.1Hz, 1H, ArH), 4.19–4.16 (m, 4H, ArOCH_2), 4.10–4.02 (m, 4H, CH_2OTs), 3.79–3.73 (m, 8H, CH_2OCH_2), 2.45 (s, 6H, TsCH_3), 1.68 (s, 2H, $(CH_3)_3$CCH_2C$(CH_3)_2$), 1.33 (s, 6H, $(CH_3)_3$CCH_2C(C$H_3)_2$), 0.71 (s, 9H, (C$H_3)_3$CCH_2C$(CH_3)_2$), ^{13}C NMR ($CDCl_3$): δ 148.4, 146.5, 144.9, 144.3 (s, Ar), 133.5, 130.0, 128.2, 119.9, 114.6 (d, Ar), 70.3, 69.9, 69.2 (t, OCH_2CH_2O), 57.3 (t, $(CH_3)_3$C*C*H_2C$(CH_3)_2$), 38.5 (s, $(CH_3)_3$CCH_2*C*$(CH_3)_2$), 31.8 (s, $(CH_3)_3$*C*CH$_2$C$(CH_3)_2$), 31.9 (q, (*C*$H_3)_3$CCH_2C(*C*$H_3)_2$), 21.6 (q, Ar*C*H_3); MS *m/z*: 706.4 (M^+). Anal. Calcd for $C_{36}H_{50}O_{10}S_2$: C, 61.21; H, 7.13. Found: C, 60.95; H, 7.15.

*General Procedure for the synthesis of 25,27-dialkoxycalix[4]arene-benzocrown-6 (**1–3**)*

25,27-Dialkoxycalix[4]arene **8a–b** (2 mmol) was dissolved in CH_3CN (300 mL) and an excess of Cs_2CO_3 (2.60 g, 8 mmol) and of the proper glycol di-*p*-toluenesulfonate (2.5 mmol) added under a nitrogen atmosphere. The reaction mixture was refluxed for 16-24 h. Then CH_3CN was removed under reduced pressure and the residue extracted with 70 mL of CH_2Cl_2 and 70 mL of 10% HCl. The organic phase was separated, washed twice with water and the solvent distilled off. The pure compounds were isolated as described below.

*25,27-Dioctyloxycalix[4]arene-dibenzo-crown-6 (**1**)*

Calix-benzocrown **1** was obtained from the oily residue after column chromatography (SiO_2, THF/esano: 1/9) and crystallisation from methanol; yield = 68%; m.p. 130 °C; ^{1}H NMR ($CDCl_3$): δ 7.10-6.99 (m, 12H, ArH), 6.80 (t, J = 6.5 Hz, 2H, ArH para), 6.78 (d, J = 6.5 Hz, 4H, ArH meta), 6.58 (t, J = 6.5 Hz, 2H, ArH para), 4.37 (s, 4H, ArOCH_2CH_2OAr), 3.77 (s, 8H, ArCH_2Ar), 3.63 (t, J = 6 Hz, 4H, ArOCH_2CH$_2$OArO), 3.47 (t, J = 6 Hz, 4H, ArOCH$_2$CH_2OArO), 3.36 (t, J = 6 Hz, 4H, ArOCH_2R), 1.36–1.1 (m, 24H, OCH$_2$(C$H_2)_6$CH$_3$), 0.92 (t, J = 6.5 Hz, 6H, —CH$_3$). ^{13}C NMR ($CDCl_3$): δ 157.3, 156.4 (s, Ar ipso), 151.7, 149.4 (s, Ar), 134.6, 134.4 (s, Ar ortho), 130.0, 129.6 (s, Ar meta), 124.4, 123.0, 122.8, 122.6, 122.1, 115.6 (d, Ar para), 70.9, 70.8, 68.8, 67.9 (t, OCH_2), 38.5 (t, Ar*C*H$_2$Ar), 32.4, 30.1, 29.8, 29.6, 26.2, 23.2 (t, *C*H$_2$), 14.6 (q, *C*H$_3$); MS *m/z*: 945.9 (M^+). Anal. Calcd for $C_{62}H_{74}O_8$: C, 78.61; H, 7.87. Found: C, 78.66; H, 7.92.

*25,27-Di-iso-propoxycalix[4]arene-bis(di-tert-butylbenzo)-crown-6 (**2**)*

Compound **2** was obtained after crystallisation with methanol; yield = 74%; m.p. 241–242 °C; ^{1}H NMR ($CDCl_3$): δ 7.12 (d, J = 2.4 Hz, 2H, ArH), 7.02 (d, J = 7.4 Hz, 4H, ArH), 6.88 (d, J = 2.4 Hz, 2H, ArH), 6.86 (t, J = 7.4 Hz, 2H, ArH), 6.82 (d, J = 7.4 Hz, 2H, ArH), 6.32 (t, J = 7.4 Hz, 2H, ArH), 4.39 (s, 4H, OCH_2CH_2O), 4.17 (q, J = 6.1 Hz, 2H, C$H(CH_3)_2$), 3.84 (s, 8H, ArCH_2Ar), 3.59 and 3.47 (t, J = 5.6 Hz, 4H each, OCH_2CH_2O), 1.48 (s, 18H, C$(CH_3)_3$), 1.32 (s, 18H, C$(CH_3)_3$), 0.80 (d, J = 6.1 Hz, 12 H, CH$(CH_3)_2$), ^{13}C NMR ($CDCl_3$): δ 156.8, 155.2 (s, Ar ipso), 153.2, 145.6, 144.6, 142.8 (s, Ar), 133.7, 133.6 (s, Ar ortho), 129.7, 129.2 (s, Ar meta), 121.9, 121.6 (d, Ar para), 118.1, 116.3 (d, Ar), 76.9 (d, *C*H$(CH_3)_2$), 70.5, 70.0, 67.8 (t, O*C*H$_2$), 39.2 (t, Ar*C*H$_2$Ar), 35.6 (s, *C*$(CH_3)_3$), 34.8 (s, *C*$(CH_3)_3$), 31.5 (q, C(*C*$H_3)_3$), 30.9 (q, C(*C*$H_3)_3$), 21.7 (q, CH(*C*$H_3)_2$); MS *m/z*: 1030.8 (M^+). Anal. Calcd for $C_{68}H_{86}O_8$: C, 79.19; H, 8.39. Found: C, 79.27; H, 8.51.

*25,27-Di-iso-propoxycalix[4]arene-(tert-octylbenzo)-crown-6 (**3**)*

Calix-benzocrown-6 (**3**) was obtained after purification on a silica gel column using first CH_2Cl_2 (100%) and then CH_2Cl_2/MeOH (10:1) as eluent; yield = 80%; m.p. 77–79 °C; ^{1}H NMR ($CDCl_3$): δ 7.03 (d, J = 7.4 Hz, 8H, ArH), 6.99–6.95 (m, 2H, ArH), 6.89 (d, J = 8.4 Hz, 1H, ArH), 6.80 (t, J = 7.4 Hz, 4H, ArH), 6.65 (t, J = 7.4 Hz, 4H, ArH), 4.26 (q, J = 6.0 Hz, 2H, $(CH_3)_2$CHO), 4.20–4.13 (m, 4H, ArOCH_2), 3.78 (d, J = 15.4 Hz, 4H, ArCH_2Ar), 3.74 (d, J = 15.4 Hz, 4H, ArCH_2Ar), 3.69–3.62 (m, 4H, ArOCH_2), 3.48–3.39 (m, 8H, CH$_2$OCH_2), 1.73 (s, 2H, $(CH_3)_3$CCH_2C$(CH_3)_2$), 1.39 (s, 6H, $(CH_3)_3$CCH$_2$C(C$H_3)_2$), 0.96 (q, J = 6.0 Hz, 12H, (C$H3)_2$CHO), 0.76 (s, 9H, (C$H_3)_3$CCH$_2$C$(CH_3)_2$); ^{13}C NMR ($CDCl_3$): δ 156.6, 154.7 (s, Ar ipso), 148.5, 147.6, 144.1 (s, Ar), 134.6, 133.6 (s, Ar ortho), 130.5, 129.9 (d, Ar meta), 121.8, 121.6 (s, Ar para), 119.7, 115.3, 114.0 (d, Ar), 70.6 (d, *C*H)CH$_3)_2$), 70.4, 70.2, 69.7, (t, OCH$_2$), 57.3 (t, $(CH_3)_3$CCH_2C$(CH_3)_2$), 38.7 (t, Ar*C*H$_2$Ar), 38.2 (s, $(CH_3)_3$CCH$_2$*C*$(CH_3)_2$), 32.3 (s, $(CH_3)_3$*C*CH$_2$C$(CH_3)_2$), 31.7 (q, (*C*$H_3)_3$CCH$_2$C$(H_3)_2$), 21.8 (q, CH(*C*$H_3)_2$). MS *m/z*: 870.4 (M^+). Anal. Calcd for $C_{56}H_{70}O_8$: C, 77.20; H, 8.09. Found: C, 77.10; H, 8.00.

Extraction from simulated waste

Calixarenes were dissolved in NPHE at a concentration of 10^{-2} M in NPHE. Liquid-liquid extraction experiments were performed by contacting for one hour the same volumes of organic and aqueous phases inside agitated closed tubes placed in a thermostated cell (25 $\pm$ 0.2 °C). Complete separation of phases was ensured by placing the tubes into a centrifuge for five minutes. Then aliquots of aqueous and organic were removed for analysis by γ spectrometry (Eurysis Mesures). The measurement times were adapted to obtain a reproducibility between $\pm$5%.

The distribution coefficients D_M were determined as the ratio of cation γ activity in the organic phase to cation γ activity in the aqueous phase. The selectivity for the cation M_1 over M_2 is expressed as α, the ratio of distribution coefficients of the two cations.

$$D_M = \frac{\sum[M]_{org}}{\sum[M]_{aq}}$$

$$\alpha = \frac{D_{M_1}}{D_{M_2}}$$

where $\sum[M]_{org}$ and $\sum[M]_{aq}$ are the sums of all the species containing the metal ion at the equilibrium in the organic and aqueous phase, respectively.

Stability constants and thermodynamic parameters determination

The stability constants of the complexes, $K_a = [ML]/[M][L]$ are expressed as concentration ratios, and are related to the equilibrium

$$M^+ + L \rightleftharpoons ML^+$$

where M^+ = metal cation and L = neutral ligand. They were determined in acetonitrile (at 25 °C and constant ionic strength 0.01 M in Et_4NClO_4) by UV absorption spectrophotometry using Li^+, Na^+, Na^+, K^+, Rb^+ perchlorates and Cs^+ nitrate. The values given in the Table 4 correspond to the arithmetic means of at least three independent determinations. The calorimetric determinations were made at 25 °C, using a precision isoperibol titration calorimeter (Tronac 450, Orem, Utah) connected to a computing system. For solubility reasons the iodide salts were titrated into 50 mL solution of the proper calixarene ligand. The temperature *vs.* time curve was automatically converted into a heat vs. mole of titrant added curve, then automatically corrected by an appropriate program. Heat-of-dilution corrections were made by titrating the metal ion solution into the solvent. When log K_a was higher than 5, the number of moles of the salt added to the ligand solution was equal to the number of moles of the complex formed and the measured heat directly related to the complexation enthalpy ΔH°. ΔS° could then be derived from the expression $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$, knowing $\Delta G^\circ = RT \ln K_a$.

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