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Synergistic Extractions of Alkali Ions by *p-tert*-Butylcalix[4]arene and Crown Ether Mixtures

I. NATATOU, M. BURGARD, Z. ASFARI and J. VICENS
Laboratoire de Chimie Minérale et Analytique (URA 405 du C.N.R.S.), Ecole Européenne des Hautes Etudes des Industries Chimiques de Strasbourg (EHICS), 1, rue Blaise Pascal. B.P. 296, F-67008 Strasbourg Cedex, France.

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Abstract. Mixtures of macrocyclic crown ethers ($L' =$ DC18C6, DB18C6, 18C6; $L'' =$ B15C5) and *p-tert*-butylcalix[4]arene (LH_4) in dichloroethane exhibit synergistic effects in the extraction of alkali ions (M^+). These extractions are described by two independent reactions:
– a two phase ion exchange:

$$LH_{4org} + M^+_{aq} \rightleftharpoons MLH_{3org} + H^+_{aq}, \quad (K_{ex})$$

– the formation of an adduct in the organic phase:

$$MLH_{3org} + nL'_{org}(\text{or } nL''_{org}) \rightleftharpoons LH_3ML'_{norg}(\text{or } LH_3ML''_{norg})(K_{fn}).$$

It is shown that $n = 1$ for all the systems including 18 membered crown ethers (M = Na, K, Rb, Cs) and for the Na^+–B15C5 system; whereas $n = 2$ in the case of the K^+–B15C5 and Rb^+–B15C5 systems. Ion size effects on the stability constant of the adducts reveal strong interactions between the crown ether and the cation in the above mentioned systems. The corresponding adduct in the Cs^+—B15C5 system has a very low stability constant in comparison with the others. This seems to show that B15C5 is unable to remove the Cs^+ ion from the calixarene 'cup' in the cesium calixarenate complex.

Key words: *p-tert*-Butylcalix[4]arene, crown ethers, alkali ions, liquid–liquid extraction, synergistic effects.

1. Introduction

The weak acidity of the calixarenes is responsible for their carrier properties in proton coupled counter transport through a liquid membrane [1, 2]. The observed selectivity is always towards cesium and is independent of the size of the calixarene ring. Particularly interesting are the investigations of the *p-tert*-butylcalix[4]arenes, which are rigid macrocycles and for which it has been shown that cesium transport is very sensitive to the size and shape of the cyclic entity including the aromatic groups [3]. Indeed, the X-ray structure has shown that in the cesium complex the cation is located within the calixarene 'cup'[4].

In addition, it has been shown that the transport properties can be considerably modified by the insertion of a polyoxyethylene chain linked to the two phenoxy groups and generating a crown ether entity (calixcrown) [5]. The complementarity between the size of the crown cavity and the size of the cation appears to be the main factor which controls the transport selectivity.

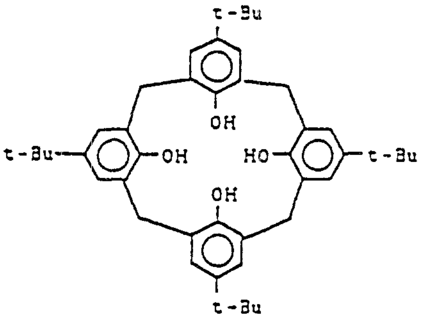
An alternative approach to the influence of crown ethers on the complexing properties of cyclic (calixarenes) and non-cyclic oligomers of phenols can be proposed by considering the liquid–liquid extraction of alkali ions by the calixarenes and the modifications brought about by the presence of a neutral crown ether on the alkali ion extraction. Such an investigation has already been carried out by considering mixtures containing a crown ether and a non-cyclic oligomer of phenol or a non-rigid calixarene (calix[6]arene) [6]. In these systems it was shown that the extraction efficiency trends follow the complementarity between the size of the crown cavity and the size of the cation.

In a similar way we investigate in this paper systems which include a crown ether and the more rigid *p-tert*-butylcalix[4]arene, and consider particularly the cesium systems in view of the known structure and stability of the cesium calixarenate complex [4].

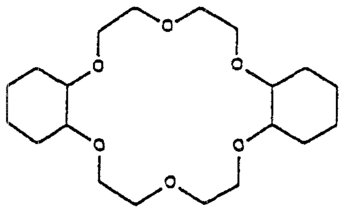
2. Materials and Experimental

Cesium chloride (99.9 %) was from Fluka, rubidium chloride (99.5 %) was from Merck, potassium chloride (99.5 %) was from Prolabo 'Normapur', sodium chloride (99.5 %) was from SDS, cesium hydroxide (99.5 %) and rubidium hydroxide (99.5 %) were from Janssen, potassium hydroxide (99 %) and sodium hydroxide (99.5 %) were from Merck. The alkali ion solutions were prepared using distilled water. The dichloroethane (SDS) was purified by pre-equilibration with water (removal of the stabiliser). The macrocyclic *p-tert*-butylcalix[4]arene (compound I) (Figure 1) was synthesized according to reference [7]. The crown ethers dicyclohexano-18-crown-6 (compound II) was the commercial isomer mixture (*cis-syn-cis* and *cis-anti-cis*), purum > 97 %, dibenzo-18-crown-6 (compound III), purum > 98 %, 18-crown-6 (compound IV), purum >97 % were from Fluka and benzo-15-crown-5 (compound V), purum > 99 % was from Merck. All these chemicals were used without further purification.

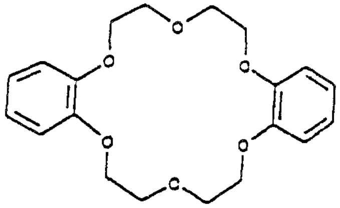
Liquid–liquid extraction experiments were carried out using a thermostated conductimetric cell. 100 mL of the aqueous phase (alkali chloride: MCl, 0.5 M) and 100 mL of the organic phase (dichloroethane solutions) were introduced and vigorously stirred by means of a rotating glass blade (500 rpm) for 20 min. The pH adjustments were carried out by adding small volumes of the corresponding M(Cl -OH) (0.5 M) mixture. The alkali organic concentrations were determined by taking aliquots (3 mL) which were stripped with 6 mL of acidic water (pH ~ 1.5). In this way, quantitative transfers of the alkali ion from the organic to the acidic water phase were obtained. This aqueous phase was sampled and analysed using a Perkin-



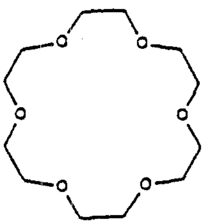
Compound I
p-tert-butylcalix[4]arene (LH_4)



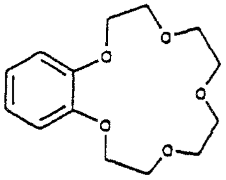
Compound II
Dicyclohexano-18-crown-6 (DC18C6)



Compound III
Dibenzo-18-crown-6 (DB18C6)



Compound IV
18-crown-6 (18C6)



Compound V
Benzo-15-crown-5 (B15C5)

Fig. 1. Compounds used as extractants.

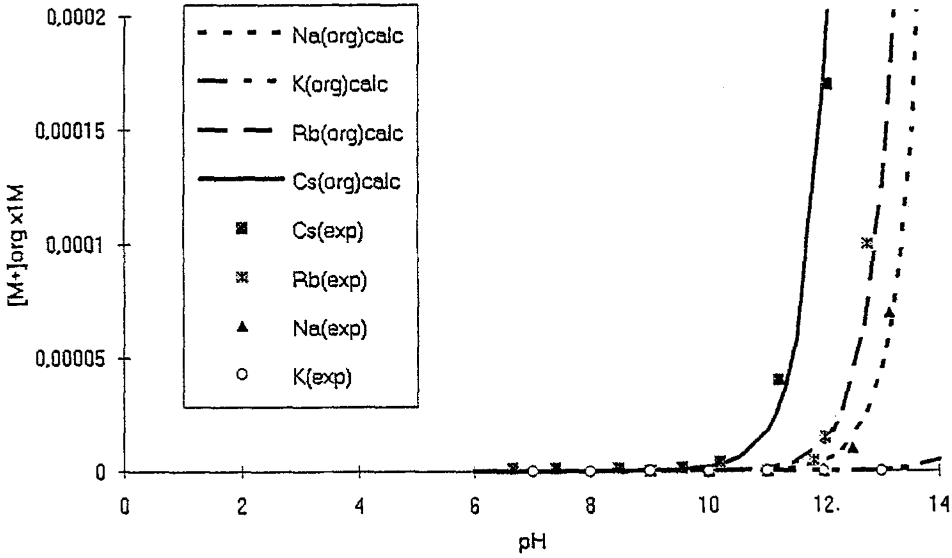


Fig. 2. Extraction of sodium, potassium, rubidium, cesium from the corresponding chlorides (0.5 M in the water phase) by *p-tert*-butylcalix[4]arene (LH_4) alone (10^{-3} M in dichloroethane). Organic alkali ion concentrations as a function of pH. The calculated curves correspond to the K_{ex} values given in Table I.

TABLE I. Extraction of M^+ by *p-tert*-butylcalix[4]arene in dichloroethane: evaluated K_{ex} values.

Metal	Cs^+	Rb^+	K^+	Na^+
$\text{Log}(K_{ex})$	−12.47	−13.60	−16	−14.05

Elmer (2380) Atomic Emission Spectrophotometer with an air–acetylene flame. Extraction experiments perfomed with pure dichloroethane showed no detectable presence of alkali ions in the organic phase.

The mass spectra of the organic phases were obtained using a fast-atom (xenon) bombardment excitation source (FAB^+MS) on a ZAB HF VG Analytical instrument. The samples were dissolved in *m*-nitrobenzyl alcohol as matrix and subjected to impingement by atoms accelerated at 8 kV. Fragments having a mass-to-charge ratio up to 900 were detected.

3. Results and Discussion

It has been shown that when the transport is controlled by the diffusion of the transported species, parameters which describe the two phase equilibria (uptake from the feed phase in the membrane and release from the membrane into the receiving phase) are key data in explaining the transport kinetics [8]. In addition, extraction

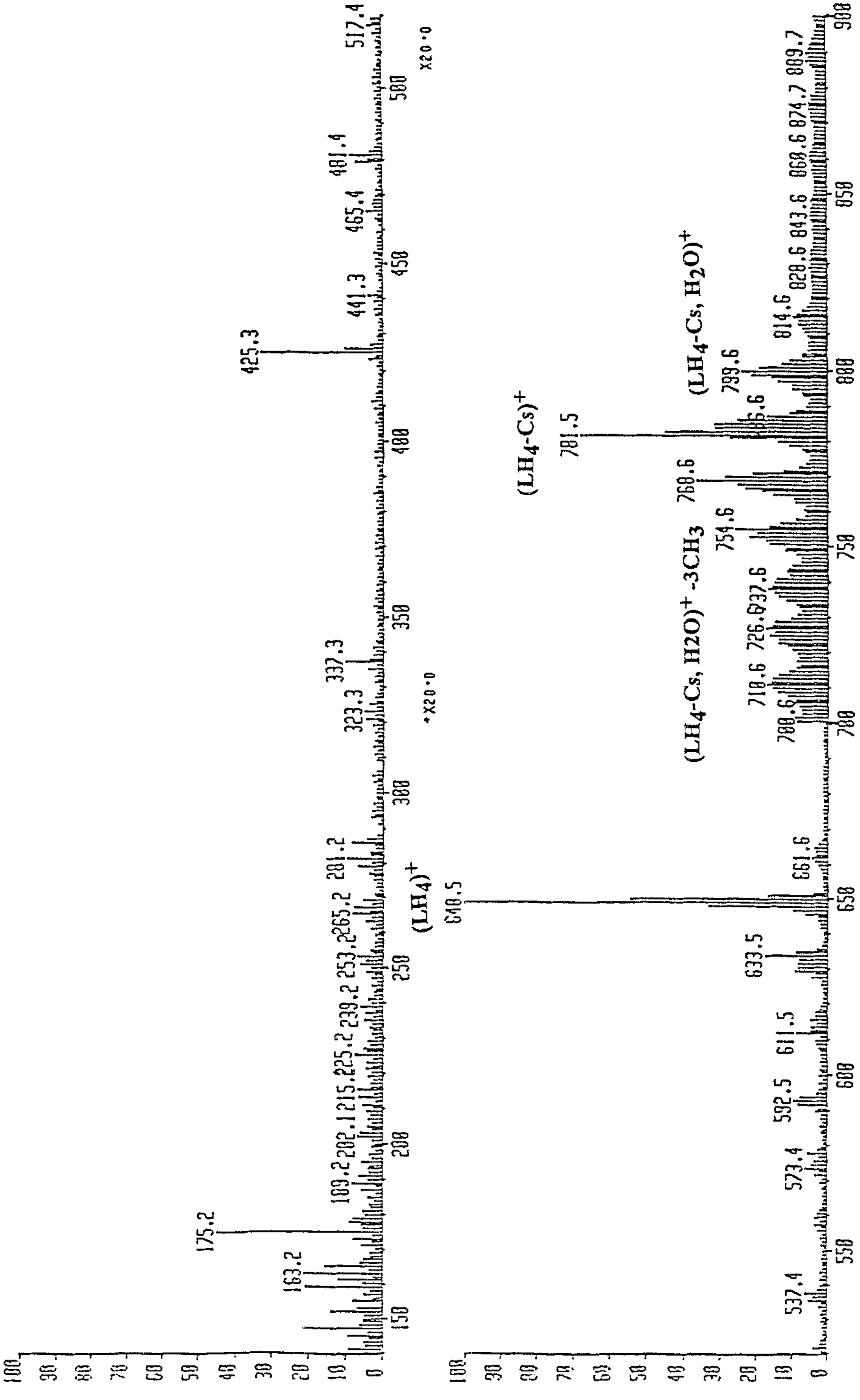


Fig. 3. Extraction of cesium by LH_4. Mass spectrum (FAB^+) of the organic phase ($LH_{4o} = 10^{-3}$ M, pH of the aqueous phase = 12).

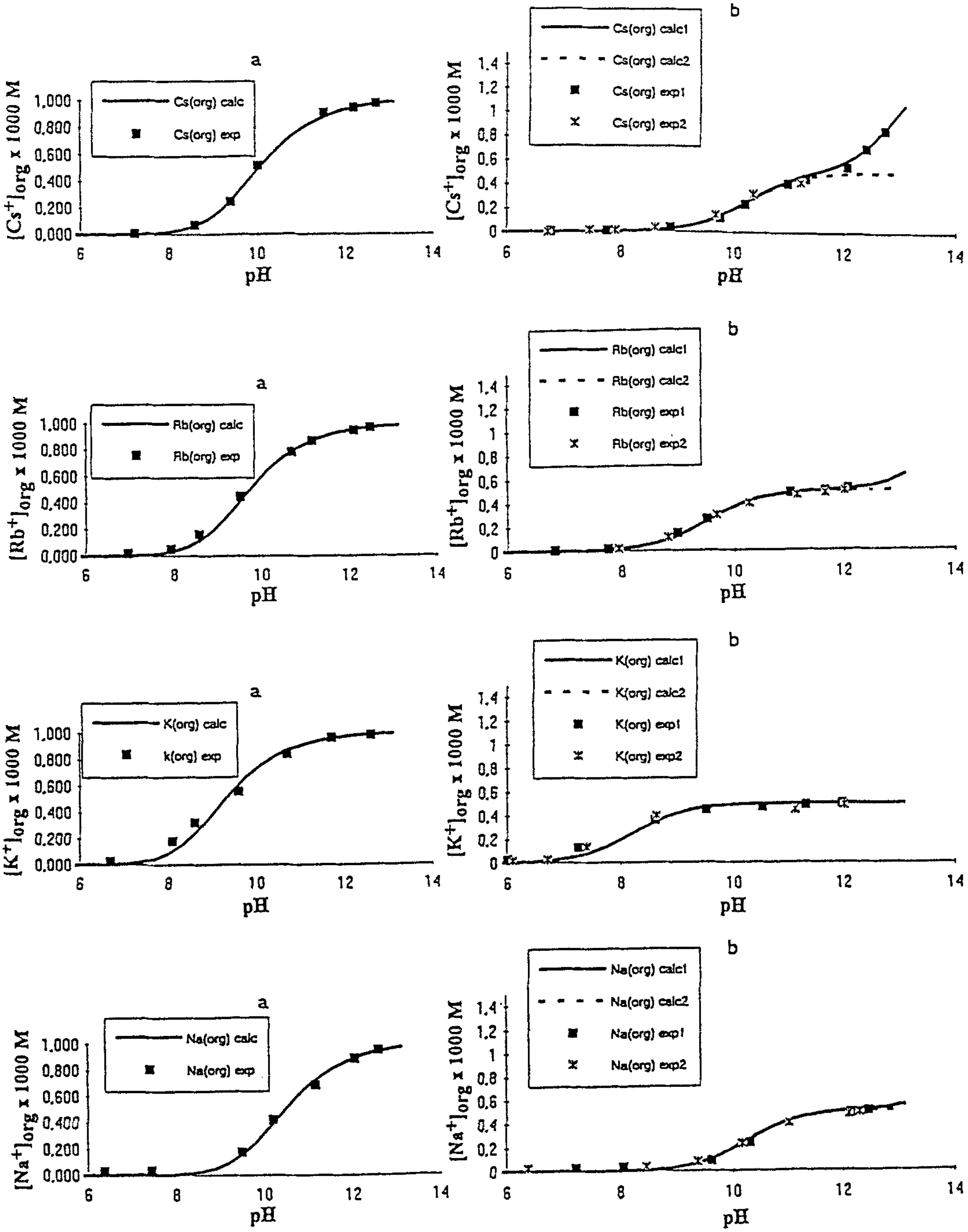


Fig. 4. Extraction of sodium, potassium, rubidium, cesium from the corresponding chlorides (0.5 M in the water phase) by *p-tert*-butylcalix[4]arene (LH_4)-dicyclohexano-18-crown-6 (L') mixtures in dichloroethane. Organic alkali ions concentration as a function of pH. (a) LH_{4o} = $L'o = 10^{-3}$ M; (b) postscript 1: $LH_{4o} = 1.5\ 10^{-3}$ M, $L'o = 0.5\ 10^{-3}$ M, postscript 2: $LH_{4o} = 0.5\ 10^{-3}$ M, $L'o = 1.5\ 10^{-3}$ M. The calculated curves correspond to the equilibrium data given in Tables I, II and III.

studies can provide a more precise description of the nature of the chemical species involved in the phase transfer process. Calix[4]arene (LH_4) extracts alkali ions via a pH dependent ion exchange (Figure 2). The fact that no more than one OH group could be deprotonated is confirmed by the fact that the experimental pH dependency of the metallic organic concentration (Figure 2) can be satisfactorily described by plotting the corresponding calculated function deduced by assuming the single coupled ion-proton exchange reaction

$$LH_{4\mathrm{org}} + M^+_{\mathrm{aq}} \rightleftharpoons MLH_{3\mathrm{org}} + H^+_{\mathrm{aq}} \quad (\text{equilibrium } a)$$

with the corresponding expression for the extraction constant

$$K_{\mathrm{ex}} = [MLH_{3\mathrm{org}}][H^+_{\mathrm{aq}}]/M^+_{\mathrm{aq}}][LH_{4\mathrm{org}}].$$

Indeed K_{ex} can be rewritten by introducing the experimental concentrations:

$$K_{\mathrm{ex}} = M_{\mathrm{org}}[H^+_{\mathrm{aq}}]/[M^+_{\mathrm{aq}}][LH_{4\mathrm{o}} - M_{\mathrm{org}}]$$

M_{org} being equal to the organic metallic concentration; $[M^+_{\mathrm{aq}}]$ being the metallic concentration in the aqueous phase which remains practically equal to the initial metallic concentration within the experimental conditions and $LH_{4\mathrm{o}}$ being the initial calixarene concentration in the organic phase. A satisfactory agreement between the experimental and calculated $M_{\mathrm{org}} = f(\mathrm{pH})$ is obtained for appropriate values of K_{ex} (Table I). FAB$^+$ mass spectroscopy (Figure 3) of the organic phase of a cesium extraction from an aqueous solution (pH = 12, $[Cs^+_{\mathrm{aq}}] = 0.5$ M, $LH_{4\mathrm{o}} = 10^{-3}$ M) confirms the presence of the postulated complex $(LH_4Cs)^+$ (781.5) in the organic phase. In addition, it shows that this complex can also contain a residual water molecule (799.6: $(LH_4Cs\ H_2O)^+$).

The extraction order, based on the K_{ex} values

$$Cs^+ > Rb^+ > Na^+ > K^+,$$

is similar to that found for the steady state flux in liquid membrane studies [1,2]. As illustrated with the systems including DC18C6 (Figure 4), the presence of a crown ether drastically modifies the extraction of the alkali ions.

Owing to the fact that neutral crown ethers exhibit very poor extraction properties towards alkali chlorides [8] and that the modifications shown are pH dependent, it is clear that the presence of a crown ether in the extracting system generates a synergistic extraction characterized by the formation in the organic phase of an adduct including a metal ion, calixarene and crown molecules.

The extracting experiments were carried out using, for each cation, a single initial total extractant concentration ($LH_{4\mathrm{o}} + L'_{\mathrm{o}} = 2.0 \cdot 10^{-3}$ M) but three different values of the extractant concentration ratio, $r = LH_{4\mathrm{o}}/L'_{\mathrm{o}}$ (Figure 4) ($a : r = 1$; $b : r = 3$ and $r = 1/3$).

All the systems including the 18-membered crown ethers (DC18C6, DB18C6, 18C6) show very similar features, namely:

TABLE II. Evaluated stability constants log K_{f1} and log K_{f2} (*) of the adduct formed between MLH_3 and a crown ether in the dichloroethane phase.

	LH_4/DC18-6	LH_4/18-6	LH_4/DB18-6	LH_4/B15-5
Cs^+	5.78	5.30	4.30	–
Rb^+	7.48	6.70	5.70	1.4*
K^+	>10.30	>9.48	>8.48	>2.3*
Na^+	7.23	5.48	5.00	5.78

TABLE III. Synergistic equilibrium constants log K_{syn1} and log K_{syn2} (*) in the extraction of alkali ions by *p-tert*-butylcalix[4]arene-crown ether mixtures in dichloroethane (conditional constants; MCl_{aq} = 0.5M).

	LH_4/DC18-6	LH_4/18-6	LH_4/DB18-6	LH_4/B15-5
Cs^+	−6.69	−7.17	−8.17	–
Rb^+	−6.12	−6.90	−7.90	−12.65*
K^+	−5.70	−6.52	−7.52	−11.75*
Na^+	−6.82	−8.57	−9.05	−8.27

- for a given pH, the highest ion extraction is obtained for $r = 1$ with a saturation corresponding to the initial common extractant concentration.
- in a large pH range, the extraction is very similar for $r = n$ and $r = 1/n$ (as shown for $n = 3$).

These facts suggest that the synergistic extraction involves a species having a 1 : 1 : 1 metal–calixarene–crown ether stoichiometry according to the corresponding synergistic equilibrium (K_{syn1}):

$$LH_{4org} + M^+_{aq} + L'_{org} \rightleftharpoons LH_3ML'_{org} + H^+_{aq} \quad (\text{equilibrium } b_1)$$

However, it should be noted that in the case of rubidium and cesium, the presence of an excess of LH_4 ($r = 3$) also shows the contribution of equilibrium a to the overall extraction.

A recombination of equilibium a and equilibrium b_1 leads to the following monophasic equilibrium

$$MLH_{3org} + L'_{org} \rightleftharpoons LH_3ML'_{org} \quad (\text{equilibrium } c_1)$$

the constant of which, (K_{f1}), is related to K_{ex} and K_{syn1} by the equation

$$K_{f1} = K_{syn1} \cdot K_{ex}^{-1}$$

K_{syn1} and K_{f1} are evaluated by analysing the experimental $M_{org} = [LH_3M_{org}] + [LH_3ML'_{org}] = f$ (pH) plots, and by carrying out appropriate mass balance with

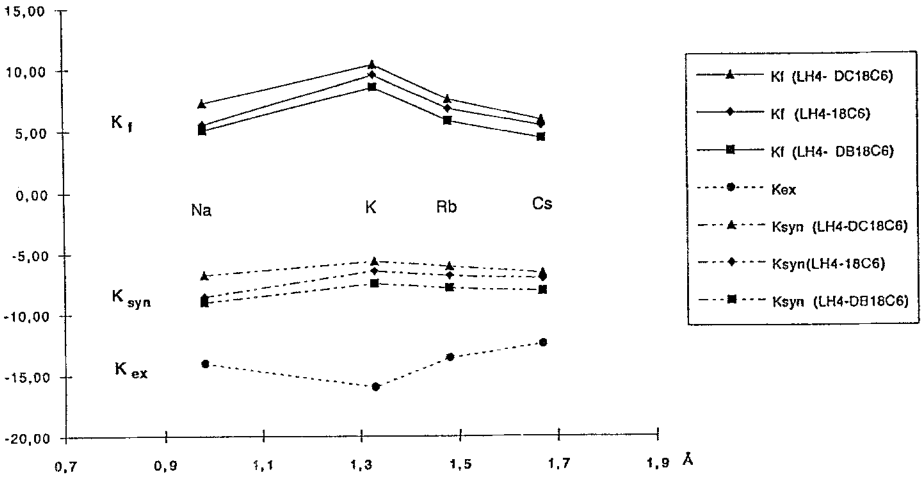


Fig. 5. Evolution of the K_{ex}s, K_{f1}s and K_{syn1}s plotted against the Pauling radii of the alkali ions.

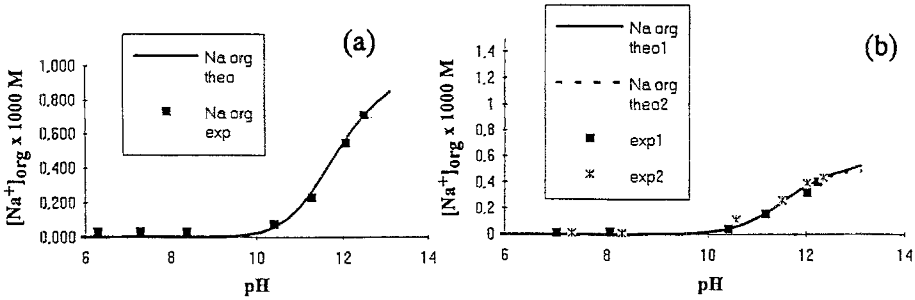


Fig. 6. Extraction of sodium from the corresponding chloride (0.5 M in the water phase) by *p-tert*-butylcalix[4]arene (LH_4)–benzo-15-crown-5 (L'') mixture in dichloroethane. Organic alkali ion concentration as a function of pH. (a) $LH_{4o} = L'_o = 10^{-3}$ M; (b) postscript 1: $LH_{4o} = 1.5\ 10^{-3}$ M, $L'_o = 0.5\ 10^{-3}$ M, postscript 2: $LH_{4o} = 0.5\ 10^{-3}$ M, $L'_o = 1.5\ 10^{-3}$ M. The calculated curves correspond to the equilibrium data given in Tables I, II and III.

the K_{ex} previously determined as well as the experimental concentrations. The best agreement is obtained for each system for values of K_f and K_{syn1} given in Tables II and III.

The very high values of the K_{f1}'s indicate the existence and high stability of the adduct formed between the LH_3M and a crown ether (L'). The correlation (Figure 5) between the K_{f1}'s and the cation size confirms that in the LH_3ML' complexes, strong interactions exist between the alkali ion and the 18-membered crown ether ring. Moreover, the fact that a similar relationship (Figure 5) is observed for K_{syn1} indicates that the crown ether–ion interactions play a major role in the overall stability of the crown ether–calixarene–ion complex. It can therefore be assumed that in the cesium system, K_{f1} measures the ability of the crown ether to 'remove'

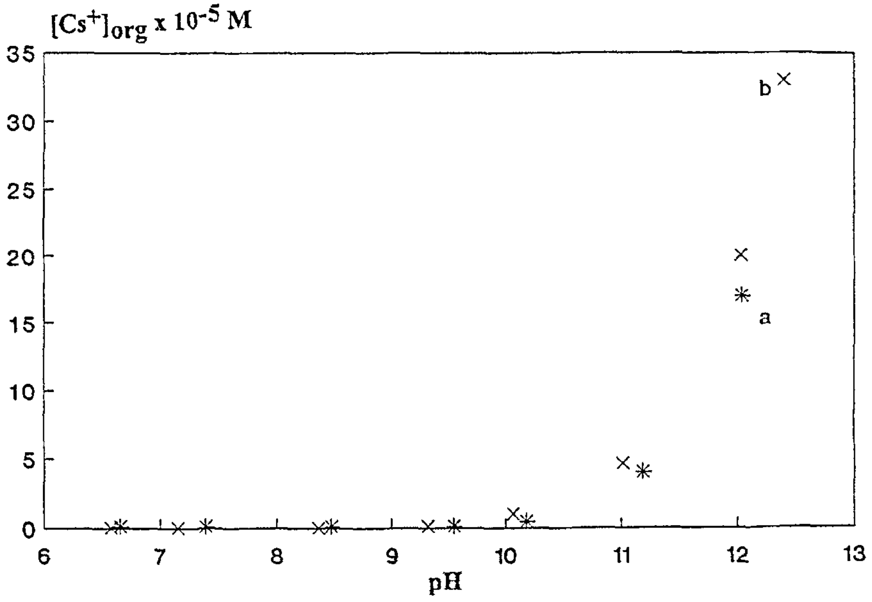


Fig. 7. Extraction of cesium from the corresponding chloride (0.5 M in the water phase) by *p-tert*-butylcalix[4]arene (LH_4)–benzo-15-crown-5 (L″) mixture in dichloroethane: (a) $LH_{4o} = 10^{-3}$ M; (b) $LH_{4o} = L''_o = 10^{-3}$ M.

the cesium ion from the calixarene cup, by forming a complex ion pair made up by a calix[4] arenate (LH_3^-) and a crown-Cs^+ cation.

In order to lower the interaction between the cation and the crown ether, liquid–liquid extractions using benzo-15-crown 5 (L″) instead of the 18-membered ring crown ethers have also been investigated by a similar procedure to that described above. The following results have been obtained:

- Stable complexes of formula $LH_3\ ML''_2$ have been characterized for potassium and rubidium from the experimental data considering equilibrium a (K_{ex}), the corresponding synergistic equilibrium (K_{syn2}):
  $$LH_{4org} + M^+_{aq} + 2L''_{org} \rightleftharpoons LH_3ML''^{+}_{2org} + H^+_{aq} \quad (\text{equilibrium } b_2)$$
  and the monophasic reaction (K_{f2})
  $$MLH_{3org} + 2L''_{org} \rightleftharpoons LH_3ML''_{2org} \quad (\text{equilibrium } c_2)$$
  The corresponding K_{f2} and K_{syn2} have been evaluated (Tables II and III).
- A stable complex ion pair is formed with sodium, the corresponding stoichiometry being $NaLH_3L''$ (Figure 6).

The presence of B15C5 in the extraction of cesium by LH_4 (Figure 7) shows a very low modification compared with other related LH_4–alkali–crown ether systems described above. This suggests that the corresponding ion pair complex is very unstable with respect to LH_3Cs.

FAB^+ mass spectra carried out on some synergistic systems (Cs–DC18C6–LH_4, Na–DC18C6–LH_4, K–DC18C6–LH_4, Na–B15C5–LH_4, Cs–B15C5–LH_4) do not confirm the existence of the corresponding complex ion pair. However they show the presence of the complex crown ether cation except in the case of the system Cs–B15C5–LH_4 which exhibits a feature very similar to that of the system Cs–LH_4.

4. Conclusion

The presence of a crown ether (L'= DC18C6, DB18C6, 18C6; L''= B15C5) in the extraction of an alkali ion ($M^+ = Na^+, K^+, Rb^+, Cs^+$) by *p-tert*-butylcalix[4]-arene (LH_4)in most cases generates a synergistic extraction characterized by the formation in the organic phase of a complex ion pair of formula LH_3ML' ($M^+ = Na^+, K^+, Rb^+, Cs^+$), LH_3ML'' ($M^+ = Na^+$) and $LH_3ML''_2$($M^+ = K^+, Rb^+$). Cation effects on the equilibrium constants K_f and K_{syn} indicate that the crown ether-metal ion interactions play a major role in the overall stability of the crown ether-calixarene-metallic ion complex. The extractions including DC18C6 lead to the formation of the most stable LH_3M–crown ether complex ion pairs whatever the nature (and size) of the alkali ion.

The results can also be interpreted in terms of the stabilization of the LH_3^- anion in relationship with the formation of large size ML'^+, ML''^+ or $ML_2''^+$ co-cations. This stabilization occurs in most cases, but remains highly questionable in the case of the LH_4–Cs–B15C5 system.

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