Solvent Extraction of Sodium and Potassium Ions by Dicarboxylated Calix[4]arenes

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Abstract. The extraction of sodium and potassium ions by 25,27-dicarboxymethyl-26,28-dimethoxy-5,11,17,23-tetra-tert-butyl calix[4]arene ($L^I H_2$) in chloroform shows the formation of $ML^I H$ and $M_2 L^I$ complexes (M = Na, K). In 1,2-dichloroethane, the $ML^I H$ species are formed in the acidic pH range, while only the $Na_2 L^I$ species is found at high pH values. The corresponding extraction equilibrium constants K_{11} (M) and K_{21} (M) have been evaluated and show a selectivity in favour of Na^+ as compared to K^+, whatever the nature of the complexes. In chloroform, this selectivity is much more pronounced considering the 2 : 1 complexes: $K_{11}(Na)/K_{11}(K) \ll K_{21}(Na)/K_{21}(K)$.

The coexistence of 1 : 1 and 2 : 1 metal : ligand complexes is also shown in the extraction of sodium in 1,2-dichloroethane by the 25,27-dicarboxymethyl-26,28-dimethoxyethoxy-5,11,17,23-tetra-tert-butyl calix[4]arene ($L^{II} H_2$), locked in the cone conformation.

Structural data of the complexes are discussed on the basis of ^{1}H-NMR spectra. In particular, for $L^I H_2$, a conformational change from cone to partial cone upon metal complexation has been evidenced for the complexes $KL^I H$, $K_2 L^I$ and $Na_2 L^I$.

Key words: Dicarboylated calix[4]arenes, sodium and potassium complexes, solvent extraction, selectivity, ^{1}H-NMR mononuclear and dinuclear species.

1. Introduction

Calixarenes are macrocyclic molecules made up of 4–8 phenolic units *meta*-linked by methylene bridges *ortho* to the OH functions [1, 2]. In particular, ionizable carboxylic calix[4]arene derivatives have been shown to be attractive complexing and extracting agents toward alkali [3–5], alkaline earth [5, 6] and rare earth cations [7, 8]. Indeed, they are rigid molecules whose properties can be modulated by the number of ionizable groups (frequently 2 or 4) which are attached to the calix[4]arene moiety as well as by the possibility to control their conformation.

In previous studies, we investigated the extraction properties of a dicarboxy-dimethoxy calix[4]arene derivative ($L^I H_2$) (Figure 1a) toward alkali ions in 1,2-dichloroethane [3, 4]. It was shown that the extraction occurs in the acidic pH range via the formation of mononuclear species for sodium, potassium, rubidium
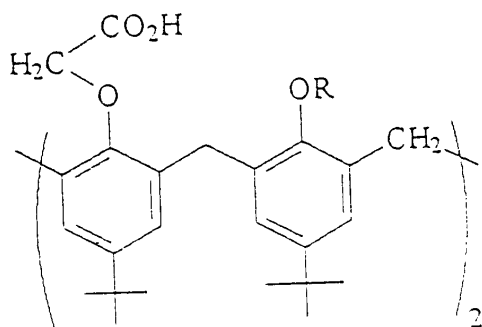
Figure 1. (a) The dicarboxymethyl-dimethoxy calix[4]arene (L^IH_2), R = CH_3. (b) The dicarboxymethyl-dimethoxyethoxy calix[4]arene ($L^{II}H_2$), R=$CH_2CH_2OCH_3$.

and caesium (L^IHM) and dinuclear species with lithium (L^ILi_2). Because of the occurrence of precipitates, the higher pH range was not investigated.

In this study, a closer investigation of the equilibria in a higher pH range is presented in connection with data obtained by using an alternative diluent, namely chloroform. Furthermore, the extraction properties of the dicarboxy-dimethoxy-ethoxy calix[4]arene ($L^{II}H_2$) (Figure 1b) with sodium in $C_2H_4Cl_2$ are studied and compared with those of the dicarboxy-dimethoxy calix[4]arene (L^IH_2). Due to the smaller size of the methoxy groups in L^IH_2 as compared to the methoxyethoxy groups in $L^{II}H_2$, allowing movement of the former through its annulus, the retention of the cone conformation upon complexation is expected to be less with L^IH_2. In both cases, ^{1}H-NMR studies have been carried out to provide information on the structure of the complexes formed and to assess the above expectation.

2. Experimental

2.1. ANALYTICAL PROCEDURES

The melting point (mp) was measured with a Büchi 500 apparatus, using capillaries sealed under nitrogen. Elemental analysis was performed at the *Service de Microanalyse* at the Institut de Chimie de Strasbourg. The ^{1}H-NMR spectra were recorded at 200 MHz on a Bruker SY200 spectrometer.

2.2. PREPARATION OF L^IH_2 AND $L^{II}H_2$

The carboxylated compound 25,27-dicarboxymethyl-26,28-dimethoxy-5,11,17,23-tetra-tert-butyl calix[4]arene (L^IH_2) was prepared according to the literature [3].

The 25,27-dicarboxymethyl-26,28-dimethoxyethoxy-5,11,17,23-tetra-tert-butyl calix[4]arene ($L^{II}H_2$) was prepared as follows: a 250 mL round-bottomed flask was equipped with a condenser and charged with a 1:1 mixture of water and ethanol (200 mL), potassium hydroxide (5 g, 89.1 mmol) and the dioxyacetate precursor $L^{II}Et_2$ [9] (3 g, 3.2 mmol). The contents were stirred while refluxing

for 2 h. After cooling to room temperature, concentrated hydrochloric acid was added to pH 1–2. A precipitate appeared which was filtered off and washed with water. Recrystallisation from ethanol–dichloromethane afforded pure L^{II}H$_2$ (2.79 g). Yield 83% mp 158–160°C.

^{1}*H-NMR* (CDCl$_3$) in ppm from chloroform (7.26 ppm): 0.84 (s, 18H, t-C$_4$H$_9$), 1.35 (s, 18H, t-C$_4$H$_9$), 3.25 (d, J_{H-H} = 13.0 Hz, ArCH$_2$Ar), 3.46 (s, 6H, OCH$_3$), 3.76 (m, 4H, ArO*CH*$_2$CH$_2$OCH$_3$, determined by NOE experiments), 3.97 (m, 4H, ArOCH$_2$*CH*$_2$OCH$_3$), 4.42 (d, J_{H-H} = 13.0 Hz, ArCH$_2$Ar), 4.75 (s, 4H, ArOCH$_2$COOH), 6.48 (s, 4H, ArH), 7.18 (s, 4H, ArH). *Elemental analysis*: C% 64.00 H% 7.29 *calculated for* C$_{54}$H$_{72}$O$_{10}$·2CH$_2$Cl$_2$; *found* C% 64.34 H% 7.17.

2.3. LIQUID–LIQUID EXTRACTION

Chloroform from Carlo Erba (99% purity) and 1,2-dichloroethane from SDS (99.5% purity) and Lancaster (99% purity) were washed with distilled water before use (removal of the stabilizer). The organic solutions, freshly prepared, were made by dissolving a weighed amount of the ligand in the organic solvent. Commercially available sodium chloride, sodium nitrate and potassium nitrate (Prolabo, SDS, 99.5% purity) were used as received and stock solutions were prepared by dissolving the salts in deionised water.

The L^{I}H$_2$ system was experimentally investigated using a radioanalytical method: aliquots of the stock solutions were neutron irradiated at the reactor of the Université de Strasbourg with a flux of 10^{12} cm^2 s^{-1} for 15 to 120 minutes, to produce the radioactive tracers ^{24}Na or ^{42}K for the Na and K solutions, respectively. The L^{II}H$_2$ system was experimentally investigated by using atomic emission spectrophotometry (Perkin Elmer 2380) with an air–acetylene flame. The measurements were carried out using standard conditions for calibration.

In both systems, the pH of the aqueous solution was adjusted to the desired values using either the acid corresponding to the anion (hydrochloric or nitric) or the base of the cation (MOH). The extraction experiments were carried out in polyethylene-stoppered tubes at (294 $\pm$ 1) K (L^{I}H$_2$) and (298 $\pm$ 1) K (L^{II}H$_2$), containing 1.6 mL (L^{I}H$_2$) and 90 mL (L^{II}H$_2$) of each phase. After shaking for more than 20 min to reach equilibrium, the tubes were centrifiuged, the final pH was measured and the phases were separated. For the L^{I}H$_2$ system, radioactivity counting of aliquots of both phases was performed with a Ge–Li detector coupled to a 4096-channel analyser, by using the 1368.55 keV and 1524.7 keV gamma rays of ^{24}Na and ^{42}K, respectively. The distribution coefficient of the alkali metal cation was calculated from the ratio of the activities, A, measured for each phase, as:

$$D_M = [M^+]_{org}/[M^+]_{aq} = A_{org}/A_{aq}. \tag{1}$$

In the extraction experiments involving L^{II}H$_2$, metal analyses of the organic phases were carried out by stripping 2 mL aliquots in contact with 10 mL of hydrochloric acid (0.1 M).

Table I. Extraction equilibrium constants $K_{ab}(M)$ with L^IH_2 in chloroform (C) and 1,2-dichloroethane (C2) at 294 K.

Metal	Figure	$K_{11}(M)$	$K_{21}(M)$
Na	Figure 3	$-4.41 \pm 0.07^*$ (C)	-10.19 ± 0.07 (C)
	Figure 5	-4.77 ± 10.07 (C2)	-11.06 ± 0.06 (C2)
		$-4.62 \pm 0.11^{**}$	
K	Figure 2	-4.74 ± 0.06 (C)	-13.24 ± 0.06 (C)
	Figure 4	-5.38 ± 0.06 (C2)	
		$-5.64 \pm 0.20^{**}$	

* Average value calculated from the parameters K_{11}(Na) obtained in Figures 3a and 3b.
** Constants derived from previous work [4] (nitrate media, 1,2-dichloroethane, 298 K).

2.4. ^{1}H-NMR STUDIES OF THE COMPLEXES

To measure the ^{1}H-NMR spectra of the complexes KL^IH, K_2L^I, NaL^IH, Na_2L^I, $NaL^{II}H$ and Na_2L^{II}, the organic solutions were loaded with the alkali cations under experimental conditions where, whenever possible, 100% of the ligand is complexed, with only one complex present in the organic phase. These conditions are specified below in Section 3.4, after the domains of existence of the various complexes have been established in the extraction experiments. After extraction, the solvent was completely evaporated under reduced pressure and the solid obtained was dissolved in $CDCl_3$. Note that the extraction experiments for $L^{II}H_2$ have been carried out in $C_2H_4Cl_2$ exclusively. By using $CDCl_3$ for the ^{1}H-NMR measurements, the absence of any significant solvent effect on the conformation of the extracted complexes is therefore assumed. This assumption is supported to some extent by the rather small solvent effect observed, in the case of L^IH_2, for the extraction constants in $C_2H_4Cl_2$ and $CHCl_3$ as reported in Table I.

3. Results and Discussion

3.1. QUANTITATIVE DETERMINATION OF THE THERMODYNAMIC EXTRACTION EQUILIBRIUM CONSTANTS

Calix[4]arenes functionalized with carboxylic acid groups are potentially proton ionizable macrocycles [3, 4, 7, 8]. Therefore, the liquid–liquid extraction of an alkali ion (M = Na, K) in the presence of a protonated complexing agent, LH_2 (with LH_2 corresponding to L^IH_2 or $L^{II}H_2$), can be represented as a proton–cation exchange process:

$$a M^+_{aq} + b LH_{2(org)} \leftrightarrows (M_a L_b H_{2b-a})_{org} + a H^+_{aq}. \tag{2}$$
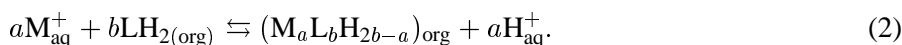
The corresponding thermodynamic extraction equilibrium constant, $K_{ab}(\mathrm{M})$, is given by:

$$K_{ab}(\mathrm{M}) = \frac{[\mathrm{M}_a\mathrm{L}_b\mathrm{H}_{2b-a}]_{\mathrm{org}}[\mathrm{H}^+]_{\mathrm{aq}}^a}{[\mathrm{LH}_2]_{\mathrm{org}}^b[\mathrm{M}^+]_{\mathrm{aq}}^a}\Gamma \qquad (3)$$

where Γ is the factor including the activity coefficients, γ, for all species. Assuming $\gamma = 1$ for the species in the organic phase, it ensues that $\Gamma = (\gamma_{\mathrm{H}}/\gamma_{\mathrm{M}})^a$; since, in the present case, the charges of these ions are the same, one may consider, on the basis of various semi-empirical expressions for γ [10], that $\Gamma = 1$ in the concentration range studied. Equation (3) may thus be rewritten as:

$$K_{ab}(\mathrm{M}) = \frac{D_{\mathrm{M}}}{a}\frac{[\mathrm{H}^+]_{\mathrm{aq}}^a}{[\mathrm{M}^+]_{\mathrm{aq}}^{a-1}[\mathrm{LH}_2]_{\mathrm{org}}^b}. \qquad (4)$$

The extraction of sodium and potassium by LH_2 was investigated under experimental conditions with an initial concentration of M much higher than that of the ligand ($[\mathrm{M}] \geq 75[\mathrm{LH}_2]$). Therefore, when only one extracted species exists and if 100% of LH_2 is complexed, the ratio r_{M} between the concentration of M complexed in the organic phase and the initial concentration of LH_2 in the organic phase gives the stoichiometry of the extracted species; r_{M} was calculated from D_{M} as

$$r_{\mathrm{M}} = [\mathrm{M}^+]_{\mathrm{org}}/[\mathrm{LH}_2]_{\mathrm{org}}^0 = (D_{\mathrm{M}}/(D_{\mathrm{M}} + 1)) \times ([\mathrm{M}^+]_{\mathrm{aq}}^0/[\mathrm{LH}_2]_{\mathrm{org}}^0) \qquad (5)$$

where $[\mathrm{LH}_2]_{\mathrm{org}}^0$ and $[\mathrm{M}^+]_{\mathrm{aq}}^0$ correspond to the initial concentrations of the ligand in the organic phase and the alkali ion in the aqueous phase, respectively.

The logarithmic form of Equation 4 may be written as:

$$\log D_{\mathrm{M}} = \log K_{ab}(\mathrm{M}) + \log a + (a - 1)\log[\mathrm{M}^+] + b\log[\mathrm{LH}_2] + a\mathrm{pH} \qquad (6)$$

and also provides direct information on the stoichiometry of the extracted species if the concentrations of free species $[\mathrm{M}^+]$ and $[\mathrm{LH}_2]$ are nearly constant, by plotting $\log D_{\mathrm{M}}$ versus pH whose slope is equal to a. In addition, in the case of mononuclear complex formation ($a = 1$), it appears from Equation 6 that $\log D_{\mathrm{M}}$ is independent of the metal concentration.

Quantitative analysis of the data was carried out by considering Equation 4 and the appropriate mass balance equations, including metal and ligand concentrations. The extraction equilibrium constants, $K_{ab}(\mathrm{M})$, are evaluated from experimental D_{M} and r_{M} values, using a nonlinear least-squares fitting program.

3.2. SODIUM AND POTASSIUM EXTRACTION BY THE DICARBOXY-DIMETHOXY CALIX[4]ARENE $\mathrm{L}^{\mathrm{I}}\mathrm{H}_2$

In the extraction by $\mathrm{L}^{\mathrm{I}}\mathrm{H}_2$ in chloroform, sodium is extracted from different aqueous media, with chloride or nitrate as counter-ions, and the results show no influence
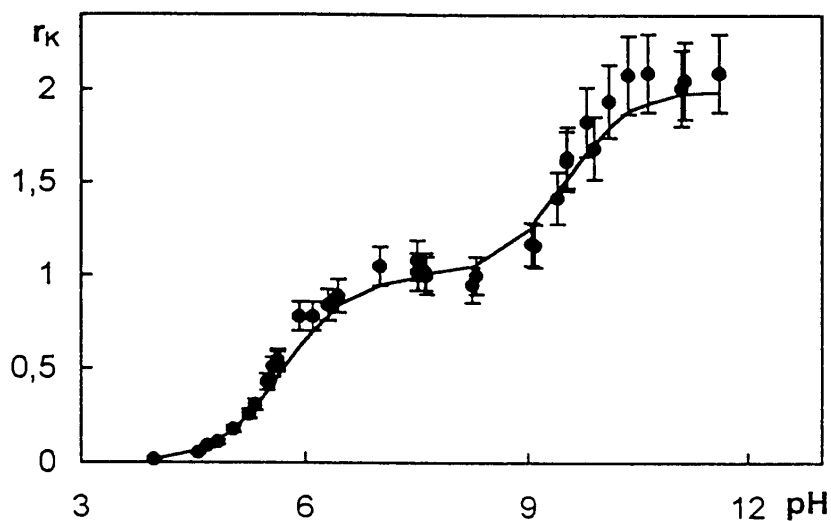
Figure 2. Extraction of potassium by L^IH_2 (2×10^{-3} M) in chloroform at 294 K; plot of r_K = f(pH). [KNO_3] = 0.1 M. The solid line corresponds to the calculated curve using $K_{11}(K)$ = $(1.80 \pm 0.27) \times 10^{-5}$ and $K_{21}(K)$ = $(5.7 \pm 0.86) \times 10^{-14}$ (see Table I).

by the latter. For potassium, only the nitrate medium was considered. The analysis of the experimental data (Figures 2 and 3) clearly shows: (i) the existence of the dinuclear 2 : 1 metal : ligand complexes corresponding to a saturation plateau at r_M = 2; (ii) the presence of the mononuclear 1 : 1 complex, evidenced in the potassium system by the presence of a second plateau for r_K = 1.

Although the plateau does not exist in the sodium system, it is shown in Figure 3a that the r_{Na} vs. pH plot is to be fitted by considering the existence of the 1 : 1 complex which is predominant at pH < 4.5. This predominance is confirmed by the log D_{Na} vs. pH plot (Figure 3b) which has a slope of one and appears to be independent of the metal concentration according to Equation (6).

Considering both the 1 : 1 and 2 : 1 complexes, the modelling leads to the determination of the corresponding extraction equilibrium constants (see Table I).

In the extraction of sodium and potassium by L^IH_2 in 1,2-dichloroethane, the existence of a single extracted species L^IHM (M = Na, K) at pH < 5.1 and pH < 7.4 for sodium and potassium, respectively, is confirmed by the log D_M vs. pH plots in the range where [LH_2] $\cong$ [LH_2]^0 (Figures 4 and 5a). Notwithstanding the small difference in temperature of the experiments, the values of the corresponding extraction equilibrium constants $K_{11}(M)$ fitted and reported in Table I are in agreement with those determined previously from an atomic absorption-based procedure [3].

The occurrence of a third phase is also observed, in the form of a precipitate above pH $\cong$ 5.1 and pH $\cong$ 7.4 for the Na and K systems, respectively. No investigations have been done to further characterize these three phase systems. However,
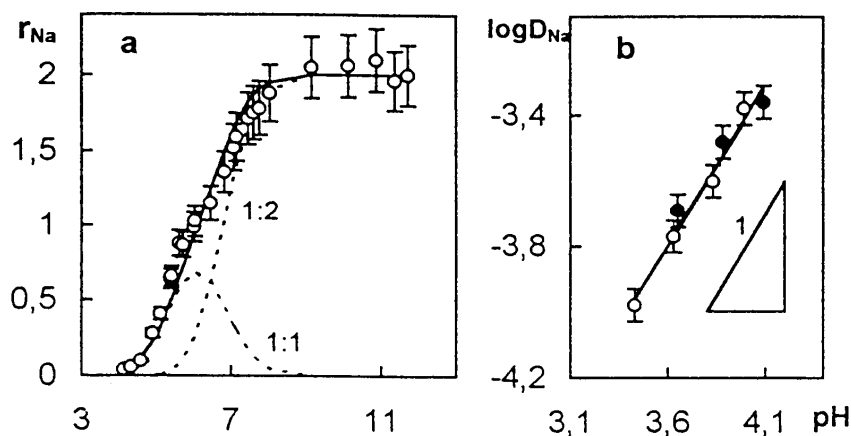
Figure 3. Extraction of sodium by $L^I H_2$ $(2 \times 10^{-3}$ M) in chloroform at 294 K. (a) Plot of $r_{Na} = f(pH)$ with $[NaNO_3] = 0.1$ M. The solid line corresponds to the calculated curve using $K_{11}(Na) = (3.70 \pm 0.56) \times 10^{-5}$ and $K_{21} = (6.5 \pm 1.0) \times 10^{-11}$ (see Table I). The dashed lines correspond to the calculated concentrations of the related mono $(1:1)$ and dinuclear $(2:1)$ extracted species. (b) Plots of $\log D_{Na} = f(pH)$ for various NaCl concentrations: ($\bullet$), 5.25×10^{-2} M; ($\bigcirc$), 0.1 M. The solid line corresponds to the calculated curve using $K_{11}(Na) = (4.09 \pm 0.61) \times 10^{-5}$ (see Table I).
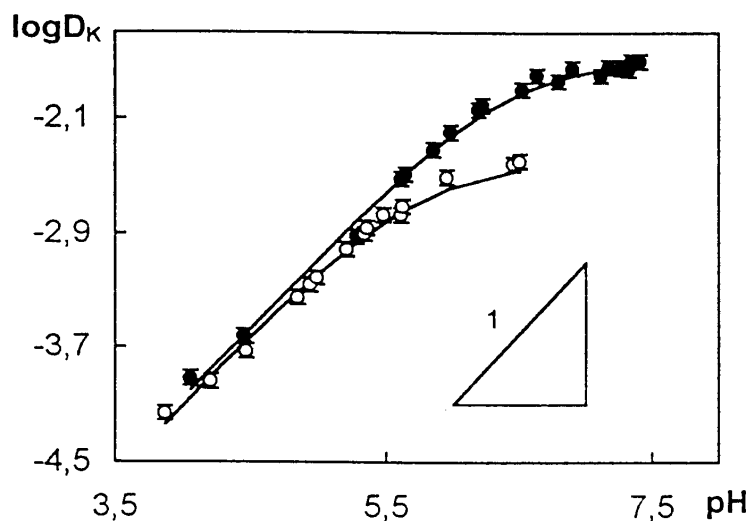
Figure 4. Extraction of potassium by $L^I H_2$ $(2 \times 10^{-3}$ M) in 1,2 dichloroethane at 294 K; plots of $\log D_K = f(pH)$ for various KNO_3 concentrations: ($\bullet$), 0.1 M; ($\bigcirc$), 0.5 M. The solid lines correspond to the calculated curve using $K_{11}(K) = (4.15 \pm 0.62) \times 10^{-6}$ (see Table I).

an exploration of the equilibrium state at higher pH values shows a redissolution of the precipitate in the sodium system for pH $\geq$ 7.3. The saturation plateau obtained (Figure 5b) corresponds to $r_{Na} = 2$ and indicates that the $L^I Na_2$ complex also exists
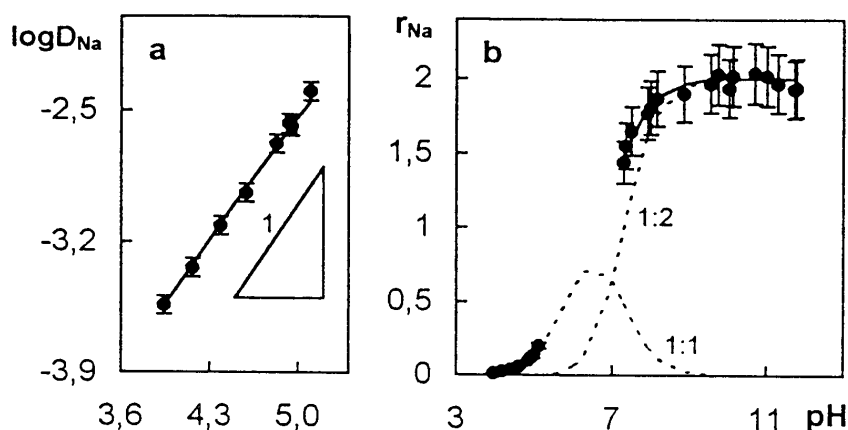
Figure 5. Extraction of sodium by L^IH_2 (2×10^{-3} M) in 1,2 dichloroethane at 294 K. [NaCl] = 0.1 M. (a) Plot of log $D_{Na} = f$(PH). The solid line corresponds to the calculated curve using K_{11}(Na) = $(1.70 \pm 0.25) \times 10^{-5}$ (see Table I). (b) Plot of $r_{Na} = f$(PH). The solid line corresponds to the calculated curve using K_{11}(Na) = $(1.70 \pm 0.25) \times 10^{-5}$ and K_{21}(Na) = $(8.7 \pm 1.3) \times 10^{-12}$ (see Table I). The dashed lines correspond to the calculated concentrations of the related mono (1 : 1) and dinuclear (2 : 1) extracted species.

in $C_2H_4Cl_2$. The corresponding K_{12} extraction equilibrium constant has been estimated (see Table I). The origin of the precipitate is difficult to explain; apparently, it appears when the 1 : 1 and 2 : 1 complexes coexist to a significant extent in the organic phase (Figure 5b).

For the potassium system, the redissolution has not been observed up to pH 13.

From the extraction equilibrium constant data, sodium is better extracted than potassium whatever the diluent and the nature of the extracted species. It is also observed that in chloroform, the ratio K_{21}(Na)/K_{21}(K), at 1.1×10^3, is much higher than the ratio K_{11}(Na)/K_{11}(K), at 2.1, suggesting a better possible Na–K separation in a range of pH and concentration where the 2 : 1 complexes are predominant. Including data on the 2 : 1 complex of lithium [4], the following order of selectivity can be given in 1,2 dichloroethane:

Na > Li > K

In addition, the extraction constants are systematically higher by a factor of 5 in chloroform than they are in 1,2-dichloroethane, leading to a better extractibility of the sodium and potassium ions in the former solvent. This difference in extraction efficiency is too small, and the data too scarce, to allow us to produce any reasonable explanation of this solvent effect in the present work. However, it may be noted that the observed tendency is in agreement with what is expected by considering the calixarene–diluent solution as a regular mixture: the cohesive energy density in chloroform is slightly lower than in 1,2-dichloroethane as expressed by the solubility parameters of 18.9 $J^{1/2}$ cm$^{-3/2}$ and 20.4 $J^{1/2}$ cm$^{-3/2}$ for chloroform and 1,2-dichloroethane, respectively [11].
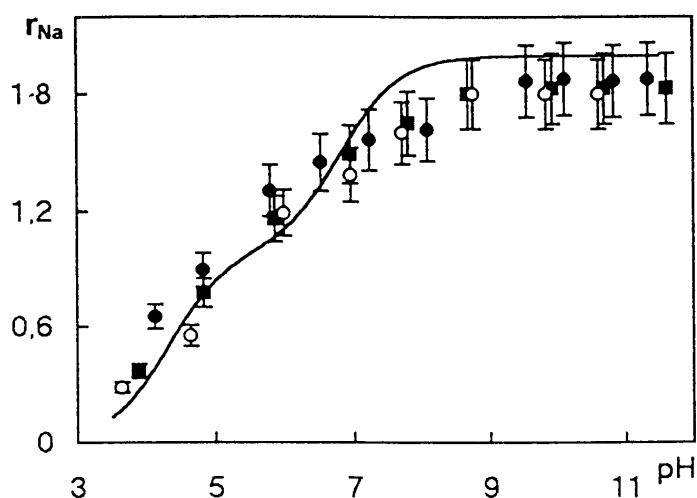
Figure 6. Extraction of sodium by L^{II}H$_2$ in 1,2-dichloroethane at 298 K. Plot of $r_{Na} = f$(pH) for various ligand concentrations: (●) 5 × 10^4 M; (■), 10^{-3} M; (○), 2 × 10^{-3} M. [NaCl] = 0.5 M. The solid line corresponds to the calculated curve using K_{11}(Na) = (9.50 ± 1.53) × 10^{-5} and K_{12}(Na) = (2.95 ± 0.86) × 10^{-11} (see text).

Stability constants (β_{11} and β_{21}) of dinuclear complexes with similar diacidic calix[4]arene derivatives have been reported by Arnaud-Neu et al. [5]. The poor selectivity in favour of sodium observed in the stability constants of the 1 : 1 complexes parallels the corresponding extraction selectivity (based on the K_{11} ratios). However this trend no longer exists when considering the relative stability of the 2 : 1 complexes. The very poor selectivity (β_{21}(Na)/β_{21}(K) $\cong$ 1) does not follow the corresponding extraction selectivity mentioned above; this suggests significant diluent–complex interactions in the extraction process leading to 2 : 1 extracted species.

3.3. SODIUM EXTRACTION BY L^{II}H$_2$ IN 1,2-DICHLOROETHANE

In order to obtain some general trends on the extraction properties of dicarboxy calix[4]arene derivatives, the extraction of sodium in 1,2-dichloroethane by a dicarboxy-dimethoxyethoxy calix[4]arene (L^{II}H$_2$) locked in the cone conformation, has been investigated by plotting r_{Na} vs. pH for three different ligand concentrations (Figure 6). A saturation plateau is observed for $r_{Na} \cong 2$ confirming the existence of a 2 : 1 metal : ligand complex. As already mentioned for the Na/L^{I}H$_2$ systems, the quantitative analysis of the data can only be made by assuming also the existence of the 1 : 1 complex in the acidic pH range. The most satisfactory fit is obtained for K_{11} = (9.50 ± 1.53) × 10^{-5} and K_{21} = (2.95 ± 0.86) × 10^{-11}, indicating that L^{II}H$_2$ is a better cation exchanger than L^{I}H$_2$, since a factor of about 4 is obtained between these constants and those evaluated with L^{I}H$_2$.
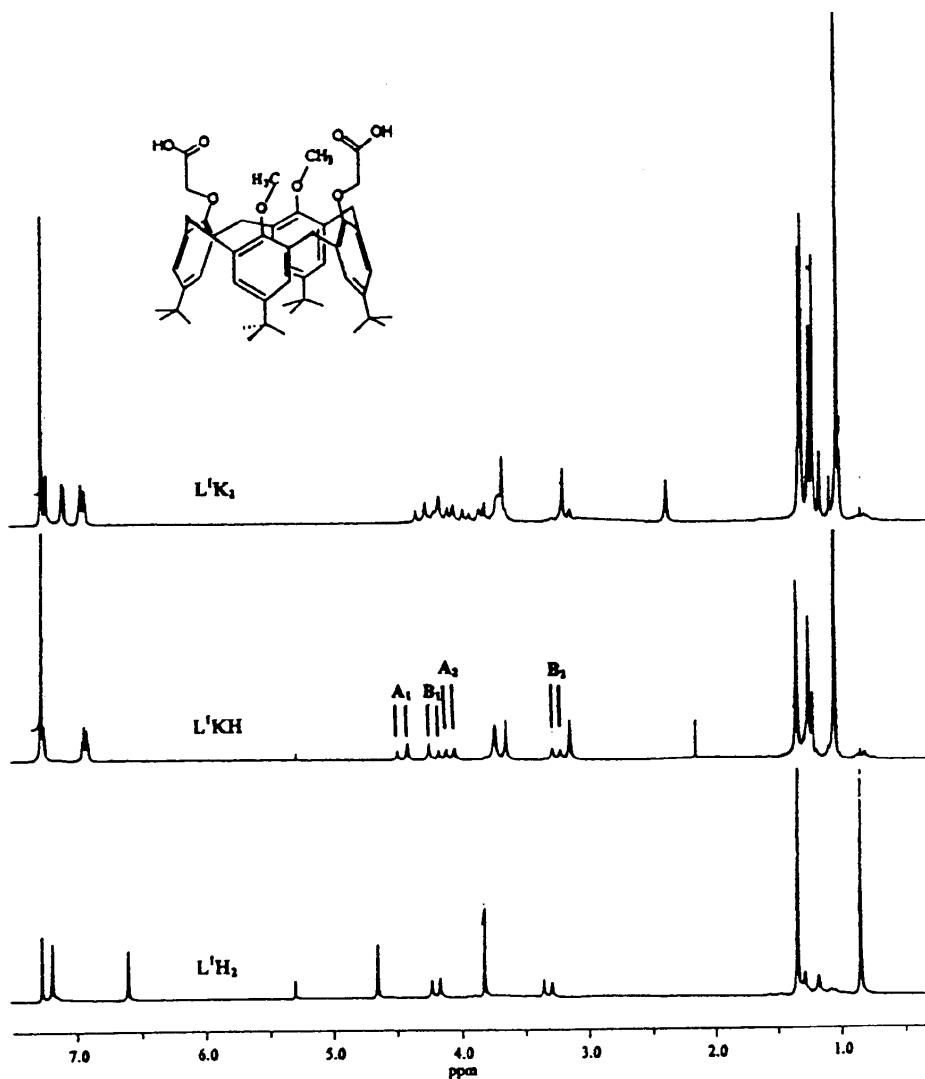
Figure 7. ^{1}H-NMR spectra (200 MHz) in CDCl$_3$ at 298 K of the free ligand L^{1}H$_2$ (bottom), the monuclear complex KL^{1}H (middle, pH = 7.3) and the dinuclear species K$_2$L^1 (top, pH = 12.3).

3.4. ^{1}H-NMR INVESTIGATIONS

^{1}H-NMR studies have been carried out to provide information on the structures of the various species characterized in the extraction experiments. To obtain nearly 100% of a single complex, the experimental conditions for preparing the loaded organic solutions were chosen in accordance with the respective extraction constants derived from the data: KL^{1}H (pH = 7.5, Figure 2), K$_2$L^1 (pH = 11.5, Figure
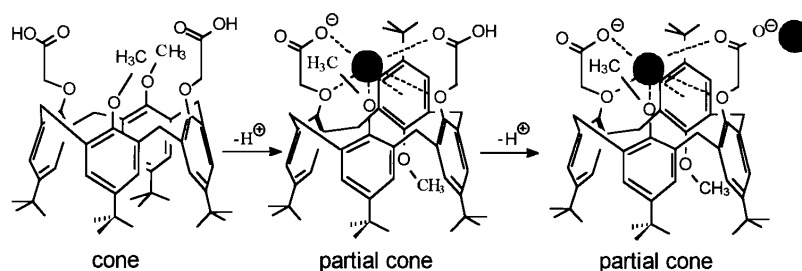
Figure 8. Hypothetical structure of the KL^{I}H and K$_2$L^I species and their formation process. ●, K$^+$.

2), Na$_2$L^I (pH = 11, Figure 3), NaL^{II}H (pH = 5.6, Figure 6), and Na$_2$L^{II} (pH = 11, Figure 6).

For NaL^{I}H, a pure solution of this species cannot be prepared, as illustrated in Figure 3 by the absence of a saturation plateau for $r_{Na} = 1$. Nevertheless, an organic solution was chosen to include both NaL^{I}H (28%) and the free ligand (72%) (pH = 5, Figure 3). After extraction and evaporation, the residue, dissolved in a minimum quantity of CDCl$_3$, to obtain a sufficiently concentrated solution for the ^{1}H-NMR analysis, is muddy. The ^{1}H-NMR spectrum measured, after filtration, corresponds to that of the free ligand, L^{I}H$_2$, indicating insufficient solubility of the NaL^{I}H complex to allow its structural characterization by ^{1}H-NMR.

Figure 7 shows the ^{1}H NMR spectra of L^{I}H$_2$, KL^{I}H and K$_2$L^I in CDCl$_3$. The free ligand L^{I}H$_2$ is characterized by an AB system representative of the cone conformation of L^{I}H$_2$. The spectrum of KL^{I}H shows a quite different pattern of signals attributed to a partial cone conformation due to the presence of 2 AB systems (noted A$_1$B$_1$ and A$_2$B$_2$ in Figure 7) with 1 : 1 integration ratio, two singlets for the OCH$_3$ groups and three singlets in 1 : 1 : 2 integration ratio for the t-butyl groups. A similar conformation change from cone to partial cone upon complexation of alkali cations has been observed in related systems [12]. This conformational change probably arises from favorable π-cation interactions stabilizing the partial cone metal complex.

The spectrum of K$_2$L^I was complicated by new signals. The L^{I}H$_2$ molecule being conformationally mobile, as expressed above, the complexity of the spectrum may be attributed to the existence of K$_2$L^I in different conformations. Due to the higher intensity of the singlet signals of the t-butyl groups in a 1 : 1 : 2 integration ratio, the partial cone conformation can be assumed to be the major product. The formation of K$_2$L^I from L^{I}H$_2$ is depicted in Figure 8.

Similarly, the Na$_2$L^I spectrum shows the existence of an equilibrium between the cone and partial cone conformations of this complex. This is indicated by the five singlets for the t-butyl groups: two singlets, at 1.17 and 1.06 ppm in a 1 : 1 integration ratio, denote the presence of the cone conformation, while the three
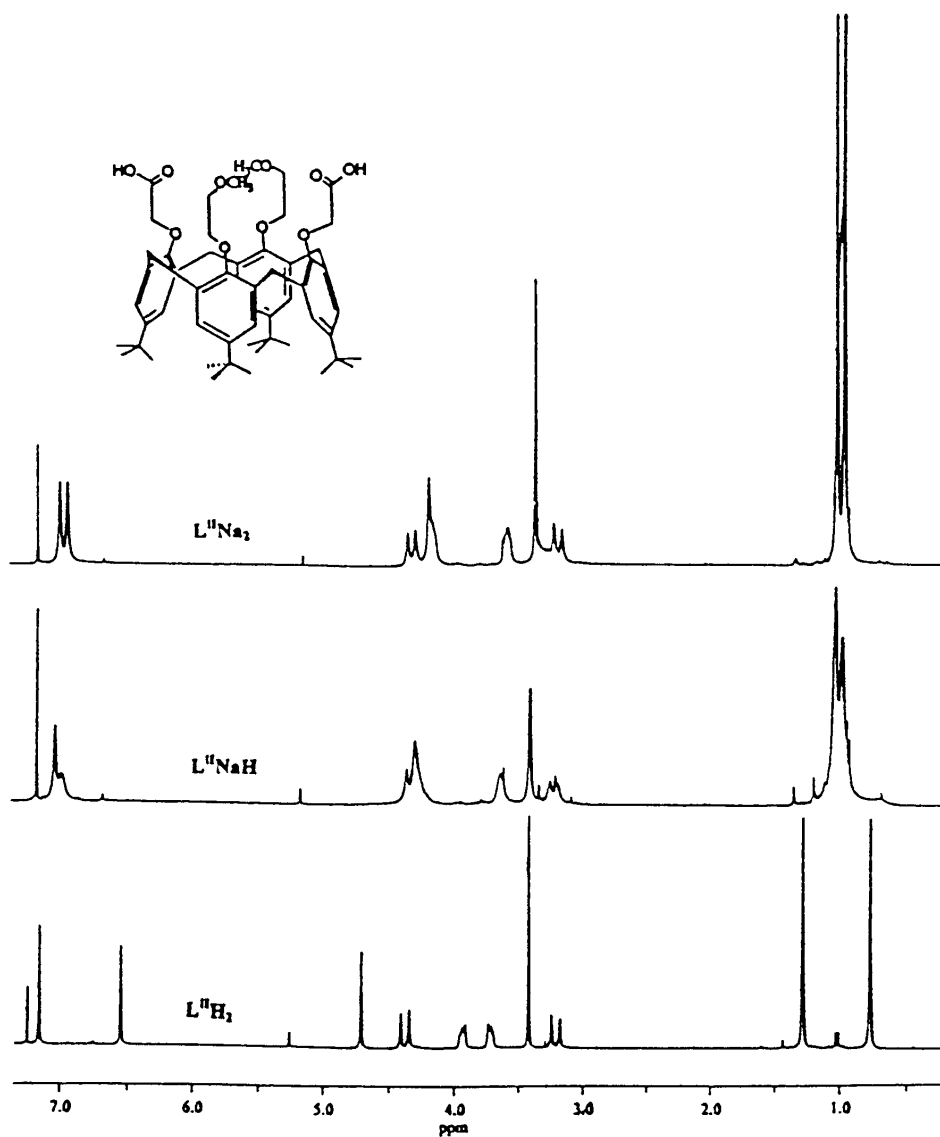
Figure 9. ¹H-NMR spectra (200 MHz) in CDCl₃ at 298 K of the free ligand L^{II}H₂ (bottom), the monuclear complex NaL^{II}H (middle, pH = 6.08), and the dinuclear species Na₂L^{II} (top, pH = 9.74).

other singlets, at 1.26, 1.22 and 1.12 ppm with a 1 : 1 : 2 integration ratio, denote that of the partial cone conformation.

In a second step, similar investigations have been carried out for the Na/L^{II}H₂ system and Figure 9 depicts the ¹H-NMR spectra of L^{II}H₂, NaL^{II}H and Na₂L^{II}. When comparing the spectra of L^{II}H₂ and NaL^{II}H, one observes large shifts of
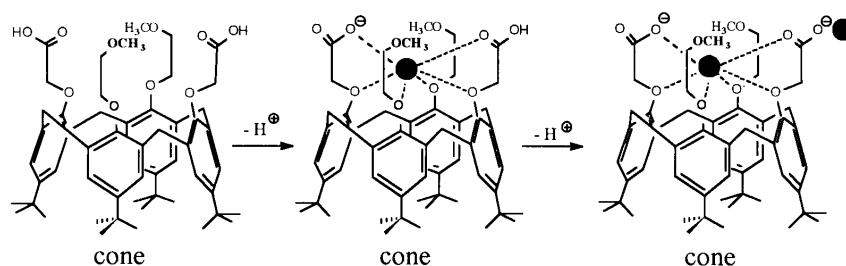
Figure 10. Hypothetical structure of the NaL^{II}H and Na$_2$L^{II} species and their formation process. ●, Na$^+$.

the t-butyl groups, aromatic protons, ArOCH_2—CH$_2$OCH$_3$ and ArOCH_2COOH signals. The shifts of the t-butyl groups and ArH signals upon complexation are attributed to a rigidification of the aromatic region of L^{II}H$_2$ in a cone conformation with approximate C$_4$ symmetry. The crystalline structure of the related dioxyacetate calix[4]arene, L^{II}Et$_2$, showed that two opposite aromatic rings are not equivalent and that the relative dihedral angles between them are 88.7 and 80.9° [9].

This rigidification is probably due to a location of Na$^+$ near the phenolic donor oxygen atoms as denoted from the shifts in the ArOCH_2—CH$_2$OCH$_3$ and ArOCH_2COOH signals. Similar findings have been encountered by Arduini et al. [13] upon the complexation of the sodium cation by the related tetraester of the p-tert-butylcalix[4]arene. As depicted in Figure 10, one can assume that Na$^+$ is also chelated by the carboxylate function of the monodeprotonated calix[4]arene. The observation of a coalescence of the ^{1}H-NMR spectrum of NaL^{II}H is also indicative of a metal–ligand exchange that is slow enough to be detected on the ^{1}H-NMR time scale. The ^{1}H-NMR spectrum of Na$_2$L^{II} is very similar to that of NaL^{II}H and one can assume the complex to behave similarly. This may indicate Na$_2$L^{II} to be as depicted in Figure 10: after deprotonation of NaL^{II}H, a sodium cation probably replaces the removed carboxylic proton.

4. Conclusion

The existence of 1 : 1 and 2 : 1 complexes is evidenced in the extraction of sodium and potassium by dicarboxylated calix[4]arenes in chlorinated diluents. In some cases however, the formation of the M$_2$L complexes is hidden by precipitation phenomena. The extractibility of sodium is more favoured via the formation of 2 : 1 complexes than via the formation of 1 : 1 complexes. The study of conformation effects on the extraction properties of alkali ions with dicarboxylated calix[4]arenes is in progress.

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