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# Extraction of Alkali-Metal Picrates by Calixarene Esters in the Water–Nitrobenzene Solvent System. The Medium Effect on the Partition and Extraction Processes

MARIA A. PUGLIESE<sup>a</sup>, MARIA T. GOITIA<sup>a</sup>, MIRTA E. MONTERO<sup>a</sup>, ALBERTO R. CASAL<sup>a</sup> and ANGELA F. DANIL DE NAMOR<sup>b,\*</sup>

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Based on distribution data involving alkali-metal ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$  and  $\text{Cs}^+$ ) picrates in the presence and in the absence of calix[n]arene ( $n = 4, 6$ ) esters, the extraction ability of these macrocycles in the water–nitrobenzene solvent system is established. Thus, partition and distribution constants in the mutually saturated solvents and ion-pair formation constants in the water saturated organic phase are calculated from distribution data in the absence of these macrocycles. From distribution data in the presence of the ligand, the extraction and the distribution constants are calculated. Within the experimental error, good agreement is found between the distribution constants calculated from distribution data in presence and absence of calixarenes. The individual processes which contribute to the overall extraction of these cations from water to nitrobenzene are discussed. The medium effect on the extraction process is analysed taking into account previously reported data for these systems in water–dichloromethane and water–chloroform.

## INTRODUCTION

Numerous investigations have been carried out to demonstrate the extracting ability of calixarene esters for alkali-metal cations in mutually saturated solvent systems [1–3]. However it was not until 1997 [4,5] that the first quantitative evaluation on the individual processes which contribute to the selective extraction of cations by calixarene derivatives in the water–benzonitrile solvent system was carried out. Indeed from distribution data of alkali-metal salts in the absence of calixarenes, the partition constant,  $K_p$ , in the mutually saturated solvent system

and the association (ion-pair) constant,  $K_a$  in water saturated benzonitrile were calculated. Combination of  $K_a$  and  $K_p$  led to the evaluation of the contribution constant,  $K_d$  in this solvent system.  $K_d$  values were also obtained from distribution data in the presence of calixarenes. The overall extraction constant,  $K_{ex}$  referred to the process in which the dissociated alkali-metal picrates are extracted from water to the organic phase by calixarenes to give the fully associated alkali-metal calixarene complex in the non-aqueous solvent was derived [6].

We report here the results obtained from distribution experiments involving alkali-metal cations as picrates in the water–nitrobenzene solvent system.

The medium effect on the extraction process is assessed taking into account previous work using calixarene esters and alkali-metal cations carried out in other solvent systems such as water–dichloromethane and water–chloroform [7].

## EXPERIMENTAL

Calixarene esters, namely, ethyl *p*-tert-butyl calix[4]arene tetraethanoate, Et Calix[4] and ethyl *p*-tert-butyl calix[6]arene hexaethanoate, Et Calix[6] were synthesised following the procedure suggested by Danil de Namor and co-workers [8–10].

Alkali-metal picrates were synthesised from picric acid (analytical grade, recrystallised as previously reported) [4–7] and the appropriate alkali-metal hydroxide ( $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ) or carbonate ( $\text{Rb}^+$  and

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Cs<sup>+</sup>). The concentration of picric acid was determined by volumetric analysis. The alkali-metal picrates were prepared 'in situ' by adding to a solution of picric acid in water (saturated with nitrobenzene), an excess of alkali-metal hydroxide or carbonate as described before [4–7].

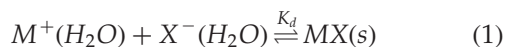
## DISTRIBUTION EXPERIMENTS

For distribution experiments in the absence of the ligand, a series of experiments were carried out. Thus, aqueous solutions (saturated with nitrobenzene) of different concentrations of metal-ion picrates (concentration range,  $1.5 \times 10^{-4}$ – $1.6 \times 10^{-3}$  mol dm<sup>-3</sup>) were shaken with equal volumes (10 cm<sup>3</sup>) of nitrobenzene (saturated with water) for 30 minutes and then these were left in a thermostat at 298.15 K for 24 hours. Following phase separation, the equilibrium concentration of picrate in water was analysed by UV spectrophotometry (Shimadzu 1603) at 355 nm.

For the distribution experiments in the presence of the calixarene ester, to solutions of alkali-metal picrates ( $6.0 \times 10^{-4}$  mol dm<sup>-3</sup>, 10 cm<sup>3</sup>), equal volumes of non-aqueous solutions containing the ligand (concentration range,  $1.5 \times 10^{-4}$ – $1.5 \times 10^{-3}$  mol dm<sup>-3</sup>) in nitrobenzene saturated with water, were added. Afterwards the procedure followed was the same as that described above for distribution experiments in the absence of the ligand.

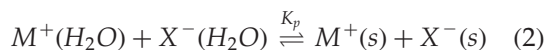
## RESULTS AND DISCUSSION

The global process involved in the distribution of alkali-metal picrates in the water–nitrobenzene solvent system is that described in Eq. (1) with ionic species (M<sup>+</sup>, metal cation and Pi<sup>-</sup>, picrate) in the aqueous phase (H<sub>2</sub>O) and ion-pairs; M<sup>+</sup>Pi<sup>-</sup> in the organic phase; (s); both phases mutually saturated,



The process described by Eq. (1) can be split into two individual processes,

- (i) the partition of the alkali-metal picrates in its ionic form in both phases Eq. (2)



- (ii) the ion-pair formation or association process in the water saturated nitrobenzene Eq. (3)

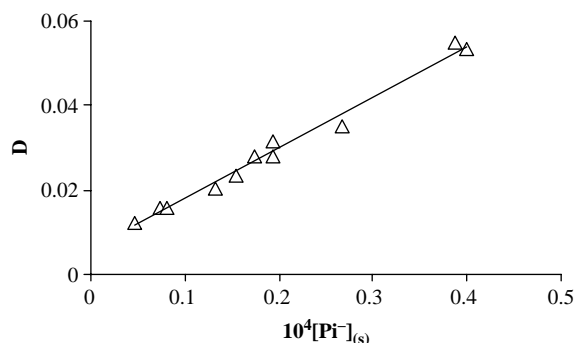


FIGURE 1 Distribution coefficients of sodium picrate in the mutually saturated water–nitrobenzene solvent system against the equilibrium concentration of picrate in the water saturated organic phase at 298.15 K.

Combination of Eqs. (2) and (3) leads to the process described in Eq. (1). Therefore

$$K_d = K_p * K_a \quad (4)$$

$K_p$ ,  $K_a$  and  $K_d$  are obtained from the relationship previously described [4] which relates the distribution coefficient, D of picrate with  $K_p$  and  $K_a$  as shown in Eq. (5)

$$D_{Pi} = K_p^{1/2} + K_p^{1/2} K_a [Pi^-](s) \quad (5)$$

In Eq. (5),  $[Pi^-]_s$  is the equilibrium concentration on the molar scale of picrate in the organic phase.

A plot of  $D_{Pi^-}$  against  $[Pi^-]_s$  should give a straight line of intercept =  $K_p^{1/2}$  and slope of  $K_p^{1/2} K_a$  from which the partition,  $K_p$ , and association constant,  $K_a$ , can be evaluated.

A representative example for sodium picrate is shown in Fig. 1 which demonstrates that the data fit into Eq. (5). Thus  $K_p$  and  $K_d$  values for alkali-metal picrates in the mutually saturated solvents and  $K_a$  for these salts in water saturated nitrobenzene are shown in Table I. The data show that as far as the partition is concerned,  $K_p$  values increase down the group while the ion-pair formation constant decreases. In fact  $K_p$  and  $K_a$  values follow the expected trend in that as the charge density of the cation decreases (i) the ability of the metal cation to enter the organic phase increases as reflected in  $K_p$  values (ii) the tendency for ion-pair formation with

TABLE I Partition,  $K_p$  and distribution,  $K_d$  constants of alkali-metal picrates in the mutually saturated water–nitrobenzene solvent system and ion-pair formation constants in water saturated nitrobenzene at 298.15 K

Alkali-Metal Picrate	$K_p^a$	$K_a$	$R^2$	$K_d$
NaPi	$3.7 \times 10^{-5}$	$2.0 \times 10^5$	0.987	7.4
KPi	$5.9 \times 10^{-5}$	$1.6 \times 10^5$	0.928	9.4
RbPi	$4.0 \times 10^{-4}$	$5.8 \times 10^4$	0.948	23.2
CsPi	$4.6 \times 10^{-4}$	$3.2 \times 10^4$	0.932	14.7

<sup>a</sup>  $K_i$  values for KPi;  $5.5 \times 10^{-5}$ ; Rb Pi;  $1.1 \times 10^{-4}$ ; CsPi;  $2.0 \times 10^{-4}$ .

the anion decreases as illustrated in the  $K_a$  values shown in Table I.

Given that  $K_a$  values are much greater than  $K_p$  values, it is concluded that ion-pairs rather than ions are the predominant species in the water saturated organic phase. At this stage it seems relevant to compare  $K_p$  values with the  $K_t$  of these electrolytes from water to nitrobenzene previously reported [9]. The latter are referred to the process involving the transfer of the electrolyte from pure water to pure nitrobenzene. These data differ from the  $K_p$  values in that these involve the mutually saturated solvents. Thus  $K_t$  values for alkali-metal picrates (derived from the combination of single-ion  $K_t$  values for the alkali-metal cation and that for the picrate anion, both based on the  $\text{Ph}_4\text{AsPh}_4\text{B}$  convention [10]) show the same trend as  $K_p$  values listed in Table I. However considerable differences are found between  $K_t$  and  $K_p$ . We believe that these differences are attributed to the  $K_t$  value for the picrate anion in the water–nitrobenzene solvent system ( $K_t = 3.90$ ) derived from a few salts containing this anion. Indeed there are practical difficulties in obtaining these salts in an anhydrous state. It is the only value which differ significantly from the calculated  $K_t$  for the picrate anion reported in the literature [11]. There is a good agreement between  $K_d$  values derived from distribution data in the absence and in the presence of the ligand as shown below. It may be emphasised that when the calculated value of 0.26 is used as the  $K_t$  value for the picrate anion; good agreement is found between  $K_p$  values shown in Table I and  $K_t$  values for these electrolytes. In fact as expected  $K_p$  values for rubidium and caesium picrates are greater than  $K_t$ . These are reported as a footnote in Table I.

In an attempt to formulate an equation representative of the process taking place when an aqueous solution (saturated with nitrobenzene) containing a 1:1 dissociated electrolyte is in equilibrium with a non-aqueous medium containing the macrocycle, it is necessary to identify the speciation in solution as well as the composition of the complex formed in the organic phase (saturated with water). The latter was confirmed by experimental work on the distribution of alkali-metal cations in the presence of the appropriate macrocycle in the organic phase.

Thus Fig. 2 shows the percentage of extraction (%E) for sodium picrate in the water–nitrobenzene solvent system at 298.15 K against the ligand:anion ratio using Et Calix[4] and Et Calix[6]. In both cases, the stoichiometry of the process obtained from the intersection of the two lines (prior and after the 1:1 ligand:anion ratio) indicates that one metal cation is taken up per unit of ligand. The same stoichiometry was found for other alkali-metal cations. It is also evident from this figure that as far as sodium is concerned, Et Calix[4] is a better extracting agent for this cation than Et Calix[6]. The results obtained

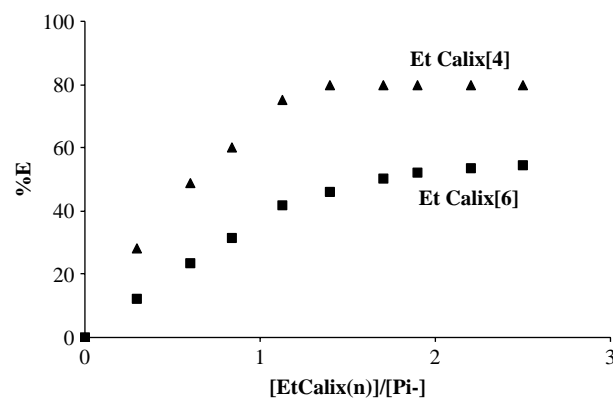
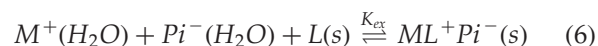


FIGURE 2 Percentages of the sodium picrate against the ethyl calix[n]arene ( $n = 4, 6$ )/picrate ratio in the water–nitrobenzene solvent system at 298.15 K.

show that the latter ligand is a better extracting agent for the larger cations such as potassium, rubidium and caesium.

Once the stoichiometry of the process was defined and taking into account that alkali-metal picrates are fully dissociated in water and the metal–ion complex salt is predominantly associated in the organic phase, the overall extraction process may be represented by Eq. (6).

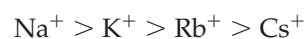


Thus using the expression previously reported [4,6,7]

$$\frac{D_{Pi^-}}{[M^+]_{H_2O}} = K_d + K_{ex}[L](s) \quad (7)$$

$K_d$  and the extraction constants,  $K_{ex}$  can be calculated provided that a plot of  $D_{Pi^-}/[M^+]_{H_2O}$  against  $[L](s)$  lead to a linear relationship.

Figures 3a and 3b show illustrative examples for the results obtained for  $\text{Rb}^+$  (as picrate) when the distribution experiments were carried out in the presence of Et Calix[4] and Et Calix[6] respectively in the water–nitrobenzene solvent system. In fact this figure shows linear relationships for both ligands when  $D_{Pi^-}/[M^+]_{H_2O}$  were plotted against the ligand:metal cation ratio. Thus  $K_d$  and  $K_{ex}$  values for all alkali-metal cations and Et Calix[4] and Et Calix[6] in this solvent system are shown in Table II. In fact  $K_d$  values shown in this table are in good agreement (within the experimental error) with those reported in Table I. Therefore an average  $K_d$  value for each alkali-metal picrate is calculated. Thus  $K_d$  values for NaPi, KPi, RbPi and CsPi are  $7.6 \pm 0.3$ ;  $9.4 \pm 0.8$ ;  $23 \pm 2$  and  $15 \pm 1$  respectively. As far as  $K_{ex}$  values are concerned for Et Calix[4] these follow the sequence,



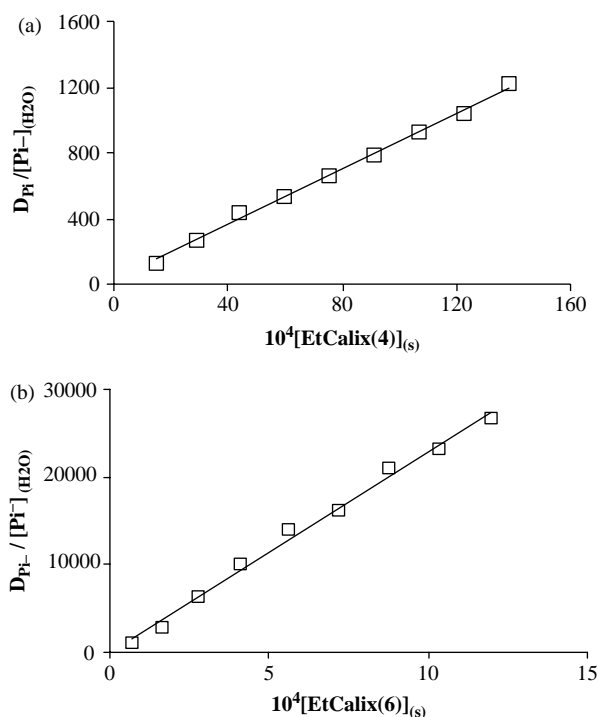


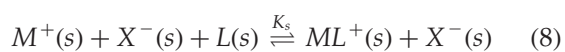
FIGURE 3 Plot of  $D_{\text{Pi}^-}/[\text{Pi}^-]_{\text{H}_2\text{O}}$  against the concentration of the EtCalix[4] (a) and Et Calix[6] (b) in the water saturated organic phase at 298.15 K.

while for Et Calix[6], the opposite trend is shown,

$$\text{Cs}^+ > \text{Rb}^+ > \text{K}^+ > \text{Na}^+$$

So far we have considered the overall extraction of alkali-metal cations from the aqueous to the organic phase where the two solvents are mutually saturated. In an attempt to analyse the individual processes which contribute to  $K_{\text{ex}}$ , two possible routes are considered for the overall process described in Eq. (6)

- (i) Partition of the dissociated electrolyte in the mutually saturated solvents (Eq. (2)) followed by cation–ligand complexation (Eq. (8)) ( $L = \text{Et Calix[4]}$  or  $\text{Et Calix[6]}$ ) in the water saturated organic phase and ion-pair formation between the complex cation and the counter-ion,  $K'_a$  (Eq. (9)) in this phase,



In Eq. (8),  $K_s$  is the stability constant of the metal–ion complex in the water saturated organic phase. Thus  $K_{\text{ex}}$  is made by the contribution of  $K_p$ ,  $K_s$  and  $K'_a$  (Eq. (10))

$$K_{\text{ex}} = K_p \times K_s \times K'_a = K_p \times K'_s \quad (10)$$

TABLE II Distribution,  $K_d$  and extraction,  $K_{\text{ex}}$  constants of alkali-metal cations in the presence of calixarenes esters in the mutually saturated water–nitrobenzene solvent system at 298.15 K

Alkali-Metal Picrate	$K_d$	$K_{\text{ex}}(\text{EtCalix[4]})$	$R^2$
NaPi	7.6	$1.6 \times 10^7$	0.994
KPi	8.6	$5.3 \times 10^6$	0.994
RbPi	21.9	$8.5 \times 10^5$	0.996
CsPi	15.9	$9.5 \times 10^5$	0.999
		$K_{\text{ex}}(\text{EtCalix[6]})$	$R^2$
NaPi	7.8	$3.7 \times 10^6$	0.999
KPi	10.1	$6.0 \times 10^6$	0.993
RbPi	25.1	$7.0 \times 10^6$	0.988
CsPi	13.5	$2.3 \times 10^7$	0.994

Therefore

$$K'_s = K_{\text{ex}}/K_p \quad (11)$$

- (ii) Partition of the dissociated electrolyte in the mutually saturated phases (Eq. (2)) followed by ion-pair formation between the free cation and the anion (Eq. (3)) in water saturated nitrobenzene, and subsequent interaction between the ion-pair and the ligand (Eq. (12))



As a result,

$$K_{\text{ex}} = K_p \times K_a \times K_{\text{ass}} = K_d \times K_{\text{ass}} \quad (13)$$

Thus

$$K_{\text{ass}} = K_{\text{ex}}/K_d \quad (14)$$

Values of  $K'_s$  and  $K_{\text{ass}}$  for these systems in water saturated nitrobenzene are shown in Table III. Given that  $K'_s > K_{\text{ass}}$  we consider that the individual processes contributing to the overall extraction of cations from water to the organic phase are those shown in Eq. (10).

The results show that although the partition of the electrolyte makes a negative contribution to the overall extraction, this is overcome by the contribution of both, the stability constant of the metal–ion

TABLE III Individual processes involved in the overall extraction of alkali-metal picrates from water by calixarene esters in the mutually saturated water–nitrobenzene solvent system at 298.15 K

Alkali-Metal Picrate	EtCalix[4]		EtCalix[6]	
	$K'_s$	$K_{\text{ass}}$	$K'_s$	$K_{\text{ass}}$
NaPi	$4.3 \times 10^{11}$	$2.2 \times 10^6$	$1.0 \times 10^{11}$	$4.9 \times 10^5$
KPi	$8.9 \times 10^{10}$	$5.6 \times 10^5$	$1.0 \times 10^{11}$	$6.4 \times 10^5$
RbPi	$2.1 \times 10^9$	$3.6 \times 10^4$	$1.8 \times 10^{10}$	$3.0 \times 10^5$
CsPi	$2.1 \times 10^9$	$6.5 \times 10^4$	$5.0 \times 10^{10}$	$1.6 \times 10^6$

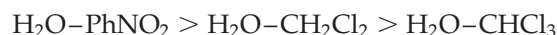
TABLE IV Partition and extraction constants of alkali-metal picrates in various solvent systems at 298.15 K

Alkali-Metal Picrate	H <sub>2</sub> O-PhNO <sub>2</sub> <sup>a</sup>			H <sub>2</sub> O-CH <sub>2</sub> Cl <sub>2</sub> <sup>b</sup>			H <sub>2</sub> O-CHCl <sub>3</sub> <sup>c</sup>		
	<i>K<sub>ex</sub></i>			<i>K<sub>ex</sub></i>			<i>K<sub>ex</sub></i>		
	<i>K<sub>p</sub></i>	Et Calix[4]	Et Calix[6]	<i>K<sub>p</sub></i>	Et Calix[4]	Et Calix[6]	<i>K<sub>p</sub></i>	Et Calix[4]	Et Calix[6]
NaPi	3.7 × 10 <sup>-5</sup>	1.6 × 10 <sup>7</sup>	3.7 × 10 <sup>6</sup>	2.4 × 10 <sup>-5</sup>	1.2 × 10 <sup>7</sup>	2.8 × 10 <sup>6</sup>	5.3 × 10 <sup>-6</sup>	8.8 × 10 <sup>5</sup>	6.6 × 10 <sup>4</sup>
KPi	5.9 × 10 <sup>-5</sup>	5.3 × 10 <sup>6</sup>	6.0 × 10 <sup>6</sup>	4.5 × 10 <sup>-5</sup>	8.3 × 10 <sup>5</sup>	2.6 × 10 <sup>7</sup>	8.4 × 10 <sup>-6</sup>	3.6 × 10 <sup>4</sup>	1.9 × 10 <sup>6</sup>
RbPi	4.0 × 10 <sup>-4</sup>	8.5 × 10 <sup>5</sup>	7.0 × 10 <sup>6</sup>	6.2 × 10 <sup>-5</sup>	3.4 × 10 <sup>5</sup>	3.8 × 10 <sup>7</sup>	1.2 × 10 <sup>-5</sup>	5.1 × 10 <sup>4</sup>	1.4 × 10 <sup>6</sup>
CsPi	4.6 × 10 <sup>-4</sup>	9.5 × 10 <sup>5</sup>	2.3 × 10 <sup>7</sup>	1.0 × 10 <sup>-4</sup>	4.8 × 10 <sup>5</sup>	2.7 × 10 <sup>7</sup>	2.0 × 10 <sup>-5</sup>	1.4 × 10 <sup>4</sup>	2.2 × 10 <sup>7</sup>

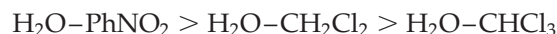
<sup>a</sup>This work, <sup>b</sup>Ref. [6], <sup>c</sup>Ref. [7]

complex and the ion-pair formation constant between the complex cation and the counter-ion,  $K'_s$  in the water saturated organic phase. Given that for a given cation, the contribution of  $K_p$  to the extraction process involving either Et Calix[4] or Et Calix[6], is the same, the overall extraction value depends on the joint contribution of  $K_s$  and  $K'_s$ . Thus among the alkali-metal cations, the extraction of  $\text{Na}^+$  is favoured in the presence of Et Calix[4] while the larger cations are better extracted in the presence of Et Calix[6].

In order to assess the medium effect on the extraction process, data for alkali-metal picrates in the water-dichloromethane [6] and water-chloroform [7] solvent systems previously reported by us are shown in Table IV. Also included in this table are the  $K_p$  values for the salts in the various solvent systems. For extraction purposes, nitrobenzene offers a more efficient medium than dichloromethane and chloroform. In fact  $K_{ex}$  values for the various solvent systems follows the sequence,



It is evident from the  $K_p$  values for alkali-metal picrates that again the partition of these electrolytes from water to nitrobenzene is more favoured than that to dichloromethane and particularly to chloroform. In fact the trend observed as far as  $K_p$  values are concerned is,



Judging solely on the permittivity of the medium, it seems reasonable to consider that as the permittivity of the medium decreases from nitrobenzene to dichloromethane and then to chloroform, the ability of the electrolyte to enter the non-aqueous medium decreases. Therefore we consider that the decrease observed in the  $K_{ex}$  values in moving from nitrobenzene to chloroform is partially attributed to the more negative contribution of the partition of the dissociated electrolyte to the overall extraction process in chloroform and to a lesser extent to dichloromethane relative to nitrobenzene. Indeed if the extraction process was only controlled by the partition process of these electrolytes, it would be expected that for a given electrolyte and ligand, the selectivity factor,  $S$ , which provide quantitative information of the solvent effect on the partition,  $S_p$  of electrolytes (Eq. (15)) or on the extraction process,  $S_{ex}$  (Eq. (16)) should be the same.

$$S_p = \frac{K_p(M^+ + X^-)(s_2)}{K_p(M^+ + X^-)(s_1)} \quad (15)$$

$$S_{ex} = \frac{K_{ex}(M^+ + X^-)(s_2)}{K_{ex}(M^+ + X^-)(s_1)} \quad (16)$$

In fact  $S_p \cong S_{ex}$  for only one system (NaPi in the chloroform–nitrobenzene solvent system and  $S_{ex}$  for the same salt and Et Calix[6]). For most systems,  $S_{ex} > S_p$  but in a few cases  $S_p > S_{ex}$ .

Given that  $K_{ex}$  is made by the contribution of  $K_s'$  and  $K_p$ , inspection of these data show that for Et Calix[4] the decrease in the  $K_{ex}$  in moving from sodium to caesium is due to the drop in the  $K_s'$  values down the Group while the opposite is true for  $K_p$ . However for Et Calix[6], the extraction constant increases as the partition increases from sodium to caesium while the maximum  $K_s'$  value is that for potassium.

## CONCLUSIONS

Given that selectivity is one of the main features of supramolecular chemistry it seems relevant to analyse selectivity in the overall extraction process in terms of the cation, the solvent and the ligand.

As far as the cation is concerned, in the water–nitrobenzene solvent system, the extraction of these metal cations in the presence of Et Calix[4] is selective for sodium relative to potassium, rubidium and caesium by factors of 3, 19 and 17 respectively. For Et Calix[6], this ligand is more selective for caesium by factors of 6, 4 and 3 relative to sodium, potassium and rubidium.

Regarding the medium effect, nitrobenzene offers a better extraction medium than dichloromethane and chloroform for Et Calix[4]. However the latter is a better medium for Et Calix[6] and the larger cations than other solvents.

In terms of the ligand, except for sodium, Et Calix[6] is a more efficient extracting agent than the tetraester.

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