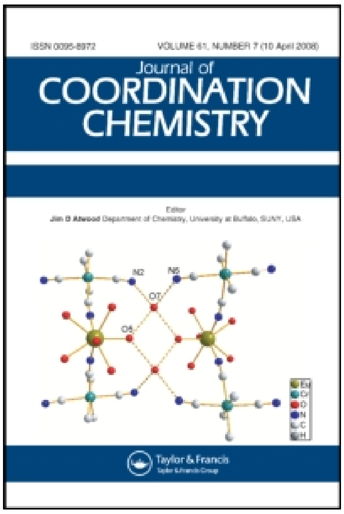

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COMPLEXATION STUDIES OF ALKALINE EARTH METAL IONS WITH MACROCYCLIC LIGANDS OF THE ANTHRAQUINONE-CROWN ETHER TYPE BY ELECTROCHEMICAL METHODS

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The electrochemical and complexation behaviour of synthetic ligands of the crown ether type attached to an anthraquinone unit has been studied using cyclic voltammetry. In the presence of alkaline earth metal ions the positions and type of the ligand redox waves were changed and the potentials of the respective redox couples were shifted to more positive values. These shifts in the potentials translate as an increase in the thermodynamic stability of complexation to the anionic when compared to the unreduced species, as well as a dependence on the complexed cation. The magnitude of the binding enhancement is larger for cations with higher ionic potential excluding Mg^{2+} and is also favoured by an increased number of donor sites in the macrocyclic cavity of the ligand. The following trends have been observed, $Ca^{2+} > Sr^{2+} > Ba^{2+} > Mg^{2+}$, with the reduced ligands studied showing a remarkably high degree of cation selectivity for Ca^{2+} over Mg^{2+}. The reduced carbonyl oxygen positioned within the crown ring makes a significant contribution to coordination; the reduced carbonyl group outside the crown ring participates weakly if at all in coordination. The results are discussed in terms of electronic properties, number of binding sites and macrocyclic ring structural flexibility in the ligands, as well as of the size and solvation of the metal cations.

Keywords: crown ether derivatives; alkaline earth; complexation; cyclic voltammetry

INTRODUCTION

Synthetic macrocyclic polyethers represent a class of compounds that is particularly interesting and very promising in several areas of research in the field

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of host-guest chemistry. They have important potential applications, from their ability, selectively, to recognize metal ions [1-4] and their use in cation sensor systems, [5, 6] to being able to act as selective carriers of metal ions across natural or artificial liquid membranes. [1, 3, 7, 8]

The structural and electronic features of these ionophoric molecules are very important for controlling and determining properties such as binding strength and selective complexation or transport processes of metal ions. [9-12] Additionally, appropriate modifications in the macrocyclic polyether systems can be made in order to enhance those properties. In particular, the presence in such systems of electroactive groups suitably positioned and oriented to allow interaction with the cation can offer more attractive properties of the macrocyclic receptor molecules induced by the charged guest. [13-17] Upon electrochemical reduction of the ligand, an additional intramolecular interaction can occur between the anionic macro-ring species generated and the bound cation, which can lead to the strengthening of the complexation of the reduced host and may influence the binding selectivity of the ligand for one metal ion over others with which it is complexed.

In the present study we report the electrochemical behaviour and investigate the complexation ability of redox-active macrocyclic molecules of the crown ether type containing an anthraquinone unit as an integral redox-active part of the macro-ring system. This study was carried out with alkaline earth metal cations using cyclic voltammetry. The quantitative enhancement of the relative complexing abilities of the reduced, compared with the unreduced, hosts has been evaluated in terms of differences in observed potentials of the respective redox couples in both the presence and absence of metal cations. A preliminary report of part of this work has already been published. [18]

EXPERIMENTAL

Calcium and strontium perchlorates were precipitated from solutions of their hydroxides (Merck) by addition of a slight excess of concentrated perchloric acid (Merck). The solids were recovered by cooling solutions that had been concentrated by prolonged gentle heating. [19] These perchlorates and also magnesium and barium perchlorates (Aldrich) were recrystallized from 1:1 water + methanol, dried in vacuum at 100°C for 24 h and then stored over P_2O_5 under vacuum. Their purities were checked by atomic absorption spectroscopy. The purification of other reagents and the synthesis of the ligands have been previously described. [17]

The electrochemical measurements were performed on a PAR potentiostat (model 273A). A glassy carbon electrode was used as the working electrode and a platinum wire as the counter electrode. A silver wire or Ag/10 mM Ag^+ in acetonitrile served as the reference electrode. More experimental details are given in the references. [17]

The potential-current curves were scanned from 0 to -2.0 V *vs* Ag/10 mM Ag^+ in acetonitrile at constant scan rates between 0.1 and 0.5 V s^{-1}. The temperature was controlled at 25.0 ± 0.1°C using a double sided glass vessel through which thermostatted water was circulated.

An anhydrous 0.1 M tetra-*n*-butylammonium perchlorate (TBAP) solution was prepared in freshly distilled acetonitrile, introduced into the experimental cell and bubbled with purified solvent-saturated nitrogen for 30 min. The solid ligand (L) was dissolved in the supporting electrolyte solution followed by the alkaline earth perchlorate. The three-electrode system was placed in the experimental cell and a stream of nitrogen was passed through the solution for 20 min., before the voltammetric experiment was initiated. An inert atmosphere was maintained over the solution during the experiments. At the lower L to M^{2+} ratios it was sometimes necessary to polish the glassy carbon electrode during the measurements because of the adsorption of electroactive species at the surface of the electrode. The concentration of the electroactive species present was in the range 1.0-5.0 mM.

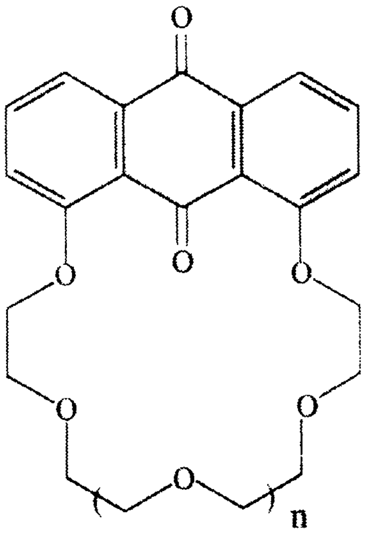
RESULTS AND DISCUSSION

The ligand molecules (L) studied are shown in Scheme I. Each of these electroactive compounds in acetonitrile solution with TBAP as supporting electrolyte exhibited two successive monoelectronic redox couples: a reversible process (*1*) at a more positive potential which corresponds to the formation of the radical anion $L^{\cdot -}$ (E°_1), followed by a quasi-reversible process (*2*) attributed to the formation of the dianion L^{2-} (E°_2) (Figure 1a)

$$L \underset{(1)}{\overset{E^0_1}{\rightleftarrows}} L^{\cdot -} \underset{(2)}{\overset{E^0_2}{\rightleftarrows}} L^{2-} \qquad (1)$$

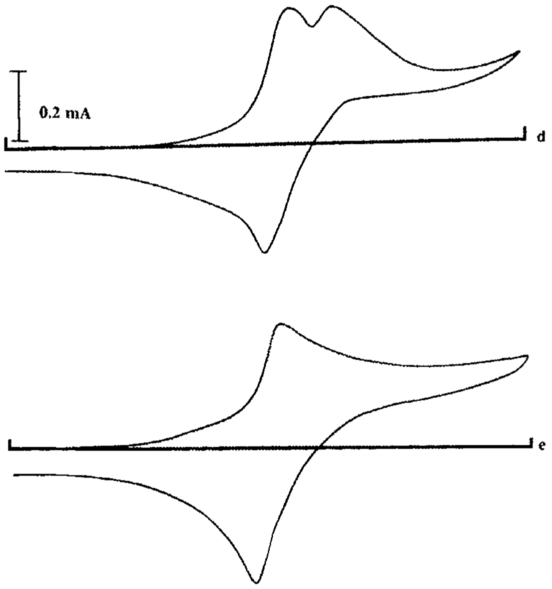
The peak currents varied according to the square root of the potential scan rate in the range 0.1-0.5 V s^{-1} and were proportional to the amount of ligand present in the solution.

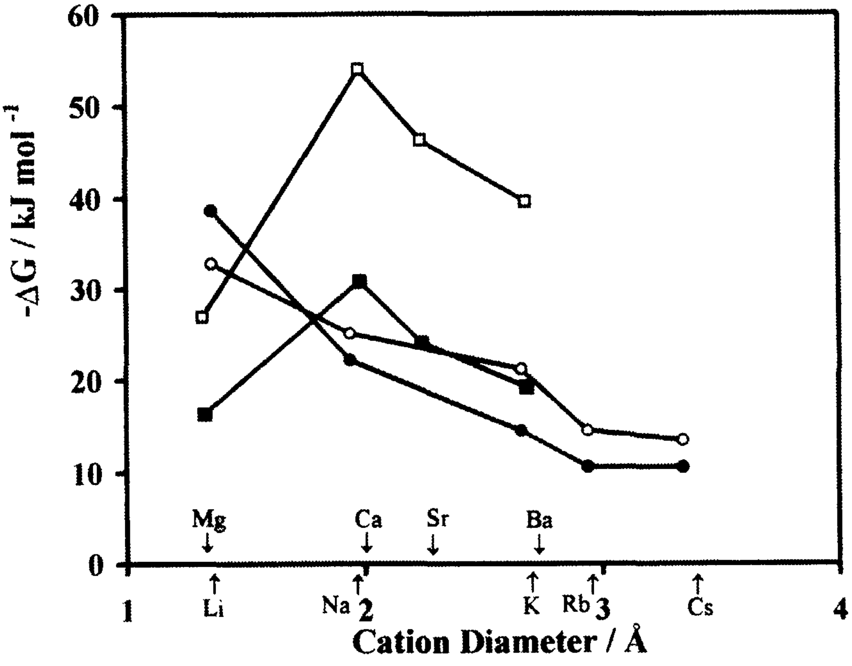
In presence of alkaline earth cations, the electrochemical behaviour was significantly altered. Figure 1 shows the changes that occurred in the cyclic voltammograms of the ligand A upon addition of successive amounts of barium



Compound	n
A	1
B	2

perchlorate to its solution. For concentration ratio L/Ba^{2+} = 2/1 and 1/1, three redox couples were observed (Figure 1b and 1c), one associated with the free ligand (E^o_1) and two additional new couples assigned to the reductions of the bound ligand $M^{2+}L$ ($E^{o\prime}_1$) and $M^{2+}L^{\cdot -}$ ($E^{o\prime}_2$), processes (*1′*) and (*2′*), both





positioned at more positive potentials than the corresponding ones for the free ligand form (E^o_1 and E^o_2).

$$M^{2+}L \underset{(1')}{\overset{E_1^{0'}}{\rightleftarrows}} M^{2+}L\cdot^- \underset{(2')}{\overset{E_2^{0'}}{\rightleftarrows}} M^{2+}L^{2-} \qquad (2)$$

The new waves indicate that the cation is able thermodynamically and accessible structurally to interact with the reduced groups and the potential shifts reflect an increase of the complexation strength between the ligand and the cation bound to the macro-ring.[17, 20] The redox couple (*2*) was absent due to the strong anion radical-cation interaction [21] which prevents the reduction of $L\cdot^-$ to L^{2-}, although the $M^{2+}L^{2-}$ specie has been formed through process (*2'*). At L/Ba^{2+} = 1/2 ratio only the waves corresponding to the processes (*1*) and (*1'*) (Figure 1d) were observed, although (*1'*) is less reversible and (*1*) becomes irreversible. The second reduction steps of the ligand are absent. We suppose that the electrochemical product $M^{2+}L\cdot^-$ associated with the increase of M^{2+} forms an insoluble layer that is adsorbed at the electrode surface. Reoxidation does not contribute to the current until the insoluble layer is stripped at the potential at which the oxidation $M^{2+}L\cdot^- \rightarrow M^{2+}L$ takes place. [17, 22, 23] For concentration ratio L/Ba^{2+} = 1/5 only the redox process (*1'*) (Figure 1e) was observed, maintaining both the wave shape and the formal potential value unaffected although the reversibility decreased. The absence of the couple (*1*) is a consequence of the strong $M^{2+} - L\cdot^-$ interaction and of the increase of metal concentration which makes the concentration of free ligand very small and its reduction, process (*1*), not detectable. [24] The current intensity of the new couples of complexed ligand are enhanced progressively with an increase in the amount of cation present in solution, while the relative intensity of the peaks of the free ligand couples was diminished or disappeared.

Qualitatively similar electrochemical behaviour has been found when Sr^{2+} is added to the solution of ligand A. There were some differences in the voltammetric characteristics obtained with the Ca^{2+} and Mg^{2+} cations, where only the redox couples corresponding to the processes (*1*) and (*1′*) are observed, (*2′*) being absent. The electrochemical behaviour of the ligand B is rather similar for each of the cations examined, with the exception of Mg^{2+} where the waves corresponding to the process (*2′*) are not detected. Table I reports the wave type, magnitude and shift of the formal potentials of the ligands investigated as a function of the amount of added metal ion. Where the electrochemical process showed a high degree of irreversibility or was totally irreversible, only the reduction potentials have been considered in estimating binding enhancements.

The $E^{o\prime}$ values obtained with each of the cations did not depend on the ligand concentration and/or on the L/M^{2+} ratio (Table I). This behaviour suggests the formation of 1:1 complexes and hence other complexation stoichiometries can be excluded under the experimental conditions used.

The binding strength and stability of unreduced complexes, in which ligands contain a crown ether system whose cavity is adjustable to the alkaline earth cation size, will be dominated by the multiple and favourable cation-oxygen interactions. It will greatly depend on the ratio of crown cavity size to cation size and on structural factors, [1, 9-11, 25] although other factors can be considered. The shift of the ligand formal potentials to more positive values in the presence of alkaline earth cations is consistent with a stronger interaction of the macroring bound cation with the reduced ligand. [14, 16]

The magnitude of the formal potential shifts $\Delta E^o = E^{o\prime} - E^o$ produced by the cations can be used as a measure of the coordination strength of the reduced compared with the neutral ligands. [26] Enhancements of cation binding K_2/K_1 and K_3/K_2 where K_1, K_2 and K_3 are the complexation constants with the unreduced, monoanionic and dianionic ligand respectively, were calculated from the ΔE^o values and are summarized in Table II. We cannot determine K_3/K_2 for some systems because no redox or reduction waves were observed for process (*2′*). Therefore the following discussion will be limited to the $L/L\cdot^-$ couple since it is the only one that shows systematic and appreciable potential shifts.

TABLE I Electrochemical data for the free and complexed ligands with alkaline earth metal ions.*

Compound	M^{2+}	L/M^{2+}	$-E^{o}_{1}/V$	$-E^{o}_{2}/V$	$-E^{o\prime}_{1}/V$	$-E^{o\prime}_{2}/V$	$\Delta E^{o}_{1}/V$	$\Delta E^{o}_{2}/V$
A			1.24	1.68				
	Mg^{2+}	2/1	1.23	1.64	1.11[a]	¶	0.17[b]	
		1/1	1.24	1.07	0.17			
		1/2	1.05	0.19				
		1/5	1.08	0.16				
	Ca^{2+}	2/1	1.18	0.86	0.32			
		1/1	1.15	0.83	0.32			
		1/2	0.81	0.34				
		1/5	0.81	0.34				
	Sr^{2+}	2/1	1.20	0.95	1.67[a]	0.25	0.10[b]	
		1/1	1.19	0.92	0.27			
		1/2	0.91	0.28				
		1/5	0.89	0.30				
	Ba^{2+}	2/1	1.23	1.03	1.58	0.20	0.10	
		1/1	1.22	1.02	1.56	0.20	0.12	
		1/2	1.25[a]	1.01	0.21			
		1/5	0.99	0.23				
B			1.32	1.77				
	Mg^{2+}	2/1	1.32	1.75	1.04	0.28		
		1/1	1.30	1.90[a]	1.01	0.29		
		1/2	-	-				
	Ca^{2+}	2/1	1.34	0.78	1.69	0.56	0.08	
		1/1	1.34[a]	0.77	0.57			
		1/2	0.76	0.58				
		1/5	0.77	0.57				
	Sr^{2+}	2/1	1.29	1.80[a]	0.81	0.48		
		1/1	1.32[a]	1.84[a]	0.81	1.74[a]	0.48	0.10[b]
		1/2	0.79	0.50				
		1/5	0.80	0.49				
	Ba^{2+}	2/1	1.35	1.85[a]	0.94	1.72[a]	0.41	0.13[b]
		1/1	1.37[a]	0.93	0.42			
		1/2	0.95	0.40				
		1/10	0.94	0.41				

*The scan rate was varied in the range 100-500 mV s^{-1}; the results presented were obtained at 100 mV s^{-1}. Potentials are reported *vs* Ag/10 mM Ag^{+} in acetonitrile solution electrode containing 0.1 M TBAP as supporting electrolyte. The potential values represent the average at the least five independent determinations and their reproducibility is ±0.02 V. E^{o}_{1} and E^{o}_{2} represent the formal potentials of the free ligands and $E^{o\prime}_{1}$ and $E^{o\prime}_{2}$ represent the formal potentials of the complexed ligands, being their values estimated as the average of the cathodic and anodic peak potentials, $E^{o} = (E_{red} + E_{ox})/2$. $\Delta E^{o} = E^{o\prime} - E^{o}$, represents the difference between the formal potentials of the complexed and free ligands.

[a] A reduction peak and not a redox couple was observed.

[b] ΔE^{o} values were deduced from the reduction potentials of the complexed and free ligands $E'_{red} - E_{red}$.

TABLE II Potential shifts (ΔE^o), enhancements of cation binding (K_2/K_1 and K_3/K_2) and Gibbs energy decreases ($-\Delta G$) in the complexation of the reduced ligands with alkaline earth metal ions at 25°C.[b]

Compound	M^{2+}	$\Delta E^o/V$		K_2/K_1	K_3/K_2	$-\Delta G/kJ\ mol^{-1}$	
		ΔE^o_1	ΔE^o_2			$-\Delta G_{2-1}$	$-\Delta G_{3-2}$
A	Mg^{2+}	0.17		7.5×10^2		16.4	
	Ca^{2+}	0.32		2.6×10^5		30.9	
	Sr^{2+}	0.25	0.10	1.7×10^4	4.9×10^1	24.1	9.6
	Ba^{2+}	0.20	0.10	2.4×10^3	4.9×10^1	19.3	9.6
B	Mg^{2+}	0.28		5.4×10^4		27.0	
	Ca^{2+}	0.56	0.08	2.9×10^9	2.3×10^1	54.0	7.7
	Sr^{2+}	0.48	0.10	1.3×10^8	4.9×10^1	46.3	9.6
	Ba^{2+}	0.41	0.13	8.6×10^6	1.6×10^2	39.6	12.5

[b] All values presented were obtained from the $L/M^{2+} = 2/1$ ratio.

The largest potential shift associated with the ligand A, $\Delta E^o_1 = 0.32$ V was induced by Ca^{2+}, indicating the largest complexation increase of 2.6×10^5 (K_2/K_1) and corresponding to a decrease in the Gibbs energy of binding of 30.9 kJ mol^{-1} ($-\Delta G$) as is indicated in Table II. The Sr^{2+} and Ba^{2+} ions, which have lesser ionic potentials, induce smaller binding enhancements; the Gibbs energy change was estimated to be $\Delta G = -24.1$ and -19.3 kJ mol^{-1} respectively. These results indicate that the largest electrochemical perturbation was induced by the cation having the greatest charge to radius ratio (Ca^{2+}) and not by the cation that is more easily fitted to the crown ether ring (Ba^{2+}). Therefore, the magnitude of the potential shifts can be considered to be dependent on the ionic potential of the bound cation and the contribution of the electrostatic interactions between the cation and the reduced carbonyl oxygen becomes the dominant factor for the increase in the complex stability. Other factors including the conformational flexibility of the macro-ring [9, 13, 25, 27] and desolvation of both the cation and ligand [4, 25, 28] although less important, can also contribute to the overall Gibbs energy of the complexation process.

The ligand molecules possess an anthraquinone unit with a rigid structure and a polyether macro-ring with some structural flexibility where the cation is accommodated. If the interaction between the cation and the macro-ring is complemented by ionic interactions and the cation size is small compared with the size of the macrocavity, the reduction of the complexed ligand can be accompanied by an energetically more favourable structural rearrangement of the crown ether cavity induced by the electric field of the cation. [4, 13] The Ca^{2+} ion has the smallest size and the highest ionic potential among the alkaline earth cations excepting Mg^{2+}. Comparatively it can produce upon electrochemical reduction a more favourable conformation of the crown cavity which allows a rearrangement of the donor atoms better to accommodate and interact with the cation, [14, 29] so contributing to a stronger complexation.

Strong cation solvation and a weak cation-neutral ligand interaction can lead to partial desolvation of the cations mainly for those with a higher electric field and too small a size to fit the macro-ring cavity size. The Ca^{2+} ion with a comparatively stronger solvation [30] and smaller size can produce upon electrochemical reduction of the ligand a more extensive and additional desolvation originated by the stronger cation-reduced ligand interaction. Thus it can contribute to more favourable enthalpy and entropy of interaction, associated with greater thermodynamic stability. The Ba^{2+} ion with the best fit to the macro-ring cavity and lower solvation energy is more competitive in the complexation process for the neutral ligands than are Sr^{2+} and Ca^{2+} ions. Therefore, its desolvation upon electrochemical reduction of the ligand should be less extensive.

The Mg^{2+} ion, despite being the most polarizing of the cations examined, showed a different trend and induced the smallest redox shift produced by the cations studied; $\Delta E^{\circ}_1 = 0.17$ V, indicating a comparatively weak enhancement of binding; $\Delta G = -16.4$ kJ mol^{-1}. This cation is too small compared with the crown ether cavity size [25] and its localization may not be necessarily at the center of the chelating cavity. [16, 31] Therefore, it is more difficult to interact with all the potential binding sites, thus weakening the total electrostatic interaction when compared with the other larger divalent cations positioned near the cavity centre where a greater number of oxygen atoms can participate in coordination. In addition, possibly only a part of the cation solvating molecules is replaced by ligand donor atoms [32] despite Mg^{2+} being the most strongly solvated ion among the alkaline earth cations. [30] Its complexes therefore may retain significant solvation upon electrochemical reduction of the ligand in contrast to the other alkaline earth cations whose desolvation is probably more extensive.

The ligand molecules contain two carbonyl groups which can be electrochemically reduced and used to bind each of the cations. The large values obtained for ΔE°_1 indicate that the position of the reduced carbonyl oxygen atom belonging to the crown ring makes it accessible to the complexed cation, thereby strongly contributing for the increase of the coordination strength. Further reduction of the radical anion $L\cdot^-$ to L^{2-} resulted either in a small shift of E°_2 to more positive potentials accompanied by an increase of the irreversibility, or in the absence of voltammetric waves even when an excess of metal cation was present (Table I). An examination of molecular models suggests that the carbonyl oxygen placed outside the macrocyclic cavity is too remote to interact appreciably with the bound cation.

The incorporation of one more ethylenoxy groups into the macro-ring (ligand B) with consequent increase of the number of donor atoms and cavity size, showed larger ΔE^{o}_{l} values (Table I). The maximum binding enhancement was also attained in the presence of Ca^{2+} ($\Delta E^{o}_{l} = 0.56$ V). Again the magnitude of the potential shifts (ΔE^{o}_{l}) was dependent on the polarizing power of the complexed alkaline earth metal ion with exception of Mg^{2+}. When the complexation of the reduced ligand A with B for the same cation is compared there is seen to be an average increase of stabilization of the complexes by approximately 22 kJ mol^{-1} (Table II). The Mg^{2+} ion induced a much smaller increase of stabilization (11 kJ mol^{-1}). This gain in stability can be attributed to the combination of two main effects: the increase in the number of donor sites in the crown cavity which enhances electrostatic interactions to the positively charged metal ions and a larger negative enthalpy, [25, 29, 32] and a more favourable macroring flexibility which can make the cation coordination more effective from the entropic point of view.[25, 33]

We have recently shown that both one- and two-electron ligand reductions led to an enhancement of cation binding with alkali metal ions. [17] The ΔE^{o}_{l} values now obtained are larger for alkaline earth when compared with those previously observed for alkali metal cations of similar size. This indicates that the ligand redox centres are electrochemically more sensitive to the presence of the doubly charged alkaline earth than to the monopositive alkali metal cations, thus inducing larger enhancement of cation binding. The relative Gibbs energy changes corresponding to the tendency of the increase of complexation are plotted as a function of cationic size in Figure 2, in which the results obtained with alkali metal cations are also presented. [17] Two observations can be confirmed from these profiles; first, the correlation appears to be more closely controlled by the charge of the complexed cation, confirming that the complexation increase is mainly of electrostatic nature; secondly, the larger number of the binding sites and larger size of the cavity induces the largest complexation increase for the same cation. Li^{+} and Mg^{2+}, two ions of comparable size, have reverse behaviour; Li^{+} is the most favoured among alkali metal cations; Mg^{2+} displays the opposite preference inducing the smallest enhancement of binding among the alkaline metal cations for the reasons already discussed.

Electrochemical studies showed that ligands of the anthraquinone-crown ether type shift their reduction potentials to more positive values in the presence of alkaline earth metal ions, indicating that complexation is increased considerably upon addition of charge to the ligand. For the redox-active ligands studied, the magnitude of the binding enhancements followed the order: $Ca^{2+} > Sr^{2+} > Ba^{2+} > Mg^{2+}$, reflecting mainly the order of decreasing of ionic potential of the cations with the exception of Mg^{2+}. The results described reveal that reduced ligands show high selectivity for Ca^{2+} over Mg^{2+}. The enhancements of binding result from a coupling of both redox and complexation reactions. The enhancement of cation binding was favoured by the ligand with the largest number of binding sites in the macrocyclic cavity. Although less important, factors such as desolvation of the cation and structural flexibility of the macro-ring cavity can also be considered in the contribution for the decrease of the Gibbs energy of complexation. The binding enhancements are still dependent on the geometry and availability of the electroactive centres relatively to the cation binding centre. The carbonyl group located within the crown ring strongly favours cation coordination because of its proximity and appropriate geometrical orientation; the contribution of the other carbonyl group is negligible.

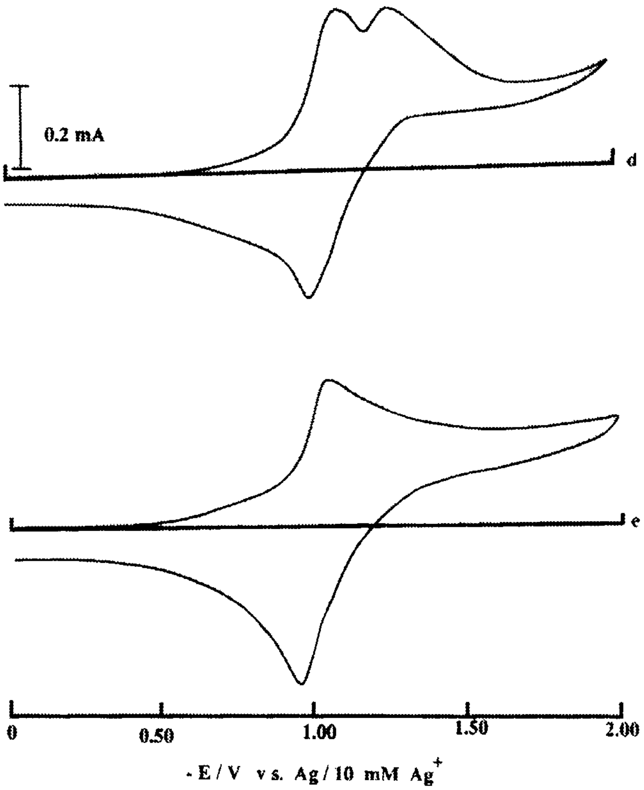


FIGURE 2 Gibbs energy decreases ($-\Delta G$) corresponding to the complexation increases of the radical anions A and B with alkali and alkaline earth metal ions as a function of the cation size. ■-ligand A + alkaline earth metal cations; □-ligand B + alkaline earth metal cations; ●-ligand A + alkali metal cations; ˆ-ligand B + alkali metal cations.

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