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Effect of the Number of Donor Atoms in Calix[4]arene Derivatives for Selective Complexation and Extraction of Mercury(II) Cations, Thermodynamics and Extraction Studies

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Abstract

Water pollution due to gold mining activity is increasingly worrying. One way to selectively mitigate it is through the use of complexing agents such as calixarenes, which selectively functionalized with soft donor atoms such as sulphur, can selectively remove this pollutant, for the selective complexation of mercury from contaminated water, which was compared by conductimetry and liquid-liquid extraction studies with results that show that the derivative with the highest sulphur atoms is its structure which presents greater selectivity compared to the derivative with the lowest number of sulphur atoms, in both cases, they present very stable complexes.

Keywords

Pollutant, Calixarene, Mercury, Selectivity, Donor Atoms

1. Introduction

Mercury (Hg) is a highly toxic metal that contaminates our water and air supplies. Approximately two-thirds of the Hg in natural environments are of anthropogenic origin [1]. Burning of fossil fuels, such as petroleum, natural gas and coal, is the most important contributor to the total environmental Hg budget, since they contain approximately 0.2 ppm of Hg^2. Mercury can be found in significant amounts in wastes from chlor-alkali manufacturing plants, electri-

cal and electronics manufacturing, and sulphide ore roasting operations. Exposure to Hg can have toxic effects on reproduction, the central nervous system, liver, and kidneys, and cause sensory and psychological impairments. Mercury in industrial effluents and flue gas is usually recovered using chelating agents, which are not reusable after Hg is removed by distillation [2]. Alternative treatment methods are greatly needed to keep Hg out of the environment.

In order to minimize the adverse effects of Hg in the environment, it is desirable to find ways to capture it before it becomes a problem. Several techniques are available for this including precipitation, ion exchange and adsorption.

The ability of a material to capture metals is controlled in part by the number of available functional groups used for binding metals. Functional groups with a known affinity for specific metals can be attached to other substances in order to create an effective adsorbent [3]. The thiol (-SH) group is known to form stable complexes with soft heavy metals of high polarizability such as Hg, Ag, Au, and to a lesser extent, Cd and Zn, while failing to coordinate well with the more abundant smaller, lighter metals such as Ca, Na, and Mg [4].

Recent studies speculated that the reaction between mercury and sulphur groups present in the adsorbent materials accounted for high adsorption capacity, in this direction, Meng *et al.* [5] reported the ability of used tyre rubber containing sulphur groups to scavenging the Hg(II) from solutions [6]. Sreedhar *et al. [7]* performed batch experiments with polysulphide treated coconut husk for Hg(II) binding. Since mercury species show a high affinity towards sulphur, a method of improving adsorption potential of activated carbon could be based on immobilising sulphur on the material. Serrano *et al.* [8] utilised commercial activated carbon loaded with sulphur groups for the removal of Hg(II), Pb(II) and Cd(II) ions from aqueous solutions.

Calixarenes [9], cyclic oligomers of phenol-formaldehyde condensates, have received much attention over the past decade as a fascinating class of cyclophanes possessing ionic and molecular-binding properties. Derivatives containing a wide range of functional groups have been synthesized and shown to exhibit different degrees of receptor ionophoric activity [10]. A number of calixarene derivatives containing pendant ether, amide, ketonic, and ester groups have been reported thermodynamic of complexation with unit and bivalent cations [11] [12].

In this work, the effect of the number of donor atoms over the binding Hg^{2+} metal cation is reported. Thermodynamic data (conductivity, calorimetry and potentiometry) and extraction result in an immiscible solvent system.

## 2. Experimental Part

2.1. Chemicals

p-tert-Butylcalix[4]arene, bromoacetonitrile, diethyl chlorothiophosphate potassium carbonate and potassium hydrogen carbonate were purchased from Aldrich, Lithium aluminium tetra hydride, 18-crown-6 (18C6), Tetra-*n*-butylammonium

perchlorate (TBAP) and tetra-*n*-butylammonium bromide were purchased from Fluka were used without further purification. Metal cation salts as perchlorate mecury(II) and potassium(I), were dried over P_4O_{10} under vacuum for several days before use.

Acetonitrile (HPLC grade, Hayman Limited, high purity reagent), THF (tetrahidrofuran), methanol (Fisher reagent, 99%) ethanol (HPLC grade Fisher) dichloromethane (Fisher) was used without further purification, picric acid analytical grade was purchased from Aldrich.

2.2. Synthesis

The ligands 5,11, 17, 23-tetra-*tert*-butyl[25, 27-bis(diethylthiophosphate amino)ethoxy-26, 28-bis(hydroxy)]-calix[4]arene, (L_1) and 5, 11, 17, 23-tetra-*tert*-butylcalix[4]arene, tetra diethyl thiophosphate; (L_2) was have synthesize, following of technique were descript by our group [13] [14] and in the search the selective macrocycle ligand for the attach mercury metal cations was found the functionalized arms groups that have donor atoms phosphorus, sulphur, nitrogen and oxygen. The oxygen as a hard Lewis base atom that interacts preferentially with cation type hard Lewis acid, while nitrogen is borderline base, sulphur and phosphorus are typical soft atoms interacts preferentially with soft cations, such as silver and mercury [2].
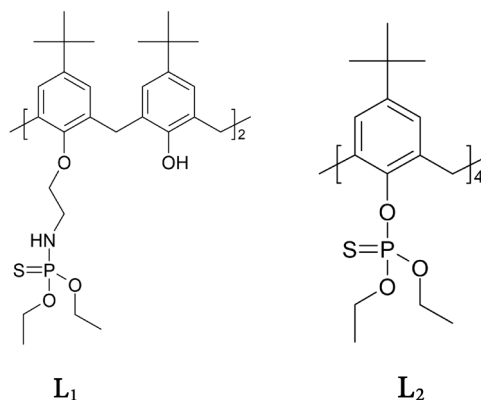
L_1 $\qquad$ L_2

Synthesis of 5,11, 17, 23-tetra-*tert*-butyl[25, 27-bis(diethylthiophosphate amino)ethoxy-26, 28-bis(hydroxy)]-calix[4]arene, (L_1)

L_1 was synthesized by the method previously described by Danil de Namor and co-workers [13], the ligand was characterized by Thermo Scientific Flash *Smart* Series Elemental Analyzers equipment. Elemental analysis was carried out at the University of Surrey, calculated % C, 64.71, H, 8.15, N 2.70; found % C 64.62, H 8.12, N 2.67. and ^{1}H and ^{13}C NMR.

[1]**H NMR** (300 MHz, in CDCl₃); δ (ppm), J (Hz); 8.59 (s, 2H, Ar-OH), 7.03 (s, 8H, Ar-H), 5.60 (t, 2H, J = 11.10, -CH₂-NH-), 4.34 (d, 4H, J = 13.20, Ar-CH₂ax-Ar), 4.13 (m, 12H, -O-CH₂-CH₂, O-CH₂-CH₃), 3.62 (m, 4H, -CH₂-CH₂-NH), 3.38 (d, 4H, J = 12.91, Ar-CH₂eq-Ar), 1.32 (t, 12H, O-CH₂-CH₃), 1.24 (s, 18H, -C-(CH₃)₃), 1.15 (s, 18H, -C-(CH₃)₃).

^{13}**C NMR** (300 MHz) (CDCl$_3$) δ_C ppm; 149.88, 148.84, 147.97, 142.41, 133.48, 127.67, 126.09, 125.62 (Ar), 77.26 (OCH$_2$CH$_2$NH), 63.08, 62.99 (OCH$_2$CH$_3$), 42.44 (OCH$_2$CH$_2$NH), 34.25, 33.88 (C(CH$_3$)$_3$, 32.41 (ArCH$_2$Ar), 31.63, 31.51 (C(CH$_3$)$_3$, and 16.15, 16.04 (OCH$_2$CH$_3$).

Synthesis of 5, 11, 17, 23-tetra-*tert*-butylcalix[4]arene, tetra diethyl thiophosphate (L$_2$)

L$_2$ was synthesized as previously reported by our group [14] [15], the ligand was characterized by Elemental analysis was carried out at the University of Surrey, calculated % C, 57.31, H, 7.37; found % C 57.13, H 7.59 and ^{1}H and ^{13}C NMR.

^{1}**H NMR** (300 MHz, in CDCl$_3$); δ (ppm), J (Hz); 8.90 (s, 8H, Ar-H), 4.85 (d, 4H, J = 14.10, Ar-CH$_2$ax-Ar), 4.29 (m, 16H, -O-CH$_2$-CH$_3$), 3.24 (d, 4H, J = 13.80, Ar-CH$_2$eq-Ar), 1.34 (t, 24H, O-CH$_2$-CH$_3$), 1.07 (s, 36H, -C-(CH$_3$)$_3$).

^{13}**C NMR** (300 MHz) (CDCl$_3$) δ_C ppm; 146.78, 143.24, 134.32, 125.92 (Ar), 65.52 (OCH$_2$CH$_3$), 34.36 (C(CH$_3$)$_3$, 32.41 (ArCH$_2$Ar), 31.80 (C(CH$_3$)$_3$, and 16.44 (OCH$_2$CH$_3$).

2.3. Conductimetric

The Wayne-Kerr B642 is an autobalance ratio arm bridge for the measurement of impedance. During the conductance measurements, the magnitude of the capacitance and the conductance are monitored on the two meters. Each of these meters has for decades, which are operated in succession. Small signal are placed between the decade control knobs to indicate the decimal points. The control knobs are selected automatically by operation of the range switch. The sensitivity of the meter can be switched to one of these normal positions to adjust the apparatus manually, the accuracy of the bridge is determinated by its internal sources and it was found to be 0.1% for all decades in use.

For the determination of the cell constant of the conductivity cell, an aqueous solution of KCl (0.10 mol·dm^{-3}) was added by steps to the deionized water containing cell. The cell was kept in the thermostatic bath at 298.15 K. The conductance of the water was measured in advance and subtracted from each conductance change recorded. The corresponding molar conductance (S·cm^2·mol^{-1}) was calculated from the equation of Lind, Zwolenik, and Fuoss [16] the molar conductance of KCl was used to calculate corresponding values of the specific conductance and then the cell constant.

2.4. Conductance Measurements at 298.15 K

Fresh solution of both the metal-ion salt and the ligands under investigation were made up for each experimental run. The conductance cell was cleaned, dried, and the accurately weighed the solution of metal-ion salt in acetonitrile and dichloromethane-water solvent system (~25 ml charged, ~3.0 × 10^{-4}), after thermal equilibrium, the ligand is added to the cell from a hypodermic syringe (~10 ml, ~1.0 × 10^{-3}). All measurements were taken at 298.15 K.

2.5. Potentiometric

The stability constant of **L** (L_1 and L_2) and mercury (II) cation were measured by potentiometry titration was using Metrohm, 716 DMS Titrinio) equipped with calomel (Hg_2Cl_2/Hg) reference double junction electrode (Russell). Its inner electrolyte was a LiCl solution saturated in ethanol, whilst the outer (salt bridge) electrolyte, separate the electrode from the titration cell, was a solution of te-tra-*n*-butylammonium perchlorate (TBAP, 0.05 mol·dm⁻³) in acetonitrile. The concentration of the free mercury ion was measured using mercury indicator electrode, both electrodes were connected to a compact automatic titrator-processor Titrinio, all titrations were carried out under a flow of nitrogen. For the calibration experiments the vessel filled with (20 ml solution TBAP 0.05 mol·dm⁻³), the burette filled with solution $Hg(ClO_4)_2$ (~3×10^{-3} mol·dm⁻³) after equilibrium starting automatic addition, collecting all data by Hyperaccess data system, the Nernstian behavior of the electrode was evaluated from the slope of a plot of potential against $-\log[Hg^{2+}]$.

For the determination of the stability constant, the ligand solution (~1.0×10^{-3} mol·dm⁻³) were prepared in TBAP solution (0.05 mol·dm⁻³) in the typical experiment filled this solution in the burette and added into the vessel solution containing a known concentration of Hg^{2+} allowing the formation of the 1:1 mercury calixarenate complex. Data collecting by Hyperaccess system used for the calculation stability constant by the use of a computer program SUPERQUAD [17].

2.6. Calorimetric

Macrocalorimetric titrations, the Tronac 450 calorimeter were used as an isoperibol titration calorimeter [18]. It is equipped with a 2 cm³ burette connected by a silicone tube to the reaction vessel. The reproducibility of the apparatus was checked by (i) calibrating the burette [19] and (ii) chemical calibration using the standard reaction of protonation of an aqueous solution of tris(hydroxymethyl)-aminomethane (THAM) in hydrochloric acid (HCl, 0.1N) at 298.15 K. Therefore, an aqueous solution of THAM was placed in the burette and incrementally titrated into the reaction vessel containing the solution of HCl (50 ml). The value determined -47.63 ± 0.19 kJ·mol⁻¹ is in agreement with the one reported by Öjelund and Wadsö (-47.49 kJ·mol⁻¹) using an LKB reaction calorimeter [20].

A direct calorimetric titration was carried out when log Ks < 6, in which a solution of the metal ion salt (concentration range 2.0×10^{-2} to 5.0×10^{-2} mol dm⁻³) was prepared in acetonitrile, placed in the burette, and titrated into the vessel containing a solution of the ligand of interest, (50 cm³, concentration range 6.0×10^{-4} to 1.5×10^{-3} mol dm⁻³) prepared in the same solvent.

2.7. Partition Experiments

Potassium picrate solution was prepare as described elsewhere [21], was used to

prepare mercury (II) picrate *in situ* by dissolving and excess of mercury (II) perchlorate, left overnight white precipitate of potassium perchlorate appears, after filter check concentration of mercury in liquid phase by technique EDTA replacement titrations [22].

Partition experiments were carried out in the absence of ligand, equal volumes (10 cm^3) of the aqueous phase containing different concentrations of metal-ion picrate in aqueous phase (5.1×10^{-5} - 1.7×10^{-4} mol·dm^{-3}), were mixed with dichloromethane, the mixtures were shaken for a period of 30 minutes, and then were left overnight in an isothermal bath at 298.15 K. Aliquots from the aqueous phase were taken and analyzed by spectrophotometric measurements.

Extraction experiments were carried out in the presence of ligand, accurate volumes of aqueous solution (10 cm^3) containing metal-ion solution (1.7×10^{-4} mol·dm^{-3}) and the (10 cm^3) organic solution containing the ligand in different concentration (4.27×10^{-5} - 2.17×10^{-4} mol·dm^{-3}) were placed in stoppered flask. The mixture was vigorously shaken were left overnight in a thermostatic bath at 298.15 K. Aliquots from the aqueous phase were taken and analyzed by spectrophotometric measurements

3. Results and Discussion

3.1. Structural Conformation of L_1 and L_2 in Solution

It is well established [23] that the difference in chemical shifts between the axial and the equatorial protons ($\Delta\delta_{ax-eq} = \delta_{ax} - \delta_{eq}$) provides information regarding the conformation of the ligand in a given solvent and the indication of the flattening degree of the "*cone*". Thus $\Delta\delta_{ax-eq}$ value of 0.9 ± 0.2 ppm is expected for the ligand in a perfect cone conformation while $\Delta\delta_{ax-eq}$ value of 0.5 ± 01 ppm corresponds to the flattened ligand in a "*cone*" conformation.

The pair of doublets found in the ^{1}H NMR spectra for L_1 and L_2 which corresponding to the axial (4.34 ppm for L_1 and 4.85 ppm for L_2) and the equatorial (3.38 ppm for L_1 and 3.24 ppm for L_2) protons of the bridging provide information to measure of the flattening of the cone. As far as the value for L_1 is $\Delta\delta_{ax-eq} =$ 0.96 ppm this corresponding when L_1 adopt a perfect *cone* conformation, while the value found for L_2 ($\Delta\delta_{ax-eq}$ = 1.61 ppm) corresponding when the ligand adopts a distorted *cone* conformation.

However these conformations for L_1 and L_2 are easily to explain, (i) L_1 is a partially substituted differently in which play a predominant role the hydrogen bond between the ethereal oxygen and phenolic proton to give to this derivative a more symmetry structure as reporting in previous works Danil de Namor *et.al.* [14], (ii) In fully substituted calix[4]derivatives most of these derivatives adopts the distorted cone conformation in solution and in solid state, in which the hydrophobic cavity decrease what that of the hydrophilic cavity increase, that may attributed to higher electrostatic repulsion between the pendant arms in L_2.

3.2. Conductance Measurements

The main aim of conductance measurements was to establish the composition

of the metal-ion complexes in acetonitrile at 298.15 K. Information that is required to proceed with the thermodynamic characterization of the complexation process involving these ligands and Hg^{2+} metal cation in acetonitrile.

Plots of molar conductance (Λ_m) against the ligand/metal-ion mol ratio showed for both ligands well-defined changes of curvature to 1:1 stoichiometry are observed, that represent strong complexes in both cases. The interesting feature is observed when moving from L_1, in which the dangling arms have two sulphur atoms as binding site, while L_2, increases the number of binding sites (sulphur atoms) to four, the changes in molar conductance are more pronounced in L_2, as shown in **Figure 1**. The decrease in molar conductance is observed with the addition of the ligand to the metal cation in acetonitrile, this can be attributed to the size of the cation as it changes from free (small) cations to cationic (large) complexes, as a result of this size change the mobility decreases until the end point or stoichiometry of the complexation is reached.
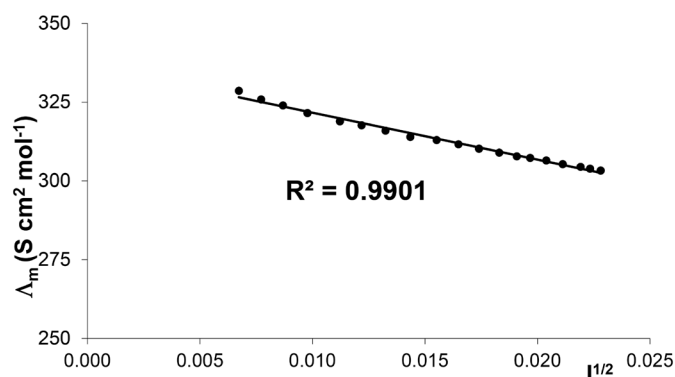
3.3. Thermodynamic of Complexations

Stability constants (log Ks) and derived Gibbs energy of complexation, $\Delta_c G^o$, enthalpies, $\Delta_c H^o$ and entropies, $\Delta_c S^o$ of these ligands with mercury(II) metal cations in acetonitrile at 298.15 K are listed **Table 1**, these data were obtained from titration macrocalorimetry and potentiometry measurements.

The complex composition found in previous discussions is required to formulate a representative equation of the complexation process. Taking into account speciation of the multicharged electrolyte in solution by conductance measurements, **Figure 2** in which a linear relationship is obtained when the
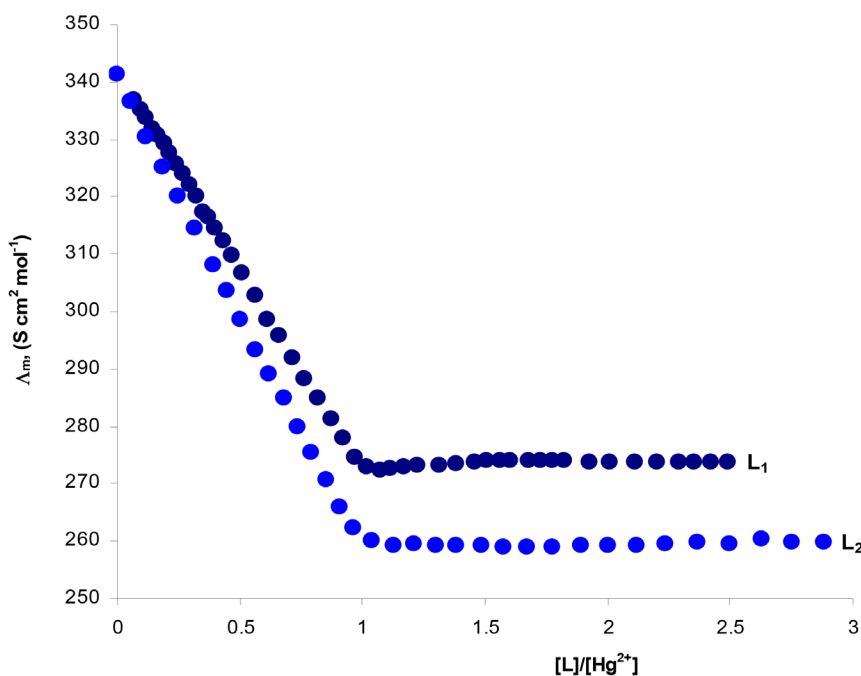
Figure 1. Conductometric curve for the titration of mercury(II), (as perchlorate) and L in acetonirile at 298.15 K.

Figure 2. Molar conductance, Λ_m, against the square root of the ionic strength, $I^{1/2}$, for Hg^{2+} (as perchlorate) in acetonitrile at 298.15 K

**Table 1.** Thermodynamic parameters for the complexation of Hg^{2+} (as perchlorate) and L (L_1 and L_2) in acetonitrile at 298.15 K by the titration classical calorimetry and titration potentiometric.

Metal	$\log K_s$	$\Delta_c G^o$ (kJ·mol^{-1})	$\Delta_c H^o$ (kJ·mol^{-1})	$\Delta_c S^o$ (J·mol^{-1}·K^{-1})
$Hg^{2+} + L_1$	10.02 ± 0.08[a]	-57.5 ± 0.4	-69.5 ± 0.7[b]	-40
$Hg^{2+} + L_2$	11.31 ± 0.01[a]	-64.51 ± 0.06	-41.9 ± 0.4[b]	76

[a]potentiometric data, [b]macrocalorimetry data.

molar conductance, (Λ_m) of $Hg(ClO_4)_2$ in acetonitrile is plotted against the square root of the ionic strength ($I^{1/2}$) of the electrolyte in solution. The results in this Figure clearly demonstrated that ionic are the predominant species in solution. These finding were also corroborated by performing thermodynamic measurements at different concentration of the electrolyte in solution, not variation in stability constant values are observed.

On basis to these findings the thermodynamic process for the complexation this ligands with mercury(II) metal cations is described as:

$$Hg^{2+}(s) + L(s) \xrightarrow{\ K_s\ } Hg^{2+}L(s) \tag{1}$$
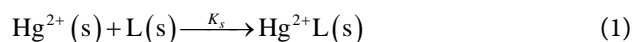
The standard deviation of the data also included in **Table 1**.

Stability constant for mercury was derived from data obtained by direct potentiometry using the calomel reference electrode and mercury indicator electrode. Typical potentiometric titration curve for the titration of mercury (II) as perchlorate with this ligand shown in **Figure 3** and **Figure 4** where potential reading in mV is plotted against legal/metal ratio was observed, indicating that one metal cation with one ligand unit as demonstrated from conductance measurements.

The enthalpy has been determined by titration calorimetry and the entropies values were calculated through the relationship

$$\Delta_c G^o = \Delta_c H^o - T\Delta_c S \tag{2}$$

The complexation curves, E/ mV versus $[L]/[Hg^{2+}]$ ratio (i) or the first derivative (ii) for the titration mercury(II), are shown in **Figure 3** (representative
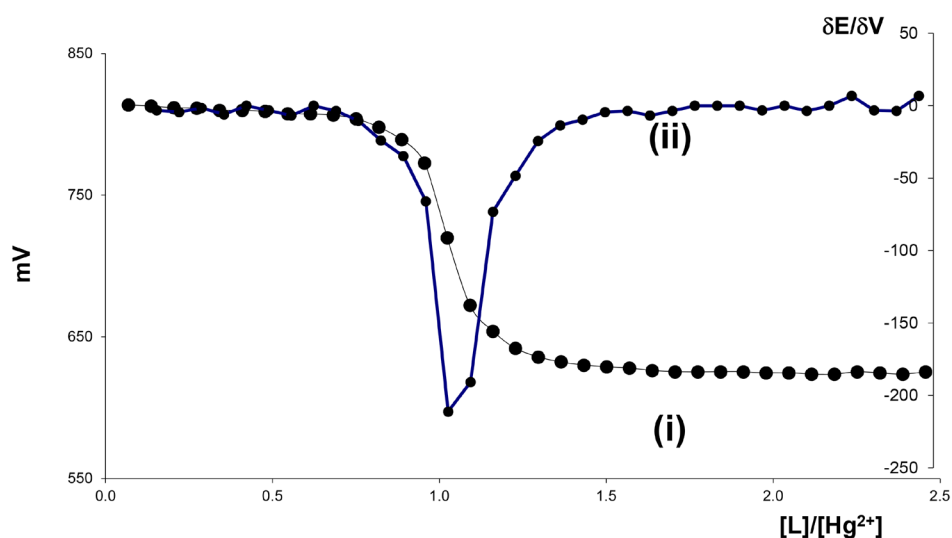
Figure 3. Potentiometric curve for the titration (i) and the first derivative to indicate the end point (ii) of the potentiometric titration of mercury(II) (as perchlorate) with L_1 in acetonitrile at 298.15 K.

example) in acetonitrile at 298.15 K. The experimental data in both cases indicate that the inflection point in (i) or the minimum point in (ii) corresponds to the 1:1 (L:Hg^{2+}) complex stoichiometry. This is in accord with the results observed from conductimetric studies. Potentiometric data were analyzed by the use of the SUPERQUAD [17] computer program.

The highest stability was found for L_2 and Hg^{2+} in acetonitrile. This stability decreases in L_1. These changes of complex stability with the ligand can be quantitatively assessed by taking the stability constant ratio for Hg^{2+} and L_2 in acetonitrile relative to L_1 ($S = [K_s(L_2)]/[K_s(L_1)]$).

Thus, the complexation of Hg^{2+} and L_2 is more stable in acetonitrile than L_1 complex by a factor of ~1.95. The difference in stability of complex formation for the same system in going from the L_1 to L_2 reveals the role of the number of the binding sites on the complexation process.

Analysis of data in Table 1, shows that the complexation process of L with mercury(II) is enthalpically controlled, possible due to the strong electrostatic (ion-dipole) interactions between these soft metal cation and the donor atoms of the ligands.

### 3.4. Phase Transfer Involving Bivalent Cations

The extraction of univalent cations from the aqueous to the organic phase in the absence and in the presence of a neutral macrocycle has been previously discussed by us [24] [25]. In this paper we formulate a treatment for the derivation of the partition, K_p and the ion-par formation, K_a, constants for the process represented in Equations (3) and (5) involving a 2:1 metal-ion salt.

$$M^{2+}(H_2O) + 2X^-(H_2O) \xrightarrow{K_p} M^{2+}(s) + 2X^-(s) \tag{3}$$
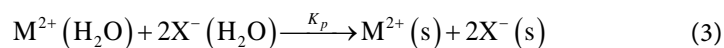
where K_p expressed in terms of concentrations may be defined as.

$$K_p = \frac{\left[M^{2+}\right]_{(s)}\left[X^-\right]_{(s)}^2}{\left[M^{2+}\right]_{(H_2O)}\left[X^-\right]_{(H_2O)}^2} \tag{4}$$

and K_a is referred to the process given in Equation (5)

$$M^{2+}(s) + 2X^-(s) \xrightarrow{K_a} MX_2(s) \tag{5}$$
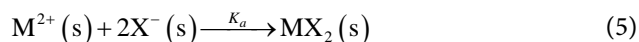
Therefore,

$$K_a = \frac{\left[MX_2\right]_{(s)}}{\left[M^{2+}\right]_{(s)}\left[X^-\right]_{(s)}^2} \tag{6}$$

Combination of (3) and (5) leads to Equation (7)

$$M^{2+}(H_2O) + 2X^-(H_2O) \xrightarrow{K_d} MX_2(s) \tag{7}$$
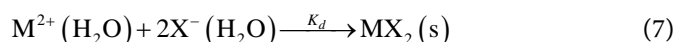
Thus, the distribution constant, K_d may be expressed as

$$K_d = \frac{\left[MX_2\right]_{(s)}}{\left[M^{2+}\right]_{(H_2O)}\left[X^-\right]_{(H_2O)}^2} \tag{8}$$

K_p and K_d are referred to the mutually saturated solvents and K_a to the water saturated organic phase.

From distribution experiments on the assumption that M^{2+} and MX_2 are the predominant species in the organic phase (saturated with water), the distribution ratio, D_M can be defined.

$$D_M = \frac{[M]_s}{[M]_{H_2O}} = \frac{\left[M^{2+}\right]_{(s)} + \left[MX_2\right]_{(s)}}{\left[M^{2+}\right]_{(H_2O)}} \tag{9}$$

Based on mass balance and electroneutrality and combining Equations ((4), (6) and (9)), it follows that.

$$D_M = K_p^{1/3} + 4K_a K_p^{1/3}\left[M^{2+}\right]_{(s)}^2 \tag{10}$$

Then a plot of D_M against $\left[M^{2+}\right]_{(s)}^2$ should give a straight line of slope equal $4K_a K_p^{1/3}$ and an intercept $= K_p^{1/3}$.

Distribution ratios for HgPi$_2$, were carried out at 298.15 K in the water-dichloromethane (mutually saturated) solvent system. Thus, plots of D_M values against $\left[Hg^{2+}\right]_{(s)}^2$ are shown in **Figure 4** The lineal relationships observed in both cases led to the calculation of K_p, K_a and K_d and these data are shown in **Table 2**.

The data show that for the system involving Hg^{2+}, K_p although small makes a favorable contribution to K_d values. However, the high K_d values observed for these systems are mostly due to the high degree of ion-pair formation of the metal-ion salts in the water-dichloromethane solvent system.
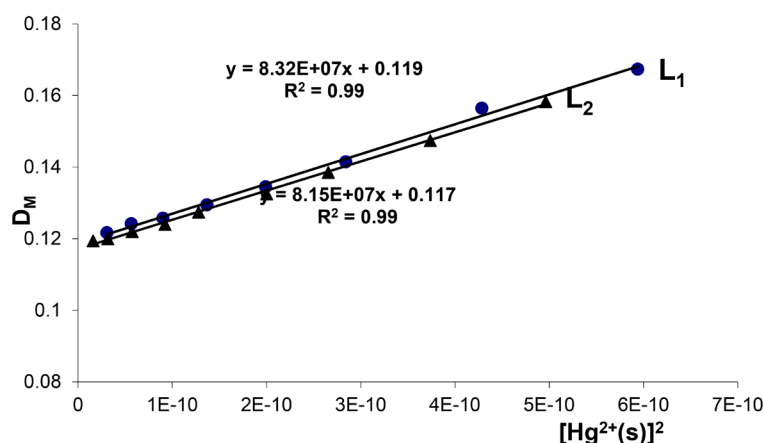
Figure 4. Distribution curve for mercury(II) (as picrate) in the water-dichloromethane solvent system at 298.15 K.

Table 2. Equilibrium data for the individual processes involved in the distribution of mercury(II) picrate in the water-dichloromethane solvent system at 298.15 K.

Const.	K_P	K_a	K_d ($K_P \times K_a$)	R^2
$Hg(C_6H_2N_3O_7)_2$ (1)	1.67×10^{-3}	1.65×108	2.76×10^5	0.99
$Hg(C_6H_2N_3O_7)_2$ (2)	1.60×10^{-3}	1.74×108	2.78×10^5	0.99

3.5. Distribution Data in the Presence of L in the Organic Phase

A general equation for the process taking place when a bivalent cation is extracted from water by the presence of a neutral macrocycle in the organic phase may be written as follows,

$$M^{2+}(H_2O) + 2X^-(H_2O) + L(s) \xrightarrow{K_{ex}} MLX_2(s) \tag{11}$$
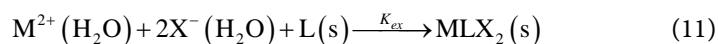
The extraction constant, K_{ex} can be defined as

$$K_{ex} = \frac{\left[MLX_2\right]_{(s)}}{\left[M^{2+}\right]_{(H_2O)}\left[X^-\right]^2_{(H_2O)}\left[L\right]_{(s)}} \tag{12}$$

Taking into account Equations ((8), (9) and (12)) it follows that

$$\frac{D_M}{\left[M^{2+}\right]^2_{(H_2O)}} = 4K_d + 4K_{ex}\left[L\right]_{(s)} \tag{13}$$

To investigate the effect of L (L_1 and L_2) on the distribution of Hg^{2+} (as picrate) in the water-dichloromethane solvent system, distribution experiments were carried out in presence of the ligands. To demonstrate the stoichiometry of the extraction process, plots of the percentage of extraction, %*E*, against the ligand:metal cation total concentration ratio, $[L]/[M^{n+}]$ are shown in **Figure 5**.

The percentage of the extraction of the metal cation was calculated from

$$\%E = \frac{\left[M^{n+}\right]_o - \left[M^{n+}\right]_F}{\left[M^{n+}\right]_o} \cdot 100 \tag{14}$$

In Equation (14); $[M^{n+}]_o$ and $[M^{n+}]_F$ are the initial and equilibrium concentrations of the metal cation in the aqueous phase.

Plots in **Figure 5** show changes in the gradient at a ligand/metal cation ratio equal to unity. Thus, the stoichiometry of the process is defined by the intercept of these two lines. These findings are in accord with conductance studies for the complexation of these ligands and this metal cation.

Therefore, a plot of $D_M/[M^{2+}]^2(H_2O)$ against $[L]_{(s)}$ should give a straight line of slope $= 4K_{ex}$ and intercept equal to $4K_d$. Distribution data (carried out in the presence of the ligand in the organic phase) against $[L]_{(s)}$ for Hg^{2+} as picrate, in the water-dichloromethane solvent system are shown in **Figure 6**. K_{ex} and K_d values are reported in **Table 3**. Excellent agreement is found between the K_d values obtained from distribution data in the absence of these ligands (**Table 3**).
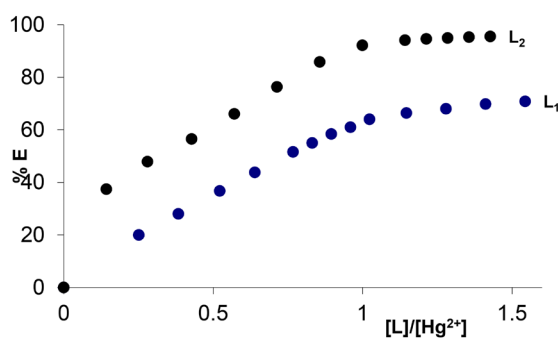

Figure 5. Percentage of extraction (% E) against $[L]/[Hg^{2+}]$ concentration ratio obtained from the distribution data for mercury(II) picrate in the presence of L in the organic phase at 298.15 K.

Table 3. Distribution and extraction data for mercury(II) and by L (L_1 and L_2) in the water-dichloromethane solvent system at 298.15 K.

Const.	$K_d{}^*$	K_d	K_{ex}	R^2
$Hg(C_6H_2N_3O_7)_2 + L_1$	2.76×10^5	2.80×10^5	2.62×10^{11}	0.99
$Hg(C_6H_2N_3O_7)_2 + L_2$	2.78×10^5	2.67×10^5	3.88×10^{13}	0.99

*Values obtained in the absence of L, $K_d = K_p \times K_a$.
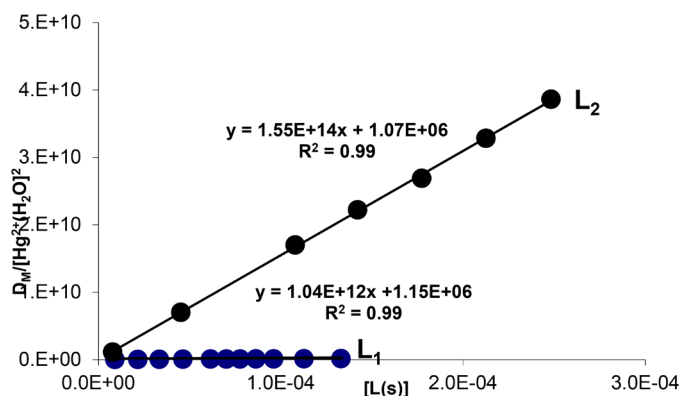
Figure 6. Plot of $D_M/[Hg^{2+}(H_2O)]^2$ against the equilibrium concentration of ligand, $[L(s)]$ in the organic phase in the water-dichloromethane solvent system at 298.15 K.

The interesting aspect of the data is that Hg^{2+} is better extracted by L_2 by a factor of ~148 times more relative to L_1.

4. Conclusions

On the basis of these discussions, can be drawn:

1) The number of the binding sites in calixarene derivatives increases the strength of the complexations process by factor ~2. From partially substituted calixarenes in which the binding sites are two, to fully substitute (four binding sites), the strength of the ion-dipole interaction increases. As a result, the mrcury(II) complex is more stable in L_2 relative to L_1 in came solvent.

2) Extraction of Hg^{2+} from water to the organic phase, also increased by a factor of 148 times for the latter relative to the former ligand.

Acknowledgements

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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List of Abbreviations

L_1: 5,11, 17, 23-tetra-*tert*-butyl[25, 27-bis(diethylthiophosphate amino)ethoxy-26, 28-bis(hydroxy)]-calix[4]arene

L_2: 5, 11, 17, 23-tetra-*tert*-butylcalix[4]arene, tetra diethyl thiophosphate

Hg, Ag, Cd, Zn, Ca, Na, Mg: mercury, silver, cadmium, lead, zinc, magnesium, respectively

-SH: Thiol group

TBAP: Tetra-*n*-butylammonium perchlorate.

18C6: 18-crown-6

THAM: tris(hydroxymethyl)aminomethane

^{1}H and ^{13}C NMR: proton and carbon, nuclear magnetic resonance