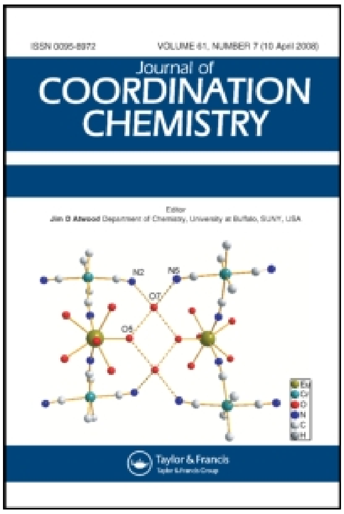

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SPECTROPHOTOMETRIC STUDY OF COMPLEX FORMATION BETWEEN SOME ALKALI AND ALKALINE EARTH CATIONS AND SEVERAL CONVENTIONAL (N,N), (N,O) AND (O,O) LIGANDS IN 95% ETHANOL

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The complexation of Li^+, Na^+, Mg^{2+} and Ca^{2+} with 1,10-phenanthroline, 2,2′-bipyridine, 1,2-phenylenediamine, 2-aminopyridine, 8-hydroxyquinoline, catechol and ethylene glycol was studied in 95% ethanol by means of a competitive spectrophotometric method using murexide as indicator. Formation constants of 1:1 conplexes were determined. In the case of all ligands used, the stability of the complexes was found to vary in the order $Mg^{2+} > Ca^{2+} > Li^+ > Na^+$. It was found that the structure influences the formation and stability of resulting complexes. Effects of various parameters on complexation are discussed.

KEY WORDS: Alkali metal, alkaline earth, complexes, stability.

INTRODUCTION

Despite the important role of alkali and alkaline earth ions in biological processes and in material science,[1,2] their coordination chemistry was very largely unknown before the 1970's. However, the discovery of crown ethers[3] and cryptands[4] opened a new chapter in the coordination chemistry of alkali and alkaline earth ions, and during the past two decades numerous thermodynamic and kinetic studies on the complexation reactions of these cations and macrocyclic ligands have been reported.[5–7]

Since in the process of complex formation the ligand must compete with solvent molecules for the cation, any variation in solvent properties is expected to change the apparent binding strength of the resulting complexes. Thus, an interesting possibility for understanding the nature of the interactions between alkali and alkaline earth cations and convetional ligands in solution is the use of nonaqueous solvents of lower solvating abilities and dielectric constants than water.

In this study we used 95% ethanol (w/w) as solvent in order to study Li^+, Na^+, Mg^{2+} ad Ca^{2+} complexes with 1,10-phenanthroline, 2,2'-bipyridine, 1,2-phenylenediamine, 2-aminopyridine, catechol and ethylene glycol (Figure 1)

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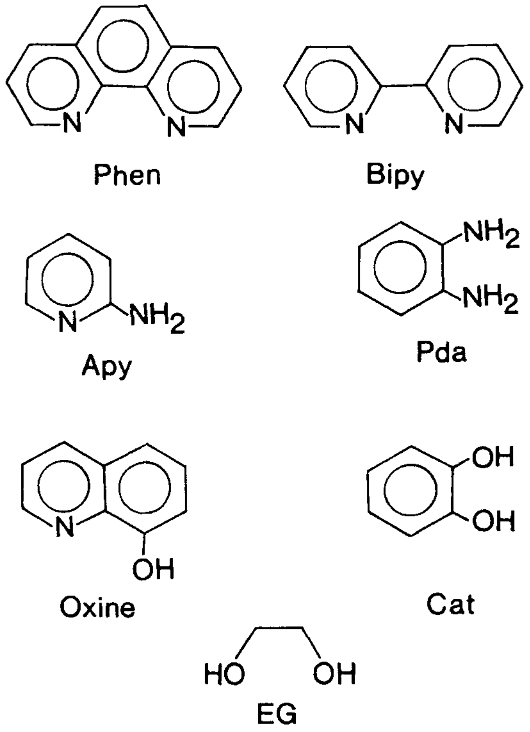

Figure 1 Structures of the ligands.

spectrophotometrically, using murexide as indicator. It should be noted, however, that there are only limited literature reports on the complexation of these ligands with alkali and alkaline earth cations due to the weak cation-ligand interactions involved.[8-13]

EXPERIMENTAL

Reagent grade lithium bromide (Merck), sodium perchlorate (Fluka), magnesium perchlorate (Fluka), calcium bromide (BDH), murexide (Fluka), 1,10-phenanthroline (Phen, Fluka), 2,2'-bipyridine (Bipy, Merck), 1,2-phenylenediamine (Pda, merck), 2-aminopyridine (Apy, GPR), 8-hydroxyquinoline (Oxine, Merck), catechol (Cat, Merck) and ethylene glycol (EG-Merck) were of the highest purity available and used without any further purification except for vacuum drying over P_2O_5 for 72 h. Tetraethylammonium perchlorate (TEAP) was prepared and dried using a previously reported method.[14] The solvent mixture (95% ethanol) was prepared from absolute ethanol (Merck) and triply distilled water.

Spectra were recorded on a Beckman DK-2A ratio recording spectrophotometer and absorbance measurements were made with a Perkin Elmer 35 spectrophotometer at $25 \pm 2°C$.

Fifteen cm^3 portions of solutions containing a fixed amount of murexide (5.0×10^{-5} M) and TEAP (0.05 M for maintaining the ionic strength) and varying concentrations of buffer ligands (0.01–0.20 M) were transferred into the titration cell. Then the solutions were titrated with standard solutions of metal ions at the same ionic strength using a calibrated burette. The final concentration of metal ions in solutions was in the range of $1.0 \times 10^{-4} - 1.0 \times 10^{-2}$ M (final volumes of 15.1 cm^3). The absorbance of solutions during the titration was measured at the λ_{max} of murexide (520 nm). It should be noted that the resulting alkali and alkaline earth complexes with murexide show a strong and ion specific shift of about 40–90 nm toward shorter wavelengths.[15,16]

The conditional formation constants of metal-murexide complexes ($K'_{ML} = [ML]/C_M[L]$) in the presence of varying concentrations of buffer ligands were determined from the intercepts of linear plots of $(A/A_0 - 1)/C_M$ *vs* A_0/A,[17] since

$$K'_{ML} - \frac{\varepsilon_{ML} K'_{ML}}{\varepsilon_L} \cdot \frac{A_0}{A} = (A_0/A - 1)/C_M \qquad (1)$$

where A_0, A, ε_{ML}, ε_L and C_M are the absorbance in the absence of metal ion, absorbance of solution during titration, molar absorptivity of metal-murexide complex, molar absorptivity of murexide and metal ion concentration, respectively. The K'_{ML} values obtained in each concentration of the buffer ligand (C_B) can be related to the metal-murexide formation constant ($K_{ML} = [ML]/[M][L]$) and the equilibrium constant for the formation of 1:1 MB complex ($K_{MB} = [MB]/[M][B]$) by the following equation.[17]

$$\frac{1}{K'_{ML}} = \frac{1}{K_{ML}}(1 + K_{MB}C_B) \qquad (2)$$

According to (2), K_{ML} and K_{MB} values can be obtained from the intercept and slope of a linear plot of $1/K'_{ML}$ *vs* C_B.

RESULTS AND DISCUSSION

The stability constants of the resulting alkali and alkaline earth complexes with the ligands used were determined from the spectrophotometric titration of murexide solutions with metal ions in the presence of varying concentration of buffer ligands. In each case, plots of $(A_0/A - 1)/C_M$ *vs* A_0/A gave a straight line, in accordance with equation (1), (Figure 2), and the conditional formation constants of the metal-murexide complexes were determined from the intercepts of the linear plots, using a computerized regression analysis. The formation constants of 1:1 metal-murexide (K_{ML}) and metal-buffer ligand (K_{MB}) complexes were determined from the intercepts and slopes of the linear plots of $1/K'_{ML}$ *vs* C_B by the use of equation (2), (Figure 3).

The formation constants of all resulting 1:1 complexes between Li^+, Na^+, Mg^{2+} and Ca^{2+} ions and different ligands are presented in Table 1. It should be noticed that murexide forms only 1:1 complexes with these cations both in aqueous[18] and non-aqueous solutions.[15,16] In the case of other ligands, although the formation of 2:1 (ligand to metal ion) and even 3:1 complexes is also possible,[8,11,19] the

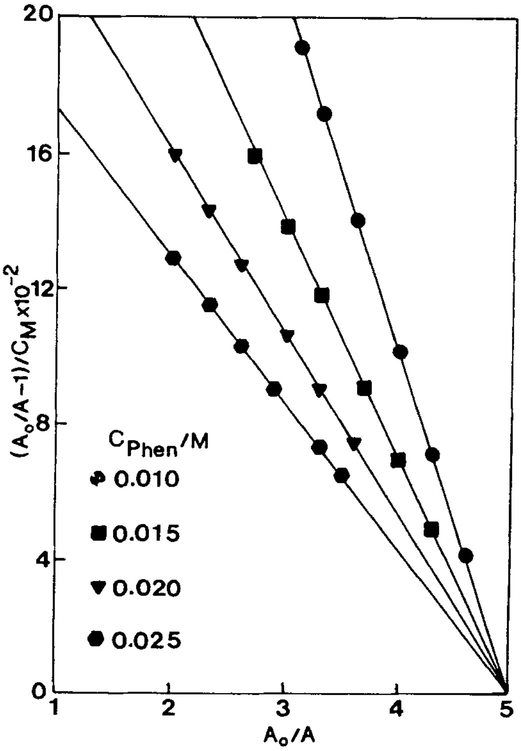

Figure 2 Plots of $(A_0/A-1)/C_M$ *vs* A_0/A for the Mg^{2+}-murexide system in the presence of different concentrations of Phen.

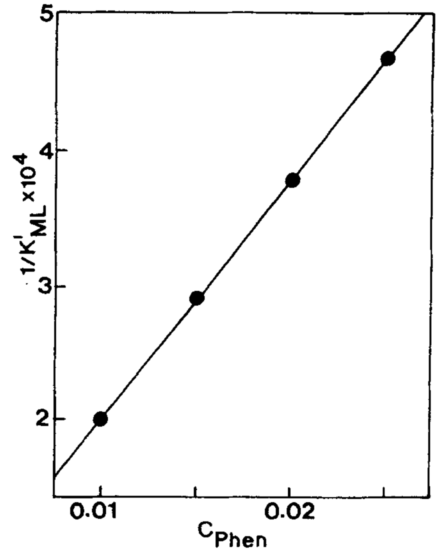

Figure 3 Plot of $1/K'_{ML}$ *vs* Phen concentration for the Mg^{2+}-murexide system.

Table 1 Stability constants of Mg^{2+}, Ca^{2+}, Li^{+} and Na^{+} complexes in 95% ethanol

	log K^{a}_{ML}			
Ligand	Mg^{2+}	Ca^{2+}	Li^{+}	Na^{+}
Murexide	4.68 ± 0.08	6.52 ± 0.10	2.44 ± 0.07	3.42 ± 0.05
Phen	2.93 ± 0.06	2.69 ± 0.04	2.24 ± 0.08	2.10 ± 0.06
Oxine	2.28 ± 0.04	2.13 ± 0.04	1.80 ± 0.07	1.42 ± 0.06
Bipy	2.20 ± 0.01	1.97 ± 0.02	1.61 ± 0.05	1.30 ± 0.06
Cat	1.98 ± 0.05	1.7 ± 0.09	1.31 ± 0.05	1.0 ± 0.04
PdA	1.73 ± 0.07	1.4 ± 0.01	1.12 ± 0.03	0.98 ± 0.04
EG	1.31 ± 0.03	1.1 ± 0.06	0.87 ± 0.04	0.9 ± 0.02
Apy	1.12 ± 0.01	0.98 ± 0.05	0.76 ± 0.05	0.8 ± 0.05

[a] $K_{ML} = [ML]/[M][L]$, 25°C.

corresponding stepwise stability constants seem to be so low that they are not detectable by the spectrophotometric method used. The stability of murexide complexes varies in the order $Ca^{2+} > Mg^{2+} > Na^{+} > Li^{+}$, the reasons for which have been discussed elsewhere.[15,16]

From the results given in Table 1 it is immediately obvious that, with the exception of murexide, the stability of the resulting complexes with a given ligand varies in the order $Mg^{2+} > Ca^{2+} > Li^{+} > Na^{+}$. It is well known that, in the cases where the size matching between the alkali and alkaline earth cations and the cavity of a ligand is not of special importance, the charge density of the cation plays a fundamental role in complexation.[19] Magnesium ion, with the highest charge density, is expected to form the most stable complexes in the series, while sodium ion, with the lowest charge desity, results in the weakest metal-ligand interactions among the cations used. However, it should be noted that the thermodynamic stability constants are not just a measure of absolute solute-solute interactions, but a measure of relative strength as compared to cation-solvent, complex-solvent and even ligand-solvent interactions.[20] Thus the highest stability of Mg^{2+} complexes results from a balance between binding and solvation energies.

The data given in Table 1 clearly show that the structural properties of the ligands (e.g. nature and position of the donating atoms, structural rigidity, etc.) play an important role in the complexation processes. As it is seen, in the case of all cations used, the stability of the resulting complexes decreases in the order Phen > Oxine > Bipy > Cat > Pda > EG > Apy.

The pyridine nitrogens seem to act as more effective donating groups than amino nitrogens and even the hydroxyl oxygens, although oxygen atoms as hard bases are expected to have stronger interactions with alkali and alkaline earth cations (as hard acids) than soft nitrogen atoms.[21] This unexpected behaviour may be due to the specific hydrogen bonding of amino and hydroxyl groups with solvent molecules, which reduces their donating abilities towards complexation. On the other hand, rigidity of the ligand is another important factor influencing the extent of metal-ligand interaction; the more rigid the ligand structure, the more fixed the spatial position of the donating group and the more stable the resulting complex. Considering the effect of these parameters on complexation, it is not surprising to observe the highest stability for the Phen complexes.

It is interesting to note that Bipy, with two donating pyridine nitrogens, forms weaker complexes than Oxine which contains one pyridine nitrogen and one hydroxyl group. It should be noted, however, that Bipy possesses a very flexible structure; the two pyridine rings can easily twist around the C-C bridge and, hence, the resulting complex would suffer from some instability. On the other hand, the two donating groups on the Oxine molecule have structurally fixed positions suitable for simultaneous bond formation with the central cation.

Table 1 shows that the alkali and alkaline earth complexes with Cat are more stable than those with Pda. This is possible because of the more suitable hard-hard interactions between the cations and donating hydroxyl groups of Cat, in comparison with the corresponding weaker hard-soft interactions of cations with soft donating amino groups of Pda.

On the other hand, despite the existence of a donating pyridine nitrogen in the structure of Apy, its resulting complexes are weaker than those of Pda. This unexpected behaviour can be explained by the unsuitable spatial position of the two donating centres of Apy which are only one carbon atom apart, compared to the two amino groups of Pda separated by two carbon atoms.

Finally, as expected, EG with the most flexible structure among the ligands used, forms the least stable complexes with alkali and alkaline earth complexes in the series.

Acknowledgements

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