Fluorimetric Study of Complexation of Alkali and Alkaline Earth Cations with 1,10-Phenanthroline, 2,2'-Bipyridine and 8-Hydroxyquinoline in Nonaqueous Solvents

Jahanbakhsh Ghasemi[a]; Mojtaba Shamsipur[a]

[a] Department of Chemistry, Shiraz University, Shiraz, Iran

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FLUORIMETRIC STUDY OF COMPLEXATION OF ALKALI AND ALKALINE EARTH CATIONS WITH 1,10-PHENANTHROLINE, 2,2'-BIPYRIDINE AND 8-HYDROXYQUINOLINE IN NONAQUEOUS SOLVENTS

JAHANBAKHSH GHASEMI and MOJTABA SHAMSIPUR*

Department of Chemistry, Shiraz University, Shiraz, Iran

Complexation of Li$^+$, Na$^+$, Mg^{2+} and Ca^{2+} with 1,10-phenanthroline, 2,2'-dipyridine and 8-hydroxyquinoline in acetonitrile, acetone and methanol solutions has been studied fluorimetrically at 25°C. The stoichiometries and stability constants of the resulting complexes were evaluated from non-linear least-squares fitting of the fluorimetric data to appropriate equations. There is an inverse relationship between the stability of the complexes and solvating ability of the solvents, as expressed by Gutmann donor numbers. In the three solvents studied, stabilities of resulting complexes vary in the order Mg^{2+} > Ca^{2+} > Li$^+$ > Na$^+$. Effects of the nature of donating atoms and the rigidity of the ligand structure on the stabilities of the complexes are discussed.

Keywords: Alkali metal, alkaline earth, complexes, stability constants, nonaqueous solvents, fluorimetry.

INTRODUCTION

Despite the profound influence of alkali and alkaline earth ions upon biological and materials sciences,[1,2] their coordination chemistry, especially with classical ligands, has received very little attention, as compared to transition metal ions.[3] This is mainly because interactions of conventional ligands with alkali and alkaline earth cations are usually quite weak and often are beyond the sensitivities of most physicochemical techniques. Therefore, in order to investigate the formation of such complexes, it is necessary to use very sensitive techniques under particular experimental conditions. Since in the complexation process the ligand must compete with solvent molecules for the cations, nonaqueous solvents of lower solvating abilities and dielectric constants than water can be employed as reaction media for studying the nature of metal-ligand interaction.

   2,2'-Bipyridine and 1,10-phenanthroline are simple polypyridine compounds which serve as chelating agents for many metal ions;[4] the photophysics and photochemistry of their complexes are under active investigation with particular interest in their application to solar energy conversion schemes.[5] However, studies of their complexes with alkali and alkaline earth ions are quite sparse.[6,7] Although frequent analytical

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* Author for correspondence.

use is made of fluorescent chelates of 8-hydroxyquinoline,[8] there have been few investigations concerning with the structure of the fluorophores and their formation.[9,10]

We have recently reported some results of the study of the coordination of alkali and alkaline earth cations with conventional and macrocyclic ligands in nonaqueous and mixed solvents.[11-15] In this paper we report a fluorimetric study of complexation between Li^+, Na^+, Mg^{2+} and Ca^{2+} ions and 2,2'-bipyridine, 1,10-phenanthroline and 8-hydroxyquinoline in acetonitrile, acetone and methanol at $25 \pm 1°C$.

EXPERIMENTAL

Reagent grade sodium and magnesium perchlorates (both from Fluka), lithium and calcium bromides (both from BDH), 1,10-phenanthroline (Phen), 2,2'-bipyridine (Bipy) and 8-hydroxyquinoline (Oxine) (all from Merck) were of the highest purity available and used without any further purification except for vacuum drying over P_2O_5 for 72 h. Spectroscopic grade acetonitrile, acetone and methanol (all from Fluka) were used as received.

Electronic spectra were recorded on a Beckman DK 2A ratio recording spectrophotometer. Fluorescence intensity measurements were made using a Perkin Elmer LS 2B instrument.

The stability constants of the resulting complexes were determined by the fluorescence intensity measurements at appropriate excitation and emission wavelengths of solutions in which varying concentrations of metal ions ($0-4.0 \times 10^{-4}$ M) were added to a fixed concentration of ligand (1.0×10^{-4} M) in different solvents. Errors associated with the stepwise formation constants reported are standard deviations.

RESULTS AND DISCUSSION

From the electronic and fluorescence spectra of the complexes of Li^+, Na^+, Mg^{2+} and Ca^{2+} and the ligands in acetonitrile, acetone and methanol solutions, the excitation (λ_{ex}) and emission (λ_{em}) wavelengths were determined. In order to determine the stoichiometry and stability of the resulting complexes, the fluorescence intensity *vs* metal ion to ligand mole ratio data were obtained at the corresponding λ_{ex} and λ_{em}.

For the evaluation of the formation constants from fluorescence intensity *vs* mole ratio data (9–13 data points), a non-linear least-squares curve fitting program, KINFIT, was used.[16] The program is based on the iterative adjustment of the calculated values of the fluorescence intensities to the observed values by using either the Wentworth matrix technique[17] or the Powell procedure.[18] Adjustable parameters are the stepwise formation constants of all complexes present and the corresponding fluorescence constants (*i.e.*, 2, 4 and 6 adjustable parameters for models I, II and III given in Table I, respectively).

The observed fluorescence intensity of solution is given by

$$(Fl)_{obs} = K'_L[L] + \sum_{n=1}^{3} K'_{MLn}[ML_n] \qquad (1)$$

TABLE I

Mass-balance equations used in computer program KINFIT for evaluation of fluorimetric data.

Model	Reactions	Stability constants	Mass-balance equations
I	$M + L = ML$	$K_1 = (ML)/(M)(L)$	$C_M = (M) + (ML)$
			$C_L = (L) + (ML)$
II	$M + L = ML$	$K_1 = (ML)/(M)(L)$	$C_M = (M) + (ML) + (ML_2)$
	$ML + L = ML_2$	$K_2 = (ML_2)/(ML)(L)$	$C_L = (L) + (ML) + 2(ML_2)$
III	$M + L = ML$	$K_1 = (ML)/(L)(M)$	$C_M = (M) + (ML) + (ML_2) + (ML_3)$
	$ML + L = ML_2$	$K_2 = (ML_2)/(ML)(L)$	
	$ML_2 + L = ML_3$	$K_3 = (ML_3)/(ML_2)L$	$C_L = (L) + (ML) + 2(ML_2) + 3(ML_3)$

TABLE II

Solution of the mass-balance equations given in Table I in terms of the free ligand concentration (L).

Model	Solution
I	$K(L)^2 + (1 + K_1(C_M - C_L))(L) - C_L = 0$
II	$K_1K_2(L)^3 + (K_1(1 + K_2(2C_M - C_L)))(L)^2 + (1 + K_1(C_M - C_L))(L) - C_L = 0$
III	$K_1K_2K_3(L)^4 + (3K_1K_2K_3C_M + K_1K_2 - C_LK_1K_2K_3)(L)^3$ $+ (2C_MK_1K_2 + K_1 - K_1K_2C_L)(L)^2 + (K_1C_M - K_1C_L + 1)(L) - C_L = 0$

where K_L' and K_{MLn}' are the fluorescence constants of the free and complexed ligand, respectively.

The mass-balance equations of all possible systems in solution, shown in Table I, can be solved in order to obtain equations for the free ligand concentration [L] (Table II). For models I–III, the free ligand concentrations were calculated by means of a Newton–Raphson procedure. Once the value of [L] had been obtained, the concentrations of all other species involved were calculated from the corresponding mass-balance equations given in Table I, by using the estimated values of the stability constants at the current iteration step of the program. Refinement of the parameters is continued until the sum-of-squares of the residuals between calculated and observed values of the fluorescence intensity for all experimental points is minimized. The output of the program KINFIT comprises refined parameters, the sum-of-squares and the standard deviation of the data. Sample computer fits of the fluorescence intensity-mole ratio data are shown in Figure 1 and all resulting formation constants for complex species present in various solvents are summarized in Table III.

It should be noted that because of the very short fluorescence life times reported for polypyridine ligands and their complexes (10–100 ns)[20] and the low concentration conditions used in this study ($1.0–4.0 \times 10^{-4}$ M), the effect of concentration quenching should be negligible.

From Table III, it is immediately obvious that the solvent plays a fundamental role in complexation. In fact, there is an inverse relationship between the stabilities of the complexes and the solvating ability of the solvents, as expressed by the Gutmann donor number (DN).[19] Since the complexation reaction takes place by replacement of the inner solvation shell of the cation by the ligand donating centres, competition exists between the ligand and solvent molecules for the cation in solution. Thus, by

TABLE III

Stability constants of Mg^{2+}, Ca^{2+}, Li^+ and Na^+ complexes with Phen, Oxine and Bipy in acetonitrile, acetone and methanol solutions.

Solvent[a]	Ligand	Cation	λ_{ex} (nm)	λ_{em} (nm)	Stepwise formation constants		
					$\log K_1$	$\log K_2$	$\log K_3$
Acetonitrile	Phen	Mg^{2+}	310	427	5.11 ± 0.04	3.45 ± 0.07	
		Ca^{2+}		417	4.11 ± 0.95	3.67 ± 0.07	1.94 ± 0.06
		Li^+		405	3.01 ± 0.03	1.87 ± 0.04	
		Na^+		405	2.64 ± 0.04	1.99 ± 0.03	
Acetone		Mg^{2+}	315	420	4.22 ± 0.05	2.40 ± 0.02	
		Ca^{2+}		415	3.93 ± 0.06	1.57 ± 0.09	1.0 ± 0.02
		Li^+		405	3.11 ± 0.01	2.00 ± 0.02	
		Na^+		405	3.04 ± 0.03	1.00 ± 0.03	
Methanol		Mg^{2+}	317	425	2.14 ± 0.01		
		Ca^{2+}		420	2.11 ± 0.03	1.21 ± 0.05	
		Li^+		408	0.95 ± 0.02		
		Na^+		405	0.81 ± 0.03		
Acetonitrile	Oxine	Mg^{2+}	380	525	4.03 ± 0.08	2.30 ± 0.09	
		Ca^{2+}		520	3.42 ± 0.05	2.38 ± 0.05	
		Li^+		480	2.82 ± 0.02	1.72 ± 0.05	
		Na^+			2.60 ± 0.04	1.72 ± 0.08	

Solvent	Ligand	Ion				
Acetone		Mg²⁺		530	2.25 ± 0.06	1.80 ± 0.01
		Ca²⁺		525	2.17 ± 0.02	1.19 ± 0.03
		Li⁺		485	1.98 ± 0.08	
		Na⁺			1.40 ± 0.05	
Methanol		Mg²⁺		535	2.01 ± 0.02	1.08 ± 0.05
		Ca²⁺		525	1.77 ± 0.07	
		Li⁺			0.91 ± 0.03	
		Na⁺			0.77 ± 0.02	
Acetonitrile	Bipy	Mg²⁺	310	420	2.80 ± 0.09	2.24 ± 0.07
		Ca²⁺		417	2.71 ± 0.04	2.10 ± 0.09
		Li⁺		415	1.87 ± 0.01	1.00 ± 0.06
		Na⁺			1.67 ± 0.02	
Acetone		Mg²⁺	310	405	2.04 ± 0.05	1.02 ± 0.06
		Ca²⁺		410	2.00 ± 0.06	0.66 ± 0.05
		Li⁺		415	1.85 ± 0.05	
		Na⁺		410	1.19 ± 0.04	
Methanol		Mg²⁺	315	405	1.90 ± 0.03	0.90 ± 0.03
		Ca²⁺			1.66 ± 0.06	
		Li⁺		400	0.45 ± 0.04	
		Na⁺			0.31 ± 0.01	

[*] Acetonitrile (DN = 14.1, ε = 38.0), acetone (DN = 17.0, ε = 20.7) and methanol (DN = 19.0, ε = 32.7)
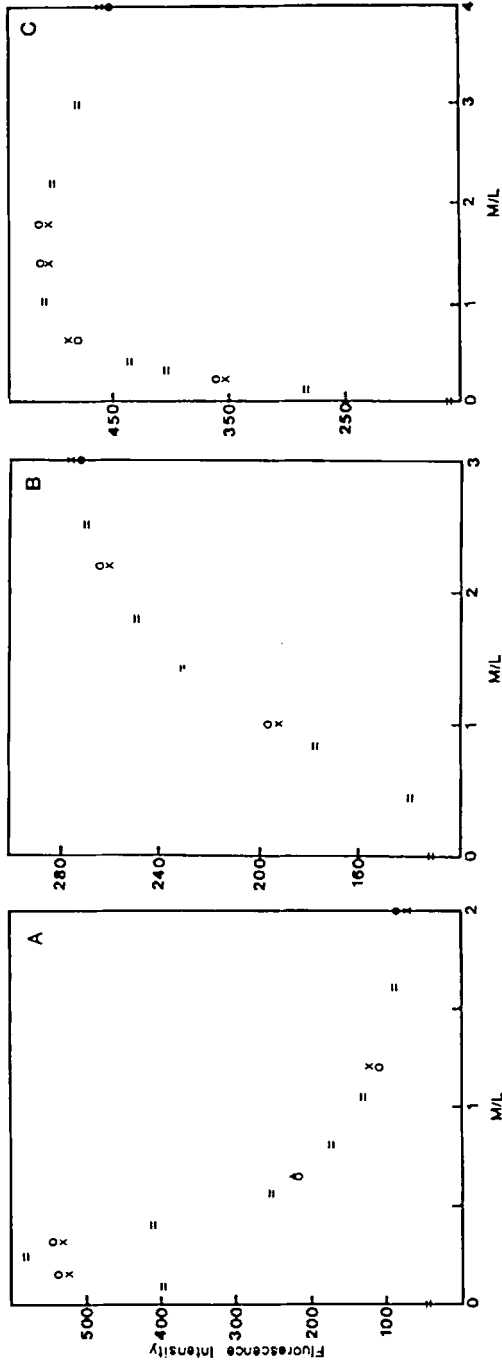
FIGURE 1   Computer fit of fluorescence intensity–mole ratio data obtained from the complexation of Ca^{2+} with 1,10-phenanthroline in various solvents: (A) acetonitrile, (B) acetone and (C) methanol; (×) experimental points; (○) calculated points; (=) experimental and calculated points are the same, within the resolution of the plot.

increasing the solvating ability of solvent from acetonitrile (DN = 14.1) to methanol (DN = 19.7), a drastic decrease (up to three orders of magnitude in some cases) in the stabilities of the resulting complexes is observed. The same kind of solvent effect has already been reported for different alkali and alkaline earth complexes in various solvents.[11–15]

It is interesting to note that in the case of the three ligands studied (and in the three solvents used) the stabilities of the resulting complexes decrease in the order $Mg^{2+} > Ca^{2+} > Li^+ > Na^+$, exactly the trend followed by the charge to size ratio of the cations. Magnesium, with the highest charge density, is expected to form the most stable complex in the series, while the Na^+ ion, having the least charge density, results in the weakest metal ion–ligand interaction. However, it should be noted that the thermodynamic stabilities are not just a measure of the absolute strength of the complexes, but also a measure of the relative strength as compared to ionic solvation. Thus the maximum stability of Mg^{2+} complexes results from a balance between the binding and solvation energies.

Moreover it seems obvious, particularly in nonaqueous solutions, that we should consider not only the solvent-cation, but also the solvent-complex and even solvent-ligand interactions as important factors in complexation. Such information seems to be largely unavailable. It has been shown that in some nonaqueous solvents there are rather strong interactions between macrocyclic ligands and solvent molecules.[21,22]

Data given in Table III clearly indicate that in a given solvent, and in the case of all cations used, the stabilities of the resulting also vary in the order Phen > Oxine > Bipy. As expected, both the nature of donating atoms and the rigidity of the ligand structure could be responsible for determining the stability of the resulting complexes. 2,2′-Bipyridine, with two donating pyridine nitrogens, forms the least stable complexes, while 1,10-phenanthroline, with the same donor centres, results in the formation of the most stable series. In contrast to 1,10-phenanthroline, 2,2′-bipyridine possesses a very flexible structure; the two pyridine rings can easily twist around the C–C bond in solution and, hence, result in some instability of entropic origin during its complexation with metal ions.

On the other hand, the two donor atoms of 1,10-phenanthroline have structurally fixed positions, suitable for simultaneous binding with metal ions in solution. However, 1,10-phenanthroline seems to act more effectively than 8-hydroxyquinoline in bond formation with alkali and alkaline earth cations.

ACKNOWLEDGEMENTS

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