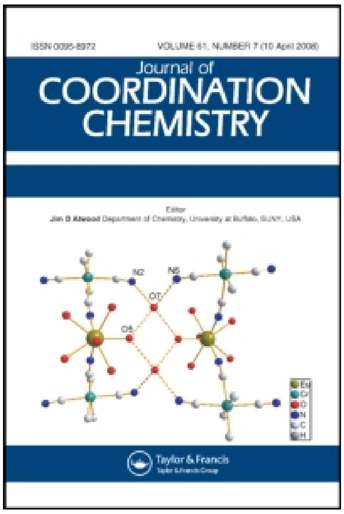

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Complex Formation Between Alkaline Earth Cations and 4-(2-Pyridylazo)Resorcinol in Ethanol-Water Mixtures

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COMPLEX FORMATION BETWEEN ALKALINE EARTH CATIONS AND 4-(2-PYRIDYLAZO)RESORCINOL IN ETHANOL–WATER MIXTURES

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The interaction between alkaline earth cations and 4-(2-pyridylazo)resorcinol in C_2H_5OH–H_2O mixtures has been studied spectrophotometrically. Formation constants for the resulting 1:1 complexes with different amounts of water in ethanol were determined. There is an inverse relationship between the complex formation constant and amount of water in the mixed solvent. In all solvent mixtures used, the stability of the complexes was found to vary in the order $Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$. A linear relationship is observed between log K_f for complexes and the mole fraction of ethanol.

Keywords: Alkaline earth, PAR, complexes, stability, mixed solvents

INTRODUCTION

Although the alkali and alkaline earth complexes occupy an important position in matter and life, their coordination chemistry has received very little atttention, as compared to transition metal ions. Perhaps the most important reason for the delayed interest in this area of research is the nature of the weak interactions between these cations and conventional ligands, especially in aqueous solutions, and which is often beyond the sensitivity range of most techniques.[1] However, because of the urgent need for understanding the vital role of cations like Na^+, K^+, Mg^{2+} and Ca^{2+} in biological systems,[2] on the one hand, and the discovery of new macrocyclic ligands such as crown ethers[3] and cryptands,[4] on the other, a new era in the coordination chemistry of the alkali and alkaline earth ions has opened during the last two decades.[5]

4-(2-Pyridylazo)resorcinol (PAR, Fig. 1A) is well known as a metallochromic indicator and a spectrophotometric reagent for determination of a wide variety of metal ions.[6] PAR usually behaves as a terdentate ligand to form a soluble coloured chelate with cations[7] (Fig. 1b). However, the stability constants for its alkaline earth complexes in aqueous solution are too low to be measured very accurately and, consequently, the use of PAR for the study of these cations in aqueous solution is quite sparse.[6,7] Since, in the process of complex formation, the ligand must compete with solvent molecules for the cation, a variation in the solvent properties is expected to change the apparent binding strength of the resulting complex.[5] Thus, the addition of solvents of lower dielectric constant and solvating ability than water to the aqueous solutions can lead to greater stability of the corresponding PAR complexes.

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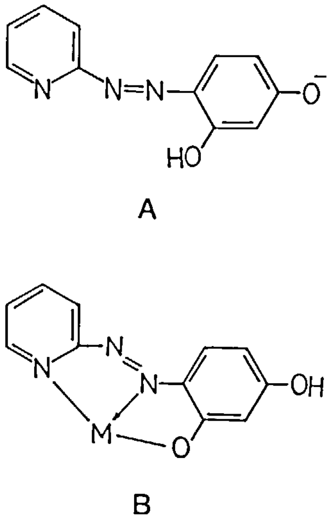

FIGURE 1 Structure of free (A) and complexed (B) PAR.

In recent years, we have been involved in a study of the coordination of alkali and alkaline earth ions with conventional and macrocyclic ligands in nonaqueous and mixed solvents.[8-12] In this paper we discuss a spectrophotometric study of PAR complexes with Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+} ions in ethanol–water mixtures.

EXPERIMENTAL

Reagent grade magnesium nitrate (Merck), calcium nitrate (Fluka), strontium bromide, barium bromide (both from BDH) and the monosodium salt of PAR (Merck) were used without any further purification except for drying in vacuum over phosphorus pentoxide for several days. Absolute ethanol (Merck, EtOH) mixtures with triply distilled water were prepared by weight. All spectra were obtained with a Beckman DK-2A ratio recording spectrophotometer and absorbance measurements were made with a Perkin-Elmer 35 spectrophotometer at $25 \pm 2°C$. All volumetric glassware used was calibrated.

The formation constants of the 1:1 complexes of PAR with alkaline earth cations were determined by previously reported methods,[13,14] as follows. The difference in the molar absorptivity of the metal–PAR complex and PAR ($\Delta\varepsilon$) was first calculated. PAR solutions of known concentration (2×10^{-5}m) were saturated with cation to convert all the ligand to complex. Saturation was confirmed by observing no change in the absorbance upon further addition of the metal ion. Absorbance measurements of the solution at a particular wavelength (usually at λ_{max} of the complex) against a PAR solution and knowledge of the concentration of the metal–PAR complex results in the calculation of $\Delta\varepsilon$.

With a value of $\Delta\varepsilon$, one can then calculate the concentration of metal–PAR complex in solution by measuring the differential absorbance ΔA at the same wavelength, (*1*).

$$\Delta A = \Delta\varepsilon\,[\mathrm{MPAR}] \qquad (1)$$

Here, the choice of metal ion concentration is critical; in all experiments, it was kept at such a value that [PAR]~[MPAR]. If [MPAR] is too small, its calculated value is in error because ΔA is small and hence its relative error is large. If, on the other hand, it is too large, [MPAR]$\sim C^T_{PAR}$ and the calculated [PAR] value (C^T_{PAR} − [MPAR]) acquires significant relative error. The equilibrium constant for reaction M + PAR = MPAR can be then evaluated from (*2*),

$$K_e = \frac{[MPAR]}{[M][PAR]} = \frac{[MPAR]}{(C^T_M-[MPAR])(C^T_{PAR}-[MPAR])} \qquad (2)$$

where C^T_M and C^T_{PAR} refer to the total concentrations of the metal ion and ligand, respectively. It has already been reported that PAR exists almost entirely as a monovalent anion (Fig. 1A) over a large pH range of from about 6 to 12.5.[21] Thus, it seems reasonable to assume that, in the neutral binary ethanol–water mixtures used, the contribution from other forms of the ligand in the complexation process is negligible.

In all experiments, equality of PAR concentrations in various solutions, and subsequent addition of metal ions were confirmed by weighing the samples in a semimicrobalance. Equilibria were assumed to be attained if there was no further change in the spectra after several hours. Errors associated with the formation constants are reported as one standard deviation.

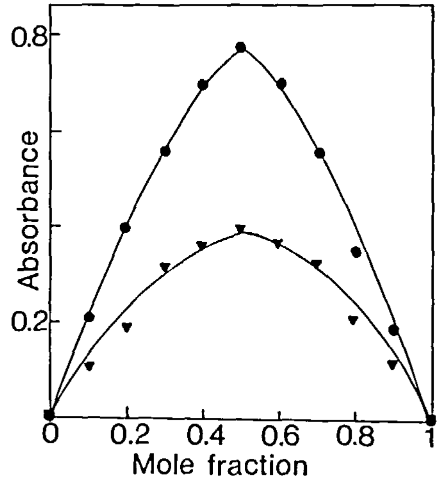

FIGURE 2 Continuous variation plots for Mg^{2+}–PAR (●) and Sr^{2+}–PAR (▲) complexes in ethanol solution.

RESULTS AND DISCUSSION

Spectra of PAR and its alkaline earth complexes were obtained in various EtOH–H_2O mixtures. In all cases, the resulting complexes are distinguished by a strong spectral shift of about 100 nm towards longer wavelengths, by comparison to the free ligand. The absorbance maxima for free and complexed PAR in different solvent mixtures were in the range 395–405 nm and 495–515 nm, respectively (see Fig. 3 as an example). Generally, the electrostatic interaction of a bound metal ion would not be able to produce such pronounced effects on the electronic structure of a dye molecule, and hence on its spectrum.[15] It thus seems reasonable to assume that a large change in the conjugation of the PAR molecule, brought about by metal ion complexation, is responsible for the spectral changes. The two six membered rings of the ligand, which are quite free to twist around the N–C bond in solution, would be fixed in the same plane as a result of complexation by a metal ion (Fig. 1). Consequently, a longer conjugated system results and complexed PAR will absorb at lower energy, as compared to its free state.

The stoichiometry of the complexes was determined by the continuous variation method,[16,17] and found to be 1:1 in all cases. The plots for the Mg^{2+} and Sr^{2+} complexes in absolute ethanol are shown in Figure 2. Moreover, the existence of a well defined isosbestic point in the spectra of PAR upon titration with alkaline earth cations (Fig. 3) is further evidence for a simple complexation equilibrium.

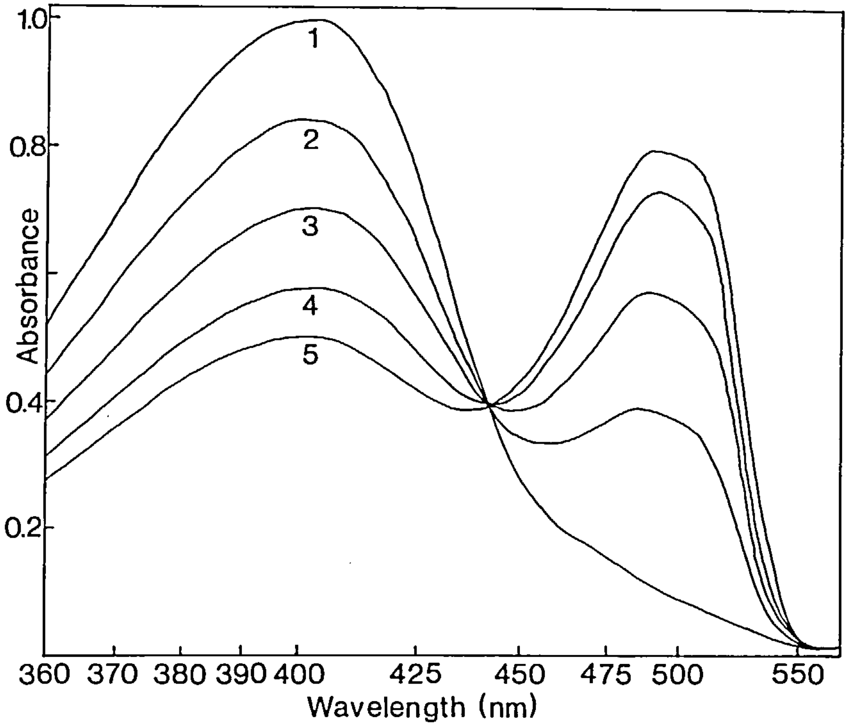

FIGURE 3 Visible spectra for titration of 2.0×10^{-5}M PAR with Mg^{2+} ion in 95% ethanol; $[Mg^{2+}]$ is 1: 0; 2: 1.0×10^{-5} M; 3: 2.0×10^{-5} M; 4: 4.0×10^{-5} M; 5: 6.0×10^{-5} M.

All calculated formation constants for the resulting complexes of Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+} in the various solvent mixtures are presented in Table I. The relationship between the logarithm of the formation constants of the complexes and the mole fraction of ethanol is shown in Figure 4. It is seen that, in all solvent mixtures used, the stability of the PAR complexes decreases with increasing ionic radius of the cations. Since the alkaline earth metal ions have a closed shell, the order of stability of their complexes cannot be a consequence of stereochemical requirements as in the case of transition metal ions. Therefore, selectivity in complex formation seems more likely to be a special property of the complexing ligand and the reaction medium.

The ligand, with two donating nitrogen atoms (Fig. 1B), can be considered as a "soft" base and is expected to have the weakest interaction with Ba^{2+} as the hardest acid. Another factor which could effect the stability constant is the relative size of the cations (with simple spherical symmetry) and the cavity formed by the ligand in its most convenient geometrical form. Obviously, the highest binding energy would be expected with a suitable spatial fit. From the results, magnesium seems to possess the best fit. Finally, it should be noted that the thermodynamic stability constant is not just a measure of the absolute solute–solute interaction, but is a measure of relative strength as compared to ionic solvation of all charged species involved in the complexation reaction (cation, ligand and complex). Thus, complex stability results from a balance between binding and solvation energies.

The data shown in Table I clearly illustrate the fundamental influence of solvent properties on the stability of the PAR complexes. In all cases, the complex formation constant decreases drastically with increasing weight percent of water in the solvent mixtures. It is well known that the solvating ability of the solvent, as expressed by the Gutmann donor scale,[18] plays an important role in complexation processes.[5,8–12,14] Water, with donor number of 33,[19] is known as a highly solvating solvent which strongly competes with the ligand for the cation. Thus it is reasonable to expect a sharp decrease in K_f upon addition of water to ethanol (as a low donicity solvent; donor number 18.5). The lower dielectric constant of ethanol (24.3) in comparison with that of water (78.5) is a further factor which could also cause the electrostatic contribution to the bond formation to increase with increasing percentage of ethanol in the solvent mixture.

TABLE I

Formation constants for alkaline earth complexes with PAR in various C_2H_5OH–H_2O binary mixtures.

Solvent Composition (wt.% C_2H_5OH)	X_{EtOH}	$\log K_f$			
		Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}
99.5	0.99	5.42±0.03	4.27±0.04	3.98±0.02	3.73±0.02
95	0.88	4.53±0.04	3.66±0.03	3.25±0.02	2.92±0.03
90	0.78	3.95±0.02	3.24±0.03	2.36±0.04	2.24±0.02
85	0.69	2.94±0.03	2.38±0.02	2.05±0.02	<2
80	0.61	2.33±0.06	2.07±0.04	<2	<2

From Figure 4, it is seen that there is a linear relationship between log K_f for the PAR complexes with Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+} and the mole fraction of ethanol in the binary mixed solvents used. The same kind of relationship is also reported between data obtained from a study of complexation in a number of ligand–metal ion systems in methanol–water,[20] acetonitrile–water[12] and ethanol–water[14] mixed solvents. It is reasonable to assume that the preferential hydration of the alkaline earth cations is mainly responsible for such a monotonic dependence of stability constant upon the solvent composition.

It is also interesting to note that the variation of the stability of PAR complexes with the solvent composition for Mg^{2+} ion is much more pronounced than that for the other cations. This exceptional behaviour must arise from inequal contributions involving solvent–cation interactions to the complexation process. While larger cations such as Ba^{2+}, with a low charge density, are expected to be rather weakly solvated by the solvent molecules, the small Mg^{2+} ion with a much higher charge density has a large tendency to interact with water molecules in the ethanol–water mixture. Thus it is not surprising to observe a drastic decrease of more than three orders of magnitude in the stability constant upon addition of water to ethanol, from 0 to 20 wt.%.

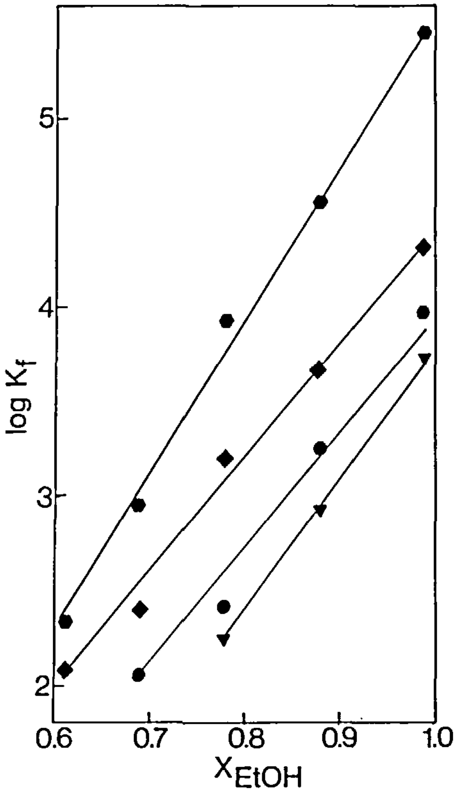

FIGURE 4 Variation of stabilities of PAR complexes with X_{EtOH} in the binary mixtures for Mg^{2+} (●), Ca^{2+} (◆), Sr^{2+} (●) and Ba^{2+} (▼).

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