

ON THE COMPLEXING ABILITY OF ERIOCHROME BLACK T AS A METALLOCHROMIC INDICATOR FOR SOME ALKALI AND ALKALINE EARTH CATIONS IN ACETONE AND DIMETHYLSULPHOXIDE SOLUTIONS

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Abstract

The interaction between eriochrome black T and Li^+ , Na^+ , K^+ , Mg^{2+} and Ca^{2+} ions in acetone and dimethylsulphoxide solutions has been investigated spectrophotometrically. The formation constants of the resulting 1:1 complexes were determined and found to decrease in the order $\text{Mg}^{2+} > \text{Ca}^{2+} > \text{Li}^+ > \text{K}^+ > \text{Na}^+$ in both solvents used. There is an inverse relationship between the stabilities of the complexes and the solvating ability of the solvents.

Introduction

O,O'- Dihydroxyaryazo dyes have found widespread use as metallochromic indicators and spectrophotometric reagents for magnesium, calcium and many transition metal ions [1-3]. A wide variety of substituents have been introduced on azobenzene and azonaphthalene derivatives in an attempt to obtain more favorable metal-binding and spectrophotometric behavior [4,5]. However, in many instances, the stability of the resulting complexes of these ligands with alkaline earth, and especially with alkali cations, is so low that their analytical uses will be faced with serious difficulties.

An interesting way to overcome the problem is to

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use the ligand-metal ion system in proper nonaqueous media instead of aqueous solutions. Since, in the complexation process, the ligand must compete with the solvent molecules for the cation, a variation in the solvent properties is expected to change the apparent binding strength of the resulting complex [6]. Thus, the use of non aqueous solvents of lower dielectric constant and solvating ability than water can lead to the greater stability of the corresponding complexes.

In recent years we have been involved in the study of the complexes between some metallochromic indicators and different metal ions in nonaqueous and mixed solvents [7-12]. In this paper we report a spectrophotometric study of the eriochrome black T complexes with Li^+ , Na^+ , K^+ , Mg^{2+} and Ca^{2+} ions in acetone and dimethylsulphoxide solutions.

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Experimental Section

Reagents

Reagent grade lithium bromide (Merck), sodium iodide (Fluka), potassium iodide (Merck), magnesium nitrate (Merck), calcium nitrate (Merck) and eriochrome black T (EBT, Fluka) were all of the highest purity available and used without any further purification except for vacuum drying over phosphorous pentoxide for 72 h. Acetone and dimethylsulphoxide (DMSO) both of Fluka A. G. quality were used without any further purification.

Apparatus

All spectra were obtained with a Beckman DK-2A ratio recording spectrophotometer and the absorbance measurements were made with a Perkin-Elmer 35 spectrophotometer at $25 \pm 2^\circ \text{C}$.

Procedure

The stoichiometry of the complexes was determined by the continuous variations method [13,14] as following. Solutions of the cation and EBT with identical molal concentrations ($1 \times 10^{-4} \text{M}$) were mixed in varying volume ratios in the calibrated 10.0 ml flasks. The absorbance of each solution was measured at the λ_{max} of the complex and corrected for any absorbance of the mixture if no reaction has occurred. The corrected absorbance was then plotted against the volume fraction (which is equal to the mole fraction) of one of the reactants. A well-defined maximum was observed at a mole fraction corresponding to the stoichiometry of the complex.

The formation constants of the 1:1 complexes EBT with alkali and alkaline earth cations were determined by the previously reported method [12,15] as following. The difference in the molar absorptivity of the metal-EBT complex and EBT ($\Delta \epsilon$) was calculated first. EBT solutions of known concentration ($2.0 \times 10^{-5} - 5.0 \times 10^{-5} \text{M}$) 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 measurement of the solution at a particular wavelength (usually at λ_{max} of the complex) against a EBT solution and knowing the concentration of metal-EBT complex results in the calculation of $\Delta \epsilon$.

Knowing the value of $\Delta \epsilon$, one can then calculate the concentration of metal-EBT complex in solutions by

measuring the differential absorbance ΔA at the same wavelength from equation (1).

$$\Delta A = \Delta \epsilon [\text{MEBT}] \quad (1)$$

In this stage, the choice of metal ion concentration is critical. In all experiments, it was kept in such a value that $[\text{EBT}] \sim [\text{MEBT}]$. If $[\text{MEBT}]$ 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, $[\text{MEBT}] \sim C_{\text{EBT}}^{\text{T}}$ and the calculated $[\text{EBT}]$ value ($C_{\text{EBT}}^{\text{T}} - [\text{MEBT}]$) acquires significant relative error. The equilibrium constant for reaction $\text{M} + \text{EBT} = \text{MEBT}$ can be then evaluated from equation (2).

$$K_f = \frac{[\text{MEBT}]}{[\text{M}][\text{EBT}]} = \frac{[\text{MEBT}]}{(C_{\text{M}}^{\text{T}} - [\text{MEBT}])(C_{\text{EBT}}^{\text{T}} - [\text{MEBT}])} \quad (2)$$

where C_{M}^{T} and $C_{\text{EBT}}^{\text{T}}$ refer to the total concentration of the metal ion and ligand, respectively.

In all experiments carried out, the equality of EBT concentrations in various solutions and the subsequent addition of metal ions were confirmed by weighing the sample in a semi-microbalance. Equilibria were assumed to be attained if there was no further change in the spectra after several hours. Errors associated with the formation constants were reported as \pm standard deviations.

In all cases studied, the complexation reactions were found to be quite fast and the complexation equilibria were attained very quickly (i.e. within a minute). The resulting complexes were stable in both solvents used for about a week. The stability of the complexes was checked by the observation of no change in their spectra after several days.

Results and Discussion

The spectra of EBT and its complexes were obtained in acetone and DMSO solution. The spectral characteristics are given in Table 1 and the resulting spectra in DMSO are shown in Fig. 1. As is seen, in all cases, the resulting complexes are distinguished by a strong and ion specific spectral shift of about 70-180 nm towards longer wavelengths, in comparison to the free ligand. Generally, the electrostatic interaction of a bound metal ion would not be able to produce such a pronounced effect on the electrostatic structure of a dye molecule, and hence on its spectrum [16]. It seems reasonable to assume that a large change in the conjugation of EBT molecule, brought about by metal

Table 1- Formation Constants and Spectral Characteristics of Alkali and Alkaline Earth Complexes with EBT in Acetone and DMSO Solutions.

Solvent	Ligand or Cation	λ_{max} (nm)	ϵ ($M^{-1} \cdot Cm^{-1} \times 10^4$)	Log K_f																																
Acetone	EBT	510	1.09±0.02	-																																
	Li ⁺	600	0.99±0.02	4.49±0.06																																
	Na ⁺	605	1.64±0.04	3.61±0.08																																
	K ⁺	610	3.72±0.05	Mg ²⁺	580	1.51±0.02	5.47±0.05	DMSO	Ca ²⁺	590	1.19±0.05	4.60±0.05	EBT	500	1.29±0.03	-	Li ⁺	570	1.46±0.04	4.37±0.06	Na ⁺	660	1.44±0.04	3.0±0.05	K ⁺	680	1.59±0.05	3.20±0.08	Mg ²⁺	570	1.41±0.03	5.22±0.04	Ca ²⁺	580	1.50±0.03	4.47±0.08
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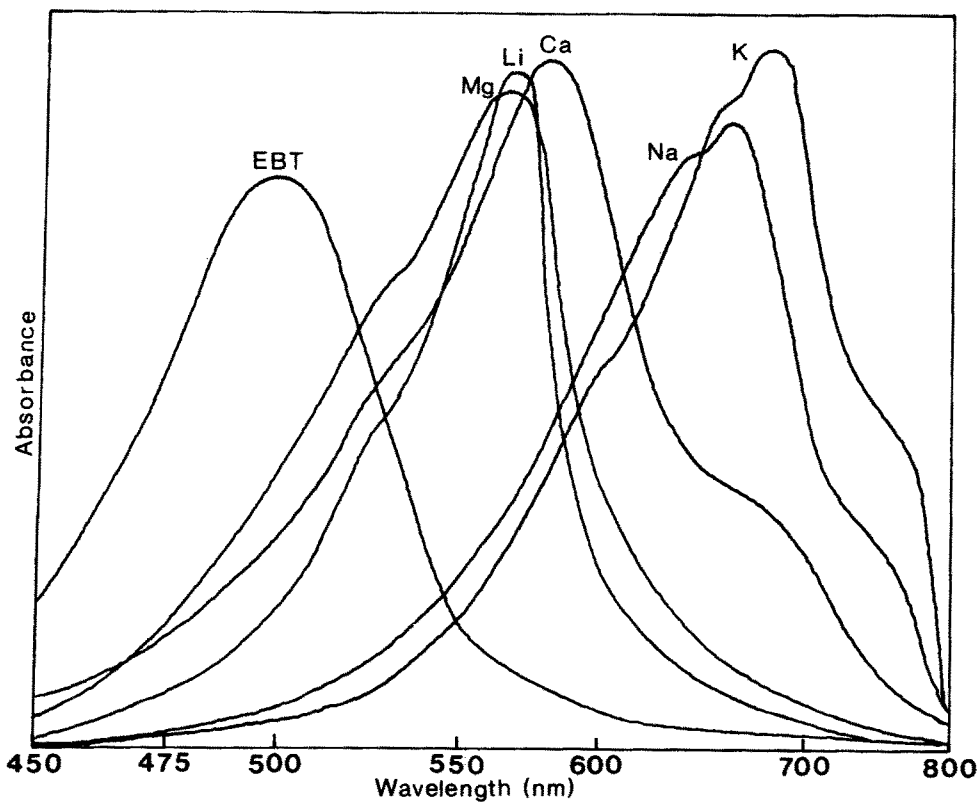


Fig. 1. Visible region spectra of eriochrome black T and its alkali and alkaline earth complexes in DMSO.

ion complexation, is mainly responsible for such spectral behavior [8,10,12].

The stoichiometry of the complexes was determined by the continuous variations method and found to be 1:1 in all cases. Moreover, the observation of a well-defined isobestic point in the spectra of EBT upon titration with all cations used is also further evidence of a simple 1:1 complexation equilibrium.

All calculated formation constants of the resulting 1:1 complexes between EBT and Li^+ , Na^+ , K^+ , Mg^{2+} and Ca^{2+} ions in acetone and DMSO solutions are presented in Table 1. The stability of the complexes vary in the order $\text{Mg}^{2+} > \text{Ca}^{2+} > \text{Li}^+ > \text{K}^+ > \text{Na}^+$. Factors affecting the stability order of the alkali and alkaline earth complexes with metallochromic dye molecules are discussed elsewhere [8,10,12].

From Table 1, it is immediately obvious that the solvent plays a very fundamental role in the complexation reaction. There is actually an inverse relationship between the donating ability of solvents, as expressed by the Gutmann donor number (DN) [17], and stability of the complexes. This result is not surprising, since the solvent molecules acting as electron donating ligands can compete with EBT for the cations in solution. The donicity of DMSO (DN = 29.8) is more than that of acetone (DN = 17.0) and, therefore, it competes the most with EBT molecules for cations, which in turn results in the least stable complexes. Moreover, the lower dielectric constant of acetone (20.7) in comparison with that of DMSO (45.0) would also cause the electrostatic contributions to the EBT complex bond formation to increase in acetone solutions.

Acknowledgements

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