SPECTROPHOTOMETRIC STUDY OF COBALT, NICKEL, COPPER, ZINC AND LEAD COMPLEXES WITH METHYLTHYMOL BLUE IN BINARY WATER-METHANOL MIXTURES

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ABSTRACT: *The complexation reactions between methylthymol blue (MTB) and Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} and Pb^{2+} ions have been studied in different water-methanol mixtures at pH 4.45 and 25 °C by a spectrophotometric technique. The stepwise stability constants of the resulting 1:1 and 2:1 (metal ion to ligand) complexes were determined from the absorbance-mole ratio data. It was found that the overall stability constants of the complexes formed increase in the order $Zn^{2+}<Co^{2+}<Pb^{2+}<Ni^{2+}<Cu^{2+}$ for all solvent mixtures studied. There is an inverse relationship between the overall stability of the complexes and amount of water in the mixed solvent. A linear relationship was observed between $\log \beta_2$ of the complexes and the mole fraction of methanol in the solvent mixture.*

KEY WORDS: *MTB complexes, Stoichiometry, Stability, Mixed solvent, Spectrophotometry.*

INTRODUCTION

Methylthymol bule, 3,3′-bis[N,N′-di(carboxymethyl-aminomethyl] thymolsulphonaphthalein (MTB, Fig. 1A), prepared and purified [1] and introduced as an excellent metallochromic indicator by *Korbl* [2]. The crystalline sodium salt of MTB is a black powder with good solubility in water but insoluble in absolute alcohol. Its aqueous solution, however, are not very stable. MTB is a six protonated ligand (H_6L) with three colour changes: yellow at $pH<6.5$, pale blue at pH 6.5-8.5, grey at pH 10.7-11.5 and dark blue at $pH>12.7$, the reason of which has been explained by the presence of H-bonds and alternating forma-

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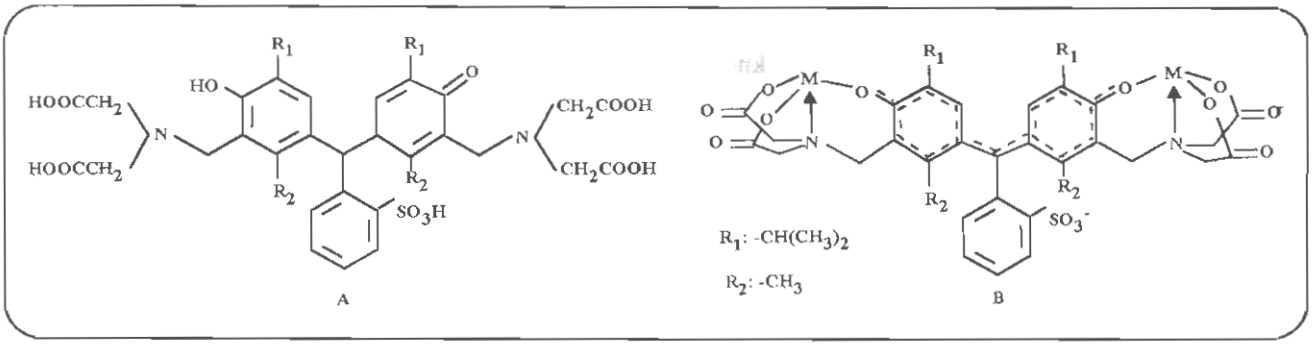

Fig. 1: Structures of MTB(A) and M_2^{2+}-MTB complex.

tion of symmetrical and unsymmetrical deprotonated forms of the indicator [3,4]. The dissociation constants of the dyestuff have been reported before [3,5,6].

The yellow colour MTB at *pH* 0 to 6 turns to blue upon complexation with many metal ions including the first series of transition metals as well as the heavy metal ions [4,7]. The stoichiometries and stabilities of the resulting complexes in aqueous solution have already been reported in the literature [3-10].

There is recently an increasing interest in the study of the complexation reactions in binary mixed solvent systems and their interpretation in terms of solute's preferential solvation by one of the mixed solvent components [11-22]. Actually, there is a simple coordination model in mixed solvents which assumes that all the thermodynamic changes in the system result from the successive replacement of the molecules of one solvent by those of a second solvent in the coordination sphere of the solute [23,24]. However, this model does not account for the changes in solvent-solvent interactions, the changes in interactions of the coordinated solvent molecules with the surrounding and the changes in the permittivity of the solvent system.

In the past, the metal-MTB interactions have only been studied in aqueous solution and information about the interactions in nonaqueous or mixed solvents is quite scarce [3-10]. Considering the fact that MTB forms quite stable complexes with transition and heavy metal ions in aqueous solution [4] with a sharp change in the indicator's colour from yellow to blue at *pH* values <6 [4,7], in this paper we used a spectrophotometric method for the study of its Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} and Pb^{2+} complexes at *pH* 4.45 in various water-methanol mixtures, in order to investigate the influence of solvent properties on the stoichiometries and stabilities of the resulting complexes.

EXPERIMENTAL

Reagents

Reagent grade nitrate salts of cobalt, nickel, copper, zinc, lead and sodium and sodium hydroxide (all from *Merck*) were used without any further purification except for vacuum drying over P_2O_5 . Analytical reagnet grade Methylthymol blue (MTB, p.a., tetrasodium salt, *Fluka*) was used as received. Triply distilled deionized water and absolute methanol *(Fluka)* were used for the preparation of the solvent mixtures by weight.

Apparatus

All spectra were recorded on a Philips PUB 700 spectrophotometer and the absorbance measurements were made with a Metrohm 662 probe type photometer. In all measurements, the cell was thermostated at 25.00±0.05 °C using a Lo-Temprol 154 Precision Scientific thermostat. Measurement of *pH* were made with a Corning 113 pH-meter using a combined electrode.

Procedure

In a typical experiment, 10 mL of the MTB solution in a given solvent mixture (1.0×10^{-5}-4.0×10^{-5}M) containing 0.1 M of sodium nitrate (for maintaining the ionic strength) and 2 mL of acetic acid-sodium acetate buffer of *pH* 4.45 was placed in

the titration cell, thermostated at the desired temperature and the absorbance of the solution at λ_{max} of the M^{2+}-MTB complex was measured. Then, a known amount of the M^{2+} ion solution in the same solvent mixture was added in a stepwise manner using a calibrated micropipette. The absorbance of solution was measured after each addition. Addition of the metal ion solution was continued until the desired metal to MTB mole ratio was achieved.

Calculations

When MTB reacts with a metal ion, M^{2+}, in solution, it may form either a 1:1 complex (model I) or both 1:1 and 2:1 (metal to ligand) complexes (model II) [9]. The mass balance equations of the two possible models in solution, shown in Table 1, can be solved in order to obtain equations for the free ligand concentration, [MTB], (Table 2). The observed absorbance of solution is given by

$$A_{obs} = \varepsilon_{MTB}[MTB] + \varepsilon_{1:1}[M-MTB] + \varepsilon_{2:1}[M_2-MTB] \quad (1)$$

where ε values are the molar absorptivities of the species denoted. For evaluation of the stability constants from the absorbance vs. C_M/C_{MTB} mole ratio data, a non-linear least squares curve fitting program KINFIT was used [25]. The program is based-on the iterative adjustment of calculated values of absorbance to observed values by using either the Wentworth matrix technique [26] or the Powell procedure [27]. Adjustable parameters are the stepwise formation constants of all complexes present and the corresponding molar absorptivities (i.e., 2 and 4 adjustable parameters for models I and II given in Table 1, respectively).

For models I and II, the free ligand concentrations, [MTB], were calculated by means of a Newton-Raphson procedure. Once the value of [MTB] had been obtained, the concentrations of all other species involved are calculated from the corresponding mass balance equations given in Table 1, by using the estimated values of the formation constants at the current iteration step of the program. Refinement of the parameters may continued until the sum-of-squares of the residuals between calculated and observed values of the absorbance for all experimental points was minimized. The output of the program KINFIT comprises the refined parameters, the sum-of-squares and the standard deviation of the data.

RESULTS AND DISCUSSION

To determine the stoichiometry and stability of the MTB complexes, the spectra of solutions containing a constant amount of the ligand at the fixed *pH* of 4.45 and varying amounts of the metal ions were obtained. A sample spectra is shown in Fig. 2. It is noteworthy that the corresponding spectra in different methanol-water mixtures have a more or less similar pattern. Fig. 2 shows Cu^{2+} can form two complexes with MTB. The maximum absorption wavelengths for 1:1 and 2:1 (metal to ligand) complexes are 465 and 600 nm, respectively. In addition, there are two clear isosbestic points in the spectra shown in Fig. 2. The first isosbestic point is at 454 nm and the second at 490 nm at *pH* 4.45. It should be noted that such a large spectral change observed, from free MTB with λ_{max}= 443 nm to the 2:1 complex with λ_{max}= 600 nm, most probably results from deprotonation of the ligand from H_4L^{2-} to H_2L^{4-} form and the corresponding changes in the conjugation of the dyestuff [25].

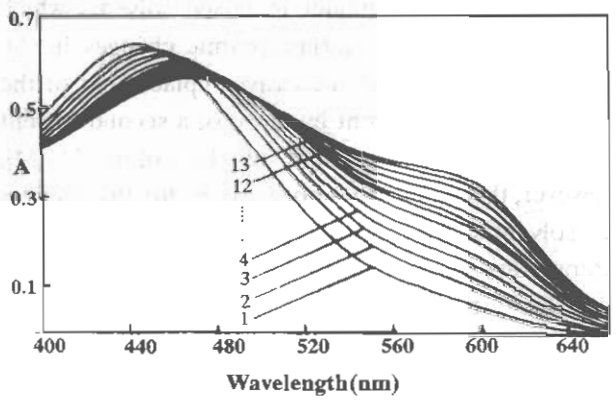

Fig. 2: Visible spectra for titration of MTB(4.6×10^{-5}M) with Cu^{2+} ion in aqueous solution at 25 °C and pH 4.45. Respective concentrations of Cu^{2+} ion (M) in different solutions are: (1) 0, (2) 1.4×10^{-5}, (3) 2.1×10^{-5}, (4) 2.8×10^{-5}, (5) 3.5×10^{-5}, (6) 4.2×10^{-5}, (7) 4.9×10^{-5}, (8) 5.6×10^{-5}, (9) 6.9×10^{-5}, (10) 9.6×10^{-5}, (11) 1.3×10^{-4}, (12) 1.6×10^{-4}, (13) 1.9×10^{-4}.

The stoichiometry of the complexes in different water-methanol mixtures was further examined by the method of continuous variation [26,27]. A sample of the resulting plots is shown in Fig. 3. It is evident that both 1:1 and 2:1 (metal to ligand) complexes are formed in solution. As it is seen from Fig. 1A, MTB is a derivative of thymolsulphonaphthalein with two N,N′-di(carboxymethyl) aminomethyl groups attached to its 3,3′-positions, each one of these groups capable to coordinate a metal ion. In other words, because of the steric hindrance of the bulky backbone of sulphonaphthalein group, the coordination of both N,N′-di-(carboxymethyl) aminomethyl groups to the same metal ion seems impossible. Thus, after the coordination of one of the donating groups to the first metal ion, the second group remains vacant and available for coordination to a second metal ion. Based on the above discussions, a possible structure for the resulting 2:1 complexes between M^{2+} ions used and MTB is proposed in Fig. 1B.

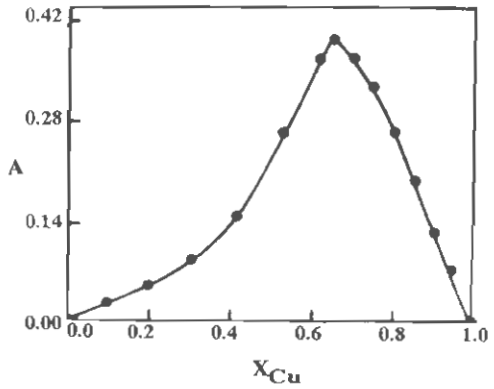

Fig. 3: Continuous variation plot for Cu^{2+}-MTB in aqueous solution.

The stepwise stability constants of the resulting 1:1 and 2:1 metal ion-MTB complexes in different water-methanol solvent mixtures were obtained at 25 °C and *pH* 4.45 by absorbance measurements, at λ_{max} of the 2:1 complex, of solutions in which varying concentrations of metal ions were added to fixed amounts of MTB in solution (see for example Fig. 2). The resulting absorbance-mole ratio data in aqueous solution are shown in Fig. 4. It should be noted that the corresponding mole ratio data in different methanol-water mixtures follow the same trend, except that in these cases the inflection points become more clear and sharper. All the absorbance-mole ratio data were best fitted to model II (Table 1 and 2), which further supports the formation of both 1:1 and 2:1 complexes in solution. A sample computer fit of the absorbance-mole ratio data is shown in Fig. 5. It is interesting to note that the existence of two inflection points at metal-to-ligand mole ratios of about 1 and 2 in the mole ratio plots (Fig. 4) are also indicative of the formation of 1:1 and 2:1 adducts in solution. Moreover, despite the absence of such clear inflection points in some cases, such as Zn^{2+}-MTB system in Fig. 4 (due to the weaker metal-MTB interactions), the model I (i.e., the formation of only a 1:1 complex) cannot be fitted to the observed data, while it is nicely fitted to model II by assuming the formation of the two complex species in solution. All the log K_1 and log K_2 values evaluated from the computer fitting of the corresponding absorbance-mole ratio data are listed in Table 3. It should be noted that the KINFIT program becomes unreliable when the stepwise stability constants are $>10^6$.

Table 1: Mass balance equations used in the computer program KINFIT for evaluation of spectrophotometric data[a]

Model	Reactions	Stability constants	Mass balance equations
I	M+MTB=M−MTB	K_1=[M−MTB]/[M][MTB]	C_M=[M]+[M−MTB] C_{MTB}=[MTB]+[M−MTB]
II	M+MTB=M−MTB M+M−MTB=M_2−MTB	K_1=[M−MTB]/[M][MTB] K_2=[M_2−MTB]/[M][M−MTB]	C_M=[M]+[M−MTB]+2[M_2−MTB] C_{MTB}=[MTB]+[M−MTB]+[M_2−MTB]

a : The charges are omitted for simplicity

Table 2: Solution of the mass balance equations given in Table 1 in terms of the free ligand concentration [MTB]

Model	Solution
I	$K_1[MTB]^2 + (1 + K_1(C_M - C_{MTB}))[MTB] - C_{MTB} = 0$
II	$K_1K_2[MTB]^3 + (K_1(1 + K_2(C_M - 2C_{MTB})))[MTB]^2 + (1 + K_1(C_M - C_{MTB}))[MTB] - C_{MTB}=0$

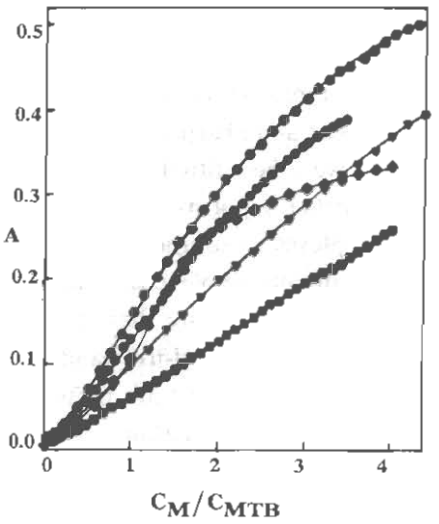

Fig. 4: The absorbance-mole ratio plots obtained from the titration of MTB with different M^{2+} ions in aqueous solution at 25.0 °C and pH 4.45: (●) Pb^{2+}, $C_{MTB}= 2.0\times10^{-5}M$; (●) Ni^{2+}, $C_{MTB}= 3.0\times10^{-5}M$; (▽) Co^{2+}, $C_{MTB}= 4.0\times10^{-5}M$; (◆) Cu^{2+}, $C_{MTB}= 2.0\times10^{-5}M$; (■) Zn^{2+}, $C_{MTB}= 4.0\times10^{-5}M$

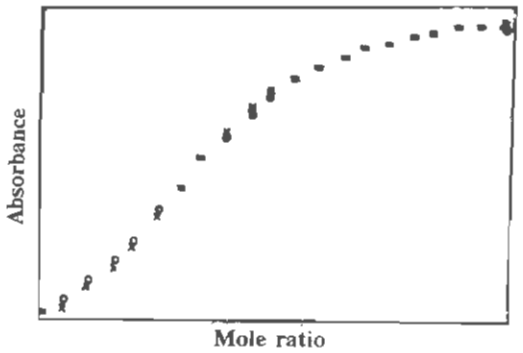

Fig. 5: Computer fit of absorbance-mole ratio data obtained from the complexation of Cu^{2+} ion with MTB in aqueous solution at 25 °C and pH 4.45: (×) experimental points; (○) calculated points; (=) experimental and calculated points are the same within the resolution of the plot.

The data given in Table 3 clearly indicate the fundamental effect of the solvent properties on the stability of both 1:1 and 2:1 complexes. In all cases studied, there is an inverse relationship between the stabilities of complexes and the amount of water in the binary mixed solvent used. Water as a solvent of high solvating ability, as expresses by donor number DN=33.0 [28], can strongly compete with the ligand MTB for metal ions, resulting in weaker MTB complexes in aqueous solution. Addition of methanol with intermediate donor number (DN=19) [29] to aqueous solution would decrease the solvating ability of medium and, as expected, results in the stronger interactions between the metal ion and ligand in solution. The lower dielectric constant of methanol (ε=32.6) in comparison with that of water (ε=78.3) is a further factor which could also cause the electrostatic contribution to the bond formation to increase with increasing percentage of methanol in the solvent mixture.

The relationship between the overall stability constants, log β_2 , of Co^{2+} , Zn^{2+} and Pb^{2+} complexes with MTB and mole fraction of methanol in the binary mixtures, X_{MeOH} , are illustrated in Fig. 6. As can be seen, there is actually a linear relationship between log β_2 and X_{MeOH} in all cases studied. The same kind of relationship is also reported between the data obtained from the study of complexation equilibria of a number of ligand-metal ion systems in different solvent mixtures [11,12,14-22]. It has been reasonably assumed that the preferential solvation of the cations by water is mainly responsible for such a monotonic dependence of the overall stability of the MTB complexes on the solvent composition.

As can be seen from Table 3, in all solvent mixtures studied, the overall stability constant of the complexes decrease in the order Cu^{2+} > Ni^{2+} >

Table 3: Stability constants for complexation reaction of Pb^{2+} , Zn^{2+} , Co^{2+} , Cu^{2+} and Ni^{2+} ions with MTB in various water-methanol mixtures at 25 °C

Metal Ion		Solvent composition (wt% MeOH in H_2O)[a]			
		0.0%	15%	30%	45%
Pb^{2+}					
	log K_1	5.09±0.02	5.67±0.03	5.92±0.02	6.05±0.14
	log K_2	4.60±0.02	4.73±0.03	5.12±0.02	5.64±0.08
	log β_2	9.69±0.03	10.40±0.04	11.04±0.03	11.69±0.16
Zn^{2+}					
	log K_1	3.93±0.05	4.54±0.03	5.10±0.05	5.75±0.05
	log K_2	3.66±0.05	4.29±0.03	4.82±0.05	5.24±0.05
	log β_2	7.59±0.07	8.83±0.04	9.92±0.07	10.99±0.07
Co^{2+}					
	log K_1	4.50±0.05	4.92±0.02	5.16±0.08	5.82±0.06
	log k_2	3.57±0.05	3.99±0.02	4.71±0.01	5.21±0.06
	log β_2	8.07±0.07	8.91±0.03	9.87±0.08	11.03±0.08
Cu^{2+}					
	log K_1	5.94±0.04	6.22±0.07	>6	>6
	log K_2	5.17±0.04	5.37±0.07	>6	>6
	log β_2	11.12±0.05	11.59±0.10	>12	>12
Ni^{2+}					
	log K_1	5.66±0.08	> 6	>6	>6
	log K_2	4.01±0.08	> 5	>6	>6
	log β_2	9.66±0.11	> 11	>12	>12

a : Mole fraction of MeOH in this solvent mixtures, X_{MeOH} , is 0.00, 0.09, 0.22 and 0.31, respectively.

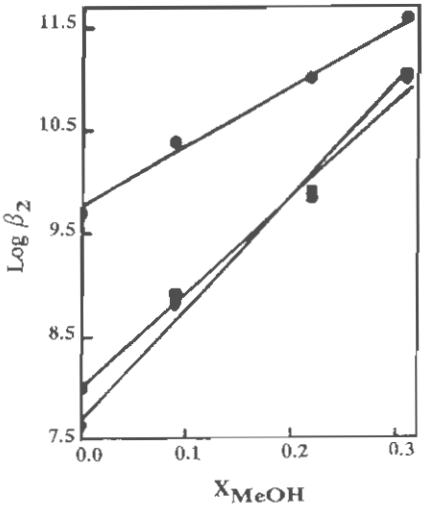

Fig. 6: Variation of overall stabilities of different metal ion complexes of MTB with mole fraction of methanol, X_{MeOH} in the water-methanol mixtures: (●) Pb^{2+} ; (■) Co^{2+} ; (▼) Zn^{2+}.

Pb^{2+}> Co^{2+}> Zn^{2+}. It is interesting to note that the stability trend observed for the first transition series (i.e., Co^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+}) follows the Irving-Williams order [22], which generally holds for the equilibrium constants of transition metals [21, 22, 31].

As can be seen from Table 3, in all solvent mixtures studied, the overall stability constant of the complexes decrease in the order Cu^{2+}> Ni^{2+}> Pb^{2+}> Co^{2+}> Zn^{2+}. It is interesting to note that the stability trend observed for the first transition series (i.e., Co^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+}) follows the Irving-Williams order [22], which generally holds for the equilibrium constants of transition metals [21, 22, 31].

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