Investigation of interaction of Mg^{2+} and Sr^{2+} with metallochromic indicators in different solvent media

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Abstract

The behaviour of complexes of Mg^{2+} and Sr^{2+} with metallochromic indicators, murexide, calmagite and Solochrome black T (EBT), in water and methanol/ water solvent systems was studied in this work. It was found that the stability of Mg^{2+} complexes of above-mentioned indicators increased when methanol was in the aqueous solvent system. Mg, which does not form complexes with murexide in water medium, was found to be able to form a fairly stable complex with murexide in methanol/ water system. Sr did not form complexes with studied three metallochromic indicators both in water and methanol/ water systems.

Introduction

The behaviour of Ca–metallochromic indicator complexes, Ca–murexide, Ca–calmagite and Ca–EBT in water and methanol/ water systems was studied previously (Edussuriya et al. 2002). According to the results of that work Ca forms relatively unstable 1:1 (metal:ligand) complexes with calmagite, murexide and EBT and the stoichiometry of these complexes changed from 1:1 to 1:2 (metal:ligand) when the medium was changed from deionised water to methanol/ water mixture. In addition to that, calculated stability constants of Ca complexes gave evidence to show that the stability of 1:2 complexes were significantly higher than that of 1:1 complexes. Therefore, in order to investigate the behaviour of the complexes of Mg and Sr, those are from the same group (II) with Ca, series of experiments were carried out using Mg and Sr salts with above mentioned three indicators using deionized water and deionized water/ methanol mixture as the solvent in this study. In this paper we report the first observation of the formation of the complex of Mg^{2+} with murexide in methanol water mixed solvent. Stability constants of the complexes in both media were calculated in order to investigate the effect of methanol on the stability of the complexes. Study of the stability of these complexes is important as they are used in the quantitative analysis of metal ions by complexometric titrations using EDTA (ethylenediaminetetraacetic acid) as the complexing agent.

A. Metal ion indicators

Metal ion indicators are used in EDTA titrations for the precise determination of the end-point. Solochrome black T (EBT) is sodium 1-(1-hydroxy-2-napthylazo)-6-nitro-2-napthol-4- sulphonate(II) and its sulphonic acid group gives up its proton long before the pH range of 7-12, which is suitable for metal ion indicators. Murexide is the ammonium salt of purpuric acid [5-(hexahydroxy-2,4,6-trioxo-5-pyrimidinyl) imino] –2,4,6-(1H, 3H, 5H)- pyrimidinyl, ammonium salt). Murexide forms complexes with many metal ions. Calmagite is 1-(1-hydroxyl-4-methyl-2-phenylazo)-2-napthol-4-sulphonic acid). Calmagite shows the colour change from blue to red in pH =10 and the colour change is somewhat clear and sharper. Calmagite functions as an acid –base indicator (Jeffery et al. 1994).

B. Complexes of alkaline earth metals with metal ion indicators

The complexes of Mg^{2+} with metallochromic indicators are coloured due to charge transfer transitions from the ligand to the metal ion and they are relatively stable compared to Ca^{2+} complexes. However Mg^{2+}-murexide complex is not formed in water media (Jeffery et al. 1994).

Sr^{2+} does not form complexes with calmagite, murexide and EBT even at low temperatures. (Jeffery et al. 1994) Sr^{2+} forms complexes with methylthymole blue and thymolpthalexone metallochromic indicators.

Mg^{2+} and Sr^{2+} do not form coloured complexes with common ions such as Cl^-, NO_3^-, PO_4^{3-}, SO_4^{2-} and F^-. Magnesium–calmagite complex is a stable complex. It may be stored for a long period of time. This complex is stable in water may mean one of two things, either that there is no reaction with water which would lead to a lower free energy of the system (thermodynamic stability) or that although a reaction would lead to a more stable system, there is no available mechanism by which the reaction can occur (kinetic stability) (Kettle 1969).

Materials and Methods

A. Instruments

Absorbance values of complexes were measured using a UV 1601 SHIMADZU spectrophotometer. pH of solutions was measured using a Jenway 3305 pH meter. Mettler AE 100 analytical balance was used for weighing purposes.

B. Chemicals

Magnesium nitrate, magnesium chloride, strontium nitrate, sodium hydrogen phosphate, sodium hydroxide, sodium hydrogen carbonate and all indicators were taken from GPR grade BDH laboratory supplies.

C. Use of Job's method

Method of continuous variations was used to determine the stoichiometry of the complexes. In this method a series of solutions was prepared such that the total number of moles of the metal and the ligand, n_{tot}, in each solution are the same. Thus, if $(n_M)_i$ and $(n_L)_i$ are the number of moles of the metal and the ligand in the i-th solution respectively, then, $n_{tot} = (n_M)_i + (n_L)_i$ (Bauer *et al.* 1979).

Absorbances of each of the solutions were measured and base line correction was done with a solution containing both indicator and the buffer solutions.

The magnesium–calmagite complex and magnesium-EBT complex were maintained between pH 10 and 11.

D. The solvent effect on the complex

This effect was investigated using solvent systems with methanol contents 20% and 40% v/v. The concentration of the stock solutions of Mg^{2+} and indicators used for measurements were 4×10^{-4} mol L^{-1}.

E. Preparation of buffer solutions

All buffer solutions (pH =11 Sodium bi carbonate buffer, pH =11 di-sodium hydrogen phosphate buffer) were prepared by method of Clark and Lubs buffer solution (Kolthof *et al.* 1969).

F. The deviation from Beer Lambert law for Mg–indicator complexes

The absorbance values of different concentrations of complexes were measured and absorbance Vs concentration graphs were plotted.

5.00 mL of **X** mol L^{-1} $Mg(NO_3)_2$ and 5.00ml of **X** mol L^{-1} indicator solutions were transferred to 25.00 mL volumetric flask and it was diluted up to the mark. Then absorbance values of complexes were measured.

Concentration **X** /mol L^{-1} = 1×10^{-4}, 2×10^{-4}, 3×10^{-4}, 4×10^{-4}, 5×10^{-4}, 6×10^{-4}

G. Determination of λ_{max} values for Sr^{2+}–ligand solution and ligand solution.

In order to determine whether the complexes, Mg-murexide and Sr-metallochromic indicators formed, over layer spectra of both metal-indicator solutions and indicator solutions were obtained. The Stability Constants were determined using a spectrophotometric method (Skoog *et al.* 1997).

Results and Discussion

Calibration curves, absorbance Vs concentration of Mg-calmagite and Mg–EBT complexes were plotted in order to find the range of concentration of the complex, which obey the Beer Lambert law. For Mg-murexide a calibration curve was unable to obtain, as Mg did not form a complex with murexide in water medium. According to the calibration curves the ranges of concentrations, which obey the Beer Lambert law for Mg–calmagite and Mg–EBT are $(2 - 12) \times 10^{-5}$ mol L^{-1} and $(2 - 8) \times 10^{-5}$ mol L^{-1} respectively. The correlation coefficients of the curves were in the range 0.92- 0.95, which ensured the good linear association of the concentration of the complexes and their absorbance values.
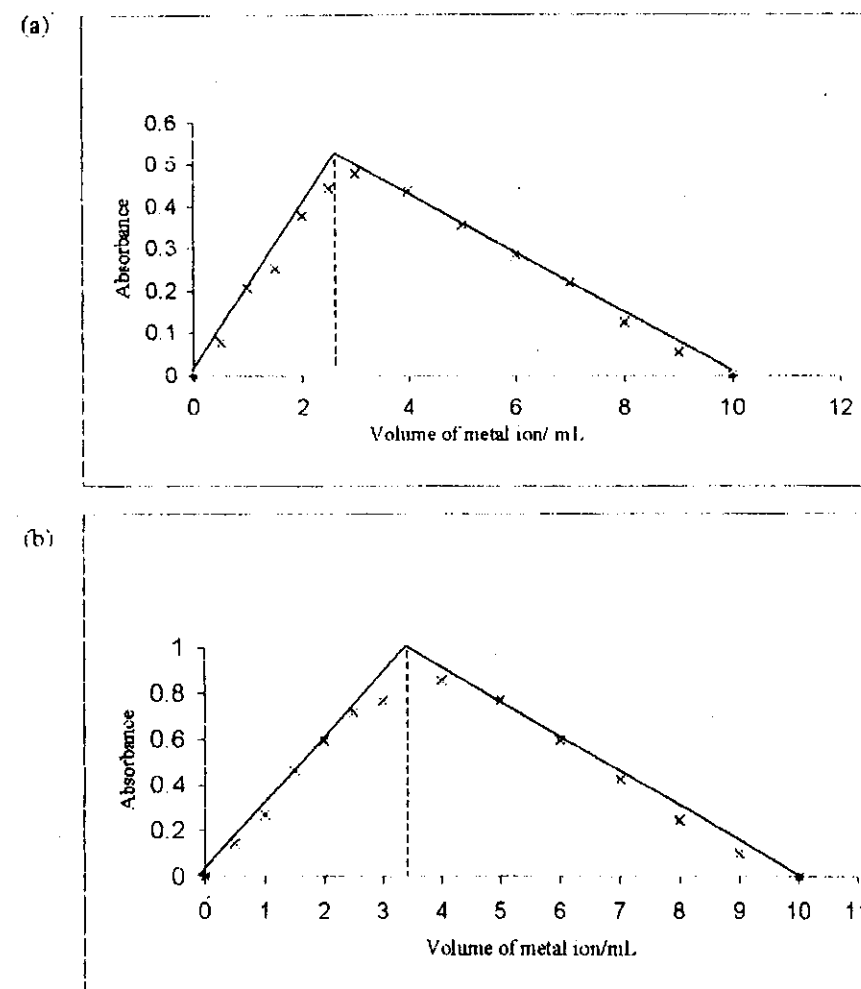

Figure 1 - Continuous variations plots for (a) Mg-calmagite in deionized water (λ_{max} =536 nm) and (b) Mg–EBT in deionized water (λ_{max} =526 nm) at pH 10-11

Mg forms complexes of 1:1 metal: ligand stoichiometric ratio with calmagite and EBT in appropriately buffered solutions (Ghasemi and Shamsipur (1995)). However the Job's plots (Figure 1) obtained from our experiments gave evidence for the formation of 1:2 (metal:ligand) complexes. In order to find out the reason for the formation of 1:2 complexes in our experiment the buffer solution used, NaHCO$_3$/NaOH was changed to NaHPO$_4$/ NaOH as their pH values are in the same range (10 -11). It was found that after using NaHPO$_4$/NaOH buffer solution the stoichiometry of complexes still remained unchanged. With the purpose of investigating the effect of anion of the Mg salt on the stoichiometry of the complexes, MgCl$_2$ was used instead of Mg (NO$_3$)$_2$ and the same experiment was carried out. Results of that experiment are given in Figure 2. From these results formation of the same 1:2 complex was substantiated.
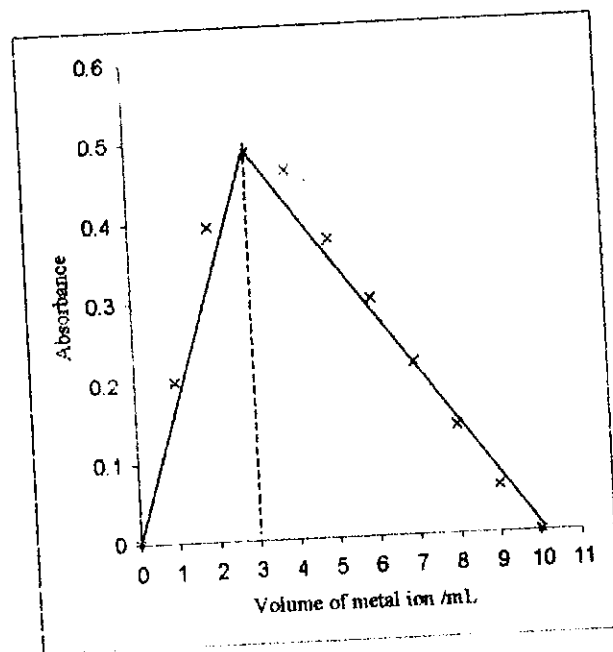

Figure 2 -   Continuous variations plot for Mg–calmagite complex obtained using MgCl$_2$ at pH 10-11

In order to investigate the effect of methanol on the behaviour of the complexes, Mg –calmagite and Mg–EBT, mixtures of methanol and deionized water were used as the medium. The percentages of methanol in the solvent mixtures were 20% and 40% v/v. Some of respective Job's plots obtained for complexes in 20% and 40% methanol solvent systems are given in Figures 3, 4 and 5.
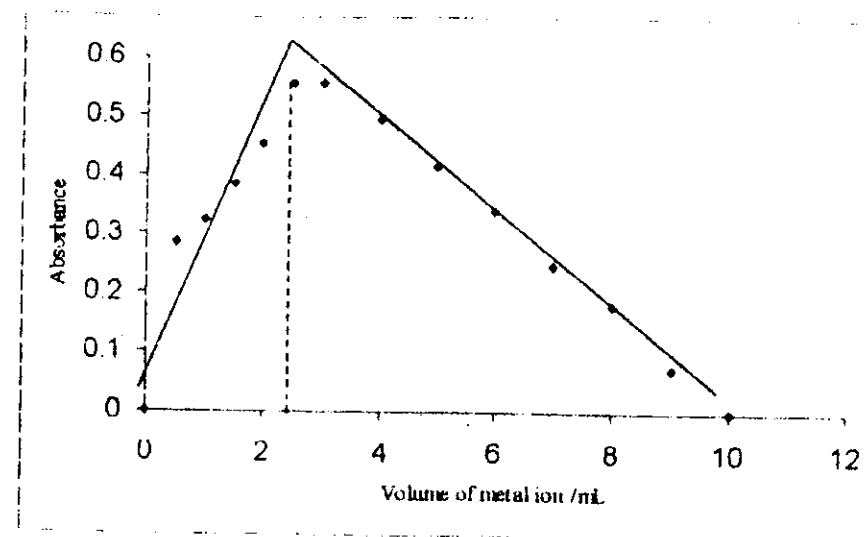

Figure 3 -   Continuous variations plot for Mg–calmagite in 40% methanol system at pH 10-11

According to the Figure 3 it was found that the metal:ligand stoichiometry of the complex was not changed even in the solvent mixture. With the indicator EBT that was used as a ligand to the Mg^{2+} ion in this study, similar job's plots were obtained for the experiments carried out using methanol/ water medium.
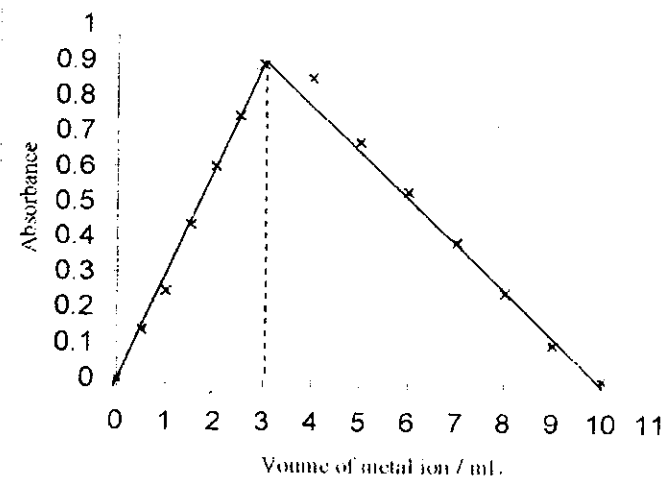

Figure 4 -   Continuous variations plot for Magnesium–EBT in 20% methanol system at pH 10-11
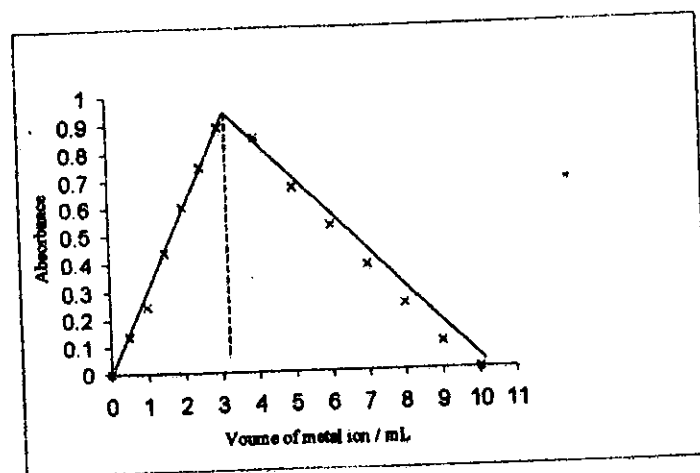
Figure 5 - Continuous variations plot for Magnesium–EBT in 40% methanol system at pH 10-11

It is evident from the Job's plots that the stoichiometry of Mg-EBT complex was 1:2 (metal:ligand) in water (Figure 1 (b)) and both, 20% and 40% methanol solvent systems, irrespective of their methanol content (Figures 4 and 5).

The over-layer spectra of the Mg–murexide complex solution and indicator solution (murexide with pH = 11 buffer solution) (Figure 6), showed that the spectrum of the complex had the same λ_{max} value as the indicator, which ensured the instability of Mg–murexide in water medium.

However, when the solvent was changed from water to methanol/ water mixture, a colour change from violet to orange was observed that was able to detect spectrophotometrically indicating a possible formation of a new complex (Figure 7).
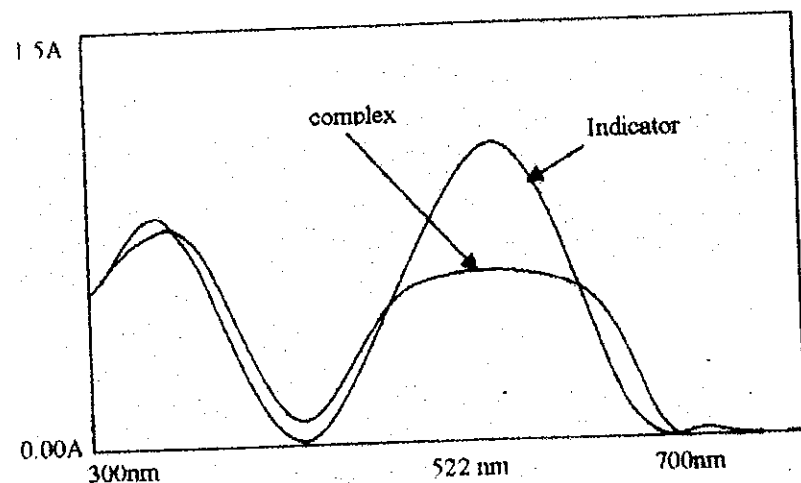

Figure 6 - Over layer spectrum of Mg-murexide complex in water medium at pH 11

According to the over layer spectra given in Figure 7 the bandwidth of the main peak of the indicator (λ_{max}= 521 nm) and the complex (λ_{max}= 476 nm) was found to be different. Also the low and high intensity peaks of the indicator shift in opposite directions, which could mean a formation of a new complex in the methanol/ water solvent mixture (Compare Figures 6 and 7).
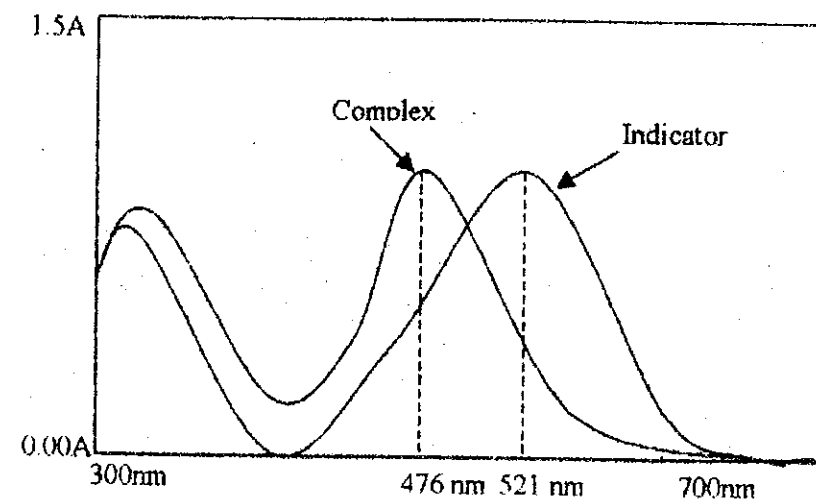

Figure 7 - Over layer spectra of Mg–murexide complex in 20% methanol at pH 11

Similar results have been reported previously, where the complexation of murexide with mono-, di- and trivalent metal cations in aqueous (Famoori and Haghgoo, (1990); Secco and Venturini (1993)), nonaqueous (Kashanian *et al.* 1988; Shamsipur and Alizadeh (1992)) and mixed solvents (Shamsipur *et al.* 1989; Shamisipur and Fat'hi (1993)) was accompanied by a relatively strong shift of the absorption band of murexide with λ_{max}= 522 nm towards shorter wavelengths, the smaller the radius of the complexed cation, the larger is the displacement.

According to the results of the work (Edussuriya *et al.* 2002) carried out previously in our laboratory, the complexation of murexide with Ca^{2+} was accompanied by a shift of the absorption band of murexide (λ_{max}= 522 nm) towards shorter wavelengths having the λ_{max} of the calcium complexes at 504 and 498 nm in water and water/ methanol mixed solvent respectively. Mg^{2+} has smaller ionic radius than Ca^{2+} and therefore the shift of the absorption band is stronger for the Mg-murexide complex ($522 \rightarrow 476$ nm) compared with the shift for the Ca-murexide complex ($522 \rightarrow 498$ nm) in the same water/ methanol mixed solvent.

The presence of OH groups in methanol may be one of the important reasons for increasing stability of Mg–murexide complexes in the methanol/ water mixture. The OH groups from methanol and water molecules are able to participate in the net work of hydrogen bond stabilizing electrostatic interactions of most Mg^{2+} binding sites, and hence its complexes with metallochromic indicators in the water /methanol mixed solvent (Natalie 1994). The calculated log value of the stability constant of Mg–murexide in methanol/ water medium was 9.36.

In order to investigate the complex formation of strontium with calmagite, murexide and EBT, in water medium, respective experiments were carried out keeping the pH value of the solutions at 11 and obtained λ_{max} values were tabulated as follows.

Table 1 - λ_{max} values for (a) calmagite/ Sr-calmagite   (b) EBT/ Sr-EBT (c) murexide/ Sr-murexide

(a)

λ_{max} of Calmagite/nm	λ_{max} of Sr^{2+}-calmagite/nm
614	615

(b)

λ_{max} of EBT/nm	λ_{max} of Sr^{2+}- EBT/nm
646	644
449	450

(c)

λ_{max} of Murexide/nm	λ_{max} of Sr^{2+}- Murexide/nm
530	532

According to the Table 1 the λ_{max} values of indicator and indicator with metal, there are no appreciable change in λ_{max} values for each of the spectra. From these results it became evident that Sr did not form any complex with none of these three metallochromic indicators under the conditions of the experiment.

When the medium was changed from water to methanol/ water mixture metal strontium did not give any colour change visually and remained with the colour of the indicator. Also in the spectrophotometric determination the over layer spectra for each indicator and indicator with strontium did not give any change in λ_{max} values (Figure 8).
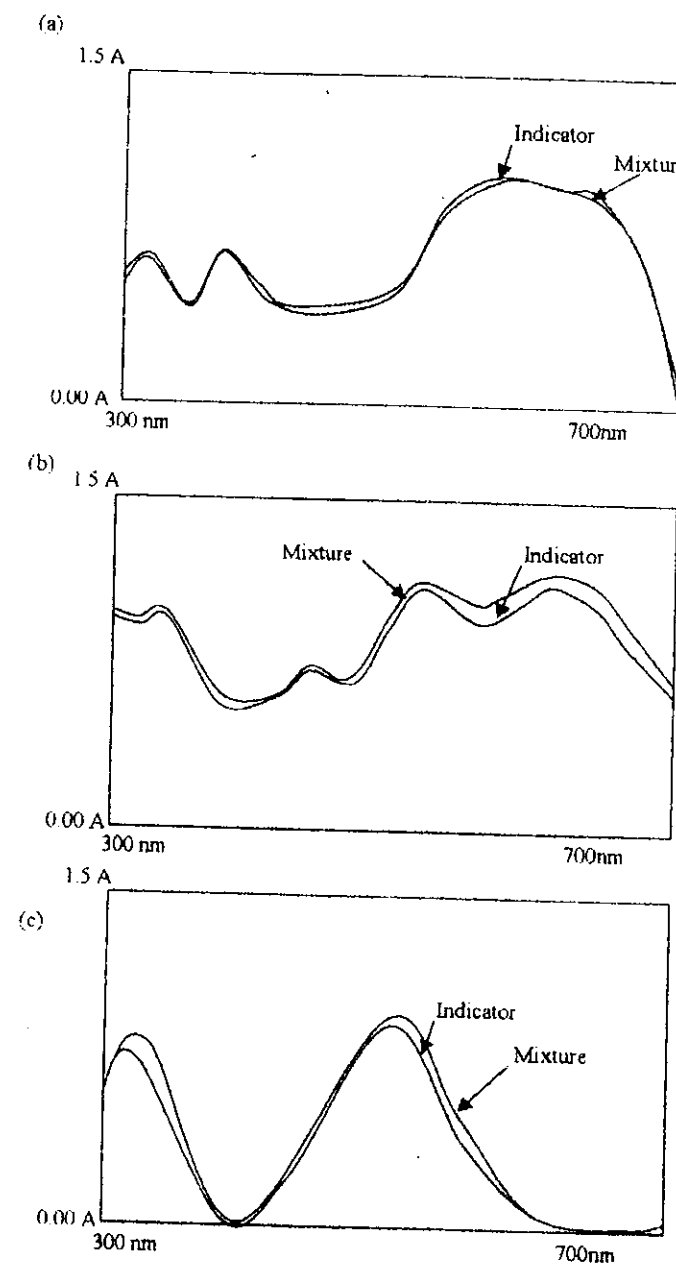

Figure 8 - Over layer spectra of (a) Sr – calmagite (b) Sr – EBT (c) Sr – murexide in 20% methanol at pH=11

The ionic radius of the strontium is 1.40 Å and it has larger ionic radius than Mg^{2+} and Ca^{2+}. The coordination number of the metal ion increases as the ionic radius increases. (1.40 Å for coordination number 8) (Oakes *et al.* 1997). For strong metal ligand binding there should be a chelating or donor functionalized feature in to the anionic ligand, so that it could satisfy the multiple coordination requirements of large cations. Thus calmagite and EBT azodyes are functioning as tri-dentate ligands and

thus these azo- dyes are of very low affinity for strontium metal. For non-transition metal ion complexes stability decreases roughly in the order of ionic potential (or polarizing power) which is defined as formal charge or ionic radius. Thus corresponding stability constant decreases in the following order. ($Mg^{2+}>Ca^{2+}>Sr^{2+}$).

The rate of complex formation is best described by the average lifetime of a particular ligand in the coordination sphere of a metal ion. Both the nature of the metal ion and that of the ligand generally influence the rate constant for ligand exchange. An example for evaluating these properties is the water exchange observed with different metal ions. In the series of Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, barium has the largest ionic radius and it has the lowest average lifetime of ligand in the coordination sphere of the metal ion. Therefore average lifetime decreases as follows, $Ba^{2+}< Sr^{2+}< Ca^{2+}< Mg^{2+}$ (Kellner *et al.* 1998). Metal srtrontium has the larger ionic radius than magnesium and calcium and thus it does not tend to form complexes with calmagite, murexide and EBT. However methylthymolblue and thymolphthalexone metal ion indicators can form coloured complexes with the metal strontium. Methylthymolblue and thymolphthalexone are hexadentate ligands. Therefore such indicators are of high affinity for strontium metal which is due to the high number of point of attachments in the ligand structure and they form stable complexes with strontium (Kettle 1969). The complex structure has some resemblance with the metal-EDTA complex (Octahedral structure).

Thymolphthalexone

Methylthymolblue

Strontium - Thymolphthalexone
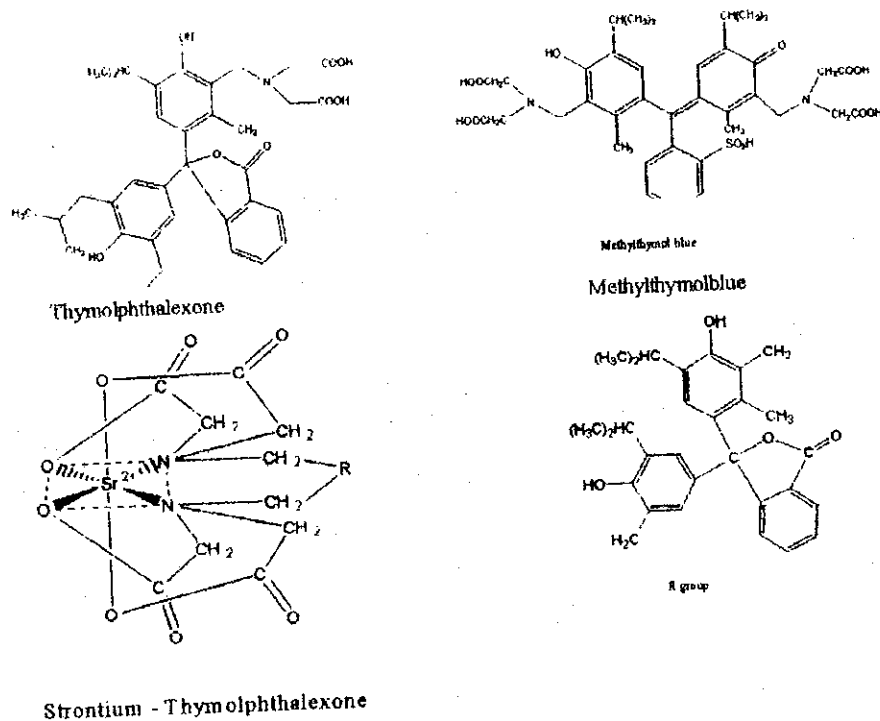
Using continuous variations plots the stability constants for Mg – complexes were calculated and tabulated in the Table 2.

Table 2 - Stability constants of complexes

(a) Stability constants, log K (theoretical values)

Metal ion	EBT	murexide	calmagite
Mg^{2+}	7.0	–	8.1
Ca^{2+}	5.4	5.0	6.1

(b) Stability constant, log K (calculated for deionized water medium)

Metal ion	EBT	murexide	calmagite
Mg^{2+}	9.15	–	9.68

(c) Stability constant, log K (calculated for 20% methanol medium)

Metal ion	EBT	murexide	calmagite
Mg^{2+}	9.59	9.36	9.80

For the comparison theoretical stability constant values for not only Mg complexes but for corresponding Ca complexes are also included. It is evident from the Table 2 that there is a fair agreement between theoretical stability constant values and values calculated for our experiments even though the stoichiometry of complexes were found different.

According to the results shown in the tables (b) and (c) the stability constant values of Mg complexes were slightly increased in the presence of methanol.

Conclusions

Mg forms complexes with calmagite and EBT according to the 1:2 (metal:ligand) stoichiometry both in water and methanol water media.

The stability of Mg–calmagite and Mg–EBT and Mg–murexide complexes were increased due to the presence of methanol in the water medium.

Formation of Mg–murexide complex was previously not has been reported and its formation in methanol/ water system was first discovered by this study.

Strontium does not form complexes with calmagite, EBT and murexide both in water and water/methanol mixed solvent.

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