

Study of the interaction of calcium (II) with metallochromic indicators in binary methanol–water mixtures

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Abstract

Generally, calcium (II) ion, Ca^{2+} , does not form stable coloured complexes due to the absence of easily excitable outer shell electrons. However, in specific pH ranges Ca^{2+} forms relatively unstable coloured complexes with metallochromic indicators such as murexide, calmagite and eriochrome black-T (EBT), where charge transfer transitions from ligand to metal are possible. One of the applications of these metallochromic indicators can be found in quantitative determination of metal ions using EDTA (ethylenediaminetetraacetic acid) as the complexing agent. However quantitative determination of Ca^{2+} using EDTA is less reliable due to the instability of Ca^{2+} -metallochromic indicator complexes. In order to investigate the effect of methanol on the stability of Ca^{2+} complexes, complexation reactions of Ca^{2+} with metallochromic indicators mentioned above in water and mixtures of methanol and water containing different amounts of methanol were studied spectrophotometrically. Ligand: Ca^{2+} stoichiometry of these complexes was determined using the well known Job's method of continuous variations. The ligand: Ca^{2+} stoichiometry of each of Ca^{2+} -murexide, Ca^{2+} -calmagite and Ca^{2+} -EBT complexes was 1:1 in water and 2:1 in methanol-water mixtures irrespective of the methanol percentage. It was found that the stability of 2:1 complexes was significantly greater than that of 1:1 complexes.

Introduction

Complexes of Ca^{2+} with metallochromic indicators are coloured due to charge transfer transitions from the ligand to the metal ion. These complexes are relatively unstable in aqueous solutions (Jeffery *et al.* 1989). Although the stability of a complex is obviously related to the complexing ability of the metal ion involved and to the characteristics of the ligand, the nature of the solvent may strongly influence the stability of Ca^{2+} -metallochromic indicator complexes and also the ligand: metal stoichiometry (Ghasemi and Shamsipur 1995). The chelating ability of the ligand also plays an important role in the formation of metal - metallochromic indicator complexes (Jeffery *et al.* 1989).

Murexide, which is the ammonium salt of purpuric acid, 5-[(hexahydroxy-2,4,6-trioxo-5-pyrimidinyl) imino]-2,4,6-(1H,3H,5H)-pyrimidinyl monoammonium salt, has been used for many years as a suitable complexing agent for a large number of metal ions over a wide range of experimental conditions (Geier 1967, Hulanicki *et al.* 1983). In most cases this ligand forms 1:1 complexes with mono, di and tri valent metal cations in aqueous, nonaqueous and mixed solvents. The metal ion-murexide equilibrium is rapidly established in aqueous and methanol solutions (Geier 1968, Winkler 1972). Murexide forms a red coloured complex (Figure 1a) with Ca^{2+} ion at pH 11.

Calmagite, 1-(1-hydroxyl-4-methyl-2-phenylazo)-2-naphthol-4-sulphonic acid, is another indicator which forms a reddish purple coloured complex (Figure 1b) with Ca^{2+}

at pH 11. Eriochrome black-T (EBT), sodium 1-(1-hydroxy-2-naphthylazo)-6-nitro-2-naphthol-4-sulphonate, forms a bluish purple coloured complex (Figure 1c) with Ca^{2+} at pH 10 (Jeffery *et al.* 1989).

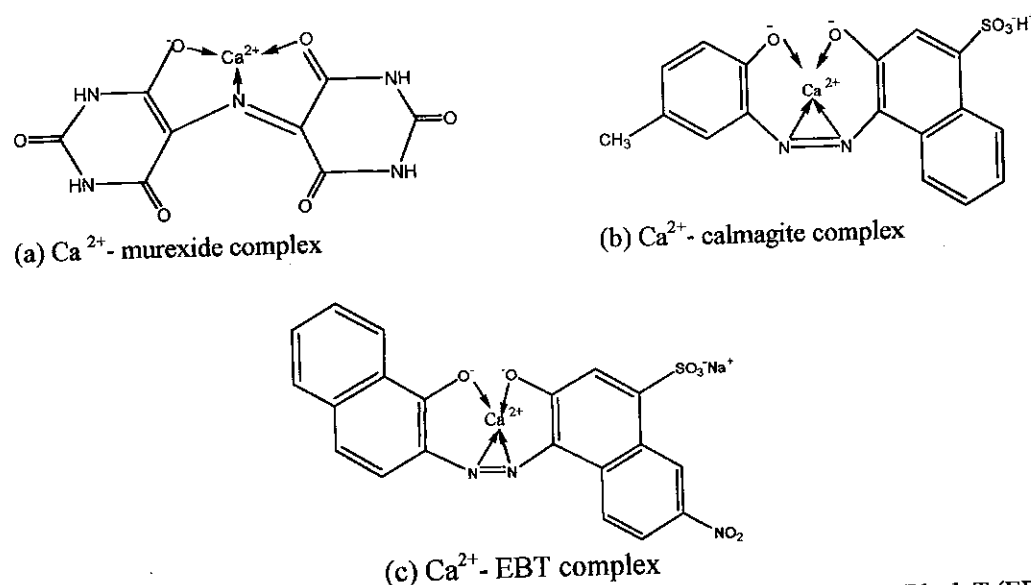


Figure 1. Complexes of Ca^{2+} with (a) murexide (b) calmagite and (c) Eriochrome Black T (EBT).

The formation constant K , of complexes can be calculated using the equilibrium,



$$K = \frac{[\text{Complex}]}{[\text{Ca}^{2+}][\text{Indicator}]^n}$$

$$K = \frac{[x/V]}{[(a-x)/V][(b-nx)/V]^n} \quad (2)$$

where, V is the volume of the solution, a is the initial concentration of the metal ion, b is the initial concentration of the indicator, x is the amount of the complex formed at the equilibrium and n is the number of ligands participated in the reaction of formation of the complex according to the stoichiometry.

Materials and methods

Absorbance values of complexes were measured using a UV 1601 SHIMADZU spectrophotometer. pH of solutions were measured using a HORIBA M-8 pH meter. Mettler AE 100 analytical balance was used for weighing purposes. All indicators, calcium nitrate, ammonium chloride, conc. ammonia, sodium phosphate, sodium hydrogen carbonate, sodium hydroxide and methanol used were GPR grade from BDH laboratory supplies. Job's method of continuous variation was used to determine the stoichiometry of the complexes.

A series of solutions with different ratios of Ca^{2+} and indicator were used. The total Ca^{2+} ion and indicator concentrations of each solution in the series were kept constant. pH of the series of solutions prepared for Ca^{2+} -murexide and Ca^{2+} -calmagite complexes was maintained between 10 and 11 while pH of the series of solutions prepared for Ca^{2+} -EBT complexes was maintained between 9 and 10, using phosphate and $\text{NH}_3/\text{NH}_4\text{Cl}$ buffer solvents, respectively.

The solvent effect on the complex formation was investigated using a series of solutions prepared by varying the methanol content in water as 10, 20, 30, 40, 50 and 60% v/v. The concentrations of Ca^{2+} and indicators used for measurements were between 1.0×10^{-4} and $2.5 \times 10^{-4} \text{ mol L}^{-1}$.

The formation constants of complexes were determined using a spectrophotometric method according to the following procedure (Skoog *et al.* 1997). The absorbance of series of complex solutions which were prepared by varying the ligand concentration and saturating each solution with $\text{Ca}(\text{NO}_3)_2$, was measured and a calibration curve, absorbance vs. ligand concentration was plotted. As the complex solution was saturated with $\text{Ca}(\text{NO}_3)_2$, according to the equilibrium (1) it was believed that the free ligand concentration is nearly zero and all of them were complexed. The concentration of the complex in the equation (2) was determined using the maximum absorbance value of the corresponding Job's plot and the calibration curve of absorbance vs. ligand concentration. As the initial concentrations of the ligand and the metal ion were known, formation constants were calculated using the equation (2).

Results and discussion

The data obtained in Job's method with Ca^{2+} -indicator complexes were plotted and the respective plots are shown in Figures 2 -4.

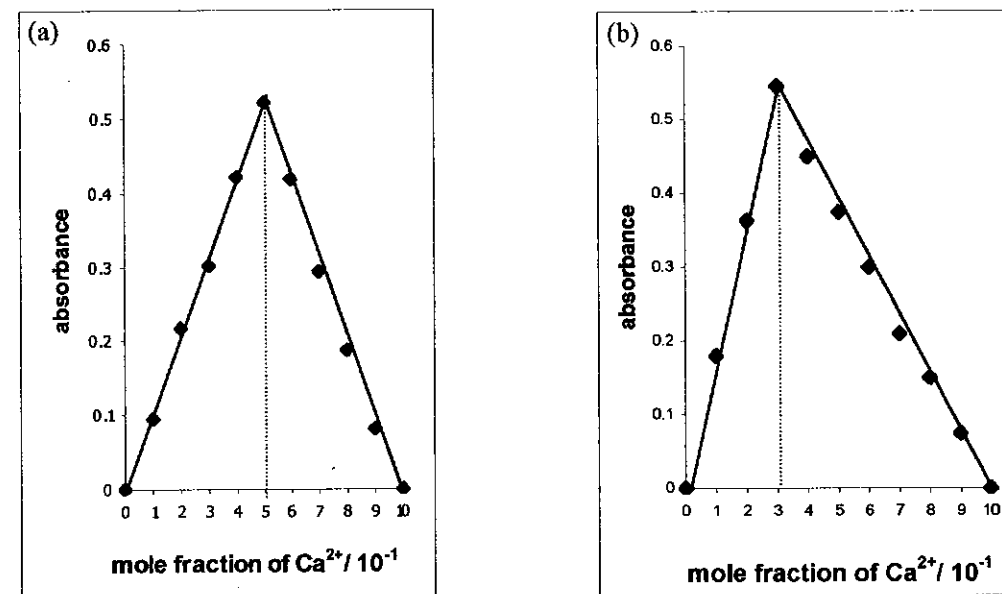


Figure 2. Continuous variations plots for calcium-murexide in (a) water ($\lambda_{\text{max}} = 504 \text{ nm}$) and (b) 40% methanol in water ($\lambda_{\text{max}} = 498 \text{ nm}$).

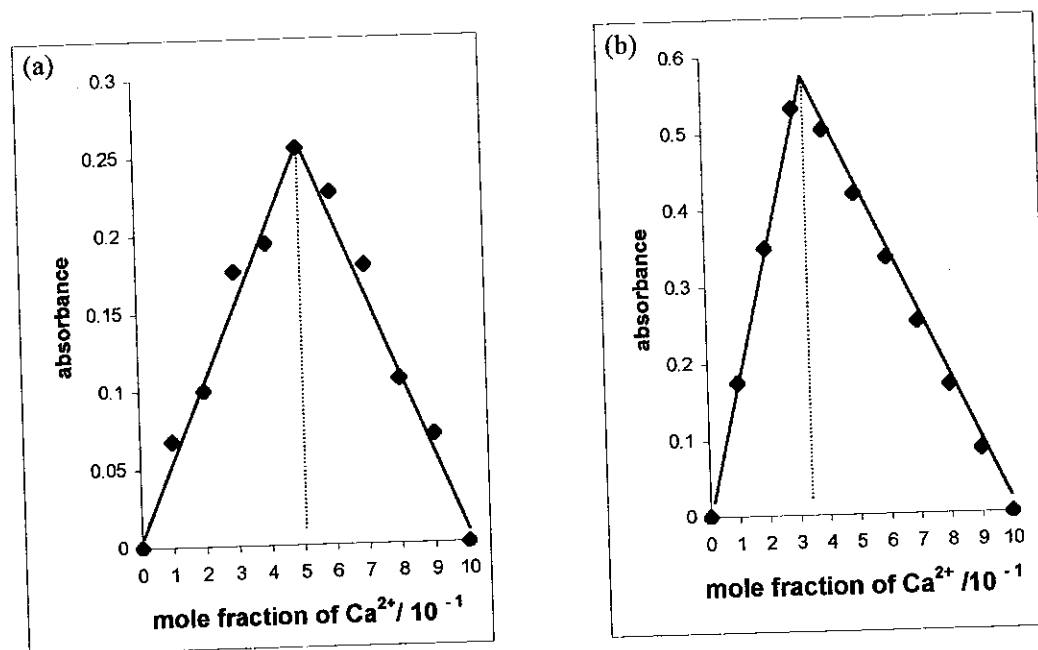


Figure 3. Continuous variations plots for calcium-calmagite in (a) water ($\lambda_{\max} = 543 \text{ nm}$) and (b) 40% methanol in water ($\lambda_{\max} = 544 \text{ nm}$).

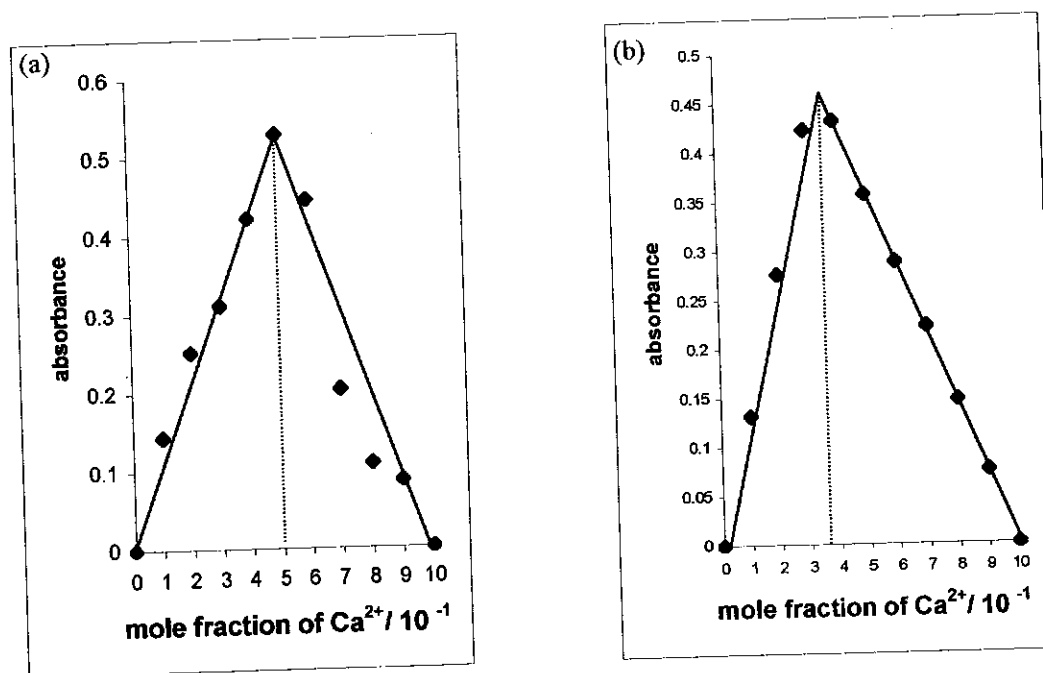


Figure 4. Continuous variations plots for calcium-EBT in (a) water ($\lambda_{\max} = 629 \text{ nm}$) and (b) 40% methanol in water ($\lambda_{\max} = 647 \text{ nm}$).

These plots were analysed using the method of continuous variations and the necessary results obtained are given in Table 1. Job's method of continuous variations states that

the stoichiometry of a complex corresponds to the mole fractions of reactants at the maximum absorbance of the complex formed. Irrespective of the methanol percentage used, similar continuous variations plots were obtained for all calcium complexes with three indicators in the binary solutions. Table 1 shows that the ligand: metal ion stoichiometric ratio for all complexes changed from 1:1 to 2:1 when the solvent system was changed from water to methanol-water mixture.

Table 1. Stoichiometry of complexes in different media

Complex	pH	Methanol percentage	Ligand:Ca ²⁺ Stoichiometry
Ca ²⁺ - murexide	10-11	0	1 : 1
		20	2 : 1
		40	2 : 1
		60	2 : 1
Ca ²⁺ - calmagite	10-11	0	1 : 1
		20	2 : 1
		40	2 : 1
		60	2 : 1
Ca ²⁺ - EBT	9-10	0	1 : 1
		20	2 : 1
		40	2 : 1
		60	2 : 1

λ_{\max} values obtained for Ca²⁺-indicator complexes in two different solvent systems are shown in Table 2. A noticeable change in λ_{\max} was observed only for Ca²⁺-EBT complex, which was not sufficient to give a noticeable colour change. The electronic transition energy has changed due to the change in ligand environment reflecting a shift in λ_{\max} , but the slight change in λ_{\max} value observed for Ca²⁺- murexide and Ca²⁺- calmagite complexes could be due to the compensation of that effect by solvent effect.

Although the formation of 2:1 complexes between murexide and Ca²⁺ in solutions has not been reported, the formation and isolation of sandwich complexes (Figure 5) of murexide with Ca²⁺, Sr²⁺, Cd²⁺, Pb²⁺ and Fe²⁺ ions in crystalline form and their structures have been reported by White and coworkers (Kepert *et al.* 1977, Favas *et al.* 1977, White and Willis 1977, Raston *et al.* 1977). However, in our study 2:1 (ligand: metal) complexes of Ca²⁺ with all three metallochromic indicators were formed in methanol-water mixtures.

Table 2. Colours and λ_{\max} values of the complexes in specific pH values

Complex	pH	Colour	λ_{\max} of the complex in water /nm	λ_{\max} of the complex in 60% methanol/ nm
Ca- murexide	11	Red	504	498
Ca- calmagite	11	Reddish purple	543	544
Ca- EBT	10	Bluish purple	629	647

The formation constants calculated for Ca^{2+} -indicator complexes are given in Table 3. The formation constants thus calculated seemed to give evidence for a remarkable difference in the stability between the 1:1 and 2:1 complexes formed in water and water/methanol respectively (Table 3).

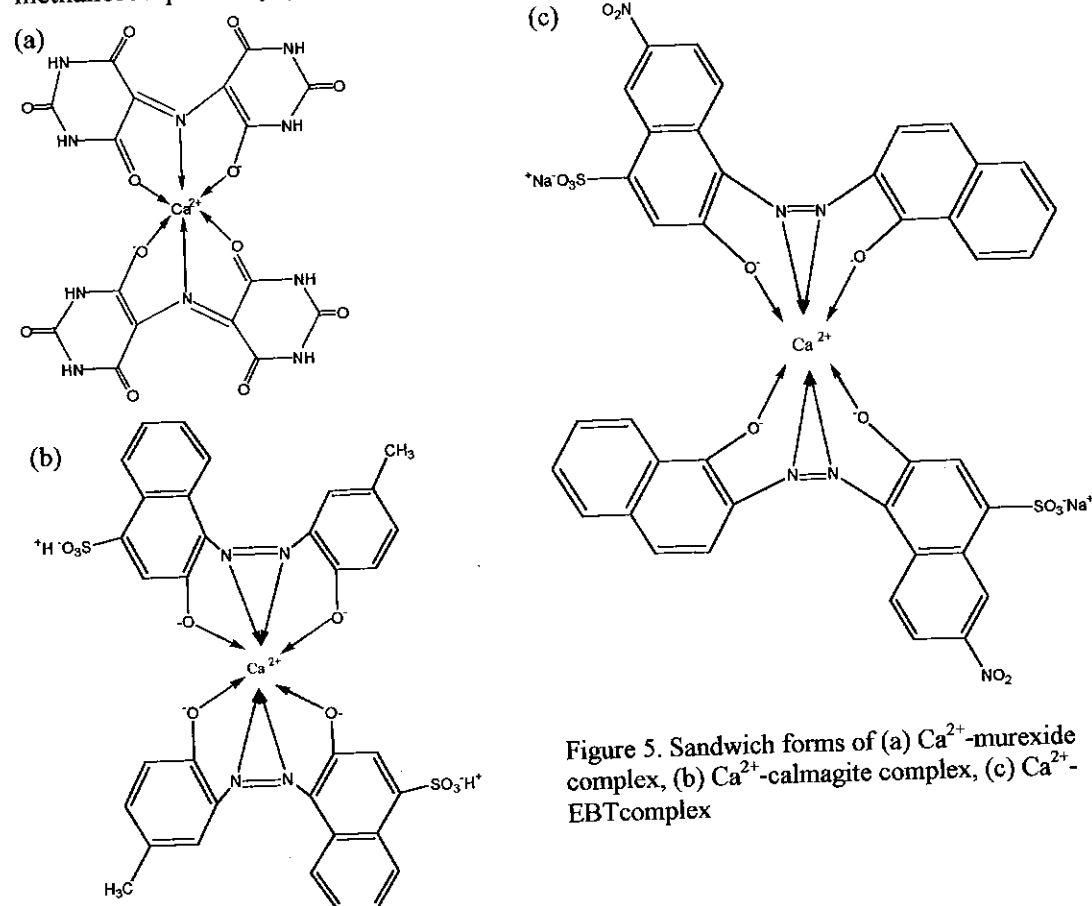


Figure 5. Sandwich forms of (a) Ca^{2+} -murexide complex, (b) Ca^{2+} -calmagite complex, (c) Ca^{2+} -EBT complex

When the stoichiometry was changed from 1:1 to 2:1, the number of points of attachment of ligands to the metal ion and the coordination number of Ca^{2+} increases enhancing the stability of complexes. Calcium, being much less restricted in its ligation requirements than other divalent cations such as Mg^{2+} , is able to accommodate from 4 to 12 oxygen ligands in their primary coordination sphere but coordination numbers of six, seven or eight are the most common (Nathalie 1994).

Table 3. Formation constants of the complexes in different media

Complex	Formation constant of the complex in water / L mol^{-1}	Formation constant of the complex in 10% methanol / $\text{L}^2 \text{mol}^{-2}$
Ca^{2+} -murexide	2.90×10^5	4.13×10^{10}
Ca^{2+} -calmagite	4.51×10^4	3.55×10^8
Ca^{2+} -EBT	1.14×10^5	6.43×10^8

In addition to that, -OH groups from methanol and water molecules are able to participate in the hydrogen bond network to stabilize the complex. Therefore it is evident that electrostatic interactions stabilize most of the Ca^{2+} binding sites increasing the stability of the complex in the solvent mixtures of methanol-water (White and Willis 1977).

Conclusion

The ligand: metal ion stoichiometric ratio for all complexes changed from 1:1 to 2:1 when the solvent system was changed from water to methanol-water mixture. Formation of 2:1 (ligand: metal) complexes between Ca^{2+} ion and murexide, calmagite and EBT in solution has not been previously reported but their formation in methanol-water mixture was evident in this study. The 2:1 (ligand: metal) complexes formed in methanol-water were found to be more stable than 1:1 complexes formed in water. In this study it was also found that the behaviour of the 2:1 (ligand: metal) complexes was independent of the methanol percentage in the medium.

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