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Dye indicator absorbance spectra and complex ions formation in chromium (III) chloride-alkali halide-water system

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ABSTRACT

Spectral absorbance of chromium (III) chloride-alkali halide-water system was studied by dye indicator i.e. methyl orange. The absorbance of a series of mixed dye, chromium (III) chloride and alkali halides solutions has been measured. Here the dye concentration and one of salt concentration was kept constant and concentration of other salt was gradually increased. The absorbance at λ_{max} against the other salt concentration shows eight peaks corresponding to complex ion formation between the salts in the ratio 6:1, 4:1, 3:1, 2:1, 3:2, 1:1, 2:3, 1:2. This can be explained on the basis of Frank-Condon principle.

Key words: absorbance, λ_{max} , dye indicator, complex, spectrophotometer.

INTRODUCTION

Transition and Inner transition metal complexes are of continuing interest mainly due to their structural and catalytical properties and their applications in diagnostic pharmaceutical and laser technology [1-6].

Critical micelle concentration of surfactants using dye indicator method has been measured by means of spectral absorbance of a series of mixtures of dye-surfactant solutions at λ_{max} of the dye, surfactant concentration increasing and dye concentration constant [7]. Here surfactant behave as electrolytes in dilute solutions and CMC is a transition from ionic micelles to neutral colloid and again charged colloidal particles, CMC being indicated by a sharp peak in absorbance – concentration curve. The chemical potential of the system goes on decreasing with increasing surfactant concentration reaching minimum at CMC, consequently showing increasing in absorbance– concentration curve reaching a peak followed by a decrease.

Hence, this characteristic abrupt change in absorbance was desirable to investigate complex ions formation in known system of chromium(III) chloride and alkali halide in aqueous solutions ; dye should not react with metal ions.

By using a number of physico-chemical properties, Nayer and coworkers [8] shown that the nature of such complex ions is unstable; showing breaks or peaks in curves obtained by plotting such physical property changes against concentration of the variant in mixed salt by mono variation method. The complex compound formed in water between lead and alkali nitrates are in the ratio of 1:1, 1:2 and 1:4, lithium nitrate is not complexing. They have also studied mercuric and alkali halid system using same physico - chemical properties and indicated formation of six complexes.[9]

Above system has been studied by Kazi and Desai[10]. They also adopted mono variation method for above system using interfacial tension method and showed three complexes for the lead system where as seven complexes for mercuric system. However they have indicated that the number of complexes decreases from seven to six to three

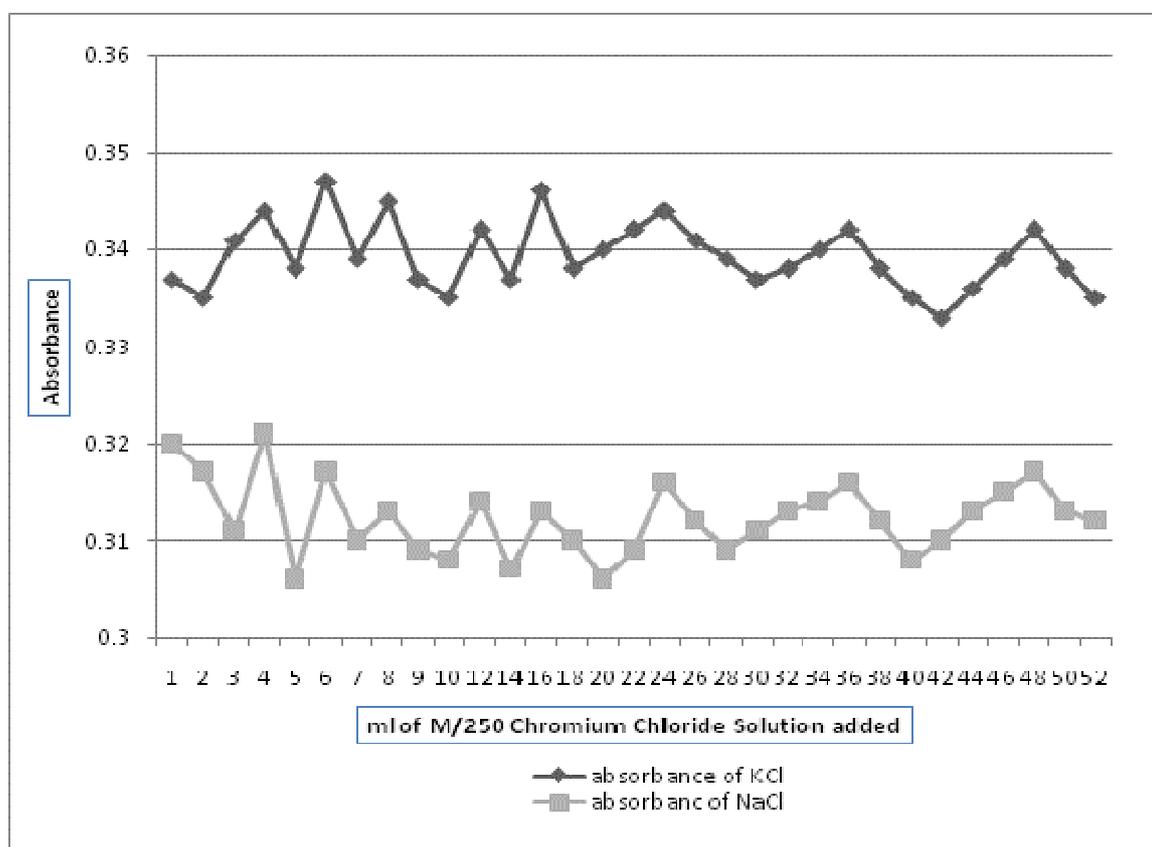
with increasing salt concentration. The interfacial tension – concentration curve peak corresponding to complex ion formation has been explained on the basis that when interfacial tension increases reaching peak value with increasing mixed salt concentration of the variant, chemical potential value becomes minimum and vice-versa.

P.Farasram and R.Farasram [11] have studied the absorbance of a series of mixed dye, mercuric halide – alkali halide - water system by mono variation method, keeping dye concentration and one salt concentration constant and increasing the concentration of HgX_2 . They indicated six peaks are in the ratio of 1:4, 1:2, 1:3, 1:1, 3:2, 2:1 for mercuric halide variable and alkali halide constant respectively.

In the present work, the absorbance of pure dye solution was measured and absorbance at λ_{max} of the dye was taken as standard in case of dye – salts system while measuring absorbance with increasing salt concentration of the variant – keeping the concentration of the other salt constant – using mono variation method – dye concentration being constant.

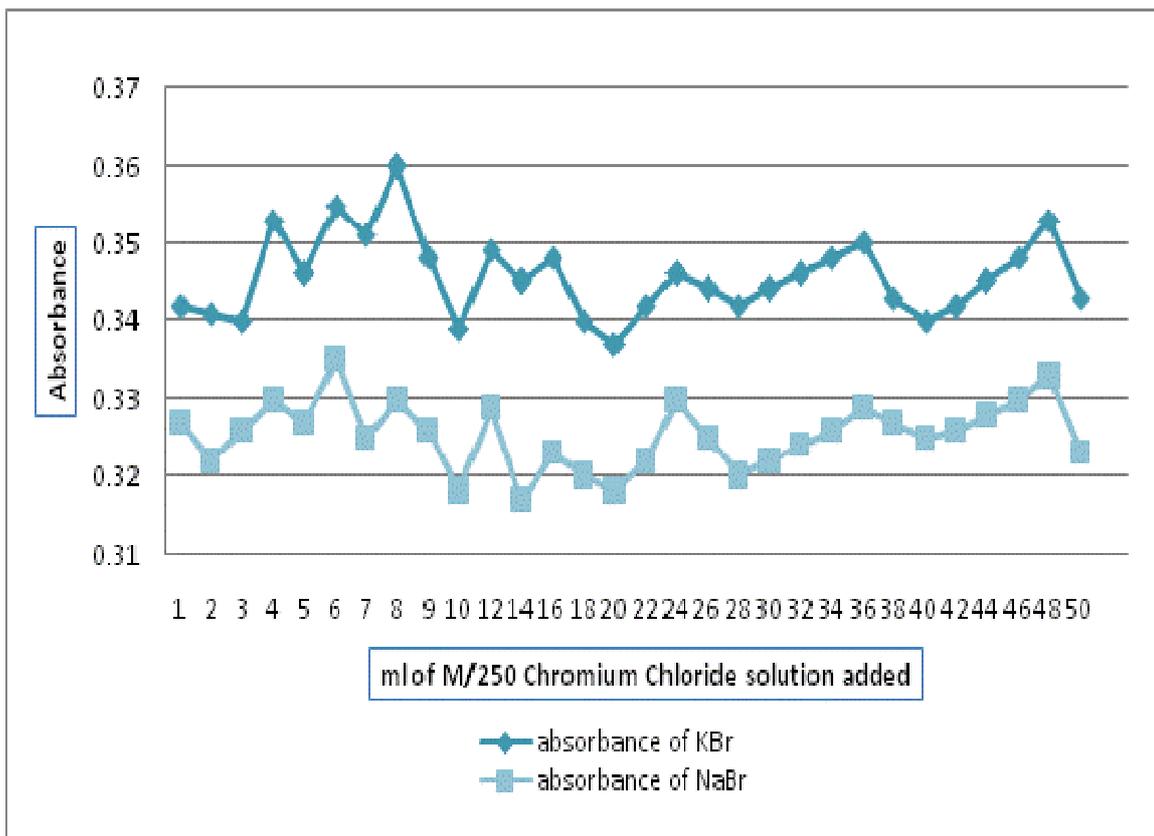
MATERIALS AND METHODS

A shimadzu double beam spectrophotometer UV-150-02 was used for spectral measurements. Salts used were of AR grade and purified ; dye methyl orange was used as indicator. Here in Chromium(III) chloride-alkali halide-water system by keeping concentration of alkali halide and dye constant with increasing concentration of Chromium(III) chloride eight peaks in the ratio of 6:1, 4:1, 3:1, 2:1, 3:2, 1:1, 2:3, 1:2 were observed.



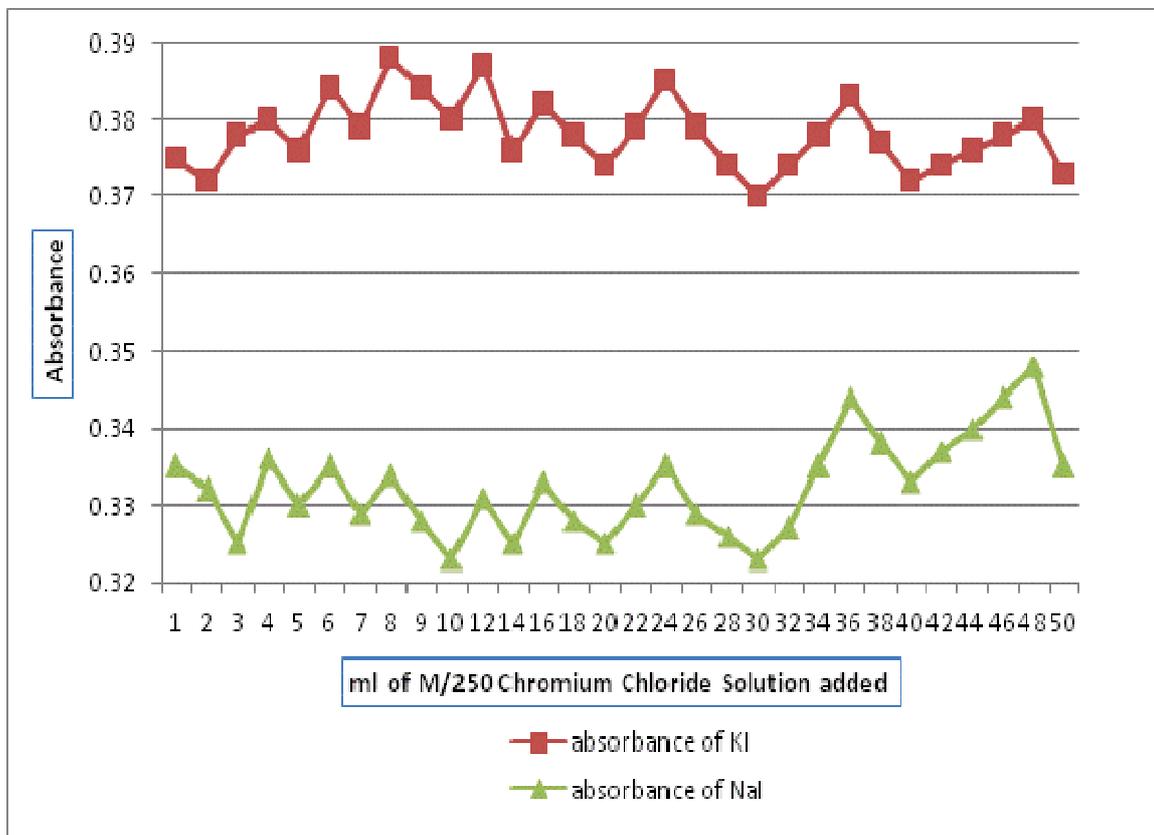
ml. of M/250 $CrCl_3$ + 24 ml. M/250 KCl + 10 ml. 2×10^{-4} M methyl orange

ml. of M/250 $CrCl_3$ + 24 ml. M/250 NaCl + 10 ml. 2×10^{-4} M methyl orange



ml. of M/250 CrCl₃ + 24 ml. M/250 KBr + 10 ml. 2×10⁻⁴M methyl orange

ml. of M/250 CrCl₃ + 24 ml. M/250 NaBr + 10 ml. 2×10⁻⁴ M methyl orange



ml. of M/250 CrCl₃ + 24 ml. M/250 KI + 10 ml. 2×10⁻⁴M methyl orange

ml. of M/250 CrCl₃ + 24 ml. M/250 NaI + 10 ml. 2×10⁻⁴ M methyl orange

RESULTS AND DISCUSSION

When such absorbance is plotted against increasing salt concentration, the graph indicate eight peaks corresponding to the ratio of concentration of two salts in stoichiometric proportion for the system forming complex compounds. The graph 1, 2 and three indicate eight peaks in the following order, sodium and potassium halide concentration constant.

6:1	6MX:CrCl ₃	M ₆ [CrCl ₃ X ₆]
4:1	4MX:CrCl ₃	M ₄ [CrCl ₃ X ₄]
3:1	3MX:CrCl ₃	M ₃ [CrCl ₃ X ₃]
2:1	2MX:CrCl ₃	M ₂ [CrCl ₃ X ₂]
3:2	3MX:2CrCl ₃	M ₃ [Cr ₂ Cl ₆ X ₃]
1:1	MX:CrCl ₃	M[CrCl ₃ X]
2:3	2MX:3CrCl ₃	M ₂ [Cr ₃ Cl ₉ X ₂]
1:2	MX:2CrCl ₃	M[Cr ₂ Cl ₆ X]

Where M = Na or K and X = Cl, Br, I

CONCLUSION

Here the absorbance peaks observed are in the order K > Na or degree of electron transition order is K > Na; because the atomic size of K > Na, so the electrostatic order Na > K.

This optical property of sudden rapid absorbance of light during complex iron formation and dissociation when electron transition occurs from equilibrium to non- equilibrium state may be correlated to chemical potential changes as well as Frank-Condon principle.

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