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NOTE

Spectral Investigation of Complex Ions Formation with Dye Indicators in Different Metal Systems

ASHWIN N. MODI* and C.M. DESAI†
Junior Laboratory Technician
Gujarat Narmada Valley Fertilizer Co. Ltd
Narmadanagar-392 015, Bharuch, India

The absorbance of zinc chloride-alkali halide, zinc chloride-alkali halide with potassium perchlorate and copper chloride/nickel chloride-zinc chloride systems were studied by dye indicators and shows peaks corresponding to complex ion formation between salts.

It was observed by means of interfacial tension, measurement against butyl or amyl acetate, using monovariation method that zinc chloride formed with alkali halide three to six or seven complexes in aqueous solution as the salt concentration decreased. The dilution of alkali salt solution has to be progressively increased in the order of Li > Na > K for formation of maximum number of possible complexes[1], as in the case of mercuric chloride or bromide systems.[2,3]. The degree of dilution is a measure of the magnitude of binding force between the anions and metal cations which is in the order $Li^+ > Na^+ > K^+$ in view of greater polarising effect of the smaller cations. It was also suggested that the formation of these complexes corresponds to

$$\left[K_4HgCl_6\right] \rightleftharpoons \begin{bmatrix}K_4HgCl_6\\K_2HgCl_4\end{bmatrix} \rightleftharpoons \left[K_2HgCl_4\right] \rightleftharpoons \begin{bmatrix}K_2HgCl_4\\KHgCl_3\end{bmatrix} \rightleftharpoons \begin{bmatrix}K_2HgCl_4\\2HgCl_2\end{bmatrix} \rightleftharpoons \begin{bmatrix}KHgCl_3\\HgCl_2\end{bmatrix} \rightleftharpoons HgCl_3^- + HgCl_2 + K^+ + Cl^-$$

The formation of complex ions between any two salts such as copper, cobalt, nickel, cadmium, mercury was also investigated forming three or four complexes. This novel spectral method has been recently applied to study complex ions formation in lead-alkali nitrate and mercuric alkali nitrate system confirming earlier findings.[4] Thus this type of specific optical property of absorbance at λ_{max}. of the dye is very significant in the study of complex formation. However, there should not be interaction of the dye with metal compounds.

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 the case of dye-salt systems. Three types of sets performed are as follows:

(1) While measuring absorbance with increasing $ZnCl_2$ salt concentration as variant, keeping the concentration of other salt alkali halide constant using mono-variation method, dye concentration being constant.

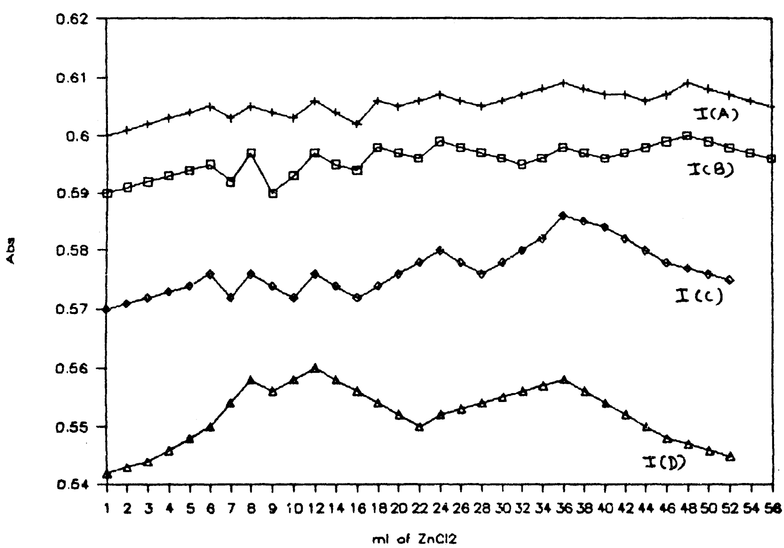
†Artemis Research Center Themis Chemicals Ltd., Vapi-396 195, India.

(2) Using the mixture of alkali chloride and potassium perchlorate salts being constants with variant $ZnCl_2$ salt.

(3) Using $ZnCl_2$ salt constant and $CuCl_2/NiCl_2$ salt as variant.

A Shimadzu double beam spectrophotometer UV-160A was used for spectral measurements. Salts used were of AR grade and purified dyes used as indicators were crystal violet and methyl orange.

In set (I) when such absorbance is plotted against increasing $ZnCl_2$ concentration as the variant the graphs indicate peaks corresponding to ratios 1:4, 1:3, 1:2, 3:2, 1:1, 2:3, 2:1 observed in graph IA and IB. While in set (II), the mixture of alkalihalide and $KClO_4$ salts concentration being constant and $ZnCl_2$ salt being variable, the graphs IC and ID indicate five and three peaks corresponding to the complexes in the ratios 1 : 4, 1 : 3, 1 : 2, 1 : 1, 2 : 3 and 1 : 3, 1 : 2, 2 : 3 respectively in the graphs IC and ID. As the $KClO_4$ mixed with alkali halide inhibits the complex formation, the peaks decrease from seven to five to three respectively in graphs IC and ID. In Set (III) the $ZnCl_2$ concentration being constant and $CuCl_2/NiCl_2$ as variant, graphs IIA and IIB indicate three peaks corresponding to complexes in the ratio 1 : 2, 1 : 1, 2 : 1.



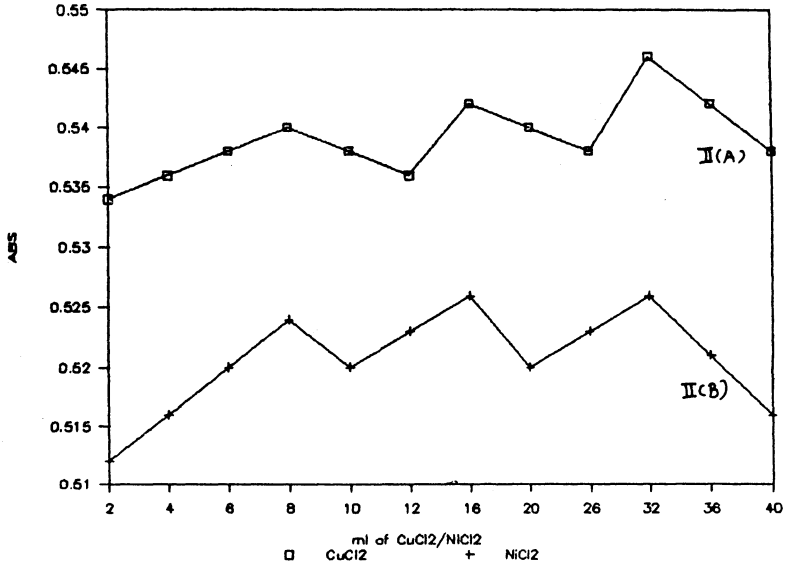
Graph-1

(A) mL of M/100 $ZnCl_2$ + 24 mL M/100 KCl + 10 mL 1.0×10^{-4} M Crystal violet +

(B) mL of M/100 $ZnCl_2$ + 24 mL M/100 LiCl + 10 mL 1.0×10^{-4} M Crystal violet □

(C) mL of M/40 $ZnCl_2$ + 24 mL M/40 KCl + 12 mL M/40 $KClO_4$ + 10 mL 3.0×10^{-4} M Methyl Orange ◊

(D) mL of M/40 $ZnCl_2$ + 24 mL M/40 KCl + 10 mL M/80 $KClO_4$ + 10 mL 3.0×10^{-4} M Methyl Orange Δ



Graph-II

(A) mL of M/100 $CuCl_2$ + 16 mL M/100 $ZnCl_2$ + 10 mL 1.0×10^{-4} M Crystal violet □

(B) mL of M/100 $NiCl_2$ + 16 mL M/100 $ZnCl_2$ + 10 mL 1.0×10^{-4} M Crystal violet ×

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