

NOTE

**Spectral Dye Absorbance Investigation of Complex Ions
Zinc-Alkali Chloride in Aqueous Methanol-Pyridine Systems**

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Absorbance spectral investigation using dye indicator has been investigated to study changes in complex ions formation with changes in aqueous phase.

Effect of increase and decrease of dielectric constant on the formation of complex ions in Zinc-alkali chloride aqueous methanol system has already been reported¹. With increasing concentration of methanol, with lower dielectric constant in solvent, the dielectric constant of water-methanol mixture decreases with consequent decrease in dissociation of anionic ions of salts and thereby decrease in complex ions formation².

Existence of seven complex ions in systems of zinc-alkali chloride in aqueous phase using novel dye indicator method has already been reported³. In the present work the system has been further investigated with aqueous methanol phase (50% methanol constant) with changes in the phase by means of pyridine addition.

Water exists as a mixture of dimers and trimers, whereas pyridine exists as mixture of dimers or an equilibrium mixture of monomers and dimers in pure state since pyridine is both N and π electron donor. The addition of pyridine to water, and associated molecular entity, may cause (1) rupture of self-association in pyridine and (2) structure breaking of water molecular H-bonding; thus the addition of pyridine to water brings about changes in their topology; thus specific interactions take place between water and pyridine resulting in their depolymerisation⁴. Nitrogen atom of pyridine with its lone pair of electrons forms H-bonding with H-atom of water; so with increase in content of pyridine, structure of water is more and more destroyed with consequent decrease in dielectric constant of mixed solvent as in the case of CH₃OH-water mixture.

The salts zinc chloride and potassium chloride M/20 concentration solution and dye crystal violet 1.0×10^{-5} M concentration solution were prepared in aqueous methanol-pyridine system using mono-variation method; different sets of solutions were prepared by increasing the zinc chloride concentration, the potassium chloride-dye crystal violet concentration being kept constant.

In the present experiments, in all sets, aqueous methanol concentration (50%) was kept constant, while the addition of pyridine was increased 5% to 30% to the aqueous methanol.

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A Shimadzu double beam spectrophotometer UV-160A was used for spectral measurements. Absorbance of pure dye solution at λ_{max} in each set of solutions was measured and plotted against increasing zinc chloride concentration. The peaks corresponding to the ratio of concentration of two salts in stoichiometric respective molecular proportions for the system are given in Table-1.

TABLE-1

S.No.	Solvent	No. of peaks with ZnCl ₂ , KCl
1.	50% methanol + 5% pyridine	7(4:1, 3:1, 2:1, 3:2, 1:1, 2:3, 1:2)
2.	50% methanol + 15% pyridine	4(4:1, 3:1, 1:1, 1:2)
3.	50% methanol + 30% pyridine	2(4:1, 3:1)
4.	50% methanol + 40% pyridine	No peak

It has been observed that in aqueous electrolyte solution the inter-ionic force may well be different for positive and negative ions in view of the electrically unsymmetrical character of water molecules; hence the negative ions would be drawn into the interior more than positive ions establishing an electrical double layer with its potential. As the ionic concentration is increased in solution, the mutual attraction between ions of opposite polarity becomes stronger than the forces between ions and water molecules causing change in the electrical double layer potential; when the double layer potential approaches zero with increasing electrolyte concentration, a double layer of opposite kind to the original is formed at the interface having again the same potential with opposite sign. In dilute solution of a mixture of salts such as zinc chloride and potassium chloride there is dissociation of positive and negative ions with increasing potential. However, with their increasing concentration, the ions may enter into complex formation and dissociation of ions taking place such as ZnCl₂. There is decrease in potential approaching zero, with still further increase in concentration. When the complex again dissociates there is potential sign change with reversal of double layer. At each state of complex formation and association and dissociation taking place there is reversal of electrical double layer with potential sign change. When this happens interfacial tension is maximum and light intensity is also maximum due to electron transition at complexing stage resulting in higher light absorbance than normal dye solution according to Franck-Condon principle.

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