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NOTE

Dye Absorbance Spectral Study of Complex Ions of Zinc-Alkali Chloride in Methanol-Water System

ASHVIN. N. MODI*, C.M. DESAI† and P.L. FARASRAM‡

Junior Laboratory Technician
Gujarat Narmada Valley Fertilizer Co. Ltd,
Namadanagar-392 015, Bharuch, India

Light absorbance spectral investigation has been studied to observe changes in complex ions formation with changes in methanol-water phase. Effect of increase and decrease of dielectric constant on the formation of complex ions, in lead-alkali nitrate and mercuric-alkali halide systems has been earlier reported. With increase in concentration of methanol, with lower dielectric constant in solvent, the dielectric constant of water-methanol mixture decreases with consequent decreasing dissociation of anionic ions of salts and thereby decrease in complex ions formation.

In the previous paper[1] we had adduced evidence for the existence of 7 (seven) complex ions in aqueous phase in zinc chloride-alkali chloride system using novel dye indicator method. However, these complex ions are unstable. In this communication same zinc system has been studied in aqueous methanol replacing aqueous phase.[2] It was observed that as the concentration of methanol gradually increased up to 90% the number of complexes decreased from seven to one.[3]

Salts (zinc chloride and potassium chloride) M/20 concentration solution and dye crystal violet 1×10^{-4} M concentration solution were prepared in aqueous methanol (60 to 90% methanol) using monovariation method. Different sets of solutions were prepared by increasing zinc chloride concentration and potassium chloride-dye crystal violet concentration being kept constant.

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 graphs indicate peaks corresponding to the ratio of concentration of two salts in stoichiometric respective molecular proportion for the systems. These are indicated in Table-1.

In zinc system the complexes found in aqueous phase between zinc and potassium chloride were in the ratio of 4 : 1, 3 : 1, 3 : 2, 1 : 1, 2 : 3, and 1 : 2 but when the system aqueous phase mixed with methanol was studied, it was observed that as the concentration of methanol increased in aqueous phase gradually up to 90%, the number of complexes decreased from seven to one with potassium chloride; this is because dielectric constant of aqueous methanol in aqueous phase

†Artemis Research Centre, Themis Chemicals Ltd, Vapi-396 195, India.
‡J.P. Arts and Science College, Bharuch-392 002, India.

TABLE-2

S. No.	Solvent	λ_{max}	Number of peaks with $ZnCl_2$-KCl
1.	Water	585 nm	07 (4 : 1, 3 : 1, 2 : 1, 3 : 2, 1 : 1, 2 : 3, 1 : 2)
2.	60% Methanol	584 nm	07 (4 : 1, 3 : 1, 2 : 1, 3 : 2, 1 : 1, 2 : 3, 1 : 2)
3.	65% Methanol	584 nm	06 (3 : 1, 2 : 1, 3 : 2, 1 : 1, 2 : 3, 1 : 2)
4.	70% Methanol	584 nm	05 (3 : 1, 2 : 1, 3 : 2, 1 : 1, 2 : 3)
5.	75% Mehanol	582 nm	04 (3 : 1, 2 : 1, 3 : 2, 2 : 3)
6.	80% Methanol	582 nm	03 (3 : 1, 1 : 1, 2 : 3)
7.	85% Methanol	582 nm	02 (3 : 1, 2 : 3)
8.	90% Methanol	582 nm	01 (3 : 1)

decrease the dissociation of complex ions and also discourages anionic ion dissociation. The number of complex ions formation decreases with increasing proportion of methanol. One explanation of this result is that a water molecule bound by H-bond to methanol molecule is less nucleophilic than a water dipole H-bonded to such another H_2O moelcule. Another reason is that the addition of methanol decreases the dissociation of complex ions with decreasing dielectric constant which also discourages anionic ion dissociation. This behaviour of H_2O-CH_3OH system can be visualised in the light of change of water structure in presence of alcohol. Many properties of liquid water suggest that it is a mixture of fluctuating regions of three-dimensional H-bonded polymers in equilibrium with randomly arranged H_2O monomer molecules. Aliphalic alcohols also have a considerable fraction of molecules joined in rings and chains, but they do not seem to participate in the formation of three-dimensional clusters characteristic of water; when alcolol is added to water the highly polar structure of water is destroyed progressively as alcohol content increases. Thus hydrogen bonding between adjacent H_2O molecules will be replaced by H-bonding with methanol and structure of water will be largely broken. Hence, the number of complex ions decreases with increasing content of methanol.[4-7]

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