NOTE

Physico-chemical Significance of Dye-Indicator Method in Complex Ions Variations in Aqueous Methanol System Mercuric Halide-Alkali Halide

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The mercuric halide-alkali halide system was studied in aqueous phase spectrophotometrically and it was found that six types of complexes were formed. The aqueous phase of the system was replaced by aqueous methanol and it was found that as the methanol concentration was increased in the system, the dielectric constant decreased and complex formation susceptibility decreased.

Several workers by different physical methods established that in mercuric halide-alkali halide system in aqueous phase six types of complex formation takes place[1–3]; however, these complex ions are unstable. An attempt has been made to study the same mercuric system spectrophotometrically by monovariation method using novel dye indicator method.[4] In this communication same mercuric halide system was studied in aqueous methanol replacing aqueous phase of the system. Effect of gradual change of concentration of methanol was studied on the number of complex ions formation. It was observed that as the concentration of methanol gradually increased up to 85%, the number of complexes decreased from six to one and no complex was observed at 90% in mercuric chloride and potassium chloride, and with potassium bromide at 90% methanol only one complex was observed. But with lithium chloride two complexes were observed at 90% methanol. This decrease of complexes can be explained on the basis of dielectric constant of the system decreasing as the concentration of methanol gradually increased in aqueous phase, which discourages the complex ions formation.[5–7]

A Shimadzu double beam spectrophotometer UV-160A was used for spectral measurements. The chemicals used in the study are of AR grade. Mercuric chloride, mercuric bromide, potassium chloride, potassium bromide and lithium chloride solution of M/100, M/100, M/200, M/200 and M/1000 concentration

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respectively and dye crystal violet (cationic) 5×10^{-5} M concentration solution was prepared in aqueous methanol (40, 50, 60, 70, 80, 85 and 90%).

For spectral study by monovariation method, different sets of solutions were prepared, increasing mercuric halide/alkali halide concentration; and alkali halide/mercuric halide-dye concentration being kept constant. Absorbance of pure dye solution at λ_{max} was taken as standard and absorbance at λ_{max} in each set of solutions was measured and plotted against increasing mercuric halide/alkali halide concentration; the graphs indicate peaks corresponding to the ratio of concentration of the two salts in stoichiometric proportioins for the system. The complexation ratio and formulae of the complexes are tabulated in Tables 1 and 2 respectively.

TABLE-1

Solvent	Number of peaks with		
	KCl	KBr	LiCl
40% Methanol	6	6	6
50% Methanol	6	6	6
60% Methanol	6	6	6
65% Methanol	5	6	6
70% Methanol	4	5	6
75% Methanol	3	4	5
80% Methanol	2	3	4
85% Methanol	1	2	3
90% Methanol	—	1	2

TABLE-2

Mole ratio	Molecular formula of complexes*
1 : 4	$HgX_2 + 4MX = M_4[HgX_6]$
1 : 2	$HgX_2 + 2MX = M_2[HgX_4]$
2 : 3	$2HgX_2 + 3MX = M_3[Hg_2X_7]$
1 : 1	$HgX_2 + MX = M[HgX_3]$
3 : 2	$3HgX_2 + 2MX = M_2[Hg_3X_8]$
2 : 1	$2HgX_2 + MX = M[Hg_2X_5]$

In mercuric halide system six types of complexes were formed in aqueous phase. When aqueous phase of the mercuric halide system was replaced by aqueous methanol and concentration of methanol increased upto 90%, number of complexes decreased from six to one. This behaviour can be explained on the basis of dielectric constant of aqueous methanol decreasing with increase in methanol concentration. The highly polar structure of aqueous phase is destroyed progressively; hence the hydrogen bonding between the adjacent aqua molecules is replaced by hydrogen bonding with methanol and structures of aqua molecules are broken to a large extent.[5–8]

Upto 60/65 % methanol six complexes were observed with KCl/KBr, because 45/40% aqua molecules can solvate salts and dissociate hence six types of complexes were formed. But after that, increasing methanol concentration, salt dissociation decreases, because lesser concentration of aqua molecules in the system is unable to solvate the salt molecules and on being surrounded by methanol molecules through hydrogen bond, the dielectric constant of salts-CH_3OH complex decreases (due to unlike inorganic-organic molecules); hence dissociation of salts decreases and complex formation also decreases and only one complex is formed with KCl and KBr at 85% and 90% methanol respectively. But with lithium chloride, as the atomic size of lithium is very small, inter-molecular attraction between LiCl and H_2O is powerful as both are alike, inorganic—like molecules and becomes weak as the concentration of methanol is increased, becaused concentration of H_2O molecules decreases and LiCl being surrounded by CH_3OH molecules through bond, dielectric constant of LiCl-CH_3OH complex decreases (due to unlike inorganic-organic molecules), hence dissociation of LiCl decreases and complex formation also decreases after 70% methanol gradually and at 90% methanol two complexes were observed.

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