Asian Journal of Chemistry Vol. 10, No. 1 (1998), 195–197

NOTE

Variation in Complex Ions Formation with Aqueous Methanol Phase Change in Lead Nitrate-Alkali Nitrate System

RAKESH FARASRAM† P.L. FARASRAM* and C.M. DESAI‡
Chemistry Department
J.P. Arts and Science College, Bharuch-392 002, India

Effect of increase and decrease of dielectric constant on the formation of complex ions in lead nitrate-alkali nitrate in aqueous methanol system was studied and and it was observed that when methanol concentration was increased in the system, the dielectric constant decreased and hence complex ions formation also decreased. When some organic liquids such as nitrobenzene, chlorobenzene and chloroform were added to the system in 60% methanol, the dielectic constant increases and hence the formation of complex ions also increases.

In the previous paper we have adduced evidence for the existence of three complex ions in aqueous phase in lead nitrate-alkali nitrate system using novel dye indicator method[1, 2]; however, these complex ions were unstable. In this communication same lead system studied in aqueous methanol replacing aqueous phase. Effect of gradual change of concentration of methanol was studied on the number of complexes. It was observed that as the concentration of methanol gradually increased upto 60%, the number of complexes decreased from three to one and no complex observed at 65% in case of potassium, sodium and ammonium nitrate with lead nitrate, but with lithium nitrate only one complex was observed. However, when organic liquids such as nitrobenzene, chlorobenzene or chloroform were added to 60% methanol the number of complexes was observed to increase again from one to three in case of potassium, sodium and ammonium nitrate with lead nitrate.

Lead nitrate and alkali nitrate M/100 and M/1000 concentration solution respectively and dye crystal violet (cationic) 5×10^{-5} M concentration solution were prepared in aqueous methanol (40, 50, 55, 60 and 65% methanol). Using monovariation method, different sets of solutions were prepared by increasing lead nitrate concentration and alkali nitrate-dye crystal violet concentration being kept constant.

*P.L. Farasram, 866, Muktinagar, G.H.B., Bharuch-392 001.
†Jr. Lab. Tech, Gujarat Narmada Valley Fertilizers Co. Ltd., Narmadanagar- 392 015, Dist. Bharuch, India.
‡Artemis Research Centre, Themis Chemicals Ltd., Vapi, India.

A Shimadzu double beam spectrophotometer UV-160A was used for spectral measurements.

Absorbance of pure dye solution at λ_{max} was taken as standard and absorbance at λ_{max} in each set of solutions were measured and plotted against increasing lead nitrate concentration; the graphs indicate peaks corresponding to the ratio of concentration of two salts in stoichiometric proportion for the system. The complexation ratio and formula of the complexes are tabulated in Table-1 and Table-2.

TABLE-1

Solvent	Number of peaks with KNO_3, $NaNO_3$, NH_4NO_3	Number of peaks with $LiNO_3$
40% Methanol	3 (1 : 4, 1 : 2, 1 : 1)	3 (1 : 4, 1 : 2, 1 : 1)
50% Methanol	3 (1 : 4, 1 : 2, 1 : 1)	3 (1 : 4, 1 : 2, 1 : 1)
55% Methanol	3 (1 : 4, 1 : 2, 1 : 1)	3 (1 : 4, 1 : 2, 1 : 1)
60% Methanol	1 (1 : 1)	3 (1 : 4, 1 : 2, 1 : 1)
65% Methanol	No peaks	1 (1 : 1)
2%Nitrobenzene in 60% Methanol	3 (1 : 4, 1 : 2, 1 : 1)	
1% Chlorobenzene in 60% Methanol	3 (1 : 4, 1 : 2, 1 : 1)	
2% Chloroform in 60% Methanol	3 (1 : 4, 1 : 2, 1 : 1)	

TABLE-2

Mole ratio	Molecular formula of complexes
1 : 4	$Pb(NO_3)_2 + 4KNO_3 = K_4[Pb(NO_3)_6]$
1 : 2	$Pb(NO_3)_2 + 2KNO_3 = K_2[Pb(NO_3)_4]$
1 : 1	$Pb(NO_3)_2 + KNO_3 = K[Pb(NO_3)_3]$

In lead system[1-5], the complexes formed in aqueous phase between lead nitrate and alkali nitrate were in the ratio of 1 : 1, 1 : 2 and 1 : 4, but when the system's aqueous phase mixed with methanol and studied it was observed that as the concentration of methanol increased in aqueous phase gradully to 60%, the number of complexes decrease from three to one with potassium, sodium and ammonium nitrate; this is because dielectric constant of the aqueous methanol decreases[6-9] with increase of methanol in aqueous phase, decreasing the dissociation of complex ions and also discouraging anionic ion dissociation. This behaviour of aqueous methanol system can be visualised in the light of change of water structure in presence of methanol. So when methanol is added to water the highly polar structure of water is destroyed progressively thus the hydrogen bonding between the adjacent water molecules will be replaced by hydrogen bonding with methanol and structure of water will be largely broken[7].

To 60% methanol set of solution in lead nitrate system, 2% nitrobenzene, 1% chlorobenzene or 2% chloroform added and the system was studied, it was observed that the number of complexes formed increased from one to three. This can be explained on the basis that the dielectric constant of 60% methanol mixed with the above three organic liquids, might have been increased and it is evident from the experiment results (Table-3).

TABLE-3

Solvent	Experimental Dielectric constant at 30°C
60% Methanol	53.98
60% Methanol + 2% Nitrobenzene	55.24
60% Methanol + 1% Chlorobenzene	57.89
60% Methanol + 2% Chlorofrom	57.16

To 60% methanol set of solution when nitrobenzene, chlorobenzene or chloroform is added, the hydrogen bonding takes place between hydrogen of methanol and highly polar oxygen of nitrobenzene or chlorine of chlorobenzene and hydrogen of chloroform and oxygen of methanol. Due to this some of the water molecules become free from hydrogen bonding with methanol; hence the dielectric constant of the solution increases and the number of complex formation increases.

In lead nitrate system three complexes were formed up to 55% methanol, but after that at 60% methanol, lead nitrate and potassium nitrate, sodium nitrate and ammonium nitrate dissociation decreases so complex formation also decreases and only one complex was formed. But with lithium nitrate as the atomic size of lithium is very small three complexes were formed up to 60% methanol and at 65% methanol, dissociation of lithium nitrate decreases and only one complex was formed.

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(*Received*: 4 August 1997; *Accepted*: 22 September 1997) AJC-1359