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Dye Indicator Absorbance Spectra and Complex Ions Formation in Solution

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

The absorbance of a series of mixed dye, lead nitrate and alkali nitrates solutions, dye concentration and one salt concentration constant and increasing the concentration of the other salt, has been measured. The absorbance at λ_{max} against the other salt concentration shows peaks corresponding to complex ion formations between the salts; this can be explained on the basis of Frank-Condon principle.

INTRODUCTION

Critical micelle concentration (CMC) of surfactants using dye indicators has been measured by means of spectral absorbance of a series of mixtures of dye-surfactant solutions at λ_{max} of the dye, surfactant concentration increasing and dye concentration constant[1]. Surfactants behave as electrolytes in dilute solutions and CMC is a transition from ionic micelles to neutral colloid and again charged colloidal particles, CMC being indicated by a sharp peak in absorbance-concentration curve. The chemical potential of the system goes on decreasing with increasing surfactant concentration reaching minimum at CMC, consequently showing increase in absorbance-concetration curve reaching a peak followed by its decrease.

Hence, this characteristic abrupt change in absorbance was desirable to investigate complex ions formation in known systems of lead and alkali nitrates and mercuric and alkali halide in aqueous solutions; dye should not react with metal ions.

The nature of such complex ions is unstable as shown by Nayar and coworkers[2] using a number of physico-chemical properties, showing breaks or peaks in curves obtained by plotting such physical property changes against concentrations of the variant in mixed salts by monovariation method. The complex compound formed in water between lead and alkali nitrates are in the ratio of 1 : 1, 1 : 2 and 1 : 4, lithium nitrate is not complexing. They have also studied mercuric and alkali halide system using some physico-chemical properties and indicated formation of six complexes[3]

Kazi and Desai[4] have studied by monovariation method the above system using interfacial tension method and showed three complexes for the lead system, whereas seven complexes for mercuric system; however, they have indicated that the number of complexes decrease from seven to six to three with increasing salt

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*Address for correspondence: P.L. Farasram, 866, Muktinagar, G.H.B. Bharuch-392 001, India

†Jr. Lab. Technician, Gujarat Narmada Valley Fertilizers Co Ltd, Narmadanagar-392 015, India.

‡Chemistry Department, South Gujarat University, Surat-395 007, India.

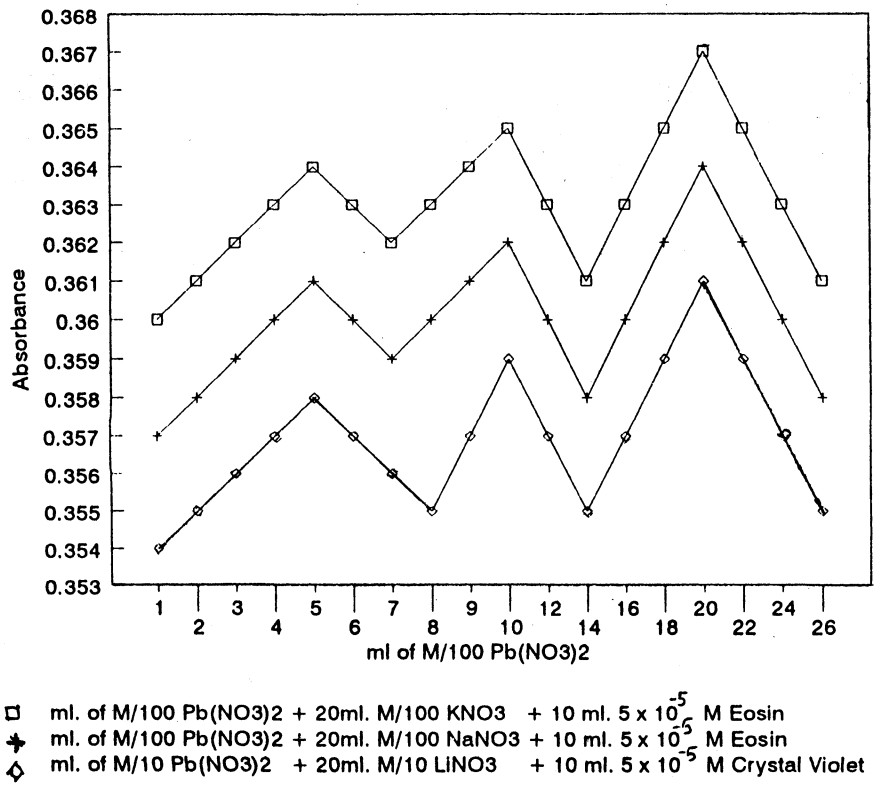
concentrations. The interfacial tension-concentration curve peak corresponding to complex ion formation has been explained on the basis that when interfacial tension increases reaching peak value with increasing mixed salt concentration of the variant, chemical potential value becomes minimum and *vice-versa.*

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 case of dye-salts system, while measuring absorbance with increasing salt concentration of the variant keeping the concentration of the other salt constant, using monovariation method, dye concentration being constant.

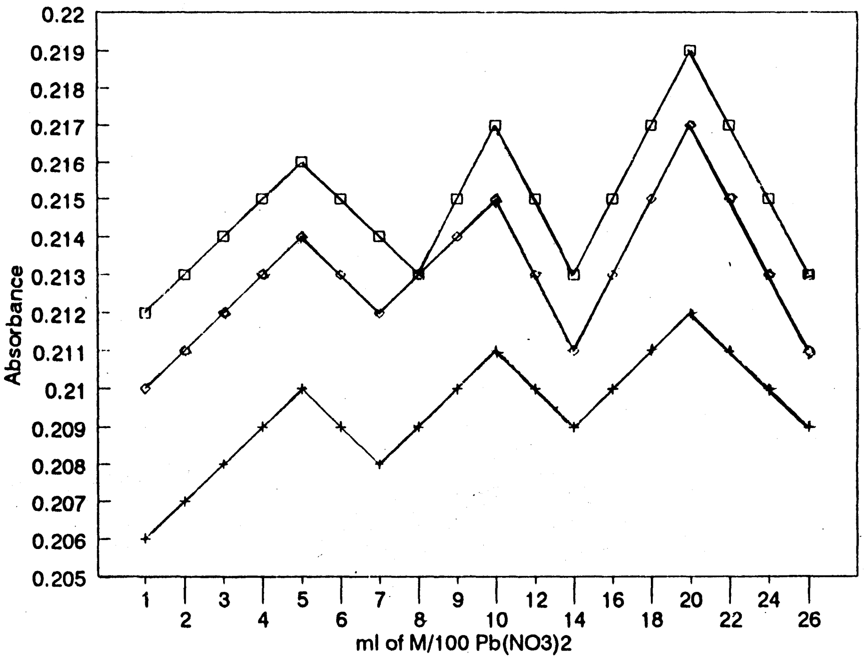
RESULTS AND DISCUSSION

When such absorbance is plotted against increasing salt concentration of the variant, the graphs indicate peaks corresponding to ratios 1 : 4, 1 : 2, 1 : 1 in graphs I and II, alkali nitrate concentration constant and ratios 1 : 1, 1 : 2, 1 : 4 in graph III, lead nitrate concentration constant. The absorbance peaks observed are in the order K > Na > Li or degree of electron transitions order is K > Na > Li; because the atomic size is in the order K > Na > Li, so the electrostatic order is Li > Na > K.

For the mercuric halide system the same procedure was observed using



GRAPH—I



□ ml. of M/100 $Pb(NO_3)_2$ + 20ml. M/100 KNO_3 + 10 ml. 1×10^{-4} M Methyl Orange

+ ml. of M/100 $Pb(NO_3)_2$ + 20ml. M/100 $NaNO_3$ + 10 ml. 1×10^{-4} M Methyl Orange

◇ ml. of M/100 $Pb(NO_3)_2$ + 20ml. M/100 NH_4NO_3 + 10 ml. 1×10^{-4} M Methyl Orange

GRAPH—II

monovariation method, dye concentration constant. The graphs IV and V indicate six peaks in the following order,potassium halide concentration constant.

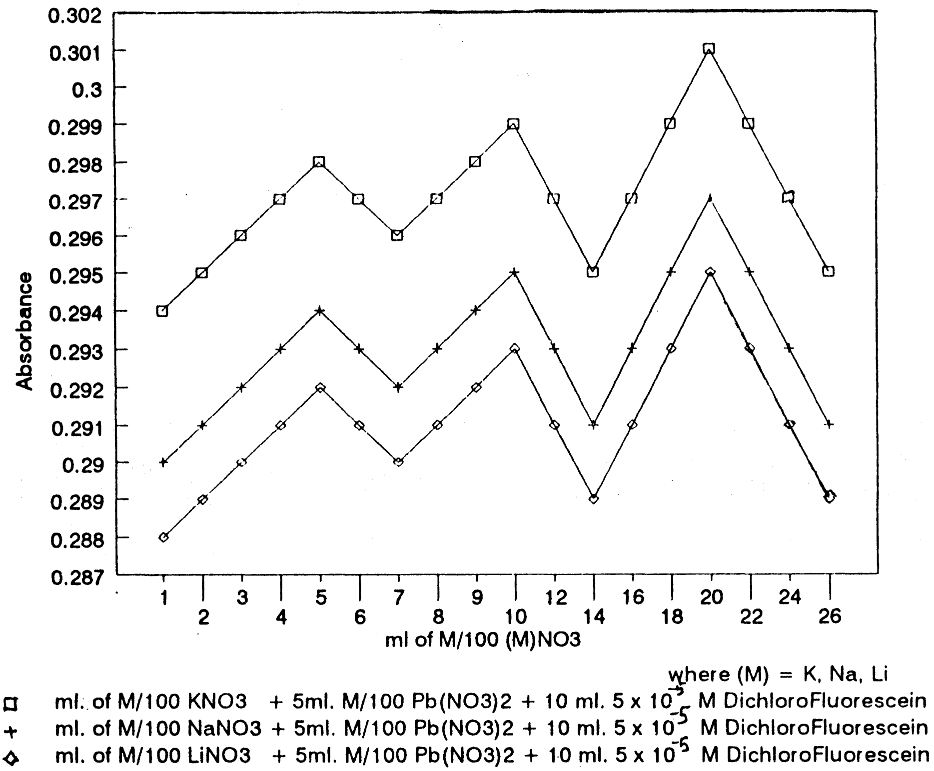
1 : 4 $HgX_2 \cdot 4KX$	$K_4[HgX_6]$
1 : 2 $HgX_2 \cdot 2KX$	$K_2[HgX_4]$
1 : 3 $2HgX_2.3KX$	$K_3[Hg_2X_7]$
1 : 1 $HgX_2.KX$	$K[HgX_3]$
3 : 2 $3HgX_2.2KX$	$K_2[Hg_3X_8]$
2 : 1 $2HgX_2.2KX$	$K[Hg_2X_5]$

This optical property of suddens rapid absorbance of light during complex ion formation and dissociation when electron transition occurs from equilibrium to non-equilibrium state may be correlated to chemical potential changes as well as Frank-Condon principle.

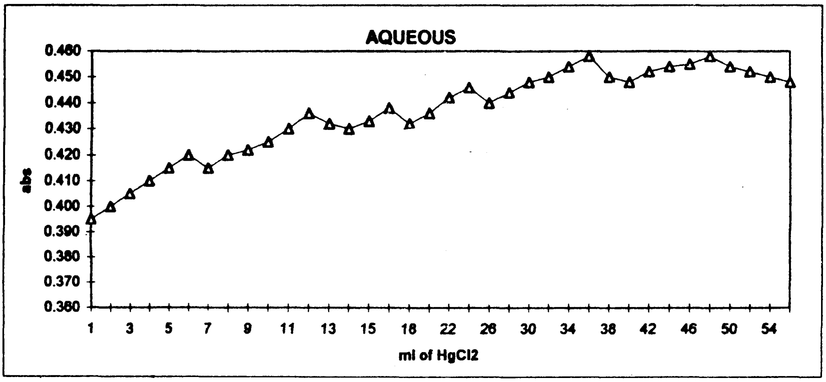
EXPERIMENTAL

A Shimadzu double beam spectrophotometer UV-160 A was used for spectral measurements. Salts used were of AR grade and purifed; dyes used as indicators were cationic crystal violet, anionic-eosin and methyl orange and nonionic 2,4-dichloro fluorescein.

Further work is in progress in aqueous phase mixed with organic liquids.

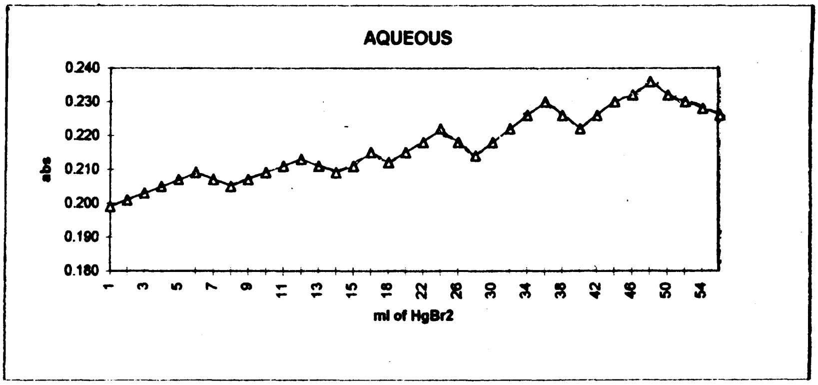


GRAPH—III



M/100 HgCl2 (1 TO 56 ml) + M/100 KCl (24 ml) + 5 x 10 ^ - 5 M CRYSTAL VIOLET (١٠ مل)

GRAPH—IV



M/100 HgBr2 (1 TO 56 mL) + M/100 KBr (24 ml) + 5 x 10 ^ -5 M CRYSTAL VIOLET (10 ml)

GRAPH—V

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