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RESEARCH ARTICLE

IRON CHELATES OF 1, (O-ARSONOPHENYL AZO) -Z- NAPHTHOL -3,6 - DISULPHONIC ACID [FE^{2+} APANS COMPLEXES]

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ABSTRACT

1(O-Arsonophenylazo)-2- naphthol - 3,6 - disulphonic acid (APANS, H_5A), an excellent agent due to presence of five electron donating functional groups, have been found to form complexes with various metal ions. It is used in determining the composition and the stability constants of a number of complexes formed under a limited p^H range using spectrophotometric methods. In the present investigation. a detailed study on the chelation reactions of APANS and pair of ligands, APANS-en and APANS-mpn with transition metal ion, fe2 has been carried out at 20^0 (r=0.10m KNO_3/Na_2SO_4) employing the p^H - metric method. From the experimental data p^H Vs volume of alkali crrves were plotted and were utilized to calculate moles of alkali used per mole of ligand (d). Further, p^H vs d, curves were platted and analysed.

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INTRODUCTION

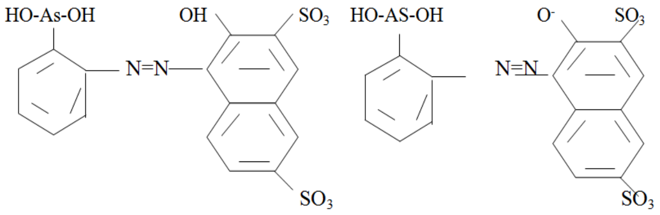
1-(O-Arsonophenylazo) -3,6- disulphonic Acid (APANS, H_2a) IN AN interesting compound of the diarylazo group of dyes which was first synthesized by kuznetsov and was used by him as a colorometric reagent. The ligand, an excellent complexing agent due to presence of five electron donating functional groups, have been found to form complexes with various metal ions. It is used in determing the composition and the stability constants of a number of complexes formed under a limited p^H range using spectro photometric methods. (3-4)

APANS Complexes

In detailed study on the chelation reaetions of APANS and pair of ligands, APANS on and APANS - Mpn with transition metal ion like - Fe^{2+} have been carried out at 20^0 (le= 0.10 M KNO_3/Na_2SO_4) employing the p^H- metric titration. From the experimental data, p^H -metric titration. From the experimental data, p^H vs volume of alkali curves were plotted and were utilized to calculate moles of alkali used per more of ligand (a) further, p^H vs a curve were plotted and analysed. Colour of the 1:1, metal - APANS Mixture gradually turns red, and the p^H vs a curves shows the formation of MH_2A species at the initial stage. But in the absence of a values below 1=1, the equilibrium constant for the reaction could not be obtained.

Proton ligand dissociation constants

APANS solution, in absence of metal ions remains orange through the titration. The p^H vs d curve for the ligand shows steep inflection at d=1, and the maximum value of a under the experimental condition of p^H is 2.0 this corresponds step wise dissociation of protons from the phenolic and one hydronyl group as shown below –



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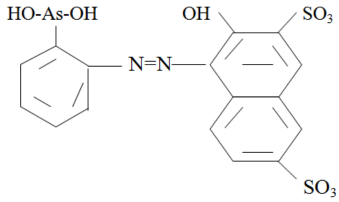
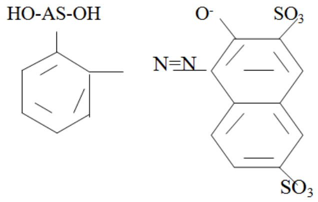




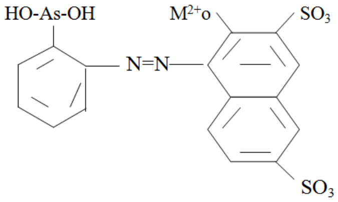
The second hydroxyproton remain associated with the ligand under the experimental condition afhus proton dissociation contents for equilibria were calculated as –

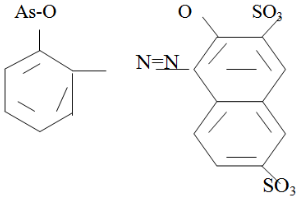
$$H_3A = H_2A + H^+ ,K^H, = \frac{(H_2A)(H^+)}{(H_3A)}$$

$$H_2A = HA + H^+,K_2^4 = \frac{(HA)(H^+)}{(H_2A)}$$

Structure

A structural change i.e. coordination through phenolic oxygen azo group, one hydrony group bound to As can be expected in the formation of MHA between d=1 and 2 where shifting of electron denisty from OH to coordinated natal ion through as would be favoured leading to dissociations of Proton from MHA between d = 2 & 3.





P^H vs d curves of 1:1:1, metal - APANS - Mp^n mixture and mpon, APANS and their binary complexes show the fomation of mixed ligand species MH_2AB at the initial p^H of titration. p^H vs a curves of APANS, en and mpn systems : complexes of Fe^{++} (20^0 r=0.10 MNa_2 SO_4).

Species concentration

P^H	Fl2+ APANS (1:1)			Fl2++ APANS - Mpn (11:1:1)	
	PMH_2A	PMHA	P^{MA}	PMH_2AB	$P^{MH}AB$
4.2	3.3207	4.7009			
4.6	3.3600	4.2248			
5.0	3.4241	3.9247			
5.4	3.6176	3.6525			
5.8	3.7880	3.4309			
6.0	3.9050	3.4309		3.3279	4.5238
6.2	4.0760	3.3874		3.3665	4.1549
6.4	4.1178	3.3625		3.3979	3.9900
6.6		4.3072	3.3532	3.4437	3.8539
6.8		3.8928	3.4385	3.5157	3.7099
7.2		3.7641	3.5690	3.5034	3.6108
8.0		3.3795	4.1329	3.9788	3.4034
8.6				4.6989	3.3187

The p^H vs d curves of the ligands, their binary and ternary complexes shows that both the ligands are attached simulatneously with the metal ion. But, nature of the p^H vs d curve is quite similar to those of mn^{++} APANS system and thus deprotonation of the protonated species can be expected involving the similar structural changes between 1 = 1 and 2. Concentrations of various species in 1:1, cl APANS and 1:1:1, Fe 2+ APANS - Mpn mixtures (20^0 u=0.1 M NO_2SO_4)

RESULT AND DISCUSSION

Concentration of the species MH_2AB, H_2A, B, M (between d=0 and 1) were calculated Beyond d=1, the following equilibria were also considered to exist:

(i)betweeen a = 1 and 2.

$$MB+HA = MBHA \quad K = \frac{(MBHA)}{(MB)(HA)}$$

$$MH_2AB = MHAB+H^+ \quad K = \frac{[MHAB](H^+)}{[MH_2AB]}$$

ii) between d = 2 and 3

$$MB+HA = MBA+H^+$$

$$K = \frac{[MBA](H^+)}{[MB](HA)}$$

$$MHAB = MBA + H^+$$

$$K = \frac{(MBA)(H^+)}{MHAB}$$

Concentration of the species corresponding to equilibria were obtained like those of binary metal - APANS system with help of K value of the reaction $MB+H_2A = MBH_2A$ the calculated equilibrium constants for Fe^{2+} complexes were equilibrium constants of Fe^{2+} - APANS complexes.
(20^0, u=0.10 M KNO_3)

Reaction	log K
$FeH_2A^- = Fe\ HA^{2-} + H^+$	-5.151+ 0.03
$FeHA^{2-} = FeA^{3-} +H^P$	-7.25+ 0.02
$FeBH_2A^- = FeBHA^{2-} +H^+$	-7.15+0.08

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