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Studies on Diazo Type Process. VI. Physico-chemical Studies on 1-(*p*-Dimethylaminophenylazo)-2-naphthol-3,6-disulfonic Acid in Aqueous Solutions

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1-(*p*-Dimethylaminophenylazo)-2-naphthol-3,6-disulfonic acid is formed in many important commercial "dry process" diazo-printing. Some physico-chemical properties of this dye in solutions have been investigated. Its absorption spectra in various solvents and in water at various acidities have been discussed on the basis of azo-quinone hydrazone tautomeric and acid-base equilibria respectively. The dissociation constants of the acid-base equilibria in the pH range of 1—14 in aqueous solutions have been determined at 25 °C and 1.0 M ionic strength. Conductivities of aqueous solutions at various concentrations and temperatures have been interpreted on the basis of the colloidal nature of the dye. The polarograms of the compound have been drawn at various pH's and discussed. Polarographic method indicates complex formation between Zn(II) salt and the dye in the mole ratio of 1:2.

The authors are presently engaged in the study of the physico-chemical properties of azo dyes formed in "diazo-printing" processes. *p*-Dimethylaminobenzenediazonium chloride and 2-naphthol-3,6-disulfonic acid (R-acid) are very commonly used in many commercial "two-component" diazo papers as the photosensitive "diazo" and "coupler" components respectively for "dry process" printing.1) The present paper reports the behaviour in aqueous solutions of the important azo dye formed by reaction between the above two components.

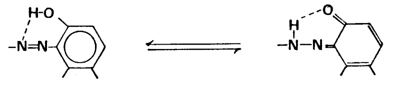
Experimental

Materials. *p*-Dimethylaminobenzenediazonium salt was prepared from the corresponding amine (analytical grade), precipitated as fluoroborate and then coupled with R-acid. The dye so prepared was recrystallized from water and stored in the absence of light. The other materials used were of analytical grade.

Methods. A Shimadzu (Model UV-180) spectrophotometer was used for absorbancy measurements. Conductance measurements were taken with a Yokokawa Denki universal bridge in conjunction with a Kikusui Denshi-Kogyo (Model 537) oscilloscope. A TOA Electronics Ltd. pH-meter (digital type, Model HM 20B) was used for pH measurement. Polarographic measurements were taken with a recording polarograph (Yanagimoto, Model PG-5). The DC current-voltage curves were obtained by measuring against saturated calomel electrode. Nitrogen gas was bubbled through the solution for 20—25 min immediately before measurement to remove dissolved oxygen. 0.02% gelatin was used as "suppressor," without which good polarographic waves were not obtained. The capillary characteristics of the dropping mercury electrode were $m=1.116$ mg s^{-1} and $\tau=3.49$ s at a mercury head of 74 cm. 1M solution of potassium nitrate was used as the supporting electrolyte.

Results and Discussion

Tautomerism. Azo dyes with a hydroxyl group located ortho- or para- to azo link are well known to exhibit azophenol-quinone hydrazone tautomerism.2) This has been the subject of study of many workers3—18) by various physico-chemical means *e.g.* IR, UV-Vis and NMR spectroscopies. Most of the works have been done in nonaqueous solvents or in the solid state and the tautomerism of the present compound has not been studied. It was thought necessary to study in greater detail the extent of tautomerism of the compound in aqueous solution.



Azo form　Quinone hydrazone form

(A)

The absorption spectrum of the dye has been drawn in different polar and nonpolar solvents and shown in Fig. 1. In nonaqueous solvents, the dye derived from *β*-naphthol in stead of R-acid was used because the presence of sulfonate groups in R-acid makes the dye insoluble in nonaqueous solvents. The presence of $-SO_3H$ group is irrelevant in spectral analysis. Two characteristic features of the spectrum are (a) a band, usually appearing as a shoulder, at ≈430 nm and (b) a strong band at ≈500 nm whose shape and position are markedly dependent upon the solvent. The two bands at ≈430 and ≈500 nm can be unequivo-

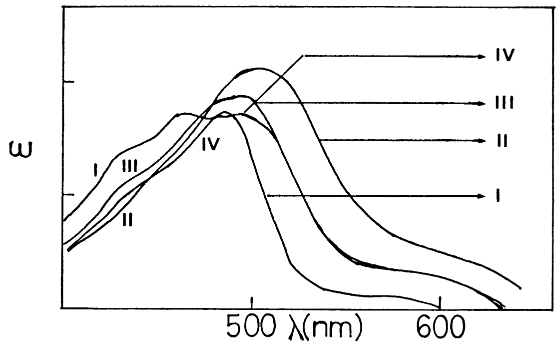


Fig. 1. Absorption spectrum of 1-(*p*-dimethylamino-phenylazo)-2-naphthol in different solvents. I: Hexane, II: formamide, III: methanol, IV: chloroform. Molar absorptivity coefficents are arbitrary.

cally assigned to azo and quinone hydrazone forms respectively.[5,6,10,13,14] The band due to the hydrazone form is a split one which is clearly observed in non-polar solvents. The split bands coalesce and move to higher wavelength region in more polar solvents due to greater solute-solvent interaction. Similar splittting of bands have been observed at low temperatures.[7] It is clear that the polarity of the solvent has a greater influence on the shape and position of the spectrum of the quinone hydrazone tautomer which has a more polar structure of the two forms. As observed in the figure, the proportion of the quinone hydrazone form increases with the increase of the polarity of the solvent.[7,12] For the purpose of quantitative interpretation, the following ratio proposed by Ospenon[9] may be used,

$$\varepsilon_{\text{quin}}/\varepsilon_{\text{azo}} + \varepsilon_{\text{quin}},$$

where ε_{azo} and $\varepsilon_{\text{quin}}$ are molar absorptivity of the azo and quinone hydrazone bands respectively, deduced from Gaussian analysis of the spectra. Table 1 gives the value of this ratio for different solvents. In water, this ratio is 0.80 which corresponds to 80% of the quinone hydrazone form in the tautomeric mixture, if the molar absorptivity of both the forms are nearly equal. This very high proportion of the quinone hydrazone form in aqueous solution of the dye may be ascribed to (i) strong polar nature of the solvent favoring more polar quinone hydrazone form[7,12] and (ii) intramolecular hydrogen bond between the hydroxyl oxygen** and the azo nitrogen atoms facilitating hydrogen transfer fom O- to N-atom,[12] which more than compensate the opposite influence of the highly electron donating $-N(CH_3)_2$ group.[15]

TABLE 1. PROPORTION OF AZO TAUTOMER PRESENT IN DIFFERENT SOLVENTS

Solvent	Hexane	Chloroform	Methanol	Water	Formamide
% Azo	33.3	24.5	23.8	20.5	17.9

The color of the dye in aqueous solutions is markedly dependent upon the pH of the solution as can be seen in Fig. 2. In highly acidic solutions (pH<1.5) the color is yellow-orange. At intermediate (7—9) and high (>12.0) pH's, the colors are violet and red respectively. The spectra of the dye at different pH's pass through clear isobestic points characteristic of equilibria (not shown in the figure). The following acid-base equilibria are obviously operative in aqueous solution.

$$\begin{tikzcd} RH_2^- \arrow[r, shift left, "K_1"] & RH^{2-} + H_3O^+ \arrow[l, shift left, "H_2O"] \arrow[d, shift left, "H_2O"] \\ & R^{3-} + H_3O^+ \arrow[u, shift left, "K_2"] \end{tikzcd}$$

Identification of the species, RH_2^-, RH^{2-} and R^{3-}, responsible for different colors, is clearly necessary.

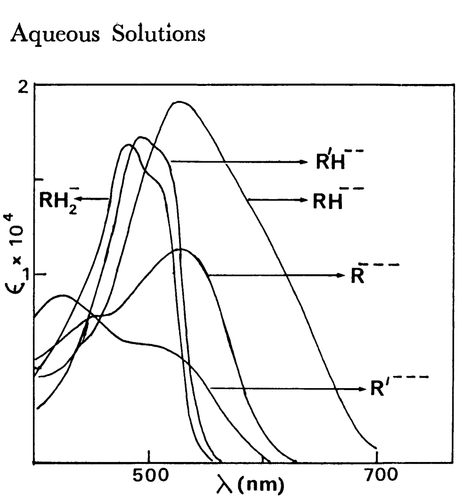
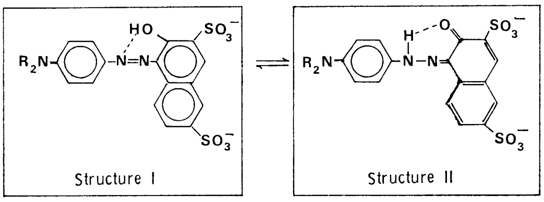


Fig. 2. Absorption spectra of different species of 1-phenylazo-2-naphthol-3,6-disulfonic acid and 1-(*p*-dimethylaminophenylazo)-2-naphthol-3,6-disulfonic acid in aqueous solutions. RH_2^-: Structure VI, RH^{2-}: structure II, R^{3-}: structure III, $R'H^{2-}$: structure VI without *p*-NR_2 group. R'^{3-}: structure III without *p*-NR_2 group.

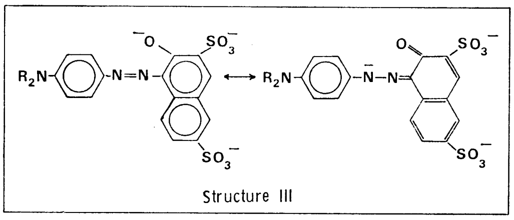
In neutral medium the dye (RH^{2-}) may have structures I and/or II.



(B)

The aforesaid discussion has clearly indicated that RH^{2-} predominantly exists in sturcture II.

In highly alkaline medium (pH>12) where the phenolic group is completely dissociated (R^{---}),*** the compound exists as structure III. The azo and quinone hydrazone structures are the different canonical forms of structure III.



(C)

The spectrum of R^{3-} contains clear bands at ≈420 and ≈520 nm.

In acidic medium (pH<1.5), the species RH_2^-, may be formed by protonation of the N-atom of the tertiary amino group or the O-atom of the phenolic group.[19] Protonation of the amino group of the azo form causes the possibility of resonance between ammonium (structure IV) and azonium (structure V) forms, the azonium form being stabilized by reson-

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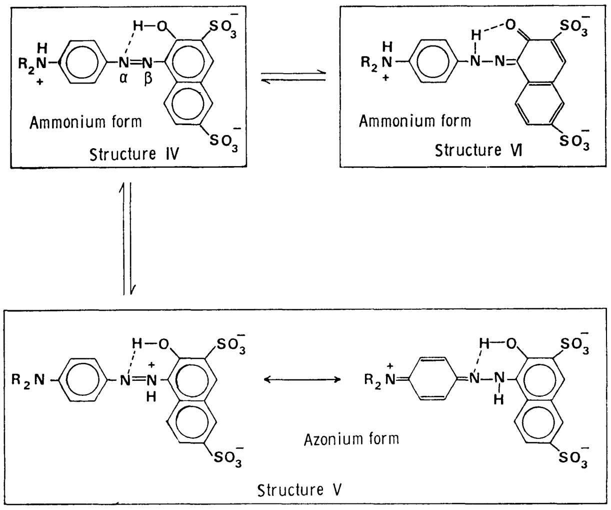
** The term hydroxyl oxygen is used in keeping with the general practice, although in this compound it is actually a quinonic oxygen.

*** Strictly speaking, the hydrogen belongs to the N-atom in the quinone hydrazone structure.

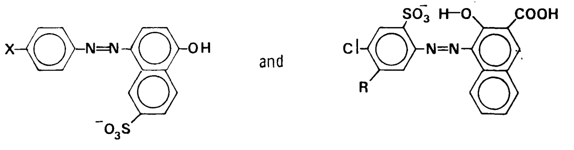
ance as shown.[20,21] Suggestion that proton could be bonded preferentially to the α-azo nitrogen in the protonated structure[22] is too untenable from theoretical argument and spectroscopic evidence[20,23] to warrant detailed discussion.



(D)

The possible azonium form of the quinone hydrazone structure (VI) lacks the resonance stabilization as in structure V and hence, may not be existing in solution, but the possibility cannot be completely ruled out. A suitable choice of structure for RH_2^- between structures IV, V, and VI can be made by comparison of the spectrum with that of the dye without the $-N(CH_3)_2$ group (1-phenylazo-2-naphthol-3,6-disulfonic acid). Figure 2 also shows the spectrum of 1-phenylazo-2-naphthol-3,6-disulfonic acid. At all pH's below 6.5 (spectrum measured upto pH 0.4) only one spectrum is observed which is similar with that of RH_2^- of the present dye. Similarly at pH's above 12, its spectrum remains unchanged. One may conclude that 1-phenylazo-2-naphthol-3,6-disulfonic acid only exists in two species containing undissociated and dissociated phenolic group (denoted as $R'H^{2-}$ and R'^{3-} respectively) at the pH range studied. The striking similarity of the spectra of RH_2^- and $R'H^{2-}$ is not surprising as it is well known that although aniline and *N*-substituted anilines in neutral solutions absorb at longer wavelengths and have higher intensities than benzene, the absorption characteristics of the anilinium ions are very similar to those of benzene.[24] From this it may be concluded that, in very acidic solutions, the protonation of the present dye takes place at the amino nitrogen atom and structure V is not present in any appreciable amount (this structure is not possible with $R'H^{2-}$) and consequently, RH_2^- probably exists predominantly in the quinone hydrazone from (structure VI). However, at very highly acidic media, there may be possibilities of protonation at other sities, particularly at the phenolic oxygen,[19] which has not been investigated in the present work.

Aggregation. Aggregation of some arylazonaphthols having formulae,† in aqueous solutions have been reported from the non-Beer's law behavior of the solution spectra by Zollinger[25] and Monahan[26,27] *et al.* respectively. This may be due to intermolecular H-bonding through the phenolic or carboxylic hydrogen atom. In the present compound the hydroxyl group, which is present at ortho position, is H-bonded with the azo nitrogen atom (intramolecular H-bonding) and there would be less possibility of intermolecular hydrogen bonding. It is found that Beer's law is followed in dilute aqueous solutions (0.5×10^{-5} to 3×10^{-4} M). But addition of some electrolytes to a concentrated solution of the dye causes precipitation. It was, therefore, thought necessary to check the aggregation by another physical method.



(E)

Whereas the plots of equivalent conductance, Λ ($ohm^{-1}\ cm^2\ g\ equiv^{-1}$) *vs.* $C^{1/2}$ (C=g eqiv dm^{-3})of a pure strong electrolyte follows Debye-Hückel-Onsager theory, the same in the case of a colloidal electrolyte has two conspicuous features: (a) a sudden deviation at low concentrations from theoretical Debye-Hückel-Onsager theory and (b) almost a constant value of Λ, or sometimes a weak minimum, at high concentrations.[28] Similar plot as prescribed for colloidal electrolytes was obtained as can be seen in Fig. 3.

Mushran and Prakash[29] have studied the conductance of several colloidal systems and have found that, in general, the "temperature of zero conductance" of a true electrolyte lies at about −40 °C, whereas in colloidal systems, this temperature ranges between −15 and −35 °C. This has been further verified by Srivastava, Seth, and Dey.[30] Conductances of three solutions of the present dye were determined at different temperatures. The plots of specific conductance, k ($ohm^{-1}\ cm^{-1}$) *vs.* temperature (°C) were linear and are shown in Fig. 4. The extrapolated value of the "temperature of zero conductance" was found to be −23 °C lending further evidence about the colloidal nature.

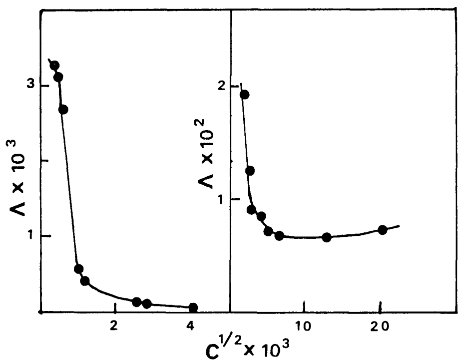


Fig. 3. Variation of equivalent conductance of 1-(*p*-dimethylaminophenylazo)-2-naphthol-3,6-disulfonic acid with square root of equivalent concentration.

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† Only the structure of the azo tautomers are presented.

Table 2. Results of $\mathrm{p}K_1$ and $\mathrm{p}K_2$ of the azo dye at 25 °C and $I=1.0\,\mathrm{M}$

Concn of azo[a] $\times 10^5$		3.019	3.321	3.623	3.925	4.227	2.717	3.623	3.019	
$[\mathrm{H}^+]$[a] $\times 10^5$		8.510	8.700	8.700	12.880	13.800	7.240	5.880	6.910	
580 nm	Abs	0.331	0.351	0.389	0.370	0.383	0.303	0.421	0.337	
	$\mathrm{p}K_1$	3.68	3.72	3.70	3.69	3.71	3.72	3.74	3.74	
620 nm	Abs	0.237	0.252	0.279	0.268	0.279	0.219	0.299	0.240	
	$\mathrm{p}K_1$	3.64	3.68	3.66	3.65	3.66	3.67	3.72	3.71	
Concn of azo[a] $\times 10^5$		1.811	2.415	2.717	3.019	3.623	3.321	3.925	2.113	3.019
$[\mathrm{H}^+]$[a] $\times 10^{11}$		3.890	2.884	3.236	3.548	1.778	2.630	2.570	3.981	1.318
540 nm	Abs	0.299	0.375	0.423	0.482	0.535	0.510	0.599	0.345	0.430
	$\mathrm{p}K_2$	10.63	10.53	10.49	10.54	10.56	10.53	10.52	10.58	10.56
600 nm	Abs	0.154	0.191	0.221	0.260	0.250	0.260	0.310	0.186	0.175
	$\mathrm{p}K_2$	10.53	10.57	10.56	10.59	10.62	10.59	10.61	10.57	10.55

Av $\mathrm{p}K_1=3.69\pm0.03$: Av $\mathrm{p}K_2=10.56\pm0.03$.

The molar absorptivities of different species as determined by separate sets of experiments are $\varepsilon_{\mathrm{RH}^{2-}(580)}=69\pm1$, $\varepsilon_{\mathrm{RH}^{2-}(620)}=0$, $\varepsilon_{\mathrm{RH}^{2-}(540)}=19270\pm120$, $\varepsilon_{\mathrm{RH}^{2-}(580)}=15380\pm98$, $\varepsilon_{\mathrm{RH}^{2-}(600)}=13069\pm98$, $\varepsilon_{\mathrm{RH}^{2-}(620)}=10772\pm82$, $\varepsilon_{\mathrm{R}^{3-}(540)}=11864\pm94$, $\varepsilon_{\mathrm{R}^{3-}(600)}=2367\pm18$

a) mol dm^{-3}.

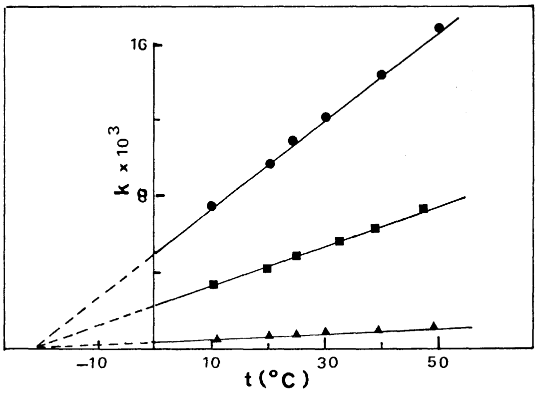

Fig. 4. Variation of specific conductance of 1-(*p*-dimethylaminophenylazo)-2-naphthol-3,6-disulfonic acid with temperature (centigrade).
Concentrations: ● 7.81×10^{-4} M, ■ 3.12×10^{-4} M, and ▲ 0.39×10^{-4} M.

From the foregoing observations one may be tempted to conclude that in the case of the aqueous solutions of the present dye, the dye-dye interaction through hydrogen bonding may not be responsible for the aggregation. More detailed study is necessary to throw light on the cause of aggregation of azo dyes in aqueous solutions.

In view of the colloidal nature of the dye, all equilibrium studies reported in the subsequent part of this paper have been carried out in as dilute solutions as possible.

Dissociation Constants. It was thought useful to determine the dissociation constants of the two dissociation processes existing in aqueous solutions. The following method was followed.

The pH's and absorbances at appropriate wavelengths of a series of solutions were measured. The $\mathrm{p}K_1$ was calculated from the data of solutions at pH's where only $\mathrm{RH_2}^-$ and RH^{2-} exist in equilibrium. Similarly $\mathrm{p}K_2$ was calculated from the data where RH^{2-} and R^{3-} co-exist. The molar absorptivity (ε) of $\mathrm{RH_2}^-$, RH^{2-}, and R^{3-} species at appropriate wavelengths were determined separately by measuring absorbances of the dye solutions at suitable pH's where singular species exist. The method of calculation is shown below.

As a general case, where the following equilibrium is operative,

$$\underset{(1-\alpha)C}{\mathrm{HA}} + \mathrm{H_2O} \rightleftharpoons \mathrm{H_3O^+} + \underset{\alpha C}{\mathrm{A}\cdot}$$

(for convenience the charge on the different species are omitted, α is the degree of dissociation and C is the molar concentration), absorbancy of the solution is given by the equation,

$$A = \varepsilon_{\mathrm{HA}}(1-\alpha)Cl + \varepsilon_{\mathrm{A}}Cl. \tag{1}$$

$\varepsilon_{\mathrm{HA}}$ and ε_{H} are molar absorptivity of HA and A respectively and l is the length of the light path. It follows from Eq. 1 that

$$\alpha C = \frac{A-\varepsilon_{\mathrm{HA}}Cl}{(\varepsilon_{\mathrm{A}}-\varepsilon_{\mathrm{HA}})}. \tag{2}$$

Knowing α, K can be calculated from Eq. 3.

$$K = \frac{[\mathrm{H}^+]\alpha}{1-\alpha}. \tag{3}$$

For the calculation of $\mathrm{p}K_1$, absorbancies at wavelengths 580 and 620 nm were measured. Similarly data at 540 and 600 nm were used for calculation of $\mathrm{p}K_2$. Table 2 gives $\mathrm{p}K_1$ and $\mathrm{p}K_2$ values at 25 °C and 1 M $\mathrm{KNO_3}$ solution. The values are 3.69 ± 0.03 and 10.56 ± 0.03 respectively. The corresponding free energy changes (ΔG) of the first and second dissociation processes are 21.1 and 60.3 kJ mol^{-1} respectively. (1 $J=0.2392$ cal)

Reaction with Metal Salts. It has been reported that the presence of zinc salts during diazo-printing improves the image area and in some cases, the prints can be used as "intermediate prints on a transparent base."[31] Zinc chloride is also often used as "stabilizer" for diazonium salts.[32] It was, therefore, thought useful to study the complexation reaction of the dye with Zn(II). Spectrophotometric method was found unsuitable as it was observed that the absorption spectrum

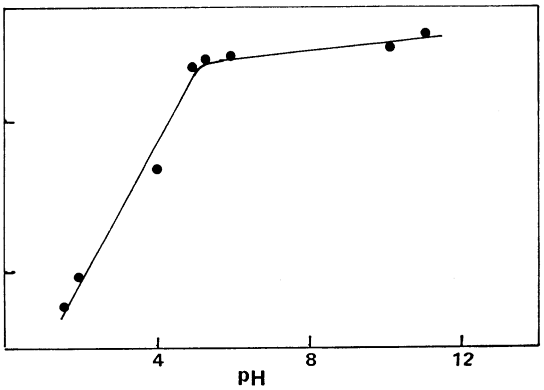

Fig. 5. Variation of half-wave potential of 1-(*p*-dimethylaminophenylazo)-2-naphthol-3,6-disulfonic acid with pH of solution. [azo] = 2.963 × 10^{-4} M.

of the dye is not sufficiently altered in the presence of zinc(II) salts to make any quantitative study possible. Hence, polarographic method was tried.

In the preliminary runs in water, the polarograms of the dye indicated a two electron process reduction as calculated from the famous Heyrovsky-Ilkovic equation,[33]

$$E_{de} = E_{1/2} - \frac{RT}{zF}\log\frac{i}{i_d - i}, \qquad (4)$$

where E_{de} is the potential at the dropping mercury electrode, $E_{1/2}$ is the half-wave potential of the dye in solution, z is the number of electrons involved in the electrode reaction, i_d is the limiting diffusion current, i is the current corresponding to the potential E_{de}, and R, T, and F have their conventional meanings. A plot of the half-wave potential of the dye against pH, as shown in Fig. 5, indicate that $E_{1/2}$ is dependent on pH of the solution. The variation of $E_{1/2}$ with pH is not surprising in view of the fact that the nature of the species existing in solution is also dependent upon the hydrogen ion concentration.

The half-wave potential of zinc nitrate changed to more negative values in the presence of the azo dye, clearly indicating complex-formation between them. The shift of half-wave potential and the overall stability constant (β_n) of the complex, ML_n, formed is related by the following equation,

$$\Delta E_{1/2} = \frac{2.303RT}{zF}\log\beta_n + \frac{2.303RT}{zF}n\log[\mathrm{L}]. \qquad (5)$$

([L] = concentration of the ligand in solution)

Figure 6 shows the plot of $\Delta E_{1/2}$ *vs.* log[L]. The slope of the plot gives $n \approx 2$. Unfortunately, it was not possible to work at high concentrations of the ligand (azo dye) because, at high concentrations, it precipitates in the presence of the zinc salt. For this reason calculation of β_2 was not attempted. Essential condition for the calculation of β is that the concentration of the ligand should be much greater than that of the metal ion.[35] Qualitative conclusion regarding the metal: ligand ratio in the complex can, however, be made from our experimental plots.[36]

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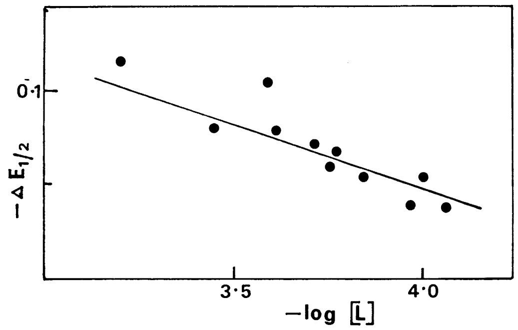

Fig. 6. Change of half-wave potential of zinc nitrate in the presence of the azo dye. Temperature: 25 °C, Medium: 1 M KNO_3, $[Zn^{2+}]$ = 6.803 × 10^{-5} M.

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