The dissociation increases with rise in temperature; but the high negative value of entropy change (Table 1) indicates that it contributes to some extent to the energy associated with the shift of equilibrium towards structure (e). At higher temperature movement of the groups by rotation similar to Berry pseudorotation[6] is surmised to account for faster dissociation at higher temperature.

The enolic OH of phenylindanedione is dissociable and the equilibrium shifts towards the enolic structure (g) suggesting easier dissociation. This accounts for the low value of proton association of the indanedionate ion. The positive entropy value also indicates that the shift of equilibrium, with rise in temperature, is favourable towards the enolic structure (g).

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Stability Constants of Complexes of Some Azo Dyes with Co(II), Ni(II) & Cu(II)

V. P. GUPTA, J. K. STHAPAK* & D. D. SHARMA

Department of Applied Chemistry, Government Engineering College, Jabalpur 482 011

Stability contants of the complexes formed by the dyes 5-(4'-sulphophenylazo)salicylic, 5-(4'-sulphophenylazo)-4-methylsalicylic and 5-(3'-nitro-4'-sulphophenylazo)salicylic acids with Co (II), Ni (II) and Cu (II) have been determined spectrophotometrically. These follow Irving-William's sequence.

AN azo substituent at 5-position in the phenyl ring of salicylic acid, or its substituted derivatives such as 4-methylsalicylic acid, shows strong electron-withdrawing effect greatly affecting the pK_a values of the molecules. Moreover, the resultant azo dyes form metal derivatives the stabilities of which determine the fastness of the dyes towards washing[1]. Hence, it was decided to study the formation constants of the complexes formed by these dyes with Co(II), Ni(II), and Cu(II).

All the chemicals used were of CP grade. The dyes were prepared as follows :

(a) 5-(4'-*Sulphophenylazo*)*salicyclic acid* (*azo-S. A*)— Sulphanilic acid (0.2 mol) was diazotised and coupled with salicyclic acid (0.2 mol) as reported

in the literature[2]. The dye was isolated as its barium salt and was then converted to the acid sodium salt. Yield of the crude product was almost quantitative. It was recrystallised repeatedly, dried over P_2O_5 at 110°C *in vacuo* (Found : N, 7.90; S, 8.75, Calc. for $C_{13}H_9O_6N_2S.Na.H_2O$: N, 7.84; S, 8.82%).

(b) 5-(4',-*Sulphophenylazo*)-4-*methylsalicyclic acid* (4-*methylazo-S.A.*) — Sulphanilic acid (0.2 mol) was diazotised and coupled with m-cresotic acid (0.2 mol) using exactly the same procedure as was followed above (Found : N, 7.52; S, 8.53, Calc. for $C_{14}H_{11}O_6N_2S.Na.H_2O$: N, 7.44, S, 8.51%).

(c) 5-(3'-*Nitro*-4'-*sulphophenylazo*)*salicyclic acid* (3'-*nitro-azo-S.A.*) — To a solution of sodium sulphite (13.1g) in distilled water (40 ml) was added m-dinitrobenzene (43 g) and the mixture heated (90-95°C) until all of it had reacted. Concentrated hydrochloric acid (125 ml) was added, the mixture boiled for 30 min, filtered, the filtrate allowed to cool when 3-nitro-aniline-4-sulphonic acid separated off. It was purified by repeated precipitation with hydrochloric acid from sodium hydroxide solution followed by recrystallisation from water and through washing with methyl alcohol, and dried at 140°C; yield 15 g.

This compound (0.2 mol) was diazotised and coupled with salicyclic acid (0.2 mol) as described above. (Found : N, 10.40, S, 7.82, Calc. for $C_{13}H_8O_8N_3S.Na.H_2O$, N : 10.32, S, 7.86%).

Equivalent weights of all the three compounds were determined by pH titration and were found to be within $\pm 0.50\%$ as against the respective calculated values.

Cu(II), Ni(II) and Co(II) sulphate solutions were prepared and standardised as usual[3]. The ligand solutions were prepared by accurately weighing out calculated quantity of the ligand, adding distilled water and an equivalent quantity of sodium carbonate, boiling, cooling and making upto the required volume in a volumetric flask.

The absorption spectra of the ligands and the complexes in solution were recorded on a Beckman DU grating spectrophotometer. pH values were recorded on a Systronics Digital pH meter. Conductometric measurements were made using Philips, GM-4144 conductance bridge with a dip-type conducticity cell.

Determination of log K^H values of the dyes— These were determined by the usual method[4] photometrically at a wavelength at which there was maximum difference in the absorbances of the ionized and the unionized species.

The sulphonic acid group of the dye was completely ionized in the entire pH range. Its carboxylic group is expected to be almost completely unionised at a pH at least 2 units below its log K_1^H value. From such a solution the molar extinction coefficient of the unionised species, E_1^U, was determined from a series of solutions of varying strengths. The carboxylic group would be completely ionized at a pH of 2-3 units above its log K_1^H value, and from such solutions the molar extinction coefficient of the first ionized species at the same wavelength,

TABLE 1— STABILITY CONSTANT DATA FOR THE AZO DYE COMPLEXES

(Temperature — 25 ± 0.01°C)

Ligand	Log K_{COOH}^H	Log K_{OH}^H	Log K^{CO}	Log K^{Ni}	Log K^{Cu}
Phenol	—	10.00	—	—	—
Salicyclic acid	2.97±0.02 (240 nm; 0.0001M)	13.80	8.09±0.03 (340 nm; 0.032M)	8.17±0.04 (340 nm; 0.33M)	10.67±0.03 (340nm; 0.033M)
3-Nitrosalicyclic acid	1.82±0.02 (440 nm; 0.002M)	10.25±0.02 (550 nm; 0.002M)	5.76±0.04 (440 nm; 0.0035M)	589±0.04 (440 nm.; 0.0037M)	8.44±0.04 (470 nm; 0.0031M)
4-Nitrosalicyclic acid	1.43±0.02 (420 nm; 0.001M)	10.32±0.02 (440 nm; 0.00056M)	5.37±0.04 (430 nm; 0.01M)	5.46±0.04 (430 nm; 0.006M)	7.43±0.04 (430nm; 0.005M)
Azosalicylic acid	2.26±0.02 (400 nm; 0.00008M)	11.26±0.03 (460 nm; 0.00003M)	6.01±0.03 (450nm;+ 0.00155M)	6.23±0.04 (450nm; 0.0006M)	9.11±0.04 (450 nm; 0.0007M)
4-Methylazosalicylic acid	2.45±0.04 (410 nm, 0.0001M)	11.45±0.04 (470 nm; 0.00002M)	5.54±0.06 (460nm; 0.00115M)	6.39±0.06 (460nm; 0.00128)	10.31±0.06 (420nm; 0.00062M)
3'-Nitroazosalicylic acid	2.16±0.03 (410nm; 0.00008M)	11.15±0.03 (510nm; 0.00006M)	6.03±0.02 (460nm; 0.00065M)	6.88±0.04 (460nm; 0.00061M)	10.14±0.04 (460nm; 0.00067M)

E_1^i was determined. Form values of apparent E experimentally obtained at $pH \sim \log K_1^H \pm 1$, the accurate $\log K_1^H$ could be calculated using the equation,

$$\log K_1^H = pH + \log \frac{E_1^i - E}{E - E_1^U} \qquad ..(1a)$$

The species with its carboxylic group completely ionized was treated as the unionized species for the second ionization, that of the phenolic group. The ionisation of the phenolic group was at a sufficiently higher pH so that no interference occurred. The analytical wavelength was chosen from the absorbance spectra; usually it had to be different from the earlier one. At the chosen analytical wavelength. the extinction coefficients of the respective, species E_2^U and E_2^i were determined as before. From the values of apparent E experimentally obtained at $pH \sim \log K_2^H \pm 1$, the accurate $\log K_2^H$ could be calculated using the equation,

$$\log K_2^H = pH + \log \frac{E_2^i - E}{E - E_2^U} \qquad ..(1b)$$

Determination of stability constants of the metal complexes — Stability constants of the complexes of the dyes with metal ions Co²⁺, Ni²⁺ and Cu²⁺ were determined using a computation method very similar to that of Janssen[5]. The absorption spectra of the complexes differ considerably from those of the corresponding azosalicyclic acid dyes. At a suitably chosen wavelength and various pH values, E_L, the molar extinction coefficient of the ligand was determined. The molar extinction coefficient, E_1, of the 1:1 complex was determined by adding as high an excess of the metal ion as possible, to a known concentration of the ligand. The stability constants were then calculated from the noted absorbances of solutions from the relationship,

$$K_1 = \frac{(A - E_L.T_L(E_1 - E_L)F}{\{(E_1 - E_L)T_M + (E_L.T_L - A)\}(E_1.T_L - A)} \qquad ..(2)$$

where A is the absorbance of the solution at equilibrium, T_L and T_M are the total concentrations of the ligand and metal ion, respectively, and,

$$F = C_L / [L] = 1 + K_1^H [H^+]$$

where [L] is the concentration at equilibrium of the free ligand, L, not bound to metal or hydrogen ions and C_L is the total concentration of the ligand not bound in a complex with the metal ion, i.e., $C_L = [L] + [HL] + [H_2L] + \ldots$. Preliminary values of E_1 and K_1 so obtained were subjected to a process of successive approximations to get the correct value of K_1.

Log K_{OH}^H of the azosalicylic dyes — LogK_1^H and log K_2^H values for the dyes are usually attributed to the carboxylic and phenolic groups, respectively (and hence often named as log K_{COOH}^H and log K_H^{OH}) (Table 1). Due to the electron-releasing effect of the methyl group and the electron-withdrawing effec of the nitro group, the highest values are foundint 4-methylazo-S.A. and the lowest in 3'-nitrozao-S.A. Log K_{COOH}^H and log K_{OH}^H values for salicyclic acid itself[4] are 3.0 and 13.8, respectively. The values obtained for the dyes are respectively 2.48 to 2.16 and 11.45 to 11.15, clearly indicating strong electron withdrawing effect of the azo-group, only slightly less strong than that of the nitro group. IR spectra of these dyes show[6] a broad absorption band between ~ 2950 and 2350 cm⁻¹ which indicates the expected hydrogen-bonded structure of these dyes. While the hydrogen-bonding causes electron-withdrawal from the carboxyl group, thus making it more acidic, the phenolic group more tenaciously held by hydrogen-bonding becomes less acidic than that in the parent phenols.

Log K^M values : Log K_1^M values for the Co², Ni²⁺ and Cu²⁺ complexes of the azosalicylate dyes are

given in Table 1. The stabilities followed the expected Irving-William sequence[7] : $Co^{2+} < Ni^{2+} < Cu^{2+}$. No evidence for the formation of any 1 : 2 complex was obtained. Thus, the apparent absorbance of mixture of metal ion solutions loaded with excess of ligand could always be explained as an additive function of the absorbance of 1:1 complex and the free ligand.

To confirm the above, specially for Cu^{2+}, for which a few workers have reported the formation of 1:2 complex, conductance studies by Job's method[8] of continuous variation were undertaken. A definite fairly sharp peak for the formation of only 1 : 1 complex was obtained.

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Spectrophotometric Determination of Aluminium with 2,4-Dihydroxyacetophenone Isonicotinoyl Hydrazone†

G. ABDUL HUQ & S. BRAHMAJI RAO*

Department of Chemistry, Sri Krishnadevaraya University, Anantapur 515 003

Aluminium forms a yellow coloured soluble 1:1 complex with 2,4-dihydroxyacetophenone isonicotinoyl hydrazone (RPINH) at pH 4.5. The system obeys Beer's law over the range 0.1-1.3 µg/ml of Al at 370 nm. The molar absorptivity and Sandell's photometric sensitivity are 2.5×10^4 litre mole^{-1} cm^{-1} and 0.001 µg cm^{-2} respectively. An indirect method for the determination of fluoride in the range 0.3 to 1.3 µg/ml is also proposed.

IT is observed that an ethanolic solution of 2,4-dihydroxyacetophenone isonicotinoyl hydrazone (resacetophenone isoniazid hydrazone, abbreviated as RPINH) is shown to give a yellow colour

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when mixed with a solution of aluminium (0.1 to 1.7 µg/ml) in acetate-phthalate buffer of pH 4.5 showing maximum absorbance in the range 370-400 nm. This colour intensity decreases linearly with the addition of fluoride. Though the yellow colour is developed in the pH range 2-8, the reagent undergoes hydrolysis[1] below pH 4.0 and the colour is not stable beyond pH 6.0. This observation has been made use for the spectrophotometric determination of aluminium and fluoride and the method is described in this note.

A 5-fold molar excess of the reagent is adequate for full colour development. The colour formation is instantaneous and stable for more than 3 hr. Job's continuous variation, molar ratio and slope ratio methods indicated a composition of 1:1 (Al: RPINH) for the complex.

Determination of aluminium — Different aliquots containing 0.1-1.7 µg/ml of Al and 5 ml of buffer (pH 4.5) were taken and to this added an ethanolic solution (2 ml) of RPINH ($2 \times 10^{-3}M$) and the volume made upto 25 ml with the deionised water. The absorbance was read at 370 nm against a reagent blank. A linear calibration curve was obtained in the range 0.1-1.3 µg/ml of Al. With amounts higher than 1.3 µg/ml, the absorbance varied nonlinearly with the amount. The total alcohol content showed no significant effect on the absorbance values. The molar absorptivity and Sandell's photometric sensitivity with respect to the metal ion are 2.5×10^4 litre mol^{-1} cm^{-1} and 0.001 µg, cm^{-2} respectively.

Effect of foreign ions — The following ions whose amounts are indicated in the parenthesis in µg/ml do not interfere in the estimation of 0.65 µg. Al/ml. K$^+$ (390), Na$^+$ (460), NH$_4^+$ (90), Co^{2+} (12), Cu^{2+} (13), Mn^{2+} (11), Ni^{2+} (12), Zn^{2+} (1500); Th^{4+}(23), Ce^{4+}(2), Cl$^-$ (500), NO$_3^-$ (310), SO$_4^{2-}$ (1500).

Uranyl(II), iron(III), zirconium(IV), titanium(IV), vanadium(V) and chromium(VI) interfere by giving a turbidity. Oxalate, citrate and tartrate interfere even when present in small amounts.

Determination of fluoride — The indirect photometric determination of fluoride based on the above colour reaction is as follows :

Ammonium alum ($2.0 \times 10^{-4}M$; 2 ml) solution, buffer solution (pH 4.5, 5 ml) and an ethanolic solution of RPINH ($2 \times 10^{-3}M$, 1 ml) were taken in different 25 ml standard flasks. Different aliquots (0.3-1.9 µg/ml) of fluoride were added and the contents made upto the mark. The absorbance of each of the solution was read at 370 nm against the reagent blank. A linear plot was obtained between the measured absorbance and the amount of fluoride (0.3-1.3 µg/ml).

The procedure described above was repeated with the solution containing the fluoride to be determined. The absorbance read at 370 nm was used to compute the amount of fluoride from the pre-determined linear calibration curve.