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Medium Effect On The Ionisation Constants of 1-and 3-Hydroxy–2–Naphthoic Acids.

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SUMMARY

The ionisation constants of 1–and 3–hydroxynaphthoic acids are determined potentiometrically in presence of some organic solvents at 25°C ± 0.2. The effect of solvent polarity on pK values is discussed.

The results are discussed in relation to medium effect. The ionisation constants were found to depend mainly on the dielectric constant of the medium. The pK values were calculated in pure aqueous medium.

INTRODUCTION

1– hydroxy–2–naphthoic acid (I) and 3–hydroxy–2–naphthoic acid (II) are used as dye intermediates for the production of several azo dyes. Molyaga(1) studied the relation between structure and antitubecular activity of some arylazo derivatives of (I). A high antitubecular activity depending on the substituent was observed. Beryllium and copper were determined potentiometrically using (I) and (II)(2). Kreshkof(3) determined some naphthoic acid derivatives alone or in binary mixtures in methanol-isopropanol (1:2) by spectrophotometric titration using sodium methylate as titrant. 1– and 3– hydroxy–2–naphthoic acids were determined potentiometrically by titration with KOH in non aqueous solvents(4). Iron (III) and U (VI) were determined spectrophotometrically at pH 2.5 and 4.6. respectively using (I) as reagent(5,6). Iron (III) and Al were determined with EDTA and (II) as reagent(7).

Since the formation of metal complexes with (I) and (II) occurs through proton displacement from the COOH or OH groups depending on the nature of the metal ion, it is of interest to determine the ionisation constants of these compounds in various media containing organic solvents. This arises from the fact that such compounds are not soluble in water.

The present investigation is a systematic study for the potentiometric determination of the dissociation constants of (I) and (II) in different media containing organic solvent to throw more insight on the factors affecting such ionisations.

EXPERIMENTAL

Stock 0.001 M solutions of (I) and (II) were prepared by dissolving the accurate weight in the requisite amount of solvent. The solvents used were methanol, ethanol, acetone, ethylmethylketone and dioxane 0.1 M aqueous solutions of HCl and NaOH were prepared and standardized as recommended(8) 1 M KCl solution was used to control the ionic strength at u = 0.1. The organic solvents were either pure or purified as described(9).

The titration mixtures were prepared as follows A) 5 ml 1 M KCl + 3 ml 0.1 M HCl + X ml organic solvent to attain the requisite percent + distilled water up to 50 ml. B) 5 ml 1 M KCl + 3 ml 0.1 M HCl + 10 ml 0.001 M (I) or (II) + organic solvent (X–10) ml + distilled water up to 50 ml.

The design of the titration cell was such that it allowed nitrogen to be passed through the solution and enabled measurements to be carried out in an atmosphere of nitrogen. The titration cell was thermostated at 25°C ± 0.2 . The titration curves were obtained by the aid of a digital corning pH meter 113 accurate to 0.01 pH unit. The pH meter readings in the organic solvent -water mixture were corrected according to Bates(10,11).

Representative titration curves for (I) in methanol are shown in Fig. (1).

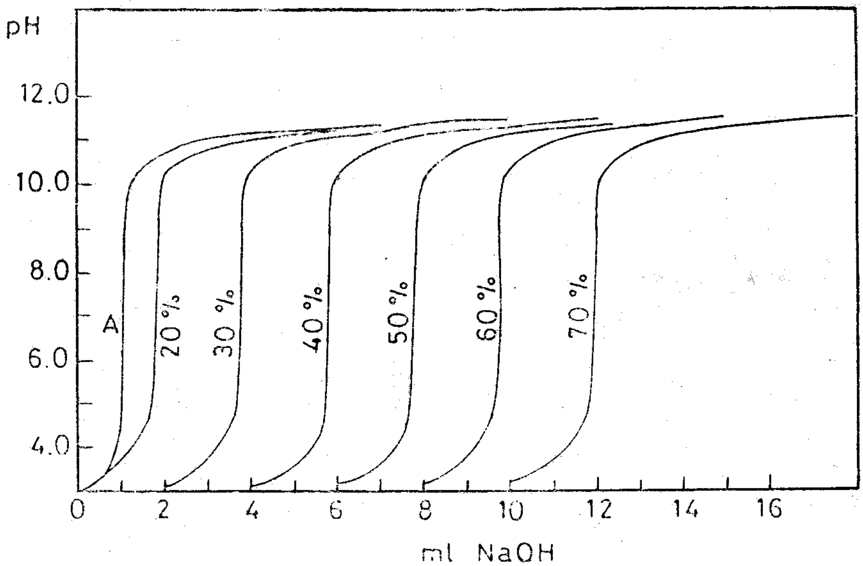

Fig. (1): Titration curves of I against NaOH in methanol-water mixtures. (curves start at 0 ml NaOH, A: free acid)

RESULTS AND DISCUSSION

The proton-ligand formation curves were obtained by plotting the $\bar{n}_A$ values ($\bar{n}_A$ = number of attached protons to the ligand) aganist pH Fig (2) and then applying various computational methods $^{(12-13)}$. The values of $\bar{n}_A$ at various pH values have been calculated from the acid and ligand titration curves (mixtures A and B, respectively). The following equation was applied:

$$\bar{n}_A = Y + \frac{(V^- - V^=)\,(N + E^\circ)}{(V + V^-)\,T^\circ_{CL}}$$

Where V^- and $V^=$ denote the volume of alkali to reach the same pH in the titration of acid and ligand respectively; T°_{CL} is the total concentration of the ligand, Y the total number of replacable protons attached to the ligand, N the normality of the alkali and E° the initial concentration of the free acid

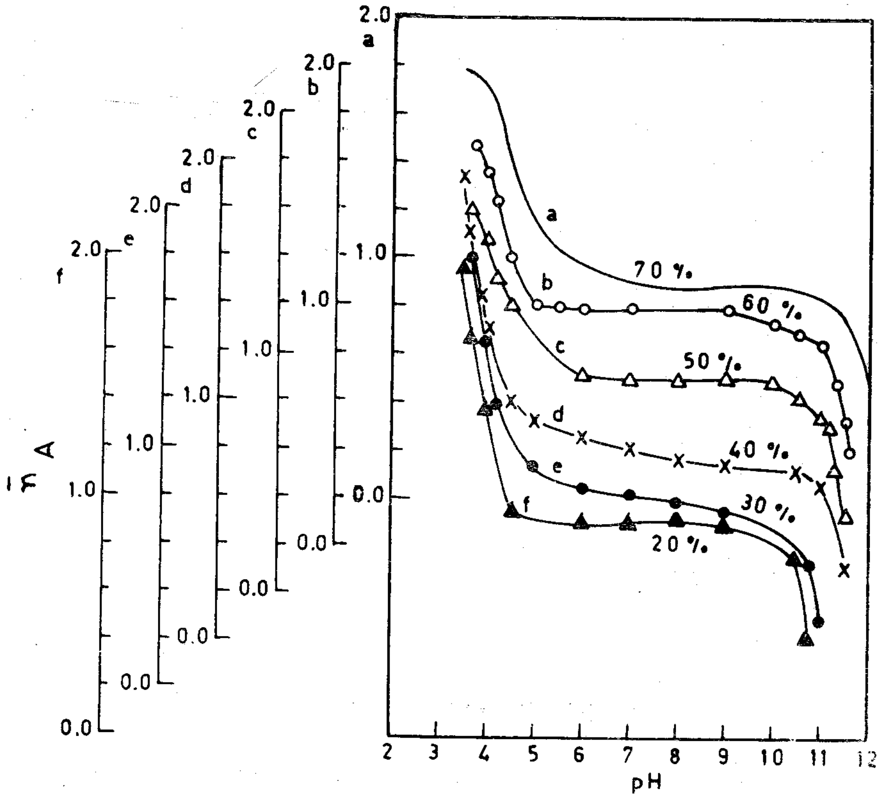

Fig. (2): Proton formation curves of I in acetone-water mixtures.

The values of pKa_1, pKa_2 and 1/D where D is the dielectric constant of the medium are shown in table 1. These data indicate that the pK values increase with increasing the percentage of organic solvent.

For a particular percent of solvent (60 % v/v). The values of 1/D decrease in the following order Dioxane > acetone > ethylmethylketone > Ethanol > Methanol

Table (1)

Ionisation constants of naphthoic acids in different media

solvent	%	$\frac{1}{D}$	I		II	
			pKa_1	pKa_2	pKa_1	pKa_2
Methanol	20	0.01432	4.06	10.62	4.12	10.62
	30	0.01541	4.15	10.82	4.25	10.82
	40	0.01665	4.05	10.93	4.05	10.92
	50	0.01809	4.05	11.02	3.95	11.03
	60	0.01977	4.15	11.32	4.00	11.30
	70	0.02175	4.22	11.42	4.10	11.50
Ethanol	20	0.01455	3.79	11.23	3.79	11.19
	30	0.01630	4.09	11.45	3.95	11.43
	40	0.01739	4.27	11.64	4.05	11.65
	50	0.01926	4.33	11.74	4.30	11.84
	60	0.02157	4.43	12.02	4.42	12.02
	70	0.02450	4.65	12.22	4.55	12.22
Acetone	20	0.01462	3.85	1.58	3.21	10.80
	30	0.01591	3.89	10.83	3.41	11.11
	40	0.01754	3.83	11.29	3.55	11.40
	50	0.01956	3.94	11.31	3.58	11.58
	60	0.02214	4.11	11.51	3.68	11.80
	70	0.02555	4.38	11.92	4.05	12.18
Ethylmethylketone	20	0.01449	4.42	11.55	3.84	11.55
	30	0.01579	4.44	11.64	4.15	11.60
	40	0.01741	5.01	11.68	4.59	11.71
	50	0.01945	5.10	11.72	4.76	11.80
	60	0.02212	5.56	11.86	5.42	11.94
	70	0.02576	6.02	11.96	6.31	12.07
Dioxane	20	0.03444	3.66	11.10	3.12	11.29
	30	0.04882	3.76	11.15	3.30	11.33
	40	0.06653	3.85	11.44	3.54	11.56
	50	0.08885	4.05	11.63	3.80	11.76
	60	0.11789	4.44	12.33	4.38	12.30
	70	0.15719	4.70	12.56	4.61	12.56

While the pKa values for the same v / v composition follow the sequence: Ethylmethylketone > Ethanol > Dioxane > Methanol > Acetone, for pKa_1 and Dioxane > Ethanol > Ethylmethylketone > Acetone > Methanol for pKa_2.

This indicates that the sequence does not follow the order of dielectric constants of the media.

In a mixed aqueous solvent the proton ligand formation constant may be influenced by different solvent characteristics. Three effects can be taken into consideration.

1– Dielectric constant of the mixed solvent,

2– Decrease in hydrogen bonding in water by organic solvent

3– Protonation of the organic solvent.

The variation of pK with dielectric constant (D) in solvent mixtures is given by the relation(14).

$$pK_a = pK_o + \frac{(0.43)}{RT} \frac{Z_1 Z_2}{r_1 r_2} \left(\frac{1}{D} \right)$$

were pK_a and pK_0 are the acid dissociation constants in the solvent mixture and in pure water, respectively, Z_1 and Z_2 are the charges carried by the ions in equilibrium and r_1 and r_2 are the radii of the ions. From this equation it is evident that if the dielectric constant of the medium is the predominant factor affecting the change of pK values with solvent concentration, the plot of pK_a aganist $1 / D$ must be linear.

On addition of organic solvent to water, the tetrahedral lattice(15) structure of water is gradually broken down and owing to the denser packing and smaller extent of hydrogen bonding between water molecules, the stability of hydroxonium ion increases and the proton donating property of the media falls. This may imply that the proton accepting property of the solvent increases. It is also said that the hydrogen bonding structure is less prevalent in pure ethanol in comparison to water and largely absent in pure acetone and pure dioxane. Gergely(16) indicated that the dioxane molecules progressively break down the hydrogen bonded structure of the water. So it is expected that the extent of hydrogen bonding in alcohol-water is greater than that in dioxane-water or acetone-water.

Protonation of the organic solvent: when the proportion of organic solvent becomes sufficiently large in water -organic solvent composition, the proton solvation of the organic solvent molecules takes place. Braude(17) reported that the basicities of the pure solvent molecules decrease in the following order. Water > dioxane > ethanol > acetone.

Thus the proton solvation of pure acetone is minimum. Now the more a solvent accepts proton the more the ligand acid is dissociated and so the pK will tend to decrease.

The foregoing solvent effects influence the pKa_1; pKa_2 for the studied compounds in the following manner: a– with decreasing of the dielectric constant of the solvent used. The pKa values of both compounds (1) and (II) increase, specially in high percentage of solvent. b– increasing proton solvation by organic solvent insreases the pK_a values. This can be proved by calculation of pK_a values in pure aqueous medium by the method of least squares(17). The mean pK_a values and standared deviation are summerized in table (2).

Table (2) : Ionisation constants of naphthoic acids in aqueous medium.

	pKa_1	S	pKa_2	S
I	3.82	± 0.08	9.12	± 0.3
II	3.50	± 0.065	9.20	± 0.10

c– The plots of pKa_1 and pKa_2 versus 1 / D Fig. (3) are always linear (except pKa_1 in methanol), this behaviour indicates that the changes in pKa with the organic solvent proportion mainely governed by the dielectric constant are also influenced by solvent basicity and by the solvation of the solute molecule by organic solvent molecules.

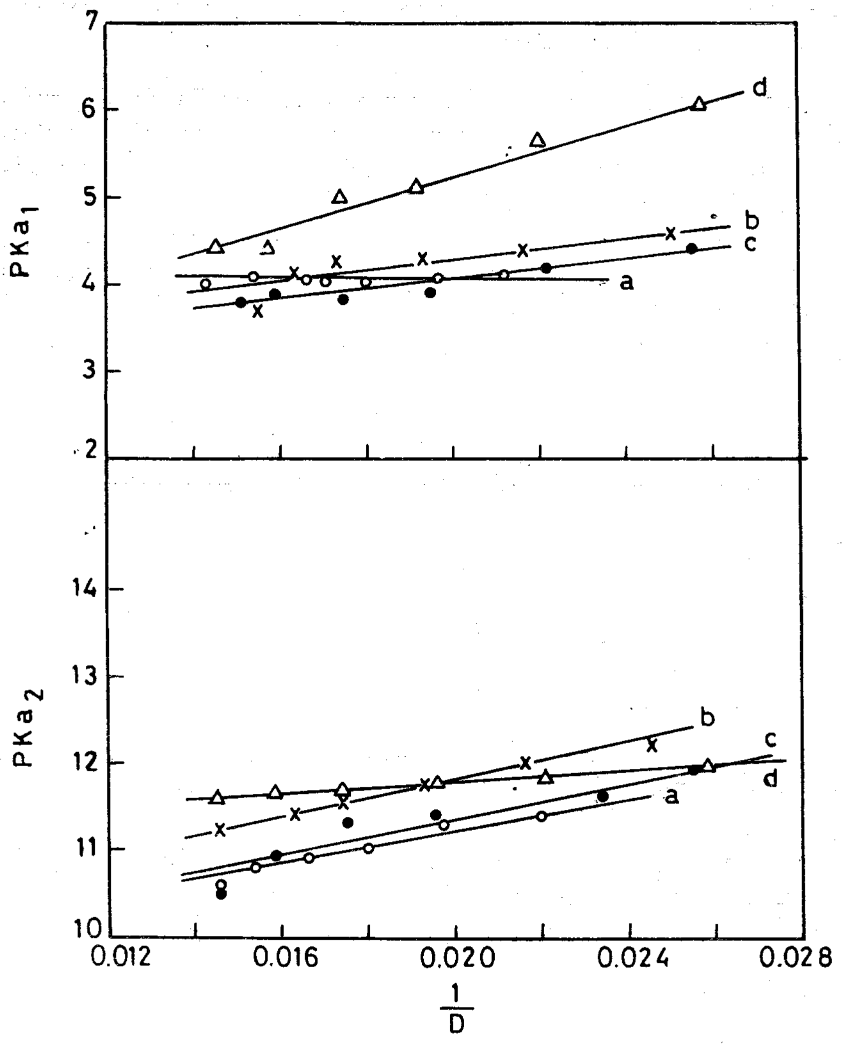

Fig. (3) :The ionisation constants of I against $\frac{1}{D}$

a) Methanol b) Ethanol c) Acetone d) Ethylmethylketone.

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