

**Spectrophotometric Studies on Some
Triphenylformazans. Medium Effect on Their Acid
Dissociation Constants**

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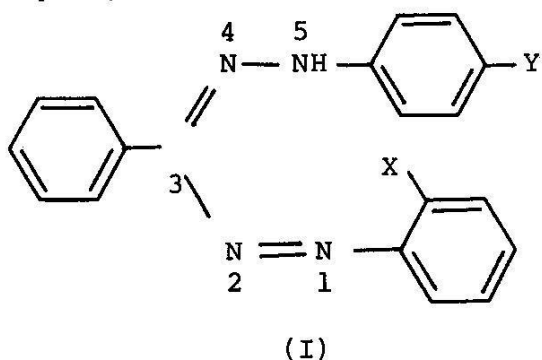
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Summary: The acid dissociation constants of some triphenylformazans are investigated spectrophotometrically. The absorption spectra are recorded in solutions of varying pH-values, the spectra indicate the existence of two equilibria in solutions for (Ia-Ic) and one equilibrium for (Ie and If). The effect of some miscible organic solvents on the ionization constant of (Ia) is also investigated and the results are correlated to solvent effect.

Introduction

Formazans are characterized by the chain of atoms N=N-C=N-NH-, such compounds form a distinct class with characteristic properties. Several reports on the use of formazans as analytical reagents have appeared [1-4].

The present investigation deals with the spectrophotometric determination of ionization constants of some 1,3,5-triphenylformazan derivatives (I).



where X, Y = o-As O(OH)₂,
H (Ia), o-AsO(OH)₂, p-Cl (Ib);
o-As O(OH)₂, p-CH₃ (Ic); o-As
O(OH)₂, p-NO₂ (Id); o-CH, H (Id);
o-COOH, H (If).

Experimental

The triphenylformazan derivatives were prepared by coupling of the corresponding diazonium salt with an equivalent amount of benzaldehyde-phenylhydrazone derivatives dissolved in sodium hydroxide [5,6]. The resulting crudes were crystallized from ethyl alcohol to constant melting point. The purity of the resulting formazans were confirmed by elemental analysis (Table-1).

0.001 M formazan solutions were prepared by dissolving the accurate amount of the acid form in proper volume of ethyl alcohol.

The absorption spectra of 1-(o-arsenophenyl)- and 1-(o-carboxyphenyl)-3,5-diphenylformazan in ethanolic solutions of varying pH values are represented graphically in Fig. (1).

The pH values were checked with the aid of a Beckman Expanded Scale pH-meter. The pH values were corrected for non aqueous media using the relation [7] : pH = pH (R) δ where

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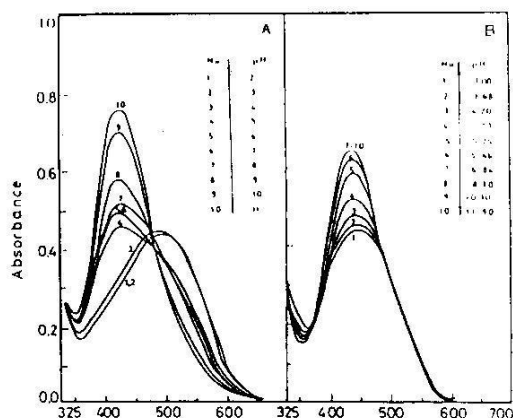


Fig.1: Absorption spectra of 4×10^{-5} M Ia [A] and 3×10^{-5} M If [B] in 40% ethanolic solutions of varying pH values.

pH (R) is the pH-meter reading. The δ values were obtained from the data given by Bates and Robinson [8].

The absorption spectra were recorded using a Beckman DK-2A spectrophotometer.

Results and Discussion

The spectra in acidic solutions of pH values 2-4.5 are characterized by broad band, absorbing maximally within the range 450-500 nm (Table-1). This band is due to absorption of the nonionized form liable to exist in such solution. This band is attributed to $\pi - \pi^*$ electronic transition within the azo linkage [9], influenced by charge migration through the whole molecule.

For compounds containing *o*-arsonic group (Ia-Id), the successive increase of pH values of the medium, leads this band to exhibit a slight decrease in absorbance meanwhile the maximum absorbance is shifted to shorter wavelength, until a certain pH values (4-5) where it attains a constant minimum value, this decrease in absorbance is

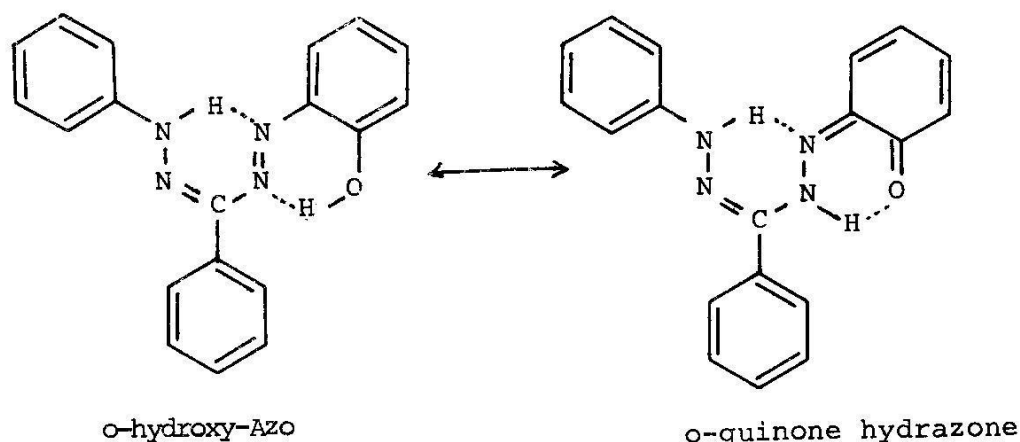
due to the ionization of the first proton of the arsonic group. On further increase of pH the absorbance increases again until it attains a limiting values at pH 12.0-12.5, also the maximum absorbance is further shifted to shorter wavelength (Table-1). This increase in absorbance is due to the ionization of the second proton of the arsonic group. A vast change in absorbance is observed within the pH range 9.00-10.50.

In case of compound (If) containing *o*-COOH group the absorbance values increase by increasing the pH values, also the maximum absorbance is slightly shifted to shorter wavelength (Table-1). These changes are attributed to the ionization of the COOH group. After pH 7.0 the absorption spectra are the same indicating the complete transfer of the compound to the anionic species i.e. complete ionization of COOH group and no further changes takes place in the molecule.

For compound (Ie) containing *o*-OH group the spectra display two overlapping bands, the first at 500 nm while the second appearing as a shoulder at 537 nm. No variation of absorbance was observed within the pH range 2.0-9.5 after which the absorbance of the first band decreases and the shoulder is shifted towards longer wavelength (λ_{\max} at pH 11.55 = 562 nm) acquiring a limiting absorbance value at pH 11.5-12.5. The existence of two overlapping bands in this compound may be attributed to the participation of the *o*-hydroxy azo-*o*-quinone hydrazone tautomerism [10].

The variation of absorbance within the pH range 9.0-12.0 is attributed to the ionization of OH group.

The spectra of triphenylformazans under investigation are characterized by the existence of the common



isosbestic points indicating the existence of an equilibrium in solutions mainly the acid-base one. The positions of the isosbestic points are listed in Table-1. Deviation from the isosbestic point is observed in compounds (Ia, Ib and Ic) this may be attributed to the presence of a second equilibrium.

Due to the limited solubility of the compounds under investigation, the studies were carried out in solutions containing 40% ethyl alcohol-water mixtures for (Ia), (Ib), (Ic), (Id) and (If) and 60% for (Ie).

The absorbance - pH curves for (Ia), (Ib), (Ic) and (Id) Fig. (2) manifest two steps, the first step is due to the ionization of the first proton of the arsonic group while the second step is due to the second ionization of the arsonic group. In compounds (Ie) and (If) containing o-OH or o-COOH group, one step curves were obtained. The variation of absorbance with change of pH is utilized for the calculation of the ionization constant using previously recommended methods [11] i.e. half height and limiting logarithmic methods.

In previous investigations [12], it was pointed out that, the ionization of acidic groups (-COOH, AsO(OH)₂

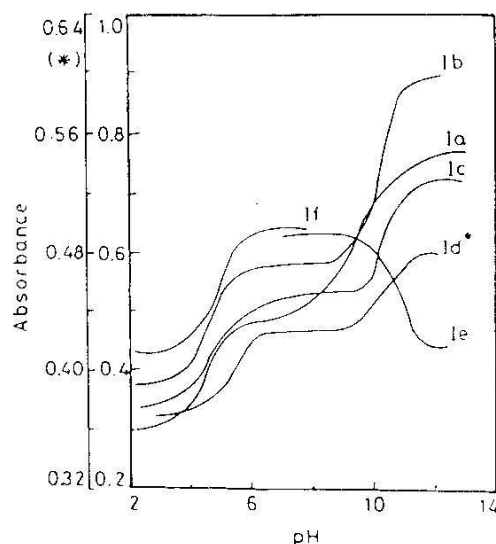


Fig. 2: Absorbance - pH curves of 4×10^{-5} M Ia (420 nm), 4×10^{-5} M Ib (440 nm), 3×10^{-5} M Ic (420 nm), 2×10^{-5} M Id (490 nm) and 3×10^{-5} M If (435 nm) in 40% and 4×10^{-5} M Ie (500 nm) in 60% ethanolic solutions.

or SO₃H) which are not directly attached to the π -resonating system in the molecule do not affect the absorption spectra. However, the ionization of groups which are participating in the π -system will cause spectral changes on ionization.

The unsubstituted triphenylformazan shows no spectral variation with

Table-1: Melting point, elemental analysis and the absorption characteristic of 1,3,5-triphenylformazan derivatives.

Formazans	MP °C Literature (found)	C	H Calculated (found)	N	Cl	Acidic (pH=3)	λ_{max} nm neutral (pH=7)	Alkaline (pH=11)	Isobestic point
Ia $C_{19}H_{17}N_4O_3As$	(163-164)	53.79 (53.11)	4.04 (4.04)	13.21 (13.15)		490 400 sh.	420	420	475 345
Ib $C_{19}H_{16}N_4O_3AsCl$	(183-184)	49.75 (50.32)	3.52 (4.32)	12.21 (11.70)	7.73 (8.21)	500 400 sh.	437	435	485 350
Ic $C_{20}H_{19}N_4O_3As$	(177-178)	54.81 (55.46)	4.37 (4.63)	12.78 (12.14)		350 420 sh.	420	425	485 355
Id $C_{19}H_{16}N_5O_3As$	(179-180)	48.63 (49.07)	3.44 (4.03)	14.92 (14.26)		500 550 sh. 375 sh.	493 375 sh.	493 375 sh.	537 433 325
Ie $C_{19}H_{16}N_4O$	(164-165) [6]	72.14	5.10	71.17		500 537 sh	500 537 sh	562	550 440
If $C_{20}H_{16}N_4O_2$	(183-184)	69.76 (69.40)	4.68 (5.55)	16.27 (15.76)		445	435	435	490 367

sh. = shoulder

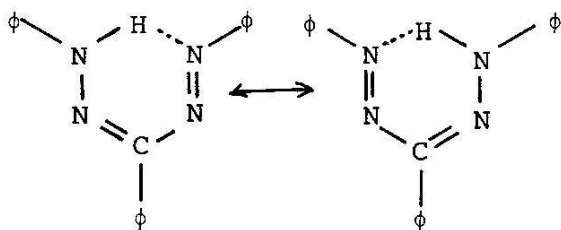
Table-2: pK-values of Triphenylformazan derivatives Ia, Ib, Ic, Id and If in 40% and Ie, in 60% ethyl alcohol-water mixture of varying pH values.

Compound	pK \pm S	
	pK ₁	pK ₂
Ia	4.40 \pm 0.09	9.40 \pm 0.10
Ib	4.67 \pm 0.03	10.10 \pm 0.07
Ic	4.86 \pm 0.09	10.38 \pm 0.10
Id	4.64 \pm 0.07	10.36 \pm 0.09
Ie	10.80 \pm 0.07	-
If	4.87 \pm 0.05	-

S = standard deviation.

change of pH value of the medium indicating that only one species exist in such solutions.

The ionization of the NH group is very difficult and is expected to have a pK value more than 14 [13]. This may be attributed to the contribution of the NH group in the formation of stable hydrogen chelate ring with the participation of the azo-hydrazone tautomerism [14], thus:



For the formazans under investigation the *o*-OH (Ie) derivative is normal in behaviour exhibiting only one ionization corresponding to the OH group with value of 10.80. It is of interest to mention that *o*-COOH derivative display a similar behaviour and

exhibits drastic changes in absorption spectra. Such changes are due to the changes of absorbing species i.e. the π -system of the molecule. This can be understood if we assume that the proton of the carboxylic group is attached to one of the four nitrogen atoms, hence the existence of the ZWITTER ion in solution. The pK value of this compound (If) amounts to 4.87 which can be assigned to nothing but the COOH group.

Compounds containing the arsono group [AsO(OH)₂] exhibit two ionization steps as shown from the absorption spectra in solutions of varying pH values and the absorbance-pH curves (Figs. 1 and 2). The two steps are due probably to the arsonic group with the pK-values in the range 4.40-4.86 and 9.40-10.38. The change in absorption spectra may be explained again by assuming the existence of a ZWITTER ion and the arsenic atom acting as electron conductor or bridge. The substituents on the other phenyl ring exhibit the normal substituent effect point of view with the exception of the unsubstituted derivative. The pK₁-values are in the order (Ia) < (Id) < (Ib) < (Ic) while for the pK₂-values the order is (Ia) < (Ib) < (Id) < (Ic).

Solvent Effect on pK-values of 1-(o-Arsonophenyl)-3,5-diphenylformazan (Ia)

The ionization constants of 1-(*o*-arsonophenyl)-3,5-diphenylformazan (Ia) were investigated in presence of some water miscible organic solvents. The mean values of the results of pK₁ and pK₂ as calculated applying the different methods [11] are listed in table-3. The standard deviations are within the range 0.02-0.10.

In a mixed aqueous solvent the proton-ligand formation constant may be influenced by different solvent

Table-3: Ionization constant values of 1-(0-arsonophenyl)-3,5-diphenylformazan (Ia) in organic solvent-water mixtures.

PK ± S	pK ₁						pK ₂							
	0 ^(*)	40	50	60	70	80	100 ^(*)	0 ^(*)	40	50	60	70	80	100 ^(*)
Methanol	3.60	4.55±0.05	4.82±0.09	5.08±0.02	5.10±0.04	-	5.90	8.60	9.59±0.08	9.91±0.09	10.31±0.05	10.55±0.04	-	11.35
Ethanol	3.65	4.40±0.09	4.99±0.02	5.23±0.04	5.42±0.05	5.73±0.03	6.20	8.15	9.40±0.10	10.00±0.02	10.39±0.03	10.78±0.07	10.80±0.07	11.85
2-Propanol	3.65	5.01±0.03	5.30±0.04	5.62±0.09	5.68±0.07	-	6.90	9.25	10.18±0.02	10.24±0.06	10.56±0.07	10.75±0.05	-	11.40
Ethyleneglycol	3.65	4.08±0.04	4.15±0.07	4.31±0.04	4.24±0.08	-	4.60	8.60	9.07±0.03	9.23±0.04	9.41±0.05	9.48±0.07	-	9.80
Glycerol	3.70	3.97±0.13	4.23±0.07	4.26±0.06	4.20±0.09	-	4.50	8.60	8.87±0.03	9.04±0.03	9.08±0.06	9.08±0.05	9.21±0.03	9.50
Acetone	3.70	4.86±0.03	5.23±0.04	5.55±0.06	5.92±0.07	-	6.75	8.25	9.96±0.06	10.44±0.04	10.73±0.06	11.41±0.08	-	12.60
Dioxan	3.70	4.99±0.04	5.50±0.07	5.72±0.03	6.18±0.05	-	7.15	9.15	10.24±0.05	10.61±0.06	10.74±0.09	11.09±0.10	-	11.90

(*) pK = values in pure solvents and water were obtained by extrapolation of pK - % solvent curves.

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 [15].

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

where pK_a and pK_o are the acid dissociation constants in the solvent mixtures and in pure water, respectively, Z₁ and Z₂ are the charges carried by the ions in equilibrium and r₁ and r₂ 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 against 1/D must be linear.

On addition of organic solvent to water, the tetrahedral lattice [16] 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 dioxan. Gergely [17] indicated that the dioxan molecules progressively break down the hydrogen bonded structure of water. So it is expected that the extent of hydrogen bonding in alcohol water is greater than that in dioxan water or acetone water.

Protonation of the organic solvent; when the proportion of organic solvent becomes sufficiently large in water-organic composition, the proton solvation of the organic solvent molecules takes place. Bradue [16] reported that the basicities of the pure solvent molecule decreases in the following order water > dioxan > ethanol > acetone.

For the results obtained in table-3 one can conclude:

- a. By increasing the amount of solvent, the pK-values increase in a

linear behaviour and thus the pK-values in pure water and solvents were obtained by extrapolation of the straight lines. The results are collected in Table-3.

b. For the same percentage of solvent dioxan shows the heighest pK values.

c. In pure solvents the order for pK₁ is dioxan > 2-propanol > acetone > ethanol > methanol > ethyleneglycol > glycerol, while for pK₂ it is acetone > dioxan > ethanol > 2-propanol > -methanol > ethyleneglycol > glycerol. The order for pK₁ is in harmony with the increase of the dielectric constant.

d. The ionization constant in pure water was obtained by extrapolation, the values are concordant in most cases and deviates only in case of 2-propanol and dioxan with pK₂.

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