PHYSICOCHEMICAL STUDIES OF SOME 2-HYDROXY-4-SULPHONIC-1-NAPHTHALENE-HYDRAZONO DERIVATIVES IN UNIVERSAL BUFFER SOLUTIONS

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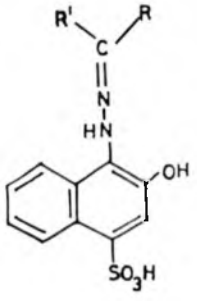
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The uv and visible spectra of some 2-hydroxy-4-sulphonic-1-naphthalenehydrazono derivatives were studied in universal buffer solutions. Evaluation of the dissociation constants of these compounds was carried out by spectral measurements in the universal buffer solutions, as well as, from pH-metric titration. The polarographic behaviour of the studied compounds has also been investigated as a function of pH. All compounds gave a single, well defined irreversible wave at pH-values ranged between 2.0 and 12.0. The half wave potential ($E_{1/2}$) of this wave as well as, its limiting current (i_d) were found to be pH dependent. The mechanism of reduction of these azo dyes over the range of pH's studied was proposed.

The electroreduction of azo compounds was studied by many authers [1-4] and it was found that the mechanism of reduction depends markedly on the pH of solution, as well as, the structure of the depolarizer. An investigation in this directions is attempted using a series of 5 compounds carrying 2-hydroxy-4-sulphonic-1-naphthalenehydrazono derivatives using pH metric, sphectrophotometric and polarographic study under different conditions.

EXPERIMENTAL

The naphthalene azo dyes used in this study were prepared as recommended [5] by coupling the diazonium salt of 2-hydroxy-4-sulphonic-1-aminonaphthalene with different melonates. Five compounds - with diethylmalonate (I_a), ethylacetoacetate (I_b), ethylcyanoacetate (I_c), ethylchloroacetate (I_d) and malononitrile (I_e) - are prepared.



	[R]		[R']
I_a ,	$COOC_2H_5$	;	$COOC_2H_5$
I_b ,	$COOC_2H_5$	;	$COCH_3$
I_c ,	$COOC_2H_5$	;	CN
I_d ,	$COOC_2H_5$	;	Cl
I_e ,	CN	;	CN

The prepared dyes were recrystallized from the appropriate solvent. The structure and the purity of these compounds were confirmed by IR spectra and elemental analysis. The stock solution (10 mM) of the studied compounds were prepared in 50% ethanol water mixture (v/v). The Britton-Robinson buffer solutions were prepared as described earlier [6].

All chemicals used in the present study are of A.R. grade. W.T.W. Degital pH-meter with combined electrode was used for pH-measurements. The pH-metric titrations were carried out in double jacket cell and bubbling oxygen-free nitrogen at 25° C as mentioned previously [7]. Perkin Elmer 550 S recording spectro-photometer was used for the u.v. and visible spectra. Polarograms were recorded on a recording polarograph LP 60a. Purified nitrogen was passed in the polarographic cell for 15 min., for deaeration. The potentials were measured against a saturated calomel electrode (SCE).

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The cell used for coulometric studies was similar to that described by Zuman [8].

RESULTS AND DISCUSSION

pH-Metric Studies

The acid form of 2-OH-4-SO_3H-naphthalene hydrazono derivatives (I_{a-e}) was titrated at constant ionic strength with 0.1M KOH solution. The pH-ml titrant plot exhibits three inflection points, the first of which is sharp whereas the others are weak. These inflections corresponding to neutralization of -SO_3 H, naphthol and hydrazono (-HN-N=C <) groups. The dissociation constants (pK's) are determined as mentioned previously [7] and given in Table 1.

The results show that Compounds I_a and I_f are less acidic with respect to the ionization of -OH and hydrazono-NH-N=C< groups compared with the other three compounds. The replacement of one of the two ethylacetate groups in compound I_a or the acetyl group in I_b by cyano (CN) or chloro (Cl) in compounds I_c and I_d respectively, increases the acidity of these compounds. This is due to the fact that (CN) or (Cl) groups are strong electron withdrawing groups which facililates the deprotonation of -OH group. Compound I_e, containing two cyano groups attached to the hydrazono moeity, was found to be the most acidic compound due to the higher electron attracting properties of the two (CN) groups.

Spectrophotometric Studies

The uv and visible spectra of compounds (I_{a-e}) of constant concentration (0.2 mM) in 10% ethanol-universal buffer solutions (of pH's 2.0-12.0) show regular change which are more or less the same for all compounds. The behaviour of a typical compound 2-OH-4-SO_3H naphthalene hydrazono ethylchloroacetate (I_d) is shown in Fig. 1.

The absorption spectra are characterized by two bands, a strong one with λ_{max} at 325-330 nm and a medium one at λ_{max} 390-393 nm. These bands do not show apparent variation with pH change up to pH 6.0. The first pKa being 3.22, at lower pH values unionized form dominates; at pH above 3.2 the monoanionic form dominates. This behaviour indicates that the ionization of the strong acid group (sulphonic group) does not cause any change in colour or in the absorption spectra [9] because the ionizable centre in the strong -SO_3 H group is not conjugated with the -N=N- centre. However, in-

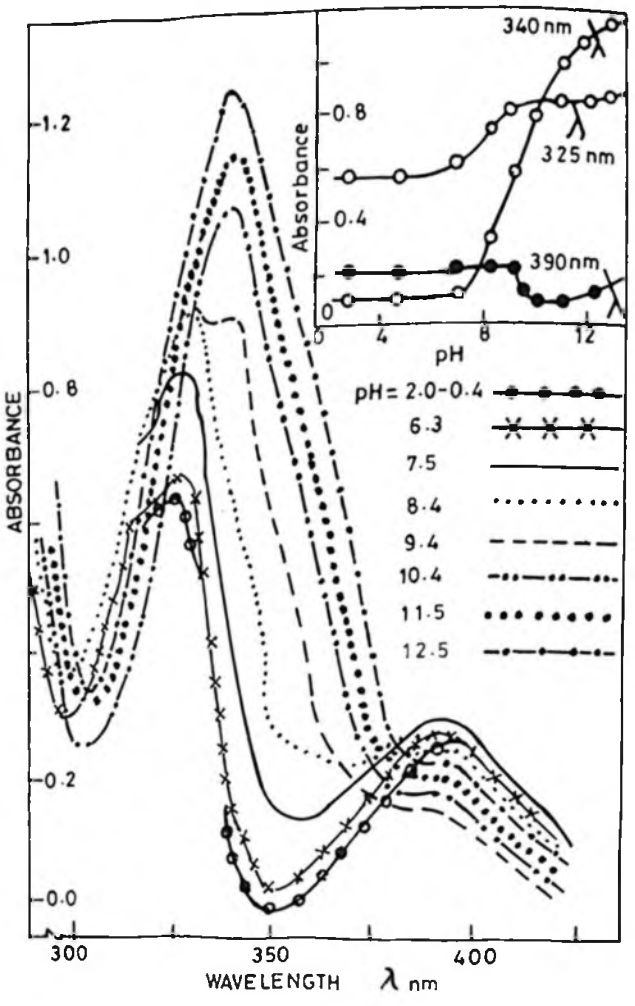


Fig. 1 Effect of pH on the spectra of 2-OH-4-SO_3 H-1-naphthalene hydrazono chloroethylacetate (I_d) in 10% Ethanol universal buffer solution.

creasing the pH of solution (6.0 - 8.0), the absorbance of the strong band (λ_{max} =330 nm), increases and a sharp increase is observed at pH 7.0. The absorbance of this band (λ_{max} = 330 nm) attains a limiting value, while a new band is developed at longer wave lengths (λ_{max}= 340 nm) at pH 9.0 Fig (1a & b). Further increasing pH (10 -12), the absorbance of the new band is markedly increased while the absorbance of the medium band (λ_{max} = 390 nm) increases slowly (Fig. 1). The first increase in absorption within the pH range 6.0 - 8.0 may be due to the ionization of the hydroxyl group of naphthalene ring as suggested by the fact that the value of the dissociation constant of the naphthalinic OH group (pK_2) is 7.8 - 8.5), Table 1. The small increase in absorption of the band at λ_{max} = 390 mm

TABLE-1

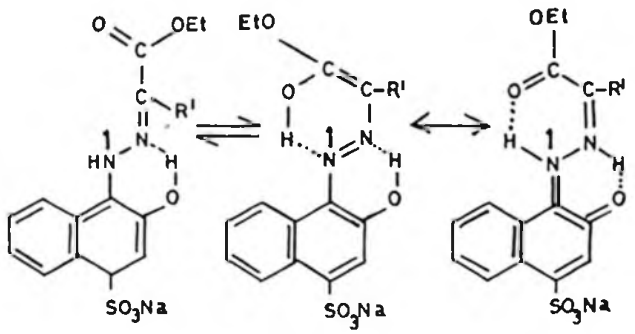
COLLECTIVE DATA OF pK VALUES FOR IONIZATION STEPS AND MAX. ABSORBANCE AT DIFFERENT pH OF COMPOUNDS (I_a - e)

Compound	pK_a	Pot. detn.	Spec. detn		Mean value of	λ_1	λ_2	λ_3
			method I	method II	pK_a	2 - 12	2 - 8.0	10 - 12
I_a	pK_1	3.22	-	-	3.22	390	330	344
	pK_2	8.90	8.75	8.75	8.80			
	pK_3	10.82	11.10	11.30	11.07			
I_b	pK_1	3.09	-	-	3.09	392	325	337
	pK_2	8.86	7.85	8.10	8.29			
	pK_3	10.80	11.05	11.50	11.12			
I_c	pK_1	3.02	-	-	3.02	390	330	345
	pK_2	8.45	7.65	7.50	7.87			
	pK_3	10.40	10.80	10.90	10.70			
I_d	pK_1	3.04	-	-	3.04	393	327	342
	pK_2	8.45	7.50	7.50	7.92			
	pK_3	10.30	11.20	10.80	10.76			
I_e	pk_1	3.02	-	-	3.02	392	329	338
	pK_2	8.24	7.65	7.40	7.76			
	pK_3	10.23	10.30	11.50	10.66			

(which is characteristic of the hydrazono moeity) [10], and also, the marked increase in the absorption of the new band at 340 in the pH(10-12,) may be attributed to the ionization of the hydrazono proton. The dissociation constant of hydrazono proton (pK_3= 10.5-11) supports the presence of a new ionized species at pH ≥ 10.0.

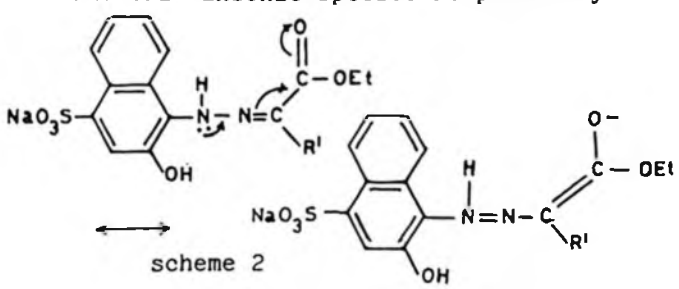
In acidic solution, the primary strong band observed at 330 nm may be ascribed to n-π^* transition of the lone pair of nitrogen atom (N^1) and the π system of naphthalene ring [11]. The resonance of hybrids corresponding to this n-π^* transition may be represented by structures (B) and (C).

Structure (B) accounts for the high values of pK_2 and pK_3 since hydrogen of the naphthoic and enolic OH groups is hydrogen bonded to the two nitrogen of the azo group rendering the ionization of these OH groups difficult; it also accounts for the splitting of the strong band. The medium band may be due to a charge transfer band in the whole molecule from the hydrazono to the aliphatic part scheme 2.



(A) (B) (C)

The spectra of Fig. 1, are characterized by two isobestic points at 315 and 380 nm denoting the set of equilibria between mono-, di- and tri- anionic species respectively:



scheme 2

$H_2B^- \rightleftharpoons HB^{--} + H^+$ (K_2; ionization of naphthyl OH)

$HB^{--} \rightleftharpoons B^{---} + H^+$ (K_3; ionization of hydrazono group

The variation of absorbance (A) with pH of the buffer solutions is used successfully for the determination of the dissociation constants of naphthaol OH (pK_2) and the hydrazono proton (pK_3) for all compounds under investigation applying the following methods:

(i) The half height method [12] for which the pK is equal to the pH at half height of A-pH curve.

(2) The modified limiting absorbance method [12] using the relation:

$$pH = pKa + \log\bar{\gamma} + \log\left(\frac{A - A_{min}}{A_1 - A}\right)$$

The values obtained from the above two methods, as well as, those obtained from the acid-base titration are collected in Table (1). The values of pK_2 obtained from the pH-metric titration are comparatively higher than those determined by spectrophotometry and this may be attributed to the partial overlap with the jump representing neutralization of the strong sulphonic group [13].

The dissociation constant of sulphonic group (pK_1) was determined only by pH-metric method owing to the absence of significant variation in the spectra at low pH values 2.0-6.0).

A mentioned before, the values of dissociation constants, (pK_2 and pK_3) of compounds (Ia) and (Ib) are higher, (less acidic) than those of compounds (Ic-e). This may be ascribed to the formation of strong intramolecular hydrogen bond and also greater participation of the hydrazono tautomer in case of compounds Ia and Ib.

Polarographic Studies

The electroreduction of 0.5 mM of the azo compounds was carried out in 10% ethanol-universal buffer solutions in presence of 0.01% gelatine as maximum suppressor. The polarograms of all compounds consist of a single, well-defined wave. Typical current-potential curves at different pH's for compounds (I_d and I_e) are shown in Fig. 2. The half wave potential, $E_{1/2}$, and the limiting current, i_d were also found to be pH dependent. The variation of $E_{1/2}$ and i_d with pH of solutions for all the five compounds studied are represented in Fig. 3. It is clear that the height of the reduction wave in acid media is approximately double its value in alkaline media. These results are in good agreement with a previous work [2,3] where the reduction of some monoazo compounds was found to consume four and two electrons in acid and alkaline media respectively. In some other azo compounds, the limiting current is pH independent. This disagreement between our results and those cited in the literature [12,13] may be ascribed to the variation of the structure of the azo compounds with special reference to the grouping attached to the hydrazono moeity

It is important to note that the polarographic reduction of 2-hydroxy-4-sulphonic-1-naphthalenehydrazono-pyrazoline-5-one [14] and 3-pyrydylazodyes [15] containing sulphonic group

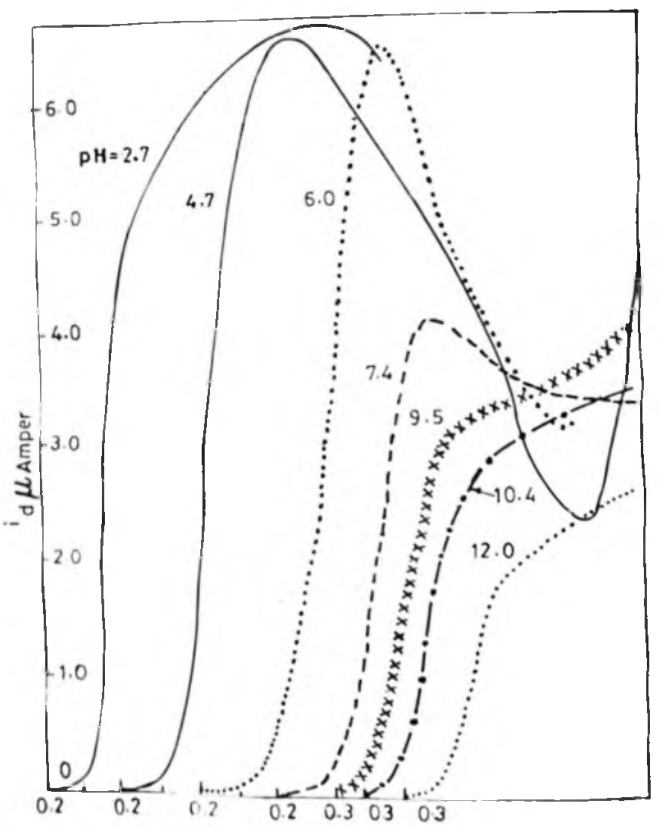


Fig. 2 Effect of pH on polarograms of 0.5 mM. hydrazono in universal buffer and 10% Ethanol-water solution.

Compound: I_d 2-Hydroxy-4-Sulphonic 1-Naphthalene hydrazono Ethylchloroacetate

were found to be characterised by a hump followed by a minimum at pH ≥ 8.0. This behaviour was attributed to the hindered reduction on the covered areas on the droping mercury electrode and the unhindered areas on the bared portions [15]. The adsorbed species are the sulphonate anions probably associated [16] with the buffer cation. The same phenomena was also noticed in this investigation but at lower pH values (i.e.at pH range 3-7) and completely disappears in alkaline media, Fig. 2.

Again, the disagreement between the polarographic reduction of the hydrazono compounds under investigation and those mentioned in the literature [1,14,16] may be mainely due to the variation of the group attached to the hydrazono moeity which is heterocyclic ring in the first case and aliphatic chain in the present study. The electron withdrawing properties of the groups in alphatic chain of compounds (Ia-e) decreases the electron density on the sulphonated anion and hence facilitate the electro reduction of the compounds at less negative potential.

The effect of mercury height (h) on the limiting current i_d represented by log i_d - log h plots are straight lines with slopes around 0.50 indicating that the wave is largely controlled by diffusion at most pH values studied.

The half wave potential $E_{1/2}$ varies with the pH of solution. The plot of $E_{1/2}$ vs. pH of solution in the pH range 3-6 is almost linear, Fig. (3). The pH dependent nature of $E_{1/2}$ indicated the participation of protons in the electro reduction. The value of p (the number of H^+ involved in the rate determining step)can be obtained from the equation

$$\frac{dE_{1/2}}{dpH} = \frac{0.056}{\alpha n a} P \quad (\text{at } 25^\circ)$$

From the slope of $E_{1/2}$ vs pH in the pH range 3-6, the value of p is found to be 1

The various criteria [17] of ascertaining the irreversibility of an electrode process were applied to the present systems and it was found that the polarographic reduction of the studied compounds was totally irreversible in acidic and alkaline media.

The plots of i_d vs molar concentration of the depolarizers are linear passing through the origin indicating the validity of Ilkovic equation.

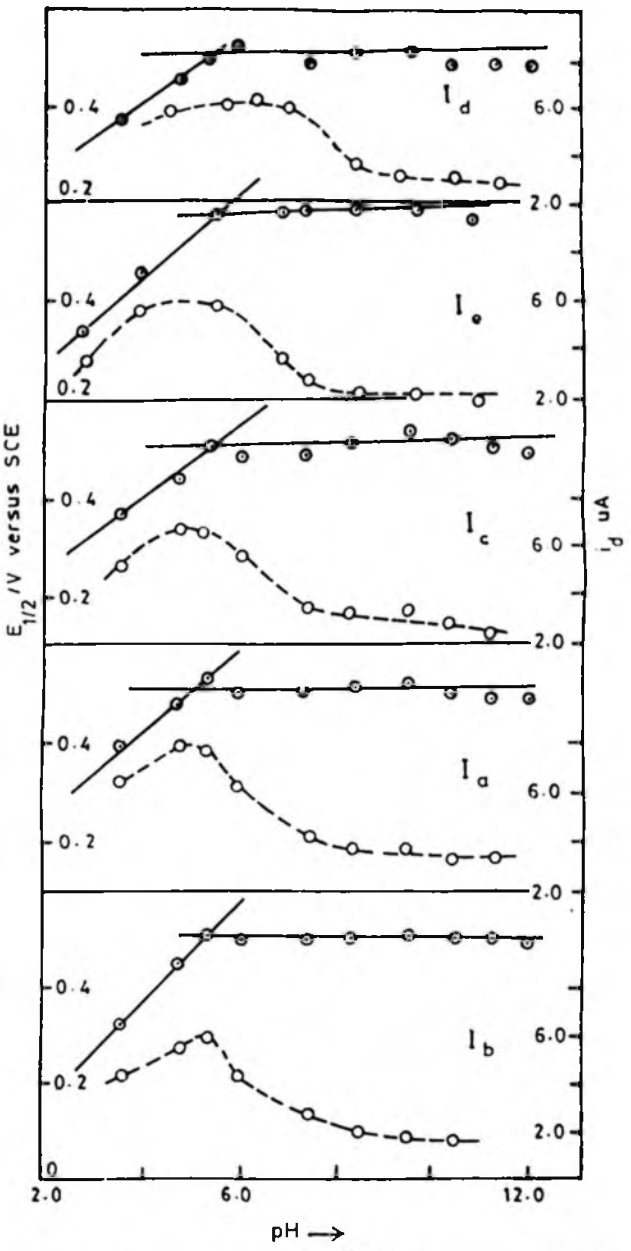
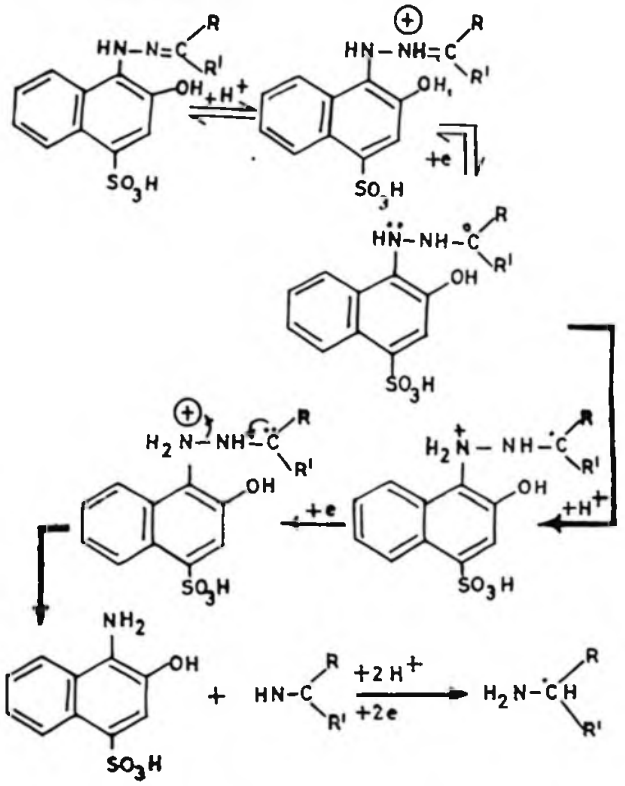


Fig.3 Effect of pH on $E_{1/2}$ and i_d or compounds —o— $I_{a\ e}$ $E_{1/2}$ V. vs. pH - - -o- - - i_d vs. pH

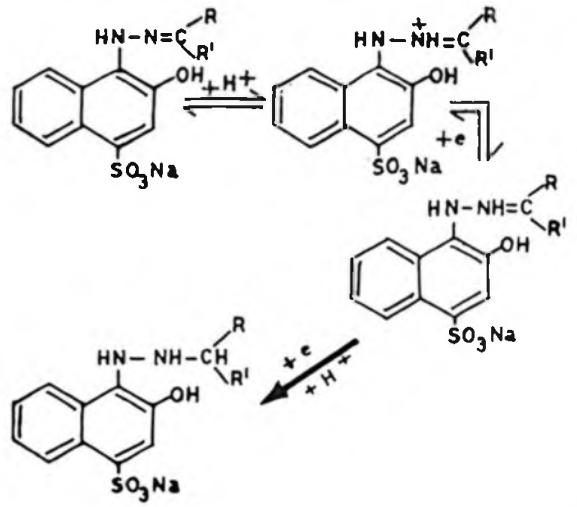
Mechanism of the Electrode Process

The compounds under investigation are characterized by the presence of hydrazone group HN-N=C< which is liable to reduction [14,18,19]. The number of electrons involved in the reduction is found to be equal to 4 in acidic and 2 in alkaline media. This was confirmed by carrying out a controlled potential electrolysis in acidic and alkaline media. The absorption spectra of all compounds under investigations exhibits a band of 390 nm, due to the hydrazono grouping [10]. This band showed gradual decrease in its intensity and

(i) Mechansim of the polarographic reduction in acid medium:



(ii) Mechanism in alkaline medium:



completely diappeared after six hour reduction in acidic medium, whereas in alkaline medium, its intensity only decreased but not disappeared even after twelve hour reduction. This indicates that cleavage of H-N-N=C group can only occur in acidic media where four electrons are consumed with the formation of primary amines [19]. On the other hand, the reduction of hydrazono group in alkaline media cannot undergo beyond the imine. Based on the above data, the following mechanism can be suggested for the polarographic reduction of the investigated compounds.

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