

Study the Effect of Concentration on Spectroscopic Properties of Fluorescein Sodium dye in Ethanol

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Abstract:

The aim of research is study The spectral properties (absorption and fluorescence) for Fluorescein Sodium dye by solving it in Ethanol ,at different concentrations ($5*10^{-5}$, $7*10^{-5}$, $1*10^{-4}$, $5*10^{-4}$, $7*10^{-4}$) mol/L at room temperature . The intensity of absorption increased and fluorescence decreased while concentration increases with agreement of Beer – Lambert Law. The absorption spectrum has been observed when it taken a wide spectral range, so when increased the concentration each peak shifted to a long wavelength. The fluorescence spectrum followed and entirely the same as absorption spectrum, so increase concentration shifted peaks to long wave length too.

The quantum efficiency of the dissolved Fluorescein Sodium dye in Ethanol has been calculated for the same above concentration were (88%,85%,70%,55%,53%) respectively. In addition to the radiative life time was (0.55,0.91,1.3,3.67,5)ns and the fluorescence life time (0.49,0.77,0.9,2.03,2.75)ns respectively.

Keywords: Xanthenes dye, Fluorescein Sodium , Fluorescence.

دراسة تأثير التركيز على الخصائص الطيفية لصبغة الفلوروسين-صوديوم المذابة في الايثانول

عدنان فالج حسن علي الحمداني فانز صالح عباس

الخلاصة:

هدف البحث هو دراسة طيفيه للامتصاص والفلورة لصبغة الفلوروسين-صوديوم والتي تمت أذابتها في محلول الايثانول للحصول على التراكيز ($5*10^{-5}$, $7*10^{-5}$, $1*10^{-4}$, $5*10^{-4}$, $7*10^{-4}$) مول/لتر وبدرجة حرارة الغرفة. أظهرت النتائج أن شدة الامتصاص تزداد مع زيادة التركيز وهذا يتفق مع قانون بير لامبرت . وكذلك تم الحصول على طيف امتصاص يمتد الى منطقة طيفية واسعة اذ بزيادة التركيز تزاح القمم نحو الاطوال الموجية الطويلة وللحاليل كافة التي تم استخدامها اما طيف الفلورة فقد سلك السلوك السابق نفسه اذ كلما زاد التركيز أزيحت القمم نحو الاطوال الموجية الطويلة أيضا. تم حساب الكفاءة الكمية للحاليل في مذيب الايثانول وحسب التراكيز أعلاه وكما يلي (88%,85%,70%,55%,53%) وأن زمن العمر الإشعاعي للتراكيز اعلاه (0.55,0.91,1.3,3.67,5) نانوثانية وزمن عمر الفلورة (0.49,0.77,0.9,2.03,2.75) نانوثانية على التوالي.

كلمات مفتاحية: الفلوروسين ، الفلوروسين-صوديوم ، صبغات

Introduction:

Luminescent solar concentrators (LSCs) do not require expensive solar tracking and concentrate both direct and diffuse light. An LSC consists of a flat transparent polymer plate doped with a luminescent dye, which has more recently been researched, with quantum dots. As incident insolation passes through the LSC device matrix, it is absorbed by the luminescent species. Red-shifted light is subsequently emitted isotropically. [1]

The dyes used in this paper contain rather large organic molecules which fluoresce. The dyes give absorption between (500- 700nm). The incoming light excites the dye molecules into the state of being ready to emit stimulated radiation, the singlet state. In this state, the molecules emit light via fluorescence, and the dye is transparent the wavelength. Within a microsecond, or less, the molecules will change to their triplet state. In the triplet state, light is emitted via phosphorescence [2]

Once a molecule has absorbed a photon it can emit a photon upon returning to the electronic ground state from the electronic excited state. As with absorbance, the strength of the transition is governed by the transition moment. The related peaks in turn will be the dominant peaks in the resulting spectrum. Two processes that emit light from a dye molecule are fluorescence, where the emitted photon is from the decay of excited state S1 to the ground state S0, and phosphorescence, which is a transition from the triplet state T1 to the electronic ground state S0. Most ground states are singlet due to the total spin being zero, cancelled out by pairs of electrons with opposite spin. The direct transition from S0 to T1 is forbidden since the value of the spin quantum number S would have to change. Similarly a transition from T1 to S0 is slow due to the same reason, resulting in a slow process called phosphorescence. Triplet-triplet absorption bands tend to heavily overlap the fluorescence region. The triplet state has a long lifetime leading to a buildup of population inversion. However since the transition from S0 to T1 is forbidden, it would require very high dye concentrations for lasing. Fluorescence can be used at relatively low dye concentrations for

laser applications. If the triplet state is at a lower energy than S1, it then competes with the buildup of the excited S1 state, lowering the quantum yield of the fluorescence.

The longevity of different excited states is important to the usefulness of a dye as a laser medium. The typical time scales for these processes are in (Figure 1) [3].

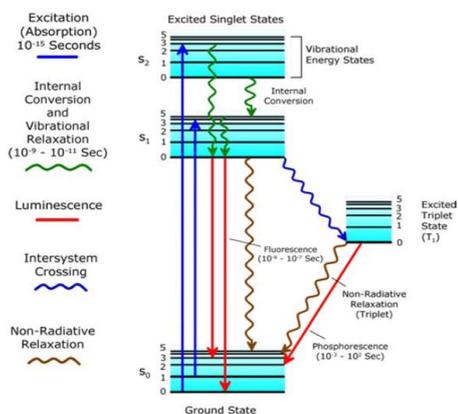


Fig (1) Jablonski diagram for the spectral process[3]

1. Fluorescence

Excitation of a molecule from absorption of a photon or thermal energy promotes the molecule to an excited energy state, setting up the possibility of emission of a photon. The excited molecules may lose energy through a non-radiative process to reach the lowest vibrational level of the excited state. Fluorescence is then the radiative loss of energy as a photon is emitted from a molecule in the excited state returning to the ground state. Since a non-radiative loss of energy occurs between the absorption and subsequent fluorescence, the emitted photon is of lower frequency than the absorbed photon producing a red shift between the absorbance and fluorescence spectra. The fluorescence from the excited state dye molecule is reabsorbed by the ground state molecule which shifts the fluorescence peak to lower energy [4].

2. Quantum Efficiency

The fluorescence efficiency q_{fm} , also known as the quantum yield, indicates the fraction of pump photons that are converted to fluorescence photons per dye molecule, where the maximum value is unity. Fluorescence

quantum yield is one of the key photophysical quantities that are amenable to direct experimental determination. The quantum yield of fluorescence is a measure of the rate of non-radiative transitions that compete with the emission of light. The knowledge of fluorescence quantum efficiency of organic dyes and its concentration dependence are essential for selecting efficient laser media [5]. The spectrum of the molecular fluorescence $F(\nu)$ gives the relative fluorescence intensity at wave-number (ν), this is related to the quantum efficiency by the following equation.

$$q_{FM} = \int_0^{\infty} F(\nu) d\nu \dots\dots(1)$$

In order to evaluate absolute quantum efficiency, we consider both the radiative and non-radiative processes taking place in the medium, therefore

$$q_{fm} = \frac{K_{fm}}{K_{fm} + \sum K_d} = \frac{K_{fm}}{K_{fm} + K_{IC} + K_{ISC}} \dots\dots(2)$$

Since

$$K_{fm} = \frac{1}{\tau_{fm}} \quad \text{and} \quad \tau_f = \frac{1}{K_{fm} + \sum K_d}$$

Therefore

$$q_{fm} = \frac{\tau_f}{\tau_{fm}} = \int_0^{\infty} F(\nu) d\nu \dots\dots(3)$$

Where τ_f is the fluorescence lifetime and τ_{fm} is the radiative lifetime of the excited state to circumscribe the possible reasons for q_{fm} variations. The radiative lifetime being a function of the absorption strength, it is invariant for any molecule unless its absorption spectrum changes. As this, to first order, is not the case in concentration quenching, the mechanism for q_{fm} variations must be changes in τ_f , caused, for example, by changes in the nonradiative lifetime of the excited state [6]

The fluorescence quantum yield of the dye solution and thin film were determined on the basis of the absorption and fluorescence spectra. This was calculated by using the following equation:

$$q_{FM} = \frac{\text{Number of quanta emitted}}{\text{Number of quanta absorbed}}$$

The radiation life time (τ_{fm}) can be calculated by:

$$\frac{1}{\tau_{fm}} = 2.88 * 10^{-9} n^2(\nu) \int \epsilon(\nu) d\nu \dots(4)$$

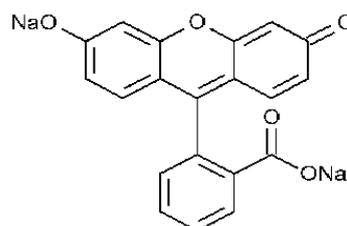
Where

n: refractive index of a medium

ν : wave number at the maximum absorption

$\int \epsilon(\nu) d\nu$: area under the absorption spectrum curve as a function of the wave number[7]

Experimental: The materials used in search Fluorescein Sodium dye:



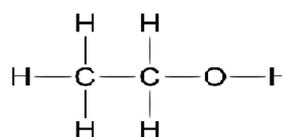
Properties

Molecular formula: $C_{20}H_{10}Na_2O_5$

Molecular weight : 376.27 g/ mol

Appearance: Orange -red to dark red crystalline powder[8]

The solvent :(Ethanol)



Properties

Molecular Formula: C_2H_5OH

Molecular Weight: 46.07 g/mol

Density: 0.7936 g/cm³

Freezing point: -114 °C

Boiling point: 78.3°C

Refractive index (n): 1.3614 [9]

Instrument used in work:

-Absorption spectrum by a (SP-8001.UV-visible spectrophotometer) by the processor (Metertech Inc)

-Fluorescence spectrum was measured by a (Spectrofluorometer SL174) by the processor (Elico).

Sample preparation:

The preparation of dye solution and different concentration and the isolation of appropriate amount of powdered dye in given volume of solvent used, according to the relationship:

$$W = \frac{M_w \times V \times C}{1000} \dots\dots\dots(5)$$

Where

W: Weight of the dissolved dye (gm)

Mw: Molecular weight of the dye (gm/mol)

V: volume of the solvent (ml)

C: dye concentration (mol/l)

The prepared solutions were diluted according to the following equation:-

$$C_1 V_1 = C_2 V_2$$

Where:

C1: primary concentration

C2: new concentration

V1: the volume before dilution

V2: the volume after dilution

Results and Discussion

The results are showing no absorption for ethanol within the spectral range of dyes Xanthine ,between (500-700) nm as in a Figure (2)

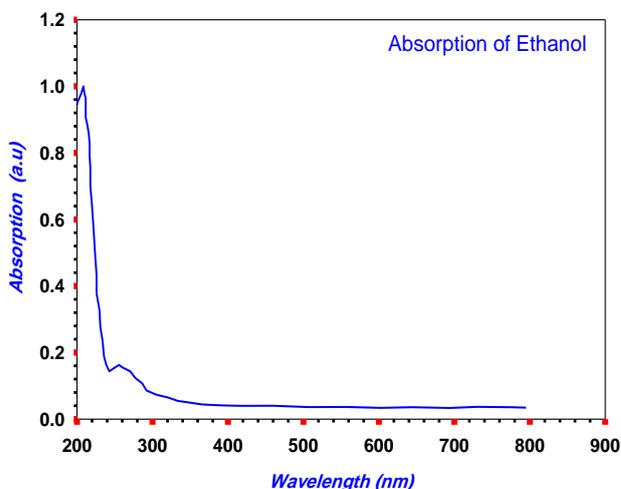
When dissolve Fluorescein Sodium in ethanol the absorption spectrum does not appear for concentrations less than 5×10^{-5} mol/L. The Absorption and Fluorescence Spectrum has been studied for five concentrations ($5 \times 10^{-5}, 7 \times 10^{-5}, 1 \times 10^{-4}, 5 \times 10^{-4}, 7 \times 10^{-4}$) mol/Las shown in Figures (3) (4) (5) (6) (7).

From above figures the Fluorescein Sodium dye has a large Absorption spectrum in (400-600) nm .

At the minimum concentration (5×10^{-5}) mol/L , the peak of absorption spectrum is at (478) nm while drift to lower energies (red shift) (22) nm at maximum used concentration (7×10^{-4}) mol/L while the peak of absorption spectrum is at (550) nm. This result agrees with the Beer-Lambert law.

The relationship between Molar Absorption Coefficient (L/mol.cm) illustated in Figure (8) to calculate the area under the curve as well as Non Radiative Life Time (τ_{fm}) and Fluorescence Life Time (τ_f)

The values of the stock shift between the absorption and fluorescence spectra, the radiated lifetime, fluorescence lifetime and the quantum efficiency of fluorescence for Fluorescein Sodium are illustated in Table (1).



Figure(2)The Absorption Spectrum of Ethanol

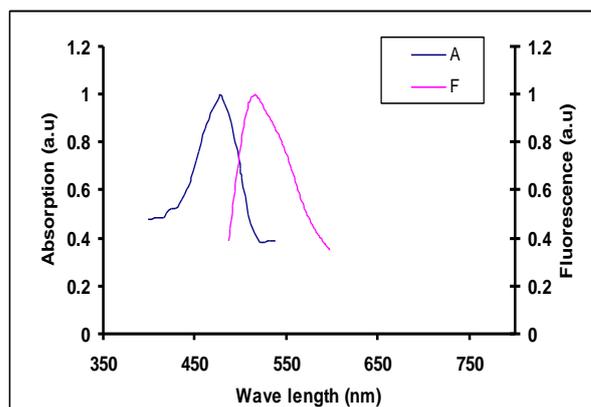


Figure (3) Absorption and Fluorescence Spectrum of Fluorescein Sodium for 5×10^{-5} mol/L

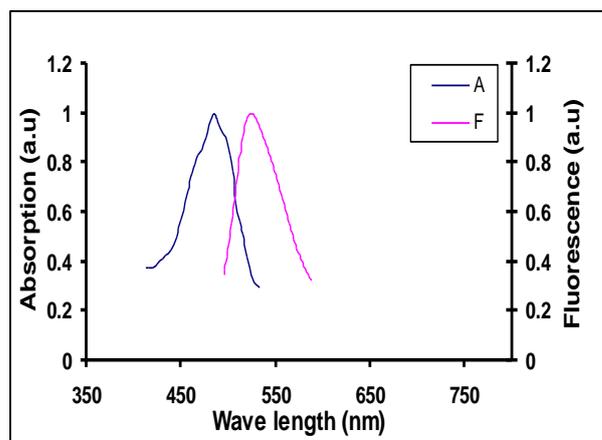
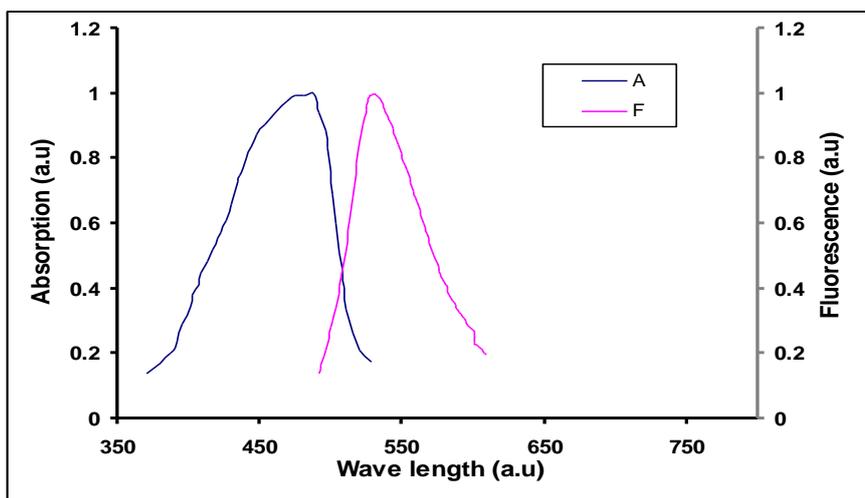


Figure (4) Absorption and Fluorescence Spectrum of Fluorescein Sodium for 7×10^{-5} mol/L



Figure(5) Absorption and Fluorescence Spectrum of Fluorescein Sodium for 1×10^{-4} mol/L

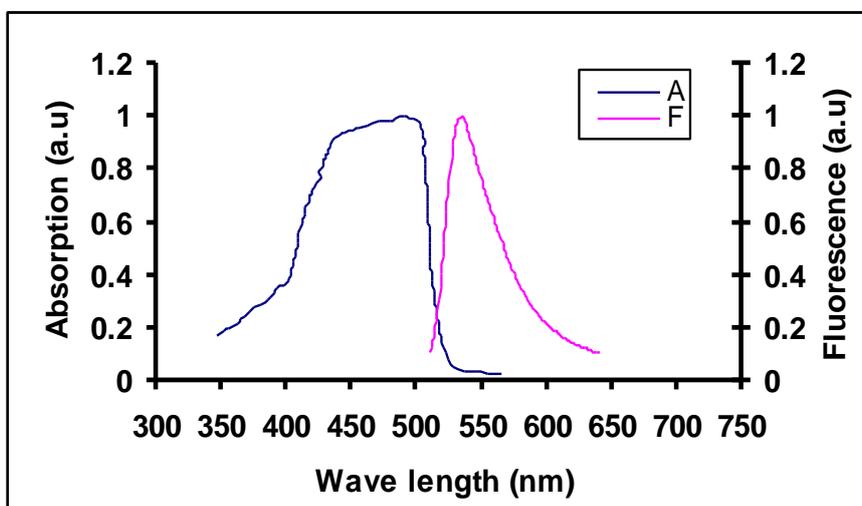


Figure (6) Absorption and Fluorescence Spectrum of Fluorescein Sodium for 5×10^{-4} mol/L

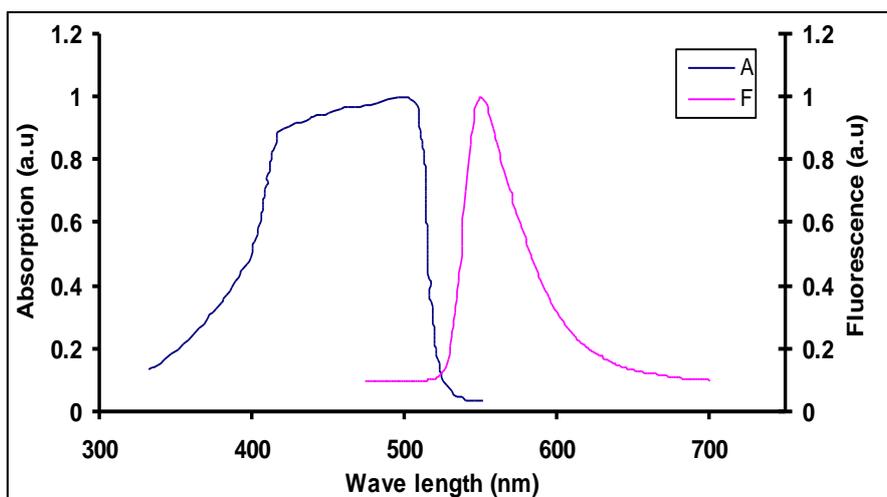
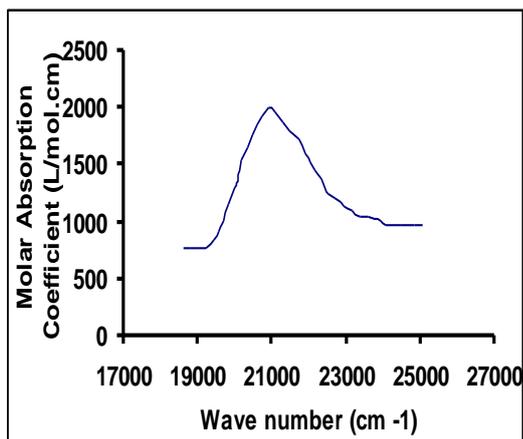
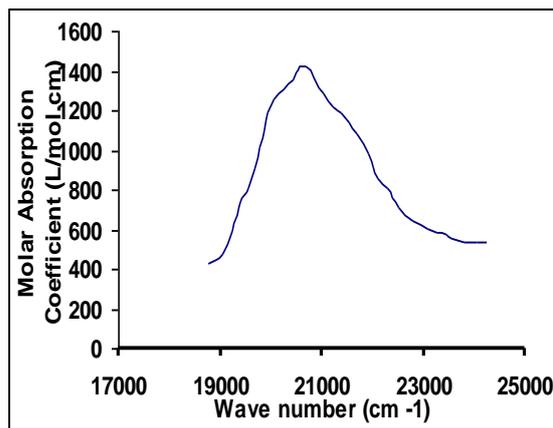


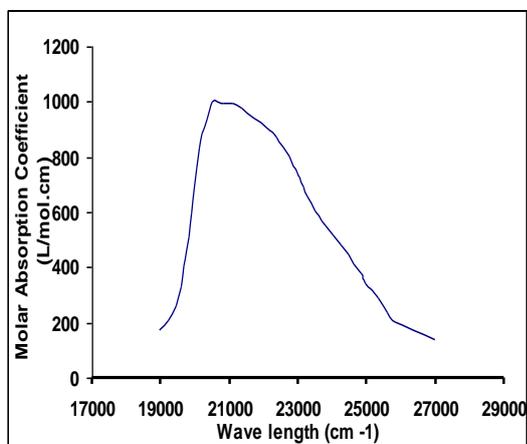
Figure (7) Absorption and Fluorescence Spectrum of Fluorescein Sodium for 7×10^{-4} mol/L



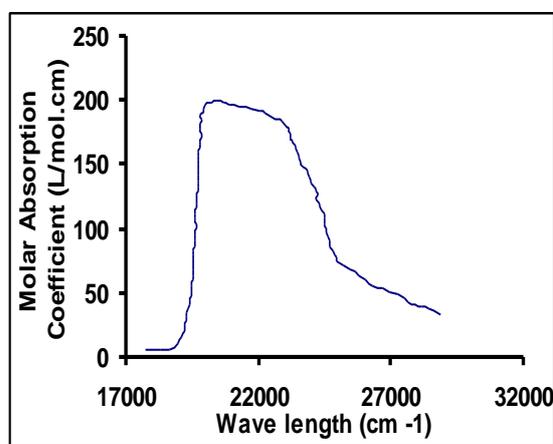
a



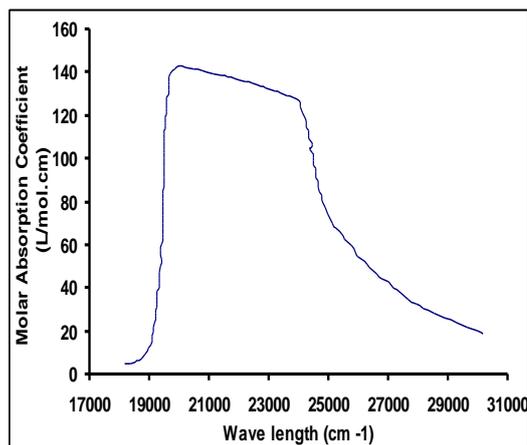
b



c



d



e

Figure(8)Spectrum of Molar coefficient (L/mol.cm) and Wave number (cm⁻¹) for
 (a) 5×10^{-5} (b) 7×10^{-5} (c) 1×10^{-4} (d) 5×10^{-4} (e) 7×10^{-4}
 (Fluorecein Sodium)

Table (1) :The stock shift between the absorption and fluorescence spectra, the radiated lifetime, fluorescence lifetime and the quantum efficiency of fluorescence for Fluorescein Sodium.

Concentration mol/L	A _{max}	F _{max}	Stokes Shift $\Delta\lambda=\lambda_{\text{flo}}-\lambda_{\text{abs}}$	The radiated Life time τ_{fm} n sec	The fluorescence Life time τ_{f} n sec	The quantum efficiency% Q_{fm}
5×10^{-5}	478	515	37	0.55	0.49	88%
7×10^{-5}	483	524	41	0.91	0.77	85%
1×10^{-4}	488	530	42	1.3	0.9	70%
5×10^{-4}	490	534	44	3.67	2.03	55%
7×10^{-4}	500	550	50	5	2.75	53%

Conclusions

1-Clear absorption spectrum of Fluorescence Sodium dye does not appear when dissolved in ethanol at concentrations less than (5×10^{-5}) mol/L.

2- Increase of concentration for all samples leads to peaks shift of the absorption and fluorescence spectra to long wavelengths, within ranges (**300-700 nm**).

3-The overlap between absorption and fluorescence was decreased with increase of concentration.

4- Increase in the value of quantum efficiency (q_{FM}) with the decrease in concentration also increases Radiative life time (τ_{FM}) and fluorescence life time (τ_{F}) where $\tau_{\text{FM}} > \tau_{\text{F}}$ for all samples.

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