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Light Scattering and NMR Studies of the Self-Association of the Amphiphilic Molecule Propranolol Hydrochloride in Aqueous Electrolyte Solutions

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Critical concentrations, aggregation numbers, and effective micellar charges of the amphiphilic drug propranolol hydrochloride have been determined from static light scattering measurements at 25 °C in the presence of added electrolyte (0.0−0.5 mol kg^{-1} NaCl). Photon correlation spectroscopy (dynamic light scattering) has shown an increase in micellar size with an increase of added electrolyte concentration. To quantify the interaction between aggregates, the correlation data have been interpreted by the DLVO theory. Micellar properties have been determined by the application of mass action theory to the concentration dependence of ^{1}H NMR chemical shifts confirming the results obtained by light scattering.

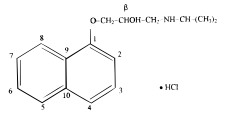
1. Introduction

The association characteristics and surface properties of a wide variety of amphiphilic drugs, examined using a wide range of techniques, have been reported in recent papers from these laboratories.[1−5] Changes in the solution properties of these drugs in aqueous solutions at critical concentrations are assumed to be indicative of the onset of association, the nature and extent of which is related to the structure of their hydrophobe.

The drug propranolol hydrochloride (see Chart 1) is a prototype of the beta-adrenergic blocking agent, and its therapeutic effect, collectively referred to as the membrane stabilizing activity, has been correlated with the hydrophobicity of the molecule.[6,7] It is a racemic compound, with only its 1-isomer having adrenergic blocking activity.

In a recent paper[8] we determined the critical concentrations for the association of propranolol in aqueous solution as a function of temperature using conductometric techniques, from which thermodynamic parameters for association were derived. We now report an extension of that study on which we have examined the influence of electrolyte on the association characteristics of propranolol hydrochloride. The concentration of the added electrolyte was restricted to less than 0.5 mol kg^{-1} NaCl. The study of the aggregation in the presence of an electrolyte is useful to understand the process of aggregate formation because the electrostatic repulsion between the charged heads is one of the factors which determine the size and shape of the aggregate.[9−11] We have used dynamic light scattering to determine diffusion coefficients, and we have interpreted the data using the Corti and Degiorgio[12] treatment

CHART 1



on the basis of the Derjaguin−Landau−Verwey−Overbeek (DLVO) theory of colloid stability.[13] This theory permits the quantification of the interactions between aggregates by means of the interaction potential, which consists of a hard-sphere repulsive part, an electrostatic long-range repulsion, and a London−van der Waals attraction. It contains only two unknown parameters, the electric potential at the shear surface of the aggregate, and the attractive Hamaker constant. These parameters have been calculated with a computational procedure.

In addition, static light scattering and NMR spectroscopy were used to determine critical concentrations and aggregation numbers in the presence of added electrolyte. NMR spectroscopy is a useful technique for the study of the association of amphiphilic molecules.[14−17] Large changes in chemical shift of aromatic protons in molecules such as propranolol on association, which are attributable to an intermolecular aromatic ring current effect,[18,19] can be used not only to determine the onset of association, but also to provide information on aggregate size.

2. Experimental Section

Materials. Propranolol (1-[Isopropylamino]-3-[1-naphthyloxy]-2-propanol) hydrochloride was obtained from Sigma Chemical Co. (No. P-0884). Water was double-distilled, deionized, and degassed before use.

Light Scattering Measurements. Static light-scattering measurements were made at 298 ± 0.1 K using a Malvern 7027 laser light scattering instrument equipped with a 2 W argon ion

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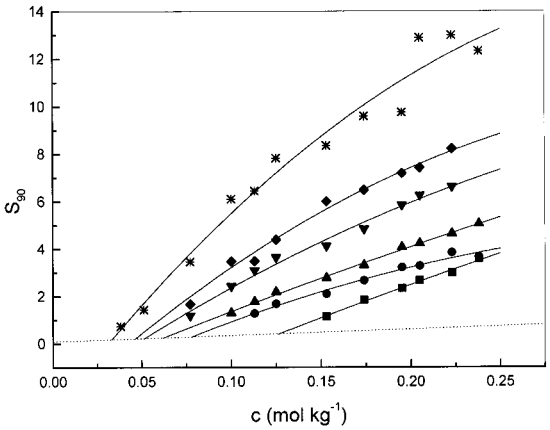


Figure 1. Variation of the scattering ratio S_{90}, with molality m, for propranolol hydrochloride in (■) water and in aqueous NaCl solutions of concentrations (●) 0.05, (▲) 0.1, (▼) 0.2, (◆) 0.3, and (∗) 0.5 mol kg^{-1} at 298 K. (− −) Monomer line.

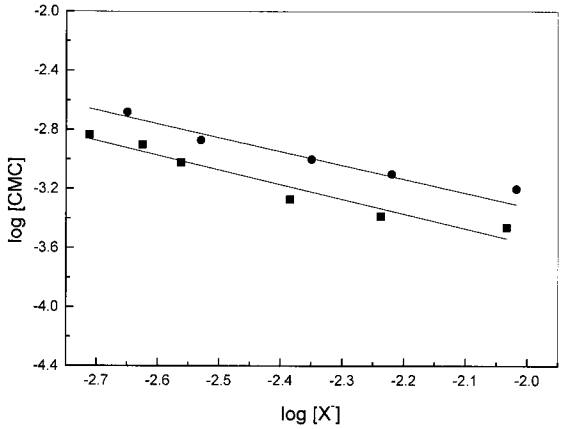


Figure 2. Logarithm of critical concentration, cmc, as a function of logarithm of counterion concentration [X$^-$]. Concentrations are in mol fraction units. (●) Values obtained from light scattering measurements. (■) Values obtained from NMR measurements.

laser (Coherent Innova 90) operating at 488 nm with vertically polarized light. Solutions were clarified by ultrafiltration through 0.1 μm filters with the ratio of light scattering at angles of 45° and 135° not exceeding 1.10.

The refractive index increments of the propranolol hydrochloride micelles were measured at 298 ± 0.1 K using an Abbé 60/DE precision refractometer (Bellingham and Stanley Ltd.), giving values of 0.0580 ± 0.0023 and 0.0055 ± 0.0026 kg mol^{-1} in water and 0.5 M NaCl, respectively. The refractive index increment of NaCl[20] is 0.0104 kg mol^{-1}.

Viscosity Measurement. Viscosity measurements were performed using an Ostwald viscometer. All the systems investigated showed a Newtonian behavior for the shear gradients available.

Dynamic Light Scattering. Measurements were made at 298 ± 0.1 K and at a scattering angle of 90° with the Malvern instrument described above combined with a Brookhaven BI 9000AT digital correlator with a sampling time range of 25 ns to 40 ms. Solutions were clarified as described above. Diffusion coefficients were determined from a single-exponential fit to the correlation curve. Hydrodynamic radii were calculated from measured diffusion coefficients by means of the Stokes−Einstein equation.

Nuclear Magnetic Resonance. ^{1}H NMR was recorded on a JEOL EX270 270 MHz spectrometer at 293 ± 1 K. The chemical shifts of peaks of interest were determined using a peak pick facility. The chemical shifts of peaks with heights exceeding the peak threshold were recorded by the computer. The peak threshold was set just below the top of the smallest peak of interest. All chemical shifts were measured relative to the internal standard sodium 3-(trimethylsilyl)proprionate (TSP).

3. Results and Discussion

In Figure 1 the concentration dependence of the static light scattering intensity, S_{90} (intensity of light scattered by the solution relative to that obtained from benzene), for propranolol hydrochloride in aqueous solution containing between 0.0 and 0.5 mol kg^{-1} NaCl are shown. Analogous studies on the amphiphilic phenothiazine drugs chlorpromazine, promazine and promethazine[21−23] in water and dilute electrolyte solution show scattering curves with two (or more) discontinuities corresponding to well-defined critical concentrations. This difference in the association pattern between propranolol and the phenothiazine drugs reflects differences in the structure of the hydrophobe; the phenothiazine drugs having a larger (tricyclic) rigid ring system, which is more conductive to the formation of stacked aggregates.[24]

TABLE 1: Micellar Properties of Propranolol Hydrochloride in Aqueous Electrolyte Solution at 298 K from Static Light Scattering (SLS) and NMR

[NaCl] (mol kg^{-1})	cmc (mol kg^{-1})		n		a
	SLS	NMR	SLS	NMR	SLS
0.00	0.124	0.108	10	15	
0.05	0.078	0.075	11	16	0.09
0.10	0.062	0.053	12	20	0.13
0.20	0.051	0.030	17	23	0.16
0.30	0.044	0.023	24	34	0.25
0.50	0.033	0.019	35	38	0.26

Critical micelle concentrations (cmc) were determined as the intersection of the scattering curves and the theoretical line (represented by a dashed line in Figure 1) for the monomers. The micellar aggregation numbers n and the degree of ionization α were calculated according to the Anacker and Westwell[25] treatment. Table 1 shows the values obtained.

Standard free energies of micellization (per mol of monomeric drug ion) were derived by the application of the mass-action model using the equation[26]

$$\log(\text{cmc}) = -(1-\alpha)\log[\text{X}^-] + \Delta G_m^0/2.303 + (1/n)\log F(m^{+p}) \quad (1)$$

where α is the degree of micellar ionization, m^{+p} is the mol fraction of micelles, and F is a term involving the activity coefficients of all species in solution. Plots of log (cmc) against log(counterion concentration), log [X$^-$], were found to be approximately linear in this system (Figure 2). ΔG_m^0 and α values were −28.7 kJ mol^{-1} and 0.12, respectively, which compare with values of −27.19 kJ mol^{-1} and 0.53 obtained in our previous study.[8] The values of the Gibbs energy are in reasonable agreement; the large discrepancies in α values may a consequence of the different techniques used for their determination. The earlier values were derived from the gradients of conductivity−concentration plots which is a more approximate method of determination.

In Figure 3 the measured apparent diffusion coefficients D are plotted as a function of micellar concentration ($c-cmc$, where c = molality of the solution) in water and aqueous electrolyte solutions. To avoid the potential source of error caused by monomers contributing to the effective value of D[27] measurements were restricted to a concentration region in which

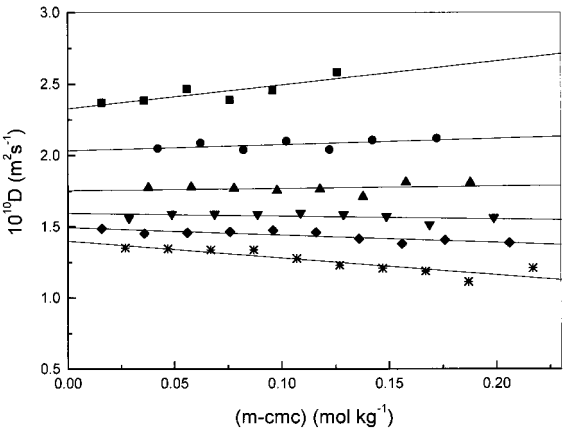


Figure 3. Diffusion coefficient D as a function of the micellar concentration for propranolol hydrochloride in (■) water and in aqueous NaCl solutions of concentrations (●) 0.05, (▲) 0.1, (▼) 0.2, (◆) 0.3, and (∗) 0.5 mol kg^{-1} at 298 K.

TABLE 2: Limiting Diffusion Coefficient D_0 and Hydrodynamic Radius r_h of Propranolol Hydrochloride in Aqueous Electrolyte Solution at 298 K

[NaCl] (mol kg^{-1})	10^{10} D_0 (m^2 s^{-1})	r_h (nm)
0.00	2.33	1.05
0.05	2.03	1.21
0.10	1.76	1.39
0.20	1.60	1.53
0.30	1.50	1.63
0.50	1.40	1.75

D was a linear function of molality. The limiting diffusion coefficients D_0 were obtained extrapolating the data to the cmc. The hydrodynamic radii r_h were calculated using the Stokes−Einstein equation where k_B is the Boltzmann constant and η

$$r_h = \frac{k_B T}{6\pi\eta D_0} \tag{2}$$

the solvent viscosity. Table 2 shows an increase of micellar size with added electrolyte concentration in agreement with the increase of aggregation number, calculated from the light-scattering data.

To correlate experimental results of diffusion with the interactive forces between micelles the data were analyzed according to the treatment proposed by Corti and Degiorgio.[12] For interacting particles, the concentration dependence of D may be described as

$$D = D_0[1 + k_D(c - cmc)] \tag{3}$$

Expressed in terms of the volume fraction ϕ of the particles,

$$D = D_0(1 + k'_D\phi) \tag{4}$$

where $k'_D = k_D/\bar{V}$ and $\bar{V}$ is the specific volume of the solute particles as determined from density measurements and taking $c > cmc$. k_D may be related to the pair-interaction potential $V(x)$ between spherical particles of radius a (equated to r_h) using the expression proposed by Felderhof[28]

$$k_D = 1.56 + \int_0^\infty [24(1 + x)^2 - F(x)][1 - \exp(V(x)/k_B T)] \tag{5}$$

where $x = (R - 2a)/2a$, R is the distance between the centers of two particles, and $F(x)$ is given as

$$F(x) = 12(1 + x) - \frac{15}{8}(1 + x)^{-2} + \frac{27}{64}(1 + x)^{-4} + \frac{75}{64}(1 + x)^{-5} \tag{6}$$

The interaction potential $V(x)$ as it is usually written in DLVO theory[13] is the sum of an attractive London−van der Waals interaction $V_A(x)$ and a repulsive interaction resulting from the electric charge of the spheres. $V_A(x)$ derived by Hamaker[29] for the case of two spheres has the expression

$$V_A(x) = -\frac{A}{12}\left[(x^2 + 2x)^{-1} + (x^2 + 2x + 1)^{-1} + \frac{2\ln(x^2 + 2x)}{(x^2 + 2x + 1)}\right] \tag{7}$$

where A is the attractive Hamaker constant. Two approximate expressions have been proposed for the repulsive interaction $V_R(x)$ for the limiting cases of $\kappa a < 1$ and $\kappa a > 1$. We have used the expression[13,30]

$$V_R(x) = \frac{\epsilon a \psi_0^2}{2} \ln [1 + \exp(-2\kappa a x)] \tag{8}$$

which is appropiate for values of to $\kappa a > 1$, although for the drug micelles investigated here ($\kappa a = 1.21$ to 4.15) neither expression is strictly valid. In eq 8 ψ_0 is the surface potential and κ the Debye−Hückel reciprocal length parameter, expressed by the eq 9:

$$\kappa^2 = \frac{8\pi c_s e^2 z^2}{\epsilon k_B T} \tag{9}$$

where ϵ is the relative dielectric constant of the suspending medium, z is the valence of the ionic species in solution, c_s is the concentration of the same species, and e is the electronic charge.

In Table 3 experimental, obtained by eq 3 and computed, obtained by eq 5, k_D values are shown. The computational procedure involved the iteration of values of A and ψ_0 to give the best fit of computed and experimental values of k_D over the range of electrolyte concentration. Agreement between computed and experimental values of k_D is reasonable in view of the assumptions inherent in these calculations.

The micellar charge q is related to the surface potential ψ_0 by the expression[31]

$$\psi_0 = \frac{2k_B T}{e} \sinh^{-1}\left(\frac{2\pi e \kappa^{-1} q e}{4\pi\epsilon k_B T}\right) \tag{10}$$

The value of q derived from eq 10 was 0.43 units of electron charge, and the Hamaker constant was 0.20×10^{-21} J. To obtain an evaluation of the unknown parameters appearing in the expression of the interaction potential $V = V_A(x) + V_R(x)$, we have made the simplifying assumption that A and q are both independent of the salt concentration. With regard to A, there are measurements of forces between two surfaces in aqueous electrolyte solutions[32] which clearly show that the attractive London−van der Waals forces are largely independent of the type and concentration of the aqueous electrolyte solution.

In Table 4 we compare the results obtained for propranolol hydrochloride with those obtained for the amphiphilic phenothiazine drugs promethazine hydrochloride (I), chlorpromazine hydrochloride (II), and thioridazine hydrochloride (III) (see Chart 2). Our values for propranolol are similar to those of the phenothiazine drugs, with the exception of the smaller Hamaker

TABLE 3: Experimental, Obtained by Equation 3, and Theoretical, Obtained by Equation 5, Slopes, k_D and Reduced Potential $e\psi_0/k_BT$ (ψ_0, Surface Potential; e, Electronic Charge; k_B, Boltzmann Constant; and T, Temperature) as a Function of Electrolyte Concentrations

[NaCl] (mol kg^{-1})	k_D		$e\psi_0/k_BT$
	experimental	theoretical	
0.00	0.72	0.77	1.82
0.05	0.21	0.27	1.29
0.10	0.08	−0.17	0.84
0.20	−0.13	−0.35	0.55
0.30	−0.35	−0.40	0.41
0.50	−0.84	−0.43	0.29

TABLE 4: Hamaker Constants A, Hydrodynamic Radii r_h, and Reduced Potential $e\psi_0/k_BT$ for Hydrochlorides of Chlorpromazine (CPZ), Promethazine (PTZ), Thioridazine (TDZ), and Propranolol (PNL)

	$A \times 10^{20}$ (J)	r_h (nm)	$e\psi_0/k_BT$[a]
CPZ[b]	0.13	0.90	2.41
PTZ[b]	0.45	0.78	1.04
TDZ[b]	0.18	1.51	1.78
PNL	0.02	1.05	1.82

[a] Values refer to micelles in water. [b] Values from ref 23.

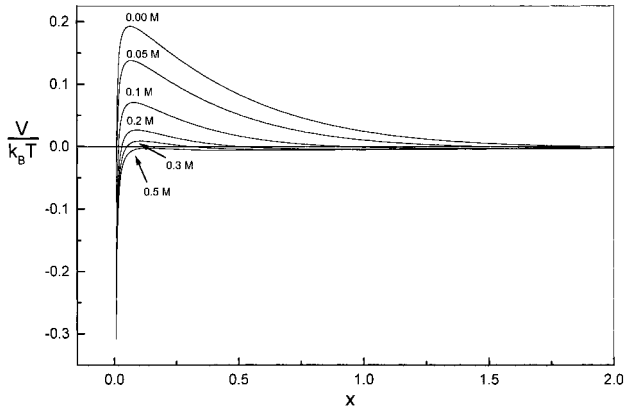
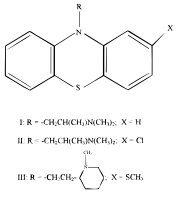


Figure 4. Plots of the pair interaction potential V calculated as sum of eqs 7 and 8 at different electrolyte concentrations. Values of the parameters are given in the text.

CHART 2



constant, indicating lower attractive forces between the propranolol aggregates. The effect of electrolyte on the reduced potential $e\psi_0/k_BT$ and $V(x)/k_BT$ are shown in Table 3 and Figure 4, respectively. From the inspection of this figure we can conclude that at low concentrations the electrostatic repulsion is predominant. When the electrolyte concentration increases the electrostatic potential becomes progressively more screened and the London-van der Waals attraction becomes more important. The concentration of 0.5 mol kg^{-1} represents the limiting electrolyte concentration at which clear solutions were obtained over the drug concentration range used; precipitation of drug was clearly observed in the presence of 0.6 mol kg^{-1} sodium chloride. Although our computations predict negative potentials at high electrolyte concentration, these may be considered to be zero within the fitting error and the observed

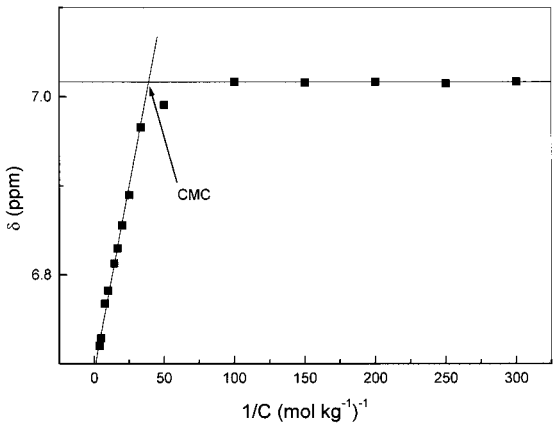


Figure 5. Variation of the ^{1}H chemical shift of the proton in position 2 of the aromatic ring as a function of the reciprocal propranolol concentration in 0.2 mol kg^{-1} NaCl solution.

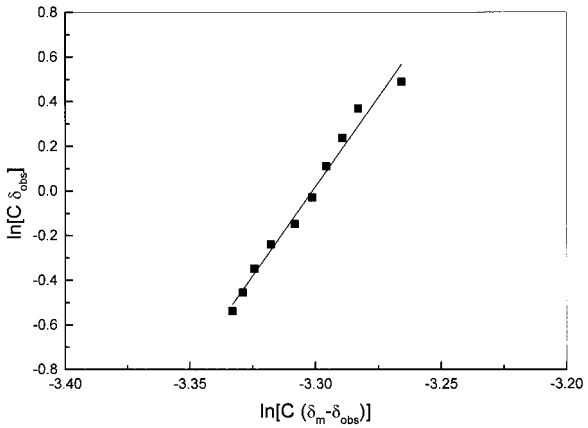


Figure 6. NMR chemical shift data plotted according to eq 14 for propranolol hydrochloride in 0.2 mol kg^{-1} NaCl solution.

precipitation is thought to be a consequence of reduced propranolol solubility rather than micellar coagulation.

The self-association behavior of propranolol hydrochloride has been investigated by the high-resolution NMR spectroscopy method. ^{1}H NMR spectra of propranolol hydrochloride solutions at a range of concentrations well below and above the cmc showed pronounced changes of chemical shift of the protons of the aromatic ring system at concentrations above the cmc resulting from the intermolecular ring current effect as the phenyl rings associate to form the micellar core. Figure 5 shows chemical shift as a function of reciprocal concentration for the proton in the 2 position of the substituted phenyl ring (see Chart 1) for solutions of propranolol in 0.2 mol kg^{-1} NaCl. Changes of chemical shift of protons of the side-chain were insignificant; for example, the change of chemical shift of the β proton was −0.057 over the concentration range of Figure 5 showing that the environment of the protons of the charged side-chains were not affected by the association process. Similar plots to Figure 5 were obtained for the electrolyte concentration range of interest.

Assuming an idealized situation where the amphiphile may exist as either a monomer or in a single type of micelle with an aggregation number n, the chemical shift can be written as[33]

$$\delta_{obsd} = \frac{C_m}{C_t}\delta_m \qquad (11)$$

where C_m and C_t are the concentration of micellized amphiphile and the total amphiphile concentration, respectively. δ_{obsd} is the

observed chemical shift, and δ_m is the shift of micellized amphiphile both taken relative to the chemical shift of the monomer as determined from measurements at high dilution. From the mass action equation, we may express the concentration of monomer as

$$[A] = C_t \frac{\delta_m - \delta_{obsd}}{\delta_m} \quad (12)$$

and the aggregate concentration as

$$n[A_n] = C_t \frac{\delta_{obsd}}{\delta_m} \quad (13)$$

Then the expression for K may be rewritten as

$$\ln(C_t\delta_{obsd}) = n\ln[C_t(\delta_m - \delta_{obsd})] + \ln K + \ln n - (n-1)\ln\delta_m \quad (14)$$

Plots of $\ln(C_t\delta_{obsd})$ against $\ln[C_t(\delta_m - \delta_{obsd})]$ may in principle give the aggregation number and the equilibrium constant. Figure 6 shows chemical shift data plotted according to eq 14 for solutions of propranolol in 0.2 mol kg^{-1} NaCl. Similar plots were obtained at all other electrolyte concentrations; cmc and aggregation numbers derived by this method are compared with light scattering values in Table 1.

It should be noted that the method of determination of aggregation number by the application of mass action theory to the concentration dependence of chemical shift as used in this study has been criticized[34] because of the influence of monomers on the shift observed at concentrations above the cmc. There is a shift difference between free and micellized amphiphile and, since the observed shifts are population weighed averages of these two environments, the shifts will change as the fraction of free monomers decreases with increase of total concentration. Table 1 shows the aggregation numbers obtained from the two techniques for the propranolol system. The cmc values derived from the intersection of lines drawn through chemical shift data above and below the cmc are consistently lower than those from light scattering. There is evidence of curvature of these plots in the cmc region, presumably as a consequence of the significant influence of monomers on the observed chemical shift in these systems of low aggregation number, which introduces error in the estimation of the cmc. However, plots of log c_1 against log[X$^-$] were linear (Figure 2), giving values of -31.9 kJ mol^{-1} and 0.1 for ΔG_m^0 and α, respectively.

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