

Ionic liquids: Solvation ability and polarity*

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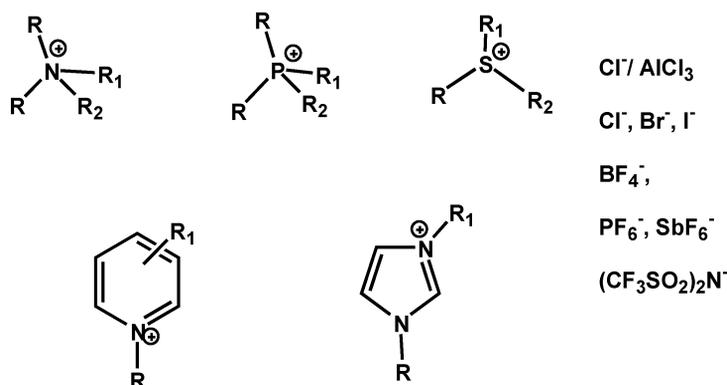
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Abstract: The role of ionic liquids (ILs) as solvents in chemistry is limited by the poor understanding of the solvation phenomenon in these media. The usual classification criteria used for molecular solvents through various experimental measurements fail to insert ILs into a univocal classification for ILs. Here, we first discuss the unsuitability of the usual interpretative scheme for molecular liquids and elucidate schematically the mechanism of solvation in ILs, pointing out the peculiarities that differentiate them with respect to molecular liquids. Second, we focus on reactivity and reaction kinetics in ILs, underlining the many problems that the complexity of these media reflects on the interpretation of kinetic data and some possible approaches to understand qualitatively the (often not trivial) kinetic problems for reactions performed in ILs.

Keywords: ionic liquids; polarity; solvation; kinetics; reactivity.

INTRODUCTION

Room-temperature ionic liquids (ILs) based on bulky asymmetric cations, such as 1,3-dialkylimidazolium salts, have been the object of intensive study owing to their wide range of applications in chemistry, electrochemistry, and materials sciences (Scheme 1) [1].



Scheme 1 Some typical IL cations and anions.

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As alternative solvents for organic reactions and catalyzed processes, ILs possess physico-chemical properties that make them improved media able to increase reactivity, selectivity, catalyst recyclability, and so on [2]. However, despite their extensive application and the number of studies published in the last few years, the nature of the solvation process in ILs remains poorly understood [3] as well as the relationship between IL structure and solvent polarity.

The reason for this lack of understanding is due to the incompatibility between results obtained with different techniques, which cannot be interpreted on the basis of the usual theories of molecular liquids. Usually, molecular solvents are classified according to their polarity or dielectric constant [4]; as mentioned above, the application of these concepts in ILs is not fruitful in rationalizing their solvent behavior.

Principally, partition methods [5] and solvatochromic dyes [6] have been used to investigate IL polarity. Moreover, some of these studies have been parametrized [5–7] by semi-empirical linear free energy relationships evidencing that ILs can be considered polar media with peculiar compositions of solvent parameters, at least in comparison to molecular solvents. Dipolar and dispersion forces, together with the ability to act as H-bond donor and/or acceptor, have been invoked to explain the capability of ILs to interact with dissolved species [7]. On the basis of the parameters arising from solvatochromic measurements [6] and related simulation studies [8], 1,3-dialkyl imidazolium salts are generally considered solvents of polarity comparable to short-chain alcohols, whereas pyridinium- and pyrrolidinium-based ILs should be more similar to polar solvents characterized by a lower hydrogen-bond donor ability. However, a behavior analogous to that of acetonitrile, a typical aprotic polar solvent, has been evidenced also for 1,3-dialkylimidazolium ILs when a specific probe, able to distinguish between protic and aprotic media, was used [9]. In agreement with these latter data, the H-bond acidity of imidazolium salts measured using ILs as stationary phase in gas-chromatography results are extremely low, if any [7a].

A first problem in utilizing these results is that, by inspecting the more recently reported data on solvation mechanism in ILs and molecular solvents [10], we cannot exclude that the solvent parameters determined in the two media (molecular and ionic) have always exactly the same meaning, even if the same probes have been used.

A second problem is given by the dielectric constant values of many ILs, recently evaluated as the zero-frequency limit of the frequency-dependent dielectric dispersion [11]. These values classify ILs as solvents of moderate-low polarity, in disagreement with the conclusions drawn by using solvatochromic dyes. However, as evidenced [10a] by the same authors and discussed in more detail in the next paragraph, “the well-established scenarios for describing dipolar interactions in molecular liquids are not easily transferred to ILs because the net charges of the ions create a fundamentally different environment with partial charge ordering and screening of dipole–dipole interactions by the sea of surrounding ions.”

In addition, ILs have other peculiar features able to affect their solvent properties. Like all molten salts, they are highly structured materials; much of the crystal lattice of the solid state is retained on melting [12]. The strong ion–ion interactions present in ILs lead to high-ordered three-dimensional supermolecular polymeric networks of anions and cations linked by H-bonds and/or Coulombic interactions [13]. The strength of the ion–ion interaction depends on the IL structure and may strongly affect the ability of the single components (anions and/or cations) to interact with dissolved species [13,14]. In addition, simulation and experiments suggest that nanoscale structures emerge in ILs incorporating long-chain hydrocarbon substituents; in these systems, the aliphatic tails form separate nanoscale domains interspersed in the ionic medium (Fig. 1) [15]. Simulation data indicate that the solute may partition preferentially into one or other domain, suggesting that regions of multiple polarity exist.

It is noteworthy that, although a number of attempts have been made to use empirical scales to elucidate the solute–solvent interactions that can occur in ILs, the mechanisms by which ILs are able to affect solvation and reactivity have been only marginally understood. In particular, no hypothesis or pre-

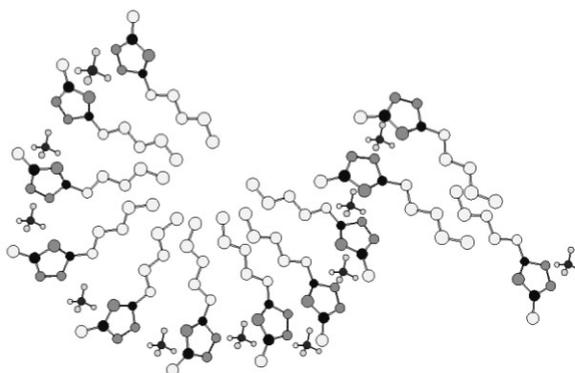


Fig. 1 Schematic representation of a typical IL incorporating a long-chain hydrocarbon substituent, in which the aliphatic tails form separate nanoscale domains interdispersed in the ionic medium.

vision has been made about the consequences of the above-mentioned “structural features” on reactivity. Dynamic or frictional solvent effects have been considered accidentally [16,17]. Only recently, a computational study of both free energetic and dynamic aspects of unimolecular charge separation and recombination processes in ILs has been published [17]. The few kinetic data of bimolecular homogeneous reactions carried out in ILs have been rationalized in terms of the transition state (TS) theory assuming that the required reorientational relaxation of the solvent molecules during the activation process is sufficiently fast and the activation complex is in thermal equilibrium with the solvent. For rapid reactions, this hypothesis may be, however, not necessarily valid, and the solvent can affect the rate through dynamic frictional effects, especially considering the slow dynamics that these systems usually display. In the case of slow solvent relaxation, significant dynamic contributions to the experimentally determined activation parameters, which are completely absent in the conventional TS theory, can exist, and in the extreme case (when the solvent re-orientation becomes the rate-limiting step), the rate depends on solvent dynamics and varies with density, viscosity, and internal pressure. These contributions may be particularly important in ILs, where dynamics, which are affected by anion–cation interactions, may be significantly slower than in molecular solvents and solvation is determined by the motions of the ions [18].

SOLVATION MECHANISM IN IONIC LIQUIDS

To understand the physics of solvation in ILs, it will be useful to recall the relative importance of the different contributions to solute–solvent and solvent–solvent interaction energy in quantitative terms. For a typical IL, such as 1-methyl-3-ethylimidazolium hexafluorophosphate, [emim][PF₆], in which ions of opposite charge are separated by about 5 Å, the Coulombic charge–charge interaction energy between a pair of these ions is about –60 kcal/mol, while the charge–dipole interaction energy is about –7 kcal/mol in the most favorable geometric disposition. In addition, dipole–dipole interactions between the cations do not exceed –0.5 kcal/mol. Therefore, charge–charge contributions are by far the most important in determining the system energy, charge–dipole are perturbations, which account for a contribution an order of magnitude less, and dipole–dipole are practically negligible.

From the thermodynamic point of view, the solubilization of a solute in a molecular solvent can be sequenced in the following stages (neglecting the mutual effect of electronic polarization on solute and solvent molecules):

1. A cavity of size suitable to accommodate the solute has to be formed in the solvent.
2. The solute is placed in the solvent.

3. The presence of the solute polarizes the solvent, reorganizing its positions and orientations around the solute itself.

On these bases, the thermodynamic behavior of ionic solutes in two model ILs, [mmim]Cl and [mmim][PF₆], has been recently evaluated using the one-dimensional reference site model (RISM) [10b]. Here, we will examine the situation in which a molecular dipole is solubilized in a molecular solvent (which is the typical situation that occurs in organic chemistry). First of all, the formation of a cavity requires the removal of some solvent molecules: this operation has a (positive) cost of some units of kcal/mol for a dipolar liquid (e.g., acetonitrile) but would have a cost of some *hundreds* of kcal/mol for an IL, in which every ion is surrounded by a discrete number of counterions (typically 5–8). If this energy cannot be counterbalanced and overcome by solute–solvent interaction (and for a molecular dipole, this will not be the case, for what was discussed above) the solvation will never take place. This gives us a first hint in supposing which kind of non-ionic species will be solvated by an IL: the ones that can be accommodated without perturbing the structure of the liquid to a considerable extent.

As a second aspect, we have to consider the solvent polarization: here, two different mechanisms play a role in the different solvents. In molecular liquids, polarization is mainly orientational polarization; the solvent molecules will be attracted toward the solute by dispersion forces and oriented by the solute local charge—solvent–dipole interaction. In ionic solvents, polarization will be mainly *translational* polarization; solvent anions will be placed close to the positive head of the solute, and vice versa (Fig. 2).

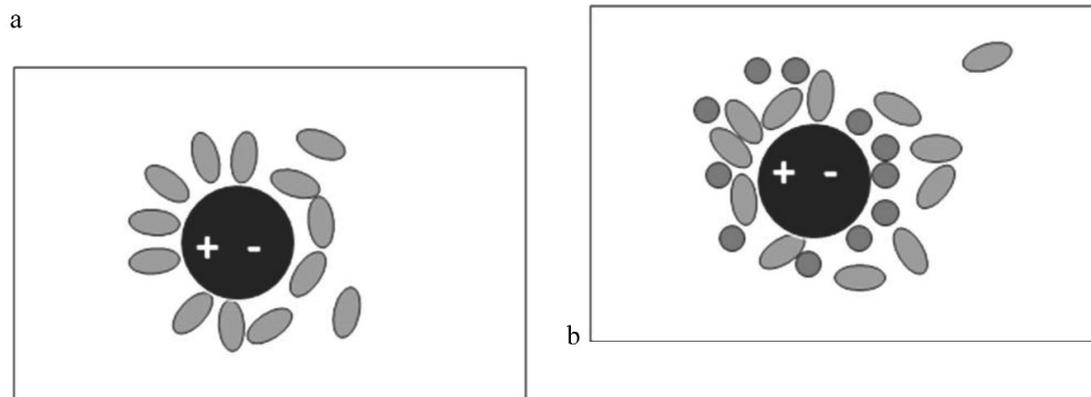


Fig. 2 Most important contributions to solvation: (a) in molecular solvents: orientational polarization of solvent dipoles; (b) ionic solvents: translational polarization of solvent ions.

Such behavior has an important consequence: the composition of the solvent varies depending on the spatial position around the solute or, in other words, is inhomogeneous. It is noteworthy that ILs should be considered inhomogeneous solvents, independently of the presence of sufficiently long alkyl chains on the cation, which are able to determine the presence of unpolar domains beside the polar ones. As a second fact, we have to remember that the disposition of the solvent around the solute will be dependent on solute–solvent interaction, but these play a minor role with respect to solvent–solvent interactions. The disposition of solvent molecules cannot thus be determined by trivial arguments considering only the solute–solvent interactions.

All these reasons—the inhomogeneity of the solvent and the difficulty of obtaining its composition in space—strongly suggest that a continuum-based description of the solvent, such as the one based on the polarizable continuum model, should be avoided. In addition, there is another pitfall that has to be avoided when considering the solvation in ILs on the basis of the methods previously adopted by

molecular liquids. The liquid polarization in molecular liquids, as explained above, is mainly given by orientational polarization of the (permanent or induced) dipoles of the solvent around the solute. In classical and quantum physics, this phenomenon is described on a macroscopic scale by the dielectric constant, which allows us to quantify the reduction of the Coulomb field around a charge through the well-known equation:

$$E(r) = \frac{q}{4\pi\epsilon_0\epsilon_S r}$$

ILs, nevertheless, are conductors, and not dielectrics: this means that, at equilibrium, their dielectric constant is “infinite”. This dielectric constant has not been confused with the frequency-dependent dynamic dielectric function: such function keeps track only of the relaxation motions occurring on a time scale faster than the inverse of the probing frequency (Fig. 3).

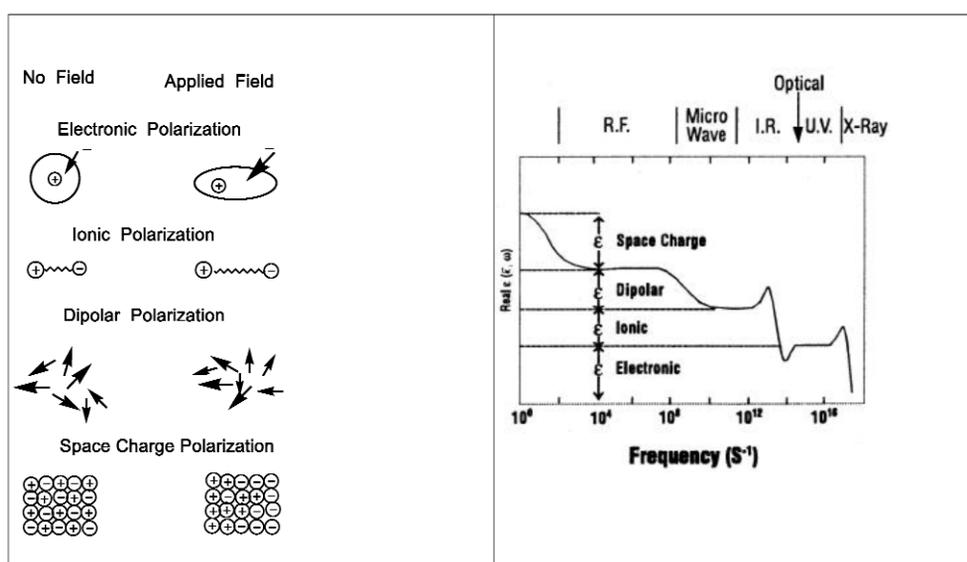


Fig. 3 Qualitative representation of the frequency-dependent dynamic dielectric function and related relaxation motions.

Dielectric spectroscopy in the megahertz/gigahertz regime is generally used to determine the complex dielectric function of ILs. This determines that only motions up to the rotational tumbling of the molecular dipoles contribute to the measurement; the slower translational rearrangement of cations and anions (charge space polarization), which should give the main contribution to screening, happens at much lower frequencies. A more suitable approach to dielectric spectroscopy of ILs, thus measuring the complex permittivity in the entire range of frequency, has been recently put forward by Leys [19]. In light of the different mechanisms of solvation in ILs and molecular solvents, the exponential increase in the dielectric constant in the low-frequency regime ($<10^4$ Hz) [19] suggests that the characterization of the equilibrium solvation properties of an IL exclusively by its high-frequency dielectric spectroscopy is probably physically meaningless. If a macroscopic quantity has to be chosen to describe the solvation, it has to be the one describing the screening of a charge or a dipole field in a conductor fluid; that is, the Debye screening length, telling us at which distance the field given by a charge will be annihilated by the screening of the conductor. The Debye length can be calculated for diluted charge systems with ease, while there are no analytic formulations for dense charged fluids. Nevertheless, theo-

retical arguments as well as experimental and molecular dynamics (MD) evidence [10a,20] seem to agree on the possibility that such length is inversely proportional to the charge density of the liquid.

Thus, the two important aspects of solvation that we recognized so far—formation of a cavity and screening interactions—appear to be ruled by charge density. It is then physically sound to propose such quantity as a macroscopic indicator for solvation properties.

ROLE OF IONIC LIQUID PECULIARITIES ON REACTION RATE

Despite the number of apparent similarities to normal polar solvents, it is evident that ILs show significant peculiarities in both structure and dynamics. In agreement with the IL solvent parameters, determined using solvatochromic dyes, these media present a high ability to interact with dissolved polar species. On the other hand, partition methods are evidence of a significant capability to interact also with unpolar compounds [7a]. Furthermore, ILs present a large electrorestrictive behavior; i.e., the radial and angular distribution of solvent ions around the solute becomes markedly structured as the solute charge separation is increased [10]. These features affect not only the possibility of these media to solvate long-lived dissolved species (reagents and products) but also transient species (TSs and intermediates), determining selectivity and reactivity.

Traditionally, reaction kinetics of homogeneous reactions are interpreted considering two factors: (1) the rate of diffusion of reactive species and (2) the time and energy required to move from the reactive complex to the TS. ILs are able to affect both factors but, more important, the effect is always determined by IL and solute structure. Anion–cation structure determines the interaction inside the IL, its three-dimensional structure and the ability of the two IL components (anions and cations) to interact with dissolved species. The solute structure determines the possibility of insertion inside the IL, its accommodation in the ionic network or in the unpolar domains as well as in the preformed cavities. At variance with molecular solvents, ILs are not homogeneous media, solute–solvent interactions are rarely of the same magnitude of the solvent–solvent interactions, solute–solvent interactions cannot be described by a simple combination of specific interactions and the alignment of the electrostatic dipole moments of the solvent molecules. Continuous theory cannot be applied to ILs, and macroscopic properties such as viscosity, cohesive pressure, and dielectric constants are not able to describe the complexity of the system. In diffusion-controlled reactions, solvent viscosity is the most important determinant of reaction rate [4]. In agreement with slow molecular diffusion characterizing ILs, diffusion-controlled processes are up to two orders of magnitude slower than in common organic solvents [21]. However, it is interesting to note that often the kinetic constants determined in ILs for diffusion-controlled processes are at least one order of magnitude higher than the kinetic constants estimated from the IL's viscosity ($k_{\text{diff}} = 8000 RT/\eta$) [21b]. Different explanations have been given [21b,22] to rationalize this behavior: (1) the presence of voids inside ILs that can favor the motion of small solutes; (2) the possibility of aromatic cations to favor electron-transfer processes, making possible the electron hopping through solvent cations; and (3) large solvent pre-exponential factors, A , that overcompensate for the large E_a values. In light of the above-discussed features of ILs, all these mechanism can contribute to the low correlation found between k_{diff} and η .

Attempts to obtain information about IL solvent properties have also been performed, investigating the kinetic and stereochemical behavior of some typical organic reactions (electrophilic additions, aliphatic nucleophilic substitutions, Diels–Alder reactions, etc.) [23]. Despite the above-mentioned peculiarities of ILs, in several reactions fairly good correlations have been obtained when kinetic and/or selectivity data have been plotted against solvents parameters [24]. However, it is noteworthy that the number of parameters necessary to describe the kinetic and stereochemical behavior is generally higher than in molecular solvents, and poor correlations have been found [25] when ILs and molecular solvents are correlated together using the sole parameters describing the reaction in molecular solvents. This suggests that the combinations of factors leading to the changes in the rates or selectivities in ILs are more complex than in molecular solvents. While specific interactions in ILs due to cations and anions

are for the most part analogous to those in molecular solvents (a potentially unique form of ion–quadrupole interactions has been proposed on the basis of MD simulations) [26], their expression depends on the ability of the dissolved species to compete with the ion–counterion interactions. On the other hand, nonspecific interactions in ILs require, as previously discussed, a deep reconsideration of solvation. ILs are conductors, and for the solute–solvent interaction it is not possible to separate the conductive and dielectric responses of the medium.

But, depending on IL structure we cannot exclude that an important contribute to the TS stabilization can arise also from the fact that ILs provide a preorganized dipolar environment, already partially oriented to stabilize the charge distribution in the TS. In molecular solvents, the solvent must always pay a significant reorganization energy to orient the polar environment toward the TS charges. The IL has already paid much of its reorganization energy to create a void during the reagents solvation. In other words, the nonequilibrium solvation effects without constituted dynamical contributions may affect reactivity contributing to the reaction barrier; molecular solvents must overcome an activation barrier to move from the reactant configuration to the product configuration when the solute is in the TS; ILs have a lower barrier, if any.

ILs are also dynamically active assemblies with a link between structure and dynamics. For ILs composed of relatively small, rigid ions a variety of IL dynamic events occur on the picosecond to nanosecond time scales [18]. The observed response functions are generally biphasic, consisting of a subpicosecond component of modest amplitude (10–20 %) and a dominant slower component relaxing of times of few picoseconds to several nanoseconds. The range of time scales of some dynamic events occurring in ILs and the time scales for the transformation of reagents in products can be similar, raising the question of their possible intercorrelation. In more detail, dynamic motions on the time scale of reaction may influence the barrier re-crossing behavior of trajectories, leading to a significant increase in the transmission coefficient (κ).

In addition, IL vibrations and motions may play a role in the fluctuation of the activation energy barrier; as in other organized systems such as enzymes [27], it is possible that the effect of IL dynamics on the activation energy, barrier height, and transmission coefficient will be interrelated. The strong coupling among ions in ILs may render solvation a collective process such that energetic perturbation brought about by a solute transition can be easily relaxed by only minor adjustments of the positions and possibly orientations of nearby ions.

Thus, in the TS framework, ILs could affect reaction rates not only by decreasing the activation barrier (Fig. 4) through specific interactions (H-bonding, dipole charge interactions, etc.), but also (1) through dynamic solvent effects, (2) reducing the solvent reorganization, (3) and/or increasing the number of trajectories that become productive after successful barrier crossing. Furthermore, entropic effects arising from the peculiar rearrangements of the solvent during the reaction may be more important in ILs than in molecular solvents.

Finally, it is noteworthy that the excitation wavelength dependence of the emission kinetics of several solutes in ILs has demonstrated the presence of *dynamic* heterogeneity in these media [28]. The rates of most of these processes vary significantly with excitation wavelength, showing that the energetically selected subpopulation relaxes at distinct rates. These studies suggest that dynamic processes taking place of the subnanosecond time scale in typical ILs near room temperature are likely to be heterogeneous in character. This heterogeneity should be considered when attempting to model fast kinetics in ILs.

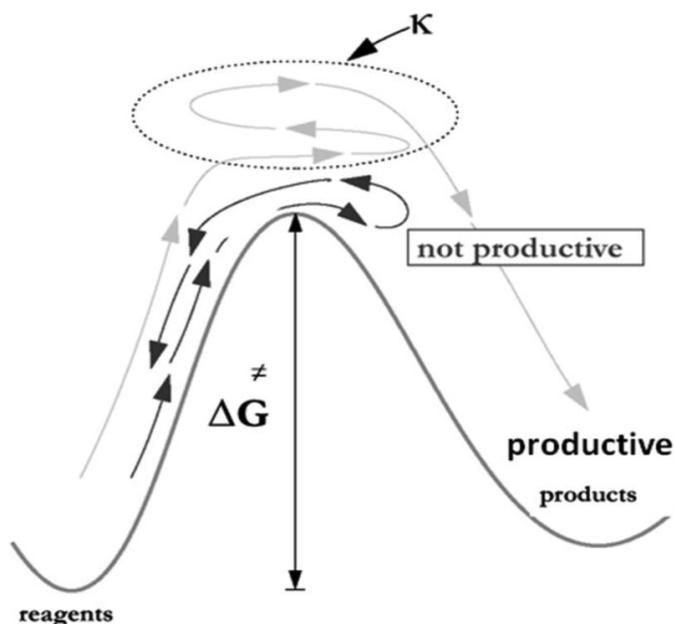


Fig. 4 Schematic illustration of a reaction in an IL. IL dynamics can affect reaction rates in two possible ways; by altering the height of the activation free energy barrier (ΔG^\ddagger) and transmission coefficient (κ).

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