



LATTICE MODEL CALCULATIONS ON AQUEOUS SOLUTIONS OF ACETONE AND TETRAMETHYLUREA

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Self-organization of aqueous acetone and tetramethylurea, caused by lyotropic phase transformations, is studied in frames of the Ising model. Using lattice Monte Carlo simulations, the concentration dependent mixing schemes in these solutions are confirmed and the molar fractions corresponding to the transitions between the mesophases of these mixing schemes are theoretically calculated.

INTRODUCTION

Binary liquid mixtures, in particular the aqueous solutions of small organic species, exhibit rather complex physicochemical properties. Their behavior is governed by the various specific interactions between the constituent molecules, such as hydrogen bonding or the longer range dipole-dipole coupling. Understanding the properties of mixtures at molecular level becomes possible with invoking experimental and theoretical methods, out of which the atomistic computer simulations proved to be particularly useful as they give a realistic insight into the structure and dynamics of the liquid.

Ising-type and lattice gas models present widespread approaches, in which the lattice sites represent the molecules of the mixture and their bonds. These models are able to reproduce the main features of thermotropic and lyotropic phase transitions in model systems of surfactant molecules in aqueous solutions.¹⁻⁴

It is of interest to explore the capabilities of such tools for studying aqueous solutions of small molecules. Apart of the well-known lyotropic transitions to various micellar phases, aqueous

solutions present more subtle features which have been investigated by Koga and coworkers.⁵ As evidenced by a series of thermodynamic studies, virtually all aqueous solutions can be characterized in terms of so-called mixing schemes, so that a particular mixture can display several characteristic behaviors in different concentration ranges. The change between two adjacent schemes occurs at characteristic concentrations, which can be identified by the sharp changes in higher order partial derivatives of thermodynamic functions. These domains in the phase diagram are called "mixing schemes", and the borders between them are named "Koga lines".⁶

In the present paper, there are selected two such mixtures, aqueous solutions of acetone and tetramethylurea, in both of them the non-ideal mixing behavior has been evidenced by thermodynamic studies.^{7,8} From structural point of view, the thermodynamic non-ideality corresponds to the enhanced clustering of the like molecules, which have been detected by radiation scattering methods, as small-angle neutron or X-ray scattering.⁸⁻¹¹

Both these co-solvents are miscible with water over the entire concentration range and at all temperatures between RT (R is the gas constant)

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and boiling points. There are no lyotropic micellar phases, as the co-solvent molecules are rather small and globular in shape. Still, according to thermodynamic data, three composition regions can be identified in these mixtures, in each of which the mixing scheme differs qualitatively from those in other regions.¹²

To receive the knowledge about phase transitions in the concentration ranges of solvent, corresponding to such phenomena, in this work we studied two mixtures, aqueous solutions of acetone and tetramethylurea, where hydrogen bonding or the longer range dipole-dipole coupling play an important role.

According to thermodynamic data, three composition regions can be identified in these mixtures,¹² in each the mixing scheme being qualitatively different from those in other regions. The structures and interactions within these regions are certainly defined by the features of the constituent molecules, and can be roughly expressed in the following way.

In the region of low concentration of the co-solvent, a small number of AC molecules are bound together by C=O dipole attraction more tightly than in pure acetone, and for TMU solution, molecules are bound together by H=CH₃ dipole attraction, respectively. In solution, such a cluster enhances the hydrogen bond network of H₂O in its immediate vicinity, with concomitant reduction in the hydrogen bond probability of bulk H₂O away from solute. So, such regions were introduced as concerning to Mixing Scheme I.¹² In the most surfactant-rich region, AC/TMU molecules form clusters in exactly the same manner as in pure liquid AC/TMU, in which AC/TMU molecules are bound together not only by C=O/H=CH₃ dipole but also van der Waals interaction. With respect to the clusters of pure AC/TMU, H₂O molecules interact as a single molecule. Hence, there is no hydrogen bond network of liquid H₂O. This is Mixing Scheme III. Mixing Scheme II is operative, in which the solution consists of two kinds of clusters each reminiscent to I and III. The transition from Mixing Scheme I to II is associated with an anomaly in a thermodynamic quantity, and it occurs in a narrow mole fraction range.

The effect of H₂O was also studied in aqueous TMU.⁵ TMU molecules directly participate in forming the hydrogen bond network of H₂O, presumably via H donor on -CH₃ and H acceptor on C=O, up to almost the saturation. Hence, the hydrogen bond connectivity in water not altered by the presence of the solute. However, the degree of

fluctuations in entropy and volume, characteristic of liquid H₂O, is reduced.⁵

Here we compare the behaviors of thermodynamical quantities, average energy and heat capacity, of aqueous AC and TMU in frames of statistical analysis, which is useful for interpretation of the hypotheses on mesomorphism caused by structures of water. In this modeling, the Ising lattice version of the free energy of the systems is involved, which was extensively studied by numerical Monte Carlo methods.³

In particular, similar binary water-surfactant systems are described¹⁻⁴ *via* the low-temperature, the mean-field, and other approximations, and which are able to predict the majority of mesomorphic states in aqueous solutions and can be tested numerically.

MONTE CARLO MODELING

The mesomorphic polymorphism of an aqueous solution depends on geometry and size of surfactant molecules, *i.e.* on its volume fraction in a solution. Chemical properties of heads and tails of surfactants, as well as their configuration thereupon, lead to formation of surfaces in solutions. The mesomorphism of aqueous AC and TMU also obeys universal phase behavior in lyotropic transitions.³

Experimental data for chemical potentials of acetone at molar fraction $0.1 < x < 0.16$, and for TMU at $0 < x < 0.03$ were taken from,¹² and calculated for the remaining concentrations by Boissonnas method. These data allowed us to perform calculations in the lattice model.

Here, applying the Ising gas lattice model,⁶ an each lattice site u is assigned a spin variable $\sigma_u = 0, 1, -1$ of face-centered cubic lattice (*fcc*). Depending on the molar fraction of particles, distributed on such a lattice, there are a vacancies, labeled as -1, water molecules (0), and surfactant's molecules (AC and TMU), which have assigned a variables 1. A few lattice sites are non-occupied, because of arithmetic demand a total number of molecules in a system should be less or equal than a total number of lattice sites, on which we distribute our system. The orientation properties of surfactants are taken into account via the coordinate variable s_u and r_{vu} , where vectors s_u are assigned each site of a lattice, and r_{vu} specify the directions from *fcc* lattice site u to v (and for s_v and r_{uv} reciprocally); for convenience, the absolute value of r_{vu} (r_{uv}) is equal to unity. The Hamiltonian of the model is

$$\begin{aligned}
H = & -\frac{J_1}{4} \sum_{\langle uv \rangle} \sigma_u (\sigma_u + 1) \sigma_v (\sigma_v + 1) \\
& -\frac{J_2}{4} \sum_{\langle uv \rangle} [(\sigma_u + 1)(\mathbf{s}_v \cdot \mathbf{r}_{uv}) + (\sigma_v + 1)(\mathbf{s}_u \cdot \mathbf{r}_{vu})] - \frac{\mu_s}{2} \sum_u \sigma_u (1 + \sigma_u),
\end{aligned} \tag{1}$$

where $\langle uv \rangle$ denotes a summation over all distinct pairs of nearest neighbor sites u and v . The term with coupling J_1 represents the isotropic interactions between nearest-neighbor sites. The terms with coupling constant J_2 describe the orientation-dependent interaction between an AC/TMU molecule and a neighboring water molecule. There is agreed that $J_2 > 0$ correspond to a surfactant orientation with its head pointing toward a neighboring water molecule. The last term gives the chemical potential energy of the AC/TMU molecules. Any operations remain in the grand canonical ensemble, when the surfactant concentration is controlled by the surfactant (AC/TMU) chemical potential μ_s , rather than in the

canonical ensemble where the surfactant concentration is fixed. Furthermore below, normalized values of excess chemical potentials μ_s^{ex} will be used, instead of μ_s . μ_s^{ex} were calculated and measured (as was reported¹² and references therein) depending on the surfactant mole fraction, they are only free of the linear terms. Such a substitution will not affect the average energy during Monte Carlo cycles, since according to (1), the reciprocal (first and second terms) and ‘‘concentration’’ (third term) spin variables are summed up independently from each other.

To simplify the calculations, the Hamiltonian (1) is normalized by the isotropic interactions $J_1/4$, and came to the form:

$$\begin{aligned}
\tilde{H} = & -\sum_{\langle uv \rangle} \sigma_u (\sigma_u + 1) \sigma_v (\sigma_v + 1) \\
& -j_2 \sum_{\langle uv \rangle} [(\sigma_u + 1)(\mathbf{s}_v \cdot \mathbf{r}_{uv}) + (\sigma_v + 1)(\mathbf{s}_u \cdot \mathbf{r}_{vu})] - 2\mu \sum_u \sigma_u (1 + \sigma_u).
\end{aligned} \tag{2}$$

The relations between j_2 and μ at non-zero temperatures t ($t = k_B T / J_1$) are chosen according to the results of low-temperature expansion.³ Here, k_B is the Boltzmann factor, $\mu = 2\mu_s / J_1$, and T is absolute temperature. In this case, the excess chemical potentials are taken as similar with the standard ones.

Fortunately, the data of^{6,12} allow to employ the known values of μ_i , connected with its molar fraction at $T = 25^\circ\text{C}$ as

$$\mu_i = RT \ln \frac{p_i}{x_i p_i^0}, \tag{3}$$

where x_i is the mole fraction of i -component in solution and p_i^0 is the vapor pressure of pure i -component, i means AC/TMU molecules.

Simulations have been performed, assigning the number of MC runs per a configuration 10^6 and the number of thermalization steps equaling 10^5 . Minimization of the energy of a configuration was performed in frames of the Metropolis algorithm built in a Fortran program.

As a trial result, to confirm the presence of a transition states, corresponding to the Ising model¹² at high temperatures, the temperature dependencies of free energy and specific heat was simulated and

shown in Figs. 1, 2 at $j_2 = 1.5$, which was obtained from the expansion of the free energy, corresponding to the *fcc* configuration.

RESULTS AND DISCUSSION

From the Gibbs energy equation, the extensive thermodynamical quantities $TS - pV$ remain after simulations, where TS is the partial molar entropy, V is the volume of a given binary system. At the constant volume, TS behaves as the free energy. In Fig. 3 the respective smoothness of the average energy, plotted for the aqueous AC and TMU systems is seen.

In the real systems, the transition from Mixing Scheme I to II starts at point X at $x \approx 0.08$ (for AC and TMU) and ends at point Y, $x \approx 0.26$.¹² However, according to the computer simulations, for both systems, the specific heat $\langle c \rangle$ exhibits an absence of extremum between the points X and Y (Fig. 4). In our MC tests, for aqueous AC, $\langle c \rangle$ has a sharp maximum in the vicinity of the 'II-III' transition (at $x \approx 0.93$) and remains smooth in the region of the 'I-II' transition.

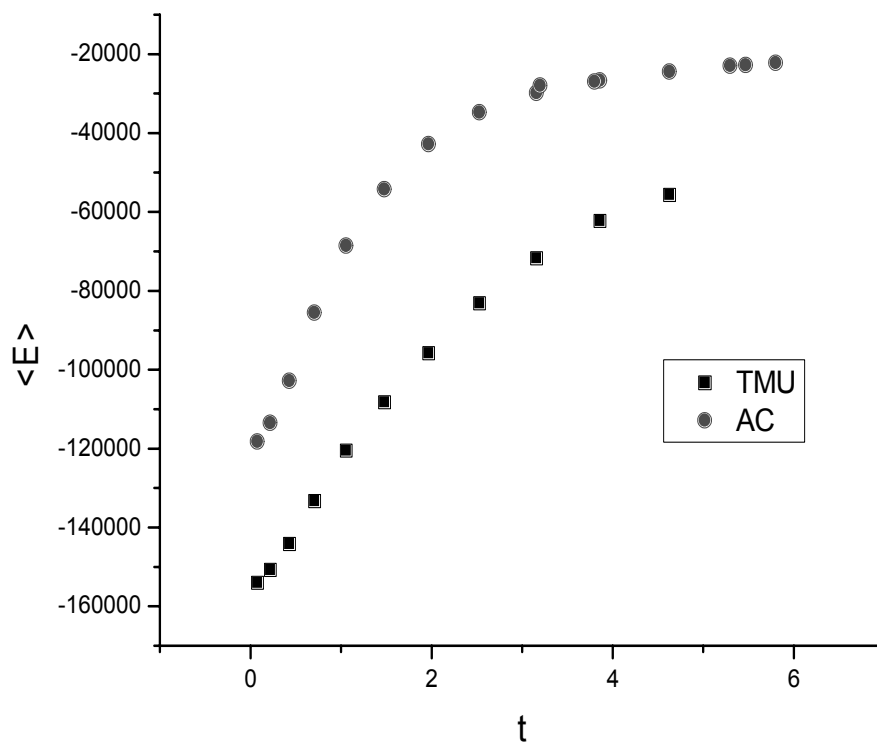


Fig. 1 – The average free energy $\langle E \rangle$ of aqueous acetone and TMU in dependence of temperature t , obeying by MC simulations, relative units. Errors of MC are of the order of 0.3 %.

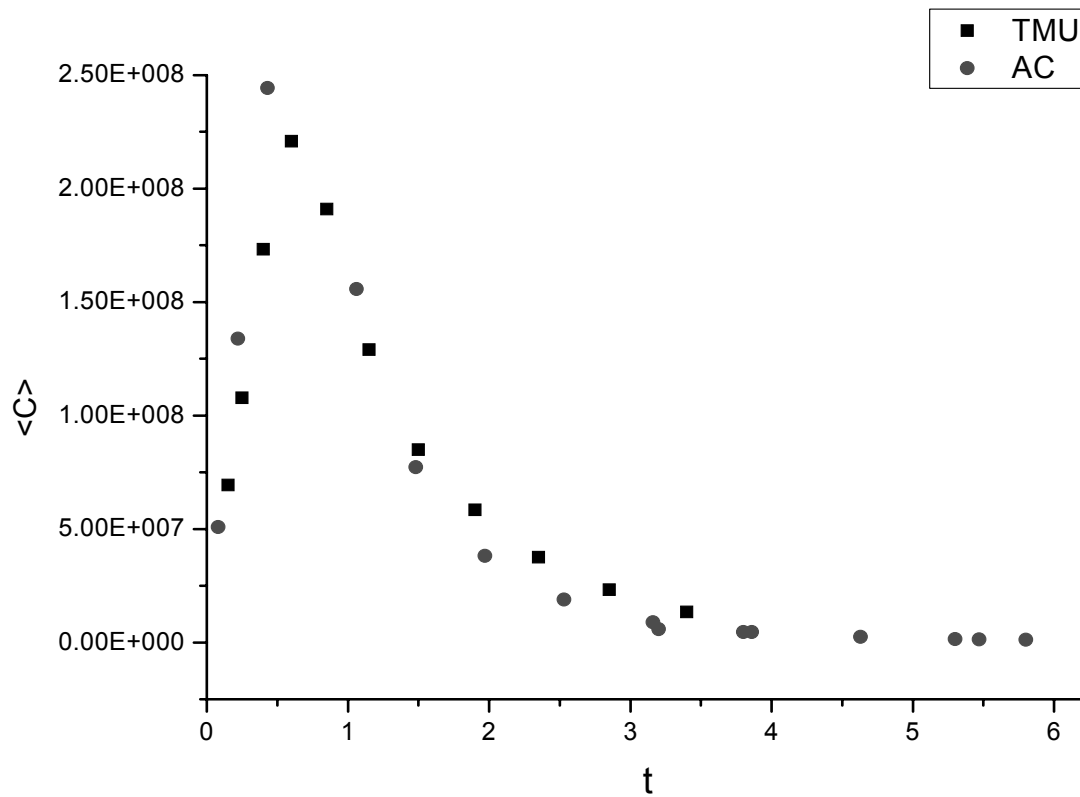


Fig. 2 – The average specific heat $\langle c \rangle$ of aqueous acetone and TMU in dependence of temperature t , obeying by MC simulations. Error bars are not shown.

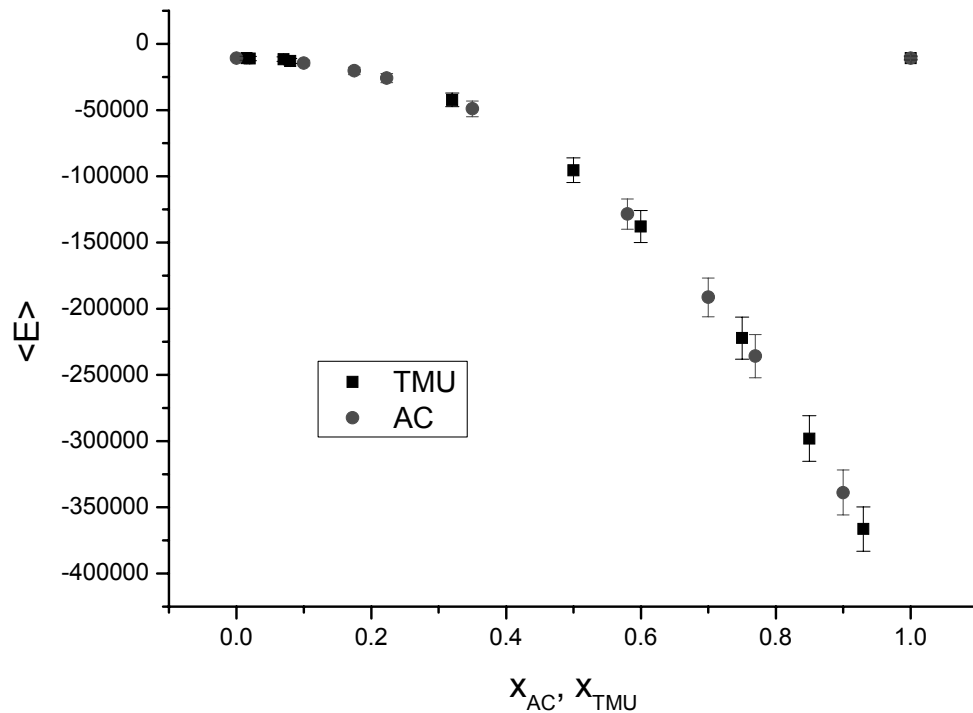


Fig. 3 – MC results for the dependence of average energy $\langle E \rangle$ on a molar fraction of aqueous acetone and TMU, relative units. Errors of MC are of the order of 0.3 %.

Fig. 5 shows the results of our MC tests, especially some typical disordered states at the Mixing Scheme II between the revealed transitions. Because of irrelevant number of empty

lattice sites, only two molecular variables 0 and 1 are visible here. The picture is similar for aqueous TMU as well. Regions with clustered acetone and clustered water molecules are clearly seen.

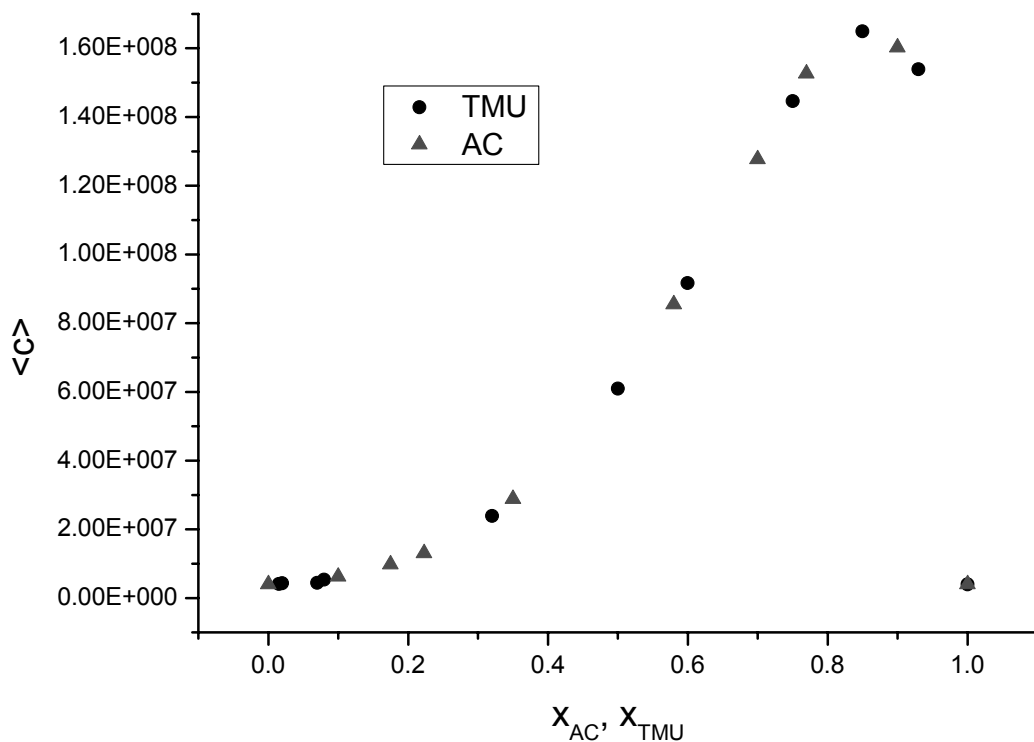


Fig. 4 – MC results for the dependence of average specific heat $\langle c \rangle$ on a molar fraction of aqueous AC and TMU. Here and at Fig. 3, points $x_{AC}=0.7, 0.9$ and $x_{TMU}=0.97, 0.85, 1.0$ are obtained by alignment of data.¹²

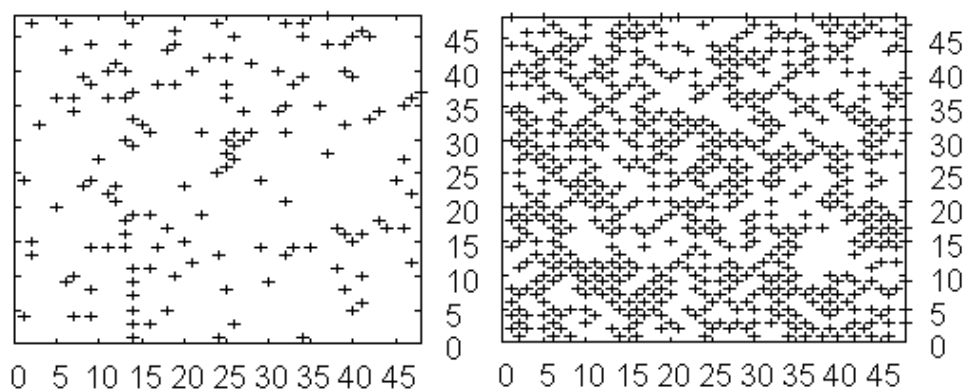


Fig. 5 – Mid slices of the simulation lattice $48 \times 48 \times 48$ for acetone in water, at molar fractions $x = 0.223$ (left), and $x = 0.770$ (right). Crosses stand for AC molecules, and empty spaces for water.

Also, for “I-II” transition in AC, the MC results have qualitative correspondence with the statements,¹³ obtained from the dielectric relaxation measurements and chemical analysis, that this is just the phase transition, connected with the second relaxation process at $x < 0.4$, at a reorientation of the water molecule, involving the disruption of the inter-molecular hydrogen bonds in the dense structure. It is however difficult to compare them directly because of the different temperatures, in which the chemical potentials were determined,^{12,13} experimental excess chemical potentials were reported, while their total values.¹³ For the system “water – acetone”, coincidence of the above calculated and reported¹² data for minimum of the free energy at $x \approx 0.8$ was revealed.

CONCLUSION

In polar aprotic solvents, the links with water are not strong, they are caused, in particular, by hydrogen bonding.¹² This paper answers the question about the role of this bonding in mesomorphism of the whole system. With regards to above statistical analysis, one may confirm the data on dielectric relaxation¹³ by revealing of the phase transition at high AC (and TMU) concentrations. Viz., at the lyotropic structure rearrangement, there is not a distinct phase transition in a system. Therefore, the expected structures stay beyond the Ising model description. Alternative computer modeling methods, such as Molecular Dynamics, where the artificial networks may be combined by oriented molecules and radicals, is actively used heretofore.¹⁴

In this problem, it is important to separate a knowledge on pure water aggregates (hydrogen networks and cluster structures^{3,4}) and on binary water mixtures (aqueous AC or TMU), comparison the behavior of hydrogen bonding in water with that in solutions may stimulate further advance in the theory of water. Other aqueous aprotic solvents might be also used to contribute such data. Using positron annihilation spectroscopy,^{15,16} also the electron density of the hydrogen bonding can be measured for systems of similar solvents, but in view of complexity of the water aggregation, such data are hard to interpret in frames of statistical analysis.

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