

Distinguishing Heteroaggregation from Homoaggregation in Mixed Binary Particle Suspensions by Multiangle Static and Dynamic Light Scattering

W. L. Yu[†]

Department of Chemistry, Clarkson University, Box 5814, Potsdam, New York 13699

M. Borkovec*

Department of Inorganic, Analytical, and Applied Chemistry, University of Geneva, 30, Quai Ernest-Ansermet, 1211 Geneva 4, Switzerland

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Time-resolved multiangle light scattering is used to measure absolute heteroaggregation (heterocoagulation) rate constants in aqueous binary colloidal particle mixtures. These measurements are possible despite the simultaneous occurrence of homoaggregation (homocoagulation). The procedure can be used with static as well as with dynamic light scattering, even though the latter technique is more accurate and more sensitive. The approach exploits the differences in the form factors of the asymmetric particles dimers. Particles of unequal size are therefore needed, but the method is sensitive already to 10% difference in size. We have applied the technique for latex particles in 100–200 nm size range, where the Rayleigh–Gans–Debye approximation is accurate, and obtained the formation aggregation (coagulation) rate constants for the asymmetric dimers as a function of the ionic strength up to 300 mM.

1. Introduction

While many studies deal with homoaggregation involving particles of the same type,^{1–7} heteroaggregation between particles of different size and properties is much more important in various applications, such as medicine, ceramics, filtration, flotation, and water purification.^{8–11} Despite the importance of heteroaggregation processes, however, careful experimental studies are scarce.^{12–14} The main reason is that homoaggregation and heteroaggregation do mostly occur simultaneously, and these processes are difficult to distinguish experimentally. Studies focusing on heteroaggregation processes have therefore often investigated somewhat artificial situations, for example, by choosing experimental conditions such that no homoaggregation occurs,^{12,13} or by selecting particles of the same size.^{15–17}

Another possibility to circumvent these difficulties is by exploiting the analogy between particle aggregation and particle deposition onto (quasi)-planar collectors. Deposition can be studied experimentally either in packed porous beds with chromatographic techniques,^{18–22} or on flat substrates by reflectometry²³ or microscopy.^{24,25} Deposition has often been used to mimic heteroaggregation processes, since the forces governing both processes are basically the same. However, in the diffusion controlled regime the analogy has its limits due to the different geometries.

While these approaches did provide some insight into heteroaggregation processes, there is an urgent need to develop reliable in-situ techniques for probing the formation of heteroaggregates without any interference from homoaggregates. In the present study we show that this aim can be achieved by modern multiangle light-scattering techniques.^{7,26,27} These techniques are capable of distinguishing homoaggregates from

heteroaggregates, and provide a straightforward means to measure heteroaggregation rate constant in various colloidal particle mixtures. We shall present, for the first time, reliable measurements of absolute heteroaggregation rate constants in a binary mixture of colloidal particles up to high ionic strengths, where homoaggregates and heteroaggregates do form simultaneously.

2. Experimental Section

Particle aggregation was monitored by an eight-angle fiber-optic static and dynamic light-scattering goniometer (ALV/CGS-8, Langen, Germany) using a krypton ion laser (Innova 301 at 647.1 nm, Coherent, CA) and eight parallel correlator channels. The angular resolution can be adjusted by rotating the goniometer during the run.

The particles used in this study were surfactant free, positively charged amidine and negatively charged sulfate lattices purchased from Interfacial Dynamics Corporation (Portland, OR). The original particle suspensions were extensively dialyzed against deionized water. The particle concentration of the suspension after dialysis was determined by static light scattering. Particle radii were measured in stable suspensions by static and dynamic light scattering yielding consistent values of 67 ± 1 nm for the amidine latex and 84 ± 1 nm the sulfate latex. The sign of the particle charge was checked by electrophoresis.

The aggregation in binary latex particle mixtures was studied in aqueous KCl solutions at pH 4 adjusted with HCl. The experiments were carried out at a total particle number concentration around 10^{14} m⁻³. The experiment was initiated by mixing both latex suspensions of appropriate concentrations in the cuvette (cleaned in boiling H₂O₂/H₂SO₄ mixture), and monitored by light scattering at 25.0 ± 0.1 °C. The data were typically accumulated for up to 1 h with a time resolution of

* To whom correspondence should be addressed. Phone: + 41 22 702 6405. Fax: + 41 22 702 6069. E-mail: michal.borkovec@unige.ch.

[†] Current address: Groton Laboratories, Pfizer, Inc., Groton, CT 06340.

25 s. The average diffusion coefficients were obtained by second order cumulant analysis. All experiments were carried out during the early stage of the aggregation process, as verified by extrapolation of the dynamic light-scattering data to time zero, and ensuring that the average diffusion coefficient did not decrease less than 20%. The apparent rate constants were obtained by linear fits of the time-dependent data in this time window.

3. Data Analysis

During the early-stage aggregation in a binary colloidal system with monomer particles A and B, three types of dimers AA, AB, and BB may form. Denoting the corresponding number concentrations of the monomers by $N_i(t)$ and of the dimers by $N_{ij}(t)$ (with $i, j = A, B$), their time evolution obeys the rate laws¹

$$\frac{dN_{AA}}{dt} = \frac{1}{2}k_{AA}N_A^2 \quad (1)$$

$$\frac{dN_{BB}}{dt} = \frac{1}{2}k_{BB}N_B^2 \quad (2)$$

$$\frac{dN_{AB}}{dt} = k_{AB}N_A N_B \quad (3)$$

where k_{AA} , k_{BB} , and k_{AB} are the corresponding rate coefficients to be determined.

In static light scattering, the aggregation kinetics can be monitored through the intensity of the scattered light $I(q, t)$, which depends on the time t and the magnitude of the scattering vector $q = (4\pi/\lambda)\sin(\theta/2)$ (where λ is the wavelength of the light in the medium, and θ is the scattering angle). In a dilute system, the scattering intensity is given by²⁶

$$I(q, t) = \sum_i I_i(q)N_i(t) + \sum_{i \geq j} I_{ij}(q)N_{ij}(t) \quad (4)$$

where $I_i(q)$ and $I_{ij}(q)$ are the static light-scattering intensities of the monomers and dimers, respectively. The apparent rate in the static light-scattering experiment can be obtained from eqs 1–4 and the corresponding mass balances. The result can be written as

$$\frac{1}{I(q, 0)} \frac{dI}{dt} \Big|_{t=0} = k_{AA}F_{AA} + 2k_{AB}F_{AB} + k_{BB}F_{BB} \quad (5)$$

where $I(q, 0)$ is the initial scattering intensity and

$$F_{ij} = N_0 x_i x_j \frac{I_{ij}(q) - I_i(q) - I_j(q)}{2[x_A I_A(q) + x_B I_B(q)]} \quad (6)$$

where N_0 is the initial total particle number concentration, and $x_i = N_i(0)/N_0$ are the respective number fractions.

In a dynamic light-scattering experiment, the aggregation process can be followed through the average translational diffusion coefficient. In a dilute suspension, this quantity is an intensity-weighted average²⁶

$$D(q, t) = \frac{\sum_i D_i I_i(q) N_i(t) + \sum_{i \geq j} D_{ij} I_{ij}(q) N_{ij}(t)}{\sum_i I_i(q) N_i(t) + \sum_{i \geq j} I_{ij}(q) N_{ij}(t)} \quad (7)$$

where D_i and D_{ij} are the corresponding diffusion coefficients of the monomers and dimers. The apparent rate from the

dynamic light-scattering experiment can be evaluated similarly as above, and reads

$$-\frac{1}{D(q, 0)} \frac{dD}{dt} \Big|_{t=0} = k_{AA}H_{AA} + 2k_{AB}H_{AB} + k_{BB}H_{BB} \quad (8)$$

where $H_{ij} = G_{ij} - F_{ij}$ with

$$G_{ij} = N_0 x_i x_j \frac{D_{ij} I_{ij}(q) - D_i I_i(q) - D_j I_j(q)}{2[D_A x_A I_A(q) + D_B x_B I_B(q)]} \quad (9)$$

and F_{ij} being given by eq 6.

These expressions can be easily evaluated within the Rayleigh–Gans–Debye approximation (RGD). The scattering intensity of a sphere of radius r_i is proportional to²⁸

$$I_i(q) \propto \frac{1}{q^6} [\sin(qr_i) - qr_i \cos(qr_i)]^2 \quad (10)$$

while for a dimer, the scattered light intensity can be obtained from

$$I_{ij}(q) = I_i(q) + I_j(q) + 2\sqrt{I_i(q)I_j(q)} \frac{\sin[q(r_i + r_j)]}{q(r_i + r_j)} \quad (11)$$

The average diffusion coefficient of the dimers D_{ij} can be expressed in terms of the dimensionless hydrodynamic coefficient defined as $\alpha_{ij} = 2/[D_{ij}(D_i^{-1} + D_j^{-1})]$, which can be accurately approximated at low Reynolds numbers as¹³

$$\alpha_{ij} \approx 1.39 + 0.61[(r_i - r_j)/(r_i + r_j)]^2 \quad (12)$$

4. Results and Discussion

Early-stage aggregation process in binary colloidal particle suspension was followed by time-resolved static and dynamic light scattering using a modern simultaneous multiangle setup. Particles used in this study are positively charged amidine latex particles of 67 nm in radius (particles A) and negatively charged sulfate latex particles of 84 nm (particles B) dispersed in KCl electrolyte solutions at pH 4. The aim is to show that multiangle static and dynamic light scattering can reliably measure the heteroaggregation rate despite the simultaneous formation of homoaggregates.

4.1. Pure Heteroaggregation. Since the particle charges are of opposite sign, electrostatic repulsion completely inhibits homoaggregation at low ionic strength, and only heteroaggregation between the different types of particles occurs. Figure 1a shows the apparent rate constants as a function of the scattering angle for different number fractions of the amidine latex particles $x_A = 0.5, 0.7$, and 0.9 at an ionic strength of 0.1 mM.

Figure 1a (top) shows the apparent rates from static light scattering, namely, the initial relative rate of change of the light-scattering intensity. No homoaggregation takes place, as can be deduced from the vanishing apparent rates in the pure systems. The nonzero apparent rates at intermediate number fractions are exclusively due to the formation of heteroaggregates AB, as further evidenced by the common crossing point of these curves at scattering angle 107° . The solid line is the result of the calculation based on RGD approximation. For the different curves, which correspond to different number fractions, we have obtained by nonlinear least-squares fit the heteroaggregation rate constant $k_{AB} = 5.42 \times 10^{-18} \text{ m}^3/\text{s}$. (The particle

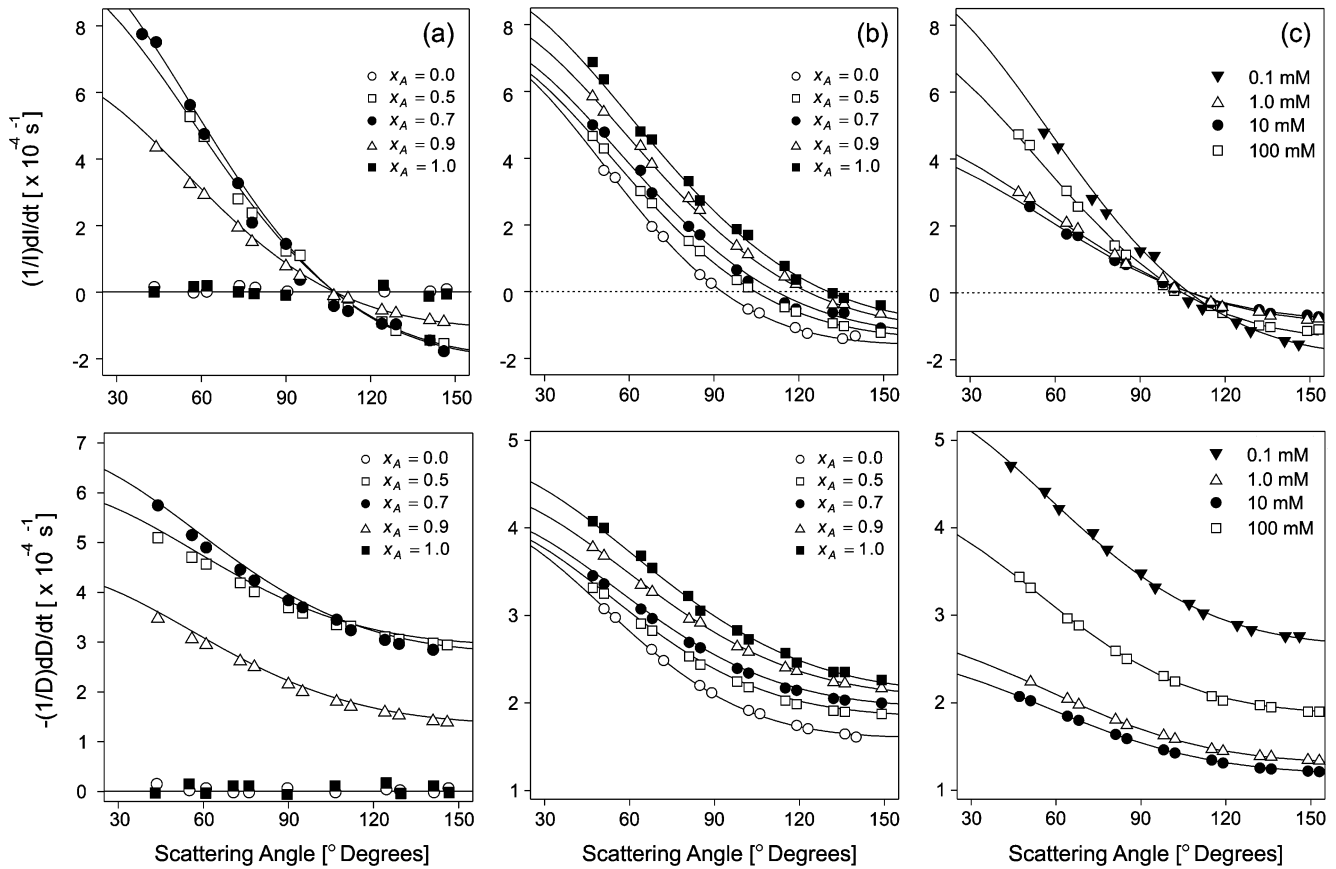


Figure 1. Apparent aggregation rates in binary mixtures of amidine (67 nm radius) and sulfate (84 nm radius) latex particles monitored by time-resolved multiangle static light scattering (top row) and dynamic light scattering (bottom row). The experimental data points are plotted as a function of the scattering angle, and compared with Rayleigh–Gans–Debye (RGD) theory (solid line). Various number fractions x_A of amidine latex at fixed ionic strength in KCl of (a) 0.1 mM (pure heteroaggregation) and (b) 100 mM (simultaneous homoaggregation and heteroaggregation). (c) Various ionic strengths at fixed number fractions $x_A = 0.5$ showing the transition from pure heteroaggregation to simultaneous homoaggregation and heteroaggregation.

TABLE 1: Absolute Aggregation Rate Constants k_{AA} , k_{BB} , and k_{AB} at Various Ionic Strengths Measured by Static Light Scattering (SLS) and Dynamic Light Scattering (DLS)

ionic strength [mM]	$k_{AA} [\times 10^{-18} \text{ m}^3 \text{ s}^{-1}]$		$k_{BB} [\times 10^{-18} \text{ m}^3 \text{ s}^{-1}]$		$k_{AB} [\times 10^{-18} \text{ m}^3 \text{ s}^{-1}]$	
	SLS	DLS	SLS	DLS	SLS	DLS
0.1	<0.01	<0.01	<0.01	<0.01	5.42	5.42
1	0.052	0.038	<0.01	<0.01	5.30	5.40
3	0.061	0.06	<0.01	<0.01	5.12	5.09
10	0.14	0.12	0.022	0.016	4.77	4.89
30	0.60	0.60	0.17	0.16	4.65	4.48
100	4.33	4.30	3.47	3.50	4.04	4.06
300	4.99	4.90	3.80	3.80	3.00	3.21

radii were set to the known values, see section 3.) The corresponding homoaggregation rate constants k_{AA} and k_{BB} are negligible within the experimental error (see Table 1).

Figure 1a (bottom) shows the apparent rate from dynamic light scattering, namely, the negative initial relative rate of change of the average diffusion coefficient. The lack of homoaggregation is again evidenced by the vanishing rate in the corresponding pure systems, and the nonzero apparent rate at intermediate number fractions solely due to the formation of heteroaggregates AB. The result is consistent with the corresponding calculation based on RGD approximation. For all the number fractions, only the heteroaggregation rate constant was fitted to $k_{AB} = 5.43 \times 10^{-18} \text{ m}^3/\text{s}$. The particle radii were set to the same values as above, and the hydrodynamic coefficient α_{AB} of the asymmetric dimer follows from eq 12 and was fixed to $\alpha_{AB} = 1.40$. The corresponding homoaggre-

gation rate constants k_{AA} and k_{BB} are again zero within the experimental error. The results are fully consistent with static light scattering (see Table 1). More details on the case of pure heteroaggregation can be found elsewhere.^{12,13}

4.2. Simultaneous Homoaggregation and Heteroaggregation. At higher ionic strengths, however, homoaggregation and heteroaggregation processes occur simultaneously. Figure 1b shows the corresponding light-scattering data as a function of the scattering angle at an ionic strength of 100 mM.

Figure 1b (top) shows the apparent rate from static light scattering. The fact that homoaggregation and heteroaggregation occurs simultaneously is manifested by a nonzero apparent rate in the pure systems, but also through the absence of a common crossing point. Fitting the two curves in the pure systems individually, we obtain the homoaggregation rate constants of $k_{AA} = 4.33 \times 10^{-18} \text{ m}^3/\text{s}$ and $k_{BB} = 3.47 \times 10^{-18} \text{ m}^3/\text{s}$. The data in the mixed systems can be fitted by $k_{AB} = 4.04 \times 10^{-18} \text{ m}^3/\text{s}$ (see Table 1). Thus, we have succeeded to extract the heteroaggregation rate constant although homoaggregation is occurring simultaneously.

The corresponding dynamic light-scattering data are shown in Figure 2b (bottom). The presence of homoaggregation and heteroaggregation is again evidenced by a nonzero apparent rate in the pure systems. Fitting these two curves individually, we obtain the homoaggregation rate constants of $k_{AA} = 4.26 \times 10^{-18} \text{ m}^3/\text{s}$ and $k_{BB} = 3.44 \times 10^{-18} \text{ m}^3/\text{s}$, whereby we have fixed the relative hydrodynamic radius of the symmetric dimer $\alpha_{AA} = \alpha_{BB} = 1.39$. The latter value follows from eq 12 and is

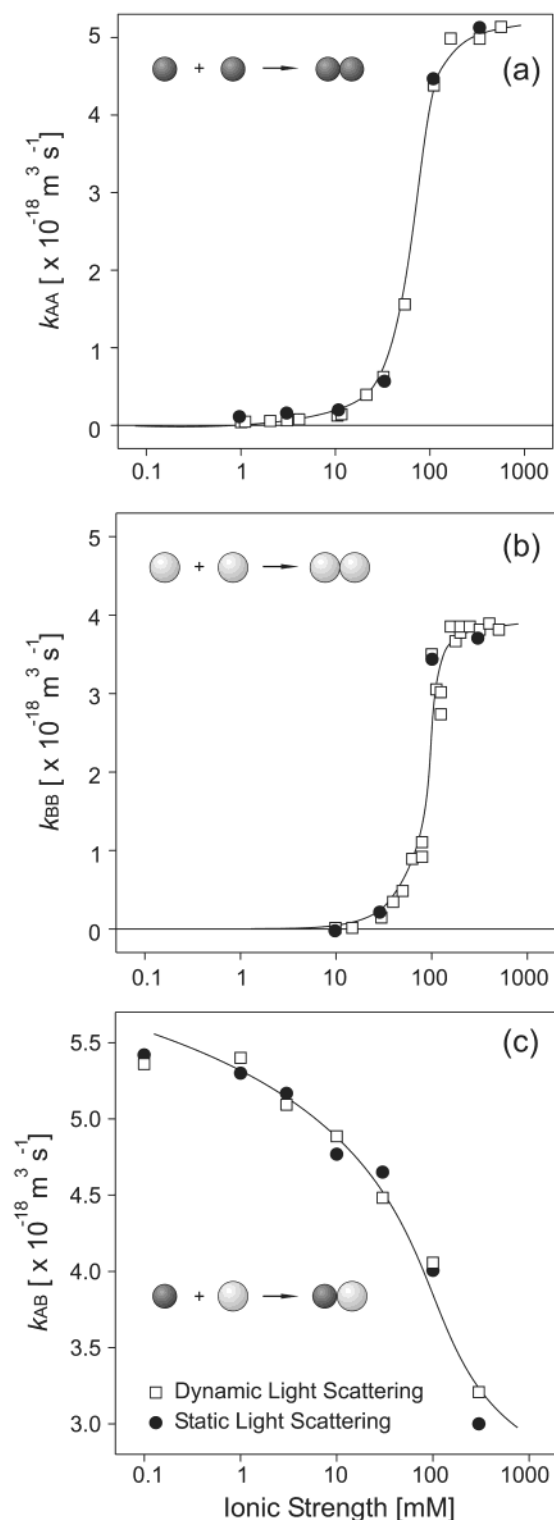


Figure 2. Aggregation rate constants obtained from static and dynamic light scattering as a function of the ionic strength. (a) Homoaggregation of amidine and (b) sulfate latex. (c) Heteroaggregation between these particles. Solid lines serve to guide the eye only.

well established experimentally and theoretically.^{26,27} The data in the mixed systems at different number fractions can be fitted with $k_{AB} = 4.06 \times 10^{-18} \text{ m}^3/\text{s}$. The resulting heteroaggregation rate constant is in accord with the value obtained from static light scattering (see Table 1). The good agreement indicates that the heteroaggregation rate constants can be accurately measured despite the simultaneous occurrence of homoaggregation.

4.3. General Procedure for the Measurement of Heteroaggregation Rate Constants. We now have an experimental technique at hand, which is capable to measure absolute heteroaggregation rate constants in binary colloidal particle mixtures, irrespective of the eventual simultaneous occurrence of homoaggregation. Due to better accuracy, dynamic light scattering is the method of choice. The combination of static and dynamic light scattering has the obvious advantage as the results can be checked for mutual consistency.

To determine the heteroaggregation rate constants in binary colloidal particle mixtures, the absolute rate constants in the corresponding pure systems must be known. Such measurements can be carried out by fitting the corresponding light-scattering data in the pure systems with RGD theory as done here, or by any alternative methods for the measurement of these constants.²⁷ With results for homoaggregation at hand, heteroaggregation rate constants can be determined. While in principle a single suitably chosen number fraction suffices for the analysis, in practice it is advantageous to study several number fractions as a means to obtain error estimates. By performing such measurements for different solution conditions, one can reliably measure the heteroaggregation rate constants as a function of various parameters (e.g., ionic strength and pH).

Let us illustrate this method by measurements of heteroaggregation rate constants in the present system as a function of ionic strength. Absolute homoaggregation rate constants were measured in the corresponding pure systems by fitting multi-angle static and dynamic light-scattering data with RGD theory (see Table 1 and Figure 2a,b). The additional data points shown in the figures were determined by conventional time-resolved dynamic light scattering.^{3,4,6,7}

With these results at hand, absolute heteroaggregation rates can be measured. Figure 1c shows the apparent rate constants obtained from static and dynamic light scattering for different ionic strengths (0.1, 1, 10, and 100 mM), and at fixed number fraction of amidine particles $x_A = 0.5$. With the known homoaggregation rate constants, the heteroaggregation rate constants were extracted independently from static and dynamic light scattering as above, and the results of these (and additional) experiments are summarized in Table 1 and Figure 2c. The results obtained from static and dynamic light scattering are again in very good agreement, giving good confidence to the method. With increasing ionic strength the observed heteroaggregation rate constant decreases due an increase of the screening of the electrostatic attraction between oppositely charged particles, but has not yet reached the expected plateau value. These findings are in line with the few available experimental measurements of heteroaggregation rates.^{12,16,18}

5. Conclusion

Heteroaggregation rate constants in binary colloidal particle mixtures can be reliably measured with time-resolved multiangle light scattering even in the presence of homoaggregation. While the procedure can be used with static as well as with dynamic light scattering, the latter is far superior in accuracy and sensitivity. The technique explores the differences in the form factors of the different particles dimers, and therefore particles of different size are required. As shown here, however, already a 10% difference in size suffices. Presently, we have applied the technique for latex particles in 100–200 nm size range for which RDG theory is accurate. The technique can be extended to cover a wider range of larger particle sizes and size disparities, but the dimer form factors must be estimated based on more sophisticated computational techniques.²⁶

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