

Rheological Properties of Highly Swollen Hydrogel Suspensions

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SYNOPSIS

The shear rheology of diluted to concentrated suspensions of weakly cross-linked sodium polyacrylate hydrogels were investigated by concentric cylinder rheometry. The size of the swollen gel particles is dependent on the initial size of the dry particle and on the nature of the added salt. Polyvalent salts are more efficient for contracting the swollen particles than monovalent ones. When suspended in water or in monovalent salt solutions, the viscosity at low concentrations shows a behaviour very similar to the one of flexible polymer solutions. Below the critical overlap concentration, the viscosity is independent of shear rate. The intrinsic viscosity is very large, on the order of 10–15 dL/g. This is in agreement with the large size of these swollen particles. Suspensions of such swollen gel particles are thus a good model for extremely high molecular weight polymer solutions. In polyvalent salt solutions different behaviour of the viscosity curves versus concentration was observed. This effect is caused by chemical cross-linking of the hydrogel by polyvalent ions. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Polyelectrolyte hydrogels have several interesting physical and chemical properties. For example, they show an extremely large volume change when the ionic strength, composition, and pH of the media or the strength of an external electric field is changed.^{1,2} They may find applications in oil recovery and in wastewater treatment.^{3,4}

Well-defined particles of polyelectrolyte hydrogels can be prepared. Their suspensions are a good model for highly swollen particles, but their rheological properties have been not systematically investigated.⁵ The purpose of this work was to start such an investigation and to compare the rheology of these suspensions with the one of a flexible polymer solution.

EXPERIMENTAL

The polymer used for this investigation is a weakly cross-linked sodium polyacrylate. It was obtained by free radical polymerization of acrylic acid in an aqueous solution using water soluble allylcarboxymethylcellulose with a degree of substitution of 0.40 of allyl groups, acting as a cross-linking agent. The synthesis has been described elsewhere.⁶ Polymer samples were washed in water and subjected to hydrolysis in a 0.1M NaOH solution. The degree of equilibrium swelling of the gel purified by washing out the excess alkali was 1000 g/g. In order to obtain a dry polymer, the hydrolysed gel was treated with excess ethyl alcohol, vacuum dried over P₂O₅, and ground in a ball mill. Three fractions of the dry powdered polymer, with particle size $d_1 = 50\text{--}60\ \mu\text{m}$, noted 60 μm ; $d_2 = 120\text{--}160\ \mu\text{m}$, noted 140 μm ; and $d_3 = 300\text{--}500\ \mu\text{m}$, noted 300 μm , were prepared. Suspensions were prepared by mixing at room temperature the dry particles with a fluid, either water or

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a salt solution. Monovalent ($K_3 [Fe(CN)_6]$, $Na_2S_2O_3$) and polyvalent ($CuSO_4$, $CoSO_4$, $NiSO_4$) metal salt solutions were investigated.

The viscosity of the hydrogel suspensions was investigated with two concentric cylinder rotational viscometers, Rheotest and Viscometer of Low Viscosities (VLV) (Institute of Petrochemical Synthesis, Moscow) with intercylinder gaps of, respectively, 1.24 and 2.30 mm. Measurements performed with the two rheometers gave identical results for the same fluid under identical conditions. The viscosity of the suspensions in water and aqueous salt solutions was also measured with an Ubbelohde viscometer with a capillary diameter of 2 mm.

RESULTS

When the hydrogel was mixed with water, a large swelling of about 10⁵% occurred. The addition of a salt contracted the swollen gel. This contraction was measured by a contraction degree, α , defined as the ratio of the sample weight in the salt solution to its weight in water in the equilibrium swollen state. The dependence of α on salt concentration C_s for several metal salts is given in Figure 1. As shown in a previous study,⁷ the amount of salt per weight of polymer in the solution is very important. As the ratio

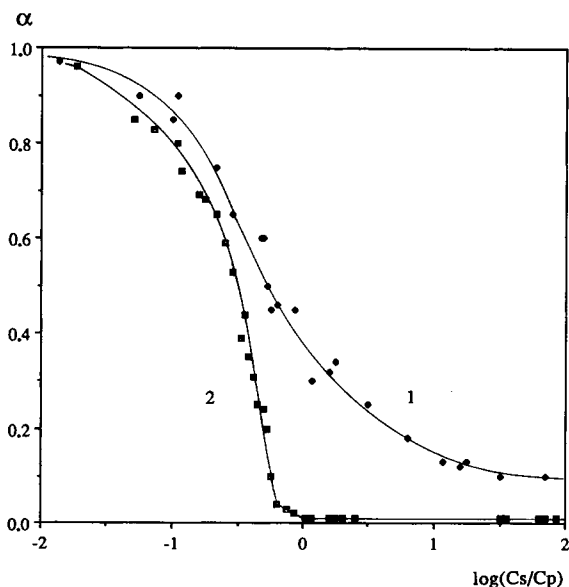


Figure 1 The dependence of the hydrogel degree of contraction, α , on salt concentration, C_s/C_p , for the salts of univalent metals $K_3[Fe(CN)_6]$ and $Na_2S_2O_3$ (curve 1) and polyvalent metals $CuSO_4$, $CoSO_4$, and $NiSO_4$ (curve 2). The concentrations are calculated in moles/litre.

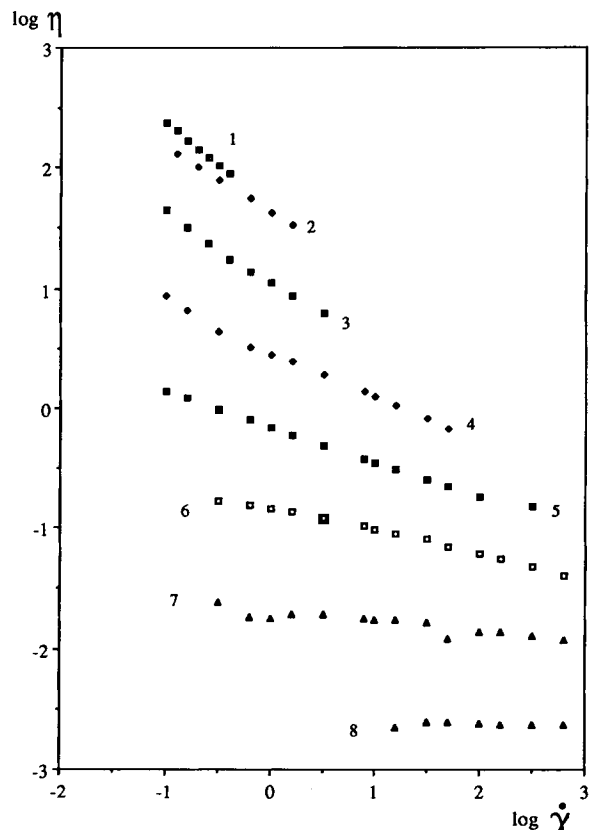


Figure 2 The dependence of viscosity, η , of the hydrogel suspension ($d_1 \approx 60 \mu m$) in water on shear rate, $\dot{\gamma}$, for different polymer concentrations: 0.63% (1); 0.39% (2); 0.20% (3); 0.14% (4); 0.1% (5); 0.074% (6); 0.046% (7); 0.016% (8).

C_s/C_p (C_p being the polymer concentration in the system) increases, a smooth contraction of the hydrogel occurs in the solutions of monovalent metal salts (curve 1, Fig. 1). However the residual swelling is still rather large, in excess of 100 g/g.

The behaviour was different in the solutions of polyvalent metal salts (curve 2, Fig. 1). The cross-linking of the hydrogel by polyvalent ions did not occur at low salt concentration and the contraction was weak. When the polyvalent metal salt concentration increased, a sharp collapse of the hydrogel took place. This was due to the cooperative effect of an avalanche-like increase of the polyvalent ions, cross-linking the hydrogel. For high concentrations of the polyvalent metal salts, the hydrogel collapsed 100-fold or more to a practically "dry" state.

The hydrogel can be prepared as a powder and suspended in water. Figure 2 shows the dependence of the viscosity, η , on shear stress for several suspensions of the 60- μm particles. The concentration

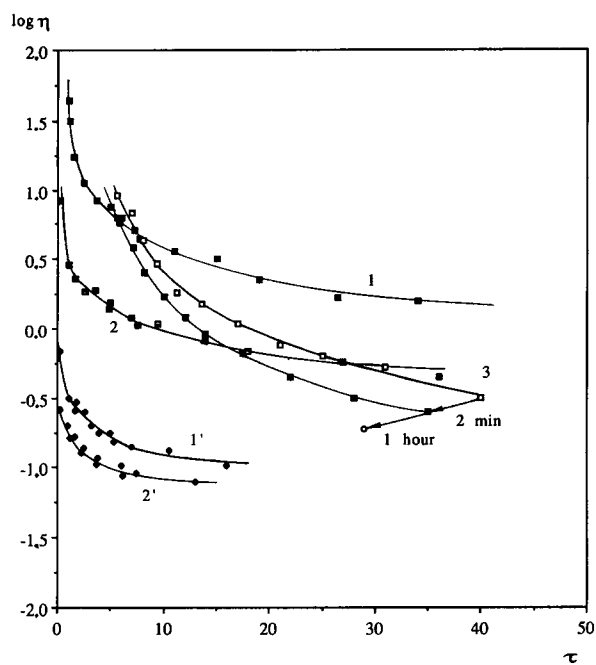


Figure 3 The dependence of viscosity, η , of the hydrogel suspensions in water on the shear stress τ (measured on two rotational viscometers) for different fractions: $d_1 \approx 60 \mu\text{m}$: 0.2% (1) and 0.1% (1'); $d_2 \approx 140 \mu\text{m}$: 0.2% (2) and 0.1% (2'); $d_3 \approx 300\text{--}500 \mu\text{m}$: 0.2% (3) (the change of viscosity with time is shown by arrows).

ranges from 0.046 to 0.63%. The viscosity was measured with the VLV rheometer. The equilibrium degree of swelling being 1000, the diameter of the largest swollen particles is about $600 \mu\text{m}$, smaller than the 2.5-mm gap of the rheometer. For the two lowest concentrations, the viscosity is independent of shear rate. The 0.074 and 0.1% suspensions show a Newtonian plateau at low shear rates and the beginning of a nonlinear regime at high shear rates. The suspensions with a concentration larger than 0.1% are shear thinning, with a power law index, m , increasing with concentration; m ranges from 0.63 for $C_p = 0.14\%$ to 0.24 for $C_p = 0.63\%$.

The most noticeable feature is the very large increase of the viscosity with the concentration. A 10-fold increase in concentration induces a 10,000-fold increase in viscosity. For the suspensions in water, the critical concentration, C^* , above which contact occurs at rest between particles, is about 0.1%, because the swelling is 10^3 . This can be observed visually, "free" water being present below 0.1%. The two lowest concentrations are thus in a diluted state while the others are in a semidilute state.

Figure 3 shows a comparison between the viscosities of the three fractions. Low stress values were obtained with the VLV rheometer, high stress values

with the Rheotest. In the overlap range, the two rheometers gave identical results. The shape of the 60- and 140- μm particle flow curves are very similar. The most noticeable result is that the viscosity of the 140- μm particles is lower than the one of the 60- μm particles in the whole range of investigated shear stresses.

The dependence of the viscosity of hydrogel suspensions with particle size $300 \mu\text{m}$ in water on shear stress was measured with the Rheotest rheometer. For the 0.2% concentration the dimension of the swollen particles is between 1.2 and 2.5 mm, which is larger than the size of the gap between the cylinders. Due to this, a mechanical degradation of the swollen particles takes place for the highest values of shear stress. For the suspensions of dry particles of 60 and 140 μm size, no degradation is noticeable after 1 h of shearing.

A closer look at the influence of the size of the dry particles is given in Figure 4. The viscosity is measured by capillary rheometry and is expressed by the relative viscosity, η_{rel} , η_{rel} being the ratio of the viscosity η of the suspension over the viscosity η_0 of the solvent. The comparison between the concentric cylinder rheometers and the capillary rheo-

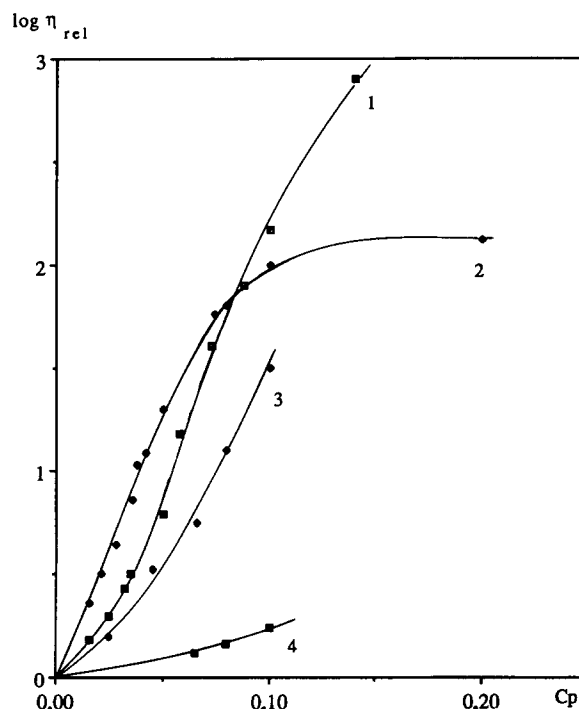


Figure 4 The dependence of the relative viscosity, η_{rel} , of the hydrogel suspensions in water-salt solutions on polymer concentration C_p : for $d_1 \approx 60 \mu\text{m}$ in water (1); 0.01% Na_2SO_4 (3); 0.1% Na_2SO_4 (4); and for $d_2 \approx 140 \mu\text{m}$ in water (2).

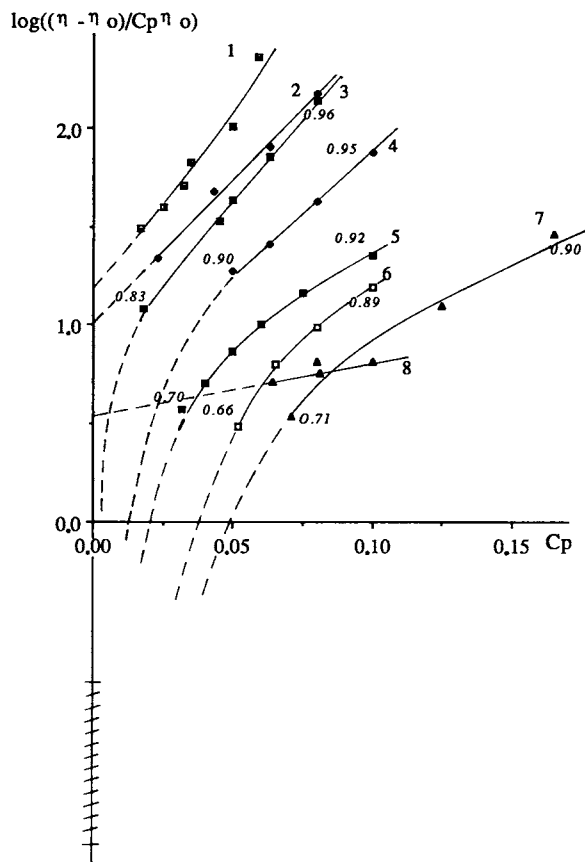


Figure 5 The dependence of $\log[(\eta - \eta_0)/\eta_0 C_p]$ of the hydrogel suspensions with $d_1 \approx 60 \mu$ on polymer concentration in the water-salt solutions: H₂O (1); 0.01% Na₂SO₄ (2); 0.0025% CuSO₄ (3); 0.01% CuSO₄ (4); 0.015% CuSO₄ (5); 0.025% CuSO₄ (6); 0.030% CuSO₄ (7); 0.100% Na₂SO₄ (8).

meter is good, given that the shear rate in the capillary rheometer is about 10^2 s^{-1} . Figure 4 shows that the viscosity of the 60- μm particle suspensions is lower than the 140- μm ones at concentrations lower than 0.1%. Above 0.1%, the viscosity of the 60- μm particle suspensions is larger than at 140- μm , as shown also in Figure 3.

The influence of a salt has been investigated and the results are shown on Figures 4 and 5. In Figure 4, the 60- μm suspension is studied in 0.01 and 0.1% Na₂SO₄ solutions. The relative viscosity of the suspension drops dramatically as the salt concentration increases. In Figure 5, $(\eta - \eta_0)/\eta_0 C_p$, C_p being the polymer concentration in g/dL, is plotted as a function of C_p for several aqueous salt solutions of Na₂ and CuSO₄. The first salt is monovalent and the contraction behaviour follows curve 1 in Figure 1 and CuSO₄ corresponds to curve 2, with a sharp contraction occurring at $C_s/C_p = 0.1$. For water and

Na₂SO₄ salt, $\log[(\eta - \eta_0)/\eta_0 C]$ versus C_p is linear. For CuSO₄, it is linear for $C_s < 0.01\%$ (or $C_s/C_p \leq 0.1$) and not linear above this salt concentration.

DISCUSSION

Different conditions have been studied, with the polymer particles suspended in water, in monovalent salts and in polyvalent salts. The rheological behaviour of the polymer particles at low concentrations suspended in water is very similar to the one of flexible coiled polymers in a solvent. As a chain in its statistical sphere, the swollen particle occupies a large volume with a very small polymer concentration. The diluted suspensions are Newtonian and the semidiluted ones have a Newtonian plateau followed by a shear thinning region, in the investigated range of shear rates.

There is a strong influence of the critical concentration $C^* \approx 0.1\%$ on the rheological behaviour. At a given concentration, in the diluted state, the viscosity is larger when the size of the particle is larger (Fig. 4), as for flexible coils when increasing molecular weight. Above C^* , the viscosity behaviour as a function of the size changes, the viscosity decreasing with the size. This points out an important difference with flexible polymers: for flexible chains, all the volume described by the mean radius of gyration is not physically occupied by the chain and above C^* , in the semidiluted state, contacts between chains are infrequent and their main effect is to screen some interchain interactions.⁸ For swollen particles, they indeed occupy all their volume, and interparticle contacts are numerous above C^* . If we define an interparticle contact surface, this surface increases when the particle size decreases. The larger this contact surface, the larger is the interparticle viscous dissipation. This mechanism can be at the origin of the behaviour above C^* , where the viscosity increases when decreasing the size of the particle.

In the diluted state, in water and monovalent salt solutions, Figure 5 shows that $\log[(\eta - \eta_0)/\eta_0 C_p]$ is linear when plotted against C_p . Extrapolation to infinite dilution is legitimate and gives an intrinsic viscosity $[\eta]$ of 15.6 dL/g for the 60- μm particles in water, 10 for Na₂SO₄, 0.01%, and 3.5 for Na₂SO₄, 0.1%. A comparison with flexible polymers would mean an extremely high molecular weight, which makes sense considering the very high degree of swelling, and thus the low concentration of polymer in the swollen particle. As an example, the molecular weight of a very flexible polymer (say polyethylene) necessary for having such a low concentration of

0.001 g/cm³ in its statistical sphere is in excess of 10⁹.

The dependence of η on C_p can be written in the form of the Martin equation⁹:

$$\log\left(\frac{\eta - \eta_0}{\eta_0 C_p}\right) = \log[\eta] + \frac{K_m}{2, 3} C_p[\eta] + \dots \quad (1)$$

K_m is a constant that expresses the hydrodynamic interactions between the particles. K_m is found to be ~ 2 from Figure 5. Such high values have been reported for several polymer solutions and dispersion of rigid spherical particles.¹⁰

Because the notion of intrinsic viscosity is valid, it is interesting to test the scaling used for flexible polymers. In Figure 6, the dependence of $\log \eta_{rel}$ on $C_p[\eta]$ for suspensions in water and monovalent salt solutions is given. As for solutions of linear polymers, a single curve can be observed, although the variations of $[\eta]$, 5 times, and of η_{rel} , 100 times for the same C_p , are wide. Comparison of this generalized curve η versus $(C_p[\eta])$ with the known theoretical correlations¹¹ shows that in the area of $C_p[\eta] > 1.5$, the experimental data lie lower than the theoretical curve. This may be caused by the effects of the viscosity dependence on the rate of strain and (or) by the virtual association of flowing particles accompanied by their deformation.

The experimental curve follows:

$$\log \eta_{rel} = 0.38(C_p[\eta]) + (C_p[\eta])^2. \quad (2)$$

For the hydrogel suspensions in the polyvalent metal salt solutions (CuSO₄) the dependence of $\log[(\eta - \eta_0)/\eta_0 C_p]$ on C_p are not linear. Such an unexpected result may be explained by taking into consideration the dependence of the degree of hydrogel contraction in polyvalent metal salt solutions versus the initial salt concentration. Indeed, during the dilution of the hydrogel suspension by the salt solution the ratio C_s/C_p increases. When $C_s > C_p$ the chemical cross-linking of hydrogel by polyvalent ions occurs. It leads to the sharp deviation of the curve $\log[(\eta - \eta_0)/\eta_0 C_p]$ versus C_p from the straight line and makes it impossible to use the concept of intrinsic viscosity. In Figure 5 the values of α calculated from Figure 1 are given. In the investigated range of concentrations, α varies from 0.99 to 0.66. Therefore, because of the shape of the curves $\log[(\eta - \eta_0)/\eta_0 C_p]$ versus C_p , when $\alpha < 0.8$, the values of $[\eta]$ cannot be obtained. In this case, they should fall in the shaded interval in Figure 5. This value at the top of this interval is calculated for hydrogel par-

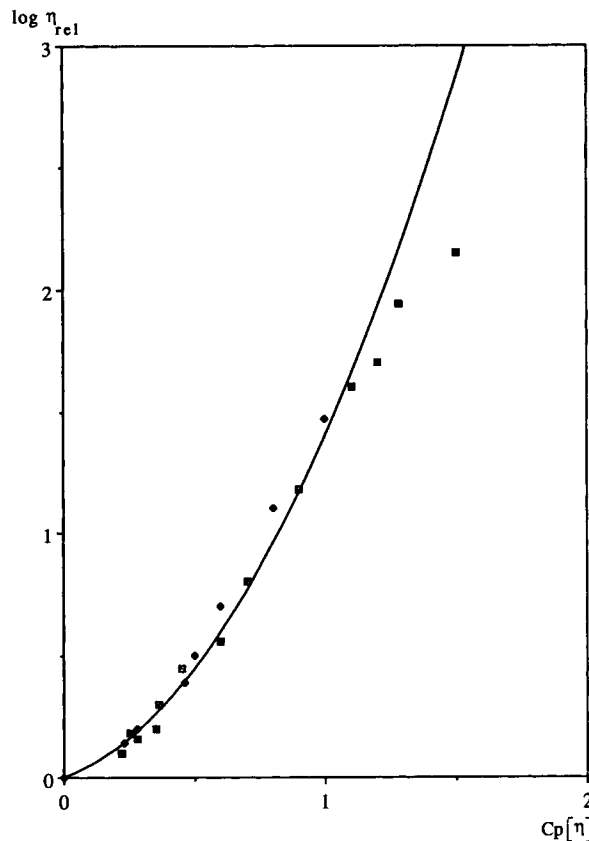


Figure 6 The dependence of $\log \eta_{rel}$ on $C_p[\eta]$. The theoretical curve is shown by a line.

ticles contracted 100 times. The value at the bottom of this interval is 0.025 dL/g, being $[\eta]$ for rigid spherical particles.

The observed differences in the behaviour of the hydrogel in the solution of salts of mono- and polyvalent metals can also be understood by a difference in the cross-linking mechanisms. The chemical cross-linking of the polymer by the polyvalent ions, with the formation of water insoluble compounds, leads not only to the suppression of the polyelectrolyte swelling, but also to the suppression of the "ordinary" network swelling. For the hydrogel in univalent metal salt solutions the network swelling mechanism (which corresponds to non hydrolysed gels) remains. That is why the contraction in these solutions is reversible¹² and α decreases only 10 times.

The sharp collapse of the hydrogel in the polyvalent metal salt solutions where the polymer falls to sediment is analogous to the behaviour of the partially hydrolysed polyacrylamide in Ca(NO₃)₂ solutions.¹² A similar phase separation in this system was also observed: at low salt concentrations poly-

acrylamide is well dissolved, and at high concentrations a separation in two phases took place.

CONCLUSION

The steady-state viscosity behaviour of highly swollen hydrogel suspensions in water and monovalent metal salt solutions at low polymer concentrations is very similar to flexible polymer solutions. The possibility of easily varying the size of the swollen particles by adding different salts opens the way for a more extended study of the detailed influence of the size on the rheological properties, including oscillatory, transients, and normal stresses.

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