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Stabilization of colloidal silica using small polyols.

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Abstract:

We have discovered that small polyols are reasonably effective at stabilizing colloidal silica against aggregation, even under the conditions of high pH and salt concentration. Both quasielastic and elastic light scattering were used to show that these polyols dramatically decrease the aggregation rate of the suspension, changing the growth kinetics from diffusion-limited cluster-cluster aggregation to reaction-limited cluster-cluster aggregation. These polyols may be useful in the treatment of tank wastes at the Hanford site.

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DISCLAIMER

Introduction

The Hanford site in Washington has numerous tanks containing solidified mixed waste material in the form of fractal aggregates. The highly aggregated nature of these materials has made their viscosity too high to easily transfer these wastes through the available pipelines. Thus preprocessing steps, such as dilution and comminution, will be necessary to reduce the waste viscosity. We are looking for ways to stabilize these materials from further aggregation, and to prevent reaggregation after comminution, that require very little addition of chemicals, so that they may be transferred through pipes to other tanks or to processing sites that will incorporate these wastes into borosilicate glass logs. We have developed a model colloidal silica suspension that mimics some aspects of these waste materials and the conditions of high pH and salt under which they are found. The tanks wastes are typically highly basic, and are several molar in salt.

Standard methods of colloidal stabilization include charge stabilization and steric stabilization. Charge stabilization requires that the colloids are far from their isoelectric point, so they have a large surface charge density. If the solvent in which they are suspended is at low ionic strength, the Debye layer will be very thick, and a significant Coulombic barrier will have to be overcome before the colloids can collide and fall into a deep, attractive van der Waals well. Clearly at the high salt concentration of the tank wastes, this is not a practical approach to stabilization. Steric stabilization uses high polymers to create so-called "hairy balls", which repel each other due to the large free energy of mixing of high polymers, much of which is due to the entropy term.

We were quite surprised to discover that low molecular weight polyols can also be surprisingly effective at stabilizing colloidal silica at high pH and multimolar salt concentrations. We have explored the homologous series of polyols; ethylene glycol, glycerin, erythritol, 1,3 propanediol, and 1,4 butanediol. These were added in various concentrations to our silica suspension and the aggregation kinetics were monitored with quasielastic light scattering (QELS). In these experiments we determined the time for a 200 nm radius aggregate to form, as a function of polyol concentration. We found that the time required to form such large aggregates increases exponentially with the stabilizer concentration, and that some polyols are much more effective than others. In general, the more hydrophilic the polyol, the better it stabilized our system. Studies of the salt and pH dependence of stabilization show that the necessary amount of stabilizer needed to achieve a target growth kinetics increases with both salt and pH.

In these experiments, the salt concentration is sufficiently high that the aggregation is diffusion limited. This was confirmed by elastic light scattering measurements that show the expected dimension $D = 1.74 \pm 0.07$ for the diffusion-limited cluster-cluster aggregation (DCLA) universality class [1]. Additionally, we observe the expected power-law growth kinetics of this class. After the polyol stabilizers are added, the fractal dimension changes to, and the growth kinetics becomes exponential in time, both of which are indicative of the reaction-limited cluster-cluster aggregation (RCLA) universality class [2].

Experimental

Our model colloidal silica suspension consists of colloidal silica in a basic solution containing a pH buffer and NaCl. Ludox SM-30 with a particle diameter of 8 nm was used as a silica source, and diluted from a 30 wt.% solution in water. The final silica concentration used in these experiments was 0.052 wt. %. Two buffered solutions were used with pHs of 8.5 and 10; the former was prepared with a borax-HCl solution and the latter with a borax-NaOH solution. The NaCl concentrations used were 1.0 M, 2.0 M, and 3.0 M.

The stabilizers used are a homologous series of polyols, Fig. 1, that vary in the number of carbons in a linear chain and the number of hydroxyl groups. Erythritol is a chain of 4 carbons and has 4 hydroxyl groups; glycerin has 3 carbons and 3 hydroxyl groups while ethylene glycol has 2 carbons and 2 hydroxyl groups. 1,3 propanediol consist of 3 carbons but only 2 hydroxyl groups while 1,4 butanediol consists of 4 carbons and 2 hydroxyl groups.

For each polyol, correlation functions were collected to determine the cluster radius as a function of time. These experiments were carried out until the aggregate had reached a radius larger than 200 nm. A plot of the radius versus time could then be fitted and the fit used to determine the time τ at which the aggregate had reached a size of 200 nm. A subsequent plot of this aggregation time τ versus polyol concentration was then made for each stabilizer.

A He-Ne laser operating at a wavelength of 632.8 nm was used as a light source and a BI-9000 AT digital autocorrelator was used to collect the correlation functions.

Kinetic Rate Equation

Before discussing the experimental results, it is helpful to review some elementary aspects of aggregation. A useful tool for investigating the kinetics of growth of aggregates is the Smoluchowski or kinetic rate equation, which provides a basis for classifying growth processes[3]. This equation relates the time evolution of the number of m-mers, *N(m)*, in terms of a reaction kernel K_{ij}. This reaction kernel gives the probability of an *i*-mer reacting with a *j*-mer.

$$\frac{dN(m)}{dt} = \frac{1}{2}\sum_{\substack{i,j \\ i+j=m}} N(i)K_{ij}N(j) - N(m)\sum_{j} K_{mj}N(j)$$

The first term takes into account the creation of *m*-mers through the collision of *i*-mers and *(m-i)*-mers while the second term accounts for the destruction of *m*-mers due to collisions with other clusters. The growth kinetics and size distributions of aggregates can vary depending on the relative sizes of clusters reacting with one another, such as having large clusters sticking to large clusters or small clusters sticking to large clusters. If the dominate process is small interacting with large, the size distribution tends to be bell shaped; if the dominate interaction is large interacting with large, a monotonically decreasing size distribution is obtained[4].

The kinetic rate equation qualitatively predicts three types of growth behavior: power-law, exponential, and gelling. These classes can be defined by two exponents λ and ν. Let the probability that a *j*-mer reacts with a *j*-mer (large interacting with large) be $K_{jj} \sim j^{\lambda}$ and the probability that a *j*-mer interacts with a monomer (large interacting with small) is $K_{1j} \sim j^{\nu}$. If the kernels have either $\lambda > 2$ or $\nu > 1$, the system is unphysical because the reactivity increases more rapidly than the cluster mass *j*. If the system has $\lambda > 1$, the kinetic rate equation predicts gelation, since an infinite cluster will form in a finite amount of time. If $\lambda \leq 1$, an infinite cluster forms in an infinite amount of time thus giving non-gelling behavior. The work herein is mainly concerned with diffusion-limited and reaction-limited conditions. In diffusion-limited conditions, interactions among small and large aggregates dominate and the kernels to the kinetic rate equation have ν less than one and λ is less than ν. Diffusion-limited conditions best describe systems displaying power-law growth. Reaction-limited conditions have neither small-large or large-large interactions as being dominant. Kernels in this regime have $\lambda = \nu \leq 1$ which show the exponential growth in time which is relevant to reaction-limited conditions. A more detailed discussion of the various growth behaviors can be found in work by Martin, *et al*[5].

Quasielastic Light Scattering

Quasielastic light scattering (QELS) was used to study the growth behavior of the aggregating colloidal silica suspension. This technique enables the determination of the cluster size over a much broader range than elastic light scattering. In QELS the radius of an object can be determined from the relaxation time associated with translational diffusion. The intensity $I(q,t)$ of the scattered light is autocorrelated to obtain the homodyne correlation function $C(t) = \langle I(q,0)I(q,t)\rangle$ [6]. The dynamic structure factor $S(q,t)$ can then be obtained from the Siegert relation

$$S(q,t) = [C(t) - \langle I(q,0)I(q,\infty)\rangle]^{1/2}$$

For a system of monodisperse spheres the dynamic structure factor is $S(q,t) = S(q)\exp(-q^2 D_t t)$ where $S(q)$ is the static structure factor, $D_t = kT/6\pi\eta R_h$ is the translational diffusion coefficient, and R_h is the hydrodynamic radius. Physically, the particle will diffuse a distance of $1/q$ during the relaxation time $\tau = 1/q^2 D_t$. An important factor to consider is whether one is in the regime where $qR_h << 1$ or $qR_h >> 1$. If $qR_h >> 1$,then other motions may contribute to the scattering. For example, the rotational motion of a rigid rod of length R can contribute to the observed relaxations in the regime $qR_h >> 1$. Also, in the case of a flexible polymer, configurational relaxations can contribute to the dynamic structure factor in this regime. In our silica system, only translational motion contributes to the dynamic structure factor when $qR_h << 1$ since there is no depolarized scattering. We then observe the dynamic structure factor due to translational diffusion where the static structure factor $S(q)$ is that of the fractal aggregate. In this case the first cumulant

$\Gamma \equiv -d\ln S(q,t \to 0)/dt$, becomes $q^2 D_t$, where D_t is a polydispersity averaged diffusion coefficient.

Aggregating systems are polydisperse, and the effects of polydispersity on the dynamics must be taken into account by averaging the correlation function, $S(q,t) = \int_0^\infty m^2 N(m) S_m(q,t) dm$ over the ensemble[7]. Here *N(m)* is the number of *m*-mers in the aggregate ensemble. The average first cumulant is then related to the so-called z-averaged diffusion coefficient.

$$\Gamma / q^2 = \int_0^\infty D_t(m) m^2 N(m) S_m(q) dm \Big/ \int_0^\infty m^2 \, N(m) S_m(q) dm$$

The subscript z denotes the z average, which is the average of a quantity over $m^2 N(m)$. The z-average hydrodynamic radius, R_z, can then be obtained from the relation $D_z = kT/6\pi\eta R_z$. For a detailed discussion of the regime $qR_z >> 1$ again see the paper by Martin *et al*[5].

Growth Kinetics

We are interested in reducing the aggregation rate as much as possible, so , experiments were carried out to see which among our series of homologous molecules slowed down aggregation the most. Once the best stabilizer was found, experiments at various pHs and salt concentrations were performed using only this stabilizer. Each experiment determines when the radius of the aggregate is 200 nm. Without the addition of a polyol, the base colloidal silica suspension takes approximately 200 s to reach an aggregate size of 200 nm in radius.

Fig. 2 displays the experimental results for erythritol with concentrations ranging from 0 M to 0.025 M. The presence of the polyol slows down the growth dramatically. The growth is linear with time when the erythritol concentration is 0 M, but the growth quickly changes over to exponential when the erythritol is added. Comparing the 0.012 M and 0.025

M curves, shows that it takes approximately 4 times as long to form a 400 nm radius aggregate when the concentration of erythritol has increased by a factor of 2.

The results of all of the polyols are in Fig. 3 which is a plot of time in seconds for the 200 nm radius aggregate to form versus concentration of polyol in mol/l. Erythritol is by far the best stabilizer, in that it takes by far the smallest amount to produce the greatest amount of stabilization. There seems to be very little difference in the stabilizing ability of 1,3 propanediol and ethylene glycol, although the 1,3 propanediol seems to be slightly better. In general, the more hydrophilic the polyol, the better it stabilizes. In Fig. 3, one can see that it takes approximately 2000 s for a 200 nm aggregate to form with a 0.01 mol/l concentration of erythritol. To produce the same growth kinetics, the concentration of glycerin needs to be almost three times as much and five times as much for 1,3 propanediol and ethylene glycol. If we look at forming a 200 nm radius aggregate in 8000 s, it takes a 0.025 mol/l concentration of erythritol and a 0.05 mol/l concentration of glycerin. As for 1,3 propanediol, a concentration of about 0.167 mol/l is necessary to achieve this same stabilization, and ethylene glycol is not far behind with a concentration of 0.18 mol/l. The stabilization properties of 1,4 butanediol were investigated, but the concentrations necessary were far too large to include in the results presented here.

We studied stabilization at a pH of 10 with erythritol, the best stabilizer. The results in Fig.4 shows the amount of stabilizer necessary increases dramatically. For example, to produce a 200 nm radius aggregate at a concentration of 0.01 mol/l of erythritol takes approximately 2000 s at a pH of 8.5. If the pH is 10 instead, a concentration of 0.215 mol/l is necessary to produce the same size aggregate at 2000 s. At an erythritol concentration of 0.025 mol/l and a pH of 8.5, an aggregate requires approximately 8000s to form, but at a pH of 10, a concentration of 0.25 mol/l is necessary to produce the same stabilization.

The effects of raising the salt concentration were studied next and again, erythritol was the only polyol studied. In Fig.5 a plot of aggregation time versus concentration of erythritol for 1.0 M, 2.0 M, and 3.0 M salt is shown. In general one notices that as the salt concentration goes up, a concomitant increase in erythritol concentration in necessary. From the original 1.0 M curve, one can see that at an erythritol concentration of 0.01 mol/l, the aggregate took 2000s to reach its 200 nm radius. If the salt concentration is increased to 2.0 M, a concentration of 0.10 mol/l is necessary and 0.17 mol/l in the 3.0 M case to produce the same stabilizing effect. If we move to higher concentrations of erythritol in the 1.0 M salt case, the 200 nm aggregate took 8000 s to form at a concentration of 0.025 mol/l. In the 2.0

M salt case, the concentration necessary to stabilize the aggregate was 0.125 mol/l and in the 3.0 M case, 0.205 mol/l.

Fractal Dimension

The elastic light scattering behavior of our model colloidal silica suspension indicates the expected mass fractal structure, in which the radius R increases with the mass M as $M \sim R^D$, where D is the fractal dimension. This fractal nature is due to the way in which the aggregates grow; smaller clusters collide to form larger clusters and these collide to form even larger clusters and so on.

In cluster-cluster aggregation models, there are two universality classes depending on the sticking probability. In diffusion-limited cluster-cluster aggregation regime the sticking probability is one and the fractal dimension is $D \cong 1.75$. The growth of these aggregates is power law with time. In the reaction-limited cluster-cluster aggregation regime, the sticking probability approaches zero and the fractal dimension is $D \cong 2.1$. In the reaction-limited case, the growth is exponential in time and the clusters are more compact than those in the diffusion-limited case.

Measuring the fractal dimension of our colloidal silica suspension was done by elastic light scattering techniques. In this technique, the intensity I is determined as a function of 1/q, where $q = \frac{4\pi}{\lambda}\sin(\theta/2)$. In a coherent scattering process for a monodisperse solution, the intensity per unit concentration c is a measure of the average mass in a box of length 1/q. For the regime 1/q<< R, the mass fractal relation $M \sim R^D$ can be used to obtain the expression $I/c \sim 1/q^D$. Once the length $1/q$ approaches the radius R of the aggregate, the scattering behavior changes over to the Porod result $I \sim 1/q$ [8]. The fractal nature of these aggregates can only then be observed in the regime $r << 1/q << R$.

In our experiments, we compared the nature of the growth kinetics before and after the stabilizer has been added and then determined the fractal dimensions in both of these cases to see if the dimensions are consistent with the known models of aggregation. Fig. 6 shows a plot of the growth of our base colloidal silica suspension as a function of time and it can be seen clearly that the growth is linear with time. From ELS experiments the fractal dimension for this system was determined to be $D = 1.74 \pm 0.07$. This is shown in Fig. 7 and is consistent with previous work on fast aggregating silica systems that has also shown that this type of growth is independent of the concentration of silica[5]. When one of the polyols is present, the growth kinetics changes over to exponential behavior as can be seen from Fig. 8 which shows a plot of the growth of our system versus time when 0.028 M glycerin has been added. When ELS was performed on this system, the fractal dimension was determined to be $D = 2.05 \pm 0.07$, which is shown in Fig. 9. Again this is consistent with the fractal dimension found for reaction-limited cluster-cluster aggregation[5].

Conclusions

We have shown that small polyols are surprisingly effective at reducing the rate of aggregation of colloidal silica at high pH and salt concentration. Erythritol turned out to be the best stabilizer by far, by virtue of its having the largest number of hydroxyl groups, and 1-4 butanediol, being far less hydrophilic, had essentially no stabilizing effect. The other stabilizers were of intermediate efficacy, indicating that the hydrophilicity is the dominate characteristic that determines stabilizing effectiveness. These hydroxyl groups apparently interact with siloxyl groups on the cluster surface, and alter the interactions between colloidal silica particles.

Both quasielastic and elastic light scattering experiments indicate that these stabilizers change the growth kinetics from diffusion-limited to reaction-limited cluster-cluster aggregation. An increase in the pH or salt concentration causes an increase in the amount of polyol necessary to produce stabilization. The addition of small amounts of erythritol should help in the prevention of aggregation of the waste materials in the Hanford waste site or in the reaggregation after these materials have been sheared.

References

1. P. Meakin, *Phys. Rev. Lett.* **51**, 1119 (1983).
2. D. W. Schaefer, J. E. Martin, P. Wiltzius and D. S. Cannell *Phys. Rev. Lett.* **52,**2371 (1984).
3. M. von Smoluchowski, *Z. Phys. Chem.* **92**, 129 (1917), *Phys. Z.* **17**, 585 (1916)
4. P. G. van Dongen and M. H. Ernst, *Phys. Rev. Lett.* **54**, 1396 (1985)
5. J. E. Martin, J. P. Wilcoxon, D. Schaefer, J. Odinek, *Phys. Rev. A*, **41,** 4379 (1990).
6. B. J. Berne and R. Pecora, *Dynamic Light Scattering* (Wiley, New York, 1976)
7. .J. E. Martin and B. J. Ackerson, *Phys. Rev. A* **31**, 1180 (1985).
8. J. E. Martin, *Phys. Rev. A* **36**, 3415 (1987).

Figure Captions

1.) Molecular structures of the homologous series of polyols used in our stabilization experiments.

2.) Aggregation curves for various concentrations of erythrtiol showing the decrease in the aggregation rate as the erythritol concentration increases. Similar families of curves were generated for each of the polyols.

3.) Aggregation curves for all of the polyols. Each curve represents the growth time for the aggregate to reach 200 nm in radius at a particular concentration of polyol. Erythritol and glycerin slow down the aggregation rate the most.

4.) Dependence of the concentration of erythritol on change in pH of the buffer solution. The pH changes from 8.5 to 10 and the change in erythritol concentration necessary to produce stabilization increases by a factor of 10.

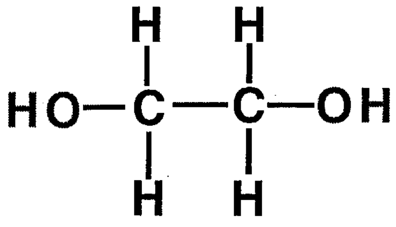
5.) Dependence of erythritol concentration on change in salt concentration. The salt concentration is increased from 1.0 M to 2.0M then to 3.0M.

6.) Power law growth of the unstabilized colloidal silica suspension without polyols..

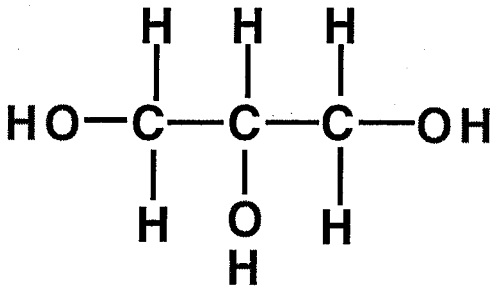
7.) Elastic light scattering results showing the fractal dimension $D = 1.74 \pm 0.07$ of the unstabilized colloidal silica suspension.

8.) Exponential growth behavior of the base colloidal silica suspension when a polyol has been added. In this plot the stabilizer used was glycerin.

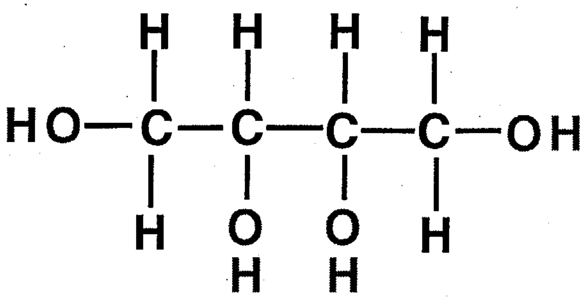
9.) Elastic light scattering results of the fractal dimension $D = 2.05 \pm 0.07$ of the colloidal silica suspension when a stabilizer has been added



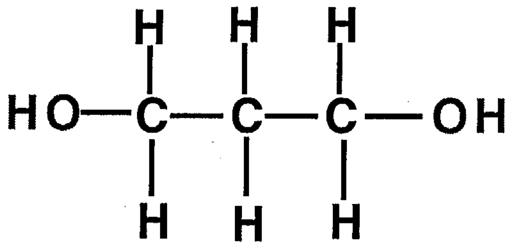
Ethylene Glycol



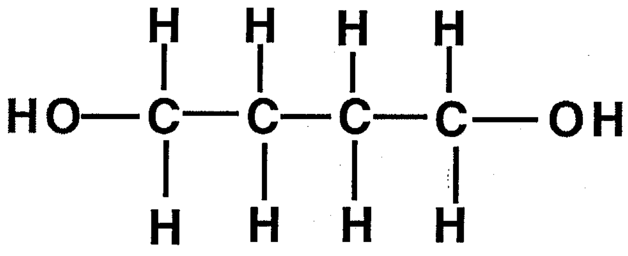
Glycerin



Erythritol



1,3 - Propanediol



1,4 - Butanediol

Legend

C	Carbon
OH	Alcohol Group
H	Hydrogen

Fig. 1

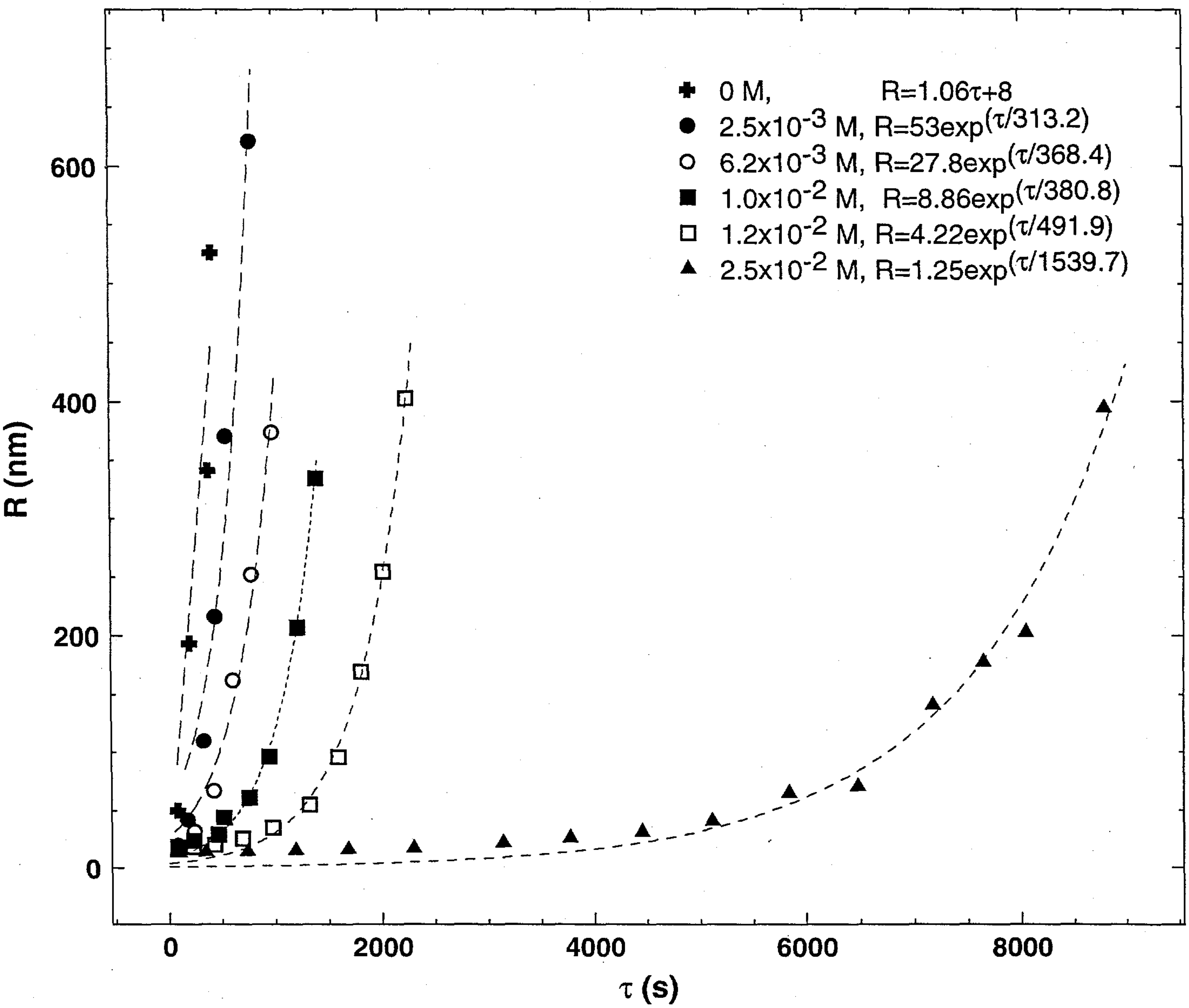

✚ 0 M, R=1.06τ+8
● 2.5x10^{-3} M, R=53exp$^{(τ/313.2)}$
○ 6.2x10^{-3} M, R=27.8exp$^{(τ/368.4)}$
■ 1.0x10^{-2} M, R=8.86exp$^{(τ/380.8)}$
□ 1.2x10^{-2} M, R=4.22exp$^{(τ/491.9)}$
▲ 2.5x10^{-2} M, R=1.25exp$^{(τ/1539.7)}$
R (nm)
600
400
200
0
0
2000
4000
6000
8000
τ (s)

Fig. 2

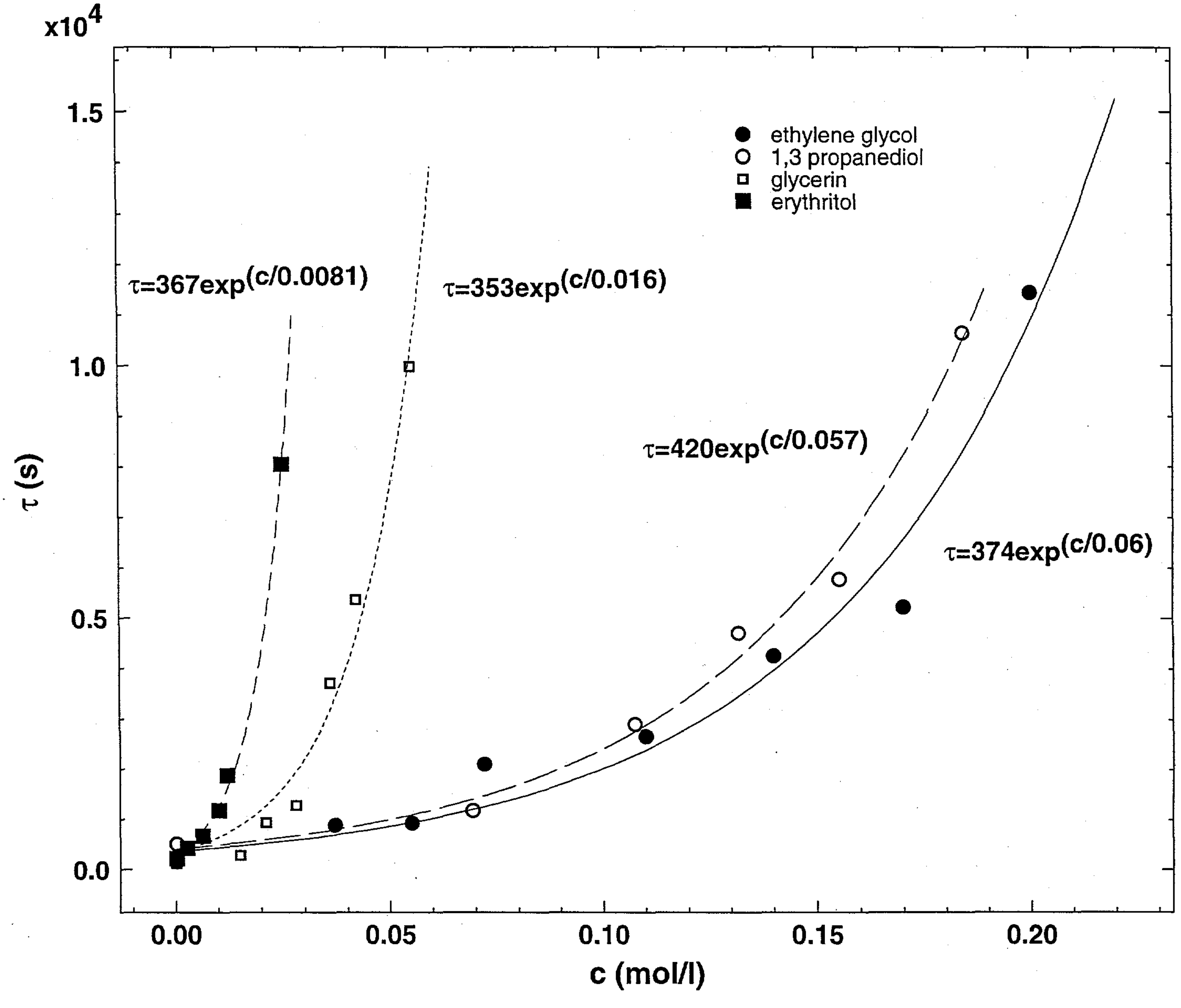

x10^4
1.5
1.0
0.5
0.0
τ (s)
0.00
0.05
0.10
0.15
0.20
c (mol/l)
● ethylene glycol
○ 1,3 propanediol
□ glycerin
■ erythritol
τ=367exp(c/0.0081)
τ=353exp(c/0.016)
τ=420exp(c/0.057)
τ=374exp(c/0.06)

Fig. 3

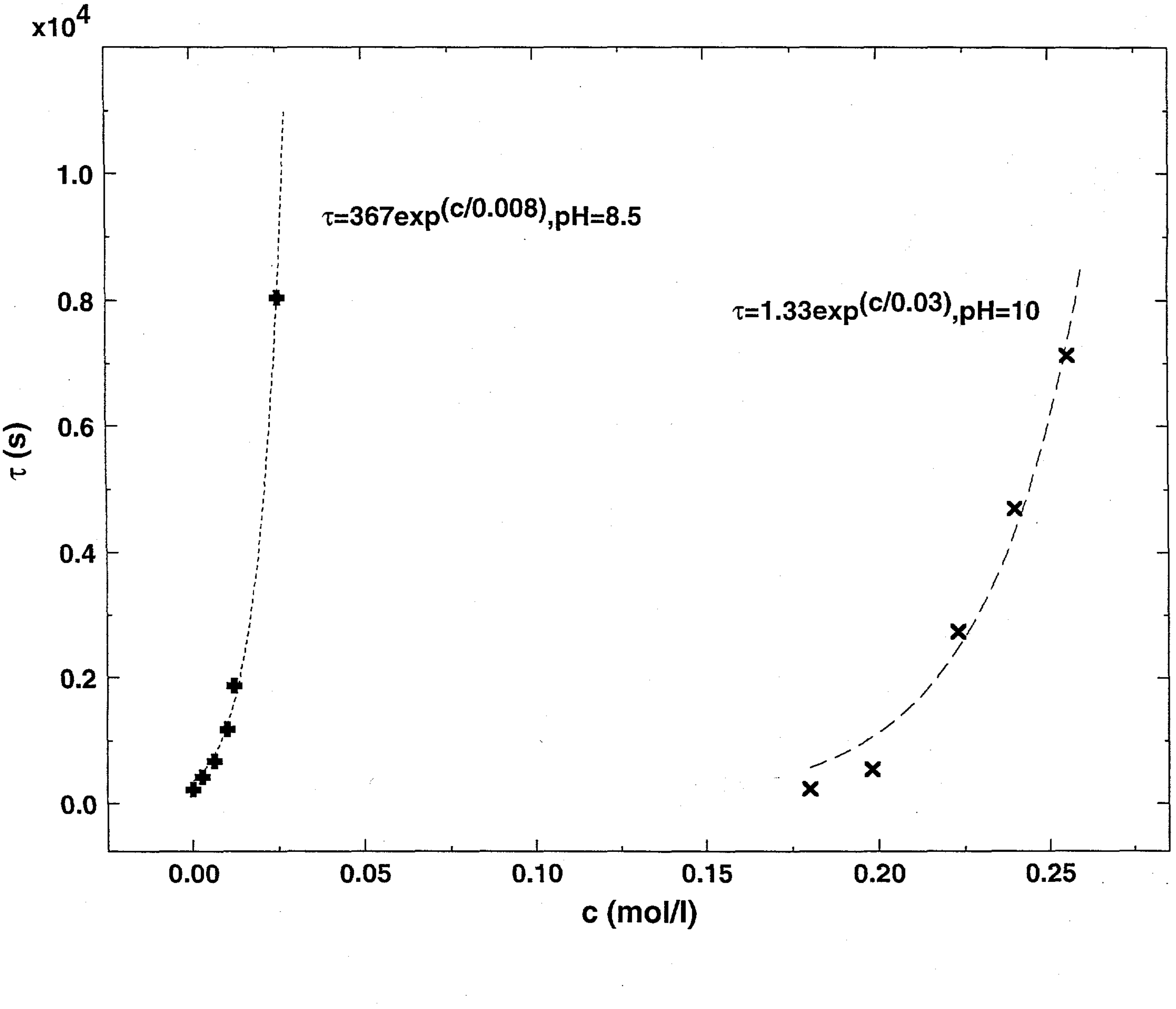

x10^4
1.0
0.8
0.6
0.4
0.2
0.0
τ (s)
τ=367exp(c/0.008),pH=8.5
τ=1.33exp(c/0.03),pH=10
0.00
0.05
0.10
0.15
0.20
0.25
c (mol/l)

Fig. 4

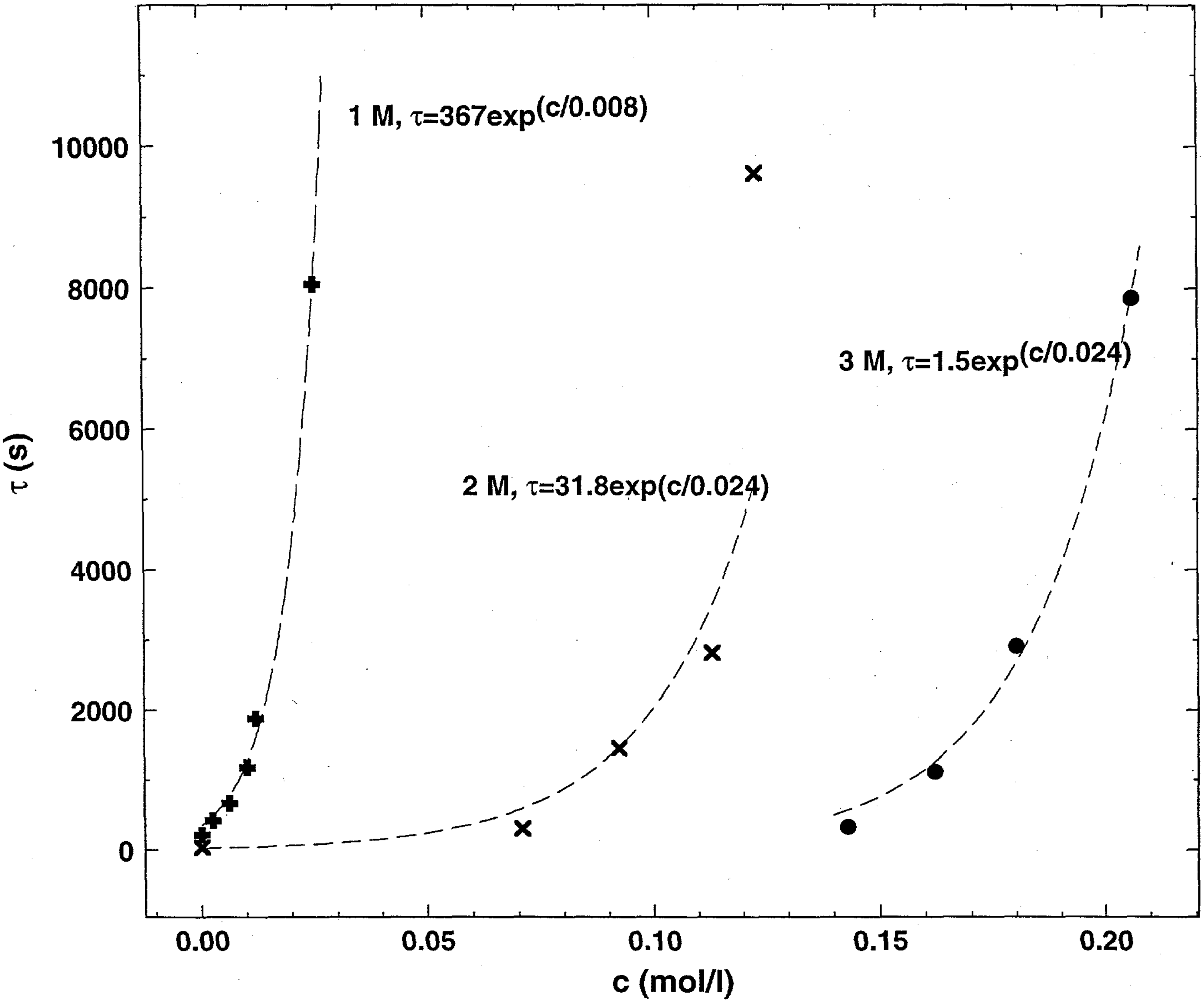

1 M, τ=367exp(c/0.008)
2 M, τ=31.8exp(c/0.024)
3 M, τ=1.5exp(c/0.024)
τ (s)
10000
8000
6000
4000
2000
0
0.00
0.05
0.10
0.15
0.20
c (mol/l)

Fig. 5

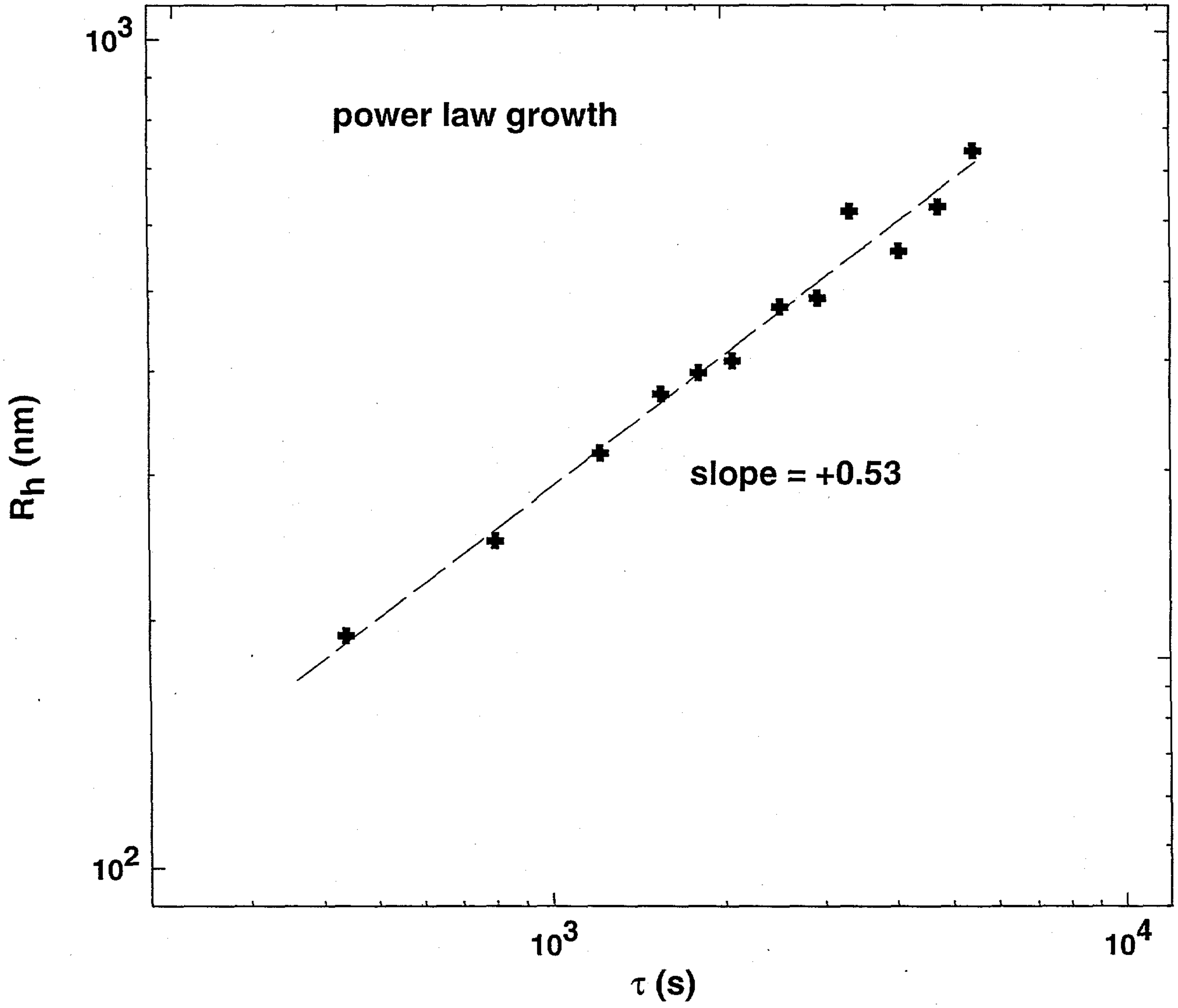


Fig. 6

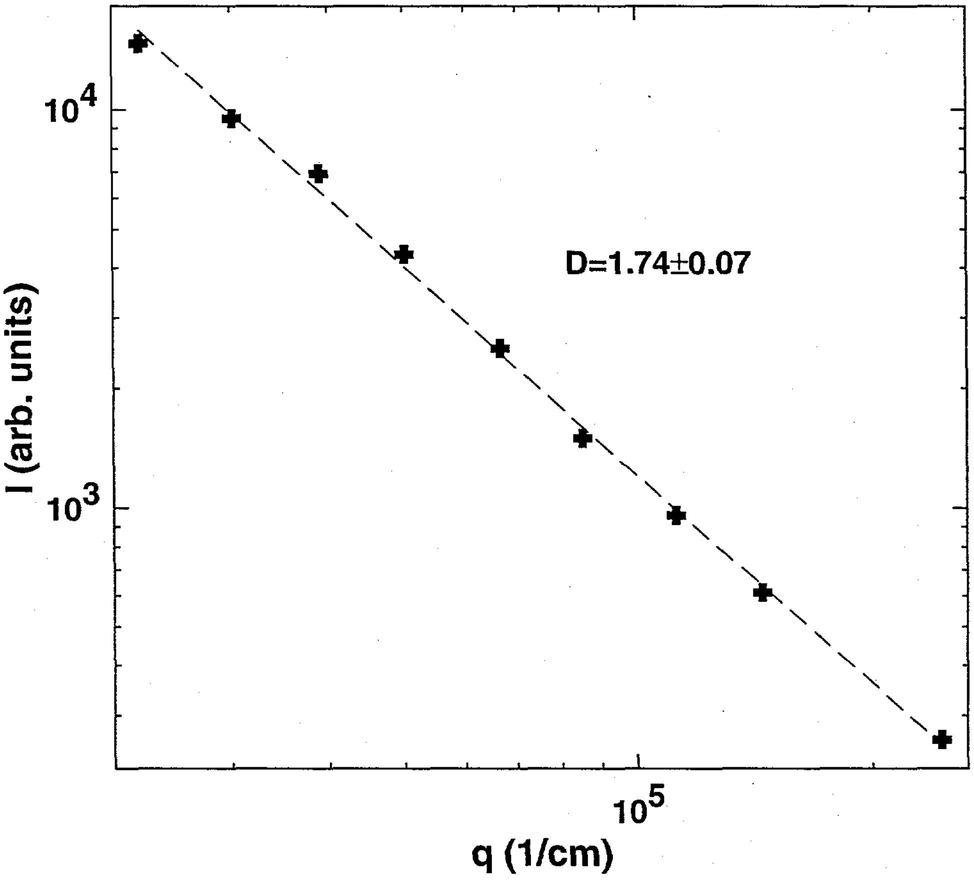


Fig. 7

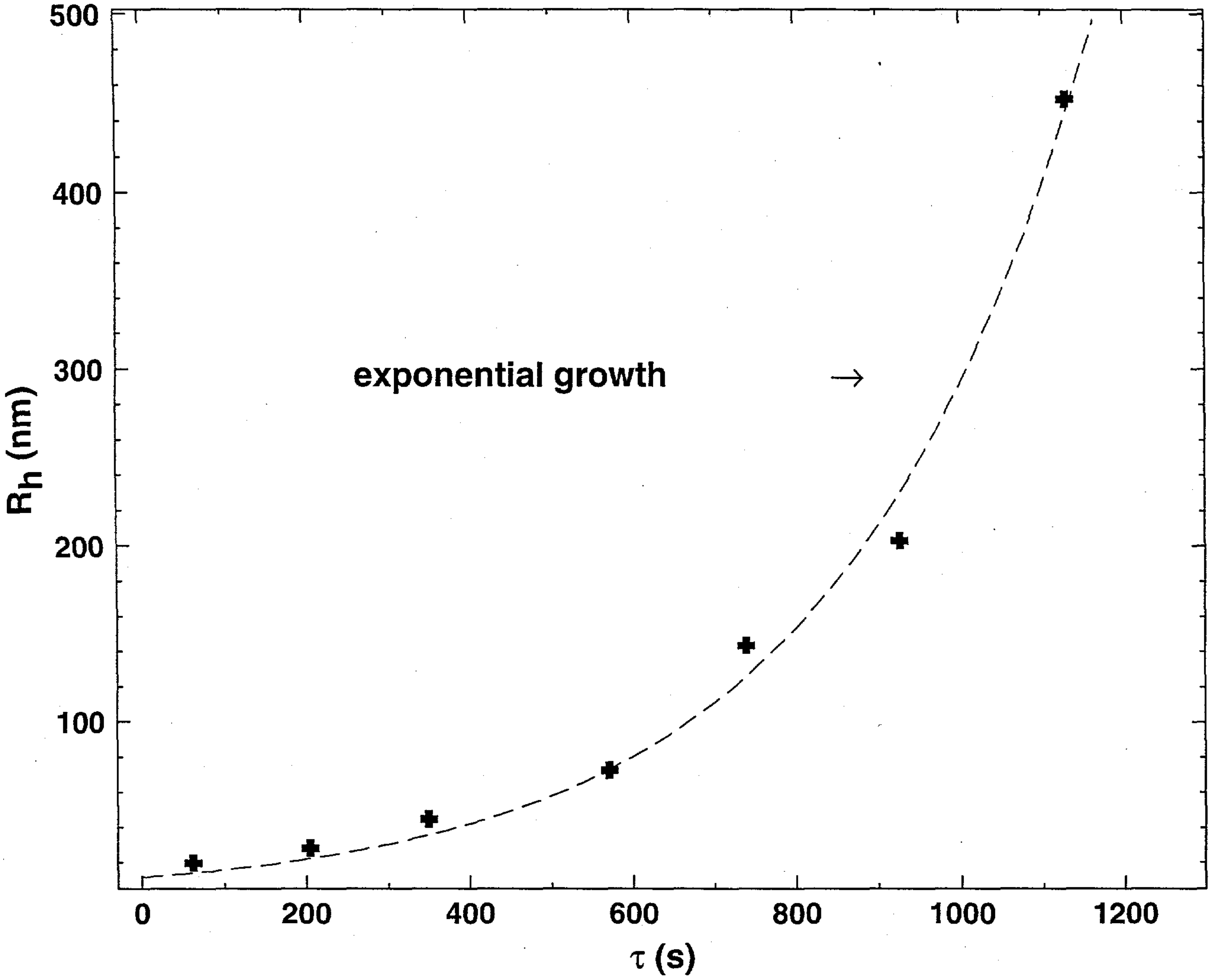

500
400
300
200
100
Rh (nm)
exponential growth →
0
200
400
600
800
1000
1200
τ (s)

Fig. 8

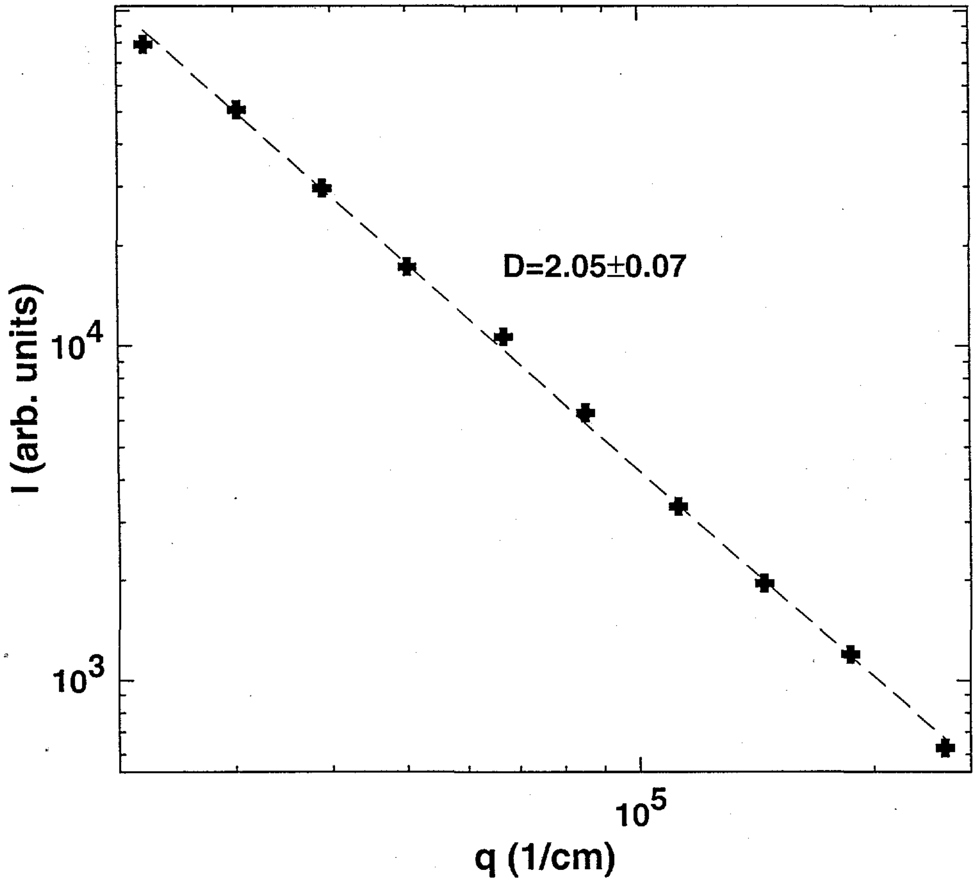


Fig. 9