K. PACŁAWSKI* J. GAPIŃSKI**

STATIC AND DYNAMIC LIGHT SCATTERING METHOD FOR ANALYSIS OF GOLD COLLOIDAL GROWTH IN AQUEOUS SOLUTION

BADANIA KINETYKI WZROSTU KOLOIDÓW ZŁOTA W ROZTWORACH WODNYCH METODĄ STATYCZNEGO I DYNAMICZNEGO ROZPRASZANIA ŚWIATŁA

In this work, the kinetics of precipitation, coagulation and growth of Au solid particles in aqueous solutions was examined. In all experiments, the Photon Correlation Spectroscopy in static (SLS) and dynamic (DLS) version was applied. Gold colloids were formed during reduction of gold(III) chloride complex ions using H_2O_2, C_2H_5OH and $NaHSO_3$ as reductants. Experiments showed that application of PCS method is not easy for these reacting systems. However, it was found that if proper conditions (e.g. temperature, initial concentrations, preliminary fast mixing of reagents) are applied, this experimental technique can be a useful tool for determination of changes in the rate of change of gold colloid size. As a result of there experiments, we evaluated the sizes of obtained Au colloidal particles in case of H_2O_2 and C_2H_5OH used as reductants. They were found to be in the range from 30 to 110 nm, and from 0.3 to 2.5 μm, respectively.

W pracy dokonano próby określenia kinetyki etapu wytrącania, koagulacji i wzrostu cząstek fazy stałej Au w roztworach wodnych. Do badań zastosowano metodę spektroskopii korelacji fotonów (PCS) w wersji statycznej (SLS) oraz dynamicznej (DLS). Koloidy złota otrzymywano w wyniku redukcji chlorkowych jonów kompleksowych złota(III) przy użyciu reduktorów H_2O_2, C_2H_5OH oraz $NaHSO_3$. Badania wykazały, że w przypadku testowanych układów reakcyjnych, użycie PCS nie jest łatwe. Stosując jednak odpowiednio dobrane warunki początkowe (temperatura, stężenia początkowe, wstępne szybkie mieszanie reagentów) testowana technika badawcza może być przydatna do rejestracji szybkości zmian rozmiarów koloidów złota. W wyniku przeprowadzonych eksperymentów stwierdzono, że w przypadku zastosowania H_2O_2 i C_2H_5OH jako reduktorów, można otrzymać cząstki koloidalne złota o rozmiarach odpowiednio od 30 do 110 nm oraz od 0.3 do 2.5 μm.

1. Introduction

Reaction of reduction of number metal ion complexes from aqueous solutions is a multi-step process. We have shown recently [1, 2] that reduction of gold(III) chloride complexes using different reductants invariably leads to a series of consecutive reactions (elementary steps), with the final step consisting in the formation of metallic phase. It also appeared that it is difficult to measure the rate of this last step. Fortunately, there exists very smart experimental technique based on the laser light scattering [3-5] which, if used properly, yields not only the rate of the processes in which i.e. solid particles or colloidal systems are formed but also may provide information about their sizes. In the present paper it will be demonstrated how it can be done in case of the re-

action reduction of gold(III) complex ions. Since this method can be realized in static and dynamic versions, at first, we'll give the description of the experimental principle.

2. Static and dynamic light scattering method

a) Static Scattering

Angular dependence of the intensity of radiation scattered by suspension of colloidal particles is often used to determine their size and shape. The wavelength of radiation is adjusted to the size of the particles – from soft X-ray for ~10 nm size particles to light scattering for sub-micron particles. Monochromatic beam of radiation

* LABORATORY OF PHYSICAL CHEMISTRY AND ELECTROCHEMISTRY, FACULTY OF NON-FERROUS METALS, AGH UNIVERSITY OF SCIENCE AND TECHNOLOGY, 30 MICKIEWICZA AVE., 30 - 059 CRACOW
** DIVISION OF MOLECULAR BIOPHYSICS, FACULTY OF PHYSICS, ADAM MICKIEWICZ UNIVERSITY, 85 UMULTOWSKA STREET, 61-614 POZNAŃ

illuminates the suspension. On the scale of the particle size it can be regarded as a plane wave. Each part of a particle can be treated as a single scattering center and the total radiation scattered at a given angle is a superposition of contributions from all those parts. This phenomenon, called intramolecular interference, gives rise to so called form factor $P(q)$, i.e. normalized angular dependencies of scattered radiation intensity characteristic for given shapes of particles. The quantity q is the magnitude of the scattering vector q defined as the vector difference between the incident and scattered beam wave vectors k_I and k_S. The value of q can be easily expressed in terms of the scattering angle θ:

$$q = \frac{4\pi n}{\lambda} \sin\left(\theta/2\right), \tag{1}$$

where n is the refractive index of the solvent and λ is the radiation wavelength.

Interaction between the particles usually induces some degree of order in relative positions of the particles. This leads to intermolecular interference in scattered radiation intensity giving rise to a different scattering angular dependence, quantified as structure factor $S(q)$. For non-interacting particles $S(q) = \text{const} = 1$. In the simple case of spherical particles the total scattered intensity $I(q)$ is a simple product of $P(q)$ and $S(q)$. When only the size and shape are measured, the proper conditions should be chosen to avoid the influence of $S(q)$ on the $I(q)$. In most cases the sample concentration below 0.1% volume fraction is enough to make $I(q)$ practically equal to $P(q)$, provided that long-range interactions are either weak or absent at all.

The analytical form of $P(q)$ for a spherical solid particle is given by:

$$P(q) = \left[\frac{3}{(qR)^3}\left(\sin(qR) - qR\cos(qR)\right)\right]^2 \tag{2}$$

and is illustrated graphically in Figure 1. In eq. (2) R denotes particle radius.

A characteristic feature of the solid sphere form factor is a series of deep narrow minima occurring at equal distances of $\Delta(qR) = \pi$ starting from $qR \approx 4.4934$. The positions of these minima are a very precise measure of the particle radius. It is obvious that any polydispersity of the particles size will decrease the depth of the minima, leading to totally "flat" form factors for mixtures of many distinctly different particles.

Interesting features can be observed in a simple mixture of two kinds of spheres with different sizes having the radii ratio of about ten (Fig. 2), and concentrations chosen in such a way that scattered intensity of small spheres at $q = 0$ is 99 times smaller than that of the
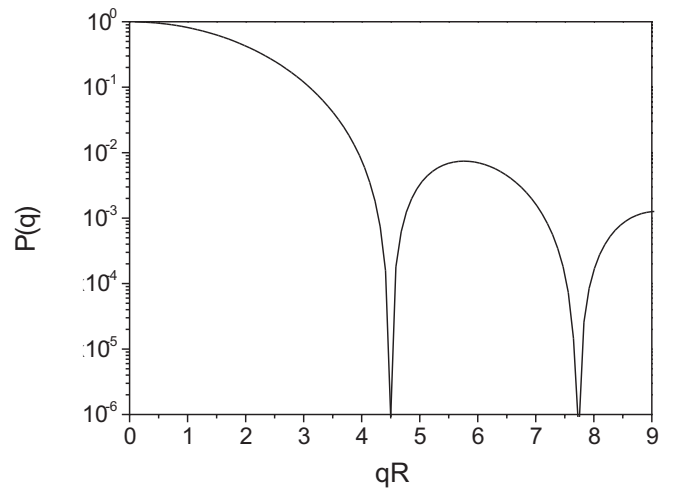

Fig. 1. Form factor of a solid sphere (simulated result of the scattering experiment, on perfectly monodisperse colloidal suspension of spherical particles with the radius R)
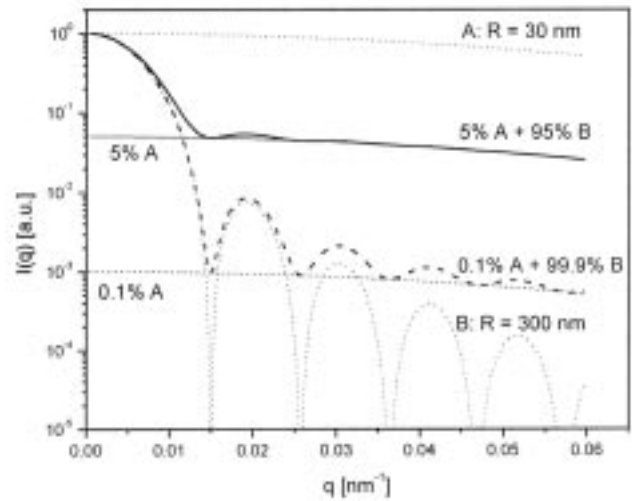

Fig. 2. Scattering profiles of mixtures of 30 (A) and 300 (B) nm solid spheres in proportions chosen such that the scattered intensity of A at q = 0 is 19 times (solid line) and 999 times (dashed line) smaller than that of B, as indicated in the figure. The dotted lines represent respective form factors of A and B. The thin solid and dashed lines show the real level of intensity scattered by A relative to B for the two sample compositions

big ones (solid line). Clearly the scattered intensity profile can be divided into two ranges: low-q range dominated by the strong scattering of the big particles and high-q range, where the rapid decay of $P(q) = I(q)$ of the big particles exposes $P(q)$ of the small ones. Even the first minimum of $P(q)$ of the big particles can hardly be recognized. Practically, if only parts of the spectrum were measured, it might happen that only one component would be found in the data analysis: the big component for the low-q range and small component for the high-q range. For the case where the fraction of the small spheres is even smaller (dashed line) an unusual phe-

nomenon is found in the narrow region around the first minimum of $P(q)$ of the big spheres: the scattered intensity is dominated by the signal returned from the small spheres. One should keep it in mind when analyzing the dynamic data in this q range.

When all components of a colloidal suspension are made of the same material (the same refractive index and density), and have identical shape, approximate quantitative information about the size distribution can also be made. Neglecting the structure factor $S(q)$, the intensity of scattered radiation $I(c, q)$ can be expressed as:

$$I(c, q) = KcMP(q), \tag{3}$$

where c is the weight concentration, M – particle molecular weight and K is a proportionality constant dependent on the studied material and the setup configuration.

For spherical particles $M \sim R^3$. To illustrate this strong dependence, we would like to point out that in order to get the dashed line in Fig. 2, proportions of concentrations (by weight) of components A nad B should be almost exactly 1:1 because the tenfold ratio of the radii gives exactly the factor of 1000 in the scattered intensity. For another sample composition, it is enough to take A and B in proportions 50:1 to have 95% intensity scattered from B (at $q = 0$).

The relative intensities of radiation scattered from the two components change strongly with the value of q. Any quantitative analysis of the sample composition based on the intensity of scattered radiation has to take into account its whole q-dependence.

b) Dynamic Scattering

Another way to measure the size of the particles suspended in simple liquids is the technique called photon correlation spectroscopy (PCS), which determines the time correlation function g(t) of the scattered radiation intensity under the assumption that the scattering volume is a coherent source of radiation. Until recently only the visible light was applied in this technique, but nowadays also synchrotron X-ray radiation is successfully used for this purpose. The fluctuations of that radiation intensity arise from particles' Brownian motion measured by their diffusion coefficient D. It was shown that such a correlation function can be expressed in terms of D as:

$$g(t) = \exp(-Dq^2t). \tag{4}$$

In turn, the diffusion coefficient of an isolated particle D_0 can be used for estimations of the particle size by combining the Einstein relation between D_0 and friction coefficient f:

$$D_0 = \frac{k_B T}{f} \tag{5}$$

which is given by Stokes formula for the sphere:

$$f = 6\pi\eta R, \tag{6}$$

where η is the solvent viscosity and R – the sphere radius. The resultant Stokes-Einstein relation:

$$D_0 = \frac{k_B T}{6\pi\eta R} \tag{7}$$

is routinely used for particle and droplet size determination in food and paint industry, biochemistry and colloidal science.

Measured diffusion coefficient D depends on particle concentration c and possible interactions between the particles. For interacting particles D_0 is determined from the extrapolation of $D(c)$ to zero concentration. For weakly interacting particles, D measured at low concentration (below 1% volume fraction) is practically equal to D_0.

In multicomponent systems, the correlation function takes a form of a superposition of exponential decays with rates proportional to respective diffusion coefficients. It is important to remember that decomposition of a multiexponential curve is an ill-posed mathematical problem (inverse Laplace transform), which means that within the experimental error there can be a lot of different combinations of exponentials that give the same shape of the correlation function. Several techniques were developed to help interpret PCS data obtained for polydisperse systems. All of them take advantage of the parsimony principle, that is the rule which allows to chose the solution with the smallest number of components that still fits well the experimental data.

c) Combined Static and Dynamic Scattering

In the case of a monodisperse colloidal suspension, both static and dynamic scattering techniques give an unequivocal and accurate result of the particle size. The numbers obtained from the two methods can be slightly different due to some subtle effects:
– influence of the hydration layer visible only in the dynamic technique,
– smeared edges of the particles leading to effectively smaller radius measured by the static scattering.

However, for polydisperse systems the decomposition procedures introduce substantial errors in the analysis of the data obtained by both techniques. Taking the advantage of the fact that the results of static and dynamic scattering are completely independent, the combined analysis increases greatly the accuracy of the solution

of the problem. In such a case the chance to get the wrong solution (i.e. wrong size distribution of the particles in the sample) that will produce scattering profiles identical to the experimental ones for both techniques is rather small. Combined static and dynamic scattering experiment is a very powerful tool used to characterize nano-scale particles in suspension.

Considering abilities of methods described above, we decided to test them as a tool to monitor kinetics of gold precipitation stage in the reaction reduction of gold(III) chloride complex ions. For reduction of these ions we applied different reductants: H_2O_2, C_2H_5OH and $NaHSO_3$. Applying the PCS method in static and dynamic form, we carried out the series of experiments in these systems, in which the intensity of scattered light and correlation function are registered. During the experiments we hoped for detection of changes in evolution of the sizes of gold particles appeared in solution. We also hope that knowledge of dynamic such process will give the chance for stabilizing obtained particles in the proper time of reaction (i.e. by freezing out or addition of stabilizers). Kinetic information could give the possibilities for preparation of colloidal gold in the proper sizes and shapes, also in nanometric scale.

3. Experimental

a) Materials

As a precursor of metallic phase of gold, tetrachloroauric acid aqueous solution ($HAuCl_4$) was used. This starting solution was prepared by dissolving of pure gold (99.99% purity, obtained from Mennica Państwowa, Warsaw, Poland) in aqua regia. After several evaporations of this solution, and dilution of the obtained solid in distilled water, the starting substrate (complexes of gold(III)) was obtained which was next used for preparation of adequate solutions with fixed gold(III) content. Prepared solutions were protected from the sunlight. Solutions of reductants (H_2O_2, C_2H_5OH and $NaHSO_3$,) were prepared by dilution of appropriate concentrated reagent grade purity (POCh, Gliwice, Poland) in distilled water. pH of this solution was determined using NaOH (reagent grade) and HCl (reagent grade), both obtained from POCh, Gliwice, Poland.

b) Method

Static and dynamic light scattering measurements were performed by using an experimental setup from ALV GmbH (Langen, Germany): ALV5000 digital correlator, avalanche photodiode (APD unit), ALV/SP-125 goniometer. A red (632.8 nm) HeNe laser (15 mW, Coherent, USA) and green (514.5 nm) Ar^+ laser (ILL 120, Zeiss, DDR) were used as a light beam source. The scheme of the whole apparatus is shown in the Fig. 3.
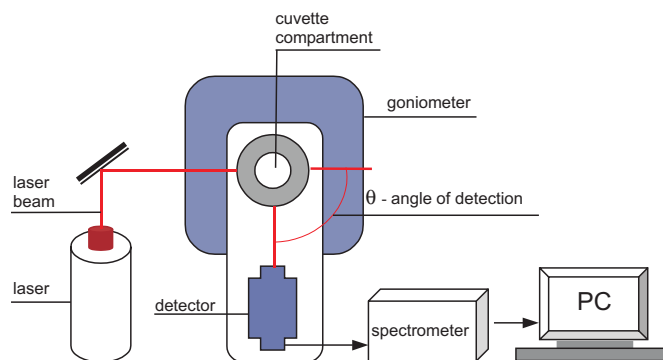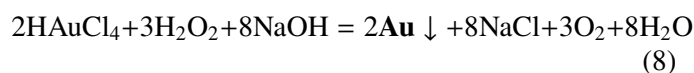

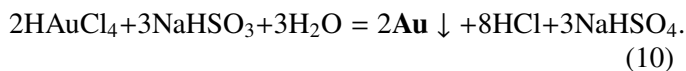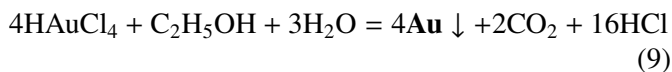Fig. 3. Scheme of the method used to measure scattered light intensity

During static experiments, procedure consisted in mixing of reagents (solution of Au(III) complexes, and the suitable reductant) in a small cylindrical glass cuvette, which was next placed as fast as possible in the compartment of the spectrometer. Next, the source of radiation (laser light beam) was switched on and the changes in the intensity of scattered light, which passed through the investigated solution, were automatically recorded with time. During dynamic measurements the correlation function, g(t), was analyzed by means of the CONTIN program. This is a common tool used to find the decay time distribution based on the inverse Laplace transform. From this dependence, value of τ is taken and next, using the appropriate equations, hydrodynamic radius of gold particles can be estimated (this procedure is described in the next chapter).

In all experiments the temperature of measurement cell was kept constant (20°C) in the range of $\pm$ 0.1°C. Initial concentrations of reagents (gold(III) complexes and reductants) used in experiments were equal to $1\cdot10^{-3}$ M for Au(III) and H_2O_2, $1\cdot10^{-2}$ M for $NaHSO_3$ and 96% by weight for the C_2H_5OH which was applied in the concentrated form. The details of experimental conditions are given in the appropriate figures captions. All experiments were repeated at least twice.

4. Results

The main product of all studied reactions was found to be pure metallic gold. The reactions, which led to gold precipitation, were the following:

$$2HAuCl_4+3H_2O_2+8NaOH = 2\textbf{Au} \downarrow +8NaCl+3O_2+8H_2O \tag{8}$$

$$4HAuCl_4 + C_2H_5OH + 3H_2O = 4\textbf{Au} \downarrow + 2CO_2 + 16HCl \tag{9}$$

$$2HAuCl_4 + 3NaHSO_3 + 3H_2O = 2\textbf{Au} \downarrow + 8HCl + 3NaHSO_4. \tag{10}$$

Kinetic experiments with these systems are possible only when the time scale of the observed processes is much longer than that of a single measurement of the scattered intensity angular dependence (static scattering) or of its time correlation function (dynamic scattering). For particles bigger then 10 nm and with sufficient optical contrast with respect to the solvent, the signal is so high that within a few seconds a good quality correlation function can be obtained. Within 1 minute, both the static scattered intensity and a full correlation function can be measured for about 15 points in the q range between ~ 0.005 nm^{-1} and 0.035 nm^{-1}.

The procedure which gives R_h vs. *time* dependencies is illustrated using Au(III) complex ions and H_2O_2 reaction system as an example. The following steps are necessary to obtain suitable data. At first, the experimentally determined intensity of scattered light on the gold particles in time is recorded (Fig. 4a). Next, for each point on I vs. *time* curve, the correlation functions g(t) vs. time is automatically (by CONTIN) determined. An example of such a dependence, for the point marked by arrow in the Fig. 4a, is illustrated in the Fig. 4b. Finally, using the simple software (i.e. TableCurve) the Γ factor in equation (11) is determined:

$$g(t) = \exp(-\Gamma t). \tag{11}$$

Since Γ is equal to $1/\tau$, and τ is expressed by equation:

$$\tau = \frac{1}{q^2 D} \tag{12}$$

the value of the diffusion coefficient (D) is obtained. From the Stokes-Einstein dependence (eq. (7)), changes in the hydrodynamic radius of gold particles during a reaction can be determined (Fig. 4c).
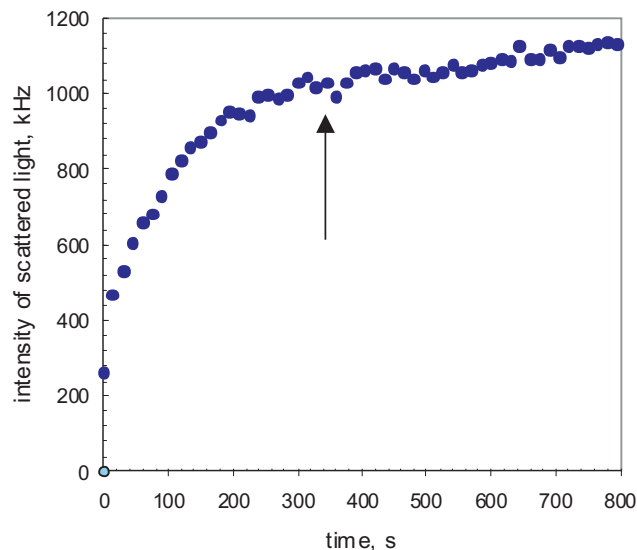

Fig. 4a. Intensity of scattered light vs time, in the reaction between Au(III) ions and H_2O_2. Conditions: alkaline solution (pH = 12), temperature 20°C, initial concentration of reagents: $C_{0,Au(III)} = 1 \cdot 10^{-3}$ M, $C_{0,H_2O_2} = 1 \cdot 10^{-3}$ M; reagents are mixed in the volume ratio 5:1 respectively
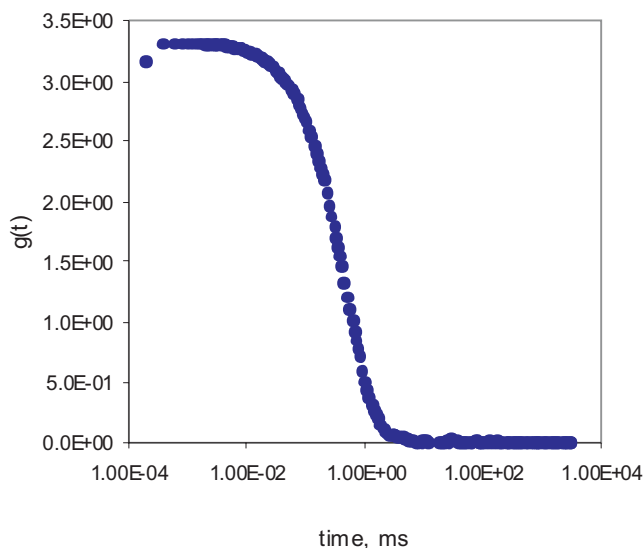

Fig. 4b. Example of the correlation function ($g(t)$ vs. *time*) for the reacting system of Au(III) ions and H_2O_2, recorded during the reaction after 360 second (for point marked by arrow in the Fig 4a). Conditions: alkaline solution (pH = 12), temperature 20°C, initial concentration of reagents: $C_{0,Au(III)}$ and $C_{0,H_2O_2} = 1 \cdot 10^{-3}$ M; reagents are mixed in the volume ratio 10:1 respectively
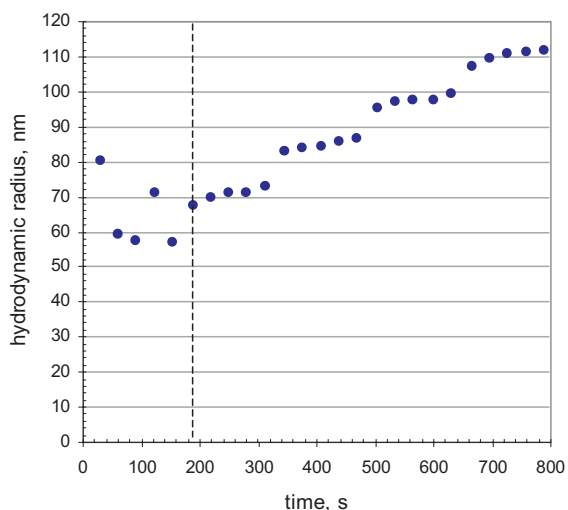
Fig. 4c. Dependence of hydrodynamic radius of gold particles in time recorded during the reaction between Au(III) ions and H_2O_2. Conditions: alkaline solution (pH = 12), temperature 20°C, initial concentration of reagents: $C_{0,Au(III)}$ and C_{0,H_2O_2} = $1 \cdot 10^{-3}$ M; reagents are mixed in the volume ratio 10:1 respectively

The procedure described above was repeated in all experiments.

In case of the reaction between the Au(III) ions and C_2H_5OH, we can see that the shape of the *I* vs. *time* dependence is sigmoidal (Fig. 5) with long induction period. The volume ratio of reagents was 1:1 and the initial concentrations were $1 \cdot 10^{-3}$ M and 96% by weight respectively.
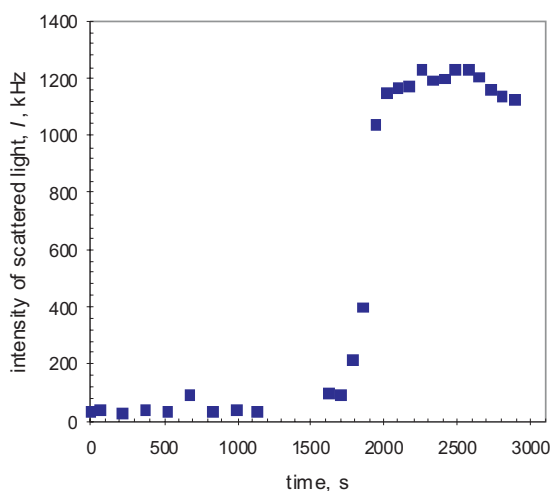

Fig. 5. Intensity of scattered light vs time, in the reaction between Au(III) ions and C_2H_5OH. Conditions: alkaline solution (pH = 12), temperature 20°C, initial concentration of reagents: $C_{0,Au(III)}$ = $1 \cdot 10^{-3}$ M, C_{0,C_2H_5OH} = 96% by weight; reagents are mixed in the volume ratio 1:1 respectively

In case of the reaction between Au(III) ions and $NaHSO_3$, an example of recorded experimental results (*I* vs. *time* dependence) is shown on the Fig. 6. We can see that *I* increases with time of the reaction and during the whole registered period, fluctuations of *I* values are present.
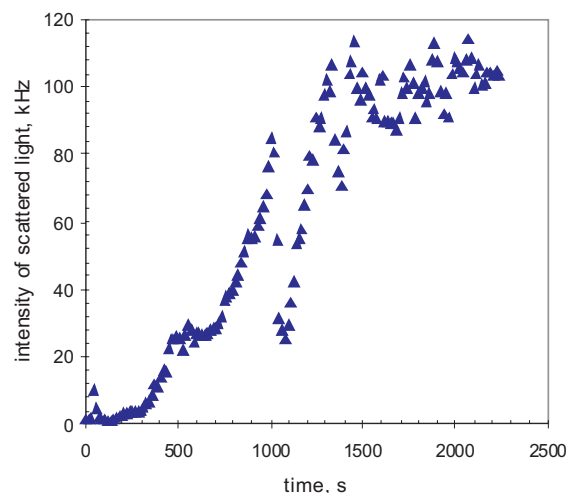

Fig. 6. Intensity of scattered light vs time, in the reaction between Au(III) ions and $NaHSO_3$. Conditions: acidic solution (pH = 1.3), temperature 20°C, initial concentration of reagents: $C_{0,Au(III)}$ = $1 \cdot 10^{-3}$ M, $C_{0,NaHSO_3}$ = $1 \cdot 10^{-2}$ M; reagents are mixed in the volume ratio 1:1 respectively

5. Discussion

Experiments of reduction of gold(III) complexes using H_2O_2 showed that dependencies of R_h vs. *time* obtained for different volume ratio of Au(III) ions and reductant solutions were similar in shape. For example, if we compare Fig. 4c with Fig. 7 it is seen that characteristic period (from 0 to 180 s) in which the large oscillations of R_h are present exists. These oscillations are probably associated with the high rate of reaction in the initial time and formation of "large" gold conglomerates. They are too heavy to produce stable colloidal system in the solution so they precipitate in the reactor. This kind of particles, as a potential scattering centers of light, is not present on the path of light and consequently, determined R_h in this period at time oscillates and decreases. Dynamical mixing of the reagents and the presence of turbulences in the system can be the next reason for registered oscillations. They may result in the changes of diffusion coefficient D, and hence on the fluctuation of sizes of Au particles. Next registered period, from about 200 to 800 s, yields the smooth increase in Au sizes.
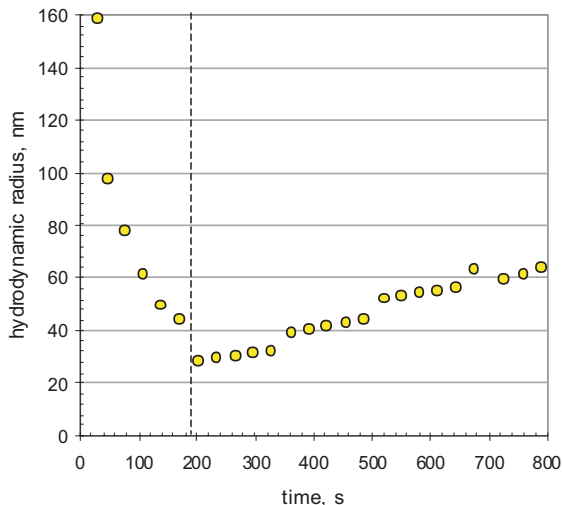
Fig. 7. Dependence of hydrodynamic radius of gold particles in time recorded during the reaction between Au(III) ions and H_2O_2. Conditions: alkaline solution (pH = 12), temperature 20°C, initial concentration of reagents: $C_{0,Au(III)}$ and C_{0,H_2O_2} = $1 \cdot 10^{-3}$ M, reagents are mixed in the volume ratio 5:1 respectively

Another factor which can influence the size of produced particles is the volume ratio. We registered that if the volume ratio of Au(III) to H_2O_2 solution increases, the particles of colloidal gold decreases. In our experiments, the R_h changed from the 30 to 65 nm for the 5:1 volume ratio, and from 60 to 110 nm for the 10:1 volume ratio of reagents. Thus, there is influence of the concentration of reductant on the size of obtained gold particles.
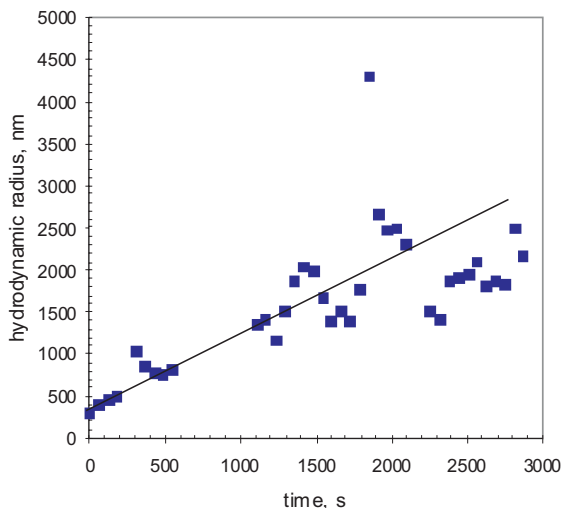

Fig. 8. Dependence of hydrodynamic radius of gold particles in time recorded during the reaction between Au(III) ions and C_2H_5OH. Conditions: alkaline solution (pH = 12), temperature 20°C, initial concentration of reagents: $C_{0,Au(III)}$ = $1 \cdot 10^{-3}$ M and C_{0,C_2H_5OH} = 96% by weight, reagents are mixed in the volume ratio 1:1 respectively

In case of reduction of gold(III) complexes by using C_2H_5OH, the changes in the values of R_h during the reaction exhibit large oscillations. An example of such dependence (R_h vs. *time*) is shown in Fig. 8.

These oscillations can be probably associated with the presence of gaseous CO_2, which appears in the system as a product of the reduction reaction (eq. 9). Coalescence of such molecules into the large bubbles can give the new scattering centers, and consequently strong oscillations are registered. Another reason can be different behavior of the Au colloids in C_2H_5OH solution. It is known that in such a system Au particles can conglomerate in the form of chains [6] and in such a case Mie theory is not valid since in other to use it an assumption about their spherical shape must be made.

Of course, precipitation of the large forms of Au colloids (which achieved critical sizes) can be the reason as well. It requires further study in which the influence of different factors, as concentration of reagents, rate of the reaction in homogeneous stage, etc. will be determined. In the experimentally studied system, where the C_2H_5OH was applied as the reductant, the values of the hydrodynamic radius o Au particles change from 0.3 to 5 μm.

Similar behavior was observed during the precipitation of Au in the reaction (10). When $NaHSO_3$ is applied as a reductant, the oscillations are already visible on the stage of registration *I* vs. *time* (Fig. 6). It can be associated with the reasons analogical to those described above (critical sizes of particles and their precipitation, evolution of SO_2 at low pH) as well as with the mechanism of periodic precipitation of Au particles. This elementary step is probably described by disproportionation of Au(I) chloride complex ions:

$$3[AuCl_2]^- \Leftrightarrow 2Au \downarrow + [AuCl_4]^- + 2Cl^-. \qquad (13)$$
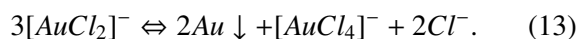
Such mechanism requires critical quantities of Au(I) in the solution, hence this process runs by the periodic precipitation of Au particles.

During the reaction of the gold(III) reduction with $NaHSO_3$, big conglomerates of Au clusters (visible to the naked eye) were formed, which immediately precipitated on the bottom and the walls of a cuvette. This situation makes the registration of *I* vs. *time* dependence difficult. In this system Au colloids do not appear and hence we didn't evaluate the size of such Au particles.

6. Conclusions

Investigations of three different systems considered in our studies give the possibility to control the prepa-

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ration of metallic gold particles of nanometric or micro-metric sizes. Applied method is useful for such estimation but it is not simple. It requires the choice of proper external conditions which give the chance for registration of *I* vs. *time* dependence without huge oscillations. From the obtained experimental results the influence of the reagents concentration and type of the reductant on the size Au particles is evident. The following conclusions can be drawn:

– The increase of the volume ratio of Au(III) and H_2O_2 solutions causes the decrease of gold particle sizes. For the 5:1 volume ratio of reagents, R_h changed from the 30 to 65 nm, and for the 10:1 from 60 to 110 nm.
– The type of reductant has an influence on the size of Au particles. Obtained R_h values varied in the following way:
from 30 to 110 nm when the H_2O_2 was applied
from 0.3 to 2.5 μm when the C_2H_5OH was applied, as a reductant.
– For the applied concentration of reagents gold precipitated on the reactor walls in all cases. In case of H_2O_2 and $NaHSO_3$ application, the walls required hydrophobizing.
– For systems in which the reaction takes place the stopped-flow system would be helpful.

– If the Dynamic Light Scattering (DLS) method is applied, the time of reaction must be suitably long in order to detect the correlation function. In our case, 15 s was enough to register $g(t)$ dependence.

This stage of experiments is treated as a test of usability of Photon Correlation Spectroscopy methods in the studies of such aqueous reacting systems. The rate equation suggested for the description of the kinetics of Au precipitation at this stage of our knowledge cannot be suggested.

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