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EXERCISE 8

Coagulation kinetics

Because of small size, colloidal particles in lyophobic sols undergo Brownian motion that results in collisions between particles. Such collisions may lead to particle aggregation. The effectiveness of the aggregation depends on the relative magnitude of the forces of attraction and repulsion between the approaching particles. According to DLVO [1, 2] theory, the interparticle forces can be regarded as the sum of two contributions. These are the electrostatic repulsion resulting from overlapping of electrical double layers of particles and van der Waals attraction, in particular its dispersion component. A very important difference between these two forces is their different dependence on the interparticle distance. To a first approximation, the repulsion is an exponential, whereas the attraction is a hyperbolic function of the distance. As a result of the combination of the two functions, the attraction is dominant at large and small distances, but in between an energy barrier may occur, as shown in Fig. 1. If the barrier is high enough to be unsurpassable by the kinetic energy, then the sol is stable against aggregation. The decrease in the barrier height caused, for instance, by the introduction of an electrolyte to the dispersion medium, involves the rise in the fraction of particle encounters leading to permanent contacts or, in other words, to coagulation. The introduction electrolyte to a sol practically does not affect the van der Waals attraction between the particles (as long as the solution is dilute). On the another hand, the electrostatic repulsion strongly depends on concentration, valences, and, to some extent, on the nature of dissolved electrolytes.

Addition of an *indifferent electrolyte*, i.e., whose ions do not adsorb specifically on the particle surface, causes compression of the diffuse part of the double layer and a reduction of the Stern potential, thus reducing the energy barrier. This, in turn, involves the increase in the fraction of collisions resulting in aggregation of particles. Thus, in kinetic terms, the increase in the ionic strength brings about the increase in the rate of coagulation. As a rule, however, for a given electrolyte there is a limiting concentration above which the coagulation rate remains constant, that is independent of the increasing ionic strength of the medium. In principle, this limiting concentration, known as the critical coagulation concentration (*c.c.c.*), is the electrolyte concentration which just makes the potential energy barrier disappear.

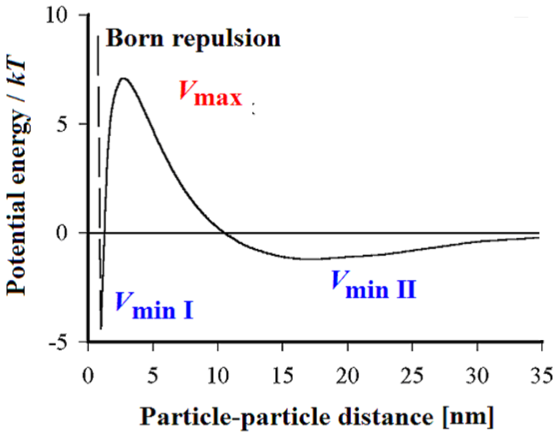

Fig. 1. Illustration of the potential energy of interaction of two spherical particles versus the distance of separation (particle diameter, concentration of 1:1 electrolyte, Stern potential, Hamaker constant and temperature are 50 nm, 0.03 M, 50 mV, $5\cdot10^{-20}$ J and 297 K, respectively).

Coagulation kinetics is classified as being "rapid" if every collision leads to aggregation and "slow" if it does not. A very simple theory of coagulation was given by Smoluchowski [3, 4] who assumed that the disappearance of primary particles can be considered as the diffusion-controlled second-order reaction.

The light scattering technique is one of the most suitable methods of observing the coagulation process, since the experimental turbidities can be interpreted in terms of the number and the size of the scattering centers. The theory of light scattering was developed br Rayleigh for systems containing monodisperse, nonabsorbing, spherical particles which are small compared with the wavelength of the light.

By combining Smoluchowski's and Rayleigh's theories, one can derive the following dependence between the intensity of light scattered by a colloidal system and the time of coagulation:

$$I_R = I_0 \cdot K \cdot N_0 \cdot V_0^2 \cdot \left(1 + \frac{2t}{t_{1/2}}\right) \quad (1)$$

where I_R is the total intensity of light scattered by the unit volume of colloidal system, I_0 – the intensity of the incident light, K denotes the constant dependent on the wavelength of the incident light and on the refractive indices of particles and of the dispersion medium, N_0 stands for initial number of particles, V_0 – the primary particle volume, t corresponds to the time of coagulation, whereas $t_{1/2}$ – to the half-period of coagulation, that is the time of coagulation in which the initial number of particles is just halved.

For low particle concentrations, the measurement of the intensity of light scattered can be replaced by that of the apparent absorbance, A. In such a case we obtain:

$$A = K_A \cdot N_0 \cdot V_0^2 \cdot l \cdot \left(1 + \frac{2t}{t_{1/2}}\right) \tag{2}$$

where K_A is a constant characteristic for a given colloidal system and l is a sample thickness which the light traverses.

Because of the restrictions imposed by the assumptions of Smoluchowski's and Rayleigh's theories, relations 1 and 2 describe well only the initial stage of the coagulation process. At higher t values a negative deviation of the measured $I_R = f(t)$ and $A = f(t)$ dependencies from the linearity is observed. Thus, in order to determine a kinetic parameter of coagulation (for instance $t_{1/2}$ value) an experimentally obtained I_R (or A) versus t dependence has to be extrapolated to $t=0$. Moreover, as it also results from the accepted assumptions, the experiment should be performed with dilute suspensions, which makes it possible to neglect the effect of secondary light scattering on the results of spectrophotometric measurements.

Experimental

The analysis of the kinetics of coagulation of a colloidal suspension induced by an indifferent electrolyte is the purpose of the experiment described. Silver iodide hydrosol is used as the colloidal system, whereas potassium nitrate is taken as the coagulating electrolyte. The analysis involves a determination of half-periods of coagulation occurring at different electrolyte concentrations in the dispersion medium and – on the basis of the obtained dependence - the determination of the critical coagulation concentration (*c.c.c.*) of the electrolyte employed, i.e., the lowest electrolyte concentration inducing a rapid coagulation.

Materials and apparatus

- aqueous solution of KI of concentration 0.088 mole/dm^3,
- aqueous solution of $AgNO_3$ of concentration 0.080 mole/dm^3,
- KNO_3 (solid)

- spectrophotometer Cary 50 and 2 glass cuvettes (1 cm path length)
- magnetic stirrer and 2-3 stir bars,
- stopclock,
- analytical balance, weighing paper and spatula,
- adjustable volume automatic pipettes
- 50 cm^3 burette,
- 20 beakers of 25 cm^3 and 3 beakers of 200-250 cm^3,
- 3 volumetric flasks of 100 cm^3
- wash bottle
- acetone and blow-dryer (hair-dryer)

Procedure

Preparation of silver iodide hydrosol

1. Prepare 100 cm^3 of aqueous $AgNO_3$ solution of concentration $0.80 \cdot 10^{-3}$ mole/dm^3 and 100 cm^3 of aqueous KI solution of concentration $0.88 \cdot 10^{-3}$ mole/dm^3 through the dilution of the corresponding stock solutions.
2. Fill the burette with the prepared $AgNO_3$ solution of concentration $0.80 \cdot 10^{-3}$ mole/dm^3.
3. To a clean and dry beaker introduce 50 cm^3 of KI solution of concentration $0.88 \cdot 10^{-3}$ mole/dm^3 and place the beaker at the magnetic stirrer. Introduce clean and dry stir bar.
4. To KI solution introduce slowly (in drops from a burette) 50 cm^3 of $AgNO_3$ solution under the continuous stirring.
5. Leave the obtained sol for about 30 minutes.

Determination of the dependence between the apparent absorbance and the coagulation time

1. Prepare a series of 8 potassium nitrate solutions in concentration range between 0.08 and 0.44 mole/dm^3.
2. Mix 5 cm^3 of prepared KNO_3 solutions with 5 cm^3 of AgI sol and measure the apparent absorbance of the solutions as a function of time t ***(assume a moment of mixing as*** $t=0$***)*** at the wavelength of 420 nm using water as a blank. Measure also the absorbance of the AgI sol diluted in ratio 1:1 with water – the obtained value can be assumed as an initial absorbance A_0 at zero time. Follow the procedure below to take the absorbance versus time readings[1].

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[1] Check that you understand how to use the spectrophotometer for kinetics study, since you will not have time to read the instructions once the process has begun.

Using the Cary-50 UV-vis spectrophotometer[2]

☐ Start the Cary 50 on.

☐ Open the folder **Cary WinUV**

☐ In the next window that appears on the screen find **Kinetics** and double click it.

☐ Select the **Setup** button to display the Setup dialog and under the **Cary tabs** set parameters as follows:

- In the **Wavelength** field enter the wavelength that you want to monitor (420 nm),
- In the **Average time** field, set the amount of time, in seconds, for which data is averaged. Average time is automatically set for 0.1000 seconds but can be adjusted if needed (we advice to set 10 s).
- Enter an upper range and lower range values in **Ymin** and **Ymax** entry fields to specify the displayed ordinate range.
- In **X mode** click on **Sec.**
- In **Collect Timing** specify the duration of the measurement run by setting **Start** 0 s and **Stop** 300 s.

Under the **Reports tab** set:

- In **X-Y Pairs Table** select **Include X-Y Pairs Table**.
- In **Autoconvert** select **ASCII (csv)** – at the end of the data collection will automatically generate a report and store the data both in the Cary format as well as ASCII XY pairs format in the current folder.

Exit the **Setup** window – select **OK** to confirm any changes you have made and close the **Setup** dialog.

☐ Place the blank solution in the sample compartment and click **Zero.** Next click first **Baseline** and then **OK.** The system will perform an instrument zero on the blank solution.

☐ Press the **Start** button to start a data collection. The system will display the **Save As** dialog box. Enter the file name for this kinetics run in the **File name** field and press **Save**.

☐ Click **OK** – a prompt will appear on the screen with a count down from 2 minutes down to zero. ***ATTENTION! Within this period of time you have to prepare your sample (by adding 5 cm^3 of AgI sol to 5 cm^3 of aqueous KNO$_3$ solution), introduce the sample into the clean and dry cuvette and place it in the sample compartment.*** Commence the data collection by

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[2] We acknowledge the assistance of Oktawia Skrzypczak and Mikołaj Pyziak, students on physical chemistry II course, in preparation of this procedure.

pressing **OK** button. ***Measure the period of time between the sample preparation (the mixing) and pressing the OK button. This value should be added to all time values recorded by the instrument.***

Data analysis

It was proved that the parabolic equation

$$A = c + bt + at^2 \tag{3}$$

is a good approximation of the experimentally obtained A vs. t dependencies. For t=0 we can assume that $A = A_0 = c$.

The derivative of absorbance with respect to time is given by:

$$\frac{\partial A}{\partial t} = b + 2at \tag{4}$$

Thus, a tangent to the obtained parabola at point (A=A_0, t=0) has a slope of b. Intercept of tangent as well as the intercept of parabola are the same and equal to A_0. Hence, the tangent equation is:

$$A = c + bt = A_0 + bt \tag{5}$$

A comparison of Eqs 2 and 5 leads to following relations:

$$K_A \cdot N_0 \cdot V_0^2 \cdot l = c \tag{6}$$

and

$$K_A \cdot N_0 \cdot V_0^2 \cdot l \cdot \frac{2}{t_{1/2}} = b \tag{7}$$

The relations permit an easy calculation of the half-periods, $t_{1/2}$, of coagulation occurring at different electrolyte concentrations (ionic strengths). Since above the c.c.c. the coagulation rate attains the maximum value, which does not change any more with further increasing electrolyte concentration, $t_{1/2}$ should reach a minimum value, $t_{1/2,\mathrm{min}}$, corresponding to the half-period of rapid coagulation. The value of $t_{1/2,\mathrm{min}}$ can be found as an arithmetic mean of $t_{1/2}$ values obtained at a certain number of the highest electrolyte concentrations used in the experiment.

Verwey and Overbeek [2] have shown that in the slow coagulation domain (low electrolyte concentration) there is a linear dependence between $\log(k/k_{\mathrm{max}})$ and $\log(c_{\mathrm{E}})$, where k and k_{max} denote rate constants of slow and fast coagulation, respectively, whereas c_{E} is the electrolyte concentration. It is a consequence of the Smoluchowski theory, but it is also intuitively obvious that $t_{1/2}$ is an inverse function of k as well as $t_{1/2,\mathrm{min}}$ is proportional to $1/k_{\mathrm{max}}$. Thus, the dependence between $\log(t_{1/2}/t_{1/2,\mathrm{min}})$ and $\log(c_{\mathrm{E}})$ should also be linear for $c_{\mathrm{E}}<c.c.c.$ Plotting $\log(t_{1/2}/t_{1/2,\mathrm{min}})$ versus $\log(c_{\mathrm{E}})$ in the sufficiently broad range of electrolyte concentrations one obtains the c.c.c. value as the lowest electrolyte concentration at which the coagulation rate reaches its maximum value or, in other words, $t_{1/2}$ attains $t_{1/2,\mathrm{min}}$. The way of the *c.c.c.* determination is schematically shown in Fig. 2.

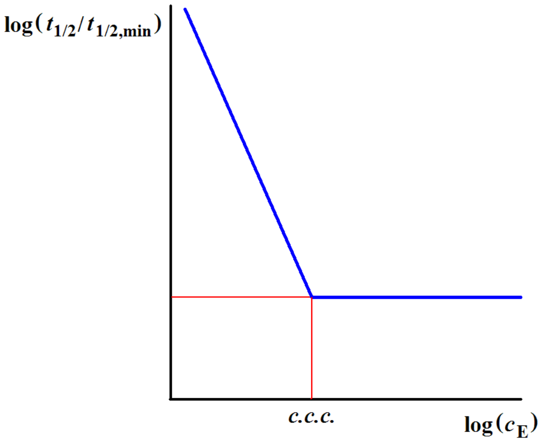


Fig. 3. Determination of the c.c.c. from $\log(t_{1/2}/t_{1/2,\mathrm{min}})$ versus $\log(c_{\mathrm{E}})$

References

1. B.V.Deryagin, L.Landau, *Acta Physicochim. URSS*, **14**, 633 (1941)
2. E.J.Verwey, J.Th.G.Overbeek "Theory of the Stability of Lyophobic Colloids", Elsevier, New York, 1948
3. M.Smoluchowski, *Phys. Z.*, **17**, 557 (1916)
4. M.Smoluchowski, *Z. Phys. Chem.*, **92**, 129 (1917)
5. W.Nowicki, G.Nowicka, *J. Chem. Educ.,* **68**, 523 (1991)

Importing of SCV formated data into Microsoft Excel

1. Start Excel
2. Go to: **Data (*Dane*)**
3. Go to: **Import external data (*Importuj dane zewnętrzne*)**
4. Go to: **Import data (*Importuj dane*)**
5. Search for the file
6. In the dialog box select: **Delimited (*Rozdzielany*)**, click **Next (*Dalej*)**, click **OK**
7. In the dialog box select: **Coma (*Przecinek*)**, click **Next (*Dalej*)**, click **OK**

If necessary change dots to commas (use "Find and Replace" dialog box)

Replace = ***Zamień***

Replace all = ***Zamień wszystko***

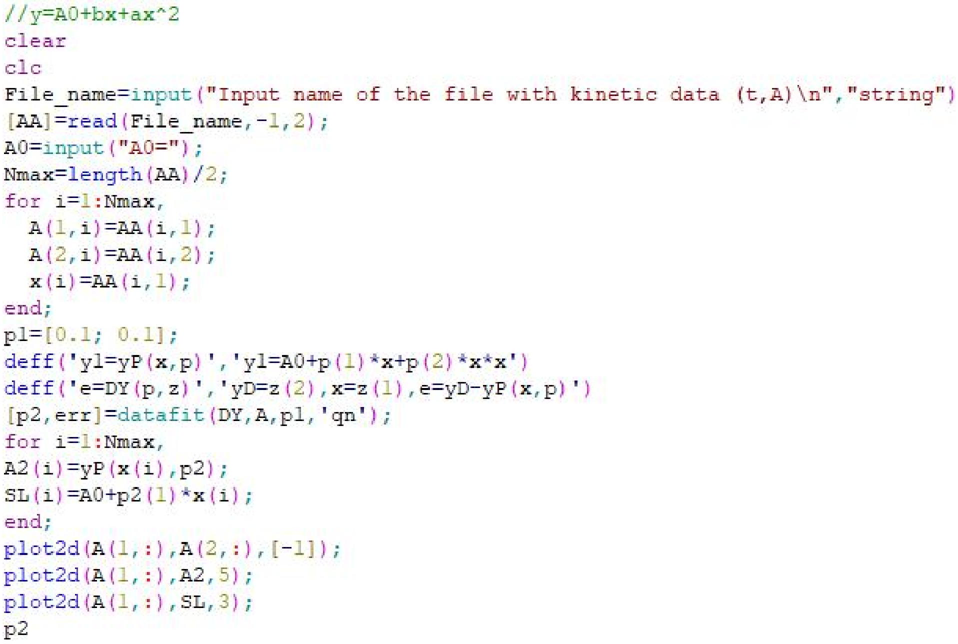
Find = ***Znajdź***

Find all = ***Znajdź wszystko***

Close = ***Zamknij***

APPENDIX: Additional calculations – Scilab script

SciLab script for calculation of initial slopes of kinetics curves:



```
//y=A0+bx+ax^2
clear
clc
File_name=input("Input name of the file with kinetic data (t,A)\n","string")
[AA]=read(File_name,-1,2);
A0=input("A0=");
Nmax=length(AA)/2;
for i=1:Nmax,
  A(1,i)=AA(i,1);
  A(2,i)=AA(i,2);
  x(i)=AA(i,1);
end;
p1=[0.1; 0.1];
deff('y1=yP(x,p)','y1=A0+p(1)*x+p(2)*x*x')
deff('e=DY(p,z)','yD=z(2),x=z(1),e=yD-yP(x,p)')
[p2,err]=datafit(DY,A,p1,'qn');
for i=1:Nmax,
A2(i)=yP(x(i),p2);
SL(i)=A0+p2(1)*x(i);
end;
plot2d(A(1,:),A(2,:),[-1]);
plot2d(A(1,:),A2,5);
plot2d(A(1,:),SL,3);
p2
```