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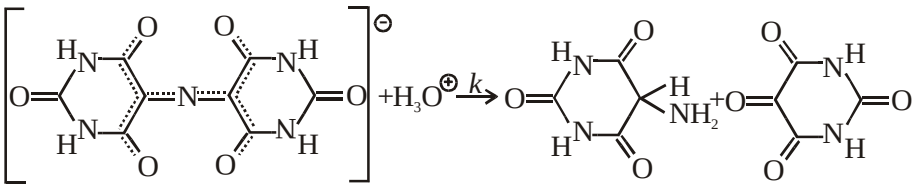
EXPERIMENT 6A

Chemical reactions in micellar systems

Basic notions: rate of reaction, micellar solutions, CMC (critical micellisation concentration), micellar catalysis, reaction rate constant, order of reaction, pseudo-first order reaction, relaxation time, absorbance

Introduction

Murexide a popular complexometric indicator is an ammonium salt of purpuric acid. In acidic water solutions the murexide anion decomposes according to the following reaction



or in short

$$Mu^- + H_3O^+ \xrightarrow{k} U + A \qquad (1)$$

where Mu^-, U and A are the murexide anion, uramil and alloxan.

The aim of the experiment is to investigate the kinetics of murexide decomposition (a) in water and (b) in a water micellar solution of sodium dodecylsulfate $C_{12}H_{25}SO_4Na$ (SDS). The rate of reaction (1) is found from spectrophotometric measurements.

Theory

Micellar solutions are formed as a result of dissolution of organic substances whose molecules are amphiphilic. The amphiphilic molecules are composed of one ionic or uncharged hydrophilic group and a nonpolar hydrophobic group. The latter usually is an aliphatic chain containing more than 8 carbon atoms. In concentrations lower than the critical micellisation concentration (CMC) the molecules exist in the solution as monomers, while above CMC they aggregate forming micelles. Above CMC the concentration of non-aggregated monomers remains constant.

The presence of micelles influences the rate constants and equilibrium constants of many chemical reactions taking place in water solutions. The reason for this effect is a separation of reagents between the bulk phase (water phase) and micellar phase so that the reaction takes place in both phases. A general scheme of the reaction taking place in micellar solutions between substrates A and B, leading to formation of the product P, can be described as follows

Bulk water phase $\mathbf{A_w + B_w \rightleftarrows P_w}$

$\uparrow\downarrow \quad \uparrow\downarrow \qquad \uparrow\downarrow$

Micelles surface $\mathbf{A_p + B_p \rightleftarrows P_p}$

Micellar phase $\uparrow\downarrow \quad \uparrow\downarrow \qquad \uparrow\downarrow$

Micelles core $\mathbf{A_r + B_r \rightleftarrows P_r}$

The rates of the direct and reverse reaction in different regions can be different. The exchange of substrates A and B and the product P between the regions is a fast and diffusion controlled process. It is assumed that the chemical reaction is much slower than the processes of exchange between the regions.

The classical definition of a catalytic process refers to the systems in which the catalyst changes the rate constant of reaction but has no effect on the equilibrium constant of reaction. Micellar catalysis refers also to the processes in which the equilibrium constant is changed as well.

If the rate of the reaction

$$A + B \xrightarrow{k} P \tag{2}$$

is defined as

$$r = k[A][B] \tag{3}$$

then the reaction is of second order. If one of the substrates, e.g. B, occurs in such large amounts that its concentration does not change significantly in the course of the reaction, so we can write that [B] ≈ const., then equation (3) becomes
where

$$r = k_{obs}[A] \tag{4}$$

$$k_{obs} = k[B] \tag{5}$$

and the reaction is of the first order. The rate of the reaction which is of the pseudo-first order is often defined in terms of the relaxation time τ as the reciprocal of the rate constant k_{obs}, $\tau = 1/k_{obs}$.

Considering the reaction between ions, the activity coefficients should be considered. Decomposition of murexide in an acidic medium takes place according to the second order kinetics

$$r = k\,[Mu^-]\,[H_3O^+]\,f_\pm^2 \tag{6}$$

where $f_\pm$ is the mean ionic activity coefficient.

In the presence of acid excess, $[H_3O^+] \gg [Mu^-]$, the value of $f_\pm$ does not change in the course of the reaction, therefore, the reaction kinetics is described by the rate constant of the pseudo-first order k_{obs}, as follows

$$r = k_{obs}\,[Mu^-] \tag{7}$$

$$k_{obs} = k\,[H_3O^+]\,f_{\pm}^2 \tag{8}$$

The aim of the experiment is to determine k_{obs} for reaction (1) of murexide decomposition.

Experiment

Method

Changes in the concentration of murexide upon its decomposition in acidic solutions are followed spectrophotometrically. In the solutions of pH ≥ 6 murexide is stable. In acidic solutions it undergoes decomposition which is manifested by gradual disappearance of the characteristic red-violet colour. The reaction progress can be observed as changes in absorbance. As the reaction is of the pseudo-first order, the concentration of the reagent decreases exponentially and the related changes in absorbance can be described by the equation

$$A_t = A_0\,e^{-k_{obs}t} \tag{9}$$

where A_0 is the initial absorbance and A_t is the absorbance at time t from the beginning of the reaction. The initial absorbance A_0 can be determined from the Lambert-Beer law, knowing that the molar absorption coefficient ε for murexide at λ_{maks} is 1.38×10^4 dm^3/(mol×cm) [1].

According to this equation, the absorbance A after the reaction completion is zero, $A_\infty = 0$. When the reaction takes place in a micellar solution, $A_\infty > 0$ as micelles scatter the incident light. The, eq. (9) should be replaced with

$$A_t = A_\infty + (A_0 - A_\infty)\,e^{-k_{obs}t} \tag{10}$$

which hold for the experiment.

A solution of murexide absorbs light in the wavelength range 420-660 nm; the maximum absorption appears at λ_{maks} = 523 nm. The time changes in absorbance are measured by an absorption spectrophotometer working in the visible range of electromagnetic radiation and measuring absorbance in the range from 0 to 2 with the accuracy of ±0.001.

Reagents and apparatuses

– murexide in solid state
– SDS solution in concentration of 0.1 mol/dm^3
– HCl solution in concentration of 0.1 mol/dm^3
– VIS spectrophotometer
– 2 glass cuvettes of 1 cm in thickness
– 2 automatic pipettes dosing the volumes of 1.5 cm^3 and 0.1 cm^3
– stopwatch
– volumetric flask of 50 cm^3 in capacity
– 4 beakers of 25 cm^3 in capacity
– scapula

Procedure

1. In a volumetric flask of 50 cm^3 in capacity prepare a solution of murexide of a concentration 5×10^{-4} mol/dm^3.

2. Prepare the spectrophotometer for absorbance measurements, using water as the reference standard. Load the cuvette with 1.5 cm^3 of murexide solution and 1.5 cm^3 of distilled water, then add 0.1 cm^3 of HCl solution of a concentration of 0.1 mol/dm^3. After covering the cuvette, quickly stir the contents by manual shaking, start the stopwatch, place the cuvette in the measuring chamber of the spectrophotometer and measure the absorbance and time on the stopwatch. All these procedures should be done as quickly as possible. Read off simultaneously time and absorbance, at first at every 30 seconds, than at every 1 minute and end the measurements for the absorbance $A \approx 0$.

3. After completion of the measurements and washing the measuring cuvette with distilled water, to the cuvette measure 1.5 cm^3 of the murexide solution and 1.5 cm^3 of SDS surfactant solution of a concentration 0.1 mol/dm^3, and add 0.1 cm^3 of a HCl solution of concentration 0.1 mol/dm^3. After quick stirring of the cuvette content and starting the stopwatch repeat the procedures described above.

Calculations

Take logarithms of the sides of eq. (10) to get the linear equation

$$\ln(A_t - A_\infty) = -k_{obs}t + \ln(A_0 - A_\infty) \tag{11}$$

whose slope with the opposite sign is equal to the observed rate constant of the reaction, k_{obs}.

Make plots of 1) kinetic curve, that is the time dependence of the measured absorbance $A = f(t)$; 2) so $\ln(A_t - A_\infty) = f(t)$. Using eq. (11) calculate by the method of the least squares the reaction rate constant k_{obs}, for murexide decomposition in the two solutions studied. Give the value of k_{obs} with the standard deviation and proper units.

Discussion

1. Compare the values of k_{obs} obtained in water and in a water micellar solution of $C_{12}H_{25}SO_4Na$ (SDS). In which solution the reaction of murexide decomposition is faster and in which it is slower? Can you interpret the difference?

2. The total reaction

$$A + B \xrightarrow{k} P \tag{12}$$

takes place according to the scheme

$$A + B \underset{k_2}{\overset{k_1}{\rightleftharpoons}} AB \xrightarrow{k_3} P \tag{13}$$

Assuming that the reactions described by the rate constants k_1 and k_2 are fast, while the reaction characterised by the rate constant k_3 is slow, express the reaction constant k of reaction (12) by the reaction rate constants k_1, k_2, k_3.

References

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Supplementing literature

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Related problems

Relaxation time. Kinetic equations. Temperature dependence of reaction rate. Light absorption. Micellar solutions: structure of micelles, CMC and methods of its determination.

Anna Stachiewicz

EXPERIMENT 6B

Chemical reactions in micellar solutions. Part 2: computer simulation of micellization process

Basic notions: Molecular dynamics, polarity of molecules, electrostatic interactions, Lennard-Jones interactions, amphiphillic molecules, micellization, critical micelle concentration.

Introduction

The second part of the exercise is aimed at the analysis of kinetics of micellization of an ionic surfactant SDS and determination of the geometric parameters of the micelle on the basis of the data obtained from molecular dynamics computer simulations.

Theory

In the molecular dynamics the motion of atoms and molecules is simulated. On the basis of the trajectory of motion (positions, velocities, energies, etc.) it is possible to conclude about the intermolecular interactions, thermodynamic properties of the system, to analyse the mechanisms of processes and to predict behaviour of new systems.

In the classical, all-atom simulation, all atoms are represented in the simulated system. For large systems the simplified, coarse-grained simulations are performed. In this technique, atoms are replaced by the pseudoatoms each of which represents a group of atoms. Due to a considerable reduction of the number of degrees of freedom, the time of simulation can be reduced from a few to a few hundred times. Despite the significant simplification of the system, in many applications the results are consistent with the all-atom simulations and the experimental data.

One of the most popular models is the so-called Martini model [1]. In this model, each pseudoatom usually represents four normal heavy (non-hydrogen) atoms (Fig. 1). One superatom represents four water molecules. In this model the non-bonded interactions of the Lennard-Jones type play an important role. Pseudoatoms are divided into groups: ionic (e.g. simple ions), strongly polar (e.g. water, alcohols), weakly polar (e.g. amines, aldehydes) and nonpolar (e.g. hydrocarbons). Two strongly polar or two nonpolar pseudoatoms interact much stronger with each other than two pseudoatoms much differing in polarity.

The Martini model can be used in computer simulations of proteins, lipids, surfactants and other systems.

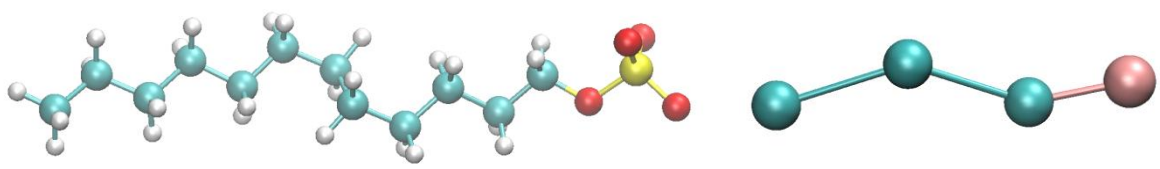

Figure 1: Structure of the SDS molecule: on the left - all-atom model, on the right the Martini

model. The radii of the balls correspond to the van der Waals radii of particular atoms.

In water solutions the amphiphillic particles make aggregates (micelles) of different geometry. The shape and size of such aggregates are determined by two types of interactions – the attraction of nonpolar tails and repulsion of the polar heads. The nonpolar hydrophobic fragments of particles are inside the aggregate and are surrounded by the hydrophilic polar parts. The attraction of tails is a consequence of the fact that nonpolar chains interact with one another stronger than with the polar solvent (hydrophobic effect). Non-ionic surfactants make relatively large aggregates, even of up to a few thousand molecules. Ionic surfactants make smaller aggregates of below 100 molecules. The distances between the polar fragments are as long as possible to minimise repulsion but small enough to restrict the penetration of water molecules inside the aggregate [2].

Micelles are most often spherical, but can have other geometry depending on the type and concentration of surfactant and the ionic strength. For the ionic surfactants, the higher the ionic force of the solution (reducing the repulsion of heads with the same sign charges), the higher the probability of formation of large non-spherical structures. The formation of bilayers is promoted by high volume of the nonpolar part of the molecule, e.g. the presence of two chains [2].

Spherical micelles can be described by the approximate model of the oil drop [3, 4]. This model assumes that the density of the interior of the micelle containing hydrocarbon chains is the same as that of the hydrocarbon solution. Moreover, it assumes that the surface of the micelle is homogeneous, the polar heads are uniformly distributed and the number of the heads is the same as the number of the tails.

On the basis of the measured density of alkanes, the formula for the volume of a spherical drop of the hydrocarbon, comprising *m* molecules, has been derived:

$$V = (27.4 + 26.9\ N_c)\ m \quad [\text{Å}^3], \tag{1}$$

where N_c is the number of carbon atoms in the chain. This volume is also equal to that of the hydrophobic core of the micelle composed of *m* molecules. The radius of the core is:

$$r = 1.26\ N_c + 0.84 \quad [\text{Å}]. \tag{2}$$

As the volume of the ball is $V = (4/3)\pi r^3$ and also $V = (27.4 + 26.9N_c)m$, the two expressions can be equated to derive the formula for the number of molecules making a micelle as a function of its radius:

$$m = \frac{(4/3)r^3\pi}{27.4 + 26.9N_c}. \tag{3}$$

An important parameter characterising a micelle is the area per one molecule of the compound of which it is made. As the surface area of the ball is $S = 4\pi r^2$, the following formula can be derived:

$$\frac{S}{m} = 4r^2\pi\frac{27.4 + 26.9N_c}{4/3r^3\pi} = \frac{3(27.4 + 26.9N_c)}{r}\ [\text{Å}^2]. \tag{4}$$

Practical realisation

Computer simulation of SDS aggregation

1. On the desktop make a folder labelled with the student's name.
2. Enter the folder `Symulacje_micele`.

3. With the right button of the mouse click on the folder, chosen by the instructor, containing the files for the simulation (e.g. `agregacja_310K_50cz`) then copy it to the folder on the desktop labelled with your name.

4. Enter the copied folder containing the files for simulation.

5. To start the console (the text field with a dark background) in the Ubuntu system, click with the right key of the mouse on the empty space between the icons and select the option `Otwórz w terminalu` or `Open in terminal`.

6. To start the simulation in the NAMD program [5], type the command in the console:

```
charmrun +p2 /usr/bin/namd2 eq.namd
```
Enter↵

The simulation takes about 1 or 2 hours, depending on the speed of the processor.

Caution: simulation, visualisation and data analysis should be performed in the same folder labelled with your name.

Visualisation of SDS aggregation

1. When the simulation is completed, perform visualisation of the results in the VMD program [6], typing in the console:

```
vmd ionized.psf eq.dcd
```
Enter↵

2. Select `Display → Orthographic`

3. In order to see the poorly visible ions present in the system:

- Select `Graphics → Representations...`
- Click `Create Rep`
- In the text field `Selected Atoms` type `ions` instead of `all`, confirm Enter↵
- From the list `Drawing Method` select `VDW`
- Change the value of `Sphere Scale` to `0.5`

4. By clicking the button `play` (in the right bottom corner of the window `VMD Main`) start the visualisation of the simulation. Repeated click on this button stops the display.

5. If the centre of mass of the micelle is significantly shifted with respect to the centre of the box, that is when the micelle is cut across, e.g. one fragment of the micelle is at the bottom of the simulation box, while another one at the top, then:

- Select `Extensions → Tk Console`
- Type the following text as a single command into the `Tk Console` window:

```
pbc wrap -centersel "resname SDS" -center com -compound residue -all
```
Enter↵

- If the centre of mass of the micelle is still shifted, you can either execute again the above command or you can replace `resname SDS` with e.g. `resid 1`:

```
pbc wrap -centersel "resid 1" -center com -compound residue -all
```

- Instead of number 1, you can choose another one from the range 1-30. Enter↵

- To close the program VMD, in the window `VMD Main` click the cross in the upper right corner and select `Yes`.

Data analysis

1. To start the script (in the Tcl language) for data analysis, type in the console the following command:

```
vmd -e aggregate.tcl -dispdev none Enter↵
```

2. The program VMD will start in the text mode. After analysis of the whole trajectory (2000 frames) the script will automatically stop working and will close the program VMD.

3. Draw the plots in the program Python, typing:

```
python plot.py Enter↵
```

4. Two plots will be displayed. Save plot 1, by clicking the diskette symbol, type the name of the file (`plot_n.png`) and confirm. In the same way save plot 2 (`plot_r.png`).

Discussion

1. On the basis of visualisation conclude if the majority of Na^+ ions are in the water phase, on the micelle surface or in the core of the micelle. What is the reason for such distribution?

2. From plot 1 read off the mean number of surfactant molecules making an aggregate and the time after which the equilibrium state has been reached, give the result in [ns].

3. From plot 2 read off the mean radius of the aggregate after reaching the state of equilibrium. Compare it to the theoretical value, calculated from equation 2, if for SDS the value of N_c, (the number of carbon atoms making the hydrocarbon chain inside the micelle) is 12.

4. Calculate the ratio of the aggregate area to the number of molecules making it, (S/m), using the previously determined value of the radius (point 3) and the number of molecules (point 2). Compare it with the theoretical value calculated from equations 2 and i 4.

Bibliography

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