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

\[
\text{Mu}^- + \text{H}_3\text{O}^+ \xrightarrow{k} \text{U} + \text{A}
\]  

(1)

where \(\text{Mu}^-\), \(\text{U}\) and \(\text{A}\) are the murexide anion, uramid 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 \(\text{C}_{12}\text{H}_{25}\text{SO}_4\text{Na}\) (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 \(\text{A}\) and \(\text{B}\), leading to formation of the product \(\text{P}\), can be described as follows
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

\[ A + B \xrightarrow{k} P \]

is defined as

\[ r = k[A][B] \] (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 \([B] \approx \text{const.}\), then equation (3) becomes

where

\[ r = k_{\text{obs}}[A] \] (4)

\[ k_{\text{obs}} = k[B] \] (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 \(\tau\) as the reciprocal of the rate constant \(k_{\text{obs}}\), \(\tau = 1/k_{\text{obs}}\).

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

\[ r = k [\text{Mu}^-] [\text{H}_3\text{O}^+] f_\pm^2 \] (6)

where \(f_\pm\) is the mean ionic activity coefficient.

In the presence of acid excess, \([\text{H}_3\text{O}^+] \gg [\text{Mu}^-]\), 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 \(k_{\text{obs}}\), as follows

\[ r = k_{\text{obs}} [\text{Mu}^-] \] (7)
\[ k_{\text{obs}} = k [\text{H}_3\text{O}^+] f_\pm^2 \] (8)

The aim of the experiment is to determine \( k_{\text{obs}} \) 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

\[ A_t = A_0 e^{-k_{\text{obs}} t} \] (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 \( \varepsilon \) for murexide at \( \lambda_{\text{maks}} \) is \( 1.38 \times 10^4 \text{dm}^3/(\text{mol}\times\text{cm}) \) [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

\[ A_t = A_\infty + (A_0 - A_\infty) e^{-k_{\text{obs}} t} \] (10)

which hold for the experiment.

A solution of murexide absorbs light in the wavelength range 420-660 nm; the maximum absorption appears at \( \lambda_{\text{maks}} = 523 \text{ nm} \). 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 \( 5 \times 10^{-4} \text{ mol/dm}^3 \).
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

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

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

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 $k_{\text{obs}}$, for murexide decomposition in the two solutions studied. Give the value of $k_{\text{obs}}$ with the standard deviation and proper units.

Discussion
1. Compare the values of $k_{\text{obs}}$ obtained in water and in a water micellar solution of C$_{12}$H$_{25}$SO$_4$Na (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

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

(12)

takes place according to the scheme

$$A + B \xrightleftharpoons[k_2]{k_1} AB \xrightarrow{k_3} P$$

(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

Supplementing literature

Related problems