Micelles in Physical Chemistry Laboratory. Surfactant Catalyzed Oxidation of Glycine by Acidic Permanganate

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요   약. 미셸 촉매 작용은 이론과 실험 화학 교과내용에서 중요한 부분이다. 산성 용액에서 도데실황산 나트륨(SDS) 을 촉매로 한 글리신과 과망가니즈산 칼륨의 반응은 미셸 촉매 작용을 보여주는 반응속도론적 실험으로 적합하며, 고등학교 와 대학 학부과정의 불리화학실험에서 사용할 수 있다. 본 연구에서는 이 반응이 계면활성제 존재하에서 반응속도가 빨라지 는 것을 관찰하기 위하여 SDS를 넣지 않은 경우와 넣은 경우 모두 실험을 진행하였고, 얻어진 k를 [SDS]에 대하여 도시하 였다. SDS의 임계 미셸 농도 이하에서부터 계면활성제에 의한 촉매 효과가 관찰되었는데, 이 선-미셸 촉매 효과는 양의 협 동효과에 의한 것임을 알 수 있다. 얻어진 양의 협동지수(n)는 2.37이다. 또한 기질과 산화제의 농도에 따른 반응속도 변화 도 논의하였다. 반응은 유사 일차 반응으로 진행되었으며, 글리신과 과망가니즈산 이온의 농도에 각각 일차 반응으로 나타나 전체 반응 차수는 이차 반응이었다. 반응 시간은 3~4시간으로 한 실험 시간에 몇 개의 실험 데이터를 얻을 수 있다. 용액 제조와 실험 과정에 대해서 자세히 기술하였으며, 또한 계면활성제에 의한 촉매 작용의 이론도 논의하였다.

주제어: Laboratory, Surfactant, Micellar, Glycine, Permanganate

ABSTRACT. Micellar catalysis is an essential part of theoretical and experimental curricular. The sodium dodecylsulfate (SDS) catalyzed reaction between glycine and potassium permanganate in acidic medium is an ideal kinetic experiment for the secondary and undergraduate physical chemistry laboratory, to show the effect of micellar catalysis on rate of the reaction. The reaction is conducted both with and without SDS to observe the rate enhancement in the presence of surfactant. To show surfactant catalysis a plot between k and [SDS] is plotted. As surfactant catalysis is observed even before the critical micelle concentration of SDS, this pre-micellar catalysis can be understood in the light of positive co-operativity. The value of positive cooperative index (n) has been found to be 2.37. Further, dependence of the reaction rate on substrate and oxidant concentrations is also discussed. The reaction follows pseudo-first-order kinetics. The overall reaction is second order, with first-order dependence on both glycine and permanganate concentrations. The theory of surfactant catalysis is also discussed. With the conditions specified in the experiment, total reaction times are in 3~4 hours lab session, thus allowing several data sets to be acquired in a single laboratory period. Preparation of solutions and procedure is also given in detail.

Keywords: Laboratory, Surfactant, Micellar, Glycine, Permanganate

INTRODUCTION

This study of micellar catalyzed and uncatalysed oxidative decarboxylation of glycine by potassium permanganate in moderately concentrated acid medium is an ideal and simple kinetic experiment for secondary level and undergraduate chemistry laboratory[1]. This shows how the presence of surfactant affects the reaction rate, dependence of the reaction rate on the concentrations of substrate and oxidant. Efforts are also made to impart training to write the most pertinent reaction mechanism for the reaction under consideration. Using excess concentrations of glycine, the depletion of permanganate is monitored iodometrically. Various graphs to ascertain the first order kinetics have been drawn. The reaction follows pseudo-first-order kinetics. The overall reaction is second order, with first-order dependence on both permanganate and glycine. Then the effect of variation of surfactant concentration on the reaction rate was studied. Positive cooperativity index value is obtained graphically to establish the pre-micellar catalysis. The experiment is feasible in 3-4 hours of lab session. Thus this has been found to be a good experimental chemical activity to be undertaken.

Theory of Surfactant catalysis[2-7]

Surfactants have attracted considerable interest in theoretical and experimental fields due to their catalytic effects and behaviour as analogous to biological membranes. They have a tendency to associate i.e. at a certain concentration in solution their monomers associate to form larger aggregates. The surfactant molecules always contain both polar (hydrophilic) and non-polar (hydrophobic) moieties they thus tend to concentrate at interfaces. Surfactants can be separated into two main types, ionic and non-ionic, the former dissociate in water. Ampholytic surfactants contain both types of functional groups but only one of them is active at a given pH of the medium. The ionic surfactant monomer is completed by an ion of the opposite charge, called a counter-ion (in cationic surfactant it is usually a halide; in anionic surfactant it can be an alkali-metal cation). The hydrophobic group is generally a

hydrocarbon chain (R) of 10 to 20 carbon atoms. The hydrophilic portion may ionise or it may not. At the lower concentration surfactant molecules consist in the monomeric state in aqueous solution. However as the concentration increases they begin to self-associate and form a new pseudophase as they reach the critical micelle concentration (cmc).

Critical micelle concentration

Surfactants dissolve completely in water at very low concentration, but above a certain concentration, they have a tendency to associate i.e. at a certain concentration in solution, their monomers associate to form larger micelle aggregates. This concentration is characteristic for each surfactant and is termed critical micelle concentration (cmc). In fact, as the concentration of surfactant in the solvent increases the diphilicity of the molecules which begins to cause association to form larger particles.

What is micellar catalysis?

One of the important properties of micellar system is their ability to affect the rates of the chemical reaction. The effect of surfactants on reaction kinetics is called micellar catalysis. The physical basis for micellar catalysis involves several contributing factors. Micellar catalysis of reactions in aqueous solutions is usually explained on the basis of a distribution of reactants between water and the micellar "pseudophase". The reaction occurs at different rates in the two media. If the solubility of the reactants is greater in the micelles than in water then the local concentration is increased in the micelle, often with suitable orientation of the reactants bound in the micelle. This leads to a large increase in the effective concentration and the observed rate (in terms of moles per unit time per liter of the entire solution) increases accordingly leading to an increase in the reaction rate. The relative free energies of the reactions and/or the transition state can be altered when reaction takes place in the micellar phase instead of bulk water. This concept is reminiscent of catalysis by an enzyme and many initial studies of rates in miceller system focussed on this possibility. Further, it was thought that only electrostatic interaction occurs between micelles and reactants,

however, later it was revealed that reaction rates are also affected by hydrophobic interactions. Catalytic effect increases with increasing hydrophobicity of the micelles and reactants. A simple surfactant catalysis can be ascertain by plotting a graph between k versus [D] but to describe the dependence of rate constant on [D] in pre-micellar region we propose a Piszk-iewicz model. If a graph between log $[k_{obs}-k_o/k_m-k_{obs}]$ versus log [D] is linear and the slope value falls between 1-6 this confirms the pre-micellar cataly-sis. Here, k_o is rate constants in the absence of sur-factant, k_{obs} is the observed rate constant at any concentration of surfactant and k_m is the maxi-mum rate constant obtained in the presence of sur-factant.

EXPERIMENTAL

Preparations of chemicals

Following chemicals were used. Potassium per-manganate (BDH), sulphuric acid (AR), glycine (Merck), soluble starch (AR), sodium thiosulphate (AR), SDS (Aldrich), potassium iodide, oxalic acid, sodium hydroxide and deionised water.

Apparatus

Burette (50 mL), pipette (10 mL), conical flask (125 mL), burette stand, porcelain white plate.

Preparation of Solutions

Students are being adviced to refer to the book "A textbook of quantitative inorganic analysis" by A. I. Vogel[8]. This gives data regarding the strength of various acids, corresponding to their percentage or normality and specific gravities and also how much volume of each acid should be taken and diluted to 1000 mL in order to prepare 1 M solu-tion.

Potassium permanganate (M/50)

By dissolving 0.790 g of potassium permangan-ate in water (deionised) so as to make the final vol-ume of solution 250 mL, thus we get M/50 per-manganate solution.

Sulfuric acid

The stock solution of sulphuric acid can be pre-pared by dilution of known volume of aci d. 667mL of (18 M) H_2SO_4 is made up to 1000 mL will give

12 M H_2SO_4. The solution is so prepared can be standardized against the solution, NaOH previously standardized against standard solution of oxalic acid. While making the sulfuric acid of desired strength, care is to be taken that concentrated H_2SO_4 should be added in installment of few mL to the water and not water to the acid. In case water is added to the acid, intense heat evolves which may break the container.

Oxalic acid (3M)

The standard solution of oxalic acid ($H_2C_2O_4$ $\cdot 5H_2O$) was prepared by direct weighing 37.8 g of oxalic acid into water to make the final volume 100 mL.

Sodium hydroxide

We want to prepare stock solutio n of 3M sodium hydroxide in 100 mL water. For this 12 g of NaOH has to be dissolved in water. It is advised to weigh about 18 g of NaOH to dissolve in water to make the final 100 mL. We have waited slightly more NaOH because quantitative dilution of this solution give us standard solution of 3 M. Before dilution the solution was standardized by titrating it against the standard oxalic acid solution.

Glycine (1.5 M)

The molecular weight of glycine is 75, therefore, 112.5 g of glycine dissolved in water to get the final volume of one liter so as to get 1.5 M solution.

Sodium thiosulphate (Hypo) (M/200)

M/200 solution of Sodium thiosulphate ($Na_2S_2O_3$ $\cdot 5H_2O$) can be prepared by dissolving 1.860 g of it in 1500 mL of water. In order to avoid standardiza-tion care is to be taken that stock solution should remain the same throughout the experiment.

Potassium iodide (1%)

This is done by weighing 1 g of KI and dissolv-ing into 100 mL of water.

Starch solution (1%)

Soluble starch was taken approximately 1 g on a watch glass, and a paste of it was prepared by add-ing a few drops of water to it. About 100 mL of water was taken in separate beaker and warmed up to 70-90 °C and then the previously prepared paste was added drop by drop with constant stirring to this warm water. A faintly opalescent solution of

1% starch is thus prepared.

Sodium dodecyl sulphate (M/100)

The stock solution of the detergent (M/100) was prepared by dissolving 0.288 g of SDS in 100 mL of water. Care is to be taken that the solution should not be shaken vigorously otherwise lots of bubbles will be formed which will take great time to settle down, consequently the work will be delayed.

PROCEDURE, RESULTS AND DISCUSSION

The reaction has been studied iodometrically. Take 35 mL of glycine solution (1.5 M), 10 mL of water and add 5 0mL of sulfuric acid (1 2M). Shake it well. Now add 5 ml. of potassium permanganate solution, in the reaction mixture bottle. Note down the time. Shake the reagent bottle for about two minutes. Need not to worry about the zero reading. After stirring and shaking thoroughly, pipette out 10 mL of the reaction mixture. Add 5 mL of 1% potassium iodide in the conical flask. Iodine will be liberated, reaction will stop between MnO_4^- and glycine. $I_2 \cdot I^- \rightarrow I_3^-$ complex will be formed, hence no loss of iodine due to evaporation. Titrate flask solution against hypo till the pale yellow colour appears now add a few drops of starch solution. The solution becomes blue. The hypo is to be added till blue color disappears. Note the burette reading. As the reaction proceeds and MnO_4^- is consumed, lesser MnO_4^- will liberate lesser I_2 and consequently less hypo is required. Readings are to be taken after every ten minutes of interval and tabulated. About 75% of the reaction is to be studied. A perusal of the table reveals that the value of rate constant k was found to be constant. This confirms that the reaction between glycine and permanganate is first order kinetics. Further, this could be confirmed by drawing various graphs. For the first order kinetics the graphs between log (a-x) vs. t and log a/a-x vs. t must be straight line, and specifically the straight line in the case of log a/a-x vs. t plot should pass through the origin. Volume of hypo added is used instead of concentrations for a and (a-x) as the advantage of first order kinetics. All the desired plots are in complete agreement with the

Table 1. Typical run

[Glycine] = 0.525 mol dm⁻³			[MnO₄⁻] = 1.0 × 10⁻³ mol dm⁻³		
[H₂SO₄] = 6 mol dm⁻³			Temp = 28 °C		

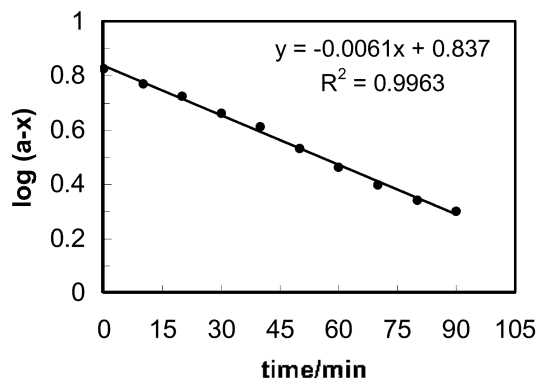| time/min	a	(a-x)	log (a-x)	log (a/a-x)	k / 10⁻² min⁻¹
0	6.7	-	0.8260		
10		5.9	0.7708	0.055	1.26
20		5.3	0.7242	0.101	1.16
30		4.6	0.6627	0.163	1.25
40		4.1	0.6127	0.213	1.22
50		3.4	0.5314	0.294	1.35
60		2.7	0.4623	0.363	1.39
70		2.3	0.3979	0.428	1.39
80		2.0	0.3424	0.483	1.38
90		1.8	0.3010	0.525	1.33

k=1.40 × 10⁻² min⁻¹

$$y = -0.0061x + 0.837$$
$$R^2 = 0.9963$$

Fig. 1. Typical run. [Glycine]=0.525 mol dm⁻³, [MnO₄⁻]= 1.0×10⁻³ mol dm⁻³, [H₂SO₄]=6 mol dm⁻³, Temp=28 °C.

expected pattern. In a typical kinetic run (*Table* 1) for the reaction [Glycine]=0.525 M, $[MnO_4^-]$=1.0×10⁻³ M, $[H_2SO_4]$=6 M, a plot of log (a-x) *versus* time gave a straight line while log a/a-x versus time yields a straight line passing through the origin [*Fig.* 1 and *Fig.* 2], which indicates that reaction under the chosen conditions follows *pseudo* first-order kinetics. Thus the order with respect to the isolated species i.e. $[MnO_4^-]$ is unity. The mean pseudo first-order rate constant k, determined from slope value of *Fig.* 1 has been found to be 1.40×10⁻² min⁻¹ i.e. the slope value multiplied by -2.303.

Order with respect to |glycine|

In order to get the order of reaction with respect to glycine concentration kinetic runs were carried out with varied concentrations of glycine [*Table* 2] and keeping the concentrations of other reagents
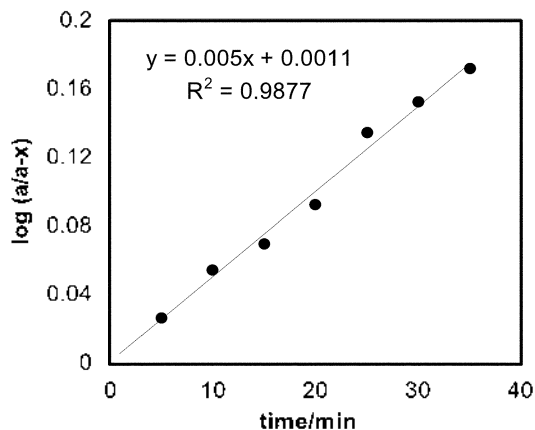
Fig. 2. log (a/a-x) vs. time plot. [Glycine]=0.525 mol dm⁻³, [MnO₄⁻]=1.0×10⁻³ mol dm⁻³, [H₂SO₄]=6 mol dm⁻³, Temp=28°C.

Table 2. Variation of substrate concentration
[MnO₄⁻]=1.0 × 10⁻³ mol dm⁻³ [H₂SO₄] = 6 mol dm⁻³
Temp = 28°C

[Glycine] / mol dm⁻³	k/10⁻² min⁻¹
0.300	0.71
0.375	0.92
0.450	1.06
0.525	1.24
0.600	1.42
0.675	1.66

constant. The plots of log k *vs.* log [glycine] gave straight lines with slopes 0.99 [*Fig.* 3], suggesting the reaction has first-order dependence with respect to [glycine].

Effect of addition of surfactant
This reaction has been found to be catalyzed by
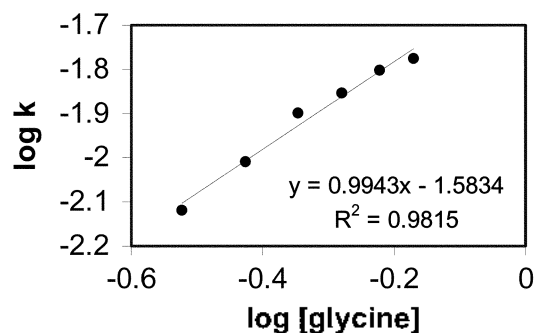
Fig. 3. Variation of substrate concentration. [MnO₄⁻]=1.0×10⁻³ mol dm⁻³, [H₂SO₄]=6 mol dm⁻³. Temp=28 °C.

Table 3. Change in rate constant on variation of [SDS]
[Glycine]=0.225 mol dm⁻³ [MnO₄⁻]=1.0×10⁻³ mol dm⁻³
[H₂SO₄]=6 mol dm⁻³ Temp.=28 °C

[SDS]/10⁻⁴ mol dm⁻³	k_{obs}/10⁻³ min⁻¹
Nil	0.47
2.0	2.02
3.0	3.63
4.0	5.65
6.0	12.40
8.0	20.70
10.0	24.49
20.0	38.60

k_m = 38.60×10⁻³ min⁻¹

addition of sodium dodecyl sulfate, [*Table* 3]. The reaction rate increases with the increase in the detergent concentration from 2.0×10^{-4} to 20×10^{-4} M. The reported cmc of sodium dodecyl sulfate is 8.1×10^{-3} M at 25 °C. Reports are available that the catalysis below cmc i.e. premicellar catalysis is also feasible.[6] As discussed earlier in the theoretical treatment for pre-micellar catalysis a graph is plotted between log [k_{obs}-k_0/k_m-k_{obs}] and log [D]. The plot is a good straight line with slope value n=2.37. This figure is drawn using the table-3. In this graph k_0 is the first value of the from the table i.e. without surfactant, k_{obs} is the value of rate constant with surfactant concentration from 2.0×10^{-4} to 20×10^{-4} mol dm⁻³ and k_m is the maximum rate constant in the presence of surfactant concentration 20×10^{-4} mol dm⁻³.In this way for every next value of surfactant we get a new k_{obs} value. Just put these values in
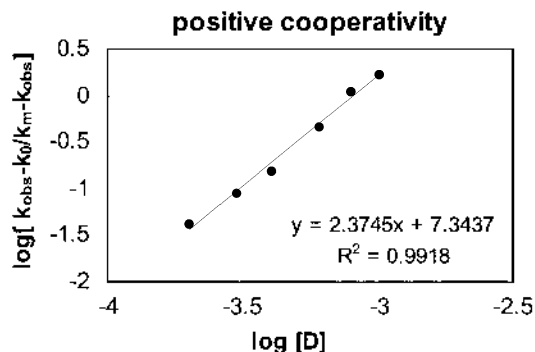

Fig. 4. Positive Cooperativity. Change in rate constant on variation of [SDS]. [Glycine]=0.225 mol dm⁻³, [MnO₄⁻]=1.0 ×10⁻³ mol dm⁻³, [H₂SO₄]=6 mol dm⁻³, Temp.=28 °C.

log $[k_{obs}-k_0/k_m-k_{obs}]$ and draw a graph against log [D]. The n value obtained is between the expected value for pre-micellar catalysis i.e. between 1 to 6. This value on n supports the substrate promoted micellization. This lower value of n suggest the pre-micellar catalysis because in the case of micellar catalysis this value has to be more than 20.

Mechanism

According to Frost and Pearson[9], a reaction mechanism is a mental model. Regarding the mechanism, it is advised for the students to read E. L. King's[10] book "How chemical reactions occur". According to this book, if the order of reaction with respect to substrate is one, then it should appear once on the left-hand side in the various steps in the form of equilibrium. Therefore, glycine should appear once on the left-hand side. The order with respect to $KMnO_4$ is also one, it should also appear once in the reaction scheme, whether it appears earlier or later it makes no difference. Glycine, which is an amino acetic acid, is an internal salt and present in the form of zwitter ion.[11] The carboxyl group has the ability to lose a proton (acidity) where as the amino group may accept a proton (basicity). Hence the molecule is polar and has a high dipole moment.

$$H_2N - CH_2 - COOH \rightleftharpoons H_3N^+-CN_2-COO^- \quad (1)$$
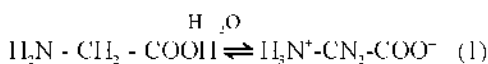
In order to avoid the precipitation of MnO_2 the reaction in being carried out in moderately concentrated acid medium, high concentration of proton will protonate the zwitter ion. Since NH_2 part is already having a positive charge, therefore, the most likely place to which proton could get attach is carboxyl oxygen. Thus, the next step is as follow:

$$H_3N+-CH_2COO^- +H^+ \overset{K_1}{\rightleftharpoons} NH_3CH_2COOH \quad (2)$$
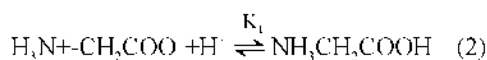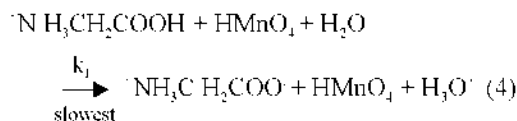
The order with respect to permanganate is also one, it should also appear on the left hand side once. Hence,

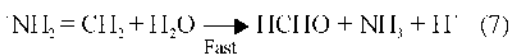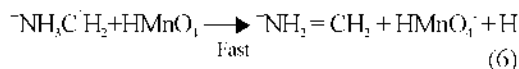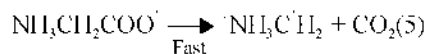$$MnO_4^- + H^+ \overset{K_2}{\rightleftharpoons} HMnO_4 \quad (3)$$
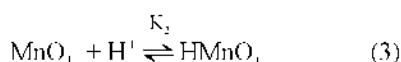
This step is consistent with the spectroscopic evidence of existence of molecular $HMnO_4$, therefore,

cumulative effect explains the catalysis by mineral acid as well[1] but not given here as beyond the scope of the students at secondary level. $HMnO_4$ a more powerful species of MnO_4^- now reacts with protonated zwitter ionic species of glycine, in the presence of water molecule.

$$^+N H_3CH_2COOH + HMnO_4 + H_2O$$
$$\overset{k_1}{\underset{slowest}{\longrightarrow}} \quad ^+NH_3C H_2COO^- + HMnO_4^- + H_3O^+ \quad (4)$$

This three-body collision is difficult and thus explains the cause of slowness in the slowest reaction. Most suitable conformation and configuration of the activated complex is necessary for this reaction to take place. Since this occur statistically per second, in a very small number, the eqs 4 becomes very slow. All subsequent steps are very fast and not of kinetic importance. Moreover, all kinetic and activation data are explainable with the help of step 2 to the rate determining step, i.e step 4. Our purpose is to deduce mechanism from kinetic data. This could be shown in the following paragraphs and from the deduction rate law expression. The probable reactions (fast) after the rate determine are as follows :

$$NH_3CH_2COO^- \overset{}{\underset{Fast}{\longrightarrow}} \ ^+NH_3C H_2 + CO_2 (5)$$

$$^+NH_3C H_2+HMnO_4 \overset{}{\underset{Fast}{\longrightarrow}} \ ^+NH_2 = CH_2 + HMnO_4^- +H \quad (6)$$

$$^+NH_2 = CH_2 + H_2O \overset{}{\underset{Fast}{\longrightarrow}} HCHO + NH_3 + H^+ \quad (7)$$

In order to derive rate law apply the law of mass action to the equations 2 - 4. from eqn.2

we get,

$K_1 = [^+NH_3CH_2COOH]/[H^+] [H_3N^+ -CH_2COO^-]$
Or $[^+NH_3CH_2COOH]=K_1[H^+][H_3N^+ - CH_2COO^-]$
$$(8)$$

From eqn.3
$$K_2=[HMnO_4]/[MnO_4^-] [H^+]$$
Or $\quad [HMnO_4]=K_2 [MnO_4^-] [H^+]$

But we know that free $[MnO_4^-]$=initial $[MnO_4^-]_i$ - $[HMnO_4]$ formed

Or $[HMnO_4]=K_2[MnO_4^-]_t[H^+] - K_2[HMnO_4][H^+]$

Or $[HMnO_4]\{1+K_2[H^+]\}=K_2[MnO_4^-]_t[H^+]$

Or $[HMnO_4]=K_2[MnO_4^-]_t[H^+]/\{1+K_2[H^+]\}$ (9)
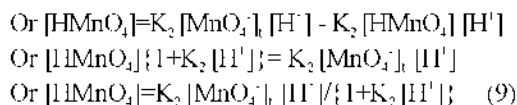
Now from eqn.4

$-d[MnO_4^-]/dt=k_1[^+NH_3CH_2COOH][HMnO_4][H_2O]$ (10)

Substituting the values of $[^+NH_3CH_2COOH]$ and $[HMnO_4]$ from 8 and 9 in eqn 10 we get

$$-d[MnO_4^-]/dt \frac{k_1K_1K_2[H^+]^2[H_2O]}{\{1+K_2[H^+]\}}$$
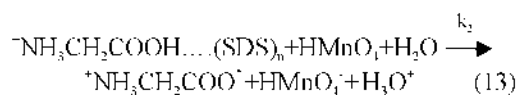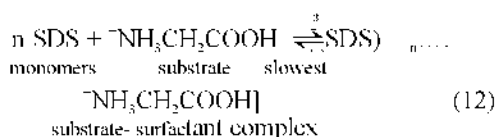
$$[H_3N^+-CH_2COO^-][MnO_4^-]_t$$

At a given concentration of acid

$$-d[MnO_4^-]/dt=k[Glycine][MnO_4^-]_t   (11)$$

where $k = \dfrac{k_1K_1K_2[H^+]^2[H_2O]}{\{1+K_2[H^-]\}}$

Surfactant catalyzed mechanism:

In the presence of an anionic surfacatnt SDS the reaction rate has been found to be substantially increased. This is most probably due to the electrostatic interaction between substrate and anionic surfactant globules. This leads to increase in effective concentration and may provide favourable orientation for the collision, thus the reaction rate increases. The first step is the formation of glycine - surfactant complex. The lower value of n substantiate this because the number of detergent molecules otherwise expected in a micelle is around 20. The substrate surfactant interaction is the main cause of pre-micellar catalysis. In this light the proposed mechanism is thus as follows:

$$n\ SDS + {}^-NH_3CH_2COOH \underset{\text{monomers}}{\overset{\text{slowest}}{\rightleftharpoons}} SDS)_n \dots$$

$$^-NH_3CH_2COOH]   (12)$$
substrate- surfactant complex

$$^-NH_3CH_2COOH\dots(SDS)_n+HMnO_4+H_2O \overset{k_2}{\longrightarrow}$$

$$^+NH_3CH_2COO^-+HMnO_4^-+H_3O^+   (13)$$

In order to derive rate law apply the law of mass action to the equations 12 -13, from

eqn.12 we get,

$$K_3=[(SDS)_n\dots{}^-NH_3CH_2COOH]/[n\ SDS]$$
$$[^-NH_3CH_2COOH]$$

Or $[(SDS)_n\dots{}^-NH_3CH_2COOH]=K_3[n\ SDS]$
$$[^-NH_3CH_2COOH]   (14)$$

From eq.13

$$-d[MnO_4^-]/dt=k_2[(SDS)_n\dots{}^-NH_3CH_2COOH]$$
$$[HMnO_4][H_2O]   (15)$$

Since the catalyzed and uncatalysed reactions take place simultaneously, substitute the values of $[HMnO_4]$ and $[(SDS)_n\dots{}^-NH_3CH_2COOH]$ from 9 and 14 in eqn 15, and combining it with the uncatalysed reaction i.e. equation 4, we get the rate law as:

$$-d[MnO_4^-]/dt = \frac{k_1k_2K_1K_2K_3[H^+]^2[H_2O]}{\{1+K_2[H^-]\}}$$

$$[SDS]^n[^+NH_3CH_2COOH][MnO_4^-]$$

At a given concentration of acid

$$-d[MnO_4^-]/dt=k''[SDS]^n[Glycine][MnO_4^-]$$

where $k'' = \dfrac{k_1k_2K_1K_2K_3[H^+]^2[H_2O]}{\{1+K_2[H^-]\}}$

or $-d[MnO_4^-]/dt = k_{obs}[SDS]^n[MnO_4^-]$ (16)

Where $k_{obs} = k''[Glycine]$

It is evident from the rate law equation 16 that substrate and surfactant complex is the cause of catalysis. Surfactant catalysis is purely a physical catalysis and there is no covalent type of bond formation takes place.

Conclusion: The proposed experimental chemical education exercise well tested and easy to perform at secondary and undergraduate level laboratory to impart an understanding of order of reaction, determination of rate constants, the surfacatnt catalysis, effect of variation of reactant concentrations on the rate of the reaction and how to write a most probable reaction mechanism.

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