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INFLUENCE OF SODIUM DODECYL SULPHATE MICELLES ON THE KINETICS OF COMPLEX FORMATION BETWEEN $Pd(H_2O)_4^{2+}$ and *S*-CARBOXYMETHYL-L-CYSTEINE

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The kinetics of complex formation between $Pd(H_2O)_4^{2+}$ and *S*-carboxymethyl-L-cysteine ($SCMCH_2$) was investigated in the presence of sodium dodecyl sulphate in the acidity range between 2 M $HClO_4$ and pH 5. Although the mechanism was not affected by the presence of anionic micelles, retardation ($2{\cdot}2 < pH < 5$) and acceleration ($pH < 2{\cdot}2$) of the complex formation were observed compared with its rate in aqueous solution. These effects were interpreted in terms of the long-range electrostatic interactions between the negatively charged micellar surface and ligand species which can be in different ionic forms depending on the pH.

1. INTRODUCTION

S-Carboxymethyl-L-cysteine ($SCMCH_2$) belongs to a group of naturally occurring amino acids containing a thioether group (see Scheme 1). $SCMCH_2$ is a biologically active substance with a mucolytic effect, which was found in the urine of cystathioninuric patients[1] and identified as an intermediate in cystamine formation.[2]

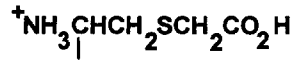
Only a few studies have been reported concerning the interaction of $SCMCH_2$ with metal ions such as Cu(II), Ni(II) and Zn(II).[3,4] A spectrophotometric method for determination of *N*-acetyl-L-cysteine and $SCMCH_2$ using palladium(II) chloride ($PdCl_2$) has been reported.[5] Also, the kinetics of complex formation between $PdCl_2$ and $SCMCH_2$ have been studied and the mechanism of the reaction has been clarified.[6]

In this work, the influence of the anionic surfactant sodium dodecyl sulphate (SDS) on the rate of complex formation between $Pd(H_2O)_4^{2+}$ and $SCMCH_2$ in aqueous solution was studied. The effects of micellar systems on chemical reactions have been studied extensively, especially for organic reactions.[7,8] However, few studies on inorganic reactions have been reported. So far, electron-transfer reactions involving metal complexes[9] and the formation of Ni(II) or Mn(II) complexes with organic ligands[10–13] have been investigated. These studies are important not only for the investigation of inorganic reaction mechanisms, but also for their biochemical aspects, as models of electron-transfer and ligand-exchange reactions at the surface of a biomembrane or at the interface of a globular protein.

EXPERIMENTAL

All reagents were commercial products of the highest purity available. A freshly prepared 2×10^{-2} M $SCMCH_2$ aqueous stock solution was used in all experiments. A standard solution of 2×10^{-3} M $Pd(H_2O)_4^{2+}$ was prepared as described elsewhere.[5] The acidity of the solution was adjusted by addition of either NaOH ($2 < pH < 5$) or $HClO_4$ ($pH < 2$). pH values were measured by a Beckman Expandomatic pH meter. The ionic strength was kept constant by the addition of $NaClO_4$ ($I = 0.1$), except for the measurements performed in concentrated perchloric acid. The acidity of the concentrated $HClO_4$ was characterized by the Hammet acidity function, H_0.[14]

The absorption spectra were recorded on a Perkin–Elmer Lambda 5UV–visible spectrophotome-



$SCMCH_2$ (2.2 <pH< 3.33)

Scheme 1

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ter. For stopped-flow experiments, a HI-TECH Model SFA 12 universal rapid kinetic accessory was fitted to the spectrophotometer. All the other reagents (surfactant, acid or inert salts) were added to the ligand and metal ion solutions at least 20 min prior to mixing. Kinetic experiments were performed by mixing equal volumes of $SCMCH_2$ and $Pd(H_2O)_4^{2+}$ solutions at 25 ± 1 °C. The rate of the complex formation was followed by monitoring the increase in the optical absorbance (A) at 250 nm with time (t). Values of k_{obs} were determined by fitting the experimental trace (A vs t) to the function $(A_{eq} - A)/(A_{eq} - A_0) = \exp(-k_{obs}t)$, where A_0 and A_{eq} are the initial and final absorbances, respectively, by using a computer program based on the least-squares method. All kinetic measurements were reproducible within limits of error of ±5%. The quoted values are the averages of at least five runs under identical experimental conditions.

RESULTS AND DISCUSSION

Absorption spectra and stoichiometry of the Pd(II)–$SCMCH_2$ complex in the presence of SDS

The formation of the complex between $Pd(H_2O)_4^{2+}$ and $SCMCH_2$ in the presence of 1×10^{-2} M SDS was investigated in the acidity range from 2 M $HClO_4$ to pH 5. The absorption spectra of solutions containing equal concentrations of $Pd(H_2O)_4^{2+}$ and $SCMCH_2$ and 1×10^{-2} M SDS at different acidities are shown in Figure 1. Isosbestic points indicating the existence of two interconverting species in solution were not observed. The Pd(II)–$SCMCH_2$ complex in the presence of anionic micelles has an absorption maximum at 250 nm and a shoulder at 320 nm. For comparison, absorption spectra of the reacting species [$Pd(H_2O)_4^{2+}$ and $SCMCH_2$] are also given in Figure 1.

The stoichiometry of the complex [Pd(II) : $SCMCH_2$ = 1 : 1] in the presence of 1×10^{-2} M SDS was determined at different acidities (1 M $HClO_4$ and pH 2 and 4) by continuous variation of the ratio between initial concentrations of $Pd(H_2O)_4^{2+}$ and $SCMCH_2$. Also, the absorption spectra at constant $Pd(H_2O)_4^{2+}$: $SCMCH_2$ ratios were followed as a function of acidity. The absorption spectra indicated that the metal chelate structure was not affected by the change in acidity. The small shifts of the absorption maxima are most likely due to the presence of different ionic forms of the ligand bound in the complex ($pK_1 = 1{\cdot}99$, $pK_2 = 3{\cdot}33$).[4] Similar effects were also found in the reaction of $PdCl_2$ with $SCMCH_2$ in aqueous solutions.[6]

Kinetics of complex formation between $Pd(H_2O)_4^{2+}$ and $SCMCH_2$ in the presence of SDS

The kinetics of the formation of the $Pd(H_2O)_4^{2+}$–$SCMCH_2$ complex in the presence of SDS micelles were followed in the acidity range from 2 M $HClO_4$ to pH 5 under pseudo-first-order conditions ([$SCMCH_2$] ≫ [Pd(II)]). The experimental rate constants (k_{obs}) followed the expression

$$k_{obs} = k_f C_L + k_r \quad (1)$$

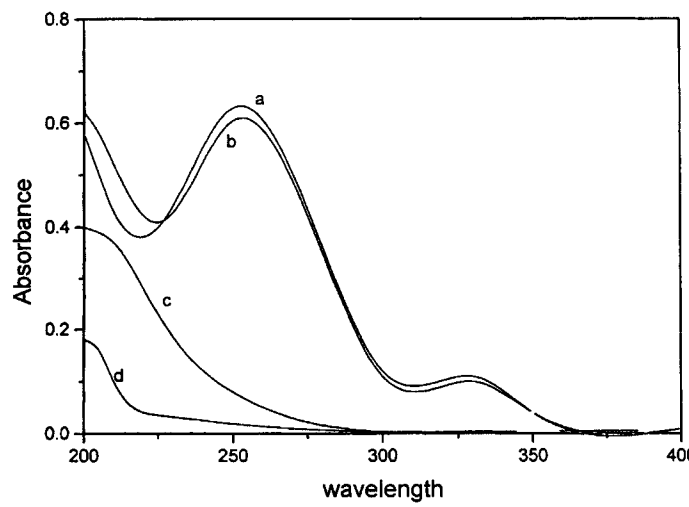

Figure 1. Absorption spectra of solutions containing equal concentrations of $Pd(H_2O)_4^{2+}$ and $SCMCH_2$ (5×10^{-5} M) and 1×10^{-2} M SDS at different acidities: (a) pH 3; (b) 2 M $HClO_4$. Absorption spectra of solutions (1×10^{-2} M SDS, pH 3) containing (c) 5×10^{-5} M $Pd(H_2O)_4^{2+}$ and (d) 5×10^{-5} M $SCMCH_2$

where k_f and k_r are the forward and reverse pH-dependent rate constants, respectively. The linear plot of k_{obs} versus C_L has a zero intercept at $0 < pH < 2$ (see Figure 2, curve b), whereas at $pH > 2$ and in strongly acidic solutions intercepts significantly different from zero are observed (see Figure 2, curves a and c) indicating the occurrence of a measurable reverse reaction. It should be pointed out that in the absence of SDS the reverse reaction exists over the entire range of acidity investigated (see Table 1). These results undoubtedly show that in the presence of micelles at $0 < pH < 2$ the stability constants of the Pd(II)–$SCMCH_2$ complex ($K = k_f/k_r$) is a few orders of magnitude higher than those obtained under the same experimental conditions but in the absence of SDS. The stability constants of the Pd(II)–$SCMCH_2$ complex in the presence of micelles in the pH range 2–5 and in extremely acidic solutions are of the same order of magnitude compared as those obtained in the absence of SDS (see Table 1).

The pH dependence of k_f in the absence and presence of 1×10^{-2} M SDS is shown in Figure 3. Although the pH profiles have similar shapes, their maximum occurs at lower pH in the presence of SDS. Similar shapes of pH profiles indicate that the mechanism of complex formation is not affected by the presence of micelles, although the rates differ from those in aqueous solutions. Also, the presence of micelles has a twofold effect on the rate of complex formation: (a) the complex formation is retarded in the presence of micelles in the pH range 2·2–5 and (b) the complex formation is accelerated at higher acidities compared with the kinetic results obtained in the absence of SDS.

Retardation of the formation of the Pd(II)–$SCMCH_2$ complex in the acidity range from pH 2·2 to 5 can be explained by the effective separation of the reacting species in the presence of anionic micelles (see Figure 3). The anionic micelles provide a dispersed negatively charged surface in solution. As a consequence, the positively charged $Pd(H_2O)_4^{2+}$ ions partition out of the bulk aqueous phase into the surface

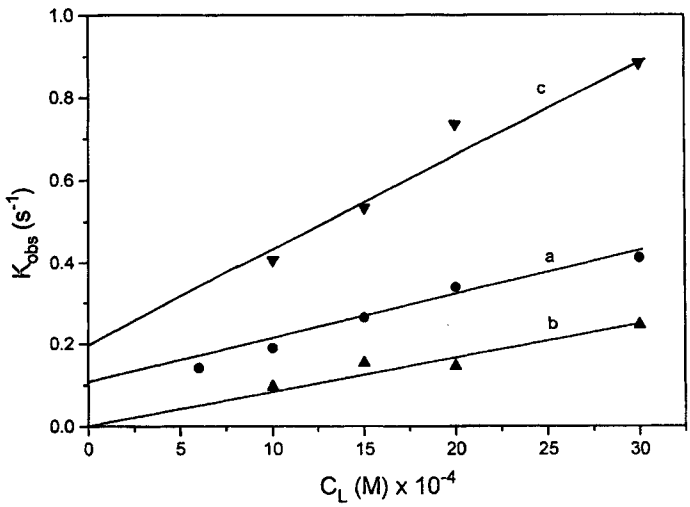

Figure 2. Experimental rate constants (k_{obs}) of complex formation between $SCMCH_2$ and $Pd(H_2O)_4^{2+}$ (2×10^{-5} M) as a function of the $SCMCH_2$ concentration in the presence of 1×10^{-2} M SDS at different acidities: (a) 2 M $HClO_4$; (b) pH 1; (c) pH 3

Table 1. k_f, k_r and K as a function of acidity in the absence and presence of 1×10^{-2} M SDS

	1×10^{-2} M SDS			Water		
pH (H_0)	k_f (l $mol^{-1} s^{-1}$)	k_r (s^{-1})	K (10^4 l mol^{-1})	k_f (l $mol^{-1} s^{-1}$)	k_r (s^{-1})	K (10^4 l mol^{-1})
−0·8	805	0·069	1·17	720	0·082	0·88
0	2622	0	$>10^3$	651	0·037	1·75
1	2702	0	$>10^3$	696	0·029	2·39
3	1335	0·084	1·58	2678	0·125	2·15
5	1651	0·043	3·86	2379	0·120	2·18

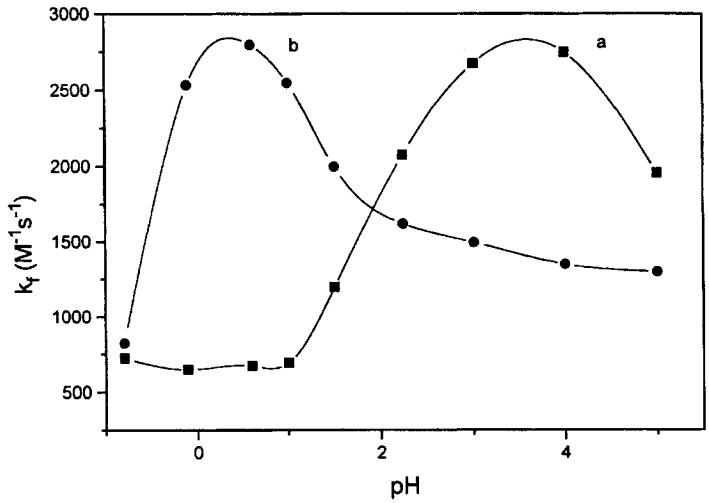

Figure 3. pH profiles of the forward rate constant (k_f) for the formation of the $Pd(H_2O)_4^{2+}$–$SCMCH_2$ complex (a) in the absence and (b) in the presence of 1×10^{-2} M SDS at 298 K

region of the micelles. The estimated binding constants for bivalent ions are in the range $1{\cdot}2 \times 10^3$–$2{\cdot}5 \times 10^3$ l mol^{-1},[15] and consequently all the $Pd(H_2O)_4^{2+}$ ions are on the micellar surface. On the other hand, the hydrophilic ligand $SCMCH_2$ in the pH range 2·2–5 is either a zwitterion (2·2 < pH < 3·33) or an anion (pH > 3·33), so it is located solely in the bulk aqueous phase. Therefore, in the presence of anionic micelles, the reacting species are effectively separated and the complex formation process is slowed. Similar retardation effects have been observed for the Pd(II)–MONO-PACA [1,8-dihydroxy-2-(pyrazol-5-ylazo)naphthalene-3,6-disulphonic acid) system.[16]

In the acidity range from 2 M $HClO_4$ to pH 2·2, formation of the Pd(II)–$SCMCH_2$ complex in the presence of 1×10^{-2} M SDS was faster than that in aqueous solution (see Figure 3). This can be explained as a consequence of the increased concentration of reagent molecules in the vicinity of the anionic micelles. The increase in the concentration of protonated ligand species ($pK_1 = 1{\cdot}99$) in the vicinity of the anionic micellar surface is electrostatically favoured. However, it is well known that the addition of electrolytes or acids can induce the growth and formation of rod-shaped micelles, which is accompanied by a considerable decrease in the 'thickness' of the diffuse double layer.[17] Also, in this pH range the local acidity in the vicinity of the micellar surface is higher than the acidity in the aqueous phase. Hence we believe that the zwitterionic species can reach the area of increased acidity in the vicinity of the interface, so that it is converted into its protonated form and reacts with $Pd(H_2O)_4^{2+}$. Consequently, the net effect is an overall increase in the concentration of protonated ligand species in the vicinity of the micellar surface where its complexation with $Pd(H_2O)_4^{2+}$ is accelerated.

The decrease in the rate of complex formation in the presence of 1×10^{-2} M SDS with an increase in acidity from pH 0·4 to 2 M $HClO_4$ can be explained by the ion exchange of the reactants [protonated ligand and $Pd(H_2O)_4^{2+}$] with H^+. Namely, the kinetic behaviour in extremely acidic micellar solutions approaches the behaviour characteristic of corresponding homogeneous systems.

The sensitivity of the rate of the formation of the Pd(II)–$SCMCH_2$ complex to anionic micelles provides a convenient experimental method for measuring the surfactant concentration at which micelle formation occurs, which is generally considered to be the critical micellisation concentration (CMC) of the surfactant. Some typical dependences of the rate constant (k_{obs}) on the concentration of SDS in the acidity range from 2 M $HClO_4$ to pH 5 are shown in Figure 4. The sharp increase and/or decrease in the rate constant indicates the first appearance of micelles or pre-micellar aggregates. The CMC values obtained (3×10^{-3} M at pH < 2·2 and 5×10^{-3} M at pH 4·5) are smaller than the reported value at zero ionic strength ($7{\cdot}75 \times 10^{-3}$ M). This effect can be explained by the well known observation that the addition of acids and divalent metal ions lowers the CMC of surfactant.[18]

The CMC is defined (in an arbitrary way) from experimental data and must depend to some extent on the experimental method used. The advantage of this method lies in the fact that all the reagents are hydrophilic, and the possibility that they induce micellization below the true CMC is negligible.

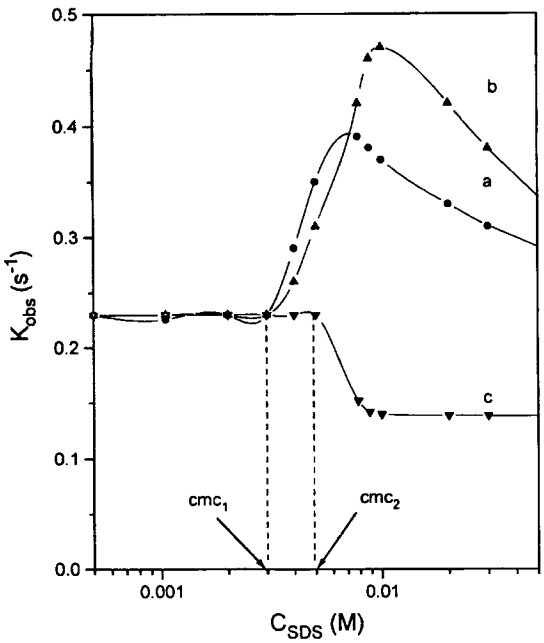

Figure 4. Experimental rate constants (k_{obs}) of complex formation between 2×10^{-5} M $Pd(H_2O)_4^{2+}$ and 2×10^{-4} M $SCMCH_2$ as a function of the SDS concentration at different acidities: (a) 2 M $HClO_4$; (b) pH 1; (c) pH 4·5. Temperature, 298 K

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