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Influence of sodium dodecyl sulfate on the kinetics of complex formation between $[\text{PdCl}(\text{dien})]^+$ and sulfur containing ligands L-cysteine and glutathione

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Abstract

The effect of sodium dodecyl sulfate (SDS) micelles on the kinetics of the complex formation between $[\text{PdCl}(\text{dien})]^+$ and sulfur containing ligands L-cysteine and glutathione (GSH) was investigated by using the stopped-flow technique under pseudo-first order conditions (ligand in excess) in the acidity range from pH 1 to 6. The presence of anionic micelles induced the acceleration of the complex formation in the entire acidity range with the maxima corresponding to the first protolytic constant of the ligands. This effect was interpreted in terms of the attractive electrostatic interaction between reacting species and the micellar surface and their effective concentration in the vicinity of micelles. An increase of the ionic strength leads to a decrease of the rate of complex formation in the presence of anionic micelles due to competition of reactive species with cations originating from inert salt for the micellar surface. The calculation of activation parameters revealed that the entropy of activation is strongly negative in the presence and in the absence of micelles, which is compatible with an associative reaction mechanism.

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1. Introduction

Interactions between Pt(II) and Pd(II) complexes with sulfur-containing biomolecules are very important from a biological and medical point of view. For instance, cisplatin (*cis*-diamminedichloroplatinum(II)) is widely used and is especially effective against testicular, head, neck and cervical cancer [1]. Although the platinum interactions with DNA are held responsible for their antitumor activity, there are many other potential biomolecules that can react with these Pt(II) complexes. Sulfur-containing biomolecules, such as amino acids (e.g. methionine, cysteine) and peptides such as glutathione (GSH), are known to be highly reactive toward

cisplatin and other platinum compounds. These interactions, traditionally, have only been associated with negative phenomena such as resistance and toxicity in the antitumor treatment [2,3]. Tripeptide GSH provides a model compound for the study of these interactions. The nephrotoxicity of antitumor platinum drugs has been ascribed to their reactions with thiol groups of proteins [4,5].

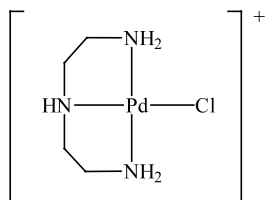
For the investigations of the reaction mechanism of platinum(II) anticancer drugs their palladium(II) analogues are suitable model compounds since they exhibit about 10^4 – 10^5 times higher reactivities, while their structural and equilibrium behavior is similar [6]. Recently, our work has been concentrated on reactions of Pt(II) and Pd(II) complexes with sulfur-bonding molecules [7–15] which could be of fundamental importance for the understanding of the nephrotoxicity of related platinum complexes. However, coordination

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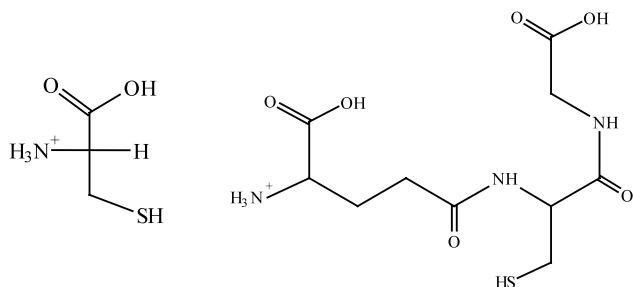
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compounds of Pt(II) and Pd(II) with various tridentate ligands form stable mononuclear complexes even at very acidic pH levels.

In order to study this process, a very suitable compound appeared to be mono-functional $[\text{PdCl}(\text{dien})]^+$ (dien = 1,5-diamin-3-azapentane). This complex, shown below, is easily available and forms stable complexes with S-donor ligands.



The naturally occurring amino acids GSH and L-cysteine are strong sulfur bonding ligands containing a thioether group. Although the complexes of some metal ions with GSH and L-cysteine have been synthesized and characterized [16–19], only a few studies have been done concerning their reactions with Pd(II). In the previous work, the kinetics of complex formation of GSH and L-cysteine with PdCl_2 and $\text{Pd}(\text{H}_2\text{O})_4^{2+}$ have been studied and the mechanism of the reaction has been clarified [20–23]. The effects of micelles forming surfactants on the reaction mechanism have also been extensively investigated [21,22].



L-cysteine

glutathione

In the present paper the influence of the anionic surfactant sodium dodecyl sulfate (SDS) on the rate of the complex formation between $[\text{PdCl}(\text{dien})]^+$ and sulfur containing ligands L-cysteine and GSH in aqueous solution is studied. These studies are important not only from a viewpoint of the inorganic reaction mechanisms, but also from biochemical aspects, i.e. as models of electron-transfer and ligand-exchange reactions on the surface of a biomembrane or at the interface of a globular protein.

2. Experimental

The complex $[\text{PdCl}(\text{dien})]\text{Cl}$ was prepared according to standard procedure [24]. The chemical analyses and

UV–VIS spectral data were in good agreement with those obtained for the previous preparation. L-cysteine (Fluka, 99.5%) and GSH (Fluka, 99%), were used without further purification. Ligand stock solutions were prepared shortly before use by dissolving the appropriate chemicals in 0.1 M HClO_4 (Merck, p.a.) as a supporting electrolyte. Under these experimental conditions, the complex $[\text{PdCl}(\text{dien})]^+$ was stable and the hydrolysis of the complex was negligible [24–27]. Triply distilled water was used. All solutions were purged with nitrogen in order to remove oxygen. The acidity was controlled by addition of Britton–Robinson buffer. The ionic strength was kept constant using NaClO_4 .

The absorption spectra were measured using a Hewlett–Packard 8452A diode-array spectrophotometer in the wavelength range from 220 to 450 nm. For the stopped-flow experiments, the universal rapid kinetic accessory HI-TECH model SFA 12 was fitted to a spectrophotometer. Reactions were initiated by mixing equal volumes of the complex and thiol solutions and were followed for at least eight half-lives. The rate of the complex formation was followed by monitoring the increase of the optical absorbance at 260 nm. All kinetic measurements were reproducible within the limits of error of $\pm 5\%$. The quoted values are the average of at least five runs under identical experimental conditions. The variable-temperature measurements were performed from 276 to 308 K.

3. Results and discussion

3.1. Absorption spectra and stoichiometry of the Pd(II) complexes in the presence of anionic micelles

The complex formation between $[\text{PdCl}(\text{dien})]^+$ and GSH or L-cysteine was studied in the absence and presence of 1×10^{-2} M SDS. The absorption spectra of solutions containing 1×10^{-4} M $[\text{PdCl}(\text{dien})]^+$ and 1×10^{-4} – 1×10^{-3} M GSH or L-cysteine were followed in the acidity range from pH 1 to 6. The concentration of SDS was higher than the critical micellisation concentration (CMC). The absorption spectra of $[\text{PdCl}(\text{dien})(\text{GSH})]^+$ complex as a function of acidity in the presence and in the absence of micelles are shown in Fig. 1. The complexes have the characteristic absorption maxima at 260 and 390 nm, and the shoulder in the wavelength range from 300 to 350 nm. Similar results were obtained for $[\text{PdCl}(\text{dien})(\text{cyst})]^+$ complex. The absorption maximum is at 250 nm, and the shoulder in the wavelength range from 300 to 350 nm, too. The presence of 1×10^{-2} M SDS in the acidity range from pH 1 to 6 did not induce any significant change of the absorption maxima position, but it slightly influenced the absorption intensity.

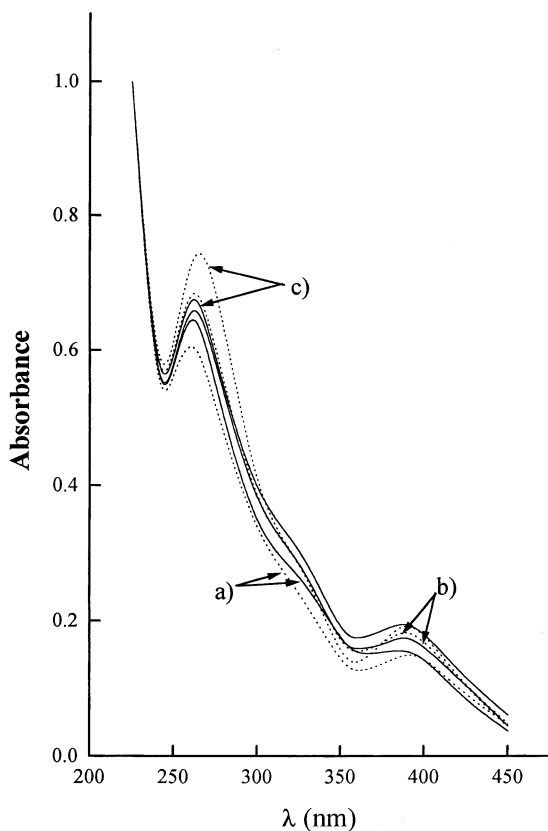
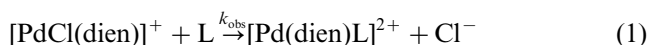


Fig. 1. Absorption spectra of solutions containing 1×10^{-3} M GSH and 1×10^{-4} M $[\text{PdCl}(\text{dien})]^+$ in the presence (solid curves) and in the absence (dot curves) of 1×10^{-2} M SDS at different acidities: (a) pH 5.3; (b) pH 3.4; (c) pH 1.9.

The slight shift of the position and intensity of the absorption maximum with the change of the acidity was most likely due to the presence of different ionic forms of the ligands at different acidities rather than the influence of micelles on the complex formation. Similar effects were also noticed in the reactions of $[\text{Pd}(\text{H}_2\text{O})_4]^{2+}$ and PdCl_2 with *S*-carboxymethyl-L-cysteine and GSH in micellar solutions [20–23].

The stoichiometry of the complexes in the presence and in the absence of 1×10^{-2} M SDS was determined by the molar ratio method at pH 1 and 3.5 keeping $[\text{PdCl}(\text{dien})]^+$ concentration constant and varying the ligand concentration. The results showed that both ligands form a 1:1 complex in the investigated acidity range, according to the relation:



3.2. The kinetics of complex formation in the presence of SDS

The influence of the micelle forming surfactant on the kinetics of complex formation between $[\text{PdCl}(\text{dien})]^+$

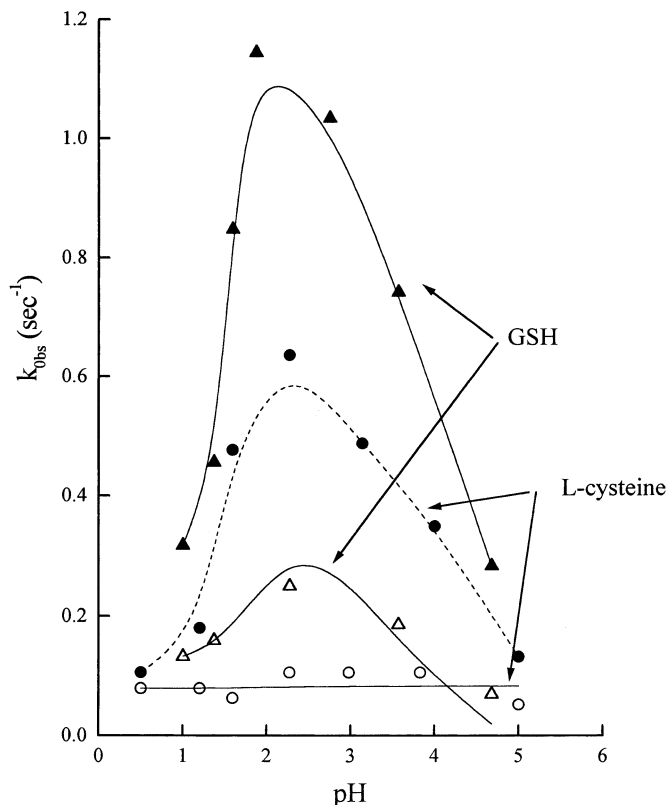


Fig. 2. pH profiles of the reaction rate constant (k_{obs}) for the formation of the $[\text{PdCl}(\text{dien})]^+$ -thiol complexes in the presence (solid symbols) and in the absence (open symbols) of 1×10^{-2} M SDS at 288 K. In aqueous media the points were experimentally obtained, while the curves were calculated from Eqs. (3) and (4).

and GSH or L-cysteine was investigated in the temperature range from 276 to 308 K at constant ionic strength (0.1 M). The kinetics traces under pseudo-first order conditions ($[\text{GSH}]$ or $[\text{L-cysteine}] \gg [\text{PdCl}(\text{dien})]^+$) in the presence and in the absence of SDS were single exponential curves, confirming that only formation of 1:1 complexes took place. The observed rate constants (k_{obs}) as a function of the total concentration of thiols can be described by the well known two term rate law common for the substitution reactions of square-planar complexes:

$$k_{\text{obs}} = k_{\text{I}} + k_{\text{II}}[\text{thiol}] \quad (2)$$

The linear plots of k_{obs} versus $[\text{thiol}]$ at constant acidity were obtained in all cases. The solvolysis rate constant k_{I} , which is independent on $[\text{thiol}]$, was determined from the intercept of the graph k_{obs} versus $[\text{thiol}]$, is small and contributes little to the observed rate. The second order rate constants (k_{II}), characterising the direct nucleophilic attack and the formation of the new complex, was determined from the slope of the plot [28].

3.3. Reaction mechanism

The effect of pH on the overall rate constant (k_{obs}) in the absence and in the presence of 1×10^{-2} M SDS was investigated in the acidity range from pH 1 to 6. The results obtained for complex formation between $[\text{PdCl}(\text{dien})]^+$ and thiols are shown in Fig. 2. In the reaction mechanism the protolysis constants of L-cysteine and GSH, which are defined in the reaction scheme presented below, must be taken into account ($\text{p}K_{\text{a}_1} = 1.9$, $\text{p}K_{\text{a}_2} = 8.10$ and $\text{p}K_{\text{a}_3} = 10.1$ for cysteine [29], and $\text{p}K_{\text{a}_1} = 2.05$, $\text{p}K_{\text{a}_2} = 3.40$, $\text{p}K_{\text{a}_3} = 8.72$ and $\text{p}K_{\text{a}_4} = 9.49$ for GSH [30]). As an example, the reaction mechanism of the complex formation between $[\text{PdCl}(\text{dien})]^+$ and L-cysteine is presented in Scheme 1:

It can be easily shown from the rate law that under the above mentioned experimental conditions for the proposed reaction mechanism pH dependence of k_{obs} for L-cysteine (Eq. (3)) and GSH (Eq. (4)) can be described as follows:

$$k_{\text{obs}} = \frac{k_1[\text{H}^+] + k_2K_{\text{a}_1}}{[\text{H}^+] + K_{\text{a}_1}} \quad (3)$$

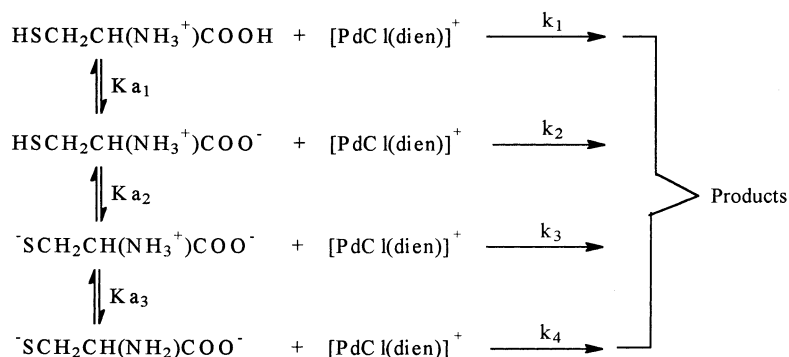
$$k_{\text{obs}} = \frac{k_1[\text{H}^+]^2 + k_2K_{\text{a}_1}[\text{H}]^2 + k_3K_{\text{a}_1}K_{\text{a}_2}}{[\text{H}^+]^2 + K_{\text{a}_1}[\text{H}] + K_{\text{a}_1}K_{\text{a}_2}} \quad (4)$$

The experimentally determined pH dependence of k_{obs} in the absence of micelles is shown by points in Fig. 2. The solid lines represent the best fit to Eqs. (3) and (4), using k_i as variable parameters. The agreement between experimentally determined and calculated values of k_{obs} was obtained for the following set of k_i : $k_1 = 7.2 \times 10^{-2} \text{ s}^{-1}$ and $k_2 = 8.3 \times 10^{-2} \text{ s}^{-1}$ for L-cysteine, and $k_1 = 0.11 \text{ s}^{-1}$, $k_2 = 0.40 \text{ s}^{-1}$ and $k_3 = 0.50 \text{ s}^{-1}$ for GSH.

It can be noticed that there is no significant influence of acidity on the reaction rate in the absence of surfactant, especially in the case of L-cysteine. In the acidity range from pH 2 to pH 8 the dissociation of $-\text{COOH}$ groups of L-cysteine and GSH do not influence the reaction rate, since the thiol group is responsible for complex formation. The reactions with rate constants

k_2 , k_3 and k_4 contribute less than 5% to the overall kinetics, which is within the limits of error of the kinetics measurements and the determinations of the activation parameters.

On the contrary, in the presence of micelles the rate constant versus pH curves are bell shaped with the maxima at pH 2 and 2.25 for GSH and L-cysteine, respectively. The rate law in the presence of micelles is the same as in aqueous medium, but the values of protolytic constants and $[\text{H}^+]$ changed, and were not determined in the present work. For this reason only the experimental points in the presence of micelles are presented in Fig. 2. As can be seen, both maxima are close to each other and correspond to the value of the $-\text{COOH}$ dissociation constant. Also, acceleration of complex formation can be observed compared with the results obtained in aqueous medium. Acceleration of the complex formation between $[\text{PdCl}(\text{dien})]^+$ and GSH or L-cysteine can be explained as a result of the increased concentration of the reactants in the vicinity of the anionic micelles. The anionic micelles provide a dispersed negatively charged surface in solution. As a consequence, the positively charged $[\text{PdCl}(\text{dien})]^+$ ions will partition out of the bulk aqueous phase into the surface region of the micelles. On the other hand, both ligands are protonated below pH 2 because the dissociation of the $-\text{COOH}$ group occurs above pH 2. The second protolytic step is the dissociation of the thiol group, and consequently L-cysteine is in the zwitterion form in the pH range from 2 to 8, while GSH is either a zwitterion ($2.05 < \text{pH} < 3.30$) or an anion ($\text{pH} > 3.40$). Therefore, in the presence of anionic micelle above pH 3, ligand species are mostly located in the bulk aqueous phase, and the complex formation process is slowed down. The decrease of the rate of the complex formation with an increase in acidity below pH 1 can be explained by the competition between reactants (protonated ligands and $[\text{PdCl}(\text{dien})]^+$) and H^+ for a place on the micellar surface. Namely, the kinetic behavior in acidic micellar solutions approaches the behavior characteristic of the corresponding homogenous system.



Scheme 1.

3.4. Dependence of rate constant on ionic strength

The rate of complex formation between $[\text{PdCl}(\text{dien})]^+$ and GSH or L-cysteine in the absence and presence of 1×10^{-2} M SDS was investigated as a function of ionic strength (0.04–0.2 M). The typical linear dependencies of $\log(k_{\text{obs}}/k_{\text{obs}}^{\circ})$ versus $I^{1/2}$ (k_{obs}° is the extrapolated value of the rate constant at zero ionic strength) at pH 3.7 and 1.7 are shown in Fig. 3. As expected, in aqueous medium for both ligands the rate of complex formation increases with the increase of ionic strength. It can be noticed that at pH 1.7 (when both reagents are mono-cations) the presence of SDS did not influence the slope of the plots (see Fig. 3, plot (a)). On the other hand, in the presence of micelles a decrease of the rate constant at pH 3.7 was observed with the increase of ionic strength for both ligands. This effect can be explained by the competition between reactant species and Na^+ ions originating from the inert salt (NaClO_4) for a place on the micellar surface. An increase of the concentration of the inert salt induces the decrease of local concentration of reactants in the vicinity of the micellar surface and a consequent decrease of the rate constant. Basically, this is the same kind of effect, which was already observed for the highly acidic media.

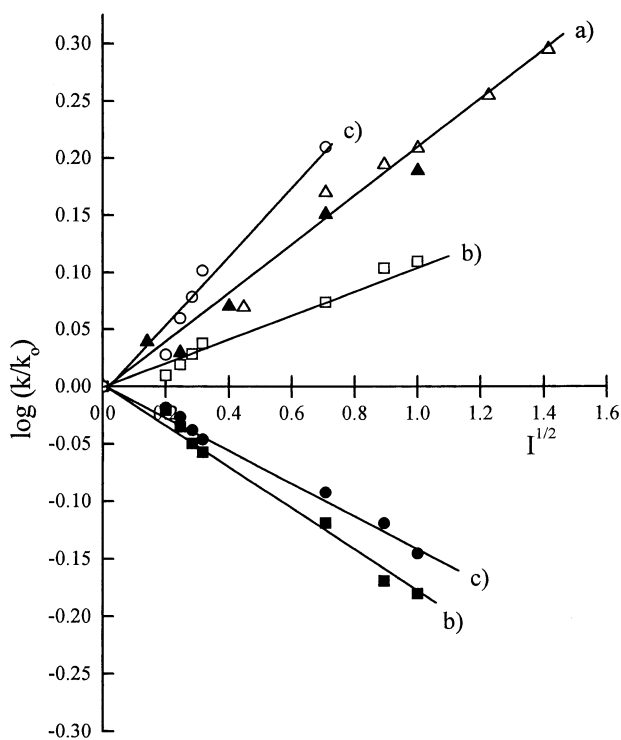
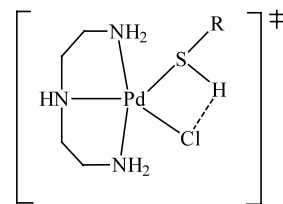


Fig. 3. The effect of the ionic strength in the presence (solid symbols) and in the absence (open symbols) of 1×10^{-2} M SDS on the reaction rate between $[\text{PdCl}(\text{dien})]^+$ and thiols. L-cysteine: (a) pH 1.7; (b) pH 3.7; GSH: (c) pH 3.7; (d) pH 4.5.

3.5. The activation parameters

The temperature dependencies of rate constants obtained for complex formation between $[\text{PdCl}(\text{dien})]^+$ and sulfur containing ligands GSH or L-cysteine in the presence and in the absence of micelles (Table 1) at pH 1.7 allowed the calculations of enthalpies and entropies of activation by use of Eyring's equation [28]. It is important to point out that under the stated experimental conditions (pH 1.7) both ligands were protonated, so the reaction pathways described by k_2 , k_3 , k_4 in Scheme 1 can be neglected.

The activation parameters derived from these experiments are summarized in Table 2. It can be seen that L-cysteine and GSH are very good entering groups for the $[\text{PdCl}(\text{dien})]^+$ complex. GSH is a better nucleophile than L-cysteine in spite of the fact that it is bigger. Moreover, GSH is considerably more reactive than expected. This anomaly seems to suggest an appreciable anchimeric effect capable of reducing the activation energy of the substitution, arising from hydrogen bonding interaction between the acidic groups located in a suitable position of the nucleophile. The anchimeric effect has been reported for other reactions of Pt(II) complexes and is well known for organic reactions [27]. A trigonal bipyramidal transition state, of reaction (1), is probably stabilized by hydrogen bonding between the entering thiol and the leaving chloro ligand as already proposed for the reaction of $[\text{Pd}(\text{H}_2\text{O})_4]^{2+}$ with monodentate acetate, propionate, glycolate, carboxylic acids [31,32] and $[\text{Pt}(\text{H}_2\text{O})_4]^{2+}$ with thioglycolic acid.



A large negative value of the entropy of activation is compatible with an associative mode of activation I_a or A mechanism. This finding indicates that bond-making with the entering ligand is important in the activation processes and that the leaving group is still tightly bound to the metal center in the transition state.

The values of the activation enthalpy obtained from the temperature dependence of k_{obs} over the range from 286 to 308 K for the complex formation at pH 1.7 in the presence of 0.01 M SDS are close, but lower than the same values measured in bulk solution for the same process (Table 2). The ΔH_f for both ligands decreased in the presence of the micellar surface, but the effect is larger in the case of the GSH reaction with $[\text{PdCl}(\text{dien})]^+$. The catalytic effect on the reaction rate is evident in both cases.

Table 1
Experimental rate constants k_{obs} (s^{-1}) for the complex formation between $[\text{PdCl}(\text{dien})]^{+}$ (1×10^{-4} M) and thiols as a function of the thiol concentration and temperature at pH 1.7

GSH		L-cysteine												
Water		1×10^{-2} M SDS					1×10^{-2} M SDS							
$10^4 \times C_L$ (M)		$10^5 \times C_L$ (M)					$10^4 \times C_L$ (M)							
Water		Water					Water							
		308 K	296 K	286 K	288 K	276 K	284 K	289 K	288 K	298 K	308 K	276 K	282 K	288 K
1	1	0.883	1.166	0.773	0.244	0.244	0.297	0.398	0.050	0.069	0.085	0.461	0.557	0.594
2	2	2.055	1.524	1.109	0.275	0.275	0.345	0.461	0.079	0.117	0.154	0.541	0.647	0.732
3	3	2.872	2.209	1.414	0.307	0.307	0.387	0.525	0.109	0.164	0.217	0.620	0.753	0.869
4	4	3.898	2.872	1.772	0.337	0.337	0.440	0.583	0.138	0.207	0.281	0.699	0.869	1.007
5	5	5.302	3.667	2.121	0.372	0.372	0.488	0.647	0.164	0.255	0.349	0.785	0.976	1.145
$10^{-3}k_{\text{II}}$ ($\text{M}^{-1}\text{s}^{-1}$)		10.671	6.350	3.359	3.200	3.200	4.772	6.203	0.286	0.461	0.657	0.806	1.060	1.379
k_1 (s^{-1})		0.20	0.38	0.43	0.21	0.21	0.25	0.30	0.02	0.02	0.02	0.40	0.44	0.46

^a Experimental error $\pm 5\%$.

Table 2

Activation parameters for the forward reactions between $[\text{Pd}(\text{dien})\text{Cl}]^{+}$ at pH 1.7 with thiols in the absence and presence of 1×10^{-2} M SDS

Ligand	SDS (M)	ΔH_f^\ddagger (kJ mol^{-1})	ΔS_f^\ddagger ($\text{J mol}^{-1} \text{K}^{-1}$)
GSH	0.01	31.9 ± 0.8	-61.6 ± 1.3
GSH		37.3 ± 3.9	-46.5 ± 4.1
L-cysteine	0.01	27.4 ± 1.5	-89.5 ± 4.3
L-cysteine		28.9 ± 1.1	-97.1 ± 3.7

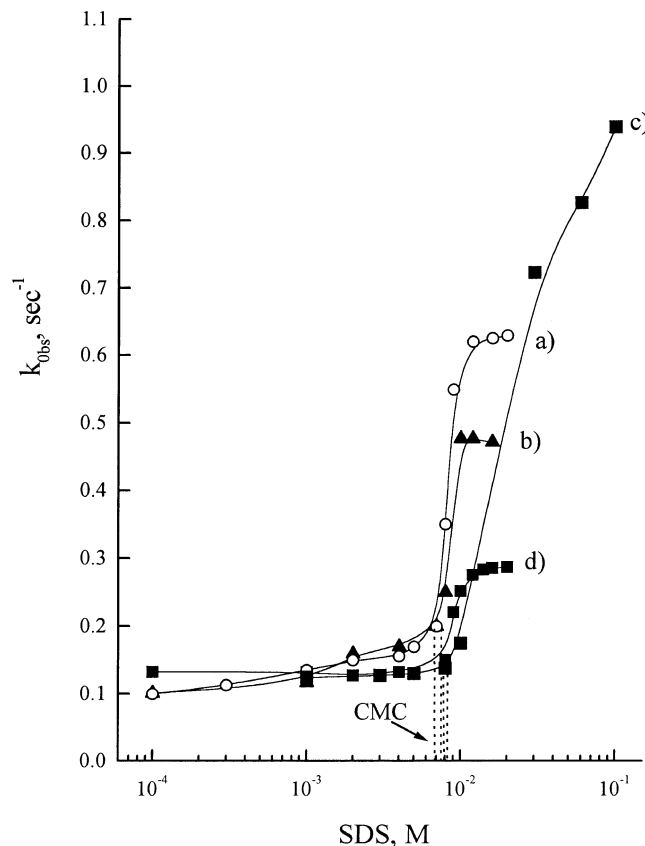


Fig. 4. Experimental rate constants (k_{obs}) of complex formation between 1×10^{-5} M $[\text{PdCl}(\text{dien})]^{+}$ and 1×10^{-4} M thiol as a function of SDS concentration at 288 K (L-cysteine: (a) pH 1.7; (b) pH 3.7; GSH: (c) pH 1.7; (d) pH 4.5).

3.6. Effect of SDS concentration

The rate of complex formation between $[\text{PdCl}(\text{dien})]^{+}$ and GSH or L-cysteine was investigated as a function of SDS concentration in the acidity range where pronounced acceleration of the complex formation was observed ($1.5 < \text{pH} < 4.5$). The sensitivity of the rate constant to the presence of anionic micelles provides the convenient method for precise detection of the surfactant concentration at which the micelle formation takes place, which is generally considered to be the CMC of the surfactant. Typical dependencies of k_{obs} on the concentration of SDS for both ligands at different

acidities are shown in Fig. 4. The increase of the rate constant indicates the first appearance of micelles or pre-micellar aggregates. The CMC values determined from the rate constant dependencies for both ligands at different pH values varied within the limits of experimental error. The obtained mean CMC value (7.0×10^{-3} M) is close to the reported value at zero ionic strength (7.75×10^{-3} M) [21,23].

Acknowledgements

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