

The effect of homocysteine and homocystine protonation on double-layer parameters at the electrode/chlorates(VII) interface

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Abstract

In this study, a comparison of the properties of homocysteine and homocystine adsorption at mercury/chlorate(VII) interface was done. The adsorption of homocysteine and homocystine is in fact the adsorption of mercury(II) cysteine thiolate and mercury(I) cysteine thiolate. The differences in the capacity curves result probably from the formation of mercurous thiolate at the mercury surface. It seems that the changes in E_z and γ_z values accompanying the change in the

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amino acid protonation in the basic electrolyte solution, confirm the altered arrangement of the cysteine mercury thiolates on the electrode surface.

Keywords

Adsorption, adsorption parameters, amino acids, differential capacity, double layer

Introduction

Adsorption processes play an important role in the phenomena occurring at interfaces including natural and technologically induced phase (Bandura et al., 2015; Chibowski et al., 2010; Jesionowski, 2002; Wiśniewska et al., 2014). Adsorption of sulphur-containing molecules from solutions into metals to form close-packed and oriented monolayers provides a convenient method to assign the desired chemical or physical properties of surfaces (Ikeda et al., 1984; Nosal-Wiercińska and Dalmata, 2010; Sieńko et al., 2006). It is important to know the adsorption behaviour of an organic additive when studying its influence on the kinetics of electrode processes or electrochemical corrosion.

This paper presents the results of measurements concerning the influence of homocysteine and homocystine protonation on double-layer parameters at the electrode/chlorates(VII) interface.

Homocysteine (HCE) and homocystine (HCY) play an important role in the maintenance of homeostasis in living organisms. For example, an elevated level of homocysteine in blood plasma (hyperhomocysteinemia) is considered a risk factor for cardiovascular and neurodegenerative diseases, some types of cancer, as well as miscarriage (Kraczkowska et al., 2005). A high concentration of homocysteine in the human body leads to a genetically determined multisystemic disorder known as homocystinuria.

Homocystine readily forms as a result of oxidation of homocysteine, and is a source of sulfur in the human body. It is excreted in urine as a result of homocystinuria (Kraczkowska et al., 2005).

As indicated in the literature (Heyrovský and Vavříčka, 1999; Heyrovský et al., 1997; Nosal-Wiercińska, 2012, 2013), the electrochemically reactive homocysteine and homocystine undergo the same reactions on the mercury electrode as cysteine (RSH). These reactions involve two steps of mercury electrooxidation: mercury(I) cysteine thiolate $\text{Hg}_2(\text{SR})_2$ and mercury(II) cysteine thiolate $\text{Hg}(\text{SR})_2$, which are strongly adsorbed on the surface of the mercury electrode (Nosal-Wiercińska, 2013).

Experimental analysis

The experiments were carried out in thermostated cells at 298 K with μ Autolab Fra 2/GPES (Version 4.9) analyser (Eco Chemie, Utrecht, the Netherlands). The working electrode was a dropping mercury electrode with a controlled increase rate and a constant drop surface (0.014740 cm^2) made by MTM, Poland. The reference was a silver chloride electrode and the auxiliary electrode was platinum.

The solutions were deoxygenated with high-purity nitrogen prior to each experiment and kept under nitrogen atmosphere during the measurements. Analytical grade chemicals from Fluka were used.

The 2, 4 and 6 mol·dm⁻³ chlorate(VII) solutions of HClO₄:NaClO₄ with the concentration ratios of (1:1) solution A, (1:4) solution B, (1:9) solution C, (4:1) solution D, (9:1) solution E were examined. The enumerated solutions were designated according to the scheme (Grochowski et al., 2016).

Amino acid solutions were prepared just before the measurements. The range of concentrations studied of amino acids were 0.1–10 × 10⁻³ mol·dm⁻³.

The differential capacity of the double layer (C_d) at the mercury/supporting electrolyte interface was measured by the impedance method. For the whole polarisation range, the capacity dispersion was tested at different frequencies between 200 and 1000 Hz. In order to obtain the appropriate equilibrium values of differential capacity, a linear dependence of capacity on the square element from frequency was extrapolated to zero frequency. This procedure assumes that the impedance of the double layer is equivalent to a series of capacity-resistance combinations and the rate of adsorption is diffusion controlled (Nosal-Wiercińska and Dalmata, 2010).

The potential of zero charge (E_z) was determined using a streaming electrode (Nosal-Wiercińska and Dalmata, 2010), with the accuracy of ±0.1 mV.

The surface tension at the potential of zero charge (γ_z) was measured using the method of the highest pressure inside the mercury drop presented by Schiffrin (Nosal-Wiercińska and Dalmata, 2010). The surface tension values were determined with an accuracy of ±0.2 mNm⁻¹.

Results and discussion

Differential capacity curves (Figure 1(a)) obtained in the studied systems for different amino acids point to changes in capacity values, compared with the supporting electrolyte.

In the region of “hump” potentials, appearing in 6 mol·dm⁻³ chlorate(VII) at HClO₄:NaClO₄ concentration ratios of 1:4 (B) solution without the amino acids (≈ -600 mV), after the introduction of homocysteine and homocystine to the solution, the height of the hump decreases. The increase in homocysteine concentration causes a further decrease in differential capacitance, whereas the increase in homocystine concentration causes an increase of differential capacitance in the region of hump potentials.

Simultaneously, in the presence of HCY, the hump moves significantly towards the negative potentials. The presence of HCE causes only a slight shift of the hump towards the negative potentials.

In the region of higher potentials (≈ 0 mV), the peaks occur in the presence of HCE and HCY owing to their above-mentioned electrochemical reactivity on mercury.

The replacement of mercury(I) cysteine thiolate Hg₂(SR)₂ and mercury(II) cysteine thiolate Hg(SR)₂ at the electrode surface is accompanied by a significant change of the electrode capacity (Heyrovský et al., 1997; Nosal-Wiercińska, 2013). The pronounced peaks ($E_p = 0$ mV), which increase with the increasing HCE and HCY concentrations in all studied chlorate(VII) solutions, are associated with adsorption of Hg(SR)₂. The area of more negative potentials (from -400 to -1000 mV) reflects the adsorption of the oriented surface layer of Hg₂(SR)₂ (Heyrovský et al., 1997; Nosal-Wiercińska, 2013). The differences in the capacity curves (for homocystine, we observe an increased differential capacity, whereas for homocysteine a decreased differential capacity) result probably from the formation of mercurous thiolate at the mercury surface.

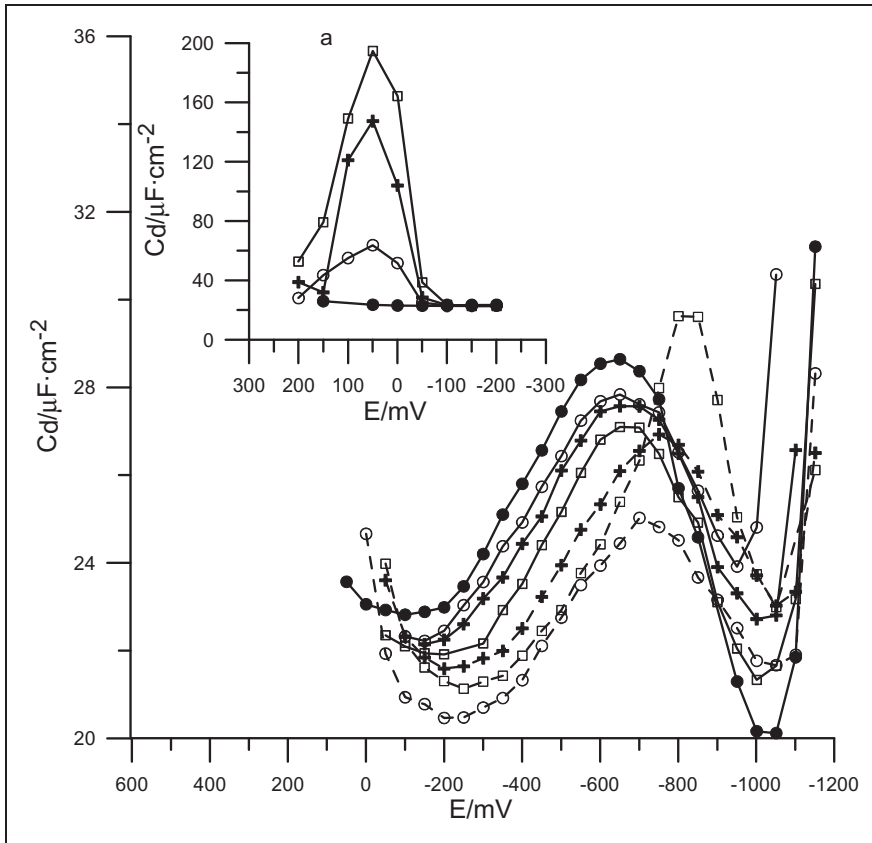


Figure 1. Differential capacity – potential curves of double layer interface Hg/6 mol·dm⁻³ chlorate(VII) with various concentrations of homocysteine (—) and homocystine (---) (in mol·dm⁻³): (●) 0, (○) 1 · 10⁻⁴, (+) 5 · 10⁻⁴, (□) 1 · 10⁻³, where HClO₄:NaClO₄ = 1:4 (B). (a) Inset shows data for homocysteine.

In the case of identical HCE concentrations (Figure 2), the hump at $C_d = f(E)$ curves decreases and shifts towards the negative potentials, with the increase of chlorate(VII) concentration, 2 mol·dm⁻³ → 4 mol·dm⁻³ → 6 mol·dm⁻³, whereas for identical HCY concentrations (Figure 2(a)), the hump at $C_d = f(E)$ curves increases and shifts towards the negative potentials, with the increase of chlorate(VII) concentration, 2 mol·dm⁻³ → 4 mol·dm⁻³ → 6 mol·dm⁻³. The peaks on the capacitance curves increased with the decrease in water activity (Figure 2(a)). Such changes indicate a considerable influence of water on the surface properties of the interface.

Figures 1 and 2 of the capacity curves point to a complicated effect proceeding at the Hg/chlorate(VII) solutions' interface in the presence of both homocysteine and homocystine. Changes in the NaClO₄ and HClO₄ concentrations in the basic electrolyte solution probably rearranged the layers of the adsorbed mercury thiolates. This may be due to the differences in the side interactions between the adsorbed mercury thiolates and protonated $-\text{NH}_3^+$ groups and dissociated $-\text{COO}^-$ groups of amino acids (Grochowski et al., 2016). It should be added that the thiolates and the amino groups of homocysteine and homocystine are fully

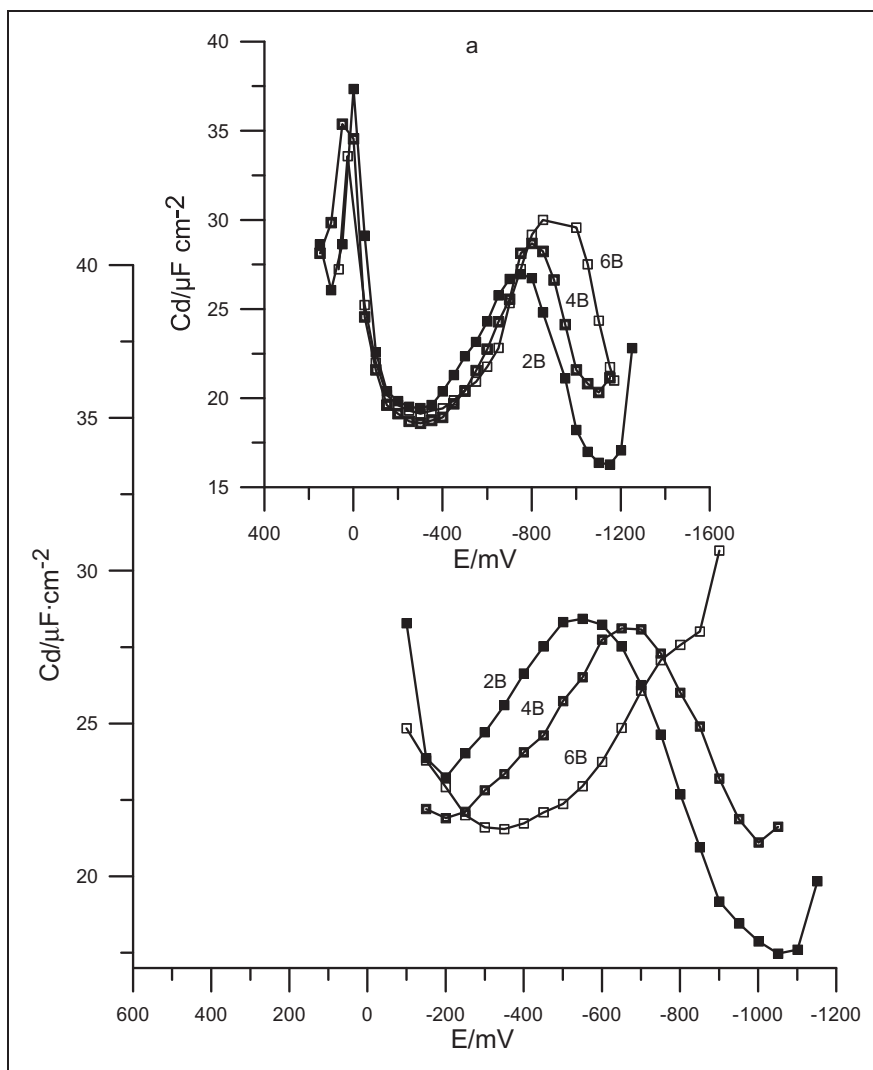


Figure 2. Differential capacity – potential curves of double layer interface Hg/2 mol·dm⁻³ chlorate(VII) (■), 4 mol·dm⁻³ chlorate (VII) (■) and 6 mol·dm⁻³ chlorate (VII) (□) with 1·10⁻³ mol·dm⁻³ homocysteine, where HClO₄:NaClO₄ = 1:4 (a) Inset shows details for homocysteine.

protonated and the carboxylic groups are totally dissociated in solutions with the prevailing amount of chloric acid(VII), whereas the thiolates and the amino groups are only partly protonated in solutions with the prevailing amount of sodium salt of the chloric acid(VII) (Grochowski et al., 2016).

Table 1 contains the values of potentials of zero charge E_z and the values of surface tension γ_z at zero charge for the studied amino acids as a function of the supporting electrolyte concentration.

The increase in sodium salt concentration in the basic electrolyte solution results in the shift of the E_z towards more positive potentials, whereas the increase in chloric(VII) acid

Table 1. Potential of zero – charge E_z vs. Ag/AgCl electrode and surface tension γ_z for E_z of chlorates(VII) solutions of concentration ratio HClO_4 : NaClO_4 (1:1) solution A, (1:4) solution B, (1:9) solution C, (4:1) solution D, (9:1) solution E + $1 \cdot 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ homocysteine (Grochowski et al. 2016) and $1 \cdot 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ homocystine systems.

	0		$1 \times 10^3 c_{\text{HCE}}/\text{mol} \cdot \text{dm}^{-3}$		$1 \times 10^3 c_{\text{HCY}}/\text{mol} \cdot \text{dm}^{-3}$	
	$-E_z/\text{V}$	$\gamma_z/\text{m Nm}^{-1}$	$-E_z/\text{V}$	$\gamma_z/\text{m Nm}^{-1}$	$-E_z/\text{V}$	$\gamma_z/\text{m Nm}^{-1}$
2 mol·dm ⁻³ chlorate(VII)						
A	0.483	469.5	0.487	466.3	0.489	467.4
B	0.481	470.3	0.487	458.9	0.485	461.4
C	0.480	474.4	0.483	467.9	0.484	466.2
D	0.494	467.1	0.497	465.4	0.504	451.6
E	0.496	466.3	0.499	462.9	0.509	461.3
4 mol·dm ⁻³ chlorate(VII)						
A	0.497	0.483	0.518	466.3	0.520	463.6
B	0.496	0.481	0.503	464.6	0.500	461.3
C	0.487	0.480	0.499	463.8	0.500	462.7
D	0.536	0.494	0.540	464.6	0.545	458.1
E	0.547	0.496	0.553	455.6	0.550	458.9
6 mol·dm ⁻³ chlorate(VII)						
A	0.528	471.2	0.535	466.3	0.554	463.3
B	0.522	468.7	0.528	460.5	0.533	457.2
C	0.519	464.6	0.526	458.1	0.535	358.4
D	0.581	466.3	0.588	462.9	0.605	454.8
E	0.607	465.4	0.619	460.5	0.621	458.7

concentration results in the shift of the E_z in the opposite direction. Such changes accompanying the change in the amino acids protonation in the basic electrolyte solution confirm the altered arrangement of the cysteine mercury thiolates on the electrode surface (Grochowski et al., 2016).

The surface tension values (Table 1) at the potential of zero charge γ_z decrease, which confirms the occurrence of the adsorption process (Dalmata and Nosal-Wiercińska, 2008; Nosal-Wiercińska et al., 2015).

Conclusion

The changes in the double-layer parameters at the mercury/chlorates(VII) interface, in the presence of amino acids under conditions of varying protonation of the homocysteine and homocystine were observed. The adsorption of homocysteine and homocystine is in fact the adsorption of mercury(II) cysteine thiolate and mercury(I) cysteine thiolate. The changes in γ_z point to the increase of adsorption of amino acids in an $\text{HCY} > \text{HCE}$ series.

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