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Adenine adsorption in different pH acetate buffer

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Abstract: The research results facilitate the description of adenine adsorption on the mercury electrode with reference to the pH of the supporting electrolyte which was the acetate buffer with pH of 3, 4, 5 and 6. The thermodynamic analysis indicates that the curves of the differential capacity of the studied systems with adenine do not overlap with the curves for the supporting electrolyte – the acetate buffer. This indicates the occurrence of adsorption of the studied compound on the mercury electrode within the whole range of applied concentrations in the case of every tested pH value of the acetate buffer. Adsorption energy and interaction constants were determined using the Frumkin isotherm and the viral isotherm. It was demonstrated that a adenine molecule is adsorbed on the mercury electrode in a buffer with pH 4, 5 and 6 through the negative pole, whereas in a buffer with pH 3 through the positive pole. Physical adsorption was observed in the studied systems. This is indicated by the occurrence of a typical maximum on the curve of the relation the relative surface excess amounts and the potential of the electrode; crossed curves of the following relation surface charge of the electrode from its potential (surface charge of the electrode from its potential $\sigma = f(E)$) at one point and, thus, the possibility of determining electrical parameters characterizing maximum adsorption as well as the absence of linearity of the function free energy of adsorption as a function of electrode potential $\Delta G^0 = f(E)$.

Keywords: adenine, adsorption, differential capacity, electroreduction, acetate buffer

1. Introduction

The fundamental adsorption theory for organic substances on an assumes that adsorption is described by an isotherm in the form determined by Frumkin and that the double electric layer can be treated as a system of two capacitors connected in parallel or in series (Frumkin, 1926). One is filled with an adsorbed organic substance and the other with a solvent. Accurate theoretical research on the adsorption is possible on mercury electrodes (Kalvoda, 2007; Vyskocil, et al ., 2009; Barek, 2013). Very good reproducibility of the results obtained on the dropping mercury electrode results from homogeneity and purity of the double layer interface mercury – solution in comparison to solid electrodes and the possibility of using various measurement methods (Nieszporek, et al., 2019; Nieszporek , 2020; Kaliszczak, et al., 2020; Nosal-Wiercinska., et al. 2020; Prado, et al., 2001; Gugała-Fekner, 2016; Sieńko et al., 2009; Nieszporek et al., 2018; Nieszporek, 2013).

Recently a rapid development of molecular genetics whose main research subject is the structure and function of DNA molecules has been observed. Therefore, it is necessary to explore the chemical properties of molecules that are DNA and RNA precursors. Purines and pyrimidines, the compounds in question, are indispensible for regulation of the cellular cycle, accumulation and transport of energy and are carriers of cellular membrane components and sugars. In a living organism they occur in several forms: as free bases, nucleosides or nucleotides. Free bases and nucleosides mainly occur in body fluids whereas nucleotides only occur in the intra-cellular area.

Purines constitute a biologically significant class of compounds with condensed heterocyclic rings. They contain the framework which consists of the pyrimidine ring condensed with the imidazole ring. The most important purines found in nature are adenine and guanine.

In five-member heterocyclic imidazole ring purines, there are two nitrogen atoms, one of which, in position 7 (N7), is alkaline due to the occurrence of a free electron pair which is not part of the aromatic

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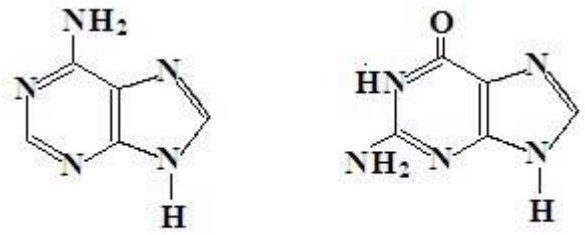
electron sextet π. This atom can become protonated. However, the second atom of imidazole, ring N9, is not alkaline because its free electron pair is part of the electron sextet π like the nitrogen atom in the pyrrole ring (Żak, et al. 2001).



adenine guanine

Fig. 1. Structural formula of purine bases

It was concluded that from neutral and acid pH solutions, only the neutral adenine is chemically adsorbed; so in very acid solutions where adenine is protonated in solution, the chemical adsorption process of the molecule must include a deprotonation step. On the contrary, at pH values around the second pKa of adenine, both species involved in the equilibrium, the neutral and the anionic adenine forms can be adsorbed, and the pKa value in the interface is very similar to the value in the bulk solution (Fig. 2)(Prieto, et al., 2017; Fontanesi, et al., 1994; Kaliszczak, et al.2020; Nosal-Wiercińska, et al., 2021).

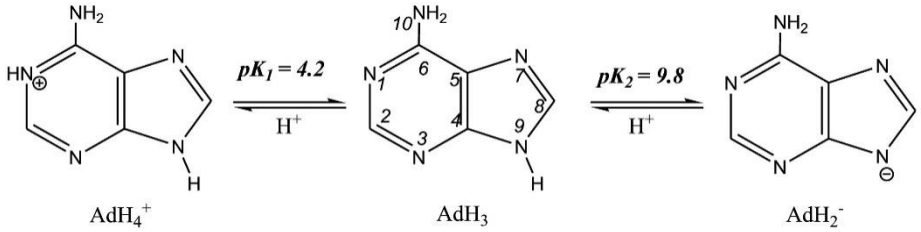


Fig.2. Acid-base equilibria of adenine in aqueous solutions (Prieto, et al., 2017)

Purine does not occur in a free form in nature, but in the form of amine and ketone (or hydroxyl) derivatives. Amine groups bound to the purine aromatic ring behave like amine groups of amino acids and can turn into a cation form after protonation. In physiological conditions, the dominant tautomeric form of adenine is lactam. Lactam pairs with cytosine, which might underlie mutagenesis.

A significant fact is that adenine is a nucleobase which causes DNA mutation in interactions with cisplatin. Therefore, despite its negative side effects, cisplatin is used in anti-neoplastic therapy. A similar therapeutic complex which would have more benign adverse effects is currently being sought (Sliwinska-Hill, et al., 2016; Rabik, et al., 2007; Suk, et al., 2005; Stenzel-Bembenek, et al., 2014). The obtained results of adenine adsorption studies can be used in biochemical studies.

It is worth noting that the applied values of potentials of the electrode are of the same order as the values of cell membranes. In addition, the surface of the electrode used is hydrophobic, as is the surface of the biological membrane. It is therefore possible to treat the surface of the electrode-biologically active compounds as a model of the effects that occur on the surface of biological membranes.

2. Materials and methods

The measurements differential capacity were performed using an Autolab (Eco Chemie) instrument in a thermostatic container at the temperature of 298 ±0.1K in a three-electrode system: the dropping mercury electrode (working electrode) with the area of the drop amounting to 0.009028cm2 (MTM Krakow), the saturated silver chloride electrode (reference electrode) and the coiled platinum (auxiliary electrode. The repeatability of the capacitance measurements was ± 5%. Measurements were carried out for five frequencies ranging from 200Hz to 2000Hz, the amplitude of the alternating signal was 50mV. Balance volumes were obtained by extrapolation to a frequency of zero.

Solutions used for tests were prepared from freshly distilled water and Fluka reagents (Sodium acetate czda. POCH, Acetic acid czda POCH, adenine czda POCH).

Each sample was deoxygenated before measurements. Oxygen as a water-soluble component of air is present in all solutions prepared in a laboratory atmosphere. It hinders the measurements because it is polarographically active, giving two waves. Therefore, it must be removed from the samples. The gas used for this purpose was nitrogen-inert gas of high purity. The average deoxygenation time was 20 minutes.

The adenine solution of concentrations, ranging from $5 \cdot 10^{-5}$mol$\cdot$dm^{-3} to $2 \cdot 10^{-3}$mol$\cdot$dm^{-3}. The maximum concentration of adenine resulted from its solubility in the conditions of the experiment.

The selection of adenine is based on the fact that it is attractive because of its potential effect on electro-reduction kinetics on the mercury electrode of depolariser ions, e.g. Zn2+ or Cd2+. The range of adenine concentrations selected for the measurements is related to the fact that the lowest concentration visibly changes the course of the differential capacity curve.

The supporting electrolyte was the acetate buffer, whose acetate ions are poorly adsorbed on the mercury electrode, with pH 3, 4, 5 and 6 (Gugała-Fekner, 2016; Gugała-Fekner, 2018; Gugała-Fekner, 2018). The choice of the acetate buffer is due to the good solubility of $ZnC_4H_6O_4$, while precipitation of this salt can be observed in other buffers.

Values of potentials of zero charge Ez were determined using a streaming electrode whereas values of surface tension γz with a potential of zero charge Ez were obtained using Schiffrin's capillary tube (Gugała-Fekner, 2016).

3. Results and discussion

Information obtained from measurements of the differential capacity facilitates qualitative determination of the condition of the electrode surface. The differential capacity curves indicate the presence of adsorbing molecules or ions. The dropping mercury electrode with a constant area of the drop was used to measure differential capacity. In order to determine whether adsorption equilibrium is obtained within the range of applied concentrations of the organic substance, measurements of the differential capacity were performed in the function of the alternating current frequency. The occurrence of frequency dispersion was observed in all the tested systems. Therefore, the values of differential capacity used for calculations constitute the result of extrapolation of correlation $C=(\sqrt{\omega})$, where ($\omega=2\pi f$ [rad$\cdot$s^{-1}]) is the angular frequency (Gugała-Fekner, 2016; Gugała-Fekner, 2018; Gugała-Fekner, 2018).

The analysis of the course of the differential capacity curves in the absence of adenine (Fig. 3) indicates a completely different change in the differential capacity in the acetate buffer with pH=3 in

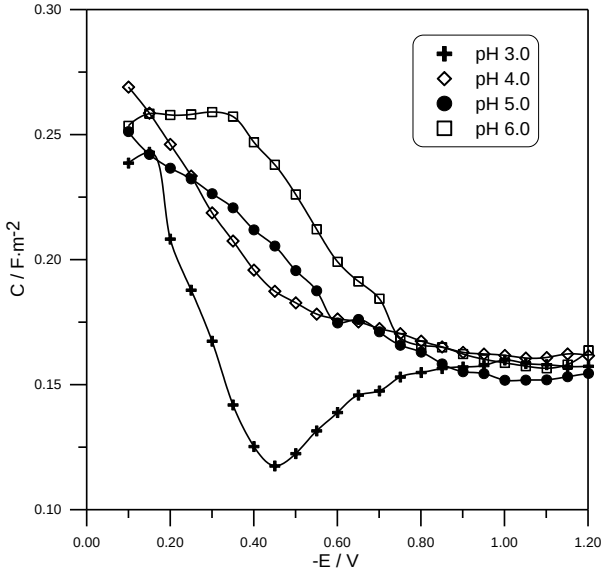


Fig. 3. Curves of the differential capacity extrapolated to zero frequency on the phase boundary: Hg/acetate buffer with varying pH

comparison to the other buffers. In buffer with pH=3 at E=-0.5V, the minimum differential capacity occurs, whereas in the other buffers the differential capacity decreases steadily. In all buffers without adenine at E>-0.8V, differential capacity values are practically constant. A different course of differential capacity curves for pH=3 in comparison to the other buffers may result from a stronger adsorption of acetic acid molecules in pH=3 buffer. In acetate buffers with a pH of 3 and 4 (Gugała-Fekner, 2018), adsorption mainly concerns acetic acid molecules, whereas in buffers with a pH of 5 and 6 - acetate ions (Gugała-Fekner, 2018).

Comparing the differential capacity curves in the presence of increasing adenine concentrations, formation of a volume peak can be observed with an increase in pH of the acetate buffer, which is typical of strongly adsorbing anions or polar substances (Fig. 4) (Gugała-Fekner, 2018; Gugała-Fekner, 2018).

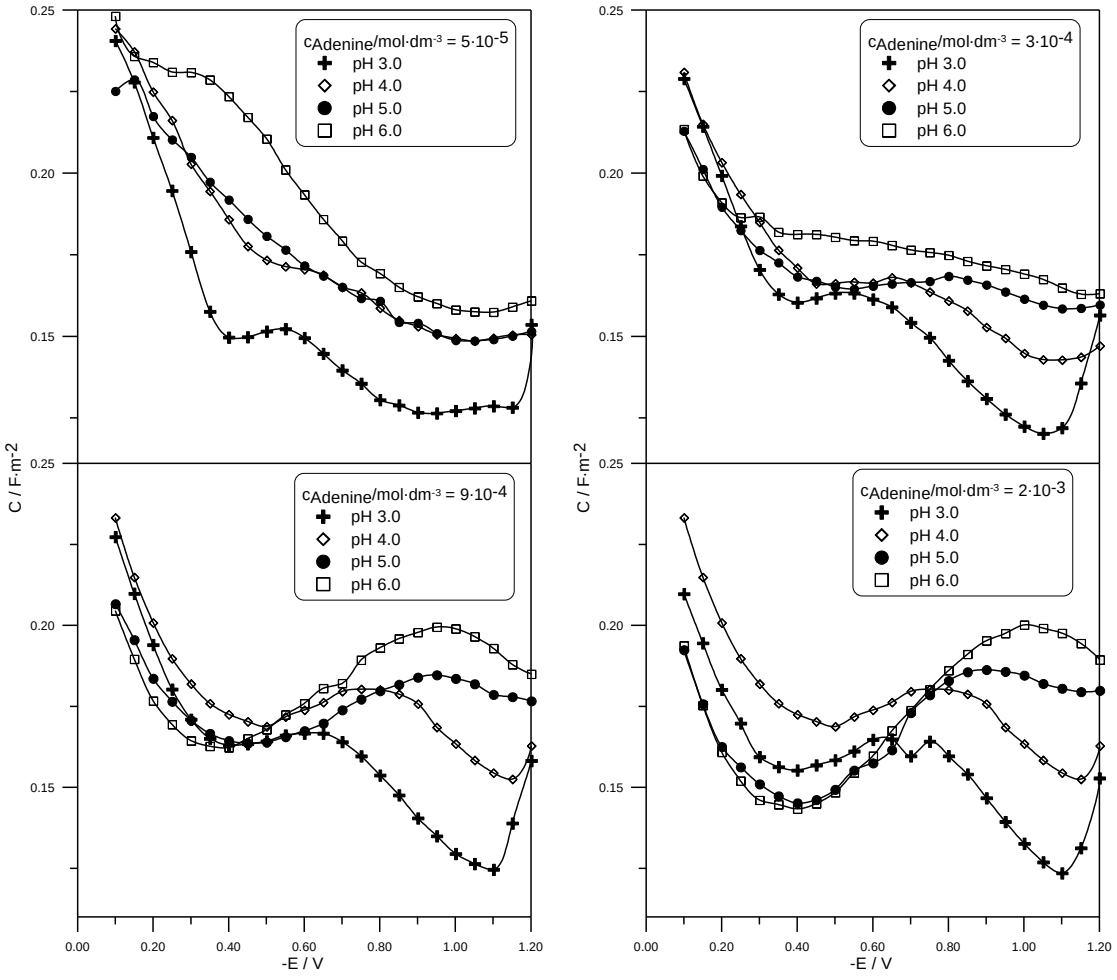


Fig. 4. Curves of the differential capacity extrapolated to zero frequency on the phase boundary: Hg/acetate buffer with varying pH for various adenine concentrations, indicated in the figure

The differential capacity curves for the whole range of concentrations do not meet at sufficiently negative potentials with the curve of the supporting electrolyte. Therefore, constants of integration are values of zero charge potentials E_z and values of surface tension determined at E_z. As correlations in Fig. 5 indicate, E_z values in buffer solutions with incremental pH without adenine shift towards negative potentials, which is associated with an increasingly higher concentration of acetate anions. Surface tension values determined at zero charge potential E_z without the organic substance remain compliant with E_z values (Fig. 5).

The analysis of information in Table 1 indicates that an increase in the concentration of adenine in the acetate buffer with pH=3 causes a shift in E_z towards less negative potentials. This might indicate the adsorption mechanism in this acetate buffer: the positive pole of the dipole molecule is directed towards the electrode surface whereas the negative pole is directed towards the solution (Gugała-

Fekner, 2018). Introduction of an organic substance in the tested buffers with pH of 4-6 causes a shift in E_z towards more negative potentials. In this case, it can be suspected that the adenine molecule is adsorbed on the surface of the mercury electrode with its aromatic ring, i.e. the negative pole (Gugała-Fekner, 2018; Gugała-Fekner, 2018). The strongest adsorption of adenine occurs at pH=6, which is indicated by the greatest shift in the γ_z value due to the maximum adenine concentration. This is also confirmed by the greatest changes in the E_z value in this buffer.

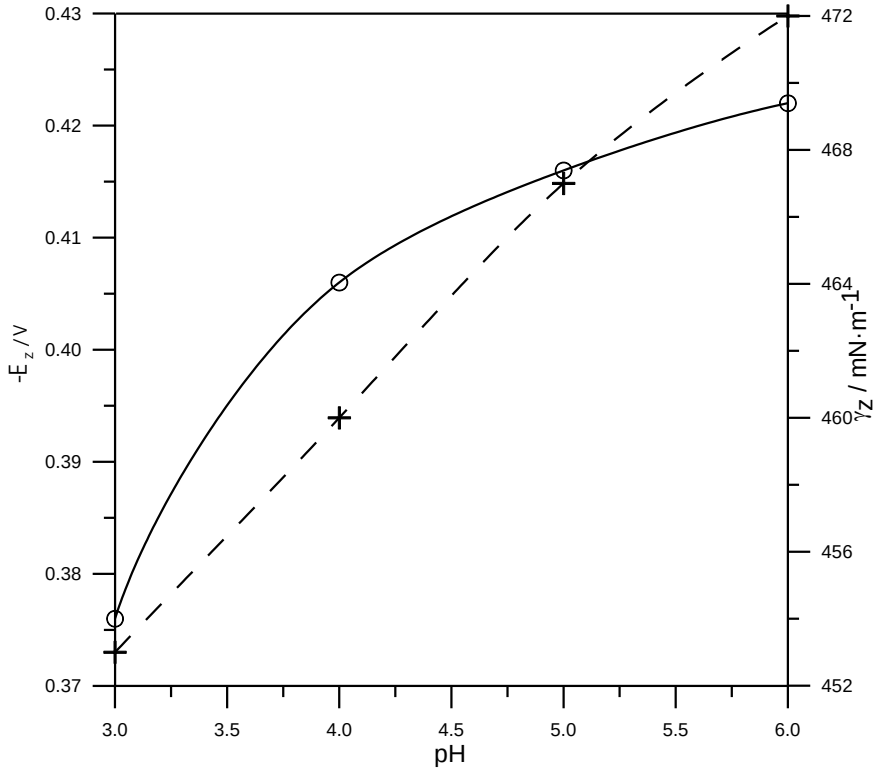


Fig. 5. Correlation of zero charge potential E_z (solid line) and surface tension γ_z with zero charge potential E_z (dotted line) against Ag/AgCl for acetate buffer with varying pH without adenine

Table 1. Correlation of zero charge potential E_z and surface tension γ_z with zero charge potential E_z against Ag/AgCl for various adenine concentrations in the supporting electrolyte with varying pH

	E_z / V							
c/mol·dm^{-3}	5×10^{-5}	1×10^{-4}	3×10^{-4}	5×10^{-4}	8×10^{-4}	9×10^{-4}	1×10^{-3}	2×10^{-3}
pH								
3	0.395	0.393	0.387	0.384	0.379	0.378	0.377	0.374
4	0.397	0.399	0.395	0.396	0.4	0.401	0.405	0.408
5	0.387	0.397	0.397	0.398	0.417	0.419	0.419	0.414
6	0.425	0.425	0.431	0.438	0.448	0.454	0.46	0.474
	γ_z / mN·m^{-1}							
c/mol·dm^{-3}	5×10^{-5}	1×10^{-4}	3×10^{-4}	5×10^{-4}	8×10^{-4}	9×10^{-4}	1×10^{-3}	2×10^{-3}
pH								
3	465	465	455	456	451	449	448	445
4	469	465	458	458	453	452	449	446
5	472	462	462	462	457	457	451	448
6	470	462	460	458	456	455	453	448

Results of measurements of Ez and γ_z were used for integration of differential capacity curves from zero charge and surface tension at this potential on the basis of the correlation (1):

$$\sigma = \int_{E_z}^{E} CdE \tag{1}$$

and calculation of the density of the charge on the electrode surface. On the basis of double integration of the differential capacity curves, the value of surface tension can be calculated from the following correlation (2):

$$\gamma = \gamma_z - \int_{E_z}^{E} \int CdE \tag{2}$$

The values of the electrode's surface charge obtained from integration of the differential capacity curves were used for determination of the maximum adsorption potential E_{max} and the maximum adsorption charge σ_{max} – values characterising maximum adsorption. Their dependence on pH of the acetate buffer is presented in Fig. 6.

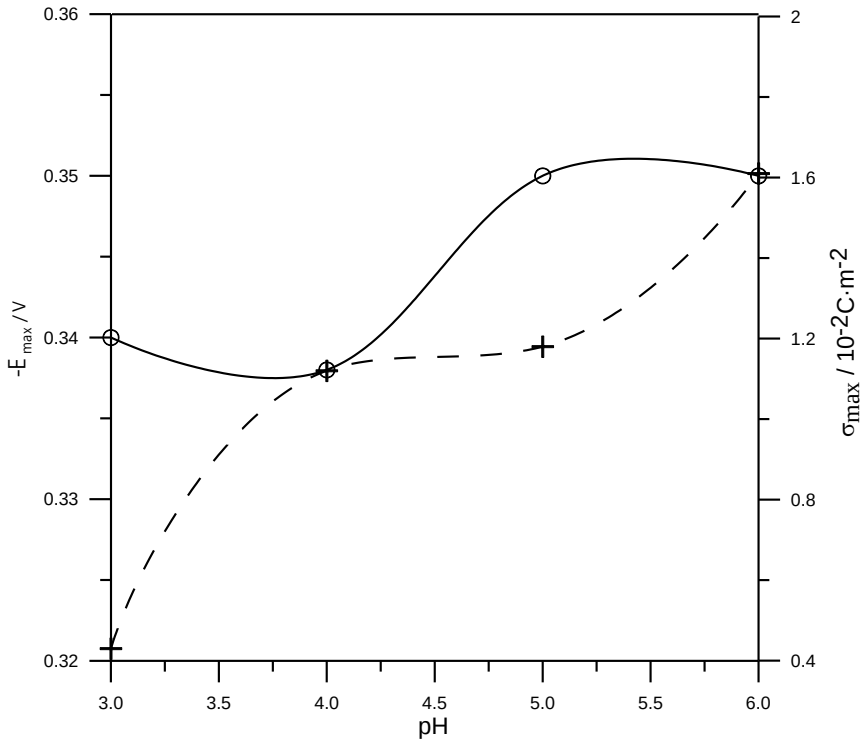


Fig. 6. Correlation between maximum adsorption potential E_{max} (solid line) and maximum adsorption charge σ_{max} (dotted line) determined for various adenine concentrations in the acetate buffer with varying pH

The analysis of the results indicates that E_{max} values are practically independent of the pH of the acetate buffer, whereas values of maximum adsorption charge increase with an increase in pH of the acetate buffer. The possibility of accurate determination of E_{max} and σ_{max} indicates the physical nature of adenine adsorption on mercury (Gugała-Fekner, 2018; Gugała-Fekner, 2018).

The surface tension values obtained from integration of the differential capacity curves were used for calculation of the inter-phase pressure Φ according to the formula (3):

$$\Delta\Phi = \Delta\gamma = \gamma^0 - \gamma \tag{3}$$

where γ^0 is surface tension of acetate buffer and γ is surface tension of a solution containing adenine.

The use of inter-phase pressure in a thermodynamic description of adsorption facilitates elimination of the adsorptive effect of supporting electrolyte ions on the value of surface excess amounts of the organic substance. Relative surface excess amounts are calculated from the interphase pressure, Φ, on the basis of the following formula (4)

$$\Gamma' = \frac{1}{RT}\left(\frac{\partial\Phi}{\partial lnc}\right)_E \tag{4}$$

Values of relative surface excess amounts in the function of the electrode's potential obtained from numerical integration of the function Φ are presented in Fig. 7. It was observed that the values of relative surface excess amounts assume the shape of a bell in acetate buffer with pH of 4-6. This shape of the curves indicates competitive electrostatic interaction between the molecules of an organic substance with the ions of the supporting electrolyte (the acetate buffer in this case) and the water molecules. A different course of changes in relative surface excess amounts in the acetate buffer with pH=3 seems to be caused by the fact that a adenine molecule is adsorbed to the surface of the mercury electrode with the positive pole in this buffer. In these cases, an increase in the concentration of adenine is accompanied by a significant increase in the values of relative surface excess amounts (Gugała-Fekner, 2018; Gugała-Fekner, 2018).

Besides the surface excess amounts, the size of adsorption can be described using the coverage rate Θ. In order to determine the coverage rate Θ, one needs to know the value of surface excess with the total coverage of the electrode surface with adsorbate Γ_s. This value can be determined using the following ways:

- from adsorption isotherm Γ = f(c) if there is a plateau in the graph. This way gives positive results in the case of adsorbates which are well soluble in the supporting electrolyte (Galus, 1979).
- from experimental correlations a set of straight lines is obtained whose intersection is determined by value $1/\Gamma_s$,
- from spherical models of the adsorbate molecule, for the specific orientation of the molecule on the surface of the electrode, the seating surface S can be calculated, and from this value we can calculate Γ_s according to the formula (5):

$$S = \frac{1}{\Gamma_s \cdot N_A} \tag{5}$$

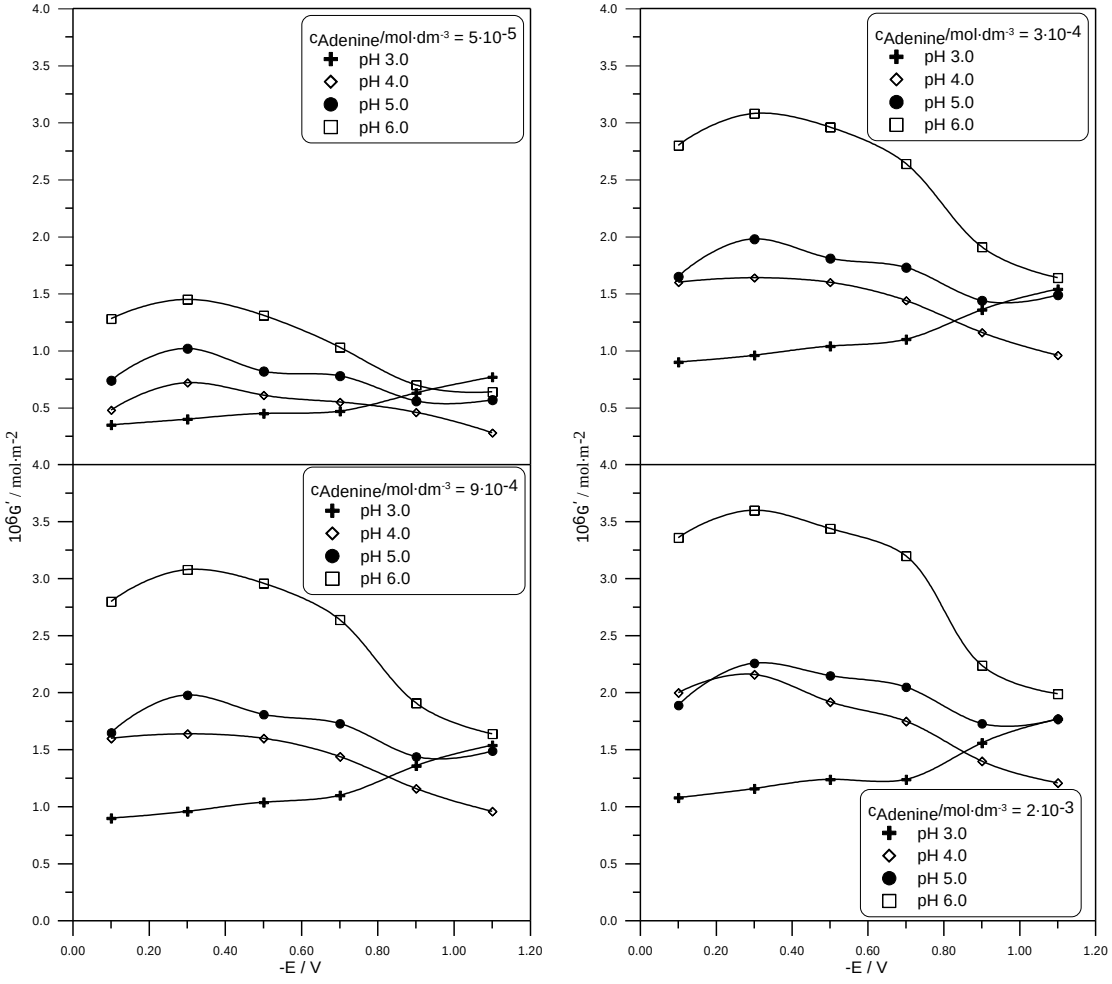


Fig. 7. Correlation between the relative surface excess amounts and the potential of the electrode for various adenine concentrations in the supporting electrolyte with varying pH

where N_A is Avogadro's number.

In the analysed case, the lowest surface excess Γ_s necessary for the calculation of the coverage rate was determined through extrapolation of straight lines $1/\Gamma'$ against $1/c$ for various electrode potentials to the value $1/c=0$.

The small values of the coverage rate obtained for one adenine molecule: 0.51 $nm^2 \cdot mol.^{-1}$; 0.48 $nm^2 \cdot mol.^{-1}$; 0.49 $nm^2 \cdot mol.^{-1}$; 0.33 $nm^2 \cdot mol.^{-1}$, respectively for pH 3, 4, 5 and 6 indicate a more oblique orientation of the adsorbed molecule with an increase in pH of the solution.

adenine adsorptions were also analysed on the basis of the Frumkin isotherm, using the obtained values of surface excess.

Constant Frumkin isotherms were determined according to the equation (6) (Gugała-Fekner, 2016; Gugała-Fekner, 2018):

$$\beta x = \frac{\Theta}{1-\Theta} e^{-2A\Theta} \tag{6}$$

where x is adsorbate molar ratio, A is adsorption equilibrium constant and $\beta = e^{-\Delta G_F^0/RT}$, where ΔG_F^0 is adsorption free energy.

The values of adsorption free energy ΔG_F^0 obtained from linear tests of the Frumkin isotherm are presented in Table 2. In the acetate buffer with pH=3, these values invariably increase towards more negative potentials, which is evidenced by electrostatic interaction of the protonated adenine molecule with the surface of the mercury electrode. In the acetate buffer with pH=4, these values barely scarcely depend on the potential. The presented adsorption parameters show that the values of adsorption free energy ΔG_F^0 for adenine in buffer solutions of pH 5 and pH 6, it is comparable and is accompanied by repulsive interactions between adsorbed adenine molecules.

This is evidenced by the mechanism of adsorption of the adenine molecule with the negative pole directed towards the surface of the electrode in these buffers. The parameters A values were calculated from the slopes of each straight line obtained from the linear test of the Frumkin isotherm. Since the linear test of the Frumkin isotherm concerns the correlation: $\ln x(1-\Theta)/\Theta$ against Θ, values $A<0$ indicate repulsive interactions whereas values $A>0$ refer to attractive interactions between adsorbed molecules. In the cases in question, parameter A values indicate repulsive interactions between adsorbed adenine molecules (Table 3).

Table 2. The values of adsorption free energy ΔG_F^0 obtained from linear tests of the Frumkin isotherm and the values of adsorption free energy ΔG_V^0 obtained from linear tests of the virial isotherm for a system containing adenine in acetate buffer with different pH values

	ΔG_F^0/kJ·mol^{-1}					
- E/V pH	0.1	0.3	0.5	0.7	0.9	1.1
3	31.56	32.45	33.49	33.56	33.54	35.42
4	31.04	33.04	32.8	32.8	32.65	30.37
5	34.68	36.73	34.68	34.68	33.09	32.75
6	34.78	35.07	35.67	33.24	32.2	32.2
	ΔG_v^0/kJ·mol^{-1}					
- E/V pH	0.1	0.3	0.5	0.7	0.9	1.1
3	109.2	110.2	110.7	111	112.3	113.7
4	108.6	111.1	110.6	110.2	109.4	107.4
5	112.4	115.1	112.4	112.4	110.6	110.6
6	113.6	119.2	113.7	112	110.7	110.7

Table 3. The values of parameter A obtained from linear tests of the Frumkin isotherm and the values of second virial coefficient B obtained from linear tests of the virial isotherm for a system containing adenine in acetate buffer with different pH values

	$-A_F$					
pH \ - E/V	0.1	0.3	0.5	0.7	0.9	1.1
3	4.7	4.8	4.9	4.6	3.7	3.5
4	1.75	2.1	2.47	3	4.13	4.13
5	3.03	2.83	2.47	2.72	3.08	2.69
6	2.44	2.3	2.32	2.14	3.22	4
	B / nm² molecula^{-1}					
pH \ - E/V	0.1	0.3	0.5	0.7	0.9	1.1
3	2.52	2.52	2.52	2.38	2.12	2.06
4	1.08	1.3	1.43	1.55	1.91	1.77
5	1.66	1.77	1.46	1.56	1.59	1.52
6	0.95	0.96	0.91	0.86	1.12	1.37

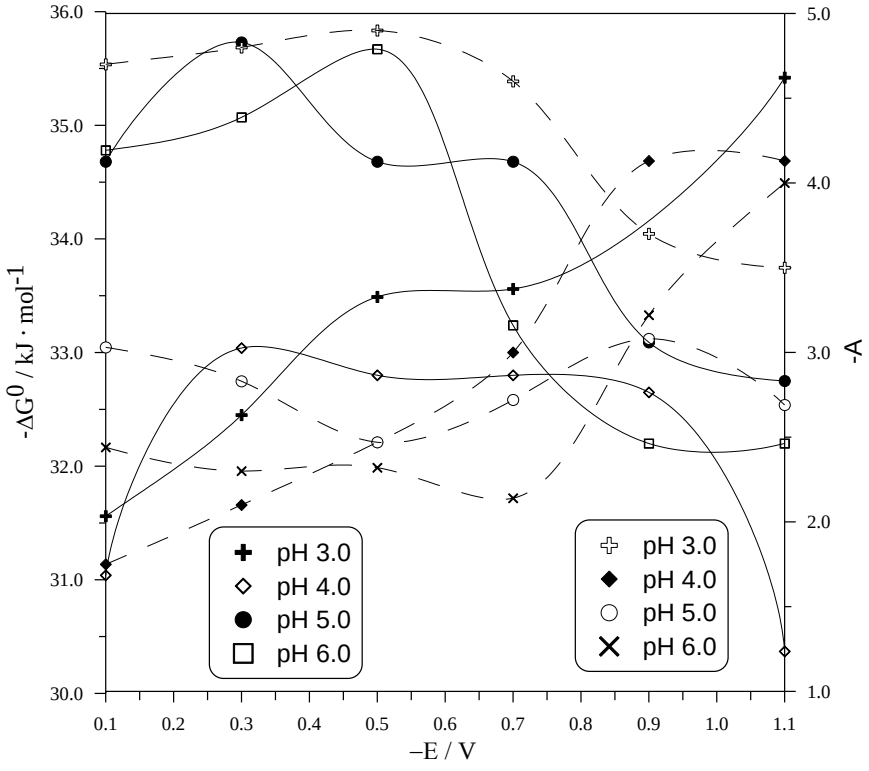


Fig. 8. The value of adsorption free energy ΔG_F^0 (solid line) determined from the Frumkin isotherm and the value of parameter A obtained from linear tests of the Frumkin isotherm $-A$ (dotted line) for the system containing adenine in the acetate buffer with varying pH

Adsorption parameters determined from Frumkin isotherms are frequently encumbered with errors. This is mainly connected with the necessity to determine Γ_s whose experimental values normally differ from the theoretical ones. Therefore, in order to verify the adsorption parameters obtained from the

Frumkin isotherm, viral isotherms were developed for the tested systems. With this end in view, the linear test of the viral isotherm was used (7)

$$\ln(\beta c) = \ln(\Gamma) + 2\beta c \quad (7)$$

The obtained adsorption energy values ΔG_V^0 and the second viral coefficient B in the function of the electrode's potential and pH of the acetate buffer are presented in Table 2, Table 3 and Fig. 8, respectively.

The obtained standard states associated with the applied isotherms are not uniform. This results in the obtainment of significantly higher values of adsorption free energy in the case of the viral isotherm in comparison to the results obtained from the Frumkin isotherm. Therefore, the discrepancies result from errors typical of numerical differentiation and extrapolation performed in order to obtain the value Γ_s and Θ (Gugała-Fekner, 2018; Gugała-Fekner, 2018).

4. Conclusions

The research results facilitate description of adenine adsorption on the mercury electrode in the function of pH of the supporting electrolyte, the acetate buffer in this case. The results of the thermodynamic analysis of the tested systems lead to numerous conclusions. One of the most crucial conclusions is the observation that the differential capacity curves of the tested systems with adenine and the differential capacity curves of the supporting electrolyte, the acetate buffer, do not overlap. This indicates the occurrence of adsorption of the tested compound on the mercury electrode within the whole range of applied concentrations. Frequency dispersion occurring in all the tested systems indicates adsorption disequilibrium during the life of a single drop. However, the differential capacity curves obtained through extrapolation to zero frequency pertain to equilibrium. The pH of the supporting electrolyte affects the course of the differential capacity curves. For pH=3 a different course of differential capacity curves in comparison to the other buffers may results from stronger adsorption of acetic acid molecules in this buffer. In acetate buffers with a pH of 3 and 4, adsorption mainly concerns acetic acid molecules whereas in buffers with a pH of 5 and 6 it concerns acetate ions. The shift of the zero charge potential value in the acetate buffer with pH=3 towards less negative potentials with an increase in the concentration of the organic substance indicates its adsorption with the positive pole towards the surface of mercury. In buffers with a pH of 4 to 6, the addition of an organic substance causes a shift of E_z towards more negative potentials; therefore, it can be assumed that in these supporting electrolytes the adenine molecule is adsorbed to the surface of the mercury electrode with the aromatic ring, i.e. the negative pole. The evidence for the physical adsorption of adenine on the mercury electrode is the possibility of determining electrical parameters characterising maximum adsorption E_{max} and σ_{max} as well as absence of linearity of the function $\Delta G^0 = f(E)$. It can be observed in all the analysed systems that the values of relative surface excess amounts increase with an increase in the concentration of the purine derivative. At the end, it was observed that the values of adsorption energy obtained from the viral isotherm demonstrate trends similar to those obtained from the Frumkin isotherm.

In conclusion, the above deliberation leads to the observation that physical adsorption occurs in the tested systems. This is evidenced by the test results, i.e. the occurrence of a typical maximum on the curve of the relation $\Gamma=f(E)$; crossed curves of the following relation $\sigma = f(E)$ at one point and, thus, the possibility of determining electrical parameters characterising maximum adsorption as well as absence of linearity of the function $\Delta G^0 = f(E)$ (Fig. 8).

The results of adenine adsorption on the mercury electrode can be used in biochemical research. Adenine as a building block of nucleic acids belongs to the group of chemical compounds called nucleosides. The synthesis of new nucleoside analogues has a huge impact on the development of modern medicine. These compounds have high antiviral, antitumor and antifungal activity. They can be used like a new class of chemotherapeutic agents.

References

BAREK, J., *2013. Possibilities and Limitations of Mercury and Mercury-based Electrodes in Practical Electroanalysis of Biologically Active Organic Compounds.* Portugaliae Electrochimica Acta. 31(6), 291-295.

GALUS, Z., 1979. Elektroanalityczne metody wyznaczania stalych fizykochemicznych PWN Warszawa, Poland.

GUGAŁA-FEKNER, D., 2016. *Adsorption of guanine at the interface electrode-acetic buffer solution and its influence on zinc cation Electroreduction.* Monatsh Chem. 147(11), 1855-1862.

GUGAŁA-FEKNER, D., 2016. *Adsorption of N-decanoyl-N-methylglucamine at the interface electrode-$NaClO_4$solution. comparison of adsorption properties of different surfactants.* Croat. Chem. Acta. 89(1), 25-30.

GUGAŁA-FEKNER, D., 2018. *Adsorption of adenine on mercury electrode in acetate buffer at pH 5 and pH 6 and its effect on electroreduction of zinc ions*. Monatsh Chem. 149, 1357-1365.

GUGAŁA-FEKNER, D., 2018. *The effect of adenine adsorption on Zn (II) electroreduction in acetate buffer*. Acta Chim. Slov. 65, 119-126.

KALISZCZAK, W., NOSAL-WIERCIŃSKA, A., 2020. *Change in the dynamics of the catalytic action of azathioprine on the electroreduction process of Bi(III) ions under the influence of surfactants in the context of controlled drug release*. J. Electroanal. Chem. 862, 114033-114041.

KALVODA, R., 2007 *Chem.Anal.* 52, 869-873.

FONTANESI, C., 1994. *Entropy change in the two-dimensional phase transition of adenine adsorbed at the Hg electrode/aqueous solution interface.* J. Chem. Soc. Faraday Trans. 90, 2925-2930.

FRUMKIN, A.C., 1926. *Über die Beeinflussung der Adsorption von Neutralmolekülen durch ein elektrisches Feld*. Z. Phys. 35, 792-802.

NIESZPOREK, J., 2013. *The mechanism and kinetics of Zn^{2+} electroreduction in the presence of octyltrimethylammonium bromide*. J. Electroanal. Chem. 706, 108-116.

NIESZPOREK, J., 2020. *Nicotinamide as a Catalyst for Zn^{2+} Electroreduction in Acetate Buffe.* Electrocatalysis. 11, 422-431.

NIESZPOREK, J., GUGAŁA-FEKNER, D., NIESZPOREK, K., 2019. *The Effect of Supporting Electrolyte Concentration on Zinc Electrodeposition Kinetics from Methimazole Solutions.* Electroanalysis. 31, 1141-1149.

NIESZPOREK, J., NIESZPOREK, K., 2018. *Experimental and Theoretical Studies of Anionic Surfactants Activity at Metal/Solution Interface: The Influence of Temperature and Hydrocarbon Chain Length of Surfactants on the Zinc Ions Electroreduction Rate*. Bulletin of the Chemical Society of Japan. 91, 201-210.

NOSAL-WIERCINSKA, A., KALISZCZAK, W., MARTYNA, M., GOLEBIOWSKA, B., WISNIEWSKA, M., 2020. *Temperature influence on the electrode process in the presence of 6-thioguanine and surfactants.* Physicochemical Problems of Mineral Processing. 56(6), 14-21.

NOSAL-WIERCIŃSKA, A., MARTYNA. M., MIRCESKI. V., SKRZYPEK. S., 2021. *Electroreduction of bi(Iii) ions at a cyclically renewable liquid silver amalgam film electrode in the presence of methionine*, Molecules. 26, 3972-3986.

PRADO, C., NAVARRO, I., RUEDA, M., FRANCOIS, H., BUESS-HERMAN, C., 2001. *Kinetics of condensation of adenine at the mercury /electrolyte interface*. J.Electroanal.Chem. 500, 353-364.

PRIETO, F., ALVAREZ-MALMAGRO, J., RUEDA, M., 2017. *Electrochemical Impedance Spectroscopy study of the adsorption of adenine on Au(111) electrodes as a function of the pH.* J. Electroanal. Chem. 793, 209-217.

RABIK, C., A., DOLAN, M., E., 2007. *Molecular mechanisms of resistance and toxicity associated with platinating agents.* Cancer Treat. Rev. 33, 9-23.

SIEŃKO, D., GUGAŁA-FEKNER, D., NIESZPOREK, J., FEKNER, Z., SABA, J., 2009. *Adsorption of tetramethylthiourea in concentrated $NaClO_4$ solutions.* Collect. Czech. Chem. Commun. 74, 1309-1321.

SLIWINSKA-HILL, U., SZUMELDA, M., 2016. *Biological aspects of anticancer therapy with platinum drugs: interactions with cytochrome c*. Journal of Oncology. 66 (2), 136-150.

STENZEL-BEMBENEK, A., SAGAN, D., GUZ, M., STEPULAK, A., 2014. *Single nucleotide polymorphisms in lung cancer patients and cisplatin treatment.* Postepy Hig Med Dosw. 68, 136-1373.

SUK, R., GURUBHAGAVATULA, S., PARK, S., ZHOU, W., SU, L., LYNCH, T., J., WAIN, J., C., NEUBERG, D., LIU, G., CHRISTIANI, D., C., 2005. *Polymorphisms in* ERCC1 *and Grade 3 or 4 Toxicity in Non–Small Cell Lung Cancer Patients.* Clin. Cancer Res. 11, 1534-1538.

VYSKOCIL, V., BAREK, J., 2009. *Mercury Electrodes–Possibilities and Limitations in Environmental Electroanalysis.* Critical Reviews in Analytical Chemistry. 39, 173-188.

ŻAK, I., BALCERZYK, A., 2001. *Chemia medyczna. Śląska Akademia Medyczna,* 307-32