



Study on electrical double layer nanostructure on zeolitic materials' surface in the presence of impurities of different nature

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Abstract

The aim of the research was to compare the adsorption mechanisms of heavy metal ions (Pb(II) and Zn(II)), as well as organic substances [diclofenac molecules and pol(acrylic acid) macromolecules on the surfaces of Na-X and Na-P1 synthetic zeolites as well their Na-X@ and Na-P1@ carbon composites]. The single and mixed adsorbate systems were considered. The more probable structures of the formed adsorption layers were proposed based on the results of the solid surface charge density and zeta potential experiments. The great applicability of the analysis of the parameters characterizing the electrical double layer in determination of the binding mechanism of simple inorganic ions and more complex organic molecules on the surface of the examined solids from the one- and two-component solutions was proved. Moreover, the changes of the surface and electrokinetic factors after the addition of the organic molecules enable specification of drug molecule orientation as well as the polymeric chain conformation at the solid/liquid interface.

Keywords Na-X synthetic zeolite · Na-P1 synthetic zeolite · Zeolite–carbon composite · Heavy metal · Electrical double layer · Mixed adsorption layer

Introduction

The specific structures of the adsorption layers formed at the solid–liquid interface in the largely dispersed systems are extremely important for their stability (Wiśniewska et al. 2012). This is essential for obtaining both long-term stable suspensions and very unstable ones. Such systems are commonly found in practice, ranging from the preparation of cosmetic and pharmaceutical suspensions, through the paint and food industries, to the treatment of groundwater and municipal wastewater (Ostolska and Wiśniewska 2015;

Wiśniewska et al. 2015; Wawrzekiewicz et al. 2017). On the one hand, the effective stabilization is greatly required (unlimited timely dispersion of one phase into another), but on the other hand, the successful separation of the solid with the adsorbed pollutants from the liquid phase (rapid destabilization) is needed (Farrokhpay 2009; Lee et al. 2014; Szewczuk-Karpisz et al. 2014).

The surface and electrokinetic studies can be very helpful in characterization of nanostructure of adsorption layers composed of simple inorganic ions, drug molecules and polymeric chains formed on the solid particles dispersed in the aqueous solutions. The parameters obtained during the solid surface (by the use of the potentiometric titration method) and zeta potential (electrophoretic mobility measurements) determination allow the specification of the arrangement of small ions and big organic molecules in the surface layer (Ostolska and Wiśniewska 2014; Wiśniewska et al. 2022). Analyzing their sign and value not only electrostatic conditions occurring in the examined system during the adsorption process, but also the location of the charged functional groups of the adsorbate in the various parts of the electrical double layer (edl) can be defined. Such information is extremely important for the determination and explanation

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of the stability mechanism of the examined suspensions which guarantees their effective application in practice.

The classical Grahame model (1947) defined the position of the stiff and movable layers within the edl. The stiff Stern layer contains the two planes: the inner Helmholtz plane (IHP) passing through the centers of specifically adsorbed ions and the outer Helmholtz plane (OHP) passing through the centers of electrostatically adsorbed ones (which have complete or partially reduced hydration shells). The OHP is also the beginning of the edl diffusion region. The Graham's model also determines the position of the slipping plane which separates the stationary part of edl from its movable part. It is determined by the outer parts of ions adsorbed rigidly on the solid surface. The potential from the slipping plane to the bulk solution is called the electrokinetic potential or the zeta potential (ζ).

The modern edl models were developed based on the dissociation reactions of metal oxide surface hydroxyl groups and their reactions with ions of the basic electrolyte (reactions of complexation and formation of ion pairs). The most important group among these models is one (Janusz 1994). The site-binding group includes the 1pK model, the 2pK model, the constant capacitance model (CCM), the double layer model (DLM), the triple layer model (TLM), the fourfold layer model (FLM) and the multisite complexation model (MUSIC). These models connect the structure of the edl proposed in the classical models with the ionization reactions of surface groups. The site-binding models reject the division into specifically and non-specifically adsorbing ions and do not use the Nernst law to describe the relationship between the surface potential and the solution pH. They are now widely applied in many variations, because they offer the opportunity to explain the dependence of the zeta potential and surface charge on the solution ionic strength.

The presence of big organic molecules and polymer chains (and in particular ionic compounds) at the interface changes significantly the structure and properties of the electrical double layer, mainly sign and magnitude of surface charge and zeta potential (M'Pandou and Siffert 1987). In the case of non-ionic substances' adsorption, the surface charge of the solid is practically unchanged or changes only slightly. If the interaction energy of the basic electrolyte ions with the surface groups is much higher than that of the non-ionic adsorbate, its adsorption does not change the position of the electrolyte ions in the Stern layer. On the other hand, Vincent (1974) took into consideration the fact that some organic molecules, especially polymeric chains, will cause the movement of counterions in the Stern layer. This displacement of the basic electrolyte ions can take place in two ways: in the direction parallel to the solid surface without causing any change in the zeta potential value or in the direction perpendicular to the solid surface, which increases the number of counterions in the edl diffusion layer

and causes the zeta potential increase. This displacement of the counterions is due to the partial blockade of the surface active sites by the adsorbed molecules of the considerable size. On the other hand, adsorption of large molecules can move the slipping plane away from the solid surface, resulting in the zeta potential decrease. In the case of the adsorbed ionic substances, their functional groups can be located in the area of the slipping plane, which results in an increase (cationic adsorbate) or decrease (anionic adsorbate) of the zeta potential.

The aim of this study was to determine and compare the nanostructure of the electrical double layers on the surfaces of the synthetic zeolites: Na-X, Na-P1 and their composites with carbon: Na-X(C), Na-P1(C) formed in the solution of the basic electrolyte and those containing additionally inorganic ions (Pb(II) and Zn(II)) or organic molecules: diclofenac drug and pol(acrylic acid) polymer. The examined suspensions were prepared in the single and mixed adsorbate systems. The parameters characterizing the surface and diffusion parts of edl were determined by the use of the potentiometric titration method and the electrophoretic mobility measurements. The changes in their values indicate not only the specific location of inorganic and organic substances in the particular parts of edl, but also the way of interactions with the solid surface (determination of the type of adsorbate functional groups directly connected with the surface). Such information is essential for the detailed description of the structure of the electrical double layer formed at the solid–liquid interface, which is very important not only for the successful removal of hazardous or undesirable substances from the aqueous solutions but also for the separation of the solid particles with adsorbed impurities from the liquid phase.

Experimental

The zeolitic materials were synthesized using the hazardous waste—high-carbon fly ash (HC FA) from the Janikowo thermal power plant. The zeolite-carbon composites (Na-X(C) and Na-P1(C)) and next the pure zeolites (Na-X and Na-P1) were obtained by the hydrothermal reaction of fly ash with the aqueous sodium hydroxide solution according to the procedure elaborated by Panek et al. (2021a) and Bandura et al. (2021). In the first stage, the zeolite–carbon composite was obtained using the fly ash from the Janikowo Combined Heat and Power Plant (product of conventional hard coal combustion). The electromagnetic separation results in obtaining of a high-carbon product which was subjected to the hydrothermal reaction of fly ash with the aqueous sodium hydroxide solution on the technological line for the synthesis of ash zeolites. For this purpose, 25 kg (in the case of Na-X(C)) or 20 kg (in the case of Na-P1(C)) of

high-carbon fly ash was mixed with 90 dm³ of NaOH solution (with the concentration 3 mol/dm³). Then, the whole system was left at 80 °C for 48 h (in the case of Na-X(C)) or at 90 °C for 24 h [in the case of Na-P1(C)]. Next, the obtained products were filtered, rinsed and dried at 105 °C. The post-reaction solution rich in silicon and aluminum was a substrate for the synthesis of pure zeolites (with no ash residue). These materials were obtained on a technological scale using the following parameters: in the case of Na-X, 50 dm³ of the waste solution was mixed with 50 dm³ of the aqueous NaOH solution (with the concentration 2 mol/dm³) in which 450 g of aluminum foil was dissolved; in the case of Na-P1, 40 dm³ of the waste solution was mixed with 10 dm³ of NaOH solution (with the concentration 2 mol/dm³), where 80 g of aluminum foil was dissolved. The final zeolites were left for 24 h at 70 °C (in the case of Na-X) or for 48 h at 100 °C (in the case of Na-P1). Then, the obtained product was filtered, washed and dried at 105 °C. The obtained materials were characterized in terms of mineralogy, structure and texture which was fully described in our previous papers (Panek et al. 2021b, c). The textural parameters were measured on an ASAP 2020 apparatus (Micromeritics Instrument Corporation, Norcross, GA, USA) using the low-temperature nitrogen adsorption/desorption isotherms.

Two heavy metals—Zn(II) and Pb(II) were selected for the studies. The initial solutions of heavy metals were prepared using Zn(NO₃)₂ and Pb(NO₃)₂ salts (POCh). Two organic substances: diclofenac sodium salt—DCF (Sigma-Aldrich) and poly(acrylic acid)—PAA (Sigma-Aldrich) were selected for studies. Both organic substances are of anionic character resulting from the occurrence of carboxyl groups in their molecules. These groups exhibit weak acidic

properties and undergo dissociation with the increasing solution pH (Gebhardt and Furstenuau 1983; Chibowski et al. 2003; Jodeh et al. 2016; Lach and Szymonik 2020). The physicochemical characteristics of the applied adsorbents and adsorbates are presented in Table 1.

Additionally, the basic electrolyte NaCl with the concentration 0.001 mol/dm³ was applied in all experiments performed in the single and mixed systems of adsorbates. The concentrations of adsorbates were as follows: C_{Zn(II),Pb(II)} 10 ppm, C_{DCF} 50 ppm and C_{PAA} 50 ppm. The compositions of the mixed systems were: Zn(II) + Pb(II), DCF + PAA, DCF + Zn(II), DCF + Pb(II), PAA + Zn(II) and PAA + Pb(II).

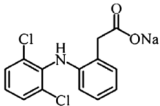
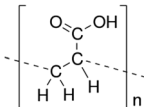
The surface charge density (σ_0) and the point of zero charge (pzc) of the zeolite suspensions were determined by the automatically controlled potentiometric titration using the computer program “titr_v3”. The difference in the volume of the titrant (NaOH with the concentration 0.1 mol/dm³) added to the suspension and the supporting electrolyte solution (obtained from the reference curve prepared earlier) providing a specific pH value (ΔV) was the basis of this method (Janusz 1994)

$$\sigma_0 = \frac{\Delta V c_b F}{m S}, \quad (1)$$

where c_b —base concentration, F —Faraday constant, m —solid mass in the suspension, and S —specific surface area of the solid.

The suspensions were prepared by adding 0.03 g of Na-X, 0.4 g of Na-P1, 0.075 g Na-X(C), or 0.2 g of Na-P1(C) to 50 cm³ of the basic electrolyte (0.001 mol/dm³ NaCl). At first, only the electrolyte was titrated. Then, the suspensions

Table 1 Physicochemical characteristics of applied adsorbents and adsorbates

Sample	BET surface area (m ² /g)	Pore volume (cm ³ /g)	Mean pore diameter (nm)	Point of zero charge (pH _{pzc})	Isoelectric point (pH _{iep})
Zeolitic adsorbents					
Na-P1(C)	69.8	0.12	6.7	8.8	3.5
Na-P1	26.7	0.05	6.9	9.4	2.6
Na-X(C)	271.9	0.17	2.6	8.6	2.9
Na-X	727.9	0.31	1.7	9.0	4.4
Sample	Molecular formula	Structural formula	Molecular weight (g/mol)	pK _a	
Organic adsorbates					
DCF	C ₁₄ H ₁₀ Cl ₂ NNaO ₂		318.1	4.15	
PAA	(CH ₂ -CHCO ₂ H) _n		240.000	4.5	

without and with inorganic or organic adsorbates in the simple and mixed systems were examined.

The electrophoretic mobility (U_e) measurements enabled the calculation of the zeta potential (ζ) and the determination of the isoelectric point (iep) of the examined suspensions (Hunter 1981; Ohshima 1994). For this purpose, there was used the following equation:

$$U_e = \frac{2\varepsilon_0\varepsilon\zeta}{3\eta}f(\kappa a), \quad (2)$$

where U_e —electrophoretic mobility, ε —dielectric constant, ε_0 —electric permeability of vacuum, η —viscosity, and $f(\kappa a)$ —Henry function.

For $f(\kappa a) < 0.1$, the above equation reduces to the Hückel one

$$U_e = \frac{2\varepsilon_0\varepsilon\zeta}{3\eta}. \quad (3)$$

On the other hand, for $f(\kappa a) > 100$, there was obtained the Smoluchowski equation

$$U_e = \frac{\varepsilon_0\varepsilon\zeta}{\eta}. \quad (4)$$

The experiments were conducted using the Zetameter Nano ZS (Malvern Instruments) equipped with the universal dip cell. The suspensions were prepared by adding 0.01 g of the solid to 200 cm³ of the supporting electrolyte solution (0.001 mol/dm³ NaCl) without and with inorganic or organic adsorbates in the simple and mixed systems. After the 3-min sonication, the suspension was divided into several parts and the specific pH value was adjusted in each of them (ranging from 3 to 10). It should be noted that all adsorbates were added to the individual suspensions after the sonication process. Then, the electrophoretic mobilities were measured.

Results and discussion

The structure of the electrical double layer (edl) formed at the solid–liquid interface determines the stability properties of suspensions. It depends on the adsorption affinity of different substances (small inorganic ions, drug, surfactant, dye molecules and polymeric macromolecules). The specific location of the adsorbed molecules, especially those with the large molecular weight and containing numerous functional groups can be characterized on the basis of the sign and magnitude of the surface charge density (σ_0) and the zeta potential (ζ). What is more, the dependencies of σ_0 and ζ versus the solution pH enable determination of values of point of zero charge (pzc) and isoelectric point (iep) of the examined solids. The pzc occurs at such pH value, at which σ_0 is equal to zero (the

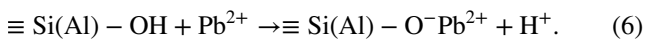
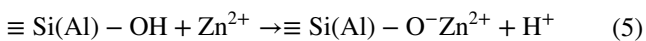
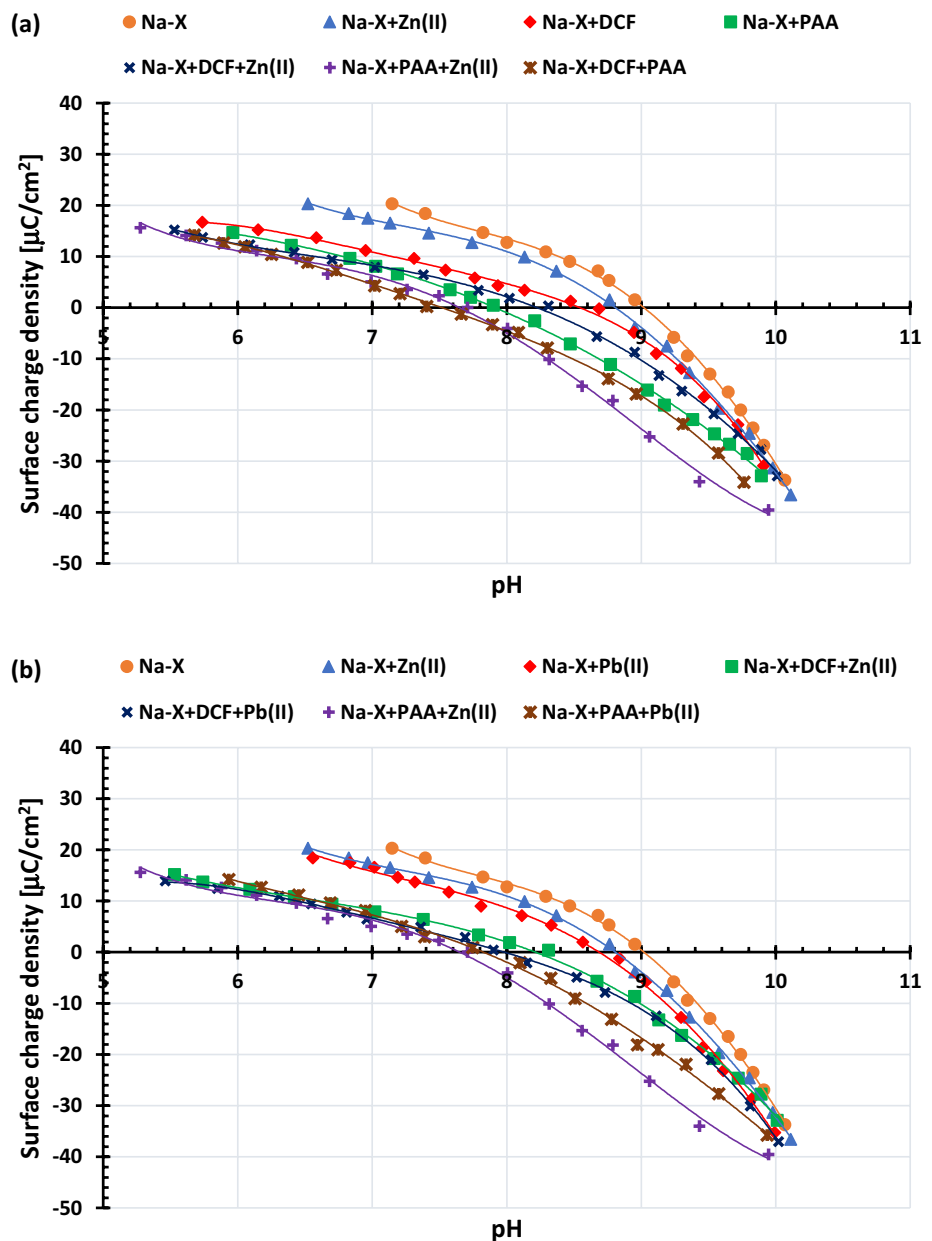
concentrations of positively and negatively charged surface groups are the same), whereas iep represents the situation, in which ζ assumes the value 0 (the concentrations of positively and negatively charged groups or ions in the slipping plane area are the same).

The values of pH_{pzc} and pH_{iep} characterizing the examined zeolites and composites are presented in Table 1. Their analysis leads to the conclusion that the points of zero charge for all examined solids are at basic pHs and assume the values changing in the range 8.6–9.4. This indicates that the solid surface over a wide pH range up to the value corresponding to the pzc, is positively charged. The isoelectric point's values (changing in the range 2.9–4.4) differ significantly from the corresponding pzc ones. The main reason for these differences is the permeation of the edl formed on the opposite pore walls of the adsorbent which changes the ionic composition of the diffusive part of the electrical double layer (Hunter 1981; Wiśniewska et al. 2020). Moreover, some impurities present in the zeolitic structure (remaining in even small amounts after the preceding washing process of the solid with the doubly distilled water) can also affect the ionic composition of surface and slipping plane layers. Such behaviour was observed for many other systems containing metal oxides, minerals, activated carbons and natural zeolites (Wiśniewska et al. 2015, 2017, 2018; Szewczuk-Karpisz et al. 2018).

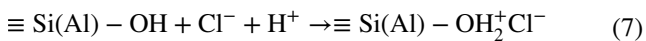
Figures 1, 2, 3, 4 show the dependencies of the solid surface charge density as a function of solution pH obtained for Na-X zeolite without and with inorganic/organic substances whereas in Figs. 5, 6, 7, 8, analogous curves present the zeta potential changes. Additionally, Figs. 1b and 5b contain the comparison of surface and electrokinetic behaviour of the examined suspensions in the Zn(II) and Pb(II) ions' presence based on the example of Na-X zeolite. The heavy metal ions' influence was similar for the other applied solids, i.e., Na-P1 zeolite as well as the Na-X(C) and Na-P1(C) composites.

The analysis of the data obtained for the simple inorganic ions [zinc(II) and lead(II) ones] indicated that the addition of divalent cations causes a decrease in the pH_{pzc} value and a noticeable decrease of the solid surface charge density in the whole examined pH range (Figs. 1, 2, 3, 4). This phenomenon is related to the formation of an additional number of negatively charged groups on the adsorbent surface. Such effect is caused by the adsorption of simple inorganic cations and observed for many experimental systems (Skwarek et al. 2014; Janusz et al. 2022). This shows that not only the typical ion exchange of cations present in the zeolite structure (e.g., Mg, Ca) with the heavy metal cations takes place in the studied systems, because it would not lead to any changes in the σ_0 values. Adsorption of divalent cations also forces the formation of positively charged surface sites by detaching a proton from the surface hydroxyl groups according to the following reactions:

Fig. 1 Dependencies of the solid surface charge density as a function of solution pH obtained for the Na-X zeolite without and with inorganic/organic substances: a) systems containing only Zn(II) ions and b) systems containing Zn(II) and Pb(II) ions



Besides the above mechanisms, the reactions of surface hydroxyl groups involving the basic electrolyte ions (Na^+ , Cl^-) take place. As a result, the surface ion pairs are formed (Janusz 1994). These reactions proceed according to the equations



Despite the fact that there are unfavourable electrostatic conditions for metal cations binding on the positively charged zeolitic materials surface in the wide pH range, their adsorption takes place—mainly through the chemisorption mechanism (Panek et al. 2021b, c). Such chemical nature of interactions refers mainly to not hydrated cations located in the Stern layer within the inner Helmholtz plane.

What is more, the greater reduction of the σ_0 values was observed for Pb(II) ions than for Zn(II) ones (Fig. 1a). The XPS studies presented in our previous paper (Medykowska et al. 2022) confirmed the presence of zinc on the solid surface in the form of mainly Zn^{2+} ions. On the other hand, lead can undergo surface precipitation, and besides its ionic form (Pb^{2+}), the hydroxides (Pb(OH)_2 , Pb(OH)_4) can be

Fig. 2 Dependencies of the solid surface charge density as a function of solution pH obtained for the Na-X(C) composite without and with inorganic/organic substances

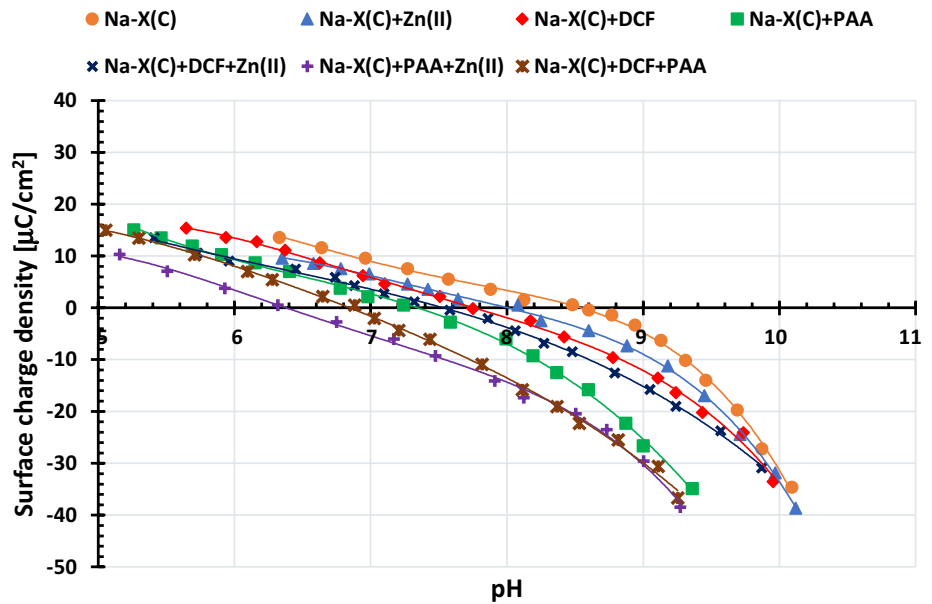
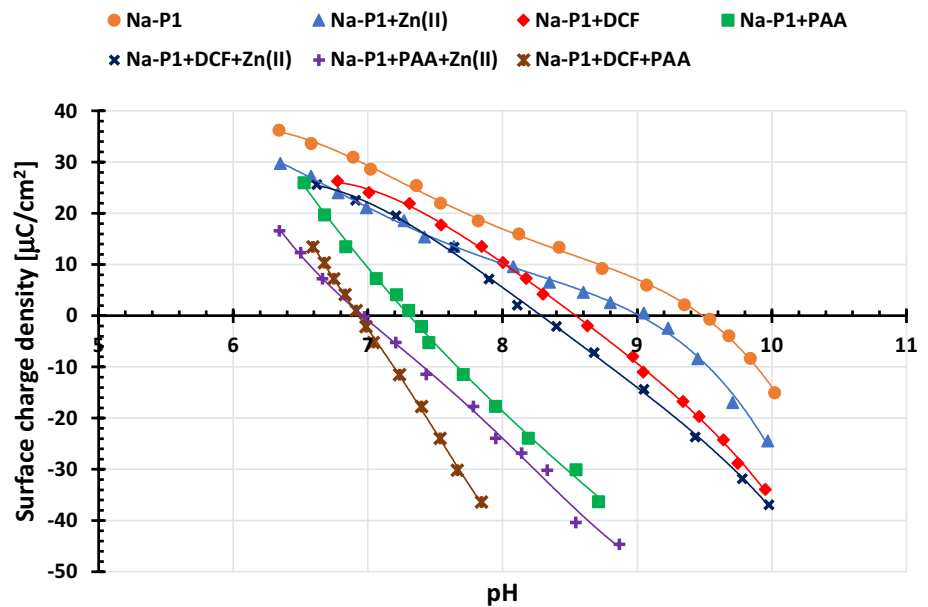


Fig. 3 Dependencies of the solid surface charge density as a function of solution pH obtained for the Na-P1 zeolite without and with inorganic/organic substances



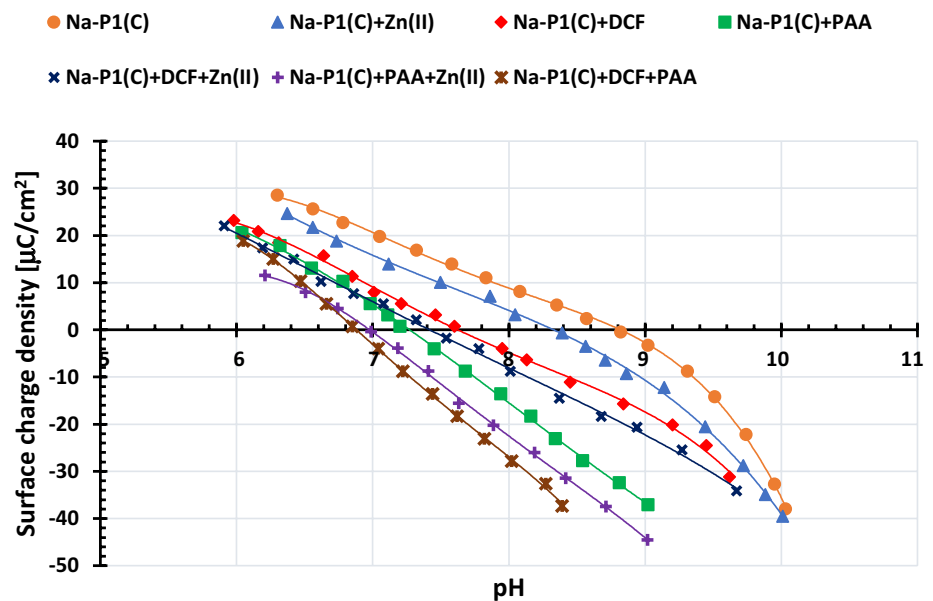
formed on the zeolitic materials' surfaces. This proves that lead can locate in both the inner Helmholtz plane (specifically adsorbed Pb^{2+} cations) and the outer Helmholtz plane (electrostatically adsorbed partially or totally hydrated Pb ions). The occurrence of lead in both Helmholtz planes causes more pronounced changes in the density of the surface charge in comparison to the zinc present mainly in the IHP area.

The second important parameter characterizing edl is the isoelectric point determined on the basis of changes in the zeta potential characterizing the charge of the slipping plane. Changes in the position of the isoelectric point of the adsorbent particles due to the addition of heavy metal ions are

noticeable (Figs. 5, 6, 7, 8). In general, a slight decrease in the zeta potential value and a decrease in the pH_{iep} value are observed. At pH equal or higher than 8.5, the zeta potential tends to increase in the systems containing zinc(II) ions. This is due to the overloading of the electrical double layer, i.e., charge reversal (Szymanek et al. 2021). This phenomenon is related to the presence of more counterions within the inner part of the electrical double layer than on the surface of the solid. Consequently, the same charge sign appears on the outside part of the electrical double layer as well as on the surface.

Additionally, the changes in the ionic composition of the diffusion part of edl are caused by the replacement of the

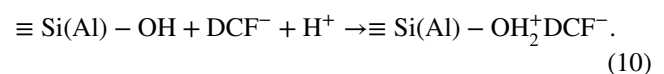
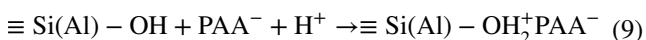
Fig. 4 Dependencies of the solid surface charge density as a function of solution pH obtained for the Na-P1(C) composite without and with inorganic/organic substances



monovalent electrolyte ions from the surface layer due to the divalent heavy metal cations.

The organic substances' [diclofenac, poly(acrylic acid)] presence influences considerably the structure of the electrical double layer formed on the examined zeolites and composites surfaces. The changes in the surface charge density and the zeta potential solid particles as a function of solution pH without and with DCF or/and PAA are presented in Figs. 1, 2, 3, 4, 5, 6, 7, 8. Both DCF and PAA have anionic character; thus, there are favourable interactions between the positively charged solid surface and the negatively charged organic molecules. The dissociation of their carboxyl groups increases with the pH increase and at pH about 6 is practically complete. The adsorption of diclofenac, poly(acrylic acid) and their mixture causes the noticeable decrease of the solid surface charge density in the whole examined pH range (Figs. 1, 2, 3, 4) for all applied zeolitic materials. As a consequence, the shift of the points of zero charge towards the lower pH values takes place. It should be noted that the greatest reduction of the surface charge density was obtained in the simultaneous presence of both adsorbates (DCF + PAA) and the smallest one occurred after the DCF addition.

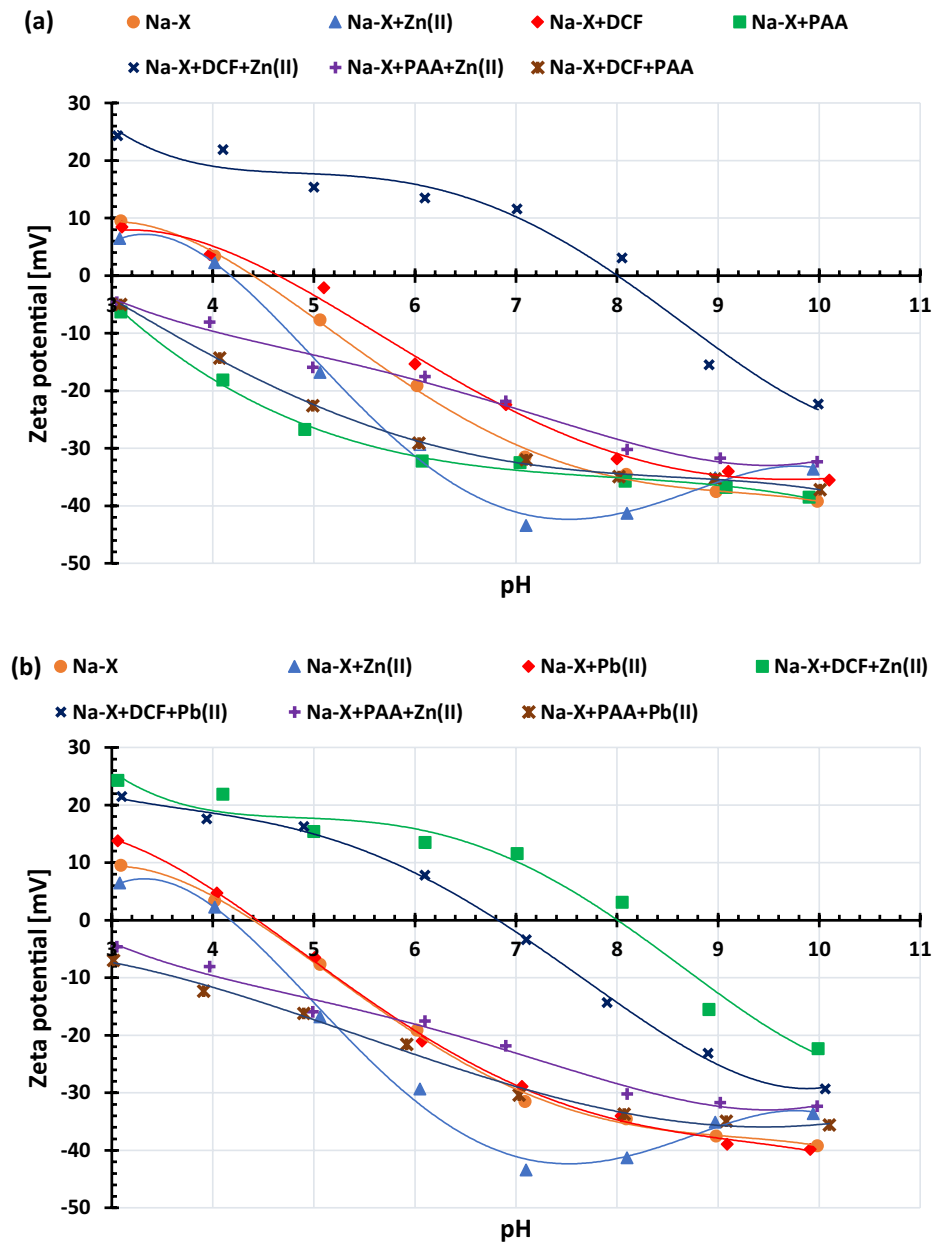
The decrease of the solid surface charge caused by the adsorption of long polymeric chains and large drug molecules with anionic character is observed, despite the fact that the direct interactions of their negatively charged functional groups with the solid surface lead to the formation of an additional number of positively charged active sites according to the reactions



Nevertheless, the total surface charge depends also on the contribution of negatively charged functional groups of the adsorbed organic molecules, unbound directly with the solid surface and located in the by-surface layer within the stiff Stern layer (Wiśniewska et al. 2015). They are more numerous than the negative groups directly interacting with the solid surface, and as a result, the total observed effect is reduction of the solid surface charge in relation to the corresponding suspension without adsorbates. Additionally, the analysis of σ_0 values suggests that not only electrostatic interactions contribute to the adsorption of DCF and PAA in the examined systems. Besides them, the hydrophobic forces and hydrogen bonds are of great importance in this process. The hydrogen bonds between the $-\text{COO}^-$ (present in both PAA and DCF molecules) and $-\text{NH}$ groups of diclofenac and zeolite hydroxyl groups can be formed. Moreover, hydrophobic interactions of the π - π electron donor-acceptor type can also occur between the aromatic rings of drug molecules and carbon structures on the composite surface (Correa-Navarro et al. 2020; Szewczuk-Karpisz et al. 2021). The obtained results suggest that the most probable mechanism of DCF adsorption includes the presence of unbound negative groups in the by-surface layer (which has an impact on the observed surface charge reduction) and direct binding of molecules takes place through the hydrogen bridges and hydrophobic interactions (in the case of composite materials containing carbon).

For all examined systems, the zeta potential of zeolitic materials particles increases in the presence of DCF, decreases in the presence of PAA, and in the case of mixed

Fig. 5 Dependencies of the zeta potential as a function of solution pH obtained for the Na-X zeolite without and with inorganic/organic substances: a) systems containing only Zn(II) ions and b) systems containing Zn(II) and Pb(II) ions



adsorbates (DCF + PAA), its value decreases in comparison with the suspension without adsorbates.

Changes in the zeta potential of solid particles in the presence of large organic molecules (polymers, drugs) are the results of three main effects (M'Pandou and Siffert 1987). There are: (1) the displacement of the counterions located in the Stern layer due to the adsorption of organic molecules leading to the desorption of basic electrolyte ions from the solid surface and their shifting towards the edl diffusion part; (2) the presence of negatively charged functional groups of the adsorbed molecules in the area of slipping plane; (3) the shift of slipping plane by the adsorbed molecules or polymeric chains from the solid surface towards the bulk solution. The obtained electrokinetic results (Figs. 1, 2, 3, 4)

indicate that the first phenomenon is dominant in the case of DCF, whose adsorption causes effective displacement of the basic electrolyte ions (especially Na^+ cations) from the stiff surface layer to the movable diffusion part of edl. For the PAA containing suspension, the shift of the slipping plane and the presence of negatively charged carboxyl groups of the polymer (each segment of the flexible polymeric chains contains such a group) in this area are dominant.

In the case of mixed adsorbates (DCF + PAA) with the same anionic character, their competition for the surface active sites occurs. The mixed adsorption layer composition is characterized by the greater accumulation of negative charges in both the surface and slipping plane layers, which is reflected in the decrease of both the surface charge density

Fig. 6 Dependencies of the zeta potential as a function of solution pH obtained for the Na-X(C) composite without and with inorganic/organic substances

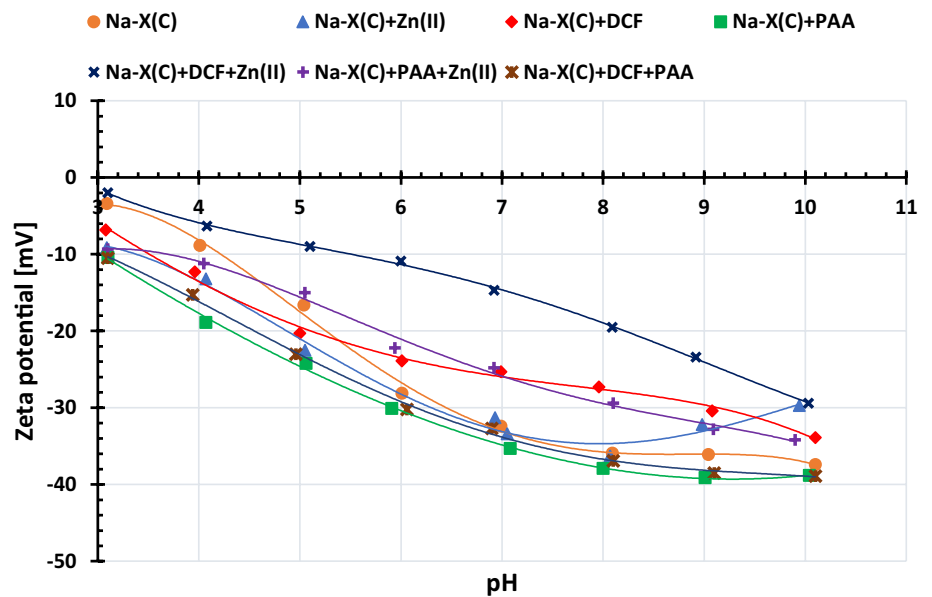
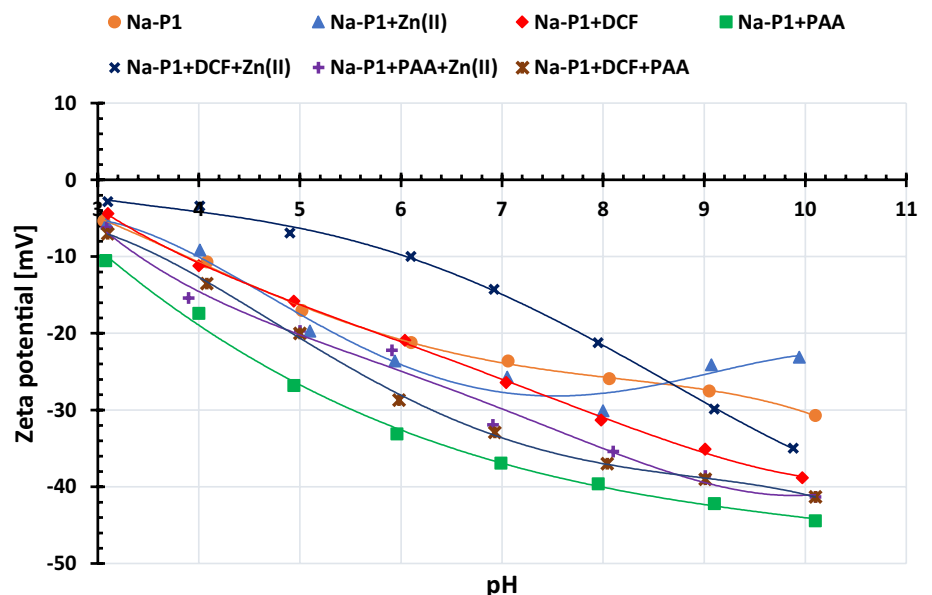


Fig. 7 Dependencies of the zeta potential as a function of solution pH obtained for the Na-P1 zeolite without and with inorganic/organic substances



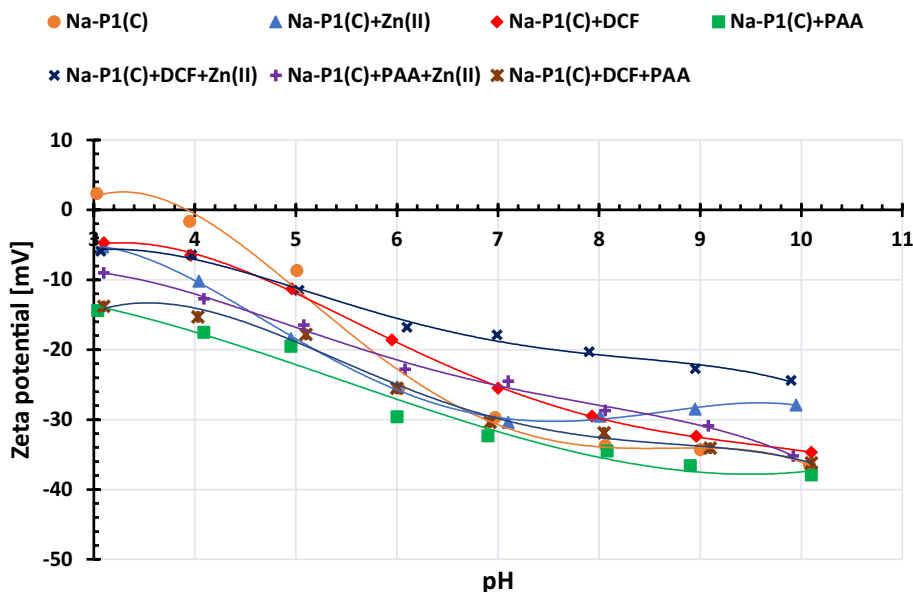
and the zeta potential values (in comparison to the systems containing single organic substances).

The simultaneous presence in the systems of heavy metals and drug/polymer molecules results in metal–DCF and metal–PAA complexes formation due to the electrostatic attraction between the inorganic actions and the organic anions (Roma-Luciw et al. 2001). In the case of long polymeric chains having numerous dissociated carboxyl groups, their complexes with divalent cations can have intra- and intermolecular character. The former are formed within one polymeric macromolecule (which leads to its more coiled conformation), and the latter ones—between two PAA chains linking them together. The adsorption of

such complexes at the solid–liquid interface causes a further decrease of the solid surface charge in relation to the suspensions containing only single DCF and PAA substances (Figs. 1, 2, 3, 4). Taking into account the type of heavy metal ions, it should be noted that their influence is minimal in the diclofenac containing systems, but for the poly(acrylic acid) containing suspensions, lead(II) ions have a greater effect on the decrease of σ_0 values [Fig. 1b)].

The changes of zeta potential of solid particles in the presence of metal–DCF and metal–PAA complexes are more complicated, and for most systems, an increase in the zeta potential values is observed compared to the suspensions containing only an organic compound (Figs. 5,

Fig. 8 Dependencies of the zeta potential as a function of solution pH obtained for the Na-P1(C) composite without and with inorganic/organic substances



6, 7, 8). Such behaviour can be a result of domination contribution of accumulation of metal cations bound with the adsorbed drug or polymer molecules in the slipping plane area. Moreover, the adsorption of such complexes causes replacement of supporting electrolyte ions and free metal cations from the surface layer towards the bulk solution, changing the ionic composition of the boundary area of compact (stiff) and movable (diffusion) parts of the

electrical double layer. Additionally, more coiled conformation of PAA chains in the form of intramolecular complexes with the metal cations adsorbed on the solid surface leads to smaller shift of the slipping plane in comparison to the suspensions containing the polymer alone.

The structure of the electrical double layer in the presence of the examined adsorbates and mechanisms of their binding are schematically presented in Fig. 9.

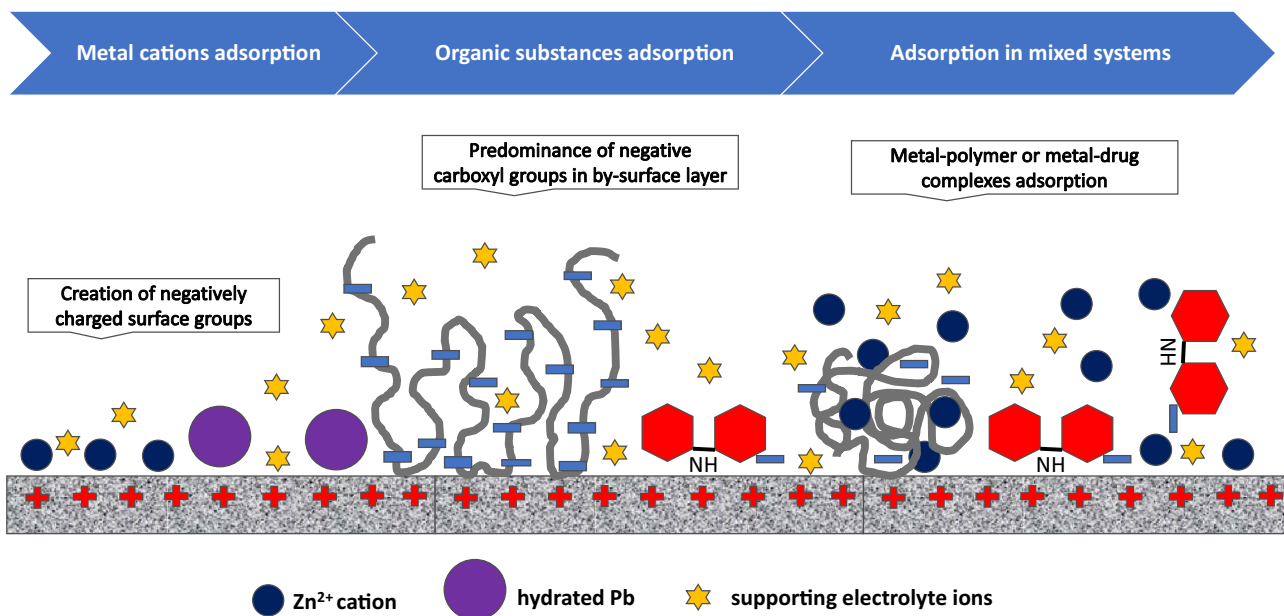


Fig. 9 Schematic representation of the structure of the electrical double layer in the presence of examined adsorbates and mechanisms of their binding

Conclusions

The obtained results show that the structure and composition of the electrical double layer can be successfully characterized by the parameters such as: solid surface charge density, zeta potential, point of zero charge, and isoelectric point. The analysis of these parameters gives important information about the specific location of both simple inorganic ions and more complex organic molecules in particular parts of edl. The structure of the adsorption layer formed on the synthetic zeolites and their carbon composites surfaces changes considerably after the organic substances addition [especially poly(acrylic acid)]. In the mixed adsorbate systems containing diclofenac or the polymer and lead(II) or zinc(II) cations, these changes are the greatest. Adsorption of formed metal–organic substance complexes results in a decrease of the surface charge density and an increase of the zeta potential of solid particles. This indicates that complexes binding with the solid surface result in replacement of the supporting electrolyte ions and free metal cations from the surface area towards the diffusion area of edl, at the same time causing accumulation of negatively charged adsorbate functional groups in the by-surface layer.

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Data availability Data are contained within the article.

Declarations

Conflict of interest On behalf of all authors, I state that there is no conflict of interest.

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