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Effective adsorption of metals on porphyrins: Experiments and advanced isotherms modeling



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KEYWORDS

Microbalance apparatus (QCM); Piezoelectric sensor; Metalloporphyrins adsorption isotherms; Statistical physics theory; Physicochemical investigation; Configurational entropy; Free enthalpy Abstract In this article, the investigation of the adsorption process of six metal compounds (aluminum chloride, aluminum sulfate, iron chloride, iron sulfate, indium chloride and indium sulfate) on the promising macromolecule named porphyrin was performed to prove new insights about the metals-porphyrin complexes. The experimental adsorption data of the six complexation systems were controlled at four reaction temperatures using the well-known microbalance apparatus (QCM). In fact, the experimental outcomes and the physical modeling treatment indicated that the complexation process of aluminium and iron should be analyzed via the mono-layer adsorption model whereas; the interaction between the two indium compounds and the porphyrin was described via the double-layer model. Actually, the physicochemical description showed that the three metals were adsorbed via a multi-docking mechanism. The fitted values of the paramount parameter density of the adsorbent sites showed the endothermic character of the studied processes. Thus, some porphyrin sites were activated only at high temperature. The down trend of the iron isotherms was explained through the van der Waals parameters which describe the lateral interactions influences. The calculation of the adsorption energies which describe the interactions between the adsorbates and the adsorbent showed that chemical bonds were carried out between the aluminum and the porphyrin. The thermodynamic study, through the two thermodynamic functions (the configurational entropy and the free enthalpy), showed that the disorder of the six processes is maximum at the level of the energetic parameters and that the six complexation mechanisms advanced spontaneously towards saturation. For the iron, the behavior of the enthalpy indicated

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1878-5352 © 2021 The Author(s). Published by Elsevier B.V. on behalf of King Saud University. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/). that the lateral interactions between the adsorbates disfavored the adsorption of iron chloride and iron sulfate at high concentration. The double-layer process of the indium was confirmed by the trends of the free enthalpies which showed two stability states for the two indium compounds.

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1. Introduction

In recent years, the macrocyclic compounds namely porphyrins played an important role in vital biological processes involved in the metabolism of living organisms such as the oxygen transport process and the photosynthesis mechanism (Ogoshi and Mizutani, 1998; Gross and Ini, 1997; Mansuy, 1993). This is due to the possibility of complexing these chemical compounds by different metals which permits the preparation of various metalloporphyrins complexes (Fuchs et al., 2000; Jasat and Dolphin, 1997; Drummond and Kappas, 1981). Thus, the macrocyclic complexes are known as pigment of life because the complexes of porphyrins with iron and magnesium appear in the hemoglobin and the chlorophyll structures (Liao and Scheiner, 2002).

Furthermore, the complexed metals favor the photodynamic activity and the sensing properties of porphyrins (Carnieri et al., 1982; Moro et al., 2011; Sayyad et al., 2010; Di Natale et al., 1998; Kadish et al., 2003). For example, metalloporphyrins were exploited as potential ionophores in ion selective sensors (Carnieri et al., 1982) and they contributed in both potentiometric and optical anion sensors such as the complexes of porphyrins with manganese and aluminum (Badr and Meyerhoff, 2005; Smith, 1975). The photosensitizing properties of cobalt-porphyrin complex have been also demonstrated to be useful in the photodynamic therapy (Fuchs et al., 2000). The increasing interest in these chemical complexes led to test the complexes of porphyrins with aluminium and indium in various potential areas such as the polymerisation reactions, the stereochemistry, the supramolecular building blocks and the molecular recognition field (Saha et al., 2019; Du et al., 2018; Stulz et al., 2003; Guo et al., 2019; Kumar and Maiya, 2003; Oin et al., 2015; Ojima, 2000). Previous research papers demonstrated also that the applicability of porphyrin-based metals could be extended to the enzymatic biosensors, the biofuel cells and other bioelectronics and organic electronics based devices (Ramanavicius and Ramanavicienne, 2009).

All these interesting applications of metalloporphyrins led researches to investigate the synthesis process of these complexes by different experimental methods (e.g. adsorption into polymer matrices, entrapment in porous metal oxides and chemical binding to polymer beads) (Hong and Mallouk, 1991; Cho et al., 2005).

Importantly, recent papers have been focused on the coating of electrodes with active polymers. These electrodes based polymers have been prepared either by applying preformed polymer or by spin coating directly on the electrode surface and they have been demonstrated to be useful in wide scope of applications (biosensors, molecular electronics and electrocatalysis...) (Hotchandani and Kamat, 1992; Ballarin et al., 1998). Interestingly, potential interest has been devoted to gold electrode based porphyrins film (Sayyad et al., 2010). In this direction, the quartz-crystal-microbalance (QCM) technique was chosen by our research team to control the complexion process of porphyrins by different metals and the spin coating method was adopted for the immobilization of porphyrins on the quartz crystal electrode. Then, the microbalance apparatus was used to control the complexed mass of the metal on the functionalized crystal for each concentration, leading to plot the isotherms curves at various reaction temperatures (Wang et al., 2005).

In fact, this article proposes the QCM technique for the study of the complexation process of 5,10,15,20-tetrakis(4-me thylphenyl) porphyrin with three metals (aluminum, iron and indium) (Fig. 1). These three complexes were selected because of their interesting fields of application and because they were not previously investigated and interpreted with a deep manner. The study of the complexation mechanism by means of the QCM setup requires the analysis of the adsorption of some compounds of these metals on porphyrin surface. Indeed, the adsorption isotherms of aluminum chloride, aluminum sulfate, iron chloride, iron sulfate, indium chloride and indium sulfate on the quartz sensor coated with the macromolecule should be carried out at various reaction temperatures.

In the literature, the analytical interpretation of adsorption isotherms could be performed via the empirical equations like the Freundlich model or the well-known Langmuir equation (Langmuir, 1918; Freundlich, 1906). These models were



Fig. 1 Chemical structure of the complexes of the 5,10,15,20-tetrakis(4-methylphenyl) porphyrin with the three metals (aluminum, iron and indium).

adopted for the examination of various adsorption problems but, they did not result in satisfying steric or energetic interpretations (Langmuir, 1918; Freundlich, 1906; Brunauer et al., 1940; Hill et al., 2010). Recently, the development of descriptive models has been improved by introducing the assumptions of the statistical physics theory, leading to the establishment of advanced models equations (Ben Yahia et al., 2016; Knani et al., 2020). The contribution of the physicochemical variables of the advanced models in both steric and energetic analysis of the adsorption phenomenon gave an interesting description of an activated surface at the ionic scale. This requires the selection of the appropriate model, being the best for the fit of experimental adsorption data.

In summary, the suggested objectives and the methodology of this paper are arranged as follows: the checking of the performance of the tetrakis(4-methylphenyl) porphyrin, acting as sensor of the three metals, is performed through the application of the QCM strategy for the achievement of experimental adsorption isotherms. The development of a theoretical description of the experimental results is carried out through the statistical physics treatment. The selection of the adequate descriptive models is established by numerical simulation. The interpretations of the steric and the energetic behaviors of the complexation mechanisms at the ionic level are performed through the parameters given by the adopted models. The estimation of the nature of bonds between the macromolecule and the three metals can be carried out based on the calculation of the adsorption energies of each system and finally, based on the statistical physics models, the macroscopic discussion around the adsorption of the three ions is evaluated through the thermodynamic study of the six complexation systems (Ben Yahia and Ben Yahia, 2020).

2. Experimental method for adsorption measurements

2.1. Piezoelectric sensor preparation

The QCM apparatus is an advanced technique of mass measurement at the nanogram scale which is based on the quartz inherent property of piezoelectricity (Buck et al., 2004; O'Sullivan and Guilbault, 1999; Sauerbrey, 1959; Bradshaw, 2000). The AT-cut of quartz, used in these experiments, is one of the favorable cut giving satisfying properties of stability. Generally, the typical quartz crystal sensor has a resonant frequency on the order of MHz. The standard frequency (f_0) of 5 MHz, which is used in this work, has a corresponding thickness of the crystal of 330 µm. The disc, having about 2.54 cm in diameter, is polished and covered with a gold layer. The gold layer area is about 1.37 cm^2 of the upper electrode and 0.4 cm² of the lower electrode (O'Sullivan and Guilbault, 1999). The quartz discs were cleaned with hydrogen peroxide and sulfuric acid at room temperature. Then, they were rinsed with deionized water and ethanol. The drying of the crystals was performed with high purity nitrogen to remove any remaining water. After that, the functionalization of the gold electrode of the quartz was carried out by spin coating 40 µL of the 5,10,15,20-tetrakis(4-methylphenyl) porphyrin (2.9 10^{-2} mol.L⁻¹) onto the crystal surface at 3000 rpm for 30 s. The adsorption cell (porphyrin coated on quartz crystal) was dried at 100 °C for 2 h.

2.2. Sauerbrey model application

The theory of the QCMs, relating a frequency change of the oscillating piezoelectric crystal to the mass change on the electrodes of the crystal, has been developed by Sauerbrey in 1959 (Sauerbrey, 1959). In recent years, the interest on the QCMs has been increased since the potential application of the quartz sensor has been expanded to the liquid environments (Nomura and Minemura, 1980; Konash and Bastiaans, 1980; Lu and Czanderna, 1984).

Then, the application of the Sauerbrey model in liquid mediums requires quantifying the variation of the oscillation frequency of quartz according to the different parameters influencing the piezoelectric crystal in liquid phase. In this case, the total resonant frequency expression of the sensor should be written according to five parameters (Hong and Mallouk, 1991; Kanazawa and Gordon, 1985; Urbakh and Daikhin, 1994; Huang et al., 2000):

$$\Delta f = \Delta f_T + \Delta f_r + \Delta f_{\eta,\rho} + \Delta f_m + \Delta f_p \tag{1}$$

In this relation, Δf_T is the frequency variation related to the temperature influence which can be neglected because the experiments are performed at constant temperature. The frequency variation Δf_r related to the roughness effect can be also neglected because the piezoelectric sensor is a polished crystal. The variation of the viscosity and the density of the solution are described by $\Delta f_{\eta,\rho}$ which are not taken into account because low impacts of the solution properties were noted during the experimental measurements (Hong and Mallouk, 1991; Kanazawa and Gordon, 1985; Huang et al., 2000). Therefore, the oscillation frequency of quartz should include only the variation of mass impact Δf_m and the pressure influence Δf_p , it can be written as follows:

$$\Delta f = \Delta f_m + \Delta f_p \tag{2}$$

However, the present investigation focused on the interactions between the metals and the adsorbent porphyrin. Then, the variation of the sensor frequency should be only due to the variation of mass on the sensor surface Δf_m without the intervention of the pressure influence Δf_p . This was taken into account in the experimental measurements in the next section.

2.3. Experimental measurements of the adsorbed quantities of metals

The experimental QCM setup presents the sensor crystal based porphyrin film (adsorption cell) which is placed in a Teflon probe and immersed in a reactor filled with a volume V_s of pure water (V_s = 100 mL). The adsorption cell was connected to the frequency-meter monitor (microbalance apparatus 'Maxtek PM 700') via a coaxial cable. The experimental measurement should be started after the stabilization of the sensor resonant frequency in the reactor. This frequency change is due to the hydrostatic pressure impact on the adsorption cell (Δf_p) and it was eliminated from the total frequency variation Δf in order to only consider the frequency change of the mass variation on the adsorbing surface ($\Delta f = \Delta f_m$).

Then, a micropipette was used to inject volumes of the adsorbates solutions of the metals (aluminum chloride/

aluminum sulfate/ iron chloride/ iron sulfate/ indium chloride/ indium sulfate) in the bain-marie. The injected adsorbates volumes were calculated through the law of matter conservation depending on the initial concentration of the prepared adsorbate solution c_0 and the final adsorbate concentration in the reactor c_f :

$$V_{ad} = \frac{c_f \times V_s}{c_0} \tag{3}$$

After each injection, the frequency-meter monitor showed the sensor resonant frequency (Δf_m) corresponding to the mass variation (Δm) of the metal on the adsorption cell. Note also that during an isotherm measurement, the added volumes did not exceed 2 mL which is negligible compared to the $V_s = 100$ mL contained in the reactor. Therefore, there is no significant influence of the volumes addition on the quartz sensor.

The complexed quantities of each metal on the sensor crystal based porphyrin was calculated based on the relation of Sauerbrey which includes the sensitivity factor of the crystal C (Hz.cm². μ g⁻¹) according to the next expression (Sauerbrey, 1959; Tsionsky and Gileadi, 1994):

$$\Delta f_m = -C \times \Delta m \tag{4}$$

Finally, the experimental data describing the adsorption of the six metals adsorbates on the tetrakis(4-methylphenyl) porphyrin were obtained at four temperatures (300–330 K) and the six adsorption systems were illustrated in Fig. 2.

2.4. Experimental results and discussion

The experimental adsorption measurements indicated the following observations:

It can be seen that the tetrakis (4-methylphenyl) porphyrin was acted as complexing sensor of the three metals but with different manner either in terms of quantity or in terms of isotherm behavior.

Concerning the quantitative manner, one can see the following order of the maximum adsorbed quantity for each adsorbate (T = 330 K): Q_a (AlCl₃) = 520.2 µg/cm² > Q_a (Al₂(SO₄)₃) = 455.3 µg/cm² > Q_a (FeCl₃) = 401.7 µg/cm² > Q_a (Fe₂ (SO₄)₃) = 359.8 µg/cm² > Q_a (InCl₃) = 309.6 µg/c m² > Q_a (In₂(SO₄)₃) = 253.7 µg/cm². The highest adsorbed amounts are shown for the two adsorbates of aluminum therefore, the aluminum-porphyrin complex is the best in terms of retained quantity.

Concerning the different behavior of isotherms curves, one can conclude that the nature of the metal is the dominant factor in the complexation mechanism. The compounds of aluminum and iron (aluminum chloride, aluminum sulfate, iron chloride, and iron sulfate) showed one saturation level for all the isotherms plots. The saturation state is reached when all the poprhyrinic sites are occupied by the metals ions leading to the formation of one adsorbed metal layer without the participation of the anionic ions (Cl^- or SO_4^{2-}) in the adsorption mechanism. The difference between the two mono-layer adsorptions of aluminum and iron can be seen at high adsorbate concentration. The stability of the saturation state of aluminum can be the result of the strong aluminum-porphyrins interaction so there is no possibility of an inverse phenomenon by cutting this bond. On contrary, the down trend of the isotherms of the two iron compounds at high concentration can be the result of the instability of the formed bond between iron and porphyrin. In fact, a desorption process took place at the saturation level and the lateral interactions between the ions have the major role of the instability of the formed ironporphyrin complex. The adsorption curves of the two indium compounds (indium chloride and indium sulfate) showed two saturation states corresponding to two formed adsorbed layers. So, the adsorption of indium was performed via the layer by layer process based on charge neutralization between materials having complementary charge signs (anions and cations) (Lvov et al., 1995; Ben Yahia et al., 2017). The two layers are formed one after the other with different energy. In fact the porphyrin can function as a sensor for the cationic metal In^{3+} which leads to the formation of the first layer. Now, if the second adsorbed layer is formed by indium ions, there will be an electrostatic repulsion between the two adsorbed layers. The role of the anionic ions (Cl⁻ or SO_4^{2-}) is to resolve this electrostatic problem in the multilayer ionic adsorption process. In this case, the formation of the two adsorbed lavers is achieved based on the laver by laver approach: first, the sensor surface acts as a template, and after the adsorption of cationic ions, it is refunctionalized and acts as a new template for the following adsorption of anionic ions (Lvov et al., 1995; Ben Yahia et al., 2017).

In what follows, these experimental observations need a deep analysis via the theoretical investigation based on the advanced statistical physics modeling.

3. Statistical physics theory: Advanced modeling and physicochemical interpretation

Theoretically, the description of isotherms by means of the classical equations of adsorption models did not give deep microscopic and macroscopic interpretations of the adsorption problem. For example, they were limited to the empirical description of a mono-layer mechanism of adsorption for all the experimental condition like the Langmuir model (Langmuir, 1918). This classical model can give wrong interpretations of a multi-layer process of adsorption like the case of indium in this work. Other models were not favorable for the investigation of the influences of some operating parameters on adsorption such as the temperature effect (Freundlich, 1906; Brunauer et al., 1940; Hill et al., 2010). On contrary, the advanced equations established based on the statistical physics assumptions introduced into their expressions some physical variables providing interesting interpretations, involving the estimation of the number of the formed layers and the influence of the reaction temperature on adsorption, for a defined adsorbate-adsorbent system.

According to the measured isotherms of the metalsporphyrin systems, the adsorption of aluminium and iron requires a model describing a mono-layer process and the adsorption of the two indium compounds should be performed via a layer by layer model describing a double-layer process.

On the basis of the statistical physics theory, the modeling of isotherms curves consists of establishing the advanced models by taking account of some assumptions then, choosing the adequate one for the isotherm description via its physical parameters (Ben Yahia and Ben Yahia, 2020; Ben Yahia et al., 2017). aluminum chloride-porphyrin

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T=300K

T=310K

T=320K

T=330K

550

500

450

400

350

300

250

200

150





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Experimental adsorption isotherms aluminum chloride, aluminum sulfate, iron chloride, iron sulfate, indium chloride and indium Fig. 2 sulfate on 5,10,15,20-tetrakis(4-methylphenyl) porphyrin given at four temperatures (300-330 K).

3.1. Methodology of adsorption models development

The first assumption of the statistical physics formalism is to consider the equilibrium between the free phase of adsorbate (A) which should be adsorbed by the surface of porphyrin sites (S) and the adsorbed phase of the formed complexes (A_n-S). The equilibrium adsorption equation involves the stochiometric variable n, representing the number of metals captured by one receptor site (Ben Yahia et al., 2017; Ben Yahia and Ben Yahia, 2020; Sellaoui et al., 2018; Ben Yahia et al., 2021):

This equilibrium between the adsorbates reservoir and the adsorbed phase of the resulting complexes should be studied in the grand-canonical situation (Ben Yahia and Ben Yahia, 2020; Sellaoui et al., 2018). Thus, the general partition function of this situation (z_{gc}) is expressed as follows:

$$z_{\rm gc} = \sum_{N_i} e^{-\beta(-E_i - \mu)N_i} \tag{6}$$

This general expression involves the parameter energy $(-E_i)$ and the chemical potential (μ). These parameters should be correctly introduced in the partition function in order to get the right expression of adsorbed quantity of the developed model.

The introduction of the energy in the models development is easy: we should consider one energy level for a mono-layer process and two energies for a double-layer mechanism.

Both mono-layer and double-layer processes can be established by introducing the chemical potential of ideal gas μ_p or the chemical potential of real gas μ_r . The first one considers that the mutual interactions between the adsorbates should be neglected (Ben Yahia et al., 2021; Diu et al., 1989; Ben Lamine and Bouazra, 1997) whereas, the second one involves a description of the lateral interactions in its expression via the parameter cohesion pressure a and the parameter covolume b. The expressions of μ_p (Ben Yahia et al., 2021; Diu et al., 1989; Ben Lamine and Bouazra, 1997) and μ_r (Ben Yahia and Ben Yahia, 2020; Ben Yahia et al., 2021) are given below:

$$\mu_p = \frac{1}{\beta} \ln\left(\frac{N}{z_{Tr}}\right) \tag{7}$$

with, N being the number of adsorbates.

$$\mu_r = \mu_p + \frac{1}{\beta} \ln \frac{1}{1 - bc} + \frac{1}{\beta} \frac{bc}{1 - bc} - 2ac$$
(8)

with, c being the adsorbate concentration.

For each model, the average occupation number (N_0) of a number P_M of identical sites of porphyrins should be calculated with the following formula (Ben Yahia et al., 2021; Ben Lamine and Bouazra, 1997):

$$N_{o} = \frac{P_{M}}{\beta} \frac{\partial \ln(z_{gc})}{\partial \mu}$$
(9)

The advanced expressions of the complexed amount (Q_a) of the two mono-layer models and the two double-layer models should be calculated from the product of the coefficient n and the average occupation quantity N₀ corresponding to each model (Ben Yahia et al., 2017; Ben Yahia and Ben Yahia, 2020; Sellaoui et al., 2018; Ben Yahia et al., 2021; Diu et al., 1989; Ben Lamine and Bouazra, 1997):

$$Q_a = n \times N_0 \tag{10}$$

Table 1 summarized the development of the four advanced adsorption models.

3.2. Selection of appropriate models for the isotherms description

The selection of the appropriate fitting model was carried out through numerical program which is based on the mathematical fitting method of the Levenberg-Marquardt iterating algorithm using a multivariable non-linear regression program (Bouzid et al., 2018). The best descriptive model is the one which shows the minimum gap between the experimental values and the theoretical estimations. This gap should be minimized to a level of confidence of 95% to indicate the best fitting result (Ben Yahia et al., 2021; Prola et al., 2013).

The numerical simulation of experimental data with the four advanced models was discussed via three errors coefficients of adjustment (Ben Yahia et al., 2017): the first one is the well-known determination coefficient R^2 which shows the best fitting result when its value is close to the unit (Prola et al., 2013; Marquardt, 1963). The second common error coefficient of adjustment is the AIC (Akaike Information Criterion) coefficient which indicates the best result for the fitting model having the lowest value of AIC (Ben Yahia et al., 2017). The Third one is the non-standardized RMSE error coefficient called (residual root mean square error) which indicates the best fitting model when its value is inferior to 2 (Marquardt, 1963; Kapoor and Yang, 1989).

Table 1 Analytical expressions of the grand-canonical partition function (z_{gc}) and the adsorbed quantity (Q_a) corresponding to the two mono-layer models of ideal gas and real gas and the two double-layers models of ideal gas and real gas.

Adsorption model	Ideal gas approach (μ_p (Eq. (7)))	Real gas approach (μ_r (Eq. (8)))
Mono-layer model	$z_{gc} = 1 + e^{\beta(E+\mu_p)}$	$z_{gc} = 1 + e^{\beta(E + \mu_r)}$
	$Q_a = \frac{nP_M}{1 + \left(\frac{c_{1/2}}{c}\right)^n}$	$Q_a = \frac{nP_M}{1 + \left(w_{1/2} - \frac{b_c}{c} e^{\beta a c_e} e^{-\frac{b_c}{1 - bc}}\right)^n}$
	Where $c1/2$ is:	Where $w1/2$ is:
	$c_{1/2} = Se^{-\frac{E_{1/2}}{k_B T}}$	$w_{1/2} = Se^{-\frac{E_{1/2}}{k_BT}}$
	S: adsorbate solubility	S: adsorbate solubility
Double-layer	$z_{gc} = 1 + e^{\beta(E_1 + \mu_p)} + e^{\beta(E_1 + E_2 + 2\mu_p)}$	$\left(\frac{c}{\left(\frac{c}{1-bc}\right)^n+2(\frac{c}{1-bc}\right)^n+2(\frac{c}{1-bc})^{2n}}\right)^{2n}$
model	$Q_a = n P_M \frac{\left(\frac{c}{c_1}\right)^n + 2\left(\frac{c}{c_2}\right)^{2n}}{1 + \left(\frac{c}{c_1}\right)^n + \left(\frac{c}{c_2}\right)^{2n}}$	$z_{gc} = 1 + e^{\rho(2_1 + \mu_r)} + e^{\rho(2_1 + \mu_r)} Q_a = n P_M \frac{\frac{1}{1 + (\frac{c}{m_1 - bc})}}{\frac{1}{m_1(1-bc)} e^{2\beta a_c} \frac{b_c}{1-bc}} \frac{e}{w_2(1-bc)} \frac{e^{-bc}}{w_2(1-bc)}}$ Where wi
	Where c1 and c2 are:	and w2 are:
	$c_{1,2} = Se^{-\frac{E_{1,2}}{k_B T}}$	$w_{1,2} = Se^{-\frac{s_{1,2}}{k_B T}}$
	S: adsorbate solubility	S: adsorbate solubility

Table 2 Values of the correlation coefficient \mathbb{R}^2 , the residual root mean square coefficient **RMSE** and the Akaike information criterion **AIC** deduced from fitting the experimental adsorption isotherms of AlCl₃ and Al₂(SO₄)₃ on 5,10,15,20-tetrakis(4-methylphenyl) porphyrin with the four advanced models.

Adsorption system		aluminum c	hloride-porph	ıyrin		aluminum sulfate-porphyrin			
Temperature (K)		300	310	320	330	300	310	320	330
Mono-layer model (ideal gas)	R ² RMSE	$0.98 \\ (\pm 0.009) \\ 1.23 \\ (\pm 0.1) \\ 1.25 \\ (\pm 0.1) \\ 1.$	$\begin{array}{c} 0.99 \\ (\pm 0.008) \\ 1.44 \\ (\pm 0.5) \end{array}$	$\begin{array}{c} 0.98 \\ (\pm 0.007) \\ 1.56 \\ (\pm 0.3) \end{array}$	$\begin{array}{c} 0.97 \\ (\pm 0.008) \\ 1.57 \\ (\pm 0.2) \end{array}$	$\begin{array}{c} 0.99 \\ (\pm 0.006) \\ 1.51 \\ (\pm 0.4) \end{array}$	$\begin{array}{c} 0.99 \\ (\pm 0.008) \\ 1.66 \\ (\pm 0.2) \end{array}$	$\begin{array}{c} 0.98 \\ (\pm 0.009) \\ 1.02 \\ (\pm 0.4) \end{array}$	0.97 (±0.007) 1.4 (±0.1)
	AIC	(± 1.9)	$16.2 (\pm 1.2)$	(± 1.5)	(± 0.9)	(± 1.8)	16.4 (±0.8)	(± 1.1)	16.26 (±2.4)
Mono-layer model (real gas)	R ² RMSE	0.90 (±0.01) 2.87 (±0.2)	0.89 (±0.03) 3.01 (±0.99)	0.88 (±0.05) 2.99 (±0.18)	0.91 (±0.01) 3.15 (±0.2)	0.89 (±0.03) 3.01 (±0.8)	0.87 (±0.02) 3.99 (±0.3)	0.88 (±0.01) 3.5 (±0.7)	0.89 (±0.01) 3.64 (±0.87)
	AIC	19.17 (±2. 3)	20.3 (± 1.9)	20.7 (±2. 5)	21.4 (±1. 8)	20.7 (± 2 . 3)	21.5 (±2. 5)	21.5 (±1. 69)	20.99 (±2. 01)
Double-layer model (ideal gas)	R ² RMSE	0.85 (±0.04) 3.99	0.84 (±0.02) 3.45	0.83 (±0.02) 3.79	0.84 (±0.03) 4.01	0.81 (±0.02) 5.2	0.84 (±0.05) 5.33	0.83 (±0.03) 6.7 (±0.1)	0.79 (±0.04) 6.2 (±0.3)
	AIC	(± 0.3) 23.5 (± 1.7)	(± 0.04) 24.7 (± 2.01)	(± 0.7) 25.3 (± 1.3)	(± 0.02) 24.9 (± 2.2)	(± 0.89) 24.6 (± 1.5)	(± 0.05) 23.98 (± 1.8)	24.79 (±2.05)	25.4 (±2.4)
Double-layer model (real gas)	R ² RMSE	0.82 (±0.06) 4.55 (±0.09)	0.78 (±0.09) 3.89 (±0.12)	0.78 (±0.04) 4.23 (±0.5)	0.81 (±0.03) 5.2 (±0.4)	0.81 (±0.05) 7.1 (±1.2)	0.81 (±0.03) 7.9 (+2.08)	0.76 (±0.09) 6.98 (±1.79)	$\begin{array}{c} 0.77 \\ (\pm 0.03) \\ 7.21 \ (\pm 2.4) \end{array}$
	AIC	25.6 (±1.8)	(± 0.12) 26.7 (± 2.9)	(± 0.3) 28.4 (± 1.3)	25.4 (±1.7)	26.7 (±1.54)	27.46 (±2.49)	(± 1.75) 28.9 (± 3.7)	27.84 (±3.2)

The values of errors fitting coefficients are indicated in Tables 2, 3 and 4.

Based on Table 2, the mono-layer model of ideal gas should be applied for the description of the isotherms of aluminum chloride and aluminum sulfate since it shows the best fitting criterion (\mathbb{R}^2 is close the unit, RMSE is inferior to 2 and AIC shows the lowest values comparing to the other fitting models). For the isotherms of iron chloride and iron sulfate, the best values of fitting coefficients are obtained for the adjustment with the mono-layer model of real gas (Table 3) thus, it is confirmed that the lateral interactions between the adsorbates are the main cause of the isotherms drop at saturation. Based on the selection criteria, the double-layer model of ideal gas is confirmed to be the best one for the description of the isotherms of indium chloride and indium sulfate (Table 4). Then, a layer by layer process took place between the metallic cations (\ln^{3+}) and the anions (Cl^-/SO_4^{2-}).

A direct comparison of experimental isotherms (T = 330 K) and the theoretical simulations with the adequate model are presented in Fig. 3: The experimental data of aluminum are fitted with the mono-layer model of ideal gas, the fit of adsorption isotherms of iron is performed with the mono-layer model of real gas and the fit of experimental data of indium is carried out with the double-layer model of ideal gas.

The microscopic investigation of the six complexation processes is developed in the following section based on the fitting values of the adopted models parameters.

3.3. Physicochemical discussion of the models' parameters

According to Table1, the three models which are selected for the description of isotherms curves involve in their expressions common steric parameters (the number of metal per porphyrin site n and the number of occupied adsorbent sites P_M) and energetic variables ($c_{1/2}$ for aluminum, $w_{1/2}$ for iron and c_1 and c_2 for indium). The lateral interactions variables (cohesion pressure a and covolume b) are only involved in the description of iron adsorption.

The parameters values of the six adsorption systems are reported in Tables 5 and 6.

i. Stereic parameters n and P_M

The performance of the six systems in terms of quantity can be compared via the steric parameters (Aouaini et al., 2014). It can be noted from Tables 5 and 6 (T = 330 K) that:

 $\begin{array}{l} n \ (AlCl_3) = \ 1.05 > n \ (Al_2(SO_4)_3) = \ 0.94 > n \ (FeCl_3) = \ 0.90 \\ > \ n \ (Fe_2 \ (SO_4)_3) = \ 0.84 > n \ (InCl_3) = \ 0.78 > n \\ (In_2(SO_4)_3) = \ 0.73 \end{array}$

 P_M (AlCl₃) = 510.7 µg/cm² > P_M (Al₂(SO₄)₃) = 421.4 µg/cm² > P_M (FeCl₃) = 389.8 µg/cm² > P_M (Fe₂ (SO₄)₃) = 3 55.2 µg/cm² > P_M (InCl₃) = 320.5 µg/cm² > P_M (In₂(SO₄)₃) = 279.4 µg/cm²

The steric comparison of the fitted values of the number of metal per porphyrin site n and the number of occupied adsorbent sites P_M confirms that the complexed quantity of

Table 3 Values of the correlation coefficient \mathbb{R}^2 , the residual root mean square coefficient **RMSE** and the Akaike information criterion **AIC** deduced from the numerical adjustment of experimental isotherms of FeCl₃ and Fe₂(SO₄)₃ on 5,10,15,20-tetrakis(4-methylphenyl) porphyrin with the four statistical physics models.

Adsorption system		Iron chlori	de-porphyrin			Iron sulfate-porphyrin			
Temperature (K)		300	310	320	330	300	310	320	330
Mono-layer model (ideal gas)	R ²	0.84 (±0.01)	0.82 (±0.04)	0.82 (±0.05)	0.84 (±0.01)	0.81 (±0.03)	0.77 (±0.09)	0.82 (±0.02)	0.83 (±0.01)
	RMSE	5.33 (±0.12)	5.44 (±0.87)	4.5 (±0.16)	5.7 (±0.93)	6.66 (±0.69)	7.3 (±0.92)	6.91 (±0.81)	7.45 (±0.89)
	AIC	28.57 (±3.04)	28.6 (±2.7)	28.3 (±3.11)	28.6 (±3.5)	29.1 (±3.7)	31.6 (±4.16)	30.67 (±4.2)	29.42 (±3.67)
Mono-layer model (real gas)	\mathbb{R}^2	$0.98 (\pm 0.002)$	0.97 (±0.004)	0.99 (±0.007)	0.97 (±0.006)	0.99 (±0.005)	0.97 (±0.009)	0.98 (±0.007)	0.98 (±0.004)
	RMSE	1.11 (±0.5)	1.23 (±0.2)	1.34 (±0.4)	1.28 (±0.5)	1.66 (±0.1)	1.78 (±0.09)	1.22 (±0.5)	1.45 (±0.2)
	AIC	20.17 (±0.94)	21.5 (±0.8)	20.81 (±1.04)	21.6 (±0.83)	19.4 (±1.52)	20.7 (±1.51)	19.47 (±1.34)	19.67 (±1.74)
Double-layer model (ideal gas)	\mathbb{R}^2	0.81 (±0.04)	$0.81 (\pm 0.01)$	0.83 (±0.02)	0.79 (±0.04)	0.81 (±0.02)	$0.82 (\pm 0.03)$	0.78 (±0.05)	0.82 (±0.01)
	RMSE	4.87 (±0.5)	3.65 (±0.22)	3.89 (±0.25)	3.21 (±0.19)	4.8 (±0.55)	3.29 (±0.12)	5.21 (±0.43)	4.95 (±0.5)
	AIC	24.8 (±1.07)	23.4 (±0.57)	25.41 (±0.79)	24.82 (±0.37)	26.6 (±1.99)	26.8 (±1.39)	27.91 (±2.7)	26.3 (±1.64)
Double-layer model (real gas)	\mathbb{R}^2	0.79 (±0.05)	0.83 (±0.04)	0.78 (±0.09)	0.82 (±0.05)	0.84 (±0.04)	0.85 (±0.02)	0.79 (±0.04)	0.8 (±0.05)
	RMSE	5.45 (±1.2)	4.81 (±1.09)	4.73 (±0.51)	5.32 (±0.08)	5.9 (±1.64)	4.89 (±0.36)	6.02 (±1.9)	5.82 (±1.88)
	AIC	27.4 (±2.46)	26.3 (±1.97)	26.64 (±2.06)	27.84 (±2.33)	28.7 (±2.7)	29.31 (±3.26)	28.5 (±3.5)	27.28 (±3.07)

aluminum by the porphyrinic surface is the best in terms of quantity compared to the other metals.

Furthermore, it is noticed that all the adsorption systems show values of n inferior to the unit, demonstrating that the complexation of the three ions took place via a multi-docking (multi-interaction) mechanism (Sellaoui et al., 2018). From the order of the values of P_M ; it is concluded that there is a fast insertion of the aluminum and iron in the porphyrins sites because there is only formation of one layer without the contribution of anionic ions. On contrary, the participation of the anionic ions (Cl^{-}/SO_4^{2-}) in the iron adsorption disfavors the complexation of porphyrin by the indium ions because of the interaction between the two adsorbed layers.

ii. Lateral interactions: Parameters a and b

The real gas model, devoted for the investigation of the adsorption of the two compounds of iron, provides a description of the lateral interactions between the adsorbates by means of the parameter a and the parameter b (Yahia et al., 2019). The first variable describes the adsorbate-adsorbate interaction which disfavors the metal complexation then, the iron compound presenting the lowest value of a is the best for the iron-porphyrin achievement. On contrary, the second variable indicates the best iron compound having the highest value of b because in this case the adsorbate-adsorbate interaction is weak which favors the iron complexation.

Tables 5 and 6 show that:

 $a(FeCl_3) = 5.2 \times 10^{-9} \text{ J.mL/mol} < a(Fe_2(SO_4)_3) = 7.13 \times 10^{-9} \text{ J.mL/mol}$

 $b(FeCl_3) = 5.9 \times 10^{-12} \text{ mL/mol} > b(Fe_2(SO_4)_3) = 4.4 \times 10^{-12} \text{ mL/mol}$

It can be concluded that the adsorbate-adsorbate interactions are the lowest for iron chloride because it presents the lowest cohesion pressure and the highest covolume. Therefore, the iron chloride-porphyrin system is more stable than the iron sulfate-porphyrin system. It can be also noticed that during the complexation process, the adsorbates compounds involving chloride ions in their chemical structures guarantees more stability of the formed complexes than the adsorbates compounds of sulfate.

iii. Energetic parameters $c_{1/2},\,w_{1/2},\,c_1$ and c_2

Using the fitted values of the energetic parameters ($c_{1/2}$ for aluminum, $w_{1/2}$ for iron and c_1 and c_2 for indium), the adsorption energies of each system can be determined through the energy expression of each adopted model (Table 1) (Ben Yahia et al., 2021; Yahia et al., 2019).

Table 7 presents the calculated energies of the six systems. It can be noted, from Table 7, the following order of modulus values of adsorption energies:

Table 4 Values of the correlation coefficient \mathbb{R}^2 , the residual root mean square coefficient **RMSE** and the Akaike information criterion **AIC** deduced from the numerical adjustment of experimental isotherms of InCl₃ and In₂(SO₄)₃ on 5,10,15,20-tetrakis(4-methylphenyl) porphyrin with the statistical physics models.

Adsorption system		indium chlo	oride-porphyri	n		Indium sulfate-porphyrin			
Temperature (K)		300	310	320	330	300	310	320	330
Mono-layer model (ideal gas)	R ²	0.74 (±0.09)	0.62 (±0.086)	0.62 (±0.03)	0.64 (±0.07)	0.71 (±0.039)	0.77 (±0.09)	0.62 (±0.05)	0.73 (±0.041)
	RMSE	7.45 (±1.25)	6.44 (±1.5)	6.89 (±1.79)	7.91 (±1.95)	8.67 (±2.67)	8.12 (±2.02)	$7.98 (\pm 1.89)$	7.56 (±1.16)
	AIC	38.7 (±3.41)	38.6 (±3.13)	38.3 (±2.95)	37.6 (±3.67)	32.7 (±1.51)	34.8 (±2.52)	34.78 (±1.92)	35.76 (±2.54)
Mono-layer model (real gas)	\mathbb{R}^2	0.88 (±0.03)	0.87 (±0.035)	0.82 (±0.06)	0.81 (±0.09)	0.79 (±0.063)	0.79 (±0.06)	0.78 (±0.07)	0.78 (±0.059)
	RMSE	5.66 (±0.09)	6.47 (±1.18)	6.78 (±0. 9)	5.39 (±0.33)	5.47 (±1.19)	6.9 (±2.05)	7.34 (±2.29)	6.57 (±1.51)
	AIC	33.78 (±1.97)	34.76 (±2.37)	33.94 (±1.56)	31.67 (±1.28)	32.4 (±2.55)	34.7 (±3.07)	35.59 (±1.85)	33.12 (±2.41)
Double-layer model (ideal gas)	\mathbb{R}^2	0.99 (±0.005)	0.99 (±0.007)	0.97 (±0.004)	0.97 (±0.007)	0.98 (±0.006)	0.99 (±0.002)	0.98 (±0.004)	0.97 (±0.006)
	RMSE	2.11 (±0.008)	1.99 (±0.019)	1.98 (±0.008)	2.02 (±0.002)	2.08 (±0.014)	1.85 (±0.065)	1.91 (±0.048)	1.95 (±0.049)
	AIC	27.61 (±2.16)	26.94 (±1.96)	27.34 (±2.8)	27.43 (±2.33)	26.94 (±1.78)	26.82 (±1.39)	26.47 (±3.04)	27.41 (±2.45)
Double-layer model (real gas)	\mathbb{R}^2	0.91 (±0.006)	0.93 (±0.005)	0.90 (±0.007)	0.92 (±0.004)	0.89 (±0.015)	0.91 (±0.007)	$0.90 (\pm 0.005)$	0.89 (±0.009)
	RMSE	5.33 (±0.39)	4.98 (±0.67)	5.27 (±1.06)	5.89 (±0.99)	5.79 (±0.25)	6.78 (±1.34)	5.94 (±1.19)	5.93 (±0.94)
	AIC	30.24 (±0.16)	31.53 (±0.31)	30.89 (±0.26)	31.67 (±0.35)	30.67 (±0.08)	31.92 (±0.19)	30.75 (±0.06)	31.98 (±1.14)



Fig. 3 Experimental adsorption isotherms simulated with the adequate statistical physics model at 330 K.

 $\begin{array}{l} |\text{-}E_1| \; (In_2(SO_4)_3) \; = \; 34.5 \; kJ \; /mol > |\text{-}E_2| \; (InCl_3) \; = \; 27.6 \; kJ \; /mol \\ > |\text{-}E_2| \; (In_2(SO_4)_3) \; = \; 20.9 \; kJ \; /mol \end{array}$

The two adsorption compounds of aluminum present the highest values of adsorption energy then, the aluminumporphrin complex is the best resulting complex in terms of stability comparing to the complexes of iron and indium. Moreover, the two adsorption processes of aluminum show adsorption energies values higher than 40 kJ/mol, indicating that chemical adsorption process occurred during the aluminum complexation (Sellaoui et al., 2018). Indeed, the aluminum-porphyrin bond can be covalent or ionic (B. yon Oepen, W. Kördel, W. Klein, 1991). The establishment of this type of bonds requires the change of particles structures and the rearrangement of the electron density between the adsor-

Adsorption isotherm/Fitting model	Models' parameters	T = 300 K	T = 310 K	T = 320 K	T = 330 K
AlCl ₃ / Mono-layer model (Ideal gas)	n	0.81	0.87	0.96	1.05
.,	P _M	324.9	386.5	441.2	510.7
	$c_{1/2}$	0.017	0.015	0.016	0.015
FeCl ₃ / Mono-layer model (Real gas)	n	0.65	0.73	0.86	0.90
	P _M	259.3	297.3	343.5	389.8
	W _{1/2}	0.012	0.011	0.011	0.012
	a $(\times 10^{-9})$	7.8	6.4	5.9	5.2
	$b(\times 10^{-12})$	2.9	4.2	4.9	5.9
InCl ₃ / Double-layer model (Ideal gas)	n	0.46	0.59	0.68	0.78
	P _M	186.9	241.7	279.2	320.5
	c ₁	0.004	0.0039	0.0037	0.0035
	c ₂	0.029	0.028	0.031	0.027

Table 5 Fitting values of the steric parameters (**n** and **P**_M), the van der Waals parameters (**a** and **b**) and the energetic parameters ($c_{1/2}$, $w_{1/2}$, c_1 and c_2) affecting the adsorption of AlCl₃, FeCl₃ and InCl₃ at four temperatures.

Table 6 Fitting values of the physicochemical parameters (n, P_M , a, b, $c_{1/2}$, $w_{1/2}$, c_1 and c_2) deduced from the adjustment of experimental isotherms of Al₂(SO₄)₃, Fe₂(SO₄)₃ and In₂(SO₄)₃ with the three adopted models.

Adsorption isotherm/Fitting model	Models' parameters	T = 300 K	T = 310 K	T = 320 K	T = 330 K
Al ₂ (SO ₄) ₃ / Mono-layer model (Ideal gas)	n	0.75	0.84	0.91	0.94
	P _M	299.2	351.6	379.5	421.4
	c _{1/2}	0.007	0.008	0.009	0.008
Fe ₂ (SO ₄) ₃ / Mono-layer model (Real gas)	n	0.55	0.64	0.72	0.84
	P _M	239.6	259.2	317.5	355.2
	W1/2	0.006	0.0067	0.0073	0.0069
	a (×10 ⁻⁹)	9.9	8.2	7.6	7.13
	b (×10 ⁻¹²)	1.4	2.1	3.8	4.4
In ₂ (SO ₄) ₃ / Double-layer model (Ideal gas)	n	0.41	0.52	0.64	0.73
	P _M	147.9	184.8	239.5	279.4
	c ₁	0.0029	0.0032	0.0034	0.0031
	c ₂	0.026	0.025	0.024	0.025

Table 7 Values of the adsorption energies $|-\mathbf{E}_{1/2}|$ for aluminum and iron adsorptions and $|-\mathbf{E}_1|$ and $|-\mathbf{E}_2|$ for indium adsorption givenin modulus values at 300, 310, 320 and 330 K.

Adsorption system	Adsorption energy	300 K	310 K	320 K	330 K
AlCl ₃ - porphyrin	$ -E_{1/2} $ (kJ/mol)	64.3	69.8	76.2	81.4
Al ₂ (SO ₄) ₃ - porphyrin	$ -E_{1/2} $ (kJ/mol)	53.1	62.4	65.1	69.5
FeCl ₃ - porphyrin	$ -E_{1/2} $ (kJ/mol)	36.2	38.4	40.7	42.1
Fe ₂ (SO ₄) ₃ - porphyrin	$ -E_{1/2} $ (kJ/mol)	32.9	36.8	38.1	40.8
InCl ₃ - porphyrin	$ -E_1 $ (kJ/mol)	29.4	33.6	36.7	37.7
	$ -E_2 $ (kJ/mol)	21.3	23.5	25.8	27.6
In ₂ (SO ₄) ₃ -porphyrin	$ -E_1 $ (kJ/mol)	25.2	28.4	33.4	34.5
	$ -E_2 $ (kJ/mol)	16.9	18.8	20.3	20.9

bate and the adsorbent. Then, chemical adsorption cannot result in a multi-layer process and cannot be affected by the lateral interactions because of the strong interaction between the adsorbed particle and the surface (Sun and Wang, 2010;

B. yon Oepen, W. Kördel, W. Klein, 1991). On the other hand, the iron and indium processes show adsorption energy values lower than 40 kJ/mol, which indicate the presence of physical adsorption process for these two metals (Sun and Wang, 2010).

Indeed, physical bonds like the hydrogen bonding or the van der Waals forces could be established between the two metals and the porphyrin cavities (Sun and Wang, 2010; B. yon Oepen, W. Kördel, W. Klein, 1991). Such binding is weakly energetic because there is no rearrangement of the electron density of the adsorbate and the adsorbent. Due to the weak binding of the adsorbate-adsorbent complex, a desorption process could take place like the case of iron and a multilayer mechanism could occur like the case of indium.

3.4. Theoretical results and discussion via the temperature

Fig. 4 illustrates the variation of all the physicochemical variables as a function of temperature. It can be noticed that the fitted values of the steric parameters (the number of metal per porphyrin site n and the number of occupied adsorbent sites P_M) and the calculated values of adsorption energies increase with the rise of temperature for the six systems. It can be concluded that the thermal agitation effect favors the adsorption dynamics which was an endothermic process.

Generally, the adsorption is an exothermic process in which the increase of temperature prevents the adsorption reaction which means that the adsorbed amount at a given pressure/concentration should reduce as the temperature increased. However, the adsorption isotherms (Fig. 2) showed that the adsorbed amounts of the six adsorbates on porphyrins increased as the temperature increased from 300 K to 330 K. This can be explained from Fig. 4b which showed that the density of receptor sites P_M increased with the rise of temperature for the six systems. The most plausible explanation is when the temperature increases, new receptor pophyrins sites which were hidden at low temperatures appeared and participated in the adsorption leading to an increase of the adsorbed quantity and the adsorption energies (Fig. 4d) (Ben Yahia et al., 2016; Knani et al., 2020).

For the iron adsorptions, it can be seen that the covolume b increases as the temperature increases (Fig. 4c) in accordance with the increase of the steric variables and the adsorption energies. However, the cohesion pressure decreases with the rise of temperature (Fig. 4c). This indicates that the rise of temperature disfavors the lateral adsorbate-adsorbate interactions while increasing the distance between the adsorbates (Ben Yahia and Ben Yahia, 2020; Yahia et al., 2019).

Overall, the steric parameters, the adsorption energies and the parameter covolume show temperature trends similar to the adsorbed quantity so, they are dominant elements in the adsorption process. On contrary, the cohesion pressure shows an opposite temperature trend then, it was not a deciding factor in the adsorption mechanism. Its usefulness was only seen for the interpretation of the decrease of adsorbed amount at saturation.



Fig. 4 Evolutions of the two steric parameters (number of metal ions per site **n** and the density of receptor porphyrins sites P_M), the lateral interactions parameters (cohesion pressure **a** and covolume **b**) and the adsorption energies $(|-E_{1/2}|, |-E_1| \text{ and } |(-E_2)|)$ as a function of temperature (300–330 K).

4. Thermodynamics

The macroscopic interpretation of the six complexation systems can be assessed through the thermodynamic properties. In fact, the expressions of the entropy and the free enthalpy of each system can be determined via the following formulas (Ben Yahia and Ben Yahia, 2020; Diu et al., 1989):

$$S_a = -\frac{P_M}{T} \frac{\partial \ln z_{gc}}{\partial \beta} + k_B P_M \ln z_{gc}$$
(11)

$$G = \mu \times Q_a \tag{12}$$

The expressions the two thermodynamic functions of each system are developed in Table 8.

The variations of the two thermodynamic functions are plotted as a function of equilibrium concentration for the six adsorption systems in (Fig. 5).

Fig. 5a shows that the entropy reaches the maximum value at the level of the energetic parameter of each adsorption system. At these specific points, the disorder of the complexation mechanism takes its maximum value (Ben Yahia and Ben Yahia, 2020). Moreover, it can be noticed that the entropy of the iron and aluminum systems show one peak because the adsorption of these compounds on the porphyrins was carried out via a mono-layer process with one energy level. However, the interpretation of indium adsorption was performed via the double-layer model with two energy levels which explains the presence of two maximums (corresponding to two energetic parameters) in the entropy of these systems. For these systems, one can see that the first peak corresponding to the first energetic parameter (disorder at the level of the first adsorbed layer) is lower than the second peak which reflects the total disorder of the adsorption system (Aouaini et al., 2014).

Fig. 5b indicates that the enthalpy values are negative for the six complexation systems, demonstrating that the adsorption of the three metals on the tested adsorbent evolved spontaneously until the saturation level. Furthermore, it is noted that the enthalpies of the two aluminum compounds present stable saturation states which means that the adsorption of AlCl₃ and Al₂(SO₄)₃ evolved spontaneously towards a stable state at high concentration. On contrary, the enthalpies of the two iron compounds expand in algebraic value at the saturation, indicating that the lateral interactions prevented the adsorption processes of FeCl₃ and Fe₂(SO₄)₃ at high concentration (Ben Yahia et al., 2021). On contrary, two stability states were shown for InCl₃ and In₂(SO₄)₃. Indeed, the double-layer adsorption of the two indium compounds on the adsorbent presents a first partial stability state corresponding to the saturation of the first layer and the second one corresponds to the total saturation of the two adsorbed layers (Aouaini et al., 2014).

5. Conclusion

The present investigation has proved that the spin coating technique was a useful method for the functionalization of quartz disc sensor with macrocyclic molecules. The piezoelectric sensor based porphyrin film was investigated in this work as complexing adsorbent of three metals leading to the measurement of experimental adsorption isotherms. The discussion of the isotherms plots indicated that the aluminumporphyrin complex is the best in terms of quantity and stability. The stability of the formed iron-porphyrin complex was influenced by the lateral interactions of adsorbates leading to a reversible phenomenon at saturation. The role of anionic ions (chloride and sulfate) was shown in the layer by layer process of indium adsorption. The contribution of these anions in the adsorption process disfavors the complexation of indium by the porphyrinic surface and affects the stability of the formed complex. The statistical physics modeling of isotherms curves, through the advanced models expressions, has explained the microscopic aspects (steric and energetic aspects) of the adsorption processes at the ionic scale. The physicochemical analysis of the models variables indicated that the complexation of porphyrin was a multi-docking process and that the aluminum-porphyrin is the best formed complex in terms of quantity and stability. The calculation of the energies of the six systems demonstrated that the adsorption of the two aluminum compounds was a chemical process and that the complexation of iron and indium took place via physical mechanism which explained the presence of a desorption process for iron and the formation of two layers for indium. The discussion of the influence of temperature on the adsorption demonstrated that the rise of temperature favors the participation of new porphyrins sites in the complexation mechanism, showing the endothermic nature of the three metals adsorption. The

Adsorption system	Entropy S_a/k_B	Free Enthalpy G/k _B T
AlCl ₃ and Al ₂ (SO ₄) ₃	$P_M \left(\ln(1 + (\frac{c}{c_{1/2}})^n) - \frac{(\frac{c}{c_{1/2}})^n \ln(\frac{c}{c_{1/2}})^n}{1 + (\frac{c}{c_{1/2}})^n} \right)$	$nP_M\left(\ln(\frac{c}{z_{tr}})\right).\left(rac{\left(rac{c}{c_{1/2}} ight)^n}{1+\left(rac{c}{c_{1/2}} ight)^n} ight)$
FeCl ₃ and Fe ₂ (SO ₄) ₃	$P_{M} \ln(1 + (\frac{c}{w_{1/2}(1-bc)c^{2\beta\alpha c}e^{-\frac{bc}{1-bc}}})^{n}) - \frac{(\frac{c}{w_{1/2}(1-bc)c^{2\beta\alpha c}e^{-\frac{bc}{1-bc}}})^{n} \ln(\frac{c}{w_{1/2}(1-bc)c^{2\beta\alpha c}e^{-\frac{bc}{1-bc}}})^{n}}{P_{M} \frac{(\frac{c}{w_{1/2}(1-bc)c^{2\beta\alpha c}e^{-\frac{bc}{1-bc}}})^{n}}{1+(\frac{c}{w_{1/2}(1-bc)c^{2\beta\alpha c}e^{-\frac{bc}{1-bc}}})^{n}}}$	$nP_M\left(\ln(rac{c}{z_{tr}}) + \lnrac{1}{1-bc} + rac{bc}{1-bc} - rac{2ac}{k_BT} ight). \ \left(rac{(rac{c}{w_{1/2}(1-bc)2^{2ar{a}c_c} - rac{bc}{1-bc})^n}}{1+(rac{c}{w_{1/2}(1-bc)e^{2ar{a}c_c} - rac{bc}{1-bc})^n}} ight)$
InCl ₃ and In ₂ (SO ₄) ₃	$P_M igg(\ln(1 + \left(rac{c}{c_1} ight)^n + \left(rac{c}{c_2} ight)^n ight) - rac{(rac{c_1}{c_1})^n \ln(rac{c_1}{c_1})^n + (rac{c_2}{c_2})^n}{1 + (rac{c_1}{c_1})^n + (rac{c_2}{c_2})^n} igg)$	$nP_M\left(\ln(rac{c}{z_{tr}}) ight) \ \left(rac{(rac{c-1}{z_{tr}})^{2\sigma}}{1+(rac{c-1}{z_{tr}})^{2\sigma}} ight)$

Table 8Analytical expressions of the entropy (S_a/k_B) and the free enthalpy (G/k_BT) of the two mono-layer adsorptions of aluminumand iron and the L.B.L double-layer adsorption of indium.



Fig. 5 Evolutions of the entropy and the free enthalpy versus concentration for the six adsorption systems at 330 K.

thermodynamic evaluation, via the analysis of the adsorption entropy, indicated that the peak of the disorder is reached at the levels of the energetic parameters for the six mechanisms. The spontaneity of the six complexation mechanisms was demonstrated by the behavior of the enthalpy. The adsorption processes of iron and aluminum presented one stability state corresponding to the saturation of the adsorbed layer (mono-layer process) whereas, the double-layer adsorption processes of the indium showed two stability states (partial stability level corresponding to the first layer saturation and total stability state of the whole system).

6. Comparison with recent papers

Theoretically speaking, the advanced statistical physics modeling of isotherms provided interesting interpretations of the adsorption mechanism concerning the number of formed layers (mono-layer/double-layer), the steric aspect (multidocking/multi-ionic), the adsorption nature (exothermic/endothermic) and the type the formed complex (chemical/physical). These microscopic results could not be explained by the previous classical models of Langmuir (Langmuir, 1918); Freundlich (Freundlich, 1906) and others (Brunauer et al., 1940; Hill et al., 2010).

Concerning the adsorption of metals on porphyrins, previous works studying the adsorption of FeCl₂, MnCl₂ and MgCl₂ on porphyrins (Ben Yahia et al., 2017; Ben Yahia et al., 2021; Yahia et al., 2019) showed that the presence of chloride ions in the adsorbate compound has no influence on the complexation process leading to a mono-layer adsorption phenomenon for all the metals. Others papers indicated that the layer by layer process (multi-layer ionic adsorption) can be shown only for the metals compounds involving the nitrate ions in their structures like the case of Co(NO₃)₂, Zn(NO₃)₂ and Mn(NO₃)₂ (Ben Yahia et al., 2016). In this work, we have shown that the anionic ions did not contribute to the adsorption of aluminum and iron but in the case of indium the chloride ions and the sulfate ions contribute to the layer by layer adsorption process of porphyrin.

7. Perspectives

The results of the present investigation should be improved in future papers by some characterization of the surface morphology of adsorption cell like scanning force microscopy (SFM) and scanning electron microscopy (SEM). The complexation process of porphyrin can be also investigated using the density functional theory (DFT) method in which the electron localization function (ELF) and electron densities plots are provided and analyzed in detail.

Moreover, the statistical physics modeling of adsorption isotherms can be improved by taking account of the dissolution of the adsorbate during the adsorption because the present treatment is carried out by considering as a first approximation that the adsorbates are globally neutral. Till now, the ionic nature of the adsorbate in the solution has not been taken into account in our knowledge. Now, to take account of the ionic nature of the adsorbate, it is important to carry out this investigation which will be an electrochemical task. That has not been taken in our search team by statistical physics treatment. This is an important investigation in which we should take into account the two different ionic natures of the anions and cations in the adsorption process. We should perhaps consider the process as a binary adsorption treated by statistical physics formalism (ref (Sellaoui et al., 2018) and consider the formed charge zone which will have an effect on the adsorption process. This is a perspective work in our statistical physics team.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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