



Adsorption Thermodynamics of Cu-Ca Ion Exchange on Nano-montmorillonite Clay System



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ERADICATION of heavy metals from water and wastewater is vital in relation of public health. Copper is discharged to the environment through the unwise use of the agrochemicals and the industrial activities such as the dyeing and mining industry. Recently clay and nanoclay exhibited efficacy as sorbent of heavy metals.

This study was conducted to analyze the thermodynamic characters of the Cu(II)/Ca(II) interactions on Ca-nano-montmorillonite to elucidate and enhance the viability of using nanoclay minerals as an effective sorbent material in reducing the bioavailable of copper, thus, reducing their environment risk.

Enhancement of the copper on the nano-montmorillonite was recorded with increasing the Cu ion fraction in the solution. Increasing the reaction temperature had a negative effect on the concentration of Cu fraction on the solid phase. The isotherms results pointed out that adsorption of Cu²⁺ ions are preferred as indicated by the negatively charged free energy (ΔG°). The preference for the Cu²⁺ ions and their influence on the nano-montmorillonite as well as the high binding strength are elucidated by the negativity of the entropy (ΔS°) and ΔS_{clay} as well as the enthalpy (ΔH°) values. The adsorption reactions of Cu²⁺ onto the clay surfaces were exothermic in nature as indicated by the negative value of ΔH° . The activity coefficient of the exchanged ions at different ionic fractions Ca:Cu in the solution are affected mainly by two factors included the distribution of the ions in the Gouy and Stern layers and the differences in the interlayer spacing according the solution composition.

Keywords: Thermodynamic, ion exchange, copper, calcium, Nano- montmorillonite clay, Gibbs free energy, enthalpy, entropy, activity coefficient, Gouy and Stern layers.

Introduction

Riddance of heavy metals from water and wastewater is vital in relation of public health and environment [1]. Pollutants enter the water bodies via numerous ways. They released from the industrial effluents, wastewater treatment services, refineries, etc. This investigation focuses on copper as one of heavy metals that attract global attention particularly when it exceeded the permissible limits. The copper discharged to the environments through the unwise use of

the agrochemicals (such as the fertilizers and fungicides). This pollutant also exist in the wastewater of industrial activities such as the dyeing and mining industry [2].

Clay minerals have wide applications in different fields. They are used in the industry field to enhance the performance of some compounds such as the production of some consumed products as well as some health-related products [3]. In addition, they are viable sorbents in the field of water remediation [4]. Recently, the

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introduction of nanoclays have been widely used as sequestering materials for heavy metals from aqueous media, in which they were used as sole or as composites [5] and [6]. The benefits of using clay minerals as the alternative adsorbents for heavy metals are related to their high ion exchange capacities (CEC) and specific surface area, besides their chemical and mechanical stability, in addition to their physical properties such as the swelling ability and the low permeability [5]; [6] and [7].

Adsorption is the most favored technique for excluding of heavy metals from aqueous solutions, due to its high efficiency and easiness of handling. [3]; [8], and [9]. Different studies introduced the using of biomaterials and agricultural residues derived biochar for the removal of heavy metals [2] and [8]. In this respect, many investigators deliberated the efficiency of several types of clays in eliminating inorganic pollutants from aqueous solutions. such as bentonite [6] and [10], montmorillonite [11]; [3], and other adsorbents [8]; [12], and [13]. Ion adsorption is one of the primary technique applied the approaches of physical chemistry to describe complications of clay suspension chemistry [14]. Thermodynamic parameters of ion exchange reactions on clays consent used to characterize the ion equilibrium in clay These parameters help in defining nature and feasibility of the sorption reaction and calculating the associated energy as well as the strength of the interactions between sorbate and sorbent [5]. The aim of the current study is to analyze the thermodynamic characters of the $\text{Cu}^{2+}/\text{Ca}^{2+}$ interactions on Ca-nano-montmorillonite for an enhanced understanding of environmental pollutions, Thus elucidates the viability of using the nanoclay minerals (nano-montmorillonite) as an effective sorbent material in reducing the bioavailable of Copper, thus, reducing their environment risk.

Experimental

Materials

Nano-montmorillonite clay (supplied by Rock wood -9023 Nanofil R., powder, and its surface area $250 \text{ m}^2/\text{g}$) was used in this study. The clay is converted to the Ca-form by extracting five times with 0.1 N CaCl_2 . The obtained Ca-homo-ionic clay samples were then dialyzed several times to remove the extra salts [15]. Finally, Ca-homo-ionic clay materials were dried at 105°C for 24 h and then crushed to collect the desired particle

size ranges of 100 nm. Two duplicate Ca-clay samples were taken to determine CEC by using 0.2 N of sodium acetate. The CEC of the clay was 215 cmol kg^{-1} .

Potentiometric Measurements

Direct potentiometric measurements of copper ion activity were carried out using an Orion digital-printer pH/mV meter model 801A. Direct measurements of copper ion concentrations were performed using a copper glass electrode has a sensitive tip highly specific to copper ion with a reference electrode (Orion research 94-82a copper electrode).

This provides direct measurements of the copper ion concentration [16] and [17]. Different molar ionic fractions of Cu: Ca (0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9 and 1.0) is prepared from CuCl_2 and CaCl_2 solutions to give an initial total concentration of 0.02 moles. The electro motif force (emf) of the different mixed solutions is determined at three different temperatures (20 , 30 and 40°C). One tenth of a gram of Ca-clay samples is added to 100 ml of the mixed electrolyte solutions. The exchange reaction is carried out in a thermostatic water bath adjusted to $20 \pm 0.1^\circ \text{C}$ in the first test series and the emf is measured after reaching equilibrium.

The difference between the suspended electrolyte solution and its corresponding pure solution represented the change in copper concentration during the exchange reaction.

Two other series of exchange reactions are carried out at 30 and 40°C . The CEC determined by 0.2 N of copper chloride is in accordance with the CEC determined by CaCl_2 in the Ca-saturated clay. This observation indicates that the CEC of the clay is constant over the entire range of the exchange isotherm.

Results

Assessment of the thermodynamic parameters

Following is the suggested ion exchange reaction in this study (eq. 1).



By implementing the mass law on the previous reaction, equilibrium constant (K) and the different thermodynamic parameters were calculated at different temperatures. The isotherms of the exchanged ions on the nano-montmorillonite at the three degree of temperature are depicted in Fig.1. Enhancement in the adsorbed Cu^{2+} ions

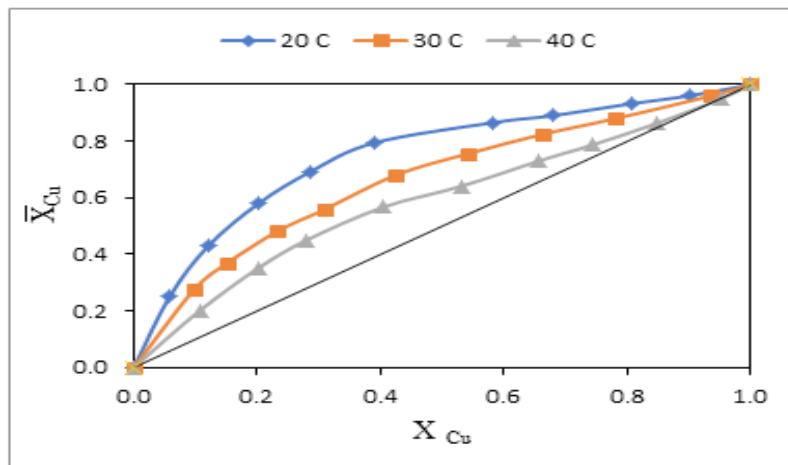


Fig.1. Isotherms of Cu-Ca Exchange on Nano-montmorillonite at the studied temperature.

fraction were obtained with increasing of the value of ion fraction in the solutions. However, these amounts were decreased with raising the reaction temperature. The uncorrected selectivity coefficient for the exchangeable reaction (1) was calculated using eq. (2).

$$K'_c = \frac{(q_{Cu}/q_o)(1 - C_{Cu}/C_o)}{(1 - (q_{Cu}/q_o)C_o)(C_{Cu}/C_o)} \quad (2)$$

where C_o and q_o are the total soluble ions concentration in the solution (equivalent per liter) and the exchanged amount on the nano-montmorillonite (equivalent per gram), respectively, C_{Cu}/C_o (X_{Cu}) and q_{Cu}/q_o (\bar{X}_{Cu}) are the copper ion fraction in the solution and on the nano-montmorillonite, respectively.

The activity coefficient, γ derived from Debye-Huckel equation [18] was involved in the estimation of the corrected selectivity K_c according the eq. (3).

$$K_c = K'_c(\gamma_{\pm CaCl_2}/\gamma_{\pm CuCl_2}) \quad (3)$$

Further, the exchange constant, K , of the thermodynamic reaction in this study is expressed by eq. (4),

$$K = K_c(f_{Cu}/f_{Ca}) \quad (4)$$

where f_{Cu} and f_{Ca} are the activity coefficients of the Cu-ion and Ca-ion on the solid surface. Previous study showed that K constant can be estimated by using eq. (5) [19]

$$\ln K = -(z_{Cu} - z_{Ca}) + \int_0^1 \ln K_c d(\bar{X}_{Cu}) = 1 + \int_0^1 \ln K_c d(\bar{X}_{Cu}) \quad (5)$$

Where Z_i is the valence of ions. By drawing the relationship between $\ln K_c$ vs. X_{Cu} , the integral was

computed as depicted in Fig. 2. It is shown from the figure that the elevation of the temperature decreases the values of K_c .

Afterward, the standard free energy, ΔG° , and the standard enthalpy change, ΔH° , of reaction (1) were then calculated from eq. (6) and from Van't Hoff eq. (7), respectively.

$$\Delta G^\circ = -RT \ln K \quad (6)$$

$$\ln \left(\frac{K_2}{K_1} \right) = -\frac{\Delta H^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad (7)$$

Where R is the gas constant, T is the temperature.

Moreover, the standard free entropy change, ΔS° , was deliberated from the thermodynamic eq. (8) [20]. All the estimated thermodynamic parameters are stated in Table 1.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (8)$$

The activity coefficient of the exchanged ion was deliberated from the equation of Gaines and Thomas [19] and [21] and as stated in eq. (9) for Cu^{2+} ion and in eq. (10) for Ca^{2+} ions. The obtained results are reported in Table 2 at different Cu^{2+} mole fractions

$$\ln f_{Cu} = (1 - q_{Cu}/q_o)(1 - \ln K_c) + \int_{q_{Cu}/q_o}^1 \ln K_c d(q_{Cu}/q_o) \quad (9)$$

$$\ln f_{Ca} = -(q_{Cu}/q_o)(1 - \ln K_c) - \int_0^{q_{Cu}/q_o} \ln K_c d(q_{Cu}/q_o) \quad (10)$$

Discussions

The adsorption characteristics of the current study are elucidated by the evaluation of the *Egypt. J. Chem.* **62**, Special Issue (Part 1) (2019)

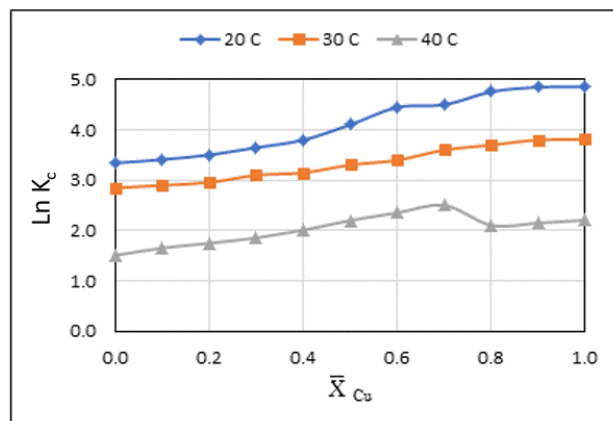


Fig. 2. Selectivity Coefficient vs Molar Ionic Fraction of Cu²⁺/Ca²⁺ on Nano-montmorillonite at the studied temperatures.

TABLE 1. Thermodynamic Parameters for Cu:Ca exchange system on nano-montmorillonite .

Parameter	20°C	30°C	40°C
K	137.6	81.7	39.5
ΔG° (kcal mole ⁻¹)	-3.08	-2.668	-2.634
ΔH° (kcal mole ⁻¹)		-12.041	
ΔS° (cal deg ⁻¹ mole ⁻¹)	-30.58	-30.94	-30.05
* ΔS° clay (cal deg ⁻¹ mole ⁻¹)	-46,68	-47.04	-46.15

*From eq. (11)

TABLE 2. The calculated activity coefficients of adsorbed Ions (f) at the studied temperature range.

X_{Cu}	20°C		30°C		40°C	
	f_{Cu}	f_{Ca}	f_{Cu}	f_{Ca}	f_{Cu}	f_{Ca}
0.1	4.177	2.230	4.905	2.813	5.702	3.247
0.2	4.051	1.938	4.310	2.541	4.514	2.692
0.3	3.801	1.908	3.961	2.572	4.637	2.735
0.4	3.603	1.790	3.833	1.805	3.974	1.893
0.5	3.342	1.509	3.407	1.794	3.561	1.825
0.6	3.200	1.468	3.308	1.651	3.572	1.736
0.7	2.947	1.175	3.107	1.248	3.225	1.371
0.8	2.314	0.947	2.462	1.150	2.657	2.701
0.9	1.807	0.795	1.946	0.869	2.145	0.887

thermodynamic parameters. Hence, the constants of the thermodynamic processes, Gibbs free energy change (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) values were estimated to confirm the viability and the spontaneously nature of the process [22]. This study is focused on the interrelations between Cu²⁺ and Ca²⁺ into the Nano-montmorillonite clay. Changing the reaction temperature is important factor in the thermodynamic adsorption

processes. Thermodynamic deliberations of any adsorption reaction are important to define whether the process is spontaneous or not. The Gibbs free energy as indicator for the spontaneity of the chemical reaction, hence it is a necessary condition for spontaneity status [23]. In addition, the enthalpy and the entropy factors must be considered in order to determine the Gibbs free energy of the process [22] and [24].

Thermodynamic parameters such as Gibbs free energy change (ΔG°), enthalpy change (ΔH°) and the entropy change (ΔS°) can be estimated using equilibrium constants changing with temperature.

Free Energy ΔG°

The negative values of Gibbs free energy variation (ΔG) denote that the product are favored for the adsorption of Cu^{2+} ions, pointing out the spontaneous nature of the adsorption process on the clay surfaces [23]. The formation of Cu-nano-montmorillonite resulted in decrease in the free energy, which means it should form spontaneously.

There is an overall character for ΔG° values in these experiments that the negative values free energy change of Cu^{2+} adsorption increased by decreasing the experimental temperature. These negative values of ΔG° (Table 1) can provide a measure for the metals binding of Cu^{2+} on the clay surfaces. The stronger the metal binding is, the more its negative value of ΔG° . This behavior is very well correlated with the electrical, physical and chemical properties of the two exchanged metals ions.

Although the free energy ΔG° had negative values indicating the strong bond of Cu^{2+} ion, this conclusion is not decisive, due to that the ΔG° parameters depends on both enthalpy ΔH° and entropy ΔS° parameters, and the binding energy is well-defined mainly by the enthalpy alone, [25]; [26] and [27].

Enthalpy ΔH°

The standard enthalpy variation, ΔH° , and the standard entropy variation, ΔS° , are two terms composed the standard free energy as realized from the aforementioned fundamental equations (eq. 8). The enthalpy of the adsorption ΔH° is a measure of the energy barrier that must be browbeaten by reacting molecules [25]. The negative ΔH° of Cu^{2+} adsorption on the clay surfaces suggests that the adsorption reactions onto the adsorbents are exothermic in nature; thereby meaning that decreasing in temperature approves the adsorption of Cu^{2+} onto these clay surfaces.

In the case of an exothermic process, when the negativity of the ΔH is exceeded over the reduction of the entropy, then the reaction could be enthalpy driven. While in the endothermic reaction it is entropy driven due to the high positivity of the ΔS . In this study and according to the thermodynamic principal, the value of ΔH

< 0 , $T\Delta S < 0$, $\Delta S < 0$ at constant pressure and volume, indicating the enthalpy driven reaction, and the arrangements or the system order improved with the existence of the Cu^{2+} on the nano-montmorillonite surface due to the reduction of the entropy [28]. Table 1 designated the formation of Cu-montmorillonite showed by the decline of the enthalpy, attaining high binding strength of the Cu^{2+} ions. The computed enthalpy in this study is a sum of different form of enthalpies: hydration, dilution, mixing and exchanging enthalpy of the ions. Those forms cannot be calculated properly due to the uncertainties concerning the hydration energy of adsorbed ions [29]. The ionic hydration enthalpy is the variation of the enthalpy that bands the dissolution of one mole of the ideal ion gas in an infinite volume of water at 298°K temperature [30]. In the current investigation, the enthalpy hydration of copper ion, ΔH_{hyd} of Cu^{2+} ions -501.9 kcal/mole, is high enough to not be overcome by the computed heat of reaction, -12 kcal/mole for Cu^{2+} adsorption, hence the Cu^{2+} remains hydrated at the temperature range in the study, which might obstacle its interface with the lattice OH groups.

Entropy ΔS°

The formation of Cu-montmorillonite according to the exchange reaction from Ca-montmorillonite is associated with reduction of the entropy, ΔS° . The values of entropy ΔS° are not significantly disturbed in the temperature range of this study, Table 1. The negative values of entropy are reliable for the Cu^{2+} preference, [21]; [31]; [32]; [33] and [34]. The obtained ΔS° is the algebraic sum of all entropy changes in the system and thus can be formulated for the reaction (1) as follow:

$$\Delta S_{\text{clay}}^\circ = (S_{\text{Cu}}^\circ - S_{\text{Ca}}^\circ)_{\text{clay}} - (S_{\text{Cu}}^\circ - S_{\text{Ca}}^\circ)_{\text{solution}} \quad (11)$$

Substituting values stated by Neilson, [35] for S_{Cu}° -65.8 and S_{Ca}° -49.7 cal/mole - degree at 25°C in aqueous solution, $\Delta S_{\text{clay}}^\circ$ becomes negative (Table 1).

The entropy of a system is related to the number of arrangement ways of the molecules or components in the thermodynamic system [25]. Due to the smaller ionic radii of Cu^{2+} (0.91 Å) comparing with Ca^{2+} (1.14 Å), the larger polarizability of Cu^{2+} (1.9) than Ca^{2+} (1.0), also the larger enthalpy of hydrations of Cu^{2+} than Ca^{2+} (-1579), therefore, Cu^{2+} ions can locate

themselves with less randomness at the solid/solute system. As a result, the probabilities of the arrangements of exchangeable ions on Cu-montmorillonite surfaces are reduced compared to that in the case of Ca-montmorillonite, thus the entropy of Cu-montmorillonite is low, and consequently ΔS° clay became negative values (Table 1). The decrease in $\Delta S^\circ_{\text{clay}}$ associated with changing the system from exchanged-Ca to exchanged-Cu could be explained due to the reduction of the exchangeable sites onto the Cu-montmorillonite compared to the Ca-montmorillonite leading to negative entropy accomplished with reducing the arrangements number of the Cu^{2+} ion in solute/solid system. In addition, Cu^{2+} ions are higher hydration and hydration ordered than Ca^{2+} ions, So that less randomness structures is accounted for the interlayer water with Cu^{2+} ions, resulting reduction in the entropy compared with the Ca^{2+} ions.

Moreover, the solution phase could also affect the entropy of the system. In which, the existence of Cu^{2+} ions in the solution tend to decrease the value of ΔS° , that might be due to induce the order of the pseudo-tetrahedral structure of the dissolving water compared to that with the existence of Ca^{2+} ions. Thus implied that the reduction of Ca^{2+} in the solution in addition to exchange it with Cu^{2+} decreased the entropy, which directed the Cu-Ca exchange reaction on nano-montmorillonite clay toward the preference of Cu sorption (Fig. 1).

Activity coefficients of adsorbed ions (f).

The activity coefficient of both ions, f_{Ca} and f_{Cu} , are declined continuously with arising the Cu fraction in the solution (Table 2), but the values of f_{Cu} are larger than that of f_{Ca} at any mole fractions. Previous studies remarked that the estimated activity coefficients of the ions are interconnected with the relative freedom of the exchanged ion at various ion saturations [19], [21], [36], and [37]. Further, they related the activity coefficient and the relative freedom to the balance between the way that the ion presented in Gouy and Stern layers and the changes in the interlayer spacing ensued.

According to Deshpande and Marshall [38]; Bansal [39] and Sposito [40], the freedom of ion movements in the Gouy layer is higher than it is in the Stern layer. There are different factors affecting ions distribution between these two

layers, including density of charge on the surface, the ions size and valence and the spreading of the ion species within the adsorbed layer. In Cu:Ca systems, the studied two ions are different in the mole fraction in the Stern layer, with the substitution of Ca by Cu ions in the diffusion layer, any small inputs of the activity coefficient of the ion in stern layer will have strong impact, leading to reduce the computed activity coefficient of copper (f_{Cu}). The results displayed the smaller values of f_{Ca} compared to the values of f_{Cu} occurred at all studied mole proportion (Table 2). That might be interpreted by the smaller mole volume of Cu^{2+} ions (7.124 ml/mole) than that of Ca ions (25.857 ml/mole), resulting in more movements of Cu^{2+} in relative to Ca^{2+} [35].

Additionally, the results depicted reducing of the f_{Cu} values with raising the Cu^{2+} molar proportion, which refer to the adsorption specification of Cu^{2+} on the nano-montmorillonite surface. That also confirmed by increasing the adsorption of Cu occurred as the f_{Cu} values reduced. Furthermore, as the movements of ions in the Stern layer is limited as compared with its movements in the Gouy layer, the adsorption of Cu^{2+} reduces the interlayer spacing of the adsorbent, which promote the specification of adsorption toward the Cu^{2+} ions. Thus inferred that f_{Cu} decreases continuously with increasing Cu saturation

Conclusion

A copper specific electrode can be used to follow the kinetics of copper ions on a nano-montmorillonite. Direct potentiometric measurements of copper ion activity technique provided direct measurements of the copper ion concentration on the clay system. The activity coefficients of copper ions on the surface reflected the relative freedom of adsorbed ions at various Cu- overloads. The distribution of the copper ions between Gouy and Stern layers influenced by density of charge on the surface, the ions size and valence and the spreading of the ion species within the adsorbed layer. The decreasing in the copper ions activity coefficient approved to a specific adsorption of these ions on the nano-montmorillonite surfaces.

Conflicts of interest

The authors declare that they have no competing interests

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الادمصاص الترموديناميكي لنظام التبادل الأيوني بين النحاس والكالسيوم على النانومونتموريللونيت الطيني

ياسر الدمراوي، فايز اسعد، رفعت يوسف، داليا مبارك

قسم الاراضى واستغلال المياه -المركز القومى للبحوث- دقى - جيزة - مصر .

يعد التخلص من المعادن الثقيلة من المصادر المائية أمراً حيوياً فيما يتعلق بالصحة العامة. يصل النحاس الى البيئة من خلال الاستخدام الغير حكيم للكيمياويات الزراعية كما يتواجد هذا الملوث ايضا فى مياه الصرف الناتجة عن الأنشطة الصناعية مثل صناعات الاصباغ والتعدين. مؤخرا اظهر الطين والطين في حجم النانو فاعلية كمواد ادمصاص للمعادن الثقيلة. اجريت هذه الدراسة لتحليل الخواص الترموديناميكية لتفاعلات التبادل لايونات النحاس/الكالسيوم على النانومونتموريللونيت الكالسيومى لتوضيح جدوى استخدام الطين النانوى كمادة ماصة فعالة تحد من تيسر ايونات النحاس، وبالتالي تقلل من خطرها البيئى.

سجلت زيادة فى قيمة النحاس المدمص على النانومونتموريللونيت مع زيادة نسبته فى المحلول. بينما ادت زيادة درجة حرارة التفاعل على خفض نسبته على الطين. أشارت نتائج الأيزوثيرم التفضيل لادمصاص أيونات النحاس والمستدل عليها بالقيمة السالبة للتغير الحراري الحر (ΔG°). هذا التفضيل لايونات النحاس وكذلك قوة ارتباطها العالية وتأثيرها على النانومونتموريللونيت تم توضيحها بالقيم السالبة لكل من الانتروبي (ΔS°) و ΔS_{clay} و الانتالبي (ΔH°). معامل النشاط للايونات المتبادلة عند مستويات مختلفة من التشبع الأيوني بين النحاس والكالسيوم يتأثر بعاملين اساسيين وهم التوزيع النسبى للايون بين طبقة جوى وطبقة اشنيرن وكذلك اختلافات المسافة البينية لسطح الارتباط المتأثرة بتركيب المحلول.