



Heat of adsorption, adsorption energy and activation energy in adsorption and ion exchange systems

Vassilis J. Inglezakis^a, Antonis A. Zorpas^{b,*}

^aSC European Focus Consulting srl, Banatului 16, 600276, Bacau, Romania

^bCyprus Open University, Department of Applied and Pure Science, Environmental Conservation and Management Program, P.O.Box 12794, 2252, Latsia, Nicosia, Cyprus

Tel. +357-22411600; Fax:+357-22411601; email: antonis.zorpas@ouc.cy.ac, antoniszorpas@yahoo.com

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ABSTRACT

The heat of adsorption, the adsorption energy and the activation energy are of the most important and frequently calculated parameters in adsorption and ion exchange systems. However, in many occasions these parameters are not clearly defined, appropriate calculated or analyzed in the related literature. A characteristic example is the use of different limits used in order to identify a process as physisorption, chemisorption or ion exchange. The present paper aims at clarifying the nature of these parameters and their interrelationship in theoretical basis and to present the paradigm of ion exchange systems involving zeolites and cations as a case study. All basic theoretical issues are presented, analyzed and discussed with the support of a large number of experimental data in order to draw secure conclusions on several critical issues. In total 46 activation energy, 32 adsorption energy and 34 heat of adsorption experimental values are collected and discussed.

Keywords: Heat of adsorption; Adsorption energy; Activation energy; Ion exchange systems; Zeolites; Clinoptilolite

1. Introduction

The heat of adsorption, the adsorption energy and the activation energy are the most important, inter-related and frequently calculated parameters relevant to the thermodynamics of any sorption system [1,2]. Although the great developments in technological, analytical and computational methods is true that the literature is frequently less accurate and insightful than expected on some theoretical subjects. This is the case of the above-mentioned parameters, which in many cases are neither clearly defined nor appropriately calculated in the related literature [3].

Inevitably, the theoretical analysis should start from the fundamentals of the subject and this is the primary target of the present paper. Furthermore, a secondary target is to discuss and clarify the relevant limits found in the related literature, which are used for defining a process as physical or chemical sorption. As it is well known, the *heat of adsorption* in physisorption process is normally lower than 80 kJ/mol while in chemisorption higher than this limit [4,5]. Concerning the *adsorption energy*, if below 8 kJ/mol the phenomenon is defined as physical adsorption, if between 8–16 kJ/mol as ion exchange and if over 16 kJ/mol as chemical adsorption [6]. Furthermore, in physisorption process the *activation energy* is lower than 40 kJ/mol, while in chemisorption higher than this limit [7,8]. In purely ion

*Corresponding author.

exchange systems, the heat involved is usually less than 2 kcal/mol (approx. 8 kJ/mol) but a maximum of 10 kcal/mol (approx. 40 kJ/mol) has been observed. In such systems, the activation energy is between 6 and 10 kcal/mol (approx. 24–40 kJ/mol) and the adsorption energy in the limits of 8 to 16 kJ/mol [9–11]. It should be noted that all above limits are empirical and approximate and should be used as a first approach in any theoretical or model calculations.

The present paper aims at clarifying the nature of the heat of adsorption, the adsorption energy and the activation energy and their interrelationship in theoretical basis and to use the paradigm of ion exchange systems on zeolites. This review is limited in particular to the zeolite clinoptilolite, which is the most commonly used zeolite for cation exchange and raw data for the analysis are readily available. The analysis is focusing on possible differences between values derived from different theoretical or analytical approaches and the target is to define the limits of the parameters under investigation rather than analyzing in detail all aspects of the available studies and data. A large number of experimental values are used; 46 for activation energy, 32 for adsorption energy and 34 for heat of adsorption.

2. Theoretical considerations

2.1. Heat of adsorption

The nomenclature and the definitions found in the related literature for the enthalpy and isosteric heat are rather confusing [3]. By definition, the isosteric heat is the ratio of the infinitesimal change in the adsorbate enthalpy to the infinitesimal change in the amount adsorbed (m) under constant temperature and pressure [1,12]:

$$Q_{st} = \left(\frac{\partial Q}{\partial m} \right)_{p,T} \quad (1)$$

The isosteric heat (Q_{st}) may or may not vary with loading (q_{eq}) and is calculated from the following thermodynamic Clausius–Clapeyron Eq. (12):

$$\frac{Q_{st}}{RT^2} = - \left(\frac{\partial \ln P}{\partial T} \right)_m \quad (2)$$

The same equation can be adopted for the case of liquid phase adsorption [5]:

$$\frac{Q_{st}}{RT^2} = - \left(\frac{\partial \ln C_{eq}}{\partial T} \right)_{q_{eq}} \quad (3)$$

where, (R) the ideal gas constant, (T) the temperature and (C_{eq}) the equilibrium liquid phase concentration at constant solid phase concentration (q_{eq}). When this equation is applied on several equilibrium isotherm models, different isosteric heat expressions are derived. As is well known, if the isosteric heat of adsorption is independent of the amount sorbed then the surface is homogeneous and if it decreases or in general varies with the amount of solute adsorbed then the surface is heterogeneous.

A typical method to measure the isosteric heat is calorimetry. The equations may vary depending on the apparatus used, but for isothermal calorimeter is [13]:

$$-Q_{st} = \frac{Q + V\Delta P}{\Delta m} \quad (4)$$

where (Q) is the heat registered for an incremental dose of gas (Δm) introduced at the temperature of the cell and (V) is the dead space in the sample cell. Normally, the term ($V\Delta P$) is small compared to (Q). Since adsorption is exothermic (Q) is negative. The differential heat of adsorption (Q_{diff}) is defined as heat evolution when unit adsorption takes place in an isolated system and is measured by calorimeter [2]:

$$Q_{diff} = \frac{\Delta Q}{\Delta m} \quad (5)$$

As is evident, (Q_{st}) is bigger than (Q_{diff}) since it requires additional work equivalent to $pV(=RT)$ [2, 14]:

$$Q_{st} = - \frac{dQ}{dm} + RT = Q_{diff} + RT \quad (6)$$

Since the term ($V\Delta P$) is small compared to Q the isosteric heat is in many occasions expressed as equivalent to the differential heat, termed as *differential* or *isosteric heat*. Finally, the *differential molar enthalpy* of adsorption (ΔH_d) is also called *isosteric enthalpy of adsorption* [15]. Then we can summarize as follows:

$$Q_{st} = -\Delta H_d = Q_{diff} + RT \quad (7)$$

It should be mentioned that the heat of adsorption most frequently used is the isosteric heat, which is equal to the differential enthalpy (ΔH_d) only for an ideal gas [3].

Tarasevich et al. used a calorimetric method to measure the heat involved in an ion exchange system but the exact calculation method for the enthalpy, termed *standard enthalpy*, is not specified [16]. In another publication, Ahmad and Dyer studied ion exchange and they used the thermodynamic equilibrium constant in order to estimate the free energy (again termed as *standard*

enthalpy) and then the heat [17]. The situation became more clear in a later work of Tarasevich and Polyakov who conducted calorimetric studies on ion exchange equilibrium systems and calculated the heat evolved and the thermodynamic equilibrium constant [18]. The integral heat $Q_{\text{int}}(\theta)$ was first measured in the calorimeter and then the differential heat was calculated as

$$Q_{\text{diff}}(\theta) = -\frac{dQ_{\text{int}}(\theta)}{d\theta} \quad (8)$$

where (θ) is the fractional loading of the solid phase ($0 < \theta < 1$). Then, the integral enthalpy (ΔH_{int}) was calculated as:

$$\Delta H_{\text{int}} = \lim_{\theta \rightarrow 1} Q_{\text{int}}(\theta) \quad (9)$$

The above equation means that the integral enthalpy is the *maximum value* of the integral heat and is this type of enthalpy, which is used for the estimation of the thermodynamic parameters of the systems.

As is evident from the above discussion, several different terms are used in the literature and there is a difficulty to relate the several types of heat with the thermodynamics of the sorption systems. In order to clarify this issue we have to go back to the classic papers of Barrer et al. [19,20]. First of all the *standard heat of partial exchange is defined* (ΔH_x°), which corresponds to a certain level of sorbate uptake (x), and for $x=1$ the *standard heat of complete exchange* (ΔH°) is obtained. In the original work of 1963, Barrer et al. use a calorimeter for the determination of heat in an ion exchange system and they underline that (ΔH_x°) and (ΔH°) do not correspond to the experimentally measured heat and a number of additional calculations and corrections should be made. Is useful to mention here that different calorimeters use different methods and thus, they result in different types of heat. For $x=1$, the *standard free energy of exchange* (ΔG°) is defined and is related to the thermodynamic equilibrium constant (K_{eq}) as follows:

$$\Delta G^\circ = -RT \ln K_{\text{eq}} \quad (10)$$

where (R) is the ideal gas constant (8.3145 J/mol K). Then, the *standard entropy* (ΔS°) is evaluated by the formula:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (11)$$

Then, by combining Eqs. (10) and (11) and deriving the Van't Hoff equation [9]:

$$-\frac{\Delta H^\circ}{RT^2} = \left(\frac{\partial \ln K_{\text{eq}}}{\partial T} \right)_p \quad (12)$$

For two different temperatures:

$$\Delta H^\circ = \left(\frac{RT_1T_2}{T_2 - T_1} \right) \ln \left(\frac{K_{\text{eq},2}}{K_{\text{eq},1}} \right) \quad (13)$$

As is evident, the thermodynamic equilibrium constant is related to the standard heat of complete exchange ($x=1$) and thus, (ΔH°) is equivalent to the integral enthalpy (ΔH_{int}) defined by Tarasevich and Polyakov [18]. The evaluation of thermodynamic parameters such as (ΔH°) necessitates the definition of an equilibrium constant that is valid over a given concentration ranges, i.e., the thermodynamic equilibrium constant. As Shahwan et al. mention, this constitutes a problem in sorption systems, as there is lack of data of an equilibrium constant that might be used to describe the system in a wide temperature range [21]. In that study is underlined that this difficulty is partially solved by using empirical distribution constants:

$$K_{\text{dist}} = \frac{q_{\text{eq}}}{C_{\text{eq}}} \quad (14)$$

However, the distribution coefficient varies with the initial concentration and liquid/solid ratio and as a consequence, enthalpy values have to be averaged over the entire concentration range leading in a rough approximation. Alternatively, for adsorption systems the equilibrium constant can be defined as follows:

$$K_{\text{eq}} = \frac{a_a}{a_s} = \frac{\gamma_a q_{\text{eq}}}{\gamma_s C_{\text{eq}}} \quad (15)$$

where (a_a) and (a_s) the activity and (γ_a) and (γ_s) the activity coefficient of the solute in the solid and solution phase, respectively [22]. Khan and Singh proposed that as the solid phase concentration approaches zero, the activity coefficient becomes unity and then [22]:

$$\lim_{q_{\text{eq}} \rightarrow 0} \frac{q_{\text{eq}}}{C_{\text{eq}}} = \frac{a_a}{a_s} = K_{\text{eq},0} \quad (16)$$

Values of ($K_{\text{eq},0}$) are obtained by plotting $\ln(q_{\text{eq}}/C_{\text{eq}})$ versus (q_{eq}), and extrapolating to zero (q_{eq}). First, a straight line is fitted to the points based on least squares analysis; its intersection with the vertical axis provides the value of (K_{eq}). The same method is used by Gunay [23]. Some authors mention that ($K_{\text{eq},0}$) is the single point or linear sorption distribution coefficient and the resulting

enthalpy corresponds to the isosteric heat of adsorption with zero surface coverage (i.e., $q_{\text{eq}} = 0$) [24]. Then:

$$-\frac{\Delta H_{\text{do}}}{RT^2} = \left(\frac{\partial \ln K_{\text{eq},o}}{\partial T} \right)_p \quad (17)$$

The thermodynamic calculations based on this method do not consider the influence of the increasing surface coverage of the solid phase on the adsorption process. Thus, the values determined for the enthalpy only represent the ideal case of an unoccupied and homogeneous surface, i.e., they describe the forces at the beginning of the adsorption process and thus, they represent only a rough approximation [25].

Concluding, by use of the zero surface coverage the differential enthalpy at zero coverage (ΔH_{do}) is calculated which is different to the differential enthalpy or isosteric heat (ΔH_d) calculated for several coverage levels and the standard heat of complete coverage or integral enthalpy (ΔH°), which express the total heat generation for the complete exchange (or adsorption) and is related to the thermodynamic equilibrium constant. Finally, if the isosteric heat is constant (i.e., independent of the amount sorbed) then it can be measured by using either the whole equilibrium curve (equilibrium constant) or individual equilibrium points. In this case, the isosteric heat of adsorption with zero surface coverage, that many authors use, is equivalent to the isosteric heat calculated by use of any other point or the equilibrium constant. Another approach is to average the isosteric heat over the whole solid phase loading range, a method which could lead to a good approximation only if the variation of heat with loading is small.

2.2. Adsorption energy

The adsorption energy is related to the Dubinin-Astakhov (DA) adsorption isotherm [11]:

$$q_{\text{eq}} = Q_M \exp \left[- \left(\frac{\varepsilon}{E} \right)^n \right] = Q_M \exp \left[- \left(\frac{RT \ln \left(\frac{P_{\text{eq}}}{P_o} \right)}{\sqrt{2}E} \right)^n \right] \quad (18)$$

where E (J/mol) is the adsorption energy, (n) the heterogeneity parameter and (E) the solid characteristic energy towards a reference adsorbate. Benzene has been used widely as the reference adsorbate. For $n=2$ the well-known Dubinin-Radushkevich (DR) adsorption isotherm is derived. The theoretical analysis of this isotherm and its use in liquid adsorption and ion exchange systems has been presented by Inglezakis [11].

The DA and DR equations can be equally used in liquid phase adsorption and ion exchange by substituting (P_{eq}/P_o) with (C_{eq}/C_s), where (C_{eq}) is the equilibrium solute concentration and (C_s) its solubility. Inglezakis and co-workers have shown that DA equation should be preferably used in systems involving zeolites and other minerals as vermiculite and bentonite [11,26]. The analysis suggests that the simplified form of the DA adsorption isotherm which is used for ion exchange systems (DR adsorption isotherm) is not adequate for systems with a heterogeneity factor different than 2.

The isosteric heat of adsorption of the DR equation can be calculated from the Van't Hoff's equation and the result is [1]:

$$-\Delta H_d = \Delta H_{\text{vap}} + E \left(\ln \frac{1}{\theta} \right)^{0.5} + \frac{E\delta T}{2} \left(\ln \frac{1}{\theta} \right)^{-0.5} \quad (19)$$

where (ΔH_{vap}) is the latent heat of vaporization and (θ) the fractional loading of the solid phase. The parameter (δ) characterizes the change of the saturation capacity (Q_M) with respect to temperature [1]:

$$\frac{1}{Q_M} \frac{dQ_M}{dT} = -\delta \quad (20)$$

Although an empirical parameter, the adsorption energy is dearly relevant (analogous) to the isosteric heat and while in the general case the heat of adsorption and in lesser extent the activation energy depend on the solid phase loading, the adsorption energy is a constant and characteristic of the system and in practice it is considered as an average or representative value of the involved energy. Finally, the net heat of adsorption is the isosteric heat minus the heat of vaporization or, the heat of immersion for liquid phase adsorption.

2.3. Activation energy

Solid phase diffusion is an activated process and the diffusivity follows the Arrhenius equation [1]:

$$D_s = D_{s0} \exp \left(- \frac{E_a}{RT} \right) \quad (21)$$

As is evident, in order to calculate the activation energy kinetic experiments in two different temperatures are needed and the diffusion coefficients are derived by use of appropriate models. Frequently, activation energy is linearly related to the integral enthalpy as follows [2]:

$$E_a = -a\Delta H^\circ \quad (22)$$

The parameter (a) could be higher or lower than 1. It is interesting to mention that the activation energy is also related to the integral heat of adsorption as follows [1]:

$$E_{\text{des}} = E_a + \Delta H^0 \quad (23)$$

where (E_{des}) is the desorption activation energy. Frequently, the latter is much higher than the adsorption activation energy (E_a) and thus becomes approximately equal to the heat of adsorption.

As is well known, ion exchange is a physical phenomenon due to the absence of chemical reaction and the formation or dissolution of any chemical bond [9]. In some cases it might involve adsorption, internal precipitation and other phenomena, however ion exchange is undoubtedly a physical phenomenon, closer to physisorption than chemisorption or any other chemical phenomenon. However, in the related literature several reaction kinetic models are used to describe the kinetics of ion exchange, as the pseudo-first and pseudo-second order equations. As a general scientific rule, the use of simple theories and models goes together with pitfalls, which are encountered in their application, and the physical significance might be reduced in meaningless approximations [27]. As Levenspiel said in his famous *Chemical Reaction Engineering* book in 1972: "...if we choose a model we must accept its rate equation, and vice versa. If a model corresponds closely to what really takes place, then its rate expression will closely predict and describe the actual kinetics; if a model widely differs from reality, then the kinetic expressions will be useless" [28]. By this, is not meant that approximate models are useless but is important to underline that the models and equations used should have some strong relevance to the physical phenomenon under investigation. Concerning the case of ion exchange, as several studies have demonstrated, is basically a diffusion-controlled process and although it differs from adsorption they share many common aspects, enough to accept the use of the same simplified kinetic and equilibrium equations. An analysis and literature review on the simplified ion exchange models can be found in the work of Inglezakis and Grigoriopoulou [29].

3. Literature review

The present review is limited to zeolite ion exchange systems and in particular for clinoptilolite, which is the most commonly used zeolite for cation exchange and raw data for the analysis needed are readily available. The analysis and approaches presented in the previous sections of the paper are all used for the treatment of experimental data in the specific systems under investigation. It is important to mention that there is no specific trend in relation to the cations exchanged and in any case,

as always the case with natural minerals, is not possible to have detailed comparisons due to the differences of zeolite samples from different parts of the world. These are the reasons why the analysis is focusing on possible differences between values derived from different modeling/measuring approaches and the main target is to define limits range of the thermodynamic parameters rather than analyzing in detail all aspects of the available studies and data. The experimental data used are for the following ions: Li^+ , Ag^+ , Cr^{3+} , Fe^{3+} , Cu^{2+} , Co^{2+} , Zn^{2+} , Mn^{2+} , NH_4^+ , Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Ba^{2+} , Rb^{2+} , Ni^{2+} , Zi^{4+} , Sr^{2+} , Cs^+ , Cd^{2+} , Pb^{2+} , and the organic cations $[\text{CH}_3\text{NH}_3]^+$, $[(\text{CH}_3)_2\text{NH}_2]^+$, $[\text{C}_2\text{H}_5\text{NH}_3]^+$ [10,11,16,18,21,26,30–48].

3.1. Heat of adsorption

In total 34 experimental values of heat of adsorption are collected, of which 50% were derived by use of distribution coefficient method and are shown in black columns on Fig. 1. Obviously, the values derived from different methods seem to be in the same range, indicating that the approximate methods using the distribution coefficients are close to reality. Furthermore, is clear that ion exchange could be endothermic or exothermic with involvement of heat in the same levels. The range of –24 to 38 kJ/mol is within the limits found in the literature, which are lower than 80 kJ/mol for physisorption and lower than 40 kJ/mol for ion exchange systems.

3.2. Adsorption energy

In total 32 experimental values of adsorption energy are collected, of which 38% were derived by use of DR model and are shown in black columns on Fig. 2. As is evident, for the same cation, the values derived from DR model are lower and the maximum values are very close to the proposed range for ion exchange from the related literature (<16 kJ/mol). However, the lower limit of 8 kJ/mol frequently used in the literature is clearly not accurate as the adsorption energy could be as low as 0.6 kJ/mol. On the other hand, DA model results in adsorption energies in the range of 12–25 kJ/mol. Thus, at least for ion exchange, the limits of the adsorption energy are in the range of 0.6 kJ/ to 25 kJ/mol. Similar results for DA method were derived by Inglezakis et al, 2007 [11]. In particular, based on 22 experimental values for ion exchange of several cations on clinoptilolite, the average value of the adsorption energy was found to be 16.7 ± 3.21 with a range of 9.47–21.74 kJ/ mol.

3.3. Activation energy

In total 46 experimental values of activation energy are collected, of which 22% were derived by use of reaction kinetic models and are shown in black columns on Fig. 3. As no data are available for the same cation, with the exception

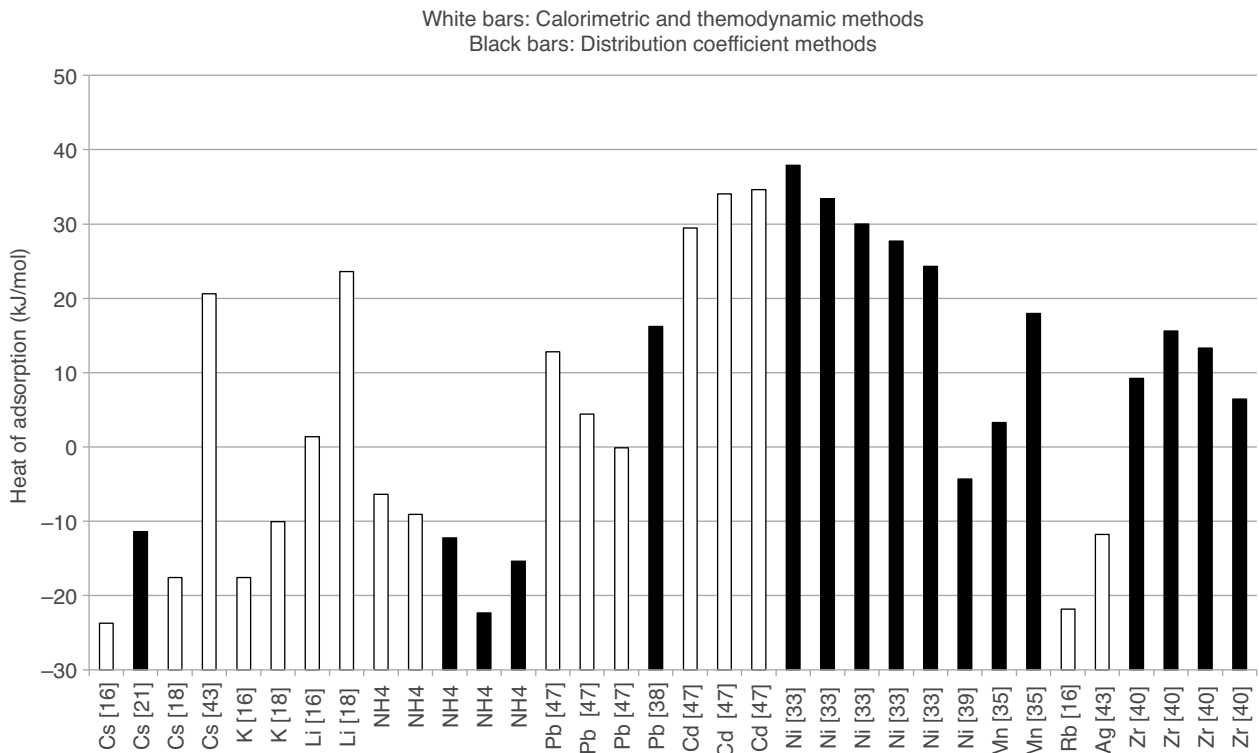


Fig. 1. Heat of adsorption in cation exchange on clinoptililite.

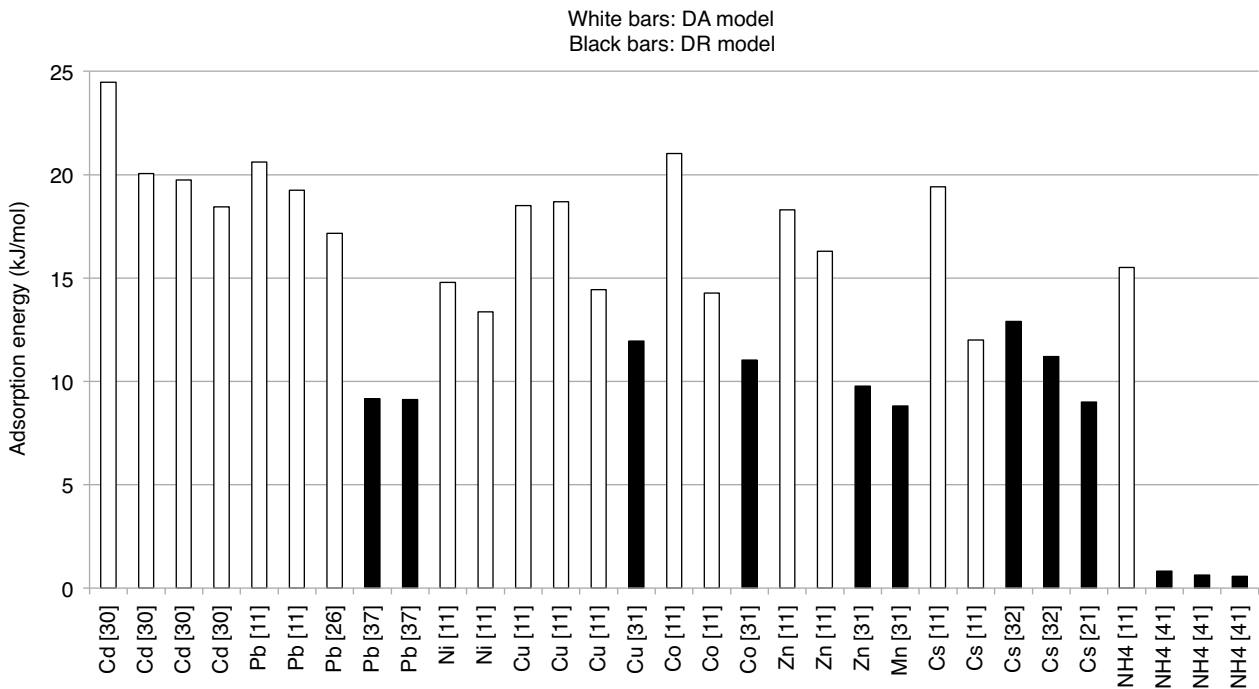


Fig. 2. Adsorption energy in cation exchange on clinoptililite.

of Cs, is not possible to derive conclusions on the trends for the two different methods, although the values calculated by use of reaction kinetic models seem to not cover the inter-

mediate range of 40–80 kJ/mol. Furthermore, about 81% of the values are below the higher limit of 40 kJ/mol found in literature while a considerable percentage of 19% of values

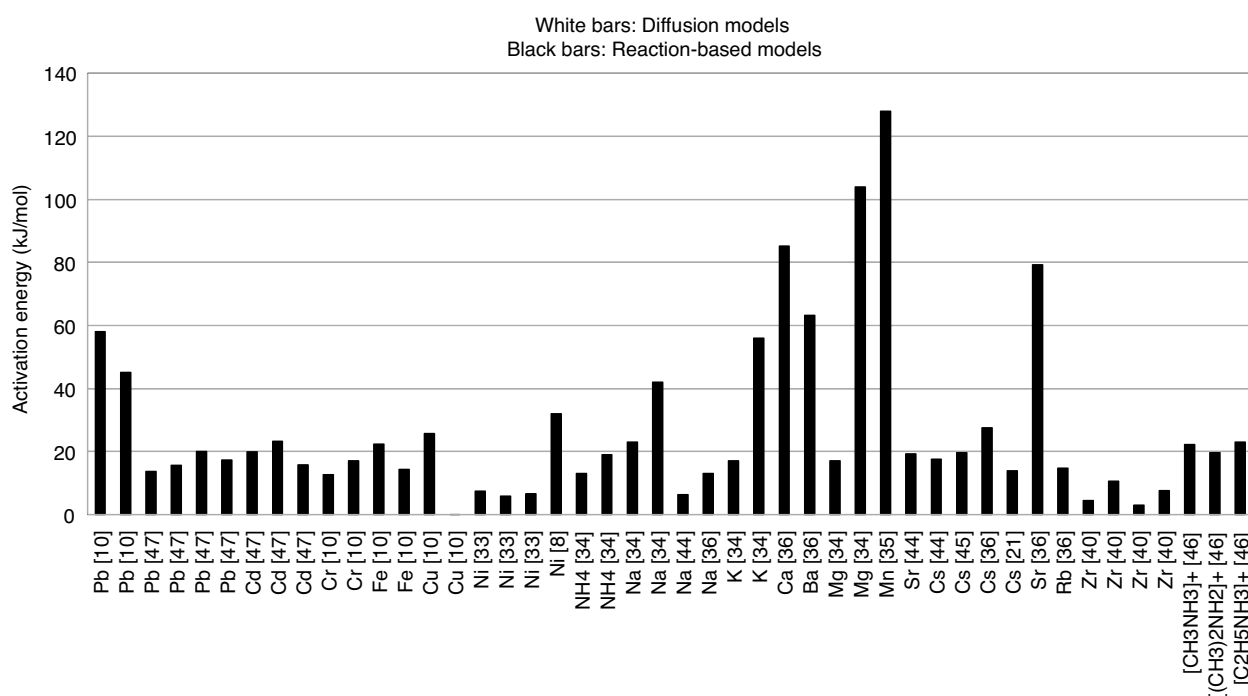


Fig. 3. Activation energy in cation exchange on clinoptilolite.

are higher. However, it should be mentioned that the general literature limit of 40 kJ/mol represents the case of meso- to macroporous materials. In microporous materials as zeolites the pore sizes are smaller than 20 Angstrom and compared to the gas phase the diffusivity of the molecules inside the zeolite channels is greatly reduced and a much stronger temperature dependence of diffusion coefficients is often observed. This regime of restricted diffusion is called *configurational diffusion* and activation energy could reach values even higher than 100 kJ/mol [49]. Going back to the collected data, approximately 96% of the values are lower than 80 kJ/mol and low values as much as 0.2 kJ/mol are found. Thus, the proposed limits are 0.2–80 kJ/mol, quite normal for diffusion of ions in the small zeolite pores.

The results of the above analysis are summarized in Table 1.

Table 1
Parameters limits

	Heat of adsorption (kJ/mol)	Adsorption energy (kJ/mol)	Activation energy (kJ/mol)
Physisorption	< 80	< 8	< 40
Ion exchange	< 40	8–16	24–40
Chemisorption	> 80	>16	> 40
Ion exchange in zeolites (current study)	–24 to 38	0.6 to 25	0.2 to 80

4. Conclusions

In the present paper three of the most important parameters in sorption systems are examined, i.e., the heat of adsorption, the adsorption energy and the activation energy. The theoretical analysis and literature review show that several theoretical approaches and experimental methods are used for the determination of these fundamental parameters, which are not always accurate, partly due to the relevant confusion in the definition of these parameters. Following the theoretical analysis, the relevant limits found in the related literature which are defining the processes as physical or chemical sorption are discussed and the case study of ion exchange on zeolites is presented. Summarizing the theoretical analysis, it can be said that the differential enthalpy at zero coverage (ΔH_{do}) is important to be distinguished from the differential enthalpy or isosteric heat (ΔH_d) and the standard heat of complete coverage or integral enthalpy (ΔH^0) which expresses the total heat generation for the complete exchange (or adsorption) and is related to the thermodynamic equilibrium constant. In the case of adsorption energy and the activation energy the difficulties are coming from the estimation methods and models used and it is concluded that the DA model and diffusion kinetic models are appropriate, respectively. In total 112 experimental values are collected and analyzed. The results show that ion exchange could be endothermic or exothermic with involvement of heat of adsorption in the range of –24 to 38 kJ/mol,

while the adsorption energy limits are found to be in the range of 0.6 kJ/ to 25 kJ/mol. For the activation energy the higher limit of 40 kJ/mol found in literature is in agreement with the 81% of the values, however this limit is not taking into account that in many cases in microporous materials the diffusion is restricted and the activation energy could be even higher than 100 kJ/mol. Thus, the limits of 0.2–80 kJ/mol are proposed as approximately 96% of the experimental values fall within this range.

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