RELATION BETWEEN IMMERSION ENTHALPY AND THE ACIDITY OF CLAY PILLARED MINERALS

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Total acidity for a series of modified clays obtained from a natural vermiculite is determined through temperature programmed desorption (TPD) using ammonia as probe molecule. Results obtained for the acidity range from 15.1 to 68.5 meq/100 g.

Immersion enthalpies of the clays in benzene, water and aqueous solutions of NH_3 0.058 M and $NaHCO_3$ 0.053 M are determined. The results obtained show that immersion enthalpies in benzene and water are between -6.26 and -25.6 J g^{-1} and -2.10 and 5.55 J g^{-1}, respectively and are smaller than the values obtained for the immersion enthalpies in the solutions.

Immersion enthalpy values in NH_3 solution are greater than the obtained using $NaHCO_3$. Linear relations between the total acidity of the clays and the immersion enthalpies in the basic solutions are determined.

An interaction factor using ammonia is calculated since the relation between the immersion enthalpy in ammonia solution and in water and it may be deduced that the relation with the total acidity is of second order tendency between them.

Keywords: *acidity, clay minerals, immersion calorimetry, TPD*

Introduction

Acidic surfaces have the ability to generate carbonium ions, which may be formed by the addition of a proton to a non-saturated hydrocarbon molecule or by the abstraction of a hydride of a saturated hydrocarbon. However, for evaluating the acidity of a surface, it is required to determine its nature, strength and acid sites number [1]; therefore, during the characterization of the acidity is necessary to use different techniques that allow getting this information. Some of the techniques for assessing acidity, directly or indirectly, are: aqueous methods, ion-exchange methods, titration of the aqueous solutions of the acid solids, titration using amines and adsorption of indicators in non-aqueous liquid phase, IR spectrophotometry, electronic spin resonance, ESR, UV spectrophotometry, RMN, calorimetric determination of the immersion and adsorption heats and desorption at programmed temperature, TPD [2]. These techniques do not provide the same specific information but they are complementary to each other and allow establishing relations.

One of the commonly used methods for determining the total acidity of acid solids is the desorption at programmed temperature of a probe molecule, i.e. $NH_{3(g)}$, due to its basic character and small size, that allow it to interact with many of the acidic sites involved in different processes [3, 4]; other works used as adsorption compound *n*-hexane to obtain TPD profiles and associate them with the acidity of adsorbent [5].

Once the clays are modified through the introduction of metals in its structure, an increase of total acidity takes place and make clays useful in linear paraffin hydroisomerization reactions, hydrocarbon hydrocraking, phenol hydroxylation, transformation of methanol to hydrocarbons, ethers synthesis, etc. [6–8].

Modified clays by ion-exchange pillarization are porous solids that show a characteristic immersion enthalpy at specific conditions. When a solid is immersed in a liquid which no reaction takes place with, some quantity of heat is generated and this immersion enthalpy is related with the formation of a layer of molecules absorbed on the solid surface.

In general, immersion enthalpies of a solid in different liquids, differ; because this is not only related with the superficial area that the liquid utilizes but the specific relations between the solid surface and the immersion liquid [9, 10]. Through the immersion calorimetry, it is possible to establish the relations between the heat generated due to the solid-liquid contact and the superficial areas of the porous solids, i.e. immersing the solid in a solvent, usually, non-polar. The relation between the superficial area and the immersion enthalpy is determined through mathematical models developed by Dubinin and Stoeckli [11, 12].

In the same way, when information is required about the thermal effects between solid and liquid, solutions of acid, bases and other solutes may be used in order to obtain the energetic interaction with functional groups that are present on the solid surface. It is then

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possible to link the total acidity of an acid solid, with the enthalpy generated due to the immersion of the clay in an aqueous phase which contains the probe molecule, NH_3; heat generated by the immersion of the clay in NH_3 aqueous solution, is related with the acidic active sites number contained in the solid [11, 13].

In the present work, the total acidity of seven clay materials is determined. The raw material is a natural vermiculite, which may be modified by different methods [14–16]. This acidity is obtained by $NH_{3(g)}$ desorption at programmed temperature. In the same way, N_2-adsorption isotherms for each clay, superficial area and immersion enthalpy of the solids in benzene, water and aqueous solutions NH_3 0.058 M and $NaHCO_3$ 0.053 M are determined. Using the obtained results, correlations are established.

Experimental

Materials and methods

Clay minerals characterized in this work, are vermiculites that have been previously modified by ion-pillarization exchange [14–16]. Each sample, the treatment applied to them and their denomination in accordance with the treatment, are summarized in Table 1. Before determination was carried out, samples were dried in a stove at 383 K.

Table 1 Clays used for the study of total acidity and immersion enthalpy

Treatment	Denomination
Vermiculite natural	Verm
Vermiculite modified with aluminium and cerium	AlCeV
AlZrV (mt). Vermiculite modified with aluminium and zirconium by the traditional method	AlZrV(mt)
AlV(mt). Vermiculite modified with aluminium by the traditional method	AlV(mt)
Hydrothermal treatment at 150°C – combined pillar–vermiculite modified with silicon and aluminium. Later hydrothermal treatment at 150°C	THT150
Hydrothermal treatment at 300°C – combined pillar–vermiculite modified with silicon and aluminium. Later hydrothermal treatment at 300°C [13]	THT300
Hydrothermal treatment at 150°C – aluminium pillar–vermiculite modified with silicon and aluminium. Later hydrothermal treatment at 400°C [13]	THT400
AlV (calcinada). Vermiculite modified with aluminium by the traditional method	AlV(cal)

Total acidity determination

The determination of the total acidity for each clay was carried out by the Temperature Programmed Desorption, TPD, with ammonia, using a CHEMBET 3000. In a glass cell, a sample of approximately 0.07 g is set out and a N_2 current is passed through at a heat rate of 373 K/15 min until it reaches a temperature of 673 K. Sample temperature is kept constant for 1 h. After that, the sample is taken to a temperature of 423 K, in which $NH_{3(g)}$ adsorption of grade AP takes place. Once the adsorption is finished, the $NH_{3(g)}$ desorption occurs from room temperature to a final temperature of 673 K. The quantity of $NH_{3(g)}$ desorbed is recorded by the Quantacrome Corporation® software.

Superficial area determination

The superficial area of each sample is determined using an AUTOSORB 03B. Between 5–100 mg of sample were weighed. The preparation of the sample included: Degasification at a constant temperature of 573 K for 3 h, which is reached at a warming speed of 25 K min^{-1}. Adsorption isotherms were carried out using N_2 at 77 K.

Immersion enthalpy determination of the clay minerals

In the present work, immersion enthalpies of the modified clays in different calorimetric liquids, benzene, water and aqueous solutions of 0.058 M NH_3 and 0.053 M $NaHCO_3$, are determined for the estimation of the energetic interactions when the solid is in contact with the solutions of these compounds. A heat conduction microcalorimeter equipped with a calorimetric cell made of stainless steel is used for the determination of the immersion enthalpies [13]. Inside the cell, approximately 10 mL of the respective solution is set out (previously kept at 298 K in a thermostat). A 50–100 mg clay sample is put in a glass bulb point inside the calorimetric cell and the microcalorimeter is assembled. When the device reaches a temperature of 298 K, it starts to record the output potential for approximately 15 min, taking data of potential every 20 s. After that, the glass bulb breakage takes place and the generated thermal effect is recorded while the potential readings continue for 15 min more. Finally, the device gets calibrated electrically. Through the electrical calibrations achieved for this work, a constant of the calorimeter, K, has been determined: 16.23 ± 0.37 W V^{-1}.

Results and discussion

The obtained results for the total acidity of each sample by the TPD method with ammonia and the superficial area value from the N_2 isotherms at 77 K data are summarized in Table 2.

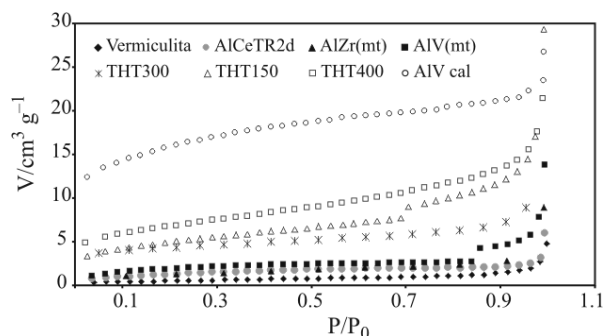**Table 2** Total acidity determination and superficial area of the clay minerals

Sample	Total acidit/ meq 100 g	Superficial area/ $m^2\ g^{-1}$
Verm	15.1	2
AlCeV	68.5	5
AlZrV(mt)	44.4	6
AlV(mt)	51.6	7
THT150	53.6	15
THT300	52.1	17
THT400	47.7	23
AlV(cal)	–	51

Fig. 1 N_2-adsorption isotherms at 77 K of the modified clays

The treatments carried out on the natural vermiculite modify both the total acidity value and the superficial area, showing higher values for the samples on which the hydrothermal treatments were applied at diverse temperatures. The greatest increase in acidity, 68.5 meq/100 g, and a reasonable superficial area modification, 5 $m^2\ g^{-1}$, corresponds to AlCeV. The AlV(cal) total acidity was not determined by the TPD method. The results of surface area can be compared with the values obtained for a vermiculite Spanish that present values of surface area of about 20 $m^2\ g^{-1}$ [17].

N_2-adsorption isotherms at 77 K of all studied clay materials are shown in Fig. 1. It may be seen from plots that vermiculite showed the lowest N_2-adsorption maintaining a similar volume through the scanning of relative pressures and it increases to a value nearby to 4 $cm^3\ g^{-1}$ as the relative pressure becomes 1. The greatest adsorption value is shown for the sample modified with Al, AlV(cal), from which the greatest superficial area value was also obtained: 51 $m^2\ g^{-1}$.

Immersion enthalpy provides information about clays physico-chemical characteristics, related with total acidity and texture, and because of this, different immersion liquids are used to allow the adsorber to specifically interact, i.e. NH_3, $NaHCO_3$ and water or to

have a physical interaction with a non-polar solvent, as the benzene. Immersion enthalpy in water is determined for subtracting its value from the immersion heat in $NaHCO_3$ and NH_3 solutions in order to find the net effect that the basic probe compounds produce, so the net immersion enthalpy will be, $\Delta H_{net\ imm}$:

$$\Delta H_{imm\ basic\ sln} - \Delta H_{imm\ water} = \Delta H_{net\ imm}$$

The net immersion enthalpy, $\Delta H_{net\ imm}$, depends exclusively on the interaction of the base with acid sites of the solid [11]. The immersion enthalpy in water was determined in order to establish whether the interaction between the solvent and the solid is important enough to not allow seeing the differences with NH_3 and $NaHCO_3$. On the other hand, when an immersion liquid as benzene is used, which solid have no chemical but physical interactions with, information about texture of the solid becomes a focus of interest.
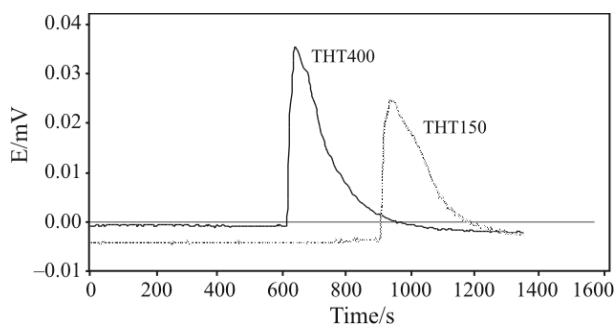
Immersion enthalpies results of the modified clays in different immersion calorimetric liquids: benzene, water, NH_3 0.058 M and $NaHCO_3$ 0.053 M in J g^{-1}, are summarized in Table 3.

Curves obtained for the immersion in benzene of the samples THT150 and THT400 are shown in Fig. 2. The heat generated when solid enters in contact with the liquid produces a peak which area under the curve is proportional to the quantity of the heat of the interaction.

Table 3 Immersion enthalpies of the modified clays in different calorimetric liquids

Sample	$-\Delta H_{imm}^{a}$ in benzene/	$-\Delta H_{imm}^{a}$ in water/	$-\Delta H_{imm}^{b}$ in NH_3 0.058 M/	$-\Delta H_{imm}^{b}$ in $NaHCO_3$ 0.053 M/
		J g^{-1}		
Verm	6.26±0.38	3.37±0.70	65.57±2.20	62.88±5.60
AlCeV	8.77±0.39	2.15±0.90	47.55±5.50	20.85±0.10
AlZrV(mt)	6.67±0.26	4.89±0.83	22.43±1.30	13.67±1.70
AlV(mt)	8.60±0.34	5.55±1.20	30.61±4.40	21.91±4.60
THT150	6.66±0.42	3.11±0.50	30.72±3.10	13.40±0.39
THT300	7.85±0.46	3.19±0.62	30.21±3.10	14.73±5.30
THT400	8.72±0.40	2.10±0.41	25.17±3.80	13.41±0.36
AlV(cal)	25.60±2.97	2.65±0.35	60.96±1.10	16.00±2.90

[a]Average of three determinations. [b]Average of five determinations

Fig. 2 Curves of the immersion of the clays THT150 and THT400 in benzene at 298 K
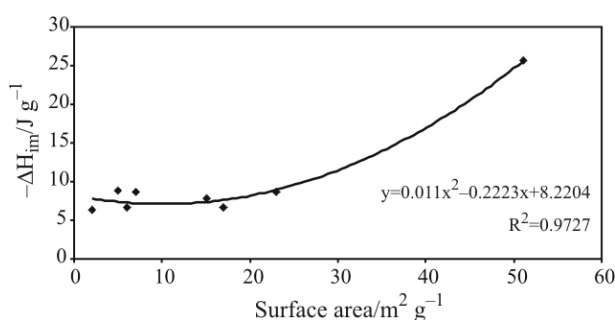
Fig. 3 Immersion enthalpy of the clays in benzene in function of superficial area

From results, it may be seen that immersion enthalpies of the clays in benzene, solvent in which physical interactions are evident, are exothermal and show values that range between -6.26 and -25.60 J g^{-1}, which are small values and agree with the previously obtained for the superficial area of the clays. The highest value for these determinations is for AlV(cal) and also shows the greatest superficial area value, 51 m^2 g^{-1}. Immersion enthalpies in water are smaller in all cases and range between -2.10 and -5.55 J g^{-1}, being AlZrV(mt) the clay with the highest value. In Fig. 3, the relation between immersion enthalpy of the clays in benzene and their superficial areas is graphed.

From relation between immersion enthalpy in benzene and the superficial area of the clays, a second order function, with a correlation coefficient, R^2 of 0.973, is obtained, suggesting that the superficial area and immersion enthalpy are directly proportional for the studied clays and that immersion enthalpy of a solid in a certain liquid constitutes a parameter for characterization. In a previous work the immersion enthalpies of activated carbons in CCl$_4$ are determined, these solids present values of surface area greater than the clay and the immersion enthalpies are between 31 and 49 J g^{-1} [18].

For all samples, immersion enthalpies in ammonia and sodium bicarbonate solutions are higher for the NH$_3$ 0.058 M than for NaHCO$_3$ 0.053 M solutions, indicating that energetic interactions are stronger with the ammonia, compound that is also used for the acidity determination by TPD. Interactions with basic solutions are stronger than with water, suggesting that solvent influence is smaller. Information about the intensity of the interaction between the acid sites of the solid and the liquid solution can be obtained. The values of acidity that are obtained for the clays used in this work are comparable with other, that appear in determinations for TPD for montmorillonite pillared with aluminum and copper polyhydroxycations, that are between 0.1 and 0.4 mmol g^{-1} [19].
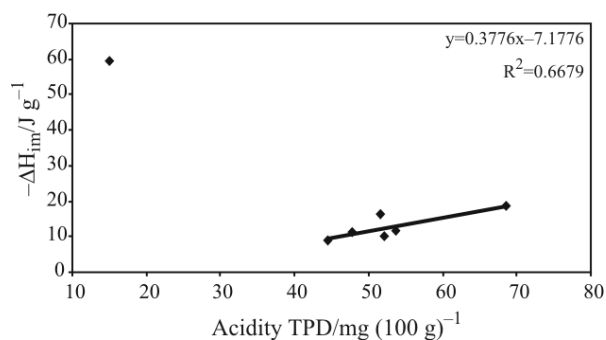
Once immersion enthalpy of the mineral clays is determined, the process is more exothermic as the total acidity of the sample increases. Besides, there is a linear relation between the net immersion heat in the NH$_3$ 0.058 M solution and the total acidity determined by NH$_{3(g)}$ desorption at programmed temperature. As the process becomes more exothermic, there is a greater energetic interaction between the adsorber and the adsorbate, which in this case and in agreement with the nature of the solids, is attributed to the contact of the acid sites of the solid with the probe molecule [20]. In Fig. 4, relation between net immersion enthalpy in ammonia solution, $\Delta H_{\text{net imm}}$ as a function of the total acidity is shown.

For the samples assessed, net immersion enthalpy in ammonia is directly proportional to the quantity of acid sites present on the solid; so the most acidic sample, 68.5 meq/100 g AlCeV, is the one with the highest net immersion heat value, 48.40 J g^{-1}. On the other hand, AlZrV(mt), the less acidic, has the lowest net immersion heat, -17.54 J g^{-1}. It is important to note that the natural vermiculite does not follow this tendency since it is the less acid of all samples studied, so produces a higher enthalpic interaction (Fig. 4). Furthermore, it deviates from linear behaviour of the rest of the samples, maybe due to the several polar groups of the hydroxyl kind in its structure that may interact with the NH$_3$ in solution due to the hydrogen bonds formation.

Through the linear relation established, it is possible to monitor the modification of a clay determining the heat generated when the solid is submerged in a solution containing a basic probe molecule because
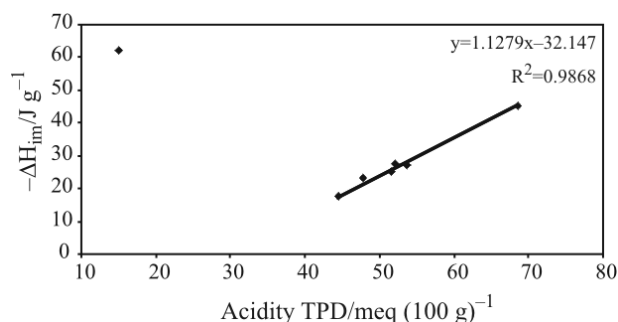
Fig. 4 Net immersion enthalpy of the clays in ammonia solution *vs.* total acidity

Fig. 5 Net immersion enthalpy of the clays in sodium bicarbonate solution *vs.* total acidity

Fig. 6 Relation between net immersion enthalpies in the NH_3 and $NaHCO_3$ solutions

the increase in the immersion enthalpy indicates that there is a higher number of acid sites available to interact with the base.

Figure 5 shows the relation between the net immersion enthalpy in $NaHCO_3$ 0.053 M solution and the total acidity of the samples. The tendency is similar to the obtained for the case of the samples immersion in ammonia solution. It may be seen that, again, the vermiculite deviates from linear behaviour of the modified clays. Similarly, the experimental plots are more scattered, with a correlation coefficient, R^2 of 0.669, than in Fig. 4. The slope also presents a smaller value, indicating that the change in enthalpy with regard to the acidity is smaller when the studied solids are in contact with the sodium bicarbonate solution and a difference between the interaction produced among the acid sites of the solids and the two basic compounds of interest is established.

Since the difference observed between the net immersion enthalpies for the NH_3 and $NaHCO_3$ solutions, the relation found for the results obtained in Fig. 6 is shown. It may be seen that experimental results are correlated and fit a second order tendency. However, some of the data deviate from the tendency, such as the case of the AlVcal sample for which net immersion enthalpy in $NaHCO_3$ solution presents a small value: -13.38 J g^{-1} regarding the curve outlined in the graph, such clay, AlVcal, and the vermiculite show behaviours that differ from those of the rest of the set, both in immersion heats and in superficial area.

Given that the enthalpic interaction of the solids with the calorimetric liquid is related with the physical surface and acidic groups; in Fig. 7, relations between immersion enthalpies in the basic solutions and the superficial area of the modified clays are shown.

The relations between superficial area and immersion enthalpy in NH_3 solution is represented by the diamonds and corresponds to the superior curve. Although the correlation coefficient is 0.629, it may be seen that the set of clays fit to the tendency proposed in the curve, indicating that even when the immersion enthalpy is mainly ascribable to the interac-
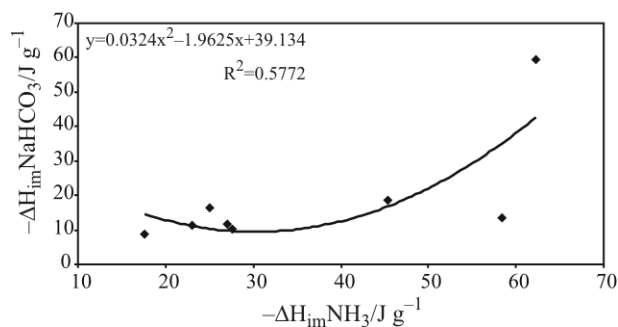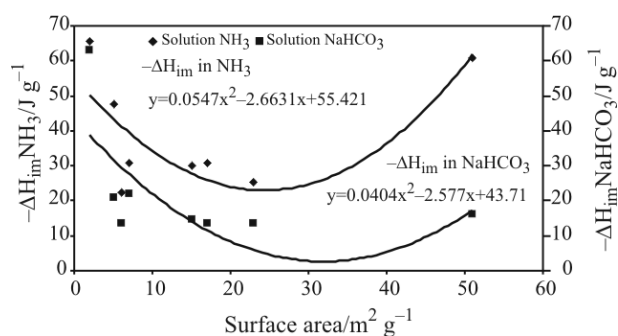

Fig. 7 Relation between immersion enthalpies in the basic solutions and the superficial area of the clays

tion with the acidic groups, it is also influenced by the superficial area that the clays show.

The plots for the immersion enthalpy in $NaHCO_3$ solution and the superficial area correspond to the squares and to the inferior curve. In this case, the plots are more scattered but the tendency is similar to the obtained with the ammonia solution. The graphs in Fig. 7. show that the immersion enthalpies in the basic solutions do not depend only on the superficial area but on another kind of interactions present among the solid, solvent and the solutes in solution.

Finally, a factor between the immersion enthalpy of the clays in NH_3 0.058 M solution and in water is calculated, indicating that the interaction with the clay increases when the immersion liquid contains the
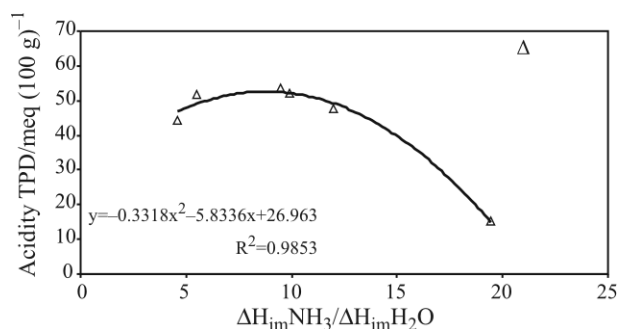
Fig. 8 Total acidity of the clays as a function of the NH_3 interaction factor

probe solute. The total acidity, determined by ammonia desorption is related with this factor and results are represented in Fig. 8.

The relation between the total acidity and the NH_3 interaction factor for the studied clays shows a second grade tendency with an optimum correlation coefficient (0.9853) that groups the set of clays with exception of the AlCV sample, which total acidity value is the highest one (68.5 meq/100 g) and immersion enthalpy value in water is the lowest one.

Conclusions

The enthalpic interaction of eight samples of clays, a natural vermiculite and materials modified by different treatments using different immersion liquids is determined. For the case of the immersion in benzene, immersion enthalpies ranging between –6.26 and 25.6 $J\ g^{-1}$ were found. Those are related with superficial interactions with the clays and values for their superficial areas are determined (2 to 51 $m^2\ g^{-1}$). Results are congruent because while superficial area values increase, immersion enthalpy in benzene does too.

Values for the immersion enthalpies in water, NH_3 0.058 M and $NaHCO_3$ 0.053 M solutions represent specific energetic interactions and for the case of the solutions, are higher than for water and benzene. Comparing the obtained values for both solutions, it may be seen that these are higher for the ammonia solution, which establishes a difference between the interaction of each base with the clays.

The total acidity of the clays is determined by TPD using $NH_{3(g)}$ as probe molecule. Obtained results are between 15.1 and 68.5 meq/100 g and are linearly related with the immersion enthalpies in NH_3 and $NaHCO_3$ solutions.

Immersion enthalpies in the basic solutions are related with each other through second order tendencies. In the same way, each result is graphed as a function of the superficial area of the solids.

An ammonia interaction factor is calculated. This is a relation between the immersion enthalpy of the clays in ammonia and in water, for which values between 4.58 and 22.1 are obtained. The factor also correlates immersion enthalpy with the total acidity for the set of the studied clays, except for the clay that show the highest total acidity.

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