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Energetic Surface Heterogeneity of Illites and Kaolinites†

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The surface properties of six clay samples (three illites and three kaolinites formed under different geological conditions) were evaluated by inverse gas chromatography at finite concentration conditions. The determination of the adsorption isotherms for several organic probes, hexane, benzene, pyridine, and 2-propanol, on these clays allows the estimation of their energetic surface heterogeneity through the determination of their adsorption energy distribution functions. It was then shown that, when the organic probe is well chosen, this method allows distinguishing between the family of clay, illite or kaolinite, and even, in a same family, between the different geological formation conditions. The illite samples are more heterogeneous than the kaolinite samples.

I. Introduction

As phyllosilicates, illites and kaolinites crystals exhibit basal and lateral surfaces giving them a macro-heterogeneous character on a molecular scale. As natural products, they contain mineral impurities, such as quartz, iron oxides, and aluminum oxides, that contribute to their surface heterogeneity too. Consequently, their surface heterogeneity will possibly vary according to their geological formation condition depending therefore on their geographical origins.

This surface heterogeneity has, of course, practical consequences. For instance, limited yield of oil recovery arising during petroleum exploitation involves the interaction of pore-filling fluids with the minerals that constitute the oil reservoir walls.¹ Among them, due to their high specific surface area and electrical charge density, clay minerals such as illites and kaolinites,² are the most active. Their water or oil wettability properties and thus their surface energies, are believed to be in relation with the heavy oil ends retention process as shown elsewhere.³

But it is not easy to measure the surface energy of divided solids with standard methods such as the liquid contact angle evaluation on an oriented clay deposit⁴ or to evaluate this liquid contact angle value from the ascending capillary rise rate of a liquid penetrating into a capillary column packed with the clay.⁵ Surface properties may be more readily established by inverse gas chromatography (IGC) at infinite dilution conditions. Hence, the dispersive component of the surface free energy (γ_s^d), as well as the morphological index (I_m) of the clays were determined.⁶ It is shown that the high values of γ_s^d (from 120 to 220 mJ/m²) obtained by this technique and correlatively the lower values of I_m were due to the surface nanorugosity and proof of the existence of an important

Table 1. Origin and Formation Conditions of the Clay Samples

family	origin	formation condition	denomination
illite	Vosges (France)	heritage	I-h
illite	Szabadság (Hungary)	neof ormation	I-n
illite	Brive (France)	agradation	I-a
kaolinite	Charentes (France)	heritage	K-h
kaolinite	Ploemeur (France)	neof ormation	K-n
kaolinite	Provins (France)	agradation	K-a

surface heterogeneity. These apparent γ_s^d values are more superior for kaolinites than for illites. These differences are certainly connected to the surface heterogeneity of the clays. The heterogeneity of the clay surface may be assessed using IGC at finite concentration conditions.

This last technique has proved to be a powerful and most suitable method for evaluating the energetic surface heterogeneity of powdered solids like micas,⁷ H-magadiite,⁸ carbon blacks,⁹ or talc.¹⁰

II. Experimental Section

Clays. Three modes of clay minerals genesis are known:¹¹ heritage, transformation (degradation, agradation), and neof ormation. For each type of formation, we selected one illite and one kaolinite sample. The origins of the selected samples, as well as their denomination, are given in Table 1. The way of preparation and purification of the clays is based on the Robert and Tessier method¹² and was presented in a previous paper.¹³ The crystallographic nature of the minerals was checked by X-ray diffraction. The specific surface areas (S) of the samples, outgassed at 120 °C, were determined from nitrogen adsorption isotherms and application of the BET theory. The cation exchange capacities (CEC) were estimated using Glaeser's method,¹⁴ which is based on the evaluation of the exchangeable protons of acidic clays by NaOH. The hydroxyl surface group density of the clay samples was established by a radiochemical method based on an esterification reaction using ¹⁴C labeled

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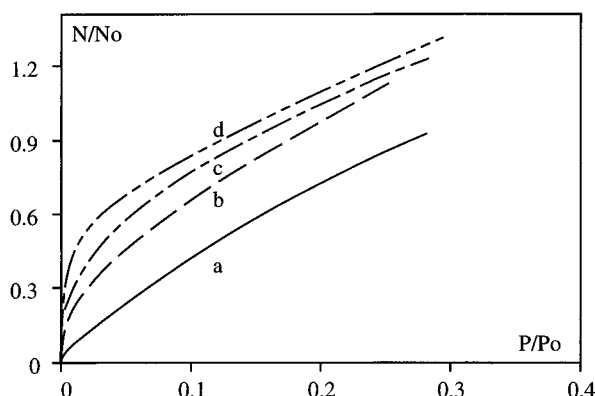
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Table 2. Specific Surface Areas (*S*), Cation Exchange Capacities (CEC), and Hydroxyl Surface Densities (OH/nm²) of the Clay Samples

samples	<i>S</i> (m ² /g)	CEC (mequiv/100 g)	OH content (OH/nm ²)
I-h	30 ± 1	9.4 ± 0.5	3.1 ± 0.3
I-n	37 ± 1	22.8 ± 0.5	6.2 ± 0.3
I-a	124 ± 2	23.2 ± 0.5	1.9 ± 0.1
K-h	21 ± 1	3.5 ± 0.5	1.7 ± 0.3
K-n	14 ± 1	2.2 ± 0.5	1.6 ± 0.5
K-a	40 ± 1	14.3 ± 0.5	3.6 ± 0.2

**Figure 1.** Reduced adsorption isotherms of (a) hexane measured at 33 °C, (b) benzene measured at 57 °C, (c) pyridine measured at 84 °C, and (d) 2-propanol measured at 43 °C, on the Charente kaolinite sample.

ethanol, following a method developed in our laboratory for the determination of the hydroxyl surface group density of silicas.¹⁵

Inverse Gas Chromatography. Since the size of the clay particles is too small (diameter below 2 μm) for making directly chromatographic supports, clay pellets were prepared by powder compression, under a pressure of 10⁸ Pa. The pellets were then hand crushed and sieved to select the fraction of particles having diameters between 250 and 400 μm. Then, the particles were introduced in a stainless steel column, 30 cm long and 3 mm in diameter. A commercial gas chromatographic apparatus (Intersmat, model IGC 120 DFL), equipped with a highly sensitive flame ionization detector, was used for this study. Helium was selected as carrier gas at a flow rate of about 25 mL/min. All employed solute probes were purchased from Aldrich. They were of chromatographic quality needing no further purification. A few microliters of liquid organic probe was injected into the column, allowing to work at finite concentration conditions. IGC experiments were performed in dry conditions (the carrier gas is connected to the chromatograph through a column filled with a dessicant).

III. Results

Characterization of Clays. The values of the specific surface areas (*S*), cation exchange capacities (CEC), and surface hydroxyl densities (OH/nm²) are summarized in Table 2. It is seen that the illite sample (I-a) has a specific surface area significantly higher than those of the other samples, like the kaolinite sample (K-a) also generated by aggradation. Concerning the cation exchange capacities, there is no direct correlation between *S* and CEC. It is also noticeable that the illite samples display a higher value of CEC than the kaolinite samples. This is explainable by the possibility of isomorphic substitution in the illite family, inducing a global negative charge balanced by exchangeable cations. We may further point out that the hydroxyl density of kaolinites is superior to that of illites: a result explainable since kaolinites possess aluminol groups also on the basal planes.¹⁶

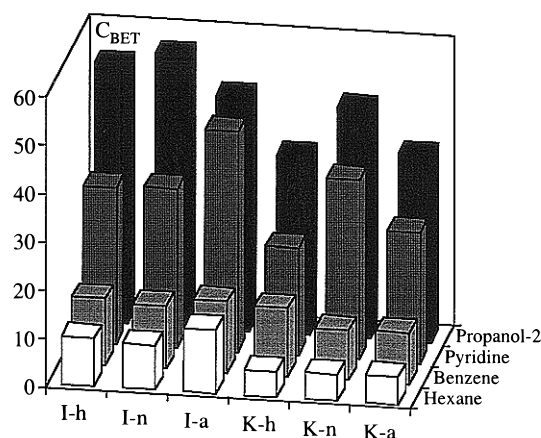
Table 3. Specific Surface Areas Measured by Nitrogen or Organic Probe Adsorption

	<i>a</i> (Å ²)	I-h	I-n	I-a	K-h	K-n	K-a
N ₂	16	30	37	124	21	14	47
hexane ^a	51	35	44	137	27	17	63
benzene ^a	40	38	51	164	23	16	54
pyridine ^a	38	54	95	293	36	29	92
2-propanol ^b	39	40	57	154	28	19	62

^a Reference 17. ^b Reference 18.

Table 4. Values of the BET Constant Measured on the Clays with the Different Organic Probes

	<i>t_m</i> (°C)	I-h	I-n	I-a	K-h	K-n	K-a
hexane	30	10	9	13	5	6	6
benzene	50	14	13	15	14	10	11
pyridine	80	32	33	45	22	37	27
2-propanol	65	53	56	48	37	47	38

**Figure 2.** Evolution of the BET constants with the nature of the probe.

Adsorption Isotherms. The reduced adsorption isotherms of four organic probes (hexane, benzene, 2-propanol, and pyridine), depicted on Figure 1, were determined on the six clay samples from the analysis of the shape of the chromatogram obtained when injecting the probe in the column filled with the clay of interest.

As expected, the curvature of the isotherms in the low-pressure range increases with the polarity of the probes. This phenomenon is related to the influence of the surface heterogeneity on the shape of the isotherm that plays a major role at low coverage ratios. In other words, a probe that is able to exchange strong interactions—acid–base or hydrogen bond—with the sites having the highest adsorption energy, gives clearer evidence of surface heterogeneity than does an apolar probe such as hexane that is able to exchange nonspecific interaction whatever the nature of the adsorption site is.

These adsorption isotherms permit determination of the specific surface area as well as the BET constant (*C_{BET}*) allowing us to evaluate approximatively the affinity of the probe for the clay surface according to the following relationship

$$C_{\text{BET}} = K \exp((E_a - E_l)/RT) \quad (1)$$

where *K* is a constant, *E_a* the interaction energy between the first adsorbed layer and the surface, and *E_l* the liquefaction energy of the probe.

The values of specific surface areas measured with nitrogen or organic probes, as well as the areas of organic molecules are summarized in Table 3. The chosen

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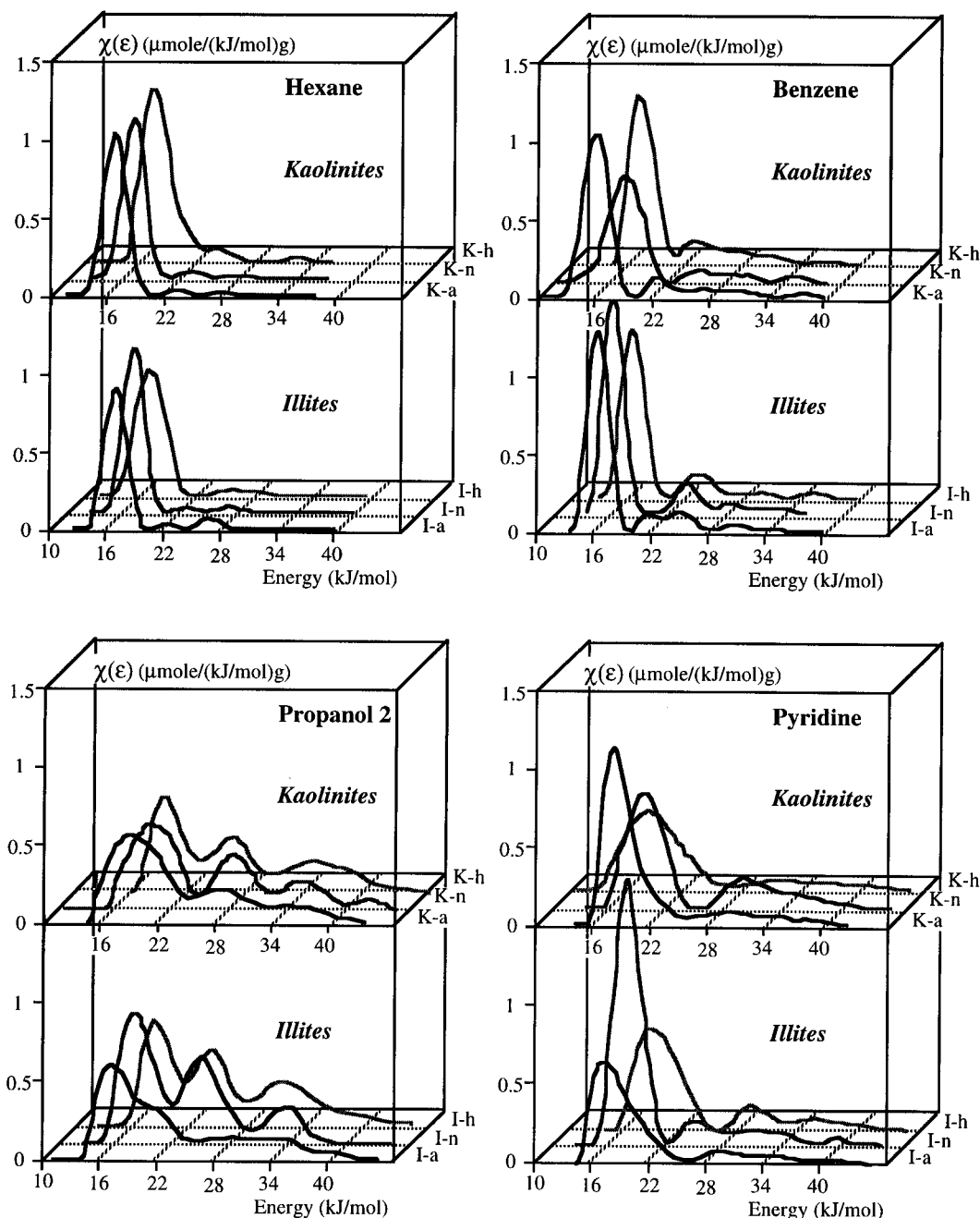


Figure 3. Energy distribution functions obtained with hexane, benzene, pyridine, and 2-propanol on the six clay samples.

molecular surface area values of the probes are those of Gray et al.¹⁷ for hexane, benzene, and pyridine, whereas the one of 2-propanol is the average of all values reported for this probe by McClellan and Harnsberger.¹⁸ It is seen that, for all organic probes, the values of the calculated specific surface areas are in relatively good agreement with those measured by nitrogen adsorption, taking into account that the molecular surface area of such organic probe is known with a precision of $\pm 5 \text{ \AA}^2$ depending on the nature of the adsorbate.¹⁸

The high values measured with pyridine may come from a poor estimation of the projected area of this probe due perhaps to a particular configuration of this flat molecule in the monolayer formed on the solid surface. The values of the BET constants (C_{BET}) were determined from more

than 3 isotherms and are known with reproducibility better than ± 1 . They allow the estimation of the interaction between the probe and the surface in the first monolayer and the calculated values are gathered in Table 4.

We may note that the values measured on the illite samples are higher than those measured on kaolinites when comparing families issued from similar geological formation processes. It follows, according to the chromatographic experiments, that illites show a higher affinity for organic probes than do kaolinites. The evolution of the BET constants is given in Figure 2, for the four probes and the six clay samples.

Significant variations are observed when increasing the polarity of the organic probes. Indeed, the two polar probes (pyridine and 2-propanol) exchange more intense interactions with the polar clay surface than do the weakly polar and apolar probes (benzene and hexane, respectively), corresponding to higher BET constant values. However,

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it is not possible to conclude which polar probe is the more interactive with the clay surface. The measured BET constants are higher in the case of 2-propanol. IGC experiments performed with pyridine, at much higher temperature, indicate a decrease of the value of the BET constant (see eq 1).

Adsorption Energy Distribution Functions. The mathematical treatment of the adsorption isotherms, using the extended Rudzinski–Jagiello approximation¹⁹ of order 4 (DFRJ4) and the Langmuir local isotherm, leads to the adsorption energy distribution functions of the clay samples, with the probe of interest. Because of the use of the Langmuir local isotherm, the global isotherm was corrected for the multilayer adsorption with $N = N(1 - x)$ and $P = P/(1 - x)$ where N and N' are respectively the experimental and corrected adsorbed amounts and x and x' are respectively the experimental and corrected relative pressure. The multiple derivations, that supposes the RJ method, were performed using Fourier's transform. Using Fourier's spectra, it is therefore possible to overcome the "ill-posed" character of the adsorption integral equation. The distribution functions were computed using a Macintosh computer and a home-made program described elsewhere.²⁰ The distribution functions obtained for hexane, benzene, pyridine, and 2-propanol probes on the six clays of interest are depicted in Figure 3.

A general trend is observed when examining these distribution functions.

The first remark is that highly polar probes lead to complex distribution functions. Distribution functions calculated from hexane isotherms exhibit one main peak, whereas peaks corresponding to higher energies of adsorption see their intensities increase with increasing polarity of the probes. As pointed out by Everett,²¹ the adsorption isotherm reflects the interaction of both partners in interaction, the sorbent and the probe. One can easily admit that an alkane like hexane can only exchange dispersive interactions and is unable to distinguish between an apolar and a polar adsorption site. Such a probe is unable to "see" specifically an adsorption site that will exchange acid–base interaction with a suitable partner. When the polarity of the probe is increased, the discrimination between polar and apolar adsorption sites will become progressively better, leading to polymodal distribution functions like those obtained with pyridine or 2-propanol. This last probe leads to the most complex distribution function because of its ability to interact

specifically with silanol and aluminol groups through hydrogen bonds.

Then looking at the distribution functions for illites, whatever the probe, one observes firstly that neoformed illite exhibits systematically a more intensive main peak than do the two other illites and, secondly, that the distribution functions of agraded illites are systematically less defined than those of the heritated and neoformed illites. These observations are coherent with the fact that agraded clays are poorly crystallized, having the highest content of associated minerals, comparatively to the two other illites. On the contrary, the better defined distribution functions of the neoformed illite suppose that this condition of geological clay formation leads to the illite having the better structure: a fact verified in the literature.

An analogous observation can be done with kaolinites since the heritated kaolinite exhibits the best defined distribution functions.

It is obvious that these interpretations have to be considered with care because of the reduced number of studied samples and the difficulties encountered in the distribution functions calculation due to the "ill-posed character" of the solution of the fundamental equation¹⁶ describing the surface heterogeneity.

IV. Conclusion

IGC is a convenient method for the evaluation of the surface properties of divided solids. This study demonstrates that it becomes possible to distinguish between not only illites and kaolinites but also their geological formation conditions. Agraded illite or kaolinite exhibit the higher surface heterogeneity, whereas heritated or neoformed clays are better defined. It is also interesting to point out the interest of using highly polar molecular probes such as pyridine or 2-propanol for examining the surface heterogeneity, in comparison with apolar or slightly polar probes that lead only to few information. Certainly, this study has to be extended to a large number of clay samples for obtaining clear-cut correlations between their physicochemical characteristics and the adsorption energy distribution functions.

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