APPLICATION OF INVERSE GAS CHROMATOGRAPHY TO THE STUDY OF THE SURFACE PROPERTIES OF SLATES

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Abstract—Inverse gas chromatography (IGC) at zero surface coverage was used for determining the surface characteristics of a slate sample. Previously this sample had been characterized by means of X-ray diffraction (XRD), chemical analysis, infrared (IR) spectroscopy and nitrogen adsorption. Quartz, muscovite and chlorite were the minerals foming the slate. A well-defined mesoporous structure with pores of 15 Å of interlayer distance was observed. Chemical analysis and IR spectroscopy corroborated the X-ray results. The surface characteristics of the slate were defined in relation to nonspecific and specific interactions with organic molecules. In accordance with the nonspecific interactions, the London component (γ_S^D) of the surface free energy gave an estimation of the surface energy of the slate sample. The obtained values for γ_S^D were 140.0, 124.8, 108.2 and 96.8 mN m^{-1} at 100, 110, 120 and 130 °C, respectively. These values were characteristic of an inorganic sample of high surface energy. The values of the thermodynamic variables—differential heat of adsorption, free energy and entropy of adsorption—were in accordance with these results. At the same time, specific interactions were characterized by the ϵ_π parameter and the acid–base (K_A, K_B) indices. The positive value of ϵ_π (0.09 kJ mol^{-1}) indicated the presence of Lewis acidic sites on the slate surface. The value of K_A (acid index) of 1.17 was higher than the value of K_B (base index) of 0.37; this result confirmed the acidic nature of the studied slate's surface.

Key Words—Inverse Gas Chromatography, Slate, Surface.

INTRODUCTION

Slates are used as building materials because they are resistant, unchanging, insulating and waterproof. They show low porosity, low water adsorption capacity, very low thermic and electric conductivity and high resistance at temperature changes. When slate vein quality is not good enough to be used as plates, the material can be crushed and used for its fire- or waterproofing characteristics. If slates are high in carbonaceous material, they can be burned at 1500 °C; a great increase in volume takes place (as much as 6 times), decreasing the density and resulting in very porous materials used as light aggregates for concrete. Sometimes slates can be ground to a fine powder used in paving roads (waterproof agent); in plastic, gums and rubbers, providing hardness; as a load in anticorrosive paintings for metals; or as a carrier of fertilizers and insecticides in agriculture. However, new applications must be found for the industrial wastes not used for the above-mentioned purposes.

Slates are formed of microporous layered minerals such as muscovite and chlorite. These minerals have many applications in the industrial field. They can be used as catalyst carriers (Pinnavaia 1983), catalysts themselves (Didams et al. 1984), molecular sieves and sorbents (Zyla and Bandosz 1987).

The structural and chemical properties of the mineral sorbent depend on the initial mineral's method of modification and on the heat treatments during processing to obtain a final product. Many researchers have studied the surface properties of clay minerals (Yamanaka and Brindley 1979; Brindley and Kao 1980; Yamanaka et al 1984).

In this work, we have studied the surface chemical properties of a slate (layered mineral) using chromatographic methods. Our objective is to demonstrate that IGC at infinite dilution provides a convenient way to evaluate surface properties of slates. These properties, such as dispersive component (γ_S^D) of surface free energy, and acid/base specific interaction parameter (I_{sp}), have been determined by adsorption of *n*-alkanes (*n*-pentane to *n*-octane) and some polar adsorbates. This IGC method has some advantages like speed, reliability of measurements and direct thermodynamic interpretation of the experimentally derived parameters.

EXPERIMENTAL

The slate sample was obtained from Pizarras Villar del Rey, S.A. (Badajoz, Spain). The slate piece of about $10 \times 10 \times 0.5$ cm was crushed and sieved and the particles in the 1 to 2 mm diameter range were ground in an agate mortar for 1 h under dry conditions (without using any liquid and with dry nitrogen atmosphere). After grinding, the slate sample was recovered and sieved. The fraction below 37 μm was used for chemical analysis, XRD and Fourier transform infrared spectroscopy (FTIR) characterization. The fraction between 0.3–0.4 mm was used for surface characterization by means of nitrogen adsorption and IGC.

Chemical analysis was carried out by ICP using a Jobin–Ivon Model JY38 VHR instrument. However, silica and SO_3 were analyzed by gravimetry. The XRD diffractogram was recorded using a Siemens Model D500 instrument with Ni-filtered Cu$K\alpha$ radiation. The FTIR spectrum was obtained in a Perkin–Elmer, Mod-

Table 1. Properties of the probes.

Molecules	DN	AN	Specific character
n-pentane	0	0	neutral
n-hexane	0	0	neutral
n-heptane	0	0	neutral
n-octane	0	0	neutral
Benzene	0.1	8.2	acid
Chloroform	0	25.1	acid
Ethylacetate	17.1	9.3	amphoteric
Acetone	17.0	12.5	amphoteric
Tetrahydrofuran	20.0	8.0	basic
Diethylether	19.2	3.9	basic

Key: DN = donor number, AN = acceptor number.

el 1760-X spectrophotometer with a 4-cm^{-1} resolution. The FTIR spectrum was measured by the KBr method in the 4000 to 400 cm^{-1} range. Ten scans were used for obtaining the final spectrum.

Nitrogen adsorption measurements were performed with an Accusorb Model 2100 ET (Micromeritics, United States) instrument at 77.5 K. Previously the slate sample was degassed at 100 °C for 24 h in order to eliminate physisorbed water and another impurities, such as CO_2, adsorbed on the surface of the sample.

IGC experiments were performed with a Perkin–Elmer, Sigma 2B gas chromatograph (GC) equipped with a dual-flame ionization detector. The stationary phase was the slate sample. The columns 30 cm long and 0.32 cm in diameter were filled with 1.7 g of slate particles. The appropriate particle size (0.3–0.4 mm) was obtained by grinding. Helium was used as the carrier gas with a flow rate of about 30 mL min^{-1}. The samples were conditioned at 423 K for 12 h in the chromatographic column under a He gas flow prior to measurements. Very small volumes of gaseous solutes were injected in order to approach conditions of Henry's region using a 1-μL Hamilton syringe. The experiments were conducted in the temperature range 373–403 K.

The dead volumes of the columns were determined by simultaneously injecting methane, which is poorly retained on the slate.

The net retention volumes, V_N, were calculated from Equation [1], as will be shown below (Results and Discussion).

The probe molecules used in the IGC measurements are listed in Table 1. The donor numbers (DN) and acceptor numbers (AN) were taken from the literature (Gutmann 1978). For this study, the semiempirical scale of Gutmann was adopted. These probes are commonly used in IGC for solid-surface characterizations.

RESULTS AND DISCUSSION

Figure 1 shows the XRD pattern of the slate sample studied. Quartz, muscovite, chlorite and small amounts of feldspars are the minerals observed in this sample. These minerals correspond to a common slate.

The chemical composition is given in Table 2. These results are in good agreement with the mineralogical composition determined by XRD. Silica and alumina are the oxides with the highest concentration. The high value of silica is associated with the presence of free quartz in the slate. In a lower concentration, alumina, iron oxide and titania are observed. The presence of magnesia suggest the mica nature of the slate sample.

Figure 2 shows the FTIR spectrum of the slate sample. The hydroxyl vibrations can be observed in the 4000–3000 cm^{-1} spectral region, and the silicate network in the 1400–400 cm^{-1} region. The 3651 and 3525 cm^{-1} IR bands can be attributed to the OH vibrations of muscovite and the bands close to 3560 and 3430 cm^{-1} can be assigned to chlorite (Farmer 1974). A very low shoulder appear at 3680 cm^{-1} which can also be assigned to chlorite. These results are in accordance with XRD analysis and the presence of quartz in the slate sample may be observed in the 1400–400 cm^{-1} region.

The bands that appear at 1165, 695, 530 and 470 cm^{-1} and the characteristic strong doublet at 798–780 cm^{-1} confirms the presence of quartz in the slate sample (Farmer 1974). The other 2 bands of quartz that normally appear at 1150 and 1084 cm^{-1} are overlapped with the silicate bands (lattice vibrations) of the muscovite and chlorite. Muscovite is clearly observed by the bands located at 1068, 1029 and 630 cm^{-1}. Alternatively, chlorite shows IR bands that are overlapped with others of muscovite (1000, 833, 752 and 471 cm^{-1}) and a low-intensity shoulder is observed at 660 cm^{-1}, which may confirm the presence of chlorite in the slate sample.

Figure 3 shows the adsorption–desorption isotherms of N_2 at 77.5 K. This isotherm can be classified as Type IV according to the International Union of Pure and Applied Chemistry (IUPAC) classification (Sing et al. 1985). The hysteresis loop is associated with capillary condensation taking place in mesopores (pores of radius between 10 and 250 Å). The adsorption hysteresis can also be classified as Type H3 (Sing et al. 1985), which is normally observed with aggregates of plate-like particles giving rise to slit-shaped pores. These results are in accordance with the presence of muscovite and chlorite in the slate.

Figure 4 shows the pore size distribution (PSD) of the slate obtained using the BJH method (Barret et al. 1951) and assuming a thickness of the nitrogen layer of 3.15 Å. The PSD shows an unimodal distribution with pores of 15 Å of interlayer distance. Specific surface area has been obtained form the Brunauer–Emmett–Teller (BET) equation (Brunauer et al. 1939) in the 0.05–0.35 partial pressure range. Mesopore area and mesopore volume have been obtained from the BJH method. The area of a nitrogen molecule is believed to be 16.2 Å^2. Table 3 gives these obtained val-
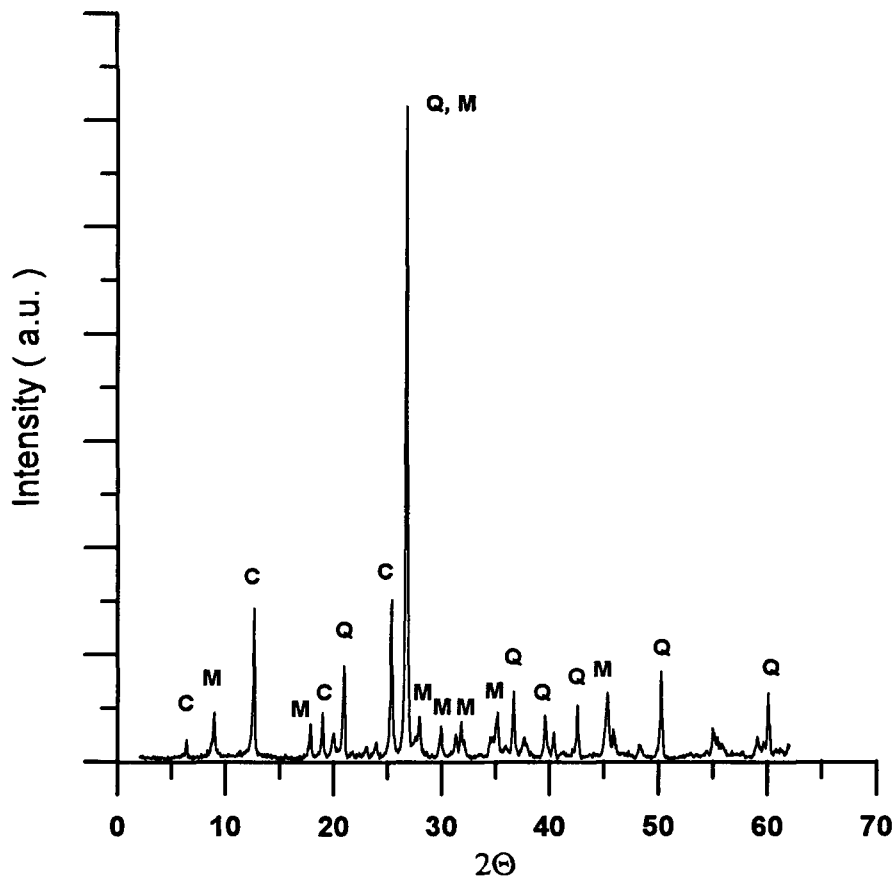
Figure 1.   XRD pattern of the slate sample; Q = quartz; C = chlorite; M = muscovite.

ues for the slate sample studied. Specific surface area and mesopore area are of the same magnitude and we may conclude that the surface area of the slate is provided by the mesopores. According to the BET theory, the constant C (Table 3) is related exponentially to the enthalpy (heat) of adsorption in the first adsorbed layer. However, it is now generally recognized that the C value does not provide a quantitative measure of the enthalpy of adsorption but merely indicates the magnitude of the adsorbent–adsorbate interaction energy.

Table 2.   Chemical analysis of the slate sample.

Component	Wt%
SiO_2	58.77
Fe_2O_3	6.72
TiO_2	2.30
Al_2O_3	20.95
CaO	0.27
MgO	1.87
Na_2O	0.53
K_2O	1.96
SO_3	0.17
MnO	0.10
Loss at 1100 °C	5.54

A high value of C (>100) is associated with a high interaction energy and therefore with a sample of high surface energy. This energy can be analyzed and quantified by the interaction of different organic vapors with the sample at infinite dilution by means of IGC.

Inverse gas adsorption chromatography is based on the study of interactions of gas molecules of known properties with solid surfaces. Small amounts of molecular probes are injected into the stream of the carrier gas flowing through the chromatographic column filled with the solid to be investigated. The net retention time, t_N, is measured as a difference between retention times of a given probe and a nonadsorbing gas used as a reference. The net retention volume, V_N, depends on the interaction energy between the gas molecule with stationary phase, and it is calculated from the formula:

$$V_N = F(t_N - t_M) \qquad [1]$$

where F is the flow rate of the carrier gas and t_M is the retention time of the nonadsorbing gas. In the case of infinite dilution chromatography, the adsorption is described by Henry's law, and we can write:
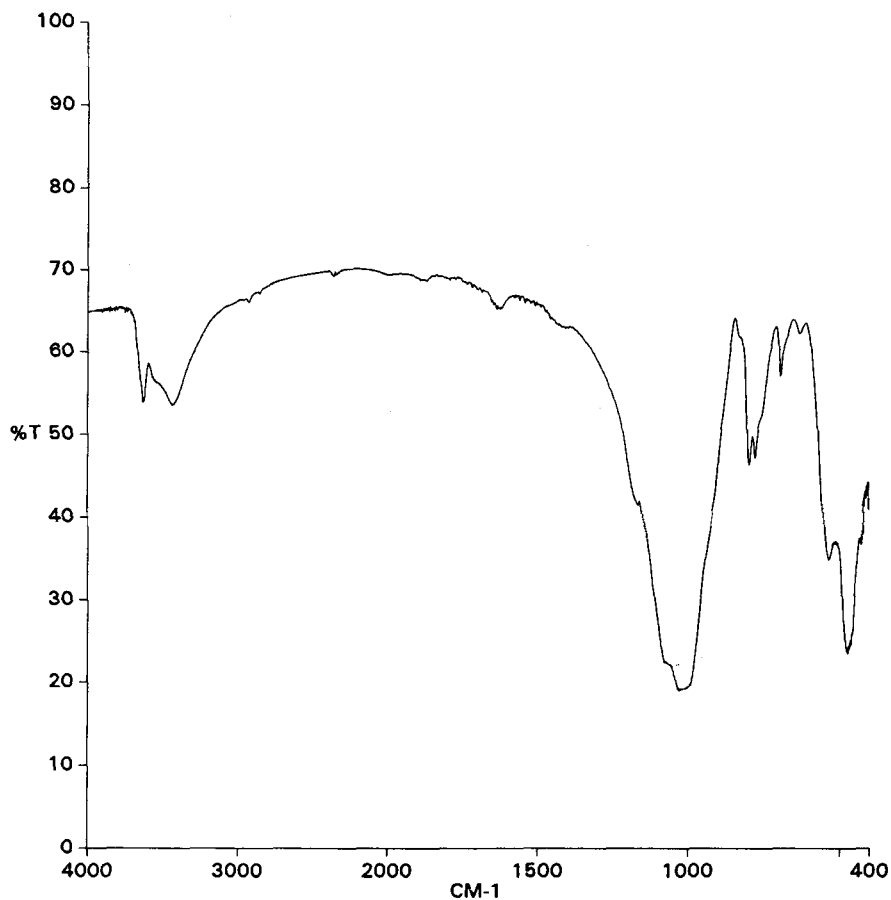
$$V_N = K_S A \qquad [2]$$

Figure 2.   IR spectrum of the slate sample.

where K_S is Henry's constant and A is the total surface area of the stationary phase. The value of K_S, characterizing an adsorbate–adsorbent equilibrium, can therefore be rapidly determined from a single retention volume measurement, provided A is known. From K_S and its temperature dependence, thermodynamic data describing the retention process can be derived. For example, the standard free energy change, ΔG_A^0, is given by:

$$\Delta G_A^0 = -RT \ln\left(\frac{P_{sg}}{\pi_s K_s}\right) \qquad [3]$$

where P_{sg} is the adsorbate vapor pressure in the gaseous standard state, π_s is the standard bidimensional pressure, R is the gas constant and T is the absolute column temperature. The standard reference states are taken as P_{sg} equal to 101 kN m^{-2} (1 atm) and π_s equal to 0.338 mN m^{-1}. The latter value, proposed by De Boer (1953), defines the standard surface pressure as that pressure where the average distance of separation between molecules in the adsorbed phase equals that in the standard gas state.

The differential heat of adsorption of the probe, $-\Delta H_A^0$, may be obtained from the temperature dependence of K_s according to:

$$\frac{-\Delta H_A^0}{R} = \frac{d(\ln K_s)}{d(1/T)} \qquad [4]$$

Provided that ΔH_A^0 is temperature independent, Equation [5] predicts a linear relationship between ΔG_A^0 and ΔH_A^0. Then, the standard entropy of adsorption of the probe at zero coverage, ΔS_A^0, can be calculated by Equation [5]:

$$\Delta S_A^0 = \frac{(\Delta H_A^0 - \Delta G_A^0)}{T} \qquad [5]$$

If we consider the adsorbate as an ideal gas, its 3-dimensional translation entropy can be written:

$$_3S_t = R \ln (M^{3/2} \, T^{5/2}) - 9.62 \qquad [6]$$

where M is the molecular weight of adsorbate. The 2-dimensional entropy is calculated by:

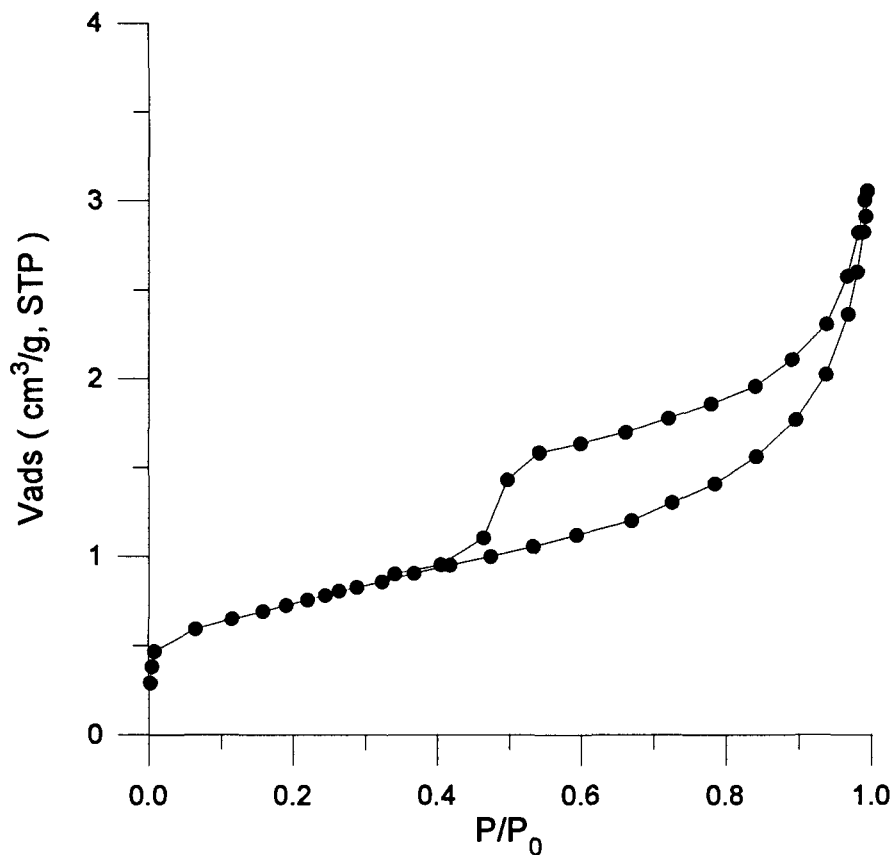$$_2S_t = R \ln (M \cdot T \cdot A_s) + 275.32 \qquad [7]$$

Figure 3. Nitrogen adsorption–desorption at 77.5 K on the slate sample.

where A_s is the available area for a molecule in standard adsorbed state. Therefore, the theoretical entropy change upon the adsorption of a vapor on a solid surface can be calculated from the difference between $_3S_t$ and $_2S_t$.

Analysis of ΔG_A^0 values obtained for appropriate molecular probes can provide information about surface properties. In general, adsorbate–adsorbent interactions can be classified as dispersive (nonspecific) and polar (specific) ones. Among probes that can undergo only dispersive interactions, n-alkanes are of great practical importance. It is well known that ΔG_A^0 for n-alkanes varies linearly with their number of carbon atoms, n. This behavior was adopted by Dorris and Gray (1980) to calculate the dispersive component of the surface free energy, γ_S^D, using:

$$\frac{-\Delta G_A^{CH_2}}{N \cdot a_{CH_2}} = 2[\gamma_{CH_2} \cdot \gamma_s^D]^{1/2} \qquad [8]$$

where a_{CH_2} is the cross-sectional area of a methylene group (0.06 nm^2), γ_{CH_2} is the surface tension of an infinite polymethylene chain, N is Avogadro's constant and $\Delta G_A^{CH_2}$ is defined as the difference in the ΔG_A^0 of 2 subsequent n-alkanes and represents the free energy of adsorption of a CH$_2$ group. It is interesting to em-

phasize the importance of the dispersive component, γ_S^D, since it depends on the standard free energy, ΔG_0^A, being a fundamental thermodynamic parameter.

The variation of the Henry's law partition coefficients at different temperatures, calculated from their respective retention volumes, are shown in Figure 5. The equilibrium partition coefficients, K_s, decrease with increase in temperature because the sorption phenomenon is less intense at high temperatures.

The differential heat of adsorption $(-\Delta H_A^0)$ at zero surface coverage as well as the free energy (ΔG_A^0), the experimental entropy (ΔS_A^0) and theoretical entropy $(_3S_t - _2S_t)$ at 403 K are given in Table 4. The high values of differential heat of adsorption suggest vigorous interactions between n-alkane molecules and the slate surface, indicating high energy sites of adsorption. These results are in accordance with the high value of the BET constant (Table 3). The increase in ΔH_A^0 illustrates the stronger surface adsorption of each n-alkane and suggests a flat orientation of the n-alkanes on the slate surface.

Additional information about the slate surface can be obtained using change data from experimental and theoretical entropies. These changes were calculated from the difference between the 3- and 2-dimensional
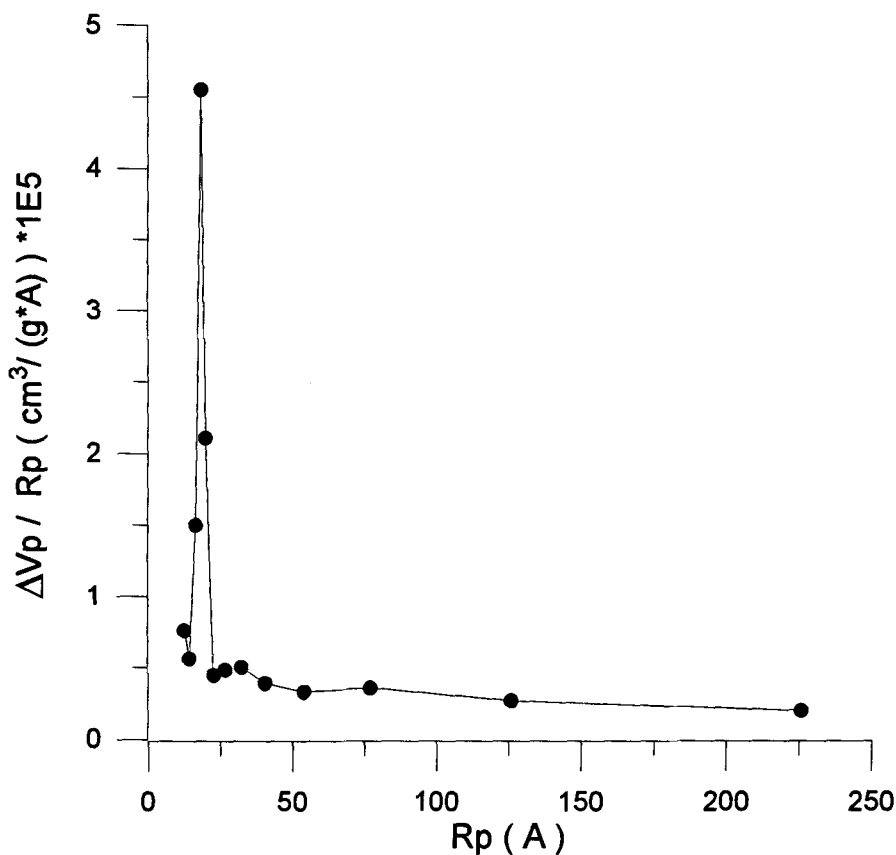
Figure 4.   Pore size distribution of the slate sample.

entropy in accordance with Equations [6] and [7]. When 1 mol of gas goes across the gas phase to the adsorbed phase, a decrease in translational entropy takes place. This change can be expressed by: $_3S_t - _2S_t$. The values for the n-alkanes are from 52.39 for n-pentane to 54.31 J mol^{-1} K^{-1} for n-octane. In the case of n-pentane, the theoretical entropy is of the same order as the experimental value (Table 4). The entropy decrease of n-alkanes upon adsorption results in part from the loss of one degree of translational freedom. When the number of carbon atoms increases, the values of $\Delta S_A{}^0$ are higher than the values of theoretical entropy. This additional entropy loss found experimentally may result from a restriction of rotational and vibrational freedom on the surface.

Figure 6 shows the variation of ΔG_0^A versus carbon

Table 3.   Specific surface area and parameters obtained from the nitrogen adsorption isotherm.

Specific surface (m^2 g^{-1})	2.60
Micropore volume (mL g^{-1})	0
Mesopore volume (mL g^{-1})	0.004
Mesopore area (m^2 g^{-1})	2.54
C (BET constant)	169

number at different temperatures of the adsorption of n-alkanes on the slate sample. The slopes of these lines decrease when the adsorption temperature increases. These slopes are used with Equation [8] to obtain the London component (γ_S^D) of the surface free energy of the slate sample studied.

Table 5 gives the γ_S^D values at experimental temperatures. This parameter (γ_S^D) is very important for the determination of surface characteristics of adsorbent materials, providing a knowledge of the force field of the high energy sites. According to general knowledge, γ_S^D is proportional to the surface density of atoms, their polarizability and their ionization energy. The obtained values of the surface free energy dispersive component correspond to a sample of high energy (Schultz et al. 1977). If we take into account the mineralogical composition of the studied slate (quartz, muscovite and chlorite), the γ_S^D of the slate must be a value close to one of those minerals. The γ_S^D of quartz is 76 mN m^{-1} (Stasczuk 1985), and for mica γ_S^D it is 30 mN m^{-1}. No value of γ_S^D has been published for chlorite. All of those values are lower than that found for the slate sample; thus, there exist some factors that can increase the surface free energy dispersive com-
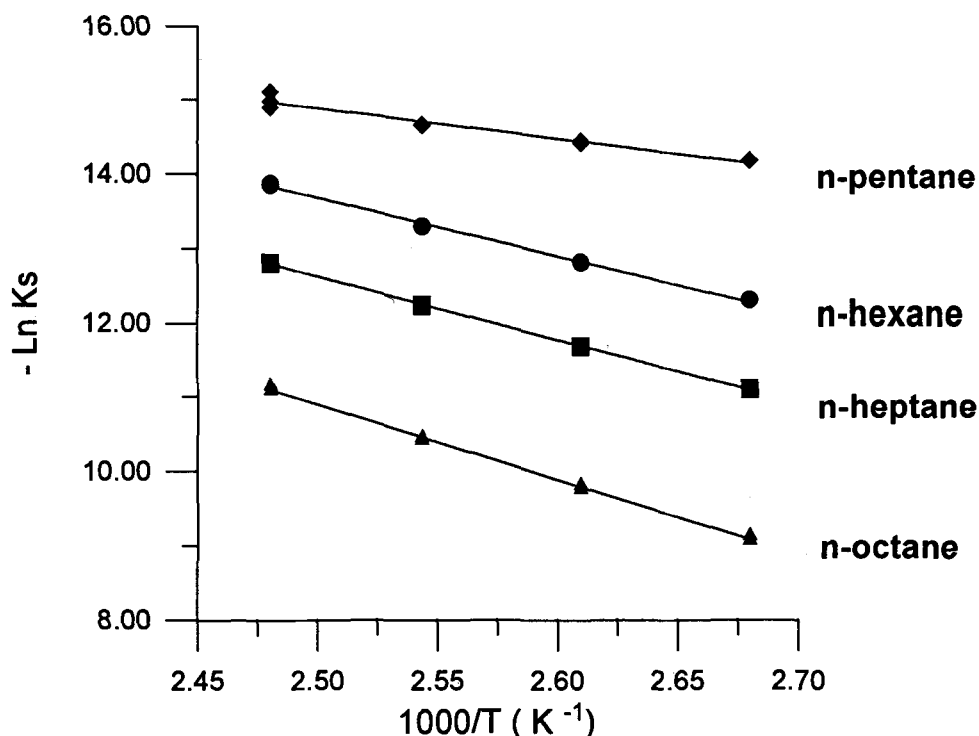
Figure 5. Variation of the Henry's Law partition coefficients with reciprocal temperature for the *n*-alkanes on slate sample.

ponent. One of them is the effect of grinding. Recently Papirer et al. (1993) have shown that an increase in the γ_S^D values may be due to the dry grinding. They found an increase from about 48 to 71 mN m^{-1} after grinding alumina samples. Papirer et al. (1986) have also found a value of 30 mN m^{-1} for a mica (muscovite) sample and this value increases up to 100 mN m^{-1} upon grinding in ethanol or water. Therefore, the high values obtained for the slate sample may be originated during the grinding process.

There is also another factor that can increase the dispersive component of the surface free energy. This is the interaction of the *n*-alkane molecules between the ends of the layers of muscovite and chlorite. This result has been observed for lamellar silicas (Ligner et al. 1989; Hadjar et al. 1995), where values higher than 220 mN m^{-1} have been found, and for smectites (Bandosz, Jagiełło, Anderson and Schwartz 1992; Bandosz et al. 1993), where values higher than 150 mN m^{-1} have been observed. Fine mesoporous structures increase the energy of adsorption (Jagiełło et al. 1992). The PSD obtained for this slate sample (Figure 4) shows a structure with well-defined mesopores in a narrow interval with 15 Å of interlayer distance. This mesopore structure may increase the values of γ_S^D for the slate sample studied. However, the values of the dispersive component of the surface free energy obtained for the studied slate are lower than those found for lamellar silicas and smectites, showing that the presence of quartz has an important influence. According to the γ_S^D values obtained for the studied slate, we can consider such a mineral as a high-energy solid (Schultz et al. 1977).

The *n*-alkanes have also been used in conjunction with unsaturated and aromatic hydrocarbons to study specific interactions of different surfaces in terms of the adsorption enthalpy. Sidqi et al. (1989) proposed a comparison of ΔG_A^0 values of *n*-alkanes and *n*-alkenes to study the effects of the double bond (π electrons) interactions with electron acceptor sites on the surface. The specific interaction parameter, ϵ_π, is defined by:

$$\epsilon_\pi = \Delta G_{alkane} - \Delta G_{alkene} \qquad [9]$$

The higher ϵ_π, the higher specific interactions. These interactions decrease with the carbon number in the probe; therefore, it should be used in alkanes with small chain.

Table 4. Thermodynamic values obtained from the slate sample at 130 °C.

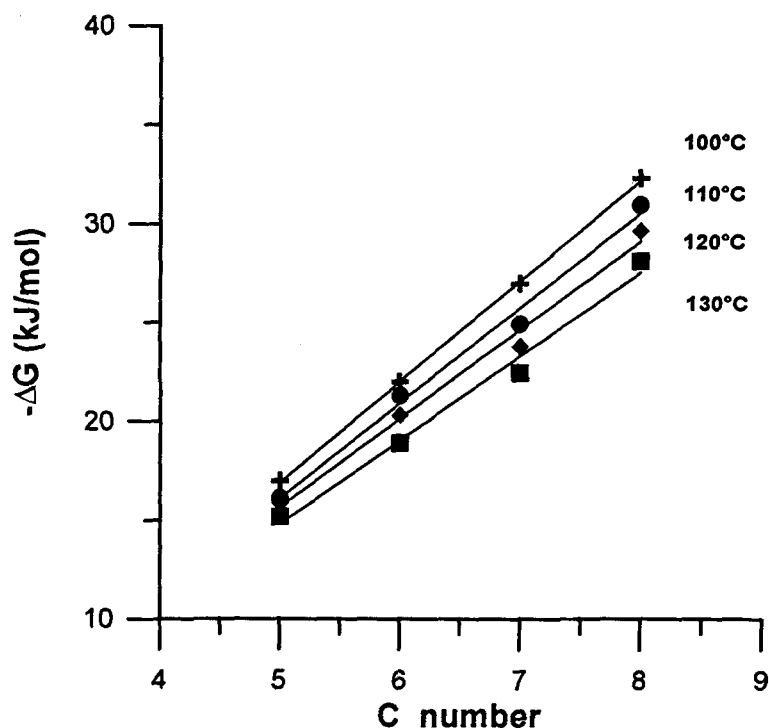| Alkane	ΔH_A^0 (kJ mol^{-1})	$-\Delta G_A^0$ (kJ mol^{-1})	$-\Delta S_A^0$ (Jmol^{-1} K^{-1})	$_3 S_t - _2 S_t$ (Jmol^{-1} K^{-1})
n-pentane	36.58	15.19	53.06	52.24
n-hexane	67.27	18.93	119.90	52.96
n-heptane	72.47	22.47	124.02	53.59
n-octane	84.10	28.15	138.78	54.13

Figure 6.   The standard free energy of adsorption for *n*-alkanes on slate sample at 4 column temperatures as a function of the number of carbon atoms in the alkane chain.

The surfaces of clay minerals are known to have strong acidic properties (Lahav et al. 1978; Occelli and Tindwa 1983; Bandosz, Jagieło, Amankawah and Schwartz 1992) which are related to layer defects, interlayer material and OH⁻ groups and oxygen atoms from the silicate layer. Cations of interlayer material and silicate layers form very strong Lewis acidic centers. The parameter ϵ_π defined by Equation [9] is adopted as a measure of the contribution of specific interaction with electron acceptor surface sites (Sidqi et al. 1989). Values of this parameter were obtained from *n*-hexane and *n*-hexene adsorption. The value of the ϵ_π parameter is presented in Table 6. The ϵ_π value is positive; therefore, the retention of 1-hexene is higher than the corresponding one for *n*-hexane, and this is due to the specific interaction of the π electrons of 1-hexene with the electron acceptor surface sites of the slate sample. The value of this parameter is dependent on the average density of these sites as well as on their

strength. Contribution of positive charges to the effective electrostatic field may be due to either Bronsted or Lewis acidic sites. For the complex structure of the slate sample studied in this work, it would be difficult to establish which may have the stronger effect on specific interactions with alkene π electrons. According to Bandosz, Jagieło, Anderson and Schwartz (1992), we should expect higher ϵ_π values for Bronsted acidic sites because they are related to the presence of H⁺ cations, whereas Lewis sites are related to metal cations. The obtained value of ϵ_π for studied slate (Table 6) is lower than the one found for smectites (Bandosz, Jagieło, Anderson and Schwartz 1992) or for pure and composite oxides (Contescu et al. 1991). The low value obtained for ϵ_π shows the presence of a low concentration of Bronsted or Lewis acidic sites on the surface of the slate sample.

On the other hand, the specific component of the surface free energy can also be obtained by IGC at infinite dilution using polar probes instead of alkenes. Specific interactions can be divided into acid or basic ones. Saint Flour and Papirer (1983) proposed a meth-

Table 5.   Dispersive component of the surface free energy (γ_s^D) on the slate sample at different temperatures.

T (°C)	γ_s^D (mN m⁻¹)
100	140.0
110	124.8
120	108.2
130	96.8

Table 6.   The ϵ_π, K_A and K_B values for slate sample studied.

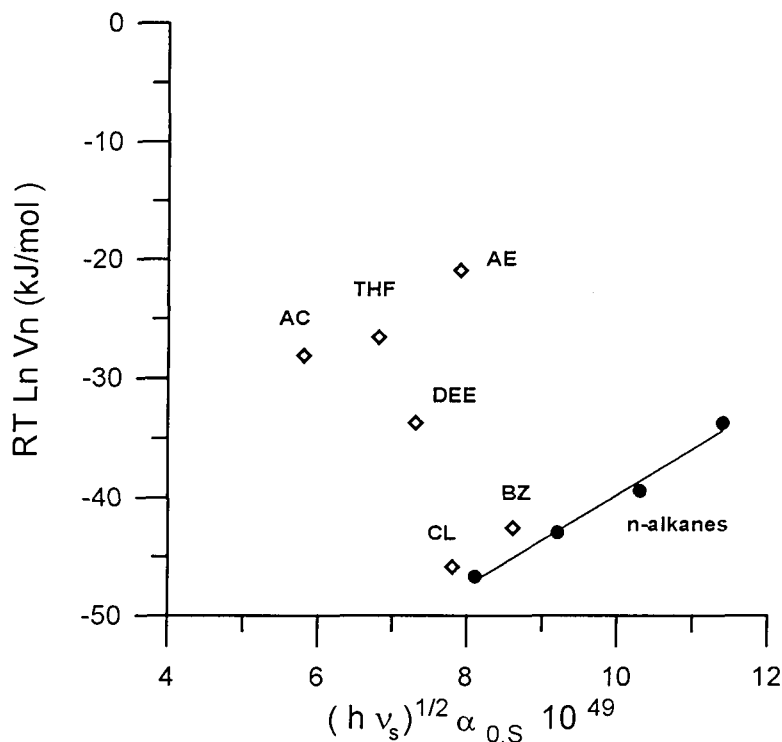| ϵ_π (kJ mol⁻¹)	K_A	K_B
0.09	1.17	0.37

Figure 7.   Plot of $RT \ln (V_n)$ vs. deformation polarizability of organic probes.

od based on the linear variation of the logarithm of the net retention volume, V_N, against the logarithm of the vapor pressure, P_0, of the n-alkane probes. This correlation is observed since n-alkanes at infinite dilution behave quite ideally. Assuming the additivity of the dispersive and specific component of the free energy, the alkane line may be taken as the reference line. The difference of ordinates between the n-alkane line and the point corresponding to the polar probe, having the same P_0 as a real or hypothetical n-alkane, gives the specific interaction parameter, I_{SP}. Recently Donnet et al. (1991) have reported a new method for evaluating the I_{sp} parameter taking into account the deformation polarizability of the probes used in the measurements. They showed that this method is more adequate than that based on the vapor pressure of the probe (Saint Flour and Papirer 1983). The Donnet et al. method (1991) relates the standard free energy of adsorption to London's equation by:

$$RT \ln (V_N) + C = K (h\nu_S)^{1/2}\alpha_{0,S}(h\nu_L)^{1/2}\alpha_{0,L} \quad [10]$$

where C is a constant, $h\nu_i$ the ionization potential of the ith interacting material, α_0 the deformation polarizability and K a constant that takes into account the permittivity in vacuum, the distance of adsorbate–adsorbent interaction and Avogadro's number. The identifiers S and L refer to solid and liquid. The main interest of this method lies in the fact that the probes are characterized by an intrinsic property derived from

London forces. Therefore, we have calculated the acid or base character of the solid surface using the Donnet et al. method with the different polar probes compiled in Table 1. Often, specific interactions are described essentially to acid/base interactions (Fowkes 1987). Indeed, it is known that the acid/base interaction energy greatly exceeds that of pure polar interactions. According to Gutmann (1978), an acid is defined by its ability to attract electrons (acceptor number, AN) and a base by its ability to release electrons (donor number, DN).

Figure 7 shows schematically the determination of the surface free energy specific component. When a polar solute is injected into the GC column containing the slate sample, both dispersive and specific interactions will take place. When the net retention volume, or ΔG_A^0, versus the polarizability of the injected solutes is plotted (Donnet et al. 1991), all points corresponding to n-alkane probes fall on a straight line, whereas the corresponding points of polar probes, interacting with the polar chromatographic support, are located well above the n-alkane line. As we have mentioned before by definition (Saint Flour and Papirer 1983) the specific interaction parameter, I_{sp}, of a given probe is given by the deviation of the experimental point from the n-alkane line.

The I_{sp} values taken from Figure 7 can be used to calculate K_A (acidity) and K_B (basicity) of the slate
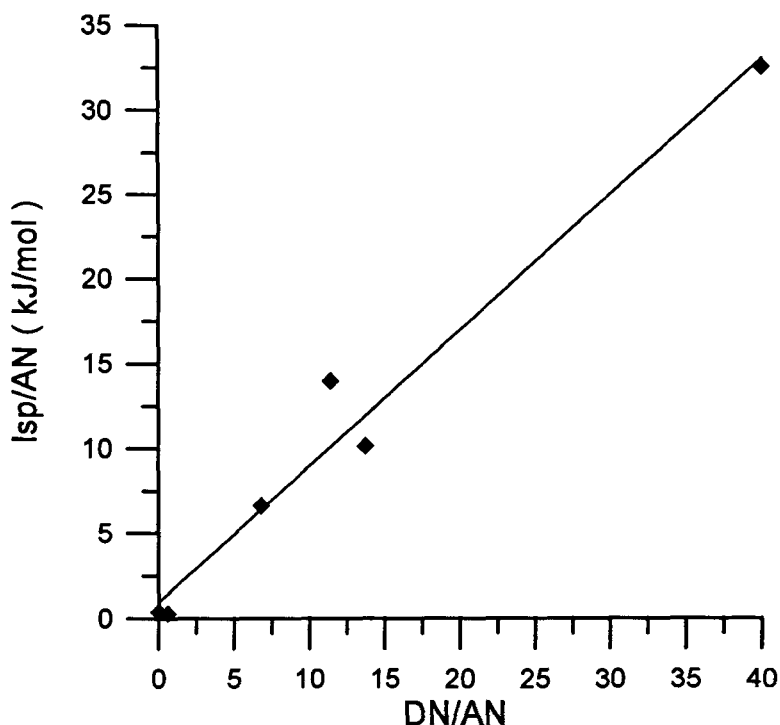
Figure 8.   Plot of I_{sp}/AN vs. DN/AN.

surface according to the following relationship (Saint Flour and Papirer 1983):

$$I_{sp} = (K_A \cdot DN) + (K_B \cdot AN) \qquad [11]$$

then dividing by AN:

$$I_{sp}/AN = K_A(DN/AN) + K_B \qquad [12]$$

which gives a linear dependence between I_{sp}/AN and DN/AN, being K_A, the slope, and K_B, the intercept. Figure 8 shows the variation between I_{sp}/AN vs. DN/AN for the polar probes adsorbed onto the surface slate used in this study.

Such a procedure has already been applied to the study of glass fibers (Saint Flour and Papirer 1983), aluminas (Papirer et al. 1991) and other mineral oxides (Morales et al. 1991). The slope of this line expresses the ability of the slate surface to accept electrons; in other words, its acidity and the y-intercept represent the surface basicity. The values obtained for K_A and K_B for the slate sample are given in Table 6 and demonstrate the acidic nature of the slate surface as it was expected, considering the presence of mica, quartz and hydroxyl groups on the slate sample. The acidity of silica and mica surfaces have been also found by Papirer et al. (1986).

The surface sites of inorganic solids usually are acidic or basic or both. Metal oxides exposed to the atmosphere normally have surface OH groups which may be acidic or basic. The surfaces of silicoaluminate

materials behave rather acidically (Ligner et al. 1990). The results obtained in this work show an acidic index (K_A) higher than the basic one (K_B) being in accordance with the ϵ_π parameter obtained previously. The OH groups observed by FTIR (Figure 2) in the muscovite and chlorite minerals forming the slate sample must be the responsible for this higher acidity.

CONCLUSIONS

In this work, it has been shown that IGC is a valuable method for the characterization of slate surfaces. The slate sample was previously characterized by XRD, FTIR, chemical analysis and nitrogen adsorption. The chemical analysis showed a chemical composition of a common slate. The minerals that form this slate are quartz, muscovite and chlorite. This result has been confirmed by FTIR spectroscopy, where the OH and skeletal vibrations of such minerals are present in the spectrum. The slate sample has a low specific surface area with pores of about 15 Å of interlayer distance.

The slate sample studied shows a high London component of the surface free energy varying between 140.0 and 96.8 mN m^{-1} with temperatures between 100 and 130 °C. These values are characteristics of high energy inorganic surfaces and are in accordance with the values obtained for the differential heat of adsorption. These high values may be due to the grinding process or to the narrow mesopore structure of the

slate. The specific component of surface energy has been characterized by means of the ϵ_π parameter and K_A and K_B indexes. The ϵ_π parameter has shown the interaction of the π-electrons of 1-hexene molecule with acidic sites of the slate sample. Alternatively, the value of K_A (acidic index) is higher than K_B (basic index). Therefore, the slate surface has an acidic character mainly due to the presence of quartz and OH groups of the muscovite and chlorite minerals.

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