INFLUENCE OF WATER ON THE RETENTION OF ORGANIC PROBES ON CLAYS STUDIED BY IGC

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Abstract—Oil recovery is strongly related to the wettability of reservoir rocks that are formed of quartz grains attached by mineral hydroxides and clay minerals. Illites and kaolinites are the most active due to their high specific surface areas and electrical charge densities. Therefore, these minerals' relative affinities for oil or water when in contact with a water–oil mix are of great importance. In order to model such a complex system, we used a mix of organic model molecules of the oil constituents and water vapor. Their interactions were estimated by inverse gas chromatography (IGC). IGC experiments were performed using a carrier gas with controlled humidity. By means of IGC at infinite dilution conditions, the dispersive component of the surface energy, γ_s^d, was determined. A strong decrease of γ_s^d, due to water molecules shielding the highest-energy sites, was observed. The energetic surface heterogeneity of the clays was examined using IGC at finite concentration conditions, allowing the determination of organic probe adsorption isotherms in the presence of water. From these isotherms, adsorption energy distribution functions were computed for propanol-2 and pyridine probes. Water mainly modifies the illite distribution functions, whereas practically no change was observed in the case of kaolinite. This observation is related to the higher hydrophilicity of illite as compared with kaolinite, and explains the different behaviors of the 2 clay families in oil reservoirs.

Key Words—Illite, Inverse Gas Chromatography, Kaolinite, Surface Energetic Heterogeneity, Water Adsorption.

INTRODUCTION

Oil recovery is strongly related to the oil wettability of an oil-field reservoir. Wettability is defined as "the tendency of one fluid to spread on or to adhere to a solid surface in the presence of other immiscible fluids" (Anderson 1986). For rock/oil/brine systems, it is a measure of the affinity that the rock has for either oil or water. Cuiec (1986) proved the existence of water-wet, mixed-wet or oil-wet rocks. Sandstones that are reservoir rocks are usually formed of quartz grains attached by clay minerals and hydroxides. The clay minerals, due to their high specific surface areas and electrical charge densities, are the most active constituents. Oil-field clays are mainly illites and kaolinites (Flandrin and Chapelle 1961). Their wettability properties, related to their surface energies and surface heterogeneities, are believed to be in relation to the heavy-oil ends retention process. In sandstones, oil wets kaolinite while illite is preferentially wetted by brine (Fassi-Fihri et al. 1992). But it is not easy to measure the surface energy of divided solids with standard methods, such as the contact angle evaluation of liquid drops deposited on an oriented clay deposit (Chassin et al. 1986), or the evaluation of this liquid contact angle value from the ascending capillary rate of a liquid penetrating into a capillary column packed with the clay (van Oss 1993). The surface properties of clays can also be determined by a chromatographic method (Saada, Siffert, Balard and Papirer 1995). Thus, γ_s^d could be measured on various minerals. The high values of γ_s^d usually obtained with layered minerals are related to clay nanomorphology. Apparently, those values are not representative of a mean behavior of the clay, particularly in the conditions of an oil reservoir, where a mix of organic species and water are in contact with the clay surfaces. In order to evaluate the surface properties of clay minerals in oil-field conditions, we examined the influence of the presence of water on the retention characteristics of organic probes, using IGC. First, IGC was applied at infinite dilution conditions, in order to measure the γ_s^d of the clay, in the presence of water. Second, IGC at finite concentration conditions was used to determine the energetic heterogeneity of the clay surfaces, also in presence of adsorbed water.

EXPERIMENTAL

Clays

Three modes of clay mineral genesis are known (Grim 1962): heritage, transformation (degradation, agradation) and neoformation. For this study, we selected 1 illite and 1 kaolinite sample, formed by heritage. Clay preparation and purification were based on the method of Robert and Tessier (1974), as described in Saada, Siffert and Papirer (1995). The specific surface areas (*S*) of the samples outgassed at 120 °C were determined from nitrogen adsorption isotherms and application of the Brunauer–Emmett–Teller (BET) theory. The cation exchange capacities (CEC) were estimated using the method of Glaeser (1954), which is based on the evaluation of acidic clay exchangeable protons by Na^+.

Water Adsorption

The hydrophilic character of the clays was estimated by water adsorption experiments. Water adsorption isotherms were obtained according to the method of Dannenberg and Opie, Jr. (1958). The clays were kept at 20.0 ± 0.5 °C in a thermostated room and then dried in a desiccator over di-phosphorus pentoxide. Every day, the weight of each sample was measured until a constant weight was obtained. Water adsorption was then measured on approximately 1 g of the dried clays. The dried clays were placed under controlled humidities obtained with saturated aqueous salt solutions. It was considered that an equilibrium adsorption state, at a given vapor pressure, was reached when the weight of the clays remained constant during the following 2 d. Then a new salt solution was used, presenting a relative pressure of water vapor slightly higher than the previous one, and the process was repeated.

Inverse Gas Chromatography

Since the clay particles are too small (diameter <2 μm) to be directly employed as chromatographic supports, clay pellets were prepared by powder compression, under a pressure of 10^8 Pa. The pellets were then hand-crushed and sieved to select the fraction of particles with 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 approximately 25 mL/min. All solute probes were purchased from Aldrich. They were of chromatographic quality needing no further purification.

INFINITE DILUTION CONDITIONS. A very small amount (approximately 10 μL vapor) of these probes was injected into the column, allowing work at infinite dilution conditions. The retention time of the probes was calculated from the 1st-order moment of the peak, measured with a Shimadzu CR4AX integrator connected with the chromatograph.

IGC experiments were performed at 3 different temperatures (40, 80 and 120 °C), under dry (when the carrier gas is connected to the chromatograph through a column filled with a desiccant) or wet conditions (the carrier gas is then flushed through a thermostated saturator filled with water). The amount of water adsorbed upon clays was determined by weighing the column after the IGC experiment.

DETERMINATION OF (γ_s^d). IGC, at infinite dilution conditions (that is, when injecting only minute amounts of probes, just at the limit of chromatographic detection), has proven to be a powerful method for evaluating the surface energy of powdered solids like alu-minas (Papirer, Perrin et al. 1991), silicas (Papirer et al. 1987), smectites (Bandoz et al. 1992) or carbon blacks (Papirer, Li et al. 1991). IGC allows the detection of the solid surface properties, using molecules of known properties or probes that are injected in a chromatographic column filled with the solid of interest. Practically, the retention time and the net retention volume, V_n (volume of carrier gas necessary to push the probe through the column), were determined in current analytical chromatographic conditions. The larger V_n will correspond to a higher affinity of the probe for the chromatographic support. Thermodynamically, affinity corresponds to the standard variation (ΔG_a^0) of the free energy of adsorption. Thus, ΔG_a^0 and V_n are connected by the following relationship:

$$\Delta G_a^0 = -RT \ln V_n + C \qquad [1]$$

where R is the ideal gas constant, T the temperature, V_n the net retention volume and C a constant depending on the total surface area of the column filling and on the arbitrary choice of the reference state of the adsorbed molecule.

The value of γ_s^d is obtained by injecting an homologous series of n-alkanes into the column (Dorris et al. 1979) and determining their retention characteristics. Generally, the logarithm of V_n (and thus ΔG_a^0) varies linearly with the number of carbon atoms of the injected n-alkanes. Therefore, it becomes possible to define the free energy of adsorption, ΔG_{CH_2}, of 1 methylene group, which no longer depends upon the arbitrary choice of the reference state:

$$\Delta G_{CH_2} = RT \ln \frac{V_{n+1}}{V_n} \qquad [2]$$

where V_{n+1} and V_n are the net retention volumes of n-alkanes having respectively $n+1$ and n atoms of carbon.

The value γ_s^d is then computed using the equation of Dorris and Gray (1980):

$$\gamma_s^d = \frac{1}{\gamma_{CH_2}} \left[\frac{\Delta G_{CH_2}}{2Na_{CH_2}} \right]^2 \qquad [3]$$

where γ_{CH_2} is the surface energy of a molecule made entirely of methylene groups (that is, polyethylene), a_{CH_2} is the surface area of 1 adsorbed CH_2 group and N is Avogadro's number.

This method holds only for molecularly flat and energetically homogeneous surfaces. Consequently, it should be noted at this point that very few injected alkane probes will experience all adsorption sites, but will be retained much more efficiently on the highest-energy adsorption sites.

In other words, it is expected that IGC, at infinite dilution conditions, will point to the existence of those active sites. For a heterogeneous solid like a clay ma-

terial, the IGC response will only be partial, that is, the γ_s^d value will certainly not be representative of a mean surface energy characteristic. Such mean values are better obtained using macroscopic methods such as liquid contact angle measurements when applicable. However, in that case, differences between clays at a molecular level will obviously not appear. That is the reason why we performed IGC at finite concentration conditions.

FINITE CONCENTRATION CONDITIONS. Here, measurable liquid amounts of molecular probes were injected into the gas chromatograph (GC) apparatus. Chromatograms were acquired, at 60 °C for propanol 2 probes and at 80 °C for pyridine probes, using the same clay-filled columns as for infinite dilution IGC. The peaks were analyzed using a Shimadzu CR4A integrator. For experiments performed under controlled humidity, helium was 1st allowed to bubble continuously through water, at a constant pressure (0.2 MPa) and at fixed temperatures (0 and 28 °C), before injecting the probes in the wet carrier gas.

The adsorption isotherms of organic compounds on clays were obtained using the so-called elution characteristic point method (Conder and Young 1979). According to this method, the 1st derivative of the adsorption isotherm can be calculated easily starting from the retention times and the signal heights of points taken on the diffuse descending front of the chromatogram. The 1st derivative of the isotherm is then related to the retention time of the characteristic point by the simplified Conder's equation:

$$\left(\frac{\partial N}{\partial P}\right)_{L,t_r} = \frac{V_n}{mRT} = \frac{JDt_r'}{mRT} \qquad [4]$$

where N is the number of absorbed molecules, P the pressure of the probe at the output of the column, L the column length, t_r the retention time corresponding to a characteristic point on the rear diffuse profile of the chromatogram, t_r' the corresponding reduced retention time, V_n the net retention volume, J the James Martin coefficient, taking into account the compressibility of the gas due to the pressure drop inside the chromatographic column, D the output flowrate, m the mass of adsorbent, R the van der Waals constant for an ideal gas and T the absolute temperature at which the measurement is performed.

DETERMINATION OF THE ENERGETIC SURFACE HETEROGENEITY. As a result of the heterogeneity of the solid surface, its interaction with adsorbing molecules will vary depending upon both the nature of the adsorption site and its location. Therefore, the determination of the adsorption isotherms using various probes can, in principle, lead to information about the surface heterogeneity of a solid in terms of adsorption energy distribution functions.

Distribution function (DF) calculation from the isotherm shape is based upon a physical model describing, in the simplest manner, the global experimental isotherm as a sum of local isotherms, each corresponding to an homogeneous adsorption surface patch.

Hence, the amount of adsorbed molecules (probes) is given by the following Fredholm integral equation:

$$N(P_m, T_m) = N_0 \int_{\epsilon min}^{\epsilon max} \theta(\epsilon, P_m, T_m)\chi(\epsilon)\, d\epsilon \qquad [5]$$

where: $N(P_m, T_m)$ is the number of molecules adsorbed at the pressure P_m and at the temperature T_m of measurement (experimental isotherm), N_0 is the number of molecules corresponding to the formation of a monolayer, $\theta(\epsilon, P_m, T_m)$ is the local isotherm defined by a discrete adsorption energy ϵ, and $\chi(\epsilon)$ is the DF of the sites seen by the probe. The solution of Fredholm's equation is widely described in 2 monographs (Rudzinski and Everett 1992; Jaroniec and Madey 1989) devoted to adsorption on heterogeneous surfaces.

The local isotherm, $\theta(\epsilon, P_m, T_m)$ has to be selected according to the physical hypothesis describing the interaction of a molecule with an adsorption site and with the neighboring adsorbed molecules. The Langmuir local isotherm that supposes localized sites and no lateral interaction between adsorbed molecules is the most familiar because of the impossibility of knowing the true values of the parameters used in the other models of local isotherms.

The characteristic energy ϵ_j of an adsorption site of type j is related to the pressure, for a coverage ratio θ_j equal to 1/2, by the following equation:

$$\epsilon_j = -RT \ln(P_m/K) \qquad [6]$$

where, for a Langmuir local isotherm, K is related to the molar mass and the temperature of measurement T (Hobson 1965), by: $K = 1.76 \cdot 10^4\ (MT)^{1/2}$.

Finally, assuming a local isotherm, one must now find a suitable numerical resolution method for solving the Fredholm equation. The oldest and simplest method of resolution is based on an approximation of the local isotherm: the condensation approximation (Jagiełło and Schwartz 1991). The condensation approximation supposes that the adsorption sites of given energy are unoccupied below a characteristic pressure and entirely occupied above it. The DF for the condensation approximation (DFCA) is directly related to the 1st derivative of the isotherm, corrected for the multilayer adsorption (Balard 1997), according to the following equation:

$$\chi_{CA}(\epsilon) = RT\frac{P'}{N_0}\left(\frac{\partial N'(P', T)}{\partial P'}\right) \qquad [7]$$

This approximation gives an exact solution only at a measurement temperature near absolute zero. At room temperature and above it, this approximation
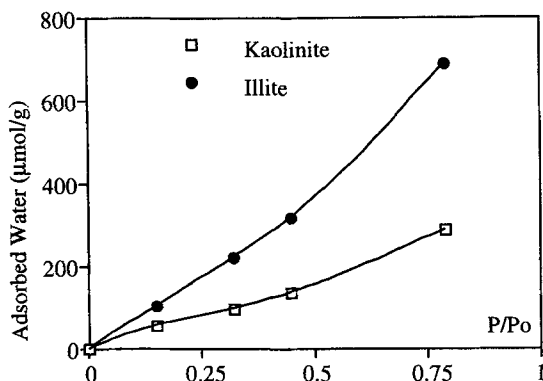
Figure 1. Water adsorption isotherms on the 2 clays.

Table 1. BET specific surface area (S), cationic exchange capacity (CEC), amount of water adsorbed at monolayer coverage completion (N) per gram and (n) per square meter.

Samples	S (m^2/g)	CEC (meq/100 g)	N (meq/g)	n (meq/m^2)
Illite	30 ± 1	9.4 ± 0.5	0.240	0.800
Kaolinite	21 ± 1	3.5 ± 0.5	0.089	0.424

fails completely. To overcome this difficulty, the Rud-zinski–Jagieło (RJ) approximation (Jagieło and Schwartz 1991) was applied for the calculation of the actual distribution function, according to the following equation:

$$\chi(\epsilon) = \sum_{j=0}^{-\infty} RT^{2j} b_{2j} \chi_{CA}^{(2j)}(\epsilon) \qquad [8]$$

where

$$b_0 = 1 \quad \text{and} \quad b_{2j} = (-1)^j \frac{(\pi^{2j})}{(2j+1)!}$$

This approximation supposes knowledge of the even derivatives of the DFCA, which are difficult to determine from the finite set of experimental points, without amplifying the experimental noise. Taking advantage of the DFCA form that looks like part of a periodic function, we proposed to fit the DFCA using Fourier's series (Balard 1997). This method permits an easy multiple derivation of the experimental DFCA and provides a simple way to separate the signal contribution from the experimental noise contribution. The remarkable robustness of this new approach, versus noise and irregular sampling, was tested using a simulation program. The energetic surface heterogeneities of silicas and talcs (Papier and Balard 1995), ground muscovites (Balard and Papirer 1994b) and carbon blacks (Balard and Papirer 1994a) were determined by applying this method.

RESULTS

Characterization of the Clay Samples by IGC in Infinite Dilution Conditions

The water adsorption isotherms, measured at 20.0 ± 0.5 °C on the 2 samples, are shown on Figure 1.

Specific surface areas, CECs and the amount of water (N_{H_2O}) adsorbed at monolayer coverage completion, determined from the BET transform of the water adsorption isotherm and the ratio (N_{H_2O}/S) that will allow

clay surface hydrophilicity to be evaluated, are summarized in Table 1.

It is evident that the illite sample having a specific surface area and CEC higher than kaolinite is consequently the more hydrophilic surface.

The γ_s^d of the clays was then measured at 3 different temperatures between 40 and 120 °C. The values of γ_s^d are listed in Table 2 with a measurement error of approximately 10 mJ/m^2.

There is no significant variation of γ_s^d within the examined temperature range, when measuring under dry experimental conditions. The values of γ_s^d reported in Table 2 are rather high, and larger than those measured, for instance, by IGC on powdered amorphous silicas (approximately 60 mJ/m^2). Such high values were also recorded with silicas or silicates having layered structures such as talc (Balard et al. 1993) or H-Magadiite (Hadjar et al. 1995). They are not representative of a mean value of layered clay surface properties. Indeed, for talc, the γ_s^d determined by IGC amounted to 130 mJ/m^2, whereas the γ_s^{LW} determined by Giese et al. (1991) by thin layer wicking is equal to 31.5 mJ/m^2. As discussed earlier, these high values may result from retention of the alkane probes in structural heterogeneities of molecular size (nanorugosities), formed by the irregular stacking of the layers, on the lateral sides of the clay. These nanorugosities would then allow a partial insertion of the alkane probes. Hence, the alkane probe would be submitted to a higher force field generated by the 2 silicate layers rather than the one resulting from a simple adsorption on a flat layer. It would consequently be more strongly retained, thus inducing a notable increase of the "apparent" γ_s^d values.

The preceding results concerning surface properties of dry clay minerals do not provide information about the behavior of the clays in wet oil-field conditions. Therefore, we used a humid carrier gas in order to detect the role played by water in the adsorption phe-

Table 2. Determination of the γ_s^d values (±10 mJ/m^2) for the 2 clay samples at different measurement temperatures.

Temperature of measurement (°C)	γ_s^d (illite) (mJ/m^2)	γ_s^d (kaolinite) (mJ/m^2)
40	174	141
80	167	171
120	179	160
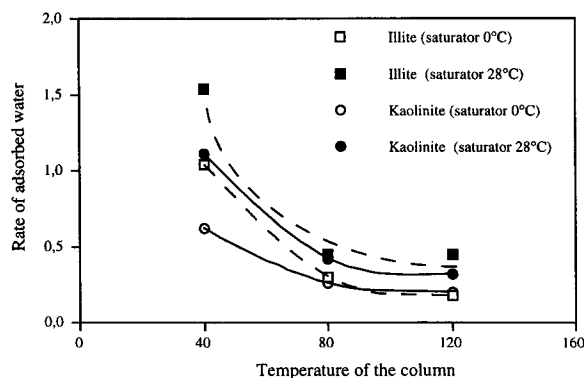
Figure 2. Amount of water fixed on clays versus the temperature of the column and of the saturator.

Table 3. Evolution of γ_s^d with the degree of humidity (temperature of the saturator) and with the measurement temperature.

Temperature of measurement (°C)	γ_s^d (mJ/m^2)					
	Illite			Kaolinite		
	40	80	120	40	80	120
Dry	174	167	179	141	171	160
Water 0 °C	91	162	155	108	142	156
Water 28 °C	57	128	154	61	112	135

nomena of n-alkane probes. The total amount of water adsorbed upon clays is measured in the chromatographic experiment conditions. Figure 2 shows the amount of water adsorbed upon clays versus the temperature of the column and of the saturator.

The amount of adsorbed water was related, as expected, to the temperature of the saturator; an increase of the saturator temperature leads to an increase of the relative pressure of water in the system, and thus to an increase in the amount of adsorbed water. We investigated the influence of this adsorbed water on the measured γ_s^d values, for each temperature of the saturator and of the column (Table 3).

As before, within the studied temperature range, the γ_s^d values remained constant when dry carrier gas was used. But with the wet carrier gas, an important decrease of the measured γ_s^d value with an increase of the clay hydration ratio was noticed. This showed that water shields the highest energy sites of the clay surface, hindering their access to the injected n-alkane probes.

Determination of the Surface Energetic Heterogeneity

The DFs of the adsorption energies were calculated from adsorption isotherms, for 4 different probes: an apolar probe (hexane), a slightly polar probe (benzene) and 2 strongly polar probes: pyridine, exhibiting a strong basic character, and propanol-2, having an acidic character.

Figure 3 displays the adsorption energy DFs of the preceding probes.

Between the 2 samples, illite exhibited the highest surface heterogeneity, as shown by the existence of more intense peaks of higher energies. When benzene was used as a probe, the main low energy peak was larger for kaolinite than for illite, whereas for hexane, both exhibited very similar behaviors. This broadening can be attributed to the fact that kaolinite presents 2 types of basal surfaces: 1 exhibiting only siloxane

bridges and the other having aluminol functions, whereas both basal surfaces of illite present only siloxane bridges.

Using other more polar probes like pyridine and propanol-2, more complex DFs were observed with more intensive peaks at the higher-energy side due to specific interactions between probes and the solid surface. Illite presented adsorption energy DFs having more fine structures than kaolinite, a proof of its lower surface heterogeneity.

Figure 4 shows the adsorption energy DFs of propanol-2 and pyridine for illite and kaolinite using either a dry vector gas or saturated gas with water at 0 and 28 °C.

With a dry vector gas, propanol-2 exhibited systematically trimodal-shaped DFs, whereas for pyridine, bimodal DFs were observed with a tail on the rightmost part, in the high-energy region.

Saturating the vector gas with water at 0 and 28 °C did not significantly change the general aspect of the DFs. For the pyridine probe, no significant changes were observed for kaolinite, whereas illite showed a slight enhancement and sharpening of the lower-energy peaks. On the contrary, for the propanol-2, this phenomenon became more apparent and an attenuation
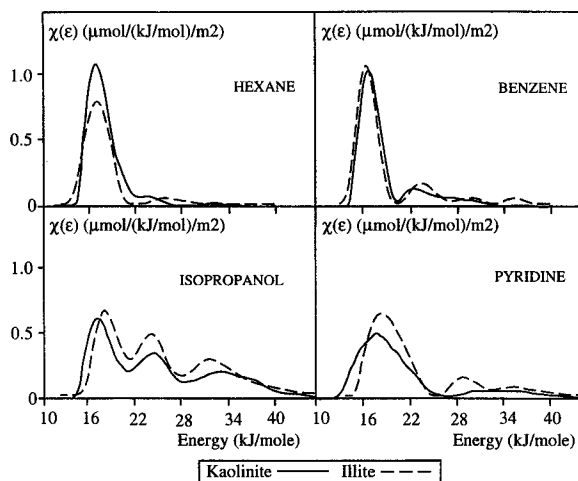

Figure 3. Energy distribution functions of adsorption sites for hexane, benzene, isopropanol and pyridine on illite and kaolinite.
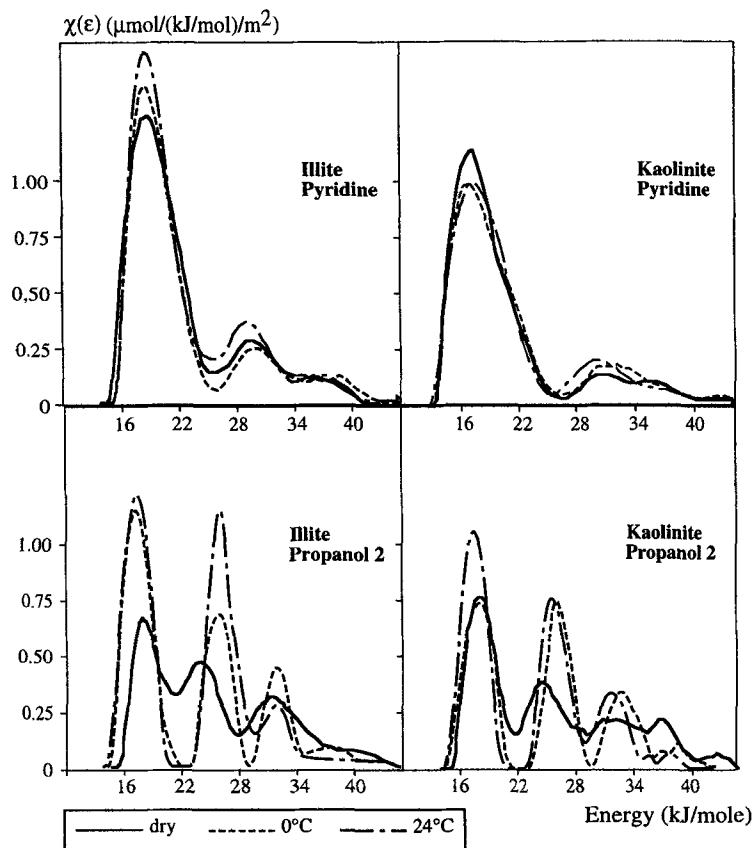
Figure 4. Adsorption energy distribution functions of propanol-2 and pyridine for illite and kaolinite using vector gas, either dry or saturated with water at 0 °C and 28 °C, under 0.2 MPa.

of the tail in the highest-energy domain was observed; again, it was more clearly evidenced for illite than for kaolinite. This difference of behavior had to be related to the higher hydrophilicity of the illite on which the adsorbed water molecules are more strongly adsorbed. In other words, the shielding of the highest-energy adsorption sites leads to the enhancement of the peaks having the lowest adsorption energy. Alternatively, the difference between the pyridine and propanol-2 probe behaviors can be attributed to the higher capacity of the strong basic probe pyridine to displace the adsorbed water from the adsorption sites on the clays surface as compared to propanol 2, because of its acidic character. To support this interpretation, we have

Table 4. Specific surface areas, BET constants and positions of DF main peaks.

	$\theta_{saturator}$	Pyridine			Propanol-2		
		Dry	0 °C	28 °C	Dry	0 °C	28 °C
Illite	S_{BET}	56	64	67	40	43	46
	C_{BET}	35	28	32	55	35	24
Kaolinite	S_{BET}	37	38	39	28	27	28
	C_{BET}	24	22	23	27	37	26

calculated the specific surface area and the BET constants for the adsorption isotherms of pyridine and propanol-2 on illite and kaolinite, in both the absence and presence of water (Table 4).

Taking into account the measurement accuracy, we may consider that partial coverage of the surface by water does not significantly influence the measurement of the solids' specific surface areas. In the case of pyridine, water does not change the BET constant values. On the contrary, for propanol-2 and the illite sample, an important decrease is observed, evidencing a strong change of the surface nature after hydration. Finally, the kaolinite BET constant values are quite independent from the hydration degree of that sample. How can we interpret these observations? The slight change of the DF of pyridine on a wet sample is certainly related to the fact that this strong basic probe is able to displace water from the acidic adsorption sites of the clay. On the contrary, if we admit that propanol-2, an acidic probe, is unable to displace water from the same acidic adsorption sites, we will observe a change in the DF and BET constants, especially in the case of the more hydrophilic solid, illite.

In other words, the higher the hydrophilicity of the solid, the lower will be the adsorption level of the propanol-2 probe on the wet sample. This fact might begin to explain the behavior of the 2 families of clays in the oil fields. Indeed, the propanol-2 type of probe is better able to displace water from the kaolinite than from illite surface. This explains why oil wets kaolinite in the reservoir while illite stays wetted by brine.

CONCLUSION

This paper demonstrates the remarkable ability of IGC to detect surface events and evaluate surface peculiarities of clay minerals. IGC can thus be used for the exploration of a macroscopic phenomenon. Our findings also highlight the complementary character of IGC at infinite dilution and finite concentration conditions in order to obtain a more realistic description of the surface characteristics of a solid. However, care should be taken in interpreting the chromatographic raw data. Only a satisfactory understanding of the molecular probe adsorption process will lead to rigorous information regarding the clay surface characteristics that strongly influence their behaviors in an oil reservoir.

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