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ADSORPTION AT THE LIQUID/SOLID INTERFACE : THE PART OF MICROCALORIMETRY IN THE FIELDS OF ENHANCED OIL RECOVERY, LUBRICATION AND WATER PURIFICATION

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ABSTRACT

After listing the problems of adsorption which are more specifically related to each of these three fields, typical results obtained by liquid/solid adsorption microcalorimetry are reported and commented on. Batch adsorption microcalorimetry is shown to be especially interesting as a sensitive detector to follow the kinetics of adsorption whereas liquid-flow adsorption microcalorimetry -although less universal- is a more convenient tool for a preliminary screening of the systems and also to study desorption.

INTRODUCTION

Although adsorption at the liquid/solid interface is of extremely high technological interest, our understanding of the phenomenon is lagging far behind what we know about gas adsorption. The main reason is of course the higher complexity of the systems which, in the simplest case, already involve 2 adsorbable components (the solvent and the solute), of which only one can be followed in terms of surface excess quantities, whereas the composition of the adsorbed layer usually remains unknown. It follows that a large number of questions usually remain unanswered. For instance, at any stage of the adsorption phenomenon :

- what is *the amount of solvent* still present *in the adsorbed phase* ?
- what is *the orientation* or, more generally, the configuration of the adsorbed molecules, especially when a large molecule of solute competes with a small molecule of solvent ?
- is *the adsorption* of the 2 (or more) components *patchwise or random* ?
- are there *any specific interactions* between the ad-molecules (like, for instance, in hemi-micelles) ?
- what is the limiting step in the *kinetics of adsorption* ?

To answer these questions, one must draw the best from the presently available techniques, especially those allowing to study the adsorbed phase without changing its immediate surroundings and without drying it. Among the available techniques, we may distinguish between :

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- those allowing to reach the *surface excess amount* (i.e. allowing to determine the so-called "adsorption isotherms") on which an up-to-date and critical general presentation, together with the appropriate processing of the data, may be found in (ref.1)
- those allowing to get direct *information on the state* of the adsorbed molecules and on their interactions with the neighbourhood : NMR (on labelled long chain adsorbates (ref.2)), IR (in the case of non-aqueous solutions), fluorescence decay (ref.3), ellipsometry ...
- those allowing to reach the *enthalpy changes* of the system during immersion of the solid into the solution or during displacement of the solvent by the solute.

For systems of technological interest (for which a few parameters are already fixed, like a low specific surface area of the adsorbent or a low range of solute concentration), most techniques above must be used at their highest sensitivity. This is also the case of calorimetry which must be used in the form of *micro*calorimetry*. We shall here present typical results obtained in the three fields of enhanced oil recovery (low surface area mineral adsorbent), lubrication (organic solutions) and water purification (dilute solutions and porous adsorbents).

ADSORPTION MICROCALORIMETRY IN THE FIELD OF ENHANCED OIL RECOVERY (EOR)

The problems to solve

a) From the viewpoint of chemical EOR, the problem to solve is *to avoid any irreversible adsorption*, on the rocks of the oil reservoir, of the components of the solutions used for the chemical flooding. Adsorption of only one component is enough to make the solution inefficient. One possible answer is to adsorb a "sacrificial" component which is not directly involved in the process of oil recovery proper, but which is adsorbed preferentially on the mineral surfaces, once the oil has been displaced. An irreversible chemisorption, leading to high enthalpies of adsorption, would then be satisfactory. Another answer is of course to find a chemical flood whose components would virtually not adsorb on the rocks at the concentrations used. Nevertheless the problem seems difficult to solve since the chemical flood is expected, among other properties, to displace the oil from the walls of the pores.

b) From the point of view of adsorption, various problems arise :
- from the fact that the adsorbable solutions are multicomponent (for instance : surfactant, co-surfactant -usually an alcohol, to make easier the microemulsion,

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* Usage seems to fix roughly the upper limits of microcalorimetry at *c.a.* 100 mJ (for the amount of heat measured in one time) or 10 mW (for the thermal power measured at any time)

water and often salt, which is already in the oil reservoir and cannot be ignored)

- from the fact that the rocks involved are not very well defined from the adsorption point of view. For instance, the adsorbing properties of a sandstone of *c.a.* 0.1 m^2g^{-1} may well be 90% determined by a 3% "impurity" clay whose specific surface area may amount to 30 m^2g^{-1}.

c) From the point of view of microcalorimetry, the problems are due :

- to the limited specific surface area of the rocks (especially of sandstone and calcite)
- to the small enthalpies of displacement to be measured (as will be seen)
- to the uncontrolled changes occurring, during the adsorption phenomenon, in the power dissipated by stirring (batch calorimeters) or by flow-through (liquid flow calorimeters) and due to changes in the thyxotropic properties of the adsorbent bed or suspension.

Typical microcalorimetric results

A very few laboratories, till now, have used the adsorption microcalorimetry approach to study systems in the scope of EOR and these works are less than 6 years old.

a) Orders of magnitude of the enthalpies of displacement.

The surfactantsmost widely used in EOR are either *sulphonates* (and especially "oil sulphonates", which are relatively cheap, although ill defined) or non-ionic *alkyl phenol polyethylenoxides* ("Triton", "Igepal" etc...) whose main interest, as compared with the sulphonates, is not to be precipitated by the Ca^{++} or Mg^{++} ions at the ionic concentrations of up to a few % which may be found in the oil fields. Typical surfactants of the above types were adsorbed onto ground sand (to play the part of sandstone, but taking advantage of an increase in specific surface area from less than 0.1 m^2g^{-1} for the sandstone to *c.a.* 4 m^2g^{-1} for the ground sand) or onto kaolin (with a nitrogen-BET specific surface area of *c.a.* 19 m^2g^{-1}). As it may be seen in Table I (taken from (ref.4)), the enthalpies of displacement are ranging from *c.a.* 6 to only 17 mJm^{-2} for the completion of the adsorbed layer corresponding to the plateau of the adsorption isotherm. One can easily understand that the highest available microcalorimetric sensitivity is needed, since the above enthalpy changes are to be recorded over times ranging from 0.5 to several hours and since the total surface area in the microcalorimeter may be of a few m^2 only (in the case of sand). The reasons for such a small enthalpy of displacement may be listed as follows :

- reaching the plateau of the adsorption isotherm *does not mean that a nearly compact monolayer* of the solute has been completed, as it would be usually the case at the gas/solid interface. From the height of the plateau and from the BET

TABLE 1

Microcalorimetric results on adsorption of a few surfactants (from water solution at 30°C) onto ground sand or kaolin (from (ref.4))

Adsorbent	Ground sand			Kaolin	
Adsorbed surfactant	TX-100	TX-102	Na-DDBS	TX-100	TX-102
Amount adsorbed (μmol m^{-2})	0.74	0.40	1.59	0.94	0.63
Apparent area (nm^2)	2.24	4.15	1.04	2.02	2.63
$\Delta_{dpl}H$(mJ m^{-2})	9.2	5.9	16.4	11.5	8.0
$\Delta_{dpl}H$(kJ mol^{-1})	12.4	14.7	10.3	12.4	14.5

surface area of the adsorbent, one may indeed derive the mean apparent area available to one adsorbed surfactant molecule. These areas (cf. Table 1) are much larger than the *c.a.* 0.3 nm^2 which may be expected, from the atomic sizes, for such surfactant molecules standing straight on the surface (ref.6). Two explanations (and all the intermediate situations) hold : either the surfactant molecules are standing normally to the surface, so that they share the surface with water molecules (which may in turn be either evenly distributed, in the case of solvatation of the surfactant, or adsorbed by patches) or the surfactant molecules cover the whole surface. To decide between the above asumptions, the shape of the adsorption isotherm may be helpful, since an S-shaped isotherm (*i.e.* beginning with an increasing slope) seems to be -as suggested by Giles (ref.7)- a safe indication of a cooperative adsorption, usually needing a parallel stacking of the adsorbed molecules. For instance, in the case of the sodium dodecylbenzene sulphonate / sand system, where the adsorption isotherm is strongly S-shaped and where the apparent area is of 1.04 nm^2 per sulphonate molecule, one may derive the following conclusions : (i) since the sulphonate molecules are likely to be stacked together (S-shaped isotherm) they are adsorbed by patches occupying about one third of the surface (*i.e.* 0.3 /1.04), (ii) this implies that an enthalpy of adhesion of (0.3/1.04) x (510 + 112.5) = 180mJ is needed (from enthalpy of immersion data given for the same sand in (ref.8)) to remove the water molecules replaced by 1.59 mol of sulphonate, (iii) considering that the transfer of a sulphonate molecule from the micellar state to the stacked state is likely to be a-thermal, then the enthalpy of adhesion of the sulphonate patches on the sand is (180 + 16.4) x (1.04/0.3) = 680 mJ.m^{-2}, *i.e.* slightly higher than that of water, (iv) if we refer it to the amount of sulphonate in the adsorbed patches, we arrive to an enthalpy of adhesion of 123 kJ.mol^{-1} whereas in the case of water, even if we only consider the first layer, we get an enthalpy of adhesion of 39 kJ.mol^{-1}, which is consistent with the 3 times smaller cross-sectional surface area, (v) immersion calorimetry experiments would have given enthalpies of 510 $mJ.m^{-2}$ (for immersion in water) and 526.4 $mJ.m^{-2}$ (for immersion in the solution), *i.e.* a 3% difference, which would have been too small to be significant

- the difference between the strong enthalpy of adhesion of water with most oxides (usually 500 to 600 $mJ.m^{-2}$ if they have been previously outgassed at 150°C) and the even slightly stronger enthalpy of adhesion of a surfactant with the same surface does not lead to a large figure (as illustrated above)
- especially, in the case of large molecules which, in favourable cases, may reach a high degree of structuration (in micelles, in the solid state, but also in the adsorbed state) it may be expected that the entropic term plays a major part in the "driving force" for adsorption, *i.e.* in the Gibbs free energy of displacement which may therefore be appreciably high, even with a small enthalpy of displacement.

Always in the scope of EOR, a number of experiments were carried by liquid-flow microcalorimetry, either to draw benefit of the simple method proposed by Groszek to measure the surface area (from the heat of displacement of n-heptane by 1-butanol (ref.9)) or to study the adsorption on silica of a series of normal alcohols which may be used as co-surfactants. The conclusions of Noll et al (ref.10) are that the still low enthalpies of displacement (22 to 29 $kJ.mol^{-1}$ for 3 to 10 carbons in the alcohol) are consistent with a merely physical process, whereas the increasing mean "parking areas" are explained by an adsorption parallel to the surface. With a similar technique, Denoyel et al (ref.11) followed the formation of a layer of TX-100 on a silica gel. The whole phenomenon (transfer of the surfactant molecules from the micelles to the surface and displacement of water) is eventually a-thermal (when the adsorbed layer is completed) whereas during the formation of the adsorbed layer the enthalpy changes observed are either exothermal (adsorption on active sites) or endothermal (growth of a two-dimensional phase of closely packed ad-molecules).

b) Specific information brought by microcalorimetry about the *kinetics* of adsorption.

Most methods used for the determination of adsorption isotherms may be used to reach the *kinetics of transfer* of the solute from the solution to the adsorption space. These are depending upon one basic parameter of the phenomenon, *i.e.* the activation energy of the displacement, and also upon the rate at which the molecules of solute are brought to the adsorption space (the latter rate depending on the stirring or flow rate and on the grain size and porosity of the adsorbent). Nevertheless, it may also be interesting to follow *further transformations occuring in the adsorption space* : this is a field in which microcalorimetry has a special part to play, as it can be illustrated by two examples.

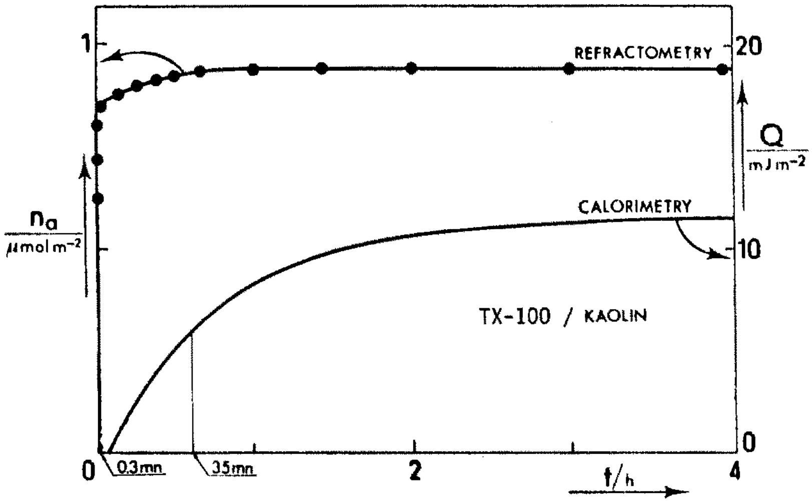

Fig. 1. Kinetical information brought by adsorption microcalorimetry : slow structuration of the adsorbed layer of TX-100 on Kaolin at 30°C (from (ref.4)).

Fig. 1. (from (ref.4)) shows two recordings (one, discontinuous, obtained by refractometry and the second, continuous, obtained by microcalorimetry). Although they both follow the same adsorption phenomenon (namely, TX-100, from aqueous solution, onto a Kaolin of 19 m^2g^{-1}), the time constants are quite different. The "half-transformation time" is indeed of *c.a.* 35 min. from the microcalorimetric recording and *more than 100 times smaller* (*c.a.* 0.3 min) from the refractometric recording. This is not due to experimental artefacts since, for other systems (for instance, the TX-100 / ground sand system) both techniques may lead to a similar time constant and since the response time of the microcalorimeter with its content lies around 3 min only. The explanation is then simply that, although the transfer of surfactant to the adsorption space is virtually immediate (due to an efficient stirring of the Kaolin suspension, either in rocking tubes or with the help of disk stirrers with vertical motion), it takes much more time (several hours) to reach the final state of the adsorbed layer. It is nevertheless puzzling that a change in the structure of the adsorbed layer does not have any measurable influence on the composition of the layer, *i.e.* on the amount adsorbed. This may be understood by the fact that although the surface is very quickly saturated with the TX-100 molecules and their cloud of solvatation molecules (in close interaction with the long oxyethylenic chain) and

although the water / TX-100 ratio in the adsorption space all at once reaches its equilibrium value (a fact in favour of the existence of a hydrated TX-100 molecule), it may take time to the adsorbed TX-100 molecules to reach the most favourable structure from the Gibbs free energy point of view. It would be of course interesting, even if not easy, to confirm this structuration by another technique than microcalorimetry.

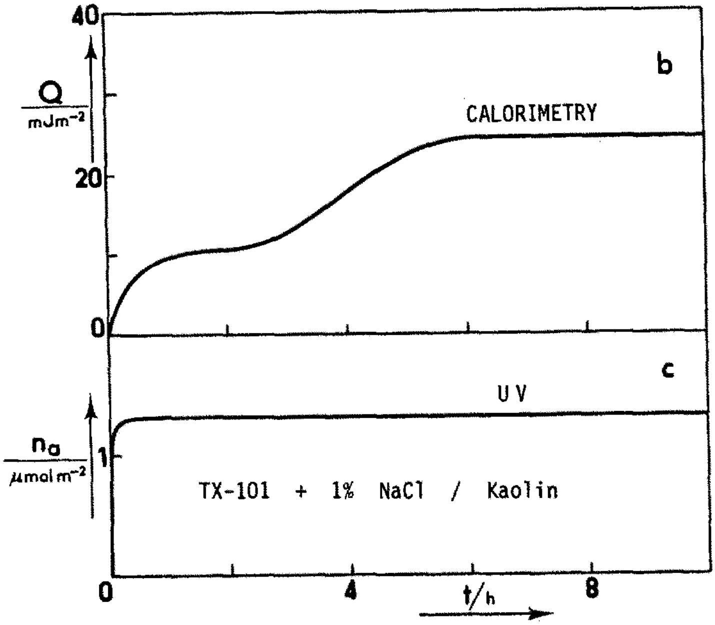

Fig. 2. Kinetical information brought by adsorption microcalorimetry : 2 step phenomenon during adsorption of TX-101 on Kaolin from a water solution with 1% NaCl, at 30°C (from (ref.4))

Fig. 2 shows an example of a phenomenon (adsorption of TX-101 on Kaolin, from a 1% NaCl aqueous solutions) which, when followed by UV on the supernatant liquid, is here again immediate. On the other hand, the microcalorimetric recording distinctly shows two steps. Since, at the top of the second step, the total amount of heat evolved is about twice as large as that recorded in the experiment of Fig. 1, we must seek for an extra phenomenon. Referring to previous work on clays by Fripiat et al. we came to the idea that the sheet-like structure of the Kaolin was partly open under the conjugated action of the salt and surfactant. This partial opening allowed water -but not surfactant- to penetrate between the sheets, giving rise to an enthalpy of immersion. If we refer to the enthalpy of immersion of the same Kaolin (outgassed at 150°C) in water (520 mJ. m^{-2} (ref.4)) we see that only 0.6 m^2g^{-1} of "fresh" surface is enough to explain the microcalorimetric data. To be more accurate, one ought to take into account the energy needed to separate the sheets of Kaolin and which lowers the exothermal phenomenon taking place during hydration. It may be that the apparent delay (nearly one hour) observed between the end of the first step and the onset of the second one is only due to a temporary cancellation of one thermal effect by the other.

It is worth pointing out that these kinetical studies need the use of a *batch* microcalorimeter in which the suspension of adsorbent in water is quickly brought in contact with the whole amount of solution (which is not possible to do with a liquid-flow microcalorimeter). Moreover, the batch microcalorimeter is practically compulsory when the adsorbent is a clay, since the latter cannot be kept on the filter of a flow-through system.

ADSORPTION MICROCALORIMETRY IN THE FIELD OF LUBRICATION

The problems to solve

One knows that modern engine lubricating oils usually consist of an oil medium acting as a vehicle for a number of additives whose activity (antiwear, anticorrosion, rust inhibitor, detergent, friction modifier, inhibitor for the catalytic activity of the metal surface etc ... (ref.13)) largely takes places on the solid surfaces which are to lubricate. Therefore, both *the stability* and *the kinetics of formation* (or re-formation) of the adsorbed layer are useful to know. Concerning the kinetics of its formation, although we have seen that, for systems in the scope of EOR, microcalorimetry was an excellent tool, we must have in mind that the time-scales are not at all the same, since in lubrication a nearly instantaneous adsorption is needed. In these conditions, the response time of microcalorimeters is usually much too long. In the absence of any direct assessment of the Gibbs free energy of the adsorbed phase, one may use the *enthalpy changes* (directly measured by microcalorimetry) as an *indicator of the stability* of the adsorbed layer. This was first pointed out by Groszek, who successfully developed the first thermal detector to follow these adsorption phenomena (ref.14). It can be especially interesting to see whether the enthalpies of interaction are *in the range of physisorption or in that of chemisorption*. Also, since the engine lubricants must be operational in a large temperature range (*i.e.* from 10 to 200°C, in a general case), microcalorimetry may be expected to be an interesting detector of *any change undergone* by the adsorption system *as the temperature is raised*.

Typical results

The above reasons were enough to launch Groszek in a series of studies carried out with a simplified -although sensitive- liquid flow apparatus. It was then possible to study the stability of a mixed adsorbed layer with respect to the relative size of the molecules and to check very easily the reversibility of adsorption, just by replacing the solution flow by a pure solvent flow. An interesting work was carried out with this equipment to study the adsorption of stearic acid onto ferric oxide (which is a frequent surface state for so-called iron objects ...) by Jaycock et al. (ref.15). Fig. 3 reports one of their typical recordings. At point A the pure heptane flow is changed to a stearic acid solution in heptane. The *exo*thermic peak first recorded is due stearic acid adsorption but it competes with the second peak, which is *endo*thermic and which is attributed either to the dissociation, on the surface, of the dimers of stearic acid (they are known to exist in the heptane solution at the concentration of 42.1 mM used here) or to the desorption of water from the iron oxide surface. At point B the solution is changed to pure heptane to produce a desorption. Successive adsorption/desorption cycles show a slow increase of the total amount which seems to be irreversibly adsorbed on the surface. Nevertheless, it is not possible, here, to disentangle the effects of time (slow chemisorption) and those of a large number of successive runs which would favour a reorganisation of the adsorbed phase. Actually, the irreversibility may be more efficiently proved by a procedure like that used by Kern and Findenegg (ref.16) with an LKB liquid-flow microcalorimeter : the possible desorption after a long-lasting period of flow-through with the pure solvent is detected by a rapid re-adsorp-

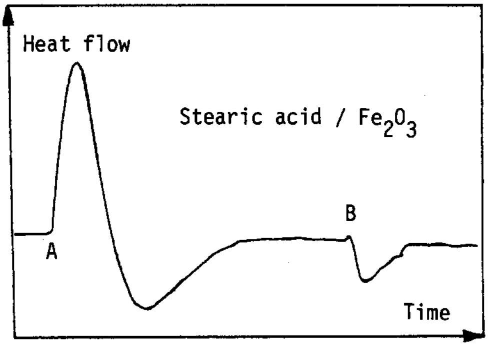

Fig. 3. Recorder output trace for the adsorption and desorption of stearic acid from a 42.1 mM solution in heptane into ferric oxide (from (ref.15))

tion taking place in the same conditions as in the first run, *i.e.* with the same final state. The interest of this procedure is to replace a very slow phenomenon (desorption from a system whose equilibrium concentration is very low) by a fast one (adsorption from a solution at appreciably high concentration).

Fig. 4 shows microcalorimetric results also obtained for adsorption of stearic acid, but on alumina (ref.17). The micron grain size of the alumina (Aluminoxid from Degussa) and the interest of working at temperatures higher than ambient were the reasons to use here a Tian-Calvet batch microcalorimeter. The enthalpies of displacement indicated are those calculated after correcting

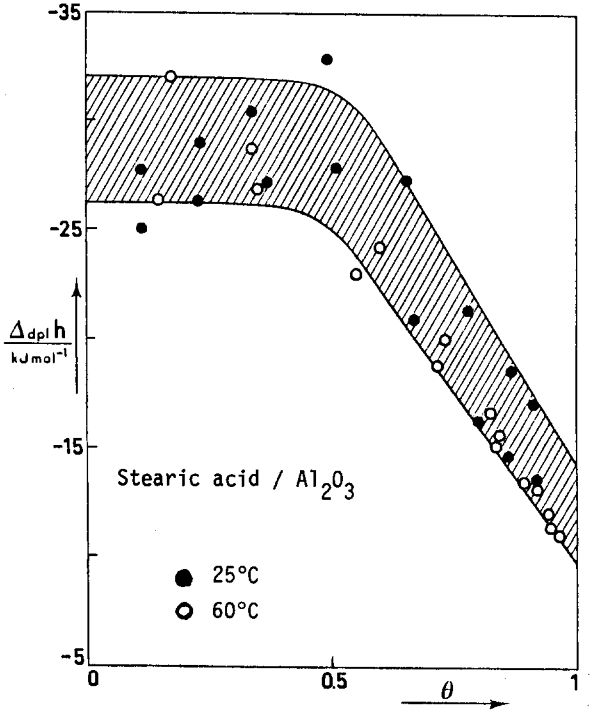

Fig. 4. Differential enthalpy of displacement of oil (Lytol) by stearic acid on alumina at 25 and 60°C (from (ref.17))

the heats measured for the heats of dilution (since any adsorption from a solution involves not only a *displacement* (of the solvent by the solute) but also a *dilution* (of the solution) which are here larger than (and opposite to) the overall thermal effects recorded. These enthalpies of displacement are practically the same at 25 and 60°C and they show that half of the adsorbed layer is fixed more strongly. Nevertheless, between 60 and 120°C, the amount of stearic acid adsorbed at "saturation" remains unchanged and twice smaller than that calculated from the specific surface area of the alumina (100 m^2g^{-1}) and from the 0.205 nm^2 cross-sectional area of the stearic acid molecule in a condensed film. Both observations are in favour of chemisorption on specific sites of the alumina. Instead of raising the temperature of adsorption, one may raise the temperature of preliminary outgassing of the alumina. This was done (between 150 and 750°C) by Stradella and Venturello (ref.18) who observed a more than 6-fold increase of the "differential heat of adsorption" of fatty acids on transition alumina. A practical consequence is that a strong bond between stearic acid and alumina is favoured by preliminary outgassing.

ADSORPTION MICROCALORIMETRY IN THE FIELD OF WATER PURIFICATION

The problems to solve

The adsorption step is known to be the last one, the safer one and also the most expensive for the purification of drinking water. The adsorbents used must have the highest possible capacity, must retain strongly an extremely large range (in size) of organic molecules (the equilibrium concentration, in weight, must often be smaller than 1 part per million) and, if possible, must be regenerated by a thermal or chemical treatment which will not damage the adsorbent. Moreover, in the case of carbons, an appreciable increase in apparent capacity is known to be due to a microbial degradation of the already adsorbed molecules. Microcalorimetry may be expected to be helpful :

- In appreciating the *stability* of an adsorbent in water.
- In appreciating the *strength of the interactions*, especially at the beginning of the adsorption, when the information is difficult to get (because of the too low equilibrium concentrations) from the adsorption isotherms.
- In following the internal migrations of adsorbate within the porous network.
- In the detection of various types of microporosity (from the enhancement of the adsorption enthalpy due to the narrowness of the pores).
- In following the long term microbial activity.

A few results

Presently, and in our knowledge, the above type of microcalorimetric work is just starting. Only two punctual examples are given here. The first one concerns the behaviour of aluminas in water. Indeed, although activated carbons are the most commonly used adsorbents in water treatment, the potential interest of aluminas is presently being considered, partly because of the variety of compounds found in water, among which those having a carboxylic function may be expected to adsorb more readily on amphoteric alumina. Moreover, the pore-size distribution of aluminas may be extremely different from, and therefore complementary to that of activated carbon.

The first aspect to consider is the long-term behaviour of aluminas in pure water. In the work reported in Table 2 (from (ref.19)) this was done by immersion microcalorimetry, starting from various states of the same samples : original beads, beads crushed into powder, beads soaked in water. Although all samples were outgassed at 150°C prior to the immersion, those in previous contact with water (crushed in air or soaked in water) give rise to a smaller enthalpy of immersion than the original beads, which shows a partial rehydration which remains irreversible on outgassing at 150°C. It follows that surface characterization of these aluminas (porosity and surface properties) must not take place without a preliminary soaking in water.

TABLE 2
Immersion microcalorimetry of five aluminas in water

Beads					
Surface area/m^2g^{-1}	90.4	123	163.7	232.9	274
$\Delta_{imm}H$ / Jg^{-1}	41.7 ±0.8	61.5 ±1.2	82.3 ±2.7	111.8 ±2.3	121.5 ±2.8
$\Delta_{imm}H$ / mJm^{-2}	502	452	443	500	480
Crushed into Powder					
$\Delta_{imm}H$ / Jg^{-1}	38.3 ±2.5	56.2 ±0.3	68.9 ±3.6	103.1 ±1.2	114.0 ±6.3
Beads pretreated in water					
$\Delta_{imm}H$ / Jg^{-1}	43.0 ±1.1	59.1 ±0.5	77.8 ±1.7	98.9 ±3.5	107.0 ±5.1

A second aspect of interest is the microporosity of activated carbons. The few methods presently available to detect and characterize microporosity are mainly the (time-wasting) adsorption of probe molecules and the analysis of nitrogen adsorption isotherms by Sing's α_S method. Any confirmation by an independent method is of course welcome. This could be done, in the case of a commercial activated carbon (Chemviron F-400) by using adsorption microcalorimetry of nitrogen at 77 K (ref. 20). The curve of differential enthalpies of adsorption *vs* coverage is made of 2 successive straight lines, indicating 2 successive mechanisms of filling of the micropores. For this carbon, indeed, the α_S analysis of the adsorption isotherm shows a first micropore filling (corresponding to 20% of the "equivalent" BET surface area) and then a second one before the completion of the monolayer. It is extremely satisfactory to see that adsorption microcalorimetry also detects the same bi-modal microporosity which is now to be taken into account for the interpretation of further adsorption experiments on this adsorbent.

CONCLUSION

The few following remarks may sum up the present status of adsorption microcalorimetry (from the liquid phase) :

- After recognizing Groszek's pioneering work, one may say that microcalorimetry is *a relatively recent tool* in the field of adsorption from liquid solutions and is still used by a small number.
- Most often, *its highest sensitivity is needed* to follow the phenomena.
- The interest of microcalorimetry is to be *both sensitive and quantitative* and not to need any special state of the system (for instance, the adsorbent may be in fine powder or in beads, the solution or suspension may be transparent or not etc...).
- Microcalorimetry is an excellent tool *to follow the kinetics* of transformation of the adsorbed phase.
- To cope with the various situations, microcalorimetry ought to be available both in the *batch mode* (necessary for fine powders and for kinetics) and in the *liquid-flow mode* (necessary for desorption).
- Although microcalorimetry may be an interesting means to get a general information on the behaviour of an adsorption system (rate and reversibility of adsorption, strength of the interactions), the best is drawn from this technique when the system studied is well defined, so that the sensitive and quantitative extra information brought by microcalorimetry is a final and safe "touch" to understand the whole ....

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