THE CONTRIBUTION OF MICROCALORIMETRY TO THE SOLUTION OF PROBLEMS INVOLVING A LIQUID/SOLID OR A GAS/SOLID INTERFACE, ESPECIALLY IN PHYSISORPTION *

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ABSTRACT

After listing a number of basic or applied problems for which it seems advantageous to determine adsorption or immersion enthalpies, this paper describes the methods currently available to determine the enthalpies of (i) immersion into a liquid, (ii) adsorption from a gas, and (iii) displacement from a liquid solution. Typical applications of each technique are reported and commented on.

INTRODUCTION

The first two steps in the quantification of adsorption phenomenon are usually: determination of the "mass exchange" (to obtain the "adsorption isotherm") and determination of the "heat exchange" (to reach, if possible, the curve of "differential" energy, or enthalpy, of adsorption).

At the "basic level", the knowledge of the energy of adsorption is indeed an extremely valuable aid to the better understanding of:

(1) physisorption of gases (nature of the interactions involved, state and stability of the adsorbed phase; influence of the crystalline structure on the adsorption phenomenon, of the porous texture and of the chemistry of the surface on the adsorption phenomenon);

(2) chemisorption of gases (see refs. 1 and 2) (chemical bonds involved and steps of catalytic reactions);

(3) wetting by pure liquids;

(4) adsorption of solutes from liquid solutions (kinetics of adsorption, structure and stability of the adsorbed layer).

At the "application level", adsorption microcalorimetry is a helpful tool for:

(1) screening adsorbents to select: (a) the strongest bonds (for energy storage and elimination of toxic gases from air, heavy metals from water,

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stains from fabrics, etc.), (b) the most stable adsorbents (for water treatment or the purification of liquid food-products, etc.);

(2) screening adsorbates to select: (a) either the strongest bonds (with a view to froth-flotation, lubrication, adhesion, dispersion of pigments into a given liquid, etc.), (b) or the weakest bonds (as usually desired in the case of enhanced oil recovery, pesticides in soil, etc.);

(3) quantitative characterization of powders, especially for factory tests (immersion calorimetry).

Because of the above variety of applications, it was found interesting, in the following presentation, to examine successively the main microcalorimetric methods, with their characteristic features and possibilities with regard to interfacial phenomena.

IMMERSION CALORIMETRY

Experimental procedure

This method was largely developed, in the past, especially by A.C. Zettlemoyer, using the bulb breaking technique in an isoperibol (or "Berthelot" or "Thomsen") calorimeter [3]. The experimental procedure appears to be extremely simple, since a glass bulb (containing the adsorbent) and a somewhat larger vessel (containing the immersion liquid) seem to be enough. Nevertheless, Fig. 1 shows that interpretation of the whole immersion phenomenon, as followed by calorimetry, needs some care. In this representation we suppose that the glass rod to which the sample bulb is fused is also used to drive the stirrer.

Depressing the glass rod starts the experiment by breaking the glass bulb against the needle on the bottom. The thermal phenomena in the calorimeter
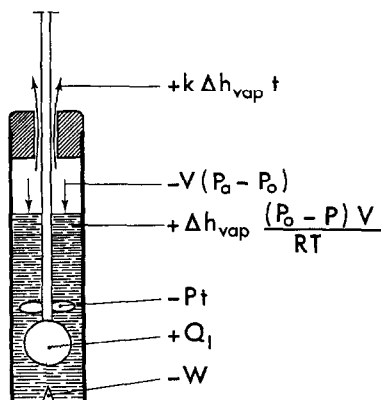

The labels in the figure read:

$$+k\,\Delta h_{vap}\uparrow$$

$$-V(P_a - P_o)$$

$$+\Delta h_{vap}\frac{(P_o - P)\,V}{RT}$$

$$-P\uparrow$$

$$+Q_1$$

$$-W$$

Fig. 1. Thermal phenomena during an ordinary immersion calorimetry experiment.

are as follows (from top to bottom) [4]:

$k\Delta_{vap}ht$ term due to continuous (but not always stable) evaporation of the liquid out of the calorimeter during time t

$V(p_a - p_0)$ term due to the work of atmospheric pressure, p_a, during the depression of the liquid level (whose saturating vapour pressure is p_0)

$\Delta_{vap}h\dfrac{(p_0 - p)V}{RT}$ term due to evaporation of the liquid into the volume left free by depression of the liquid level during filling of the glass bulb, in which the equilibrium pressure (before breaking) was p, i.e., very often, a vacuum

Pt stirring energy

Q_I heat effect corresponding to the enthalpy of immersion proper

W energy of bulb breaking, which may amount to more than 1 J for complete breaking of a thin-walled glass ampoule

Any modification allowing one or more of these "corrective terms" to be eliminated is clearly welcome, as a means of increasing the accuracy of the method (and, therefore, of lowering the surface area needed for a meaningful experiment). Starting from a former design [5], we have progressively reached the assembly shown in Fig. 2. This air-tight assembly (where O-ring 5 allows tight up-and-down displacement of glass rod 4) is used with a Tian–Calvet isothermal microcalorimeter. Its advantages are (i) elimination of continuous evaporation of the liquid (usually responsible for drifts of the baseline); (ii) elimination of the work of atmospheric pressure; (iii) elimination of the need for stirring, hence the upper void volume 2 which is eventually filled with the liquid passing through the sample (if necessary, an intermediate constriction can be made to stop the adsorbent during its upwards movement and so enhances the "percolation" effect of the system [6]); and (iv) minimisation of bulb breaking heat (ca. 5 mJ) and also its scattering (so that values from blank experiments with other bulbs can be used with a satisfactory degree of confidence). Also using a closed system, but with a magnet-suspended glass bulb of increased brittleness, Everett et al. [7] succeeded in obtaining reproducibilities of the order of 1 mJ. The practical problems associated with the blowing and sealing of these thin ampoules with a brittle end can be avoided by means of a stop-cock [8] which makes the experiment much easier. Nevertheless, new problems arise with regard to the initial outgassing of the adsorbent (the stopcock is closed and usually cannot whithstand being heated) and the tightness of the system (it is difficult to maintain the starting vacuum and, therefore, the starting state, in the small sample ampoule during thermal equilibration of the calorimeter; enthalpies of immersion are extremely sensitive to this initial state of the adsorbent). The device shown in Fig. 2 needs more practical skill but it is safer and more universal. It allows
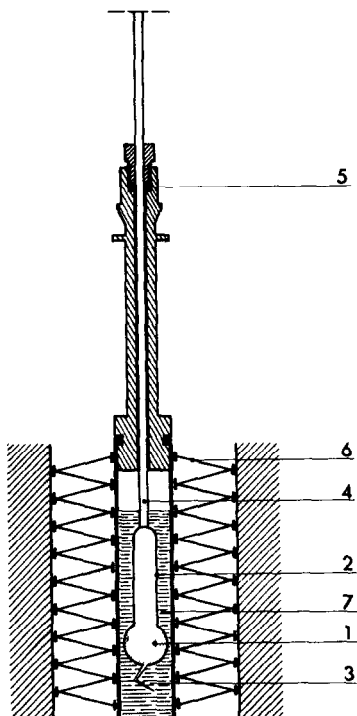
Fig. 2. Air-tight device for immersion microcalorimetry experiments.

the performance of experiments with an overall inaccuracy of ca. 25 mJ. This means that samples of only a few $m^2 \ g^{-1}$ may be studied by this technique.

Main applications

Immersion microcalorimetry may be regarded as simple, sensitive and quantitative. It can be used in various ways, as described below.

(1) To follow any change in the surface state of a sample (surface area, microporosity, surface crystallinity or chemical nature). Interaction with a polar liquid, such as water, as well as a number of organic molecules, may be extremely sensitive to small changes in these surface-state parameters. The accuracy increases when the saturating vapour pressure, and therefore the corrective term for the heat of vaporization, decreases with the temperature of the experiment. Immersion microcalorimetry may thus be used as a complete sensitive factory test, provided it is remembered that the experiment proper, i.e., recording of the microcalorimetric signal, may last ca. 30 min if there is no long-term phenomenon, whereas preparation, outgassing and final thermal equilibration of the sample may last a number of hours; on the other hand, there is no objection to using both cells of a differential microcalorimeter, one after the other, as "active" cells, to double the speed.

As to microporosity, an interesting study by Widyani and Wightman [9] follows the size of the micropores in natural coals by comparing their availability to a series of normal alcohols. Greater availability to the smallest molecules gives rise to a larger specific (i.e., related to the unit mass of adsorbent) enthalpy of immersion and a quicker phenomenon, because of easier diffusion into the micropores. Immersion calorimetry, indeed, yields both thermodynamic information i.e., the enthalpy of immersion obtained by comparing the initial and final states of equilibrium, and intermediate kinetic information from the continuous calorimetric recording, expressible, in its simplest form, as the "half-time of reaction" or half-time of heat evolution". Similar work has been successfully performed on microporous charcoals and associated with gas adsorption studies (both volumetric and microcalorimetric) [10].

(2) To follow changes in the chemical nature of the surface only, provided another method is available to determine the specific surface area of the sample, and provided microporosity is shown (or known) to be absent. The specific surface area may be determined by the BET method but also by the modified Harkins and Jura calorimetric method which is described hereafter and which has the practical advantage of using exactly the same equipment.

(3) To follow changes in specific surface area only, using a modification of the Harkins and Jura "absolute" method (original principle shown in Fig. 3). The basic idea is to screen the "active centres" of the surface with a thick layer of adsorbed water (obtained by pre-equilibration with saturating water vapour) and then immerse the wetted powder in water inside a calorimeter. The water/air interface surrounding every particle or assembly of particles disappears during immersion, giving rise to a heat release, Q_1, which solely depends on γ (the water/air interfacial tension), its dependence on tempera-
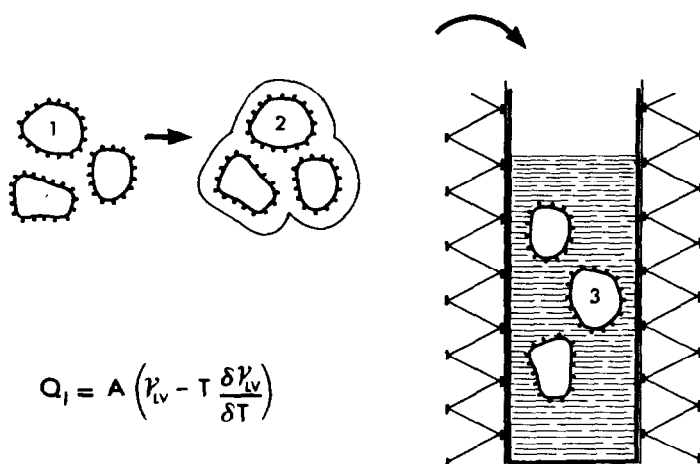
$$Q_1 = A \left(\gamma_{lv} - T \frac{\delta \gamma_{lv}}{\delta T} \right)$$

Fig. 3. Principle of the "absolute" Harkins and Jura method for the calorimetric determination of surface areas.

ture, and *A* (the area of the water/air interface). The method is elegant since, unlike the BET method, it does not require any assumption concerning the content of a monolayer and the cross-sectional area of the adsorbed molecules. Nevertheless, considerable uncertainty may remain as to the relationship between the area of the water/air interface (actually measured) and the surface area of the solid in question. Fortunately, systematic studies on a number of adsorbents show that, as a general rule, only two layers of water are enough to screen, from the point of view of the enthalpy function, the active centres of the surface. Since two layers of water are not enough to cause any appreciable capillary condensation, and since their thickness is usually small with respect to the mean diameter of the particles, it is felt that this method can be used with sufficient confidence, especially for specific surface areas between 0.5 and 100 m^2 g^{-1}, either as a complement to the BET method or instead of it when the adsorbent must be studied in a wet state (either because it cannot stand thorough drying, or because the porous texture opens in the presence of water, as has been observed with a kaolin) [4]. Practically, the sample must be (i) outgassed, (ii) pre-equilibrated with ca. half the saturating vapour pressure of water, and (iii) immersed in the microcalorimeter.

GAS ADSORPTION MICROCALORIMETRY

Since chemisorption and catalytic reactions are dealt with elsewhere [1,2], we will focus our attention here on physisorption of gases on solids.

Experimental procedure

We shall deal with microcalorimetry only (taking this to mean the measurement of thermal powers smaller than 10 mW or amounts of heat smaller than 100 mJ), because physisorption does not give rise to large thermal phenomena. Since the widest information on the adsorbing surface and the adsorption mechanism (including structural changes in the adsorbed layer) is obtained from the so-called curves of "differential (or "derivative") enthalpy of adsorption vs. amount adsorbed, it is interesting to devise an experimental assembly and procedure able to produce these curves with the highest possible resolution. Actually, two sets of equipment are needed for simultaneous determination of the amount adsorbed and the heat exchanged.

The latter is conveniently determined with an isothermal and differential microcalorimeter (such as the Tian–Calvet microcalorimeter). This allows one (i) to carry out the whole experiment at one temperature, whatever the amount of gas introduced, (ii) to use, if necessary (e.g., for the initial outgassing stage) large permanent pipes to connect the adsorption calorimetric cell to the external equipment needed to determine the adsorption

isotherm, and (iii) to operate over a wide range of temperature (at present up to ca. 400°C in good conditions and at higher temperatures with a lower sensitivity). The adiabatic microcalorimeters sometimes used by physicists for the study of adsorption lend themselves to good low-temperature work, especially below 100 K [11], and when the C_p value of the adsorbed phase is wanted, though changing the sample (in the midst of a series of insulating and vacuum-tight vessels) and outgassing it (in a metal cell evacuated through a capillary) is not so easy as with an isothermal microcalorimeter, in which changing the sample is a matter of minutes and the outgassing temperature is only limited by the pyrex or fused silica of the sample bulb. The adiabatic procedure also demands a discontinuous introduction of the adsorptive to bring the system back to its initial temperature after each adsorption step. As we shall see, this is a limitation. The amount adsorbed may usually be determined by gravimetry or volumetry. For these experiments associated with calorimetry, gravimetry is not often used, either because the calorimetric yield, in the case of a sample cell suspended on a microbalance in the middle of a calorimeter (without touching it, of course) tends to depend on the pressure (especially when this is below 1 Torr), or because, in the case of two simultaneous determinations on different samples (one in the microbalance, the other in the microcalorimeter) it is difficult to
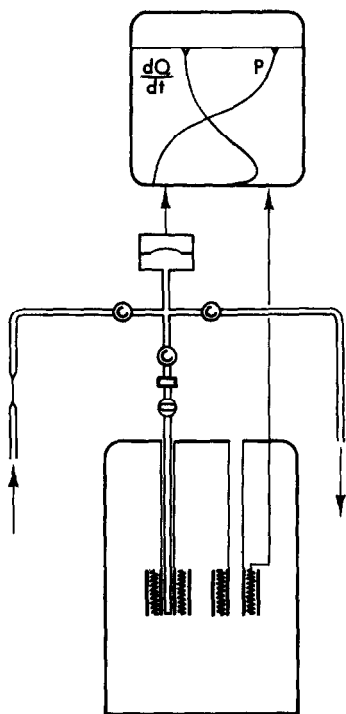

Fig. 4. Association of quasi-static gas adsorption volumetry with isothermal microcalorimetry.

ensure that the temperatures of both samples are as identical as the interpretation of the experiment requires. Furthermore, the whole assembly (with its gas connections between both components) is somewhat difficult to build and operate.

For these reasons, gas adsorption microcalorimeters are usually combined with gas volumetry apparatus. The most popular are known as "BET" volumetric apparatus. While these allow a discontinuous introduction of adsorptive, they also have their shortcomings: (i) the resolution of the final curve of differential enthalpies of adsorption is limited by the width of the introduction steps, (ii) except for computer-controlled equipment, an operator is needed at each step, and (iii) discontinuous introduction of adsorbable gas may lead to concentration gradients within the sample (with the highest concentration on the top, where the gas flow arrives) that may take a long time to disappear (especially when the pressure in the adsorption cell is still low and the adsorbent is highly microporous), or may even never disappear (when the pressure is such that a hysteresis loop of the adsorp-
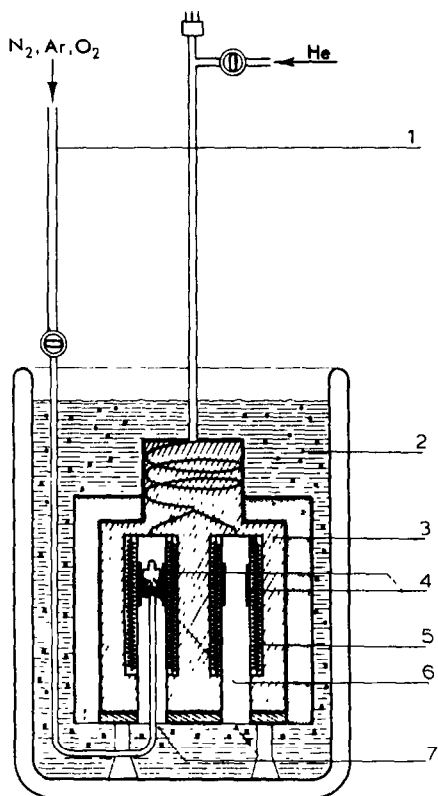

Fig. 5. Low-temperature isothermal gas adsorption microcalorimeter for use at 77 or 87 K.

tion–desorption isotherm is observed). All these shortcomings are eliminated, without complicating the equipment, by the quasi-static volumetric method, in other words continuous, slow, steady introduction of the adsorptive [12]. As illustrated in Fig. 4, in association with a standard Tian–Calvet micro-calorimeter, provision is made for continuous introduction of the adsorptive (left arrow) at a constant rate towards the adsorbent (assumed to be in the left cell). Because of the low rate (usually ca. 1 cm^3 STP per hour), quasi-equilibrium conditions are usually achieved. This can be easily checked by introducing the adsorbable gas at a different rate. It the results of both experiments coincide, a satisfactory "quasi-equilibrium" is present. In this method, two quantities are simultaneously recorded vs. time (i.e., vs. the amount of adsorptive introduced), namely the quasi-equilibrium pressure P and the thermal power dQ/dt released by the sample. These curves are converted into a continuous curve of differential enthalpy of adsorption vs. the amount adsorbed.

The same procedure is usually adopted with the low-temperature isother-mal adsorption microcalorimeter represented in Fig. 5. Here, two Tian–Calvet thermopiles are located in a kind of "diving bell" under helium pressure and directly immersed in the cryogenic liquid (nitrogen or argon) [13].

Applications

These techniques provide valuable information in several physisorption areas.

Study of phase transitions in the adsorbed layer

This is a field in which a number of demonstrative experiments have been carried out with energetically homogeneous surfaces. The first results were obtained for the nitrogen/graphite or argon/graphite systems [14,15]. After completion of the monolayer, an energy change corresponding to RT, i.e., to the loss of two degrees of freedom (in the kinetic theory of gases) is clearly observed with argon, showing that at 77 K the monolayer passes from a 2D hypercritical fluid state to a 2D solid state.

In the case of nitrogen, this solid state can be monitored via substrate lattice whereas in the case of argon it cannot. For this reason, when the carbon is imperfectly graphitized, the phase transition is easier to detect with argon (less sensitive to the "border" or "edge" effects). These results have been confirmed by neutron diffraction studies and Monte-Carlo simulations [16]. Similar studies have been carried out on boron nitride [17] and on titania [18].

Study of the state of the nitrogen monolayer on heterogeneous surfaces

This type of study is directed at the cross-sectional area of the adsorbed nitrogen molecule in the scope of the BET theory. A number of studies with silica, titania and zirconia have consistently shown that changes in the

chemical nature of the surface (concentration of surface hydroxyl groups or unscreened cations) have less influence on the adsorption enthalpy of argon than on that of nitrogen. For instance, the specific energy of interaction of nitrogen with surface hydroxyls amounts to 3 kJ mol^{-1}. Such an interaction leads to mean orientation of the nitrogen molecule, which in any event cannot occur with the spherical argon molecule. This is enough to explain all the discrepancies between the nitrogen and argon BET surface areas. In other words, the usually accepted cross-sectional area of 0.162 nm^2 for the nitrogen molecule may currently be seen as a maximum value (except in the special case of a 2D crystallization seen from the adsorbent lattice, where some "dilation" may be observed), since any mean orientation of this molecule allows closest packing [19].

Study of adsorption into micropores

The present lack of a method for determining pore size distribution in the microporous range (i.e., smaller than 2 nm) makes it of interest to look for a relationship between the pore size and the enthalpy of adsorption, since a three-fold increase may be expected for the "primary filling" process [20]. Systematic work still needs to be done in this respect.

LIQUID ADSORPTION MICROCALORIMETRY

Experimental procedure

We may distinguish between the batch and the liquid flow method. In the batch method, a given amount of solution is brought into contact with a suspension of the adsorbent in the solvent. The techniques used may thus be similar to those for reaction calorimetry (reaction of one liquid with another). One experimental possibility is to break a glass bulb (containing, say, the solution) in the suspension of adsorbent [21] or vice versa [22]. Alternatively, the contents of two open reservoirs (with or without cover) can be mixed by revolving the whole calorimeter [23]. Nevertheless, the highest sensitivity and flexibility appears to be currently obtained with the system shown in Fig. 6, where the solid is first brought into suspension in the pure solvent by means of the stirrer. The mother solution is then progressively introduced from outside by an appropriate pump through the 8 m long coil of a heat-exchanger. The critical question of stirring (whose thermal effect must not be large compared with the enthalpy changes of the system) is solved in the following way: the vibrations from the driving motor are damped by a magnetic transmission [24], whereas the stirring efficiency/thermal power evolved ratio is substantially improved by limiting the basic motion of the propellers to a very fast half-turn followed by an approximately ten times slower return to the starting position [25]. The assembly in Fig. 6 is of rather general application. It can be used at temperatures up to 200°C (for work
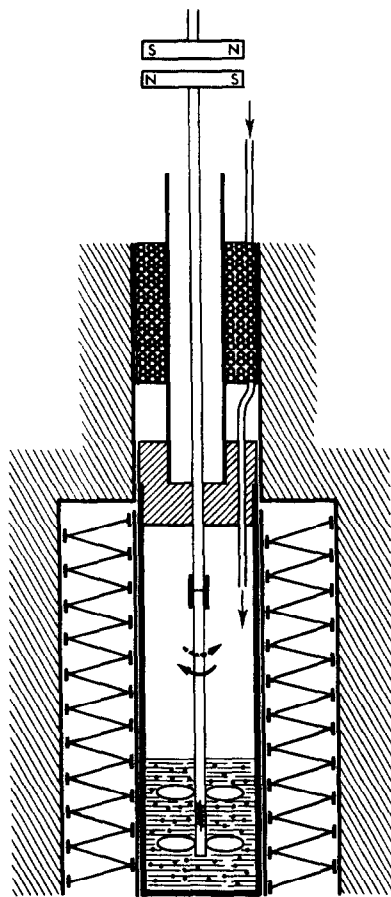
Fig. 6. Liquid adsorption microcalorimetry: batch system with slow–fast rotation of magnet-driven propellers.

with organic liquids) and allows adsorption phenomena to be followed for several hours (e.g., the slow structuring of an adsorbed layer).

The liquid-flow method is less universal, since it does not accept fine powders or clays as adsorbents, but it has its own interesting features. Indeed, it permits (i) the establishment of higher concentrations (in the case of limited solubility of the solute) than the batch method (where some dilution always take place), (ii) the study of desorption phenomena, and (iii) "on-line" determination of the amount adsorbed or desorbed by connecting an analytical device (refractometer, UV or IR spectrometer) to the exit port of the calorimeter [26,27]. The microcalorimeters used are either available commercially [28,29] or specially built for this purpose [27]. The latter can accommodate larger samples (in order to increase the number of adsorption steps and, therefore, the resolution of the study) and also smaller surface areas (2.7 m^2 in the example given in ref. 27). These microcalorimeters may

be considered as the successors of Groszek's apparatus [30] whose simplicity did not alter sensitivity and resolution but brought limitations to the quantitative character of the measurement.

As to the thermodynamic presentation of the data it is worth noting that:

(1) all the calorimetric experiments mentioned in this section involve displacement from the surface of the solid of solvent molecules by solute molecules;

(2) the heats measured are "experimental heats" that depend on both the system studied and the experimental procedure, so that they cannot be called, in the absence of any appropriate correction (which must be clearly indicated), "enthalpies of displacement" or still less, "enthalpies of adsorption" (cf. above), though this is sometimes done;

(3) calculation of the enthalpy of displacement, $\Delta_{dpl}H$, from the experimental heat, Q_{exp}, always requires (i) knowledge of the amount adsorbed and (ii) consideration of the dilution enthalpy of the solute in the conditions of the experiment;

(4) the path to follow for a strict derivation of $\Delta_{dpl}H$ from calorimetric measurements has been described for the liquid-flow method [27,28,31] and the batch method [32];

(5) as a rule, the enthalpy of adsorption proper cannot be determined since the exact number of solvent molecules displaced by one molecule of solute and, hence, the corresponding enthalpy of desorption included in the overall enthalpy of displacement derived from the calorimetric data are not known.

Applications

Among the adsorption phenomena studied with liquid adsorption microcalorimetry we may quote:

(1) adsorption of 1-butanol from *n*-hexane on alumina, silica, ferric oxide, zinc oxide or iron to determine the specific surface area of the adsorbent from the heat evolved [33];

(2) adsorption of fatty acids on alumina and iron oxide mainly as part of lubrication studies [25,34,35];

(3) adsorption of iodine [36] and of pyridines [37] on aluminas from alkane solutions;

(4) adsorption of surfactants on silica gel, sand, sandstone or kaolin in the scope of enhanced oil recovery. The enthalpies of displacement are then very small [38] and sometimes the heat evolution allows either slow kinetics of restructuration of the adsorbed layer [39] or the building up of a monolayer of non-ionic surfactant on silica, proceeding from dominant adsorbate/adsorbent to dominant "lateral" interactions of the same order of magnitude as those in the micellar state [27];

(5) adsorption of polymers on silica [21,40] to determine the fraction of polymer bound to the surface;

(6) adsorption of organic compounds on graphite [28] to determine the structure of the adsorbed layer.

CONCLUSIONS

In order to guide the reader in his decision to use the microcalorimetric approach in the study of adsorption phenomena, it was considered useful to end with the following list of typical conclusions drawn from recent papers.

Concerning the surface area

(1) Specific orientations are likely to orientate the nitrogen molecule and to lower its mean cross-sectional area [19].

(2) Argon may also have specific interactions, though smaller than those of nitrogen, with some cations [19].

(3) At 77 K, argon is likely to be in a two-dimensional liquid state up to the completion of the monolayer: p_0 is then to be taken as that of the supercooled liquid.

(4) The modified Harkins and Jura "absolute" method is of interest if the adsorbent is to be used in a liquid medium [4].

Concerning microporosity

(1) A small BET c value does not prove the absence of microporosity [41].

(2) Molecular size microporosity alone (giving rise to Sing's "primary filling") enhances the enthalpy of adsorption.

Concerning chemical or structural heterogeneities

(1) Macroscopic detection of surface homogeneity on a crystalline surface (stepwise isotherm + calorimetric evidence of a two-dimensional transition) is a matter of minimum size of the homogeneous patches [15].

(2) Two layers of water are usually enough (from the energetical point of view) to screen the chemical functions of the surface [4].

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