192. The Characterization of Natural and Artificial Calcium Carbonates by Adsorption and Immersion Techniques

by Daniel Morel, Fritz Stoeckli*, Francis Krähenbühl, Laurent Misteli, and Paulin Munyazikwiye

Institut de Chimie, Université de Neuchâtel, Avenue de Bellevaux 51, CH–2000 Neuchâtel

Dedicated to Prof. *Tino Gäumann* on the occasion of his 60th birthday

(14.VI.85)

Nitrogen adsorption isotherms at 77K and enthalpies of immersion into water at 293K have been measured for a series of artificial and natural calcium carbonates. It appears that the external surface area and the micropore system can be fully characterized if a non-porous sample, present in the series, is used as an internal reference. Data are given for the reference isotherm. Owing to high specific interactions, immersion into water only provides information on the total surface area of the samples.

Introduction. – In spite of the progress achieved in the study of solid surfaces, classical techniques [1] such as adsorption at the gas-solid interface and immersion calorimetry still play an important role. This paper illustrates this point in the case of the characterization of calcium carbonates, which play a role in a variety of industrial applications (dispersions, filters, coating).

The two limiting cases for the physical adsorption of gases by solids are represented by open surfaces and by micropores [1][2]. The latter are cavities of molecular dimensions, not exceeding 1.5 nm, and found in a variety of solids such as zeolites, active carbons and a number of polycrystalline materials. Adsorption occurs as a process of micropore volume filling, usually described by the classical equation of *Dubinin* and *Radushkevich* [1] [2]

$$W = W_o \exp\{-B(T/\beta)^2 \log^2(p_o/p)\} \tag{1}$$

W is the volume of micropores filled by the liquid-like adsorbate at relative pressure p/p_o and temperature T; W_o is the total volume of the micropores, and B and β are parameters characterizing the solid and the adsorptive, respectively.

In the case of adsorption by an open surface, the classical BET treatment [1] can lead to the equivalent monolayer capacity of the surface and hence to the so-called BET surface area. In spite of the simplicity of the underlying model, the corresponding surface area is often in good agreement with the true area of non-porous surfaces [1] [3].

Since micropores and an external surface area can be found simultaneously, their contributions must be extracted from the overall adsorption data. This can be achieved by comparing the adsorption isotherm with a reference isotherm, obtained under similar conditions for a non-porous surface [1] and ideally of the same chemical nature. A plot of the amounts of gas adsorbed by the unknown sample *vs.* the amounts adsorbed by the reference at the same pressures leads to a linear section if the mechanisms are identical (mathematically speaking, one tests whether the two isotherms are affine or not). If the

linear section does not extrapolate through the origin, as in *Fig. 1*, microporosity must be present in the sample under investigation. The intercept corresponds to the amount adsorbed in the micropores, and the slope is equal to the ratios of the non-porous areas.

Immersion calorimetry [1] [4–6] can also be used for the characterization of external surface areas and of micropores. For open surfaces of the same chemical nature, the enthalpies of immersion into a given liquid must be proportional to the corresponding surface areas. In the case of micropores on the other hand, the enthalpies of immersion reflect the structure and the volume of the cavities, as shown for active carbons [5]. This is a consequence of the enhanced energy of adsorption in micropores. However, if strong specific interactions are present, such as hydration for example [6], the effect of the micropore size may become small and the enthalpy of immersion reflects the total area, *i.e.* the area of the micropore walls and the external surface.

Experimental. – Adsorption and immersion experiments were carried out on two artificial and four natural calcium carbonates of different origins, listed in *Table 2*. All samples were of high purity and had average particle sizes in the range of 1–3 μm. Adsorption of N_2 vapours at 77K, and of H_2O at 293K in the case of solid *Calofort U*, were carried out volumetrically [1], the pressures being recorded with transducer gauges in the range of *ca.* 10^{-3} to 500 Torr. The absence of a hysteresis loop, for all the samples, indicates the systematic absence of mesoporosity. Enthalpies of immersion into H_2O, at 293K, were measured in a calorimeter of the *Tian-Calvet* type [6] described in [5]. Prior to adsorption and immersion experiments, the samples were outgassed for 36–48 h under 10^{-4}–10^{-5} Torr and at temp. not exceeding 120°, in order to prevent any structural damage and to ensure a standard treatment.

Results and Discussion. – The N_2 adsorption isotherms were subjected to the analytical treatments described above. From the relatively low *c* value (13.5) of the BET plot and the comparison with *Halsey*'s reference isotherm [1], it appears that *Grade 81* has no microporosity. This is also in agreement with direct observations in transmission electron microscopy, showing a highly crystalline material.

Table 1. *The Adsorption of N_2 at 77K ($p_0 = 720$ Torr) by Sample* Grade 81 (reference isotherm for calcium carbonates)

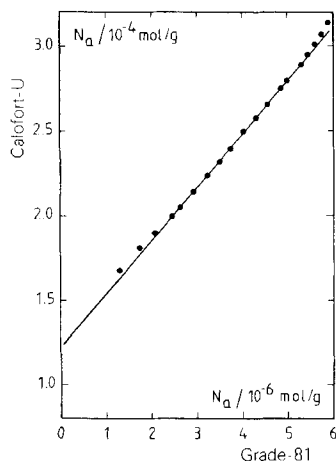| Pressure [Torr]	20	30	50	70	100	120	150	170	200	230	250
Amount adsorbed [10^{-6} mol/g]	1.75	2.05	2.50	2.80	3.20	3.50	3.90	4.15	4.60	5.00	5.30

Figure. *The comparison of the amounts of N_2 adsorbed at 77K, at the same pressures, by samples* Calofort U *and* Grade 81 (non-porous reference)

This sample, with a BET surface area of $0.37 \text{ m}^2/\text{g}$, was, therefore, used as an internal reference for the other solids. Their adsorption data for N_2 at 77K were plotted against those of *Grade 81* given in *Table 1*. A typical plot, as obtained for *Calofort U* is shown in the *Fig.* The linear section, which includes the monolayer capacity, corresponds to the domain in which the adsorption mechanism is the same for both samples. The slope (31.9) is, therefore, equal to the ratio of the two areas and it follows that the external surface area of the sample is $S_e = 11.8 \text{ m}^2/\text{g}$. As discussed in [1], the extrapolation of the linear section ($1.21 \cdot 10^{-4}$ mol/g) should correspond to the amount W_o of N_2 which practically fills the micropores before multilayer adsorption starts on the surface. In the present case, the micropore volume is $4.2 \cdot 10^{-3} \text{ cm}^3/\text{g}$.

Table 2. *Data from the Adsorption of N_2 at 77K and the Immersion into H_2O at 293K, for a Series of Calcium Carbonates*

Sample	S_e [m²/g]	W_o [10^{-3} cm³/g]	S_t [m²/g]	$\Delta H_i(H_2O)$ [J/g]	$\Delta H_i/S_t$ [J/m²]
Grade 81	0.37	–	0.37	0.192	0.52
Calofort U	11.83	4.2	23.68	11.76	0.50
H-30	4.11	0.94	6.75	3.94	0.58
S-51	7.58	2.3	14.05	7.71	0.54
CAL-2	3.30	0.87	5.74	3.43	0.59
H-V	4.7	1.26	8.25	4.55	0.55

The results for W_o *(Table 2)* are in good agreement with those obtained by fitting the low-pressure region ($p/p_o < 0.01$) of the N_2 isotherm to *Eqn. 1*. This confirms the validity of the comparison method. Since neopentane, a molecule of *ca.* 0.63 nm in diameter, is adsorbed slowly even at room temperature and leads to low-pressure hysteresis [1], the micropores must be near 0.65–0.70 nm in width. Such pores can accommodate two layers of N_2 or H_2O, their thicknesses being 0.34 [1] and 0.30 nm [7] [8], respectively.

It follows that the volume of N_2 or H_2O adsorbed in the micropores should correspond to the surface area of their walls, S_{mi}. An approximate total surface area $S_t = S_{mi} + S_e$ can, therefore, be obtained for the solids listed in *Table 2*.

As confirmed by experiments with H_2O vapour on *Calofort U* at 293K, this adsorptive is adsorbed in the same way as N_2 at 77K. The H_2O isotherm is of a well-defined type II [1], suggesting relatively strong interactions with the surface.

The immersion of the samples into water, at 293K, leads to the results given in *Table 2*. For the non-porous reference *Grade 81*, an enthalpy ΔH_i of 0.193 J/g or 0.52 J/m² is obtained, in good agreement with an earlier determination in [6] for the system H_2O/calcite (0.500 J/m^2). It appears that the specific interactions of H_2O with a number of hydrophilic surfaces [6] are much larger than for classical systems involving organic liquids [9] with nonspecific interactions. This means that the effect of the micropore structure, depending essentially on dispersion forces, will be relatively small and the enthalpy of immersion into H_2O reflects primarily the specific interactions with the sites on the surface. This is confirmed by the values of $\Delta H_i/S_t$ *(Table 2)*, which vary between 0.50 and 0.59 J/m², in good agreement with the result for the non-porous reference.

Immersion into H_2O can, therefore, be used for the determination of the total surface area, but it does not provide information on the micropore system itself. The comparison

of the adsorption and immersion data shows consistency, as far as the total surface areas of the calcium carbonates are concerned. On the other hand, a reliable and rapid assessment of microporosity can only be provided by the comparison of the adsorption data with the reference given in *Table 1*.

REFERENCES

[1] S. J. Gregg, K. S. W. Sing, 'Adsorption, Surface Area and Porosity', Academic Press, New York, 1982.
[2] M. M. Dubinin, in 'Progress in Surface and Membrane Science', Ed. D. A. Cadenhead, Academic Press, New York, 1975, Vol. 9, pp. 1–69.
[3] V. R. Deitz, N. H. Turner, in 'Surface Area Determination', Ed. D. H. Everett and R. H. Ottewill, Butterworths, London, 1970, pp. 43–54.
[4] H. F. Stoeckli, F. Kraehenbuehl, *Carbon* **1984**, *22*, 297.
[5] H. F. Stoeckli, F. Kraehenbuehl, *Carbon* **1981**, *19*, 353.
[6] S. Partyka, F. Rouquérol, J. Rouquérol, *J. Colloid Interface Sci.* **1979**, *68*, 21.
[7] J. Hagymassy, S. Brunauer, R. S. Mikhail, *J. Colloid Interface Sci.* **1969**, *29*, 485.
[8] R. M. Barrer, *Phil. Trans. R. Soc. London A* **1984**, *311*, 333.
[9] L. Robert, *Bull. Soc. Chim. Fr.* **1967**, 2309.