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SHORT COMMUNICATION

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Surface areas of kaolin, α-Fe_2O_3 and hydroxy-Al montmorillonite

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Abstract Adsorption of eight organic molecules on kaolin, α-Fe_2O_3 and hydroxy-Al montmorillonite was studied to examine the effect of sorbate area on the values of the surface area of these materials. For each sorbent, the number of molecules at monolayer coverage per gram produced a single hyperbola when plotted as a function of the area occupied by an adsorbate. The equations of the hyperbolas are: $NA = 22.23\ A^{0.098}$ for the kaolin, $NA = 53.70\ A^{-0.399}$ for α-Fe_2O_3 and $NA = 161.81\ A^{0.322}$ for the hydroxy-Al montmorillonite. These equations give accessible surface areas and not the true surface areas of the solids studied, which remain elusive.

Key words Evaluation of surface areas – kaolin – hematite – hydroxy-Al montmorillonite

Introduction

The specific surface area is a highly significant parameter in nearly all physical and chemical processes involving powdered solids. The specific surface area is obtained from the number (N, per g) of molecules adsorbed at monolayer coverage using the relation [1]

$$NA = S \qquad (1)$$

where S is the surface area (m^2/g) and A is the area that occupies an adsorbate (m^2/molecule). However for many solids Eq. (1) is not obeyed, though in some applications its validity is presumed [2]. The surface area of solids which do not obey Eq. (1) remain elusive as will be shown below.

In the present work the suitability of Eq. (1) for the determination of the surface areas of kaolin, α-Fe_2O_3 and hydroxy-Al montmorillonite is investigated, making use of 8 organic compounds frequently used in surface area determinations.

Materials and methods

The following materials were used as sorbents:

1. Kaolin (Davison Chem. Co., Birch Pit, Macon, GA). It has a cation exchange capacity of 0.054 meq/g for the fraction used ($< 2\ \mu$m). Samples were centrifuge washed first with 0.5 M KCl then with water until excess salt was eliminated. The clay was then dried and pulverised.
2. The $< 0.2\ \mu$m fraction from a local montmorillonite was intercalated with aluminium hydroxide [3]. Analysis showed that it contained 60.1 mg Al per g (11.35% Al_2O_3), it had an exchange capacity of 0.5 meq/g and produced a basal spacing (0 0 1) of 18.2 Å in the X-ray diagram.
3. A hematite (α-Fe_2O_3) sample from Riedel De Haën (Hannover, Germany).

As adsorbates the following were used:

1. 1,10-phenanthroline (OP), ($C_{12}H_8N_2 \cdot H_2O$), Merck.
2. 2,2′-bipyridine (BP), ($C_{10}H_8N_2$), Merck.
3. Quinoline (Q), (C_9H_7N), BDH.

4. 8-hydroxyquinoline (oxine), (C_9H_7NOH), Riedel de Haën.
5. Methylene blue (MB), ($C_{16}H_{18}ClN_3S$), Anedra.
6. Glycerol, [$HOCH_2CH(OH)CH_2OH$], Anedra.
7. Ethylene glycol (EG), ($HOCH_2CH_2OH$), Sintorgan.
8. Ethylene glycol mono-ethyl ether (EGME), ($C_2H_5OCH_2CH_2OH$), Riedel de Haën.

Adsorption of OP, BP, Q, oxine and MB by the sorbents were carried out by adding to 0.1 g material samples in 40 ml bottles 25 ml of aqueous solutions of different concentrations of the above mentioned compounds. The bottles were shaken for 1 h then left for 24 h at 28 °C with occasional shaking. Filtrates were analyzed by spectrophotometric methods described in the cited references for each compound [4–7]. The amounts adsorbed were calculated as the differences between initial and equilibrium concentrations.

The adsorption values corresponding to unimolecular surface coverage were obtained by the application of the usual Langmuir treatment and for glycerol by heating a clay glycerol mixture in presence of partially saturated atmosphere of glycerol vapor until adsorption equilibrium was attained [9]. For the EG and EGME the procedure described by Eltantawy and Arnold [10, 11] was adopted, using an evacuated system containing a free liquid surface and dry $CaCl_2$ as separate phase. For methylene blue monolayer coverage was obtained by the extrapolation procedure given in ref. [8].

The basal spacings of the montmorillonite was obtained by the X-ray powder diffraction technique using air dried sample.

The molecular areas used in the calculations of surface areas are given in Table 1. In case of montmorillonite, the area/molecule of oxine, quinoline and bipyridine are twice the values given in the table because each molecule comes in contact with two surfaces within the clay interlayers.

Results and discussion

As shown in Fig. 1 the curves resulting from plotting the numbers of molecules, at monolayer coverage, against the corresponding sorbate areas are equilateral hyperbolas. The equations that represent the hyperbolas are:

$$\text{For kaolin: } NA = 22.23\,A^{0.098},\quad r^2 = 0.70\ (n = 8)\,, \tag{2}$$

$$\text{For } \alpha\text{-Fe}_2\text{O}_3\text{: } NA = 53.70\,A^{-0.399},\quad r^2 = 0.80\ (n = 8)\,, \tag{3}$$

$$\text{For hydroxy-Al montmorillonite: } NA = 161.81\,A^{0.322},\quad r^2 = 0.80\ (n = 5)\,. \tag{4}$$

In logarithmic form, the above equations give straight lines with negative slopes (Fig. 2):

$$\text{For kaolin: } \log N = 21.347 - 0.902 \log A\,, \tag{5}$$

$$\text{For } \alpha\text{-Fe}_2\text{O}_3\text{: } \log N = 21.730 - 1.399 \log A\,, \tag{6}$$

for hydroxy-Al montmorillonite:

$$\log N = 22.209 - 0.679 \log A\,. \tag{7}$$

A negative slope reflects the fact that as the adsorbed molecule increases in size, less amounts could be accommodated per unit area of sorbent, a fact already reported for other systems [12–15].

For all the solids studied the slope of the lines is different from the value −1 required by Eq. (1). For kaolin and hydroxy-Al montmorillonite the lines have slopes greater than −1, while for α-Fe_2O_3 it is less −1. Slopes greater than −1 are usually attributed to surface irregularities, and in the case of montmorillonite could be the result of intercalating the clay interlayers with hydroxy-Al polynuclear cations. Slopes less than −1 as obtained for α-Fe_2O_3 may be explained by the idea that the sorption process involves other mechanisms in addition to physical adsorption [16, 17].

The functional dependence of the amounts adsorbed at monolayer coverage on the sorbates used signifies that

Table 1 Molecular dimensions, molecular areas and number of molecules adsorbed at monolayer coverage (N) on kaolin, α-Fe_2O_3 and hydroxy-Al montmorillonite

Dimensions [Å]	Area [Å^2/molecule]	10^{-19} N [molecule/g]		
		Kaolin	α-Fe_2O_3	Hydroxy-Al mont.
OP: 11 × 7.5 × 3.25	60.0 [18]	3.38	1.20	67.8
BP: 11 × 7 × 3.25	71.5 [5]	3.70	1.51	66.9
Quinoline: 9 × 7 × 3.25	58.5 [3]	5.63	1.92	22.1
Oxine: 11 × 7.5 × 3.25	73.8 [2]	2.51	0.723	55.4
MB: 11 × 7.5 × 3.25	135.0 [1]	4.30	0.843	26.5
Glycerol	29.3 [9]	9.82	8.91	203.6
Ethylene glycol	22.4 [10]	15.72	5.54	195.0
Ethylene glycol mono-ethyl ether	39.6 [8]	10.78	3.07	135.7

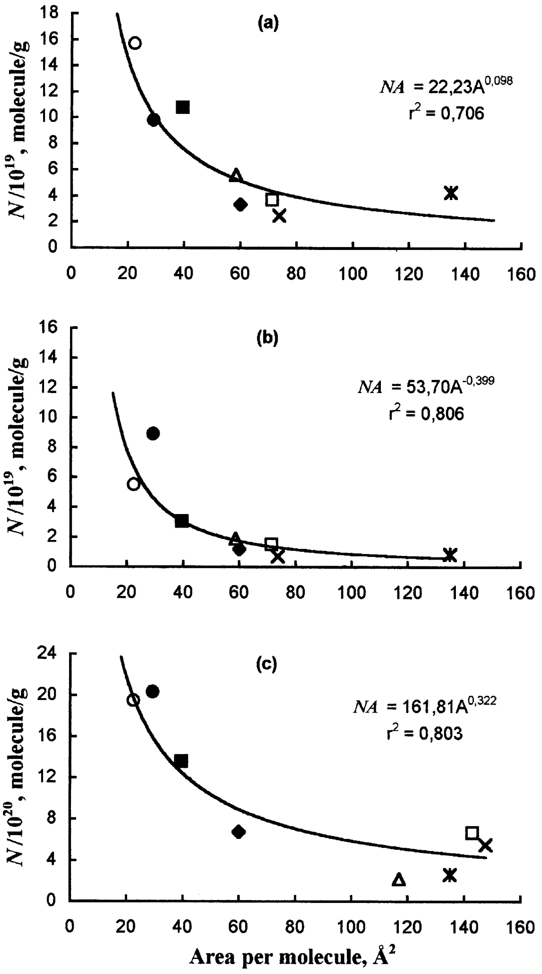

Fig. 1 Relation between number of molecules at monolayer coverage on kaolin (a), α-Fe_2O_3 (b) and hydroxy-Al montmorillonite (c) and the areas occupied by: (◆) 1,10-phenanthroline; (■) bipyridine; (△) quinoline; (×) oxine; (□) glycerol; (●) ethylene glycol; (○) ethylene glycol mono-ethyl ether; (⁎) methylene blue

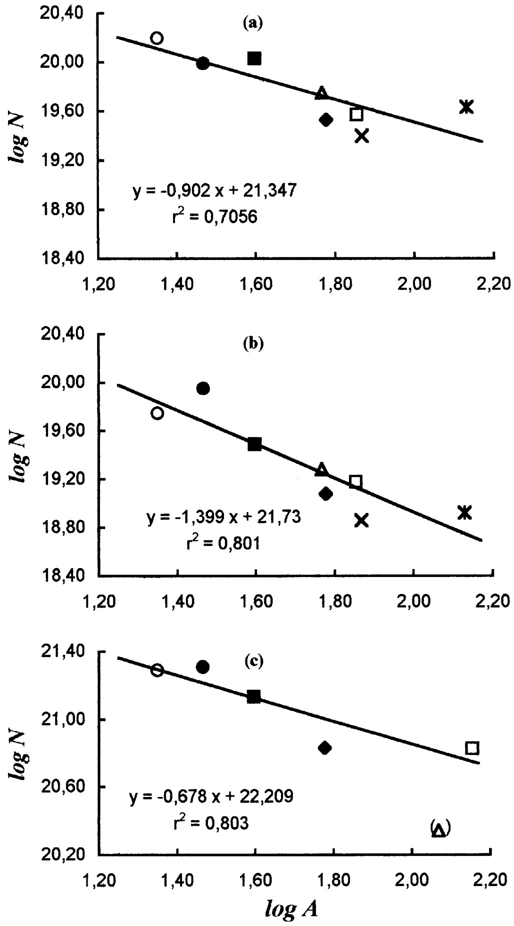

Fig. 2 Relation between the logarithm of the numbers of molecules at monolayer coverage on kaolin (a), α-Fe_2O_3 (b) and hydroxy-Al montmorillonite (c), and the logarithm of the areas occupied by: (◆) 1,10-phenanthroline; (■) bipyridine; (△) quinoline; (×) oxine; (□) glycerol; (●) ethylene glycol; (○) ethylene glycol mono-ethyl ether; (⁎) methylene blue

Eq. (1) cannot be used for obtaining the surface areas of the solids studied. The product NA in Eqs. (2–4) represents for the solids studied accessible surface areas and not true ones. The latter remains out of reach.

Two important points follow from the present work:

1. The value of the surface area of a given solid is uncertain unless Eq. (1) is shown to be valid using various sorbates.

2. Knowledge of the value of the exponent z in the equation

$$NA^z = k \qquad (8)$$

where z is a constant for each solid and $k \rightarrow S$ for $z = 1$, is essential for evaluation of solid areas and for calibration of molecular areas.

With respect to the problem of whether the measured accessible area of a given solid can be transformed into a true area, by selecting an adsorbate of a certain size, it is worth stating that no adsorbate as small or as large as can be imagined can transform the measured surface areas of the solids studied into true surface areas in place of accessible ones. This conclusion follows from the experimental fact: The constant (z) in Eq. (8) is different from unity and is independent of adsorbate size.

In order to show that it is a general result valid for sorbents other than those studied in this report, namely that each sorbent has characteristic z value (Eq. (8)) we give in the appendix results obtained by the application of Eq. (8) to data published by many authors, as well as a comment on the ideas behind both our approach and fractality.

Conclusions

For the sorbents studied the equation $NA = S$ is not obeyed and a modified version is obtained:

$$NA^z = k$$

where z is a constant different from unity while k is another constant different from S and with no clear physical significance.

Accordingly, the surface areas obtained are accessible areas and not the true surface areas of the solids.

Appendix

In Fig. 3 are shown the relations between the number of molecules at monolayer coverage for various sorbents and molecular areas of different sorbates. Also given in the figures are the equations that fit the experimental data as obtained using least square methods.

As appears from the equations, the z values differentiate the sorbents into only 3 categories.

1. Sorbents with $z = 1$. Samples of charcoal, anatase and silica gel belong to this category.

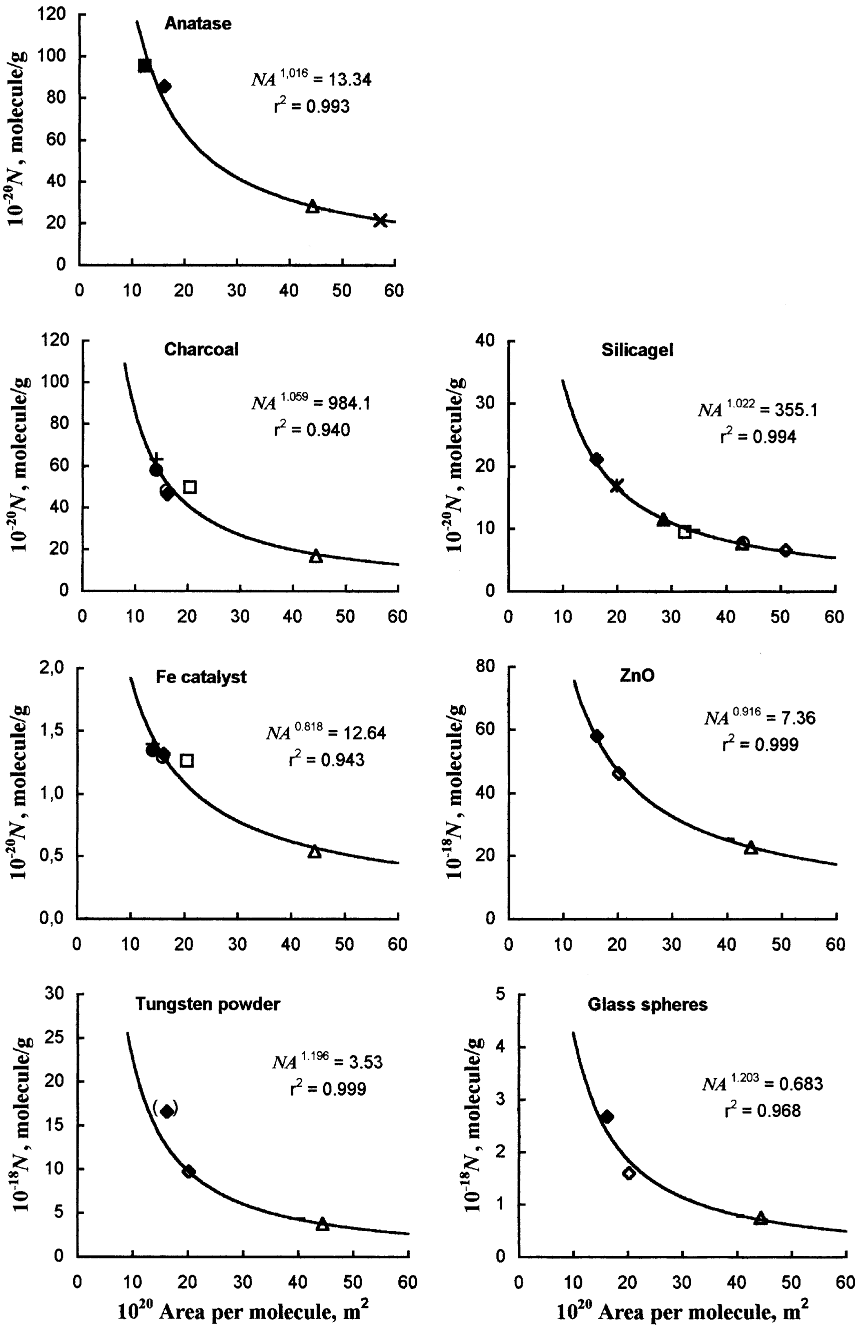

Fig. 3 Relation between number of molecules at monolayer coverage (N) for various sorbents and molecular areas of: (■) H_2O; (◆) N_2; (△) n-butane; (◇) n-hexane; (×) n-heptane; (□) CO_2; (●) Argon; (+) O_2; (○) CO; (▲) CCl_4; (*) Methanol; (-) Ethanol; (–) Propanol; (◭) Benzene; (◑) Diethylamine; (◪) Butylamine; (◈) Krypton and (▼) Freon ($CHCl_2F$). References: Anatase: ref. [1]; Charcoal: [20]; silicagel: [21]; Iron catalyst: [22]; ZnO, tungsten powder and glass spheres: [23]

2. Sorbents with $z < 1$. Samples of zinc oxide and iron catalyst belong to this category.
3. Sorbents with $z > 1$. Samples of glass spheres and tungsten powder belong to this category.

Only for the sorbents with $z = 1$ that true values for the surface areas can be determined. The true surface areas of sorbents with z values different from unity cannot be obtained by adsorption methods and only areas accessible to each sorbate can be calculated using Eq. (1).

Fractality and equations of hyperbolas as tools for sorbent characterization:

Fractality and the treatment of adsorption data adopted in the present work are two tools for sorbent characterization which resort to different concepts. In fractality geometric assumption are implicated. The surface area is presumed to depend on a dimension of an individual unit, hence the $D/2$ exponent, i.e. the fractal dimension (see refs. [2, 15, 16] and the references there in).

In our approach, no assumptions of any kind are made. Simply the experimental results plotted on appropriate coordinates, describe hyperbolas whose equations contain constants characteristic for each sorbent. The equation of the hyperbola is nothing else than the formula used to calculate the surface area from adsorption data at monolayer coverage. As is well known, this formula is an equation of a rectangular hyperbola.

The present approach is a novel way of representation of experimental data and the equations disclose aspects of the properties of sorbents and sorbates not emphasised before.

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