Determination of Specific Surface Areas of Dispersed Materials. Comparison of the Negative Adsorption Method with Some Other Methods[1]

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Abstract: In this paper specific surface areas are reported of dispersed silver iodide, hematite, and silica that have been measured using six different methods including the negative adsorption method, based on the expulsion of co-ions. Both the BET and negative adsorption give internally consistent results, but in the case of silver iodide negative adsorption areas are consistently about a factor of 3.3 higher than BET areas. Consideration of the available experimental evidence suggests that at least in this case the negative adsorption area should be preferred over the BET area when one is concerned with the area of materials dispersed in aqueous solution.

In many scientific and industrial applications of dispersed materials, the specific surface area of the material is an important quantity. A number of methods are available to determine this parameter. However, different methods do not always give the same area.[3-5]

A discrepancy can arise because one of the methods is not valid for the case in which it is used or because different methods "see" a different surface area. In the latter case a closer inspection of the conflicting results of the different methods can reveal interesting details on the surface structure, especially on surface porosity.

Another source of discrepancy, often overlooked, has to do with the state of the surface. Measurements of gas adsorption or gas permeability are carried out on dried samples (we will refer to these techniques as "dry methods"), whereas methods based on adsorption from solution, negative adsorption, and liquid permeability are carried out on samples dispersed in a liquid ("wet method"). It is evident that results from dry and wet methods agree only if no changes in the size and other characteristics of the surface occur on drying, *e.g.*, by aggregation of the particles or by rearrangements in the particle surface.

It is the purpose of this paper to compare results obtained by some dry methods with results obtained by applying wet methods, particularly those obtained by measurement of the negative adsorption of co-ions.[5-7] The principle of this method is that at a charged surface the co-ions (bearing the same sign as the surface charge) are expelled from the surface; *i.e.*, they are negatively adsorbed. Just as *positive* adsorption causes a *decrease* in concentration of the bulk solution, *negative* adsorption causes an *increase* in concentration. This increase, reflecting the number of ions expelled by the surface, is evidently proportional to the surface area. The proportionality constant can be derived with the aid of the diffuse double-layer theory. The principal advantage over conventional adsorption methods is that no size parameters of molecules or ions are needed. It has the additional advantage of measuring surface areas *in situ.*

The method was originally developed by Schofield and successfully applied to clay minerals with areas of 10–500 m^2/g.[6] Recently we refined the method and investigated the dependency on surface potential.[5,7] As a result, the method is now applicable to surface areas as low as 1 m^2/g. A comparison between the results of our method and conventional methods is now possible, which is the object of this paper.

The material used in this study was precipitated silver iodide. Some results on hematite (α-Fe_2O_3) and silica will also be included.

Experimental Section

Materials. Silver iodide suspensions were prepared by the following methods: (1) to a 0.1 *N* KI solution was added 0.1 *N* $AgNO_3$ under vigorous stirring; (B) small portions of 0.1 *N* KI and 0.1 *N* $AgNO_3$ were added alternatively to conductivity water; (C) a dialyzed and well-aged negative AgI sol was flocculated with $AgNO_3$. All precipitates were thoroughly washed and aged for 3 days at 80°. Precipitates, treated in this way, give no detectable change in surface area over a period of several years. The preparations were stored without drying.

Hematite was prepared by hydrolysis of a 0.4 *M* solution of ferric nitrate at 100°. The liberated acid was neutralized by slow addition of 12 *N* KOH. The precipitate was washed thoroughly and stored without drying. Silica was dry BDH material, used without further treatment.

Triple distilled water was further purified by percolating over a column of the material under study. All chemicals were Analar grade and were used without further purification.

Gas Adsorption. A number of surface areas were determined by a continuous flow technique with the Perkin-Elmer/Shell sorptometer 212C. This instrument was developed by Nelson and Eggertsen[8a] and described in its present form by Ettre, *et al.*[8b] The principle of its operation is as follows. A mixture of adsorbate gas (nitrogen) and inert carrier gas (helium) is passed over the sample. The mixture composition (*i.e.*, the partial pressure *p* of the N_2) is calculated from the flow rates of the carrier gas and the mixture

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(1) Carried out under the auspices of the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for the Advancement of Pure Research (ZWO).

(2) Plastics Department Research Laboratory, The Dow Chemical Co., Midland, Mich. 48640.

(3) C. Orr and J. M. Dallavalle, "Fine Particle Measurement," The Macmillan Co., New York, N. Y., 1959, pp 4, 281 ff.

(4) A. W. Adamson, "Physical Chemistry of Surfaces," Interscience Publishers, New York, N. Y., 1960, p 426.

(5) H. J. van den Hul, Thesis, State University of Utrecht, 1966; available on request.

(6) (a) R. K. Schofield, *Nature*, **160**, 408 (1947); (b) R. K. Schofield and O. Talibuddin, *Discussions Faraday Soc.*, **3**, 51 (1948); (c) H. van Olphen, "An Introduction to Clay Colloid Chemistry," Interscience Publishers, New York, N. Y., 1963, pp 270–274.

(7) H. J. van den Hul and J. Lyklema, *J. Colloid Interface Sci.*, **23**, 500 (1967).

(8) (a) F. M. Nelson and F. T. Eggertsen, *Anal. Chem.*, **30**, 1387 (1958); (b) L. S. Ettre, N. Brenner, and E. W. Cieplinski, *Z. Physik. Chem.* (Leipzig), **219**, 17 (1962).

as determined with a calibrated soap bubble flow meter. The amount of gas adsorbed at liquid nitrogen temperature is determined by a concentration determination of the effluent which is passed through a heat conductivity cell. The amount of gas desorbed after removal of the liquid N_2 bath is measured in the same way. At each flow rate the detector signal, which is recorded continuously, is calibrated by admitting a known volume of nitrogen into the gas stream. An advantage of this method over the classical gas adsorption method is that dead-space corrections are not required. Moreover, the instrument is simple and robust in construction, rendering it suitable for routine measurements.

For comparison, a few AgI surface areas were determined by static methods. The adsorption of benzene and carbon tetrachloride at 20° was measured in a simple Pyrex glass volumetric apparatus.[5] Nitrogen, argon, and krypton isotherms were recorded on conventional devices; one nitrogen adsorption determination was carried out with the Adsorptomat[9] of American Instrument Co.[10]

Silver iodide samples were degassed for 3 hr at 110°, which was shown to be equivalent to 48 hr at room temperature. Degassing at higher temperatures (*e.g.*, 200°) resulted in a considerable loss[11] in surface area, explained by irreversible structural changes at the transition point (146°). The other materials were heated overnight at 200°. Prior to static measurements the degassing was carried out *in vacuo:* in the sorptometer experiments degassing was effected in a stream of helium.

Microscopy. Particle counts were made with an optical microscope (Reichert) with a calibrated grid eyepiece. Small samples of dried powder were dispersed in a few milliliters of a 20% solution of collodion in butyl acetate. A drop of the mixture is placed on a clean water surface and the film resulting after evaporation transported to a microscope slide and dried.

Electron Microscopy. Diluted sols or suspensions were spread over a formvar film held by a small woven Pt grid and viewed in a Phillips EM 100 electron microscope. One AgI sol was spread over a microscope slide and shadowed under 30° with platinum. Then the particles were covered with carbon and the resulting replicas, after removal of the AgI particles, viewed in a Siemens Elmiskop I.[12]

Air Permeability. Air permeabilities were measured with a modified Rigden[13] apparatus of Pyrex glass.[5] The cell was made of Perspex and provided with a perforated Perspex disk and a piece of filter paper for support. Plugs were pressed layer-wise to the desired porosity. The gas flow rate was determined as a function of the pressure drop over the plug with an U-tube manometer filled with dibutyl phthalate.

Dye Adsorption. Samples (250 mg) of adsorbent were agitated for 1 hr in dye solutions of the desired concentrations and allowed to settle for the next 24 hr. The concentrations of the dye in the supernatant solution were determined spectrophotometrically, methylene blue (MB) at 660 mμ, 1,1′-diethyl-2,2′-cyanine (DEC) at 520 mμ. MB was adsorbed from aqueous solution and DEC generally from alcoholic solution.

Negative Adsorption. A wet paste containing about 5 g of AgI was suspended in 20 ml of a solution containing potential-determining electrolyte (*i.e.*, KI of sufficiently high concentration to provide for a surface potential of about −300 mV) and the anion to be negatively adsorbed (*i.e.*, SO_4^{2-} or HPO_4^{2-}). The systems were agitated for 1 hr. After settling the precipitate for 2 days, the supernatant equilibrium solution was pipetted off and analyzed. Phosphate concentrations were determined spectrophotometrically by the molybdenum blue method and sulfate concentrations radiometrically after addition of tracer amounts of $K_2{}^{35}SO_4$.

The above procedure is suitable only for AgI. The negative adsorption from hematite and silica must be measured using a membrane equilibrium; although the slow sedimentation could be accelerated by centrifugation, the sediment volume is so small in these cases that the negative adsorption is considerably decreased because of double-layer overlap.[14]

In the case of hematite the negative adsorption of Ca^{2+} ions was measured at pH 4, where the particles are positive. To 80 ml of a 12% hematite suspension in $Ca(NO_3)_2$ solution of pH 4, two cellulose dialysis bags, each containing 10 ml of water, were added. The systems were rotated end over end for 10 days. The calcium concentration in the bags was determined in an Eppendorf flame photometer.

In the case of silica the negative adsorption of SO_4^{2-} ions was measured at pH 9, where the particles are negative. The procedure was the same as for hematite; the sulfate concentrations were determined radiometrically.

Capacitance. Differential double-layer capacitances have been obtained by differentiation of adsorption isotherms of potential-determining ions, plotted as surface charge *vs.* surface potential.[15,16]

Results

In order to obtain reliable values, the conventional gas adsorption areas of two silver iodide samples were determined in different laboratories with different adsorbates.[10] The results are shown in Table I. It is clear that these results are in good agreement.

Table I. Comparison of Gas Adsorption Areas of AgI Samples B2 and C1

AgI[a]	Adsorbate	a_0, Å^2 [h]		S, m^2/g
B2	Ar[b,d]	13.8		0.49
B2	N_2[b,e]	16.2		0.53
B2	N_2[c,f]	16.2		0.46
B2	Kr[b,g]	19.5		0.49
B2	C_6H_6[b,f]	40		0.62
B2	CCl_4[b,f]	37		0.55
			Av	0.52 ± 0.05
C1	Ar[b,d]	13.8		0.88
C1	N_2[c,f]	16.2		0.94
C1	C_6H_6[b,f]	40		1.10
			Av	0.97 ± 0.09

[a] B and C refer to mode of preparation (Experimental Section). [b] Static method. [c] Dynamic method. [d] Lehigh University. [e] American Instrument Co. [f] Authors. [g] Loughborough Technical University. [h] Molecular cross section of the adsorbate.

In Table II the results of the various surface area determinations on six AgI samples are tabulated for comparison. The negative adsorption areas are average values of at least four determinations, the gas adsorption areas of at least two.

As this table shows, the dry methods, gas adsorption and air permeability (internal surface), are in mutual agreement. So are the two wet electrochemical methods, negative adsorption and capacitance. However, the two wet surfaces are consistently higher by a factor about 3.3 than the dry methods. This factor remains roughly the same even though the absolute value of the area varies by a factor of 6. The other results reproduced in the table suffer from some interpretational difficulties as will be set forth in the discussion below.

In connection with the apparent and reproducible discrepancy between the "dry" and "wet" surface area, the following experiment was performed. The negative adsorption was measured of a AgI sample stored in aqueous dispersion. Then the sample was dried and

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(9) E. V. Ballou and O. K. Doolen, *Anal. Chem.*, 32, 532 (1960).

(10) We gratefully acknowledge the cooperation of Mr. N. H. de Boer (Koninklijke/Shell lab., Amsterdam), the American Instrument Co. (Silver Spring, Md.), Drs. A. C. Zettlemoyer and D. R. Bassett (Lehigh University, Bethlehem, Pa.), and Dr. M. J. Jaycock and Mr. E. W. Sidebottom (Loughborough Technical University, Loughborough, England).

(11) This loss in surface area is also reflected by a decrease in the capacity for the adsorption of dyes from solution.

(12) We are grateful to Mr. H. G. Elerie of the Service Institute for Techn. Physics in Agriculture, Wageningen, and to Mr. J. Pieters of the Centre for Submicroscopical Study on Biological Objects, State University, Utrecht, for technical assistance.

(13) P. J. Rigden, *J. Soc. Chem. Ind.* (London), 62, 1 (1943).

(14) F. A. M. de Haan, *J. Phys. Chem.*, **68**, 2970 (1964).

(15) (a) J. Lyklema and J. Th. G. Overbeek, *J. Colloid Sci.*, **16**, 595 (1961); (b) B. H. Bijsterbosch and J. Lyklema, *ibid.*, 20, 665 (1965).

(16) G. A. Parks and P. L. de Bruyn, *J. Phys. Chem.*, **66**, 967 (1962).

Table II. Surface Areas of Silver Iodide (m²/g) as Determined by Various Methods

	Gas	Air permeability[b]			Neg		Dye adsorp		Ratio
AgI[a]	adsorp	External	Internal	Microscopy	adsorp	Capacitance	MB[c]	DEC[d]	wet/dry[e]
A1	0.45	...	...	0.25	1.5	1.4	0.87	0.78	3.2
A2	0.38	0.27	0.35	0.18	1.3	1.35	0.61	0.65	3.8
B2	0.52	0.34	0.51	0.32	1.6	1.5	0.98	1.00	3.1
B3	0.30	0.19	0.26	0.22	0.9	0.85	0.65	...	3.2
C1	0.97	0.48	0.88	0.45	3.3	3.5	2.18	1.92	3.6
C2	1.99	...	...	...	5.5	5.6	2.14	...	2.8

[a] A, B, and C refer to mode of preparation (see Experimental Section). [b] See discussion. [c] Methylene blue, molecular cross section a_0 = 108 Å². [d] 1,1′-Diethyl-2,2′-cyanine bromide, a_0 = 138 Å². [e] Calculated as the ratio between the (dry) gas adsorption area and the (wet) negative adsorption area.

Table III. Surface Areas (m²/g) in Successive Determinations on the Same Sample

Sample	Neg adsorp	Gas adsorp	Neg adsorp	Gas adsorp
A2	1.4	0.38	1.3	...
B1	2.55	0.66	2.85	0.68

the gas adsorption area determined. The dry sample was again suspended and the negative adsorption measured, followed again by drying and determination of the BET area. The results are shown in Table III.

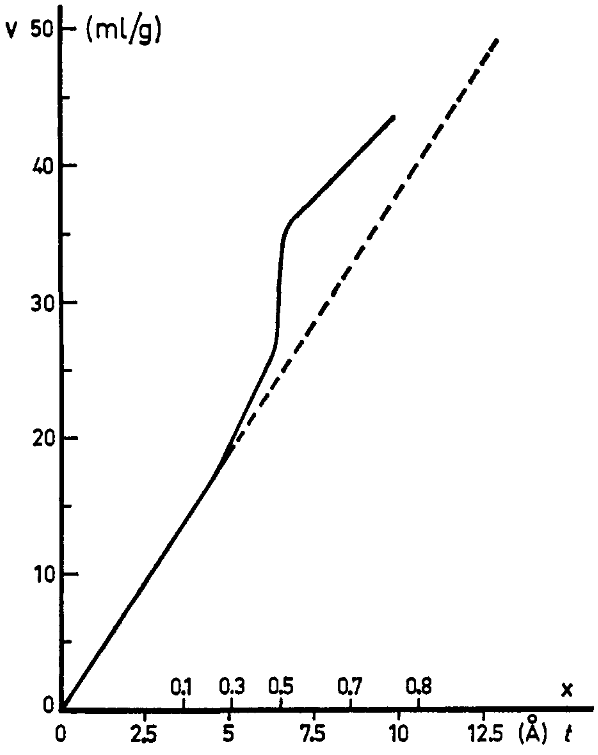

Figure 1. Comparison of volume of nitrogen adsorbed on silica *vs.* *t* (drawn line) and volume adsorbed on nonporous solids *vs.* *t* (dashed line, de Boer[17]).

This table shows that the difference between the wet and dry area is reproducible and independent of the sample history.

In Table IV, the nitrogen adsorption areas of hematite and silica are compared with negative adsorption areas. The negative adsorption area of hematite is calculated from a series of experiments at a range of Ca^{2+} concentrations between 5×10^{-3} and 10^{-4} *M*.

Table IV. Surface Areas of Hematite and Silica

	Microscopy	N_2 adsorp	Neg adsorp
Hematite	20	40	35
Silica	...	56.0	34.5

In a typical experiment with silica we found a negative adsorption of 0.14 μequiv/g as measured by the membrane equilibrium *vs.* 0.06 μequiv/g as measured after sedimentation of the silica. Thus double-layer overlap decreased the negative adsorption by as much as 42%.

In order to establish whether silica is porous, the nitrogen adsorption was measured at a number of relative pressures (x) between 0.1 and 0.75 and analyzed by the t method of de Boer, *et al.*,[17] The measured volume of nitrogen adsorbed (v) is plotted as a function of the statistical thickness of the adsorbed layer (t), taken from a master curve of t as a function of x, prepared by de Boer. The experimental curve is compared with de Boer's curve for the adsorption of nitrogen on nonporous solids (Figure 1). Below $x = 0.3$, the two curves are identical; from the slope a surface area of 56.5 m²/g is calculated. Beyond $x = 0.3$, the volume adsorbed increases significantly more than on a nonporous surface, indicating the presence of micropores. At still larger pressures, these pores are apparently filled and adsorption now occurs only at the outer surface. From the slope of the high-pressure part of the curve, an external surface area of 40 m²/g is calculated, which is close to the negative adsorption area.

Discussion

Before discussing the observed remarkable and systematic differences in surface areas, it is useful to review briefly some assumptions and approximations to be made in the application of the various methods.

Gas Adsorption. The calculation of surface areas from gas adsorption data requires the evaluation from these data of the monolayer volume v_m and the knowledge of the effective molecular cross section a_0. The value of v_m is usually obtained from slope and intercept of the linearized BET plot.[18] Although the validity of the BET equation is open to doubt,[19] it is widely used because it has given satisfactory results in a variety of experiments. It is also possible to calculate v_m from the knee-bend in the

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(17) J. H. de Boer, B. C. Lippens, B. G. Linsen, J. C. P. Broekhoff, A. van den Heuvel, and Th. J. Osinga, *J. Colloid Interface Sci.*, 21, 405 (1966).

(18) S. Brunauer, P. H. Emmett, and E. Teller, *J. Am. Chem. Soc.*, **60**, 309 (1938).

(19) See, *e.g.*, ref 4, pp 514–515.

isotherm (point B), which is said to represent the completion of a monolayer.[20] In our experiments the difference between v_m from point B and from the BET plot never exceeded 20% and was generally much smaller. In a typical experiment with krypton, v_m was 0.104 ml calculated from point B *vs.* 0.106 ml calculated from the BET plot.

The effective molecular area a_0 depends not only on the geometry of the adsorbate molecule, but also on the density of packing and the orientation of the molecules. It can be calculated from the second virial coefficient or with the aid of a model packing, or derived from adsorption on solids with known surface area. However, the choice of a_0 will be rather arbitrary because its value can vary with the adsorbent.[21,22] Notwithstanding the uncertainties in a_0, the very fact that in Table I the same values are obtained using different adsorbates, demonstrates that the results are reliable.

A possible cause for the low gas adsorption area of the AgI is insufficient outgassing. (The temperature should remain well below 146°; see Experimental Section.) Thus part of the surface may be blocked by water molecules. However, Tcheurekdjian, Zettlemoyer, and Chessick[23] have shown that AgI is essentially hydrophobic and that water is completely desorbed from it, even at room temperature. Moreover, different outgassing procedures (3–12 hr at 110° or 48 hr at 25°) and drying techniques (oven drying at 100°, freeze-drying at room temperature after successive washing with alcohol, acetone, and ether) did not change v_m significantly.

Microscopy. Although microscopy is a useful tool for the determination of the average particle size of a suspension, calculation of the surface area is possible only for particles of simple geometry. Flocculated sols consist of irregularly shaped aggregates of primary sol particles which grow together in the aging process. Hence microscopic areas tend to be low (see Tables II and IV). The reported surface areas were calculated assuming the particles to be spherical.

The average microscopically determined radii of the AgI precipitates are 0.5–2 μ; the primary sol particles are much smaller. An electron micrograph of the mother sol of precipitate C1 shows some large hexagonal crystals (0.3 μ) together with many smaller crystals (0.1 μ) of fairly regular shape. Thus, if there would be no aggregation, the surface area of the sol would have been about 6 m²/g.

Electron micrographs of hematite sols show more or less spheroidal particles. The average particle radius is about 0.025 μ.

In conclusion, microscopy gives only a rough idea of the outer surface of irregularly shaped particles. Elucidation of the discrepancy between wet and dry areas is doubtful in view of the difficulty in avoiding artifacts. However, the large difference between the radii of the precipitate particles and the sol particles demonstrates the possibility of aggregation as a cause for a large loss in surface area.

Air Permeability. In gas permeability one deals essentially with two types of flow: viscous or Poiseuille flow and molecular or Knudsen flow. Viscous flow measures only the smoothed area of the capillaries in the plug, as it depends on the radius of the capillaries, not on surface irregularities. The surface area, calculated by the Kozeny–Carman equation,[24] which is an extension of the Poiseuille law to porous plugs, is the external area.

Molecular flow measures the total nonporous area, as it is determined by collisions of the gas molecules with the capillary wall. The surface area, calculated by the Carman–Maleherbe equation,[25] which is the Kozeny–Carman equation corrected for molecular flow, is the internal area. It depends on the gas pressure whether one measures either one of these types or a combination.

Both equations are empirical because, in replacing the capillary radius in the Poiseuille law by the effective radius of the plug, an empirical tortuosity factor is introduced. Carman and Maleherbe have shown that their equation applies well at porosities[26] between 0.4 and 0.5. Therefore, our experiments were performed with plugs of these porosities, and the same tortuosity factor[5] was adopted in the calculation as the one given by Carman and Maleherbe. Indeed, the internal areas in Table II agree well with the BET areas, whereas the external areas compare better with microscopically determined areas. These results support the Carman–Maleherbe theory.

Dye Adsorption. Although adsorption from solution experiments are in general very simple, the evaluation of surface areas from the adsorption isotherms is problematic, as both the amount of adsorbate in a monolayer and the molecular cross section a_0 are difficult to assess.

First, the basic fact that a solution is at least a binary mixture implies that only the preferential adsorption of one component over the other is measured.[27] Only in very dilute solutions can concentration changes in the bulk solution due to adsorption of the solvent be neglected.

Secondly, the adsorption depends on many variables (some of which are difficult to control), such as the nature of the solvent,[27] presence of electrolytes,[5] and surface charge, even if the adsorbing molecules are nonionic.[15b,23] These variables can affect either the orientation of the adsorbed molecules or the saturation adsorption (which is not necessarily equal to the monolayer capacity, notably when the adsorbate is not physically bound but chemisorbed).

In the case of adsorption of cyanine dyes on silver halides, chemisorption was indicated by Boyer, *et al.*[29] These dyes have been used for the measurement of surface areas and in studies on dye orientation at crystal surfaces.[30] However, chemisorption would invalidate

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(20) D. M. Young and A. D. Crowell, "Physical Adsorption of Gases," Butterworth & Co., Ltd., London, 1962, pp 187–190.

(21) Sometimes a_0 is determined entirely by the surface structure of the adsorbent; *e.g.*, N_2 molecules on graphite occupy 20–21 Å², as they fit into the carbon hexagons; see C. Pierce and B. Ewing, *J. Phys. Chem.*, **68**, 2562 (1964).

(22) Smith and Ford found different ratios between the N_2 area and the Ar area on different adsorbents: W. R. Smith and D. G. Ford, *ibid.*, **69**, 3587 (1965).

(23) N. Tcheurekdjian, A. C. Zettlemoyer, and J. J. Chessick, *ibid.*, **68**, 773 (1964).

(24) See, *e.g.*, ref 3, Chapter 6.

(25) (a) P. C. Carman and P. le R. Maleherbe, *J. Soc. Chem. Ind.* (London), **69**, 134 (1950); (b) ref 3, Chapter 6.

(26) The porosity is defined as the ratio between void volume and total volume of the plug.

(27) J. J. Kipling, "Adsorption from Solution of Non-electrolytes," Academic Press Inc., London, 1965.

(28) E. Blomgren, J. O'M. Bockris, and C. Jesch, *J. Phys. Chem.*, **65**, 2000 (1961).

(29) S. Boyer, B. Malingrey, and M. C. Preteseille, *Sci. Ind. Phot.*, **36**, 217 (1965).

surface area measurements because the dye molecules do not "see" the total surface but rather specific sites.

We established both for MB and for DEC a strong dependency of the amount adsorbed on surface charge, the nature of the solvent, and the nature of salt added.[5] The surface areas in Table II are calculated from the isotherm plateaus of MB adsorbed from water and DEC adsorbed from alcohol on neutral AgI, taking the theoretical area of a flat adsorbed dye molecule. The results do not agree with either the BET area or the negative adsorption area. Conversely, molecular areas calculated from the plateaus on the basis of the BET area or the negative adsorption area do not compare with known orientations of these dyes. These molecules seem to "see" only part of the wet area, apparently the same part because the agreement between the areas determined by both dyes is remarkable. When DEC is adsorbed from water, no saturation plateau is reached, but the extrapolated saturation value would lead to areas that compare with the negative adsorption area.

In the case of oxidic materials (hematite, silica), the surface charge depends strongly on pH. Perhaps as a consequence, we found it impossible to obtain reproducible results, small pH fluctuations exerting a marked effect on the adsorption.

In conclusion we do not consider dye adsorption methods as a reliable absolute procedure to evaluate specific surface areas of dispersed materials.

Negative Adsorption. As outlined in the introductory section the increase in concentration of co-ions (Δc_i) caused by negative adsorption from charged particles is proportional to the total surface area of the particles. The proportionality constant is derived from diffuse double-layer theory. For the case of bivalent co-ions in aqueous solutions at 25° we arrived at[5,7]

$$S = 1.89 \times 10^7 V_t(\Delta c_i/c_i)\sqrt{c_i} \quad (\mathrm{cm}^2) \qquad (1)$$

in which S is the surface area in cm^2, V_t the total liquid volume, and c_i the equilibrium concentration of co-ions (g of ions/l.). The factor 1.89×10^7 contains natural constants, the dielectric constant, and the temperature but not the molecular cross section of the negatively adsorbing ion. The assumptions made in the derivation of eq 1 are that (a) the concentration of potential-determining ions is small as compared to that of the co-ions; (b) the potential of the outer Helmholtz plane ($\psi\delta$) is sufficiently high; (c) the double layers are flat; and (d) there is no double-layer interaction.

Condition a is easily controlled by measuring the concentration of potential-determining ions; if it was comparable to the co-ion concentration, a more complex expression was used.[5] Condition b is fulfilled at surface potentials of 250 mV and up; in that case the negative adsorption is independent of potential. The dependence of the negative adsorption on potential at surface potentials below 250 mV was also theoretically derived and experimentally corroborated, which is a good check of the correctness of the underlying theory.[5] Condition c depends on the value of κa (the ratio of the particle radius a and the thickness of the diffuse double layer $1/\kappa$); at large κa values, *i.e.*, with large particles and high concentrations, the flat double-layer approximation is warranted. In some cases corrections for low κa had to be applied. Condition d depends on the ratio of $1/\kappa$ and the interparticle distance; at large separations and high concentrations there is no interaction. Corrections to be applied when the particles approach each other closely have been given by de Haan.[14]

Most nonswelling clays are ideal systems in that the particles are flat plates at large separations. Silver iodide precipitates are also satisfactory in that κa is large (large particles), whereas the aggregates in the sediment are so loosely packed that no appreciable double-layer interaction occurs.[5,7] On the other hand Δc_i is small (1–10%), requiring accurate analytical techniques. The lowest area that can be determined with an accuracy of 20% is about 1 m^2/g.

In the case of hematite and silica the curvature of the double layer cannot be neglected at salt concentrations below 10^{-3} M. Assuming spherical double layers, we derived[5,7]

$$S = (2.32/I_-)10^7 V_t(\Delta c_i/c_i)\sqrt{c_i} \quad (\mathrm{cm}^2) \qquad (2)$$

in which I_- is a quantity calculated from the Poisson–Boltzmann equation for spherical double layers and tabulated by Loeb, *et al.*,[31] as a function of κa. Equation 1 is simply the limiting case for $\kappa a = \infty$.

As reported above, sediments of SiO_2 and Fe_2O_3 are too compact to warrant the neglect of double-layer overlap. This difficulty was avoided by using a membrane equilibrium. In a typical experiment with silica, in which no membrane was used, we found that the negative adsorption was 42% lower because of double-layer overlap, comparing well with the theoretical prediction of 40%, calculated from average particle size and sediment volume. In the case of AgI, agitated precipitates, examined by a membrane equilibrium, gave the same negative adsorption as settled, unagitated precipitates.

A definite proof for the correctness of the theory is the verification of the concentration dependence of the negative adsorption as predicted by eq 1 and 2. For AgI this was already reported.[5,7] For hematite it was checked in the concentration range 10^{-4}–5×10^{-3} M. The concentration dependence described by eq 2 was verified; at the highest concentration, eq 1 applies.[32]

Thus the dependence of the negative adsorption on all important variables, wherever it was possible to check it, was in excellent agreement with theoretical predictions. This demonstrates the correctness of the negative adsorption method.

Capacitance. Capacitance areas are calculated by dividing the measured differential capacitance per gram at the point of zero charge by the theoretical value per unit area. For AgI in the presence of 10^{-3} M KNO_3 this value is 5.3 μF/cm^2 ± 10%. A strong argument for the correctness of the capacitance area is that the capacitance of smooth AgI electrodes, measured directly by an ac-bridge method, is close to our value of 5.3 μF/cm^2.[33] As apparent from Table II the agreement

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(30) (a) J. F. Padday, *Trans. Faraday Soc.*, 60, 1325 (1964); J. F. Padday and R. S. Wickham, *ibid.*, 62, 1283 (1966); (b) E. Günther and E. Moisar, *J. Phot. Sci.*, 13, 280 (1965); (c) A. H. Herz and J. O. Helling, *J. Colloid Interface Sci.*, 22, 391 (1966); (d) S. Boyer and M. C. Preteseille, *Sci. Ind. Phot.*, 37, 129 (1966).

(31) A. L. Loeb, P. H. Wiersema, and J. Th. G. Overbeek, "The Electrical Double Layer around a Spherical Colloid Particle," The MIT Press, Cambridge, Mass., 1960.

(32) Details of the calculation will be published.

(33) (a) D. J. C. Engel, private communication; (b) R. S. Hansen, private communication.

between negative adsorption and capacitance areas is excellent for AgI.

Unfortunately this method does not apply for hematite and silica. On these materials the classical Gouy–Stern theory cannot be used to estimate the capacitance per unit area, because of a different double-layer structure (hematite,[34] silica[35]).

Comparison of Results. We have shown above the self-consistency of the determinations of the dry area as well as that of the determinations of the wet area. However, for silver iodide, the average value of the wet area is 3.3 times higher than the average value of the dry area. It may be noted that, if negative adsorption and BET yield different results, a lower value for the first is always easier to explain than the reverse. A lower value can be attributed to surface roughness or surface porosity "seen" by the BET method, but not by the negative adsorption, as long as the size of the irregularities is small as compared to the double-layer thickness. This can be the reason for the low negative adsorption from silica. See also the discussion of Figure 1. The negative adsorption area of hematite is in reasonable agreement with the gas adsorption area. Earlier, good agreement was reported for nonswellable kaolinite clays.[36]

Apparently the difference in dry and wet area of AgI must be attributed to a loss in surface area on drying, perhaps by aggregation. If the cause is aggregation, it is obviously reproducible (compare Table III). Giles and Nakhwa give a similar explanation for the difference between the wet area (adsorption of *p* nitrophenol from solution) and dry area (N_2 adsorption) of metal powders and organic pigments, the wet area being also two to four times the dry area.[37]

Thus evidently in wet experiments the wet area of the adsorbent should be used, at least for nonporous solids like AgI. Several results in the literature in which the dry area was used in wet experiments are indeed better explained on the basis of the wet area.

Padday[30a] reports an adsorption of DEC and other dyes per unit area which is 3.8 times higher on AgI than on AgBr. He suggests a dye monolayer on AgBr and multilayer formation on AgI. However, if DEC is chemisorbed (as proposed by Boyer, *et al.*[29]), formation of second and higher layers will be unlikely. An alternative explanation is that for AgBr the wet area equals the dry area, whereas for AgI a wet area 3.8 times the dry area should be used. In that case on both solids a monolayer of like orientation is built.

Likewise, Mathai and Ottewill[38] suggest a layer of three molecules thick of polyoxyethylene glycol monoalkyl ethers on silver iodide on the basis of the dry area. The limiting area of the adsorbed molecules on this basis was 18 Å^2 for C_{10} E_6 and C_{12} E_6 and 24 Å^2 for C_8 E_6, whereas at the air–solution interface the close-packed area is 60 Å^2. However, on the basis of the wet area, a more realistic close-packed monolayer of the nonionics would be computed. We think it most likely that the molecules are adsorbed in a monolayer with their hydrocarbon parts to the surface, as was found for butanol on AgI by Bijsterbosch and Lyklema.[15b] The voluminous C_{16} E_9 molecule would then be adsorbed in a more loosely packed layer with a limiting area of 180 Å^2 per molecule.

Finally Abramson, Jaycock, and Ottewill[39] measured directly the adsorption of La^{3+} ions at pH values between 2 and 5 at pI 4, *i.e.*, at a surface potential of about -400 mV. At an equilibrium concentration of 10^{-3} *M*, the La^{3+} adsorption was about 3×10^{-7} g of ions /g, which on the basis of the dry area amounts to a countercharge of 12 μC/cm^2; there is no reversal of charge. However, under these conditions the surface charge is 4 μC/cm^2.[40] This discrepancy can again be automatically resolved if the negative adsorption area is used instead of the BET area. The alternative explanation of hydrolysis to $La(OH)_2{}^+$ ions is rejected because the adsorption is independent of pH between pH 2 and 5.

Conclusions

The examples show that comparative surface area studies can be very helpful in studies of the electrochemistry of the phase boundary. The indiscriminate use of the BET surface area in studies concerning the wet area is open to doubt. The negative adsorption method can give more meaningful results in these studies.

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(35) (a) Th. F. Tadros, private communication; (b) G. H. Bolt, *J. Phys. Chem.*, **61**, 1166 (1957); (c) W. M. Heston, R. K. Iler, and G. W. Sears, *ibid.*, **64**, 147 (1960).

(36) (a) R. K. Schofield, *Trans. Brit. Ceram. Soc.*, **48**, 207 (1949); (b) R. K. Schofield and H. R. Samson, *Discussions Faraday Soc.*, **18**, 135 (1954).

(37) (a) C. H. Giles and S. N. Nakhwa, *J. Appl. Chem.* (London), **12**, 266 (1962). (b) Only with zinc powder the wet area was 60 times the dry area.

(38) K. G. Mathai and R. H. Ottewill, *Trans. Faraday Soc.*, **62**, 750 (1966).

(39) M. B. Abramson, M. J. Jaycock, and R. H. Ottewill, *J. Chem. Soc.*, 5034 (1963).

(40) J. Lyklema, Thesis, State University, Utrecht, 1957.