16 Specific Surface

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16–1 INTRODUCTION

Surface area largely determines many physical and chemical properties of materials. Physical adsorption of molecules, heat loss or gain resulting from that adsorption, swelling and shrinking, and many other physical and chemical processes are closely related to surface area. Surface or exposed area is also closely related to and often the controlling factor in many biological processes. Soils vary widely in their reactive surface because of differences in mineralogical and organic composition and in their particle-size distribution. Water retention and movement, cation exchange capacity, and pesticide adsorption are closely related to the *specific surface* (defined as the surface area per unit mass of soil). Specific surface is usually expressed in square meters per gram (m^2/g).

Clay-size particles, and particularly some layer silicate minerals, contribute most of the inorganic surface area to soils. Nonexpanding layer silicates such as kaolinite and some micas have only external surfaces. The specific surface of these minerals ranges from 10 to 70 m^2/g. Expanding layer silicates, such as montmorillonites, other smectites, and vermiculites, have extensive internal as well as external surface, giving specific surfaces up to 810 m^2/g, depending upon the amount of internal surface exposed by expansion. Consequently, the types of minerals present in soil largely determine soil specific surface and related properties.

Many methods and approaches have been employed to measure the specific surface of soils and minerals. Some methods are thermodynamically sound but too time-consuming, or they require too much spe-

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cialized apparatus to be used on a routine basis. Therefore, other more rapid but less accurate methods have been developed. Cihacek and Bremner (1979) suggested that the assumptions required and the several factors influencing results from most of these latter proceedures give us an assessment but not a real measure of surface area. Absolute measurements are difficult to attain and interpret because of the interaction of factors such as the adsorbed cation, the orientation of the adsorbed molecules, mono- or duo-layer coverage in the interlayer spacing, and sample water-content.

The purpose of surface-area measurements is commonly to determine the accessibility of internal surfaces of the clay mineral complex to molecules or ions which can be adsorbed thereon. This accessibility is generally determined by the relative adsorption forces of the introduced molecules or ions to the clay mineral surfaces as compared to the attraction forces between adjacent clay mineral platelets. The systems of most general interest are hydrated systems. Consequently, a measurement procedure which estimates surface area that would be accessible under hydrated conditions is commonly desired. Both ethylene glycol and ethylene glycol monoethyl ether appear to be adsorbed on clay mineral surfaces and to adsorbed cations to essentially the same extent, and probably by the same mechanisms, as is water in hydrated systems.

16–2 PRINCIPLES

16–2.1 Adsorption Isotherms

Gas molecules close to the solid surface are attracted by forces arising from solid-phase surface atoms. Essentially, all gases tend to be adsorbed on solid surfaces in response to the force field at or very near the surface. The quantity of gas adsorbed can provide a measure of surface area.

Langmuir (1918) provided the equation

$$P/V = 1/k_2V_m + P/V_m$$

where V is the volume of gas adsorbed per gram of adsorbent at pressure P, k_2 is a constant, and V_m is the gas volume adsorbed per gram when a complete monomolecular layer has been formed. The surface area is obtained by plotting P/V vs. P at constant temperature. The slope of the plot is equal to $1/V_m$. Knowing this value, the specific surface of the adsorbent may be calculated by determining the number of molecules in V_m and multiplying by the cross-sectional area of the adsorbate. The Langmuir equation is based upon assumptions that (i) only one layer of molecules is adsorbed and (ii) the heat of adsorption is uniform during adsorption of the monomolecular layer.

Brunauer, Emmett, and Teller (1938) derived an equation, now commonly called the BET equation, from multimolecular adsorption theory

that provided for calculating the number of adsorbate molecules in a monolayer. The BET equation is

$$P/V(P_0 - P) = (1/V_m C) + [(C - 1)P/V_m C P_0]$$

where V is the gas volume adsorbed at pressure P, V_m is the volume of gas required for a single molecular layer over the entire adsorbent surface, P_0 is the gas pressure required for saturation at the temperature of the experiment, and $C = \exp [E_1 - E_2]/RT$, where E_2 is the heat of liquification of the gas, E_1 is the heat of adsorption of the first layer of adsorbate, R is the gas constant, and T is the absolute temperature. The BET equation involves assumptions that (i) the heat of adsorption of all molecular layers after the first is equal to the heat of liquification and (ii) at equilibrium, the condensation rate on the surface is equal to the evaporation rate from the first or subsequent layers. The BET equation is most useful between relative pressures (P/P_0) of 0.05 to 0.45. By plotting $P/V(P_0 - P)$ vs. P/P_0, V_m can be calculated from the intercept and slope of the linear portion of the curve. The surface area can then be calculated by multiplying V_m by the adsorbate molecule cross-sectional area. The density of the adsorbate is usually assumed to be either that of the liquified or solidified gas. Since the calculated area per molecule depends upon the density used, there is a degree of uncertainty in the absolute surface areas measured.

The BET equation has been applied by many researchers utilizing nitrogen, ethane, water, ammonia, and other gases on soils and minerals. The apparent surface area of montmorillonites has been shown to depend upon the nature of the adsorbate used. Weakly adsorbed nitrogen, for instance, does not penetrate the interlayer surfaces, so that the measurement obtained is only for external surfaces—whereas polar molecules such as water and ammonia are strongly adsorbed and penetrate into the interlayer surfaces, giving more nearly total surface-area measurements. The use of the BET equation in determining surface area of clay minerals from water adsorption has been criticized because water molecules tend to cluster around cation sites (Quirk, 1955).

16–2.2 Retention of Polar Liquids

Dyal and Hendricks (1950) introduced a method for estimating surface area of clays based upon adsorption of ethylene glycol to form a monomolecular layer over the entire surface. Their work suggested that other polar liquids could also be used for measuring surface area. The method involves adding ethylene glycol to properly pretreated soil or clay mineral samples and evaporating the excess in an evacuated system. The evaporation rate decreases when all free ethylene glycol is gone and only that adsorbed in a monomolecular layer is left. The quantity of glycol retained at the moment the evaporation rate decreases should be pro-

portional to the surface area. Utilizing a theoretically specific surface for bentonite of 810 m^2/g and the amount of ethylene glycol retained when the evaporation rate decreased, Dyal and Hendricks (1950) found that 0.00031 g of ethylene glycol was needed to form a monomolecular layer on each square meter of bentonite surface.

Bower and Gschwend (1952) utilized ethylene glycol adsorption as a measure of surface area and interlayer swelling of layer silicates. Samples were weighed at consecutive time intervals to determine the transition from a high rate of free glycol loss to a lower loss rate for that bound to the clay surface. The vapor pressure of ethylene glycol was considered of critical importance in gravimetric methods for estimating surface area. Where ethylene-glycol-saturated samples were maintained in an evacuated chamber over dry $CaCl_2$, the vapor pressure was low and losses beyond the transition from high to low rate loss occurred. Martin (1955) included a free surface of ethylene glycol with the samples in order to maintain a higher ethylene glycol vapor pressure. As long as both free ethylene glycol and $CaCl_2$ are present, the amount of ethylene glycol retained by a sample should reach and maintain a constant value.

Bower and Goertzen (1959) introduced the use of a $CaCl_2$–ethylene glycol complex ($CaCl_2$-monoglycolate) to maintain an ethylene glycol vapor pressure slightly lower than required for monolayer formation. Mixtures of an anhydrous and a solvated form, or mixtures of two solvated forms of salts, have a definite vapor pressure at a given temperature. This pressure is independent of the relative proportions of the two forms of the salt present. (For an explanation of this phenomenon, see Prutton & Maron, 1951, p. 372–375.)

Another approach was to include a large quantity of bentonite, containing just enough ethylene glycol to form a monomolecular on all surfaces, to maintain an ethylene glycol vapor pressure in the evacuated desiccator equal to that necessary for forming a monomolecular layer on the surfaces of small samples. The environment provided by this system allows a true equilibrium value to be reached (Sor & Kemper, 1959). The ethylene glycol retained by samples in this latter system is slightly higher than the amount retained in the environment provided by the presence of both the $CaCl_2$–monoglycolate and free $CaCl_2$. Using a $CaCl_2$–monoglycolate with $CaCl_2$ to stabilize the ethylene glycol vapor pressure in an equilibrium procedure has the advantage of using pure, commercially available materials.

Glycerol has also been used as a polar molecule to measure the surface area of layer silicate minerals (Diamond & Kinter, 1956). They found that montmorillonite forms a stable complex with glycerol in the presence of glycerol vapor at high temperatures, and that a monomolecular layer of glycerol molecules occurs in the interlayer spacings of most layer silicates.

Carter et al. (1965) introduced the use of ethylene glycol monoethyl ether (EGME) as the polar molecule for determining the surface area of

layer silicate minerals and soils. This polar liquid has a higher vapor pressure at room temperature than does ethylene glycol. Hence, it evaporates more rapidly from treated samples, requiring a shorter time to evaporate free liquid and to attain equilibrium with a monomolecular layer. In addition to the advantages of being more rapid, the EGME method generally has greater precision than the ethylene glycol method because samples are handled fewer times and the opportunities for introducing water vapor and other sources of errors are decreased.

Molecular coverage for EGME was calculated with the same assumption applied earlier by Dyal and Hendricks (1950) for ethylene glycol. Using 810 m^2/g as the theoretical specific surface for montmorillonite, and a measured value of 23.7 mg EGME retained per gram of clay, the calculated quantity of EGME to cover 1 m^2 of clay surface with one molecular layer is 0.000286 g, with a molecular coverage of 5.2×10^{-15} cm^2/molecule. Applying these coverage values for EGME and assuming 0.00031 g of ethylene glycol per square meter as reported by Dyal and Hendricks (1950), extensive comparisons for layer silicates, layer silicate mixtures of known composition, and soils were made between the EGME and ethylene glycol methods. Excellent agreement was found in all comparisons, indicating that the two polar molecules cover the same surface (Carter et al., 1965; Heilman et al., 1965).

The EGME forms a solvate with $CaCl_2$ that is stable at 70 °C. The EGME/$CaCl_2$ ratio is 1.5:1, indicating that three molecules of EGME solvate two molecules of $CaCl_2$. This solvate may be used in the desiccator with $CaCl_2$ to assure an EGME vapor pressure near that of an adsorbed monomolecular layer. Maintaining the adsorbate vapor pressure in the sample environment is generally easier with the EGME method than with the ethylene glycol method because of the shorter time required for attaining a monomolecular layer and the fewer sample-handling events. Samples must be weighed within a reasonable time after evacuating the desiccator. It is advisable to include the solvate along with $CaCl_2$ when time periods such as overnight or over a weekend are involved, in order to prevent some EGME from being lost from the monolayer. Eltanawy and Arnold (1973) suggested that such losses occur even in the presence of EGME–$CaCl_2$ solvates and contended that a free EGME surface is required in the desiccator to provide sufficient vapor pressure to assure a monomolecular layer. Their own data, however, indicate that EGME in excess of that required to form a monomolecular layer is retained under conditions involving a free EGME surface.

The convenient and rapid EGME method for estimating surface area of soils and clays has been widely accepted. Nevertheless, it involves assumptions and has limitations. One assumption involves the method used to calculate molecular coverage. Similar to the assumption made for ethylene glycol, it was assumed that EGME covered all interlayer and external surfaces. This assumption is difficult to prove. It is possible that the 0.000286 g of EGME required for a monomolecular layer on 1 m^2

of surface is not absolutely correct. It is probable that EGME molecules are associated with exchangeable cations in thicknesses greater than required for a monomolecular layer, as has been reported for ethylene glycol (McNeal, 1964). It is also possible that some voids occur on certain minerals so that coverage is incomplete in the interlayer spaces (Dowdy & Mortland, 1967). There are also questions regarding the density of adsorbed EGME in comparison to the density of bulk liquid EGME. The latter has been used in calculations of molecular coverage.

As is the case with ethylene glycol, vermiculite likely adsorbs only one layer of EGME molecules between adjacent clay platelets. Hence, the assumption that all surfaces are covered with a monomolecular layer of EGME probably does not hold for vermiculite, hydrated halloysite, and possibly some intergrade layer silicates, as is the case for ethylene glycol.

The wide acceptance of the EGME method is related to the simplicity and ease with which it can be used in the laboratory. This, in turn, has led to more widespread relation of surface-area values of soils and layer silicates to various physical, chemical, and biological processes. Ross (1978) and Low (1980) have shown that shrink-swell properties are highly correlated with the surface areas of soils and clays. Supak et al. (1978) related the adsorption of aldicarb by clays to their specific surface values. Van der Staay and Focht (1977) investigated the effects of soil surface area upon bacterial denitrification rates. Moreale and Van Bladel (1979) related specific surface to herbicide-derived aniline residue. Also, because surface-area estimates are easily obtained by the EGME method, the property is commonly used in characterizing soils and in relating specific surface to other soil properties (Bingham et al., 1978; DeKimpe & Laverdiere, 1980; DeKimpe et al., 1979; Farrar & Coleman, 1967; Galindo & Bingham, 1977; Gallez et al., 1976; Singer & Navrot, 1977).

Some other organic chemicals may have equal or greater potential for use in estimating surface area of soils and clay minerals. Porter (1971) reported that 2-h desorption curves for dioxane, 2-methoxy-ethanol, and tetrahydrofluran from Na-saturated bentonite were quite similar to the desorption curve for EGME. He found excellent relationships between the EGME retained by various ratios of Na-kaolinite to Na-bentonite and the 2-methoxyethanol, dioxane, and tetrafluran retained by the same mixtures. He concluded that these materials should be as effective and rapid as EGME in measuring surface areas of Na-saturated systems.

A method for measuring surface area of clays involving methylene blue as the adsorbate has been published by Pham and Brindley (1970). An advantage of this method is that adsorption is carried out in fully hydrated systems. Clays are exposed to various concentrations of methylene blue and the amount adsorbed is measured spectrophotometrically by measuring the decrease in concentration of the supernatent solution. The surface area is calculated by taking the area of the adsorbed molecule as 1.30 nm^2, which corresponds to flat orientation of the molecule on the mineral surface. A good relationship was found between surface area by this method and by use of a BET method.

16-3 METHOD

16-3.1 Special Apparatus

1. Vacuum desiccator 25 cm or larger in diameter with a plate to hold samples above the desiccant.
2. Vacuum pump capable of reducing pressure to 0.250 mm of Hg.
3. Aluminum cans having a diameter of 6 to 7 cm and a height not exceeding 2 cm, with lids.
4. Culture chambers consisting of a glass dish with cover, having a diameter of about 20 cm and a height of about 7.5 cm.
5. Support for holding aluminum cans in each culture chamber approximately 2 cm above the bottom of the chamber. The support may consist of a circular piece of hardware cloth with openings of 0.5 to 1.0 cm, with brass machine screws or similar devices for legs attached near the perimeter of the hardware cloth by means of nuts and washers. Alternatively a square piece of hardware cloth with the corners bent down to serve as legs may be used.

16-3.2 Chemicals

1. Ethylene glycol monoethyl ether (2-ethoxyethanol) (EGME), reagent grade.
2. Phosphorus pentoxide (P_2O_5).
3. Calcium chloride ($CaCl_2$), 40-mesh (0.425 mm opening) anhydrous, reagent grade.

16-3.3 Procedure

16-3.3.1 PREPARATION OF $CaCl_2$-EGME SOLVATE

Weigh approximately 120 g of 40-mesh $CaCl_2$ into a 1-L beaker and dry in an oven at 210 °C for 1 h or more to remove all traces of water. Weigh 20 g of EGME into a 400-mL beaker. Remove the $CaCl_2$ from the oven, weigh out 100 g without cooling, and add it to the beaker containing the EGME. Mix immediately and thoroughly with a spatula. The heat of the $CaCl_2$ facilitates solvation. After the solvate has cooled, transfer it to a culture chamber and spread it uniformly over the bottom. Store the chamber and contents in a sealed desiccator.

16-3.3.2 SAMPLE PRETREATMENT

Treat the sample with H_2O_2 as described in chapter 5, to remove organic matter. Saturate the sample with Ca by leaching or repeated shaking and centrifuging with an excess of 1.0 *M* $CaCl_2$. Remove the excess $CaCl_2$ with three successive water washings. Air dry the sample and pass it through a 60-mesh sieve, grinding if necessary. If a measure

of only the external surface is desired, heat the sample at 600 °C for 2 h to suppress interlayer swelling.

16-3.3.3 SORPTION TECHNIQUE

Weigh approximately 1.1 g of soil or clay into a tared aluminum can, including a lid, and spread the sample evenly over the bottom of the can. Place the can, with lid beneath, in a vacuum desiccator over about 250 g of P_2O_5, evacuate the desiccator by applying a vacuum pump for one hour, close the stopcock, and dry to constant weight. Constant weight is usually attained in about 6 to 7 h for groups of four to six samples. The drying is most conveniently accomplished overnight. Weigh the dried sample, using care to minimize adsorption of atmospheric water. Wet the sample with approximately 3 mL of reagent-grade ethylene glycol monoethyl ether (EGME) to form a soil- or clay-adsorbate slurry. Place the can containing the sample-adsorbate slurry, with lid beneath, in a culture chamber on the hardware cloth support over the $CaCl_2$–EGME solvate. Place the lid on the culture chamber. (Elevation of the lid with a small block to leave a space approximately 2 mm wide between lid and chamber will better allow gases to escape.) Place the entire culture chamber in a vacuum desiccator containing $CaCl_2$. Allow 30 min or more for the sample-solvate slurry to equilibrate. Evacuate the desiccator with a vacuum pump for about 45 min. Allow the desiccator to stand at room temperature for 4 to 6 h, release the vacuum, open the desiccator and culture chamber, and place the lid on the aluminum can to prevent the sample from adsorbing atmospheric water. Weigh the can, lid, and sample. Return the can, with lid beneath, to the culture chamber and the culture chamber to the desiccator. Evacuate the desiccator by applying a vacuum pump for 45 min. Weigh the samples at 2- to 4-h intervals, evacuating between weighings, until constant weight is attained. Generally constant weight will be indicated by the second or third weighing. If surface area determinations are made on several samples concurrently, a point is often reached when some samples appear to gain and some to lose a fraction of a milligram between two successive weighings. This is good indication that equilibrium has been attained. Use the mean of two successive weights that agree within a few tenths of a milligram to calculate the quantity of ethylene glycol monoethyl ether retained by the sample.

16-3.3.4 CALCULATING SPECIFIC SURFACE

Calculate the specific surface by the equation

$$A = W_a/(W_s \times 0.000286)$$

where A = specific surface in m^2/g, W_a = weight of ethylene glycol

monoethyl ether (EGME) retained by the sample in g, W_s = weight of P_2O_5-dried sample in g, and 0.000286 is the weight of EGME required to form a monomolecular layer on a square meter of surface.

16–3.4 Comments

Smaller samples, 0.3 to 1.1 g, may be used for samples having high specific surface.

The vacuum pump and desiccators should be connected with tight-fitting, vacuum-type rubber tubing. A glass tube filled with the 8-mesh anhydrous $CaCl_2$ should be inserted in the line to prevent undesirable vapors from entering the pump. High-vacuum stopcock lubricant should be used to seal glass joints.

Adsorption of atmospheric water by the sample during weighing operations is controlled by allowing air to flow back through the $CaCl_2$ tube into each desiccator when releasing the vacuum, by placing the lid on each can promptly after releasing the vacuum, and by weighing rapidly. Determinations may be made on as many as six samples concurrently.

Use of the $CaCl_2$–EGME solvate and the associated culture chamber is optional for this method. Inclusion of the solvate insures equilibrium with approximately a monomolecular layer. However, reasonable results are also attainable without the solvate (Heilman et al., 1965; Cihacek & Bremner, 1979). The migration of excess EGME vapor to the $CaCl_2$ spontaneously forms a small amount of $CaCl_2$–EGME solvate.

It is desirable to prepare fresh $CaCl_2$–EGME solvate, where used, for each set of determinations, as some absorption of atmospheric water with continuing use is unavoidable. The P_2O_5 employed for drying may be used until it absorbs sufficient water to develop a syrupy consistency.

According to Diamond and Kinter (1956), some montmorillonites re-expand after being heated at 600 °C. Therefore, measurements on samples which have received this pretreatment do not always provide an unbiased estimate of external surface. Prior saturation with a less readily hydrated cation, such as K^+, should help in this regard, though recalibration of the procedure with pure montmorillonite will also be required.

Specific surface determinations for large numbers of samples can be completed in a 2-day routine (Heilman et al., 1965). Drying over P_2O_5 is accomplished the 1st day or overnight. The equilibration to constant weight, indicative of a monomolecular layer, can then be accomplished the 2nd day or overnight.

Specific surface determinations for many samples can be made with reasonable accuracy by this method without H_2O_2 pretreatment to destroy organic matter (Cihacek & Bremner, 1979).

Samples may be oven-dried at 110 °C for 24 h instead of drying over P_2O_5 in most situations. Eltanawy and Arnold (1973) claim more complete drying in the oven at 110 °C.

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