

## ETHYLENE GLYCOL MONOETHYL ETHER FOR DETERMINING SURFACE AREA OF SILICATE MINERALS

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Total surface area is a fundamental property of layer silicates, and it has been used as a criterion for identification. Early methods for determining surface area used nitrogen or ethane gas and were based on the principle that solid materials will adsorb a monomolecular layer of the gas at a particular pressure (4, 6). Dyal and Hendricks (6) introduced a method for determining surface area with ethylene glycol. Their method has been adapted to determining surface area of soils and soil minerals (2) and, although it is not an equilibrium method, much useful information has been provided by its use.

The Dyal and Hendricks method has been modified to include a source of free ethylene glycol or an ethylene-glycol-solvated material to control the vapor pressure of the ethylene glycol at the adsorbing surface (1, 10, 13). Several workers have used glycerol successfully to determine surface area of both layer silicates and soils (5, 7, 9, 12). Both ethylene glycol and glycerol molecules are polar, and at present both materials are in use. Other methods in limited use include application of the B.E.T. theory (4), using ethylene dibromide (8) and the adsorption of organic molecules from solutions (3).

All surface-area methods are rather tedious and time-consuming. A more rapid technique to provide surface area data with precision equal to or better than present methods would be useful.

This paper reports the use of ethylene glycol monoethyl ether (2-ethoxyethanol) (hereafter referred to as EGME) for determining the total surface area of three reference-layer silicates. Results are compared with those obtained from the ethylene glycol method proposed by Bower and Goertzen (2).

### METHODS AND MATERIALS

The layer silicates used for most of the study were montmorillonite 21 from Chisholm Mine,

Polkville, Mississippi; illite 36 from Morris, Illinois; and kaolinite 5 from McNamee Pit, Bath, South Carolina. They were obtained from Ward's Natural Science Establishment, Rochester, New York. Their numbers refer to corresponding minerals as classified by the American Petroleum Institute.

The minerals were ground to pass a 60-mesh sieve, treated with  $H_2O_2$  to destroy organic matter, and washed with three successive portions of  $N CaCl_2$  for Ca-saturating. Excess salt was removed by three successive water washings. The samples were air-dried and again ground to pass a 60-mesh sieve.

To determine the retention of EGME, 1.1-g. samples of each mineral were placed in shallow aluminum weighing cans and dried to a constant weight over  $P_2O_5$  in an evacuated desiccator. Approximately 3 ml. of reagent grade EGME was added to each dried sample to form a mineral-adsorbate slurry. The slurry was allowed to equilibrate for at least 1 hour. Samples were then placed in culture dishes (2) over an EGME- $CaCl_2$  solvate, and the culture dishes were placed in desiccators to determine the equilibrium retention of EGME at room temperature. The desiccators were evacuated with a high-vacuum pump for 45 minutes. This procedure attained a vacuum of 0.250 mm. of Hg. The samples were first weighed 1 hour after evacuation, then at successively longer time intervals until constant weight was attained. After each weighing, samples were returned to the desiccators, and the 45-minute evacuation was repeated.

After constant weight had been attained, several samples were composited and heated to drive off the adsorbate. The adsorbate vapors were condensed in an ice trap. Samples of the condensed material were passed through a recording laboratory vapor fractometer. The peaks recorded from the vapor fractionation were compared with those for reagent-grade samples of ethylene glycol and EGME.

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For comparison, the surface area was determined with ethylene glycol by the Bower and Goertzen method (2).

Another group of montmorillonite 21 samples was dried over  $P_2O_5$ , treated with EGME, evacuated, and weighed at short intervals to give data for plotting EGME retention vs. time.

To determine if EGME formed a solvate with  $CaCl_2$ , 0.01-mole quantities of dried  $CaCl_2$  were weighed into aluminum dishes and treated with approximately 0.08 mole of EGME. One set of samples was heated at  $110^\circ C$ . and another set at  $70^\circ C$ . To determine weight loss with time, the samples were at first weighed at 30-minute intervals and thereafter at longer time intervals.

### RESULTS AND DISCUSSION

The EGME retained by montmorillonite 21 at equilibrium averaged 231.7 mg./g. Using the Dyal and Hendricks (6) value of  $810 \text{ m.}^2/\text{g.}$  as the surface area for montmorillonite, it can be calculated that  $2.86 \times 10^{-4}$  g. of EGME is required to form a monolayer on  $1 \text{ m.}^2$  of surface. The corresponding molecular coverage is  $52 \times 10^{-16} \text{ cm.}^2/\text{molecule}$ . These values were used to calculate the surface area of the three layer silicates studied. The average quantities of EGME and ethylene glycol retained, the latter measured by the Bower and Goertzen method (2), and the corresponding calculated surface areas for the three reference-layer silicates are given in table 1. Mixtures of montmorillonite 21 and kaolinite 5 retained quantities of EGME in proportion to the amount of each mineral present; for example, a 50:50 mixture retained 123 mg. of EGME per g. of the mineral mixture, corresponding to a surface area of  $430 \text{ m.}^2/\text{g.}$

TABLE 1

*Ethylene glycol and ethylene glycol monoethyl ether retained by three reference-layer silicates and the corresponding total surface area of the minerals*

Adsorbate	Amount Retained			Surface Area		
	Kaol. 5	Illite 36	Mont. 21	Kaol. 5	Illite 36	Mont. 21
	mg./g.			$\text{m.}^2/\text{g.}$		
Ethylene glycol monoethyl ether	13.8	55.1	231.7	48.3	192.6	810.0
Ethylene glycol	17.3	64.7	250.1	55.4	208.8	806.7

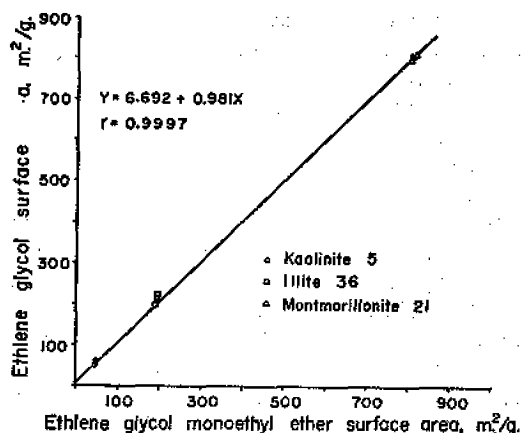


FIG. 1. Relations between surface-area measurements by ethylene glycol and ethylene glycol monoethyl ether for three reference-layer silicates.

The relation between the total surface area of the three layer silicates by the two methods is illustrated in figure 1. The slope of the line is slightly less than unity, and the intercept misses the origin by approximately  $7 \text{ m.}^2/\text{g.}$  It appears that two of the surface-area values, both for illite 36 by the glycol method, are slightly high, and these values shifted the line a small amount from a 1:1 relationship. It is evident that the two adsorbates precisely measure the same surface area.

Plotting the data as milligrams retained per gram of layer silicate gave an equally good relationship for both compounds. In this case, however, the slope was slightly greater than unity, because differences in molecular weights and molecular coverage for the two compounds are such that a slightly greater weight of ethylene glycol is required to cover a unit surface with a monomolecular layer. The greater the surface area, the greater will be the difference between the weights of the two compounds retained. For example, kaolinite 5 retained 3.4 mg. more ethylene glycol than EGME, whereas montmorillonite retained 18.4 mg. more ethylene glycol per g. of clay.

It was considered possible that layer silicates may react with EGME and cleave the molecules, leaving ethylene glycol adsorbed on the mineral surface. Vapor fractometer traces of reagent grade EGME and of adsorbed material collected by heating minerals containing an equilibrium monolayer of EGME were the same shape,

and both materials passed through the column at the same rate. It is evident that the EGME is not cleaved by layer silicate minerals (fig. 2). The difference in peak height resulted from different sample sizes. Ethylene glycol required slightly more time to pass through the fractometer column, and it gave a broader peak (fig. 2).

Bower (3) reported that *o*-phenanthroline molecules were too large to diffuse between lattice layers of vermiculite and halloysite. As a result, total surface area values for these minerals cannot be determined with *o*-phenanthroline. Small samples of vermiculite and halloysite used in previous studies at the U. S. Salinity Laboratory (3, 11) were obtained for determining surface area. The data (table 2) indicate that EGME molecules diffuse between the lattice layers of the two minerals and adsorb to interlayer surfaces.

For additional comparison of results obtained with the two adsorbates duplicate samples of halloysite 29 from Wagon Wheel Gap, Colorado, hectorite 34 from Hector, California, and pyrophyllite 49 from Robbins, North Carolina, were

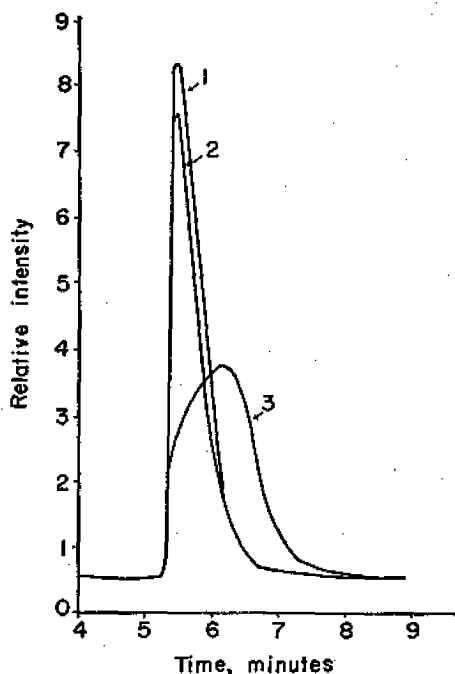


FIG. 2. Vapor fractometer peaks for ethylene glycol monoethyl ether before (curve 1) and after (curve 2) adsorption by minerals, and for ethylene glycol (curve 3) before adsorption by minerals.

TABLE 2

Total surface area for vermiculite and halloysite by three methods

Adsorbate	Vermiculite	Halloysite
	m. <sup>2</sup> /g.	
Glycol*	237.0	326.0
<i>O</i> -phenanthroline*	43.7	43.6
Glycol†	339	—
Glycol‡	340	170
Ethylene glycol monoethyl ether‡	350	173

\* Bower (3).

† McNeal (11).

‡ This study.

subjected to surface-area measurement with each adsorbate. The agreement between the two adsorbates was excellent (table 3). The tabled data (table 3) closely follows the plot for the three major groups of minerals (fig. 1).

The principal advantage of using EGME is the short time required for the excess to evaporate, leaving a monolayer. Figure 3 illustrates that an equilibrium monolayer on montmorillonite 21 was obtained approximately 2 hours after evacuation was begun, even when considerable excess EGME was added. In contrast, 22 days were required to obtain an equilibrium monolayer of ethylene glycol on montmorillonite 21. The Bower and Goertzen method (2) recommends that the first weighing be made 48 hours after evacuation and at 8- to 16-hour intervals thereafter. Although their method is precise, it is very time-consuming. Using EGME allows an equilibrium monolayer to be attained easily within 1 day. Since this time period is less than that required for drying samples over  $P_2O_5$ , the drying becomes the most time-consuming part of the procedure.

The properties of EGME differ considerably from those of ethylene glycol (table 4). Both compounds are formed from ethylene oxide. The reaction with water gives ethylene glycol, and the reaction with ethanol gives EGME. Ethylene glycol has two hydroxyl groups whereas EGME has only one. For their original method using ethylene glycol, Dyal and Hendricks (6) used the basis that polyhydroxylate compounds formed solvates with montmorillonite. Our data show that similar solvates with montmorillonite are formed by compounds with one hydroxyl

group, with ethyl ether in place of a second hydroxyl group.

Visual observation indicates that EGME is adsorbed more rapidly by layer silicates than is the more viscous ethylene glycol. Samples wet immediately and the EGME disappears into the sample, whereas ethylene glycol tends to remain in droplet form and moves through the sample rather slowly.

EGME forms a solvate with  $\text{CaCl}_2$  that is stable at  $70^\circ\text{C}$ . (fig. 4). The ethylene glycol monoethyl ether: $\text{CaCl}_2$  ratio is 1.5:1. Therefore, 3 molecules of ethylene glycol monoethyl ether

TABLE 3

Average surface area values of three minerals with two adsorbate methods

Mineral	Ethylene Glycol	Ethylene Glycol Monoethyl Ether
	m. <sup>2</sup> /g.	
Halloysite 29	75.2	76.2
Hectorite 34	464.0	461.8
Prophyllite 49	7.0	6.2

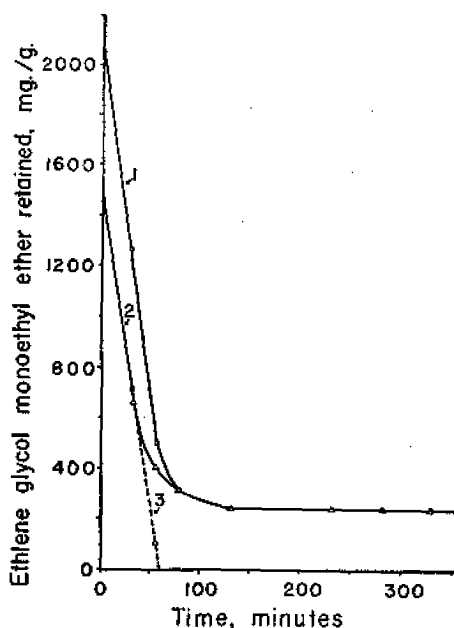


FIG. 3. Ethylene glycol monoethyl ether retained by montmorillonite 21 after various evacuation times: 2107 mg./g. added (curve 1); 1515 mg./g. added (curve 2); 1512 mg./g. of solvate alone (curve 3).

TABLE 4

Properties, names, and formulas of ethylene glycol and ethylene glycol monoethyl ether

	Ethylene Glycol	Ethylene Glycol Monoethyl Ether
Formula.....	$\text{HOCH}_2\text{CH}_2\text{OH}$	$\text{C}_2\text{H}_4\text{OCH}_2\text{CH}_2\text{OH}$
Other names.....	1,2-ethanediol	Ethanol, 2-ethoxy
Molecular weight (g./mole).....	62.07	90.12
Density at $20^\circ\text{C}$ . (g./cc.).....	1.1185	0.9311
Boiling point ( $^\circ\text{C}$ ).....	197.2	135.1

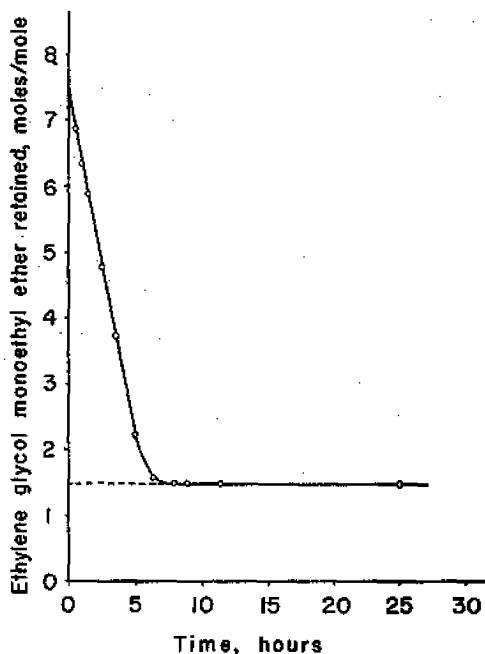


FIG. 4. Ethylene glycol monoethyl ether retained by  $\text{CaCl}_2$  as a function of time at  $70^\circ\text{C}$ .

solvates 2 molecules of  $\text{CaCl}_2$ . Bower and Goertzen (2) reported a glycol: $\text{CaCl}_2$  ratio of 1:1 for a solvate stable at  $110^\circ\text{C}$ . The EGME- $\text{CaCl}_2$  solvate decomposes at  $110^\circ\text{C}$ .

Since the two compounds give identical measures of surface area for Ca-saturated minerals, it is probable that the measured surface area with EGME would differ with different saturating cations, as is the case with ethylene glycol (11). It is also probable that EGME molecules are associated with the saturating cations in thicknesses greater than monolayers, as McNeal (11) recently reported for ethylene glycol.

Additional work is underway to adapt ethyl-

ene glycol monoethyl ether to a rapid technique for determining soil surface area.

#### SUMMARY

Ethylene glycol monoethyl ether (EGME) is a useful adsorbate for determining the surface area of layer silicate minerals. With this compound, surface area of dry montmorillonite can be determined in less than a day compared to more than 20 days when ethylene glycol is used as the adsorbate. Both compounds precisely measure the same surface area, and it is probable that they are similarly influenced by the saturating cations.

#### REFERENCES

- (1) Bower, C. A., and Gschwend, F. B. 1952 Ethylene glycol retention by soils as a measure of surface area and interlayer swelling. *Soil Sci. Soc. Am. Proc.* 16: 342-345.
- (2) Bower, C. A., and Goertzen, J. O. 1959 Surface area of soils and clays by an equilibrium ethylene glycol method. *Soil Sci. Soc. Am. Proc.* 23: 289-292.
- (3) Bower, C. A. 1963 Adsorption of *o*-phenanthroline by minerals and soils. *Soil Sci. Soc. Am. Proc.* 27: 192-195.
- (4) Brunauer, S., Emmett, P. H., and Teller, E. 1938 Adsorption of gases in multimolecular layers. *J. Am. Chem. Soc.* 60: 309-319.
- (5) Diamond, S., and Kinter, E. B. 1958 Surface area of clay minerals as derived from measurements of glycerol retention. *Clays and Clay Minerals* 5: 334-347.
- (6) Dyal, R. S., and Hendricks, S. B. 1950 Total surface of clays in polar liquids as a characteristic index. *Soil Sci. Soc. Am. Proc.* 69: 421-432.
- (7) Jackson, M. L. 1956 "Soil chemical analyses—advanced course." Published by the Soils Dept., University of Wisconsin, Madison, Wisconsin.
- (8) Jurinak, J. J., and Volman, D. H. 1967 Application of Brunauer, Emmett, and Teller equation to ethylene dibromide adsorption by soils. *Soil Sci. Soc. Am. Proc.* 31: 487-496.
- (9) Kinter, E. B., and Diamond, S. 1958 Gravimetric determination of monolayer glycerol complexes of clay minerals. *Clays and Clay Minerals* 5: 318-333.
- (10) Martin, T. R. 1955 Ethylene glycol retention by clays. *Soil Sci. Soc. Am. Proc.* 19: 160-164.
- (11) McNeal, B. L. 1964 Effect of exchangeable cations on glycol retention by clay minerals. *Soil Sci. Soc. Am. Proc.* 28: 96-102.
- (12) Milford, M. H., and Jackson, M. L. 1961 Specific surface determinations of expansible layer silicates. *Science* 135: 929-930.
- (13) Sor, K., and Kemper, W. D. 1959 Estimation of hydrateable surface area of soils and clays from the amount of adsorption and retention of ethylene glycol. *Soil Sci. Soc. Am. Proc.* 23: 105-110.

Dear Reader:

Since this paper has been published, I have learned that comparisons of the data on line 1 with that on lines 3, 4 and 5 of table 2 are not strictly valid. The vermiculite sample used for obtaining the data on line 1 is not the same material that was used for the data on lines 3, 4 and 5. The assumptions used in obtaining the surface area for halloysite on line 1 differed from those used for obtaining the data on lines 4 and 5. Other comparisons in the table are valid.

The discrepancy in the comparisons of table 2 in no way detracts from the surface area methods used in this study or other studies. The discrepancy should have been more fully explained in the text.

Respectfully yours,

*David L. Carter*