

## THE EFFECT OF HEATING *IN VACUO* ON THE MICROPOROSITY OF SEPIOLITE

A. J. DANDY

School of Natural Resources, University of the South Pacific, Suva, Fiji

and

M. S. NADIYE-TABBIRUKA

Department of Chemistry, Makerere University, Kampala, Uganda

(Received 11 August 1975; and in final form 16 September 1975)

**Abstract**—The *t*-plot method has been applied to the results of nitrogen adsorption at 76°K on sepiolite first heated *in vacuo* at various temperatures. Heating sepiolite samples *in vacuo* at 427°K results in a large decrease in surface area compared with samples outgassed at 373°K. A change in structure and a consequent collapse of micropores is postulated. However, the *t*-plots indicate that some microporosity remains. Outgassing at 623°K appears to destroy completely the micropores.

### INTRODUCTION

The *t*-plot method (Lippens *et al.*, 1964; Lippens and de Boer, 1965; de Boer *et al.*, 1966) for the calculation of the surface areas of solids has been extended by Mikhail *et al.* (1968a) to the determination of both internal and external surface areas of microporous solids, i.e. solids with pores of radii 1.0–1.5 nm or less (Dubinin, 1966). According to the authors a single gas adsorption isotherm can yield information concerning the extent of the micropore system and the external surface area of solids which is not obtainable by methods such as the BET method (Brunauer *et al.*, 1938). Complete pore structure analyses have been made using the *t*-plot approach by Mikhail *et al.* (1968b).

In the *t*-plot method, the adsorption isotherm data (volumes,  $V_a$  (STP), or weights,  $x_a$ , of gas adsorbed/g adsorbent at a series of equilibrium pressures) is converted into a plot of  $V_a$  (or  $x_a$ ) against *t*, the statistical thickness of the adsorbed layer, by means of a “master” *t*-curve for non-porous adsorbents, several of which have been published (Shull, 1948; Cranston and Inkley, 1957; de Boer *et al.*, 1966). Such curves have been derived for a large number of non-porous solids by calculating the statistical thickness, *t*, from  $V_a/S_{\text{BET}}$  values (where  $S_{\text{BET}}$  is the specific BET surface area), assuming close packing of adsorbate molecules, and plotting these against the corresponding relative pressures at equilibrium. Smoothed-out (“universal”) *t*-curves are obtained for groups of solids. Non-porous solids yield linear *t*-plots ( $V_a$  vs *t*) which pass through the origin if no capillary condensation takes place. A surface area,  $S_s$ , may be calculated from the slope of such a linear plot. However, the choice of the master *t*-curve influences the results obtained. The interpretation of the results continues to be a matter of controversy (Sing, 1973).

Microporous solids yield linear plots which intercept the  $V_a$  (or  $x_a$ ) ordinate at a finite value at  $t = 0$  ( $P/P_0 = 0$ , where  $P$  = equilibrium pressure and  $P_0$  = saturated vapour pressure of adsorbate). It has been suggested that this linear plot can be used to calculate the external surface area of the solid and that the slope of the line drawn from the origin to the “monolayer point” can be used to calculate the surface area of the micropores and the external surface (de Boer *et al.*, 1966); geometric considerations show that this interpretation is equivalent to using the intercept at  $t = 0$  as a measure of the amount of gas adsorbed by the micropores. A different interpretation is that micropores are filled in this region and that the micropore volume is estimated from the intercept at  $t = 0$  (Day and Parfitt, 1967; Sing, 1967).

### RESULTS

In this instance the *t*-plot is used to interpret the results of a study of gas adsorption on sepiolite, a microporous clay mineral from Amboseli, Tanzania. It has been shown by Dandy (1971) that the BET surface area calculated from the nitrogen adsorption isotherm at 76°K,  $S_{\text{BET}}(\text{N}_2)$ , is  $364 \text{ m}^2\text{g}^{-1}$  for sepiolite samples first outgassed (*in vacuo*) at 373°K. If samples are outgassed at temperatures above 378°K, the value of  $S_{\text{BET}}(\text{N}_2)$  decreases and is reduced to  $180 \text{ m}^2\text{g}^{-1}$  for samples outgassed at 427°K. It was postulated that under these conditions the structure was changed in such a way as to make access of nitrogen molecules to micropores difficult, i.e. the value of  $180 \text{ m}^2\text{g}^{-1}$  may represent the external surface area. Preisinger (1963) has shown that such a change in structure takes place on heating sepiolite *in air* to temperatures above 623°K; a phase transformation to “sepiolite anhydride” takes place and the

silicate layers become tilted. The loss of bound water associated with this change commences above 523°K in air, according to Hayashi *et al.* (1969) and Nagata *et al.* (1974). The uptake of ammonia on sepiolite samples first outgassed *in vacuo* at 373°K is very high (due to extensive penetration of micropores and exchange processes) but is decreased to a value corresponding to a surface coverage of 193 m<sup>2</sup>g<sup>-1</sup> on samples first outgassed at 427°K, assuming a molecular cross-sectional area of 0.137 nm<sup>2</sup> for the ammonia molecule. This appears to support the postulate that a change in structure has occurred and that there is very limited access to micropores.

The nitrogen adsorption isotherm data for sepiolite, outgassed at 373°K, has been re-plotted in the form of a  $x_a$ - $t$ -plot (Fig. 1, A) using the  $t$ -curve of Cranston and Inkley (1957). This curve was chosen because it corresponds to a higher BET  $c$ -value than that of de Boer's curve (de Boer *et al.*, 1966); the BET  $c$ -value for nitrogen on sepiolite is very large, the intercept of the BET plot being practically zero. Mikhail *et al.* (1968a) maintain that the  $t$ -curve should be chosen to have the same  $c$ -value as the system under consideration in order to ensure that  $S_t$  is equal to  $S_{BET}$ . However, this begs the question of the significance of  $S_{BET}$  values and Sing (1973) has pointed out that pore-narrowing effects are ignored by adopting this approach.

The equation used by de Boer *et al.* (1966) to calculate  $S_t$  was modified for uptakes expressed as weights rather than volumes of adsorbate:

$$S_t = 1.238 (x_a/t) \quad (1)$$

where  $x_a$  is the weight of nitrogen adsorbed at 76°K in mg/g of adsorbate, and  $t$  is expressed in nm.

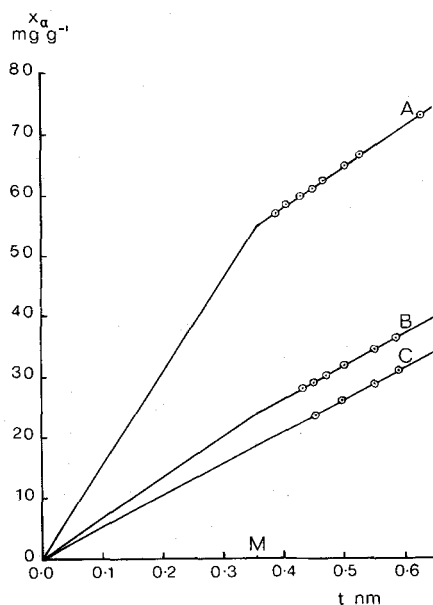


Fig. 1.  $x_a$ - $t$  plots of nitrogen adsorption at 76°K on sepiolite samples. (A) sepiolite outgassed at 373°K; (B) outgassed at 427°K; (C) outgassed at 673°K.

Table 1. Specific surface areas of sepiolite samples, calculated from N<sub>2</sub> adsorption at 76°K

Outgassing Temperature °K	373 (100°c)	427 (154°c)	673 (400°c)
Specific area, m <sup>2</sup> /g			
BET method (Dandy, 1971)	364	180	133
$t$ -plot, $S_{total}$	380	168	130
$t$ -plot, $S_{external}$	168	133	130

If the slopes of the lines drawn beyond the monolayer point (Fig. 1, M) are associated with the external surface and those from the origin to this point for individual plots can be interpreted in terms of the total surface area,  $S_{total}$ , of microporous solids, the values obtained for  $S_{total}$  and  $S_{ext}$  from plot A (sepiolite outgassed at 373°K) are 380 m<sup>2</sup>g<sup>-1</sup> and 168 m<sup>2</sup>g<sup>-1</sup> respectively. A comparison of the latter value with the BET (N<sub>2</sub>) surface area of sepiolite outgassed at 427°K (180 m<sup>2</sup>g<sup>-1</sup>) appears to support the interpretation that outgassing at this higher temperature decreased the surface area of sepiolite samples to that of the external surface only. However, the  $t$ -plot obtained from the adsorption isotherm for these samples outgassed at 427°K (Fig. 1, B) does not pass through the origin; this is indicative of the continued presence of micropores. Values of  $S_{total} = 168$  m<sup>2</sup>g<sup>-1</sup> and  $S_{ext} = 133$  m<sup>2</sup>g<sup>-1</sup> were calculated from the slopes of this plot. Thus the external surface area also is decreased when sepiolite is outgassed at 427°K rather than at 373°K. A change in structure of the kind postulated could be expected to affect the external surface, particularly at the micropore openings. An even higher outgassing temperature (673°K) produces sepiolite samples of BET (N<sub>2</sub>) surface area = 133 m<sup>2</sup>g<sup>-1</sup>. The  $t$ -plot (Fig. 1, C) passes through the origin, which is indicative of non-microporosity. The slope of this plot gives  $S_{total} (= S_{ext}) = 130$  m<sup>2</sup>g<sup>-1</sup>. Table 1 summarises the values of specific surface area of sepiolite samples prepared under various conditions, calculated by the BET method and by the  $t$ -plot method, as detailed above.

## DISCUSSION

The changes in BET (N<sub>2</sub>) surface areas cannot be used with any certainty to draw conclusions concerning the presence of micropores in sepiolite outgassed at 427°K: the decrease in BET surface area which results from outgassing at 673°K rather than 427°K could be attributed to sintering of the external surface. In this situation the  $t$ -plot appears to afford a means of obtaining information concerning the micropores. No firm evidence is available to decide whether the initial slopes of  $t$ -plots of microporous solids should be used to calculate surface areas or whether the intercepts at  $t = 0$  should be regarded as indicating the completion of micropore filling by

adsorbate. It should be noted that sepiolite micropores have cross-sectional areas only 4–5× larger than those of nitrogen molecules at 76°K. Their widths are comparable with those of nitrogen molecules. In addition, internally projecting water molecules are present within the micropores. Neither complete area coverage nor complete volume filling is an appropriate concept. It is unlikely that monolayers of nitrogen molecules on all internal surfaces are achieved.

## REFERENCES

- Brunauer, S., Emmett, P. H. and Teller, E. (1938) Adsorption of gases in multimolecular layers: *J. Am. Chem. Soc.* **60**, 309–319.
- Cranston, R. W. and Inkley, F. A. (1957) The determination of pore structures from nitrogen adsorption isotherms: *Adv. Catalysis* **9**, 143–154.
- Dandy, A. J. (1971) Zeolitic water content and adsorptive capacity for ammonia of microporous sepiolite: *J. Chem. Soc. A*, 2383–2387.
- Day, R. and Parfitt, G. D. (1967) Characterization of the surface of rutile by nitrogen and water vapour adsorption: *Trans. Farad. Soc.* **3**, 708–716.
- de Boer, J. H., Lippens, B. C., Linsen, B. G., Broekhoff, J. C. P., van den Heuvel, A. and Osinga, Th. J. (1966) The *t*-curve of multimolecular N<sub>2</sub>-adsorption: *J. Colloid Interface Sci.* **21**, 405–414.
- Dubin, M. M. (1966) Modern state of the theory of gas and vapour adsorption by microporous adsorbents: *Pure appl. Chem.* **10**, 309–321.
- Hayashi, H., Otsuka, R. and Imai, N. (1969) I.r. study of sepiolite and palygorskite on heating: *Am. Miner.* **53**, 1613–1624.
- Lippens, B. C. and de Boer, J. H. (1965) Studies on pore systems in catalysts—V. The *t* method: *J. Catalysis* **4**, 319–323.
- Lippens, B. C., Linsen, B. G. and de Boer, J. H. (1964) Pore systems in adsorbents and catalysts: *J. Catalysis* **3**, 32–37.
- Mikhail, R. Sh., Brunauer, S. and Bodor, E. E. (1968a) Investigations of a complete pore structure analysis—I: Analysis of micropores: *J. Colloid Interface Sci.* **26**, 45–53.
- Mikhail, R. Sh., Brunauer, S. and Bodor, E. E. (1968b) Investigations of a complete pore structure analysis—II: Analysis of four silica gels: *ibid.* **26**, 54–61.
- Nagata, H., Shimoda, S. and Sudo, T. (1974) On dehydration of bound water of sepiolite: *Clays and Clay Minerals* **22**, 285–293.
- Preisinger, A. (1963) Sepiolite and related compounds: its stability and application: *Clays and Clay Minerals* **10**, 365–371.
- Shull, C. G. (1948) The determination of pore size distribution from gas adsorption data: *J. Am. Chem. Soc.* **70**, 1405–1410.
- Sing, K. S. W. (1967) Assessment of microporosity: *Chem. Ind.*, 829–830.
- Sing, K. S. W. (1973) *Colloid Science* (Edited by Everett, D. H.), Vol. 1, Chap. 1. The Chemical Society, London.