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A NOVEL DIFFERENTIAL THERMAL ANALYSIS METHOD FOR QUANTIFYING THE SORPTION CAPACITY OF SMECTITE CLAY

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Abstract—The enthalpy of freezing of methyl salicylate sorbed by four commercial montmorillonite clays was used to estimate the absorption/adsorption capacity of the clay. Differential thermal analysis was therefore employed to give a quantitative estimate of the sorption capacity of the clay for methyl salicylate. The absorption capacity of the clay depended on the state of hydration and ranged from 30.4% for an 8% water content to 9.7% for a montmorillonite containing 24% water.

Key Words—Adsorption, Differential thermal analysis, Hydration, Methyl salicylate, Smectite.

INTRODUCTION

Smectite clays are widely used as adsorbents/absorbents in a variety of applications, including spillage control, the safe disposal of toxic waste, and in pharmaceuticals (Hall, 1987). The ability of smectite clays to absorb (and adsorb) large quantities of organic material is related to the ability of the negatively charged aluminosilicate layers to move apart and provide a larger interlamellar space, in which the host molecules can be held, (van Olphen, 1977). Binding within this space may involve several mechanisms, including coordination to the counter ion located between the layers and binding to acidic or basic sites on the surface of the clay.

The interaction of water with clays has been particularly well studied, and a semi-fluid model best describes the properties of water within the clay (Sposito and Prost, 1982). Studies of the partial molar Gibbs energies (and the corresponding enthalpies) for the adsorption of water enable the water associated with the clay to be classified, in a simplified way, as bound and free (Sposito and Prost, 1982; Zografi and Kontny, 1986). In related work Fielden *et al.* (1988) used differential thermal analysis (DTA) to study the enthalpy of freezing of water associated with microcrystalline cellulose and estimated the amount of water bound to the surface of this material. In the present paper a further quantification of this DTA method, for estimating the binding capacity of solids, is presented, in this case for smectite clays.

EXPERIMENTAL

Materials

The following clay samples were obtained from commercial sources and used as provided: Wyoming bentonite (Volclay, Birkenhead, United Kingdom), sodium bentonite (of unknown location, supplied by Steetley Minerals, Woburn, United Kingdom), BDH montmorillonite (for adsorption) (of unknown location, supplied by British Drug Houses, Poole Dorset, United Kingdom), and montmorillonite (Surrey Finest, Laporte Industries). Each was characterized as a smectite by X-ray powder diffraction (XRD) (Wilson, 1987). Their properties are as follows:

The Surrey Finest sample had a water content of 12% w/w (by thermal gravimetric analysis (TGA)) and a d(001) value of 14.7 Å, characteristic of two layers of intercalated water. The principal interlamellar ion was calcium. The Wyoming bentonite had a water content of 8% w/w (by TGA) and a d(001) value of 12.30 Å, characteristic of one layer of intercalated water. The principal interlamellar ion was sodium. The sodium bentonite had a water content of 7% w/w (by TGA) and a d(001) value of 12.20 Å, characteristic of one layer of intercalated water. The principal interlamellar ion was sodium. The BDH montmorillonite (for absorption) had a water content of 14% w/w (by TGA) and a d(001) value of 15.2 Å, characteristic of two layers of intercalated water. The principal interlamellar ion was calcium.

Methyl salicylate was obtained from British Drug Houses, distilled under reduced pressure, and dried over molecular sieves. Clay samples were prepared by direct mixing of known weights of methyl salicylate and the clay, followed by a gentle mixing in a mortar and pestle. Similar values for the enthalpy of fusion were obtained immediately after sample preparation or 24 hr later.

Instrumentation

Water content was estimated by thermal gravimetric analysis with Stanton Redcroft TG-750. A Stanton Redcroft DTA Model 671 was used throughout the study, calibrated with high purity indium. The sample was referenced against an empty sample pan, and liquid nitrogen was used as a coolant. In all experiments the same operating conditions were used—a heating rate of 10°C/min in an atmosphere of static air. Peak areas

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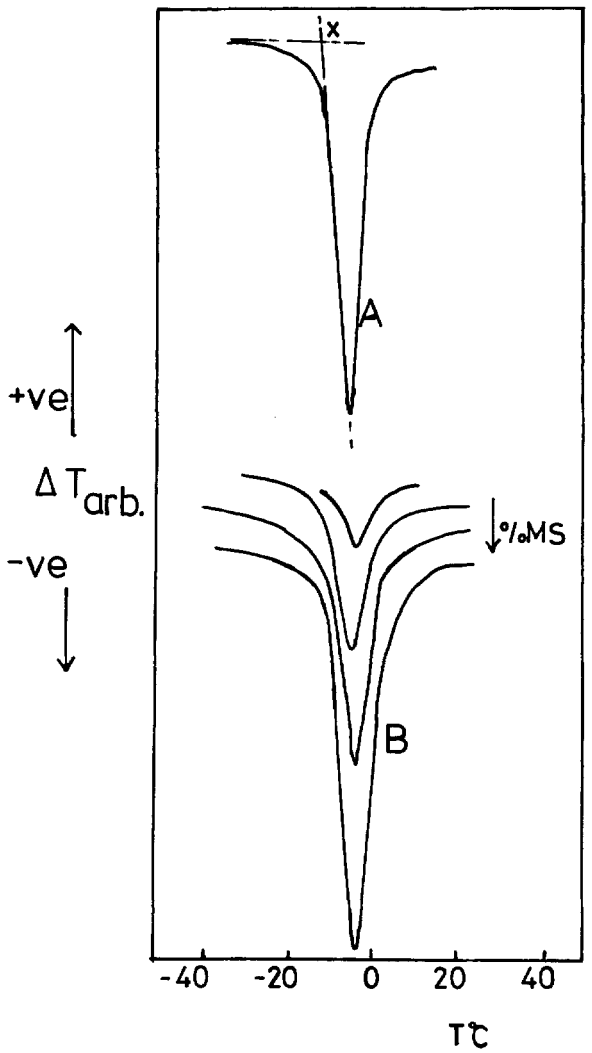


Figure 1. Typical differential thermal analysis traces for (A) methyl salicylate and (B) methyl salicylate-sodium bentonite complex (31%, 39%, 53%, and 77% w/w). x = marks the extrapolated onset temperature.

were determined by cutting out the traces and weighing the paper.

In a typical set of experiments three aliquots of each clay-methyl salicylate sample were analyzed by DTA (sample weights were in the range 20 to 40 mg). Plots of ΔH_{obs}/[methyl salicylate] vs. 1/P were subjected to a conventional least squares analysis. A non-linear fitting of the data was accomplished using the Marquard alogarithm, a program from Project Seraphim (Eastern Michigan State University, Ypsilanti, Michigan) was used.

RESULTS AND DISCUSSION

Methyl salicylate (MS) is an organic compound of moderate hydrophobicity, with an accessible freezing point (−8.6°C); it is also a common reagent of moderate toxicity (Merck, 1983). MS was therefore used to study the interaction of a moderately polar organic molecule with various smectite clays.

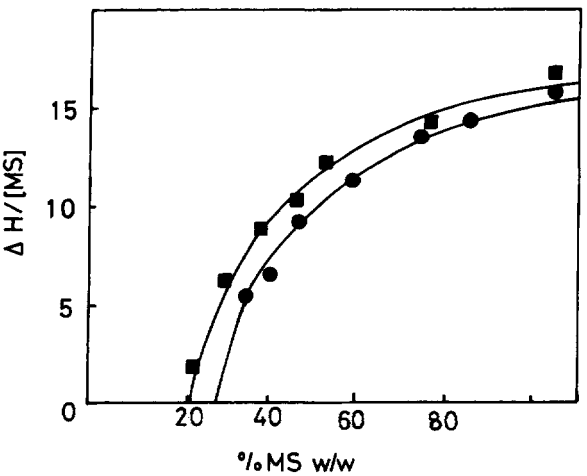


Figure 2. Variation of observed enthalpy (ΔH_{obs}/[methyl salicylate] kJ/mole) with percentage of absorbed methyl salicylate (w/w) for: ●, Wyoming bentonite and ■, sodium bentonite. Solid lines are theoretical curves calculated using results in Table 1 and Eq. (2). The thermal results for the Surrey Finest and the Wyoming bentonite samples almost overlay each other. The Surrey Finest sample is omitted from this figure and from Figure 4.

Initial work

The freezing behavior of MS in the presence and absence of montmorillonite was studied by DTA. Typical traces are shown in Figure 1 for work with the methyl salicylate/sodium bentonite system. MS freezes at −8.6°C (Merck, 1983), consistent with the extrapolated onset temperature of −8°C as measured in DTA experiments on pure MS. The enthalpy of fusion of MS was estimated by DTA as 19.1 ± 1.3 kJ/mole (six determinations). On the addition of MS to a clay sample, no freezing endotherm was observed until a critical amount of MS had been added (usually about 25% w/w). Above this critical percentage (P_c), the observed enthalpy per mole of MS added increased as illustrated in Figure 2.

The DTA experiments were correlated with established procedures by measuring the dependence of the d(001) value on the quantity of added MS. For the Wyoming bentonite and the Surrey Finest samples, plots of d(001) value vs. percentage of MS (w/w) are shown in Figure 3. These results indicate that the clays were fully expanded at MS percentages >20%. The limiting values of d(001) was 18.03 Å for the Wyoming bentonite, 18.60 Å for the Surrey Finest, and 18.5 Å for the sodium bentonite samples. These values may be compared with data from Brindley (1966) and Wilson (1987) for the "well characterized" ethylene glycol

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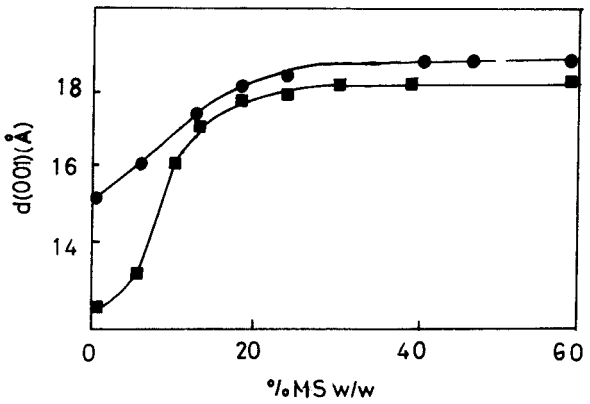


Figure 3. The variation of d(001) with percentage of methyl salicylate (w/w) absorbed on the clay for: ●, Surrey Finest and ■, Wyoming bentonite samples.

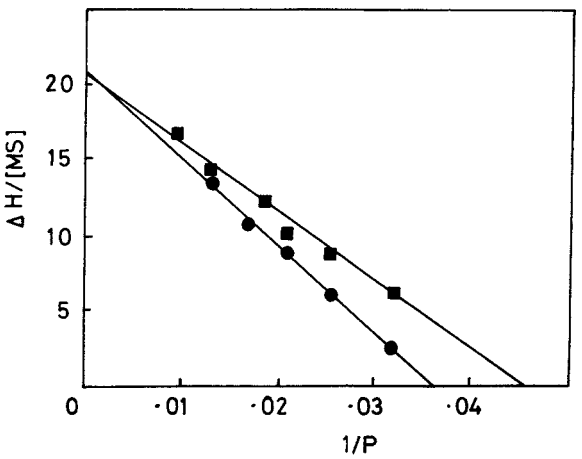


Figure 4. Plots of ΔH_{obs}/[methyl salicylate] kJ/mole vs. reciprocal percentage (1/P, w/w) of methyl salicylate absorbed on clay. Eq. (2) for: ●, Wyoming bentonite and ■, sodium bentonite.

(16.9–17.1 Å) and glycerol (17.8 Å) adducts of montmorillonite. The quantification of the XRD data and the determination of the maximum absorption capacity of the clay are difficult, and, compared with DTA, the XRD method is slow.

Changes in the infrared spectra of adsorbed MS were small, and no evidence for the displacement of water from the interlamellar space of the clay was found (either by Fourier Transform Infrared Spectroscopy (FTIR) or DTA). In contrast, Bowen *et al.* (1988) showed that if dimethyl methylphosphonate binds to smectite, water, easily observed by FTIR, is displaced from the interlamellar space.

Quantification of results

To quantify the DTA results a simple model based on the assumption that absorbed (and adsorbed) MS does not freeze at the normal freezing point of MS was developed. The observed enthalpy (ΔH_{obs}), thus, appeared to be solely due to liquid MS in the sample pan. Hence,

$$\Delta H_{obs} = \Delta H_{melt}[MS]_{total} - \Delta H_{melt}[MS]_{abs}, \quad (1)$$

where $[MS]_{total}$ is the total number of moles of MS added to the sample, and $[MS]_{abs}$ is the number of moles of MS adsorbed and absorbed by the clay.

If all of the salicylate added, up to a critical percentage (w/w), was immobilized on the clay, Eq. (1) may be rewritten as:

$$\Delta H_{obs}/[MS]_{total} = \Delta H_{melt} - \Delta H_{melt}P_c/P, \quad (2)$$

where P is the percentage (w/w) of MS on the clay, and P_c is the critical percentage above which no more MS was absorbed.

Hence, a plot of $\Delta H_{obs}/[MS]_{total}$ vs. 1/P should give a straight line from which the critical percentage can be obtained as the reciprocal of the x-axis intercept and the heat of fusion from the y-intercept. The slope gives the product $\Delta H \cdot P_c$. Typical linear plots are shown in Figure 4, and values for the critical percentage and the heat of fusion of MS are tabulated in Table 1. To establish P_c a calibrated instrument was not used; plots may be constructed using any suitable measure of peak area per mass of MS. The method as presented here provides the enthalpy of fusion of MS as an additional check. The value for the enthalpy of fusion of MS, however, as determined from these plots was consistently and significantly higher than that measured in experiments on pure MS (19.96 kJ/mole) (Table 1).

Table 1. Maximum absorption capacity of smectite samples (P_c w/w) and heat of fusion[1] of methyl salicylate as obtained by linear and non-linear methods.

	P_c[2]	P_c[3]	ΔH[2]	ΔH[3]
Wyoming bentonite	27.7 (1.0)	27.0 (0.2)	20.8 (0.3)	20.0 (0.5)
Sodium bentonite	22.1 (1.1)	22.0 (0.4)	20.4 (0.5)	20.5 (2.3)
Surrey Finest	26.5 (1.7)	26.4 (0.8)	20.7 (0.5)	20.5 (0.7)

Values in parentheses are estimated errors; the clays are named as by the suppliers; for details see experimental section.
[1] ΔH kJ/mole.
[2] From linear regression (see Figure 4).
[3] From non-linear fitting of Eq. (2).

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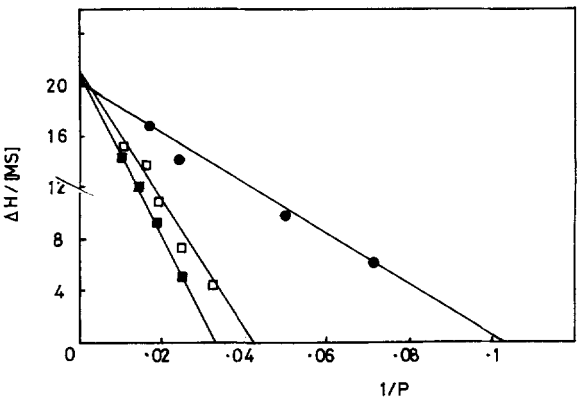


Figure 5. Plots of ΔH_{obs}/[methyl salicylate] kJ/mole vs. reciprocal percentage (1/P, w/w) of methyl salicylate absorbed on clay. Eq. (2) for various water contents (British Drug Houses montmorillonite): ●, 8%; □, 15%; and ■, 24% water.

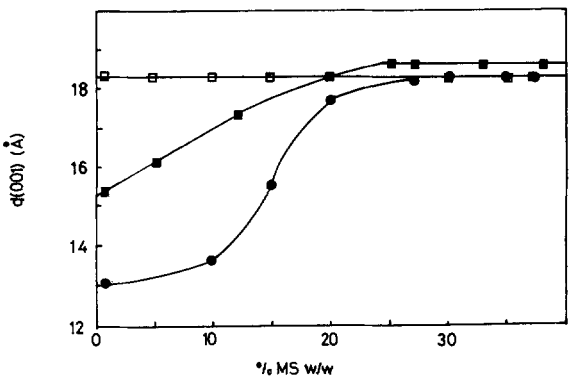


Figure 6. The variation of d(001) with percentage of methyl salicylate for montmorillonite in various hydration states. ●, 8%; ■, 15%; and □, 24% water.

The form of Eq. (2) means that the plotted values are highly correlated; thus, the weightings given to the various points in a conventional linear least squares treatment will result in slightly unreliable estimates of both P_c and ΔH. The results were subsequently investigated by a non-linear least squares procedure in which Eq. (2) was fitted directly using the Marquard algorithm. The results of this treatment are also summarized in Table 1. The value of ΔH_{melt}, as estimated by this method, was generally lower than that from linear regression and had consistently a greater error. The values were always within experimental error of our independently determined value for the heat of fusion of MS. Using linear regression does not appear to have affected P_c, and P_c can therefore be reliably determined from a linear plot. The solid lines in Figure 2 were calculated from Eq. (2) using the parameters derived from non-linear fitting (Table 1).

Effect of water on the absorption/adsorption of MS by montmorillonite

The BDH montmorillonite was studied as supplied, after partial dehydration (60°C, 1 hr, d(001) = 15.2 Å, 8% H_2O) and after hydration (in an atmosphere saturated with water vapor for 2 days, d(001) = 18.3 Å, 24% H_2O). The thermal behavior of the samples containing 8% and 15% water, after the addition of MS, was similar to that discussed above; critical percentages are reported in Table 2 and Figure 5.

Table 2. Effect of water content on the absorption capacity of British Drug Houses montmorillonite.

H_2O (%)	P_c[1]	ΔH[1]
24	9.7 (0.9)	19.5 (0.6)
15	24.5 (1.6)	21.1 (0.8)
8	30.4 (1.3)	21.7 (0.3)

Values in parentheses are the estimated errors.
[1] From linear fitting of Eq. (2), ΔH kJ/mole, P_c = critical percentage.

The behavior of the sample containing 24% water was somewhat different, in that an endotherm was observed at about 0°C in the absence of MS (~0.05 J/g) due to the freezing of mobile water within the clay. This endotherm persisted as MS was added to the clay and remained at a constant size (0.05 J/g). Consequently, to interpret the results in the presence of MS, the contribution from the freezing of water had to be subtracted from the area used in Eq. (2) (Table 2, Figure 5). The results indicate a reduced absorption capacity for this more hydrated sample. Similar observations were reported, many years ago, for the ethylene glycol intercalate of montmorillonite (Mackenzie, 1948).

X-ray powder diffraction results for these samples indicated that the maximum expansion of the 001 spacing was to about 18.3 Å (Figure 6). The highly hydrated clay absorbed/adsorbed MS without further expansion, suggesting that the organic molecule did not compete with water and was weakly held within the lamellar space.

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