Downloaded from rsta.royalsocietypublishing.org

Interaction of Water with Clay Surfaces [and Discussion]

J. J. Fripiat, M. Letellier, P. Levitz and J. M. Thomas

Phil. Trans. R. Soc. Lond. A 1984 **311**, 287-299
doi: 10.1098/rsta.1984.0029

Email alerting service Receive free email alerts when new articles cite this article - sign up in the box at the top right-hand corner of the article or click here

To subscribe to *Phil. Trans. R. Soc. Lond. A* go to: **http://rsta.royalsocietypublishing.org/subscriptions**

This journal is © 1984 The Royal Society

Downloaded from rsta.royalsocietypublishing.org

Phil. Trans. R. Soc. Lond. A **311**, 287–299 (1984) [287]
Printed in Great Britain

Interaction of water with clay surfaces

BY J. J. FRIPIAT, M. LETELLIER AND P. LEVITZ
Centre de Recherche sur les Solides à Organisation Cristalline Imparfaite, 1B, rue de la Férollerie 45045 Orléans, France

[Plate 1]

In clay suspensions and gels water molecules are distributed between two populations in fast exchange. The physical meaning of this distribution is discussed here. From the molecular dynamics point of view it is shown that the surface force fields perturb the rotational motion on a distance z^* extending to approximately 10^{-9} m. The product z^* times the surface area available to water defines the volume of a surface phase b. In the bulk phase a the rotational diffusional correlation time is not affected and the pulsed field gradient nuclear magnetic technique shows that the self-diffusion coefficient of water in that phase is the same as in pure liquid.

The effects of salt concentration, pressure and temperature on phase b are studied, the main finding being that in the surface phase the well-developed random hydrogen bond network characteristic of liquid water is, at least, partly destroyed. Freezing the the gel suppresses the rapid exchange between the two phases.

From the thermodynamic point of view it is not possible with the present data to decide whether phase b has thermodynamic significance or if it constitutes a heterogeneity within the aqueous phase.

1. INTRODUCTION

It was recently shown (Fripiat *et al.* 1982) that water molecules in clay gels and suspensions are distributed between two populations: phase a contains the so-called free water in the pores between the clay tactoids, whereas phase b is made from about 3 layers of molecules directly affected by surface force fields. Thus these fields extend only to approximately 10^{-9} m. This conclusion was reached by measuring the variation of the heat of immersion with respect to the average degree of coverage with water or the variation of the ^{1}H or ^{2}H spin–lattice n.m.r. relaxation time (T_1) with respect to the concentration Cf of the gel ($C = m_s/m_w$ with m_s: mass of air-dried solid and m_w mass of water respectively; f is a correction factor accounting for the hydration of the air-dried sample).

The heat of immersion decreases rapidly as the degree of coverage is increased until it becomes equal to the internal energy of bulk water in equilibrium with its vapour, namely 119.5 mJ m^{-2}. This occurs when the solid is covered with about 3–4 layers of water.

The variation of the relaxation rate T_1^{-1} with Cf is linear in a large range of concentration in solid. The intercept is proportional to the rotational–diffusional correlation time in phase a and therefore inversely proportional to the self-diffusion coefficient of water in that phase. The diffusion coefficient computed in that way is very close to that of pure liquid water, irrespective of C. This is rather surprising considering that clay gels with very high shear strength are eventually obtained. The slope of the linear variation T_1^{-1} against Cf is proportional to the volume of phase b. Knowing the surface available to water, the average number of water layers in phase b is determined. It was practically equivalent to that obtained from heat of immersion measure-

The Royal Society is collaborating with JSTOR to digitize, preserve, and extend access to
Philosophical Transactions of the Royal Society of London. Series A, Mathematical and Physical Sciences.
www.jstor.org

Downloaded from rsta.royalsocietypublishing.org

ments. This also was not necessarily expected since these two techniques operate in domains of energy that are about 7 orders of magnitude apart.

The linear behaviour of T_1^{-1} against Cf results from the fast molecular exchange between populations a and b

$$T_1^{-1} = x_a\, T_{1a}^{-1} + x_b\, T_{1b}^{-1} \approx T_{1a}^{-1} + x_b\, T_{1b}^{-1}, \tag{1}$$

with $x_a + x_b = 1$ and $x_b \ll x_a$; x_a and x_b are the molar fractions of water in the two phases and T_{1a}^{-1} and T_{1b}^{-1} are specific relaxation rates in pure water and in the first layers of water in contact with the surface respectively. The latter can be estimated from relaxation rate measurements on clay surfaces that have adsorbed one or a few layers of water.

In operating in this way it was assumed that the surface effects are ruled by a step function. Phase b would be defined in a thermodynamic sense similar to that used according to the concept of the Gibbs dividing plane.

The aim of this contribution is to check to what extent such a concept is valid. From the experimental point of view it should be first established that the direct measurement of the self-diffusion coefficient by the n.m.r. pulsed field gradient gives for phase a values in good agreement with those of pure liquid water. Then using a non-microporous solid with a well known surface area fully available to water, the slope of the T_1^{-1} against Cf should permit one to obtain the volume of phase b and therefore its surface area by assuming an average thickness of 10^{-9} m for the surface phase.

If reasonable agreement were obtained for these two sets of experiments, the principle on which (1) is founded would be considered as valid and various consequences for water–clay systems could be developed.

2. EXPERIMENTAL

(a) *Samples*

Kaolinite from Georgia (U.S.A.), a synthetic magnesium phyllosilicate (trade name laponite (Laporte Industrie G.B.)), and hectorite from Hector (California, U.S.A.) were described earlier (Fripiat *et al.* 1982). Their properties pertinent to the present subject can be found also in the same reference.

Hectorite and laponite are swelling clays, kaolinite is not. Kaolinite could have been an interesting sample for measuring the surface area available to water. However, xonotlite, a synthetic non microporous calcium silicate, was preferred for that purpose because of two essential chacteristics, namely, a low iron content and a high surface area.

Its classical composition was the following (percentage mass); SiO_2: 49.0; Al_2O_3: 0.25; CaO: 42.9; MgO: 0.35; NaO_2: 0.05; K_2O: 0.1; CO_2: 1.55. Constitutional and hydration water content of the air-dried material was *ca.* 7 %. The iron content in the particularly pure sample used here was about 200 µg/g. It was most probably homogeneously spread into the bulk of the solid and not mainly concentrated on the surface, as is most often the case for kaolinite. The b.e.t. surface area was 62 ± 2 m^2: it was equal to that obtained by the Harkins & Jura technique (Harkins & Jura 1944), using the heat of immersion in water.

From the extent of the surface area, the iron content and a specific mass of 2.6 g cm^{-3}, the number of paramagnetic centres per unit surface is $k = 0.88\ 10^{12}$ Fe atoms per square centimetre. This parameter is important for the interpretation of the ^{1}H n.m.r. relaxation rate.

The xonotlite material is made from fibres aggregated in hollow spheres with average diameter of about 80 µm, as shown in figure 1, plate 1.

Downloaded from rsta.royalsocietypublishing.org

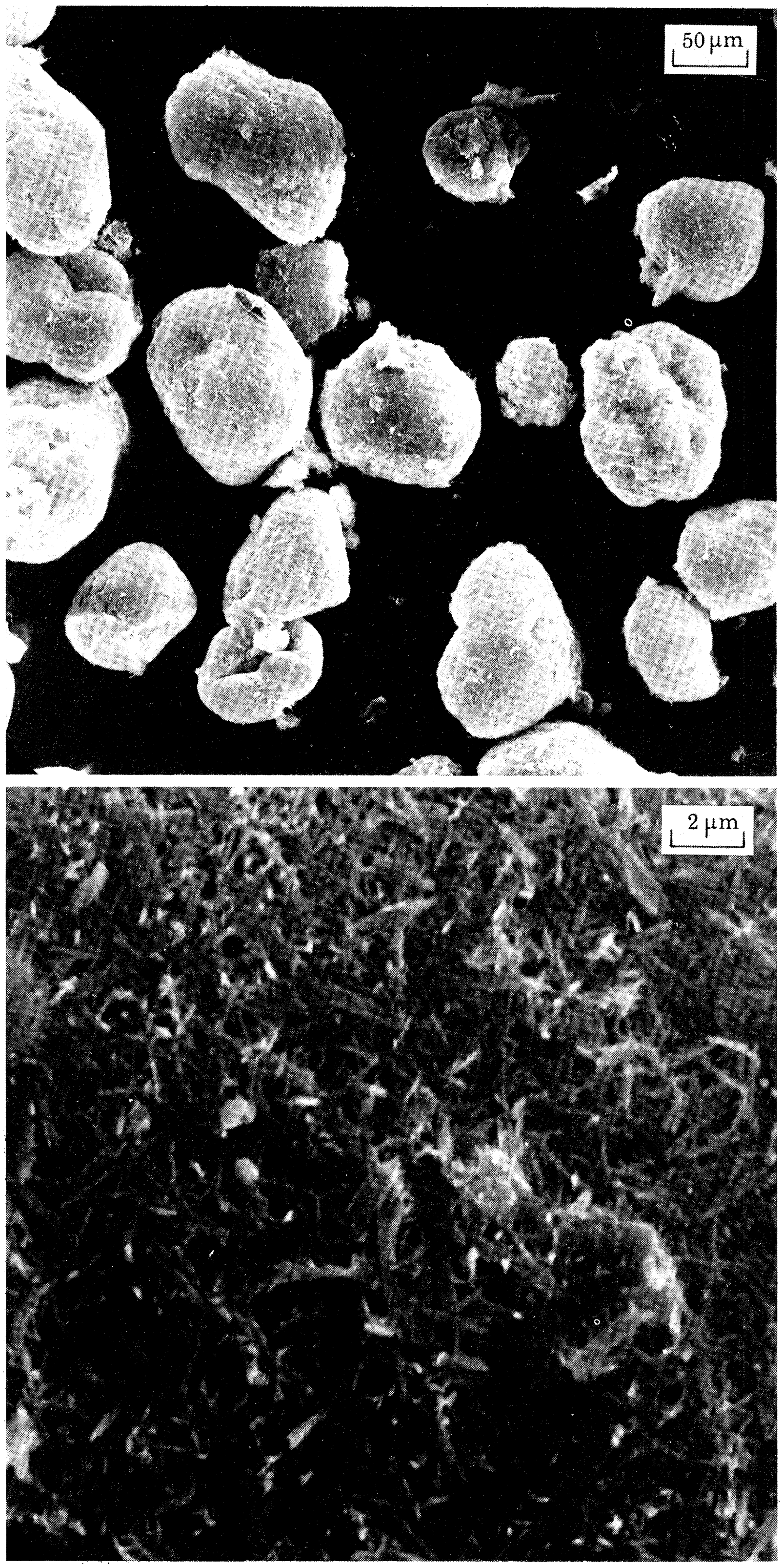


FIGURE 1. Scanning electron micrographs of xonotlite particles: two magnifications (thanks due to the courtesy of Dr O. Anton, Redco, Belgium).

PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

Downloaded from rsta.royalsocietypublishing.org

For self-diffusion coefficient measurements, a defibrated sepiolite (trade name Pangel, Tolsa, Spain), forming good thixotropic gel for $C > 0.05$ was also used. Sepiolite is a fibrous non-swelling mineral which contains zeolitic channels parallel to the fibre axis. The Spanish sample is very pure from the mineralogical point of view. After outgassing at 100 ° during 20 h the N_2 b.e.t. surface area is $330 \pm 10\ \mathrm{m^2\,g^{-1}}$. Because of the microporous nature of this material the significance of this value is surely questionable as will be discussed later on.

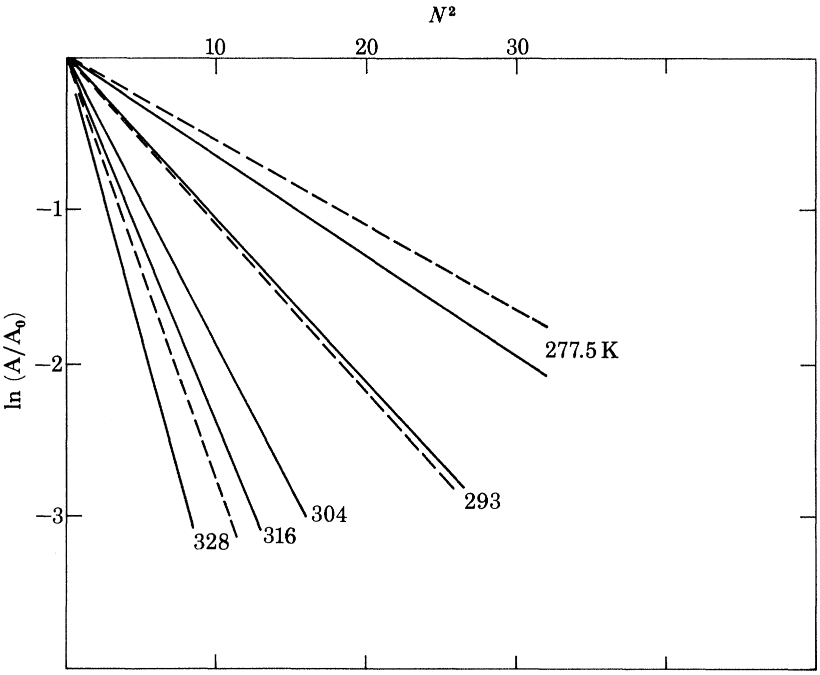


FIGURE 2. Example of application of the pulsed field gradient technique to the measurement of the self-diffusion coefficient of water in sepiolite suspension and in pure liquid at different temperatures (see equation (2)). N is proportional to the field gradient G_t.

(b) *Measurements*

^{1}H or ^{2}H relaxation rates T_1^{-1} were measured by the classical π, τ, $\frac{1}{2}\pi$ pulses sequence at 90 MHz or 13.85 MHz, respectively. The pulsed field gradient (p.f.g) measurements were done with the $\frac{1}{2}\pi$, t_1, p.f.g., π, p.f.g. sequence (Stejskal *et al.* 1964). The echo amplitude in presence (A) or absence (A_0) of field gradient G_t is given by the relation

$$\ln (A/A_0) = -\alpha D G_t^2, \tag{2}$$

where α contains time parameters adjusting the position of the p.f.g. with respect to the $\frac{1}{2}\pi$ and π pulses. An example of the practical determination of D is shown in figure 2.

The self-diffusion coefficient of water at 293 K, i.e. $2.2 \times 10^{-5}\ \mathrm{cm^2\,s^{-1}}$ was taken as reference to obtain α. Then with α constant, self-diffusion cofficients in the pure liquid at other temperature or in the suspensions were obtained.

Downloaded from rsta.royalsocietypublishing.org

PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

3. Results

(*a*) *Self-diffusion coefficient measurements*

Diffusion coefficients obtained for water are compared in figure 3 with those obtained by other experimentors, whereas table 1 gives the ratio D_s/D_0 of the diffusion coefficient in the suspensions (or gels) to that of water at the same temperature, and the average values M of these ratios. Knowing that the p.f.g. technique has an accuracy of about $\pm 10\,\%$ the clear conclusion is that D_s is effectively equal to D_0 within the experimental errors. The main source of experimental uncertainty here is the temperature stability of the n.m.r. probe which is surely not better than $\pm$ 1 K. Also the non-Arrhenius behaviour of D compared with $1/T$ looks very similar for water and for the suspensions or gels.

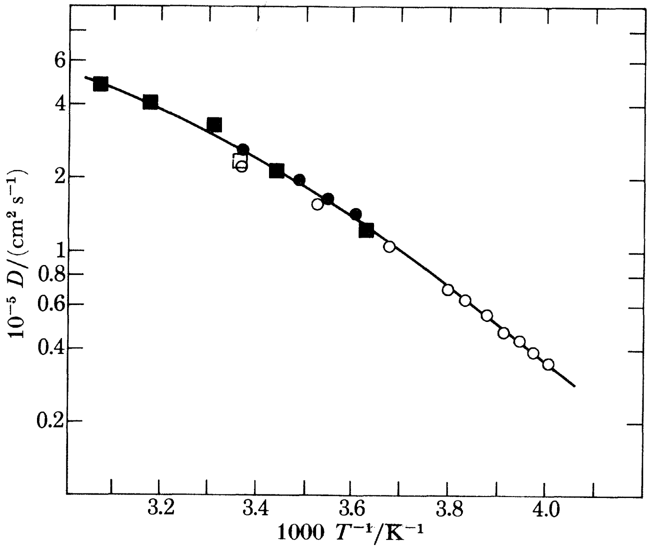


FIGURE 3. Self-diffusion coefficient of water with respect to $1000/T$. Experimental data of: ○ Gillen (1972); ● Wang (1965); □ Goldammer (1970); ■ this work.

The agreement between D_s and D_0 is striking for gels with high viscosity such as those obtained for laponite or sepiolite. When the diffusion coefficient was obtained indirectly from T_1^{-1} by using the rotational diffusional correlation time τ_{ra} in phase a and Einstein's equation $D = \langle l^2 \rangle / 6\tau_{\mathrm{ra}}$, $\langle l^2 \rangle$ being the mean quadratic jump distance approximated as the square of the molecular diameter, the agreement was not surprising because at the molecular scale, the thermal fluctuations that allow diffusion could be considered easily as not influenced by the intricate network of solid particles. With the p.f.g. technique the agreement is more surprising since during the duration of the field gradient pulses, the water molecules diffuse through distances much larger than the molecular diameter. Thus from the molecular dynamics point of view, even in thick gels, the behaviour in phase a is identical with that in the pure liquid.

(*b*) *Surface area available to water*

Figures 4 and 5 show the variation of $^2\mathrm{H}\,T_1^{-1}$ and $^1\mathrm{H}\,T_1^{-1}$ measured for the system xonotlite–water at increasing solid content (Cf). The linear relation predicted by (1) is well obeyed. This agreement confirms the previous findings recalled in § 1.

Downloaded from rsta.royalsocietypublishing.org

PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

TABLE 1. RATIO OF THE DIFFUSION COEFFICIENT OF WATER IN THE SUSPENSIONS (D_s) TO THE DIFFUSION COEFFICIENT OF THE PURE LIQUID (D_0) BETWEEN 328 AND 277.5 (± 1) K

suspension	temperature	D_s/D_0
kaolinite, $C = 0.65$	328	0.74
	316	0.90
	304	0.96
	293	1.04
	283	1.10
	277.5	1.12
		$M = 0.98$
hectorite, $C = 0.12$	328	1.09
	316	1.04
	304	1.15
	293	1.13
	283	1.33
	277.5	0.92
		$M = 1.11$
$C = 0.07$	316	1.13
	304	1.25
	293	1.36
	283	0.98
	277.5	0.87
		$M = 1.12$
laponite, $C = 0.1$	316	0.85
	293	1.05
	283	1.13
	277.5	1.31
		$M = 1.08$
$C = 0.05$	316	0.94
	304	1.04
	293	1.0
	283	1.08
		$M = 1.02$
sepiolite, $C = 0.1$	328	1.27
	316	1.20
	304	1.26
	293	1.0
	277.5	1.04
		$M = 1.15$
$C = 0.06$	328	0.66
	316	0.64
	303	0.82
	293	1.0
	283	0.98
	277.5	0.86
		$M = 0.828$

The straightforward treatment for obtaining the surface area available to water is to use the the ^{2}H relaxation rate because of the intramolecular mode of relaxation. Indeed for rapid exchange between the two phases, the observed relaxation rate is

$$({}^{2}\mathrm{H})\,T_1^{-1} = F_a x_a \tau_{ra} + F_b x_b \tau_{rb} \approx F_a \tau_{ra} + F_b x_b \tau_{rb}, \tag{3}$$

where $F = \frac{3}{8}(2\pi\ \text{q.c.c.})^2$, q.c.c. being the quadrupole coupling constant. The subscripts a or b denote phases a or b respectively; τ_r is the correlation time; the q.c.c. of pure liquid D_2O is

Downloaded from rsta.royalsocietypublishing.org

2.26×10^5 Hz at 298 K. In the one layer hydrate of halloysite (Cruz *et al.* 1978), q.c.c. = 1.65 $\times 10^5$ Hz. By using this value, F_b can be computed.

The correlation time in phase a is $\tau_{ra} = 3 \pm 0.2 \times 10^{-12}\,s^{-1}$ at 298 K (Eisenberg & Kauzman 1969) whereas the rotational correlation time obtained for the one- or two-layer hydrates of Na and Ca montmorillonites, the two-layer hydrate of Na vermiculite and the one-layer hydrate of Li hectorite is about $10^{-10}\,s^{-1}$ (Fripiat 1980) at this temperature; τ_{rb} can be approximated by that value.

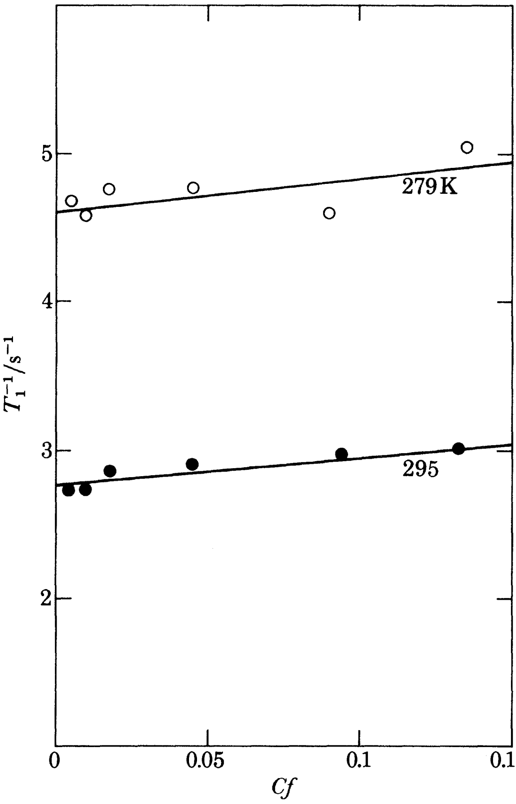


FIGURE 4. Deuteron relaxation rate against *Cf* (the concentration of solid in water, grams per gram) for xonotlite suspensions at two temperatures.

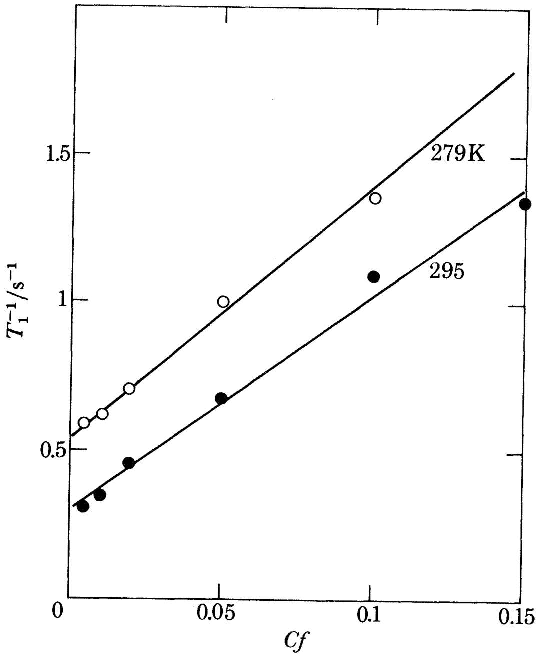


FIGURE 5. Proton relaxation rate against *Cf* (the concentration of solid in water, grams per gram) for xonotlite suspensions at two temperatures.

The average experimental slope (figure 4) obtained from the plot $^2\mathrm{H}\,T_1^{-1}$ against *Cf* is $2.2 \pm 0.2\ s^{-1}$. The relation between x_b and *Cf* is

$$\rho_w S_b z^* Cf = V_b/V_a \approx x_b, \tag{4}$$

obtained by neglecting V_b with respect to the total volume of water and assuming that the molar volume is the same in the two phases. In (4) S_b is the specific surface area available to water, z^* the average thickness of phase b and ρ_w the specific mass of water. It is assumed that $\rho_{wa} \equiv \rho_{wb}$. Since $F_b \tau_{rb} = 40$, $S_b z^* = 0.055\ \mathrm{cm^3\ g^{-1}}$ of xonotlite, and $S_b = 55\ \mathrm{m^2\,g^{-1}} \pm 10\,\%$, with $z^* = 10^{-9}$ m. This too perfect agreement with the b.e.t. surface area can be checked by using the proton relaxation data. The situation here is more complex because relaxation in the

Downloaded from rsta.royalsocietypublishing.org

surface phase is mainly controlled by the paramagnetic impurities in the surface layers. It was shown in that case that the slope K' of the experimental relation

$$^{1}\mathrm{H}T_{1}^{-1} = K + K'Cf \tag{5}$$

was

$$K' = 1.7 \times 10^{-10} S_{\mathrm{b}} z^{*} k. \tag{6}$$

The average value of the experimental slopes in figure 5 at 295 and 279 K is 8.9 $\mathrm{s}^{-1} \pm 10\,\%$. Using $k = 0.88\ 10^{12}$ paramagnetic (Fe^{3+}) centres per square centimetre yields $S_{\mathrm{b}} z^{*} = 0.058\,\mathrm{cm}^{3}\,\mathrm{g}^{-1}$ with $S_{\mathrm{b}} = 59\,\mathrm{m}^{2}\,\mathrm{g}^{-1} \pm 10\,\%$. The main source of uncertainty here is the actual value of k, since it has been assumed that the paramagnetic centres are homogeneously distributed.

The very good agreement between the specific surface areas calculated from by the $^{2}\mathrm{H}$ and $^{1}\mathrm{H}$ relaxation rates and those observed by the N_{2} b.e.t. method and the Harkins & Jura technique may be partly fortuitous. It shows at least that the thickness z^{*} assigned to the surface phase b of the right order of magnitude.

4. Discussion

The two main conclusions from § 3 (*a*) and § 3 (*b*) reinforce those obtained previously and the rest of this paper will be devoted to the analysis of the significance of the distribution in clay suspensions and gels of water molecules between two phases and of the various implications of this situation.

(*a*) *Thermodynamic aspect*

We know that at 298 K the life-time in phase b is of the order of magnitude of, or longer than, 10^{-9} s (Fripiat *et al.* 1982), and that the rotational correlation time in phase b is about 10^{-10} s whereas it is 3×10^{-12} s in phase a. What we do not know is whether or not the so-called 'phase b' has a thermodynamic meaning!

Suppose that the life time in phase b is long (with respect to τ_{rb}), so that phase b can be considered as distinct from phase a. The free energy of the suspension is

$$F = F_{\mathrm{a}} + F_{\mathrm{b}}. \tag{7}$$

Then, from the cell theory of liquids (Hill 1962)

and

$$\left.\begin{aligned} F_{\mathrm{a}} &= -N(1-x_{\mathrm{b}})\,kT\ln(\bar{V}\mathrm{e}Z_{\mathrm{b}}),\\ F_{\mathrm{b}} &= -Nx_{\mathrm{b}}\,kT\ln(\bar{V}\mathrm{e}Z_{\mathrm{b}}),\end{aligned}\right\} \tag{8}$$

where $N = N_{\mathrm{a}} + N_{\mathrm{b}}$, $\bar{V}$ is the molecular volume of water or the volume of the cell (equal in phases a and b), Z_{a} and Z_{b} are the partition functions of the water molecule in phases a and b respectively and $\ln \mathrm{e} = 1$. The chemical potential of water in the system is $\mu(x_{\mathrm{b}}, T) = (\partial F/\partial N)_{T, x_{\mathrm{b}}}$:

$$\mu(x_{\mathrm{b}}, T) = -(1-x_{\mathrm{b}})\,kT\ln(\bar{V}\mathrm{e}Z_{\mathrm{a}}) - x_{\mathrm{b}}kT\ln(\bar{V}\mathrm{e}Z_{\mathrm{b}}). \tag{9}$$

Moreover

$$\mu(x_{\mathrm{b}}, T) = \mu_{0}(T) + kT\ln P,$$

whereas for $x_{\mathrm{b}} = 0$

$$\mu(0, T) = \mu_{0}(T) + kT\ln P_{0}.$$

Thus

$$RT\ln(P/P_{0}) = x_{\mathrm{b}}RT\ln(Z_{\mathrm{a}}/Z_{\mathrm{b}}) = x_{\mathrm{b}}[(\bar{E}_{\mathrm{b}} - \bar{E}_{\mathrm{a}}) - T(\bar{S}_{\mathrm{b}} - \bar{S}_{\mathrm{a}})] = x_{\mathrm{b}}\overline{\Delta F}, \tag{10}$$

where $\bar{E}$ and $\bar{S}$ denote the molar energy and entropy, respectively. It follows that

$$RT\ln(P/P_{0}) = \overline{\Delta F}\,x_{\mathrm{b}}, \tag{11}$$

where $\overline{\Delta F}$ is the transfer molar free energy of water from phase a to phase b.

Downloaded from rsta.royalsocietypublishing.org

The presence of a solute or of colloid particles decreases the free energy and thus the vapour pressure ($P < P_0$). Equations (11) and (4) predict that $RT\ln(P/P_0)$ must be a linear function of x_b and thus of Cf for a specified clay suspension (constant $S_b z^*$).

Now suppose that the lifetime in phase b is too short (with respect to τ_{rb}) such that phase b can no longer be considered as distinct from phase a. The clay suspension is then, from the solvent point of view, a heterogeneous medium to which the mixture model approach of Ben-Naim (1974) can be applied.

Then

$$F = kTN\ln[\mathrm{e}(Z_a V_a + Z_b V_b)/N], \tag{12}$$

where

$$V_a = (1-x_b)\,\bar{V}N, \tag{13}$$

$$V_b = x_b\bar{V}N, \tag{14}$$

and

$$\mu(x_b, T) = -kT\ln[(Z_a\bar{V}(1-x_b) + Z_b\bar{V}x_b)\,\mathrm{e}]. \tag{15}$$

Using the same procedure as above yields

$$RT\ln(P/P_0) = -RT\ln[1 - x_b(1 - Z_b/Z_a)]. \tag{16}$$

Since $P < P_0$, $\overline{\Delta F}$ must be negative, and for small x_b (15) becomes

$$RT\ln(P/P_0) = RTS_b z^* \rho_w[1 - \exp(-\overline{\Delta F}/RT)]\,Cf. \tag{17}$$

For small values of $\overline{\Delta F}$ (17) is indistinguishable from (11). In both cases $RT\ln(P/P_0)$ should be proportional to Cf.

A gel made from sepiolite was used to check these models. Two types of measurements were carried out. The gels were made by stirring various amounts of sepiolite in D_2O or H_2O at about 10000 r.p.m. for a few minutes.

Figure 6 shows the variation of the ^{2}H T_1^{-1} relaxation rates with respect to Cf at 297 and 279 K. The slopes are 15.7 and 18.7 s^{-1} respectively. Applying equation (3), one obtains $S_b z^* \approx 0.5\ \mathrm{cm^3\,g^{-1}}$ which means that the $S_b \approx 500\ \mathrm{m^2\,g^{-1}}$. This is the highest value so far obtained for a surface phase in rapid exchange with bulk water. Because of the formation of tactoids, the corresponding specific surface areas are smaller for swelling clays (under 100 m^2 g^{-1}).

On the other hand $(RT/N_A\bar{V})\ln(P/P_0)$ (N_A is the Avogadro number) was measured for $C = 0.03$ and $C = 0.06$ sepiolite gels with a thermocouple psychrometer, as described by Brown (1970).

The plot against Cf was observed to be linear and passed through the origin. At 295 K, the slope was 7 bar.† From (11) or (17), it may be easily calculated that $\overline{\Delta F} \approx 5$ cal mol^{-1}‡ or *ca.* 10^{-2} kT per molecule.

This is a rather astonishing result since, from heats of immersion measurements, we know that $\bar{E}_b - \bar{E}_a$ is far from negligible. Therefore in order for $\overline{\Delta F}$ to be that small, the entropic term must cancel most of the energetic contribution. Thus on the basis of the present data it is impossible to draw any conclusion about which of the two thermodynamic models is applicable to the clay–water system.

---

† 1 bar = 10^5 Pa. ‡ 1 cal = 4.184 J.

Downloaded from rsta.royalsocietypublishing.org

MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES
THE ROYAL SOCIETY A
PHILOSOPHICAL TRANSACTIONS OF

(*b*) *Effects of salt concentration, pressure and temperature on the surface phase volume*

It could have been expected that compressing the electrical double layer by increasing the ionic strength of the solution may affect the volume of phase b.

Sepiolite was chosen for these experiments because of its high surface area and because an electrolyte concentration as high as 1 M KCl does not affect the viscosity of the gel to a noticeable extent. Therefore the fibrous network should not be considerably modified. The pH of the suspension in presence or absence of KCl was about 8.2. Note that sepiolite has a rather small cation exchange capacity (c.e.c. ≈ 0.2 meq g^{-1}).

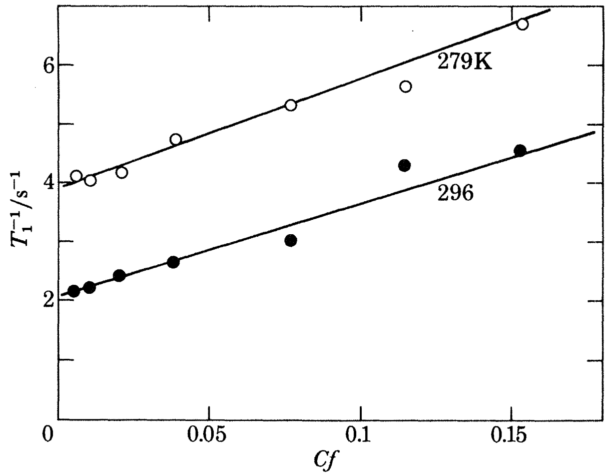


FIGURE 6. Deuteron relaxation rate against *Cf* (the concentration of solid in water, gram per gram) for sepiolite suspensions at two temperatures.

TABLE 2. COMPARISON OF THE SLOPE OF THE EMPIRICAL EQUATION (3) OBSERVED FOR 1 M KCl SEPIOLITE D_2O SUSPENSIONS WITH SEPIOLITE SUSPENSIONS IN PURE D_2O

temperature/K	$(KCl+D_2O)/s^{-1}$	$(D_2O)/s^{-1}$
299	16	15.7
279	19	18.7

In a 1 M KCl aqueous solution, according to Endom *et al.* (1967), T_1^{-1} is not appreciably affected. For instance at 299 K, ^1H T_1^{-1}(KCl 1 M) = 0.273 s^{-1} whereas it is 0.28 s^{-1} in water. In table 2, the slopes of the empirical equation (3) observed for sepiolite suspensions with solid contents up to about 0.15 are shown to be the same.

It may be concluded that the volume of phase b is not influenced by the ionic strength in spite of the fact that the osmotic pressure in a 1 M KCl (H_2O) solution is 44.5 bar. That the effect of such a pressure is too small to be observed agrees with the conclusions of an experimental study by Jonas *et al.* (1982) on the effect of a high mechanical pressure on the deuterium relaxation rate in the kaolinite D_2O system. Indeed it was shown that $T_{1\mathrm{b}}^{-1}$ increases only by about 20 % when the pressure increases from 1 bar to 5 kbar.

The temperature effect was also determined for the same kaolinite–water system by measuring $^2H(T_1^{-1})$ or $^1H(T_1^{-1})$ with respect to temperature. The activation energy obtained in that way is

Downloaded from rsta.royalsocietypublishing.org

that of τ_{ra} or of τ_{rb} as shown in table 3. The activation energy in phase b is noticeably different from that in phase a.

As the main intermolecular interactions are due to hydrogen bonding, it may be concluded that the energy required to activate these bonds is lower in phase b than in phase a. This would suggest that the kaolinite surface destroys the well developed random hydrogen bond network characteristic of liquid water. Jonas *et al.* (1976), Wilbur *et al.* (1976) and De Fries & Jones (1977) have shown that the compression of pure liquid water distorts the optimal tetrahedral order. An increase in temperature is an efficient way to produce these perturbations. The surface force field is thus at the same time more efficient than an increase in pressure and temperature in that respect.

TABLE 3. ACTIVATION ENERGY OF THE ROTATIONAL CORRELATION TIMES IN THE TEMPERATURE RANGE 10–60 °C FOR PHASE a AND PHASE b IN A KAOLINITE SUSPENSION ($C = 2.65$)

solvent	pressure/bar	phase a/(kcal mol^{-1})	phase b/(kcal mol^{-1})
D_2O	1	5.2	1.8
	5×10^3	4.6	1.8
H_2O	1	4.1	1.1
	5×10^3	4.0	0.7

This conclusion can be generalized to hydrophylic surfaces in general since the lengthening of the rotational correlation time in phase b by about two orders of magnitude with respect to that in phase a is observed for all the minerals studied so far.

On the other hand the insensitivity with respect to the ionic strength of phase b volume in a sepiolite gel cannot be generalized to swelling silicates. In fact, as shown by Fripiat *et al.* (1982), the volume of phase b for a suspension of Ca-hectorite is about $\frac{2}{3}$ of that observed for a suspension of Na-hectorite. Since z^* seems to be constant, this observation could be interpreted as an increase in the number of clay layers forming the tactoids with the simultaneous decrease of the specific surface area available to water (S_b).

(c) *Phase transition upon freezing*

Anderson & Tice (1971) have shown that below the freezing point (f.p.) a fraction of the water molecules in a clay gel remains unfrozen. This fraction contains the water molecules influenced by the surface force fields and also those that are in very narrow pores between clay tactoids. As expected, the larger the freezing point depression, the narrower are the pores in which freezing occurs. The interlayer water within the tactoids freezes at the lowest temperature. The water in phase b on the external surface of the tactoid should behave differently from that in pores with diameters over 2×10^{-9} m (i.e. over $2z^*$).

Suppose an ideal model where phase a is frozen whereas phase b is not. It may be expected that the rapid exchange averaging the n.m.r. relaxation rate T_1^{-1} (equation (1)) should be suppressed and that the decay of the longitudinal component of the magnetization could be the sum of two exponentials:

$$(M(\infty) - M(t))/2M_\infty = P'_a \exp(-t/T'_{1a}) + P'_b \exp(-t/T'_{1b}), \tag{18}$$

where the apparent proton populations and relaxation rates are P'_a and P'_b, $1/T'_{1a}$ and $1/T'_{1b}$, respectively.

This was actually observed by Fripiat & Letellier (1984) for a Na-hectorite H_2O suspensions with $0.05 < C < 0.18$. T'_{1b} was near that observed for the monohydrate of Li-hectorite (Fripiat

Downloaded from rsta.royalsocietypublishing.org

et al. 1980), whereas T'_{1a} was about 4 times larger than T'_{1b}. For the proton, the suggested relaxation mechanism in the frozen phase was spin diffusion toward 'freely' rotating water molecules either in phase b and, or within the tactoids. For D_2O suspensions with $0.05 \leqslant C \leqslant 0.18$, a single T_1^{-1} was observed and the deuteron resonance line intensity below f.p. was not more than 2 % that above f.p. The deuterium signal was hardly observable below f.p. for more diluted suspensions.

Below f.p. the ^2H resonance line was a doublet which splitting increased with temperature, in contrast with what was observed for pure D_2O polycrystalline ice (Jackson & Rabideau 1964*a, b*). The T_1 behaviour with respect to temperature is represented in figure 7.

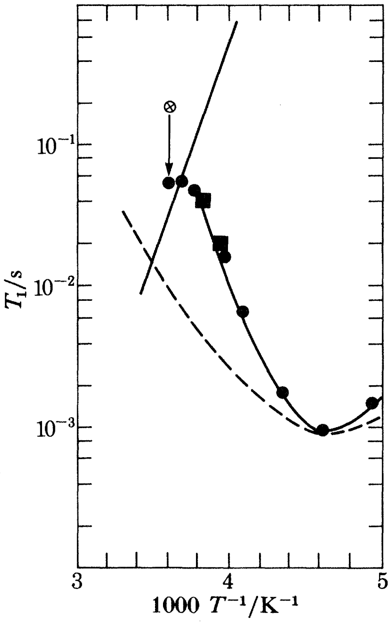


FIGURE 7. Deuteron relaxation rate against 1000/T. The solid straight line is computed from the ^1H spin lattice relaxation time and q.c.c. = 195 KHz, (Jackson *et al.* 1964*b*). The dashed line represents the values obtained for the one-layer D_2O hydrate of halloysite by Cruz *et al.* (1978). Experimental values observed for a Na-hectorite gel with $Cf = 0.05$, ● and $Cf = 0.18$, ■, ⊗ indicates the drop of T_1 at freezing point.

These results were interpreted by assuming that below f.p. the resonance of unfrozen D_2O molecules (in phase b or within the clay tactoids) was the only one observed with the n.m.r. instrument used for this study. The frozen D_2O molecules in phase a would display a signal too large to be recorded. The relaxation time fitting the experimental T_1 shown in figure 7 is

$$\tau_r(s) = 1.9 \times 10^{-20} \exp(11\,700\,\text{cal}/RT), \tag{19}$$

the activation energy being about 2 kcal mol^{-1} lower than that reported for dielectric relaxation and for the proton T_1 in H_2O polycrystalline ice, (Barnall & Lowe 1968). The q.c.c. at the $^2H\,T_1^{-1}$ minimum is about 160 kHz, in agreement with the value given in § 3 (*b*). This value is about $\frac{3}{4}$ that of polycrystalline D_2O (Jackson & Rabideau 1964*b*).

Using the activation energy for D_2O, shown in table 3, the correlation time τ_{rb} in phase *b* is 0.8×10^{-10} s at f.p. (277 K). At the same temperature, τ_r calculated from (19) is 0.4×10^{-10} s. This discrepancy is within the limits of the experimental errors but what is amazing is the large increase of the activation energy (equation (19)) with respect to that observed for phase b above f.p. It may be suggested that hydrogen bonding at the interface between unfrozen and frozen molecules is stronger than at above f.p.

Downloaded from rsta.royalsocietypublishing.org

MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES
THE ROYAL SOCIETY A
PHILOSOPHICAL TRANSACTIONS OF

(*e*) *Conclusions*

From the preceding discussions it may be safely concluded that from the microdynamic point of view the surface and bulk phases have a physical significance in clay suspensions and gels. However, it cannot be concluded that these phases have a real thermodynamic meaning since the transfer molar free energy is undoubtedly very small (see § 4 (*a*)). Since the lifetime in the surface phase is between ten to one hundred times longer than the rotational correlation time in phase b which itself is about one hundred times larger than the rotational correlation time in phase a, the use of a step function differentiating phase b from phase a is justified.

For minerals without internal surface (kaolinite and xonotlite), the surface phase has an area that is well approximated by the N_2 b.e.t. or by the Harkins & Jura techniques. For minerals with internal surfaces, the situation is more ambiguous.

In suspensions, swelling clays such as hectorite and laponite display surface areas available to water much less in extent than the sum of internal and external surface areas. This is because the internal surface is not available for rapid exchange. This observation supports the concept of tactoids, the interesting point being that these tactoids can be considered as textural units already present in dilute suspensions, ($C < 0.01$).

In suspensions, the non-swelling sepiolite develops a very high surface area available to rapid exchange in spite of its zeolitic fabric. According to Cases & François (1983), personal communication) the surface area available to CO_2 and to N_2 (after outgassing at 100 °C for 20 h) is of the order of 350 $m^2\,g^{-1}$ whereas that computed from the product $S_b\,z^*$ (assuming that $z^* = 10 \times 10^{-10}$ m) is between 450 and 500 $m^2\,g^{-1}$. The observation of a surface area available to water higher than that measured with N_2 of CO_2 may find its origin in the fact that the zeolitic channels ($\phi \approx 4 \times 10^{-10}$ m) are open on larger pores ($10 \times 10^{-10}\,\mathrm{m} < \phi < 30 \times 10^{-10}$ m). Therefore a large fraction of the zeolitic water could participate in the exchange.

As far as the mechanism of gel formation is concerned, this contribution has again emphasized the fact that the influence of the surface force field on the molecular dynamics does not extend to more than about 10×10^{-10} m and that the diffusion coefficient of water in phase *a* is, within the experimental error, the same as in pure liquid. Thus the formation of a clay gel cannot be attributed to surface forces ordering water molecules on long distances.

This research was supported by a D.G.R.S.T. contract no. 81.D.1109. The authors are very grateful to Dr J. M. Cases and Miss M. François for specific surface area measurements as well as for numerous discussions. Tolsa (Spain) and Redco (Belgium) gave well characterized samples of pure sepiolite and xonotlite respectively.

REFERENCES

Anderson, D. M. & Tice, A. R. 1971 *Proc. Am. Soil Sci. Soc.* **35**, 47–54.
Barnall, D. E. & Lowe, I. J. 1968 *J. chem. Phys.* **48**, 4614–4618.
Ben-Naim, A. 1974 *Water and aqueous Solutions*, p. 201. New York, London: Plenum.
Brown, R. W. 1970 *Measurement of water potential with thermocouple psychrometers: construction and application.* U.S.D.A. Forest Serv. Res. pap. INI-80 (27 p.)
Cruz, M. I., Letellier, M. & Fripiat, J. J. 1978 *J. chem. Phys.* **69**, 2018–2027.
De Fries, T. & Jonas, J. 1977 *J. chem. Phys.* **66**, 896–901.
Eisenberg, D. & Kauzman, W. 1969 *The structure and properties of water*, p. 215. Oxford University Press.
Endom, L., Hertz, H. G., Thul, B. & Zeidler, M. D. 1967 *Ber. BunsenGes. phys Chem.* **71**, 1008–1031.

Downloaded from rsta.royalsocietypublishing.org

Fripiat, J. J. 1980 *Bull. Soc. Française Mineral.* **103**, 440–443.
Fripiat, J. J., Kadi-Hanifi, M., Conard, J. & Stone, W. E. E. 1980 In *Magnetic resonance in colloid and interface science* (ed. J. Fraissart & H. A. Resing), pp. 529–535. Dordrecht: Reidel.
Fripiat, J. J., Cases, J., François, M. & Letellier, M. 1982 *J. Colloid Interface Sci.* **89**, 378–400.
Fripiat, J. J. & Letellier, M. 1984 *J. magn. Reson.* (In the press.)
Gillen, K. T., Douglass, D. C. & Hoch, M. J. R. 1972 *J. chem. Phys.* **57**, 5117–5119.
Goldammer, E. V. & Hertz, H. G. 1970 *J. phys. Chem.* **74**, 3734–3755.
Harkins, W. D. & Jura, G. 1944 *J. Am. chem. Soc.* **5**, 1366–1373.
Hill, T. L. 1962 *An introduction to statistical thermodynamics*, 2nd edn, p. 286. Reading, Massachusetts: Addison Wesley.
Jackson, J. A. & Rabideau, S. W. 1964*a* *Bull. Am. phys. Soc.* **9**, 142–147.
Jackson, J. A. & Rabideau, S. W. 1964*b* *J. chem. Phys.* **41**, 4008.
Jonas, J., De Fries, T. & Wilbur, D. J. 1976 *J. chem. Phys.* **65**, 582–588.
Jonas, J., Brown, D. & Fripiat, J. J. 1982 *J. Colloid. Interface Sci.* **89**, 374–377.
Stejskal, E. O. & Tanner, J. E. 1964 *J. chem. Phys.* **42**, 288–292.
Wang, J. H. 1965 *J. phys. Chem.* **65**, 4412.
Wilbur, D. J., De Fries, T. & Jonas, J. 1976 *J. chem. Phys.* **65**, 1783–1786.

Discussion

J. M. THOMAS, F.R.S. (*University of Cambridge, Department of Physical Chemistry, Cambridge, U.K.*). Could Professor Fripiat tell us how the rotational correlation times that he has measured for the rather strongly bound (so-called 'phase b') H_2O and D_2O in sepiolite compare with corresponding values for water in:

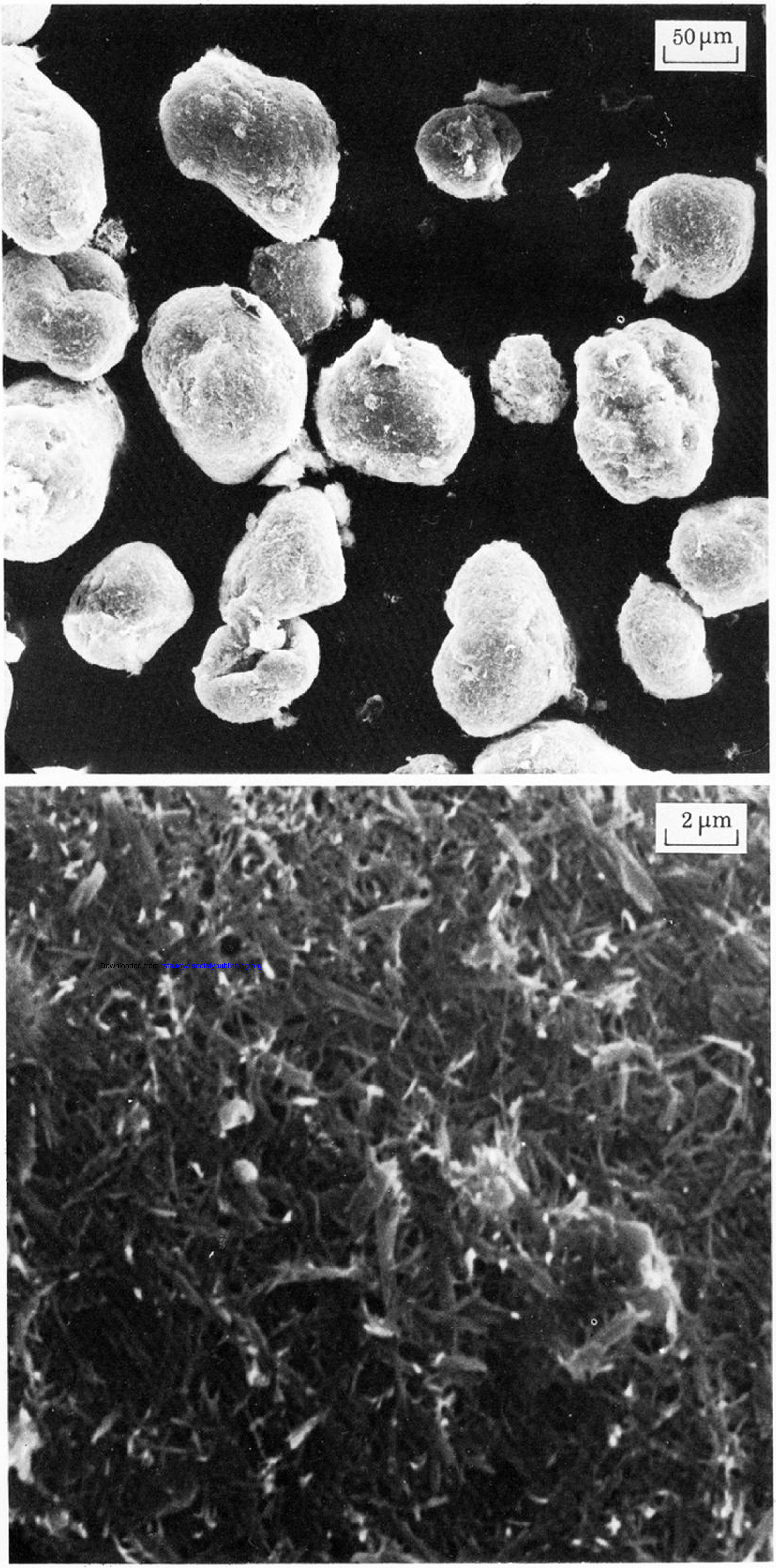
(i) one-layer, two-layer and three-layer montmorillonites; and
(ii) vermiculite?

Could he also tell us how these values compare with those obtained by other workers, using, for example, neutron scattering studies, in assessments of ease of diffusion in interlamellar water?

J. J. FRIPIAT. In phase b and for the one-layer or two-layer hydrates of Na, Ca-montmorillonites and Na-vermiculite the n.m.r. correlation times observed at 298 K were between 1 and 2×10^{-10} s whereas in liquid water it is 3×10^{-12} s.

The comparison with quasi-elastic neutron scattering (q.e.n.s.) studies is not direct since this technique gives inter-jump residence times. It may thus be expected that the activation energies observed with the two techniques will not be the same since their physical meanings are different.

However the correlation and the residence times observed in phase b, as measured by n.m.r. and q.e.n.s. are within the same order of magnitude.



Downloaded from rsta.royalsocietypublishing.org

IGURE 1. Scanning electron micrographs of xonotlite particles: two magnifications (thanks due to the courtesy of Dr O. Anton, Redco, Belgium).

PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES