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Neutron Scattering Study of Vermiculite–Poly(vinyl methyl ether) Mixtures

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A four-component clay–polymer–salt–water system, consisting of *n*-butylammonium vermiculite, poly(vinyl methyl ether), *n*-butylammonium chloride, and heavy water, was studied by neutron scattering. The volume fraction of clay in the system and the salt concentration were held constant, at $r = 0.01$ and $c = 0.1$ M, respectively, and the volume fraction of polymer v was varied between 0 and 0.04. The addition of polymer, up to $v = 0.04$, had no effect on the phase transition temperature between the tactoid and gel phases of the clay system. However, even for v values as low as 0.001, the clay plates in the gel phase were more parallel and more regularly spaced than in the system without added polymer. In the gel phase, the lattice constant along the swelling axis of the clay colloid decreased exponentially as a function of the polymer volume fraction, from 12 nm at $v = 0$ to 8 nm at $v = 0.04$. In the tactoid phase, at $T > 14$ °C, the c -axis lattice constant in the crystalline regions was equal to 1.94 nm at $v = 0$ and 0.04, showing that the spacing between the clay plates is not affected by the added polymer when they are collapsed by an increase in temperature.

Introduction

Two books published in 1979 pointed out a need for experimental advances in two very different areas of polymer science. From the polymer physics point of view, de Gennes,¹ predicting that a segregated model would apply in two-dimensional situations, hoped that future experiments using chains trapped in lamellar systems would be able to probe how the degree of chain interpenetration depends on dimensionality. The interlayer region in a lamellar clay gel is an obvious candidate for such a trapping experiment. From a more practical point of view, the importance and potential of the four-component clay–polymer–salt–water system in agricultural and industrial applications could hardly be understated, being the central problem of soil science. As pointed out by Theng,² “progress in our understanding of this system is at present limited more by experimental than theoretical inadequacies.” Although substantial progress has been made during the past 17 years,³ there remains a strong element of truth in this statement. We hope that the present study will contribute significantly to improving the experimental situation, by describing an investigation into the effect of adding a polymer to a model clay system, the *n*-butylammonium vermiculites.

The *n*-butylammonium vermiculite system is the best characterized clay colloid system. The raw swelling phenomenon illustrated by Figure 1a,b was first reported^{4,5} in

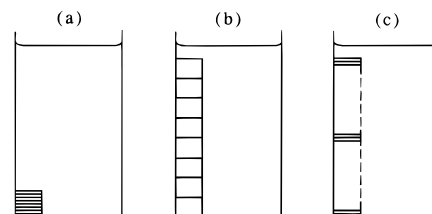


Figure 1. Schematic illustration of the swelling of *n*-butylammonium vermiculite in an 0.1 M *n*-butylammonium chloride solution: (a) the *n*-butylammonium vermiculite crystal ($d \approx 2$ nm) prior to swelling, (b) the gel ($d \approx 12$ nm) formed by a homogeneous 6-fold expansion at $T < 14$ °C, and (c) the tactoid formed when the gel collapses at $T > 14$ °C. In (c), the dashed line represents the fact that the tactoid structure occupies the same volume as the gel structure.

the early 1960s. It involves the absorption of large amounts of water by *n*-butylammonium vermiculite crystals placed in dilute *n*-butylammonium salt solutions, the extent of swelling being strongly dependent on the salt concentration in the soaking solution.⁴ It leads to the formation of coherent gels, which show no tendency to disperse into the surrounding solution. The (b)–(c) process was discovered more recently⁶ and has been investigated as a function of the salt concentration c , temperature T ,⁷ hydrostatic pressure P ,⁶ uniaxial stress along the swelling axis p ,⁸ and, most recently, volume fraction r of the clay in the condensed matter system.⁹ See ref 10 for a recent review.

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Adding polymer to the system adds three new variables to be considered: the chemical nature of the polymer x , the molecular weight of the polymer M , and the volume fraction of the polymer in the condensed matter system v . There are therefore a total of eight variables to be considered in these studies, creating an enormous phase space to be investigated. We therefore proceeded cautiously, eliminating six of the variables in the present study, as follows.

First, attention was restricted to the unstressed systems, namely all the experiments were carried out at $P = 1$ atm and $p = 0$; the gels were allowed to swell freely to equilibrium at atmospheric pressure. Second, attention was restricted to the case $r = 0.01$ (the clay occupied 1% of the volume in the condensed matter system) and $c = 0.1$ M; the two concentration variables determining the composition of the three-component clay-salt-water system were held fixed. Third, attention was restricted to $x = \text{PVME}$ (poly(vinyl methyl ether)) and $M = 18\,000$; a particular polymer was chosen for the study. The experiments were therefore reduced to studying the (v, T) behavior of the system, a two-variable problem.

We note that the PVME-water system has itself an interesting (v, T) phase diagram of LCST (lower critical solution temperature) type,¹¹ but that the polymer and water were miscible over the temperature range of the present study. For a PVME sample of weight-average molecular weight 98 000, the phase separation temperature between PVME and water occurs at 33.0 ± 0.2 °C in the v range between 0 and 0.1.¹¹ For the lower molecular weight PVME sample used, the LCST is shifted to higher temperatures, well above the range (8 °C $< T < 20$ °C) of interest here.

Our main aims were to determine (i) the lattice constant (d -value) along the swelling axis of the clay colloid in the gel phase (Figure 1b) and (ii) the phase transition temperature T_c between the gel phase (Figure 1b) and the tactoid phase (Figure 1c) of the system, as functions of the polymer volume fraction v .

Experimental Section

The vermiculite crystals were from Eucatex, Brazil. Crystals about 30 mm² in area by 1 mm thick were washed and then treated for about a year with 1 M NaCl solution at 50 °C, with regular changes of solution, to produce a pure Na vermiculite, with the chemical formula $\text{Si}_{6.13}\text{Mg}_{5.44}\text{Al}_{1.65}\text{Fe}_{0.50}\text{Ti}_{0.13}\text{Ca}_{0.13}\text{Cr}_{0.01}\text{K}_{0.01}\text{O}_{20}(\text{OH})_4\text{Na}_{1.29}$.

To prepare the *n*-butylammonium vermiculite, the Na form was soaked in 1 M *n*-butylammonium chloride solution at 50 °C, with regular changes of solution, for about a month. Chemical analysis of the *n*-butylammonium vermiculite thus obtained showed that the amount of interlayer sodium remaining was less than 1%. The crystals were stored in a 1 M *n*-butylammonium chloride solution prior to the swelling experiments.

The PVME was synthesized by cationic polymerization in toluene at -78 °C with boron trifluoride etherate as the initiator. The number-average molecular weight (M_n) of the PVME, measured by gel permeation chromatography (GPC) in chloroform, was 27 000 in terms of the polystyrene equivalent, and the polydispersity ratio (M_w/M_n , where M_w is the weight-average molecular weight) was 1.40. Experiments on PVME samples with narrow molecular weight distributions ($M_w/M_n < 1.1$) in the molecular weight range between 500 and 4000 have shown that the absolute value of M_n obtained by ¹H NMR is equal to 0.67 times the polystyrene equivalent value obtained by GPC.¹² If we assume that this factor holds for our sample, although it may depend on the GPC conditions (temperature, kind of column used, solvent, etc.) and the polymer structure (stereoregularity, etc.), then the true value of M_n would be 18 000, corresponding to a degree of polymerization of 310.

Solutions of the required volume fraction of PVME were prepared by dissolving a known mass of the polymer ($\rho = 1.03$ g/cm³) in a known volume of a 0.1 M *n*-butylammonium chloride solution, prepared by dissolving a known mass of *n*-butylammonium chloride in D₂O. It was necessary to swell the crystals in D₂O rather than H₂O solutions because of the large incoherent scattering cross section of hydrogen which would otherwise have obscured the scattering of interest.

Prior to performing an experiment on the clay, the crystals were first washed thoroughly to remove any molar solution that may be trapped in surface imperfections. This was achieved by rinsing the crystals with 500 cm³ of distilled water at 60–80 °C 15 times before drying on filter paper. The distilled water was heated in order to prevent any swelling occurring during this washing process since, although the absorption of distilled water is rapid, it does not occur above 40 °C as this is above the phase transition temperature for tactoid formation.⁹ After drying, the crystals were cut to dimensions of approximately $0.5 \times 0.5 \times 0.1$ cm. These were individually weighed, and the volume of a crystal in its fully hydrated state was calculated using the density ($\rho = 1.86$ g/cm³). After weighing, a single vermiculite crystal was placed into a quartz sample cell of dimensions $1 \times 1 \times 4.5$ cm, and an appropriate amount of the polymer solution (typically 2.5 cm³) was added to prepare an $r = 0.01$ sample. The cells were then sealed with parafilm and allowed to stand at 7 °C for 2 weeks prior to the neutron-scattering experiments, to ensure that full equilibrium swelling had been achieved.⁹

The neutron diffraction experiments were carried out at the JRR-3M Research Reactor, Japan Atomic Energy Research Institute (JAERI), Tokai-mura, using the SANS-J instrument, described in ref 13. A monochromatic beam of neutrons of wavelength $\lambda = 6$ Å was used, and the incident beam was collimated by passage through a 5 mm diameter circular aperture. The samples were mounted on a temperature-controlled four-position sample changer under the control of the instrument computer. Neutrons scattered by the gel samples were recorded on a two-dimensional area detector, software coded as 128×128 pixels, situated 1.5 m behind the samples, covering the approximate q range between 0.2 and 2 nm⁻¹, where the wave-number q is defined by the equation

$$q = \left(\frac{4\pi}{\lambda} \right) \sin\left(\frac{\theta}{2}\right)$$

with θ being the scattering angle.

The quartz sample cells used were practically transparent to neutrons at the wavelength utilized on the SANS-J, and the small angle neutron scattering from D₂O was of low intensity and completely unstructured over the q range studied. All of the sample runs were corrected for the background scattering arising from the cell and D₂O; after making the appropriate transmission corrections, the scattering arising from a cell containing D₂O was subtracted from the sample runs. In this way the scattering patterns analyzed arose purely from the gels.

Results

Two typical scattering patterns from gel samples are shown in Figure 2, which represents the raw data observed on the detector as intensity contours plotted as a function of the pixel row and column numbers. The scattering pattern consists of two lobes of intensity above and below the plane of the layers in the gel. If the layers were perfectly parallel, then coherent scattering would occur only along the axis perpendicular to the layers, but in reality there are defects in the gel so scattering occurs on either side of the axis. The width of the lobe is an indication of the parallelity of the gel stack. For the pure aqueous sample (no PVME), almost all of the scattering falls within two cones of 60° azimuthal width, as observed previously;⁹ see Figure 2a. The scattering from a $c = 0.1$ M PVME sample is shown in Figure 2b. The first remarkable feature of this pattern is that the cones of scattering have

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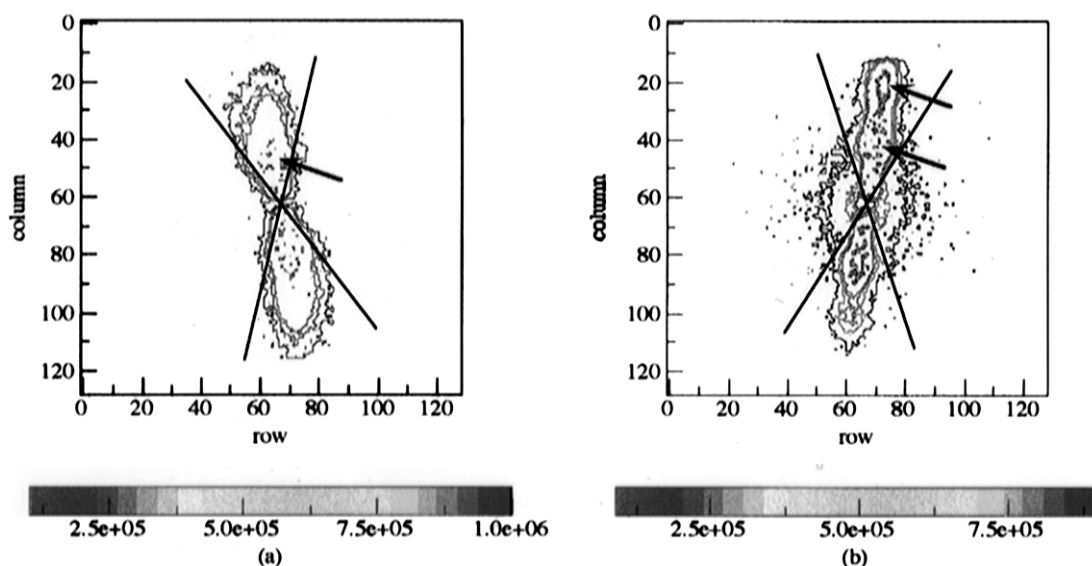


Figure 2. Contour plots of typical neutron-scattering patterns for $r = 0.01$ and $c = 0.1$ M gels at $T = 8^\circ\text{C}$. The numbers show the pixel code. (a) No added polymer. The arrow marks the first-order diffraction maximum at $q_{\text{max}} = 0.5\text{ nm}^{-1}$. (b) With 1% PVME. The arrows mark the first maximum at $q_{\text{max}} = 0.7\text{ nm}^{-1}$ and the second maximum at $q_{\text{max}} = 1.4\text{ nm}^{-1}$.

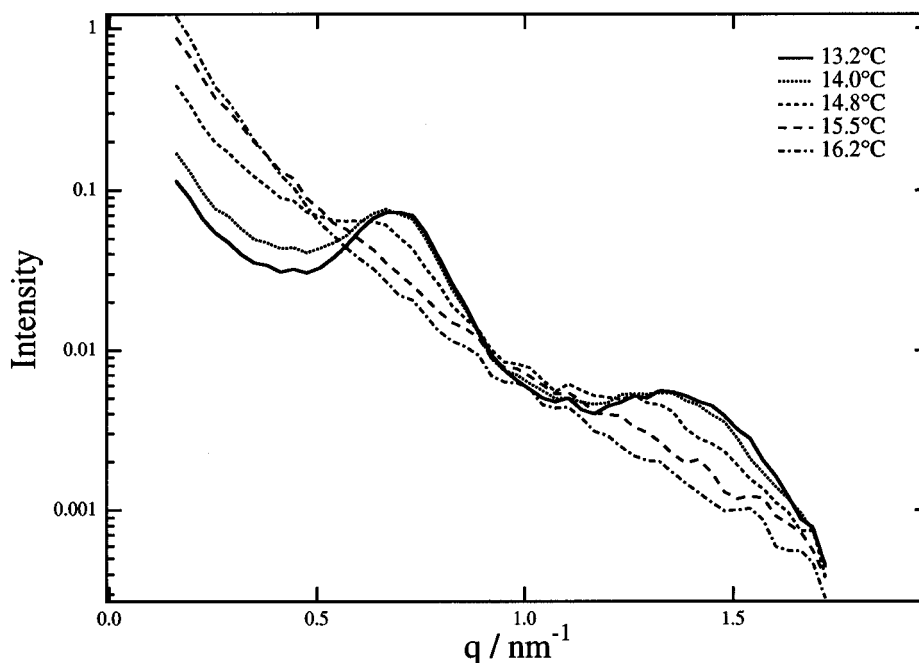


Figure 3. $I(q)$ (arbitrary units) vs q plots obtained for one sample at $r = 0.01$ and $c = 0.1$ M, 2% PVME. The solid line shows the scan obtained at 13.2°C , and the dots (\cdots), short dashes ($- - -$), long dashes ($- - -$), and dot-dashes (\cdots) show those obtained at 14.0 , 14.8 , 15.5 , and 16.2°C , respectively. The phase transition temperature $T_c = 15 \pm 1^\circ\text{C}$.

become narrower than those observed in the pure aqueous system, almost all of the scattering now lying within a cone of azimuthal angle of 50° , rather than 60° . This effect was observed for all the polymer-added samples studied. Since the width of the cone is a measure of the mosaic spread of the clay plates, this shows that (1) *the addition of polymer causes the clay plates to become more strongly aligned (more parallel) in the gel phase.*

The existence of intensity maxima within the cones of scattering is due to a pronounced interference effect between the clay plates, which have a well-defined separation. The second remarkable feature of Figure 2a,b is that the diffraction pattern from the polymer-added sample is much sharper; it exhibits a more pronounced first-order diffraction maximum and a strong second-order diffraction maximum, which is rare for a pure aqueous sample.⁹ This was also observed for all the PVME-added samples and means that (2) *the addition of polymer causes*

the clay plates to be more regularly spaced in the gel phase. It is also clear that the first-order diffraction maximum has shifted to higher q as compared with the pure aqueous $c = 0.1$ M sample. This was also a general effect and means that (3) *the addition of polymer causes a decrease in the interlayer spacing between the clay plates in the gel phase.* In order to quantify this effect, the scattering patterns were radially summed within the appropriate azimuthal cones. One example of the result of such a radial summation, for a $c = 0.1$ M sample containing 2% PVME, is shown by the solid line in Figure 3.

The solid line in Figure 3 shows a strong first-order diffraction maximum at $q_{\text{max}} = 0.70\text{ nm}^{-1}$ and a weaker second-order diffraction maximum at $q_{\text{max}} = 1.40\text{ nm}^{-1}$, at $T = 13.2^\circ\text{C}$. Identical diffraction traces (not shown on the figure) were obtained at 1°C intervals in the range between 9 and 13°C . At 14°C , there is a slight change

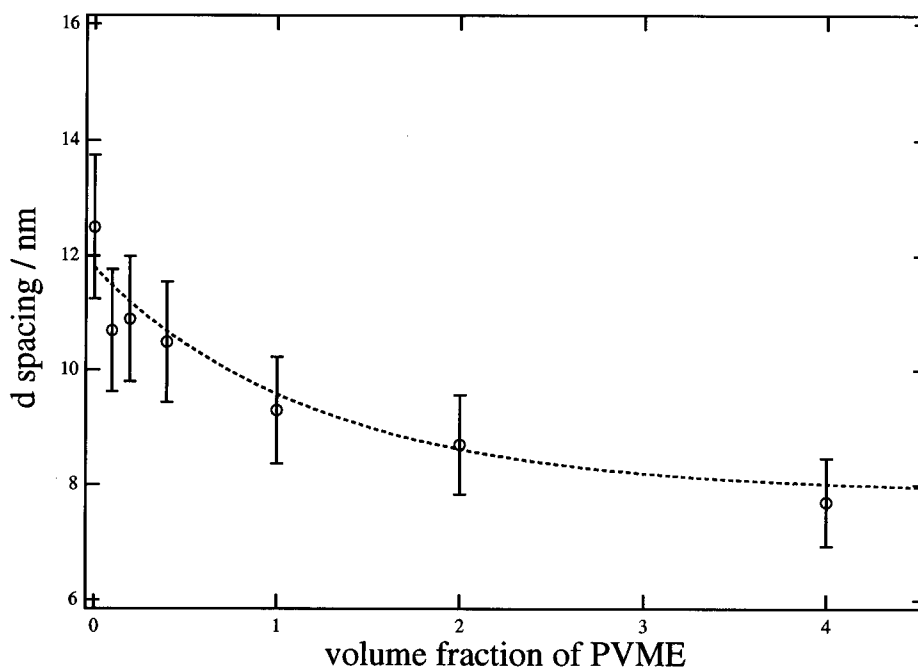


Figure 4. The average d value (nm) as a function of the PVME volume fraction (%) for $r = 0.01$, $c = 0.1$ M, and $T = 8$ °C.

in pattern, followed by a profound change in the range between 14 and 16 °C. This corresponds to the phase transition illustrated in Figure [1(b)–(c)]. The trace at 14.8 °C is intermediate between the pure gel pattern observed at lower temperatures and the smooth decay observed in the scattering function at higher temperatures. It therefore corresponds to T_c , which is 15 ± 1 °C in this case. The phase transition was always observed to be within the range between 14 and 16 °C irrespective of the volume fraction of PVME in the system. We therefore conclude that (4) *the addition of polymer has no effect on the phase transition temperature between the tactoid and gel phases of the clay system.*

In order to extract the most precise information from the neutron diffraction patterns it would be necessary to analyze them quantitatively using a one-dimensional paracrystalline lattice model.¹⁴ Although such an analysis can be performed for small angle X-ray diffraction patterns from clay gels,^{15,16} it is not so straightforward for small angle neutron scattering data because of the poorer resolution due to the larger size of the beam and the wider spectral distribution, $\Delta\lambda/\lambda \approx 0.1$. However, the sharpness of the diffraction effect permits an immediate approximate evaluation of the average d value by measuring q_{\max} , the q value at the maximum of the first-order diffraction effect, and applying the simple equation

$$d = \frac{2\pi}{q_{\max}}$$

The results of this analysis are shown in Figure 4, where the error bars represent $\pm 10\%$ of the average values obtained, due to sample-to-sample variability.⁹

The number of samples studied in each case was between four and eight, and the variation of the average d value with the volume fraction seems to be well represented by the exponential fit shown by the dotted

line in Figure 4.

$$d = 7.9 + 3.9 \exp(-1.0v)$$

where d is expressed in nm and v is expressed as a percentage.

It was not possible to determine the d value in the collapsed phase within the q range of the SANS-J instrument. However, our recent X-ray scattering studies¹⁶ have shown that above 16 °C a strong diffraction peak is visible at $q = 3.24 \text{ nm}^{-1}$, corresponding to a d value of 1.94 nm. This is identical to the value obtained in the pure aqueous system,^{7,9} showing that (5) *the spacing between the clay plates is not affected by the added polymer when they are collapsed by an increase in temperature.*

Discussion

Brandrup and Immergut¹⁷ give the end-to-end distance r_0 of a PVME chain in solution as

$$r_0 = 900M^{1/2} \times 10^{-4} \text{ nm}$$

Inserting $M = 18\,000$ into this formula gives $r_0 \approx 12$ nm, and dividing this number by $\sqrt{6}$ gives the radius of gyration $R_g \approx 5$ nm. Since the d value of 12 nm in the pure aqueous system at $c = 0.1$ M is composed of a clay plate of approximate thickness 1 nm and an interlayer spacing of approximate thickness 11 nm, it would seem that the polymer chain should be able to "fit" into the clay gel. There are therefore three likely sites for a polymer molecule in and around the clay gel: (A) adsorbed onto the surface of a single plate, in a flattened configuration, (B) as free chains inside the gel phase, and (C) as free chains in the supernatant fluid surrounding the gel. The approximate matching of the size of the polymer to the interlayer separation suggests another possibility, that the PVME molecules could act (D) as bridges between the clay plates, adsorbed onto the surfaces of two neighboring plates.

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We might expect that A and C would be the most favored sites. Adsorption isotherms for neutral polymers on the more widely studied montmorillonite clays invariably show high affinity of the polymer for the surface,² and the conventional wisdom^{2,3} is that because a large number of solvent molecules must be desorbed in order to accommodate a single polymer molecule, the translational entropy so gained by the system provides a strong driving force for polymer adsorption. This driving force outweighs the loss of conformational entropy of the polymer and favors type A adsorption. The same reasoning suggests that type D adsorption would be the least favorable; in this case, only short trains of the polymer could be attached to the two surfaces and a severe loss of conformational entropy would not be compensated for by translational entropy gain of the solvent. Similarly, site B would involve conformational entropy loss for the polymer without solvent entropy gain. In advance of the experimental results, it would be natural to predict that the polymer concentration would vary as $A > C > B \approx D$.

The idea that $C > B$ gains support from results 1–3. In these circumstances, the excess of polymer molecules in the supernatant fluid, as compared with the fluid in the gel phase, would exert an osmotic pressure on the gel and the effect should be similar to that of applying an external pressure to the gel. The effects of two different types of pressure on *n*-butylammonium vermiculite gels have been studied by neutron scattering.^{7,9} The application of hydrostatic pressure, when the whole condensed matter system is compressed uniformly from outside, has an effect quite different from what we have observed for the polymer addition; the phase transition temperature changes but the *d* value within the gel phase remains approximately constant.⁷ However, the effect of uniaxial stress on the gels, when a piston inside the condensed matter system compresses a gel along its swelling axis, causes the diffraction patterns to sharpen and the *d* value to decrease,⁹ just as we have described here. Indeed, the *d* value also decreases exponentially as a function of uniaxial stress,⁹ so the analogy of polymer volume fraction to uniaxial pressure is an attractive one and supports the hypothesis that the free chains are fractionated into the clear fluid surrounding the gel. The hypothesis $C > B$ is also consistent with result 4, since the small number of chains in site B in the gel phase would be expected to have little effect on the phase transition process, as they would be squeezed out of the interlayer region when the plates collapse.

Result 5, that the *c* axis *d* value of 1.94 nm in the collapsed regions in a sample with added polymer is equal to that in the pure aqueous system, is the most interesting. Since the clay plates themselves have a thickness of approximately 1 nm, the interlayer spacing in the crystalline regions is also approximately equal to 1 nm, so it is not possible for a polymer with a radius of gyration of approximately 5 nm to exist as *free chains* inside the tactoids. Although it is possible for the polymer to be adsorbed into the 1 nm gap between the clay plates in a flattened configuration, it is unlikely that substantial polymer adsorption into the tactoids would lead to an interlayer spacing identical to that obtained in the pure aqueous system, so result 5 suggests that only a very small

number of polymer molecules can be included in the crystalline regions. Whether or not this in turn suggests that there is little adsorption in the gel phase is then a question of kinetics. As the dynamics of polymer desorption are normally considered to be slow,^{2,3} and the dynamics of the *n*-butylammonium vermiculite phase transition have been reported to be surprisingly rapid, on the order of 10 min,⁷ it seems unlikely that the polymer could desorb during the time it takes for the plates to collapse. Result 5 therefore throws some doubt on the hypothesis $A > C$.

In an extreme case, we note that none of our results are inconsistent with the assumption that the concentration of polymer in type A, B, and D sites is *effectively* zero, namely that almost no polymer molecules exist in the region bounded by the clay plates. In particular, this crude assumption immediately explains result 5 and offers a natural explanation for result 4, that the phase transition temperature is unaffected; if there are no polymer molecules trapped between the clay plates in either phase, the transition between the two phases should resemble the process in the pure aqueous system. The decrease in the *d* value would then be explained by the osmotic pressure mechanism. In another extreme case, nor are the results inconsistent with the assumption that type D adsorption is important, namely that a substantial number of polymer molecules are physically adsorbed onto both of two neighboring clay surfaces, bridging them. Such 'bonds' between the clay plates might have the effect of binding them more strongly and so explain results 1–3. If the kinetics of polymer desorption were rapid compared with the kinetics of the plate rearrangement, this idea would be compatible with results 4 and 5.

Other mechanisms are possible. In type A adsorption, displacement of small ions from the surface could lead to an increase in the effective surface charge, which would again produce a decrease in the *d* value and an increase in the strength of binding between the plates.¹⁸ Yet another possible mechanism is that the addition of polymer to the system could perturb the distribution of salt between the gel and the supernatant fluid,¹⁰ again affecting the plate-plate interaction. Further investigations are in progress in an attempt to distinguish between these various mechanisms.

Whatever the mechanisms, the facts are interesting. It seems unlikely that any theory could have predicted results 1–5 in advance of the experiments, and they are all clear-cut results on a well-defined four-component system.

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