

Neutron Scattering Study of Vermiculite–PEO Mixtures

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A four component clay–polymer–salt–water system, consisting of *n*-butylammonium vermiculite, poly(ethylene oxide), *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 d along the swelling axis of the clay colloid decreased as a function of the polymer volume fraction, from 12 nm at $v = 0$ to 6 nm at $v = 0.04$. This behavior is qualitatively similar to that observed in the vermiculite system with added poly(vinyl methyl ether). Possible mechanisms for the observed contraction are discussed, including the possibility of bridging flocculation of the clay plates. In one experiment, the d value in the gel phase was observed to increase with temperature prior to collapse into the tactoid phase, which is a new effect that seems to depend on cycling of the system between the gel and tactoid phases.

Introduction

The *n*-butylammonium vermiculite system is the best-characterized clay colloid system. The raw swelling phenomenon illustrated by Figure 1a–b was first reported^{1,2} in 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.¹ The swelling leads to the formation of coherent gels, which show no tendency to disperse into the surrounding solution. The gel-to-tactoid transition illustrated by Figure 1b–c was discovered more recently.³ The phase transition between the gel and tactoid phases is reversible and has well-defined thermodynamic properties. This reversibility is of great theoretical interest because it constitutes a counterexample to the standard theory of colloid stability, the DLVO theory,^{4,5} which is based on the assumption that the secondary minimum (gel) state is always thermodynamically unstable with respect to the primary minimum (tactoid) state. It is also of some practical interest because of the widespread importance of charge-stabilized colloids in industrial applications.⁶

The other main mechanism involved in colloid stability is steric stabilization, brought about by the adsorption of polymers onto the surfaces of colloidal particles. The sharp characterization of the three-component clay–salt–water system composed of *n*-butylammonium vermiculite, *n*-butylammonium chloride, and water,^{7–10} which has established it as a model clay colloid system,¹⁰ offers a special opportunity for unravelling the mechanisms of steric stabilization by studying the corresponding four-component clay–polymer–salt–water system. The uni-

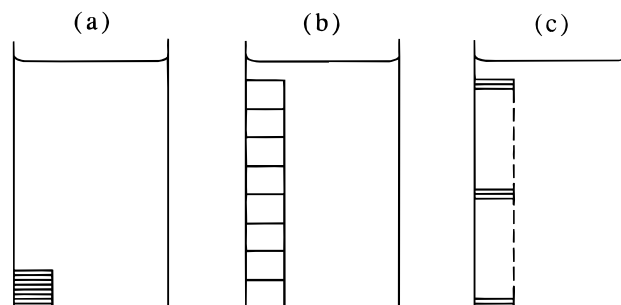


Figure 1. Schematic illustration of the swelling of *n*-butylammonium vermiculite in an 0.1 M *n*-butylammonium chloride solution: (a) represents the *n*-butylammonium vermiculite crystal ($d = 2$ nm) prior to swelling; (b) the gel ($d = 12$ nm) formed by a homogeneous 6-fold expansion at $T < 14$ °C; 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 approximately the same volume as the gel structure.

axial nature of the swelling, the fact that the d value along the swelling axis is sharply defined and easy to measure by neutron scattering,^{7–10} and the existence of the unusual phase transition with a well-defined transition temperature T_c make the system an ideal one for investigating the effect of added polymers on clay swelling in particular and on colloid stability in general.

In a previous study,¹¹ the effect of adding poly(vinyl methyl ether) (PVME) to the *n*-butylammonium vermiculite system was investigated by neutron scattering. Although it would be interesting to add a charged polymer to the system to further investigate the electrostatic interaction between plate macroions,^{12–14} the present study has been restricted to the vermiculite–poly(ethylene oxide) (PEO) system to investigate the steric interaction. PEO seems an obvious candidate because the

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PEO-salt-water system is one of the best characterized polymer-salt-water systems.¹⁵⁻¹⁷ Such a gradual approach is necessary because care has to be taken in controlling the myriad variables in a four-component system. The three component clay-salt-water system has been investigated as a function of the salt concentration c and the temperature T ,⁷ hydrostatic pressure P ,³ uniaxial stress along the swelling axis p ,⁸ and the volume fraction r of the clay in the condensed matter system.⁹ In addition to the five variables (r, c, T, P, p), adding polymer adds three new variables to be considered; they are, 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 . In the previous study,¹¹ six of the variables were eliminated, as follows. First, attention was restricted to the unstressed systems; namely, all the experiments were carried out at $P = 1$ atm and $p = 0$, and 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 clay-salt-water system were held fixed. Third, attention was restricted to $x = \text{PVME}$ 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.

In the present study, P, p , and r were held constant as before. We also chose a polymer with a molecular weight of 18 000, eliminating M , and concentrated mainly on the case $c = 0.1$ M, again studying the (v, T) behavior of the system, this time with $x = \text{PEO}$. We also made a preliminary investigation of the case $c = 0.01$ M. Our main aims were to determine (i) the lattice constant (d value) along the swelling axis of the clay colloid in the gel phase (b), and (ii) the phase transition temperature T_c between the gel phase (b) and the tactoid phase (c) of the system, as functions of the polymer volume fraction v .

Experimental Section

The vermiculite crystals were from Eucatex, Brazil. Crystals $\sim 30\text{ mm}^2$ in area and 1 mm thick were washed and then treated for ~ 1 year with 1 M NaCl solution at 50 °C, with regular changes of solution, to produce a pure Na vermiculite, with the chemical formula¹¹ $\text{Si}_{6.13}\text{Mg}_{5.44}\text{Al}_{1.65}\text{Fe}_{0.50}\text{Ti}_{0.13}\text{Ca}_{0.13}\text{Cr}_{0.01}\text{K}_{0.01}\text{O}_{20}(\text{OH})_4\text{Na}_{1.29}$.

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 ~ 1 month. Chemical analysis of the *n*-butylammonium vermiculite thus obtained showed that the amount of interlayer sodium remaining was $\ll 1\%$. The crystals were stored in a 1 M *n*-butylammonium chloride solution prior to the swelling experiments.

The PEO was purchased from Scientific Polymer Products Ltd. (Church Stretton, UK) with manufacturers specifications $M_w/M_n = 1.02$, where M_w and M_n are the weight-average and number-average molecular weights, respectively, and used without further purification. Solutions of the required volume fraction of PEO were prepared by dissolving a known mass of the polymer ($\rho = 1.13\text{ g/cm}^3$) in a known volume of a 0.1 (or 0.01) M *n*-butylammonium chloride solution, itself prepared by dissolving a known mass of *n*-butylammonium chloride in D_2O . It was necessary to swell the crystals in D_2O rather than H_2O solutions because of the large incoherent scattering cross-section of hydrogen that 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 washing was achieved by rinsing the crystals with 500 cm^3 of distilled water at 60–80 °C fifteen times before drying on filter paper. The distilled water was heated to prevent any swelling occurring during this washing process because, although the absorption of distilled water is rapid, it does not occur above 40 °C, which is the phase transition temperature for tactoid formation.⁹ After drying, the crystals were cut to dimensions of $\sim 0.5 \times 0.5 \times 0.1$ cm. These crystals were individually weighed, and the volume of a crystal in its fully hydrated state was calculated using the density (ρ) of 1.86 g/cm^3 . After weighing, a single vermiculite crystal was placed into a quartz sample cell of internal dimensions $1 \times 1 \times 4.5$ cm and an appropriate amount of solution (typically 2.5 cm^3) was added to prepare an $r = 0.01$ sample. The volume fractions of the clay and salt were fixed such that their numbers were the same in all of the studies and not varied to accommodate the addition of the polymer. That is, addition of the polymer was assumed to have negligible effect on the calculation of the other volume fractions. The volume fraction of polymer was varied between $v = 0.0010$ and 0.0400, with accuracy to the fourth decimal place. The difficulty in controlling the concentration variables r, c , and v was a strong motivation in using neutron scattering. Good quality X-ray diffraction traces can be obtained from vermiculite gels,¹⁸ but the tiny samples required make it very difficult to rigorously control the concentration variables.⁹ The cells containing the four components were 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 ISIS spallation source, using the time-of-flight small-angle scattering instrument LOQ, described previously.¹⁹ A white beam of neutrons with wavelengths in the range between $\lambda = 2.2\text{ \AA}$ and $\lambda = 10\text{ \AA}$ was used, and the incident beam was collimated by passage through 8-mm wide, 2-mm high rectangular slits. The samples were mounted on a temperature-controlled, 20-position sample changer. Neutrons scattered by the gel samples were recorded on a two-dimensional area detector, software coded as 64×64 pixels, situated 4.5 m behind the samples, covering the approximate Q range between 0.02 and 0.2 \AA^{-1} . The quartz sample cells used were practically transparent to neutrons at the wavelengths utilized on LOQ and the small-angle neutron scattering from D_2O 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 D_2O ; after making the appropriate transmission corrections, the scattering arising from a cell containing D_2O was subtracted from the sample runs. In this way, the scattering patterns analyzed arose purely from the gels. The way in which the patterns recorded on the two-dimensional multidetector were reduced to plots of intensity against the Q vector perpendicular to the clay layers, expressed as $I(Q)$ versus Q in the following, is described fully in refs 11 and 20. Here we note that the rectangular beam used was oriented approximately parallel to the vermiculite plates by using the vertical growth of the gel stacks inside the confining quartz cells. In the majority of the cases studied, the intensity of the Bragg peaks on opposite sides of the multidetector was approximately equal, reflecting both the parallel orientation of the beam to the net orientation of the clay layers and the mosaic spread of

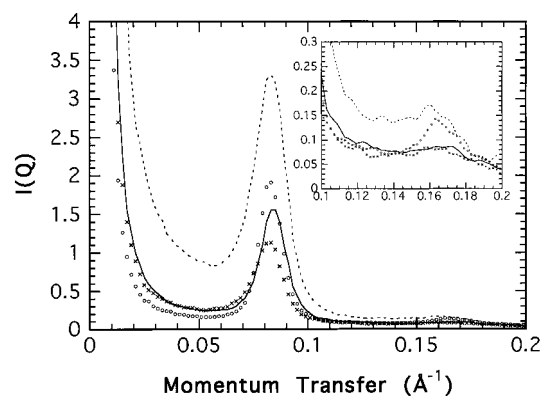


Figure 2. The scattering patterns obtained from four different samples at $r = 0.01$, $c = 0.1$ M, $v = 0.02$, and $T = 7$ °C. The insets show the weak second-order peak on an expanded scale.

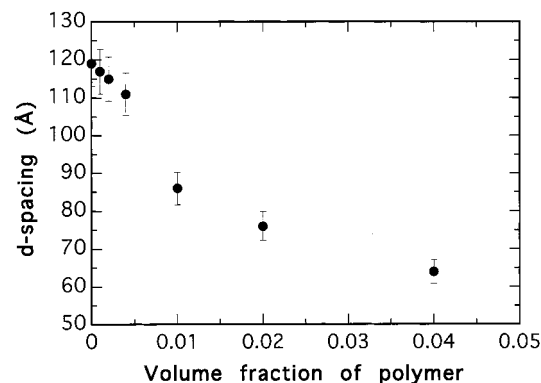


Figure 3. The average d value (Å) as a function of the PEO volume fraction at $r = 0.01$, $c = 0.1$ M, and $T = 7$ °C.

the orientations, which has been established to be of the order of 5° to 10° in the *n*-butylammonium vermiculite system.⁷

Results

The main study was at $c = 0.1$ M, for which $d = 120$ Å and $T_c = 14$ °C in the system without added polymer. Four samples were prepared at each of the following volume fractions of PEO: $v = 0, 0.001, 0.002, 0.004, 0.01, 0.02$, and 0.04 . First, the scattering from all 28 samples was measured at $T = 7$ °C. The sample-to-sample variability study, which is necessary because the crystals are prepared from a naturally occurring mineral, at $v = 0.02$ (2% PEO) is shown in Figure 2, where the scattering patterns observed on the two-dimensional multi-detector have been reduced to plots of scattering intensity $I(Q)$ versus scattering vector Q , as described previously.^{9,11} It is clear that the scattering is reproducible between gels prepared from different pieces of vermiculite. All four samples exhibit a sharp first-order diffraction peak at $Q_{\max} = 0.083$ Å⁻¹, with a weaker second-order diffraction peak (shown on the insets in Figure 2) at twice this Q value. The d value at this volume fraction is therefore equal to 76 Å.

The d values obtained as a function of the polymer volume fraction v are shown in Figure 3. They can be represented by the approximate exponential fit $d = 60 + 60 \exp(-1.0v)$, where d is expressed in Angstroms and v as a percentage. This result is remarkably similar to the fit obtained for the effect of PVME volume fraction,¹¹ showing that two chemically different neutral polymers bring about a similar contraction of the gel phase. The effect of PEO on the phase transition temperature T_c between the gel phase and the crystalline phase of the system was also similar to that observed for PVME; namely, no effect

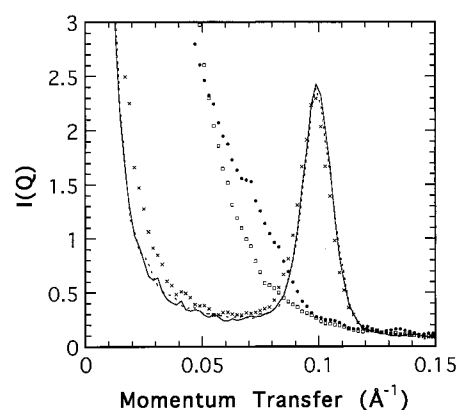


Figure 4. $I(Q)$ versus Q plots obtained for one sample at $r = 0.01$, $c = 0.1$ M, and 4% PEO. The solid line shows the scan obtained at 7 °C and the dashes, crosses, open squares, and solid circles show those obtained at 10, 12, 14, and 16 °C, respectively. The phase transition temperature $T_c = 13 \pm 1$ °C.

at all up to volume fractions of 4%. The diffraction traces obtained as a function of temperature for the 4% PEO sample are shown in Figure 4. It is clear that the gel peak disappears between 12 and 14 °C, corresponding to $T_c = 13 \pm 1$ °C. The same effect was observed for all the samples studied.

The diffraction patterns shown in Figure 4 were obtained at approximately hourly intervals, as the temperature was increased in 2 °C steps. This procedure for measuring T_c was the same as that employed in previous studies of the pure aqueous system⁹ and the system with added PVME.¹¹ A recent, more detailed small-angle X-ray diffraction study of the phase transition in the PVME-added system has revealed more subtle effects of the polymer addition around T_c when the sample is cycled through its phase transition temperature.²⁰ Accordingly, a second study was carried out at $c = 0.1$ M, measuring the temperature-dependent scattering from a sample with 4% PEO that had been taken several times through the b–c process illustrated in Figure 1. A pure aqueous sample that had been through the same treatment was also studied for comparative purposes. Because the second study was carried out with a new batch of samples, it was first necessary to check the sample-to-sample variability again, and four samples were prepared at each of the following volume fractions v of PEO: $v = 0, 0.004, 0.01, 0.02$, and 0.04 . The scattering from 20 samples was measured at $T = 10$ °C, and typical results are shown in Figure 5. The d values obtained from the new batch of samples were higher, but within 15% of the previous results, confirming that PEO has a remarkably similar effect on the swelling at $c = 0.1$ M to PVME. The collapse of the gels to the crystalline phase at $T = 16$ °C, when we cycled the temperature, was also expected on the basis of the previous results, but some new effects came when we varied the temperature. The scattering patterns obtained from a gel with 4% added PEO at six temperatures between 9 and 15 °C are shown in Figure 6.

The position of the maximum in the first-order Bragg peak from the gel phase shows that the gel expands on heating prior to its collapse at 16 °C. This result was quite unlike the effect of heating on the system without added polymer, for which the d value remained constant below T_c . A further repeat of this experiment with a sample containing 4% PEO that had been through its phase transition once only gave the familiar result that d is constant with respect to T prior to collapse; so this new effect seems to depend on cycling of the system between the gel and tactoid phases.

In ref 20, a first attempt was made to determine the effect of varying c in PEO solutions at $c = 0.01$ M. We continued to

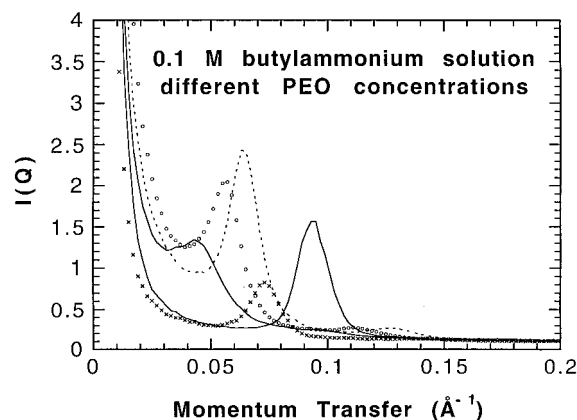


Figure 5. Scattering patterns obtained from gels prepared in 0.1 M *n*-butylammonium chloride solutions at 10 °C. The solid line with the weak diffraction maximum at $Q_{\max} = 0.05 \text{ \AA}^{-1}$ is for a gel without added polymer and that with the strong maximum at $Q_{\max} = 0.1 \text{ \AA}^{-1}$ is for a gel with 4% added PEO. The open circles, dashes, and crosses correspond to 0.4, 1, and 2%, added PEO, respectively.

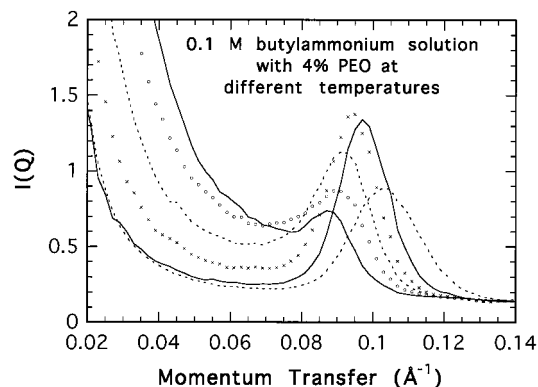


Figure 6. Scattering patterns obtained from a gel prepared in 0.1 M *n*-butylammonium chloride solution with 4% added PEO. The temperatures of 9, 11, 12, 13, 14, and 15 °C are represented, respectively, by dashes (with $Q_{\max} > 0.1 \text{ \AA}^{-1}$), a solid line (with a strong maximum at $Q_{\max} \approx 0.1 \text{ \AA}^{-1}$), crosses, dashes, open circles, and a solid line with $Q_{\max} = 0.09 \text{ \AA}^{-1}$.

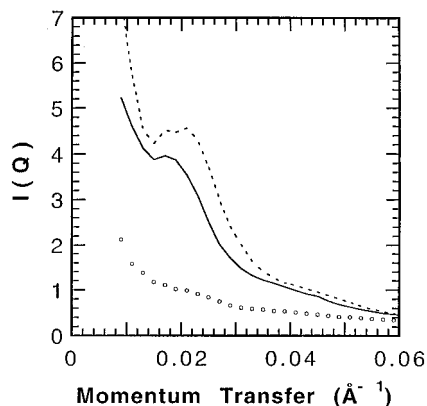


Figure 7. Scattering patterns obtained from gels prepared in 0.01 M *n*-butylammonium chloride solutions at 20 °C. The dashes, solid line, and circles correspond to 0.4, 1, and 4% added PEO, respectively.

investigate the effect of diluting the simple electrolyte, the main aim being to sketch out the d value along the swelling axis of the clay colloid in the gel phase as a function of the polymer volume fraction v by measuring four samples at $v = 0.004$, 0.01, and 0.04. Three typical traces are shown in Figure 7. The weak diffraction effects in the region of $Q = 0.02 \text{ \AA}^{-1}$, corresponding to a d value of $\sim 300 \text{ \AA}$, are typical of $c = 0.01$

M gels without added polymer, so it would seem that the PEO has a much weaker effect in this case, in agreement with the preliminary results.²⁰ This result may throw some light on the mechanism of the effects observed, as discussed next.

Discussion

There are four sites for a polymer molecule in and around the vermiculite gel: (A) adsorbed onto the surface of a single plate, (B) as free chains inside the gel phase, (C) as free chains in the supernatant fluid surrounding the gel, and (D) as bridges between the vermiculite layers, adsorbed onto the surfaces of two neighboring layers. It should be possible to estimate the relative contribution of site C by direct chemical analysis of the supernatant fluid, and such measurements are in progress. At present, we can give only a qualitative discussion of the data, which should provide a basis for further enquiries by theorists as well as experimentalists.

In the main case studied, at $c = 0.1 \text{ M}$ and $M = 18\,000$, we chose an approximate matching of the size of the polymer to the interlayer separation in the clay–salt–water system, expressed as $d \approx 2R_g$, where R_g is the radius of gyration of the polymer. With 400 monomer units, approximately equal to the number studied in the vermiculite-PVME system,^{11,20} a fully extended chain could have a length of 1000 \AA or more. However, such a stretched configuration is so entropically unfavorable with respect to a random walk of the polymer segments that such configurations will make a negligible contribution to the thermodynamic free energy of the system. The statistically favored configuration for the polymer is the random walk, and studies of aqueous PEO solutions give the end-to-end distance r_0 of a PEO chain in solution as²¹ $r_0 = 900 M^{1/2} \times 10^{-4} \text{ nm}$.

Inserting $M = 18\,000$ into this formula gives $r_0 = 12 \text{ nm}$, and dividing this number by $\sqrt{6}$ gives the radius of gyration $R_g = 5 \text{ nm}$. Because the d value of 12 nm in the pure aqueous system at $c = 0.1 \text{ M}$ is composed of a clay plate of $\sim 1 \text{ nm}$ and an interlayer spacing of $\sim 11 \text{ nm}$ thickness, it would seem that the polymer chain should be able to ‘fit’ into the clay gel and bridge the plates at the spacings shown in Figure 3. The matching condition $d \approx 2R_g$ is suggestive of possibility D; that is, that the PEO molecules act as bridges between the clay plates, adsorbed onto the surfaces of two neighboring plates. This mechanism fits well with the apparent insensitivity of the d value to polymer addition at $c = 0.01 \text{ M}$, because in the latter case, the d value of 30 nm in the pure aqueous system is too large to permit bridging. Further systematic variations of M , v , and c are in progress to test this bridging flocculation mechanism.

There are various other possible mechanisms for the d versus v plot shown in Figure 3. Apart from bridging, the obvious ones are that the gel is compressed either by osmotic pressure due to an excess of polymer molecules in the supernatant fluid or by an electrical effect due to type A adsorption being accompanied by a redistribution of charge within the gel, affecting the layer–layer interaction. The addition of polymer to the system could also perturb the distribution of salt between the gel and the supernatant fluid,⁹ again affecting the layer–layer interaction.

Adsorption isotherms for neutral polymers on the more widely studied montmorillonite clays invariably show high affinity of the polymer for the surface,²² and the conventional wisdom^{22,23} is that because a large number of solvent molecules must be desorbed 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 and D adsorption. In the latter case, a balance between conformational entropy loss of the polymer and a free energy gain in surface adsorption might lead to the kind of drawing force between the clay plates that we observe. Similar considerations suggest that site B, free polymer chains inside the gel, would be unfavorable because conformational entropy loss for the polymer in a nearly two-dimensional environment (compared with its statistical size) is not compensated by a free energy of adsorption in this case.

The idea that $C > B$ gains support from Figure 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, known as depletion flocculation,²³ should be similar to that of applying an external pressure to the gel. This mechanism also fits with the apparent insensitivity of the d value to polymer addition at $c = 0.01$ M, as the polymers may be homogeneously distributed when the confinement by the clay plates is relaxed at the higher interlayer spacing. It is interesting to compare the effect of such an osmotic pressure with the effects of two different types of pressure on *n*-butylammonium vermiculite gels, which have also been studied by neutron scattering.^{3,8} 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.³ 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,⁸ just as we have described here. Indeed, the d value also decreases approximately exponentially as a function of uniaxial stress,⁸ 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 that $C > B$ is also consistent with the constancy of T_c because the small number of chains in site B in the gel phase would be expected to have little effect on the phase transition process. It is worth noting, however, that Figure 3 could also be explained by the bridging mechanism.²⁴

If type D adsorption was the leading contribution to the contraction of the gel phase, the constancy of T_c could still be explained if polymer molecules were squeezed out of the interlayer region when the plates collapse. 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.¹⁴ Likewise, the addition of polymer to the system could perturb

the distribution of salt between the gel and the supernatant fluid,⁹ 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 in their own right. It seems unlikely that any theory could have predicted in advance of the experiments the two major results; that is, (i) that the lattice constant (d value) along the swelling axis of the clay colloid in the gel phase decreases exponentially with v , and (ii) that the phase transition temperature T_c remains constant with respect to v . These results are clear cut for a well-defined four-component system.

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