Intercalation Adsorption of Poly(ethylene oxide) into Montmorillonite

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Adsorption of poly(ethylene oxide)s (PEO) having molecular weights from 400 to 1×10^6 on calcium montmorillonite from their aqueous solution was studied. High molecular weight polymers showed high affinity type adsorption isotherm. Concomitant measurement of d(001) spacing of the clay indicated intercalation adsorption of the polymers, and it was concluded that the adsorbed PEO takes a form of thin pancake shaped disk in the interlamellar region, whose radius was proportional to the square root of molecular weight. Free energy of adsorption calculated from the adsorption isotherm became more negative with increase in molecular weight and the entropy change became increasingly positive. The positive entropy probably originated from a desorption of water from the interlammella region of clay as PEO was adsorbed.

KEY WORDS: Adsorption/ Clay/ Intercalation/ Poly(ethylene oxide)/ Montmorillonite/

INTRODUCTION

Much progress has been made for the last three decades in understanding the adsorption behavior of polymers at the solid/solution interface.[1,2] Research has been stimulated by the importance and potential applications of polymer adsorption phenomena in industry, biology and agriculture. In the most of studies, silica, metallic and/or metal oxide surfaces and polymer latex particles have been used as adsorbent. There are other important adsorbents, namely clay minerals and the adsorption studies of water soluble non-ionic polymers, polyelectrolytes as well as biological macromolecules have already been done.[3]

Recently, adsorption of polymers on clay minerals has been of interest from two reasons. The first is the introduction of surface force apparatus in the study of polymer adsorption.[4] On the apparatus operation, polymers are adsorbed on mica surfaces and the force-distance curve is measured. Hence the understanding of polymer adsorption from organic solvent or water on the mica surface is the crucial importance in the analysis of the results. However, the adsorption study of polymers on mica surface is, in the authors opinion, insufficient at the present stage. The second is the implication that the clay-polymer interaction is the very origin of life on the earth as proposed by Cairns-Smith.[5]

One of the peculiar feature of layer type clay minerals is that the interlayer spacing can be swelled by water and intercalated organic substances together with the electrical

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double layer repulsion.[3]   Furthermore, it has been found that many polymers can be also intercalately adsorbed into layers of clays such as montmorillonite and bentonite by expanding the interlayer spacing.

The interlayer adsorption of polymers may be regarded as a special case which has been interested from the point of view of macromolecules in slit i.e. macromolecules in restricted dimensions as Daoud and de Gennes have suggested.[7,8]   In such a system, not only the information of adsorbed amount of polymer but also the knowledge of interlayer spacing expansion and polymer dimensions in the adsorbed state must be required.   Especially the latter information is very important to infer the conformation of polymers in the restricted dimension.   Parfitt and Greenland[6] have studied the intercalation adsorption of low molecular weight poly(ethylene oxide) (PEO) on montmorillonite, and reached the conclusion that the adsorption of PEO is driven by the increasing of entropy caused by liberation of preadsorbed water molecules.

Despite the adsorption studies of PEOs by clay minerals, the study of conformation of adsorbed polymers in the layers of clay minerals has not been reported.   The purpose of this article is to calculate the radii of poly(ethylene oxide) molecules, which has been intercalately adsorbed into the interlayer of calcium montmorillonite.

Calcium montmorillonite was used to avoid the electrostatic repulsive interaction between silicate layers.   From the molecular weight dependences of interlayer swelling and the radii of poly(ethylene oxide), the conformation of PEO is inferred.

Experimental

Materials

Clay Minerals: The montmorillonite was obtained from Nakarai Chemical Co. (Lot No. M4F 4169) as sodium form.   Calcium montmorillonite (Ca-M) was prepared as follows: an aqueous sodium montmorillonite (Na-M) suspension (20 g/100 ml) was mixed with H-form Amberlite IR-120 cation exchange resin and was converted to hydrogen form montmorillonite.   The hydrogen form montmorillonite (H-M) was separated from the resin and pH of the resultant suspension was 3.   The H-M suspension was neutralized by standardized calcium hydroxide solution, then Ca-M was separated by centrifugation, and dried in a vacuum oven at 180°C.
Poly(ethylene oxide):   Samples of poly(ethylene glycols) with average molecular weight from 400 to 9.96×10^5 were used.   Their suppliers and molecular characteristics are shown in Table I.
Water: Twice distilled water by a pyrex apparatus was used as solvent.

Methods

Adsorption procedure: Adsorption isotherms were determined by mixing 0.2 g Ca-montmorillonite with 7 ml of aqueous polymer solutions of different concentrations in polythylene tubes.   Normally after the tubes were shaken for 1 to 3 days at 25°C, equilibrium was reached for low molecular weight PEOs.   For high molecular weight PEOs ($Mw > 20 \times 10^3$) a shaking period of two weeks was required.   (See Figure 1). After equilibration the samples were centrifuged at 20,000 g for 20 min in a Kubota

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Table I. Molecular Characteristics and Suppliers of Poly (ethylene oxide)

Code and M_w		Degree of Polymerization, N	M_w/M_n	Supplier
PEo	400	9.1	—	Wako Pure Chemicals
	4,000	90.9	—	do.
	6,000	136.3	—	do.
	20,000	454.5	—	Katayama Chemical Co.
	86,000	1954	1.02	Tosoh Co.
	145,000	3295	1.03	do.
	594,000	13500	1.04	do.
	996,000	22636	1.06	do.

centrifuge in capped tubes. The supernatant was removed and the polymer concentration was determined from the measurements of refractive index increment by a Wood differential refractomer.

Amounts of polymer adsorbed A are expressed as g per g clay.

X-ray diffraction: Samples, which are dried, hydrated and then polymer adsorbed, are prepared. X-ray diffraction traces were obtained by using these samples, which were spreaded on glass plates and covered with a thin polyethylene terephtalate sheet. The traces were obtained by a Rigaku, Geigerflex RAD-1A using CuKα radiation. The unit cell dimensions for Ca-M (orthorombic) were $a = 0.520$, $b = 0.900$ and $c = 1.545$ nm, respectively.

Chemical composition of Ca-M was determined by the fusion method with Na_2CO_3[9]. The result was

$$(Si_{7.9}Al_{0.1})(Al_{1.84}Fe_{2.1}Mg_{0.51}Ca_{0.59}Na_{0.18}K_{0.01})O_{20}(OH)_4.$$
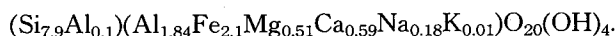
The unit-cell weight w for this formula is determined as 715.45, and the specific surface area S was calculated to be 788 m^2/g by using van Olphen's equation[10]

$$S = (1/w) \cdot 2 \cdot a \cdot b \cdot N_A \tag{1}$$

where a and b are unit cell dimension and N_A the Avogadro number.

RESULTS AND DISCUSSION

Figure 1 shows the time dependence of adsorbance of PEO with molecular weight 20,000. Adsorption of PEO proceeded stepwisely and to reach equilibrium. It is clear that 2 weeks are necessary. Below $Mw = 6 \times 10^3$, 1~3 days were sufficient to attain adsorption equilibrium. In Figure 2, the adsorption isotherms thus obtained are shown for samples with different molecular weight. Below $Mw = 6 \times 10^3$, the adsorption isotherms are Langmuir type, however, for samples above $M_w = 2 \times 10^4$, high affinity type adsorption isotherms are obtained. The plateau adsorbance A first increases with
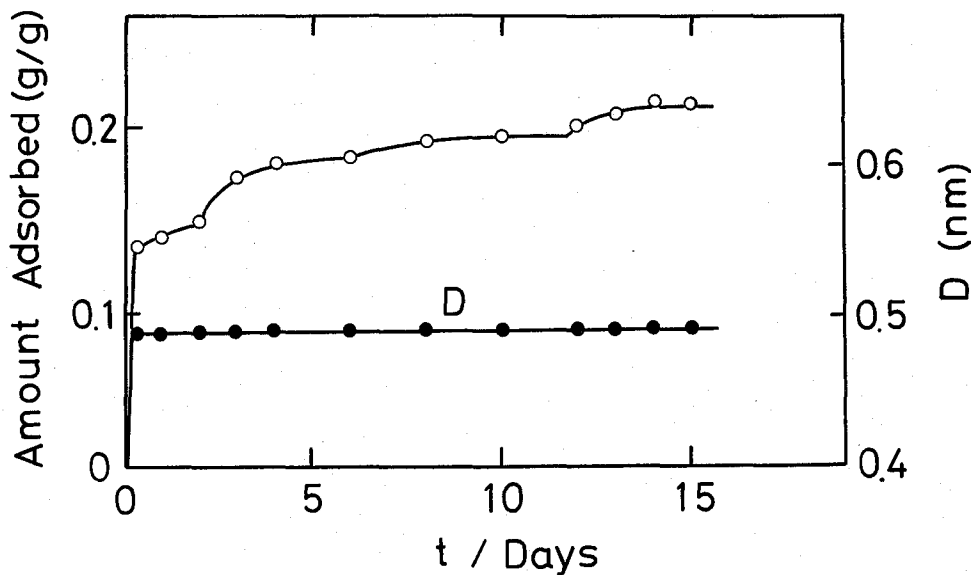
Figure 1. Time dependences of both amount adsorbed and interlayer spacing D for PEO 20,000 adsorbing on Ca montmorillonite at 25°C.
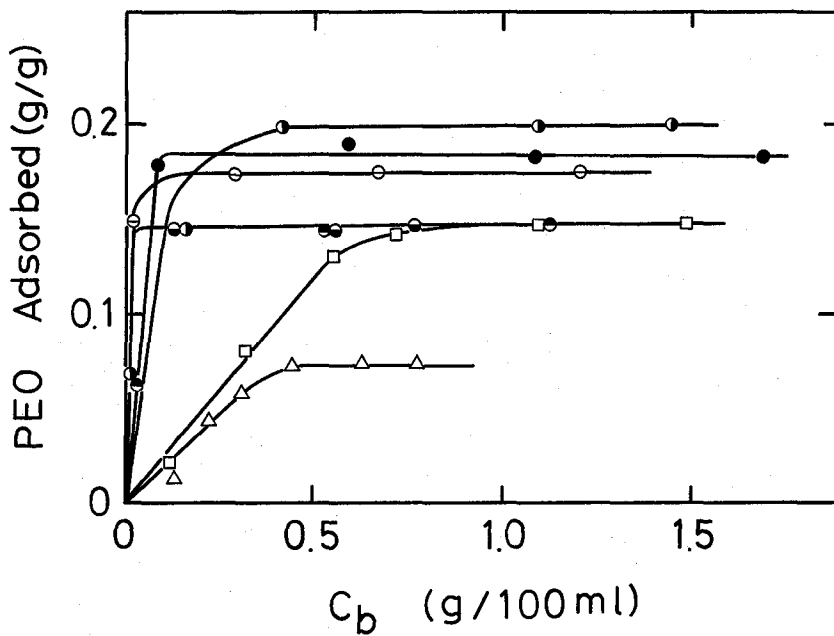

Figure 2. Isotherms for the adsorption of PEO 400, △; PEO 6,000, □; PEO 20,000, ◐; PEO 86,000, ●; 145,000, ⊖; PEO 594,000, ◓; PEO 996,000, ◒ on Ca montmorillonite at 25°C.

increasing molecular weight, showing maximum around $Mw = 2 \times 10^4$, then decreases slightly and eventually becomes independent on molecular weight above $Mw \simeq 6 \times 10^5$.

The amount adsorbed $0.15 \sim 0.20$ g/g of clay corresponds to the adsorbance $1.5 \sim 2.5 \times 10^{-8}$ g/cm^2, since 1 g clay has the specific surface area 788 m^2/g. The adsorbance is slightly lower than the adsorbance of PEO on silica particles from water.

With the proceeding of PEO adsorption, the basal spacing beetween 001 plane of Ca-M was also measured by X-ray diffraction. Figure 3 shows the shift of (001) peak of Ca-M. The peak in water moves to lower angle upon adsorption of PEO. The result clearly demonstrates the interlayer expansion or swelling of Ca-M and it is the evidence of intercalation adsorption. Denoting the basal plane spacing (i.e. d-spacing) of dry Ca-M as d_o ($=1.58$ nm) and the d-spacing of PEO adsorbed clay as d, then $D = d - d_o$ can be regraded as the measure of increase of interlayer spacing by adsorption. The time dependence of D is shown in Figure 1 and the result indicates that while A increases gradually with adsorption time, nevertheless D first steeply increases and then takes a constant value. This means that even the intercalation of a small number of PEO molecules is sufficient to increase the d-spacing from d_o to d.

The values of D evaluated at the plateau region of adsorbance for samples with
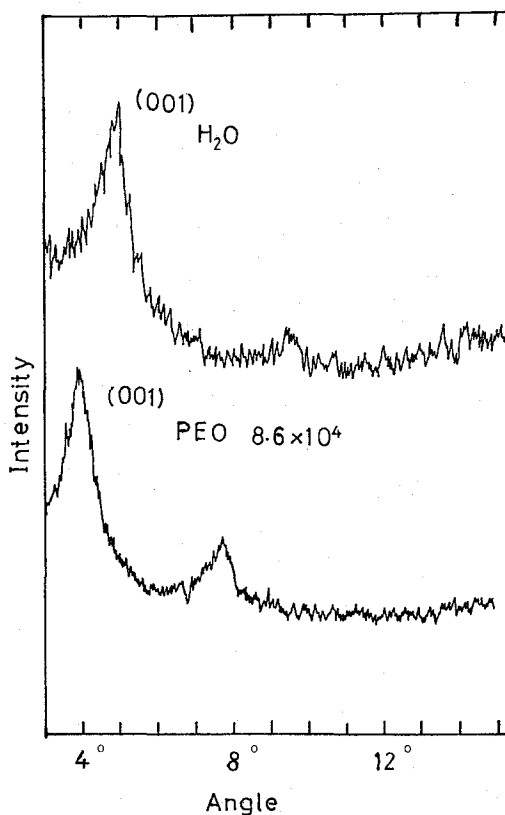

Figure 3. X-ray diffraction patterns of Ca montmorillonite (A) in water and (B) after adsorption of PEO 86,000.

different molecular weight are plotted against degree of polymerization N in Figure 4. Below $N = 10^3$, D increases with increasing N, however, above $N = 10^3$, D is about 0.7 nm and behaves as independent of molecular weight. Since D and S give the interlayer volume V per unit weight of clay and the adsorbed amount per g of clay gives the number of intercalately adsorbed PEO molecules, we can calculate the occupied volume v_a per PEO molecule. Since D is the order of monomer size, we may suppose to be the form of PEO molecules as a very thin disk of radius R_{F_2}, then v_a is given by

$$v_a = \pi R_{F_2}^2 D \tag{2}$$

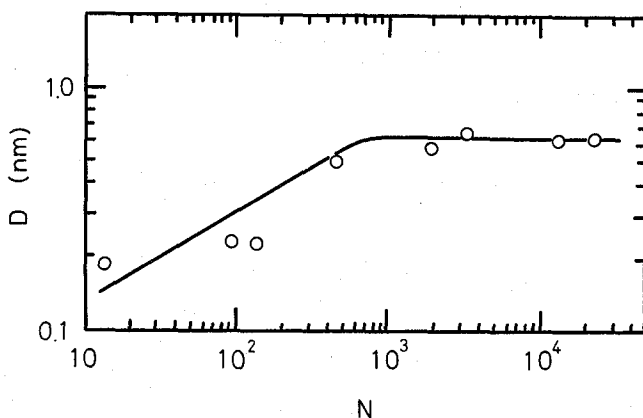In Figure 5, the calculated R_{F_2} is plotted against degree of polymerization N in

Figure 4. Interlayer spacing of PEO adsorbed on Ca montmorillonite plotted against degree of polymerization N of PEO.
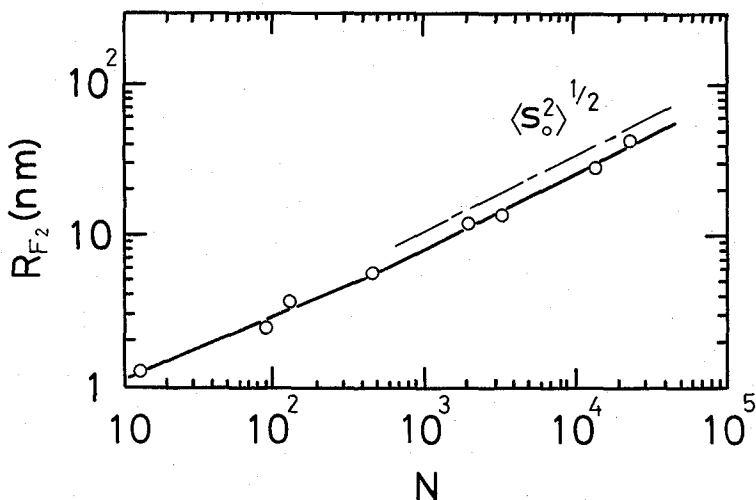

Figure 5. Chain length dependence of radii of intercaletely adsorbed PEO and the unperturbed radii of gyration in three dimension.

logarithmic scale. In the Figure 5, the unperturbed radii of gyration of PEOs evaluated by Flory equation from intrinsic viscosity measurements are also shown. Below $N = 10^3$, the slope of R_{F_2} vs. N plot is less than 0.5. However, above $N = 10^3$, $R_{F_2} \propto N^{0.5}$. Furthermore, the unperturbed radius of gyration is about 1.4 times larger than R_{F_2}.

The above result clearly demonstrates that the PEO molecules, whose molecular weight is as high as 10^6, can penetrate in the interlayer of clay and can expand it.

Furthermore, the affinity of PEOs for the clay surface, as can be judged from the initial slope of the isotherm, increases with increasing molecular weight. In order to understand the intercalation adsorption mechanism, the temperature dependence of adsorption isotherms were measured at 15° and 35°C, respectively. Following the procedure reported by Parfitt and Greenland,[6] when the adsorption follows a linear isotherm, as shown in Figure 6, C_A/C_b is constant (Km), where C_A is the concentration of polymer in the interlayer, C_b is the bulk concentration. Hence the equlibrium constant K_a is
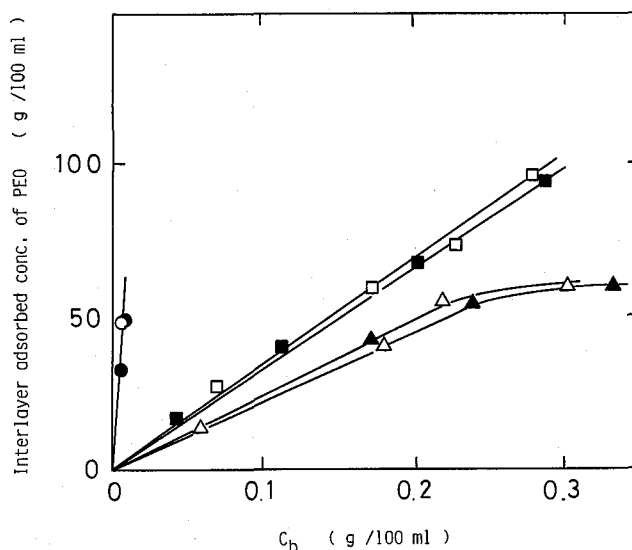

Figure 6. Initial slope of isotherms for the adsorption of PEO 400 at 35°C, △ and at 15°C; ▲; PEO 6,000 at 35°C, □ and ■ at 15°C; PEO 20,000 at 35°C, ○ and at 15°C, ● on Ca montmorillonite.

$$K_a = K_m \times \text{constant.} \tag{3}$$

surface concentration was calculated by using the adsorbance, the specific surface area, and the interlamellar distance calculated from the d spacing of polymer adsorbed clay.

Since $K_a = K_m \times C$, and the standard free energy $\Delta G°$ is geven by $-\Delta G° = RT\ln K_a$, $\Delta G° = \Delta G^m + C$. The non standard free energy ΔG^m was calculated by $RT\ln K_m$. The thermodynamic data of intercalation adsorption of PEO into the interlayer are summarized in Table II. The adsorption enthalpy is negative, i.e. exothermic as expected for

Table II. Non-standard Thermodynamic Data for the Adsorption of PEO by Calcium Montmorillionite

MW of PEO	15°C $-\Delta G^m$ cal/mol	35°C $-\Delta G^m$ cal/mol	$-\Delta H^m$ cal/mol	ΔS^m e.u.
400	783	821	716	0.34
6,000	3385	3621	1102	7.9
20,000	4698	5140	1674	11.5

adsorption process. On the other hand, the adsorption entropy is positive. In general, for adsorption of low molecular weight species from bulk to an interface, ΔS is usually negative. In case of intercalation adsorption of PEO, the total entropy change may be considered as the sum of two terms, the first is the conformational term ΔS^m_{conf} and the other is hydration term ΔS_H^m. Upon the intercalation adsorption of PEO, conformation is restricted and thus entropy is lost and this opposes the adsorption. On the other hand, ΔS_H^m term consists of (1) loss of water from the polymer, (2) desorption of water from the clay srface to bulk phase and (3) entropy of dilution of the bulk phase. As Parfitt and Greenland[6] already reported, it is considered that the most significant contribution to ΔS_H^m is probably (2). That is, the preadsorbed water molecules on the clay surface are released to the bulk phase. Since ΔS^m_{conf} is negative, ΔS_H^m should be positive and larger than $|\Delta S^m_{conf}|$. We may conclude that the intercalation adsorption of PEO is driven by entropical change, together with the adsorption enthalpy for which interaction between ether oxygen in PEO and clay surface is responsible.

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