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Adsorption of Polymeric Inclusion Compounds on Muscovite Mica

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ABSTRACT: α-Cyclodextrin, α-CD, which does not adsorb on mica, can be bound to this surface as a polymeric inclusion compound that is formed by threading many α-CD rings on a cationic polyelectrolyte, poly(decamethylenebipyridinium dibromide). The major driving force of the adsorption of the polymer and the polymeric inclusion compound is ion exchange with surface ions of mica. Somewhat less polymer is adsorbed when it is engaged in the inclusion complex than as pure polymer. The rates of adsorption for both the polymer alone and for the polymer in the inclusion compound depend strongly on the particular cation initially present at the mica surface (Li^+ or K^+); it is much more rapid with Li^+. The equilibrium between complexed α-CD and uncomplexed α-CD, found in solution, is modified upon adsorption of the complex to favor the release of α-CD from the complex. However, the α-CD is only slowly released from the complex on the surface and, as a result, mica-bound complex can be isolated.

Introduction

Cyclodextrins (CDs) have been known for a long time to include small molecules, called guests, in their molecular cavity.[1] This happens in aqueous solution, driven primarily by "hydrophobic interactions".[2] Recently, the nearly complete inclusion of polymer chains by many CD rings has also been reported,[3−6] where polymeric inclusion compounds resembling a necklace are formed (Figure 1). These are related to polyrotaxanes, a class of compounds with potential for interesting material properties.[7]

The thermodynamic stability of monomeric and polymeric CD inclusion compounds increases with the length of the hydrophobic segments of the guest.[4−6] Poly(ethylene glycol), poly(iminooligomethylene)s, and ionenes have been found to be suitable guests for α-CD. The rates of formation and dissociation strongly depend on the molecular structure of the guest,[8] and the process of threading α-CD onto a polymer chain might take between hours and several months. Often the process of dissociation is even slower, and these polymer inclusion compounds are, therefore, generally quite stable.[4−6] The adsorption behavior of polymeric inclusion compounds has not been previously studied. In particular, it is not known how the rings and the polymer influence each other.

In the present work, a poly(viologen), PV-10 (see Figure 2), and α-cyclodextrin (α-CD) form the inclusion complex. The substrate was a muscovite mica with ultrahigh specific surface area. Muscovite has a well-defined flat surface, well suited for the study of surface reactions, and it has inorganic cations at the surface.[9,10] Muscovite with ultrahigh specific surface area is obtained by chemical delamination of muscovite powders with $LiNO_3$.[11] As a consequence of this treatment, the mica contains lithium ions at the surface[10,11] that readily exchange with other inorganic ions, e.g., K^+, or with organic ions when the mica is treated with aqueous solutions of these ions.[10] Similarly, when a cationic polyelectrolyte is present in solution, adsorption via ion exchange can occur.[10]

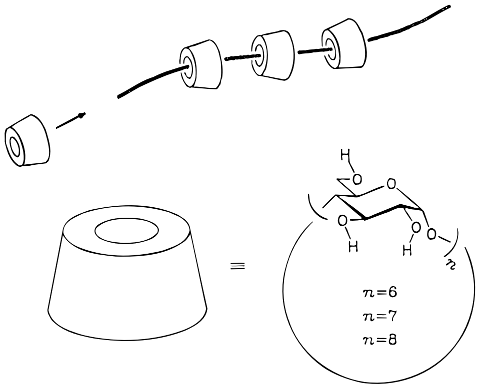

Figure 1. Schematic representation of a polymeric inclusion compound and the structure of α-CD (n = 6), β-CD (n = 7), and γ-CD (n = 8).

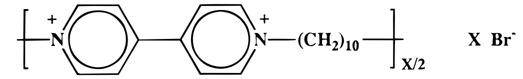

Figure 2. Chemical structure of PV-10.

The primary questions we wished to investigate were (i) whether the adsorption of a cationic polyelectrolyte inclusion compound proceeds in a manner analogous to that of the polyelectrolyte alone and (ii) whether through this method it is possible to attach rings to a surface that otherwise would not adsorb.

Experimental Section

Preparation of Poly(*N*-4,4′-bipyridinium-*N*-decamethylene dibromide) (PV-10). 4,4′-Bipyridyl [15.61 g (0.100 mol)] and 1,10-dibromodecane [30.01 g (0.100 mol)] were dissolved in 100 mL of methanol/*N*-methylformamide and stirred at room temperature for 10 days and thereafter at 50 °C for 3 days. The polymer was precipitated by pouring the reaction mixture into *tert*-butyl methyl ether (TBME), filtered, washed with TBME, and dried in vacuum. The product was

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dissolved in water and purified by dialysis against water for 1 day using a hollow fiber module. After dialysis, the resulting solution was frozen and freeze-dried at 50 °C in vacuum. The yield was 33.2 g (70%).

Analysis. Bromide content: 34.8%. ^{1}H-NMR (CD$_3$OD) (δ in ppm, J in Hz): 1.32−1.67 (m, 12 H), 2.07 (m, 4 H), 4.81 (t, 4 H, J = 6.8), 8.74 (d, 4 H, J = 6.8), 9.35 (d, 4 H, J = 6.8). ^{13}C-NMR (CD$_3$OD) (δ in ppm): 27.2, 30.0, 30.3, 32.5, 63.3, 128.4, 147.1, 151.3. IR (KBr) (w = weak, m = medium, s = strong): 3040 (m), 2920 (s), 2860 (m), 1550 (w), 1500 (w), 1450 (m), 1350 (w), 1225 (w), 1180 (m), 840 (m), 720 (w). The number-average degree of polymerization was 20, estimated from end group analysis by ^{1}H-NMR spectroscopy. The polymers were obtained by condensation and most probably have a polydispersity of 2.

Mica Delamination. The starting material consisted of mica fines supplied by Isola, Breitenbach (Switzerland), and designated by them as Mica 21. The delamination procedure was described previously.[10,12] Here, micas with specific surface areas of 101 and 104 m^2/g were used, as measured with methylene blue.[13−15]

The mica obtained by delamination contains Li$^+$ ions on the surface ("Li-mica").[10,11] Mica with K$^+$ surface ions ("K-mica") was prepared from the delaminated mica by ion exchange:[10] 3 g of delaminated mica was suspended in 35 mL of 1 M KNO$_3$ solution, the mixture stirred for 1 h, and the suspension filtered; this treatment of the mica was repeated twice. Finally, the mica was suspended in 100 mL of doubly distilled water, filtered, and dried.

Adsorption of PV-10 and PV-10-*complex*-α-CD. For adsorption studies, micas with lithium or potassium ions at the surface were used. The micas were suspended in aqueous solutions of PV-10 or of a mixture of PV-10 and α-CD. The initial concentrations were 2 mM with respect to α-CD and PV-10 (for PV-10, the concentrations are based on "constitutional repeat units").

All the adsorption experiments were performed with double distilled water. For experiments with PV-10 and α-CD in a ratio of 1:1, 1 mL each of 10 mM PV-10 and 10 mM α-CD stock solutions were pipetted into plastic tubes and diluted with water to 5 mL. The tubes were capped, and the solutions allowed to stand for 24 h. Then mica was added, the amount depending on the desired ratio of surface cations to polymer cations (the mica contains ca. 4 μmol of surface ions per m^2 [10]). After 24 h in the case of Li-mica and 8 days in the case of K-mica, the suspension was centrifuged in a Hettich Universal centrifuge at 4000 rpm for 10 min. A sample of the supernatant solution was removed with a pipette for analysis. For atomic absorption spectroscopy, the solution was filtered through syringe filters with a pore diameter of 0.45 μm (Nalgene Co., Rochester, NY).

The PV-10 concentrations in the supernatant solutions were determined by UV spectroscopy, and the α-CD concentrations by polarimetry (see the Results and Discussion section for details); the estimated errors are ca. 1%. The amounts of adsorbed PV-10 and α-CD were calculated from the differences between the concentrations in solution before and after adsorption.

Investigations were also carried out with PV-10 alone (i.e., in the absence of α-CD), with PV-10 and an excess of α-CD present (more than 1 α-CD molecule per viologen group), and in 1 M LiCl as solvent. The experiments were all carried out in the same way, except when large excesses of α-CD (5−20 times) were to be studied, where 50 mM (instead of 10 mM) α-CD stock solution was added.

Desorption Experiments. Mica (100 mg), with either adsorbed PV-10 or PV-10-*complex*-α-CD, was suspended in either 1.25 mL of water or 1.25 mL of 1 M LiCl solution. After 6 days, the suspension was treated by centrifugation and filtration, as described above. The filtrate was analyzed by UV spectroscopy and polarimetry.

Polarimetry. The optical rotation was measured on a Perkin-Elmer 241 polarimeter using a precision 10 cm quartz glass cuvette at a wavelength of 589 nm if not otherwise indicated and a temperature of 24 °C. To follow the formation of polymeric inclusion compound by the change in optical rotation of the α-CD, 1 mL of a 10 mM solution PV-10 and 1 mL of a 10 mM α-CD solution were added to 3 mL of water.

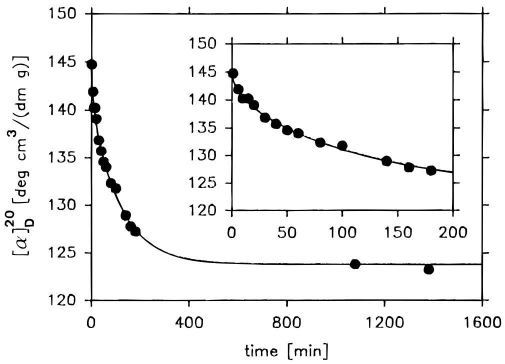

Figure 3. Optical rotation at 589 nm of a solution containing 2 mM α-CD and 2 mM PV-10 as a function of time. Lines represent a model fit (see text).

Table 1. Values for $[\alpha]^{20}_\lambda$ [deg·cm^3/(dm·g)] of a 2 mM α-CD Solution Containing Different Concentrations of PV-10 (*c*) at Different Wavelengths λ (after 24 h)

	$[\alpha]^{20}_\lambda$			
λ (nm)	c = 0	c = 1 mM	c = 2 mM	c = 3 mM
365	+430.9	+338.7	+313.2	+313.2
436	+286.7	+226.2	+213.7	+214.8
589	+147.0	+119.9	+112.5	+112.5

UV Measurements. UV spectroscopy was performed at a wavelength of 262 nm with a diode array spectrophotometer (Model 8542 A, Hewlett-Packard, Palo Alto, CA) using quartz glass cells with a path length of 1 mm. After each measurement, the cuvette was rinsed three times with water and once with acetone.

Atomic Absorption Spectroscopy (AAS). The supernatant solutions from the adsorption experiments (0.75−1.5 mL) were added to 10 mL of a solution containing 0.2 M HNO$_3$ and 0.02 M CsCl, and this solution was diluted with water to 20 mL. The AAS measurements were carried out by the analytical service group of the Laboratorium für Anorganische Chemie der ETH Zürich.

Results and Discussion

Inclusion Complex in Solution. The optical rotation of an α-CD solution depends on the wavelength of the light (see Table 1). Upon addition of PV-10, the optical rotation at a given wavelength decreases with time until a final value is reached. This is displayed in Figure 3, where the variation of optical rotation with time for the given initial concentrations of PV-10 and α-CD is shown. Since the optical rotation of cyclodextrins can change markedly when they include other molecules,[16] we attribute the changes observed with PV-10 to the formation of the polymeric inclusion compound. The line in Figure 3 is a model fit for one-dimensional Fickian diffusion of the rings along the chain and equilibrium at the chain end. The model is detailed in the Appendix and has two constants, the diffusion constant and the equilibrium constant, fitted to the data. The time dependence of the optical rotation suggests that, under the conditions used, it requires several hours to reach equilibrium in the formation of the inclusion compound. In consequence, the solutions were allowed to stand for at least 24 h to reach equilibrium at room temperature.

Equilibrium values of optical rotation for a total α-CD concentration of 2 mM and different total PV-10 concentrations are shown in Table 1. A solution of 2 mM

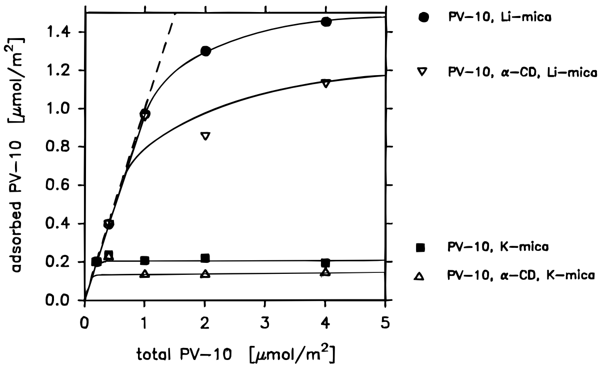

Figure 4. Adsorbed amount of PV-10 as a function of the total amount in the system after 24 h (Li^+) and 8 days (K^+). The dashed line represents a slope of unity.

each of α-CD and PV-10 displays an optical rotation significantly lower than pure α-CD at the same concentration, and addition of PV-10 to the solution does not lead to an additional decrease in optical rotation. It seems, therefore, that no additional α-CD is complexed for PV-10 concentrations above 2 mM. If it is assumed that every α-CD is complexed with a monomer unit, if the decrease in rotation in equilibrium depends linearly on the number of complexed α-CD per polymer chain, and if the equilibrium is established after 24 h, the fraction of complexed α-CD in a 2 mM equimolar solution, calculated from the values in Table 1, then is 0.8.

This value can be confirmed with ^{1}H-NMR spectroscopy: Some signals stemming from the inclusion compound change upon complexation, allowing the determination of the complexed fraction of α-CD.[4] The fraction of complexed α-CD determined by ^{1}H-NMR spectroscopy is 0.5 in a solution containing 2 mM α-CD (total) and 2 mM PV-10 (total). Putting higher confidence in the NMR determination, one must conclude that the assumptions taken for the calculation based on the optical rotation cannot all be in complete agreement with the real situation.

Polymer Adsorption. Mica readily adsorbs PV-10 from aqueous solution. The rate of adsorption is much faster for Li-mica than for K-mica. With Li-mica, adsorption equilibrium is reached within 24 h. With K-mica, equilibrium is not yet established after 8 days. On Li-mica, the kinetics cannot be measured quantitatively because significant adsorption takes place also during sample workup. On K-mica, the low amount of adsorbed polymer does not allow a precise determination of the kinetics.

In Figure 4, the amount of PV-10 adsorbed per m^2 in the system for Li-mica and for K-mica after 24 h and 8 days respectively, is displayed as a function of *a*, the total amount of PV-10 added per m^2 of mica in the system. The amount of adsorbed PV-10 is always less on K-mica than on Li-mica. While there is certainly a kinetic reason for the slow uptake of the polymer by K-mica, it might also be that the driving force in this case is significantly lower since potassium ions have a higher affinity (by a factor of ca. 80) for the mica surface than lithium ions.[10] An adsorbing polyelectrolyte molecule must, if the mechanism is ion exchange, compete with the existing surface ions for the surface ion exchange sites.

Quantitative adsorption of PV-10, where essentially all of the PV-10 added is taken up by the surface, is indicated in Figure 4 by a line of unit slope. This was observed with Li-mica for *a* values up to about 1 μmol/m^2, but, with K-mica, only for very low *a* values.

The ion exchange capacity of the mica is about 4 μmol/m^2.[10] For Li-mica, in Figure 4, there appears to be a maximum adsorption of about 1.5 μmol/m^2 PV-10 at high *a* values. With two ion charges per PV-10 monomer unit, the number of charges in the adsorbed polymer is not far from the ion exchange capacity of the surface (i.e., 1.5 μmol/m^2 of polymer constitutional repeat units adsorbed means 3 μmol charges/m^2, and the surface capacity is about 4 μmol charges/m^2), and a certain fraction of the charges in an adsorbed PV-10 chain are probably present in loops and tails and therefore not ion-exchanged.

With K-mica, the potassium ions released upon PV-10 adsorption were determined in the supernatant solution by atomic absorption spectroscopy for *a* values of 0.2, 0.4, and 1 μmol/m^2. Solutions containing PV-10 alone and also both α-CD and PV-10 (see below) were investigated. In all cases, ca. 0.65 potassium ion was found to be released per charge of adsorbed polymer. That less than 1 potassium ion is released per charge adsorbed may again be due to some of the charges being found in chain loops and tails and unable to exchange with the surface potassium ions.

With cationic polyelectrolytes on silicate minerals such as montmorillonite, it has been found that adsorbed chains lie predominantly "flat" on a surface.[9] Even at full coverage of the surface, not more than ca. 25% of the segments are present in loops and tails.[9] It is not clear, however, if similar behavior should be expected for mica, since with minerals such as montmorillonite, adsorption of the polymers in interlayers is likely to occur ("adsorption at an inner surface"),[9] while this is not expected for mica.[9] It has been claimed, on the other hand, that the loops and tails at low ionic strength are less probable for polyelectrolytes because of electrostatic repulsion of the chain segments.[17]

Complex Adsorption. The adsorption experiments were repeated for solutions containing both PV-10 and α-CD, and the results are also displayed in Figure 4. For high values of *a*, the amount of PV-10 adsorbed is significantly lower, for a given *a*, in the presence of α-CD than in its absence, at least for $a > 1$ μmol/m^2 in the case of Li-mica or $a > 0.5$ μmol/m^2 in the case of K-mica. That α-CD indeed was present as inclusion complex on the adsorbed polymer is indicated by the fact that α-CD was removed from solution upon the adsorption of PV-10. In contrast, in the absence of PV-10, α-CD is not adsorbed by either Li- or K-mica. The reduction of the propensity to adsorb is presumably the effect of α-CD rings threaded onto the adsorbed polymer. The rings could increase the separation between the positive charges on the polymer and the negative charges at the silicate layer and thereby weaken the ionic interactions. The affinity of the ions for the surface would thus be reduced, and the equilibrium would be less favorable to polymer adsorption. Other factors may also contribute to the reduced adsorption of polymer in the presence of α-CD.

For *a* values of 0.1−0.5 μmol/m^2 with Li-mica and of 0.1 μmol/m^2 with K-mica, 96−100% of the polymer present in the system is adsorbed. As a consequence, the α-CD remaining in solution is always to significantly more than 50% in the form of free α-CD. Hence, its concentration can be estimated from the optical rotation. For $a \geq 1$ μmol/m^2 with Li-mica and for $a \geq 0.2$ μmol/m^2 with K-mica, less than 40% of the total polymer

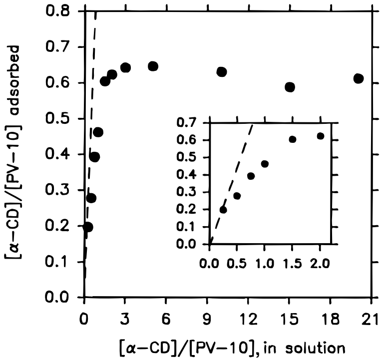

Figure 5. Ratio α-CD to PV-10 in the adsorbed material at different total ratios of α-CD to PV-10 ([PV-10] = 0.8 μmol/m^2). The dashed line has unit slope.

amount is adsorbed. Consequently, the calculation of the α-CD concentration becomes less precise because the optical rotation is strongly influenced by the presence of polymer, as is obvious from Table 1. The values reported below are only for cases where more than 95% of polymer is adsorbed.

For Li-mica, the ratio of α-CD to PV-10 in the adsorbed material (r_{CD}) is found to be 0.41−0.46, while for K-mica it is 0.13, i.e., clearly lower for K-mica than for Li-mica. At least the value for K-mica is well below the value of 0.50 found (as previously discussed) in solution, in the absence of mica, at concentrations of (total) 2 mM α-CD and 2 mM PV-10. Thus it appears that the equilibrium between free and complexed α-CD changes upon adsorption of PV-10-*complex*-α-CD to favor the release of α-CD from the complex.

In order to confirm that the ratio of [α-CD]/[PV-10] in the adsorbed material was determined, at least in part, by kinetic effects, mica containing adsorbed PV-10 was suspended in a 2 mM α-CD solution. The total amount of PV-10 in the system was equal to the total amount of α-CD. No adsorption of α-CD was observed within 12 days, and no desorption of PV-10 was detected. When mica with adsorbed PV-10-*complex*-α-CD was suspended in water or 1 M LiCl for 6 days, 3−5% of the adsorbed α-CD desorbed (no significant desorption of PV-10 was observed). Thus it appears that kinetic effects are indeed important, and it can be surmised that in adsorption equilibrium α-CD is more or less completely released from the complex.

In another series of experiments, the PV-10 concentration was kept constant (0.8 μmol/m^2), but the concentration of α-CD was varied. The PV-10 was adsorbed completely within the adsorption time (24 h), as confirmed by UV investigations of the supernatant solutions. Hence, fractionation of polymer molecules on the surface due to differences in chain length or fraction of complexed constitutional repeat units cannot occur.

The ratio of α-CD to PV-10 in the adsorbed material was determined from the change in α-CD concentration in solution. The results are displayed in Figure 5. The ratio r_{CD} increases with increasing [α-CD]/[PV-10] in the starting solution to a limiting value of ca. 0.6. The general principles of chemical equilibria imply that r_{CD} should increase upon increasing CD concentration up to a saturation value of 1. However, the data in Figure 5 seem to indicate that a plateau value of ca. 0.6 is reached at an [α-CD]/[PV-10] ratio of ca. 3. This suggests that, upon adsorption, α-CD is released from the chain; presumably the equlibrium changes upon adsorption of the inclusion compound to favor the release of the α-CD from the complex. As to the cause of this change in equilibrium, one could speculate that the attraction between the positively charged chain and the negatively charged surface in effect "squeezes" the rings off the chain, or that the release of rings is favored for entropic reasons.

Table 2. Processes with Polymeric Inclusion Compounds under the Experimental Conditions Indicated in the Text

	Li-mica	K-mica
inclusion of α-CD with PV-10		
in solution	equil	equil
at the surface	not equil	not equil
adsorption/desorption of polymer	equil	not equil

While changes in equilibria can account for many of the observations, kinetic effects appear to play an important role even for Li-mica (Table 2). In this view, the inclusion compound is adsorbed quickly onto Li-mica, "freezing" the rings on the polymer from which they are released only very slowly. In contrast, the adsorption is slow on K-mica, allowing the rings to desorb from the polymer at a rate comparable to the rate of adsorption, and as a result the system is closer to the equilibrium of the inclusion process in the adsorbed state (recall that the time required for adsorption of the complex was more than 8 days in the case of K-mica and not more than 24 h in the case of Li-mica).

From the adsorbed mass per area, an average layer thickness of 9 Å can be estimated for the polymeric inclusion compound on Li-mica in the plateau region, compared to ca. 0.8 Å on K-mica and ca. 4 and 0.6 Å, respectively, for PV-10 alone on Li-mica and K-mica, respectively. However, the thickness of the adsorbed layers is hardly uniform on a molecular level. Included cyclodextrin molecules and, maybe, loops and tails will give rise to an enhancement in the local thickness. It might be possible that the release of cyclodextrin molecules depends on the presence of loops and tails and the length of the PV-10 molecules. Considering the average layer thickness, the formation of loops and tails is not conclusive; i.e., the average thicknesses would agree with molecules adsorbed flat.

Experiments with Added LiCl. The expanded coil conformation of polyelectrolytes at low ionic strength can be transformed into that of a near-Θ coil form by addition of mineral salts.[17] The reduced repulsion between charged chain segments at high ionic strength could lead to the frequent formation of loops and tails in the adsorbed state,[17] and it has been found that the amount of adsorbed polyelectrolyte on mica can change when mineral salts are added.[17] Another possible effect upon addition of mineral salts stems from the competition for adsorption sites between the mineral salt's ions and the ionic groups in the polymer. To keep this latter effect to a minimum, LiCl was selected since the affinity of Li$^+$ ions for the muscovite surface is weak.[10]

Addition of LiCl in concentrations up to 1 M does not change the optical rotation of a 2 mM α-CD solution significantly, and the change in optical rotation upon addition of PV-10 is not significantly affected. When mica with adsorbed PV-10 or PV-10-*complex*-α-CD is suspended in 1 M LiCl for 6 days, the fraction of desorbed PV-10 is less than 1%, indicating that the affinity of the Li$^+$ ions is much below that of the polymer.

The adsorption from solution of PV-10 or a PV-10-*complex*-α-CD in the presence of 1 M LiCl leads to effects similar to those described for the experiments without LiCl: The adsorbed amounts are in the same range as without LiCl, and the presence of α-CD results in a decrease in adsorbed PV-10. It seems, therefore, that the expected change in conformation in solution at higher ionic strength is of minor importance with respect to the adsorbed PV-10.

Conclusions

Polymeric inclusion compounds can be used to bind molecules to surfaces that normally do not adsorb. This was shown for α-CD, which normally does not adsorb on mica but which can be bound to the surface via a polyelectrolyte inclusion compound. Polymer adsorbed whether or not α-CD was present, but the amount adsorbed is lower in the presence of α-CD. The presence of 1 M LiCl does not influence the adsorption process significantly.

At least with K-mica, the adsorption of PV-10 and of PV-10-*complex*-α-CD proceeds predominantly via ion exchange. The major fraction (ca. 65%) of the charges in the adsorbed polymer chains have exchanged with surface ions. Apparently, only a small fraction of the charges, 35% at most, are present in loops or tails; i.e., the chains must lie relatively flat on the surface.

In solution, at high [PV-10]/[α-CD] ratios, the rings are for the most part in the complexed form. When the complex is adsorbed on the surface, the equilibrium is shifted to favor free α-CD. The rings in the adsorbed complex detach only very slowly from the polymer chains, on a time scale of at least weeks. As a result, mica with adsorbed α-CD can readily be isolated. This is especially the case with Li-mica, where the adsorption of complex is much faster (complete within a few hours) than the detachment of the rings. In contrast, with K-mica, the adsorption of polymer is much slower (equilibrium requires several days), and, as a consequence, the ratio of α-CD to PV-10 in the adsorbed complex is lower.

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Appendix. Simulation Model for Inclusion Complex Formation

Inclusion complex formation in solution can be simulated with a computer model based on one-dimensional Fickian diffusion for the transport of rings along the chain and time-varying equilibrium at the chain end between uncomplexed rings and rings on the chain.

The diffusion of ring molecules along a chain is assumed to be given by eq A1, analogous to Fick's second law of diffusion:

$$\frac{\partial c}{\partial t} = \mathrm{D}\,\frac{\partial^2 c}{\partial x^2} \tag{A1}$$

Here c is the local "concentration" of rings on the chain expressed as the number of rings per chain repeat unit at point x measured from the chain end in chain repeat units, D is the linear diffusivity, assumed to be constant, and t is the time. Basically, what is sought is a solution of this equation giving $c = c(x,t)$ for the applicable initial and boundary conditions.

The rate-controlling step in inclusion complex formation is assumed to be diffusion of the rings along the chain. The chain ends are in that case essentially in equilibrium with the solution, with a ring concentration c_{eq}. It is assumed that the initial concentration of rings on the chains is 0. It is also assumed that diffusion takes place from both ends of the chain and that the concentration profile is symmetrical about the chain center. There is, therefore, no diffusion across the center and it is convenient to consider only half the chain, from $x = 0$ to $x = l/2$, where l is the chain length in repeat units. The initial and boundary conditions are then

$$\text{at } t = 0 \text{ and } 0 \le x \le l/2\text{:}\ \ c = 0$$

$$\text{at } t > 0 \text{ and } x = 0\text{:}\ \ c = c_{\mathrm{eq}}$$

$$\text{at } t \ge 0 \text{ and } x = l/2\text{:}\ \ \partial c/\partial x = 0$$

This system resembles diffusion into a plane sheet from a stirred solution of limited volume, and a number of analytical (series) solutions of this problem have been presented in the literature.[18] It may be possible to obtain an analytical solution for the present system in a similar way. However, numerical solution of the relevant system of equations by computer using a dynamic simulation program[19] is convenient and was used in the present study.

For computational convenience, the chain was conceptually divided into 40 "segments", i.e., 20 segments between chain end and chain center, each of length $\Delta x = l/40$. As the polymer had ca. 20 constitutional repeat units per chain, each segment represents about half a repeat unit. The change of ring concentration in a given segment i per unit of time $\Delta c_i/\Delta t$, is determined using a stepwise linear approximation to eq A1:

$$\frac{\Delta c_i}{\Delta t} = D\,\frac{(c_{i-1} - c_i) - (c_i - c_{i+1})}{\Delta x^2} \tag{A2}$$

In particular, from the boundary conditions, for the segment at the chain end ($i = 1$), $c_{i-1} = c_{\mathrm{eq}}$ and for the segment at the chain center ($i = 20$), $c_i - c_{i+1} = 0$.

To calculate c_{eq}, it is assumed, for simplicity, that the complex formation reaction can be represented by

$$\mathrm{C} + \mathrm{P} \rightleftharpoons \mathrm{CP} \tag{A3}$$

where C represents the (cyclodextrin) rings, P the polymer chain repeat units, and CP the inclusion complex (a repeat unit complexed with a ring), i.e., that one repeat unit complexes with at most one ring. The equilibrium constant K will then be given by

$$K = \frac{x_{\mathrm{CP}}}{x_{\mathrm{C}}x_{\mathrm{P}}} \tag{A4}$$

where x_{CP}, x_{C}, and x_{P} are respectively the mole fractions of CP, C, and P in the solution at equilibrium. For dilute solutions, in good approximation,

$$x_i \approx [\mathrm{i}]/[\mathrm{L}] \tag{A5}$$

where [i] refers to the amount of substance concentration of species i and L represents the solvent (in this case water with [L] = 55.5 mol/L). Substituting eq A5 into eq A4 gives

$$K = \frac{[\mathrm{CP}][\mathrm{L}]}{[\mathrm{C}][\mathrm{P}]} \tag{A6}$$

The value of c at the chain end, c_{eq}, will then be given by

$$c_{eq} = \frac{[CP]_{eq}}{[P]_{eq} + [CP]_{eq}} \tag{A7}$$

where the right-hand side of eq A7 refers to concentrations at *equilibrium*, i.e., in the relationship fixed by eq A6. Combining eqs A6 and A7 gives after rearrangement

$$c_{eq} = \frac{K[C]}{[L] + K[C]} \tag{A8}$$

Note that c_{eq} will lie in the range 0 to 1, the value depending on the magnitude of K and [C]. Naturally, as the complex forms, with rings diffusing onto and along the chain molecules, [C] decreases, together with c_{eq}. [C] (as well as [P]) at any given time can be found from [CP] by material balance. [CP] is obtained from

$$[CP] = \langle c_i \rangle([P] + [CP]) = \langle c_i \rangle [P_{tot}] \tag{A9}$$

where $\langle c_i \rangle$ is the mean value of c along the chain. The sum $[P] + [CP] = [P_{tot}]$ represents the concentration of chain repeat units, complexed or uncomplexed, and is a constant. The above set of simultaneous equations can then be solved numerically to obtain c as a function of x and t, and [C], [P], and [CP] as a function of t.

The optical rotation of the rings in solution when a fraction of the rings is inclusion-complexed, for the case where total repeat unit concentration and total ring concentration are both 2 mmol/L, is assumed to be given by

$$[\alpha]_D^{20} = 145\frac{[C]}{[C] + [CP]} + 113\frac{[CP]}{[C] + [CP]} \tag{A10}$$

(Determination of the optical rotations for the uncomplexed rings alone and for the complexed rings alone is discussed in the text.) Thus from the [C] and [CP] values obtained by simulation for a given set of K and D values, a plot of optical rotation against time can be generated. The model values of optical rotation can then be compared with the experimentally determined values and, using a suitable search algorithm, the values of K and D providing the best fit can be determined. In the present work, the search algorithm for the best fit values of K and D was Nelder–Mead with fifth-order Runga–Kutta–Fehlberg as the integration algorithm. The dynamic simulation program was SimuSolv (Dow Chemical, Midland, MI).

From the data fit, we found $K = 2.4 \times 10^5$ and $D = 7.8 \times 10^{-3}$ (repeat unit)^2/s. As the length of a repeat unit measured along the chain backbone is ca. 25 Å, this corresponds to $D \approx 48$ Å^2/s $\approx 5 \times 10^{-15}$ cm^2/s. In Figure 3, the experimental values of optical rotation and the simulated values obtained with the fitted constants are plotted against time.

Given the assumptions made and the discrepancy discussed in the text between the NMR and optical rotation data, the values of K and D can be regarded as only rough estimates. However, the good fit of the model to the data displayed in Figure 3 shows that this type of model can at least qualitatively describe the complex formation process.

References and Notes

(1) Saenger, W. *Angew. Chem.* **1980**, *92*, 343.
(2) Schneider, H.-J. *Angew. Chem.* **1991**, *103*, 1419.
(3) Harada, A.; Kamachi, M. *Macromolecules* **1990**, *23*, 2821.
(4) Wenz. G.; Keller, B. *Angew. Chem.* **1992**, *104*, 201.
(5) Keller, B.; Wenz. G. In *Minutes of the 6th International Symposium on Cyclodextrins*; Hedges, A. R., Ed.; Editions de Santé: Paris, 1992.
(6) Wenz, G.; Keller, B. *Polym. Prepr.* (*Am. Chem. Soc., Div. Polym. Chem.*) 1993, *34* (1), 62.
(7) Gibson, H. W.; Marand, H. *Adv. Mater.* **1993**, *5*, 11.
(8) Saito, H.; Yonemura, H.; Nakamura, H.; Matsuo, T. *Chem. Lett.* **1990**, 535.
(9) Theng, B. K. G. *Formation and Properties of Clay–Polymer Complexes*; Elsevier: Amsterdam, 1979.
(10) Shelden, R. A.; Caseri, W. R.; Suter, U. W. *J. Colloid Interface Sci.* 1993, *157*, 318.
(11) Caseri, W. R.; Shelden, R. A.; Suter, U. W. *Colloid Polym. Sci.* **1992**, *270*, 392.
(12) Meier, L. P.; Shelden, R. A.; Caseri, W. R.; Suter, U. W. *Macromolecules* **1994**, *27*, 1637.
(13) Blake, P.; Ralston, J. *Colloids Surf.* **1985**, *15*, 101.
(14) Giles, C. H.; Trivedi, A. T. *Chem. Ind.* **1969**, *40*, 1426.
(15) Hang, P. T.; Brindley, C. W. *Clays Clay Miner.* **1970**, *18*, 203.
(16) Schlenk, C. D.; Sand, D. M. *J. Am. Chem. Soc.* **1961**, *83*, 2312.
(17) Davies, R. J.; Dix, L. R.; Toprakcioglu, C. *J. Colloid Interface Sci.* **1989**, *129*, 145.
(18) Crank, J. *The Mathematics of Diffusion*; Oxford University: Oxford, 1975.
(19) Ingham, J.; Dunn, I. J.; Heinzle, E.; Prenosil, J. E. *Chemical Engineering Dynamics. Modelling with PC Simulation*; VCH: Weinheim, 1994.

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