Colloid & Polymer Science Colloid Polym Sci 272:986–990 (1994)

Adsorption of polymers with crown ether substituents on muscovite mica

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Abstract: Ultrahigh specific surface area muscovite with different ions at the surface (Li^+, Na^+, K^+, Rb^+, Cs^+, Ca^{2+}, Sr^{2+}, Ba^{2+}, Cu^{2+}) was treated with aqueous solutions of low molecular weight crown ethers and polymers with crown ether substituents. The adsorption was assessed by UV analysis of the supernatant solution, and with TGA and IR spectroscopy of the mica solids. In contrast to other layered silicates, the low molecular weight crown ethers show no affinity to any of the muscovite surfaces. The polymers can adsorb, however, depending on the type of surface cation. The results indicate that at least some of the crown ether moieties are complexed to surface cations and that the diameter of the ions at the surface plays an important role in the adsorption process.

Key words: Adsorption – muscovite mica – polymers – crown ethers

Introduction

Due to its well defined, flat surface [1], muscovite mica is a suitable substrate for surface studies [2, 3]. Recently, a muscovite mica with ultrahigh specific surface area (100 m^2/g and more) has been prepared [4] that is well suited for surface studies [5, 6]. It is obtained by chemical cleavage of muscovite particles with $LiNO_3$ and, as a consequence, has lithium instead of potassium ions at the surface [4, 6]. These lithium ions can be exchanged by treatment of the muscovite with aqueous solutions containing other ions [6].

Crown ethers are neutral, multidentate ligands that coordinate to a variety of metal ions, including alkaline ions [7–10]. Low molecular weight crown ethers form complexes with metal ions in layered silicates, such as montmorillonite, hectorite or vermiculite, that are saturated with lithium, sodium, potassium, calcium, barium or copper ions [11–17]. The crown ethers form intercalation complexes with these minerals [12–17] that can be so strong that the crown ethers do not desorb by treatment with water, salt solutions or organic solvents [12, 13].

While intercalation of organic compounds is frequently found for several layered silicates [18–21], this is not common for muscovite [22]. In contrast to minerals that participate in intercalation processes, the entire muscovite surface is accessible to the reaction partners "immediately," and the space limitations in intercalation processes are not relevant for studies with muscovite.

Polymers with crown ether functionalities have not been applied to minerals, to our knowledge, but their preparation and complexing behavior with alkaline or earth alkaline ions has been described [9, 11]. Crown ether monomers have been synthesized on the basis of styrene (vinylbenzo crown ethers), and they have been polymerized with radical initiators (9, 11, 23]. In the following, we report on adsorption experiments with low molecular weight crown ethers and polymers with crown ether functionalities on muscovite with different ions at the surface.

Experimental

Crown ether compounds

Benzo-15-crown-5 was purchased from Fluka, Buchs (Switzerland). 4′-Vinylbenzo-15-crown-5 (VB15C5) and poly(4′-vinylbenzo-15-crown-5)

(PVB15C5) were prepared according to the literature [11]. The number-average molecular weight (determined by vapor osmometry) of a "short" polymer obtained by radical polymerization was $4.3 \cdot 10^3$, and the weight-average of the molecular weight (determined by light scattering) was $1.1 \cdot 10^5$ for a "long" polymer.

Preparation of the mica

The preparation of mica with ultrahigh specific surface area has been described previously for amounts in the mass range of 15 g by chemical treatment of mica powders with lithium salts [24]. The specific surface areas of the resulting mica is typically 100–110 m^2/g (determined by methylene blue adsorption [4, 6, 25]). That of the mica used here was 108 m^2/g.

For surface cation exchange, 1 g cleaved mica was stirred for 1 h in 40–60 ml of a 1 M solution of the chloride salt of the metal to be exchanged. The mica was filtered and stirred again for 1 h in 40–60 ml of a 1 M solution of the salt. The mica was filtered, washed four times with 8 ml of bidistilled water, and dried over KOH at ca. 100 torr for 48 h.

Adsorption of crown ether compounds

Low molecular weight crown ethers were adsorbed from 5 ml of a 0.26 mM VB15C5 solution or 0.52 mM B15C5 solution, respectively, in which 50 mg (in the cases of monovalent surface cations) or 100 mg (in the cases of bivalent surface cations) of mica were suspended. The solutions were stirred for 4 h. For adsorption experiments with polymers, 15–180 mg mica and 4–250 ml of a 0.46 mM (monomer units) solution were stirred for 7 d.

The solutions of the "long" polymer were close to saturation. Occasionally, polymer precipitated from the adsorption solution, especially when the solution was stirred or shaken. Since the polymer is more soluble at lower temperatures, the suspensions were cooled to 7 °C during 3 h before analysis and then allowed to warm up to room temperature during 3 h without stirring or shaking. The cooling was sufficient to dissolve precipitated polymer, if present.

Desorption of crown ether compounds

100 mg mica containing adsorbed polymer were suspended in 5 ml water and shaken in a mechanical shaker for 3 d. After centrifugation, the supernatant solution was examined by UV spectroscopy, and the mica was filtered and analyzed by thermogravimetric analysis.

UV and thermogravimetric analysis

Solution concentrations were measured by UV spectroscopy at the wavelength of maximum absorption of light, i.e., at 290 nm for VB15C5 ($\varepsilon = 4700\ M^{-1}cm^{-1}$), at 274 nm for B15C5 ($\varepsilon = 2270\ M^{-1}cm^{-1}$) and at 280 nm for PVB15C5 ($\varepsilon = 2450\ M^{-1}cm^{-1}$) using a Hewlett-Packard Diode Array Spectrophotometer, Model 8542 A.

Thermogravimetric analyses (TGA) were performed under nitrogen on a Perkin-Elmer TGA 7 with a heating rate of 20 °C/min.

Results

Adsorption experiments were performed with benzo-15-crown-5 (B15C5), 4′-vinylbenzo-15-crown-5 (VB15C5) and poly(4′-vinylbenzo-15-crown-5) (PVB15C5) (Fig. 1). Among the alkaline ions, the affinity of these crown ethers is expected to be strongest to potassium and weakest to lithium ions [9, 11]. A "short" polymer with $M_n = 4.3 \cdot 10^3$ and a "long" polymer with M_w of $1.1 \cdot 10^5$ were prepared according to the literature [11]. Since the crown ethers absorb in the UV region, the adsorption on mica was monitored by UV spectroscopy of the supernatant solution and confirmed qualitatively by infrared spectroscopy and quantitatively by thermogravimetric analysis (TGA) of the mica after filtration.

The Li^+ ions present on the ultrahigh specific surface area muscovite [4, 6] were exchanged with Na^+, K^+, Rb^+, Cs^+, Ca^{2+}, Sr^{2+}, Ba^{2+}, and Cu^{2+} ions and adsorption experiments with the crown ether compounds were conducted. No adsorption of VB15C5 was found with any of these ions, neither by UV spectroscopy of the supernatant solution nor by TGA of the solids. B15C5 was applied to mica with Na^+ and K^+ ions on the surface, and no adsorption was found, either. For the polymers, adsorption could be detected, particularly on the micas with K^+, Rb^+ and Ba^{2+} ions at the surface (Table 1.). No difference in adsorbed

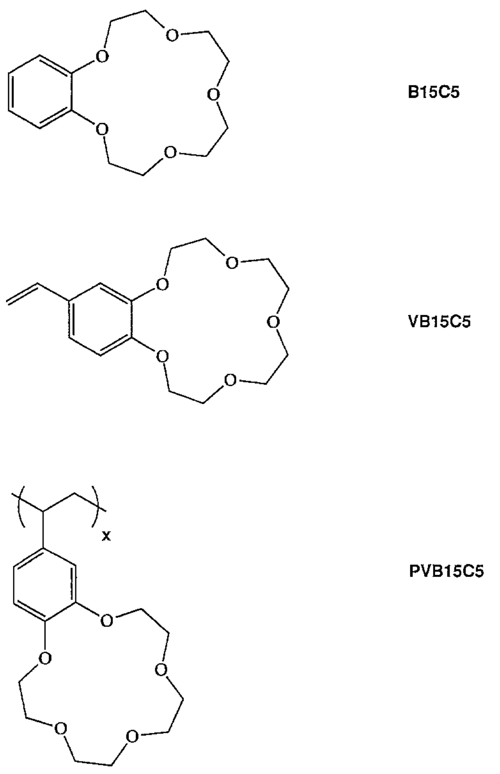

Fig. 1. Formula schemes of benzo-15-crown-5 (B15C5), 4′-vinylbenzo-15-crown-5 (VB15C5) and poly(4′-vinylbenzo-15-crown-5) (PVB15C5).

Table 1. Ionic radii [26], r, adsorbed amount of poly (4′-vinylbenzo-15-crown-5) ($M_n = 4.3 \cdot 10^3$) per surface area of mica, Γ, and adsorbed amount of polymer as a fraction of the total amount of polymer in the system, q, when adsorption was performed from 5 ml of a 0.462 mM (monomer units) solution containing 25 mg of muscovite.

	r[pm]	Γ [μmol/m^2]	q [%]
Li^+	68	≤ 0.05	≤ 6
Na^+	97	0.08	9
K^+	133	0.21	27
Rb^+	147	0.26	34
Cs^+	167	0.12	13
Ca^{2+}	99	≤ 0.05	≤ 6
Sr^{2+}	112	≤ 0.05	≤ 6
Ba^{2+}	134	0.13	15
Cu^{2+}	72	≤ 0.05	≤ 6

mass was found between adsorption times of a few hours and several days. The following results refer to adsorption times of 7 days, and it is assumed that equilibrium has been established in this period.

Infrared spectra of the polymer-treated micas confirmed the presence of adsorbed poly (4′-vinylbenzo-15-crown-5). No significant band shifts were observed compared to the spectra of films of the pure polymers in the range of 1300–4000 cm^{-1} (below 1300 cm^{-1}, an analysis is prevented by the strong absorptions of the mica bulk).

Thermogravimetric analysis (TGA) of the pure polymers shows a weight loss at 450 °C. The adsorbed polymers obviously decompose at 400 °C. The weight loss at 400 °C is in agreement with the amounts of adsorbed polymer expected from UV measurements of the supernatant solutions. Occasionally, a second TGA peak was found close to the decomposition temperature of the pure polymer. This second peak, however, is not reproducible. Addition of 11 mg "short" PVB15C5 to 60 mg of mica with Ba^{2+} ions at the surface yields, after intense mixing with mortar and pestle, the weight loss characteristic for the pure, non-adsorbed polymer. It seems, therefore, that the above-mentioned peak at 400 °C is characteristic for the adsorbed polymer, while the peak at higher temperature, occasionally found after adsorption of the polymers, is most likely due to precipitated bulk polymer adventitiously present on the filtered mica.

A theoretical treatment of the adsorption process would be complex. In addition to the fact that the polymers are polydisperse, polymer chains with the same number of monomer units could coordinate by different numbers of crown ether moieties, thus leading to a superposition of many equilibria with unknown and different equilibrium constants. However, the affinity of the polymers to the surface may be demonstrated qualitatively by plotting the total amount in the system of polymer/m^2 mica surface, a, vs. the adsorbed amount of polymer/m^2 mica surface, Γ [6]. Figure 2 displays Γ as a function of a for the "long" polymer on mica with K^+ ions at the surface; Ba^{2+} at the surface yields identical results, the "short" polymer identically shaped curves. In all cases, Γ increases rapidly with increasing a until a plateau is reached. The plateau is higher for the "long" polymer (ca. 0.4 μmol monomer units/m^2).

Desorption of the adsorbed polymer was investigated by immersing samples in water for

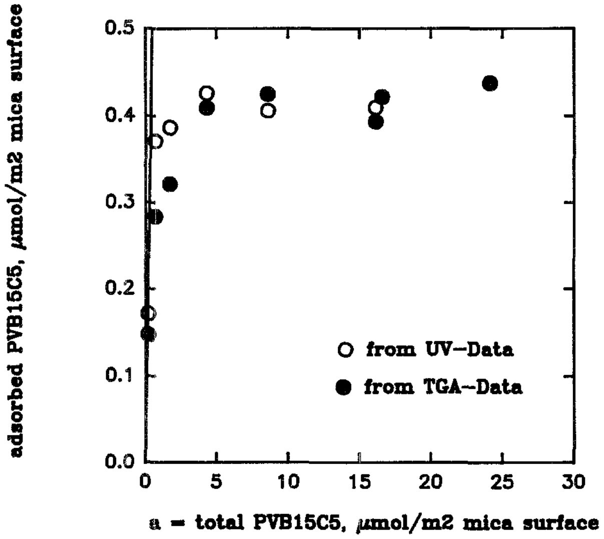

Fig. 2. Total amount in the system of polymer/m^2 mica surface, *a*, vs. adsorbed amount of polymer/m^2 mica surface, Γ, for poly (4'-vinylbenzo-15-crown-5) (PVB15C5, $M_w = 1.1 \cdot 10^5$) on muscovite with K^+ ions at the surface. The straight line is of slope 1 and represents complete adsorption.

3 days. The desorption process was followed by UV analysis of the supernatant solution and TGA of the remaining mica. During the observed period, ca. 30% of the "short" and ca. 3% of the "long" polymer desorb on mica with potassium ions at the surface, and the corresponding values for the mica with barium ions at the surface are ca. 20% for the "short" as well as for the "long" polymer.

Discussion

No adsorption of low-molecular weight crown ethers was found on mica, in contrast to reports on related systems involving montmorillonite, vermiculite or hectorite [11–17]. This is probably due to the different behavior of mica and these other minerals: Organic molecules commonly intercalate in interlayers of vermiculite, montmorillonite or hectorite, but not in mica (see Introduction), where the adsorption process is usually limited to the surface at room temperature. It seems that the equilibrium between VB15C5 adsorbed on the surface and in solution is strongly on the solution side.

The adsorbed amount of polymer depends on the surface ions. This indicates that the surface ions are strongly involved in the adsorption process, i. e., that van-der-Waals interactions are not of prime importance for the difference in the behavior of VB15C5 and the polymers. Extraction of cations from PVB15C5-complexes with picrate salts are reported to have yielded relative complexing strengths of cations with PVB15C5 in the order $K^+, Rb^+ > Cs^+ > Na^+, Ba^{2+} > Li^+$ [11]. This ranking is similar to that of the mass of adsorbed polymer on the corresponding adsorbed cations, where an increased amount of adsorbed polymer is found in the order K^+, $Rb^+ > Cs^+ >$ Na^+, $Ba^{2+} > Li^+$ (Table 1). This is consistent with the assumption that at least a part of the crown ether moieties in the polymers is complexed to the ions at the surface. When the size of the ions is compared, an optimum in polymer adsorption is found for ions with a radius in a range of ca. 130–150 pm (Table 1). The ion radius is known to play a crucial role in the complexing behavior of crown ethers [9, 12–15]. The ionic charge seems to be immaterial.

It seems that the affinity of a single crown ether moiety to mica surfaces is low since the low molecular weight compounds do not adsorb on mica with any of the surface ions investigated here. Hence, the adsorption of the polymers is due to the large number of coordination sites per molecule or to solubility effects (the solubility is in the order monomer > "short" polymer > "long" polymer).

The plateau values observed for the "short" polymer (ca. 0.25 μmol/m^2) differ from those for the "long" polymer (ca. 0.4 μmol/m^2). They are far below the ion density on the muscovite surface (ca. 4 μmol/m^2 [6]). Since it is not certain that the apparent plateau represents saturation of the surface, it is imaginable that much higher concentrations than those used here could lead to higher amounts of adsorbed polymer; however, since the solubility of the polymer is limited, this possibility cannot be pursued.

The plateau values seem to be determined by the chain length of the polymer rather than the ions present at the surface. This could be explained by formation of loops: Due to the higher number of coordination sites in the "long" polymer, those chains could be adsorbed even if a relatively large number of crown ether moieties per polymer molecule does not coordinate to surface ions. This would lead to an increase in the amount of adsorbed polymer with higher chain length.

Acknowledgements

We would like to thank Dr. Peter Schurtenberger and Martin Colussi for determining the molecular weights of the polymers. We also gratefully acknowledge financial support for this work through the (Swiss) Kommission zur Förderung der wissenschaftlichen Forschung (KWF) and the (Swiss) Schwerpunktprogramm Werkstofforschung (SPWF) as well as stimulating discussions with several members of the Research Divisions of the Schweizerische Isola-Werke, Breitenbach (Switzerland), and Asea Brown Boveri, Baden (Switzerland).

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Received October 12, 1993
accepted October 27, 1993

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