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ORIGINAL CONTRIBUTION

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The structure of chiral phenylethylammonium montmorillonites in ethanol-toluene mixtures

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Abstract Chiral phenylethyl alkylammonium montmorillonites were prepared by ion exchange of Na montmorillonite (from Wyoming). The structure of chiral montmorillonite organocomplexes was studied in the dry state by X-ray diffraction, IR spectroscopy and ^{13}C cross-polarized MAS NMR and after swelling by X-ray diffraction. The phenylethylammonium ions are intercalated in montmorillonite in a monolayer structure, while higher derivatives containing alkyl chains with lengths of $n_c = 10-16$ take up a bilayer orientation. The hydrophobized clay mineral is readily dispersed in organic solvents, for example in ethanol, toluene and their binary mixtures. Due to selective adsorption, the liquids penetrate into the interlamellar space under significant interlayer expansion producing a great variety of alkyl chain orientations within the interlamellar space, depending on the length of alkyl chains and on the mixture composition. Such interlamellar spaces are possible chiral nanoreactors with adjustable volume and may be prospectively utilized for shape-selective catalytic reactions and the production of enantiomers.

Key words Chirality – Clay organocomplexes – Intercalation – Nanophase reactors – Binary liquid mixtures – X-ray diffraction

Introduction

Despite the large number of important chiral pharmaceuticals and agrochemicals there is still growing interest in developing new synthetic routes for the preparation of these compounds. Due to environmental considerations extensive efforts involving asymmetric synthesis have been carried out to replace the sensitive soluble metal complexes and to design chiral heterogeneous catalysts. Clay minerals are one of the most promising candidates for this purpose, especially montmorillonites, which have relatively high acid strength [1] and are excellent catalysts for electrophilic organic reactions [2]. Due to the structural character of clay minerals their properties can be modified by ion exchange or intercalation [3]. Both processes are excellent methods for immobilizing organic modifiers on the surface or in the interlamellar space. As a result, modification of clay minerals by organic compounds [4–13] is one of the most popular research areas in clay chemistry. Swelling layer silicates are especially easy to hydrophobize using organic cations (alkylammonium, alkylpyridinium), exchanging Na^+ or Ca^{2+} ions of montmorillonite for organic cations [3–9]. The structure of the resulting clay mineral organocomplexes is determined primarily by the length of the alkyl chains and the charge density of the mineral [4–8]. The structure of the organocomplexes changes significantly when the samples are dispersed in liquids, since liquid molecules penetrate into the hydrophobized lamellae, into the so-called interlamellar space, and the organocomplex swells. As a consequence of swelling, the lamellae move apart and their distance can be determined by X-ray diffraction [10–12]. Depending on the polarity of the liquids, the extent of swelling may vary over a wide range. Swelling is most extensive in

aromatic solvents, while in alcohols it is limited: the process should rather be termed as interlamellar sorption of alcohols. It has been pointed out by Dékány and coworkers [8–12] that in binary mixtures of aromatic solvents and alcohols interlamellar swelling is a function of the mixture composition.

It is surprising that this idea was only sporadically applied for the preparation of chirally modified clay minerals. The examples are related to the intercalation of chiral metal complexes and their use in hydrogenation reactions [14, 15]. However, we are not aware of any data with respect to the modification of clays with chiral compounds concerning the development of new chiral solid acid catalysts or chiral supports for heterogeneous catalytic processes.

In the present paper we disclose the modification of the well-known Wyoming montmorillonite using enantiomerically pure ammonium salts. As a consequence of the chirality of the ammonium-clay mineral complexes prepared, enantioselective reactions are expected to occur in the interlamellar space through preferential adsorption of the reaction partners. An additional aim of the present work is to develop an interlamellar reactor of adjustable volume containing (*R*)–(+) enantiomers of alkylammonium derivatives with various chain lengths. Interlamellar distances can be controlled by the composition of the liquid phase, allowing the realization of shape-selective reactions.

Experimental

Materials

(*R*)- and (*S*)-1-phenylethyl amines (Fluka) were alkylated by decyl bromide, dodecyl bromide or hexadecyl bromide (each from Aldrich) to produce the ternary ammonium salts, which were characterized by ^{1}H and ^{13}C NMR spectroscopies. The synthetic procedure and the detailed spectral characterization has been published elsewhere [15]. Sodium montmorillonite was fractionated from Wyoming bentonite ($d < 2$ μm) and exchanged with Na^{+} cations. Ethanol and toluene (Fluka) were used after drying on by a 0.4 nm Merck molecular sieve.

Preparation of chiral ammonium montmorillonite complexes

Na-Wyoming montmorillonite (2.0 g) was suspended in 100 ml deionized water and after 48 h swelling the mixture was filled up to 200 ml with deionized water (1% suspension). To this montmorillonite suspension the appropriate amount (in 1.5-fold excess with respect to the cationic exchange capacity) of 0.1 mol dm^{-3} solution of the alkylammonium chlorides was then added during continuous stirring. Ion exchange was allowed to take place for 6 h at 25 °C under stirring, then the suspension was filtered. The solid material was washed 3 times with 100 ml ethanol:water mixture (1:1) and dried. The dry samples were ground and passed through a 60 mesh sieve and kept in a dessicator.

Characterization

X-ray diffractometry

The basal spacings (d_L values) of the organocomplexes were determined with a Philips PW-1830 diffractometer (CuK radiation, $\lambda = 1.54$ nm) in a 1–20 $2\Theta^{\circ}$ angle range. A powder diffraction goniometer was used for powder tests and also for the investigation of suspensions. In the latter case the suspension was covered by Mylar foil (25 μm) to prevent evaporation of the dispersion liquids. The experimental results were reproducible within 0.02 nm.

MAS NMR spectroscopy

^{13}C and ^{29}Si MAS NMR spectra were recorded with a Bruker AM 400 spectrometer in a 7 mm rotor. Tetramethylsilane was used as a reference sample and the spectral parameters were SF: 79.469, LB: 50 with a 6 s relaxation delay.

Infrared spectroscopy

FT-IR studies were carried out with a Mattson Genesis 1 spectrometer in KBr pellets. The spectra were recorded both at the regular position relative to the infrared beam (90°) and tilted to 45°. Since the same samples were used for both experiments no further corrections or normalization were necessary.

Results and discussion

Preparation of the ammonium montmorillonite complexes were carried out by the standard ion-exchange procedure. After complete removal of the physically adsorbed ammonium salts the samples were dried and characterized in the dried state by spectroscopic methods. Since the physical parameters of the chiral compounds are the same except for the optical rotation only the characterization of the (*R*)–(+) derivatives will be shown. The FT-IR spectra of the parent Wyoming montmorillonite and the ion-exchanged complexes are shown in Fig. 1.

The characteristic bands of the organic cations are found at 600–800 cm^{-1} (benzene ring deformation and tertiary C-H out-of-plane stretchings), 1400–1500 cm^{-1} (benzene ring stretching) and 2600–3000 cm^{-1} (CH_2 skeletal stretching) (Fig. 1a). Other significant changes were observed relative to the parent Wyoming montmorillonite in the 3000–3700 cm^{-1} region. The broad OH band belonging to the Al-O-H positions practically disappeared after ion exchange while the second OH band characteristic of Si-O-H groups did not change.

For the determination of the perpendicular or parallel position of the phenyl ring in the ammonium salts relative to the siloxane sheet, infrared dichroism measurements were carried our for each sample [17]. The absorbance of the ν_{19a} and ν_{19b} bands (C-H out-of-plane ring deformation) was measured for pellets

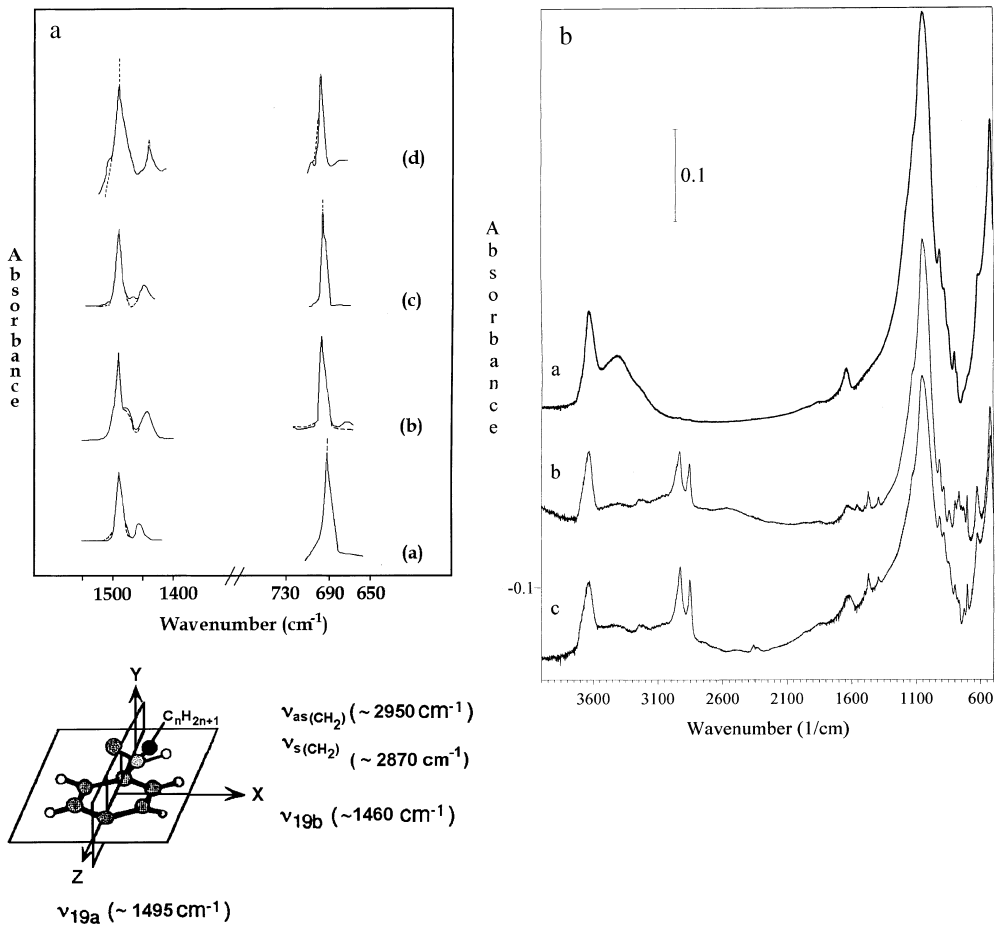

Fig. 1 (**a**) FT-IR spectra of the parent Wyoming montmorillonite (*a*) and derivatives ion exchanged with (*R*)–(+)-*N*-decyl phenylethylammonium (*b*) and (*R*)–(+)-*N*-hexadecyl phenylethylammonium ions (*c*). (**b**) Selected infrared vibrations of *N*-alkylated (*R*)–(+)-phenylethylammonium ion-exchanged Wyoming montmorillonite for 90° (—) and 45° (- - -) angles of incidence. The molecular axes associated with these vibrations are indicated

perpendicular or with 45° orientation to the beam. According to Serratosa [17] and Stevens and Anderson [18], the absorbance of the ν_{19a} peak should increase by at least a factor of 2 when the *x*-axis is perpendicular to the siloxane sheet. Similarly, if the *z*-axis and the phenyl ring are perpendicular to the siloxane surface, the ν_{19b} band should exhibit dichroism. Finally, in the case of dichroism of the C-H out-of-plane band, the geometry of the phenyl ring is parallel to the surface (Fig. 1b).

The spectra unambiguously indicate that the selected absorbances only slightly changed due to the tilting of the samples relative to the infrared beam; none of the bands exhibit significant dichroism. As a result, the above-mentioned special geometries for the phenyl group (parallel or perpendicular) are not indicated, most likely, the pillaring effect of the alkyl chain provides enough room for the rotational mobility of the phenyl group. Although the infrared dichroism measurements clearly indicate that the *x*- and *z*-axes of the ion-exchanged compounds are not parallel or perpendicular to the surface, it cannot be excluded on the basis of these experiments that the phenyl ring itself is perpendicular to the surface [17].

As an additional tool, multinuclear MAS NMR spectroscopy was used to obtain information about the structure of the Wyoming montmorillonite and the derivatives prepared. First, ^{29}Si MAS NMR spectra of the parent montmorillonite and the ion-exchanged products were recorded. Some spectra are shown as representative examples in Fig. 2.

The spectra contain two major peaks at −93 and −107 ppm. These signals are characteristic of silicon atoms in the tetrahedral sheet of montmorillonite (−93) and quartz (−107). These spectra agree with data in the literature, the only difference being the lack of kaolinite in the sample (characteristic peak was expected at −100 ppm) indicating the high purity of the Wyoming-type montmorillonite. The intercalated chiral ammonium salts induced a slight, but upfield shift (~2 ppm relative to the quartz peak) of the signal of the tetrahedral sheet.

Parallel with ^{29}Si NMR the position of the organic guests was studied by ^{13}C MAS NMR. Since the simple ^{13}C MAS spectra were completely uninformative, cross-polarization (CP) experiments were run. The ^{13}C CP MAS NMR spectrum of the decyl alkylammonium-clay complex is shown in Fig. 3.

The peaks observed are characteristic of organic guest cations; however, the signal-to-noise ratio is worse than described by Bank et al. [13] for adsorbed racemic phenylethylamine. In our opinion, the main reasons of this phenomenon are that our samples are not ^{13}C-labeled compounds and in our case the organic guests are bound between the montmorillonite layers, in contrast with the above-mentioned paper where the amine was adsorbed on the external surface. Taking into account a recent paper related to ^{13}C CP MAS NMR of intercalated benzene [19] this explanation is the most probable.

The structure of chiral montmorillonite organocomplexes was also studied by X-ray diffraction in the dried state to gain more insight into the changes of the lamellar structure. After ion exchange the organocomplexes were first washed with a 1:1 mixture of ethanol and water in order to remove chiral molecules bound by physical adsorption in the interlamellar space. The basal spacings of the dried organocomplexes are listed in Table 1.

As discussed by Lagaly and Weiss [6, 7], alkyl chains (thickness 4.6 Å) on montmorillonite – a mineral with a low charge density – lay down on the silicate lamellae which are 9.6 Å thick. When chiral phenylammonium ions are adsorbed, a monolayer orientation requires a spacing $d_L = 9.6 + 4.6 = 14.2$ Å (Fig. 4a).

In the case of bilayers (one alkyl chain on each silicate layer), the calculated basal spacing is

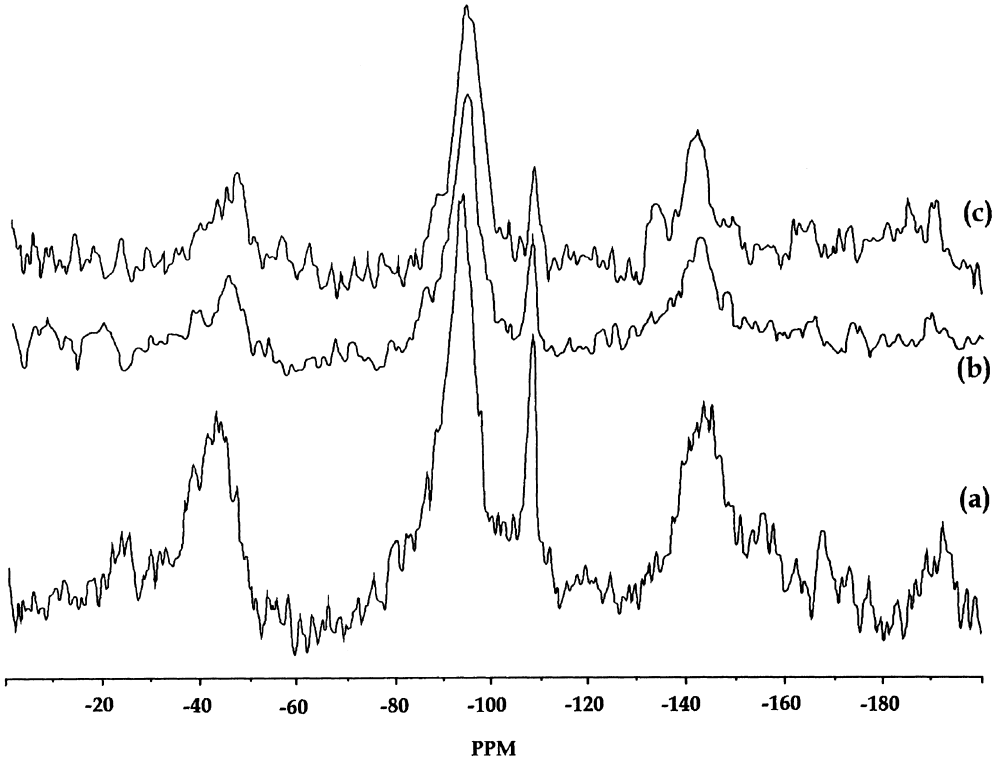

Fig. 2 ^{29}Si MAS NMR spectra of the Na-Wyoming montmorillonite (*a*) and derivatives ion exchanged with (*R*)–(+)-*N*-decyl phenylethylammonium (*b*) and (*R*)–(+)-*N*-hexadecyl phenylethylammonium ions (*c*)

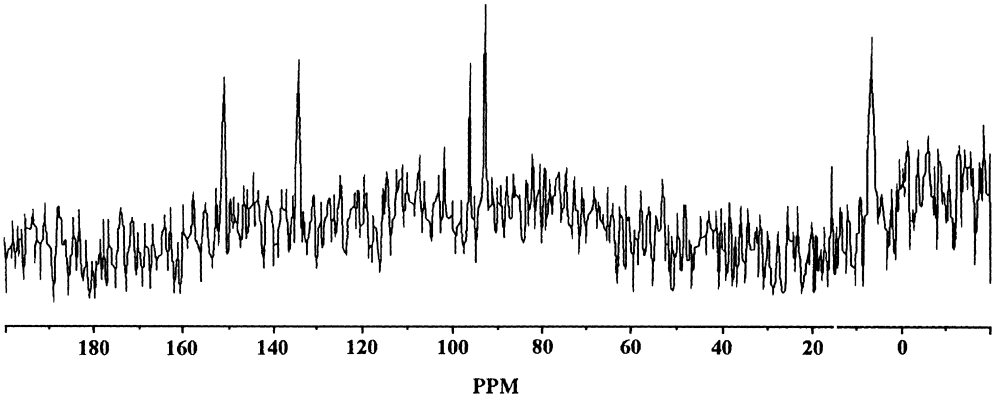

Fig. 3 ^{13}C cross-polarized MAS NMR spectra of (*R*)–(+)-*N*-decyl phenylethylammonium ion-exchanged Wyoming montmorillonite

$d_L = 9.6 + 2 \times 4.6 = 18.8$ Å (Fig. 4b) with relatively short alkyl chains ($n_c = 10$–12) it may also occur that the alkyl chain comes into contact with the phenyl group of the opposite chiral molecule, in which $d_L = 9.6 + 3.5 + 4.6 = 17.7$ Å. The experimental results are in good agreement with these models (Table 1).

An entirely different interlamellar orientation of alkyl chains becomes possible when the chiral clay mineral organocomplex is dispersed in a liquid medium. In this case liquid molecules penetrate into the interlamellar space, the liquid(s) are adsorbed on the free silicate surfaces and solvate the chiral molecules. As a result, the alkyl chains rise from the surface and, for chemical-structural reasons, take up a position at an angle of 55° with the surface [5–7] (Fig. 4c, d). When alkyl chains come into contact with the opposite silicate layer, the so-called monolayer orientation is established (Fig. 4c); penetration of even more liquid into the lamellae leads to further swelling and values of d_L(calc) may increase up to 39–47 Å, depending on chain length (Fig. 4d). Comparison of the calculated data with experimental results reveals that in ethanol the alkyl chains of chiral organocomplexes are tilted to the surface at an angle of 55° and the thickness of the liquid layer separating the silicate layers varies between 12.3 and 18.8 Å, depending on chain length. The organocomplex does not swell in toluene until the chain length reaches $n_c = 12$. The interlamellar sorption of toluene then increases the spacing to 17 Å (Table 1).

When ethanol is added to toluene, the interlamellar space opens at $n_c = 12$ due to preferential adsorption of ethanol. The extent of swelling is significant: $d_L = 38.2$–39.0 Å [10–12]. The process can be efficiently monitored by X-ray diffraction. Selected patterns are shown in Fig. 5a–d.

The X-ray diffractograms indicate that the layer expansion is strongly dependent on the environment of the organocomplexes. As a result, the effect of the solvent composition on the basal distances was also studied. The swelling of the montmorillonite organocomplexes as a function of the solvent composition is displayed in Fig. 6.

When the composition of the mixture changes, the basal spacing of the underivatized and decyl phenylethyl organocomplex remains constant, while the interlamellar expansion passes through a maximum for the dodecyl phenylethyl and hexadecyl phenylethyl derivatives. The maximum of the interlamellar distance in ethanol is found at $x_1 = 0.2$–0.4. Ethanol penetrates into the interlamellar space irrespective of the length of the alkyl chain, while toluene produces significant interlamellar swelling only in the case of the hexadecylammonium sample. Extensive swelling is due to preferential adsorption of ethanol on the free silicate surfaces in the interlamellar space which promotes penetration of toluene between silicate layers as a solvating agent of the alkyl chains [11, 12, 20]. Thus, in this case the so-called bilayer orientation is established, with a tilting angle of 55° to the surface.

Thus a desired layer separation can be achieved by careful selection of the solvent composition. This phenomenon calls attention to the intriguing possibility of regulating the space available for catalytic transformations. In this way various shape-selective processes can be carried out by setting the appropriate ethanol-toluene mixture composition.

Conclusion

New chiral phenylethylammonium montmorillonite complexes were prepared by cation-exchange reactions, and the orientation of the organic component between the silicate lamellae was characterized. The surface orientation of the phenyl group was investigated by IR and MAS NMR measurements. It was concluded from these experiments that the phenyl group has limited mobility in the dried state and is oriented neither parallel nor perpendicular to the surface of the montmorillonite lamellae. The orientation of alkyl chains was also studied by X-ray diffraction for dried samples and on particles suspended in ethanol, toluene and their binary mixtures. Ethanol penetrated into the interlamellar space irrespective of the length of the alkyl chain, while toluene brought about significant interlamellar swelling only in the case of hexadecylammonium sample. The interlamellar distance was significantly increased for the $C_{12}H_{25}$ derivative at molar fractions $x_1 = 0.2 - 0.4$

Table 1 Basal spacings (in Å) of chiral *n*-alkylphenylethylammonium montmorillonites

Chiral organoclay	d_L (calc) dried	d_L (exp) sample	d_L (calc) monolayer $\alpha = 55°$	d_L (calc) bilayer $\alpha = 55°$	d_L (exp) in ethanol	d_L (exp) in toluene	d_L (exp) in $x_1 = 0.2$ mixture
Phenylethyl	14.2 (monolayer)	14.5	–	–	16.8	15.7	17.1
Decyl phenylethyl	17.7 (bilayer)[a]	17.0	22.31	39.18	21.9	17.0	17.1
Dodecyl phenylethyl	17.7 (bilayer)[a]	17.6	24.40	43.34	24.9	17.0	38.2
Hexadecyl phenylethyl	18.8 (bilayer)[b]	19.1	28.56	47.52	28.4	36.0	39.0

[a] Alkyl chain in contact with phenyl groups
[b] Alkyl chain in contact with another alkyl chain

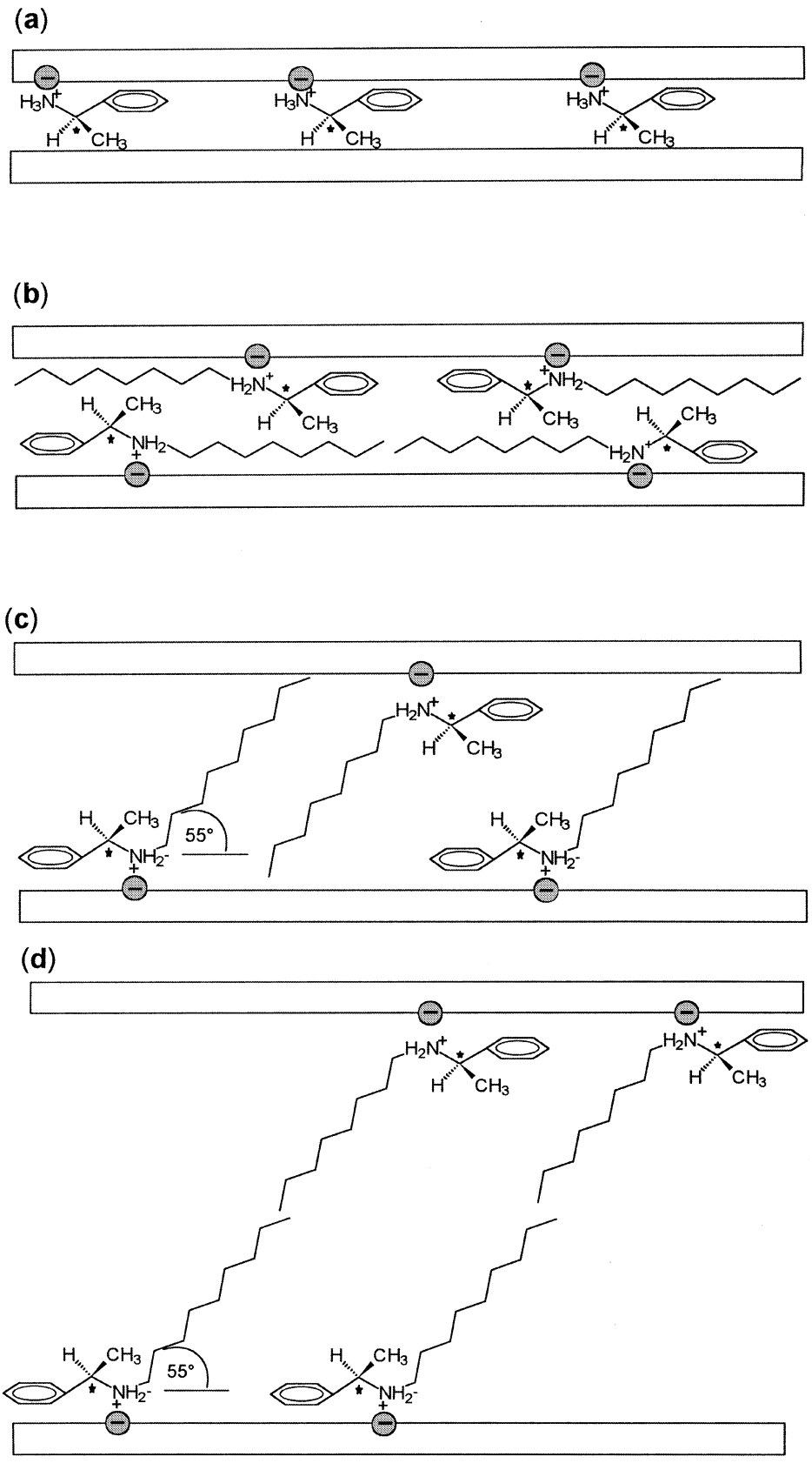

Fig. 4a–d Interlayer orientation of chiral organic molecules in the interlayer of montmorillonite. (**a**) Intercalation of phenylethylammonium cations between the silicate layers. d_L(calc) = 14.2 Å. (**b**) Bilayer orientation of alkyl chains between the silicate layers. d_L(calc) = 18.8 Å. (**c**) Monolayer orientation of alkyl chains between the silicate layers at a tilting angle of 55°. (**d**) Bilayer orientation of alkyl chains between the silicate layers at a tilting angle of 55°

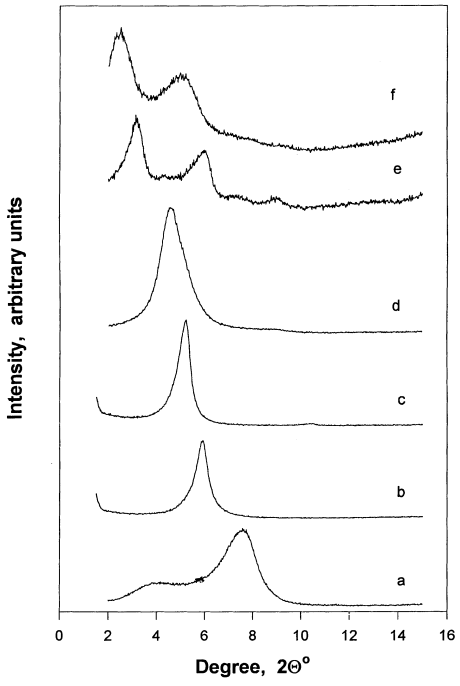

Fig. 5 X-ray diffraction patterns of different chiral phenylethylammonium montmorillonite complexes. (*a*) phenylethylammonium montmorillonite (dry). (*b*) phenylethylammonium montmorillonite (in ethanol). (*c*) hexadecyl phenylethylammonium montmorillonite (dry). (*d*) hexadecyl phenylethylammonium montmorillonite (in ethanol). (*e*) hexadecyl phenylethylammonium montmorillonite (in toluene). (*f*) hexadecyl phenylethylammonium montmorillonite [in $x_1 = 0.2$ ethanol toluene (1:2) mixture]

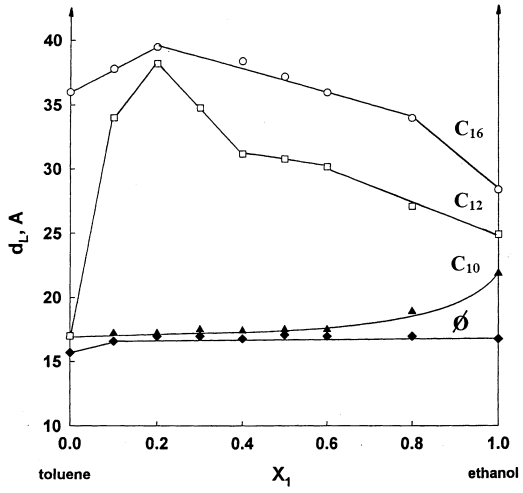

Fig. 6 Basal distances of phenylethylammonium and alkylated phenylethylammonium montmorillonite complexes in toluene-ethanol mixtures as a function of the molar fraction x_1 of ethanol. (◆) phenylethylammonium, (▲) decyl phenylethylammoniummo, (□) dodecyl phenylethylammonium, and (○) hexadecyl phenylethylammonium montmorillonites

(ethanol-toluene). The unique process described here provides new ways to carry out shape-selective heterogeneous catalytic reactions. In addition, due to their chiral character these new montmorillonite organocomplexes may open up new unexplored fields in material science increasing the potential of these intriguing clay minerals.

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