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ORIGINAL CONTRIBUTION

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Bilayer studies in mixed *n*-decanol / *n*-tetradecanol complexes of *n*-decylammonium beidellite

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Abstract Complexes have been prepared by treatment of *n*-decylammonium beidellite with mixtures of *n*-decanol and *n*-tetradecanol with different concentrations. Measurements of the basal spacings of the obtained complexes have been performed in a wide range of temperatures. Three different bilayer phases have been established between (20 and 70 °C: the $\beta_i(C_{10})$ phases (= bilayers of *n*-decyl chains); the $\beta_i(C_{10}/C_{14})$ phases (= mixed bilayers of *n*-decyl and *n*-tetradecyl chains in molar ratio approximately 1:1) and the $\beta_i(C_{14})$ phases (= bilayer of *n*-tetradecyl chains with the *n*-decylammonium ions included). In all bilayer phases the chains stand perpendicular to the silicate interfaces. In definite concentration ranges two of the phases coexist, i.e., miscibility gaps occur, which disappear at temperatures higher than the temperature of the β_i/α transition. The miscibility gaps are reversible with temperature. The composition of the intercalated bilayers has been studied by HPLC of the excess alkanol mixture separated from the beidellite complexes after the equilibrium has been reached. There is preferential adsorption of one of two alkanols from the mixture, which is in agreement with the observed miscibility gaps. The space filling problem as well as the structure of the three bilayer phases observed have been discussed.

Key words Decylammonium-alkanol-beidellite complexes – miscibility gap in mixed alkanol complexes – structure of intercalated bilayers – coexistence of phases

Introduction

By intercalation of *n*-alkanols into *n*-alkylammonium layer silicates (smectities) bilayers of alkanol and ammonium ions are formed in the interlayer region [1–4].

In a previous paper [5] we have studied the phases and phase transitions in two relatively simple cases: *n*-tetradecylammonium-*n*-tetradecanol-beidellite as well as *n*-tetradecylammonium-*n*-tetradecanol-montmorillonite. Beidellite and montmorillonite are layer silicates with low, but slightly different mean layer charge densities. Their *n*-tetradecylammonium derivatives have been treated with different amounts of *n*-tetradecanol (the number of C-atoms in the alkanol molecule being equal to that of the cation, $N_A = N_C = 14$), i.e., the intercalate complexes have been studied for different ratios C mole *n*-tetradecanol per $(SiAl)_4O_{10}$-unit. With increasing C no continuous increase of the interlayer distance was observed, but only three phases exist with characteristic and limited alkanol concentrations. These phases are structurally characterized by: i) alkyl chains lying flatly on the silicate interfaces; ii) monolayers of all-anti alkyl chains tilted under 55° to the silicate layers; iii) bilayers of alkyl chains standing perpendicular to the silicate interfaces. Each of these phases has a small range of composition. Intermediate alkanol concentrations lead to coexistence of two phase regions. The miscibility gaps disappear at higher temperatures.

A more complex situation is obtained by treatment of the *n*-alkylammonium derivatives with mixtures of two *n*-alkanols of different chain lengths.

In this case the questions arise:

a) what kind of intercalate structures will be obtained if we change the ratio of the amounts of both alkanols in the mixture?
b) Is there a monotonous increase of the interlayer thickness (= distance between the silicate interfaces = basal spacing minus thickness of the silicate layer) with increasing concentration of the longer molecules in the mixture and
c) are there discontinuities with a limited number of intermediate phases and mixing gaps?

The answer to these questions is interesting since such mixed bilayers are spread in nature. Some studies on intercalation bilayer structures of different molecules have already been performed [3].

In our present investigation *n*-decylammoniumbeidellite was chosen as a model system and treated with mixtures of *n*-decanol + *n*-tetradecanol with different concentrations. That means two alkyl chains of different lengths are included in the intercalate structure: the *n*-decyl chain (*n*-decylammonium cation as well as *n*-decanol, $N_C = N_A = 10$) and the *n*-tetradecyl chain of the *n*-tetradecanol ($N_C \mp N_A = 14$). Because of the relatively large equivalent area per unit charge of the beidellite, the average ratio cations: alkanol molecules in the saturated intercalate complex is approximately 1:4. Hence, when there is a dense packing of the alkyl chains in the intercalate, the composition of the complex can be idealized by the formula

$$(C_{10}H_{21}NH_3)^+_{0.43} \cdot (C_{10}H_{21}OH)_z \cdot (C_{14}H_{29}OH)_{1.63-z} \cdot$$
$$[Al_2(OH)_2(Si_{3,57}Al_{0,43}O_{12})]^{0,43-}$$

Obviously, the concentration of the decyl chains can vary from $X_{10c} = 0.21$ (*n*-decylammonium cations plus tetradecanol only, no *n*-decanol) up to $X_{10c} = 1$ (decyl chains only, no *n*-tetradecanol). Here, X_{10c} is the molar fraction of all decyl chains. The question in the present paper is whether z increases monotonously with monotonously increasing X_{10c}.

Experimental

The *n*-alkylammonium-beidellites have been prepared by cation exchange, as described earlier [6–8]. The beidellite used has a mean layer charge of 0.44 eq/$(Si, Al)_4O_{10}$ (charge distribution within 0.39 – 0.46), CEC = 111 meq/100 g and an equivalent area of 54 Å^2/charge.

Alkanol-complexes have been prepared with different amounts of decanol plus tetradecanol mixtures [9]. There are 2.06 alkyl chains per $(Si, Al)_4O_{10}$ -unit at dense, incommensurate packing of the chains in the intercalate. The stoichiometric amount of alkanols, calculated on this basis, usually is multiplied by a factor f: when $f > 1$, there is excess of alkanols and when $f < 1$, there is defficiency of alkanols. A dense packing of the alkyl chains in the complex is obtained when f is between 1.05 and 1.1. However, in many cases essentially larger excess of alkanol mixture has been used, f being up to 10. Such a large excess offers the possibility of preferential intercalation of one alkanol from the mixture. This can be established quantitatively by making analysis of the excess alkanol mixture after the equilibrium has been reached. For this purpose the alkanol mixture has been separated from the silicate complex by centrifugation and then analyzed chromatographically.

In other series of experiments the amount of the alkanol mixture has been less than the stoichiometrically calculated ($f < 1$). In order to distribute the small amount of alkanols uniformly over all particles of the alkylammonium-beidellite solution in diethyl ether has been used, e.g., 100 mg alkanols in 5 cm^3 ether for 200 mg *n*-alkylammonium-beidellite. After obtaining a uniform suspension, the ether has been removed during 4-week storage in an exsicator over paraffin.

In all cases the suspension {alkanol mixture – alkylammonium beidellite} has been kept for a long time at different temperatures in order to obtain equilibrium intercalate complexes. First the suspension has been stored for 2 days at temperature above the melting point of the alkanol, but below the point of β/α phase transition. Then its storage was continued at alternately increasing and decreasing temperature (gradient ca. 5° per hour) in the range between 35 °C and 80 °C for several days.

The basal spacings of the obtained alkylammonium-alkanol beidellite complexes with decanol and tetradecanol intercalated have been measured at room temperature with a Philips Norelco diffractometer as well as in a Debye–Scherrer powder camera with Cu-K$_\alpha$ radiation. The beidellite complex has been transferred into the sample holder with preferential orientation of the layers and covered by Mylar membrane to prevent evaporation of the alkanols.

The composition of the beidellite complex has been calculated from the concentrations of both alkanols in the excess mixture, which has been separated from the suspension after the equilibrium had been reached. These concentrations have been measured by High Pressure Liquid

Chromatography (HPLC) using a 250 mm column filled with 5 μm Hypersil Shandon ODS, the flow liquid being 8% water in methanol.The alkanol mixture has been dissolved in pure methanol (10% solution), the flow rate was 2 cm^3/min at column pressure 68 bar. A differential refractometer has been used as detector connected with a $X(t)$ recorder. Two separate peaks are recorded from the decanol and tetradecanol respectively. The area A enclosed by a peak is taken proportional to the concentration of the corresponding alkanol. The molar fraction X_{10} of the decanol in the alkanol mixture is given by

$$X_{10} = \frac{A_{10}}{A_{10} + K_{10} A_{14}}, \tag{1}$$

where A_{10} and A_{14} are the peak areas of decanol and tetradecanol respectively and the constant K_{10} is obtained from

$$K_{10} = A^S_{10} n^S_{14} / A^S_{14} n^S_{10}, \tag{2}$$

n^S_{10} and n^S_{14} being the moles of exactly known standard quantities of decanol and tetradecanol.

The molar fraction X_{10c} of the decyl chains (decylammonium cations plus decanol molecules) in the intercalate complex can be calculated using the expression:

$$X_{10c} = (1 - n_c/n_\infty)[f X^0_{10} - (f-1)/(1 + K_{10} A^e_{14}/A^e_{10})] + n_c/n_\infty . \tag{3}$$

Here, X^0_{10} is the molar fraction of decanol in the initial alkanol mixture, A^e_{10} and A^e_{14} are the peak areas of decanol and tetradecanol respectively in the mixture separated after the equilibrium had been reached, n_c is the number of decylammonium cations and n_∞ – the number of all alkyl chains (cations plus both alkanols) per (SiAl)$_4$O$_{10}$– unit in the intercalate complex, dense packing of the chains being supposed.

The X_{10c} values calculated using Eq. (3) for 10 n-decanol + n-tetradecanol mixtures studied at 25 °C are presented in Table 1. X^0_{10c} denotes the molar part of all chains (decylammonium cations plus decanol molecules) in the intercalate, calculated from the molar fraction X^0_{10} of the alkanol mixture with the assumption that there is no preferential adsorption of any alkanol. For the denotation of the bilayer phases see part 3.1.

Results and discussion

Bilayer intercalate phases at different concentrations of the n-decanol/n-tetradecanol mixtures and different temperatures

Detailed mesurements of the basal spacings d of the intercalation complexes have been performed for nine n-decanol/n-tetradecanol mixtures with different concentrations X^0_{10}. The d-values have been measured at different temperatures in the range 20°–120 °C, the sample holder being heated or cooled by a special device. In each case series of d measurements have been performed, the temperature being first decreased from 120 °C down in steps of 3°–5° C and then increased in the same steps. At each step the sample has been annealed for a long time and then the basal spacings were measured. It turned out that the difference between the d-values, obtained when cooling the sample and those obtained when heating it, are minimal. This fact indicates that the obtained basal spacings are very close to the equilibrium values. The d-values presented in Figs. 1–3 are from the cooling series only; in general, there should be less kinetic hindrances in these series. The d-values in the figures are denoted as follows: full circles denote a value obtained from a x-ray diffraction pattern, in which (0 0 1) and higher order reflections are available; open circles – only (0 0 2) and higher order reflections, respectively; the smaller the circles, the larger the number of basal reflections available. For instance, the smallest full circle denotes a d-value obtained from a diffraction patern with five basal reflections including (0 0 1), i.e., the d-value has been determined with the best accuracy. Figure 1 presents both limiting cases. In the case $X^0_{10c} = 1$ (Fig. 1a) n-decanol only has been offered, i.e., there are decyl chains only in the intercalaction complex. This simple case has been already studies [2]. The d-values measured show that one phase appears only up to about 70°–80 °C; this is obviously the $\beta_i(C_{10})$ phase: bilayer of n-decyl chains in all-anti conformation standing perpendicular to the interfaces. With increasing temperature cooperative conformational changes occur and the d-values decrease stepwise; these changes are characterised by (+)gauche-anti-(−)gauche kink formations [3]. At about 70°–80 °C the

Table 1

X^0_{10c}	0	0.21	0.3	0.4	0.5	0.61	0.7	0.8	0.9	1
X_{10c}	0	0.21	0.27	0.29	0.5	0.54	0.56	0.87	0.96	1
Bilayer phases	(14)	(14)	(14) (10/14)	(14) (10/14)	(10/14) (14)	(10/14)	(10/14)	(10) (10/14)	(10) (10/14)	(10)

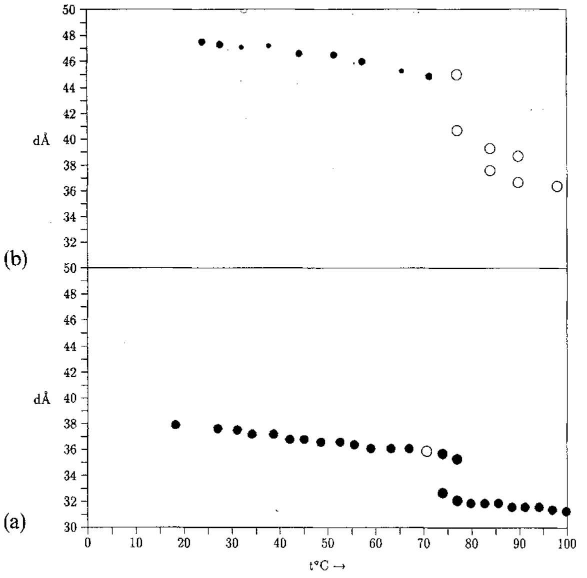


Fig. 1 Basal spacings *d* of decanol-tetradecanol-decylammonium beidellite as a function of temperature *t*: a) $X^0_{10c} = 1$; b) $X^0_{10c} = 0.21$; in both cases $f = 10$

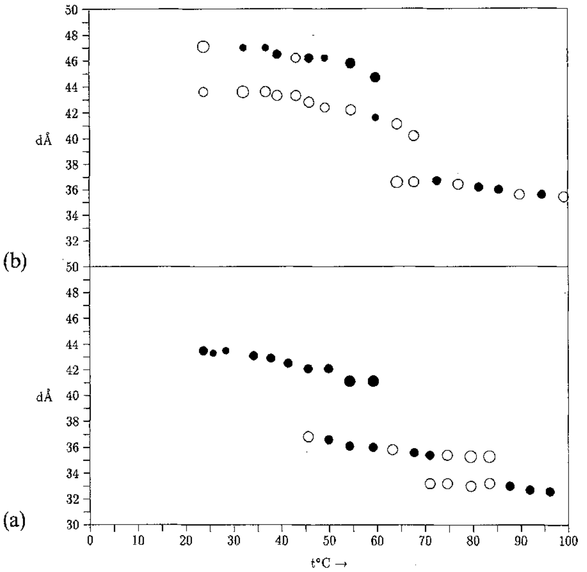


Fig. 2 Basal spacings *d* of decanol-tetradecanol-decylammonium beidellite as a function of temperature *t*: a) $X^0_{10c} = 0.7$; b) $X^0_{10c} = 0.5$; in both cases $f = 10$

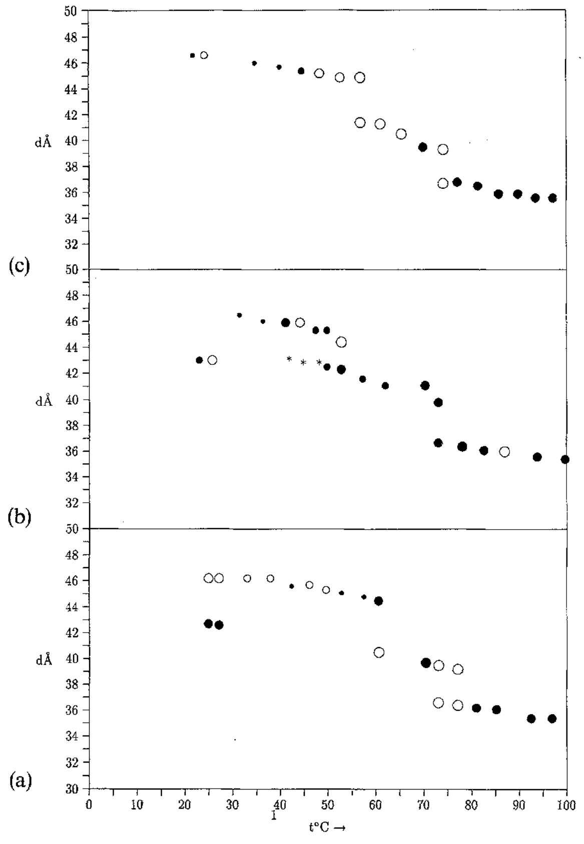


Fig. 3 Basal spacings *d* of decanol-tetradecanol-decylammonium beidellite as a function of temperature *t*: a) $f = 10$; b) $f = 2.5$; c) $f = 1.2$; in all cases $X^0_{10c} = 0.4$

phase transition $\beta_i \rightarrow \alpha$ phase happens and at higher temperatures the α phase remains only.

The other limiting case $X^0_{10c} = 0.21$ is presented in Fig. 1b. In this case *n*-tetradecanol only is intercalated into the *n*-decylammonium beidellite. The results (Fig. 1b) show that one phase only appears below the $\beta_i \rightarrow \alpha$ phase transition temperature. This is the $\beta_i(C_{14})$ phase: bilayer of *n*-tetradecyl chains standing perpendicular to the silicate sheets. The single β_i steps appear with the increasing temperature. Obviously, the number of the decyl chains in the intercalate is small and the number of voids (10/14) (void volume proportional to the chain length difference of C_{14}- and C_{10}-chains Δd) is very small as well. Chains pairings C_{10}/C_{10} and consequently voids (10/10) (void volume proportional to $2\Delta d$) are extremely rare. This makes a miscibility gap impossible and the $\beta_i(C_{14})$ phase obtained is almost the same as in the case of *n*-tetradecylammonium-*n*-tetradecanol-beidellite.

While in both limiting cases considered there is one β_i phase only (the $\beta_i(C_{10})$ or $\beta_i(C_{14})$ phase respectively), in the case $X^0_{10c} = 0.5$ (Fig. 2b) two β_i phases coexist in the whole temperature range from room temperature up to the temperature of the $\beta_i \rightarrow \alpha$ transition. This is the typical case of a miscibility gap. Besides the $\beta_i(C_{14})$ phase, a new β_i phase appears; its *d*-values correspond to an intercalated bilayer with chain pairings C_{10}/C_{14} perpendicular to the silicate interface. We shall call this new β_i phase the $\beta_i(C_{10}/C_{14})$ phase. In the case $X^0_{10c} = 0.61$ this is the only phase appearing at low temperatures; neither $\beta_i(C_{10})$ nor

$\beta_i(C_{14})$ exist at this concentration of the alkanol mixture. It is interesting to point out that for $X^0_{10c} = 0.61$, $X_{10c} = 0.54$ (see Table 1), i.e., the amount of decyl and the tetradecyl chains is almost equal in the intercalate complex.

When the concentration of the decyl chains is increased at $X^0_{10c} = 0.7$ (Fig. 2a) the $\beta_i(C_{10})$ phase appears also at about 45 °C, the $\beta_i(C_{10}/C_{14})$ phase remaining the main phase. Both phases coexist in a limited temperature range (45–60 °C), i.e., there is again a miscibility gap. If the concentration of the tetradecyl chains is increased $X^0_{10c} = 0.4$. (Fig. 3a), just the opposite happens: the $\beta_i(C_{14})$ is the main phase at temperatures above 30 °C, however the $\beta_i(C_{10}/C_{14})$ phase remains the main phase at room temperature, coexisting with the $\beta_i(C_{14})$ phase – the miscibility gap occurs at room temperature only.

All these results clearly demonstrate that there is no monotonous increase of the d-values, respective the interlayer thicknesses, with monotonous increase of the concentration of tetradecanol in the decanol/tetradecanol mixture. Just the opposite occurs: three well defined phases only appear at the different X^0_{10c} values, one of them being the main phase depending on the concrete values of X^0_{10c} and t °C. Often two of these three phases coexist in a limited range of conditions, i.e., there are miscibility gaps in these ranges. The values X_{10c} of the composition of the intercalate complexes, obtained by HPLC-analysis (Table 1) show that there is preferential adsorption of one of both alkanols from the mixture, which is in agreement with the observed miscibility gaps.

Effect of alkanol excess on bilayer intercalate phases

The results discussed before have been obtained from experiments with large excess of decanol/tetradecanol mixture (10 fold, $f = 10$). In order to examine whether this excess is sufficient to guarantee equilibrium, experiments have been carried out with less ($f = 2.5$) and almost stoichiometric amounts ($f = 1.2$) for bilayer formation. The results for $X^0_{10c} = 0.4$ are presented in Fig. 3 as follows: a) $f = 10$; b) $f = 2.5$; c) $f = 1.2$. The curves are similar at higher temperatures, but interesting differences occur at room temperature. At this temperature a part of tetradecanol of the mixture crystallizes. When there is a large excess of the alkanol mixture (Fig. 3a) the main phase is the $\beta_i(C_{10}/C_{14})$ phase; however the $\beta_i(C_{14})$ is still observed, and both phases coexist at room temperature. At higher temperatures tetradecanol is melted and only the $\beta_i(C_{14})$ phase exist. If the alkanol excess is diminished ($f = 2.5$, Fig. 3b) only the $\beta(C_{10}/C_{14})$ phase is observed at room temperature obviously this phase is in equilibrium with a liquid mixture rich in decanol, because of the partial crystallization of the tetradecanol. In the case of practically stoichiometric amount of alkanol mixture (Fig. 3c) almost all the decanol and tetradecanol are intercalated into the n-decylammonium-beidellite at higher temperatures and the $\beta_i(C_{14})$ phase is obtained. After cooling to room temperature this phase persists, since there is no excess of the alkanol mixture with which an exchange of one of the alkanols could take place. One concludes from Fig. 3 that the studied bilayer intercalate phases are equilibrium phases.

The space filling problem of the C_{10}/C_{10}-, C_{10}/C_{14}- and C_{14}/C_{14}-bilayers

The dependence of the basal spacing on X_{10c} at room temperature (23°–27 °C) is presented in Fig. 4b. Again, the existence, respectively coexistence, of the three β_i phases is clearly seen. There are two miscibility gaps at this temperature: the $\beta_i(C_{14}) + \beta_i(C_{10}/C_{14})$ phases at $X_{10c} = 0.27 - 0.5$ and the $\beta_i(C_{10}/C_{14}) + \beta_i(C_{10})$ phases at $X_{10c} = 0.87 - 0.96$. The basal spacing (Fig. 4b) can be compared with the dependence ΔV (X_{10c}) (Fig. 4a), ΔV being the difference between the experimentally obtained volume (from d-measurements) and the calculated volume of the intercalated bilayer, using the following expressions

$$\Delta V = V_{\mathrm{exp}} - V_{\mathrm{cal}} \tag{4}$$

$$V_{\mathrm{exp}} = 23.2(d - 9.8) \tag{5}$$

$$V_{\mathrm{cal}} = 23.2 \cdot 2.03[X_{10c}(1.265(10-1) + 2.9) + (1 - X_{10c})(1.265(14-1) + 2.9)]\,. \tag{6}$$

The comparison shows that the ΔV value is close to zero only in those cases when one β_i phase exists. Conversely, there are large ΔV values (both positive and negative) in the ranges of miscibility gaps when two β_i phases coexist.

It is interesting to juxtapose the results presented in Fig. 4 with the distribution of the statistical probabilities Z_{ij} for the formation of C_{10}/C_{14} or C_{14}/C_{14} alkyl chain pairs in the intercalated bilayer. If we assume that these probabilities depend on the concentration X_{10} of the decyl (respectively tetradecyl) chains only, the Z_{ij} values can be calculated using the following equations:

$$Z_{10/10} = \frac{n_{10}^2}{n^2} \tag{7}$$

$$Z_{10/14} = \frac{2n_{10}n_{14}}{n^2} \tag{8}$$

$$Z_{14/14} = \frac{n_{14}^2}{n^2}\,, \tag{9}$$

where n_{10} is the number of moles decyl chains (both decylammonium cation and decanol), n_{14} – the number of

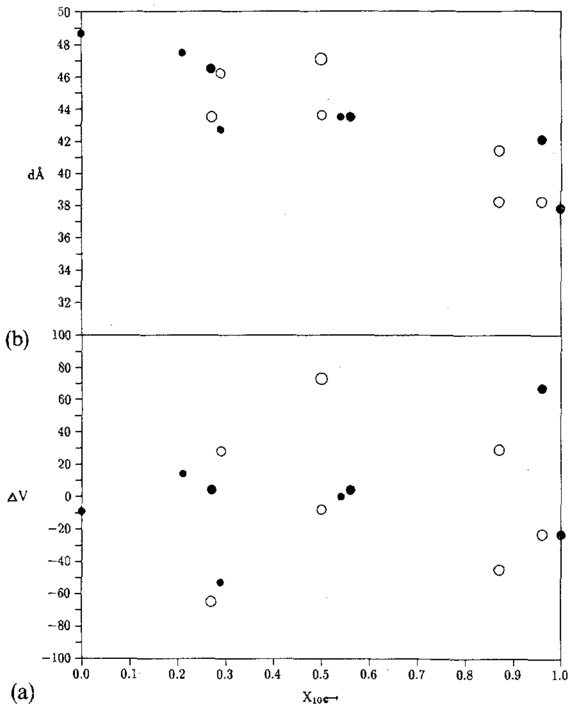


Fig. 4 Basal spacings d and volume difference $\Delta V = V_{exp} - V_{cal}$ of the intercalated bilayer of *n*-decanol and *n*-tetradecanol in *n*-decylammonium beidellite as a function of experimentally determined molar fraction X_{10c} of the decyl chains in the bilayer

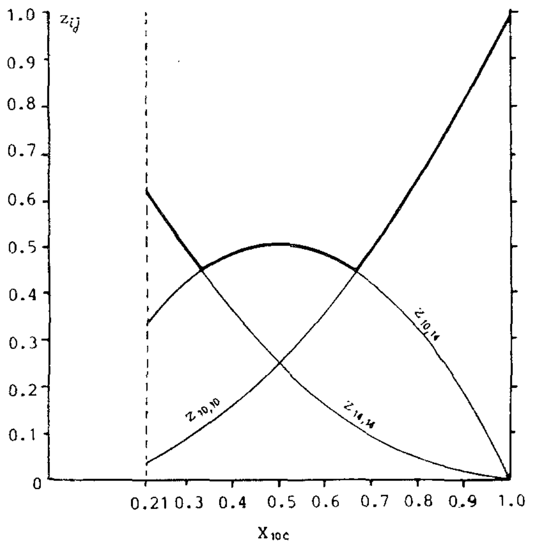


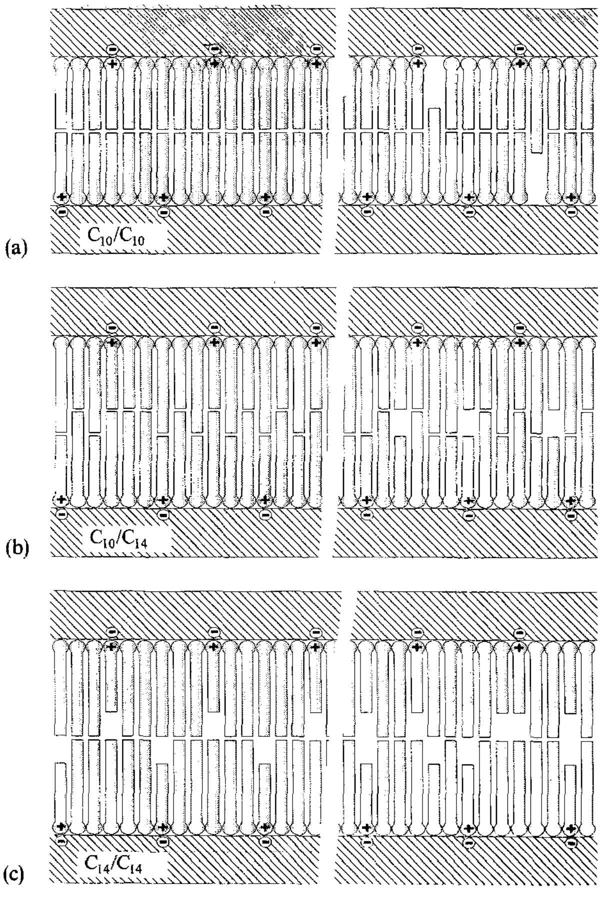
Fig. 5 Statistical probabilities Z_{ij} for the formation of alkyl chain pairs as a function of the molar fraction X_{10c} of the decyl chains in the bilayer

moles tetradecyl chains and n – the total number of moles alkyl chains. Figure 5 shows the three Z_{ij} as function of the molar fraction X_{10c} of the decyl chains in the intercalated bilayer. This picture is in good agreement with the data of Fig. 4. Miscibility gaps occur in those ranges in which two of the three Z_{ij} values are close to each other. In contrast, when one of the Z_{ij} values is essentially larger than both others – only one β_i phase exists. Obviously, the space-filling argument is decisive whether there is a miscibility gap or not.

The structure of the β_i phases

The bilayer structures may include a considerable amount of defects within the stability range. The decisive defects are due to the voids caused by chain length differences. However, we have to distinguish between positive voids (holes) and negative voids (interstitial sites) which might be compared with Schottky and Frenkel defects in solid-state chemistry (vacancies and interstitial lattice sites). Positive

Fig. 6 Arrangement of the *n*-decylammonium ions and *n*-decanol and tetradecanol molecules in the bilayers. a) left: bilayer with decyl chains only. right: as left, but a small number of tetradecanol molecules in the bilayer. b) left: bilayer with regular chain pairing decyl-/tetradecyl. right: as left, but a small excess of decyl chains. c) left: bilayer with tetradecanol only, but decylammonium cations. right: as left, but an additional small amount of decanol, too



voids are connected with a corresponding decrease in the mean bilayer density, negative voids with an increase in the density. Due to the huge interstitial volume required for excess chain lengths, defects of this type are not observed in our systems. In Fig. 6 the three different structural bilayer types are shown schematically. On the left side a) represents an ideal C_{10}/C_{10} bilayer and b) shows a regularly mixed C_{10}/C_{14} bilayer with idealized chain pairing. Part c) indicates a C_{14}/C_{14} bilayer. However, in this case voids have to be built in, because $X_{10c} = 0$ cannot be realized with the *n*-decylammonium beidellite.

On the right parts of Fig. 6 " Schottky defects" are introduced. In Fig. 6a the volume of these defects corresponds to $4 \cdot V_{-CH_2-} + V_{-OH}$. ($V_{-CH_2}$ = volume of a $-CH_2$-group in a bilayer structure, V_{-OH} = volume of an alcoholic OH-group, involved in hydrogen bonding to oxygen). In this case the H-bonding interaction of an alcoholic OH-group with the oxygen atoms of the silicate layers is lost in addition to the loss of van der Waals interaction between the alkyl chains in the void area. In Fig. 6b the idealized void volume corresponds to $4 \cdot V_{-CH_2-}$. In Fig. 6c two different void types are possible with idealized void volumes $4 \cdot V_{-CH_2}$ and $2 \cdot (4V_{-CH_2-})$. The voids within these structures may be mobile via change of sites of the alkylchains.

If we postulate an attractive interaction between the voids W_{VV}, they will be distributed randomly, as long as $W_{VV} < kT$. With $W_{VV} \geq kT$, the voids will segregate. As a consequence of void segregation, two phases are formed.

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References

1. Lagaly G, Weiss A (1971) Kolloid Z u Z Polymere 248:968, 979
2. Lagaly G, Weiss A (1972) Proc Intern Clay Conf p 637
3. Lagaly G, Fitz St, Weiss A (1975) Clays Clay Minerals 23:45
4. Platikanov D, Weiss A, Lagaly G (1977) Colloid Polym Sci 255:907
5. Weiss A, Holm C, Platikanov D (1993) Colloid Polym Sci 271:891
6. Lagaly G, Weiss A (1970) Kolloid Z u Z Polymere 237:266, 364
7. Lagaly G, Weiss A (1970) Kolloid Z u Z Polymere 238:485
8. Lagaly G, Weiss A (1971) Kolloid Z u Z Polymere 242:48
9. Schick P, PhD Thesis, Univ München, 1982