

of a thickness comparable to the average microbead diameter needs to be investigated. In spite of these omissions, however, the principal results concerning the optics of the glass microbeads covered by monocrysal TiO_2 are valid.

Acknowledgment. We thank Dr. Schechter for numerous helpful discussions. We would also like to thank Dr. Bezman from Chevron for providing us with samples of the crude oils. We are grateful to the Department of Energy for the support of this work.

Thionine in the Cage of Zeolite L

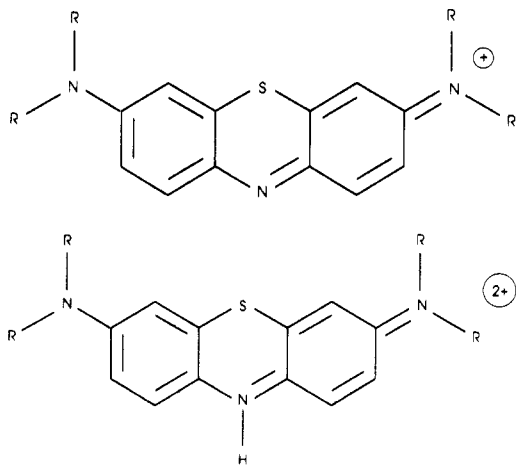
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(Received: October 14, 1991)*

The room temperature exchange isotherm of thionine (TH^+) in aqueous potassium zeolite L dispersions shows that TH^+ can exchange up to 7.5% of the cations belonging to the main channel from which an average thionine-thionine center to center distance of 27 Å is calculated. This corresponds to a 0.2 M TH^+ concentration with respect to the zeolite L volume. We conclude that the maximum number of TH^+ that can be incorporated is limited by the space available in the channel. Even at these high concentrations the electronic spectrum is that of a monomer. It is more structured than in diluted aqueous or alcoholic solutions, thus indicating the restricted freedom in the channel. The spectrum observed just after mixing the dye with a zeolite L dispersion is that of aggregates, easily recognized by the sudden color change from blue to purple. With time the short-wavelength absorption decreases and the monomer spectrum develops. Intercalation kinetics is slow at room temperature in the case of a potassium zeolite L and takes about 2 weeks to be completed. It is much faster at 70 °C where it takes about 10 h for a potassium zeolite and only about 1 h for a proton zeolite. We have observed that the acid-base behavior of thionine in the channels of a proton zeolite L is comparable to that otherwise observed in 2.5 M hydrochloric acid. Methylene blue and ethylene blue being slightly larger than thionine do not show any cage effect since they do not go into the main channel of zeolite L. Their electronic spectra observed even after 2 weeks are those of aggregates. We conclude that they remain adsorbed at the outside of the zeolite particles because the geometry of a zeolite L does not allow the formation of parallel dimers inside the main channel.

Introduction

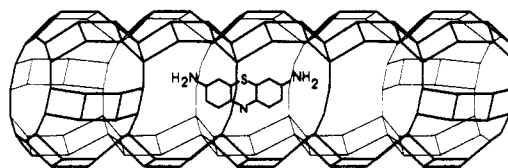
The van der Waals radii of the thionine molecule **1** are about $7.2 \times 15 \text{ \AA}^2$. This suggests that it should fit into the main channel of a zeolite L which has an opening of about 7.1 Å,¹ shown in Scheme I. Thionine is a cationic dye and this is why it can fill



in the cylinder shaped cage by ion exchange. A channel of 200 nm length, the average size of commercially available zeolite L particles, is long enough to swallow up to 100 dye molecules one after the other, resulting in concentrations of about 0.2 mol/L. Methylene blue **2** and ethylene blue **3** are molecules of similar structure and shape but slightly larger.

formula 1	formula 1'
1: R = H	1': R = H
2: R = CH ₃	2': R = CH ₃
3: R = C ₂ H ₅	3': R = C ₂ H ₅

SCHEME I: Schematic View of a Thionine Molecule in the Main Channel of a Zeolite L

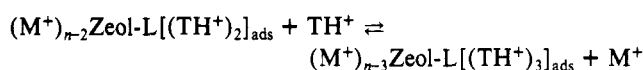
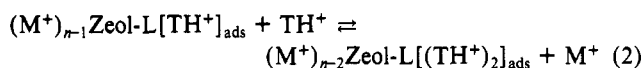
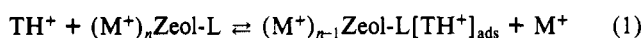


Photochemical and photophysical properties of these molecules have been studied extensively in homogeneous²⁻¹¹ and in heterogeneous environment.¹²⁻¹⁶ Thus we know enough to meaningfully investigate their interactions with a zeolite environment. The characteristic differences between the electronic absorption spectra

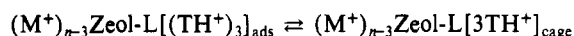
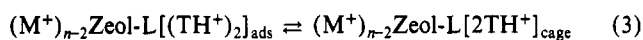
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of the monomers, the dimers, and the higher aggregates^{2,3,8,9} have been used to distinguish them. The geometry of a zeolite L does not allow the formation of parallel dimers, so called H-type aggregates,¹⁰ inside the main cage. This can be used to distinguish between molecules within the cage and molecules only adsorbed on the surface of a zeolite particle since those on the surface have a strong tendency to form aggregates. To find out how many thionine molecules TH⁺ are adsorbed on zeolite L or located in the main channel, we have measured exchange isotherms. Reactions of the following type are discussed: adsorption of thionine molecules on the surface of the zeolite particles as monomers (1); adsorption of larger amounts of thionine leading to aggregates on the surface of the particles (2); intercalation of surface adsorbed thionine into the main channel (3). We apply electronic ab-

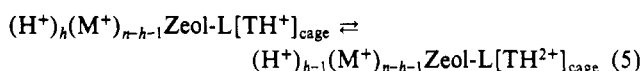
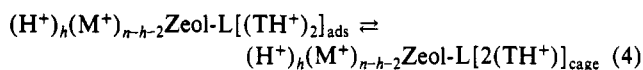


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sorption spectroscopy to differentiate between dye molecules adsorbed on the surface only and molecules inside the main channel. For comparison we also report the exchange isotherms of 2 and 3. The spectrum of the protonated form 1', TH²⁺, is well known and characteristically different from that of 1. This allows the study of acid-base reactions such as (5) in the main channel of the proton zeolite L and the comparison of the intercalation kinetics of the type (3) and (4).



Experimental Section

Dyes. Thionine 1 was purified by converting the hydrochloride form (Merck, Art. 1421, for microscopy) to the free base by adding 10% NaOH to an aqueous solution of thionine. The free base was collected and dissolved in hot 2-propanol, treated with activated charcoal, filtered, and left overnight under nitrogen at room temperature. The precipitated crystals were separated by decantation, treated with 25% hydrochloric acid, and stirred for 1 h. The resulting crystals were recrystallized from 2-propanol/water (1/1) and washed with cold 2-propanol. Further purification was achieved by chromatography on aluminum oxide (CAMAG, 5016-A, basic, Brockmann No. 1) with 95% ethanol.

Methylene blue 2 (Fluka, puriss) was used without further purification.

Ethylene blue 3 was prepared¹⁷ by dissolving 10 g of *N,N*-diethylphenylenediamine in 600 mL of cold 3 M hydrochloric acid. Three grams of zinc sulfide was added and the solution was saturated with hydrogen sulfide; 150 mL of a 40% solution of ferric chloride was added dropwise. The product was extracted with methylene chloride, purified by flash column chromatography on silica gel (Baker Analysed 70241) with chloroform/methanol (4/1), and analyzed by ¹H NMR.

Zeolite L. Zeolite Linde type L with the stoichiometry K₆-Na₃(SiO₂)₂₇(AlO₂)₉·21H₂O and a particle size of about 0.2 μm (obtained from Union Carbide, Molecularsieves Type ELZ-L) was saturated with K⁺ by stirring in a 1 M KCl aqueous solution at 50 °C for 5 h, resulting in a zeolite in which all exchangeable

TABLE I: Extinction Coefficient at the Absorption Maxima of the Dyes 1, 2, and 3 in 10⁻⁵ M Aqueous Solutions

	ε/10 ⁵ M ⁻¹ cm ⁻¹
thionine	0.53 ¹ (597 nm)
methylene blue	0.85 ¹² (664 nm)
ethylene blue	1.01 ¹⁷ (670 nm)

cations consist of K⁺. The exchanged zeolite was washed several times with bidistilled water and dried overnight at 80 °C. To obtain the protonated form of zeolite L, a suspension in diluted aqueous HCl was stirred at 70 °C. In intervals of 1 h, hydrochloric acid was added to adjust the pH of the suspension to 2.5. This procedure was repeated several times until the pH remained stable at about 3.

Procedure To Determine the Exchange Isotherm of Dye Zeolite L. Weighed amounts (1–40 mg) of dried K⁺-zeolite L were added to 25 mL of an approximately 10⁻⁵ M aqueous dye solution. The concentration was determined by absorption spectroscopy using the extinction coefficients ε in Table I. After treatment in the supersonic bath for about 5 min the suspensions were shaken with a lab shaker for 2 weeks at room temperature (22 °C). The suspensions were centrifuged at 5000g during 10 min. The absorption spectrum of the supernatant was similar to that of an aqueous dye solution. We therefore assume that the measured absorbance was not influenced by the remaining zeolite particles. The concentration of the residual dye in the supernatant was determined by UV-vis spectroscopy. The number of exchanged dye molecules was calculated from the difference between the initial and the equilibrium state dye concentration in the supernatant. All manipulations were performed in polyethylene vessels to avoid adsorption on glass surfaces and in the dark to minimize thermal and photochemical degradation of the free dye molecules.

Spectroscopy. Absorption spectra were measured with a single-beam spectrophotometer (Philips PU8700) on both homogeneous solution and dilute dispersions of zeolites. Because of the small particle size and the high dilution good quality, transmission spectra could be measured. When necessary, a dye-free diluted zeolite L dispersion was used to determine the baseline. To measure the spectra of zeolites containing dyes prepared as described above, a small amount of dye zeolite L was washed with bidistilled water until the water remained colorless. The samples were then dried at 60 °C overnight. About 2 mg of it was then dispersed in 5 mL of water and a spectrum was taken. For other measurements a typical procedure with zeolite dispersions was as follows: 100 μL of zeolite L suspension (1 g/50 mL) was mixed with 2.5 mL of bidistilled water and different amounts (10–100 μL) of a 2 × 10⁻³ M aqueous dye solution were added. This leads to suspensions with a zeolite L concentration of 0.8 g/L and dye concentrations in the range 8 × 10⁻⁶–8 × 10⁻⁵ M.

Results

Ionic Exchange. The stoichiometric formula of a potassium zeolite L is K₆(SiO₂)₂₇(AlO₂)₉·21H₂O, its cations being distributed among different sites. Only the cations belonging to the main channel can be exchanged by other cations for steric reasons. According to Breck,^{18–20} 3.6 cations per unit cell belong to this channel on the average. We therefore define the exchange degree θ as the number of cations exchanged per unit cell, with respect to the average number of cations belonging to the main channel.

$$\theta = \text{number of cations exchanged per unit cell}/3.6 \quad (6)$$

This can also be expressed as

$$\theta = [\text{D}^+]_{\text{Z}}/[\text{K}^+]_{\text{Z}}^0 \quad (7)$$

If not otherwise stated, concentrations refer to the whole volume

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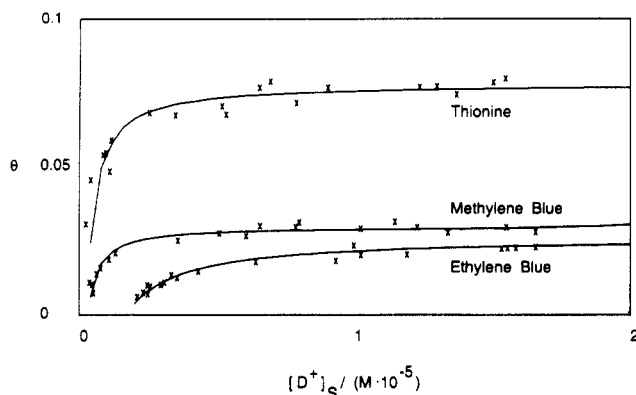


Figure 1. Exchange isotherms of thionine, methylene blue, and ethylene blue on potassium zeolite L. The crosses represent experimental values and the solid line is a fit of eq 16 to the experimental data.

TABLE II: Maximum Exchange Degrees (θ_{\max}) of Thiazine Dyes on Zeolite L

	θ_{\max} , %
thionine	7.5
methylene blue	3.06
ethylene blue	2.36

of the suspensions which are treated as they would not settle. The exchange degree θ (6) has close analogy to the fractional coverage θ' as defined in the description of adsorption isotherms:²¹

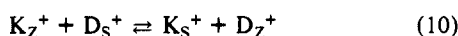
$$\theta' = \frac{\text{no. of adsorption sites occupied}}{\text{no. of adsorption sites available}} \quad (8)$$

As we will show later, not all cation sites belonging to the main channel are available for adsorption of the dyes. Thus

$$\theta' = \frac{[D^+]_Z}{[D^+]_{Z_{\max}}} = \frac{\theta}{\theta_{\max}} \quad (9)$$

The experimentally determined room temperature exchange isotherms of the three thiazine dyes 1, 2, and 3 in Figure 1 show on the abscissa the dye concentration $[D^+]_S$ in the solution and on the ordinate the exchange degree θ at equilibrium. The saturation values θ_{\max} for the three dyes are reported in Table II. θ_{\max} refers to the maximum exchange degree for a specific dye. The thionine can exchange about 7.5% of the cations belonging to the main channel. The difference between θ_{\max} of the thionine and θ_{\max} of the other dye cations will be shown to be indicative for a remarkable dissimilarity to the nature of sites that can be populated by the different molecules. The slope of $\theta([D^+]_S)$ does not go through $[D^+]_S = 0$ for $\theta = 0$ as one would eventually expect, because some residual KCl was adsorbed on the zeolite; see below. $[D^+]_Z$ and $[K^+]_Z$ are the concentration of the dye and of the potassium cations located in the main channel which are exchangeable by the dye. The subscripts Z and S refer to zeolite and solution and the superscript zero indicates initial concentrations.

To develop a quantitative description, we apply the treatment of ion-exchange reactions in zeolites according to Breck¹⁸



where $[K^+]_Z$ represents the exchangeable sites and the equilibrium constant K is defined as

$$K = \frac{[K^+]_S[D^+]_Z}{[D^+]_S[K^+]_Z} \quad (11)$$

We obtain formal analogy to the Langmuir isotherm²¹ by defining $K' = K/[K^+]_S$. The total ion concentration in solution $[K^+]_S + [D^+]_S$ varies between 2×10^{-5} and 2×10^{-4} M and it does not

TABLE III: Limiting Concentration $[D^+]_S^{\theta \rightarrow 0}$, $m = 0.3$

	limiting concn $[D^+]_S^{\theta \rightarrow 0}$
thionine	<0.02
methylene blue	0.04
ethylene blue	0.17

seem a first priority to discuss its influence on activity coefficients. The following concentration relations hold:

$$[D^+]_S^0 = [D^+]_Z + [D^+]_S \quad (12a)$$

$$[K^+]_a^0 + \theta_{\max}[K^+]_Z^0 = [K^+]_Z + [K^+]_S \quad (12b)$$

$$\theta_{\max}[K^+]_Z^0 = [K^+]_Z + [D^+]_Z \quad (12c)$$

Equation 12b takes into account that by the pretreatment of the zeolite two types of potassium cations are brought into the system, namely $[K^+]_Z^0$, corresponding to the total number of exchangeable cations, and the residual KCl adsorbed on the particles denoted as $[K^+]_a^0$. It is convenient to express $[K^+]_a^0$ in terms of the relative number m which we have determined experimentally.

$$[K^+]_a^0 = m[K^+]_Z^0 \quad (13)$$

In our experiments m was in the order of 0.3. This means that the number of adsorbed potassium cations was approximately one per unit cell. Inserting (7), (12), and (13) into (11) we get after some rearrangement for the equilibrium constant K

$$K = \frac{m \left(\frac{[D^+]_S^0 - [D^+]_S}{\theta} \right) + ([D^+]_S^0 - [D^+]_S)}{[D^+]_S \left(\frac{\theta_{\max}}{\theta} - 1 \right)} \quad (14)$$

which leads to

$$K = \frac{1}{[D^+]_S} \frac{m + \theta}{\theta_{\max} - \theta} ([D^+]_S^0 - [D^+]_S) \quad (15)$$

From this we calculate the exchange degree θ

$$\theta = \frac{[D^+]_S(K\theta_{\max} + m) - m[D^+]_S^0}{[D^+]_S(K - 1) + [D^+]_S^0} = \frac{K\theta_{\max} + m \left(1 - \frac{[D^+]_S^0}{[D^+]_S} \right)}{K - \left(1 - \frac{[D^+]_S^0}{[D^+]_S} \right)} \quad (16)$$

This equation can be used to determine the equilibrium constant K and θ_{\max} from the experimental data. It explains also the observation that the slope $\theta([D^+]_S)$ does not go through $[D^+]_S = 0$ for $\theta = 0$. Let us assume that we add to a given amount of dye solution a large amount of potassium zeolite. This leads to a very small θ with a dye concentration $[D^+]_S^{\theta \rightarrow 0}$ defined as follows:

$$[D^+]_S^{\theta \rightarrow 0} = \lim_{[K^+]_Z \rightarrow \infty} [D^+]_S \quad (17)$$

In the limit $\theta \rightarrow 0$ the numerator of eq 16 must vanish:

$$[D^+]_S(K\theta_{\max} + m) - m[D^+]_S^0 = 0 \quad \text{for } \theta \rightarrow 0 \quad (18)$$

Solving this equation for $[D^+]_S^{\theta \rightarrow 0}$ results in

$$[D^+]_S^{\theta \rightarrow 0} = [D^+]_S^0 \frac{m}{K\theta_{\max} + m} \quad (19)$$

In Figure 1 $[D^+]_S^{\theta \rightarrow 0}$ corresponds to the intersection of the isotherms with the abscissa at $\theta = 0$. The thus determined $[D^+]_S^{\theta \rightarrow 0}$ are reported in Table III. We have fitted the experimental data points in Figure 1 to the theoretical expression (16) by independently varying the equilibrium constant K and θ_{\max} . The theoretical curves drawn as solid line show no systematic deviation from the experimental values. We conclude that eq 16 is adequate

(21) Atkins, P. W. *Physical Chemistry*; W. H. Freeman and Co.: New York, 1990; p 885.

TABLE IV: Equilibrium Constants K of Reaction 10^a

	K
thionine	320
methylene blue	520
ethylene blue	135

^aFor MB⁺ and EB⁺ the equilibrium constants do not refer to main channel equilibria.

to describe our data. The thus obtained equilibrium constants are given in Table IV from which follows that the zeolite strongly prefers thionine in comparison to the exchangeable potassium cations in the main channel. The maximum number of thionine molecules that can be incorporated is therefore only limited by the space available in this channel. We will come back to this later.

Let us compare this result with the Langmuir isotherm equation²¹

$$K' = \frac{1}{[D^+]_S} \frac{\theta'}{1 - \theta'} \quad (20)$$

from which we get for the fractional coverage θ'

$$\theta' = \frac{K[D^+]_S}{1 + K[D^+]_S} \quad (21)$$

It is obvious that when $\theta' = 0$ it follows that $[D^+]_S^{\theta' \rightarrow 0} = 0$. This corresponds in (19) to $m = 0$. When $m = 0$ it follows from (12) that $[D^+]_S^0 - [D^+]_S = [K^+]_S$. Inserting this in eq 15, dividing by $[K^+]_S$ and applying the definitions $\theta' = \theta/\theta_{\max}$ and $K' = K/[K^+]_S$ this leads to the Langmuir equation (20) or (21), respectively. Thus, formal similarity of the ion-exchange isotherm with the hyperbolic Langmuir isotherm has been proven.

Absorption Spectra of Thionine on Zeolite L. Electronic absorption spectra of thionine TH⁺ 1, methylene blue, MB⁺ 2, and ethylene blue, EB⁺ 3, were studied many years ago by several authors under different conditions.²⁻¹² In very diluted aqueous solutions ($<10^{-5}$ M) at about neutral pH the spectra of the pure monomers are observed. With increasing concentration a new blue-shifted band grows in. This band can be correlated with the appearance of dimers (TH⁺)₂, (MB⁺)₂, and (EB⁺)₂. At concentrations above 10^{-3} M a further blue shift in the spectra is observed which is caused by the formation of trimers (TH⁺)₃, (MB⁺)₃, and (EB⁺)₃. A new band red-shifted by 70–80 nm appears in strongly acidic dye solutions of about pH = 0, indicating that the protonated forms 1', 2', and 3' are stable under these conditions. Metachromasy in clay minerals of thionine,¹⁶ methylene blue,^{12,15} acridineorange,²² and pyronine Y²³ has been studied.

The geometry of a zeolite L does not allow the formation of H-aggregates inside the main cage. The easiest way to find out if the isotherms in Figure 1 describe molecules that are really located inside the main channel is to compare the absorption spectra of the dyes on zeolite L with their absorption spectra in homogeneous solution. In Figure 2 we show the thionine absorption spectrum of a sample corresponding to the second last experimental point in Figure 1 at an exchange degree of $\theta = 0.075$. It is important to realize that the dye concentration with respect to the volume of the zeolite particles is very high. $\theta = 0.075$ corresponds to 0.27 dye molecules per unit cell or the stoichiometric equation $(\text{TH}^+)_{0.27} \text{K}_{8.73} (\text{SiO}_2)_{27} (\text{AlO}_2)_9 \cdot 21\text{H}_2\text{O}$. The mass of a unit cell is 2880 g/mol and the density of the zeolite L is about 2.11 g/cm³. From this we calculate a dye concentration on the zeolite of about 0.2 M. The spectrum of thionine in ethanol is the one of pure monomers. The spectrum in sucrose and the more pronounced one in water indicate the beginning of some dimer formation. The spectrum of thionine in zeolite L is even more structured than the one in ethanol with respect to which it is red-shifted by 20 nm. Spectra measured at all exchange degrees

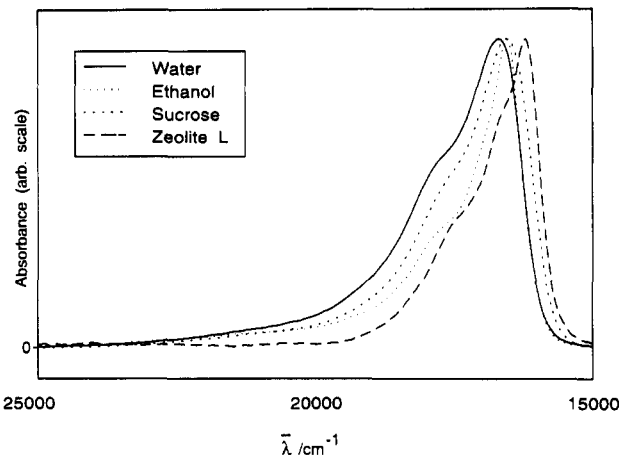
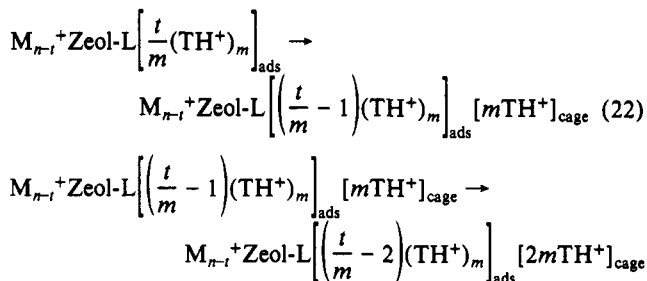


Figure 2. Absorption spectra of 10^{-5} M thionine solutions in different solvents scaled to identical heights. The thionine-zeolite spectrum corresponds to the pure dye-zeolite part of the second last point at $\theta = 0.075$ of the thionine exchange isotherm, Figure 1, and therefore to a concentration of 0.2 M with respect to the zeolite volume.

have exactly the same shape. It corresponds to the one expected for monomers. We conclude that the thionine is really located inside the main channel of zeolite L since we have observed the spectrum of the monomer $M_{n-1}^+ \text{Zeol-L}[\text{TH}^+]_{\text{cage}}$. The more pronounced structure of the thionine-zeolite spectrum in comparison to the spectra in solution might indicate the restricted freedom in the channel.²⁴

Our interpretation is supported by an experiment that shows how the dye-zeolite spectrum develops in time. The kinetics of the dye adsorbed on the zeolite particles going into the channel can be expressed as follows



It is very slow at room temperature and takes about 2 weeks to be completed. We have therefore carried out experiments at elevated temperature. In Figure 3a we show the spectra observed when adding 20 μL of a 2×10^{-3} M aqueous thionine solution to 2.5 mL of an aqueous dispersion at 70 °C containing 2 mg of zeolite L. The spectrum measured just after mixing the dye with the dispersion shows the typical form expected for aggregates. These aggregates may not only consist of dimers but also of trimers and perhaps of some higher agglomerates. Because we cannot clearly distinguish between them we will always speak of aggregates $(\text{TH}^+)_{\text{m}}$, $m = 2, 3, \dots$ With time the short-wavelength aggregate absorption decreases and the monomer spectrum develops and we finally end up with the spectrum shown in Figure 2. Decomposition of the spectra in the monomer and the aggregate absorption gives a more quantitative impression on the kinetics of the intercalation reaction (18). This is illustrated in Figure 3b where the increase of the concentration of dye intercalated in the main channel $[\text{TH}^+]_{\text{cage}}$ and the decrease of dye adsorbed on the surface $[(\text{TH}^+)_{\text{m}}]_{\text{ads}}$ are shown. The reaction rate cannot be described by a single exponential.

How do the spectra look like immediately after mixing different amounts of dye to the zeolite suspension? To answer this question 10 μL of a 10^{-3} M thionine solution have been added step wise

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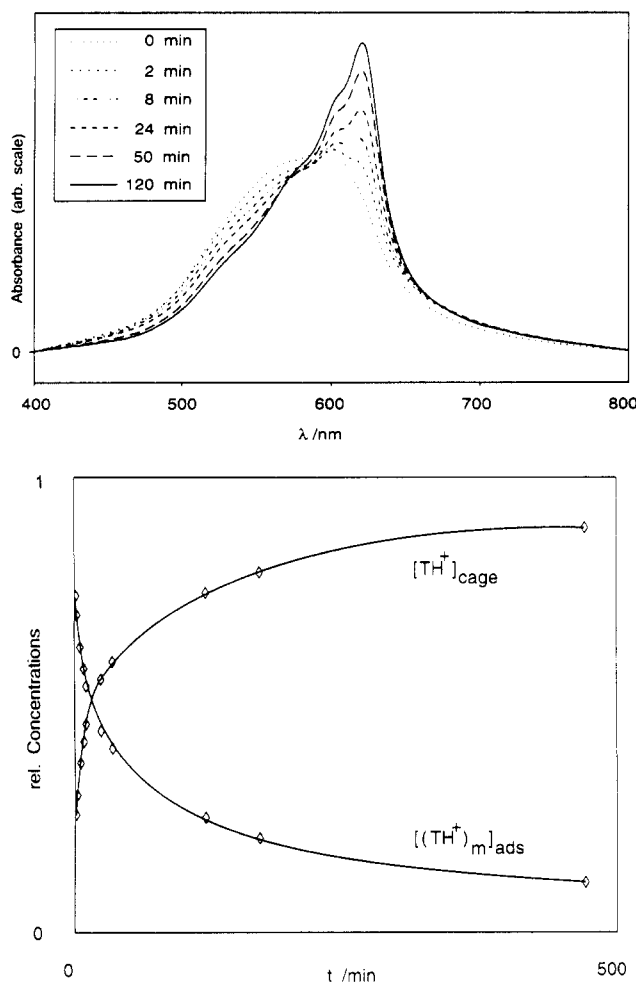
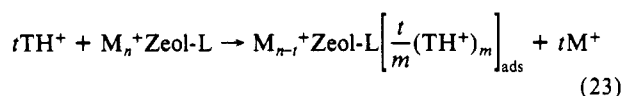


Figure 3. (a, top) Spectra of a thionine-zeolite L dispersion at 70 °C measured at different times after mixing of an aqueous zeolite dispersion with the dye. (b, bottom) Kinetics of intercalation of the aggregates formed in the first step into the main channel at 70 °C.

to 2.5 mL of a dispersion containing 2 mg of zeolite L at pH 6.5. This corresponds to dye concentrations of 8×10^{-6} – 6.4×10^{-5} M. A spectrum was taken immediately after mixing. The results obtained are shown in Figure 4a. Surprisingly, we have observed the aggregate spectrum 1 at concentrations of only 8×10^{-6} M at which in pure aqueous solutions a monomer spectrum is observed. Visual demonstration of this observation is obtained if to a diluted thionine solution containing monomers only a small amount of zeolite dispersion is added. The violet color of the thionine monomer immediately turns into purple. This means that at this concentration the dye molecules stick immediately on the zeolite surface where their tendency to form aggregates is very high. If the dye-zeolite dispersion is separated from the water by centrifuging, a completely colorless supernatant solution results. This means that the dye has gone quantitatively on the zeolite according to the following equation:



The spectra change continually with increasing concentration. Up to about 2×10^{-5} M situations, however, similar behavior is observed. At higher concentrations the supernatant becomes colored, indicating that now part of the dye molecules remain in solution. This is also demonstrated by Figure 4b where spectrum 1 is compared with the difference spectra 3 – 2, 5 – 4, and 8 – 7 normalized to equal maxima. The shapes of the spectra 1 and 2 are identical. Spectrum 3 is a superposition of spectrum 1 and the difference spectrum 8 – 7. The difference spectra 4 – 3 to 8 – 7 correspond to thionine solved in water. From this we know

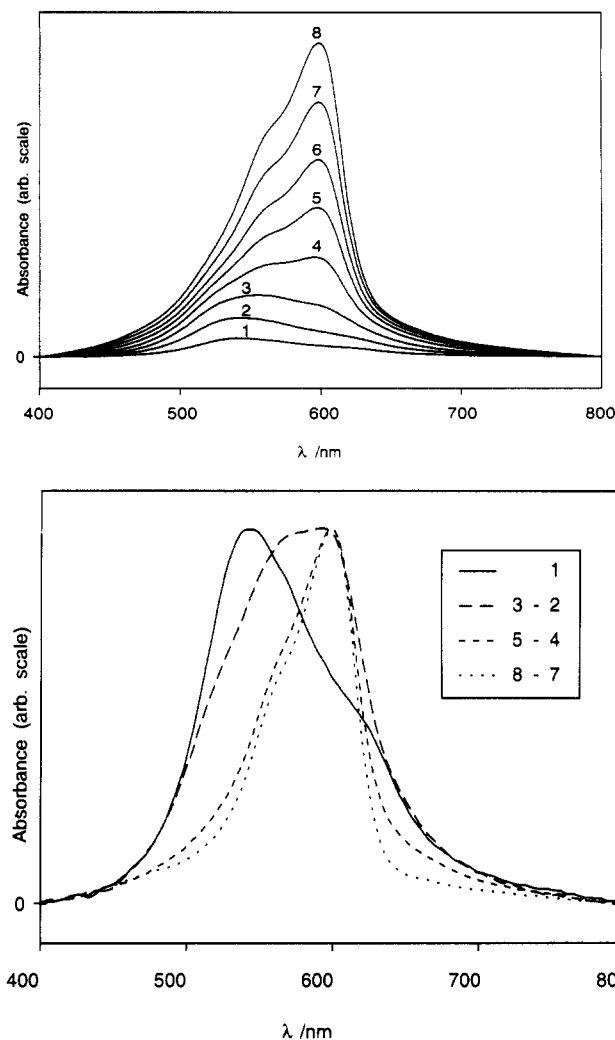
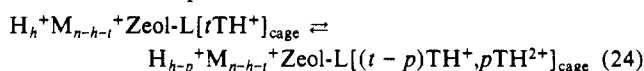


Figure 4. (a, top) Spectra obtained by step wise addition of thionine to an aqueous zeolite L suspension at room temperature. (b, bottom) Magnified spectrum 1 and difference spectra 3 – 2, 5 – 4, and 8 – 7 normalized to the same maximum.

that the first two additions and half of the third dye addition stick immediately on the zeolite particles while later additions remain in solution. Expressed as exchange degree this corresponds to $\theta = 0.02$, a value close to $\theta_{\text{max}} = 0.024$ observed for ethylene blue and comparable to $\theta_{\text{max}} = 0.03$ for methylene blue.

If our interpretation thus far is correct, it should be possible to observe the protonated form $1' \text{TH}^{2+}$ within the main channel of zeolite L under conditions where the aqueous solution is not acidic enough to stabilize TH^{2+} . An elegant experiment can be carried out applying a similar procedure as described before to observe the intercalation kinetics of a potassium zeolite L as shown in Figure 3. One gram of proton zeolite L was dispersed in 50 mL of water resulting in a pH of 5.5; 100 μL of this dispersion was diluted with 2.5 mL of water and kept at 70 °C. To this dispersion 10 μL of an aqueous 10^{-3} M thionine solution was added and the first spectrum measured immediately after mixing. Further spectra were taken in time intervals of 1 min. The result is shown in Figure 5a. In Figure 5b we show the spectrum of thionine in an aqueous 2.5 M HCl solution, for comparison. The first spectrum in Figure 5a is similar to the aggregate spectrum in Figure 4 with already some shift to the red thus indicating that the kinetics of this system is faster. The red band of the protonated form is already well developed after 1 min. After 3 min the intensity of the 670-nm absorption belonging to TH^{2+} and the 619-nm band belonging to TH^+ increase at the same speed. This means that the equilibrium



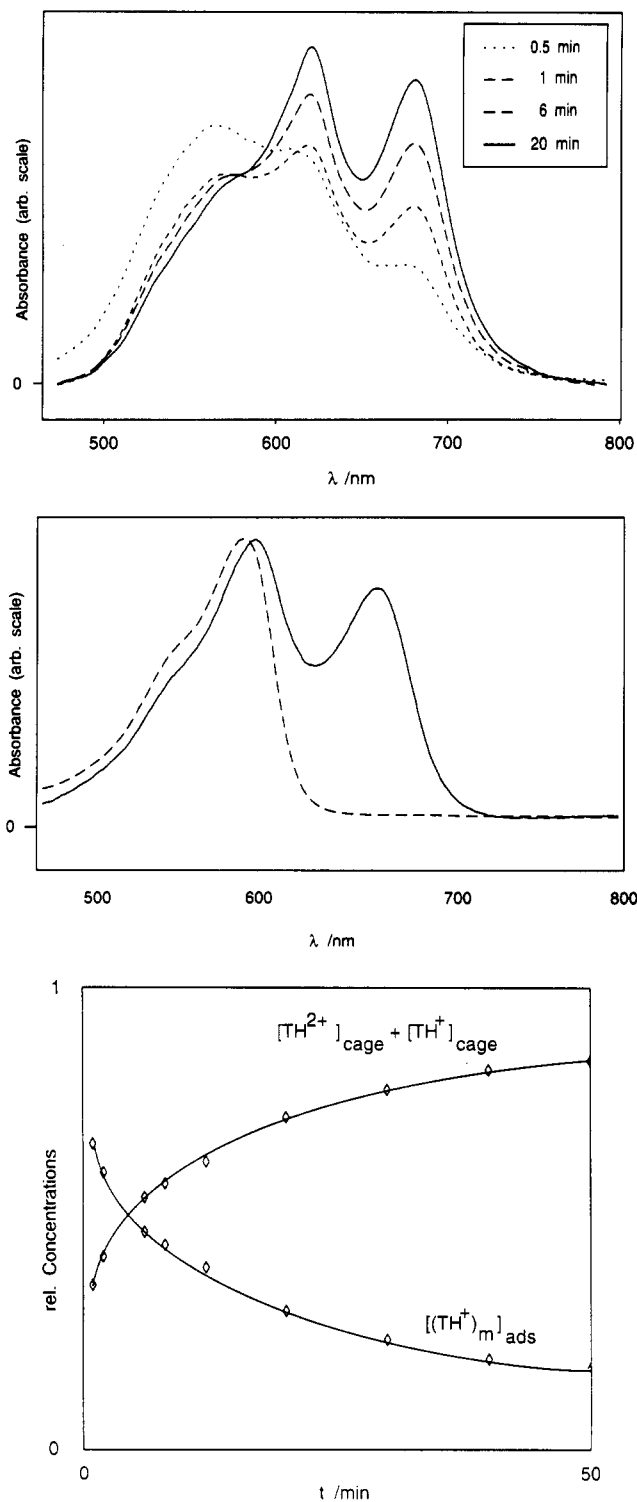


Figure 5. (a, top) Time-dependent behavior of the absorption spectrum of thionine in the protonated form of zeolite L at 70 °C. (b, middle) Absorption spectra of 10⁻⁵ M thionine solutions in water at neutral pH (dashed line) and in 2.5 M HCl (solid line) at room temperature. (c, bottom) Kinetics of intercalation of the aggregates formed in the first step into the main channel at 70 °C.

has been reached. As before, decomposition of the spectra in Figure 5a in the monomer and the aggregate absorption gives a more quantitative impression on the kinetics of the intercalation reaction (22). This is illustrated in Figure 5c where the increase of the concentration of dye intercalated in the main channel $[(\text{TH}^{2+})_{\text{cage}} + (\text{TH}^+)_{\text{cage}}]$ and the decrease of the dye adsorbed on the surface $[(\text{TH}^+)_{\text{m}}]_{\text{ads}}$ are shown. Comparing this result with Figure 3b we conclude that at 70 °C the intercalation of the proton zeolite L reaction is about 10 times faster than that of the potassium zeolite L. Again the reaction rate shown in Figure 5c cannot be

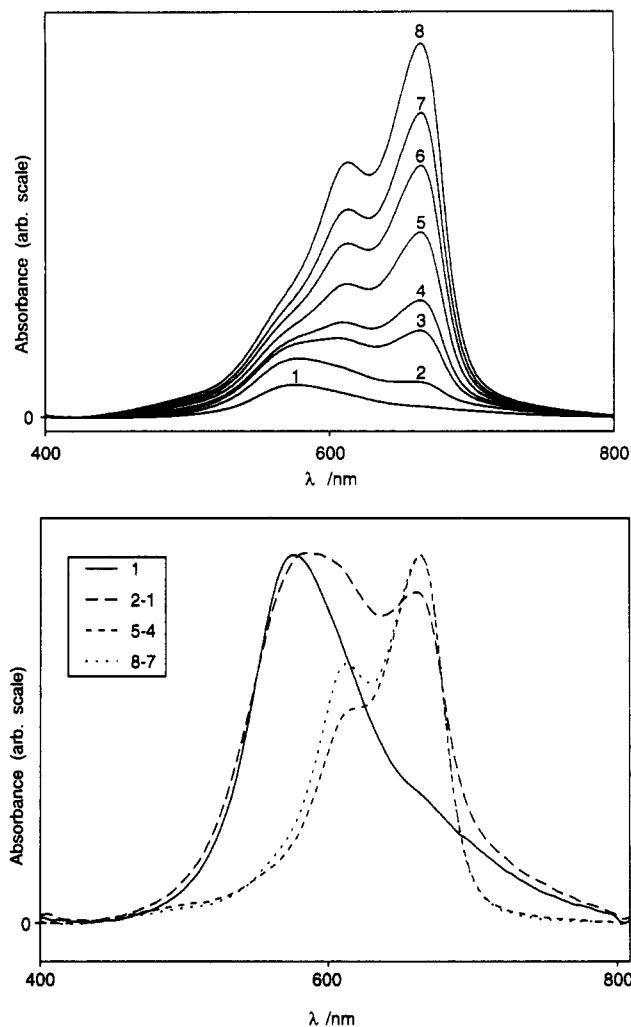


Figure 6. (a, top) Spectra obtained by stepwise addition of methylene blue to an aqueous potassium zeolite L suspension at room temperature. (b, bottom) Magnified spectrum 1 and difference spectra 2 - 1, 5 - 4, and 8 - 7 normalized to the same maximum.

described by a single exponential.

These data provide also an understanding of the proton activity of zeolite L. In the main channel of zeolite L the number of water molecules is comparable to the number of Zeol-OH groups and can therefore not be neglected. We estimate the ratio of water molecules to Zeol-OH groups per unit cell in the main channel as about 6. The acid-base reaction within the main channel can be expressed in simplified terms by eq 25 in which the concentration of water molecules can not be assumed as constant. We

$$K_{a,\text{Zeol}} = \frac{[\text{H}_3\text{O}^+][\text{Zeol-O}^-]}{[\text{H}_2\text{O}][\text{Zeol-OH}]} \quad (25)$$

do not include activity coefficients in our formulas, because of lack of data. On the basis of the ratio of the TH^{2+} extinction and the TH^+ extinction in the absorption spectrum of equilibrated thionine in the protonated zeolite L we find that the proton zeolite L behaves toward thionine like 2.5 M aqueous HCl with a ratio of $[\text{H}_3\text{O}^+]/[\text{H}_2\text{O}] = 0.047$. Assuming that this ratio can be applied to approximate the proton activity in the main channel we get $[\text{Zeol-O}^-]/[\text{Zeol-OH}] = 0.4$. Inserting these number into (25) we get $K_{a,\text{Zeol}} = 0.02$ for the main channel.

Absorption Spectra of Methylene Blue and Ethylene Blue on Zeolite L. The spectra of methylene blue (MB^+) and ethylene blue (EB^+) on zeolite L behave similar to that of thionine immediately after mixing. This is illustrated in the case of MB^+ in Figure 6, a and b, which has been obtained by exactly the same procedure as described for Figure 4. In contrast to thionine, however, no time evolution of the spectra can be observed. Even after 2 weeks at room temperature or 24 h at 70 °C their form

remains identical. A small decrease in intensity has been observed. This means that methylene blue and ethylene blue do not go into the main channel under these conditions. Similar experiments with proton zeolite L as described for the thionine have been carried out for these two dyes. In sharp contrast to the thionine case we have not been able to observe the spectrum of the protonated form of these dyes under these conditions. This is a convincing proof that they have not been intercalated.

Discussion

We have observed that thionine molecules all enter the channel of a potassium and of a proton zeolite L after they have been adsorbed on the surface. In contrast to this, methylene blue and ethylene blue are only adsorbed on the surface of the zeolite. Thionine is only slightly larger than methylviologen which has already been incorporated in different types of zeolites,²⁵⁻²⁷ but for which to our knowledge no exchange isotherm has been reported so far. From the maximum exchange degree θ_{\max} of thionine, its maximum equilibrium concentration is calculated as about 0.2 M with respect to the zeolite volume. Even at this high concentration, its electronic absorption spectrum is that of a monomer, shifted by 25 nm to the red with respect to that observed in water. As regards methylene blue and ethylene blue, however, only the spectrum of aggregates has been observed. While θ_{\max} of thionine is a measure of the space available inside the main channel, θ_{\max} of methylene blue and ethylene blue is a measure of the space available at the outer surface. The ratio of θ_{\max} of the two dyes is 1.3. Where does this difference come from? Let us assume that the first layer of methylene blue covers the surface completely and that the aggregation number for both dyes is the same. In this case the difference of θ_{\max} of the two dyes is only a question of their size. The number n of methylene blue molecules that can stick on a zeolite L surface F is given by

$$n = F/F_{\text{MB}} \quad (26)$$

F_{MB} is the area of the methylene blue (MB^+). Ethylene blue (EB^+) is larger by ΔF and therefore N is smaller by Δn . This can be expressed as follows:

$$n - \Delta n = \frac{F}{F_{\text{MB}} + \Delta F} \quad (27)$$

From this we obtain

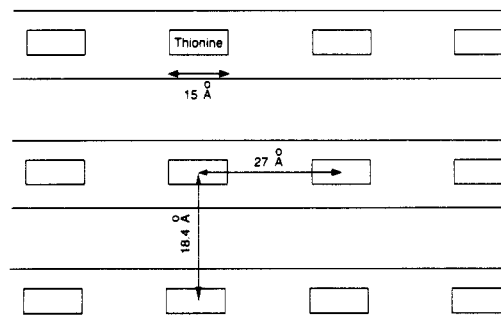
$$\Delta n = n - \frac{F}{F_{\text{MB}} + \Delta F} = F \left(\frac{1}{F_{\text{MB}}} - \frac{1}{F_{\text{MB}} + \Delta F} \right) \quad (28)$$

and thus

$$\Delta n = n \left(\frac{\Delta F}{F_{\text{MB}} + \Delta F} \right) \quad (29)$$

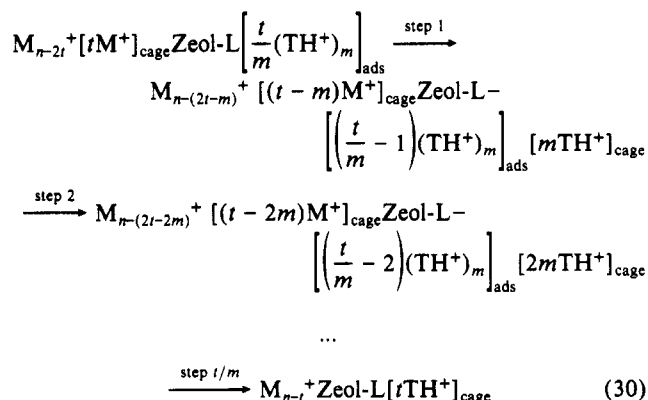
F_{MB} is approximately $18 \times 9 \text{ \AA}^2$ and ΔF is in the order of 60 \AA^2 , and we get $\Delta n \approx 0.27n$. From this follows $\theta_{\max}(\text{MB})/\theta_{\max}(\text{EB}) \approx n/(n - \Delta n) = 1.37$, a value close to the experimentally observed ratio of the maximum exchange degrees (Table II). This is why it seems reasonable to assume that the differences in θ_{\max} of MB^+ and EB^+ are due to the different size of the two molecules. It is remarkable that the same formalism can be used to describe the exchange isotherms of thionine, MB^+ and EB^+ despite the fact that the thionine monomers are located inside the main channel and the other dyes are on the surface of the zeolite particles. We assume that this is explained by the fact that in each case an ion-exchange reaction and not a less specific adsorption occurs. It seems that after saturation via ion exchange has been completed an excess positive charge on the zeolite particles does not allow more dye molecules to stick onto the

SCHEME II: Scheme To Illustrate the Mean Distance of Thionine Molecules in the Main Channel of Zeolite L at Maximum Exchange Degree



surface. Surface phenomena of this kind are well known in colloidal chemistry.²⁸

What is the specific situation of a dense package of thionine molecules in the main channel of a zeolite L? We start with the observation that its electronic absorption spectrum is more structured than that observed in ethanol, water, and other solvents at room temperature. It resembles more a low-temperature spectrum. This can be understood considering the limited space available in the main channel. The molecule is embedded in a rigid environment and therefore a more uniform distribution results in which otherwise at room temperature accessible low-energy states are not available. This leads to the more structured absorption spectrum. Another typical cage effect is the high Brønsted acidity probed by the thionine in the main channel of the proton zeolite L. The absorption spectrum of the protonated form 1' of thionine is characteristically different from that of 1. Comparison of the thionine spectrum in the channel of the proton zeolite L with that in a 2.5 M aqueous HCl solution shows that the acidity the thionine feels in the channel corresponds to the acidity it feels in a 2.5 M HCl solution. Disregarding activities, we estimate the $[\text{H}_3\text{O}^+]/[\text{H}_2\text{O}]$ ratio in 2.5 M HCl as 0.047. From this we get $[\text{Zeol-O}^-]/[\text{Zeol-OH}] \approx 0.4$. The aqueous environment of the proton zeolite particles was at pH 5.5 in our experiments, just as a reminder. One has to be cautious in reporting acidity constants in such an environment²⁹ and we leave this out in the present investigation. It is striking that the intercalation kinetics of a proton zeolite is much faster than that of a potassium zeolite L. A possible explanation of this observation has to take into account that the protons have a higher mobility than the potassium cations. Each TH^+ entering the channel substitutes a cation that has to leave. Once a TH^+ has entered from both sides the leaving cation has to pass between the dye and the empty space left. This seems to be much harder for the potassium cations than for the protons that can travel by a chain mechanism. A stoichiometric description of the reaction sequences of the intercalation kinetics is obtained by writing eq 22 in more detail:



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In each step the thionine has to slip farther into the channel and the leaving cation has to pass more dye molecules being already in the channel. After a short initial period the mean path lengths a cation has to travel to escape the channel is the same in both directions. This means that the fast intercalation rate observed at the beginning slows down (Figures 3b and 5c).

To get a better feeling of what it means that the dye concentration at θ_{\max} is about 0.2 M with respect to the zeolite volume we have to realize that due to the limited space available in the channel, each molecule has to be aligned along the same axis. The mean size of a zeolite L particle is 200 nm. Assuming that the mean length of a channel corresponds to about the same value, one gets a linear chain of about 70 molecules. The distance between two channels is 18.4 Å and the mean distance between the centers of two thionines along the axis of the channel is 27

Å. This geometric situation is illustrated in Scheme II. It is fascinating that such a dense package can be realized without formation of aggregates and it will be exciting to investigate the photochemical and photophysical properties³⁰ of this system.

Acknowledgment. We thank Prof. Frank Wilkinson and Dr. Silvano Bergamasco for helpful discussions. This work was supported by grant BEW-EPA 217.307 financed by the Schweizerisches Bundesamt für Energiewirtschaft and grant No. 2-5.542 of the Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung.

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Growth Shapes of a Two-Dimensional Solid in a Langmuir Monolayer. Role of Impurities

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Two-dimensional solid domains in a monolayer of a fluorescent amphiphile, 12-NBD-stearic acid, are observed with a optical microscope. When oxidation products of the molecule are absent, domains have a rodlike shape showing two long, parallel facets. The introduction of even a few oxidized molecules (less than 1%) leads to needlelike shapes. These needles can be understood as the result of a gradient of impurity concentration, appearing in the beginning of growth. This explanation, based on isotherm measurements and structural observations, implies that impurities segregate in the solid with the growth of the domains. The fluid becomes more pure; this feature is confirmed by observations. The faceted rods are probably growth shapes. Since concentration gradients transform rods into needles, it is proposed that needles are growth shapes as well as rods.

I. Introduction

Two-dimensional phase transitions in amphiphilic monolayers at the air-water interface are an old but still fascinating question.^{1,2} The controversial problem of the so-called liquid expanded-liquid condensed transition was partially resolved recently, with strong evidence that the transition is first order for three different systems.³ However, rheological⁴ and structural⁵ properties of the condensed phases are difficult subjects, different from case to case and not yet totally understood. Epifluorescence microscopy⁶ brought the possibility of direct optical observations in the coexistence region of such a transition. This technique made possible the study of shapes and macroscopic arrangements⁷ of domains. When polarized light is used, fluorescence microscopy is also a powerful tool to investigate molecular order in the phases² and to reveal defects in ordered phases.^{5b}

Presumed equilibrium shapes are generally explained by the competition of line tension and long-range electrostatic interactions of dipolar origin.⁸ Particularly, spiral 2D crystals,⁹ made of chiral lipids, can be interpreted as equilibrium shapes due to the combination of dipolar interactions and non-mirror-symmetric line tension.⁸ However, if the condensed phase is solid, the relevance of this type of explanation is not clear, because of the difficulty for a solid to relax toward its equilibrium shape. For spiral crystals, an alternative interpretation has been given,¹⁰ assuming the phase to be a true solid: the shapes would be growth properties of the solid. In this view, growing crystals are caused to spiral by a gradient of impurity concentration, imposed in the structure during

the growth and creating a lattice-spacing gradient. The impurity could be for example cholesterol, incorporated in the spiral system at a concentration of 1 or 2%. The concentration gradient does not relax during experimental time, because molecular diffusion in the solid phase is very slow. To my knowledge, no experimental result to date can discriminate between the two models.

This article concerns monolayers of a fluorescent amphiphilic molecule, NBD-labeled stearic acid (NBDS), which shows a first-order transition between an isotropic fluid and an anisotropic solid.¹¹ I have studied monolayers of NBDS alone as well as

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