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X-Ray Diffraction, Differential Scanning Calorimetry, and Spectroscopic Studies of Phase Transitions in FeOCl-*n*-Alkylamine Intercalation Complexes

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$\beta \rightleftharpoons \alpha$ Phase transitions in the layered compound FeOCl–$C_nH_{2n+1}NH_2$ (n = 10, 12, 14, 16, and 18) have been studied by X-ray diffraction, differential scanning calorimetry (DSC), and IR. The transition temperature (T_c) is approximately 20°C higher than the melting point of each corresponding amine and increases with the alkyl chain length. The enthalpy of transition has been estimated from DSC measurements as ca. 6 kJ/mole. The conformational changes of the alkyl chains during the $\beta \rightleftharpoons \alpha$ transition could be confirmed by infrared studies.

Introduction

Intercalation between guest compounds and layered materials can be divided into three classes according to the bonding between host layers and guest molecules. In sorption-type complexes organic molecules are loosely bound to the host layers by hydrogen bonds, ion–dipole interactions, and charge-transfer bonds (*1*, *2*). Many intercalation complexes, for example, transition-metal chalcogenohalides, belong to this type. Clay–organic complexes form another class (*3*). In these complexes organic cations are bound to the aluminosilicate layers by electrostatic interaction. The third group comprises organic derivatives of layered inorganic compounds, where organic molecules are directly bound to the host layers by covalent bonds or by replacing the outermost atoms of the layers. Only a few examples of this type have been reported in the literature (*4–9*).

In metal oxyhalides charge-transfer interactions between guest molecules and the layers are predominant. FeOCl, a member of the metal oxyhalides, has a layered structure similar to γ-FeOOH and belongs to the orthorhombic space group *Pmmn* with cell dimensions a = 3.780, b = 3.302, c = 7.917 Å and z = 2 (*10*). The crystal structure consists of stacks of double layers of *cis*-$FeCl_2O_4$ octahedra sharing edges with their neighboring ones (Fig. 1). The outermost Cl atoms form a two-dimensionally infinite layer. The sheets are held together by

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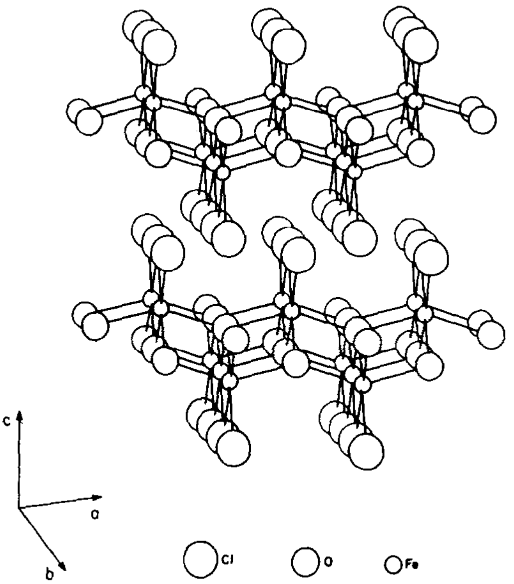

FIG. 1. The structure of FeOCl, viewed 5° off the *b* axis.

van der Waals bonds, which allow FeOCl to be expanded by the intercalation of guest molecules. Iron(III) oxychloride intercalates ammonia, aniline derivatives (*11*), pyridine, pyridine derivatives (*12, 13*), phosphine, and phosphite (*14*). Intercalation of *n*-alkylmonoamine also has been reported (*15–17*). The basal spacings of *n*-alkylamine intercalation complexes vary slightly depending upon thermal treatment. In the present paper, the temperature-dependent phase transition of FeOCl–alkylamine intercalates has been studied (see Fig. 2). Such phase transitions occur in many layered systems such as lipid biomembranes (*18*), layered silicates (*3*), transition metal disulfides (*20*), and perovskite-type layer compounds (*21–24*). In layer perovskites and in lipid biomembranes, the transitions are mainly governed by the dynamics of the chains; they imply reorientational motions of the rigid chains and conformational transitions leading to a partial "melting" of the hydrocarbon part.

Experimental

(*A*) *Preparation*

Iron(III) oxychloride, FeOCl, was prepared from α-Fe_2O_3 and $FeCl_3$ (mole ratio 1 : 1.3) in a sealed Pyrex tube by a chemical vapor transport technique. Dark-brownish, thin, and plate-like crystals were obtained in a temperature gradient of 350–450°C for 7 days. Excess of adhering $FeCl_3$ and $FeCl_2$ was washed out by repeated treatment with water-free ethanol. Powder X-ray diffraction patterns agree with the literature (a = 3.780, b = 3.302, and c = 7.917 Å) (*7*).

The intercalates were obtained by direct reaction between FeOCl and water-free amine. The reaction temperatures were slightly higher than the melting points of the corresponding amines. Completion of intercalation was monitored by powder X-ray diffraction. The basal spacings of the complexes were calculated from the d_{00l} values of the basal reflections.

(*B*) *Analysis*

Powder X-ray diffraction patterns were

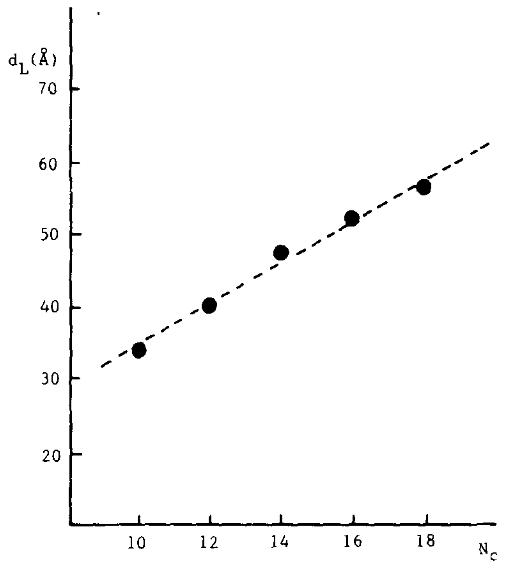

FIG. 2. Basal spacing of FeOCl–alkylamine complex at room temperature as a function of chain length.

obtained with a JEOL JDX-5 apparatus (Ni-filter, Cu*K*α radiation). For measurements above room temperature, a special sample holder for the X-ray diffractometer was constructed. It could be heated electrically up to 80°C, and the temperature could be maintained constant within ±0.5°C during the measurement. The temperature was measured by a Ni–NiCr thermocouple.

Infrared spectra of the FeOCl–octadecylamine complexes were obtained by a Bruker 113 V FT-IR spectrometer equipped with an MCT detector. The samples were in an evacuated sample chamber, where the temperature was kept stable within 1°C. The resolution was 1 cm^{-1} and 400 scans were accumulated. The samples were dispersed, in Nujol mull sandwiched between CsI windows.

Differential scanning calorimetry (DSC) was carried out with a Rigaku TAS-100 apparatus, and the scanning rate was 5°C min^{-1} between 25 and 95°C.

Results and Discussion

(*A*) *X-Ray Studies*

The reaction conditions and basal spacings (at room temperature) of FeOCl–*n*-alkylmonoamine intercalation complexes are summarized in Table I. The basal spacings of the intercalates are dependent upon reaction conditions, especially temperature. Phases, β and α, are defined according to the basal spacings of the intercalates (*3, 4, 19*): the phase stable at room temperature is the β-phase and the stable one at high temperature is the α-phase.

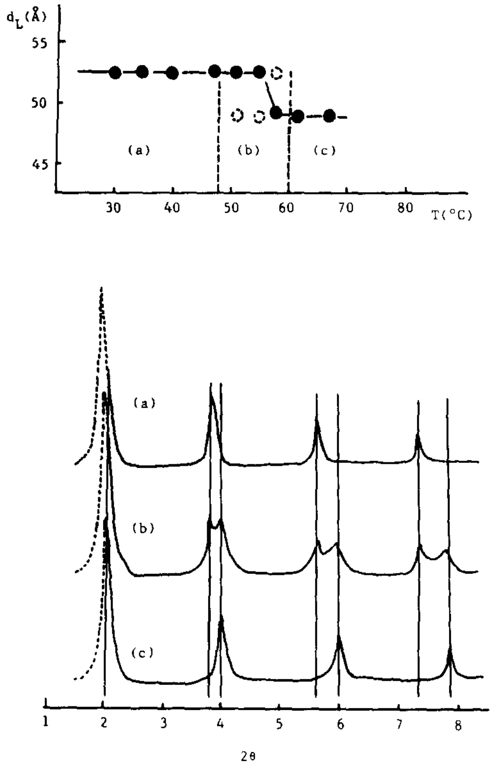

FIG. 3. Temperature dependency of basal spacing of *n*-tetradecylamine intercalate of FeOCl.

TABLE I

BASAL SPACINGS AND REACTION CONDITIONS OF INTERCALATION COMPOUNDS

Guest comp. $C_nH_{2n+1}NH_2$ (n=)	Reaction conditions Temp. (°C)	Time (hr)	Basal spacings Obs. (Å)	Calc.[a] (Å)
10	27	40	34.6	40.1
12	45	40	40.2	45.1
14	45	40	47.5	50.2
16	65	40	52.0	55.2
18	65	40	56.3	60.3

[a] The calculated basal spacings are obtained by assuming extended perpendicular alkyl chains in bilayers.

As depicted in Fig. 2, the basal spacings at room temperature increase gradually with increasing chain length. The average increment of the basal spacing per carbon atom is 2.73 Å/C atom. The maximum increase in a monolayer is 1.265 Å/C atom if the chains in all-*trans* conformation and perpendicular to the layer. The observed values are higher than those calculated for perpendicular chains in bilayers (1.265 × 2

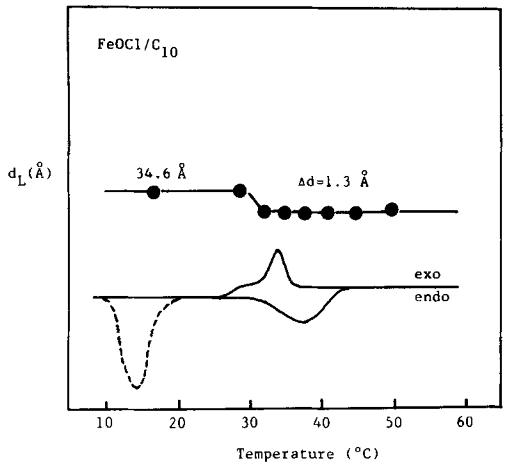

FIG. 4.1. Temperature-dependent basal spacing and DSC curve of FeOCl–decylamine. (Dotted line is the curve of free decylamine.)

= 2.53 Å/C atom). This might be explained by a gradual increase of the tilting angle of the alkyl chains with increasing chain length (*17*).

Similar to many other intercalation complexes (*3*, *16*, *24*), FeOCl–alkylamine complexes show the abrupt decrease of basal spacing at critical temperature. In Fig. 3 the temperature dependency of the basal spac-

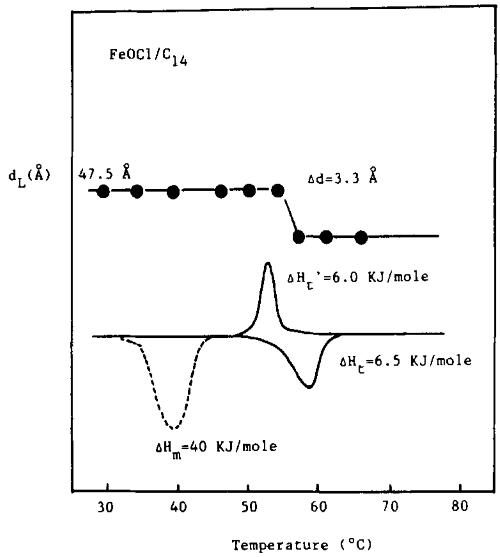

FIG. 4.3. Temperature-dependent basal spacings and DSC curve of FeOCl–tetradecylamine. (Dotted line is the curve of free tetradecylamine.)

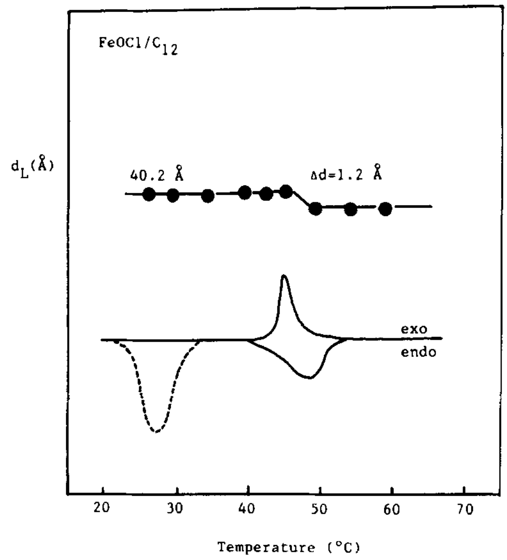

FIG. 4.2. Temperature-dependent basal spacing and DSC curve of FeOCl–dodecylamine. (Dotted line is the curve of free dodecylamine.)

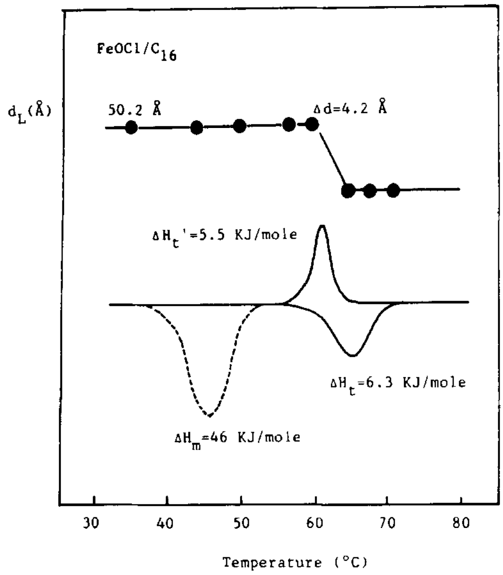

FIG. 4.4. Temperature-dependent basal spacing and DSC curve of FeOCl–hexadecylamine. (Dotted line is the curve of free hexadecylamine.)

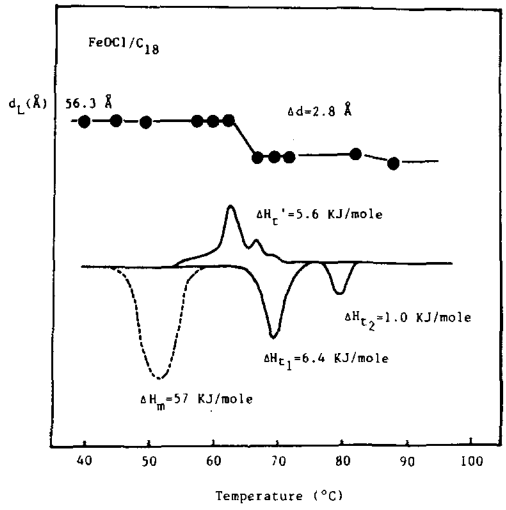

FIG. 4.5. Temperature-dependent basal spacing and DSC curve of FeOCl–octadecylamine. (Dotted line is the curve of free octadecylamine.)

ing in FeOCl–tetradecylamine intercalation complex is shown. Three regions may be distinguished by the basal spacings. The low temperature phase in region a is the β-phase. If it is heated above 60°C, the high temperature α-phase is observed (region c). In region b, two phases coexist, but the coexistence may disappear when the heating rate is slow enough to attain equilibrium.

The differences of the basal spacings between β- and α-phase vary from 1 to 4 Å, depending on the alkyl chain length (Figs. 4.1–4.5).

(*B*) *Differential Scanning Calorimetry*

Calorimetric study of each intercalation compound also proved the $\beta \rightleftarrows \alpha$ phase transition. The transition temperatures obtained by DSC are almost identical to those determined by X-ray diffraction (Figs. 4.1–4.5).

Although some hysteresis between heating and cooling cycle is observed, the value of the enthalpy of exothermic peak in cooling is nearly the same as the corresponding values of the endothermic peak in the heat-

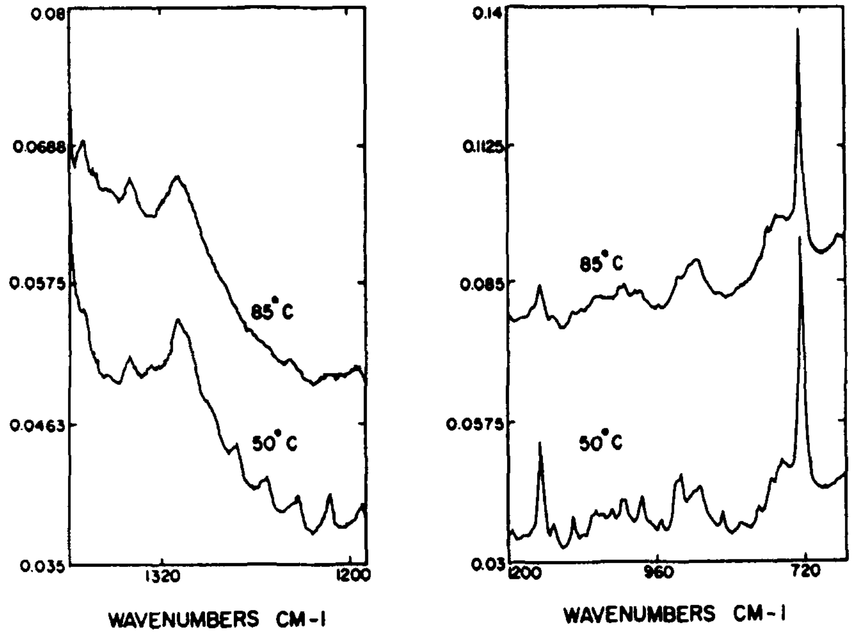

FIG. 5. FT-IR spectra of FeOCl–octadecylamine at 85°C (above) and 50°C (below). The intensities are taken in different scales to reflect the different wavenumber regions.

TABLE II

THE $\beta \rightleftharpoons \alpha$ PHASE TRANSITION TEMPERATURE AND THE ENTHALPY CHANGE FOR FeOCl–ALKYLAMINE INTERCALATION COMPOUNDS COMPARED WITH THOSE FOR THE CORRESPONDING AMINES

Guest	Melting of amine		$\beta \rightleftharpoons \alpha$ transition	
$C_nH_{2n+1}NH_2$ (n =)	Temp. (°C)	ΔH_m (kJ/mole)	Temp. (°C)	ΔH_t (kJ/mole)
10	12	—	30–40	—
12	27	—	43–50	—
14	39	40	48–60	6.5
16	46	46	55–65	6.3
18	51	57	60–72	6.4

ing curve. Therefore, this phase transition seems to be reversible.

FeOCl–octadecylamine exhibits two peaks in each cycle (Fig. 4.5). The first belongs to the $\beta \rightleftharpoons \alpha$ phase transition. The peak at high temperature is probably caused by a $\alpha_1 \rightleftharpoons \alpha_2$ phase transition (*3, 4*).

The transition temperature of the intercalates are about 20°C higher than the melting points of the corresponding amines, and the enthalpies of transition are about 6 kJ/mole which are less than those of melting. According to Lagaly (*3*), the enthalpies of transitions $\beta_i \rightleftharpoons \beta_{i+1}$ and $\beta \rightleftharpoons \alpha$ in alkylammonium–alcanolbeidellite systems are calorimetrically estimated as 2.9–3.4 kJ/mole and ca. 5.8 kJ/mole, respectively. The latter is well consistent with our experimental value of ca. 6.0 kJ/mole for $\beta \rightleftharpoons \alpha$ transition in alkylamine–FeOCl system (see Table II).

(*C*) *Infrared Spectroscopy*

Temperature-dependent infrared spectra prove the proposed model of phase transitions (Fig. 5). The spectra of the β-phase of the octadecylamine complex exhibit well-defined bands which can be assigned to progression bands, by analogy to the spectra of solid *n*-paraffins. They are due to nonlocalized modes and are sensitive to the length and conformation of the alkyl chains. Progression bands are characteristic of the extended chains with all conformations of the C–C bonds. In the high-temperature phase, the progression bands are no longer observed. They are replaced by much weaker and broader bands due to transitions into several conformers. Some bands between 1300 and 1370 cm^{-1} result from the localized vibration modes related to short sequences of bonds with specific conformations as in liquid *n*-alkanes (*24*) and perovskites (*21–24*). The band at 1309 cm^{-1} and perhaps the shoulder near 1370 cm^{-1} correspond to kink (· · ·ttgtg′tt· · · or · · ·ttgtgtt· · ·) defects. The maximum at 1340 cm^{-1} in α-phase appears at the same frequency as a progression band in the spectrum of β-phase; its relative intensity in the α-phase increases while the intensity of the other progression bands decreases. It is therefore assigned to a defect vibration, namely end gauche mode (near the methyl group). A very weak absorption near 1352 cm^{-1} could be due to a small number of · · ·gg· · · forms. This proves that the $\beta \rightleftharpoons \alpha$ transition is caused by the occurrence of gauche defects in the hydrocarbon part. The frequency of the fundamental methylene rocking mode (rocking of the CH bonds in the HCH plane) at 720 cm^{-1} is not modified, which indicates that sequences of at least 4 *trans* bonds still exist (*24*).

Table III summarizes an estimation of the amine content from the volume increase after intercalation and the molecular volume of the amine. The change in basal spacing is related to the change in packing density of the alkyl chains. The average amine/FeOCl ratio is 0.55 at low temperature and 0.51 at high temperature. The studies show that the phase transitions in the FeOCl–alkylamine complexes are of the same type as in clay minerals (*3, 4, 17*): an ordered β-phase and a more disordered α-phase probably with lower packing density.

TABLE III

CALCULATION OF AMINE CONTENT OF INTERCALATION COMPOUNDS

		$FeOCl \cdot xC_nH_{2n+1}NH_2$—Intercalate with n =				
Intercalate:		10	12	14	16	18
Molecular weight (M):		157.30	185.36	213.41	241.47	269.52
Density (g/cm^3) (ρ):		0.7936	0.8015	0.8079	0.8129	0.8618
V_M (Å^3):		329.1	384.0	440.3	493.3	519.3
Low-temp. phase	ΔV	332.8	402.7	493.7	549.8	603.5
	Z (molecule/unit cell)	1.01	1.05	1.12	1.11	1.16
	x	0.505	0.525	0.560	0.555	0.580
				$x = 0.55 \pm 0.03$		
High-temp. phase	ΔV	316.6	388.9	452.6	497.5	568.6
	Z (molecule/unit cell)	0.96	1.01	1.03	1.01	1.09
	x	0.480	0.505	0.515	0.505	0.545
				$x = 0.51 \pm 0.02$		

Note. $V_M = M_{RNH_2}/\rho N_L$; N_L, Avogadro number; $\Delta V = \Delta d \cdot a \cdot b$; Δd, basal spacing increment; a, b, lattice constants; $Z = \Delta V/V_M$; Z, number of molecules in the unit cell; $x = Z/2$.

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