

CORRELATION BETWEEN LAYER CHARGE AND ACTIVATION ENERGY OF THERMALLY INDUCED DEINTERCALATION IN ORGANO-LAYER SILICATES

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The intercalation reaction of organic molecules with montmorillonite has been widely studied [1-3]. Some studies on the thermal behavior of n-alkylammonium-montmorillonite complexes has also been reported [4-5], but no research on the reaction kinetics of desintercalation.

The montmorillonite is a three layer lattice type of clay mineral having layer charge due to the isomorphous substitution in tetrahedral or octahedral sites where  $Si^{4+}$  or  $Al^{3+}$  are replaced by other cations of lower valence [6]. To compensate the layer charge in their natural state, the equivalent amount of cations must be introduced into the interlayer positions. These cations are exchangeable with other inorganic ions in aqueous solution or with organic cations, particularly with surface active agents such as n-alkylammonium cations. Since excess negative charge is delocalized over all oxygens in the lattice, n-alkylammonium cations are held to the interlayer surface by ionic bonding and van der Waals attraction. The bonding force of intercalated n-alkylammonium ions in the interlayer space is strengthened depending upon the extent of surface charge density of silicate.

The thermally stimulated alkylammonium complexes are desintercalated at a specific temperature domain of 320-470°C. Therefore, we have attempted to find the correlation between layer charge due to the isomorphous substitution of layer silicate and activation energy which represents the energy barrier to be surmounted of thermally induced desintercalation reaction of its decylammonium complex.

The preparation and characterization of n-decylammonium-montmorillonite complexes have been systematically studied in this work with the variation of charge density in the natural montmorillonite. The layer charge was estimated by n-alcohol method as follows [2-3]. At first, n-decylammonium complexes are synthesized by ion exchange reaction and by successive molecular intercalation of primary n-alcohol (ROH, where R =  $C_{10}H_{21}$ ,  $C_{12}H_{25}$ ,  $C_{14}H_{29}$ , etc....). The layer charge can be calculated from the basal spacings of n-decylammonium derivatives under n-alcohol by the following equations (1) and (2);

$$N_{CH_2} = [(x + y)n_C + \{2.0 - (x + y)\} n_A] \dots\dots\dots (1)$$

for  $n_A > n_C$

$$d = 1.4 N_{CH_2} + 9.6 \overset{\circ}{\text{A}} \dots\dots\dots (2)$$

where  $n_A$  is no. of carbon atoms in n-alcanol,  $n_C$  is no. of carbon atoms in n-alkylammonium,  $N_{CH_2}$  is total no. of carbon atoms in  $(Si,Al)_4O_{10}$  unit,  $(x+y)$  corresponds to layer charge ( $\xi$ ) in formula unit. The obtained basal spacings, layer charge and interlayer C.E.C are listed in Table I.

TABLE I. Basal spacings (pm) of n-decylammonium-montmorillonites after swelling under n-alcanols and calculated layer charges and interlayer C.E.C.

MONT.	OBSERVED BASAL SPACINGS [d(00k)] (pm)			$\xi(x+y)$	IL-C.E.C. (meq./100g)
	$\bar{C}_{10}-\bar{C}_{10}$ mont.	$\bar{C}_{10}-\bar{C}_{12}$ mont.	$\bar{C}_{10}-\bar{C}_{14}$ mont.		
A	3843±25	4215±5	5667±5	0.38±0.01	102.57±0.5
B	3864±15	4200±5	4642±10	0.44±0.01	118.24±0.5
C	3837±5	4175±5	4618±5	0.49±0.02	138.27±1.0

$\bar{C}_{10}$  : n-decylammonium                       $\xi$  : layer charge  
 $\bar{C}_{10}, \bar{C}_{12}, \bar{C}_{14}$  : n-alcanol                      IL : Interlayer

For the kinetic study of desintercalation reaction along with the estimation of activation energy, Kissinger's [7] and Ozawa's [8] methods were employed by using a differential scanning calorimetry (DSC). As suggested by Kissinger, the activation energy of first order process may be estimated from the variation of the temperature at maximal intensity of DTA peak ( $T_m$ ) with various heating rates. The kinetics of the thermal decomposition of volatile products can be described by the equation (3).

$$-\frac{dX}{dt} = DX^b \dots\dots\dots (3)$$

where  $D = Z \exp(-E/RT)$ ,  $X$  is the fraction of the sample not yet reacted ( $0 < X < 1$ ),  $b$  is the order of kinetics,  $E$  is the activation energy,  $R$  is the gas constant and  $Z$  is the pre-exponential factor. Assuming first order kinetics and simplifying eq. (3) gives

$$\frac{d(\ln(\phi/T_m^2))}{d(1/T_m)} = -\frac{E}{R} \dots\dots\dots (4)$$

The activation energy can be therefore obtained from the slope, by plotting the  $\ln(\phi/T_m^2)$  vs  $1/T_m$ . Ozawa also proposed that the activation energy may be estimated from the shifting of DSC curve as the heating rate is changed. It is based on the general equation (5),

$$-\frac{dx}{dt} = Z.f(x) \exp(-E/RT) \dots\dots\dots (5)$$

where  $f(x)$  can be general function of  $X$ . Assuming a constant heating rate and simplifying eq. (5) gives

$$\log \phi + 0.4567 E/RT = \text{constant.} \quad \dots\dots\dots (6)$$

Thus, plotting  $\log \phi$  versus  $1/T_m$  gives the slope of which is equal to  $-0.4567 E/R$  and the activation energy can be obtained.

In this study, the temperature of maximal peak intensity of desintercalation was detected with the variation of heating rate of 5, 7, 10, 15 and 20 deg./min. in an inert atmosphere. The estimated activation energies by Kissinger's and Ozawa's methods are shown in Fig. 1, 2 and 3.

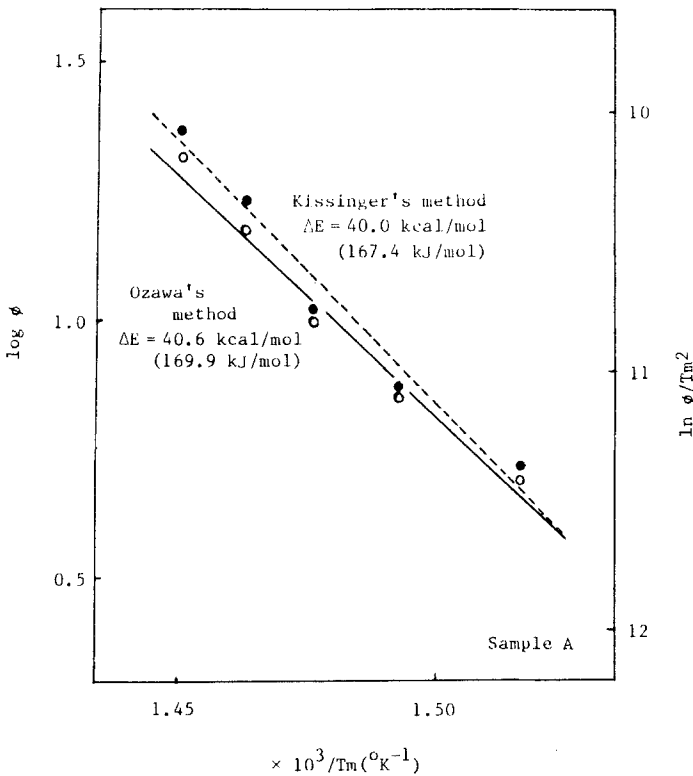


Figure 1. Plots of  $\log \phi$  vs.  $1/T_m$  and  $\ln \phi/T_m$  vs.  $1/T_m^2$  in montmorillonite A. ( $\xi=0.38$ )

The values obtained by Ozawa method are slightly higher than those of Kissinger's, but they have a good coincidence within the limit of experimental error. (Table 2) The activation energy in desintercalation process seems to be increased as the layer charge increases. Such a phenomenon might be well understandable by considering the enhanced bonding between silicate surface and decylammonium ion.

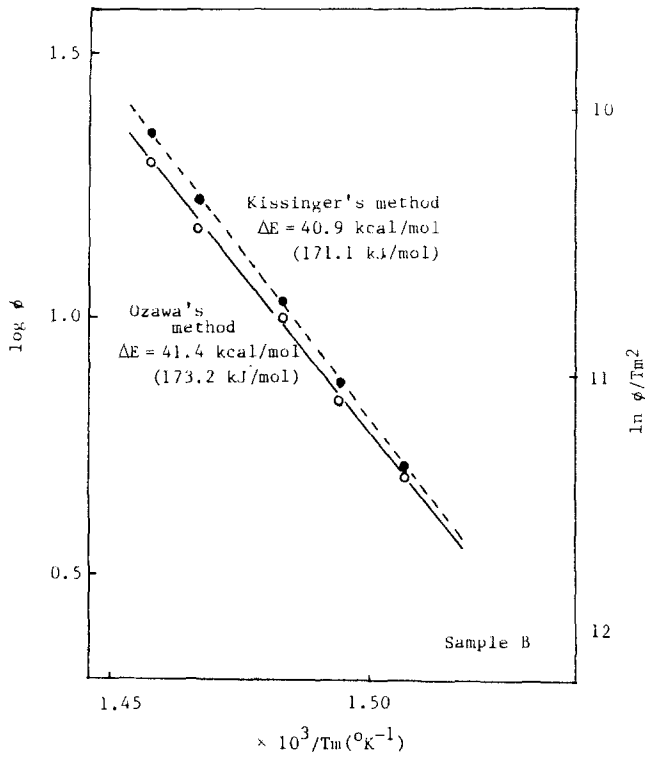


Figure 2. Plots of  $\log \phi$  vs.  $1/T_m$  and  $\ln \phi/T_m^2$  vs.  $1/T_m^2$  in montmorillonite B. ( $\xi=0.44$ )

TABLE II. Linear correlation between layer charge and activation energy (kJ/mol)

MONT.	$\xi$	$\Delta E$ KISSINGER (kJ/mol)	$\Delta E$ OZAWA (kJ/mol)
A	0.38	167.4	169.9
B	0.44	171.1	173.2
C	0.49	214.6	214.6

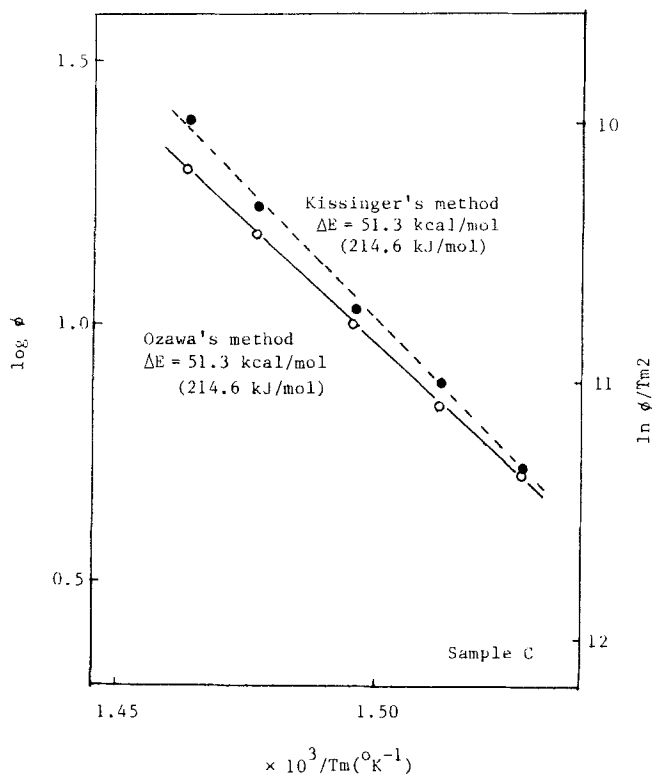


Figure 3. Plots of  $\log \phi$  vs.  $1/T_m$  and  $\ln \phi/T_m^2$  vs.  $1/T_m^2$  montmorillonite C. ( $\xi=0.49$ )

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