Concentration−Dependent Conformation of Alkyl Tail in the Nanoconfined Space: Hexadecylamine in the Silicate Galleries

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Concentration-Dependent Conformation of Alkyl Tail in the Nanoconfined Space: Hexadecylamine in the Silicate Galleries

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The conformation and melting of both hexadecylammonium ion, n-$CH_3(CH_2)_{15}NH_3^+$, and neutral hexadecylamine, n-$CH_3(CH_2)_{15}NH_2$, within the clay silicate galleries have been studied by Fourier transform infrared spectroscopy (FTIR). The conformational ordering of the alkyl tail in the confined system shows strong dependence on amine concentration and orientation. While the amine chains with orientation parallel to the silicate layers are in various disordered states, those with orientation radiating from the clay surface take mostly ordered conformation. Ammonium ion shows a similar trend of ordering dependence on the concentration as neutral amine, although the former has lower ordering than the latter, under the same concentration level. Temperature-dependent FTIR study shows that the melting behavior of confined amine corresponds to the chain melting process.

Introduction

Materials in confined geometries show remarkable difference in static and dynamic properties from the correspondent bulk because of the introduction of finite size effect, the restriction in the dimensionality, and the competition between the molecule−wall and molecule−molecule interaction forces.[1,2] Understanding the molecular origin of confinement-induced changes is of fundamental interest to many processes, such as lubrication, adhesion, coating, chromatography, and membrane separation. The most prominent feature for molecules confined between two solid walls as well as adsorbed on a single wall is that the molecules tend to organize into layered structure. Such structures can be seen in the Langmuir−Blodgett multilayers on a substrate,[3] an example of single-wall confinement, and surfactant molecules within silicate layers, an example of double-sided solid wall confinement.[4] The organization and orientation of these single-sided or double-sided wall confined molecules have been the subject of interest for many years. Extensive theoretical and experimental studies have been reported on the molecules confined by single-sided restriction.[5−7] However, because of the experimental difficulties, except for many works on molecular simulation,[8,9] few experimental results on the double-sided wall confinement exist.[10−12] The special parallel structure of the silicate layers in clay provides an ideal model for fundamental understanding of molecules in one-dimensional confined space. The most widely used technique for the study of intercalated materials in the silicate galleries is X-ray diffraction (XRD), which provides information on the layering structure and the basal d spacing of the layer. The orientation of the intercalated alkylamine molecules was indirectly obtained on the basis of the basal d spacing, with the assumption that all the molecules have all-trans conformation. As we reported in our previous work,[13] hexadecylamine in the clay silicate layers does not have the same melting behavior as bulk. Instead, stable thermal transitions at a temperature 20−30 °C higher than the bulk amine were observed. This means that confined hexadecylamine forms different ordered structure within the nanoscale silicate galleries. However, on the basis of the differential scanning calorimetric (DSC) heat flow, the highest crystallinity of confined hexadecylamine is only about 35%, indicating that a significant amount of confined amine has amorphous or liquidlike structure. Moreover, the crystallinity of confined amine strongly depends on the amine concentration. It brought out the question about what kind of ordered structure the amine would form within the silicate layers. Fourier transform infrared spectroscopy (FTIR) has been extensively used in the investigation of Langmuir−Blodgett multilayer systems.[5,23] The wavenumber, frequency shift, and bandwidth of infrared absorption bands provide detailed information of alkyl chains in the single-sided confinement. Therefore, FTIR is used in this study to molecularly understand the nature of the stable thermal transition shown in the DSC result and the order and disorder structure the amine molecules may have in the confined space.

Experimental Section

The montmorillonite used was Bentolite-L, from Southern Clay Products, with a cation-exchange capacity (CEC) of approximately 80 meq/(100 g). It was dried in a vacuum oven at 120 °C for 48

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(1) Bhushan, B.; Israelachvili, J. N.; Landman, U. *Nature* **1995**, *374*, 607.

(2) Granick, S. *Phys. Today* **1999**, 26.

(3) Blodgett, K. B. *J. Am. Chem. Soc.* **1934**, *56*, 495.

(4) Lagaly, G, *Solid State Ionics* **1986**, *22*, 43

(5) Porter, M. D.; Bright, T. B.; Allara, D. L.; Chidsey, C. E. D. *J. Am. Chem. Soc.* **1987**, *109*, 3559.

(6) Chernyshova, I. V.; Rao, K. H.; Vidyadhar, A. *Langmuir* **2000**, *16*, 8071.

(7) Perry, M. D.; Harrison, J. A. *Langmuir* **1996**, *12*, 4543.

(8) Cui, S. T.; Cummings, P. T.; Cochran, H. D. *Fluid Phase Equilib.* **2001**, *183*, 381.

(9) Gao, J.; Luedtke, W. D.; Landman, U. *J. Chem. Phys.* **1997**, *106*, 4309.

(10) Vaia, R. A.; Teukolsky, R. K.; Giannelis, E. P. *Chem. Mater.* **1994**, *6*, 1017.

(11) Wang, L. Q.; Liu, J.; Exarhos, G. J.; Flanigan, K. Y.; Bordia, R. *J. Phys. Chem. B* **2000**, *104*, 2810.

(12) Venkataraman, N. V.; Vasudevan, S. *J. Phys. Chem. B* **2000**, *104*, 11179.

(13) Li, Y. Q.; Ishida, H. *Chem. Mater.* **2002**, *14*, 1398.

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h prior to use. Hexadecylamine with purity of 98% was purchased from Aldrich Chemical Co. and used directly. The nature of the impurity is not known, though we suspect that the majority of the impurity is alkylamine with different chain length. Since it is not the crystal structure but the chain conformation of hexadecylamine within the silicate layers we are studying here, the effect of the impurity of this level is expected to be very small.

Neutral hexadecylamine was intercalated into silicate galleries via ion−dipole interaction by melt-mixing. Clay and various amounts of amine were mixed and annealed at 120 °C for 40 min, and the obtained clay is designated as C16-clay. Hexadecylammonium ion was intercalated into the silicate galleries by the cation exchange method following ref 14, and the obtained clay is designated as C16H⁺-clay. The degree of cation exchange was controlled by using different hexadecylammonium ion-to-clay ratios and was determined by the organic content from the weight loss in the range of 165−750 °C by thermogravimetric analysis (TGA), using a TA Instruments Hi-Res 2950 thermogravimetric analyzer. The scanning rate was 10 °C/min with a nitrogen purge rate at 90 mL/min.

Differential scanning calorimetric measurement was made with 2920 MDSC, from TA Instruments Inc. Dry nitrogen gas with a flow rate of 80 mL/min was purged through the DSC cell. A heating rate of 3 °C/min was used. The temperature and heat flow were calibrated using water, indium, and zinc at 3 °C/min. Wide-angle X-ray diffraction study was performed by a Philips XRG 3100 diffractometer with Cu Kα radiation, using a scanning speed and step size of 0.06°/min and 0.01°, respectively. A Fourier transform infrared spectrophotometer (Bomem Michaelson MB110) with a wide band gap, nitrogen-cooled mercury−cadmium−telluride (MCT) detector was used at a resolution of 2 cm⁻¹. The specific detectivity of the detector is 1×10^{10} Hz$^{1/2}$·cm/W, and 128 scans were typically used to obtain a good signal-to-noise ratio. The spectrometer was constantly purged by dry nitrogen gas. Temperature-dependent infrared measurement was carried out by making a KBr pellet of an organoclay, which was placed between two KBr windows of the heating cell (Watlow 965, Connecticut Instrument Corp.). After the desired temperature was reached, the sample was kept for at least 15 min prior to the measurement in order to ensure thermal equilibrium. The frequency of absorption bands was determined with the raw edge detection method by a commercial software (Grams 32) from Galactic Inc. The bandwidth (full width at half-maximum, fwhm) was obtained after curve resolving using the same software. The band contour used was a mixture of Gaussian and Lorentzian functions. The frequency accuracy of the measurement is better than 0.01 cm⁻¹. Therefore, the error bars in terms of frequency are less than the size of the data point dot. The intensity reproducibility from scan to scan is typically around ±2% and again less than the size of the data point dots.

Results and Discussion

Effect of Amine Concentration and Chain Orientation in C16-Clay. Confined amine shows completely different thermal behavior from the correspondent bulk, which provides a convenient and direct way to differentiate the confined amine from the bulk counterpart.[13] Therefore, by the DSC measurement, we can confirm the intercalation state of amine so that the FTIR information obtained is from the confined amine alone rather than from the bulk amine or from a mixture. To obtain direct correlation between the DSC and FTIR results, the sample for the FTIR measurement was directly obtained from the DSC pan after the DSC examination. Furthermore, the absence of clay absorption in all the frequency regions mentioned below allows direct observation for the amine absorption, avoiding the complexity of frequency and intensity determination.

The infrared absorption bands between 1475 and 1420 cm⁻¹, due to the methylene scissoring modes, are quite

(14) Weiss, A.; Holm, C.; Platikanov, D. *Colloid Polym. Sci.* **1993**, *271*, 891.
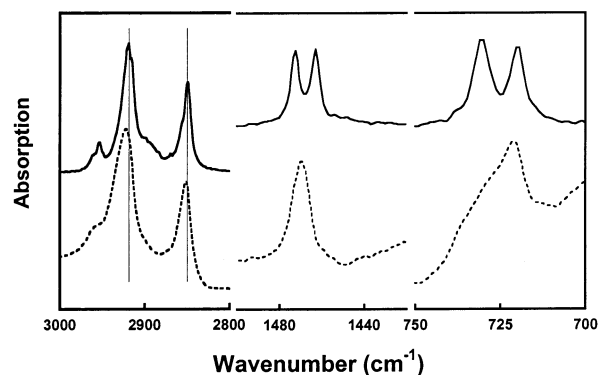

Figure 1. Comparison of FTIR of (−) pure hexadecylamine and (···) C16-clay with hexadecylamine concentration at 0.79 CEC.

similar to the 735 to 715 cm⁻¹ methylene rocking modes in the disposition and shape of the bands. Doublets are observed for the pure crystalline hexadecylamine, shown as the solid line in Figure 1. These doublets appear at 1473 and 1463 cm⁻¹ for the scissoring modes and 730 and 720 cm⁻¹ for the rocking modes, respectively. The splitting of 10 cm⁻¹ of the CH₂ scissoring and rocking bands is due to the intermolecular interaction between the two adjacent hydrocarbon chains in a perpendicular orthorhombic subcell[15,16] and further requires an all-trans conformation for its detection.[17] Singlets at 1468 and 721 cm⁻¹, respectively, both with a bandwidth around 11 cm⁻¹, appeared in the C16-clay with amine concentration at 0.79 CEC, shown as the dotted line in Figure 1. These broad single absorption bands are related to either a liquidlike structure or relatively disordered hexagonal subcell packing, where the hydrocarbon chain freely rotates around its long axis.[17,18] This observation of singlet scissoring and rocking absorption bands for the confined amine is the same for all C16-clay samples studied in this paper and is independent of amine concentration. This phenomenon indicates that the alkyl tails of confined hexadecylamine are poorly packed within the silicate layers. In other words, the confined amine does not have the same three-dimensional order as the pure amine. This conclusion is consistent with the result from X-ray diffraction that no diffraction signal from the amine crystal structure is observed for the confined amine.[13] The intense IR absorption bands at 2917.8 and 2850.1 cm⁻¹ for the pure amine, shown as the solid line in Figure 1, are from the antisymmetric and symmetric CH₂ stretching modes. It is well-established[19,20] that the frequencies of the CH₂ stretching bands of hydrocarbon chains are extremely sensitive to the conformational changes of the chains. Only when the chains are highly ordered (all-trans zigzag conformation), the narrow absorption bands appear around 2918 (ν_{as}(CH₂)) and 2850 cm⁻¹ (ν_s(CH₂)) in the infrared spectrum. On the other hand, if conformational disorder is included in the chains, their frequencies shift upward, depending upon the average content of gauche conformers. Both of these bands shifted to high frequencies

(15) Casal, H. L.; Mantsch, H. H.; Cameron, D. G.; Snyder, R. G. *J. Chem. Phys.* **1982**, *77*, 2825,

(16) Snyder, R. G. *J. Chem. Phys.* **1979**, *71*, 3229.

(17) Flach, C. R.; Gericke, A.; Mendelsohn, R. *J. Phys. Chem. B* **1997**, *101*, 58.

(18) Snyder, R. G. *J. Mol. Spectrosc.* **1961**, *7*, 116.

(19) Horn, A. In *Spectroscopy for Surface Science*; Clark, R. J. H., Hester, R. E., Eds.; John Wiley and Sons: New York, 1998; Vol. 26, pp 273−339.

(20) Mendelsohn, R.; Brauner, J. W.; Gericke, A. *Annu. Rev. Phys. Chem.* **1995**, *46*, 305.
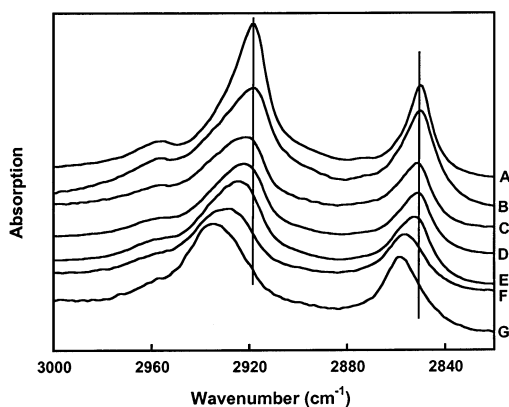
Figure 2. FT-IR spectra (region $2800-3000$ cm^{-1}) of C16-clay with amine concentration at (A) 3.84, (B) 1.94, (C) 0.92, (D) 0.79, (E) 0.52, (F) 0.35, and (G) 0.10 CEC.
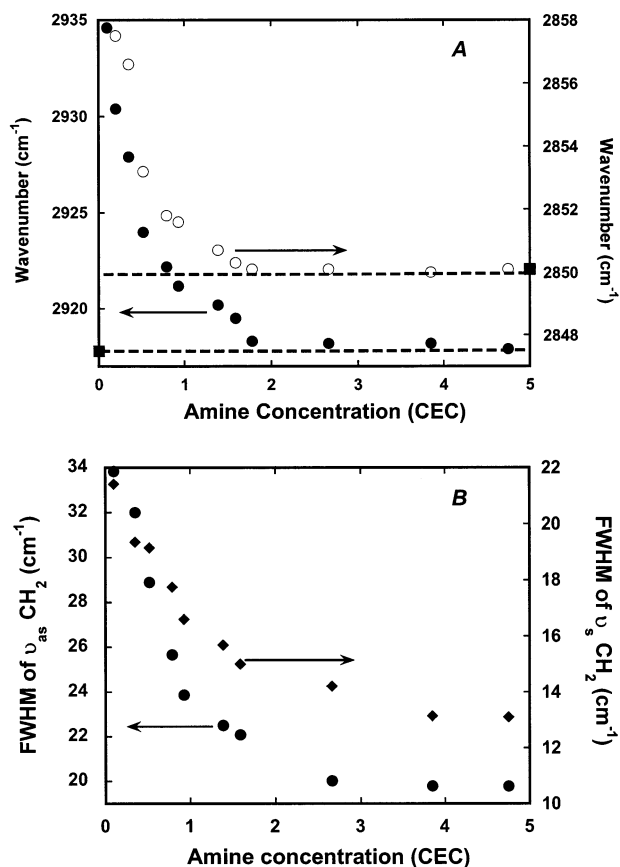

Figure 3. Change of (A) frequency and (B) fwhm of the methylene ν_{as} and methylene ν_s of C16-clay as a function of amine concentration.

Figure 4. Change of d spacing for C16-clay as a function of amine concentration, with inserted figure indicating the amine chain orientation for different concentration ranges.

high concentration range, the confined hexadecylamine chains adopt an essentially all-trans conformation despite poor chain packing. Defects, if they exist, due to gauche conformers are few in number. However, in the relatively low amine concentration range, the frequency shifted significantly to high wavenumber, indicating that a large number of the gauche conformer is introduced into the amine chain. The bandwidth, which is proportional to the degree of molecular mobility,[21] changed from the narrowest around 20 and 13 cm^{-1}, respectively, which is comparable to crystalline hexadecylamine, to the widest of 34 and 21 cm^{-1}, respectively, experiencing the same variation trend as a function of amine concentration, as shown in Figure 3B.

Either for the frequency shift or bandwidth change, there is a critical concentration for the change, which appears around $1.6-2$ CEC. The basal d spacing of the amine-intercalated clay can be obtained from the X-ray diffraction result, which shows a discrete d spacing increment as a function of amine concentration.[13] On the basis of the amine chain length, diameter, and the d spacing increment, especially the clear stepwise d spacing increment rather than continuous changes, the orientation of the confined amine can be determined. They are either lying parallel to the silicate layer to form a single-layered or double-layered structure or standing up with an angle about 55° to the silicate layers to form a single-layered or double-layered structure, as shown in Figure 4. Therefore, the chain orientation of the confined amine within the silicate galleries depends on the amine concentration. The critical concentration for the orientation is around 1.7 CEC. Amine chains are parallel to the clay surface below 1.7 CEC, whereas they radiate away from the clay surface above 1.7 CEC. The critical concentration of 1.7 CEC for the amine orientation from the X-ray diffraction result agrees well with the critical concentration for the amine conformational change determined by FTIR. For amine molecules confined within the silicate layers, they face the competition of interactions between the amine molecule–silicate surface and the amine–amine molecules. The interaction among amine molecules leads to ordered chain conformation and dense chain packing. Theoretical calculation[22] and experimental results[23] indicate that the most important factors governing the conformational

in the sample of C16-clay at 0.75 CEC, shown as the dotted line in Figure 1, indicating the introduction of gauche conformer in the hydrocarbon tail.

The frequency and bandwidth of both antisymmetric and symmetric stretching modes for the confined amine strongly depend on amine concentration, which can be seen in Figure 2. Conformational changes of the confined amine as a function of amine concentration can be qualitatively monitored by the wavenumber shift and bandwidth change, as shown in Figure 3. In the high concentration range, the frequency of both antisymmetric and symmetric absorption bands for the confined amine keeps relatively constant. They are very close to the frequency of the pure amine, which is shown by the solid squares in Figure 3A. This means that, in this relatively
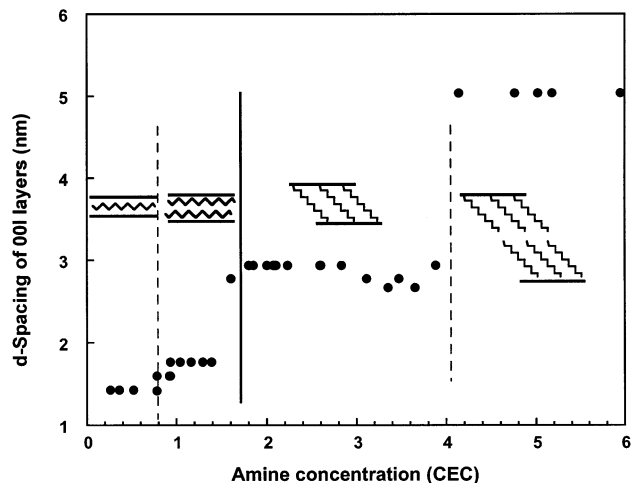
(21) Katayama, N.; Enomoto, S.; Satao, T.; Ozaki, Y.; Kuramoto, N. *J. Chem. Phys.* **1993**, *97*, 6880.
(22) Tasi, Mizukami, G. F. *J. Math. Chem.* **1999**, *25*, 55.

behavior of free *n*-alkanes are the nonbonded van der Waals interactions between the hydrogen atoms. The weakening of the interaction would result in the increased number of gauche conformer. On the other hand, since the silicate surface of clay is hydrophilic whereas the hydrocarbon chains of amine molecules are hydrophobic, the silicate surface−hydrocarbon chain interaction is of repulsive nature. Therefore, such repulsive force from the silicate surface would increase the mobility of the alkyl tails of amine molecules, resulting in increased number of gauche conformers. The forces from the silicate wall to the confined amine molecules are limited by the distance. Through computer simulation, Gupta et al.[24] found that the surface effect is only restricted to the layer in contact with the surface. At the same time, the interaction among amine molecules is a function of amine concentration.

The density of hexadecylamine is approximately 0.81 g/cm³; hence, its molecular volume is 0.50 nm³, which yields an area per molecule of 0.76 nm². The cation exchange capacity of the clay used is 80 meq/(100 g). Therefore, the cation density is approximately 1 charge/(1.54 nm²), which is about twice the area per amine molecules. For C16-clay with very low amine concentration where amine molecules form a single layer parallel to the silicate layers, amine molecules are individually separated; therefore, the interaction among amine molecules is very weak. This dilution effect causes the formation of gauche conformer; meanwhile, the hydrocarbon tails that are parallel to the silicate layers have full contact with the silicate surface. The hydrocarbon tails have two different kinds of interaction with the clay surface: the van der Waals forces that act as an attractive force and the hydrophilic environment that acts as repulsive force. Although the hydroxyl groups are inside the clay layers, it does impose a hydrophilic environment through the long-range effect. Besides, the existence of a small amount of water on the clay surface makes the repulsive force stronger. Therefore, the total effect between the clay surface and the hydrocarbon tail is considered to be repulsive. The repulsive forces from the silicate surface increase the mobility of the hydrocarbon tail and therefore results in high concentration of gauche conformer. Hence, the formation of gauche conformer is enhanced by the combination of these two effects. This is the reason the highest frequency shift for the confined amine is as much as 17 cm⁻¹, while the frequency shift of hexadecylamine in dilute solution of carbon tetrachloride is only 10 cm⁻¹. When amine concentration increases, but within the range that amine chains still keep full contact with the silicate surfaces and face strong repulsive forces from them, the increased concentration results in increased interchain interaction among amine molecules. This is reflected by the increased number of trans conformer with the frequency shifting to low wavenumber. Molecules have the tendency to take more ordered trans conformer and more dense packing structure to minimize the energy. As amine concentration increased, increased interchain interaction competes with the silicate surface−amine chain interaction. When the interchain interaction among amine molecules overcomes the repulsive forces from the silicate surface, the orientation of the hydrocarbon tail suddenly changes from parallel to radiate away from the silicate surface to minimize the energy. The hydrocarbon tail with orientation radiating away from the silicate surface hardly face the force from the silicate surface, while the van der Waals forces among

hydrocarbon tails keep the fully ordered trans conformation. However, the amine chains are still not in the three-dimensionally ordered state, which may be due to the ion−dipole interaction between the headgroup of NH₂ and the silicate surface.

This concentration- and orientation-dependent conformation of confined hexadecylamine in the layered silicate galleries is quite different from the situation of cetyl trimethylammonium (CTA) ions within galleries of layered CdPS₃. It was reported that hydrocarbon tails of CTA adopt mostly trans conformation in the samples with both low and high CTA concentration within the layered CdPS₃.[12,25] It is possible that the silicate surface and CdPS₃ surface have opposite effect on the hydrocarbon chain mobility

Order−Disorder Transition of C16-Clay. Pure hexadecylamine shows a melting temperature around 46 °C in the DSC measurement, while the confined amine shows stable thermal transitions between 60 and 80 °C, depending on the amine concentration and chain orientation.[13] To understand the molecular origin of this different thermal behavior, temperature-dependent FTIR measurement was used to follow the melting process. When temperature increases, drastic change happened in the FTIR spectrum of pure hexadecylamine. Doublets at 1463−1473 cm⁻¹ due to the methylene scissoring mode and at 720−730 cm⁻¹ due to the methylene rocking mode disappear, and singlets at 1468 and 721 cm⁻¹ appear during the melting temperature range. This indicates the destruction of perpendicular orthorhombic subcell and the formation of relatively disordered hexagonal subcell packing and then liquidlike structure. As well, the frequency shift of the methylene antisymmetric and symmetric bands at 2917 and 2850 cm⁻¹, respectively, is also observed, reflecting the increase of disordered gauche conformer. The conformational isomerization happens via rotation about C−C bonds. This brings one or more trans bonds into gauche bonds, leading to the introduction of the "kinks".[26] Kink formation is a cooperative process in which the number of kinks per alkyl chain increases by 1 within a relatively small temperature range since the energy difference between the trans and gauche conformers for an isolated alkyl chain is rather small value of 0.6 kcal/mol.[27] Therefore, the kink formation is a function of temperature, which can be reflected in the temperature-dependent FTIR of pure hexadecylamine, shown as the solid square in Figure 5. The frequency shifts to high wavenumber continuously as temperature increases. However, in addition to the continuous frequency shift above and below the melting temperature at 46 °C, a sudden transition is observed around the melting temperature. This phenomenon is very similar to crystalline *n*-alkanes, with conformational disorder appearing discontinuously at the solid−solid phase transition.[28] Müller pointed out that, at this phase transition, interchain distances increased in a way that suggested an increased freedom for chain rotation about the molecular axis.[29] On the other hand, the situation is quite different for the confined amine. No obvious change is observed in the methylene scissoring and rocking mode when the temperature changes, indicating little change in the interchain packing. For the CH₂ antisymmetirc stretching band, the frequency keeps shifting to high wavenumber, with a large

(23) Okamura, E.; Umemura, J.; Takenaka, T. *Biochim. Biophys. Acta* **1985**, *812*, 139.
(24) Gupta, S.; Koopman, D. C.; Westermann-Clark, G. B.; Bitsanis, I. A. *J. Chem. Phys.* **1994**, *100*, 8444.
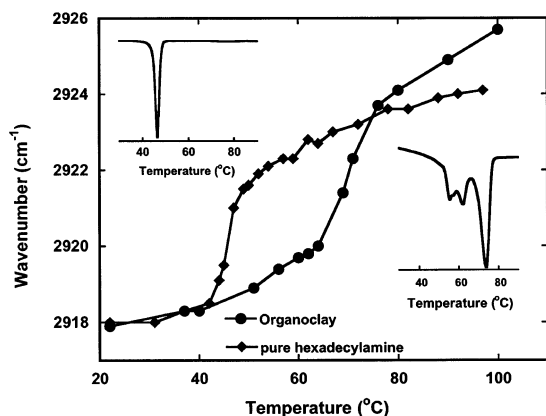
(25) Venkataraman, N. V.; Vasudevan, S. *Proc.−Indian Acad. Sci., Chem. Sci.* **2001**, *113* (5−6), 539.
(26) Blasenbrey, S.; Pechhold, W. *Rheol. Acta* **1967**, *6*, 174.
(27) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953; pp 399−431.
(28) Kim, Y.; Strauss, H. L.; Snyder, R. G. *J. Phys. Chem.* **1989**, *93*, 7520.
(29) Müller, A. *Proc. R. Soc. London, Ser. A* **1932**, *138*, 514.

Figure 5. Methylene ν_{as} wavenumber shift as a function of temperature for the pure hexadecylamine and C16-clay with 4.75 CEC of hexadecylamine.
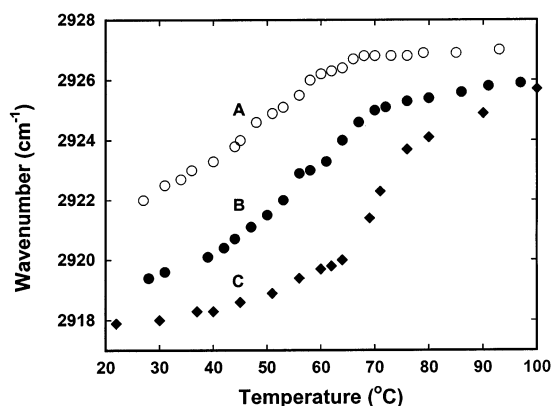

Figure 6. Comparison of temperature-dependent methylene ν_{as} frequency shift for C16-clay with amine concentration at (A) 0.92, (B) 1.44, and (C) 4.75 CEC.

Figure 7. Comparison of methylene ν_{as} frequency shift for heating (♦) and cooling (●) processes for C16-clay with amine concentration at 4.75 CEC.

discontinuous frequency shift occurring around 75 °C. There is also some hint of two small discontinuous frequency shifts around 50 and 65 °C, which are shown as the solid dots in Figure 5, with amine concentration at 4.75 CEC. The CH_2 symmetric stretching band gives practically the same results, the overall change in frequency being smaller. These three temperature regions for the discontinuous frequency shift agree well with the thermal transition temperature observed by DSC which is inserted in Figure 5. These results strongly suggest that the DSC endothermic peaks for the confined amine correspond to the conformational order−disorder change process. Therefore, the melting behavior of confined amine is fundamentally different from bulk amine. While the melting of bulk amine is related to three-dimensional crystal structure melting, the melting of confined amine is related to chain conformational order−disorder transition, or called chain melting.[30]

Figure 6 compares the temperature-dependent frequency shift for the antisymmetric CH_2 stretching band for C16-clay samples with amine concentration at 0.92, 1.44, and 4.75 CEC. The magnitude of the steep frequency shift varies with amine concentration. This magnitude corresponds well with the amount of heat flow, i.e., crystallinity, obtained from DSC for different amine concentrations.[13] This can be used as evidence for the conclusion that the melting process of confined amine is related to chain conformational order to disorder transi-
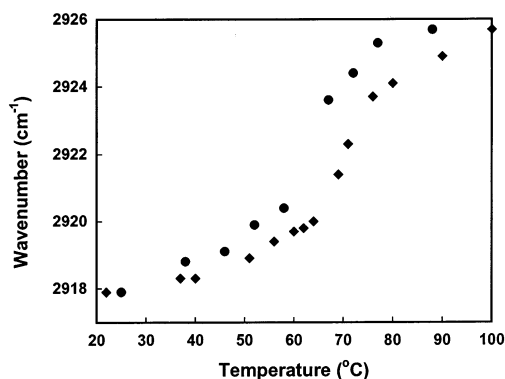
tion, although the reason confined amine with different orientation has different melting temperature is not clear yet at this stage.

Chain melting behavior of confined amine can also be verified through cyclic thermal treatment in conjunction with spectroscopic measurements. The results of these studies are shown in Figure 7, where C16-clay with amine concentration at 4.75 CEC was gradually raised to elevated temperatures, its IR spectrum recorded and then lowered to room temperature, and a subsequent IR spectrum obtained. Comparing to the heating process, the frequency of the sample during the cooling process is slightly higher and the discontinuous change of the frequency happens at a temperature slightly lower than that of the heating process. It is apparent, however, that the frequency (ordering) of the sample, when it was cooled to room temperature and kept at room temperature for a long enough time, is the same as that before the heating process, indicating that the process is reversible, although there is a hysteresis phenomenon.

Headgroup Effect: Comparison of C16-Clay and C16H⁺-Clay. Amine can intercalate into the silicate galleries as neutral molecules or in the form of ammonium ion. The confined molecules with these two different forms, therefore, have different interactions with the clay surface through the headgroup. Neutral amine molecules coordinate with the clay surface through the ion−dipole interaction between the headgroup and cation. On the other hand, after cation exchange with the metal cation on the clay surface, hexadecylammonium ions coordinate with the clay surface through ion−ion bond between the headgroup and O^{2-}. To study the effect of the interaction between the headgroup and clay surface on the ordering behavior of the nanoscale confined molecules, these two kinds of confined structures were compared. With similar amine concentrations, similar basal d spacings were observed for C16-clay and C16H⁺-clay from the X-ray diffraction results, suggesting the same chain orientation dependence on the amine concentration for these two kinds of samples. However, a different thermal behavior was observed for them. The thermal behavior of C16H⁺-clay is similar to the C16-clay with much lower amine concentration, as shown in Figure 8. Besides, the normalized heat flow shows that, in the confined silicate layers, ammonium ion has weaker thermal transition than neutral amine, indicating less ordered structure in ammonium ion. This agrees well with the result from IR spectrum. Figure 9 compares the CH_2 antisymmetric stretching band for hexadecylammonium ion and neutral hexadecylamine confined in the silicate layers as a function of amine concentration. Although the hexadecylammo-

(30) Badia, A.; Singh, S.; Demers, L. M.; Cuccia, L. A.; Brown, G. R.; Lennox, R. B. *Chem. Eur. J.* **1996**, *96*, 2657.
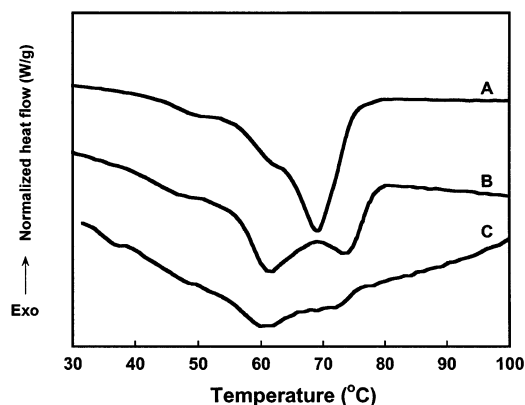
Figure 8. Comparison of the DSC thermal behavior of (A) C16-clay with amine concentration at 2.94 CEC, (B) C16-clay with amine concentration at 1.40 CEC, and (C) C16H$^+$-clay with amine concentration at 2.90 CEC.
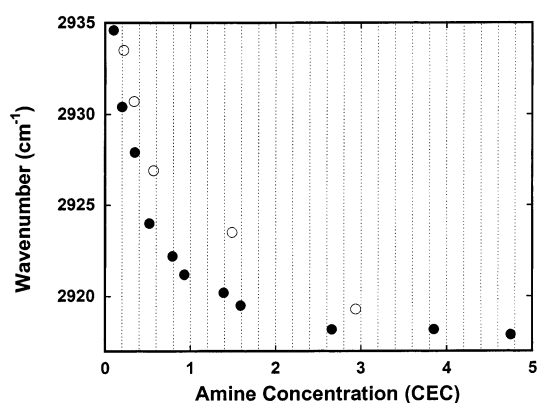

Figure 9. Comparison of methylene ν_{as} frequency shift for (●) C16-clay, and (○) C16H$^+$-clay as a function of amine concentration.

nium ion shows a concentration-dependent frequency shift similar to that of the neutral amine, the former shows a generally higher frequency shift than the latter at the same amine concentration level. This suggests that the interaction between the headgroup of alkylamine and the clay surface influences the ordering of the hydrocarbon tail: strong ion−ion interaction resulting in more disordered conformation than weak ion−dipole interaction. This headgroup effect is distinguished from the well-known terminal effect of the chain ends on melting temperature (T_m) or glass transition temperature (T_g). In

the context of the headgroup effect in this paper, the chain length of the alkyl tail is kept constant while the strength of the interaction between the amine headgroup and silicate surface varies. On the other hand, for the situation of terminal effect on the T_m or T_g, the chain end structure remains the same while the length of the main chain varies. It appears that increasing the strength of the headgroup has an effect similar to shortening the chain length. As we mentioned, the disordered structure of the alkyl tail within the silicate layers is caused by the combinational effect of the repulsive force between the tail and the silicate surface and the dilution effect of amine molecules. It is possible that the electrostatic repulsion between ammonium ion headgroups keeps the amine chain in the more separated state, which would further enhance the dilution effect.

Conclusion

FTIR spectroscopy has provided a detailed observation of the ordering state of hexadecylamine within the nanoscale silicate layers. By monitoring the frequency shift of the CH$_2$ antisymmetric and symmetric stretching modes, it is found that the confined amine chains exist in states with varying degrees of order in conformation with a relatively disordered hexagonal subcell packing or liquidlike structure. The ordering of conformation strongly depends on amine concentration and orientation. The chains adopt an essentially all-trans conformation with orientation radiating away from silicate surface when amine concentration is high. On the other hand, disordered gauche conformer is introduced to the chain when amine chains have orientation parallel to the silicate layers, with the amount of gauche conformer increasing as amine concentration decreases. The competition between the forces from hydrocarbon tail−silicate surface and amine−amine molecules is considered to be the cause for orientation-dependent ordering in conformation. The interaction between the headgroup of amine molecules and the silicate surface also influences the ordering of the hydrocarbon tail. C16H$^+$-clay with strong ion−ion interaction shows more disordered structure in chain conformation than C16-clay, at the same concentration level. In addition, temperature-dependent FTIR spectroscopy revealed that the DSC determined stable thermal transition for the confined amine, which is much higher than bulk amine, corresponds to the chain melting process: order to disorder or disorder to more disordered chain conformational transition.