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INTERMOLECULAR INTERACTION IN MONTMORILLONITES: NH–CO SYSTEMS*

H. E. DONER and M. M. MORTLAND†
Department of Soil Science, Michigan State University, East Lansing, Mich. 48823

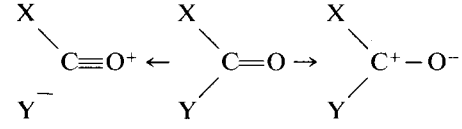
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Abstract—The mechanism of interaction between cationic organic molecules satisfying exchange sites in montmorillonite and organic molecules with carbonyl groups was investigated. Dialkyl amides adsorbed on trimethyl-ammonium- and tetramethylammonium-montmorillonite were studied by i.r. spectroscopy. The electronegativity or basicity of the amides, expressed as a summation of the Taft polar factors ($\Sigma\sigma^*$), was found to be linearly related to the C–O stretching frequency after adsorption on trimethyl-ammonium-montmorillonite. Furthermore, the changes in the C—O and N—H stretching frequencies of the amides and trimethylammonium ion respectively, exhibited a direct linear relationship. Thus, the dialkyl amides were shown to be hydrogen bonded through the oxygen of the carbonyl group to the hydrogen of the trimethylammonium. The (001) spacing of trimethyl-ammonium-montmorillonite was 12·9 Å. Only after the adsorption of amide molecules of the size of N,N-diethylacetamide or larger did this spacing change. Dialkyl amides were adsorbed on tetramethylammonium-montmorillonite, but less energetically than on trimethylammonium-clay. The (001) spacing of tetramethylammonium-montmorillonite was 13·8 Å and remained the same after adsorption of the dialkyl amides. Evidence of hydrogen bonding between the hydrogen of trimethylammonium-ion and some other carbonyl compounds was also noted.

INTRODUCTION

A RECENT investigation by Mortland (1968) showed that pyridinium-montmorillonite forms a relatively stable complex with ethyl N,N-di-*n*-propylthiolcarbamate (EPTC). Hydrogen bonding was proposed as a mechanism for the complex formation, based on the observation that both C—O stretching and N—H bending frequencies changed with complex formation. Lailach and Brindley (1969), on the basis of X-ray diffraction data, have hypothesized a hydrogen bonding mechanism for co-absorption of purines and pyrimidines by montmorillonite. Where metal cations occupy the exchange sites on montmorillonite, organic molecules containing a carbonyl group may be bonded to the surface either by the formation of a coordination compound (Tahoun and Mortland, 1966) or by hydrogen bonding through a "water-bridge" to the exchange cation (Farmer and Mortland, 1966; Yariv *et al.*, 1966; Parfitt and Mortland, 1968).

The basicity of molecules containing a carbonyl group depends on the electronegativity of other groups bonded to the carbon atom. Thus, with a compound such as F·CO·F the C—O vibrational frequency is 1928 cm^{-1}, while in urea, $NH_2 \cdot CO \cdot NH_2$, the frequency is 1655 cm^{-1}. Kagarise (1955) proposed that the carbonyl group may assume a bond character ranging from a single to a triple bond as follows:



I II

The extent to which structures I and II are formed depends on the electron-attracting or electron repelling nature of X and Y. When the character of the carbonyl group is more like structure II, the electrons will be more available for bonding. Taft (1956, pp. 586–675) has reported the relative electron withdrawing constants of various possible substituents. A summation of the electron withdrawing constants or Taft polar factors (σ^*), provides a theoretical basis for estimating relative basicity of compounds independent of steric considerations. Adelman (1964) found a linear relationship between summation of Taft polar

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†Research Associate and Professor of Soil Science, respectively.

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factors ($\Sigma\sigma^*$) and basicity when formamides and acetamides were the electron donors and $HClO_4$ was the electron acceptor.

A series of organic compounds containing carbonyl groups were selected to investigate the bonding mechanism between the organic molecules and clays saturated with organic cations. The compounds were selected to obtain a range in the basicity. The organic cation selected for saturation of the clay was trimethylammonium which could interact with the carbonyls of other molecules by hydrogen bonding. The degree of association would then be observed by shifts in the N—H and C—O stretching frequencies, the amount of shift depending on the basicity of the carbonyl compound involved. For comparison, similar experiments were performed where tetramethylammonium ion saturated the clay and where no such interaction was possible. The objective was to determine whether organic cations in clay would complex with carbonyl compounds by hydrogen bonding and if the degree of association was related to the basicity of the compound with the carbonyl group.

EXPERIMENTAL

Trimethylammonium- and tetramethylammonium-montmorillonites were prepared by treating the $< 2\mu$ fraction of Wyoming montmorillonite (Reference Clay Mineral No. 25, Ward, Rochester, N.Y.) with several washings of either trimethylammonium or tetramethylammonium chloride salt solutions. The samples were then washed with distilled water until no chloride appeared in the washings upon testing with $AgNO_3$. Thin self-supporting clay films (2 mg/cm²) were prepared by evaporation of the water suspensions in aluminium foil dishes. Trimethylammonium- and tetramethylammonium-montmorillonite films were soaked overnight in liquid N,N-dimethylformamide (DMF), N,N-diethylformamide (DEF), N,N-dimethyl-acetamide (DMA), N,N-diethylacetamide (DEA), or N,N-dipropylacetamide (DPA). Excess amide was evaporated from the clay films by mild heating. Spectra were obtained by placing the treated film at right angles to the beam in an i.r. spectrophotometer (IR-7). Infrared spectra were also obtained of the liquid dialkyl amides between NaCl crystals. The amides were used as provided by the supplier without further purification. The (001) spacings of the clay-organic systems were obtained with a Philips X-ray diffractometer using filtered copper radiation.

RESULTS AND DISCUSSION

The N—H stretching frequency of dry trimethylammonium-montmorillonite was 3200 cm^{-1} compared to 2735 cm^{-1} for trimethylammonium chloride in Nujol (Bellanto and Barcelo, 1956). After treatment with a dialkyl amide the N—H stretching was found at a lower frequency, for example, 2725 cm^{-1} when treated with DEA (Fig. 1). Corresponding, the C—O stretching vibration of liquid DEA decreased from 1645 to 1613 cm^{-1}. The broad band at 2500 cm^{-1} may be O—H stretching from protonated DEA. It is assumed that the nitrogen in all dialkyl amides is unavailable for accepting a proton, based on the results of Cook (1964) with DMA.

Figure 2 shows the decrease in C—O stretching frequency with decrease in $\Sigma\sigma^*$ (summation of Taft polar factors) or, alternatively, with increase in polarity when dialkyl amides were adsorbed on trimethylammonium- and tetramethyl-ammonium-montmorillonite compared to either the liquid amide or amide dissolved in isoctane. The summa-

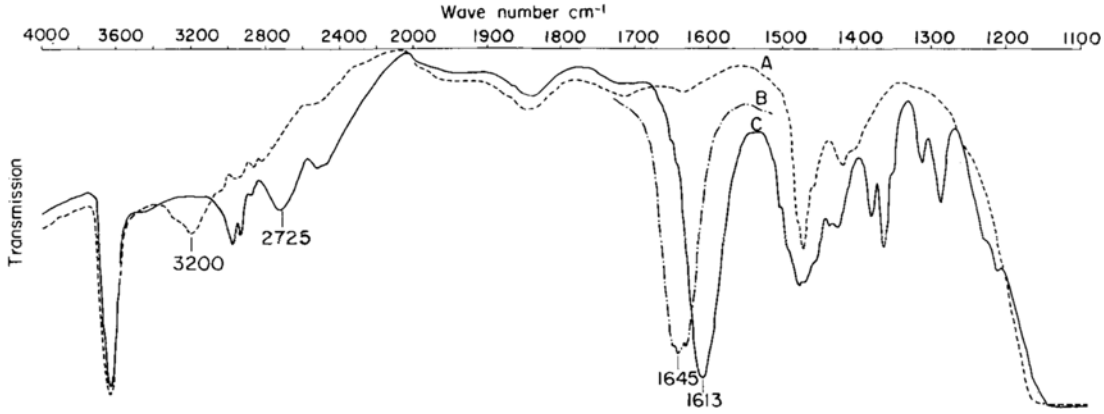


Fig. 1. I.R. spectra of trimethylammonium-montmorillonite (A), liquid DEA (B), and DEA complexes with trimethylammonium-montmorillonite (C) comparing the N—H and C—O stretching frequencies.

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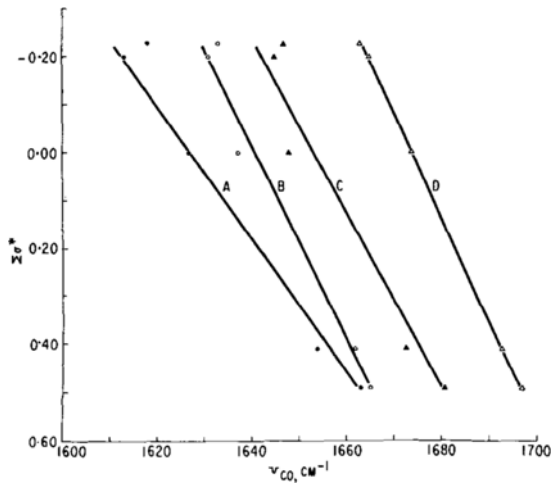


Fig. 2. Summation of Taft polar factors $\Sigma\sigma^*$ for some dialkyl amides compared with C—O stretching frequencies (ν_{CO}) in different environments. Complexed with trimethylammonium-montmorillonite (A), tetramethylammonium-montmorillonite (B), liquid (C), and in isooctane (D) (Adelman, 1956), where $\Sigma\sigma^*$ for DMF = +0·49, DEF = +0·41, DMA = 0, DEA = −0·20, and DPA = −0·23.

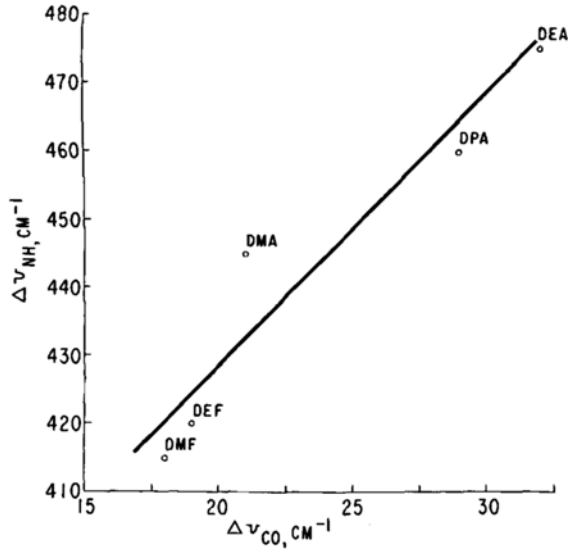


Fig. 3. Change in the N—H and C—O stretching frequencies of some complexes of dialkyl amides with trimethylammonium-montmorillonite compared to the N—H stretching frequency of untreated trimethylammonium-montmorillonite and the C—O stretching frequencies of liquid dialkyl amides.

tion of the Taft polar factors, as reported by Adelman (1964), ranged from −0·23 for DPA to +0·49 for DMF while the C—O stretching frequency varied from 1613 cm^{-1} for DEA to 1663 cm^{-1} for DMF in complexes with trimethylammonium-montmorillonite. The points fell on essentially a straight line with the exception of DPA where it was 1618 cm^{-1}. DPA may be somewhat sterically affected on adsorption which causes it to deviate from the linear relationship. The C—O stretching frequency for the individual dialkyl amides was less when adsorbed on trimethylammonium-montmorillonite than on the tetramethylammonium system. However, the stretching frequencies for both systems were less than those reported for the amides dissolved in isooctane (Adelman, 1964) or those found for the liquid amides.

A positive linear relationship was found between the C—O stretching frequency change ($\Delta\nu_{CO}$) and the N—H stretching frequency change ($\Delta\nu_{NH}$) when dialkyl amides were adsorbed on trimethylammonium-montmorillonite (Fig. 3). The C—O stretching frequency change was found by taking the difference between the frequency of the liquid amide and that frequency after adsorption on the trimethylammonium-montmorillonite. The difference between the N—H stretching frequency of the dry trimethylammonium-montmorillonite, 3200 cm^{-1} and the frequency after treatment with dialkyl amides determined the change, $\Delta\nu_{NH}$. DEA showed the greatest $\Delta\nu_{CO}$ and $\Delta\nu_{NH}$, 32 cm^{-1} and 475 cm^{-1}, respectively, while DMF showed the least, 18 cm^{-1} and 415 cm^{-1}, respectively. In reconsidering Fig. 2, it can be observed that a decrease in $\Sigma\sigma^*$ resulted in increasingly greater values for both $\Delta\nu_{CO}$ and $\Delta\nu_{NH}$ with the possible exception of DPA. These frequency changes represent energy losses which may be accounted for primarily by the formation of a hydrogen bond between the proton and the oxygen, N—H--O—C. Pullin and Werner (1965) reported similar kinds of frequency shifts in solutions containing NH—CO systems and attributed these shifts to hydrogen bonding. Those compounds with the largest $\Delta\nu_{CO}$ and $\Delta\nu_{NH}$ values would have the strongest hydrogen bond.

Observations of the loss of the H_2O deformation frequency, 1634 cm^{-1}, and the O—H stretching frequency, 3450 cm^{-1}, showed that the dialkyl amides displaced all the water in trimethylammonium-montmorillonite. Even though dialkyl amides were adsorbed in tetramethylammonium-montmorillonite, the clay films remained at least partially hydrated. Water was readily removed from both untreated trimethylammonium- and tetramethylammonium-montmorillonite by a partial vacuum and both were quickly rehydrated when exposed to room conditions.

The dialkyl amides were adsorbed on tetra-

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methylammonium with decreases in C—O stretching frequencies; however, these decreases were less than with trimethylammonium-montmorillonite. Since the tetramethylammonium ion has no proton available for bonding, some other interaction must be involved. The energy of bonding was less in the case of tetramethylammonium-montmorillonite compared to trimethylammonium-montmorillonite based on the following three observations: (1) When the amides were adsorbed, part, if not most, of the water was retained in the tetramethylammonium clay films, whereas the clay films of trimethylammonium were essentially dry; (2) Tetramethylammonium clay films appeared to lose dialkyl amides faster than trimethylammonium films after soaking in the amides; (3) As has been mentioned above, the C—O stretching frequency for the amides on tetramethylammonium-montmorillonite was greater than trimethylammonium-montmorillonite. The mechanism for adsorption of dialkyl amides on tetramethylammonium-montmorillonite may involve primarily van der Waal's forces.

Spacings obtained by X-ray diffraction (Table 1) showed that the (001) spacing for trimethylammonium-montmorillonite was 12·9 Å compared to 13·0 Å reported by Barrer and Reay (1957). For the purposes of this report, the difference is probably of little significance. The layers were sufficiently expanded to allow adsorption of the dialkyl amides without further expansion except in the case of DEA and DPA. When DEA and DPA were adsorbed the layers expanded 0·5–0·6 Å. The larger size of the DEA and DPA molecules combined with their greater bonding ability may account for much of the observed expansion. With both the untreated and treated tetramethylammonium-montmorillonite the (001) spacing was found to be 13·8 Å. Barrer and Reay (1957) reported 13·5 Å for the (001) spacing of tetramethylammonium-montmorillonite. They may have reported only first order peaks which may account for part of the discrepancy. The distance between the tetramethylammonium ions was calculated to be approximately 5 Å, assuming uniform surface charge distribution on the clay. Thus, sufficient space exists for the adsorption of the dialkyl amides without further expansion.

Other carbonyl compounds investigated were acetone, propionaldehyde, *o*-chlorobenzaldehyde, *p*-chlorobenzaldehyde, N,N-diphenylformamide, N-N-diphenylacetamide, and ethyl N,N-di-*n*-propylthiolcarbamate (Table 2). All these compounds exhibited a decrease in the C—O stretching frequency when adsorbed on trimethylammonium-montmorillonite compared to tetramethyl-ammonium-montmorillonite. This lends support to the utility of the hydrogen bond as a complexing mechanism on organic cation saturated clays. It was not possible to compare these compounds directly with the dialkyl amides reported for the following reasons: (1) With aromatic compounds other bonding mechanisms may become important, such as, π bonding; (2) Larger molecules may exhibit more steric interferences; (3) The functional

Table 1. (001) spacings, Å, of trimethylammonium and tetramethylammonium montmorillonite after adsorption of dialkyl amides

Adsorbed dialkyl amide	(001) Spacing of montmorillonite, Å	
	$(CH_3)_3NH^{+*}$	$(CH_3)_4N^{+*}$
Check	12·9	13·8
DMF	12·8	13·8
DEF	13·0	13·8
DMA	12·9	13·8
DEA	13·5	13·8
DPA	13·4	13·8

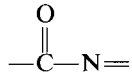
*Estimated accuracy, ±0·1 Å.

Table 2. C—O stretching frequencies of some carbonyl compounds adsorbed on trimethylammonium- and tetramethylammonium-montmorillonite

Carbonyl compound	C—O stretching frequency, cm^{-1}	
	$(CH_3)_3NH$-montmorillonite	$(CH_3)_4N$-montmorillonite
Acetone	1710	1712
Propionaldehyde	1695	1717
O-Chlorobenzaldehyde	1667	1712
p-Chlorobenzaldehyde	1666	1711
Benzaldehyde	1665–1670	1695
N,N-diphenylacetamide	1638	1663
N,N-diphenylformamide	1650	1679
Ethyl N,N-di-*n*-propylthiolcarbamate	1611	1637

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group considered for calculation of $\Sigma\sigma^*$ for the dialkyl amides was



whereas the other compounds may not have this group.

Trimethylammonium and tetramethylammonium cations are not found in soils and sediments. However, their use here as model systems demonstrate the possible importance of hydrogen bonding between protonated and polar organic molecules on the clay surface to form organic-organic complexes. Many pesticides contain carbonyl groups which may hydrogen bond with natural organic components in the soil. Further, hydrogen bonding may reduce the biological availability of certain organic compounds. Not only those compounds containing carbonyl groups can be hydrogen bonded, but other electronegative groups such as amines.

In summary, the results of this investigation show that carbonyl groups were able to hydrogen bond with trimethylammonium-montmorillonite. The greater the polarity or basicity, the greater the change in C—O and N—H stretching frequencies. This is directly related to the strength of the hydrogen bond. The sum of the Taft polar factors ($\Sigma\sigma^*$) provided a useful measure of the relative polarity or basicity of a compound. Tetramethylammonium-montmorillonite adsorbed dialkyl amides, but less energetically than the trimethylammonium-clay system.

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Résumé – On a étudié le mécanisme d'interaction entre les molécules organiques de cations se déplaçant dans les montmorillonites et les molécules organiques avec groupes de carbonyle. Des amides bi-alcoyle adsorpbées sur des montmorillonites trimethylammonium et tetramethylammonium ont été étudiées par spectroscopie à l'infra-rouge. On a trouvé que l'électronégativité ou la basicité des amides, exprimée en tant que somme des facteurs polaires Taft ($\Sigma\sigma^*$), était linéaire par rapport à la fréquence d'allongement C–O après adsorption sur le montmorillonite triméthylammonium. En plus, les changes en fréquence d'allongemont C–O et N–H des ions amide et trimethylammonium, une liaison hydrogène par l'intermédiaire de l'oxygène du groupe carbonyle avec l'hydrogène du triméthylammonium. L'écart (001) du montmorillonite était de 12,9 Å. Cet écart changeait seulement après adsorption des molécules d'amide de la grosseur de N,N-diethylacétamide ou plus grandes. Les amides bi-alcoyle étaient adsorpbées sur le montmorillonite tetraméthylammonium, mais moins énergiquement sur l'argile triméthylammonium. L'écart (001) du montmorillonite tetraméthylammonium était de 13,8 Å, et ne changeait pas après adsorption des amides bi-alcoyle. On a aussi noté la liaison évidente de l'hydrogène de l'ion triméthylammonium et de quelques autres composés de carbonyle.

Kurzreferat – Der Mechanismus der Interaktion zwischen kationischen, organischen Molekülen an Austauschpunkten in Montmorillonit und organischen Molekülen mit Carbonyl-gruppen wurde untersucht. Auf Trimethylammonium und Tetramethylammonium-Montmorillonit adsorbierte Dialkylamide wurden durch Infrarotspektroskopie untersucht. Die Elektronegativität oder Basi-

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zität der Amide ausgedrückt als eine Summe der Taft Polarfaktoren ($\Sigma\sigma^*$) steht, wie erwiesen wurde, zu der C–O Spannungs-frequenz nach Adsorption auf Trimethylammonium-Montmorillonit in Beziehung. Außerdem bestand eine unmittelbare lineare Beziehung zwischen den Änderungen in den C–O und N–H Spannungsfrequenzen der Amide bzw. des Trimethylammonium-Ions. Es wurde somit erwiesen, daß die Dialkylamide durch des Sauerstoff der Carbonylgruppe über Wasserstoff mit dem Wasserstoff des Trimethylammoniums in Verbindung stehen. Die (001) abstand des Trimethylammonium-Montmorillonits betrug 12,9 Å. Diese abstand änderte sich erst nach der Adsorption der Amidmoleküle vom Größenbereich des N,N-Diäthylazetamid aufwärts. Dialkylamide wurden auf Tetramethylammonium-Montmorillonit adsorbiert, doch weniger energisch als auf Trimethylammonium-Ton. Die (001) abstand des Tetramethylammonium-Montmorillonits betrug 13,8 Å und blieb die gleiche nach Adsorption der Dialkylamide. Es wurden auch Anzeichen für Wasserstoffbindung zwischen dem Wasserstoff des Trimethylammonium-Ions und gewisser anderer Carbonyl Verbindungen festgestellt.

Резюме—Был изучен механизм взаимодействия катионных органических молекуп, занимающих обменные позиции в монтмориллоните, с органическими молекулами, содержащими карбонильные группы. Диалкил-амиды, адсорбированные на триметиламмоний— и тетраметиламмониймонтмориллонитах изучались с помощью инфракрасной спектроскопии. Показано, что электроотрицательность или основность амидов, выраженная как совокупность полярных факторов Тафта ($\Sigma\sigma^*$), линейно связана с частотой натяжений С—О после адсорбции на триметиламмониймонтмориллоните. Изменения частот натяжений С–О и N–H соответственно амидов и иона триметиламмония обнаруживают также прямую линейную зависимость. Так, было показано, что диалкил-амиды имеют водородные связи через кислород карбонильных групп с водородом триметиламмония. Расстояние (001) триметиламмонийного монтмориллонита составляло 12,9 А. Только после адсорбции амидных молекул, сходных по размерам с молекулами N, N- —диэтилацетамида или более крупных, это расстояние изменилось. Диалкил-амиды адсорбировались тетраметиламмониймонтмориллонитом, но менее энергично, чем триметиламмонийной глиной. Расстояние (001) тетраметиламмонийного монтмориллонита составляло 13,8А и не изменялось после адсорбции диалкил-амидов. Получены указания о существовании водородной связи между водородом иона триметиламмония и некоторых других карбонильных соединений.

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