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ADSORPTION STUDIES ON KAOLINITES – II ADSORPTION OF AMINES

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Abstract– An investigation of the reaction between amines and hydrogen kaolinites having a broad range of crystallinites and particle sizes has been made. Aqueous and non-aqueous adsorption isotherms, conductivity titrations, rheological measurements and sediment volume studies give strong evidence that edge sites are dominantly involved in the reaction and basal surfaces remain essentially unaltered. The acid–base reaction produces a localized adduct rather than an ionized, protonated amine. The amine-hydrate adduct adsorbs with greatly modified geometry.

INTRODUCTION

KAOLINITE is known and exploited for its amine adsorption characteristics (Conley and Torok, 1964). Adsorption of nitrogeneous materials occurs most likely at acidic sites believed to originate on edge crystal faces, i.e. {010}, {$\bar{1}$10} and {110} surfaces (Lloyd and Conley, 1970). Langmuir adsorption isotherms yield 32 Å^2 per butylamine molecule as the effective adsorption area. This is slightly in excess of the minimum molecular cross sectional area, 25 Å^2 (Betts and Pethica, 1956), for adsorption. Wettability of the kaolin surface, both the rate and extent, is strongly affected by amine adsorption (Kitahara and Williamson, 1964). Vapor adsorption data on kaolins gave an average value of 150 Å^2 per unit cation exchange capacity. For kaolinite morphology with the common 6:1 aspect ratio, this area reduces to about 37 Å^2, if each silanol group is interpreted as an acidic edge site and ion exchange site. The population of these sites per g is termed χ.

The adsorption pattern, particularly with respect to orientation, of complex amines has received attention by Thompson and Brindley (1969), Raman and Mortland (1969), Yariv, *et al.* (1969), Tahoun and Mortland (1966) and others. Amine adsorbate behavior is not altogether clear. Some polyamines (ethylenediamine) peptize clay suspensions while others (hexamethylenediamine) produce flocculation. Ammonia, however, as a peptizing agent is superior to short chain monoamines and long chain polyamines.

Long chain fatty amines are observed (Wilcox, 1961b) to impart hydrophobic character to the kaolinite surface. However, the method of application influences strongly the thermal stability of the adduct. Hydrazine appears to diffuse rapidly between certain basal planes and expand the *c* axis dimension (Weiss *et al.*, 1963).

Amine adsorption carries important commercial implications in the fields of paint, plastics, cosmetics, pharmaceuticals, etc. Some evidence exists that clay adsorption of nitrogenous materials was instrumental in life building processes early in the earth's history.

The present work is part of a study to evaluate more quantitatively the mechanisms and functionality of the kaolinite surface in adsorption phenomena.

EXPERIMENTAL

Adsorption studies were performed at 25°C on a variety of kaolins selected to represent a broad range in both particle size and crystallinity and, hence, adsorptivity. Crystallinity was determined from the ratio of X-ray peak heights, $I_{02\bar{1}}/I_{060}$ and is termed the crystallinity index, C.I. For the 28 samples in this suite, C.I. varied from 0·00 to 1·00 with the mean being 0·41. Particle size (e.s.d.), surface area and crystallinity data for the samples are given in Table 1. Additional data pertinent to the samples appear in previous work (Lloyd and Conley, 1970).

The kaolinites were converted to the hydrogen form just prior to adsorption experiments by elutriation with H_2SO_4 at pH3 (10 per cent solids) followed by water washing to remove traces of salts and free acid and drying for 16 hr at 125°C. Previous work demonstrated no significant variations in clay adsorptivity within eight hours of the terminal drying time.

Rheological specimens, both aqueous and non-aqueous (mineral oil, resin, etc.), were prepared with a Waring blendor. Dispersion viscosities were determined with a model RVF Brookfield viscosimeter. Sediment volume studies employed 2 per cent dispersed samples prepared at maximum shear. Graduated centrifuge tubes (A.S.T.M.

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Table 1. Physical properties of kaolinite samples

Sample	Particle size $\bar{D}(\mu)$	Particle size % < 2μ	Crystallinity $I_{02\bar{1}}/I_{060}$	Surface area M^2/g	Acidity pK_a
Ia	7·3	13·0	0·15	9·7	6·20
Ib	0·57	83·0	0·61	22·7	6·25
Ic	0·35	97·0	0·16	29·4	6·30
Id	0·32	97·5	0·27	30·5	6·20
IIa	9·4	7·0	0·17	6·4	6·05
IIb	0·68	81·5	0·67	12·8	6·35
IIc	0·42	95·5	0·49	20·6	6·25
IId	0·31	98·0	0·59	19·3	5·90
IIIa	7·6	12·5	0·20	11·6	6·10
IIIb	0·63	83·0	0·14	(16)	6·05
IIIc	0·37	94·5	0·10	29·5	5·65
IIId	0·31	98·0	0·18	29·4	6·30
IVa	7·8	8·0	0·20	8·4	(6·75)
IVb	0·64	82·5	0·36	15·8	6·35
IVc	0·38	97·0	0·45	19·7	6·80
IVd	0·29	99·5	0·33	20·3	6·75
Va	9·1	6·5	0·25	5·1	6·35
Vb	0·80	77·0	0·27	12·8	6·45
Vc	0·49	94·5	0·29	14·7	6·35
Vd	0·33	99·0	0·41	17·6	6·35
VIa	9·0	6·0	0·46	7·0	6·40
VIb	0·92	77·5	0·48	13·2	6·15
VIc	0·53	94·5	0·73	16·6	5·90
VId	0·42	98·5	0·55	12·0	6·65
VIIa	7·8	5·0	0·61	5·6	6·60
VIIb	0·85	80·0	0·87	11·6	5·85
VIIc	0·45	97·0	0·43	23·2	6·60
VIId	0·35	99·0	1·00	21·1	5·85

D-96) assisted in determining accurately the sediment volumes over a 100 day period.

Adsorption isotherms (25°) were obtained with five solution concentrations within the Langmuir region, from about 400μM to 1800μM. One g of kaolinite was suspended in 50 ml solvent for 30 min, then centrifuged and the supernatant removed. Analysis for amine concentration was by HCl titration for aqueous solutions and by aqueous HCl extraction and NaOH back titration for non-aqueous (repurified, anhydrous heptane) solutions.

Computer fits were made to the general Langmuir adsorption equation

$$\frac{C}{A} = \frac{C}{A_s} + \frac{1}{A_s K}$$

where C = solution concentration of adsorbate
A = amount adsorbed per unit mass adsorbent
A_s = amount adsorbed at monolayer (saturation) coverage
K = adsorptivity constant.

Only data sets with correlation coefficients above 0·96 were accepted.

Conductivity measurements were performed under a nitrogen atmosphere on aqueous solutions with a precision 1000 Hz conductivity bridge.

RESULTS

Characteristically, strong amines ($pK_b < 5$) follow a particle size dependent, adsorption process shown typically in Fig. 1. The steep initial slopes of the data suggest amines to be held to the clay surface by strong dipole interactions. As the adsorbate in this region is not fugitive upon drying at 110°C, the adsorption energy must exceed 4–5 kcal/mole. Some amines adsorbed were observed to be retained in entirety above 150°C.

The assumption that Langmuir adsorption describes processes operative on clay surfaces is not always justified. Ross and Olivier (1964) have shown that most materials exhibit a distribution in adsorptive potentials. Such "patch" inhomogeneity may exist on both a molecular and crystal facet scale. The authors (1970) have observed various

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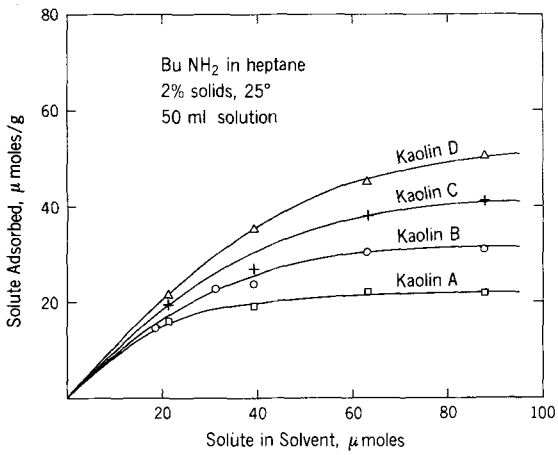

Fig. 1. Langmuir adsorption isotherms for kaolinite samples.

adsorptive surfaces on kaolinite with respect to H_2O resulting in part from restricted adsorbate orientation. Similar results on oxide surfaces have been reported by Holmes *et al.* (1968). Thus, the basic premises of the Langmuir isotherm, (a) localized adsorption, (b) mono-molecular adsorption, and (c) enthalpy of adsorption independent of surface coverage, must be examined critically for adsorbate-surface systems before an accurate interpretation can result.

An acid–base association complex on kaolinite as a consequence of amine adsorption fulfills the Langmuir premises. Further, the enthalpy of adsorption should exceed considerably that for other, non-acid, surfaces. Thus, the adsorption curves in Fig. 1 may be considered exclusively Langmuir and the surface mono-energetic in character. The computed monolayer for the adsorption process, which corresponds to complete "coverage" of high energy sites, varies from 10–60 μ moles/g (1–6 meq./100 g), depending on particle size and geometry.

Marshall (1949) has shown that kaolinite exhibits weak monoprotism during strong base conductometric titrations, i.e. smooth titration curves result. While it is generally impractical to titrate poorly dissociated acids with poorly dissociated bases, the high energy nature of amine adsorption is substantiated by this technique. The aqueous conductometric (resistivity) measurements were obtained with equipment shown schematically in Fig. 2.

Ethylenediamine (EN) is a good dispersant for kaolinites in H_2O. It is also a weak electrolyte as shown in Fig. 3. In pure water titration (lower curve), hydrolysis of the amine takes place

$$R\text{–}NH_2 + H_2O \leftrightarrow R\text{–}NH_3^+ + OH^-$$

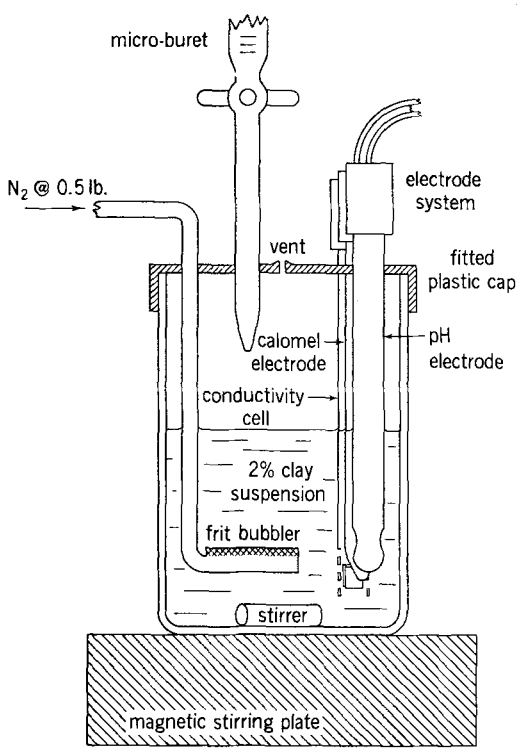

Fig. 2. Titrimetric arrangement for kaolinite suspensions.

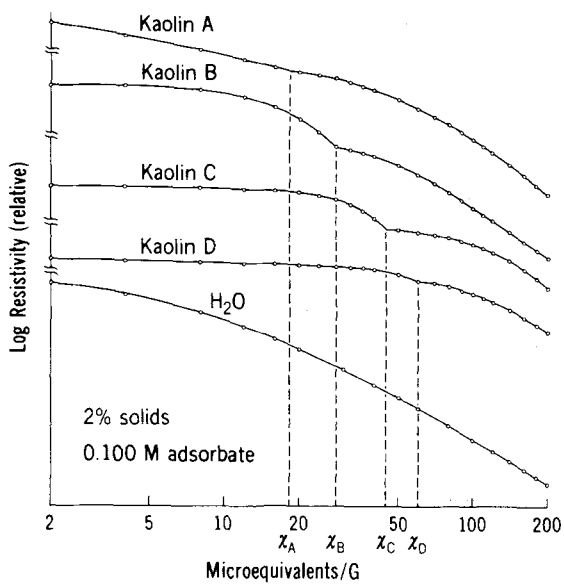

Fig. 3. Aqueous conductometric curves for ethylenediamine adsorbed per unit mass kaolinite.

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and generates ionic, conductive species. The hydroxyl ion, however, dominates the conductivity. From the equilibrium equation,

$$K_b = \frac{[R\text{NH}_3^+][\text{OH}^-]}{[R\text{NH}_3\text{OH}]}$$

it follows that, if the conductivity by OH^- far exceeds that by RNH_3^+, resistivity should be inversely proportional to amine concentration, which would appear as a -1 slope with increased titre on a log–log plot. However, in very dilute solution EN undergoes partial hydrolysis of both amine groups:

$$\text{H}_2\text{N}\text{–}R\text{–}\text{NH}_3^+ + \text{H}_2\text{O} \leftrightarrow {}^+\text{H}_3\text{N}\text{–}R\text{–}\text{NH}_3^+ + \text{OH}^-.$$

The pK_b for the second ionization process is of the order of 10 and its contribution cannot be neglected in the adsorption range studied ($C \simeq 10^{-5}$ M). Thus, the slope $\Delta R/\Delta C$ approaches -1 with high titre and -2 with low titre. The slope at the low titre end may be decreased slightly by the semi-flocculated state of the suspension. The absolute value of the resistivity is not significant since trace ions, total protonation and other factors may be influencial.

The presence of kaolinite in the conductivity system offers a competitive reaction where the protonated, surface silanol groups exhibit greater acidity than H_2O.

$$\text{kaolinite H} + R\text{–}\text{NH}_2 \rightarrow \text{kaolinite} \text{—H—}\text{H}_2\text{N}\text{–}R$$

circumventing OH^- ion generation and maintaining high resistivity. The early portion of the clay titration curves in Fig. 3, particularly for large values of χ, is significantly flattened. As the protonated surface is hydrated prior to amine introduction, the amine adsorption reaction must be more energetic than the hydration of the proton. A sharp change in $\Delta R/\Delta C$ occurs for all clays at the χ value. The values for χ correspond closely to those for the monolayer taken from Fig. 1. As EN is a diamine, χ is measured in microequivalents rather than micromoles ($1\,\mu$mole EN $= 2\,\mu$ eq). At higher concentrations of titre, the slope rapidly approaches the value for simple hydrolysis. The rate of slope change just prior to these "end points" and the flattened tendencies just following suggest that any additional adsorption process operative on the clay surface, e.g. on basal planes, must be of very low energy with the equilibrium shifted strongly to the solution phase. While occasional substituents as Al for Si may generate basal acid sites, the correlation between amine adsorption and edge area, rather than total area, indicates that these sites are a secondary contribution.

The acid flushing experiment plotted in Fig. 4 measures further the tenacity of edge-adsorbed amine. The adsorption of ethylenediamine was followed conductimetrically far past the adsorption break. The suspension was then back titrated with HCl of equal concentration (0·100 N). Free amine should react

$$R\text{–}\text{NH}_3\text{OH} + \text{HCl} \rightarrow R\text{–}\text{NH}_3^+ + \text{Cl}^- + \text{H}_2\text{O}$$

and generate two highly ionized and fairly conductive species. At the return point, corresponding to the molar value in adsorption, a discontinuity in resistivity appears in the otherwise smooth transition. The only available species more conductive is H^+. This could be introduced if, during the back titration, amines were incompletely neutralized. Thus, adsorbed molecules on the kaolinite surface are partially restrained from protonation.

The basicity of amines is quite variant and displays marked conductivity variations. This is observed in the selection plotted in Fig. 5. Stronger amines, EN and propylamine, ($pK_b < 4$) give pronounced breaks in the titration curve, while the very weak aniline ($pK_B \simeq 9{\cdot}3$) shows an imperceptible one. In contrast to this behavior glycine and formamide, both very polar molecules, but very weak bases (note early slopes), also produce well defined breaks, while ammonium hydroxide ($pK_b \simeq 4{\cdot}8$), one of the stronger nitrogen bases, shows very little discontinuity in the curve.

Mortland (1968) has shown that excess NH_3

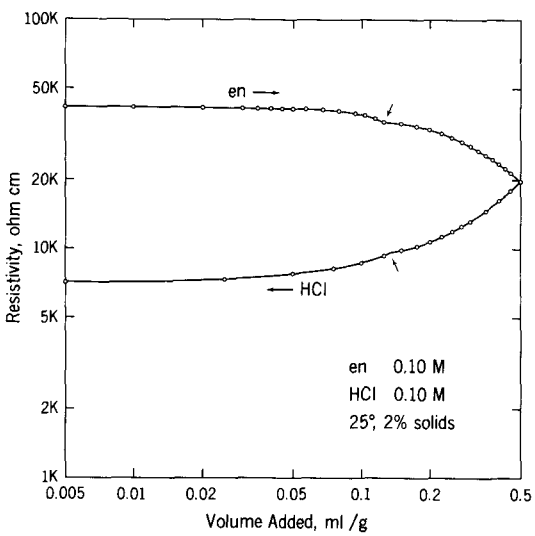

Fig. 4. Conductometric curves for acid flusing of amine-kaolinite.

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adsorbate on montmorillonite tends to dimerize and to become localized and monoprotonated. This mechanism likely derives from the acidic water of cation hydration. In aqueous environment this phenomenon is not in evidence with H kaolinite as little conductivity change with electrolyte occurs prior to or following the adsorption discontinuity.

Thus, acid–base behavior is not exclusively responsible for the curve shape. The acid sites on the clay must be a contributory factor in the adsorption mechanisms inasmuch as all curve discontinuities occur very near the same molar titre. Steric factors are suspect in these polar adsorption processes even though the molecules chosen (excepting aniline) have similar molecular cross sections. Whalen (1967) in adsorption studies on silica surfaces has demonstrated strong adsorption dependence on molecular geometry both of the substrate and adsorbate. Similarly, quarternary amines adsorb in varying degrees on kaolinite resulting from molecular geometry dependence of the adsorbate (Weiss, 1969). Both the titration profile in Fig. 4 and the conductance endpoint data in Fig. 5 suggest that EN functions as a monoamine with a single amine group exhibiting ready protonation.

Non-aqueous butylamine adsorption shows a 1:1 correlation with a reaction process at each Si–Al edge site (A = 32 Å^2) independent of crystallinity. Aqueous adsorption data showed lesser quantities of $BuNH_2$ to adsorb. The combined study on the 28 sample suite yielded the data shown in Fig. 6. An origin-biased, least squares line through the data yields a slope of 2·0. It appears conclusive that aqueous adsorption precludes 50 per cent of the acid adsorption sites independent of crystallinity. This observation is in keeping with the low χ values observed on conductivity plots in Fig. 3 (1 meg EN = 0·5 μmoles). The disparity may be resolved by considering the primary difference between organic solvent and aqueous butylamine solutions, i.e. the hydrated nature of the molecule in the latter.

$$BuNH_2 + H_2O \rightleftarrows BuNH_3OH \rightleftarrows BuNH_3^+ + OH^-.$$

The configuration in Fig. 7a involves orbital overlap of the lone-paired, 2 p (or sp^3) orbital* on nitrogen with a hydrogen s cloud from the water molecule.

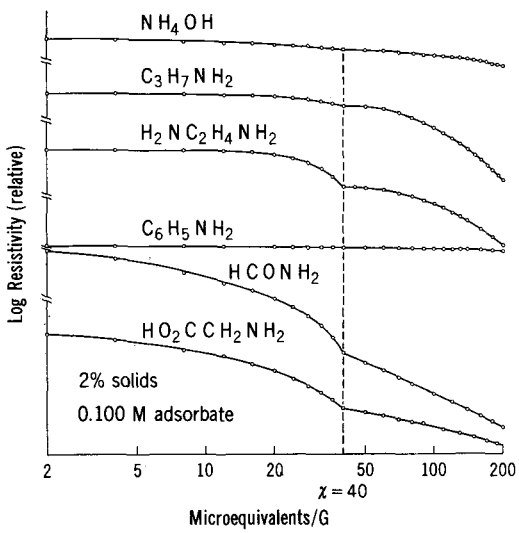

Fig. 5. Aqueous conductometric curves for various adsorbates per unit mass kaolinite.

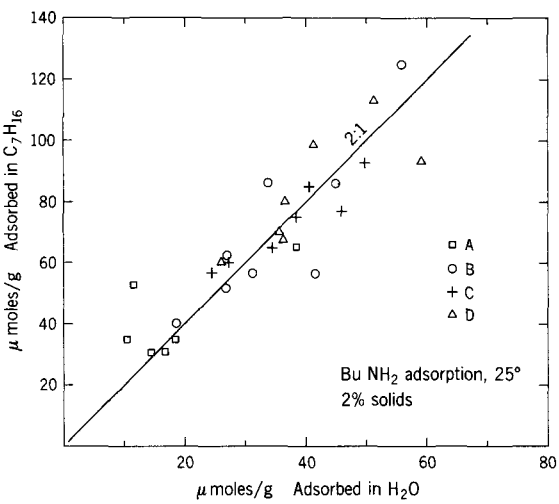

Fig. 6. Monolayer values for butylamine on various kaolinites in water and heptane.

The remaining paired s and p orbitals on the H_2O molecule orient to produce hindered overlap onto each of the amine hydrogen s orbitals. Thus, three very weak hydrogen bonds hold the $BuNH_3OH$ adduct together. Upon association of anhydrous $BuNH_2$ with silanol surface groups similar coordination results as depicted in Fig. 7b. As the pK_a of the silanol group is approximately 6 (Conley and Althoff, 1971), proton transfer to the amine has small likelihood. However, the acidity of the

*NH_3 and amines experience varying degrees of sp^3 hydridization depending upon environmental influences (Kauzmann, 1957).

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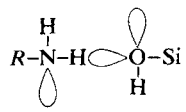
silanol, being stronger than that of H_2O, yields a stronger amine–silanol complex than $BuNH_3OH$. Once formed the



adduct remains stable toward hydrolysis at ambient temperatures.

After hydration, the butylamine molecule becomes sterically hindered from coordinating at the silanol surface. While an exchange reaction should result from the higher stability of the amine–silanol complex vs. the hydrate, the activation energy of the weak, amine complex about 4 kcal, is only slightly above the enthalpy of adsorption of the hydrate complex, 2–3 kcal (Martin, 1962; Nair and Adamson, 1970). This condition diminishes severely the rate constant of the exchange reaction. A second operative factor involves the uncoordinated H atom on the H_2O molecule in the complex. The *s* cloud from the H_2O molecule may hydrogen bond to the silanol group in characteristic fashion but the remaining sets of filled orbitals on the oxygen and nitrogen atoms produce hindrance with any coaxial orientation. Inclining the $BuNH_3OH$ molecule to the kaolinite edge yields an orientation wherein the free water hydrogen orbital overlaps one siloxy *p* orbital pair and the water *p* orbital overlaps both the amine hydrogen and the hydrogen on an adjacent silanol group. This concept has additional merit, since alternate edge silanol groups by virtue of skewed tetrahedra and the inclined $BuNH_3OH$ molecule would be sterically hindered from adsorbing amine. The adsorption scheme appears diagrammatically in Fig. 7c.

Because one hydrogen orbital is shared between *p* orbitals, and less energetically held, and because the various *p* clouds contribute antibonding to the association complex, $BuNH_3OH$ should be held more weakly to the surface than $BuNH_2$. This is borne out by surface chemical modification studies. Aliphatic amines, either dry blended (Wilcox, 1961a) or added via non-aqueous solution (Conley and Golding, 1965) to dry kaolinite, yield surface modified products with notably superior thermal

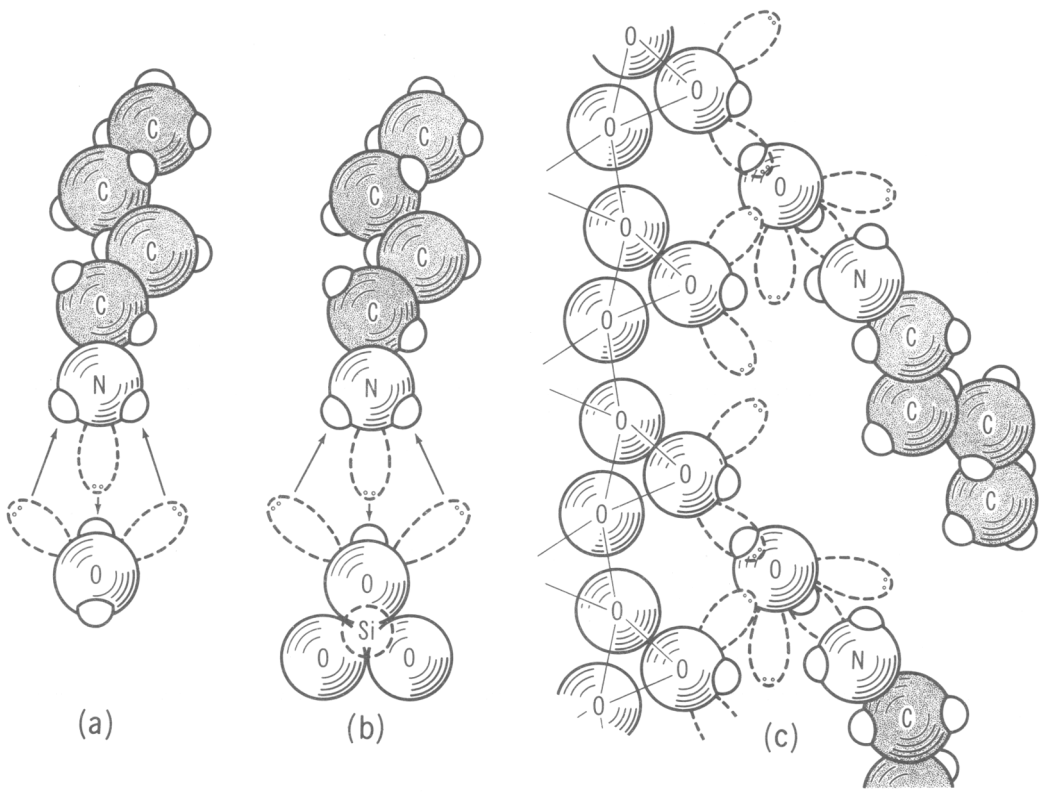


Fig. 7. Molecular model for butylamine adsorption on kaolinite edge.

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stability to those produced via aqueous contact systems. The amine-hydrate model serves to explain more clearly the variability in interlayer adsorption behavior of aniline and cyclohexyl amine on montmorillonites (Yariv, Heller and Kaufherr, 1969).

Fatty amines employed to generate hydrophobicity on pigment surfaces require quantities suggestive of edge coverage only. Typical is the rheology plot in Fig. 8. Bifunctional amines, as ethylenediamine, Quilon*, hydroxy paraffin amines, etc. display a more complex amine–rheology relationship as shown generally in Fig. 9.

*Trade name for heterocyclic organo-chromium-amine complex.

The α component represents the bifunctional amine and the β component the epitaxially modified phase (usually a polymeric resin containing chemically reactive groups). The symbol η designates low shear viscosity and N, the number of equivalents. Viscosity minima for a series of kaolinites surface modified by the α–β process, i.e. EN and polyester resin (Bundy, 1963) were obtained within 10 per cent of the graphically indicated values for χ.

Polyamines have been suspect as undergoing chelation based on Weiss (1959) interlayer phenomena. If this activity occurred with EN, the surface should become hydrophobic as depicted in Fig. 10a. The effective dispersant action of EN in water suggests polar "tail" activity, Fig. 10b, where EN functions as a monoamine (see also Fig. 3). Lang-

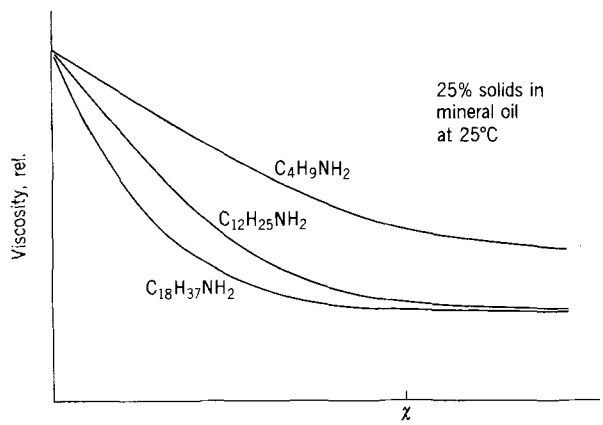

Fig. 8. Rheology of amine-treated kaolinites.

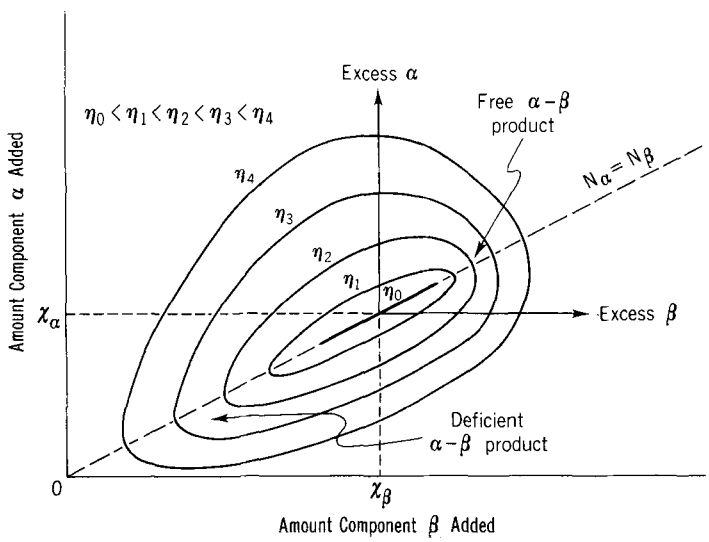

Fig. 9. Rheology of amine-adduct treated kaolinite.

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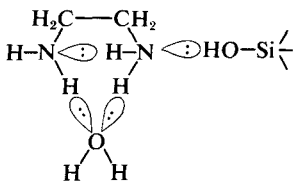
muir adsorption plots for aqueous $BuNH_2$ and EN on the crystallinity suite yield the monolayer data in Fig. 11. Slightly less EN is observed to adsorb for a given surface than $BuNH_2$ by an average factor of about 20 per cent (least squares slope $\simeq 0{\cdot}83$). Earlier conductivity and adsorption data lend additional support for these phenomena. The amount of $BuNH_2$ adsorbed in μmole is equal to or somewhat less than the amount of EN in μeq. As 1 μmole EN = 2 μeq, the data in Fig. 1, 3, 6 and 11 are self consistent. Some form of chelation activity by ethylenediamine is suggested. The molecule is too short, 5·6Å, to span the 7·2ÅC axis spacing and coreact with vertically adjacent silanol groups. Lateral interaction by the unhydrated molecule with adjacent silanol groups, 5·1Å, is plausible only in the oleophilic orientation of Fig. 10a.

A more reasonable proposal is based on the configuration of ethylenediamine in H_2O proposed by Schaap and Schmidt (1970)



Each lone pair orbital of the H_2O molecule shares one H each from the two amine groups. This

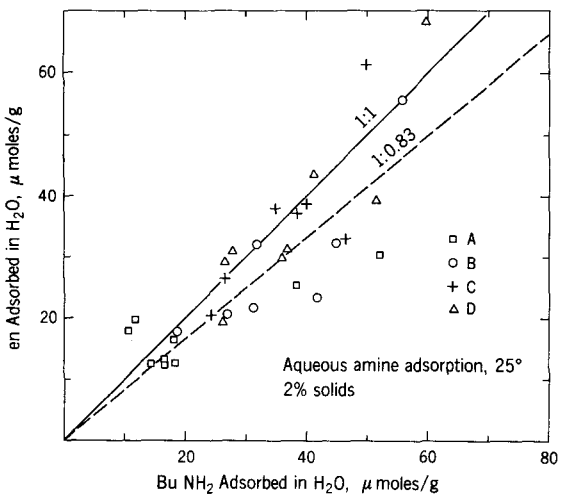


Fig. 11. Monolayer values for ethylenediamine and butylamine on various kaolinites in water.

results in an extremely stable, five-membered ring structure (EN retains the hydrate through the boiling process). Adsorption of the ring intact would require hindered coordination of one amine group with a silanol. The hydrate portion of the molecule would adsorb similarly hindered at an adjacent silanol. Thus, one amine group remains uncoordinated with the clay surface and is directed toward and displays dipole character to the liquid phase. The bulkiness of this configuration should exert serious steric hindrances toward adsorption

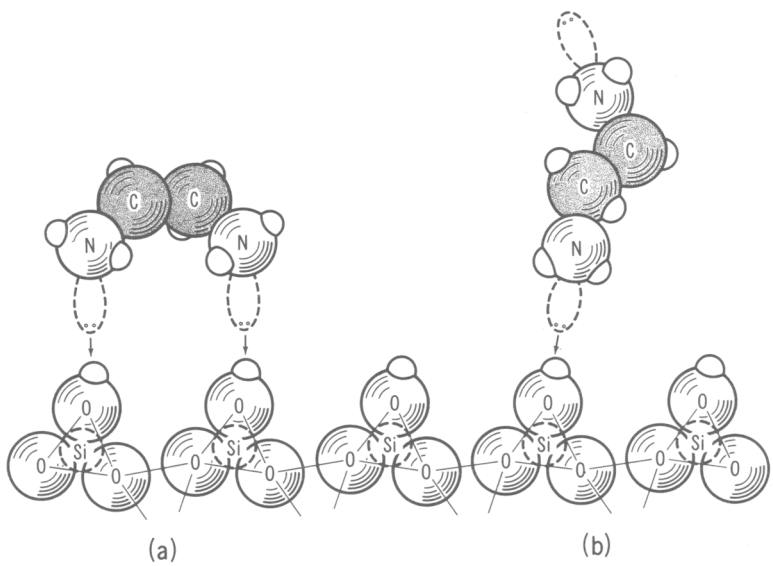


Fig. 10. Molecular models for ethylenediamine adsorption on kaolinite edge.

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upon adjacent (third) silanols along the edge face. As several orientations of the subgroups, $-NH_2-H_2O-$, are possible with two silanol groups and as a separate mode of pairing can exist between a silanol group and the associated edge Al octahedron (Conley and Althoff, 1971), a variety of conformations may take place. Reduced adsorption compared with $BuNH_3OH$ is expected with this model.

While the application of i.r. spectroscopy has been of value in interpreting other amine adsorption work on clays (Mortland, 1966; Farmer and Mortland, 1965), the quantities of adsorbate involved on kaolinites, 10–60 μeq/g, are too low for practical interpretation. In addition water, which occurs to the extent of 100–200 μeq/g, produces severely interfering absorption bands in the amine region.

Most sensitive to the polar-non polar surface configuration of adsorbed molecules are the double layer phenomena, in particular the zeta potential. Wolff (1957) has shown that both sedimentation rate and terminal sediment volume (T.S.V.) are manifestations of the surface characteristics interpretable where polar and non-polar media are employed. For kaolinite sedimentation volume is a complex function of its zeta potential and adsorbed water film (Tamamushi and Shirai, 1954). Heptane and water sedimentation media lend themselves to a simple, semi-quantitative evaluation technique. While all solute-solvent combinations are not practicable, e.g. anhydrous ammonia/heptane, sufficient are available so as to obtain an insight into orientation and charge phenomena associated with adsorbates. In Table 2 are listed a series of adsorbates, solvents and terminal sediment volume data.

In the high C.I.–H_2O system ammonia exhibits a better dispersant activity than EN or $BuNH_2$. Yet its T.S.V. is not as compact. More interestingly, the hydrophobic character of the C_4H_9 tail appears little different than the hydrophilic EN ring, TETA and hydrazine. Hexamethylenediamine apparently does bridge silanol groups, as floc volumes (card-house structure) are produced. Glycine, an essentially neutral base, acts as an excellent dispersant due likely to the polar carboxylic tail. Formamide, with a similar, but aldehydic, tail is considerably poorer.

The high C.I.–C_7H_{16} system yields T.S.V.'s considerably in excess of card-house structures. On the average two particles approach no closer than 1·5 diameters in the polar solute (adsorbate) systems. The data suggest a superstructure levitation phenomenon in non-polar liquids. The hydrophobic influence generated by hexamethylenediamine, and to a lesser extent by butyl amine, is further supported by reduced T.S.V.'s with these solutes. The degree of compaction is still significantly less than floc volumes would suggest.

Table 2. Terminal sediment volumes (rel.) for kaolinites sedimented in polar and non-polar media*

Liquid system Kaolinite sample Solute	H_2O VIc† T.S.V.	H_2O IIIc‡ T.S.V.	C_7H_{16} VIc T.S.V.	C_7H_{16} IIIc T.S.V.
NH_3	5·2	5·2		
en	3·4	5·2	38	11·7
$BuNH_2$	3·6	5·2	27	13·5
Hex-EN	13·0	12·5	23	13·0
TETA	3·8	6·2	36	15·0
N_2H_4	3·6	6·4	36	13·0
$C_6H_5NH_2$	4·4	5·7	31	13·0
Glycine	3·4	5·2		
Formamide	4·6	5·2	36	15·0

*100 μM solution, 1 per cent solids.
†C.I. = 0·73 (from Table 1).
‡C.I. = 0·10 (montmorillonite impurity) (from Table 1).

As the available adsorbate in solution is several times that required for monolayer coverage (see Fig. 1), as $BuNH_2$ fails to produce hydrophobic character in H_2O, and as considerable electrostatic repulsion exists for the $BuNH_2$–C_7H_{16} system it appears conclusive that an appreciable fraction of the kaolinite surface takes up little, if any, adsorbate. Thus, much of its native polar character, likely derived from basal surfaces is retained.

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Résumé – Ce travail porte sur l'étude des réactions entre des amines et les formes hydrogène de kaolinites ayant des cristallinités et des tailles particulaires très variées. Les isothermes d'adsorption en milieux aqueux et non aqueux, les titrations conductimétriques, les mesures rhéologiques et les études de volume de sédiment montrent avec évidence que les sites de bord sont concernés d'une façon prédominante dans la réaction et que les surfaces basales restent essentiellement non touchées. La réaction acide-base entraîne l'apparition d'une amine protonée, formée plus par une action locale que par une ionisation. Le complexe amine-hydrate formé s'absorbe avec une géométrie profondément modifiée.

Kurzreferat – Es wurde eine Untersuchung der Reaktion zwischen Aminen und Wasserstoff-Kaoliniten mit einem weiten Bereich von Kristalliniten und Teilchengrössen durchgeführt. Wässrige und nichtwässrige Adsorptionsisothermen, Leitfähigkeitstitrationen, rheologische Messungen und Sedimentsvolumenuntersuchungen deuten stark darauf hin, dass in erster Linie Kantenstellen an der Reaktion beteiligt sind und Grundflächen im allgemeinen unverändert bleiben. Die Säure-Basenreaktion ergibt eher ein örtliches Anlagerungsprodukt als ein ionisiertes, protontragendes Amin. Das Amin-hydrat Anlagerungsprodukt adsorbiert mit weitgehend veränderter Geometrie.

Резюме — Проведено изучение реакции между аминами и водородными каолинитами, значительно различающимися по кристалличности и величине частиц. Изучение изотерм водной и неводной адсорбции, титрование проводимости, геологические измерения и определение объема осадка служат важным доказательством преимущественного участия в реакции реберных позиций; базальные поверхности существенно не меняются. Кислотно-основная реакция более легко создает локализованный аддукт, чем ионизированный (протонизированный) амин. Амино-гидратный аддукт адсорбирует с весьма видоизмененной геометрией.

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