Clays and Clay Minerals, 1969, Vol. 17, pp. 301–308. Pergamon Press. Printed in Great Britain

EFFECT OF ACIDITY IN MONTMORILLONITE INTERLAYERS ON THE SORPTION OF ANILINE DERIVATIVES

S. YARIV and L. HELLER
Department of Geology, The Hebrew University, Jerusalem, Israel
and
N. KAUFHERR
Department of Inorganic and Analytical Chemistry, The Hebrew University, Jerusalem, Israel

(*Received* 24 *April* 1969)

Abstract – Sorption of aniline and its derivatives by montmorillonite substituted by cations of widely different acidity depends upon the polarizing power of the interlayer cations. Infra-red spectra indicate that the anilines are mostly bound to the interlayer cations through water molecules, except in Cs montmorillonite, where bonding to the oxygen surfaces of the alumino-silicate sheets seems to predominate. Anilines are weak bases, which compete with the oxygen surfaces for protons of acidic interlayer water. Consequently, the tendency of anilines to act as proton donors in the clay interlayers increases with the polarizing power of the exchangeable cation. The concept of 'basic' water is introduced to account for some of the features of the spectra of Cs montmorillonite treated with the organic ligands.

THE TERM 'surface acidity' applied to smectites may be misleading. The oxygen sheets are, in fact, electron donors and only the interlayer water is acidic, imparting an overall acidic character to the clay. In reactions with strong bases such as ammonia (e.g. Mortland and Raman, 1968) or with aliphatic amines (Fripiat, 1963) only the net acidic effect has to be considered. However, in the presence of weak amphoteric organic bases such as aniline, the clay surfaces may compete with the organic base sorbed for the protons of the interlayer water molecules. The polarization of the interlayer water depends on the exchangeable cations present.

The reactions of different cations in the clay interlayers with water and aniline and of transition metal cations with water and various aniline derivatives have been described previously (Yariv *et al.*, 1968; Heller and Yariv, 1969). The present study is devoted to the sorption of various aniline derivatives by Wyoming bentonite saturated with ions of widely different acidity: Cs, K, Na, Mg, Al and H.

EXPERIMENTAL

The materials used and the experimental procedures followed were the same as those previously described (Heller and Yariv, 1969). Unless otherwise stated, samples were immersed for 24 hr in the organic liquids and subsequently wiped with filter paper.

RESULTS AND INTERPRETATION

Infra-red spectra

The frequencies observed in the NH_2, NH–O and CN stretching regions are listed in Table 1.

K, Na, Mg, H *and* Al *montmorillonites.* Interlayer associations of cations, water and various anilines have been divided into two types, I and II, with direct N–Me and N–H_2O–Me bonds respectively (Yariv *et al.*, 1968; Heller and Yariv, 1969). Type I associations are predominantly formed when the metal ions display a strong tendency to form complexes with the organic bases.

The interlayer cations of the present samples do not tend to form type I complexes; faint indications of such complexes were detected with Mg, K and Na montmorillonite samples and aniline, which show a very small band at 3270 cm^{-1}*. However, with hydrogen montmorillonite, at least, direct protonation of the organic bases might be expected, by analogy with the reactions of such clays with ammonia (Fripiat, 1963) or pyridine (Farmer and Mortland, 1966). But the spectra obtained with H montmorillonite treated with ani-

---

*The results obtained for aniline associations in this study are more accurate than those previously reported (Yariv *et al.*, 1968) due to the more powerful grating instrument now available, which permits more accurate assessment of the positions and relative intensities of the peaks.

Table 1. Frequencies of NH_2, NH—O and CN bands (cm^{-1})

Montmorillonite		Al	Mg	H	Na	K	Cs	Pure liquid
Aniline	NH_2 stretching	3315, 3385	3320, 3390	3320, 3390	3320, 3390	3320, 3390	3345, 3390*, 3420*, (3475)†	
	NH . . . O band	3200 (3140)*	3135–3185	3130–3200	3140–3190	3150	3215	
	CN stretching	1243, 1250* (1283, 1315)	1250	1250	1254	1254	1270 (1315)	1276
o-toluidine	NH_2 stretching	3310, 3385	3320, 3390	3320, 3390	3320, 3390	3320, 3390	3345, 3390 (3425)†, 3475*	
	NH . . . O band	3150–3200	3140–3205	3130–3200	3185‡	3185‡ (3125)†	3215*	
	CN stretching	1243	1248	1250	1248	1248	1258	1268
m-toluidine	NH_2 stretching	3310, 3385	3320, 3390	3320, 3390	3320, 3390	3320, 3390	3345, 3390, 3420* (3475)†	
	NH . . . O band	3175–3200, (3140)*	3180–3200, (3140)*	3150–3210 (3120)†	(3155)†	(3160)†	3215	
	CN stretching	1275	1275	1278	1280	1279	1288	1290
p-toluidine	NH_2 stretching	3310, 3385	3315, 3385	3315, 3385	3320, 3390	3320, 3395	3320, 3390, 3430	
	NH . . . O band	3205 (3145)*	3185–3230 (3140)*	3150–3230	(3200)†, (3125)†	(3200)†, (3130)†	3225*	
	CN stretching	1243	1245	1238 (1250)*	1250	1250	1260	1262
2,5 dimethylaniline	NH_2 stretching	3310, 3385	3315, 3385	3315, 3380	3315, 3385	3315, 3385	3385, 3430 (3470)*	
	NH . . . O band	3210 (3140)*	3210 (3135)†	3210‡	(3200)*		3245*	
	CN stretching	1258–1262	1261	1263	1262	1262	1270	1282
2,6 dimethylaniline	NH_2 stretching	3325, 3395	3335, 3400	3330, 3400	3330, 3400	3335, 3395	3330*, 3395, 3475*	
	NH . . . O band	3200 (3135)*	3200 (3130)*	3200 (3135)†	3130–3200§	3165–3225§	3225*	
	CN stretching	1266	1265	1265	1267	1267	1272	1270
2,4,6 trimethylaniline	NH_2 stretching	3330, 3395	3330, 3405	3330, 3395	3335, 3400	3330, 3395	3390, 3475* (3345)†	
	NH . . . O band	3200, 3135*	3205, 3135*	3210		3200	3250‡	
	CN stretching	1226–1236 (1250)†	1232	1232‡	1238–1250	1230–1235	1243‡	1251
o-chloroaniline	NH_2 stretching	3315, 3390	3330, 3395	3325, 3395	3330, 3400	3325, 3390	3345, 3385, 3425, 3480	
	NH . . . O band	3195‡	3170–3230	3190‡	3200	3200	3230‡	
	CN stretching	1288	1288	1288	1292	1292	1300	1312
m-chloroaniline	NH_2 stretching	3315, 3385	3330, 3995	3330, 3395	3330, 3395	3330, 3390	3350, 3390, 3430*, 3475*	
	NH . . . O band	3200	3200 (3120, 3165)†	3200‡	3200§	3200	3215	
	CN stretching	1245, 1267	1245 (1265)†	1248, 1266*	1260 (1248)†	1263 (1248)†	1260	1298

*Shoulder.
†Very small shoulder.
‡Very broad.
§Small broad band. Brackets signify that the peaks are indistinct.

line derivatives show features similar to those of K, Na, Mg and Al montmorillonites and of type II complexes obtained with transition metals (Heller and Yariv, 1969) and differ entirely from the spectra of the corresponding anilinium or anilinium aniline samples (Fig. 1). Only the spectra of Al montmorillonite immersed in aniline or *m*-toluidine show some resemblance to those of the corresponding anilinium aniline samples*).

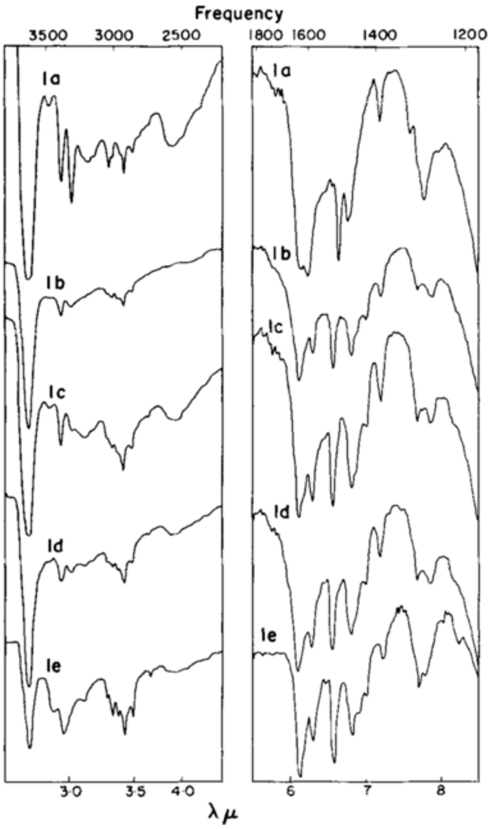
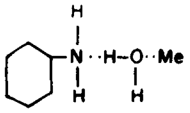
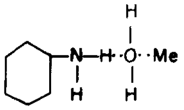


Fig. 1. Infra red spectra of self-supporting films of (a) Al montmorillonite-m toluidine; (b) K montmorillonite-2,5 dimethylaniline; (c) Al montmorillonite-2,5 dimethylaniline; (d) H montmorillonite-2,5 dimethylaniline; (e) 2,5 dimethylanilinium montmorillonite-2,5 dimethylaniline.

Two structures of type II, designated C and D, were previously postulated for aniline derivatives, in which the organic molecules act as proton acceptors and proton donors respectively (Heller and Yariv, 1969).



(C)



(D)

Structure C contains a free NH$_2$ and structure D a free NH group. Two bands, corresponding to asymmetric and symmetric NH$_2$ frequencies should therefore appear for structure C, at 3400 ± 100 cm^{-1}, but only one band for structure D in the same region. The spectra observed show two bands, but, as previously noted, their relative intensities differ greatly. It is concluded that both structures occur in varying proportions and that the NH stretching frequency of structure D either coincides with the asymmetric NH$_2$ frequency of structure C or is too close to it to be resolved by the i.r. instrument used.

Whenever the band corresponding to the asymmetric vibration is intense, so also is a broad band at 3130–3210 cm^{-1}, the assignment of which is uncertain. It might be a combination band of NH$_2$ deformation vibrations. However, Lippincott and Khanna (1965) ascribed it to N–H . . . O vibrations in glycine and Peri (1965) suggested that a band at 3100 cm^{-1} may be due to hydrogen bonding of ammonia to surface oxygens of γ alumina.

The intensity ratios, R_1 and R_2, of the asymmetric to symmetric NH$_2$ vibrations and of the broad band at about 3200 cm^{-1} to the symmetric NH$_2$ vibrations respectively are given in Table 2. Since only relative values were considered, these were calculated from transmittance values, measured from an idealised base-line. Accurate values are difficult to determine and only general trends are significant. An increase in both R_1 and R_2 indicates an increase in the proportion of structure D relative to C.

The CN bond in structure D has much more double bond character than that in structure C. It is to be expected that the CN stretching of structure C should be lower than that of the pure liquid, while that of structure D should be similar or higher. Indeed, one CN stretching of lower frequency than that of the pure liquid is always observed. With aniline a band at higher frequency can be unequivocally assigned to CN with more

---

*See footnote on page 301.

Table 2. Intensity ratios of some selected bands of i.r. spectra

Montmorillonite		K	Na	Mg	H	Al
Aniline	R_1	0·58	0·59	0·70	0·72	0·91
	R_2			0·09	0·07	0·22
	R_3					0·40
o-toluidine	R_1	1·0	0·92	1·60	1·15	2·57
	R_2	0·05	0·03	0·47	0·08	0·57
	R_3	0·37	0·39	0·60	0·60	0·85
m-toluidine	R_1	0·68	0·70	0·85	0·82	1·00
	R_2			0·38	0·09	0·26
	R_3	0·20	0·21	0·23	0·25	0·50
p-toluidine	R_1	0·70	0·60	0·78	0·75	1·00
	R_2			0·23	0·15	0·40
	R_3*					
2,5 dimethylaniline	R_1	2·10	1·75	2·87	2·00	4·60
	R_2		0·25	1·25		1·57
	R_3	1·25	1·06		1·40	1·67
2,6 dimethylaniline	R_1	1·50	1·50	2·25	2·00	5·50
	R_2	0·30	0·20	1·50	1·30	3·60
	R_3		0·20	0·25	0·23	0·45
2,4,6 trimethylaniline	R_1	1·71		2·87	2·00	5·50
	R_2	0·71		2·20	1·30	6·50
	R_3	1·43	1·37	1·45	1·60	1·75
o-chloroaniline	R_1	1·27	0·95	1·04	1·37	2·25
	R_2	0·30	v. sm.	0·32	0·51	1·50
	R_3	0·90	0·67	0·80	1·00	1·37
m-chloroaniline	R_1	0·85	0·90	0·93	1·11	1·63
	R_2	0·23	v. sm.	0·29	0·28	1·27
	R_3	0·96	1·08	0·93	1·17	1·38

*Reference peak is too broad to be useable (For definitions of R_1, R_2, R_3 see text).

double bond character. With the other ligands, bands are observed in the appropriate region, but due to overlap with CH bands they could not be identified with any degree of certainty.

In Table 2, intensity ratios (R_3) are included of two bands in the CN stretching region: the one at higher frequency either corresponds to the CN bouble bond and is intensified by increasing proportions of structure D, or to a CH vibration, which is not appreciably affected by changes in structure from C to D. The band at lower frequency is assigned to CN with single bond character. An increase in R_3, like that in R_1 or R_2, therefore indicates an increase in the amount of structure D relative to C and the three intensity ratios generally show similar trends.

Cs montmorillonite. The spectra of Cs montmorillonite with aniline derivatives differ from those of the other clays studied. A very broad band occurs in the NH_2 stretching region, which sometimes shows three, but more frequently four maxima. (Table 1 and Fig. 2a–c). With ortho-substituted anilines the strongest maximum appears at higher frequencies than with other ligands – at 3385–3395 cm^{-1} instead of 3345 cm^{-1}. This suggests that in the absence of ortho-substituents the NH vibrations may be more affected by the field of the Cs ions.

The broad band at 3130–3210 cm^{-1} observed with other montmorillonites is sharpened with Cs montmorillonite–aniline associations and is shifted to higher frequencies (3215–3250 cm^{-1}).

Fig. 2. Infra red spectra of self-supporting films of (a) Cs montmorillonite-*m* toluidine; (b) Cs montmorillonite-2,5 dimethylaniline; (c) Cs montmorillonite-2,4,6 trimethylaniline; (d) K montmorillonite-2,4,6 trimethylaniline; (e) K montmorillonite-2,4,6 trimethylaniline, heated *in vacuo* at 100°C; (f) K montmorillonite-2,4,6 trimethylaniline, after 48 hr immersion in organic liquid.

Another feature distinguishing the spectra of Cs samples is the high intensity of the NH_2 deformation band at 1620–1630 cm^{-1}. This band is intense for aniline dissolved in CCl_4 and becomes weaker as H bonding increases. Its high intensity in the spectra of the Cs samples suggests that there is little H bonding of the NH_2 groups. This conclusion is supported by the observed CN stretching frequencies, which are close to those of the pure liquids, indicating that the vibrations are only slightly perturbed.

With aniline, however, an additional weak band is observed at 1315 cm^{-1}. This must be regarded as a CN stretching frequency and indicates that a small proportion of the CN vibrations are strongly perturbed. Similar but weaker high frequency bands were also observed with Al montmorillonite and very faintly with K and Na montmorillonites. They disappear on heating in vacuo at 100°C. Simultaneously a maximum at 3345 cm^{-1}, the lowest frequency observed in the NH_2 stretching region, is weakened. It thus appears that the perturbed CN vibrations and a strongly perturbed NH_2 vibration may be assigned to the same molecules of the organic ligand. Since they are attenuated by heating at 100°C, they are probably associated with water.

Cs has little tendency to retain water or to form complexes with organic molecules. The spectra show that most of the anilines in the Cs montmorillonite interlayers are held by weak hydrogen bonding, probably to the oxygen surfaces, either directly or through water molecules. However, on the clay surfaces there are regions of higher local charge concentration in the vicinity of positions of tetrahedral substitution. Water held in these positions by H bonding becomes strongly polarized, with the negative ends of the dipoles projecting into the interlayers. Association of some aniline with such water molecules would account for the strong perturbation of part of the CN and NH vibrations. The fact that a similar, though weaker, effect is detected with montmorillonite saturated with Al ions, which are acidic, may perhaps be attributed to the high valency of this cation, which gives rise to a more localized neutralization of interlayer charge. Regions of negative charge concentration on the oxygen surfaces may attract water molecules, giving rise to effects similar to those observed with Cs montmorillonite. As the valency of the cation decreases, the charge distribution in the interlayers becomes more homogeneous and the intensities of the highly perturbed CN and NH vibrations decrease.

Effect of prolonged immersion in the organic liquids or of heating the specimens under vacuum. Prolonged treatment of the samples with the organic bases or heating the clay aniline associations under vacuum have one effect in common: to displace water molecules from the clay interlayers (on heating, some organic material is also lost). The spectra acquire a certain similarity to those of Cs montmorillonite, although most of the features of the original spectra persist. In the NH_2 stretching region a broad band appears with several maxima (Fig. 2e, f). The NH_2 bands become much broader and overlap; small shoulders detectable at 3345–3425 cm^{-1} may be used as a criterion for the extent to which the original spectra tend to resemble those of the corresponding Cs montmorillonite samples. For similarly treated montmorillonites, resemblance to Cs decreases in the order K > Na > H > Mg > Al. Analogous results are obtained with the other ligands, though the effect is sometimes very weak and the position of H in the series varies.

Chemical analyses

The percentage of N retained by samples dried *in vacuo* at 100°C depends upon the interlayer cation and the organic ligand, as previously discussed (Heller and Yariv, 1969). There is a pronounced tendency for this percentage to increase in the order Cs < K < Na < Mg < Al, i.e. with increasing hydration energy of the cation. The position of H in this series depends upon the ligand. The amount of N retained by Cs montmorillonite ranges from 0·6 per cent for *o*-chloroaniline to 1·2 per cent for aniline, while corresponding samples of K montmorillonite retain 0·85 and 1·78 per cent and Al 1·7 and 2·5 per cent respectively. The effect of the nature of the organic ligand has been discussed previously (Heller and Yariv, 1969).

Samples stored in tightly closed vessels in the presence of $Mg(ClO_4)_2$ lose much of the sorbed aniline. With Cs montmorillonite most of the organic material was lost after 4 months' storage.

DISCUSSION

The effect of 'surface acidity' of smectites in relation to hydration, exchangeable cation and smectite structure has been discussed by Mortland and Raman (1968). They showed that protonation of sorbed ammonia occurred to a degree depending upon the hydrolysis constant (pK) of the interlayer hydration complexes and that the degree of protonation may be regarded as a measure of the acidity of the system. Mortland (1968) pointed out that a correlation appears between the degree of protonation and the basicity of the sorbed nitrogen bases ammonia, pyridine and urea.

With weak amphoteric bases such as aniline or its derivatives, acidic water molecules do not necessarily donate protons to the interlayer organic material. The oxygen surfaces of the clay, which are negatively charged, also act as bases, competing with the organic base for the protons of the water molecules. A distinction must therefore be made between the acidity of the interlayer water and the surface basicity of the clay layers. The acidity of interlayer water increases with increasing polarizing ability of the exchangeable cations.

Although it has been contended that Cs, K and Na ions are unhydrated in the clay interlayers (Grim, 1968) this has been disputed for Na and K (e.g. Fripiat *et al.*, 1960; Mackenzie, 1964; Russell and Farmer, 1964). The spectra of Na and K montmorillonites immersed in various anilines resemble those of all the other samples studied except Cs (Table 1, Fig. 1). It appears that type II complexes are formed, indicating that some water molecules directly coordinated to the cations were not only present initially, but were sufficiently strongly bound not to be displaced by the organic molecules. The relative intensities of the bands show that the amount of organic base sorbed increases in the order Cs < K < Na < Mg < Al, i.e. with increasing hydration energy of the cation.

In Cs montmorillonite, interlayer water is probably associated with negative charge maxima on the oxygen surfaces. Some water molecules will be oriented with the positive ends of the dipoles towards the oxygen surfaces, thus imparting a basic character to the interlayer water. Such 'basic' water molecules are probably also present with other montmorillonites, as discussed. However, the greater the polarizing power of the interlayer cation, the more acidic the associated hydration shell. Thus, 'acidic' water predominates over 'basic' water and obscures its presence. The more acidic the hydration shell of an exchangeable cation, the stronger the hydrogen bonding to the clay surfaces, break them. Consequently the anilines tend to swelling in an aqueous medium.

The present results show that with aniline and its derivatives, the ratio of structure D to C increases in the series K < Na < Mg < Al, i.e. with increasing polarizing power of the cations (Table 2). This suggests that, as the strength of the hydrogen bonds between the clay surfaces and the water of hydration of the cations increases, the basicity of the aniline molecules becomes insufficient to break them. Consequently the anilines tend to act as proton donors and a metastable equilibrium is probably established.

The NH_2 and CN stretching frequencies observed with Al associations are consistently lower than those given by the other interlayer cations, indicating stronger hydrogen bonding. This is in agreement with the results of the chemical analyses, which show that after heating *in vacuo* at 100°C Al montmorillonite retains appreciably larger amounts of anilines than the other samples.

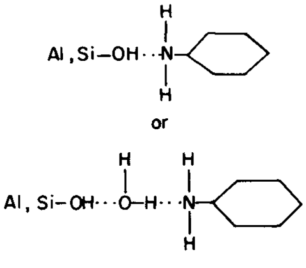
The formation of structure D is favoured by ortho-substitution of the aniline molecules (Table 2). This may be attributed to the reduced accessibility of the electron pair of the N atoms to H, due to steric hindrance, as previously discussed. (Heller and Yariv, 1969). Anilines with two ortho-substituents generally give rise to bands of slightly higher frequency than monosubstituted ones, indicating weaker bonding.

In a previous study (Yariv *et al.*, 1968) bands at 2625 and 2650 cm^{-1} were ascribed to combination bands of interlayer anilinium ions. On immersion in excess aniline, these bands turned into a broad band at 2500–2600 cm^{-1}, which was assigned to anilinium aniline. In the present experiments some spectra showed a broad band at 2600 cm^{-1}, which, however, cannot be entirely attributed to anilinium aniline, since it is more intense with the Al- than with the corresponding H or anilinium saturated samples. The significance of this band is under investigation.

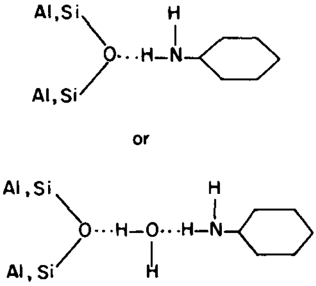
The fact that the spectra of H montmorillonite with anilines differ from those of the corresponding anilinium associations proves that protonation of the aniline molecules does not predominate. It seems that the interlayer protons are 'fixed' by the oxygen sheets and that hydroxonium ions persist in the presence of weak bases, giving rise to structures of type II.

The spectra of montmorillonites saturated with various anilines and heated *in vacuo* at 100°C show a slight resemblance to the corresponding Cs montmorillonites. The similarity increases with decreasing hydration energy of the cation (except H). The amount of organic material retained, which is much less than that originally sorbed, decreases in the same order, as also does the sharpness of the X-ray patterns (unpublished). These observations suggest that, as the interlayer cations become dehydrated, the organic molecules retained are partly bonded directly to the alumino-silicate surfaces.

Hydrogen bonding of anilines to alumino-silicate surfaces also occurs in allophane (Yariv and Heller, paper in preparation). Yet the spectra of allophane–aniline associations differ entirely from those of the variously substituted montmorillonites with anilines. With all cations except Cs this difference could be attributed to the bonding of the organic molecules to the interlayer ions in montmorillonite. However, the striking difference between the spectra of corresponding samples of aniline-treated Cs montmorillonite and allophane must largely be due to the intrinsic properties of the alumino-silicate surfaces. These are acidic in allophanes and basic in montmorillonites. Bonding of type (a) and (b) may therefore be envisaged for anilines held by allophane and Cs montmorillonite respectively.



(a)



(b)

CONCLUSIONS

Different types of acid-base equilibria obtain in the clay interlayers: the clay surfaces are basic and water molecules associated with centres of negative charge acquire a 'basic' character. However, water of hydration associated with interlayer cations is 'acidic', the degree of dissociation increasing with increasing polarizing power of the cations. Except with Cs montmorillonite, 'acidic' water greatly predominates.

In K, Na, Mg, H and Al montmorillonites aniline and its derivatives are bound to the exchangeable cations through water molecules. The oxygen sheets compete with the weak organic bases for protons of the water molecules and anilines consequently act as either proton donors (structure D) or proton acceptors (structure C). Structure D is favoured by increasing polarizing power of the interlayer cation and by steric hindrance arising from ortho-substitution of the organic ligand.

The associations of Cs montmorillonite with aniline and its derivatives differ from those of the other samples. The exchangeable cations are largely unhydrated and the sorbed organic molecules are probably primarily attached to the oxygens of the alumino-silicate sheets, either directly or through water molecules, but the organic ligands are also affected by the field of the interlayer Cs ions.

Acknowledgments—Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. We also wish to thank Dr. H. Feilchenfeld and S. Cohen and G. Zinnan of the Department of Organic Chemistry, Hebrew University, for the i.r. spectra.

REFERENCES

Farmer, V. C., and Mortland, M. M. (1966) An i.r. study of the coordination of pyridine and water to exchangeable cations in montmorillonite and saponite: *J. chem. Soc.* A 344–351.

Fripiat, J. J., Chaussidon, J., and Touillaux, R. (1960)

Study of dehydration of montmorillonite and vermiculite by i.r. spectroscopy: *J. Phys. Chem.* **64**, 1234–1241.

Fripiat, J. J. (1963) Surface properties of alumino-silicates: *Clays and Clay Minerals*, Pergamon Press, New York, **12**, 327–358.

Grim, R. E. (1968) *Clay Mineralogy*: McGraw-Hill, New York, 260 pp.

Heller, L., and Yariv, S. (1969) Sorption of some anilines by Mn-, Co-, Ni-, Cu-, Zn- and Cd montmorillonite: *Proc. Intern. Clay Conf.* Vol. I, in press.

Lippincott, E. R., and Khanna, R. K. (1965) A study of hydrogen bonds in some addition compounds of glycine: *12th Colloq. Spectroscopic. Intern. Exeter.* Hilger and Watts, 513–522.

Mackenzie, R. C. (1964) Hydrationseigenschaften von Montmorillonit: *Ber. Deut. Keram. Ges.* **41**, 696–708.

Mortland, M. M. (1968) Protonation of compounds at clay mineral surfaces: *Trans 9th Intern. Congr. Soil Sci.* **1**, 691–699.

Mortland, M. M., and Raman, K. V. (1968) Surface acidity of smectites in relation to hydration, exchangeable cation and structure: *Clays and Clay Minerals* **16**, 393–398.

Peri, J. B. (1965) Infra-red study of adsorption of ammonia of dry γ alumina: *J. Phys. Chem.* **69**, 231–239.

Russell, J. D., and Farmer, V. C. (1964) Infra-red spectroscopic study of the dehydration of montmorillonite and saponite: *Clay Minerals Bull.* **5**, 443–464.

Yariv, S., Heller, L., Sofer, Z., and Bodenheimer, W. (1968) Sorption of aniline by montmorillonite: *Israel J. Chem.* **6**, 741–756.

Résumé—La sorption de l'aniline et de ses dérivés par du montmorillonite subsitué par des cations d'une acidité très différente dépend du pouvoir de polarisation des cations des couches intermédiaires. Des spectres à l'infra-rouge indiquent que les anilines sont surtout liées aux cations des couches intermédiaires par des molécules d'eau, à l'exception des montmorillonites Cs, où semblent dominer la liaison des surfaces d'oxygène aux feuilles de silicate d'alumine. Les anilines sont des bases faibles, en concurrence avec les surfaces d'oxygène pour les protons de l'eau acide des couches intermédiaires. En conséquence, la tendance que montrent les anilines agissant en tant que donneurs de protons dans les couches intermédiaires d'argile, accroît le pouvoir de polarisation du cation échangeable. On introduit la conception d'une eau "basique" tenant compte de quelques caractéristiques des spectres de montmorillonite Cs traité avec des ligands organiques.

Kurzreferat—Die Sorption von Anilin und seinen Derivaten durch Montmorillonit, das mit Kationen sehr verschiedener Azidität substituiert ist, hängt von der Polarisierleistung der Zwischenschicht-Kationen ab. Infrarotspektren deuten darauf hin, daß die Aniline im wesentlichen durch Wassermoleküle mit den Zwischenschicht-Kationen verbunden sind, außer bei Cs Montmorillonit, wo die Bindung an den Sauerstoffflächen der Aluminium-Silikatladen vorzuherrschen scheint. Aniline sind schwache Basen, die ebenso wie die Sauerstoffflächen Protone saueren Zwischenschichtwassers anziehen. Die Neigung der Aniline als Protonspender in den Tonzwischenschichten zu wirken, nimmt daher mit der Polarisierleistung des austauschbaren Kations zu. Der Begriff "basisches" Wasser wird eingeführt, um einige der Merkmale der Spektren von Cs Montmorillonit, das mit organischen Bindern behandelt wurde, zu erklären.

Резюме—Сорбция анилина и его производных монтмориллонитом с обменными катионами весьма различной кислотности зависит от поляризующей силы межслоевых катионов. Инфракрасные спектры показывают, что анилины большею частью связаны с межслоевыми катионами посредством молекул воды; исключение составляет Cs -монтмориллонит, в котором связь с кислородными поверхностями алюмосиликатных листов, по-видимому, преобладает. Анилины представляют слабые основания, которые, как и кислородные поверхности, стремятся присоединить протоны кислотной межслоевой воды. Следовательно, тенденция анилинов действовать в качестве протонных доноров в межслоевых промежутках глинистых минералов возрастает с увеличением поляризующей силы обменного катиона. Предложено понятие об 'основной' воде для характеристики некоторых особенностей спектров Cs -монморидлонита, обработанного органическими лигандами.