MONTMORILLONITE–ORGANIC COMPLEXES – GAS CHROMATOGRAPHIC DETERMINATION OF ENERGIES OF INTERACTIONS

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Abstract – Gas–solid chromatographic measurements of interaction energies were made for the systems ethanol and acetone with K-, Na-, Ba-, and Ca-montmorillonites. The results revealed an increased interaction energy in the order:

K-mont. < Na-mont. < Ba-mont. < Ca-mont.

Interaction energies ranged from about 14 kcal/mole for K-montmorillonite to about 30 kcal/mole for Ca-montmorillonite. A very good agreement was observed between experimental heats of adsorption values and theoretical values for the electrostatic attractive energy between the respective cations and polar molecules.

These results confirm our earlier suggestions that complex formation takes place through cation-dipole interactions and that the polar molecules solvate the exchange cations in a manner similar to the hydration of cations in aqueous solutions.

INTRODUCTION

THIS report is the second of two parts concerned with the evaluation of the role of exchange cations on the adsorption of polar non-cationic compounds by homoionic montmorillonite. These investigations were carried out in an attempt to clarify the mechanism of formation of clay-organic complexes of the type mentioned (Bissada, Johns, and Cheng, 1967).

Acetone and ethanol were selected as typical representatives of two classes of polar organic molecules. From the standpoint of local distribution of electron density the ethanol molecule $(C_2H_5—O—H)$ possesses an electronegative oxygen atom with two free pairs of electrons as well as an active hydrogen atom, and is capable of specific interaction both with local centers of positive charge as well as with other oxygen-bearing species, resulting in the formation of mutual hydrogen bonds. Acetone $\left[\begin{smallmatrix} CH_3 \\ \\ CH_3 \end{smallmatrix} \!\!>\!\! C\!=\!O\right]$ is capable of specific interactions by virtue of posses-

sing an electro-negative atom with two lone electron pairs, but in contrast to ethanol, it does not possess an active hydrogen, and cannot enter into hydrogen bonding unless some other species supplies the proton.

Similarly, the electron structures of the atoms and bonds disposed at the surfaces of clay minerals control the specificity of their interaction with organic molecules. Montmorillonite possesses two distinctly different types of centers of adsorption: on the one hand the silicate basal surfaces have local centers of negative charge by virtue of the lone electron pairs of the oxygen atoms forming that surface, and are potential interaction loci specifically for ethanol. Thus hydrogen bonding of the type —O—H . . . . . O—Silicate has been postulated by several authors (Emerson, 1957; Brindley and Ray, 1964; Brindley and Moll, 1965). On the other hand, the interlayer region contains positively charged ions (the exchangeable cations) capable of interacting specifically with the oxygen atoms of ethanol or acetone through electro-static cation-dipole attraction.

In the preceding paper (Bissada, Johns and Cheng, 1967) it was shown that the adsorption of ethanol and acetone from dilute solutions on homoionic montmorillonites was significantly

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Table 1. Composition and basal spacing for ethanol- and acetone-complexes with homoionic montmorillonites

		K-Mont.	Na-Mont.	Ba-Mont.	Ca-Mont.
Ethanol complexes — Fully expanded	Molecules/cation	2	3	8	10
	d(001) spacings	13·0 Å	13·5 Å	17·2 Å	17·3 Å
Partially collapsed	Molecules/cation	—	—	4	5
	d(001) spacings	—	—	13·6 Å	13·7 Å
Acetone complexes — Fully expanded	Molecules/cation	2	3	8	8
	d(001) spacings	13·4 Å	13·2 Å	17·3 Å	17·3 Å
Partially collapsed	Molecules/cation	—	—	4	4
	d(001) spacings	—	—	13·3 Å	13·5 Å

controlled by the exchangeable cations. Thinking in terms of cation-organic complex groups the number of molecules associated with each exchange cation was determined. The results, which are summarized in Table 1, show increasing organic molecular association in the order $K^+ < Na^+ < Ba^{2+} < Ca^{2+}$. It was therefore concluded that cation-dipole interactions play a very important role in the adsorption process, and that the polar molecules solvate the exchangeable cations, in a manner analogous to water molecules. I.R. spectroscopic studies carried out by Dowdy and Mortland (1967) and Parfitt and Mortland (1968) support these conclusions. For example when acetone is complexed with homoionic montmorillonites the C=O stretching frequency of the ketone shifts to lower values and at the same time its C—C stretching vibration shifts to higher frequencies; the extent of these shifts being controlled by the kind of exchangeable cation and by the amount of water on the clay.

The main objective of the work reported in the present paper was to investigate experimentally the physical-chemical nature of the interactions involved in the formation of these complexes, and specifically to demonstrate the variations in the measured energies of adsorption of polar molecules by montmorillonite as a function of the exchangeable cations. A gas-chromatographic approach was used to measure adsorbent-adsorbate interaction energies for the systems K-, Na-, Ba-, and Ca-montmorillonites with ethanol or acetone. The method is based upon the principle that the heat of interaction of an active stationary phase with a solute vapour carried in an inert mobile gas phase is related to the chromatographic "specific retention volume" by the expression:

$$\Delta H_a = -2 \cdot 303\, R\, \frac{d(\log_{10} V_g)}{d(1/T)} \qquad (1)*$$

*The theoretical development of the chromatographic method of measuring heats of interaction, and the assumptions underlying the derivation of equation (1) may be found in various sources (e.g. Dal Nogare and Juvet, 1965).

where ΔH_a is the heat of adsorption, V_g is the chromatographic specific retention volume, defined qualitatively as the volume of carrier gas required to elute one half of the solute from a column containing one gram of stationary phase (with no pressure drop or free gas space); T is the absolute temperature; and R is the molal gas constant.

Determination of sorption energies by the gas chromatographic method, where conditions of infinite dilution may be approached, is preferred over the static calorimetric determinations made at considerably higher coverages. Chromatography yields heat of adsorption values that approach the true values of the potential energy of interaction computed for adsorption of individual molecules, whereas calorimetry yields much higher values due to contribution from adsorbate–adsorbent interactions as well as adsorbate–adsorbate interactions. The method has been used successfully to measure heats of interaction for the adsorption of various classes of organic compounds on graphitized carbon black (Belyakova et al., 1964; Kiselev et al., 1964 a,b; and Gale and Beebe, 1964), on cationic zeolites (Eberly, 1961), and on dimethyldioctadecylammonium bentonite (White and Cowan, 1958).

The results obtained in our laboratory and described in the present report revealed an increased interaction energy in the order $K^+ < Na^+ < Ba^{2+} < Ca^{2+}$, and a very good agreement between experimental and theoretical interaction energies.

EXPERIMENTAL PROCEDURES

The montmorillonite used for this study was from Belle Fourche, S. Dakota. The less than 1μ fraction was separated by sedimentation procedures. Homoionic montmorillonite suspensions with Na^+, K^+, Ca^{2+}, or Ba^{2+} as exchangeable cations were prepared from a fractionated stock suspension by the procedure described previously (Bissada, Johns, and Cheng, 1967). Each homoionic slurry, containing at least 25 g of clay, was allowed to dry in a deep narrow evaporating dish, forming hard clay lumps which were subsequently crushed. The 40–60 mesh fraction was retained for use as column packing in the gas–solid chromatographic studies.

Equation (1) indicates that a plot of $\log_{10} V_g$ vs. $1/T$ will have a slope of $-\Delta H_a/2\cdot303\,R$. The first step in the determination of ΔH_a, therefore, was to develop a method for measuring V_g values for systems involving homoionic montmorillonites as adsorbents and ethanol or acetone as adsorbates. After considerable experimentation the method outlined below was developed.

Four 2-ft. columns of 1/4-in. O.D. chromatographic grade copper tubing (supplied by F and

M Scientific Corporation) were each packed with one of the homoionic granular clays (40–60 mesh) using a technique described by Dal Nogare and Juvet (1965). In the filling operation, care was taken to avoid fracturing the grains and production of fine particles which may increase flow resistance. The weights of the 250°C-dry clays used as packing material in the columns were:

11·678 g . . . . K-montmorillonite column
10·802 g . . . . Na-montmorillonite column
11·760 g . . . . Ba-montmorillonite column
11·865 g . . . . Ca-montmorillonite column.

The columns were then installed in an F&M model 700 gas chromatograph equipped with a thermal conductivity detector operating at 115°C. The recorder was a 1-mv unit, operating with a chart speed of $\frac{1}{4}$ in. per min. Grade A helium, dried by passing it through a tube containing molecular sieve type 4A, was used as carrier gas. The flow rates were measured by means of a soap-film flow meter. The outlet pressure was atmospheric. The inlet pressure was measured with a pressure gauge and set at a value of 10 Psig. The temperature of the column was monitored by a Leeds and Northrup potentiometer in conjunction with chromel-alumel thermocouples attached to various points in the vicinity of the column.

Samples of ethanol or acetone were introduced into the carrier gas stream by means of a 0·25 ml hypodermic syringe inserted through a self-sealing silicone rubber diaphragm at the tip of the heated injection port.

The injection port temperature was maintained at 150°C. Injected samples ranged between 0·1 ml to 0·2 ml, depending on the polarities of adsorbate and adsorbent. Care was taken to keep the sample size of a given adsorbate, introduced into a particular column, constant throughout a given series of runs covering the range of temperatures at which V_g values were to be measured.

The general procedural steps leading to the development, recording of elution curves, and measurement of V_g values, were as follows:

Before making a series of runs, a column under study was heated in the column-oven compartment of the chromatograph at 180°C for approximately 6 hr while a helium flow was maintained at 120 ml/min to flush the column free of any adsorbed water.

The column-oven temperature was then adjusted to a selected value for a chromatographic run and the system allowed to equilibrate thermally for 2 hr. The helium flow rate was adjusted to the value desired (varied between 100 ml and 120 ml per min, depending upon the system under considera-
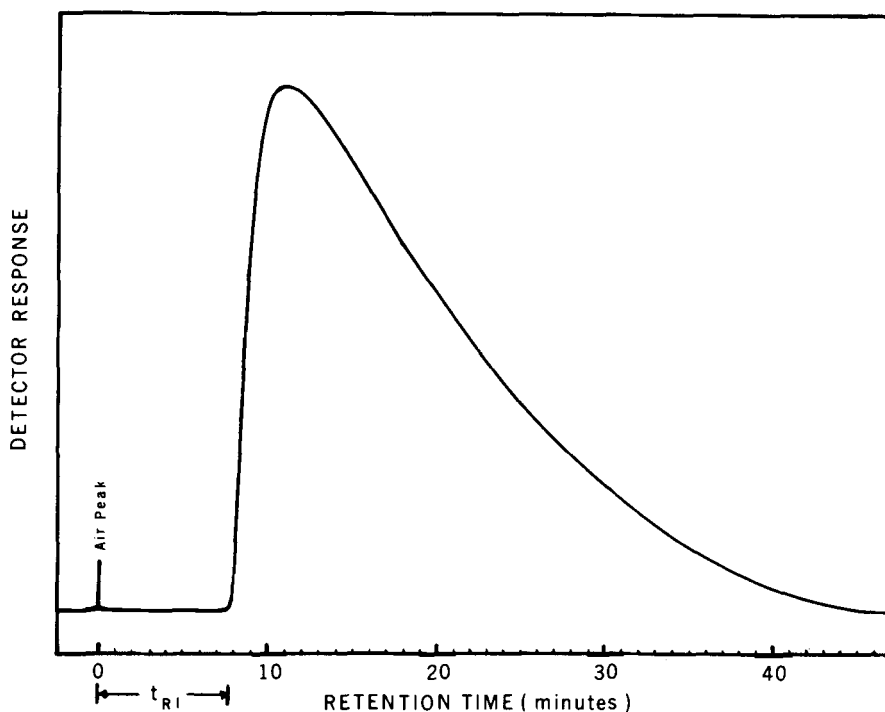
Fig. 1. A typical elution chromatogram of ethanol obtained on Na-montmorillonite column.
Temp.: 73°C; helium flowrate: 98·4 ml/min; sample size: 0·1 ml.

tion). The ambient temperature and pressure were recorded and the column temperature accurately measured. A sample was injected and an elution curve recorded. A typical chromatogram for the elution of ethanol through a Na-montmorillonite column at 73°C is reproduced in Fig. 1. The initial retention time past the air peak was measured and the V_g value calculated from the equation:

$$V_g = \frac{V_{RI}}{W_a} = \frac{t_{RI} \cdot F_c \cdot j}{W_a}$$

where V_{RI} = initial retention volume
t_{RI} = initial retention time*
F_c = flow rate of carrier gas in ml/min, corrected to column temperature, T_c, and outlet or ambient pressure, $P_0(= P_a)$; thus:

$$F_c = F \cdot \left(\frac{T_c}{T_a}\right) \cdot \left(1 - \frac{P_w}{P_a}\right).$$

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*Everett and Stoddart (1961) have observed that in runs with increasing sample size the initial retention time remains constant while the peak retention time increases, suggesting that the initial retention time is the significant quantity.

F being the measured flow rate at ambient temperature, T_a, and ambient pressure. Since a soap-film flow-meter was used, a correction for the vapor pressure of water was introduced, hence the term P_w.

j = compressibility factor for the gas, defined by James and Martin (1952) in terms of the inlet pressure, P_i, and outlet pressure, P_0, as:

$$\frac{3[(P_i/P_0)^2 - 1]}{2[(P_i/P_0)^3 - 1]}$$

W_a = weight of adsorbent used as column packing.

The initial retention time, t_{RI}, varied from a few minutes to more than 4 hr depending upon the system being studied and upon the column temperature. Retention data and operating conditions are tabulated in Table 2.

Following each run the helium flow was increased to 200 ml per min and a sample of water (~ 0·2 ml) injected to displace any organic compound retained by the clay. After about 1 hr the

Table 2. Experimental retention data for ethanol and acetone on
montmorillonite columns

	Ethanol			Acetone		
	Column temp. (°C)	t_{Ri} (min)	V_g (ml)	Column temp. (°C)	t_{Ri} (min)	V_g (ml)
K-montmorillonite	43·1	55·00	382·30	50·5	127·60	901·10
	43·5	55·16	384·42	50·5	118·90	866·70
	48·5	34·40	242·72	57·3	76·60	541·89
	56·5	21·50	153·31	61·5	55·20	401·20
	63·0	14·00	103·07	67·5	35·65	274·47
	66·5	10·60	79·04	75·0	23·70	181·15
	75·8	5·60	42·72	83·0	14·60	111·77
	85·0	3·20	24·82			
Na-montmorillonite	44·0	76·10	514·81	44·5	128·40	887·23
	48·0	53·70	367·94	51·0	95·80	668·75
	57·9	24·20	174·96	59·0	49·40	349·72
	73·0	7·80	58·51	68·9	24·00	173·81
	84·1	3·55	27·50	79·0	11·80	89·04
	90·0	2·55	20·20	90·0	5·35	42·59
				112·0	1·52	12·56
Ba-montmorillonite	75·8	288·70	2149·58	87·5	141·30	1208·94
	80·5	176·60	1338·47	92·4	87·30	757·64
	85·5	123·30	941·58	98·8	52·99	472·70
	92·6	67·30	523·59	102·0	38·20	345·15
	97·0	45·30	359·37	109·0	24·45	224·05
	104·0	27·20	218·70	112·5	16·60	153·00
	109·0	17·75	146·64			
Ca-montmorillonite	78·0	195·20	1454·60	92·0	158·40	1171·40
	81·0	143·25	1080·51	101·3	54·30	407·89
	86·3	84·00	641·76	102·3	45·40	363·20
	90·0	50·70	391·40	107·0	23·70	192·68
	99·2	20·50	163·88	107·5	24·25	185·84
	105·5	10·70	85·87	111·0	19·50	160·68
				113·3	15·10	116·53
				114·5	12·00	99·12

temperature of the column was increased to approximately 180°C, the flow rate reduced to 120 ml/min, and the column flushed for at least 6 hr before the next run was begun.

Plots of $\log_{10} V_g$ against $1/T$, for each of the systems studied are shown in Fig. 2.

DISCUSSION AND CONCLUSIONS

From the slopes of the plots of $\log_{10} V_g$ vs. $1/T$, the heats of adsorption were determined, being given by

$$\Delta H_a = -2\cdot 303R \text{ (slope)}.$$

(ΔH_a is expressed in kcal/mole if R is given as $1\cdot 987 \times 10^{-3}$ kcal/mole deg.). The results, shown in Table 3, revealed the striking influence of the exchange cation species of the clay mineral on the heat of adsorption values for the systems studied. The energy involved in the sorption of ethanol or acetone by homoionic montmorillonites increases in the order K-mont. < Na-mont. < Ba-mont. < Ca-mont. This order is the same as the one observed earlier (Bissada, Johns, and Cheng, 1967) for the numbers of molecules associating with each exchangeable cation.

These observations confirm our earlier suggestion that the polar molecules do solvate the exchangeable cations and that the "solvation number" is related to the electrostatic field strength associated with each exchangeable cation.
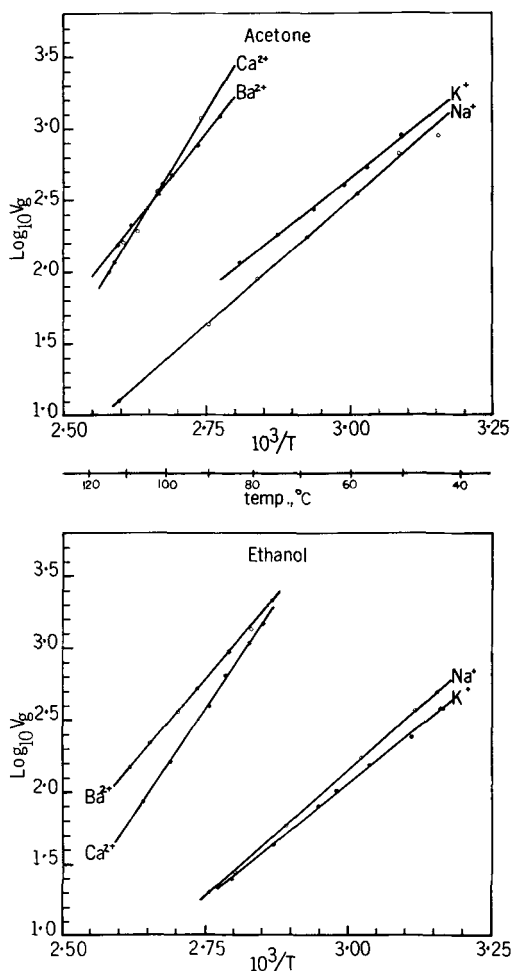
Fig. 2. Variation of $Log_{10}V_g$ with $1/T$ for ethanol- and acetone-homoionic montmorillonite systems.

Table 3. Comparison between measured heats of adsorption and theoretical cation-dipole interaction energies

		Chromatographically determined heat of adsorption $\Delta H_a = -2\cdot303\,R \cdot \dfrac{d(\log V_g)}{d\frac{1}{T}}$	Theoretical cation-dipole interaction energy $\phi_p = \dfrac{-\mu_p \cdot C_A{}^+}{r_0{}^2}$
		(kcal/mole)	(kcal/mole)
Ethanol	K^+	14·4	11·3
	Na^+	16·1	14·0
	Ba^{2+}	21·8	22·1
	Ca^{2+}	29·3	27·5
Acetone	K^+	14·3	11·9
	Na^+	16·0	14·4
	Ba^{2+}	23·1	23·6
	Ca^{2+}	30·1	28·1

The theoretical electrostatic attractive energy between an ion and a polar molecule ϕ_p, can be computed from the expression:

$$\phi_p = -\frac{C_A{}^+ \cdot \mu_p}{r_0{}^2}$$

where $C_A{}^+$ is the charge of the cation, μ_p is the dipole moment of the polar molecule, and r_0 is the interaction distance, taken as the distance from the center of the cation to the center of the organic dipole. Values for r_0 could be computed from molecular models of ethanol and acetone by assuming that the cation makes contact with the oxygen atom of the organic molecule [ionic radii from Ahrens (1964), bond angles, bond lengths and atomic radii from Pauling (1960)]. In the case

of acetone, the center of the cation is assumed to be coaxial with the $\diagdown C{=}O$ bond; in ethanol, the point of contact is assumed to be at the point of emergence of the lone-pair resultant of the tetrahedrally hybridized oxygen atom of the molecule.

ϕ_p values for K^+-, Na^+-, Ba^{2+}-, and Ca^{2+}-ethanol and acetone interactions were computed (dipole moments from McLellan, 1963). These are compared with the chromatographically measured heat of adsorption values in Table 3. The agreement between the theoretically computed cation-dipole interaction energy and the measured heats of adsorption is very good. The 1–3 kcal/mole difference may be due to non-specific dispersion forces between the whole adsorbed molecule and the clay surface, and perhaps due to a weak contribution from the interaction of active methylene or methyl groups of ethanol or acetone respectively with the oxygens of the silicate surface through C—H . . . . . O bonding as has been suggested by Bradley (1945) and MacEwan (1948). The close agreement between measured and theoretical energies, and the magnitude of the observed heat of adsorption values, confirm that cation-dipole attractive interactions play the dominant role in the mechanism of adsorption of small polar molecules by montmorillonite. Had the mechanism involved only hydrogen bonding of the type R—O—H . . . . . O—Silicate, as usually suggested, the measured heat of adsorption should have been of the order of 7–11 kcal/mole. If the bonding was only through C—H . . . . . O bonds, as suggested by Bradley (1945) and MacEwan (1948), the total energy of adsorption should not have exceeded 2–3 kcal/mole.

It may be interesting at this point to refer to the work of Keay and Wild (1961) on the heats of hydration of vermiculite. These authors have shown that the heats of hydration of homoionic vermiculites, measured calorimetricly, increase in the order Na-vermiculite < Ba-vermiculite < Ca-vermiculite.

From the discussion presented above we can arrive at the following conclusions:

(i) Strong cation/dipole attractive forces play the most predominant role in the adsorption of "polar" molecules on montmorillonite and similar layer silicates.

(ii) The sorption phenomenon results from specific interaction between the small exchangeable cations and electronegative oxygen (or nitrogen) atoms possessing lone electron pairs in the adsorbate molecules, regardless of whether the molecule possesses an active hydrogen atom.

(iii) The mechanism is that of solvation of the cations by the polar molecules, similar to hydration of cations in aqueous solutions.

(iv) The interaction energy is determined mainly by the magnitude of the field strength of the exchangeable cation, the dipole moment of the adsorbate molecule, and the distance separating the two interacting species.

REFERENCES

Ahrens, L. H. (1964) The significance of the chemical bond for controlling the geochemical distribution of the elements: In *Physics and Chemistry of the Earth*, Vol. 5, pp. 1–54. Macmillan, New York.

Belyakova, L. D., Kiselev, A. V., and Kovalova, N. V. (1964) Gas chromatographic determination of energy of hydrogen bonds in the adsorbed layers of alcohol on graphitized carbon black: *Anal. Chem.* **36**, 1517–1519.

Bissada, K. K., Johns, W. D., and Cheng, F. S. (1967) Cation-dipole interactions in clay-organic complexes: *Clay Minerals* **7**, 155–166.

Bradley, W. F. (1945) Molecular association between montmorillonite and some polyfunctional organic liquids: *J. Am. Chem. Soc.* **67**, 975–981.

Brindley, G. W., and Moll, W. F., Jr. (1965) Complexes of natural and synthetic Ca-montmorillonites with fatty acids: *Am. Mineralogist* **50**, 1355–1370.

Brindley, G. W., and Ray, S. (1964) Complexes of Ca-montmorillonite with primary monohydric alcohols: *Am. Mineralogist* **49**, 106–115.

Dal Nogare, S., and Juvet, R. S., Jr. (1965) *Gas-liquid chromatography: Theory and Practice*: Interscience, New York.

Dowdy, R. H., and Mortland, M. M. (1967) Alcohol-water interactions on montmorillonite surfaces: I. Ethanol: *Clays and Clay Minerals* **15**, 259–271.

Eberly, P. E. (1961), High temperature adsorption studies on 13X molecular sieve and other porous solids by pulse flow techniques: *J. Phys. Chem.* **65**, 68–72.

Emerson, W. W. (1957), Organo-clay complexes: *Nature* **180**, 48–49.

Everett, D. H., and Stoddart, C. T. H. (1961) The thermodynamics of hydrocarbon solutions from G.L.C. measurements: Part I. Solution in Dinonylphthalate: *Trans. Faraday Soc.* **57**, 746–754.

Gale, R. L., and Beebe, R. A. (1964) Determination of heats of adsorption on carbon blacks and bone mineral by chromatography using the elution pulse technique: *J. Phys. Chem.* **68**, 555–567.

James, A. T., and Martin, A. J. P. (1952) Gas-liquid partition chromatography: A technique for the analysis of Volatile materials: *Analyst* **77**, 915.

Keay, J., and Wild, A. (1961) Hydration properties of vermiculite: *Clay Minerals Bull.* **4**, 221–228.

Kiselev, A. V., Paskonova, E. A., Petrova, R. S., and Shcherbakova, K. D. (1964a) The adsorption properties of carbon blacks by the gas chromatographic method: *Zh. Fiz. Khim.* **38**, 161–169.

Kiselev, A. V., Petrova, R. S., and Shcherbakova, K. D. (1964b) Gas chromatographic characteristics of the unit surface of an adsorbent: *Kinetics and Catalysis* **5**, 456–461.

MacEwan, D. M. C. (1948) 1. Complexes of clays with organic compounds: *Trans. Faraday Soc.* **44**, 349–367.

McLellan, A. L. (1963) Tables of experimental dipole moments: Freeman & Co., New York.

Parfitt, R. L., and Mortland, M. M. (1968) Ketone adsorption on montmorillonite: *Soil Sci. Soc. Am. Proc.* **32**, 355–363.

Pauling, L. (1960), *The nature of the chemical bond:* 3rd edn, Cornell University Press, New York.

White, D., and Cowan, C. T. (1958) The sorption properties of dimethyldioctadecylammonium bentonite using gas chromatography: *Trans. Faraday Soc.* **54**, 557–561.

Résumé — Des mesures chromatographiques gaz–solides d'énergies d'interaction ont été effectuées pour les systèmes éthanol et acétone avec les montmorillonites K-, Na-, Ba-, et Ca-. Les résultats ont révélé une énergie d'interaction accrue de l'ordre de:

K-mont. < Na-mont. < Ba-mont. < Ca-mont.

Les énergies d'interaction se trouvaient dans la gamme d'environ 14 kcal/mole pour montmorillonite K à environ 30 kcal/mole pour montmorillonite Ca. On a observé une très bonne corrélation entre les chaleurs expérimentales des valeurs d'absorption et les valeurs théoriques pour l'énergie électrostatique d'attraction entre les cations respectifs et les molécules polaires.

Ces résultats confirment nos suggestions antérieures établissant que la formation complexe a lieu dans les interactions cation-bipôle et que les molécules polaires semblent donner une solvatisation similaire à l'hydratation des cations dans des solutions aqueuses.

Kurzreferat -- Mittels Gas–Feststoff Chromatographie wurden Messungen von Wechselwirkungsenergien für die Systeme Äthanol und Aceton mit K-, Na-, Ba-, und Ca-Montmorilloniten durchgeführt. Die Ergebnisse zeigten eine steigende Wechselwirkungsenergie in der Reihenfolge:

K-Mont. < Na-Mont. < Ba-Mont. < Ca-Mont.

an. Die Wechselwirkungsenergien bewegten sich in einem Bereich von etwa 14 kcal/Mol für K-Montmorillonit bis zu etwa 30 kcal/Mol für Ca-Montmorillonit. Es konnte ausgezeichnete Übereinstimmung zwischen den in Versuchen beobachteten Werten der Adsorptionswärme und den theoretischen Werten für die elektrostatische Anziehungsenergie zwischen den betreffenden Kationen und polaren Molekülen festgestellt werden.

Diese Ergebnisse bestätigen unsere früheren Annahmen, wonach es durch Kation-Dipol Wechselwirkungen zu Komplexbildungen kommt, und die polaren Moleküle in einer der Hydratisierung von Kationen in wässrigen Lösungen ähnlichen Weise die Austauschkationen "solvatisieren".

Резюме—Были выполнены измерения энергий взаимодействия ацетона и этанола с калиевым, натриевым, бариевым и кальциевым монтмориллонитами с помощью метода газовой хроматографии. Показано что по изменению энергии взаимодействия монтмориллониты образуют ряд: К-монтм. < Na-монтм. < Ba-монтм. < Ca-монтм. Энергии взаимодействия составляют от 14 килокал./моль для К-монтмориллонита до ∾ 30 килокал./моль для Ca-монтмориллонита. Экспериментально определенные теплоты адсорбции хорошо согласуются с теоретическими значениями энергии электростатического притяжения между соответствующими катионами и полярными молекулами.

Полученные результаты подтверждают ранее высказанные автором предположения о возникновении комплексов путем катионно-дипольного взаимодействия и о сольватации полярными молекулами обменных катионов таким же путем, как происходит гидратация катионов в водных растворах.