ADSORPTION OF XYLENE BY ORGANOCLAYS

W. H. Slabaugh and R. W. Vasofsky*

Oregon State University, Corvallis, Oregon 97331, U.S.A.

Abstract—Based on X-ray powder diffraction measurements of swelling, thermodynamic analysis of adsorption and kinetics, a mechanism of interaction between xylene isomers and two organoclay complexes was derived. The work is intended to resolve the factors which make possible the chromatographic separation of the xylene isomers with organoclays. Significant differences between the behavior of fresh organoclays and xylene vapor-conditioned organoclays were noted. Only small differences were apparent between the montmorillonite and the hectorite organoclays. Force constants, enthalpy changes, entropy changes, free energy changes and two specific rate constants were derived from the information obtained from this study.

INTRODUCTION

Hughes, White and Roberts (1959) are credited with chromatographically separating the three xylene isomers with an organo-clay material, Bentone 34. The present study adds to the efforts of others, such as Barrer and Kelsey (1960), White (1964) and Taramasso and Timidei (1970), to understand the mechanism of this separation.

This study is limited to two organoclays in which the identical organic group, dimethyldioctadecylammonium, is attached to montmorillonite and to hectorite. These two materials, Bentone 34 and Bentone 38, respectively, were used as supplied by the Baroid Division of N.L. Industries, Inc. Adsorption characteristics were examined in terms of basal expansion, thermodynamics, and kinetics.

MATERIALS AND METHODS

Early in this work, it was discovered that the organoclays exhibited characteristics that are influenced by their history. Fresh samples and xylene vapor conditioned samples, for instance, showed appreciable differences that are described in later sections of this report. Samples for the X-ray powder diffraction analysis were prepared by troweling a toluene slurry onto a glass slide, then removing the toluene in a vacuum oven at 40°C overnight.

Measurements of the expansion or swelling of the organoclays were made with a General Electric XRD-5F diffractometer concurrently with gravimetric adsorption measurements. Adsorption and desorption behavior, as noted in Fig. 1, revealed a substantial increase of about 2Å for Bentone 38 and 1Å for Bentone 34. This increase in *c*-spacing as the result of undergoing adsorption and desorption of xylene vapor is attributed to the re-orientation of the organic groups in the organoclay. Once this re-orientation is achieved, usually after only one or two adsorption–desorption cycles, it appeared to remain unchanged in successive adsorption–desorption runs. Complete removal of adsorbed xylene after an adsorption–desorption run was substantiated by concurrent gravimetric measurements.

Once the organoclays were conditioned with xylene vapor, the expansion occurred more gradually than with the fresh, untreated samples. Both Bentone 34 and Bentone 38 expanded from about 28 to 45Å in adsorbing 0·80 relative vapor pressure of xylene, with Bentone 34 absorbing slightly more xylene vapor at this vapor pressure.

By means of Cornet's thermodynamic model of swelling (1950), force constants were derived for the expansion of the organoclays. The free energy of xylene adsorption, ΔG, is related to the relative vapor pressure of xylene, P/P_0, which in turn is related to the interplanar force (f) acting against the work of
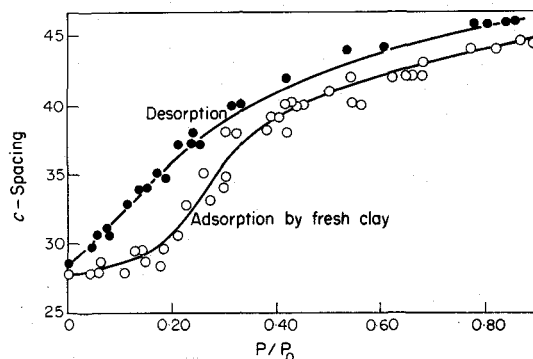

Fig. 1. X-ray powder diffraction measurements of the expansion and compaction of Bentone 34 by ortho-xylene at 25°C.

* Present address: Department of Physics, Clarkson of Technology, Potsdam, New York 13676, U.S.A.
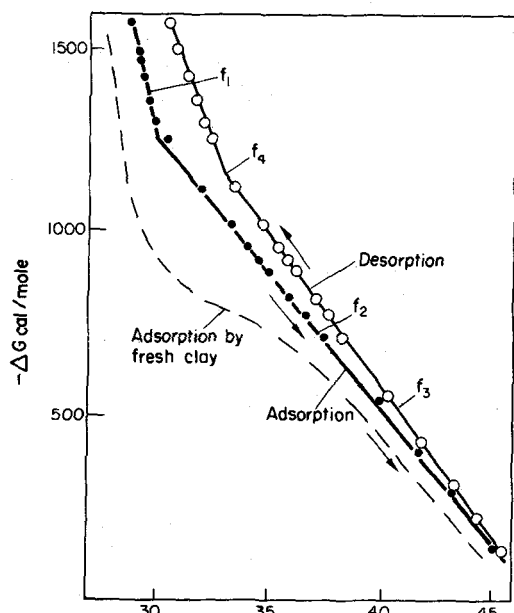
Fig. 2. Free energy change as a function of c-spacing during the intercalation of ortho-xylene by Bentone 34 at 25°C.

Fig. 3. Entropy and enthalpy changes in the adsorption of meta-xylene by Bentone 38 at 25°C.

separation and the actual distance of separation, dx:

$$\Delta G = RT \ln (P/P_0) = -f \, dx$$

values of ΔG derived in this way are shown in Fig. 2. It is noted from this figure that the force constants define two distinctly different steps in both the expansion (adsorption) and compaction (desorption) processes. That is, a transition occurs where f_1 gives way to f_2 on adsorption and f_3 changes to f_4 on desorption. There are significant changes in the magnitude of these force constant changes although they occur at almost identical c-spacings and in a small range of the amount of adsorbed xylene. Table 1 summarizes these values for Bentone 34. Similar data were found for Bentone 38.

For adsorption isotherms at $18.0 \pm 0.1°C$ and $32.0 \pm 0.1°C$ the isosteric heats of adsorption were calculated by means of the integrated Clausius–Clapeyron equation. These values of ΔH_i, along with ΔG values derived above, gave entropy data ΔS as sum-

marized in Fig. 3. Again, appreciable differences between fresh samples and xylene vapor-conditioned samples were found.

Upon comparing the ΔH_i, ΔS, and ΔG for the adsorption of xylene on Bentone 34 and Bentone 38 it is reasonably valid to extrapolate these nearly linear differences to zero adsorption (Fig. 4). Bentone 38, for instance, showed a ΔH_i of about 2.3 kcal/mole more exothermic than did Bentone 34 at zero coverage. The entropy change for Bentone 38 was about
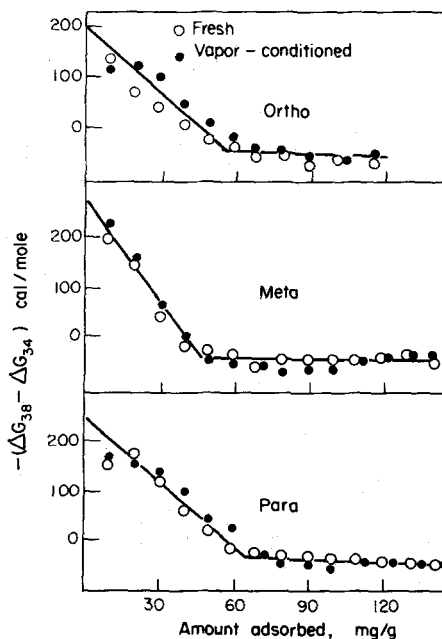

Fig. 4. Difference between the free energy changes for the adsorption of xylenes by Bentone 38 and Bentone 34 at 25°C.

Table 1. Expansion and compaction of Bentone 34

	f_1 cal/mole	f_2 cal/moleÅ	At transition $f_1 \rightarrow f_2$		
Adsorbate			C-spacing Å	Amount absorbed mg/g	P/P_0
o-xylene		-245	-73	30.0	34
m-xylene		-258	-79	31.3	44
p-xylene		-335	-62	30.8	45

	f_3	f_4	at transition $f_3 \rightarrow f_4$		
o-xylene	$+86$	$+165$	33.0	47	0.13
m-xylene	$+90$	$+160$	33.9	53	0.18
p-xylene	$+76$	$+180$	33.0	63	0.16

2·3 e.u. greater than that of Bentone 34. The values of ΔG (Fig. 4) showed that less work is required to penetrate and be adsorbed by Bentone 38. Further comparison of thermodynamic values for fresh vs vapor-conditioned samples were made.

These thermodynamic measurements showed that the intensity of the xylene–organoclay interaction was in the order ortho > meta > para. The dipole moments of the three xylene isomers are in the same order and it is believed that the intensity of xylene interaction with the hydrocarbon chains in the organoclay is essentially influenced by the ability of the xylene to penetrate the micelle and to solvate the hydrocarbon chains. Entropy measurements indicate that steric factors may also play a role in distinguishing or separating the xylene isomers by adsorption.

Kinetic measurements were conducted gravimetrically by exposing samples to a fixed vapor pressure of xylene vapor and observing the rate of adsorption. Two observed rate constants for the xylene adsorption were found by applying the rate law $dS/dt = -kS$, where S is the amount of xylene remaining to be adsorbed at a given pressure P. That is, two adsorption components, k_1 and k_2, are shown in Fig. 5.

Further analysis was made of these two rate constants in terms of the relative vapor pressure (P/P_0) and the extent of adsorption at the transitions between k_1 and k_2. S is defined as A_e, the amount of xylene adsorbed at equilibrium, minus A_t, the amount of xylene adsorbed at time t. When values of k_1 and k_2 were plotted as a function of $(1 - P/P_0)$, transitions between these two rate constants occurred at identical relative pressures $(P/P_0 = 0.32)$ as noted in Fig. 6. Furthermore, this transition occurs at the same point in the expansion of the organoclay micelle, at 31Å c-spacing, where the force constant f_1 changes to f_2.

The amount of xylene adsorbed at the $k_1 \rightarrow k_2$ transition varies even though the c-spacing is always 31Å. By plotting the amount of xylene adsorbed at the $k_1 \rightarrow k_2$ transition vs P/P_0, a linear relationship that permits extrapolation to $P/P_0 = 1$ is possible. At saturation of the organoclay with xylene vapor,
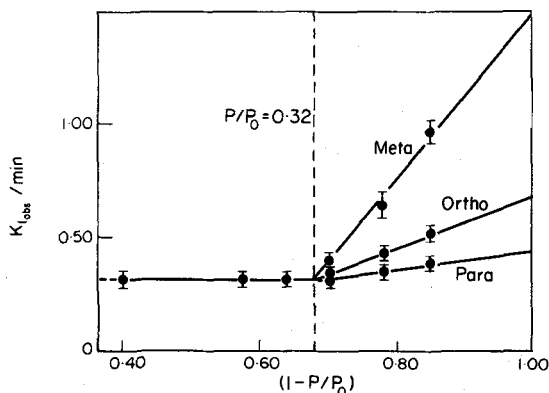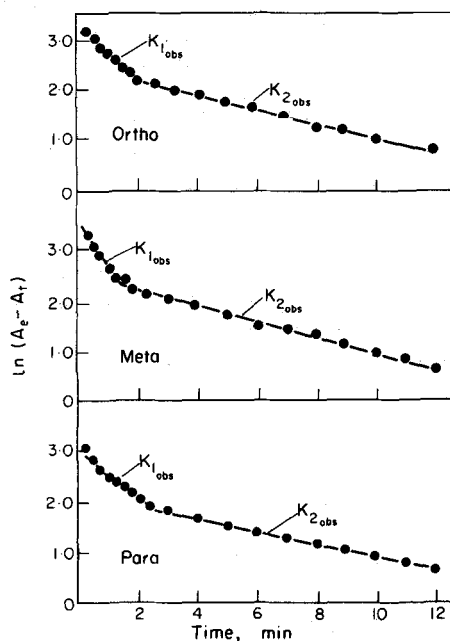

Fig. 6. The relationship of the rate constant k_1 for the adsorption of xylenes by vapor-conditioned Bentone 38 at 25°C vs time at $P/P_0 = 0.32$.

130 mg/g of adsorption should occur. At a c-spacing of 31Å, where the size of the exchangeable cation and the number of cations/unit cell are accounted for (Barrer et al., 1960), the free volume capable of accommodating xylene vapor would be 365Å^3 per unit cell. If liquid xylene completely occupied this free volume, then there would be 134 mg/g of xylene adsorbed. Rather than a trivial coincidence that these two amounts are nearly identical (130 and 134 mg/g), it is probable that at the 31Å c-spacing the organic groups in the clay complex have become ordered or activated to the extent that a second mechanism begins at this transition point.

RESULTS AND DISCUSSION

In chromatographic separation of the xylene isomers by organoclays, the order of retention is meta > ortho > para (Taramasso et al., 1970). In the thermodynamic analysis, the free energy of adsorption and intercalation gives the same order, and the same order is shown in the kinetic study. The relative extent of interaction between xylene vapor and organoclay is in the order ortho > meta > para. However, because chromatographic separations involve the overall adsorption–desorption cycle, it is apparent that the free energy and the kinetic factors take precedence over other factors.

The differences between Bentone 34 and Bentone 38 are largely attributed to the number of platelets per average aggregate. Barren and Millington (1967) have found an average of 9 platelets/particle for hectorite and 26 platelets/particle for montmorillonite. The method of preparation is also a factor in these

Fig. 5. Rates of adsorption of xylenes by vapor-conditioned Bentone 38 at $P/P_0 = 0.15$ and 25°C.

differences as are the factor of conditioning to the adsorbate.

REFERENCES

Barrer, R. M. and Kelsey, K. E. (1960) Thermodynamics of interlamellar complexes—II: sorption by dimethyldioctadecylammonium bentonite: *Trans. Farad. Soc.* **57**, 625–640.

Barrer, R. M. and Millington, A. D. (1967) Sorption and intercalation by methylammonium montmorillonites: *J. Colloid Interface Sci.* **25**, 359–372.

Cornet, I. J. (1950) Expansion of the montmorillonite lattice on hydration: *J. Chem. Phys.* **18**, 623–636.

Hughs, M. A., White, D. and Roberts, A. L. (1959) Separation of the meta- and para-iisomers of the xylenes, cresols and toluidines by gas–solid chromatography: *Nature, Lond.* **184**, 1796–1797.

Taramasso, M. and Timidei (1970) Correlation between gas chromatographic behavior and surface properties of organic derivatives of clay minerals: *Gas Chromatogr., Proc. Int. Symp.* (Europe) **8**, 55–69.

White, D. (1964) The structure of organic montmorillonites and their absorptive properties in the gas phase: *Proc. 12th Nat. Conf. Clays and Clay Minerals* **12**, 257–266.