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SURFACE HETEROGENEITY OF TRIMETHYLPHENYLAMMONIUM-SMECTITE AS REVEALED BY ADSORPTION OF AROMATIC HYDROCARBONS FROM WATER

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Abstract—Adsorption studies of aromatic hydrocarbons of various molecular sizes on organo-clays in aqueous solution were carried out for characterizing the surface heterogeneity of organo-clays. Benzene, toluene, *p*-xylene, ethylbenzene and *n*-propylbenzene adsorption by a smectite with 5 different exchange degrees of trimethylphenylammonium (TMPA) cations for Ca^{2+} was measured. The Langmuir isotherm equation did not adequately describe the experimental data, especially for small molecules, whereas the Dubinin–Radushkevich (DR) equation combined with a gamma-type adsorption energy distribution function described all experimental data well, suggesting the surface and structural heterogeneity of TMPA-smectites. The calculated adsorption energy distributions indicated that the apparent heterogeneity depends on the molecular size of adsorbates. Small adsorbate molecules such as benzene explore a highly heterogeneous surface of TMPA-smectites while large molecules such as *n*-propylbenzene detect a relatively homogeneous surface. The surface fractal dimension was dependent on the extent of TMPA exchange for Ca^{2+}. When TMPA content is less than 75% of the cation exchange capacity (CEC) of the smectite, the heterogeneity decreases as TMPA content increases; it increases with TMPA content thereafter. These results are related to the size distribution of micropores in TMPA-smectites, which are defined by the 2 semi-infinite aluminosilicate sheets and the interlayer cations. The micropore size distributions and, hence, heterogeneity are created in part by the inhomogeneity of the charge density of clay surfaces and the tendency for cation segregation in these systems.

Key Words—Adsorption Energy Distribution, DR Equation, Fractal Dimension, Heterogeneity, Micropore Size Distribution, Organoclay.

INTRODUCTION

Organo-clays are formed when inorganic cations such as Ca^{2+} and Na^+ in natural clay minerals are replaced by organic cations. Such organo-clays are effective sorbents for a variety of aqueous organic compounds including many common groundwater contaminants (Boyd, Lee and Mortland 1988; Boyd, Mortland and Chiou 1988; Boyd et al. 1991; Jaynes and Boyd 1991a; Lee et al. 1990; Sheng et al. 1996; Xu et al. 1996; Sheng and Boyd 1997). When relatively small organic cations, such as TMPA cations, are employed, the organo-clays function as solid adsorbents and manifest Langmuir-type adsorption isotherms (Jaynes and Boyd 1990, 1991b). The Langmuir adsorption equation is often used to represent this type of experimental data.

Langmuir adsorption theory (Langmuir 1918) has been extensively used in various monolayer adsorption systems because of its simplicity of form and directness of derivation. However, difficulties often arise in applying the Langmuir equation to practical adsorption systems (Rudzinski and Wojciechowski 1993). One of the major assumptions underlying the Langmuir adsorption equation is that the solid surface is energetically homogeneous (Langmuir 1918), which is often not true, especially for naturally occurring solids such as clays. It is now well known that geometric and energetic heterogeneity is a fundamental feature of many solid surfaces (Rudzinski and Wojciechowski 1993). The main sources of heterogeneity are the complexity

of crystallographical and geometrical structure of solids and their complex chemical compositions.

Adsorption energy distribution of solid surfaces, and pore-size distribution and fractal dimension of fractally porous solids, are among the most important quantities for characterizing the heterogeneity of solids (Jaroniec and Madey 1988). Adsorption energy distribution, which characterizes the overall energetic heterogeneity of solid surfaces, has been extensively studied on microporous activated carbons (Dubinin 1975; Jaroniec and Madey 1989; Rudzinski and Wojciechowski 1993). Pore-size distribution of porous solids is usually calculated from the low-temperature nitrogen adsorption–desorption isotherm using the Kelvin equation. Empirical relationships between pore size and characteristic adsorption energy of activated carbons have been established (Dubinin 1988; Stoeckli et al. 1989). Fractal dimension depends on the microporosity of solids, and has recently been used to characterize surface irregularity. Pfeifer et al. (1983) and Avnir et al. (1983, 1984) were the first to introduce and apply Mandelbrot's non-Euclidean fractal geometry to characterize adsorption systems. By using adsorbates of varying molecular cross section, they showed that most solid surfaces are fractals, and that the fractal dimension measures the irregularity of surface accessible to molecules during adsorption processes. Linear relationships between the monolayer adsorption and the molecular size of adsorbates have

been established to determine fractal dimension of a given solid surface (Avnir et al. 1984).

Most of the work on the heterogeneity of solid surfaces has been focused on activated carbons and other inorganic adsorbents and catalysts (Jaroniec and Madey 1988). Comparatively little work on the heterogeneity of clay minerals (Lagaly 1979, 1981, 1982; Barrow et al. 1993), and none on organo-clays, has been done. In this study, the adsorption of toluene, p-xylene, and n-propylbenzene in aqueous solutions by Ca-smectite partially and fully exchanged with TMPA cations was measured. The resulting isotherms were analyzed by several adsorption equations to characterize the heterogeneity of such organo-smectites. In these systems, individual pores are defined by 2 semi-infinite parallel silicate sheets which have permanent negative charge, and by adsorbed interlayer Ca^{2+} and TMPA cations which neutralize this charge. The interlayer cations act as pillars to separate silicate sheets, and to define the dimensions of the micropores. As such, the size and structure of micropores in organo-smectites are largely dependent on the nature of the exchange cations (for example, Ca^{2+} and TMPA), the proportion of the CEC they occupy and their distributions on the surface.

The objectives of this study were to evaluate the applicabilities of different adsorption equations (the Langmuir equation, the DA equation and the DR equation) for describing the uptake of aromatic hydrocarbons from water by mixed Ca/TMPA- and TMPA-smectites, and to characterize these organo-smectites as heterogeneous adsorbents through an analysis of adsorption energy distribution, fractal dimension and micropore size distribution.

BACKGROUND AND THEORY

Based on the Polanyi potential theory of adsorption (Goldman and Polanyi 1928; Polanyi and Welke 1928), and extensive gas and vapor adsorption studies, Dubinin and Astakhov (Dubinin 1975) developed a theory for the volume filling of micropores, expressed semiempirically by the following equation (DA equation):

$$\theta(A) = \exp\left[-\left(\frac{A}{\beta E_0}\right)^n\right] \quad [1]$$

with

$$A = RT \ln\frac{p_0}{p} \quad [2]$$

where θ is the degree of volume filling, expressed as the ratio of the amount adsorbed in the micropores at temperature T and relative pressure p/p_0 to the maximum adsorption amount. R is the gas constant, A is the Polanyi adsorption potential and E_0 is the characteristic adsorption energy of a reference adsorbate, and depends only on the adsorbate. The similarity (affinity) coefficient β is a shifting factor, and is a measure of the similarities be-

tween the characteristic vapor adsorption for the adsorbate being studied and that of a reference adsorbate. The value of β depends only on the adsorbate and can be defined as the ratio of the characteristic adsorption energy of any adsorbate, E, to the characteristic adsorption energy of a reference adsorbate, E_0, that is, $\beta = E/E_0$. By convention, benzene is selected as the reference adsorbate, as Dubinin (1975) suggested ($\beta C_6H_6 = 1$). The exponent n varies between 1 and 3, depending on the nature of adsorbent used. The value of n approaches 3 for adsorbents with homogeneous micropores, whereas n approaches 1 for adsorbents with highly heterogeneous micropores. When $n = 2$, for average adsorbents, Equation [1] becomes:

$$\theta(A) = \exp\left[-\left(\frac{A}{\beta E_0}\right)^2\right] \quad [3]$$

This equation is the DR equation mentioned previously (Dubinin 1975). The DR equation is a good mathematical description of both vapor adsorption and adsorption in dilute liquid/solid systems (Jaroniec and Derylo 1981). In liquid/solid systems, the DR equation is written as:

$$\theta(A) = \exp\left[-\left(\frac{A}{\beta E_0^*}\right)^2\right] \quad [4]$$

with

$$A = RT \ln\frac{C_0}{C} \quad [5]$$

where C and C_0 are the respective equilibrium liquid phase concentration and the solute solubility, and E_0^* is the characteristic adsorption energy of a reference adsorbate (C_6H_6) in such adsorption systems.

Choma et al. (1993) introduced an "interfacial" similarity (affinity) coefficient β^* to relate the characteristic energies E_0 and E_0^*:

$$\beta^* = \frac{E_0^*}{E_0} \quad [6]$$

They examined β^* value for benzene by using 8 different activated carbons of different sources. The resulting β^* value was 0.052 ± 0.004 and did not depend on the heterogeneity of the activated carbons used, illustrating the usefulness of β^* as a measure of the similarity between the characteristic adsorption curves of any adsorbate in the gas/solid and liquid/solid systems. Thus, the DR equation in the dilute liquid/solid adsorption systems can be rewritten as:

$$\theta(A) = \exp\left[-\left(\frac{A}{\beta\beta^* E_0}\right)^2\right] \quad [7]$$

It should be emphasized that β defines the similarities between gas/solid adsorptions for an adsorbate compound and a reference compound, while β^*, which is equal to 0.52 for benzene, defines the similarities be-

Table 1. Properties of mixed Ca/TMPA- and TMPA-smectites.

Clay	Sample name	OC%†	% of CEC occupied by TMPA	d (001) (Å)
1	SAC-TMPA.17‡	1.66	17	14.42, 18.89
2	SAC-TMPA.38	3.57	38	14.12, 18.97
3	SAC-TMPA.65	5.88	65	14.16
4	SAC-TMPA.75	6.75	75	14.95
5	SAC-TMPA1.0	8.84	100	14.38

† OC% stands for the percent organic carbon content in organo-clays.

‡ SAC stands for the smectite clay from American Colloid Company; TMPA.XX and TMPA1.0 represent that SAC is treated with TMPA and the degree of the CEC occupied by TMPA is .XX and 1.0, respectively.

tween liquid/solid and gas/solid adsorptions for an adsorbate.

Recent studies (Innes et al. 1989; Stoeckli 1989; Stoeckli et al. 1990) have shown that the DR equation satisfactorily describes adsorption only in uniform and weakly heterogeneous micropores. Stoeckli et al. (Stoeckli 1977; Dubinin and Stoeckli 1980) suggested an integral equation combined with an adsorption energy distribution function to describe adsorption in heterogeneous micropores. The DR equation is rewritten as:

$$\theta(A) = \exp\left[-\frac{\pi}{4}\left(\frac{A}{\bar{A}}\right)^2\right] \qquad [8]$$

where $\bar{A} = (\pi^{1/2}/2)\beta\beta^*E_0$ is the average adsorption potential. Letting $z = 1/\bar{A}$, adsorption in heterogeneous micropores can be expressed as:

$$\theta(A) = \int_0^\infty \exp\left(-\frac{\pi}{4}A^2z^2\right)G(z)\,dz \qquad [9]$$

where $G(z)$ is the distribution function of z correlated to the characteristic adsorption energy E_0. Dubinin and Kadlec (1987) assumed a Gaussian distribution for representing the adsorption energy distribution function. However, because the Gaussian distribution has a non-zero value at zero point argument, and the resulting adsorption isotherm equation contains the error function of the adsorption potential, Jaroniec and Madey (1989) proposed a gamma-type distribution function for representing adsorption energy distribution function, which is physically and mathematically meaningful and leads to a simple adsorption isotherm equation. The following distribution function was obtained:

$$G(z) = \frac{2q^{v/2}}{\Gamma(v/2)}z^{v-1}\exp(-qz^2);$$

$$q > 0 \quad \text{and} \quad v > -1 \qquad [10]$$

with

$$\int_0^\infty G(z)\,dz = 1 \qquad [11]$$

where $\Gamma(v/2)$ is the gamma function, q and v are parameters associated with the dispersion σ_z of the distribution and mean $\bar{z}$.

Integration of Equation [9] with the substitution of $G(z)$ leads to the following adsorption isotherm equation:

$$\theta(A) = \left[\frac{q}{q + (\pi/4)A^2}\right]^{v/2} \qquad [12]$$

Equations [10] and [12] are good mathematical representations of adsorptions in gas/solid and dilute liquid/solid systems. The simplicity of these equations allows one to properly characterize adsorption with only the parameters q, v, β^* and β, which can be calculated from experimental adsorption data.

MATERIALS AND METHODS

Smectite from a Wyoming bentonite (SAC) with a CEC of 90 $cmol_c$/kg was obtained from the American Colloid Company (Chicago, Illinois). The <2 μm clay fractions were obtained by wet sedimentation and subsequently saturated with Ca^{2+} cations by washing the clay repeatedly with $CaCl_2$ solution (0.1 mol/L). TMPA bromide (Aldrich Chemical Co.) was dissolved in distilled water and used to prepare TMPA organo-smectites (SAC-TMPA). Clay suspensions containing 25 g of Ca-clay were treated by adding different amounts of TMPA bromide solution (0.03 mol/L) to form either mixed Ca/TMPA-clays or fully saturated TMPA-clay (SAC-TMPA). To prepare mixed Ca/TMPA-clays, the amounts of TMPA added were 0.2, 0.4, 0.65 and 0.75 times the CEC. To prepare the saturated TMPA-clay, TMPA was added at 3 times the CEC. The mixtures were agitated overnight on a magnetic stirrer at room temperature. The organo-clay suspensions were then washed with distilled water repeatedly until free of bromide ions as indicated by $AgNO_3$, and stored in bottles for later use. Organic carbon contents of clays were determined using Dohrmann DC-190 high-temperature TOC analyzer (Rosemount Analytical Inc., Santa Clara, California), and were used to calculate the fraction of CEC occupied by TMPA cations. These organo-clays are referred to as SAC-TMPA.17, SAC-TMPA.38, SAC-TMPA.65, SAC-TMPA.75 and SAC-TMPA1.0, respectively, in which the numerical value represents the fraction of the CEC occupied by TMPA. The properties of these SAC-TMPAs are given in Table 1.

Adsorption of benzene, toluene, ethylbenzene, p-xylene and n-propylbenzene by the organo-clays was conducted using a batch equilibration technique. Corex glass centrifuge tubes were filled with 100 mg of organo-clay and 25 mL of distilled water. Organic solutes were added neat using a Hamilton microliter syringe to produce a range of initial and final concentrations. The tubes were capped immediately with Teflon-backed septa. The tubes were shaken for 24 h on a rotator at room temperature. Preliminary experi-

ments showed that sorption reached equilibrium within 18 h. After equilibration, the tubes were centrifuged at 8000 rpm (relative centrifugal force = 4302 g) for 10 min to separate liquid and solid phases. A volume of 5 mL of supernatant was extracted with 10 mL of carbon disulfide in a glass vial.

Analysis of organic solutes in the carbon disulfide extracts was made by gas chromatography. A Hewlett–Packard 5890 A gas chromatograph fitted with a flame ionization detector and a packed column (Alltech Co.) was used; N_2 was the carrier gas. Peak areas were recorded by a Hewlett–Packard 3392A integrator, and compared to external standards to determine the concentrations of organic solutes. The recovery of organic solutes in blanks not containing organo-clays was >90%. The amount of organic solutes sorbed was calculated from the differences between the amount of organic solutes added and that remaining in the final equilibrium solutions. Sorption isotherms were made by plotting the amount sorbed versus the equilibrium concentration in solution.

Basal spacings [$d(001)$] of SAC-TMPA organo-clays with organic solutes sorbed were determined by XRD analysis. Organo-clay suspensions were dropped on glass slides, and immediately covered by Teflon tape to prevent vapor loss. X-ray diffraction (XRD) patterns were recorded using CuKα radiator and a Philips APD3720 automated X-ray diffractometer using an APD3521 goniometer fit with a θ-compressing slit, a 0.2-mm receiving slit and a diffracted-beam graphite monochromator, from 2 to 10 °2θ, in steps of 0.03 °2θ, 1 sec/step.

Pore size distributions of the organo-clays were determined by QuantaChrome Co. (Romeoville, Illinois). The organo-clays were outgassed for 16 h at 70 °C. The N_2 sorption measurements were analyzed using the Brunauer–Emmett–Teller (BET) equation (Brunauer et al. 1938) and the Horvath–Kawazoe (H–K) method (Horvath and Kawazoe 1983).

RESULTS AND DISCUSSION

The adsorption isotherms of benzene, toluene, p-xylene, ethylbenzene and propylbenzene are shown in Figure 1. All isotherms are type I, indicating that the adsorption occurs on the surfaces and in the micropores of SAC-TMPAs. Benzene shows the highest uptake by the organo-clays; progressively lower uptake occurs for larger molecules in the order of benzene > toluene > p-xylene ≈ ethylbenzene > n-propylbenzene. At Ce/Cs (equilibrium concentration in water/ aqueous solubility) = 0.5, the sorbed concentration on SAC-TMPA.65 is about 78 mg/g for benzene, 51 for toluene, 41 for p-xylene and ethylbenzene and 36 for n-propylbenzene. X-ray analysis showed that SAC-TMPAs do not undergo interlayer expansion after adsorption of the test compounds over the experimental concentration range used, indicating that the microstructures of SAC-TMPAs were not altered.

Choice of the Adsorption Isotherm Equation

All adsorption isotherms were fit to the Langmuir isotherm equation and the DA isotherm equation with $n = 2$ and $n = 3$. Typical fitting results are represented in Figure 2. For small adsorbates such as benzene, the Langmuir equation overestimates adsorption at low concentrations and underestimates adsorption at high concentrations (Figure 2). For larger molecules like n-propylbenzene, the Langmuir equation gives a better fit, but it still deviates slightly from the experimental data (Figure 2). The DA equation with $n = 3$ provides a good description of adsorption of gases and aqueous compounds on activated carbons that contain uniform micropores (Innes et al. 1989; Stoeckli 1989; Stoeckli et al. 1990). When combined with the gamma-type adsorption energy distribution function, it also describes adsorption on heterogeneous activated carbons. However, it does not give a good fit for our experimental data in water/SAC-TMPA systems. The DR equation, which is suitable for weakly heterogeneous activated carbons (Kraehenbuehl et al. 1986; Innes et al. 1989; Stoeckli 1989), combined with the gamma-type adsorption energy distribution, does provide an excellent fit for our experimental data over the whole concentration range used (Figure 2).

The DR equation is a fundamental mathematical description of gas adsorption on porous and microporous solids. It is also very useful for describing gas adsorption on mesoporous, macroporous and nonporous solids, although there is no theoretical basis for the equation (Hobson 1961; Cerofolini 1974). Our results suggest that the DR equation may be extended to the aqueous organo-clay adsorption systems presented here, as described below.

Adsorption Energy Distribution Function

Adsorption energy distribution functions are dependent on the heterogeneity parameters q and v (Equation [10]). In order to obtain q and v for calculating the adsorption energy distribution functions for SAC-TMPAs, all isotherms were fit to Equation [12]. The resulting values of q and v, together with the maximum adsorption amount Q_m, are listed in Table 2.

The adsorption energy distribution functions versus the inverse value of the average adsorption potential, z, calculated from Equation [10], are shown in Figure 3. All are asymmetrical gamma-type distributions with a broadening toward lower energies. To better describe those adsorption energy distributions, the z_{max} values (at which adsorption energy distributions reach a maximum), the average $\bar{z}$ values, and the dispersion σ_z values were calculated according to the following equations (Jaroniec and Madey 1989):
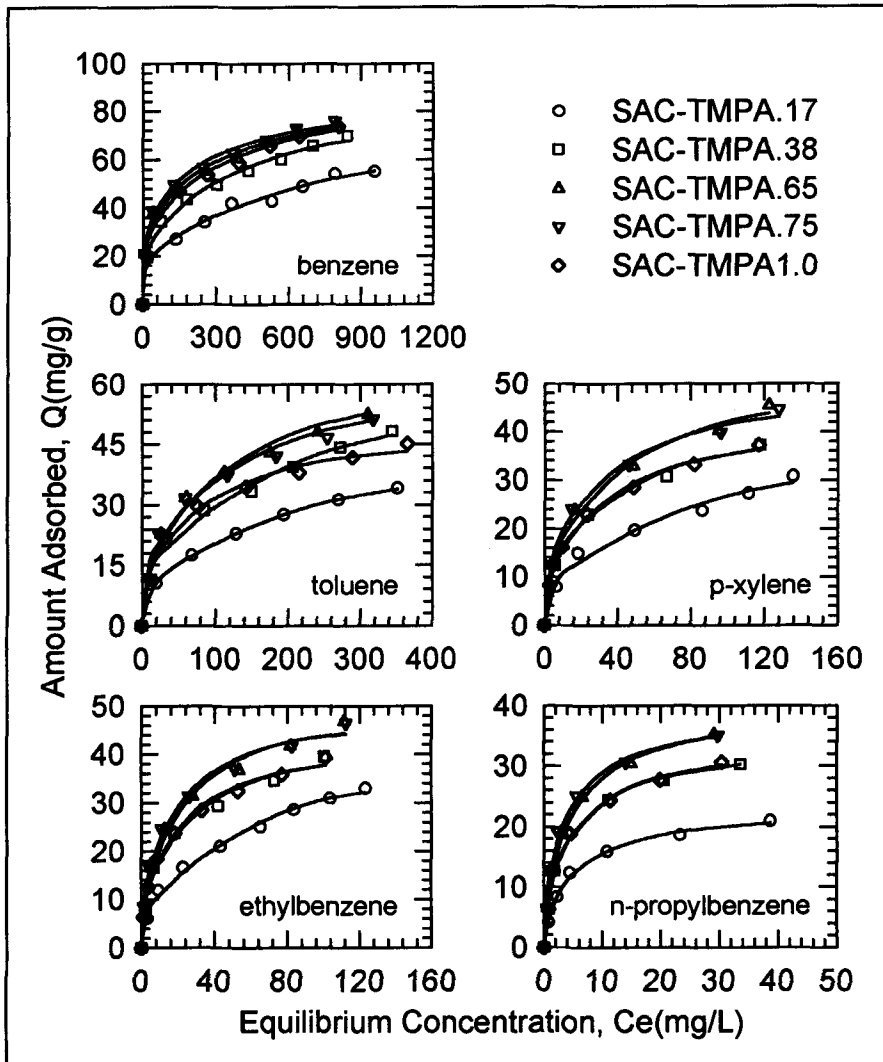
Figure 1. Adsorption of aqueous phase alkylbenzenes by SAC-TMPAs.

$$z_{max} = \sqrt{\frac{v-1}{2q}} \qquad [13]$$

$$\bar{z} = \int_0^\infty zG(z)\, dz = \frac{\Gamma\left(\dfrac{v+1}{2}\right)}{\Gamma\left(\dfrac{v}{2}\right)}\frac{1}{\sqrt{q}} \qquad [14]$$

$$\sigma_z = \sqrt{\int_0^\infty z^2 G(z)\, dz - \bar{z}^2} = \sqrt{\frac{v}{2}\frac{\Gamma^2\left(\dfrac{v+1}{2}\right)}{\Gamma^2\left(\dfrac{v}{2}\right)}\frac{1}{\sqrt{q}}} \qquad [15]$$

The results are listed in Table 3. For all SAC-TMPAs, the energy distributions of benzene reach a maximum at higher adsorption energies as compared to the alkylbenzenes studied, with an average z_{max} value of 0.0028 mol/kJ. By comparison, z_{max} values for toluene, p-xylene, ethylbenzene and n-propylbenzene were all about 0.0040 mol/kJ. As indicated by σ_z, the energy distributions of toluene are broader than that of benzene, and then progressively narrower for larger molecules in the sequence: benzene $<$ toluene $>$ p-xylene $\approx$ ethylbenzene $>$ n-propylbenzene. For n-propylbenzene, the adsorption energy distributions are very sharp and nearly symmetrical. For the adsorption of the same adsorbate on different SAC-TMPAs, SAC-TMPA.17 gives the broadest distributions. The adsorption energy distributions for the other 4 SAC-TMPAs are similar to each other, particularly in the case of larger molecules such as ethylbenzene, but remarkably different from
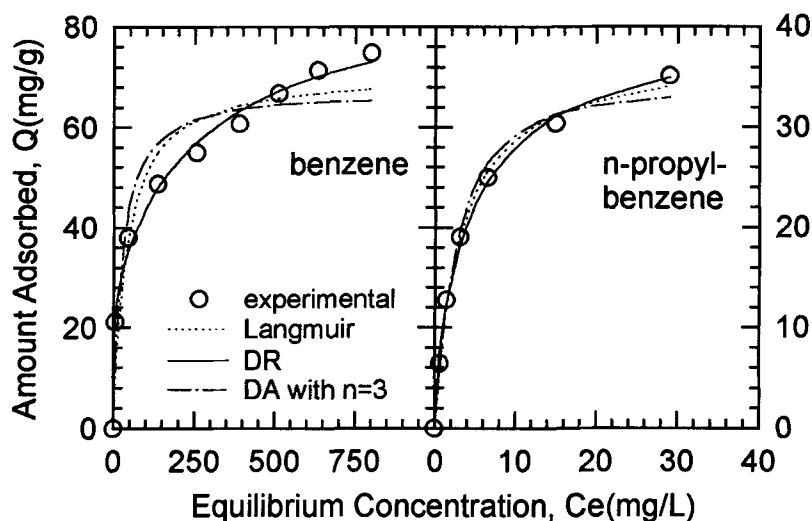
Figure 2. Adsorption by SAC-TMPA.65 of benzene (left) and n-propylbenzene (right) in aqueous solutions, fitted to the Langmuir equation (dotted line), the DA equation with $n = 3$ (dashed dotted line), and the DR equation (solid line).

SAC-TMPA.17, the general trend in width being SAC-TMPA.38 ≈ SAC-TMPA1.0 > SAC-TMPA.65 ≈ SAC-TMPA.75. In the case of n-propylbenzene, they actually overlap, and only 1 curve is shown in Figure 3 for n-propylbenzene.

As a probe for the heterogeneity of adsorbents, adsorbate molecules only detect those sites that interact with the probe molecules during the adsorption process. Therefore, the adsorption experiments provide information concerning the "relative" heterogeneity. It is apparent from the adsorption energy distributions summarized above that there is a steric effect involved in adsorption. Benzene molecules, due to their small sizes, are adsorbed at sites of (comparatively) high energies, whereas toluene and larger molecules can only be adsorbed at sites of lower energies. Stoeckli et al. (1989) have shown that the characteristic adsorption energy and micro-

pore size of activated carbons have an inverse relationship. A similar relationship correlating the characteristic adsorption energy and micropore sizes may exist in TMPA organo-smectites. This suggests the existence of fine micropores of high adsorption energies in SAC-TMPAs which are accessible for benzene molecules but sterically exclude toluene and larger molecules. Such molecules can only be adsorbed in larger micropores, and on mesoporous, macroporous and flat surfaces which have the sites of lower energies, as indicated by the shift of z_{max} values for these molecules. These results also suggest that sites of benzene adsorption have micropore diameters larger than the length of the benzene molecules (5.6 Å) but smaller than the length of toluene molecules (7.1 Å), and that molecular planes of the adsorbates must be parallel to the basal plane of the clay as indicated previously by Jaynes and Boyd

Table 2. Parameters Q_m, v, q for adsorption of aromatic hydrocarbons in water/TMPA-smectite systems.

| SAC-TMPA		0.17	0.38	0.65	0.75	1.0
benzene	Q_m (mg/g)	60.61	73.24	77.84	78.51	77.36
	v	1.09	1.59	1.48	1.59	1.51
	q(kJ/mol)^2	1.03×10^4	2.59×10^4	3.44×10^4	4.24×10^4	3.03×10^4
toluene	Q_m (mg/g)	35.50	49.65	55.30	53.22	43.90
	v	1.33	1.22	1.98	1.60	2.47
	q(kJ/mol)^2	9.95×10^3	9.49×10^3	2.48×10^4	2.03×10^4	4.28×10^4
p-xylene	Q_m (mg/g)	30.87	38.00	45.51	44.16	37.63
	v	1.22	2.11	2.17	2.36	2.98
	q(kJ/mol)^2	8.37×10^3	3.22×10^4	3.02×10^4	4.14×10^4	5.20×10^4
ethylbenzene	Q_m (mg/g)	32.72	38.62	44.98	44.64	38.48
	v	1.35	2.70	3.40	3.06	3.47
	q(kJ/mol)^2	8.52×10^3	4.54×10^4	5.98×10^4	6.14×10^4	6.57×10^4
n-propylbenzene	Q_m (mg/g)	21.31	31.54	37.16	36.97	31.88
	v	33.4	65.4	87.0	56.3	75.8
	q(kJ/mol)^2	9.80×10^5	2.15×10^6	2.85×10^6	2.12×10^6	2.43×10^6
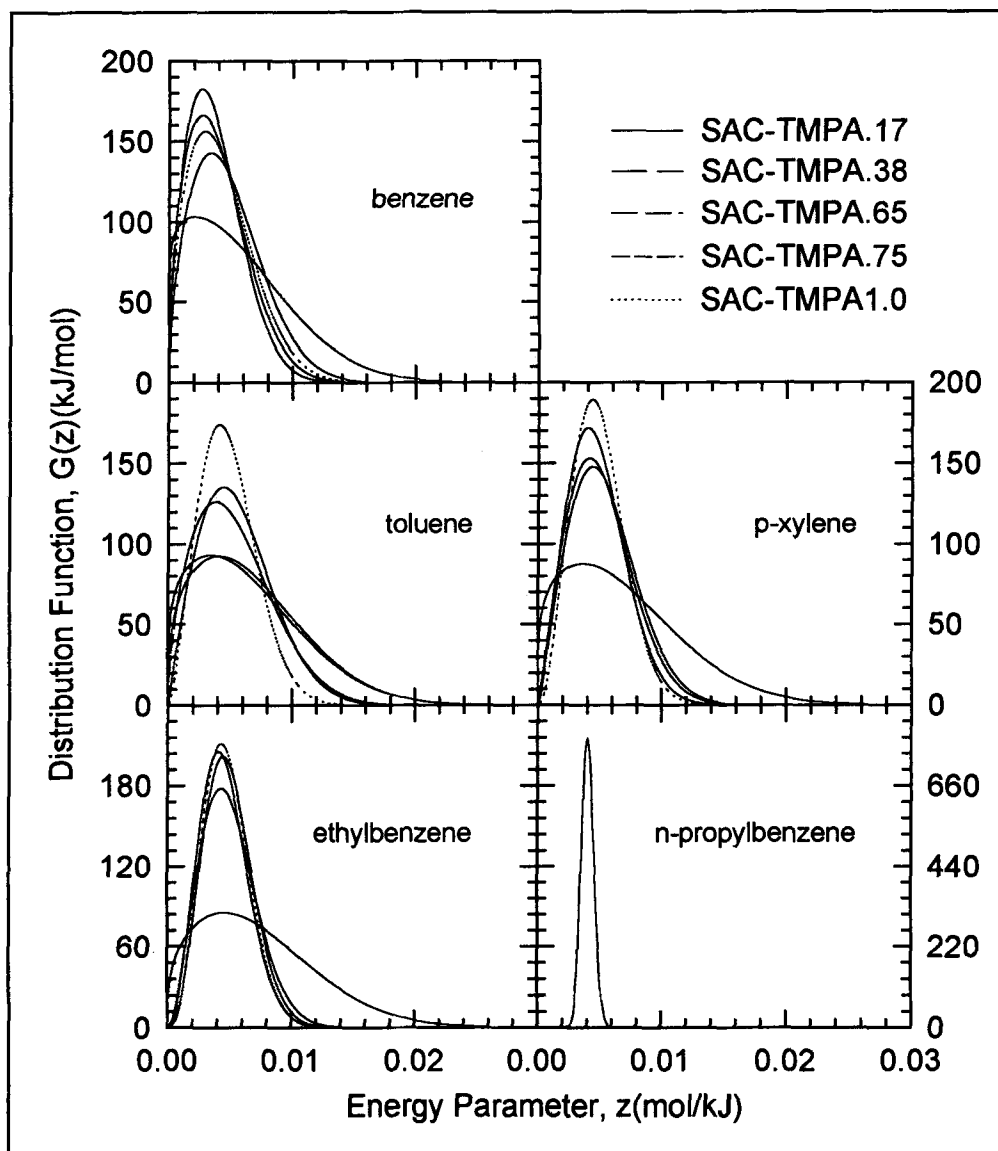
Figure 3.   Adsorption energy distributions for SAC-TMPAs.

(1991b). If adsorbed molecules were oriented vertically to the clay surfaces, all 5 adsorbates used in this study would fill micropores, since they have the same widths of 4.8 Å.

The above discussion is supported by the measured pore size distributions of SAC-TMPAs shown in Figure 4. All pores are in the micropore region. A significant portion of the micropores have pore diameters about 6.5 Å, larger than the length of the benzene molecule and smaller than the length of toluene.

Although benzene molecules can fill the fine micropores, toluene, p-xylene, ethylbenzene and n-propylbenzene are adsorbed in larger micropores and on surfaces. The smaller toluene molecules explore more sites of different energies on the clay surfaces than the

larger alkylbenzenes. As a result, toluene detects a more heterogeneous surface and gives broader adsorption energy distributions. The adsorption energy distribution narrows and the heterogeneity is concealed gradually as the adsorbate molecular size increases. In the case of n-propylbenzene, the heterogeneity is concealed completely so that the adsorption isotherms can be fit to the Langmuir equation (Figure 2).

Non-uniform distribution of cations, especially at low TMPA content, may lead to a broadening of the energy distribution profile. McBride and Mortland (1973) observed the segregation of different cations in a smectite when ethylammonium was partially exchanged by tetrapropylammonium up to about 55% of the CEC. Faver and Lagaly (1991) reported that large

Table 3. The characteristics of adsorption energy distribution.

SAC-TMPA		0.17	0.38	0.65	0.75	1.0	Average
benzene	z_{max}(mol/kJ)	0.0029	0.0034	0.0026	0.0026	0.0029	0.0028
	z(mol/kJ)	0.0059	0.0048	0.0040	0.0037	0.0043	
	σ_z(mol/kJ)	0.0043	0.0028	0.0024	0.0022	0.0026	
toluene	z_{max}(mol/kJ)	0.0041	0.0035	0.0044	0.0038	0.0041	0.0041
	z(mol/kJ)	0.0068	0.0066	0.0056	0.0054	0.0049	
	σ_z(mol/kJ)	0.0045	0.0045	0.0029	0.0032	0.0023	
p-xylene	z_{max}(mol/kJ)	0.0036	0.0041	0.0044	0.0040	0.0044	0.0040
	z(mol/kJ)	0.0071	0.0051	0.0054	0.0048	0.0049	
	σ_z(mol/kJ)	0.0048	0.0026	0.0027	0.0023	0.0021	
ethylbenzene	z_{max}(mol/kJ)	0.0046	0.0043	0.0045	0.0041	0.0043	0.0044
	z(mol/kJ)	0.0075	0.0050	0.0050	0.0046	0.0048	
	σ_z(mol/kJ)	0.0048	0.0022	0.0020	0.0019	0.0019	
n-propylbenzene	z_{max}(mol/kJ)	0.0041	0.0039	0.0039	0.0036	0.0039	0.0039
	z(mol/kJ)	0.0041	0.0039	0.0039	0.0036	0.0039	
	σ_z(mol/kJ)	0.0005	0.0005	0.0005	0.0005	0.0005	

quaternary ammonium cations (such as hexadecyltrimethylammonium) are preferentially adsorbed on low charge density clay surfaces while small organic cations such as TMPA prefer to be adsorbed on surfaces of high charge density. We observed that Ca^{2+} and TMPA cations are randomly distributed in SAC-TMPAs (Sheng and Boyd 1997). However, the inhomogeneity of layer charge density may cause a nonuniform distribution of Ca^{2+} and TMPA cations, resulting in a distribution of micropore sizes. This type of topographical heterogeneity is especially significant for SAC-TMPA.17, producing the broad adsorption energy distributions. As the TMPA content increases in

Figure 4. Micropore-size distributions of SAC-TMPAs.

these clays, Ca^{2+} and TMPA distribution becomes more uniform and hence the surfaces more homogeneous. This is indicated by the progressively narrower adsorption energy distributions of SAC-TMPA.38, SAC-TMPA.65 and SAC-TMPA.75. Once the CEC is fully saturated by TMPA (in SAC-TMPA1.0), the adsorption energy distribution is slightly broader. This may be related to the formation of more fine micropores due to the high TMPA density on the surfaces.

Surface Fractal Dimension

Surface fractal dimension is useful for characterizing heterogeneous adsorbents. For a series of spherical molecules, Pfeifer et al. (1983) and Avnir et al. (1983, 1984) derived the following relationship which relates the monolayer amount adsorbed (Q_m) to the spherical radius of the adsorbate molecule (r) and the surface fractal dimension (D), which is between 2 and 3:

$$Q_m \propto r^{-D} \quad [16]$$

However, the adsorbate molecules need not be spherical, provided they are adsorbed flat on the adsorbent surface and belong to a homologous series for which the ratio of the square of the linear extent (that is, largest distance, r, between any 2 points on the probe) to the effective cross-sectional area is the same for all members (Pfeifer et al. 1983). For the sorption data presented here, a plot of logarithm Q_m versus logarithm r yields a straight line (Figure 5), indicating that these requirements are satisfied. Values of D are obtained from the slopes of these plots and listed in Table 4 together with the lengths of the aromatic molecules (r) which were used to estimate the fractal dimensions. Correlation coefficients (R^2) in Table 4 verify the highly linear relationship between log Q_m and log r. The high D value for SAC-TMPA.17 suggests a comparatively high degree of heterogeneity for SAC-TMPA.17. This high heterogeneity can be attributed to the formation of TMPA-rich patches in regions of
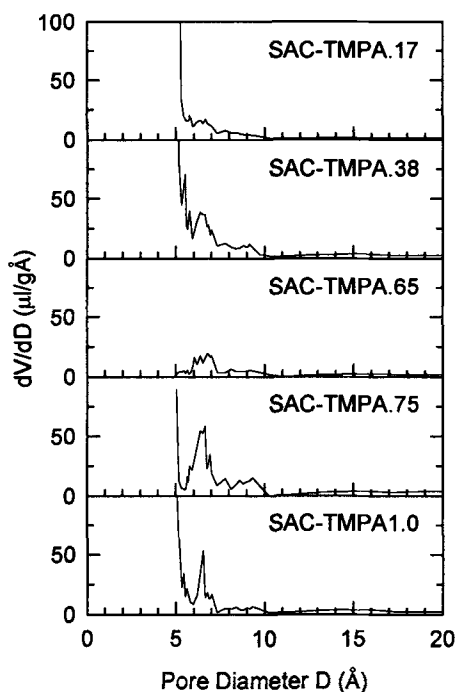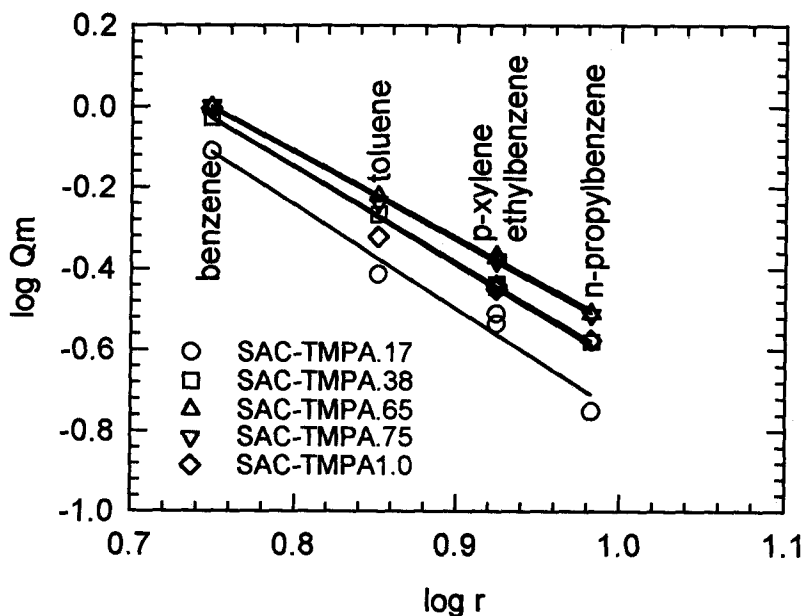
Figure 5.   Dependence of adsorption capacity on molecular size.

higher charge density and the associated formation of numerous fine micropores. The D value decreases from 2.55 for SAC-TMPA.17 to 2.15 as the TMPA content increases to about 0.65 CEC, indicating that TMPA-smectite becomes less heterogeneous. This can be attributed to the adsorption of TMPA on the layers of lower charge density, and the resultant formation of larger pores which lowers the (molecular scale) fractal dimension. The D value increases again to 2.40 for SAC-TMPA1.0 as the TMPA content increases to 1.0 CEC due to the formation of additional micropores. The analysis of fractal dimension results is consistent with the previous analysis of adsorption energy distributions.

These results are also consistent with the measured pore size distributions of SAC-TMPAs shown in Figure 4. The volume fraction of the portion of the micropores with pore diameters of about 6.5 Å increases (as the D value decreases) in the order: SAC-TMPA.17 < SAC-TMPA.38 <SAC-TMPA.65, decreases thereafter (as the D value increases) in the order: SAC-TMPA.65 > SAC-TMPA.75 > SAC-TMPA1.0.

Based on the theory of adsorption on fractally porous solids, Avnir et al. (1983) have developed the

following theoretical proportionality relationship between pore-size distribution $J(x)$ and fractal dimension:

$$J(x) \propto x^{2-D} \qquad [17]$$

In the micropore region, Jaroniec et al. (1990) derived the following equation:

$$J(x) = \frac{3 - D}{x_{max}^{3-D} - x_{min}^{3-D}} x^{2-D} \qquad [18]$$

where x_{max} is the upper limit of micropore size, and x_{min} is the lower limit of micropore size. Plotting fractal dimension against mean pore size, shown in Figure 6, gives the following linear relationship:
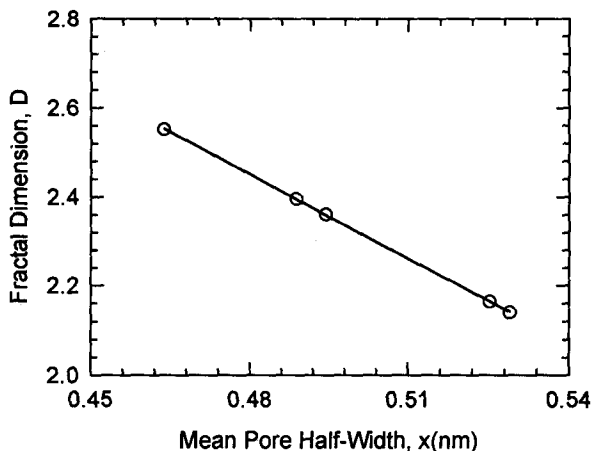
Table 4.   Molecular lengths of adsorbates and fractal dimensions of SAC-TMPAs.

Adsorbate	Benzene	Toluene	p-xylene	Ethyl-benzene	n-propyl-benzene
Length (Å)	5.6	7.1	8.4	8.4	9.6
SAC-TMPA	0.17	0.38	0.65	0.75	1.0
D	2.55	2.36	2.15	2.16	2.40
R^2	0.9704	0.9998	0.9989	0.9984	0.9842

Figure 6.   Dependence of fractal dimension on mean pore size of SAC-TMPAs.

$$D = 5.478 - 6.308 \bar{x} \quad R^2 = 1.000 \qquad [19]$$

This type of linear relationship was also obtained for activated carbons and consistent with the theoretical analysis (Jaroniec et al. 1993). This relationship could be used to estimate the fractal dimension from experimental micropore size distribution of TMPA-smectites. In the above relationship, the mean pore size is calculated via the following expression using $x_{max} = 1.0$ nm and $x_{min} = 0.1$ nm:

$$\bar{x} = \frac{\displaystyle\int_{x_{min}}^{x_{max}} x J(x) \, dx}{\displaystyle\int_{x_{min}}^{x_{max}} J(x) \, dx} \qquad [20]$$

Our experimental results of micropore size distribution and the theoretical linear relationship between D and $\bar{x}$ illustrate that D is simply correlated to the microporosity of SAC-TMPAs and reflects the fact that the surface irregularities of SAC-TMPAs are largely generated by their microporosity.

In summary, as effective adsorbents for aqueous aromatic hydrocarbons, SAC-TMPAs possess both the surface and structural heterogeneity. The DR equation with a gamma-type distribution function describes the adsorption isotherm data better than the Langmuir equation (Figure 2). The heterogeneity of SAC-TMPAs can be characterized by adsorption energy distribution, fractal dimension and microporosity. The relative heterogeneity revealed by adsorption experiments depends on the size of adsorbate molecules. Small molecules probe the highly heterogeneous surface while large molecules detect a relatively homogeneous surface. TMPA content and inhomogeneity of charge density in smectite also affect the heterogeneity of SAC-TMPAs by affecting the distribution of TMPA cations in smectite and possibly the interaction between TMPA cations.

Our results suggest here that the heterogeneity is the intrinsic property of organo-clays. The DR equation for sorption onto heterogeneous surfaces would be the better choice than the Langmuir equation for describing the adsorption of organic compounds on organo-clays containing relatively small exchange cations like TMPA.

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