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Linear Solvation Energy Relationships Used To Evaluate Sorption Mechanisms of Volatile Organic Compounds with One Organomontmorillonite under Different Humidities

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ABSTRACT: Organic-cation-modified clays are usually used as sorbents to reduce the spread of organic contaminants in remediation or landfill sites and to remove them at contaminated sites. To effectively design organomontmorillonite to remove volatile organic compounds (VOCs) and predict the fate of VOCs in the environment, the sorption equilibrium and mechanisms of VOCs on organomontmorillonite under different humidities are needed to be studied. In this study, organomontmorillonite was synthesized through exchanging inorganic cations by hexadecyltrimethyl ammonium (HDTMA) into montmorillonite. The surface area of organomontmorillonite was smaller than the unmodified clay because of the incorporation of organic cations into interlayers of clay. As compared to sorption coefficients in montmorillonite under different humidities, surface adsorption on organomontmorillonite surface and partition into the incorporated HDTMA in organomontmorillonite both play roles on the sorption process. The sorption coefficients of VOC vapors on organomontmorillonite were further characterized using a linear solvation energy relationship (LSER). The fitted LSER equations were obtained by a multiple regression of the sorption coefficients of 22 probe chemicals against their solvation parameters. The coefficients of the five-parameter LSER equations show that organomontmorillonite interacts with VOC molecules mainly through dispersion, partly through dipolarity/polarizability and hydrogen-bonds and with negative π-/n-electron pair interaction. The interaction analysis by LSERs suggests that the potential predominant factors governing the sorption of VOCs are dispersion interactions under all tested humidity conditions, whereas hydrogen-bond interactions or both interactions dominate the sorption process with the increase of relative humidity. The derived LSER equations successfully fitted the sorption coefficients of VOCs on organomontmorillonite. A better understanding of the effect of relative humidity on the organo−inorganic complexes sorption mechanism via the LSER approach is important to the design of the toxic-vapor removal and the assessment of organic contaminants in the environment.

INTRODUCTION

Organomontmorillonite is a type of organically modified montmorillonite comprising montmorillonite mineral that has organocations instead of the original layer of interlayer cations. By adding organic cation molecules, the hydrophilic property of clay becomes increasingly more hydrophobic to sorb organic compounds. Organoclay has been used in a number of environmental applications because of its ability to remediate organic pollutants in the environment.[1−3]

Sorption plays an important role in designing filters (especially air filters[4]) and liners made of various organoclays to remove organic pollutants.[5] The sorption of volatile organic compounds (VOCs) into the organic−inorganic complex also governs their transport, fate, and effect in the environment.[6−9] Moreover, because clays show decreasing sorption of VOCs with increasing relative humidity (RH),[10−13] humidity plays a key role in the sorption of VOCs on organomontmorillonites. To improve the design of proper filter and cleanup procedures, further understanding of the sorption of organic vapors on organomontmorillonites under different RHs is needed.

The quantitative structure−activity relationships are also used to improve the understanding of sorption phenomena in organomontmorillonites. The linear solvation energy relationship (LSER) approach, developed by Abraham et al.,[14−16] was used to understand the sorption mechanism of VOCs with sorbents.[16−19] Various coefficients obtained from the multiple regression of sorption coefficients and solvation parameters of compounds represent the surface properties of adsorbents. The relative magnitudes of the terms in the LSER can be related to each interaction that contributes to the overall process.[16−19]

In this study, montmorillonite is modified with hexadecyltrimethyl ammonium (HDTMA) to form organomontmorillonite. Sorption capacities of VOCs with the organomontmorillonite at different levels of RH were investigated by inverse gas chromatography (IGC). The relationship between intermolecular interactions of VOCs with organomontmorillonite at different levels of RH was investigated with the LSER approach. The resultant sorption equilibrium, mechanisms, and LSER equations give us further insight to a fundamental understanding of the sorption of VOCs in organo−inorganic complexes and an improved technical base for predicting and designing organomontmorillonite for VOC removal.

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Table 1. Octanol−Water Partition Constant and Molecular Descriptors of Organic Sorbates Used in This Study

class of compounds	compounds	log K_{ow}[a]	E[b]	S[b]	A[b]	B[b]	L[b]
alkane	*n*-pentane	3.39	0.000	0.00	0.00	0.00	2.162
	n-hexane	4.00	0.000	0.00	0.00	0.00	2.688
	n-heptane	4.66	0.000	0.00	0.00	0.00	3.173
	n-octane	5.15	0.000	0.00	0.00	0.00	3.677
	2,2,4-trimethylpentane	4.09	0.000	0.00	0.00	0.00	3.106
	cyclohexane	3.44	0.305	0.10	0.00	0.00	2.964
aromatic	benzene	1.48	0.610	0.52	0.00	0.14	2.786
	toluene	2.42	0.601	0.52	0.00	0.14	3.325
	ethylbenzene	2.88	0.613	0.51	0.00	0.15	3.778
chloroalkane	dichloromethane	2.17	0.387	0.57	0.10	0.05	2.019
	trichloromethane	2.69	0.425	0.49	0.15	0.02	2.480
	tetrachloromethane	3.20	0.458	0.38	0.00	0.00	2.823
chloroalkene	1,1-dichloroethylene	1.31	0.362	0.34	0.00	0.05	2.110
	trichloroethylene	1.95	0.524	0.53	0.12	0.03	2.997
	tetrachloroethylene	2.77	0.639	0.42	0.00	0.00	3.584
alcohol	methanol	−0.77	0.278	0.44	0.43	0.47	0.970
	ethanol	−0.31	0.246	0.42	0.37	0.48	1.485
	2-propanol	0.05	0.212	0.36	0.33	0.56	1.764
ether	diethyl ether	0.69	0.041	0.25	0.00	0.45	2.015
ketone	acetone	−0.24	0.179	0.70	0.04	0.49	1.696
ester	ethyl acetate	0.89	0.106	0.62	0.00	0.45	2.314
nitrile	acetonitrile	−0.34	0.237	0.90	0.07	0.32	1.739

[a] Data were obtained from Schwarzenbach et al.[31] [b] Data obtained from Abraham.[14]

EXPERIMENTAL SECTION

Organomontmorillonite. The montmorillonite, STx-1, was obtained from the Clay Minerals Society Source Clays Repository (Columbia, MO, USA). The basal spacing is 1.17 nm. The cation exchange capacity (CEC) and the surface area of montmorillonite are 84.4 meq/100 g and 80.1 $m^2 \cdot g^{-1}$, respectively.[20] The C, N, H, and O element contents are 0.01 %, 0.05 %, 2 %, and 17 %, respectively. The organomontmorillonite was prepared by the following procedure. The desired amount of HDTMA bromide solution was added to montmorillonite suspensions. After mixing, the organomontmorillonite suspensions were shaken overnight at ambient temperature. Suspensions were then centrifuged at 30 000 g for 20 min. Deionized water was used to wash the precipitates three times. The precipitates were frozen in liquid nitrogen and dried in a freeze-dryer. Lastly, the organomontmorillonite was stored in a sealed bottle for later use. The contents of C, N, O, and H were measured by an elemental analyzer (Heraeus CHN-OS Rapid F002). The Brunauer−Emmett−Teller (BET) surface area and pore size were determined to be 77 K on the basis of nitrogen adsorption by an ASAP2100 analyzer (Micrometrics Instrument Corporation, Norcross, GA, USA). Basal spacings at three levels of humidity were determined by Synchrotron X-ray diffraction (XRD) in the National Synchrotron Radiation Research Center, Taiwan.

Chemical Probes. A total of 22 VOCs, including nine main classes of common VOCs, were selected as the probe solutes. Toluene, *n*-pentane, *n*-octane, 1,1-dichloroethylene, trichloroethylene, tetrachloroethylene, 2,2,4-trimethylpentane, ethylbenzene, and 2-propanol were purchased from Acros Organics. Cyclohexane, *n*-hexane, *n*-heptane, dichloromethane, trichloromethane, methanol, ethyl acetate, and acetonitrile were purchased from J.T. Baker. Tetrachloromethane and benzene were purchased from Merck. Acetone was obtained from Mallinckrodt Baker. Diethyl ether was purchased from Riedel-de Haën. The solvation parameters of the selected VOCs are listed in Table 1 and have been verified that they are independent. All chemicals utilized in the experiment had purity grades of > 95 % and no visible peaks of impurities for any solutes via our preliminary IGC analysis.[20]

Sorption Experiments. IGC was used to measure the sorption equilibrium coefficients of the selected VOCs as previous described.[20,21]

LSER Fit. The LSER equation we used is[14]

$$\log K_d = c + eE + sS + aA + bB + lL \tag{1}$$

where each term represents a type of contribution among various intermolecular interactions and the coefficients characterize the physicochemical properties of the sorbent material. E is the excess molecular refractivity of the sorbate that reflects its ability to interact with a sorbent through π or n-electron pairs. S is the dipolarity/polarizing ability of the sorbate. A and B are the sorbate hydrogen-bond acidity and basicity, respectively. L is the Ostwald solubility coefficient on hexadecane at 298 K (which accounts for the dispersion/cavity formation). a and b are complementary to the chemical hydrogen-bond acidity and basicity; they represent hydrogen-bond basicity and acidity of the sorbent phase, respectively. The s coefficient is related to the sorbent phase dipolarity/polarizability. The l coefficient is related to dispersion interactions. The e coefficient refers to the ability of the phase to interact with solute n- and π-electron pairs and provides an indication of polarizability. The constant, c, is derived from the method of multiple linear regressions used to find eq 1.

The solvation parameters mentioned above have been derived from physicochemical and thermodynamic measurements and are available for hundreds of organic compounds.[15,22−24] The obtained sorption coefficients from IGC in this study are regressed against all solvation parameters of the selected VOCs (Table 1) by multiple linear regression analysis using Microsoft Excel 2003.[20] The coefficients, c, e, s, a, b, and l, were fitted to capture differential interactions of the set of compounds interacting with the gas phase against those interacting with the organomontmorillonite in the solid phase.

Table 2. Basic Properties of the Organomontmorillonite

properties	
elemental contents (%)	
C	6.3
N	0.44
H	3.0
O	10.0
BET surface area ($m^2 \cdot g^{-1}$)	49.7
average pore diameter (nm)	8.83
pore volume of mesopore and macropore[a] ($cm^3 \cdot g^{-1}$)	0.145

[a] Total volume for pores with diameters between 17 nm and 3000 nm.

Table 3. Basal Spacing of the Organomontmorillonite at Different Levels of Relative Humidity

condition	basal spacing$_{(d001)}$ (nm)
low RH (∼0 % RH)	1.36
ambient RH (∼50 % RH)	1.45
high RH (∼90 % RH)	1.82

RESULTS AND DISCUSSION

Characteristics of Organomontmorillonite. The basic properties of our synthesized organomontmorillonite are listed in Table 2. The C, N, H, and O element contents in the organomontmorillonite are 6.3 %, 0.44 %, 3 %, and 10 %, respectively. Compared to the original element contents of montmorillonite above, the increasing percentage of C, N, and H supports the incorporation of HDTMA into montmorillonite and indicates that 35 % of CEC is replaced by HDTMA. The surface area of the organomontmorillonite is 49.7 $m^2 \cdot g^{-1}$, which is around half of that of the original montmorillonite. Since nitrogen can only adsorbed on the outer surface of the organomontmorillonite,[25] the lower surface area of HDTMA modified organomontmorillonite might due to the aggregation of particle and no internal surface area accessible to nitrogen gas.[25] A similar result was also observed for organobentonites modified by two quaternary ammomiun cations.[26] The average pore diameter is 8.83 nm and slightly larger than 7.25 nm for the original montmorillonite. The total pore volume of 0.145 $cm^3 \cdot g^{-1}$ is less than 0.205 $cm^3 \cdot g^{-1}$ for the original montmorillonite. Besides, the total volume of pore less than 1.7 nm is undetectable, while it is 0.00401 $cm^3 \cdot g^{-1}$ in the original montmorillonite. These results might be caused by the incorporation of HDTMA in pores.

Under different relative humidities, the basal spacing of HDTMA modified organomontmorillonite was investigated by XRD (Table 3). The spacing increases from 1.36 nm at 0 % RH, to 1.45 nm at 50 % RH, and then to 1.82 nm at 90 % RH. The increment of d-spacing between original montmorillonite and this organomontmorillonite under 0 % RH indicates the

Table 4. Equilibrium Sorption Coefficients K_d of VOCs on Organomontmorillonite at Different Levels of Relative Humidity at 303 K

compounds	K_d $(mg \cdot g^{-1})/(mg \cdot L^{-1})$		
	∼0 % RH	∼55 % RH	∼90 % RH
n-pentane	0.0677 ± 0.0042	0.0172 ± 0.0010	0.0164 ± 0.0011
n-hexane	0.351 ± 0.0076	0.0497 ± 0.00023	0.0193 ± 0.0024
n-heptane	2.07 ± 0.031	0.143 ± 0.0010	0.0537 ± 0.0015
n-octane	10.5 ± 0.586	0.444 ± 0.012	0.147 ± 0.0027
2,2,4-trimethylpentane	2.08 ± 0.153	0.156 ± 0.00023	0.0588 ± 0.0012
cyclohexane	0.244 ± 0.0034	0.0596 ± 0.0010	0.0244 ± 0.0014
benzene	7.44 ± 0.70	0.386 ± 0.0045	0.0976 ± 0.0016
toluene	31.9 ± 1.2	0.957 ± 0.0014	0.225 ± 0.00036
ethylbenzene		2.49 ± 0.11	0.503 ± 0.0030
dichloromethane	1.31 ± 0.072	0.136 ± 0.00061	0.0509 ± 0.0010
trichloromethane	1.26 ± 0.22	0.137 ± 0.00061	0.0545 ± 0.0013
tetrachloromethane	0.830 ± 0.12	0.0715 ± 0.00023	0.0299 ± 0.00079
1,1-dichloroethylene	0.222 ± 0.0058	0.0398 ± 0.0013	0.0169 ± 0.0033
trichloroethylene	2.82 ± 0.27	0.156 ± 0.00092	0.0549 ± 0.0023
tetrachloroethylene	5.08 ± 0.24	0.278 ± 0.0034	0.105 ± 0.0027
methanol		1.64 ± 1.031	1.43 ± 0.051
ethanol	17.4 ± 1.3	2.40 ± 1.5	1.36 ± 0.0016
2-propanol	36.1 ± 1.6	2.89 ± 1.8	1.28 ± 0.015
diethyl ether	7.74 ± 0.88	0.153 ± 0.17	0.0467 ± 0.0011
acetone	18.4 ± 1.1	0.949 ± 0.092	0.428 ± 0.0025
ethyl acetate	37.1 ± 2.3	1.45 ± 0.92	0.279 ± 0.0067
acetonitrile	17.8 ± 0.95	4.76 ± 0.11	1.51 ± 0.061

incorporation of HDTMA into the interlayer of montmorillonite. Furthermore, the *d*-spacing of organomontmorillonite increases from 0.09 nm to 0.46 nm with increasing relative humidity from 50 % to 90 %, indicating that, even though some inorganic cations are replaced by HDTMA, water molecules still could enter into the interlayer of organo-modified montmorillonite. The larger *d*-spacing under higher relative humidity reflects a larger amount of incorporated water. Due to only 35 % CEC replacement by HDTMA, the spacing values under these two RHs are similar to those for the original montmorillonite under the same conditions.

Sorption Equilibrium and the Effect of Relative Humidity. The sorption equilibrium coefficients (K_d) of 22 VOCs on organomontmorillonite at 303 K are shown in Table 4. In general, these sorption equilibrium coefficients in each group increase with their hydrophobicity (K_{ow} in Table 1) under different RHs, indicating that organic vapor partition into the increase of carbon content from exchanged organic cations in the organomontmorillonite may play a role in this sorption process. Boyd et al.[27] also indicated a much greater contribution of the partition of benzene vapor into organic phases of organomontmorillonites in dry conditions. However, under 0 % RH, the K_d value for most compounds (except that of diethyl ether, acetone, and acetonitrile) are smaller than that of the original montmorillonite.[28] It may result from the reduced surface area of the organomontmorillonite as compared to montmorillonite. Goss[29] also indicated the reduced surface area might contribute to the decrease of the adsorption ability for VOCs under dry conditions. The surface adsorption of organic vapors on the organomontmorillonite plays a key role under 0 % RH.

The adsorption capacity becomes weaker in wet conditions as compared to dry conditions,[6,9] which might be because a rigid water structure in the crystal lattice is built up by hydrogen bonds between water molecules and oxygen atoms of the crystal sheets.[29] Goss and Eisenreich[13] also indicated that at least one molecular layer of water completely covering the surface of mineral surfaces could affect the sorption behavior of VOCs. The effect of water on the adsorption ability was also found in the organomontmorillonite. The K_d value for all compounds adsorbed on organomontmorillonite significantly decreases with increasing relative humidity; the K_d values obtained under 55 % RH declines 3 to 50 times as compared to those under 0 % RH. The decline trend increased with the increase of relative humidity. However, the repression magnitude of water on the adsorption ability of VOCs on the original montmorillonite from dry to wet conditions is larger than that of the organomontmorillonite. Furthermore, the adsorption abilities of most VOCs (except alcohol, ether, ketone, and ester at 50 % RH) on organomontmorillonite under hydrate conditions are larger than those on the original montmorillonite. In organomontmorillonite, HDTMA incorporation increase the interaction tendency between sorbate and sorption sites and reduces the competition from water.[5] With the increase of RH, the sorption of organic vapors into the exchanged organic cations play a important role in the organomontmorillonites.

LSER Approach. The observed sorption equilibrium coefficient data under three RHs were regressed against five solvation parameters of the probe solutes shown in Table 1. Although the sorption equilibrium coefficients of two compounds were not obtained under dry conditions, other data points more than three times the number of descriptors. The LSERs for three different levels of relative humidity are given as the following equations:

For low relative humidity (~ 0 % RH),

$$\begin{aligned}\log K_d = &(-0.929 \pm 0.44)E + (1.64 \pm 0.41)S \\ &+ (3.13 \pm 0.68)A + (3.93 \pm 0.50)B \\ &+ (1.25 \pm 0.14)L + (-3.76 \pm 0.43)\end{aligned}$$

$$R^2 = 0.931, \quad SD = 0.248, \quad F = 37.9, \quad n = 20 \qquad (2)$$

For ambient relative humidity (~ 55 % RH),

$$\begin{aligned}\log K_d = &(-1.23 \pm 0.45)E + (1.97 \pm 0.42)S \\ &+ (3.06 \pm 0.68)A + (2.09 \pm 0.46)B \\ &+ (0.863 \pm 0.14)L + (-3.64 \pm 0.40)\end{aligned}$$

$$R^2 = 0.895, \quad SD = 0.257, \quad F = 27.1, \quad n = 22 \qquad (3)$$

For high relative humidity (~ 90 % RH),

$$\begin{aligned}\log K_d = &(-1.12 \pm 0.48)E + (1.62 \pm 0.45)S \\ &+ (3.47 \pm 0.72)A + (1.7 \pm 0.49)B \\ &+ (0.667 \pm 0.14)L + (-3.43 \pm 0.43)\end{aligned}$$

$$R^2 = 0.869, \quad SD = 0.274, \quad F = 21.2, \quad n = 22 \qquad (4)$$

where R^2 is the coefficient of determination, SD is the standard deviation of the regression, *F* is the Fisher *F*-statistic, and *n* is the number of samples.

The relatively higher sample decisive coefficients R^2 mean satisfactory goodness of these fittings. The analyses of variances were also performed for the regression significance test of the equations by the *F*-test. The fact that *F* values are greater than $F_{0.01}(5, 14)$ for the dry condition or $F_{0.01}(5, 16)$ for the hydrated condition and *p* values of significance are close to zero indicates that the regression equations are highly significant. To check for possible chance correlations, the observed sorption equilibrium coefficient data under three RHs were randomly organized 100 times and regressed against these five solvation parameters of the probe solutes shown in Table 1. The random number correlations do not lead to significant values of R^2, so these LSER correlations are not by chance. These results demonstrate that the largest difference of sorption coefficients can be reliably referred to these five solvation parameters.

The physicochemical properties of the organomontmorillonite can be characterized through the constants in the LSER equations under different relative humidity. Under these three RHs, the positive *s*, *a*, *b*, and *l* values show that organomontmorillonite has the tendency to interact with VOCs through dipolarity/polarizability, hydrogen-bond, and dispersion/cavity formation interactions, respectively. The negative *e* values reveal that the organomontmorillonite is not favorable for the sorption of sorbates with π-/*n*-electron pairs. The significance of explicative variable seems to be hydrogen-bonding, which also has been found to be the most important contribution on adsorption of organic vapors to natural mineral surfaces.[30] Furthermore, the suppression effect from π-/*n*-electron pairs (relating to constant *e*) increases at both 50 % and 90 % RH. The *a* value increases at 90 % RH, suggesting the enhanced importance of hydrogen-bond basicity on the organomontmorillonite only when the surface of organomontmorillonite is entirely covered with water molecules. The declining *b* and *l* value with increasing relative humidity also indicates that the water layer inhibits the organomontmorillonite to form a cavity and provide dispersion and hydrogen-bond acidity interactions for VOCs.

The relative interaction abilities of organomontmorillonite with VOC molecules at ~0 % RH generally follow the order dispersion > dipolarity/polarizability > hydrogen-bond acidity > hydrogen-bond basicity > π-/n-electron interaction (data not shown). Compared to the relative interaction abilities of montmorillonite with VOC molecules at ~0 % RH,[28] the interaction results from dispersion and hydrogen bonds obviously increase in organomontmorillonite; the interaction results from dipolarity/polarizability increase slightly; and the suppression effect results from π-/n-electron interaction are reduced. Furthermore, under hydrated conditions (data not shown), the relative interaction abilities of organomontmorillonite with VOCs molecules generally follow a similar order of dispersion > dipolarity/polarizability > hydrogen-bond basicity > hydrogen-bond acidity > π-/n-electron interaction. However, for some polar compounds at hydrated conditions, the dominant interactions change to hydrogen-bond interactions instead of dispersion. Compared to the relative interaction abilities at these two RHs, these interactions do not change a lot except that dispersion interaction obviously decreases. However, compared to the relative interaction abilities at these three RHs with montmorillonite,[28] the decrease magnitude of dispersion in the organomontmorillonite is less than that in only montmorillonite because of the increased contribution of the incorporated HDTMA in inorganic clay.

■ CONCLUSIONS

The sorption equilibrium and mechanisms of VOCs with HDTMA modified organomontmorillonite under different levels of relative humidity were studied and evaluated via a LSER approach. The sorption coefficients of all tested compounds decreased as the relative humidity increased. Furthermore, due to the decrease of surface area after modification with HDTMA, the sorption coefficients in the organomontmorillonite are smaller than those for montmorillonite under dry conditions. For hydrophobic compounds, sorption coefficients in the organomontmorillonite are higher than those in montmorillonite under hydrated conditions, indicating the partition of these compounds into the exchanged organic cations in the organomontmorillonite. Surface adsorption on the organomontmorillonite surface and the partition into the incorporated HDTMA in organomontmorillonite both play roles on the sorption process. The LSERs can further characterize surface properties of organomontmorillonite in terms of molecular interactions under different relative humidities. In general, the dispersion interaction is the predominant molecular force for the sorption of most VOC vapors in organomontmorillonite; unless particularly strong hydrogen-bonding and/or dipolarity/polarizability interactions take place between VOCs and organomontmorillonite, the π-/n-electron interactions make a negative contribution for all VOCs. However, with the increase of relative humidity, the dominant interactions for some polar compounds change to hydrogen-bond interactions instead of dispersion. These LSER equations can be used to predict the sorption ability of VOCs on organomontmorillonite and to potentially apply them in the removal treatments of VOCs.

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