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Characterization of Adsorption Mechanisms of Volatile Organic Compounds with Montmorillonite at Different Levels of Relative Humidity via a Linear Solvation Energy Relationship Approach

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The sorption mechanisms of volatile organic compounds (VOCs) with montmorillonite, a clay, need to be studied adequately to predict the fate of VOCs in the environment and to fully employ the sorption characteristics of clays to control VOC pollution. The sorption of VOCs as vapors to a typical montmorillonite, STx-1, at different levels of relative humidity were characterized using a linear solvation energy relationship (LSER). The fitted LSER equation was obtained by a multiple regression of the partition coefficients of 22 probe chemicals against their solvation parameters. The coefficients of the five-parameter LSER equations show that montmorillonite interacts with VOC molecules mainly through dispersion, partly through dipolarity/polarizability and hydrogen bonds, and with negatively π-/n-electron pair interaction under dry conditions. With an increase of relative humidity, hydrated montmorillonite behaves both as a hydrogen-bond donor (HBD) and hydrogen-bond acceptor (HBA) and interacts with chemicals by dispersion interactions and dipolarity/polarizability and also with negatively π-/n-electron pair interaction. The related terms in LSERs suggest that the potential factors governing the sorption of VOCs are dispersion interactions on dry montmorillonite that become hydrogen-bond acidity and hydrogen-bond basicity interactions for hydrated montmorillonite. The dispersion interaction is recognized to be the predominant parameter for most VOCs, whereas the contributions of the other parameters depend on specific VOCs. The derived LSER equations successfully fitted the sorption coefficients of VOCs on montmorillonite. The LSER approach coupled with inverse gas chromatography (IGC) has been used to characterize the sorption mechanism of VOCs with clay under different conditions.

Introduction

The sorption of organic compounds to mineral surfaces is one of the key processes in determining the transport, fate, and the effect of organic pollutants in the environment.[1−4] The role of sorption is also important for the proper design of filters and linears constructed using clays (especially air filters[5]).[6] Furthermore, vapor-phase sorption is one of the most important factors governing the mobility and distribution of volatile organic compounds (VOCs) in the subsurface. In soils, the sorption of VOCs from the aqueous phase is usually dominated by organic matter, but mineral surfaces are important for adsorption from the gas phase under dry conditions.[7] The understanding of the sorption of organic vapors on clays under different relative humidities is of critical importance to improve our ability to estimate risks and to design cleanup procedures.

Humidity plays a key role on the sorption of VOCs on clay minerals. Minerals generally show decreasing sorption of VOCs with increasing relative humidity.[2,8−10] Pennell et al.[11] summarized the sorption mechanisms of organic vapors to mineral surfaces including adsorption on mineral surfaces, adsorption at the gas−liquid interface, and dissolution into adsorbed water. The adsorption of VOCs to quartz and different minerals has been reported.[3,12] The influence of important variables (e.g., temperature and humidity) on the sorption of VOCs has been evaluated.[10] However, the molecular interactions between organic vapors and clays under different relative humidities have not yet been conclusively studied, especially for the expandable 2:1 layer silicate clay, montmorillonite, which is particularly important because of its wide distribution, high surface area, and cation exchange capacity as well as surface reactivity.[13]

To improve our fundamental understanding of such sorption phenomena, as well as develop practical means for estimating sorption coefficients of VOCs on montmorillonite, we use the quantitative structure−activity relationships. The linear solvation energy relationship (LSER) approach developed by Abraham et al.[14−16] is an effective means of elucidating the sorption mechanism of VOCs with sorbents.[16−19] The contribution of each interaction to the overall process can be related to the relative magnitudes of the terms in the LSER.[16,17]

In this study, we attempted to ascertain the relationships between intermolecular interactions and sorption capacities of VOCs with a representative clay, montmorillonite, at different levels of relative humidity (RH) by the LSER approach. These better understandings and resultant LSERs are expected to provide an improved technical base for the prediction of VOC sorption and the design of effective sorbents of VOC control.

Experimental Section

Montmorillonite. The clay mineral used in this study was montmorillonite, STx-1, obtained from the Clay Minerals Society Source Clays Repository (MO, USA). The montmorillonite had a cation exchange capacity (CEC) of 84.4 meq/100 g. The specific surface area was determined on the basis of nitrogen adsorption at 77 K by an ASAP2100 analyzer (Micrometrics Instrument Corporation, USA). The basal spacings of montmorillonite at three different levels of relative humidity

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Table 1. Octanol−Water Partition Constant K_{ow} and Molecular Descriptors E, S, A, B, and L 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 given for 25 °C and were obtained from Schwarzenbach et al.[30] [b] Data obtained from Abraham.[14]

(~ 0 %, ~ 50 %, and ~ 100 % RH) 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 obtained 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 selected VOCs are listed in Table 1. The cross-correlations between solvation parameters have been calculated by using the SAS software, and we verified that the values of all solute descriptors are independent. All chemicals were of purity grade greater than 95 % and were used as received. In our preliminary experiments, no visible peaks of impurities were observed during inverse gas chromatography (IGC) for all solutes.

Sorption Experiments. The measurement of the sorption equilibrium coefficients of these selected VOCs was carried out using IGC. This chromatographic method has been widely used for studying sorption coefficients for gaseous sorption at low concentrations,[3,17,20−24] thus enhancing the environmental relevance of the results. The equilibrium sorption isotherm for a compound is linear at low concentrations, and the equilibrium sorption behavior can be described by a sorption coefficient.[25] In this chromatographic method, the investigated montmorillonite is used as the stationary phase. The montmorillonite was placed into a 10 cm (length) stainless steel column (o.d. 1/8 in.). The two ends of the column were plugged with silane-treated glass wool. The column filled with montmorillonite was mounted into the injector and the detector in a gas chromatograph (GC). While a substance is injected into this column, the retention observed is a measure of its sorption behavior. When the sorption equilibrium process is reversible and the injected concentrations are sufficiently low to achieve a linear isotherm, the following relationship exists:[20]

$$K_d = (t_r - t_o)\frac{F_c}{m} \tag{1}$$

where K_d is the equilibrium sorption coefficient for a compound between the montmorillonite and the gas phase (mg·g^{-1})/(mg·L^{-1}), t_r is the retention time of the compound (min), t_o is the retention time of the nonsorbing gas methane (min), F_c is the corrected flow rate of the carrier gas (mL·min^{-1}), and m is the mass of montmorillonite packed in the column (mg). The correction of the flow rate followed the relationship below:[20]

$$F_c = F_m \cdot \frac{3}{2} \frac{\left(\frac{P_i}{P_o}\right)^2 - 1}{\left(\frac{P_i}{P_o}\right)^3 - 1} \tag{2}$$

where F_m is the flow rate of the carrier gas (mL·min^{-1}), P_i is the inlet pressure of the column (bar), and P_o is the outlet pressure of the column (bar). The apparatus used for measuring sorption of VOCs on montmorillonite at different levels of relative humidity in this study is shown in Figure 1. Nitrogen gas (purity of 99.995 %) was used as carrier gas. The gas flow rate was regulated by a mass flow controller. For montmorillonite under humid conditions, nitrogen gas flows through a gas-washing bottle containing pure water. By controlling the flow rates, the desired relative humidity of carrier gas can be achieved. A China chromatograph 8700F (Taiwan) equipped with flame ionization detector was used in this study. The carrier gas flow rate was measured by a soap bubble meter, and the maximum rate was less than 30 mL·min^{-1}. The inlet carrier gas pressure and the outlet gas pressure were measured with a manometer. The packed column was conditioned at 443 K for at least 48 h. The temperatures of the injector and the detector were set at (393 and 453) K, respectively. The chemical probe was taken with a gastight syringe from the headspace of its pure chemical and injected in the gaseous state. The injected volumes for all chemicals were 100 μL. The maximum error for mean retention time values of three to five measurements was 5 %. The detector was set to the highest sensitivity, and

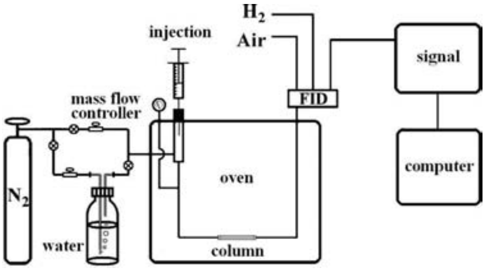

Figure 1. A schematic experimental setting of IGC.

the data were collected with a chromatography data handling system (Peak-ABC, Great Tide Instrument Company). The equilibrium sorption coefficients can be obtained from eqs 1 and 2.[3,17,24,26]

LSER Fit. The typical LSER equation is as follows:[14]

$$\log \mathrm{SP} = c + eE + sS + aA + bB + lL \qquad (3)$$

Each term in eq 3 represents a type of contribution among various intermolecular interactions. For explicative variables (solvation parameters), E is the excess molar refractivity of the sorbate that reflects the ability of the sorbate to interact with a sorbent through π-/n-electron pairs. S is the dipolarity/polarizability 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. The coefficients in eq 3 characterize the physicochemical properties of the sorbent material. The a and b coefficients, being complementary to the chemical hydrogen-bond acidity and basicity, represent the 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, arises from the method of multiple linear regression used to obtain eq 3.

In eq 3, log SP is the dependent variable, where SP refers to some sorbate properties on a given sorbent. For our gas−solid sorption process of VOCs with montmorillonite, SP can be the partition coefficient, K_d, of the sorbate between the gas and the solid phases. The magnitude of K_d illustrates the sorption capacity of a given sorbate to a sorbent. K_d can be defined according to eq 4

$$K_d = (q/C_g) \qquad C_g \rightarrow 0 \qquad (4)$$

where q is sorption capacity ($\mathrm{mg \cdot g^{-1}}$) and C_g is the concentration of the sorbate in the gas phase ($\mathrm{mg \cdot mL^{-1}}$).

The above-mentioned solvation parameters are derived from physicochemical and thermodynamic measurements. These parameters are available for hundreds of organic compounds.[15,27,28] The obtained equilibrium sorption coefficients K_d in this study are regressed against all solvation parameters for the selected VOCs shown in Table 1 by multiple linear regression analysis using Microsoft Office Excel 2003.[16] The coefficients c, e, s, a, b, and l were fitted to capture the differential interactions of the set of compounds interacting with the gas phase versus those interacting with the montmorillonite solid phase. The statistical analyses were also confirmed by using the SAS software. The prediction of sum of squares (PRESS), the statistical parameter for the predictive ability, was obtained from the SAS software to calculate the predictive standard deviation (PSD).

Table 2. Equilibrium Sorption Coefficients, K_d, of VOCs on Montmorillonite at Different Levels of Relative Humidity at 303 K

	K_d ($\mathrm{(mg \cdot g^{-1})/(mg \cdot L^{-1})}$)		
compound	~ 0 % RH	~ 55 % RH	~ 90 % RH
n-pentane	1.2 ± 0.090	0.015 ± 0.0017	0.0056 ± 0.0010
n-hexane	4.2 ± 0.21	0.027 ± 0.00	0.0071 ± 0.0012
n-heptane	11 ± 0.81	0.076 ± 0.00073	0.012 ± 0.00098
n-octane		0.22 ± 0.00044	0.024 ± 0.00066
2,2,4-trimethylpentane	6.4 ± 0.052	0.088 ± 0.0017	0.016 ± 0.0030
cyclohexane	2.0 ± 0.019	0.029 ± 0.0010	0.012 ± 0.0018
benzene	6.6 ± 0.30	0.15 ± 0.020	0.017 ± 0.0023
toluene		0.31 ± 0.0015	0.031 ± 0.0010
ethylbenzene		0.71 ± 0.019	0.068 ± 0.0014
dichloromethane	1.6 ± 0.11	0.041 ± 0.0013	0.0085 ± 0.0012
trichloromethane	3.2 ± 0.14	0.063 ± 0.0018	0.011 ± 0.00047
tetrachloromethane	2.2 ± 0.30	0.038 ± 0.0014	0.0084 ± 0.0011
1,1-dichloroethylene	1.4 ± 0.047	0.018 ± 0.0025	0.0068 ± 0.00085
trichloroethylene	9.2 ± 0.41	0.059 ± 0.00029	0.013 ± 0.0011
tetrachloroethylene	18 ± 1.6	0.11 ± 0.0012	0.026 ± 0.0030
methanol		3.5 ± 0.030	1.4 ± 0.052
ethanol		6.7 ± 0.049	1.1 ± 0.084
2-propanol		9.5 ± 0.43	0.92 ± 0.014
diethyl ether	5.7 ± 0.70	1.1 ± 0.20	0.030 ± 0.0049
acetone	16 ± 1.0	3.2 ± 0.44	0.36 ± 0.0076
ethyl acetate		4.6 ± 0.61	0.17 ± 0.0021
acetonitrile	8.6 ± 1.3	2.0 ± 0.13	0.50 ± 0.015

Results and Discussion

Results from Montmorillonite. The specific surface area of this clay mineral was determined by nitrogen adsorption, yielding a value of 80.1 $\mathrm{m^2 \cdot g^{-1}}$. Under different relative humidities, water molecules adsorb on the surface of montmorillonite and into its interlayer. The basal spacing of montmorillonite increased from 1.17 nm at 0 % RH to 1.54 nm at 50 % RH and then to 1.89 nm at 100 % RH. Our XRD analysis results showed that the increment of d-spacing between two layers of montmorillonite increased from (0.37 to 0.72) nm with increasing relative humidity from 50 % to 100 %. With increasing relative humidity, more water molecules entered and swelled the interlayer of montmorillonite.

Effect of Relative Humidity on Sorption. The sorption equilibrium coefficients (K_d) of 22 VOCs on montmorillonite at different levels of relative humidity at 303 K are obtained from the IGC method and are shown in Table 2. The K_d value of one compound significantly decreases with increasing relative humidity. The K_d values for nonpolar compounds under 55 % RH decline 40 to 160 times as compared to those under 0 % RH. For polar compounds, the K_d values only decrease around five-fold. The declining trend increased with the increase of relative humidity. For example, the average K_d for n-heptane under 90 % RH decreased 910 times as compared to that under 0 % RH. This agrees with the results presented by Chiou and Kile[1] and Shih and Wu,[7] who have indicated that inorganic matter has a strong adsorption capacity under dry conditions but becomes a weak adsorbent in wet conditions. Although the expandable montmorillonite swells, no sorption on the internal surface was observed at a higher moisture content.[12] It could result from a rigid water structure in the crystal lattice of montmorillonite caused by hydrogen bonds between water molecules and oxygen atoms of the crystal sheets of montmorillonite.[12] Goss and Eisenreich[10] also indicated that the surface of clays is completely covered by at least one molecular layer of water and the sorption behavior thus is dominated by sorption onto the adsorbed water film. Water behaves both as a hydrogen-bond donor (HBD) and a hydrogen-bond acceptor (HBA) when it sorbs on clays. So, water suppresses the sorption of organic compounds onto montmorillonite by competing for hydrogen-bond active sites of clays with these organic compounds.

Five-Parameter LSERs. The observed sorption equilibrium coefficient data were regressed against five solvation parameters of the probe solutes shown in Table 1 by multiple linear regressions to generate three LSERs. Although some sorption equilibrium coefficients were not obtained under dry conditions, the data points are equal to three times the number of descriptors. Because of the limit of chemical properties and the experimental setting, the sorption data points for LSER are around three times the number of independent variables such as 14 chemicals[16] and 22 chemicals.[17] The LSERs for three different levels of relative humidity are given as the following equations.

For a low relative humidity (~ 0 % RH),

$$\begin{gathered}\log K_\mathrm{d} = (-1.23 \pm 0.365)E + (1.33 \pm 0.399)S + \\ (0.239 \pm 1.11)A + (1.62 \pm 0.445)B + \\ (0.948 \pm 0.119)L + (-2.05 \pm 0.327) \qquad (5) \\ R^2 = 0.900,\ \mathrm{SD} = 0.152,\ F = 16.1,\ \mathrm{PRESS} = 0.645, \\ \mathrm{PSD} = 0.803,\ n = 15\end{gathered}$$

For an ambient relative humidity (~ 55 % RH),

$$\begin{gathered}\log K_\mathrm{d} = (-1.22 \pm 0.251)E + (1.19 \pm 0.234)S + \\ (2.32 \pm 0.380)A + (4.17 \pm 0.258)B + \\ (0.734 \pm 0.759)L + (-3.45 \pm 0.222) \qquad (6) \\ R^2 = 0.981,\ \mathrm{SD} = 0.144,\ F = 166,\ \mathrm{PRESS} = 0.687, \\ \mathrm{PSD} = 0.829,\ n = 22\end{gathered}$$

For a high relative humidity (~ 90 % RH),

$$\begin{gathered}\log K_d = (-0.990 \pm 0.489)E + (1.12 \pm 0.456)S + \\ (3.18 \pm 0.741)A + (2.51 \pm 0.503)B + \\ (0.446 \pm 0.148)L + (-3.32 \pm 0.433) \qquad (7) \\ R^2 = 0.905,\ \mathrm{SD} = 0.280,\ F = 30.3,\ \mathrm{PRESS} = 2.900, \\ \mathrm{PSD} = 1.703,\ n = 22\end{gathered}$$

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 specimens.

The relatively higher sample decisive coefficients R^2 indicate a 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 $F_{0.01}(5,9)$ for the dry condition or $F_{0.01}(5,16)$ for the hydrated condition and p values of significance are close to zero ($2.93 \cdot 10^{-4}$, $3.37 \cdot 10^{-13}$, and $1.27 \cdot 10^{-7}$, respectively) indicates that the regression equations are highly significant. The small values of PRESS and PSD also indicated the predictive ability of these equations. The $\log K_\mathrm{d}$ values estimated using these LSERs are plotted versus the experimental data in Figure 2. These results demonstrate that most differences of $\log K_\mathrm{d}$ can be reliably referred to these five solvation parameters.

The physicochemical properties of the adsorbent can be characterized through the constants in the LSER equations. According to the results of the significance test for the regression coefficients at the dry condition (~ 0 % RH), the explicative variable of A (relating to constant a) is statistically nonsignificant, suggesting that hydrogen-bond basicity for montmorillonite is negligible. For montmorillonite at the dry condition, the negative e accounts for the fact that π-/n-electron interaction has a negative contribution for the sorption of VOCs on montmorillonite. The positive s, b, and l values show that montmorillonite has the tendency to interact with VOCs through dipolarity/polarizability interaction, hydrogen-bond acidity, and dispersion/cavity formation interaction, respectively. The relative interaction abilities of montmorillonite with VOC molecules at ~ 0 % RH can be determined by the significance of explicative variables, following the order hydrogen-bond basicity > π-/n-electron interaction > dispersion > dipolarity/polarizability. The hydrogen-bond basicity also has been found to be the most important contribution on the adsorption of organic vapors to natural mineral surfaces.[19]

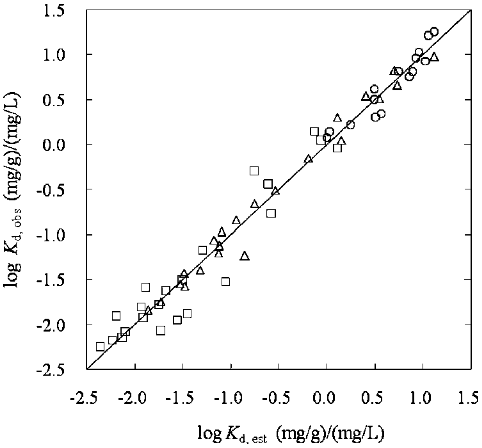

Figure 2. Overall correlation of the sorption coefficients estimated using these LSER eqs 5 to 7 versus the measured values. ○, ~ 0 % RH; △, ~ 55 % RH; □, ~ 90 % RH.

Under hydrated conditions (~ 55 % RH and ~ 90 % RH), the negative e values reveal that π-/n-electron pairs contribute to a decrease in the sorption of VOCs on montmorillonite. The positive s, a, b, and l values show that each corresponding interaction promotes the VOC sorption on montmorillonite at hydrated conditions. In contrast to dry conditions, the much greater a value for hydrated montmorillonite suggests the enhanced importance of hydrogen-bond basicity when the mineral surface is entirely covered with water molecules. The declining l value with increasing relative humidity indicates that the water layer inhibits cavity formation and dispersion interactions. The irregularly changing b values with increasing relative humidity imply that the hydrogen-bond acidity interaction of montmorillonite becomes more significant as the mineral surface is covered with water molecules at ~ 55 % RH and then becomes a little weaker with the increase of adsorbed water molecules to around the saturated condition. The relative interaction abilities of montmorillonite with VOC molecules at ~ 55 % RH follow the order hydrogen-bond acidity > hydrogen-bond basicity > dipolarity/polarizability > dispersion. In addition, the relative interactions at ~ 90 % RH follow the order hydrogen-bond basicity > hydrogen-bond acidity > dipolarity/polarizability > dispersion.

By all accounts, the dispersion interaction is the predominant molecular force for the sorption of most VOCs from the gas phase on montmorillonite; unless particularly strong hydrogen-bonding and/or dipolarity/polarizability interactions take place between VOCs and montmorillonite, the π-/n-electron interactions make a negative contribution for all VOCs. Apparently π-/n-electron interactions depend on whether the solute has π-/n-electron pairs or not. The hydrogen-bond interaction depends on whether the solute is the HBD or HBA.[29] Furthermore, under hydrated conditions, the three major interactions governing water sorption on clays are hydrogen-bond basicity > hydrogen-bond acidity > dispersion. Sorbed water molecules behave as both HBD and HBA, which result in the different sorption interactions of VOCs onto montmorillonite under hydrated conditions as compared to dry conditions.

Conclusions

The LSER approach coupled with IGC was used to characterize the sorption mechanisms of VOCs with clay under different levels of relative humidity. The coefficients of the five-parameter LSER equation indicated that montmorillonite is a sorbent which can mainly interact with VOC molecules by dispersion interactions, partly through dipolarity/polarizability, and behaves as a HBD with a negative π-/n-electron pair interaction. The related terms in five-parameter LSERs suggest that the potential factors governing the sorption of VOCs on montmorillonite are dispersion interactions, hydrogen-bond basicity interactions, dipolarity/polarizability, and π-/n-electron interactions. The dispersion interaction is recognized to be the predominant parameter under dry conditions, whereas the contributions of the other parameters change as the relative humidity increased. The sorption coefficients of all tested compounds decreased rapidly as the relative humidity increased. With the increase of relative humidity, the dominant interactions for polar compounds change to hydrogen-bond interactions instead of dispersion. The LSER approach can characterize surface properties of montmorillonite in terms of molecular interactions under different relative humidities. This characterization allows the prediction of the sorption behavior of VOCs on montmorillonite at different relative humidities and the potential application of this in the design of VOC control.

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