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Sorption interactions of volatile organic compounds with organoclays under different humidities by using linear solvation energy relationships

Yu-Huei Peng · Shih-Min Chou · Yang-Hsin Shih

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Abstract Organoclays are usually used as sorbents to reduce the spread of organic compounds and to remove them at contaminated sites. The sorption equilibrium and the mechanisms of volatile organic compounds (VOCs) on organoclays under different humidities are helpful for developing efficient organoclays and for predicting the fate of VOCs in the environment. In this study, the organoclay was synthesized through exchanging inorganic cations by hexadecyltrimethyl ammonium (HDTMA) into montmorillonite, resulting in 12 % of organic content. The surface area of organoclay was smaller than the unmodified clay due to the incorporation of organic cations into the interlayer. Both adsorption on organoclay surface and partition into the incorporated HDTMA in organoclay played roles on the sorption process. Compared the sorption coefficients in montmorillonite and different modified clays, the incorporated organic cations overcame the inhibition effect of hydrophilic surface of clay on the sorption process of hydrophobic organic compounds from water.

The sorption coefficients of VOC vapors on organoclay 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 showed that high HDTMA-content montmorillonite interacts with VOC molecules mainly through dispersion, partly through dipolarity/polarizability and hydrogen-bonds as well as 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, similar with the lower level modified clay. The derived LSER equations successfully fit the sorption coefficients of VOCs on organoclay under different humidity conditions. It is helpful to design better toxic vapor removal strategy and evaluate the fate of organic contaminants in the environment.

Keywords Organoclay · Volatile organic compounds · Sorption · Inverse gas chromatography · Linear solvation energy relationship

1 Introduction

Clay minerals bear nano-sized structure and contain exchangeable inorganic cations in the interlayer space. They are abundant in nature and are widely used in a variety of industries. Montmorillonite is the most commonly used clay minerals, because its cation exchange ability, swelling properties, surface area and adsorption/absorption efficiency are relative higher than others. In addition, through exchanging the interlayer cations with organocations, the basal spacing between layers increases and new sorption sites of clays are exposed. The modified montmorillonites, i.e. organoclays, possess more hydrophobicity and exhibit larger capacity for organic compounds. Therefore, organoclay have been used as efficient sorbents to remove organic pollutants in different applications (Brixie and Boyd 1994; Juang et al. 2007; Wagner et al. 1994).

The sorption of volatile organic compounds (VOCs) into organic–inorganic complex governs their transport, fate and effect in the environment (Chiou and Kile 1998; Goss 1992; Johnson et al. 2007; Shih and Wu 2004). Sorption also plays the major role in the function of organoclay-made filters

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Y.-H. Peng · S.-M. Chou · Y.-H. Shih (✉)
Department of Agricultural Chemistry, National Taiwan University, Taipei 106, Taiwan
e-mail: yhs@ntu.edu.tw

(Zhu and Su 2002) and linears to remove organic pollutants (Borisover et al. 2008). The more we understand the sorptive characteristics of organocalys, the more is helpful for designing sorbent with larger sorption capacity or developing lower cost remediation methods. It has been proposed that the hydrophobic siloxane surface of clay mineral and the alkyl chain aggregates formed by cationic surfactants played important roles in the sorption of VOCs (Chen et al. 2005; Sheng et al. 1996). Therefore, the type of surfactant (Zhao and Burns 2012), surfactant loading level (Chen et al. 2005), and the surfactant packing density (Zhu and Zhu 2008) all influence the sorption efficiency. Besides, humidity (Borisover et al. 2008; Kukkadapu and Boyd 1995; Shih et al. 2011), the basal spacing of the organoclay (Sheng et al. 1996), and the ratio of intercalated surfactants (Wang et al. 2010) also affect the sorption capacity. Because the sorption mechanism is complicated, the best condition for preparing the organoclays and the ways to analyze their sorption behabiors are still under investigation.

In order to understand the sorption mechanism of VOCs in organoclays, the linear solvation energy relationship (LSER) approach was used. This quantitative structure–activity relationships was developed by Abraham et al. (Abraham 1993; Abraham et al. 2004) and has been applied to explore the sorptive characteristics of VOCs on various sorbates (Burg et al. 2002; Nguyen et al. 2005; Shih and Chou 2010; Shih et al. 2011; Shih and Gschwend 2009; Tian et al. 2004). The surface properties of sorbents could be described by various coefficients obtained from the multiple regression of sorption coefficients and solvation parameters of compounds. The contribution of different interactions to the whole event can be related to the relative magnitudes of the terms in the LSER.

In this study, the sorption capacities of VOCs on organoclay, the hexadecyltrimethyl ammonium (HDTMA) modified montmorillonite, at different levels of RH were measured. The relationship between intermolecular interactions of VOCs with the organoclay at different levels of RH was investigated by the LSER approach. Finally, the sorption characteristics was compared with mineral clay and organoclay with lower carbon content. These results provide further insight to a fundamental understanding of the sorption of VOCs in organo-inorganic phases and offer an improved technical base for predicting and designing organoclay for VOCs removal.

2 Experimental methods

2.1 Materials

The montmorillonite, STx-1, was purchased from the Clay Minerals Society Source Clays Repository (Columbia, MO, USA). The basal spacing and the surface area of the clay mineral are 1.17 nm and 80.1 $m^2\,g^{-1}$, respectively. The cation exchange capacity (CEC) is 84.4 meq/100 g (Shih and Chou 2010). The C, N, H, and O element contents are 0.01 %, 0.05 %, 2 % and 17 %, respectively. A total of 22 VOCs, including nine main classes of common VOCs, were chosen as the chemical probes. Toluene, *n*-pentane, *n*-octane, 1,1-dichloroethylene, trichloroethylene, tetrachloroethylene, 2,2,4-trimethylpentane, ethylbenzene and 2-propanol were obtained 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 obtained from Merck. Acetone was purchase from Mallinckrodt Baker. Diethyl ether was purchased from Riedel-de Haën. The solvation parameters of the selected VOCs were described previously and their independences have been verified (Shih et al. 2011). All chemicals utilized were of purity grade greater than 95 % and there were no visible peaks of impurities for any solutes via our preliminary IGC analysis (Shih and Chou 2010).

2.2 Synthesis and characterization of organoclays

The procedure for preparing the organoclay is the same as described previously (Shih et al. 2011). The contents of C, N, O, and H were measured by elemental analyzer (Heraeus CHN-OS Rapid F002). With an ASAP2100 analyzer (Micrometrics Instrument Corporation, Norcross, GA, USA), the Brunauer–Emmett–Teller (BET) surface area and pore size were determined to be 77 K on the basis of nitrogen adsorption. Basal spacings at different humidity were determined by Synchrotron X-ray diffraction (XRD) in the National Synchrotron Radiation Research Center, Taiwan.

2.3 Procedures of sorption

The measurement of the sorption equilibrium coefficients of the selected VOCs was carried out by IGC as previous described (Shih and Chou 2010; Shih and Li 2008).

2.4 The LSER Approach

A widely accepted LSER model is given as

$$\log K_d = c + eE + sS + aA + bB + lL \qquad (1)$$

where the $\log K_d$ refers to the sorbate properties on a given sorbent. Each term in the right side represents a type of contribution among various intermolecular interactions. For the solute-dependent Abraham descriptors, E, S, A and B are which are related to the ability of the sorbate to interact with a sorbent through π-/n-electron pairs, dipolarity/polarizing ability, hydrogen-bond donating ability (acidity) and hydrogen-bond acceptin ability (basicity), respectively. L is the Ostwald solubility coefficient on hexadecane at 298 K, accounting for the dispersion/ cavity formation. The coefficients e, s, a, b, l , representing the complementory interaction abilities of the sorbent phase. The constant, c, is derived from the method of multiple linear regressions used to find (1) (Abraham 1993).

The above solvation parameters mentioned are derived from physicochemical and thermodynamic measurements and their values for hundreds of organic compounds are available (Abraham et al. 1990, 2000, 2004; Hickey and Passino-Reader 1991). The obtained sorption coefficients of the selected VOCs from IGC in this study were regressed against the solvation parameters (Shih and Chou 2010) by multiple linear regression analysis using Microsoft Excel 2003.

3 Results and discussions

3.1 Characteristics of organoclays

The basic properties of our synthesized organoclay are list in Table 1. The C, N, H, and O element contents are 12 %, 0.79 %, 3.6 %, 7.7 %, respectively. Compared to the original element contents in montmorillonite, the increasing percentage of C, N and H supports the incorporation of HDTMA into montmorillonite and indicates that 65 % of CEC is replaced by HDTMA.

The nitrogen sorption isotherms at 77.3 K for clay and organoclay are presented in Fig. 1. According to the classification, the isotherm type for montmorillonite (Fig. 1a) and the orgonoclay (Fig. 1b) belong to type II (Sing et al. 1985). The sorption amount is little when the relative nitrogen pressure is low. However, due to the interaction between nitrogen, the sorption amount increases dramatically with the relative nitrogen pressure. The desorption isotherm does not overlap with the adsorption isotherm under higher nitrogen concentration, indicating that hysteresis occurs in pores with long-and-thin shape.

Table 1 Basic properties of the organoclay

Properties	
Elemental contents (%)	
C	12
N	0.79
H	3.6
O	7.7
BET surface area ($m^2\ g^{-1}$)	37.5
Average pore diameter (Å)	100.4
Pore volume of mesopore and macropore[a] ($cm^3\ g^{-1}$)	0.145

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

The surface area of the organoclay is 37.5 $m^2\ g^{-1}$ (Table 1), below the half of value for the surface area of the original montmorillonite (80.1 $m^2\ g^{-1}$). As compared to surface area of the original montmorillonite and organoclay with 6.3 % carbon content (49.7 $m^2\ g^{-1}$), the reduced degree in the surface area was proportional to the carbon content of the modified clays. The relationship between pore volume and pore diameter in clay and organoclay are shown in Fig. 2. In montmorillonite, the most contribution for pore volume is from micropores (0.00401 $cm^3\ g^{-1}\ Å^{-1}$), whose diameter is below 17 Å (Fig. 2a). In the organocaly, the micropores are not detectable. The most contribution for pore volume is from mesopores in the diameter of 30–40 Å (Fig. 2b). Although the average pore diameter in organoclay (100.4 Å, Table 1) is larger than that of the original montmorillonite (72.5 Å). The total pore volume for mesopore and macropore in organoclay (0.145 $cm^3\ g^{-1}$, Table 1) is less than that in the original montmorillonite (0.205 $cm^3\ g^{-1}$). These results indicates that the incorporation of HDTMA into montmorillonite shelters the adsorption surface of the clay, especially those pores in small diameter. A similar result is also observed for organo-bentonites modified by two quaternary ammomiun cations and organo-montmorillonite modified by HDTMA (Bartelt-Hunt et al. 2003; Shih et al. 2011). The lower surface area in organoclays with higher modifier

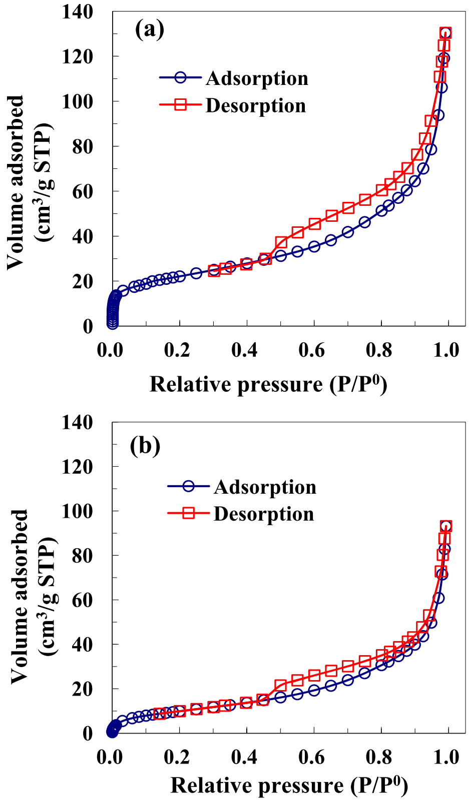

Fig. 1 Adsorption and desorption isotherms of nitrogen on (**a**) montmorillonite and (**b**) organoclay at 77.3 K

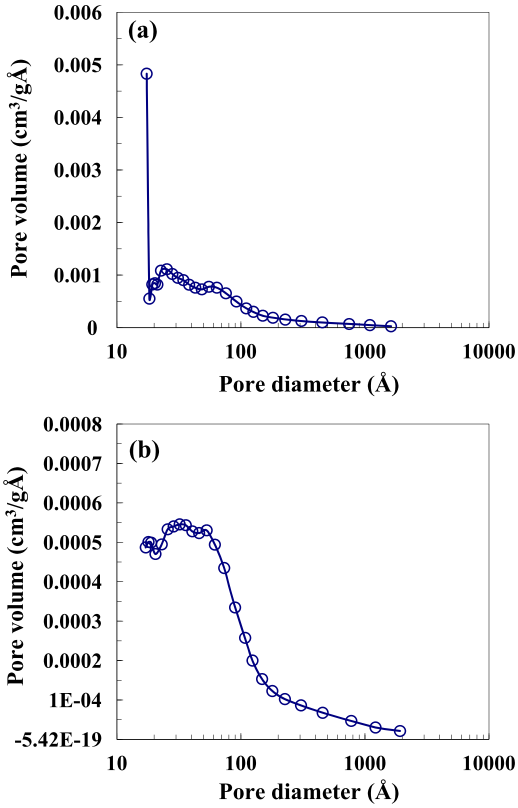

Fig. 2 Pore volume changes with pore diameter of (**a**) montmorillonite and (**b**) organoclay

Table 2 Basal spacing of the organoclay at different levels of relative humidity

Condition	Basal spacing$_{(d001)}$ (nm)
low RH (∼0 % RH)	1.75
ambient RH (∼50 % RH)	1.78
high RH (∼90 % RH)	2.29

content might due to the aggregation of particles and no internal surface area accessible to nitrogen gas (Jaynes and Vance 1996). Our results consistently indicate that the sheltered effect in organocalys was more obvious when more HDTMA is incorporated.

The basal spacing of the organoclay under different relative humidity is investigated by XRD (Table 2). The spacing increases from 1.75 nm at 0 % RH, to 1.78 nm at 50 % RH, and then to 2.29 nm at 90 % RH. Under 0 % RH, the d-spacing in organoclay is larger than that in the original montmorillonite (1.17 nm) or the organoclay with lower HDTMA content (Shih et al. 2011), suggesting the incorporation of HDTMA to the interlayer of montmorillonite. In addition, the d-spacing enlarges with the increasing of relative humidity: 0.03 nm under 50 % and 0.54 nm under 90 %. Even though some inorganic cations are replaced by HDTMA, water molecules still enters into the interlayer of organo-modified montmorillonite. The larger d-spacing under higher relative humidity reflects a larger amount of incorporated water.

3.2 Sorption equilibrium and the effect of relative humidity

The sorption equilibrium coefficients (K_d) of 22 VOCs on organoclay under different RHs were measured and were shown in Table 3. In general, the sorption equilibrium coefficients increase with the hydrophobicity (K_{ow}) of VOCs, indicating that organic vapor partition into the organoclay might play a role in the sorption process. This coincides with the conclusion that the HDTMA-modified montmorillonite is a powerful partition medium for uptaking VOCs (Boyd et al. 1988). Under the dry condition (0 % RH), the K_d values from organoclay are less than that from the original montmorillonite or the lower-modified organoclay (Shih and Chou 2010; Shih et al. 2011). The reason might due to the smaller surface area which is resulted from the incorporation of HDTMA into the clay, as what indicated by Goss that the adsorption abilities of clay minerals for VOCs are apparently determined by their surface areas (Goss 1993). While under ambient (55 %) and high (90 %) relative humidity, the K_d values from organoclay are more than that from the original montmorillonite and even more than that from the less-modified organoclay (Shih and Chou 2010; Shih et al. 2011), coincided with the enhanced sorption capability due to the incorporation of organic cations.

The K_d values for all chemical probes adsorbed on organoclay significantly decrease through the increasing of the relative humidity. The reduction rate is about 0.5 to 14 times when the relative humidity shifts from 0 % RH to 55 % RH. The suppression effect of water is not as huge as that on the original montmorillonite (4 to 164 times) and the suppression level is less than that on the clay mineral with lower HDTMA content (3 to 50 times) (Shih and Chou 2010; Shih et al. 2011). Although the reduction rate for most VOCs increases when the elevated humidity shifts from 55 % RH to 90 % RH, the organoclay still presented a better VOCs adsorption ability and could resist the suppression effect from water under the general atmosphere environment.

The adsorption capacities of soil or clay minerals become weaker in wet conditions as compared to dry conditions (Chiou and Kile 1998; Shih and Wu 2004). A rigid water structure built up by hydrogen bonds between water molecules and oxygen atoms of the crystal sheets might account for this observation (Goss 1993). Goss and Eisenreich also indicated that at least one molecular layer of water completely covering the surface of mineral surfaces could affect the sorption behavior of VOCs (Goss and Eisenreich 1996). The adsorption ability of organoclay with low HDTMA content is reduced through the elevation of humidity (Shih et

Table 3 Sorption coefficients K_d of VOCs on organoclay at different levels of relative humidity at 303 K

Compounds	K_d (mg g^{-1})/(mg L^{-1})		
	∼0 % RH	∼55 % RH	∼90 % RH
n-pentane	0.0409 ± 0.0025	0.0781 ± 0.0021	0.0134 ± 0.0076
n-hexane	0.172 ± 0.0037	0.185 ± 0.017	0.0379 ± 0.0034
n-heptane	0.784 ± 0.0042	0.512 ± 0.018	0.119 ± 0.00043
n-octane	2.99 ± 0.19	1.31 ± 0.0086	0.350 ± 0.0078
2,2,4-trimethylpentane	0.657 ± 0.084	0.458 ± 0.0083	0.131 ± 0.0027
cyclohexane	0.420 ± 0.024	0.304 ± 0.0051	0.0530 ± 0.0027
benzene	5.61 ± 0.13	0.805 ± 0.014	0.286 ± 0.017
toluene	16.4 ± 0.54	2.08 ± 0.020	0.740 ± 0.017
ethylbenzene	–	4.37 ± 0.10	1.77 ± 0.12
dichloromethane	1.05 ± 0.065	0.293 ± 0.0046	0.0836 ± 0.0013
trichloromethane	0.522 ± 0.075	0.376 ± 0.022	0.111 ± 0.0022
tetrachloromethane	0.160 ± 0.0088	0.408 ± 0.0075	0.0605 ± 0.0037
1,1-dichloroethylene	0.339 ± 0.022	0.110 ± 0.0042	0.0278 ± 0.00073
trichloroethylene	1.68 ± 0.048	0.639 ± 0.0099	0.123 ± 0.0063
tetrachloroethylene	2.46 ± 0.14	1.27 ± 0.024	0.232 ± 0.0037
methanol	9.90 ± 0.64	0.695 ± 0.019	0.511 ± 0.023
ethanol	16.7 ± 0.74	1.23 ± 0.017	0.861 ± 0.029
2-propanol	–	2.12 ± 0.019	1.13 ± 0.033
diethyl ether	0.725 ± 0.059	0.151 ± 0.0084	0.0729 ± 0.0013
acetone	7.18 ± 0.31	0.879 ± 0.030	0.444 ± 0.014
ethyl acetate	16.0 ± 0.16	1.53 ± 0.051	0.510 ± 0.014
acetonitrile	–	4.91 ± 0.14	2.19 ± 0.059

al. 2011). The interaction between water and the organic compounds would weaken the suppression effect from water (Borisover et al. 2008). Our results ellucidates the influence of water on the sorption ability of higher level HDTMA-modified clay, which would be a better material for VOCs removal.

3.3 LSER approach

The LSER equation under each RH was obtained from the multiple linear regressions by using the observed sorption equilibrium coefficients data to regress against five solvation parameters of the probe solutes. Except the sorption equilibrium coefficients of three compounds under dry conditions were not obtained, other data points were more than three times the number of descriptors. The LSERs for three RHs are given as the following equations:

For low relative humidity (∼0 % RH),

$$\begin{aligned}\log K_d = {} & (-0.251 \pm 0.71)E + (1.31 \pm 0.74)S \\ & +(3.00 \pm 0.93)A + (3.27 \pm 0.75)B \\ & +(1.02 \pm 0.20)L + (-3.47 \pm 0.58) \\ R^2 = 0.854,\ & SD = 0.34,\ F = 20.6,\ n = 19 \end{aligned} \tag{2}$$

For ambient relative humidity (∼55 % RH),

$$\begin{aligned}\log K_d = {} & (-1.04 \pm 0.36)E + (1.67 \pm 0.34)S \\ & +(2.36 \pm 0.55)A + (0.95 \pm 0.37)B \\ & +(0.835 \pm 0.11)L + (-2.99 \pm 0.32) \\ R^2 = 0.858,\ & SD = 0.21,\ F = 19.4,\ n = 22 \end{aligned} \tag{3}$$

For high relative humidity (∼90 % RH),

$$\begin{aligned}\log K_d = {} & (-1.09 \pm 0.44)E + (1.85 \pm 0.41)S \\ & +(2.83 \pm 0.67)A + (1.65 \pm 0.45)B \\ & +(0.880 \pm 0.13)L + (-3.79 \pm 0.39) \\ R^2 = 0.865,\ & SD = 0.25,\ F = 20.6,\ n = 22 \end{aligned} \tag{4}$$

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

The relatively high sample decisive coefficients R^2 represent a satisfactory goodness of these fittings. The analyses of variances are also performed for the regression significance test of the equations by the F-test. The fact that F values are greater than $F_{0.01}(5, 13)$ for the dry condition or $F_{0.01}(5, 16)$ for the hydrated condition. The p values of significance are close to zero, indicating that the regression equations are highly significant. The sorption coefficients estimated using these LSERs are plotted versus the experimental data

Table 4 The contribution for the relative interaction between organoclay and VOCs

Chemicals	eE			sS			aA			bB			lL		
	LH	AH	HH	LH	AH	HH	LH	AH	HH	LH	AH	HH	LH	AH	HH
n-pentane	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	2.20	1.80	1.90
n-hexane	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	2.73	2.24	2.37
n-heptane	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	3.22	2.65	2.79
n-octane	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	3.73	3.07	3.24
2,2,4-trimethylpentane	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	3.15	2.59	2.73
cyclohexane	−0.077	−0.32	−0.33	0.13	0.18	0.19	0.00	0.00	0.00	0.00	0.00	0.00	3.01	2.47	2.61
benzene	−0.15	−0.63	−0.67	0.68	0.92	0.96	0.00	0.00	0.00	0.46	0.13	0.23	2.83	2.33	2.45
toluene	−0.15	−0.62	−0.66	0.68	0.92	0.96	0.00	0.00	0.00	0.46	0.13	0.23	3.38	2.78	2.93
ethylbenzene	–	−0.64	−0.67	–	0.90	0.94	–	0.00	0.00	–	0.14	0.25	–	3.15	3.33
dichloromethane	−0.097	−0.40	−0.42	0.75	1.0	1.1	0.30	0.24	0.28	0.16	0.047	0.083	2.05	1.69	1.78
trichloromethane	−0.11	−0.44	−0.46	0.64	0.86	0.91	0.45	0.36	0.42	0.065	0.019	0.033	2.52	2.07	2.18
tetrachloromethane	−0.12	−0.48	−0.50	0.50	0.67	0.70	0.00	0.00	0.00	0.00	0.00	0.00	2.87	2.36	2.49
1,1-dichloroethylene	−0.091	−0.38	−0.40	0.45	0.60	0.63	0.00	0.00	0.00	0.16	0.047	0.083	2.14	1.76	1.86
trichloroethylene	−0.13	−0.54	−0.57	0.70	0.93	0.98	0.36	0.28	0.34	0.098	0.028	0.050	3.04	2.50	2.64
tetrachloroethylene	−0.16	−0.66	−0.70	0.55	0.74	0.78	0.00	0.00	0.00	0.00	0.00	0.00	3.64	2.99	3.16
methanol	−0.070	−0.29	−0.30	0.58	0.78	0.81	1.3	1.0	1.2	1.5	0.45	0.78	0.985	0.810	0.854
ethanol	−0.062	−0.26	−0.27	0.55	0.74	0.78	1.1	0.88	1.0	1.6	0.46	0.79	1.51	1.24	1.31
2-propanol	–	−0.22	−0.23	–	0.63	0.67	–	0.78	0.93	–	0.53	0.93	–	1.47	1.55
diethyl ether	−0.010	−0.043	−0.045	0.33	0.44	0.46	0.00	0.00	0.00	1.5	0.43	0.75	2.05	1.68	1.77
acetone	−0.045	−0.19	−0.20	0.92	1.2	1.3	0.12	0.095	0.11	1.6	0.47	0.81	1.72	1.42	1.49
ethyl acetate	−0.027	−0.11	−0.12	0.81	1.1	1.1	0.00	0.00	0.00	1.5	0.43	0.75	2.35	1.93	2.04
acetonitrile	–	−0.25	−0.26	–	1.6	1.7	–	0.17	0.20	–	0.30	0.53	–	1.45	1.53

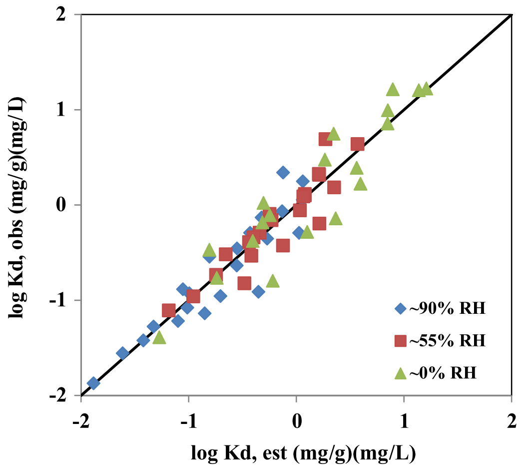

Fig. 3 Overall correlation of the sorption coefficients of VOC on the organoclay estimated by LSER equations 3–5 versus the measured values under different relative humidity

in Fig. 3. These results demonstrate that the largest difference of sorption coefficients can be reliably referred to the solvation parameters.

The contribution for the relative interaction between organoclay and VOCs can be evaluated by each LSER term (the product of Abraham descriptor and the coefficient, Table 4). At ~ 0 % RH, the interactions generally follow the order: dispersion $>$ dipolarity/polarizability $>$ hydrogen-bond basicity $>$ hydrogen-bond acidity $\gg$ π-/n-electron interaction. Dispersion also plays a major role the original montmorillonite and the lower-HDTMA modified clay (Shih and Chou 2010; Shih et al. 2011). Under 55 % RH, the contribution from dispersion in the interaction between organoclay and VOCs is also dominant. The interaction for dispersion, dipolarity/polarizability and hydrogen-bond basicity are larger than that in the original montmorillonite while no difference with that in the lower-HDTMA modified clay. At 90 % RH, the trend for the contribution of each term in the interaction between organoclay and VOCs remains.

The physicochemical properties of the organoclay under different relative humidity can be characterized through the coefficients in the LSER equations. The negative e values reveal that the organoclay does not favor to sorb the sorbates through π-/n-electron pairs. The positive s, a, b, and l values mean that the organoclay has the tendency to interact with VOCs through dipolarity/polarizability, hydrogen-bond, and dispersion/cavity formation interactions, respectively. Among these coefficients, a value is stable through the change of humidity, indicating the hydrogen-bond donor acidity for the organoclay does not affected by water. The *b* value is also prominent under dry condition while it decrease though the elevation of humidity, suggesting that the hydrogen-bond accept basicity on the organoclay could be suppressed by the coverage of water molecules. The *s* value increases while the *l* value declines with the increasing relative humidity, indicating that water layer promotes dipolarity/polarizability but inhibits dispersion in the organoclay. Furthermore, the π-/n-electron interaction (relating to coefficient *e*) is also suppressed through the increase of the relative humidity. Compare to the coefficients of the original montmorillonite and the lower-HDTMA modified clay, under dry condition, the more the HDTMA content, the stronger hydrogen-bond ability and the less π-/n-electron interaction would present from the sorbent. Under hydrated conditions, the hydrogen-bond accept basicity decreases obviously with the increasing content of HDTMA in the clays.

4 Conclusions

The sorption equilibrium of VOCs with HDTMA modified organoclay under different levels of relative humidity was investigated and the sorption mechanisms were evaluated via a LSER approach. The incorporation of HDTMA reduce the surface area while increase the interlayer spacing of the clay. Due to the decrease of surface area after modification with high content of HDTMA, the sorption coefficients of the organoclay under dry condition are smaller than those for montmorillonite or the low HDTMA-content organocly. When the relative humidity increased, the sorption coefficients of all tested compounds decrease. However, the suppression effect on the sorption coefficients from water is more potent in the original montmorillonite and the low HDTMA-content organocly. Therefore, it turns that the sorption ability in the high HDTMA-content organocly under hydrated environment is the strongest. Surface adsorption on organoclay surface and the partition into the incorporated HDTMA in organoclay are two major factors in the sorption process. The LSERs can further characterize surface properties of organoclay in terms of different molecular interactions. Generally, dispersion interaction is predominant and π-/n-electron interaction makes a negative contribution on the interactions between VOC vapors and the organoclays. Incorporation of HDTMA into clay or the changed relative humidity change the molecular interaction characteristics on the clays. These LSER equations can be used to predict the large sorption ability of VOCs on the high HDTMA content organoclay and the organoclay presents the potential to apply in the removal treatments of VOCs.

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