Linear Adsorption of Nonionic Organic Compounds from Water onto Hydrophilic Minerals: Silica and Alumina

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To characterize the linear adsorption phenomena in aqueous nonionic organic solute–mineral systems, the adsorption isotherms of some low-molecular-weight nonpolar nonionic solutes (1,2,3-trichlorobenzene, lindane, phenanthrene, and pyrene) and polar nonionic solutes (1,3-dinitrobenzene and 2,4-dinitrotoluene) from single- and binary-solute solutions on hydrophilic silica and alumina were established. Toward this objective, the influences of temperature, ionic strength, and pH on adsorption were also determined. It is found that linear adsorption exhibits low exothermic heats and practically no adsorptive competition. The solute–solid configuration and the adsorptive force consistent with these effects were hypothesized. For nonpolar solutes, the adsorption occurs presumably by London (dispersion) forces onto a water film above the mineral surface. For polar solutes, the adsorption is also assisted by polar-group interactions. The reduced adsorptive forces of solutes with hydrophilic minerals due to physical separation by the water film and the low fractions of the water-film surface covered by solutes offer a theoretical basis for linear solute adsorption, low exothermic heats, and no adsorptive competition. The postulated adsorptive forces are supported by observations that ionic strength or pH poses no effect on the adsorption of nonpolar solutes while it exhibits a significant effect on the uptake of polar solutes.

Introduction

Soil/solid organic-matter (SOM) content dictates the extent and mode of uptake of organic compounds by geologic materials. Normally, if natural solids contain more than 0.1–

0.2% of SOM and little charcoal-like substance or soot, adsorption of low-polarity nonionic solutes from water by solid surfaces is insignificant compared to the concurrent solute partition into SOM (1–5); this is attributed to the strong competitive adsorption of water for usually polar mineral/inorganic surfaces (2, 5). However, for solids containing little or no SOM, adsorption with mineral/inorganic surfaces becomes the major/dominant process, even if the overall uptake is weak. Although a significant advance has been achieved in modeling the uptake of organic ligands and ionizable solutes (e.g., carboxylic acids) by some hydrophilic minerals (6 and references therein), the mechanism for relatively weak adsorption of low-polarity nonionic solutes by these minerals remains to be elucidated. The latter subject has not been well attended in conventional adsorption studies, where such solutes or vapors normally condense under strong adsorptive forces onto solid surfaces (or the pore space), producing highly nonlinear isotherms with large exothermic heats. Knowledge on adsorption of low-polarity solutes on hydrophilic minerals is needed for fate assessments of various environmental chemicals (7–11).

It is recognized that adsorption isotherms of low-polarity nonionic organic solutes (e.g., lindane, chlorobenzenes, and PAHs) from water on virtually organic-free hydrophilic minerals (e.g., silica and alumina) and low-organic-carbon clays (e.g., kaolinite and smectite) are essentially linear over a wide range of relative concentrations (C_e/S_w) (7–12), where C_e is the equilibrium solute concentration and S_w is the solute water solubility. In many of these systems, the isotherm linearity extends to $C_e/S_w > 0.5$ (8, 10). The adsorption data with organic-free silica and alumina suggest that in these solute–mineral systems water must be preferentially adsorbed, thus making the competitive solute adsorption weak and linear. The specific solute–mineral layout that yields linear solute adsorption, which resembles superficially the linear solute partition with SOM, has been a subject of interest to be further resolved, since the conventional adsorption isotherms are typically nonlinear and no significant solute partition with solid inorganic material is anticipated.

Characteristics for weak linear adsorption of low-polarity nonionic solutes (e.g., PAHs) on hydrophilic solids (e.g., alumina, silica, and iron oxide) include (i) a rapid solution-solid equilibrium time (9); (ii) a dependence of the adsorption coefficient (K_d) on the surface area (SA) of a given mineral (8, 13); (iii) a dependence of K_d on solute water solubility (S_w) (8, 10); (iv) no marked dependence of K_d on solution pH, ionic strength, and solid surface charge and its sign (10); and (v) the solute adsorption heat being less exothermic than the solute condensation heat from water (i.e., the reverse solute heat of solution, $-\Delta\bar{H}_{w,s}$) (13). With noted low adsorption heats, the adsorption is envisioned by some researchers to be driven by a gain in solvent (water) entropy when the solutes detach from surrounding structured water to adsorb onto the solid (8, 13). Such a viewpoint is, however, not conciliatory with the significant (entropy-reducing) solute concentration onto or near the solid and the exothermic heat (13, 14) accompanying the adsorption. Generally, the adsorption of a dilute solute proceeds with an exothermic heat that is large enough to offset the overall reduction in system entropy (15). Up to now, the particular solute–solid assembly leading to weak linear solute adsorption remains to be scrutinized.

With the stated characteristics of nonionic solutes on hydrophilic minerals, it is conceivable that a layer (film) of water adheres strongly on mineral surfaces (16); hence it can be hypothesized that the solutes could only adsorb weakly with reduced forces from minerals onto the water layer. If

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TABLE 1. Physicochemical Properties of the Organic Compounds Used in Adsorption Experiments^a

compound	abbrev.	MW	ρ	mp	S_w	$\Delta\bar{H}_w$	log K_{ow}
1,2,3-trichlorobenzene	TCB	181.5	1.45	53	16.3	NA ^b	4.04
lindane	LIN	290.9	1.87	113	7.87	NA	3.72
phenanthrene	PHN	178.2	1.17	101	1.29	40.0	4.46
pyrene	PYR	202.3	1.27	156	0.135	45.3	4.88
1,3-dinitrobenzene	DNB	168.1	1.37	90	533	26.8	1.49
2,4-dinitrotoluene	DNT	182.1	1.52	71	300	NA	1.98

^a MW = Molecular weight; ρ = density at room temperature (g/mL); mp = melting point (°C); S_w = water solubility at 25 °C (mg/L); $\Delta\bar{H}_w$ = molar heat of solution in water at 25 °C (kJ/mol); K_{ow} = octanol–water partition coefficient. The density (ρ), mp, S_w , and K_{ow} values are from those cited in Mackay et al. (19–22) except those of 1,3-dinitrobenzene from Syracuse Research Corporation database (23). The $\Delta\bar{H}_w$ values of PHN and PYR are from May et al. (24) and that of DNB is from Li et al. (25). ^b NA = not available.

such adsorbed solutes take up a small fraction of the relatively energetically uniform water surface, the adsorption will then be linear and noncompetitive; it would also display a low exothermic heat, to the extent that the adsorbed solutes do not form a separate phase. To avoid the difficulty in determining the water-film SA, the latter is approximated to equal the dry-mineral surface. The theoretical solute monolayer capacity with the water film surface may then be established to determine the fraction of film SA covered by the solute. To this effect, a solid (adsorbent) with a SA of 1000 m²/g adsorbing a substance of ca. 1 g/mL in density will have an adsorbed monolayer capacity (AMC) of ca. 0.25 mL/g (17). The AMC values in units of adsorbed volume per solid mass are fairly constant for different adsorbates (solute) on a porous solid (15). Thus, by using the linear relation between AMC (volume/mass) and solid SA, the AMC (mass/mass) for a solute with the water film of a solid can be computed as follows to test the requirement for linear noncompetitive solute adsorption:

$$\text{AMC (mg/g)} = 250\rho(\text{SA}/1000) \quad (1)$$

where ρ is the solute density (g/mL) and SA is the solid's surface area (m²/g).

The primary objectives of this study are (i) to examine the competitive adsorption, if any, between nonionic solutes with hydrophilic minerals and (ii) to determine the fraction of water-film surface covered by the solutes for verifying the consistency with linear adsorption behavior. This study is warranted for model validation and for assessing the influence of coexisting solutes on the adsorption of a given nonionic solute in multi-solute natural systems. In this work, the adsorption isotherms of several nonpolar nonionic compounds (1,2,3-trichlorobenzene, lindane, phenanthrene, and pyrene) and polar nonionic compounds (2,4-dinitrotoluene and 1,3-dinitrobenzene) as single and binary solutes on pure silica and alumina were obtained to examine the competitiveness of the solute adsorption. Organic-free synthetic silica and alumina with high SAs were employed to enhance the accuracy of the adsorption data. To eliminate complications of the solute uptake by trace SOM in natural solids, no natural clay minerals (e.g., kaolinite and montmorillonite) were used in the present work. Inclusion of polar nonionic solutes into the present study expands the scope of the investigation. In addition to measuring the adsorption isotherms at room temperature (25 ± 1 °C), the isotherms of some solutes at 45 °C were also secured in order to determine the adsorption heats for comparison with earlier reported values.

Experimental Section

Adsorbents. Two highly pure synthetic mineral oxides (adsorbents) with large specific surface areas were selected for experiments. An active silica gel, short as “silica”, with a particle size of 100–200 μm and an average pore size of 6 nm, was obtained from Scientific Adsorbents Inc. (Atlanta,

GA). This sample has a SA by the BET-N₂ method of 563 m²/g, as determined with a Gemini 2360 surface-area analyzer from Micromeritics. An activated aluminum oxide (neutral, Brockmann 1), short as “alumina”, having a particle size of ca. 150 mesh and a BET SA of 155 m²/g (reported in the Aldrich Catalog) was obtained from Aldrich. Both solids show no detectable organic carbon level (<0.01%, by Leco WR-112 Instrument). The respective points of zero charge (PZC) for silica and alumina are 5.7 and 7.0 (by electrophoretic mobility), 5.2 and 6.8 (potentiometric titration) (16), and 5.3 and 6.3 (pH-drift) (18). From the potentiometric titration, the acidity constants of surface hydroxyls for silica are 3.3 (pK_{a1}) and 6.9 (pK_{a2}). These constants for alumina are 5.2 and 8.5.

Solutes. 1,2,3-Trichlorobenzene (TCB) (purity, 99%), lindane (LIN) (97%), phenanthrene (PHN) (98%), pyrene (PYR) (98%), 1,3-dinitrobenzene (DNB) (99.3%) and 2,4-dinitrotoluene (DNT) (99.4%) were purchased from Sigma-Aldrich Co. They all were used as solutes in adsorption experiments without further purification. The fundamental physicochemical properties of these solutes are given in Table 1.

Adsorption Isotherms. A series of water solutions with a fixed level of background salts (0.01 M or 0.05 M CaCl₂ plus 400 mg/L NaNO₃) and varied levels of a test solute (or binary solutes) were prepared using either 15-mL or 30-mL centrifuge tubes. For a solute–solid pair, fixed amounts of the solid were added to the solute solutions for determining the isotherm. The solid-to-solution ratios (w/v) ranged between 1:3 and 1:4 for TCB, LIN, DNB, and DNT and between 1:10 and 1:20 for PHN and PYR depending on specific solute–solid systems. The solution volumes were 10 mL for TCB, LIN, DNB, and DNT and 20 mL for PHN and PYR. The solid–solution mixtures were equilibrated for 48 h on a horizontal-motion shaker under a nearly constant temperature of 25 ± 1 °C or 45 ± 1 °C, maintained by a thermostated water bath. The differences in metal oxide crystal properties at the two temperatures were neglected. Preliminary experiments indicated that all solid–solution mixtures reached equilibrium in 48 h. Other than PHN and DNT from 0.01 M CaCl₂ on alumina at 25 °C and pH = 8 adjusted using 0.1 M NaOH, all solid–solution mixtures were equilibrated without pH adjustment. After equilibration, the solution and solid phases were separated by centrifugation at 3000g. Aliquots of supernatant solutions were then removed with a pipet and extracted with *n*-hexane for analysis of the solute concentration (C_e). Remaining supernatant solutions were used to determine equilibrium pH.

In the binary-solute experiments, concentrations of the two solutes were chosen such that they had about equal initial relative concentrations (C_i/S_w), where C_i is the initial solute concentration and S_w is the solute solubility. This was done to ensure that the two solutes have comparable competitive adsorption potentials, if the adsorption on the solid is competitive in nature.

In all experiments with the solid–solution ratios used, the solute concentrations in water following the equilibration exhibited a significant (usually, 30–70%) decrease relative to the respective control solutions (containing only solutes and background salts without solids) for improving accuracies of the established adsorption isotherms. The recoveries of control solute samples, by the method described below, were $96.7 \pm 1.4\%$ for TCB; $98.5 \pm 4.0\%$ for LIN; $89.3 \pm 1.0\%$ for PHN; $97.3 \pm 3.7\%$ for PYR; $95.2 \pm 1.8\%$ for DNB; and $91.3 \pm 1.5\%$ for DNT. Amounts of the solute adsorbed by the solid were determined by differences of the measured solute concentrations between the control and study samples.

Solute Analyses. Aliquots of water solutions were extracted with *n*-hexane. Solute concentrations were quantified by gas chromatography using the external standards of respective solutes in *n*-hexane analyzed in conjunction with the experimental samples. LIN and TCB in extracts were quantified by an Agilent 6820 gas chromatograph with a ^{63}Ni electron capture detector (ECD) and a DB-1 capillary column (0.53 mm $\times$ 15 m, 0.5 μm thick); extracts of DNB, DNT, PHN and PYR were also analyzed by the same chromatograph using a flame ionization detector (FID) and a HP-5 MS capillary column (0.32 mm $\times$ 30 m, 0.25 μm thick).

Data Analyses. Isotherms for each solute–solid system were constructed by plotting the mass of solute adsorbed per unit weight of the solid (adsorbent), Q (mg/kg), against the respective equilibrium solute concentration, C_e (mg/L). In view that the isotherms for all test solutes were essentially linear, the distribution coefficients (K_d) and the standard errors ($\pm\text{SE}$) for individual solute–solid pairs were computed using a linear statistical program (SPSS Version 11.5). Average K_d and associated SE values at $P < 0.01$ are listed in Table 2.

Results and Discussion

The representative adsorption isotherms of selected nonpolar nonionic compounds (TCB, LIN, PHN, and PYR) and polar nonionic compounds (DNB and DNT), as single and binary solutes, on silica and alumina at $25(\pm 1)^\circ\text{C}$ and $45(\pm 1)^\circ\text{C}$ are presented in Figures 1–4, in which the mass of adsorbed solute per unit weight of the solid (Q) is plotted against the equilibrium solute concentration in water (C_e). As shown, the isotherms are all practically linear, with C_e/S_w extended to 0.14 for DNT/alumina and 0.56 for PHN/silica. This high isotherm linearity is similar to that found earlier in uptakes of PHN and other PAHs by silica and alumina (8, 9, 13). Treating these isotherms in linear form with zero intercept, the linear solute adsorption coefficients (K_d) (L/kg) for related solute–solid systems are determined (Table 2). As noted, whereas the K_d is the highest for the least water-soluble PYR, the K_d for relatively soluble polar DNB is also quite appreciable (especially, the K_d with alumina). Overall, the K_d values for all solutes with either silica or alumina are not dictated primarily by their water solubilities (S_w) or octanol–water partition coefficients (K_{ow}), meaning that the solute hydrophilicity is not the predominant determinant of K_d . In all pH-unadjusted adsorption experiments, the final solution pH values were 5.25 ± 0.10 for silica and 6.28 ± 0.10 for alumina, all being close to the mineral PZC.

With the hypothesis that the solute adsorbs on top of the water film over the mineral (solid), one would anticipate the K_d for a solute with a given mineral to be largely proportional to the solid SA and the heat of adsorption per mole of the solute ($\Delta\bar{H}_{ad}$) to be independent of the K_d . To the SA effect, the present PHN K_d of 6.48 with the silica ($SA = 563\text{ m}^2/\text{g}$) is similar in magnitude to the PHN K_d of 3.08 with silica gel 150 ($SA = 314\text{ m}^2/\text{g}$) and of 4.65 with silica gel 40 ($SA = 521\text{ m}^2/\text{g}$), reported by Huang et al. (9). Similarly, on the SA basis, the present PYR K_d of 12.0 with the alumina ($SA = 155\text{ m}^2/\text{g}$) is of the same order of magnitude as that (0.231) with

TABLE 2. Adsorption Coefficients (K_d) of Selected Organic Solutes on Silica and Alumina

solute/ cosolute ^a	<i>t</i> (°C)	K_d (silica) (L/kg)	K_d (alumina) (L/kg)	ionic strength (with CaCl_2)
TCB	25	5.49 ± 0.29	0.98 ± 0.05	0.01 M
TCB	45	4.13 ± 0.43	0.63 ± 0.04	0.01 M
TCB/LIN	25	5.37 ± 0.60	0.92 ± 0.14	0.01 M
TCB/PHN	25	5.81 ± 0.19	0.93 ± 0.05	0.01 M
LIN	25	7.37 ± 0.48	1.53 ± 0.07	0.01 M
LIN	25	7.65 ± 0.53	1.20 ± 0.13	0.05 M
LIN	45	4.61 ± 0.34	0.93 ± 0.05	0.01 M
LIN/PHN	25	7.70 ± 0.34	1.51 ± 0.07	0.01 M
LIN/TCB	25	7.56 ± 0.27	1.43 ± 0.13	0.01 M
PHN	25	6.48 ± 0.18	2.28 ± 0.10	0.01 M
PHN	25	6.66 ± 0.44	2.37 ± 0.22	0.05 M
PHN (pH = 8)	25		2.20 ± 0.11	0.01 M
PHN/TCB	25	6.39 ± 0.36	2.24 ± 0.11	0.01 M
PHN/PYR	25	6.34 ± 0.13	2.19 ± 0.23	0.01 M
PHN	45	4.31 ± 0.12	1.49 ± 0.08	0.01 M
PHN/LIN	25	6.14 ± 0.66	2.71 ± 0.16	0.01 M
PHN/DNT	25	5.90 ± 0.37	2.41 ± 0.17	0.01 M
PYR	25	18.9 ± 0.33	12.0 ± 0.43	0.01 M
PYR	25	18.6 ± 0.41	11.5 ± 0.52	0.05 M
PYR	45	10.5 ± 0.29	7.45 ± 0.44	0.01 M
PYR/PHN	25	18.5 ± 1.08	11.6 ± 0.55	0.01 M
DNT	25	4.77 ± 0.37	4.48 ± 0.04	0.01 M
DNT	25	3.77 ± 0.10	1.36 ± 0.04	0.05 M
DNT (pH = 8)	25		53.7 ± 4.46	0.01 M
DNT	45	2.98 ± 0.27	2.03 ± 0.17	0.01 M
DNT/DNB	25	4.82 ± 0.30	4.32 ± 0.34	0.01 M
DNT/PHN	25	4.95 ± 0.51	4.43 ± 0.39	0.01 M
DNB	25	3.17 ± 0.24	3.63 ± 0.12	0.01 M
DNB	45	2.17 ± 0.08	2.22 ± 0.22	0.01 M
DNB/DNT	25	3.30 ± 0.14	3.63 ± 0.18	0.01 M

^a If not specified, the pH values of solute–solid suspensions are 5.25 ± 0.10 for silica and 6.28 ± 0.10 for alumina.

FIGURE 1. Adsorption isotherms of LIN from 0.01 M CaCl_2 on silica at pH = 5.25 ± 0.10 .

α -alumina ($SA = 11.7\text{ m}^2/\text{g}$) observed by Mader et al. (10). To the adsorption heat effect, the solute molar heats of adsorption are first obtained by application of the van't Hoff equation using the linear adsorption coefficients (i.e., K_d values) at two temperatures, i.e.,

$$\Delta\bar{H}_{ad} = -2.303R \left[\frac{\log(K_{d,2}/K_{d,1})}{1/T_2 - 1/T_1} \right] \quad (2)$$

where $\Delta\bar{H}_{ad}$ is adsorption heat per mole of the solute (kJ/mol), R is the gas constant (8.31 J/K·mol), and $K_{d,1}$ and $K_{d,2}$

FIGURE 2. Adsorption isotherms of PHN from 0.01 M CaCl_2 on silica at $\text{pH} = 5.25 \pm 0.10$ and on alumina at $\text{pH} = 6.28 \pm 0.10$.

FIGURE 3. Adsorption isotherms of PYR from 0.01 M and 0.05 M CaCl_2 on silica at $\text{pH} = 5.25 \pm 0.10$.

FIGURE 4. Adsorption isotherms of DNT from 0.01 M and 0.05 M CaCl_2 on alumina at $\text{pH} = 6.28 \pm 0.10$.

are (linear) adsorption coefficients at absolute temperatures T_1 and T_2 . Using the present K_d at 25 and 45 °C under 0.01M CaCl_2 , the $\Delta\bar{H}_{ad}$ is -18.5 kJ/mol on silica and -19.6 kJ/mol on alumina for LIN; -16.1 kJ/mol on silica and -16.8 kJ/mol on alumina for PHN; -23.2 kJ/mol on silica and -18.8 kJ/mol on alumina for PYR; -14.9 kJ/mol on silica and -19.4 kJ/mol on alumina for DNB. These values compare well with the reported $\Delta\bar{H}_{ad}$ of ca. -20.9 kJ/mol for LIN on aquifer sand (11); -12.6 to -17.9 kJ/mol for PHN on silica gel 150 and -19.6 to -22.8 kJ/mol for PHN on silica gel 40 (13); and

TABLE 3. AMC, S_wK_d , and S_wK_d/AMC Values of Solute–Solid Systems at 25 °C^a

solute/solid	AMC	S_wK_d	S_wK_d/AMC
TCB/silica	204	8.95E-2	4.39E-4
TCB/alumina	56.2	1.60E-2	2.84E-4
LIN/silica	263	5.80E-2	2.21E-4
LIN/alumina	72.5	1.22E-2	1.66E-4
PHN/silica	165	8.36E-3	5.07E-5
PHN/alumina	45.3	2.94E-3	6.49E-5
PYR/silica	179	2.55E-3	5.19E-5
PYR/alumina	49.2	1.62E-3	3.29E-5
DNT/silica	214	1.43	6.68E-3
DNT/alumina	58.9	1.34	2.28E-2
DNB/silica	193	1.69	8.75E-3
DNB/alumina	53.1	1.94	3.65E-2

^a AMC = adsorbed solute monolayer capacities on solids (mg/g); S_wK_d = maximum solute concentrations on solids (mg/g), where the K_d are values at 0.01M CaCl_2 ; S_wK_d/AMC = maximum fractions of monolayers occupied by solutes.

-20.8 kJ/mol for PYR on α -alumina (10). Thus, the results from present and earlier studies are mutually consistent and well in line with theoretical expectations.

As seen, all solute $\Delta\bar{H}_{ad}$ values are notably exothermic but less in extent than the respective solute $-\Delta\bar{H}_w$ values; here $\Delta\bar{H}_w$ is 40.0 kJ/mol for PHN (24), 45.3 kJ/mol for PYR (24), and 26.8 kJ/mol for DNB (25) at ~ 25 °C. The magnitudes and signs of $\Delta\bar{H}_{ad}$ relative to $-\Delta\bar{H}_w$ manifest that adsorbed solutes do not form a condensed phase on mineral surfaces; if a condensed phase were formed, the $\Delta\bar{H}_{ad}$ would be more exothermic than $-\Delta\bar{H}_w$ because the solute condensation heat ($-\Delta\bar{H}_w$) is a component of the adsorption heat (26). A typical solute condensation effect is illustrated by PHN on graphite (13), where $\Delta\bar{H}_{ad}$ is about -47.1 kJ/mol and the isotherm is highly nonlinear (with a concave downward shape). This disparate adsorption characteristic is attributed to the low affinity of water for graphite that makes the solute (PHN) a powerful competitor over water for adsorptive condensation on the solid surfaces. The present system is also dissimilar to the complex formation of reactive solutes (e.g., carboxylic acids) with mineral surface sites (6), since this occurrence would likely result in high exothermic heats and a nonlinear uptake due to site saturation.

The present study manifests the absence of competitive adsorption between coexisting solutes with hydrophilic minerals. This effect is attributed to the weak solute adsorption over a strongly adsorbed water film, on which the solute molecules occupy supposedly only a small fraction of the relatively (energetically) uniform surface. Under this condition, the adsorbed solute is at a discrete molecular state rather than at a condensed state (because the latter situation will make $\Delta\bar{H}_{ad}$ more exothermic than $-\Delta\bar{H}_w$). Using eq 1, the AMC values are obtained for all solutes. Taking the water solubility (S_w) as the linear-adsorption limit, the highest adsorbed solute concentration on the solid will then be S_wK_d and the largest fraction of the monolayer occupied by the solute will be S_wK_d/AMC .

Calculated AMC, S_wK_d , and S_wK_d/AMC values for low-polarity TCB, LIN, PHN, and PYR are listed in Table 3. As found, the S_wK_d/AMC values are generally very small (<0.001) for these solutes, supporting the notion that at low water-surface coverage the adsorption of multiple solutes on hydrophilic solids would be largely linear and noncompetitive. As noted, the S_wK_d/AMC values for polar DNB and DNT are greater by 1–2 orders of magnitude over those of the low-polarity solutes, although the values for DNB and DNT (0.00668–0.0365) correspond nonetheless to a low surface coverage. The cause for the higher surface coverage for polar solutes will be considered later.

The water film on silica or alumina referred to is considered to be only about one molecular-layer thick, formed supposedly via the H-bonding of water with surface hydroxyls (16, 27), and thus does not extend much beyond the first layer. As such, an organic solute may adsorb more effectively than excess water by London forces on the water film because the solute has a greater molar polarizability than water (15). Thus, for relatively nonpolar solutes, London forces should be the main cause for adsorption. Here the solute adsorption heat should be low because of the rapid decrease of the London force with the distance of separation by the water film and the absence of solute condensation onto the water film. For polar solutes (e.g., DNT), the adsorption is presumably facilitated by additional polar-group interactions with the water film, considering their moderately high K_d and very high S_w values. This interaction enhances the polar-solute monolayer coverage and partially offsets the solute hydrophilicity. Thus, the K_d values for a mixed group of polar and nonpolar solutes would not likely be dictated by the solute water solubility (S_w) or the octanol-water partition coefficient (K_{ow}). The previously observed correlation of K_d with solute hydrophilicity (8, 10) could have resulted from the use of limited low-polarity solute K_d data. As shown in Table 1, the log K_{ow} values of the studied solutes differ by more than 1000 fold, whereas the measured K_d values in Table 2 differ only by 6 fold on silica and by 10 fold on alumina.

It is noted with interest that the adsorption of polar solutes on poorly hydrophilic mineral surfaces yields contrasting results on solute uptake and isotherm linearity. A good example of such surfaces is the siloxane plane in montmorillonite, which is more readily wet by a polar liquid (e.g., EGME) than by water because water has an exceptionally high cohesive-energy density (28). In essence, the availability of siloxane layers in a montmorillonite for adsorbing solutes depends strongly on the hydrating power of the exchangeable cation(s) intercalated between the siloxane layers (29). Typical strongly hydrating cations are Ca^{2+} , Mg^{2+} , and Na^+ , and weakly hydrating cations are K^+ , Cs^+ , and NH_4^+ (29). As observed, adsorption of polar nitroaromatic solutes (e.g., DNT) from water on clays saturated with poorly hydrating cations (e.g., K^+) is substantial and nonlinear, reflecting that polar solutes adsorb (condense) more readily than water onto available poorly hydrating siloxane planes (30, 31). However, by replacing K^+ with Ca^{2+} in the clay, the availability of siloxane layers is seriously inhibited by the Ca^{2+} -solvated water and the solute adsorption is thus sharply reduced (29, 31–33). This result is similar to that with hydrophilic silica and alumina, in which the preferred adsorption of water on minerals weakens the competitive solute adsorption. The observed low-concentration K_d values for all nitroaromatic solutes with clay siloxane surfaces show no significant correlation with the solute hydrophilicity (S_w or K_{ow}) (31).

As noted here, the K_d values of low-polarity solutes with silica are always greater than those with alumina, in which the differences for TCB and LIN are closely related to the solid surface areas, as recognized earlier (8, 13), whereas the results for PHN and PYR are only partially related to the surface areas. Reasons for these discrepancies are not immediately clear and will be subject to further investigations. Moreover, the K_d values of low-polarity solutes also show no strong dependence on the solid surface charge (10). In contrast, the K_d values for the polar solutes (DNT and DNB) with the two solids are relatively comparable and much higher in magnitude than expected from their high water solubilities. The latter finding suggests that the adsorption of polar solutes involves additional polar interactions and/or H-bonding with the water-film surface.

The different ionic-strength effects on K_d observed for polar and nonpolar solutes support the presumed solute

polarity effect. As shown in Table 2, when the solution ionic strength increased from 0.01 to 0.05 M CaCl_2 , no significant change in K_d occurred for LIN, PHN, and PYR, a result conciliatory with the assumed primary adsorptive force (i.e., London force) for nonpolar solutes. Contrarily, the same change in ionic strength resulted in a significant decrease in K_d for polar DNT, consistent with the notion that the net surface charges, which attract polar solutes, decrease with increasing ionic strength. Similarly, when the solution pH increased to 8.0 (i.e., ≥ 1 unit above the PZC), the K_d for PHN/alumina did not vary significantly, whereas the K_d for DNT/alumina showed a substantial increase, the latter being indicative of an increased surface charge that promotes the solute dipole-surface charge interaction.

In summary, the postulated molecular interactions of polar and nonpolar solutes with hydrophilic silica and alumina account effectively for the observed outstanding adsorption characteristics, i.e., the isotherm linearity, low exothermic heats, and noncompetitive uptakes. The noncompetitive adsorption between solutes as illustrated in this study has an important implication on individual solute behaviors in multi-solute natural systems. The different adsorptive forces hypothesized for polar and nonpolar solutes are underscored by the different solute K_d responses to ionic strength and pH. At this point, however, more fundamental inputs are still needed to shed light on all relevant molecular and surface parameters that influence the linear adsorption of both polar and nonpolar solutes on various hydrophilic minerals.

Acknowledgments

The research was supported by the Ministry of Science and Technology (2007CB407301), the Chinese Academy of Sciences (KZCX3-SW-431), and the Chinese Natural Science Foundation (20667003). The use of trade, brand, or product names in this article is for identification purposes only and does not imply endorsement by the U.S. Government.

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Received for review April 24, 2006. Revised manuscript received September 6, 2006. Accepted September 11, 2006.

ES0609809