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Thermodynamics of phenanthrene partition into solid organic matter from water

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Abstract: The thermodynamic behavior of organic contaminants in soils is essential to develop remediation technologies and assess risk from alternative technologies. Thermodynamics of phenanthrene partition into four solids (three soils and a bentonite) from water were investigated. The thermodynamics parameters (ΔH , ΔG° , ΔS°) were calculated according to experimental data. The total sorption heats of phenanthrene to solids from water ranged from -7.93 to -17.1 kJ/mol, which were less exothermic than the condensation heat of phenanthrene-solid (i.e., -18.6 kJ/mol). The partition heats of phenanthrene dissolved into solid organic matter ranged from 23.1 to 32.2 kJ/mol, which were less endothermic than the aqueous dissolved heat of phenanthrene (i.e., 40.2 kJ/mol), and were more endothermic than the fusion heat of phenanthrene-solid (i.e., 18.6 kJ/mol). The standard free energy changes, ΔG° , are all negative which suggested that phenanthrene sorption into solid was a spontaneous process. The positive values of standard entropy changes, ΔS° , show a gain in entropy for the transfer of phenanthrene at the stated standard state. Due to solubility-enhancement of phenanthrene, the partition coefficients normalized by organic carbon contents decrease with increasing system temperature (i.e., $\ln K_{oc} = -0.284 \ln S + 9.82$ ($n = 4$, $r^2 = 0.992$)). The solubility of phenanthrene in solid organic matter increased with increasing temperatures. Transports of phenanthrene in different latitude locations and seasons would be predicted according to its sorption thermodynamics behavior.

Keywords: soil; bentonite; phenanthrene; sorption; thermodynamics

Introduction

Sorption of an organic pollutant to soil has a major influence on its transport, bioavailability and fate in natural environments and developing soil pollution remediation technologies. Extensive research (Chiou, 1979; 1983; 1985; 1998a; Karickhoff, 1979; Kile, 1995; Rutherford, 1992) suggested that sorption of nonionic organic compounds (NOCs) from water to soil is due primarily to the partitioning into soil organic matter (SOM). Adsorption of NOCs from water by relatively polar soil minerals is suppressed by the strong competitive adsorption of water (Chiou, 1985). Accordingly, the soil-water distribution (K_d) of a nonpolar contaminant (solute) is strongly dependent on the soil organic matter content (f_{om}) or, alternatively, on the soil organic carbon contents (f_{oc}), unless either is extremely low.

For a given organic compound, partition coefficients (K_d) normalized by soil organic carbon contents (f_{oc}) (i.e., $K_{oc} = K_d/f_{oc}$) are about the same on a large set of soils and similarly on a large set of bed sediments, the samples being from dispersed locations in the world (Chiou, 1998b). Because natural soil/sediment organic matter may vary greatly with their location, origin, and soil/sediment profile, the values of K_{oc} are dependent on SOM composition and polarity. The K_{oc} values for the sediments are about twice as those of the soils due to the sediment organic matter has a somewhat lower overall polarity than the soil organic matter (Chiou, 1995; 1998a). Trichloroethylene K_{oc} in the shale samples containing condensed organic carbon was more than

one order of magnitude greater than that in young surface soils (Grathwohl, 1990). K_{oc} of a solute increased with soil profile depth because aromatic carbons of humic substance increased with depth (Chen, 1995; Xing, 1999). Liu *et al.* (Liu, 2002) observed that K_{oc} values changed inversely with effective polarity and directly with aromaticity, and that young surface organic matter had lower sorption capacity than the old organic matter in shale.

K_{oc} values of NOCs increase with increasing octanol-water partition coefficients (K_{ow}) and decreasing aqueous solubilities of NOCs (S_w), so K_{oc} values of NOCs can often be estimated with sufficient accuracy from their related physical parameters, such as the octanol-water partition coefficients or the solute aqueous solubilities (Chiou, 1979; 1983; Karickhoff, 1979). The relationship between $\log K_{oc}$ and $\log K_{ow}$ established by Chiou *et al.* for substituted aromatic compounds (primarily chlorinated benzenes and PCB) over a range of $\log K_{ow}$ (2.11 to 5.62) on soil gives (Chiou, 1983).

$$\log K_{oc} = 0.904 \log K_{ow} - 0.543 \quad (n = 12, r^2 = 0.996). \quad (1)$$

The relationship between $\log K_{oc}$ and $\log K_{ow}$ presented by Karickhoff *et al.* for polycyclic aromatic hydrocarbons (PAHs) and their derivatives over a range of $\log K_{ow}$ (2.11–6.43) on river sediments gives (Karickhoff, 1979).

$$\log K_{oc} = 1.00 \log K_{ow} - 0.21 \quad (n = 10, r^2 = 1.00). \quad (2)$$

All above, both soil geologic properties and organic compound properties are two major influential factors on sorption behavior of NOCs in soil-water system. Of physical, chemical and biological processes, sorption is one of the most

important in soils because it regulates its fate, transport and remediation technologies. The knowledge of sorption thermodynamics of organic pollutants to soil is essential to develop remediation technologies and assess risk from alternative technologies, and also significant to develop regional or global transport model of organic pollutants in different latitude locations and seasons. The objectives of this study are to determinate sorption behavior of a solute to soils at different temperatures and the corresponding aqueous solubility of the solute; to calculate thermodynamic parameters (i.e., ΔH , ΔG , and ΔS) of the solute partition into solid organic matter and solubility of the solute in SOM at different temperatures; to offer some thermodynamics data to precisely predict the transport of a solute at different seasons and latitude locations.

1 Materials and methods

1.1 Materials

Phenanthrene was of analytical grade and was used without further treatment. Three soils and one original bentonite were selected for sorption experiments. The three soils collected from Zhejiang Province, China. The bentonite used was primarily Ca^{2+} -montmorillonite, collected from Inner Mongolia National Autonomous Region, China. The air-dried soil and bentonite samples were sieved to obtain particles less than 100 mesh in all experiments. The selected properties of studied soils and bentonite, such as BET- N_2 surface area (SA), organic carbon contents (f_{oc}), and cation-exchanged capacity (CEC), are presented in Table 1. The organic carbon contents were analyzed using LECO CS-344 type Carbon-Sulphate analyzer under the condition of 50% relative humidity and 25 °C. The BET- N_2 surface areas were determined using Coulter-100CX surface area analyzer. The cation-exchange capacities were determined with ion exchange methods.

Table 1 Selected properties of studied four solids

Solids	Bentonite	Soil 1	Soil 2	Soil 3
CEC, meq/100 g	104.5	3.51	19.81	27.17
SA, m^2/g	60.9	3.82	5.51	6.54
f_{oc} , %	0.04	0.51	1.28	6.48

Notes: CEC = cation exchange capacity, SA = BET-(N_2) surface area, and f_{oc} = fraction of organic carbon contents

1.2 Analytical methods

Aqueous phenanthrene was quantified by ultraviolet spectrophotometry at absorbance wavelength 245 nm. All analysis utilized standard external calibration curves over their linear response regions and was made well above the instrumental and method detection limits.

1.3 Sorption of phenanthrene to solids

Sorption of phenanthrene from water onto solids were determined by adding various amount of organic pollutant to the 50 ml Erlenmeyer flasks with glass caps, which contained

appropriate amount of solid and 20 ml 0.005 mol/L CaCl_2 solution. The flasks were shaken for 12 h on a gyratory shaker at 150 r/min, at 5, 15, 25 and 35 \pm 0.5 °C respectively. After equilibration, the solution and solid phase were separated by centrifugation at 4000 r/min for 10 min at corresponding temperature. An amount of supernatant was removed and analyzed for organic pollutant by UV. The equilibrium concentrations of organic solute were computed from the final UV readings, while the sorbed amounts were computed simply from the difference of the initial and final solute concentrations. The losses of the compounds by photochemical decomposition and sorption to the flask and volatilization were found to be negligible.

1.4 Solubility of phenanthrene in water

Solubilities of phenanthrene in water at different temperatures were determined. A 0.005 mol/L CaCl_2 solution was placed in 50 ml Erlenmeyer flasks with glass caps, and phenanthrene was added to Erlenmeyer flasks in an amount more than required to saturate the solution. Duplicate samples were prepared for each temperature; these samples were then equilibrated on a gyratory shaker for 48 h at 5, 15, 25, 35 \pm 0.5 °C and 150 r/min. The samples were subsequently centrifuged at 4000 r/min for 20 min to separate the undissolved solute. An appropriate aliquot of the supernatant was then carefully withdraw with a volumetric pipet and diluted to appropriate volume with deionized water. Phenanthrene in aqueous solution was analyzed by UV. The solubilities of phenanthrene in aqueous solution were computed from the final UV readings.

2 Results and discussion

2.1 Sorption of phenanthrene to solids at different temperatures

Sorption isotherms of phenanthrene to four solids (i.e., three soils and a bentonite) with organic carbon contents ranged from 0.04% to 6.48% at four different temperatures (i.e., 5, 15, 25, 35 °C) were presented in Fig. 1. The distributions of phenanthrene in solid-water systems were linear. According to the slope of linear isotherms, the sorption coefficients (K_d) of phenanthrene could be calculated (Table 2). At a given temperature, the values K_d of phenanthrene were positively correlated with solid organic carbon contents (f_{oc}). The relationships between K_d and f_{oc} at different temperatures were all linear (regression equation presented in Table 2), which suggested that sorption of phenanthrene to solids was dominated by partition into solid organic matter. On the base of the linear slope of $K_d - f_{oc}$, the sorption coefficients of phenanthrene normalized by solid organic contents (i.e., K_{oc}) were calculated as 13778, 11984, 11006 and 10036, respectively, at 5, 15, 25 and 35 °C. For a given solid, the values K_d decreased with increase of temperature which indicated that apparent sorption

heat was exothermic, those results would be discussed in later. According to $K_d = K_{oc} \times f_{oc}$, the observation of decrease of K_d values was due to K_{oc} values decreased with

the increase of temperature, because f_{oc} values were generally constant at different temperatures.

Table 2 Sorption coefficients (K_d , K_{oc}) of phenanthrene to solids at different temperatures (T) and the regression equation between K_d and organic carbon contents (f_{oc})

T , K	K_d				Regression equations	Relation coefficients, r^2	K_{oc}
	Bentonite	Soil 1	Soil 2	Soil 3			
278	8.98	110	220	917	$K_d = 13778f_{oc} + 27.74$	0.998	13778
288	6.79	100	191	798	$K_d = 11984f_{oc} + 25.06$	0.998	11984
298	5.25	86.3	144	725	$K_d = 11006f_{oc} + 11.52$	0.998	11006
308	4.04	66.7	134	653	$K_d = 10036f_{oc} + 1.103$	0.998	10036

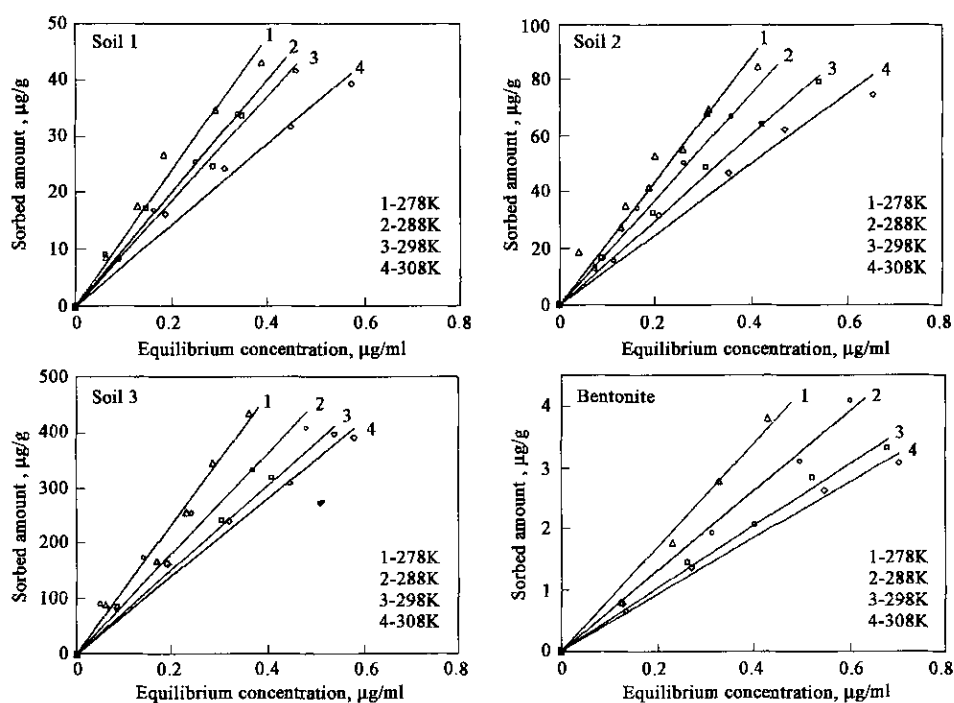


Fig. 1 Isotherms of phenanthrene to solids at different temperatures

2.2 Solubilities of phenanthrene in water and in solid organic matter

Solubilities of phenanthrene in aqueous solution at different temperatures (i. e., 5, 15, 25, and 35°C) were determined by experiment in duplicate samples. The solubilities data at 5, 15, 25, and 35°C were 0.34, 0.62, 1.08, 1.84 µg/ml. The solubilities of phenanthrene increased with increasing temperature indicated that the solubilization process was endothermic.

Accountability of phenanthrene partitioning in solid organic matter is further substantiated by the estimated magnitude of the solute solubility in solid organic matter. Since the isotherms are practically linear, the solubility of the phenanthrene into organic matter may be calculated (Chiou, 1998b).

$$S_{om} = S_w \cdot K_{om}, \quad (3)$$

where S_{om} is the solubility of phenanthrene in organic matter and S_w is the solubility in water, K_{om} is the partition coefficient normalized by organic matter. When carbon

content in solid organic matter is about 58% (generally), the relationship K_{om} and K_{oc} is

$$K_{oc} = 1.72 K_{om}. \quad (4)$$

Based on Equation (1) and Equation (2), S_{om} can be transferred as

$$S_{om} = \frac{S_w \cdot K_{oc}}{1.72}. \quad (5)$$

According to the data of S_w and K_{oc} at different temperatures, the solubilities of phenanthrene in solid organic matter were 4.66, 7.43, 11.9 and 18.5 g/kg, respectively, at 5, 15, 25, and 35°C. S_{om} of phenanthrene increased with temperature increasing. At 25°C, partition coefficient between octanol and water (i. e., K_{ow}) is 28000 and solubility of phenanthrene is 1.08 µg/ml, so the calculated value of solubility of phenanthrene in pure octanol is approximately 30.2 g/L, which is some 3 times its solubility in solid organic matter.

For solid DDT with $S_w = 5.5$ µg/L and $K_{om} = 1.5 \times 10^5$ at 25°C, one therefore gets $S_{om} = 0.83$ g/kg. By

comparison, the solubility of DDT in pure octanol is approximately 42 g/L (Chiou, 1982), which is some 50 times its solubility in soil organic matter. On the premise of solute partitioning, one expects organic compounds with higher water solubility to give lower K_{om} but higher S_{om} values because these compounds are usually also more compatible with organic solvents (Chiou, 1998b).

2.3 Thermodynamic process of phenanthrene partitioning into solid organic matter from water

It is useful to consider the equilibrium heat associated with the partition of a solute to predict of thermodynamics of phenanthrene in natural environments. For linear isotherms, the molar isothermic heat of sorption is independent of the amount of sorption and can be calculated from the Clausius-Clapeyron equation:

$$\ln K = -\frac{\Delta H_1}{RT} + A, \quad (6)$$

where K is the linear sorption coefficient (i. e., K_d); ΔH_1 is the total molar heat of sorption; R is the gas constant (equal to 8.314 J/(K·mol)); T is the system temperature (unit is K); A is a constant. Plots of $\ln K$ vs $1/T$ for given solids are presented in Fig. 2, and yields a slope of $-\Delta H_1/R$ and an intercept of A . Calculated values of ΔH_1 were negative (Table 3) indicated that sorption of phenanthrene to solid is exothermic.

Table 3 Total sorption heat of phenanthrene to solid and solubility heat of phenanthrene in water and organic matter (kJ/mol)

Solids	ΔH_1	ΔH_w	ΔH_o	ΔH_{wnet}	ΔH_{onet}
Bentonite	-17.1	40.2	23.1	21.6	4.5
Soil 1	-11.7	40.2	28.5	21.6	9.9
Soil 2	-16.0	40.2	24.2	21.6	5.6
Soil 3	-7.93	40.2	32.3	21.6	13.7

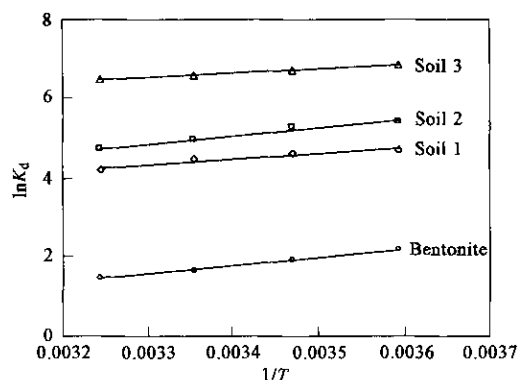


Fig. 2 The relationship between temperatures and partition coefficients of phenanthrene

Because sorption of phenanthrene to solid is dominated by partition into its organic matter, the total molar heat of sorption can also be calculated as,

$$\Delta H_1 = \Delta H_o - \Delta H_w, \quad (7)$$

where ΔH_o is the molar heat of solution in the organic matter and ΔH_w is the molar heat of solution in water, both of which

are usually positive. According to the plot of $\ln S_w$ vs $1/T$ (Fig. 3), ΔH_w value was calculated as, i. e., 40.2 kJ/mol. The molar heats of phenanthrene partition into different solid organic matter (ΔH_o) can be calculated by Equation (7) (Table 3), which are less than ΔH_w . For solid phenanthrene, ΔH_w and ΔH_o include molar heat of fusion (ΔH_f) as a part of heats of solution, which are constant for phenanthrene, i. e., 18.6 kJ/mol (Chiou, 2002), so ΔH_w and ΔH_o are also expressed as,

$$\Delta H_w = \Delta H_{wnet} + \Delta H_f, \quad (8)$$

$$\Delta H_o = \Delta H_{onet} + \Delta H_f, \quad (9)$$

where ΔH_{wnet} and ΔH_{onet} are the net molar heat of phenanthrene solution in water and in organic matter, which are presented in Table 3. The sorption heats of phenanthrene to solids from water are less exothermic than the heat of phenanthrene-solid condensation (i. e., -18.6 kJ/mol). The heats of phenanthrene partition into solid organic matter are less endothermic than the heat of phenanthrene solubility in water and are more endothermic than the heat of phenanthrene-solid fusion.

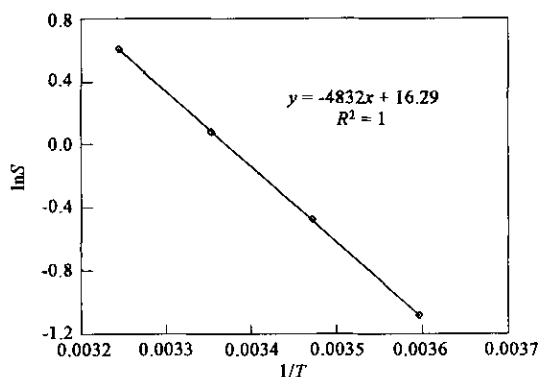


Fig. 3 The relationship between temperatures and aqueous solubilities of phenanthrene

Based on the heat of sorption (i. e., ΔH_1) and K_{oc} values, one can calculate the standard entropy change for the transfer of phenanthrene from water to the soil organic matter as

$$\Delta G^\circ = -RT \ln K_{om} = -RT \ln \frac{K_{oc}}{1.72} \quad (10)$$

and

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T}, \quad (11)$$

where ΔG° is the molar standard free energy change for the transfer of one mole (or a unit mass) of the solute from water at unit concentration to the organic matter phase at unit concentration, ΔH° and ΔS° are the corresponding standard enthalpy and entropy changes. The calculated data of ΔG° and ΔS° are presented in Table 4. The standard free energy changes, ΔG° , for the phenanthrene partition into solids are in the range of -20.8—-22.2 kJ/mol, which is similar to the results for sorption picloram (Biggar, 1973) fluridone

(McCloskey, 1987) on soils, and pentachlorophenol(Xing, 1993) on montmorillonite. The values of ΔG° were all negatives suggested that phenanthrene sorption to solid was automatic process, and the trend increased with the temperature increasing. The magnitudes of ΔS° would show a gain in entropy for the transfer of phenanthrene at the stated standard state. Such a gain in entropy deviates from the expectation for a decrease in entropy for adsorption of a trace component from solution(Chiou, 1998b).

Table 4 Thermodynamics parameter (ΔG° and ΔS°) of phenanthrene partition into solid

Temperature, K	ΔG° , kJ/mol	ΔS° , J/(K·mol)			
		Bentonite	Soil 1	Soil 2	Soil 3
278	-20.8	13.2	32.6	17.2	46.2
288	-21.2	14.2	32.9	18.0	46.0
298	-21.7	15.5	33.6	19.2	46.3
308	-22.2	16.6	34.1	20.1	46.3

2.4 Implications

Solubilities of phenanthrene both in water and in solid organic matter enhanced with increasing system temperature, but the resulted sorption coefficients(K_d) decreased. Due to ΔH_w higher than ΔH_o , the magnitude of solubility-enhancement in water was more larger than that in organic matter by increasing temperature. K_d value decreases were contributed to K_{oc} values decrease, which arised from aqueous solubility enhancement by temperature increasing. The relationship between K_{oc} and S_w is presented in Fig.4. Young and LeBoeuf(Young, 2000) found that peat humic acid and Suwannee River fulvic acid had their glass transition temperatures(T_g) values between 43–62°C and 36–49°C, respectively. Due to variable temperature isotherms below T_g (36°C), the structure and properties of SOM should not be changed with the variance of temperature (Gunasekara, 2003).

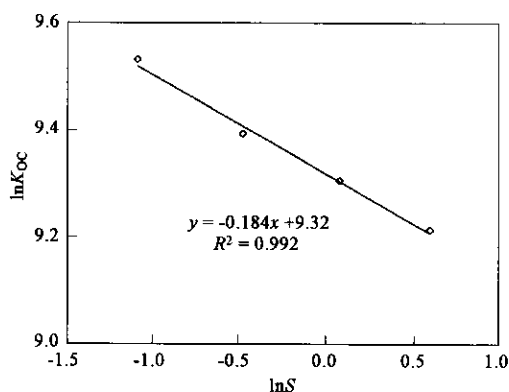


Fig. 4 The relationship between phenanthrene aqueous solubilities and partition coefficients normalized by solid organic carbon content in different temperature

Temperature, as an important parameter of environmental condition, is a significant effect factor on transport of a solute at different seasons and latitude regions

with different temperature. Soil organic pollutants would mobilize more easily in summer with higher temperature than in winter with lower temperature because K_{oc} values decrease with temperature increasing. Organic pollutants are usually desorbed from hot region and transported to cold region in the earth, because sorption of organic pollutants to soils is a spontaneous process. It also suggests a persistence and resistance to degradation of organic pollutants in soils because the sorption reduces their bioavailability. According to the thermodynamics of sorption process, one would predict the transport and fate of organic contaminants in natural environments; and design remediation technologies to maximize the performance efficiency and minimize the remediation cost.

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