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Adsorption of Trace Hydrophobic Compounds from Water on Surfactant-Coated Alumina

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Abstract

The adsorption of several hydrophobic organic compounds (HOCs) from water on alumina coated by sodium dodecylsulfate surfactant "hemimicelles" is discussed. This provides a convenient way of concentrating them on a metal oxide solid support such as alumina. Alumina can be subsequently regenerated with a minimum effort such as a change of pH of the aqueous solution. Adsorption studies showed that the partition constants of HOCs with hemimicelles of sodium dodecylsulfate on alumina is linearly related to their octanol–water partition constants. Surfactant-coated alumina was a better adsorption surface for HOCs than natural soils.

INTRODUCTION

Surfactant molecules form self-aggregate structures called "micelles" above a certain aqueous concentration of monomers called the "critical micellar concentration" (CMC). The formation of micelles is aided by a cooperative interaction (due to van der Waals forces) between the long hydrocarbon chains of the surfactant molecules. The same interaction is believed to be responsible for the formation of surfactant aggregates on solid surfaces such as silica and alumina. A typical isotherm for the adsorption of an anionic surfactant such as sodium dodecylsulfate on alumina is shown in Fig. 1. Four regions are distinguishable. Region I is the Henry's law region for adsorption. As adsorbed concentration increases to a certain value when cooperative interactions between adsorbed molecules become significant (Region II), a sudden phase transition occurs leading to the formation of aggregate structures called "hemimicelles." The concentration at which they are formed is called the "hemimicellar concentration" (HMC) (*1*). In Region III, adsorption increases only slowly, reaching a plateau above the CMC, i.e., Region IV. In Region IV the monomer

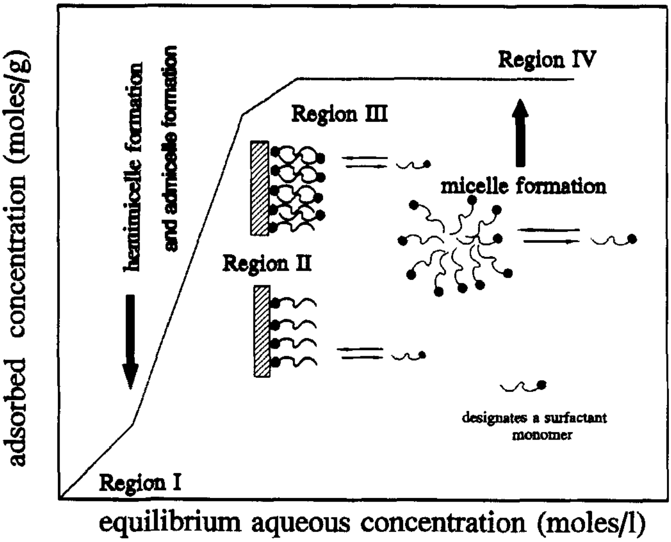

FIG. 1. A typical adsorption isotherm for an anionic surfactant on alumina.

concentration in the aqueous phase is constant and the number of micelles in the aqueous phase increases linearly with added surfactant concentration. As the concentraton of surfactant increases from Region III to Region IV, bilayered surfactant aggregates called "admicelles" are also known to exist (*2*, *3*).

The structures of hemimicelles and admicelles have been probed using a variety of spectroscopic techniques (*4–6*). It has been shown that the interior of the hemimicelles is remarkably similar to those of a micelle and that it is a conducive situation for the incorporation of hydrophobic organic compounds just as micelles are known to do (*7*). Several investigators, including the author, have shown that hemimicelles are capable of solubilizing hydrophobic compounds and thus increase the adsorptive capacity of alumina (*8*, *9*). The process of solubilization of compounds in hemimicelles and admicelles is termed "adsolubilization." Since hemimicelle formation on alumina is a strong function of pH, the surfactants and the adsolubilized material in them can be recovered easily by a change of pH of the aqueous phase. Alumina can then be reused for subsequent adsorption of hemimicelles and adsolubilization without loss of efficiency. The recovery and reuse of surfactants and alumina provide a strong incentive for research for using this process as a possible wastewater treatment process.

In this paper we describe some of our preliminary investigations into the adsorption of a nonvolatile hydrophobic compound (pentachlorophenol) on alumina modified by the presence of hemimicelles of an anionic surfactant (sodium dodecylsulfate). We also summarize some of our earlier work on the adsorption of volatile organic compounds (chloroform, benzene, dichlorobenzene) and some of the existing literature on other compounds (styrene, heptanol, hexanol) with a view to correlating the partition constants between hemimicelles and water with a hydrophobicity indicator such as the octanol–water partition constant. We also compare the binding capacity of surfactant-coated alumina with those of a natural soils for hydrophobic compounds.

EXPERIMENTAL

The sodium dodecylsufate (SDS) used in the experiments was of electrophoresis-grade purity (99%, Bio Rad Labs). 99% pure pentachlorophenol (PCP) and other HOCs were supplied by Aldrich Chemicals. A stock solution of SDS was prepared by dissolving 20 g in 1 L distilled water. A stock solution of 1 *M* NaCl was used for ionic strength adjustment. All chemicals were used as supplied without further purification. Solutions of the desired HOC concentrations were made by appropriate dilution of a saturated aqueous solution of known HOC concentration.

Experiments were performed in glass hypo-vials sealed with Teflon-lined silicone septa and aluminum crimp caps (Pierce Chemical Co.). The total volume of the vial was 157 mL; the final aqueous solution had a volume of 70 mL in each of the experiments. The solution contained 1.5 g alumina (EM Sciences, Chromatographic grade). 3.5 mL of 1 *M* NaCl was used as "swamping electrolyte," and an appropriate volume of SDS was added. The pH was adjusted using 1 *M* sulfuric acid and/or 1 *M* sodium hydroxide. All experiments with PCP were conducted at a pH of 2.2 ± 0.2 to assure that PCP existed as neutral molecules. Experiments with chloroform, benzene, and dichlorobenzene were conducted at pH 6.8. An appropriate volume of standard HOC solution was added and the bottle was immediately capped with a crimp sealer and equilibrated for 24 h at 25°C in a shaker water bath (Techne Instruments). Several such bottles were prepared, each containing varying amounts of SDS and HOC.

After equlibration, a head space analysis of the vapor was carried out to ascertain the adsorbed concentration of chloroform, benzene, and dichlorobenzene; this has been discussed (*8*).

For PCP determination after equlibration, 5 mL of the supernatent solution was withdrawn into a cuvette, the solution acidified using 1 *N* sulfuric acid, and the UV absorbance of PCP at 214 nm determined. The concentration of PCP in the supernatent was determined from a calibration curve of PCP concentration versus absorbance. The amount of PCP adsorbed was determined by difference.

The supernatent aqueous solution was analyzed for the surfactant (SDS) using the classical methylene blue assay method (*10*). Knowing the total added SDS concentration, the amount of SDS adsorbed was determined by difference.

RESULTS AND DISCUSSION

The adsorption isotherms for SDS on alumina at different pH values are shown in Fig. 2. The four regions of the isotherm as described earlier are clearly evident. Notice that in each case even the maximum equilibrium aqueous concentration of SDS is smaller than the CMC (8 × 10^{-3} mol/L), indicating that under these conditions the surfactant exists as an individual monomer with no micellar entities present. The adsorption is a strong function of pH. Since hydrogen (H^+) and hydroxyl (OH^-) ions are the potential-determining ions on mineral oxides, there is an increase in surface potential with decreasing pH. Therefore, negatively charged SDS surfactant ions are adsorbed at low pH values due to increased interactions between the alumina and SDS (*11*). The adsorption reaches a plateau value above aqueous SDS concentrations of approximately 0.0027 mol/L. The maximum SDS adsorbed at pH 4.1 is almost five times as large as at pH

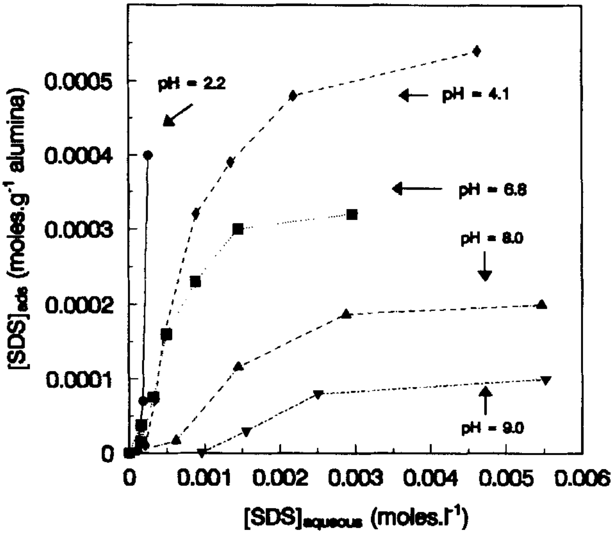

FIG. 2. Experimental adsorption isotherms of SDS on alumina at various pH values.

9.2. At pH 2.2, the adsorption still did not reach a plateau. The onset of hemimicellar phase formation was delayed as the pH increased.

The adsorption of HOCs on alumina was observed to increase with adsorbed SDS concentration on alumina. As an example, the adsorption of PCP onto alumina with and without hemimicelles is shown in Fig. 3. All experiments with PCP were conducted at pH 2.2 ± 0.2. Experiments with chloroform, benzene, and dichlorobenzene were conducted at pH 6.8. The concentrations of SDS adsorbed on alumina were in the rising portion of the adsorption isotherm for SDS on alumina (Fig. 2).

At pH 2.2, PCP exists as neutral molecules and hence the adsorption of neutral PCP is the only process of concern. The adsorption of PCP on alumina in the absence of any SDS in the solution was seen to be negligible; the adsorption following a typical Type III isotherm (*12*). A Type III isotherm indicates that as the maximum PCP solubility in the aqueous phase is reached, multilayer adsorption of PCP on the alumina surface occurs. Since the pK_a of PCP is 4.7 and the pH of the aqueous solution in contact with alumina is 2.2, electrostatic interactions have a negligible effect on the adsorption of neutral PCP on alumina (*13*). Hydrophobic exclusion of the species from bulk aqueous solution is the primary mechanism of adsorption of neutral PCP on alumina. Figure 3 shows that as the concentration of adsorbed SDS increases, the concentration of PCP on the alumina

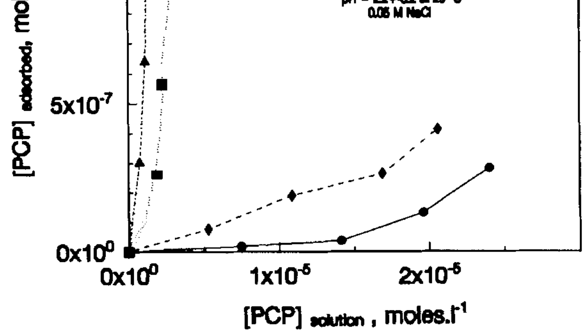

FIG. 3. Adsorption isotherms for pentachlorophenol on alumina with and without hemimicelles of SDS.

surface also increases. The adsorption isotherm becomes linear as the SDS concentration on alumina increases. A similar behavior was observed for chloroform, benzene, and dichlorobenzene (*8*).

The linear portion of the isotherm for each of the HOC was analyzed to obtain a linear adsorption constant for HOC on alumina, i.e.,

$$K_m = [\mathrm{HOC}]_{\mathrm{ads}}/[\mathrm{HOC}]_{\mathrm{aq}} \quad (1)$$

where $[\mathrm{HOC}]_{\mathrm{ads}}$ is the adsorbed concentration (mol/g alumina) and $[\mathrm{HOC}]_{\mathrm{aq}}$ is the equilibrium concentration in the aqueous phase (mol/L). The value of K_m is a function of $[\mathrm{SDS}]_{\mathrm{ads}}$ as shown in Fig. 4. Figure 4 includes the relationship for the four HOCs: pentachlorophenol, chloroform, benzene, and dichlorobenzene (*8*).

The slope (K_h) of the linear relationship between K_m (in L/g) versus $[\mathrm{SDS}]_{\mathrm{ads}}$ (mol/g) is the partition constant for HOC between the hemimicellar phase on alumina and water. The value of K_h for a particular HOC is dependent on the type of surfactant forming the hemimicellar phase.

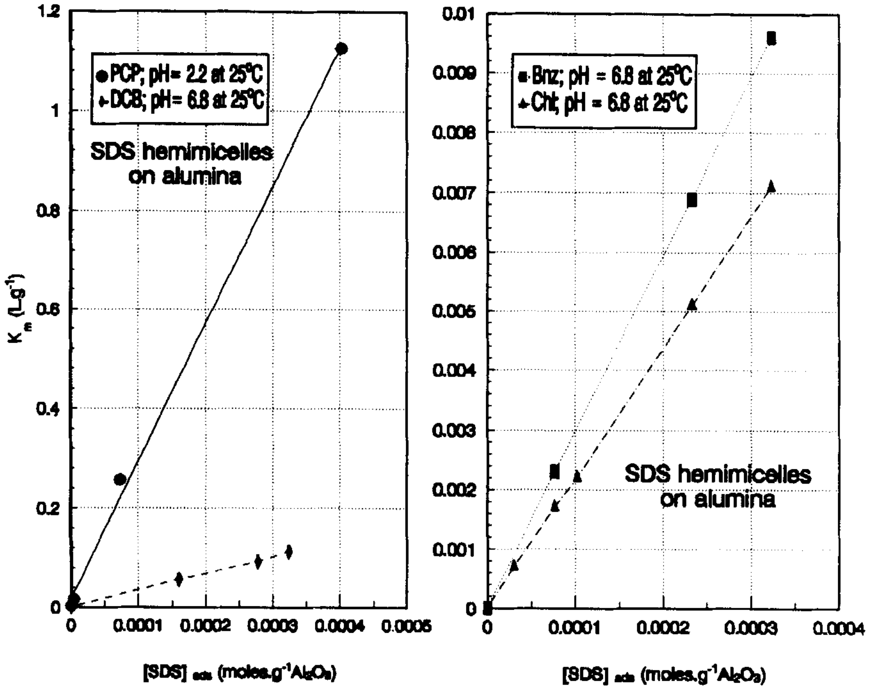

FIG. 4. Dependence of K_m on $[\mathrm{SDS}]_{\mathrm{ads}}$ for various organic compounds on SDS-coated alumina.

Our results, along with those of some other investigators, for other compounds are summarized in Table 1. The values of K_h in Table 1 are in L/kg.

It is well known that partition constants of hydrophobic compounds between sediment or soil surfaces and water and those between surfactant micelles and water are linearly related to hydrophobicity indicators such as octanol–water partition constants, K_{ow}, because of the linear free energy relationships for the transfer processes (*14–16*).

The micelle–water partition constant, P_m, increases with K_h as shown in Table 1. This should be anticipated since the incorporation of HOCs into both micelles and hemimicelles is due to the same entropic driven process of hydrophobic exclusion from water structure. However, it is not clear why the micelle–water partition constants for chloroform, benzene, *n*-heptanol, and dichlorobenzene are lower than the respective K_h values, while for pentachlorophenol they are similar. P_m values are, in general, smaller than their respective K_{ow} values for all compounds except *n*-heptanol.

The relationship between log K_h and log K_{ow} is shown in Fig. 5. Generally, log K_h increases with log K_{ow}. This can serve as a convenient way of correlating log K_h with log K_{ow} for those compounds for which K_h values are as yet unavailable. However, it has to be expected that log K_h versus log K_{ow} correlations will be specific for classes of compounds just as for micelle–water systems (*15*). Knowledge of K_h is essential in ascertaining

TABLE 1
Partition Constants for Solutes between SDS-Coated Alumina and Water

Compound	K_h (L/kg)	Reference	$K_{oc}{}^{d}$ (on alumina)	$K_{oc}{}^{a,d}$ (natural soil)	$P_m{}^{c}$	K_{ow}
Chloroform	76	8	158	35	53	85
Benzene	120	8	207	54	85	135
1,2-Dichlorobenzene	1,216	8	2,432	937	588	3,162
Pentachlorophenol	9,600	This work	20,810	16,937[b]	10,232	100,000
Styrene	1,047	9	2,364	305	—	891
n-Heptanol	643	20	1,311	95	468	251
3-Heptanol	167	20	356	50	—	126
2-Methyl-2-hexanol	61	20	209	41	—	100

[a] Calculated from log K_{oc} = 0.92 log K_{ow} − 0.23 [18].

[b] Obtained from the sorption data on chlorophenols: log K_{oc} = 0.884 log K_{ow} − 0.199 [19].

[c] P_m is the micelle–water partition constant, dimensionless mole fraction ratio given by (mol HOC/L micellar pseudophase)/(mol HOC/L aqueous phase). Values are from Ref. 15.

[d] K_{oc} has dimensions of L/kg.

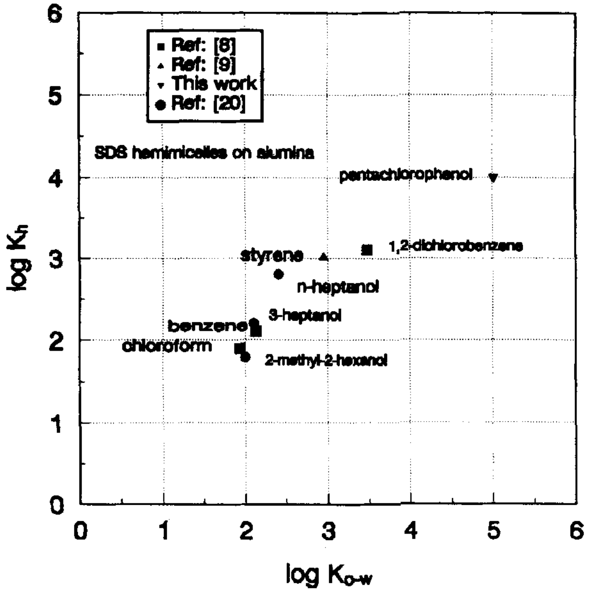

FIG. 5. Relationship between log K_h and log K_{ow}.

the efficacy of the method as a possible tertiary wastewater treatment process.

Since 288.8 g SDS contains 144 g organic carbon, the fractional organic carbon, f_{oc} (in the form of SDS), adsorbed per gram of alumina can be calculated from the known values of $[\mathrm{SDS}]_{\mathrm{ads}}$. Therefore an organic-carbon-based partition constant (K_{oc}, L/kg) for HOC on SDS-coated alumina can be obtained by plotting K_m versus f_{oc}. f_{oc} values ranged from 0 to 0.1 for the various reported experiments. The K_{oc} values thus obtained are given in Table 1. The amount of HOC sorbed on natural soil surfaces can be predicted from the soil organic carbon content, HOC solubility, and its octanol–water partition constant. The predicted K_{oc} values for sorption of HOCs on natural soil using available correlations are given in Table 1. The measured values of K_{oc} for sorption of HOCs on surfactant-coated alumina are greater than the predicted values of K_{oc} on natural soil. For pentachlorophenol, the K_{oc} on surfactant-coated alumina is only marginally higher than the predicted value on natural soil.

K_{oc} values for several compounds such as toluene, trichloroethylene, and xylene adsorption on ferrihydrite covered with SDS surfactant were reported by Holsen et al. (*17*), the alumina coated with commercial humic

TABLE 2
Comparison of K_{oc} Values for HOCs on Various Substrates

		K_{oc} (L/kg)				
Substrate	Coating	Benzene	Toluene	Xylene	Chloroform	Trichloroethylene
Alumina	SDS[a]	207	—	—	158	—
Alumina	Humic acid[b]	—	74	—	—	58
Ferrihydrite	SDS[c]	—	524	1280	—	359
Natural soil	Humic acid[d]	54	176	466	35	75

[a] This work.
[b] For commercial (ICN) humic acid, see Ref. 21.
[c] Ref. 17.
[d] For natural humic acid, see Ref. 18.

acids were reported by Lion and coworkers (*21*). These values are compared with predicted K_{oc} values on natural soils in Table 2. In general, the organic carbon normalized adsorption constants for HOCs on humic acids present on natural soils and humic acid-coated alumina are smaller than those for SDS-coated alumina and ferrihydrite. It can therefore be concluded that surfactant-coated metal oxides are more hydrophobic surfaces than natural soil containing organic matter (humic acids, for example) for the sorption of hydrophobic compounds. Soil organic matter contains a higher polar group content and therefore is less effective in solubilizing nonpolar compounds.

CONCLUSIONS

Adsorbed sodium dodecylsulfate increased the adsorption capacity of alumina surfaces for many hydrophobic organic compounds from water. The partition constant of hydrophobic compounds between surfactant-coated alumina and water was related to hydrophobicity indicators such as octanol–water and micelle–water partition constants. The adsorption constants for HOCs on surfactant-coated alumina were in many cases larger than those for natural soils and sediments. An overall scheme utilizing this process for wastewater treatment with efficient recovery and reuse of surfactants and alumina should be considered for further research.

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