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Partitioning of Hydrophobic Nonpolar Volatile Organics between the Aqueous and Surfactant Aggregate Phases on Alumina

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Abstract

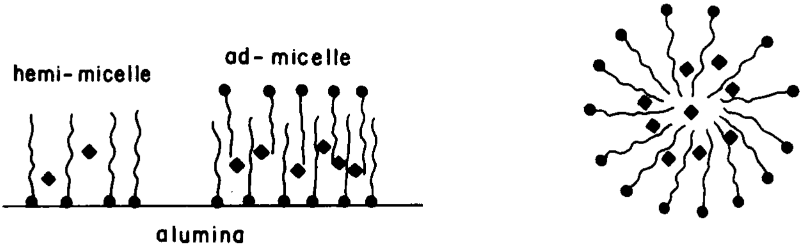
The partitioning of three hydrophobic volatile organic compounds (VOCs)—chloroform, benzene, and 1,3-dichlorobenzene—between the aqueous and two surfactant aggregate phases (sodium dodecylsulfate and sodium dodecylbenzenesulfonate) on alumina was studied using the technique of equilibrium partitioning method in closed systems. Facile incorporation of these compounds into hemimicelles were observed. The partition constants correlated well with traditional hydrophobicity indicators such as octanol-water partition constants and molar solubilities of the hydrophobic compounds in the aqueous phase.

INTRODUCTION

Volatile organic compounds (VOCs) form an important class of groundwater contaminants in many parts of the United States (*1*). The solubility of hydrophobic VOCs in the aqueous phase is an important parameter required in modeling the transport and fate of these compounds in aquifers. Several factors can modify their aqueous solubilities and hydrophobicities. The presence of highly soluble alcohols (e.g., ethanol, methanol) and ketones are known to increase the aqueous solubility of VOCs (*2, 3*). Similarly the presence of surfactant micelles and dissolved organic compounds (e.g., humic and fulvic acids) are also known to enhance the aqueous solubilities of VOCs (*4*).

Most of the hydrophobic VOCs are known to adsorb onto the natural organic matter coating on solid mineral surfaces (*5*). It is also known that many of the VOCs undergo photocatalytic decomposition upon selected mineral oxide surfaces (*6*). Photodechlorination of compounds such as polychlorinated biphenyls (PCBs) in micelles in aqueous solutions have also been reported recently (*7*). It may therefore be possible that surfactant aggregates on mineral oxide surfaces will enhance the photolysis reactions of chlorinated VOCs. The study of the interaction of hydrophobic VOCs with modified mineral oxide surfaces deserves special attention. Hydrophobic bonding of aliphatic acids on alumina has been reported most recently (*8*). Such studies are important since alumina surface is representative of that encountered by other aquatic particles such as hydrous oxides and aluminum silicates which are major constituents of mineral surfaces. There is much controversy as to whether the incorporation of VOCs and other hydrophobic compounds into the natural organic matter (humic and fulvic acid components) on mineral oxide surfaces (e.g., kaolinite and montmorillonite) is a simple two-phase partitioning process or an adsorption process (*9*). Only further detailed studies of adsorption of VOCs on surfaces such as modified alumina can shed light on such questions. It has been reported recently that when long chain amphiphilic surfactant ions such as hexadecyltrimethylammonium ions are exchanged for metal cations like calcium in clays, the sorptive capacity of these clays for nonpolar organics is enhanced considerably (*34*). Such studies show the importance of modified clay surfaces in retaining nonpolar VOCs and other hydrophobic compounds with potential applications in enhancing containment capabilities of clay landfill liners and bentonite slurry walls.

It is well established in the literature that mineral oxides such as alumina and silica form surfactant aggregates on their surfaces called "hemimicelles" well below the critical micellar concentration (CMC) of the surfactant in the aqueous phase. These aggregate structures have properties very similar to those of a micelle and can act as solubilizers of hydrophobic compounds. We have previously shown the ability of micelles, i.e., surfactant aggregates in the aqueous phase formed above the CMC, to solubilize the VOCs (*4*). The structural similarities and the incorporation of hydrophobic molecules within micelles and hemimicelles are shown schematically in Fig. 1. In this paper we report our study on the capacity of hemimicelles to solubilize VOCs and thereby enhance the adsorptive potential of alumina for VOCs in the presence of



(a) HYDROPHOBIC MOLECULE (◆) TRAPPED IN A HEMI–MICELLE OR AD–MICELLE

(b) HYDROPHOBIC MOLECULE (◆) TRAPPED IN A MICELLE

FIG. 1. Schematic of incorporation of hydrophobic molecules in hemimicelles and micelles.

ionic surfactants in the aqueous phase. The equilibrium partitioning technique in closed systems that we described earlier for micellar solubilization of VOCs (*4*) is extended to the hemimicellar solubilization of VOCs to determine the partition constants of VOCs between hemimicelles and water.

EXPERIMENTAL

A series of experiments was performed for each VOC. The VOCs used were chloroform, benzene, and 1,3-dichlorobenzene, all supplied by Fisher Scientific and Eastman Kodak. A saturated stock aqueous solution of each was prepared by overnight stirring. Stock solutions of sodium dodecylsulfate (DDS) and sodium dodecylbenzenesulfonate (DDBS) were prepared by dissolving 20 g in 1 L water. A stock solution of 1 *M* sodium chloride solution was used for ionic strength adjustments. The DDS used was of electrophoresis-grade purity (99%, Bio Rad Labs), and DDBS was supplied by Sigma Chemical Company. These chemicals were used as supplied without further purification.

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 volume was 70 mL in every one of the experiments. The solution contained 1.5 g of alumina (EM Science, Chromatographic grade, BET surface area 240 m^2/

g). 3.5 mL of 1 *M* NaCl and an appropriate volume of surfactant solution to obtain a specific hemimicelle concentration on alumina were added. The pH was adjusted using 1 *M* sulfuric acid and/or 1 *M* sodium hydroxide. 5 mL of the standard stock solution of VOC was added and the bottle was immediately capped with a crimp sealer and equilibrated for 24 h at 25°C in a circulating water bath (Techne Tempette TE-8A). Several such bottles, each containing varying amounts of surfactant, were prepared for each VOC. One additional bottle contained only alumina, NaCl, and VOC with no surfactant, while another bottle contained no alumina or surfactant. These served as control samples. The bottles were periodically removed from the bath and shaken vigorously for approximately 30 s.

After equilibration, 50 μL of the gas phase was injected into a gas chromatograph using a Pressure-Lok gas tight syringe (Dynatech). A Hewlett-Packard 5890A gas chromatograph equipped with a flame ionization detector was used for analysis of the VOCs. The column used for the analysis of benzene and chloroform was a 6-ft long, 1/8 in. i.d. stainless steel column packed with 80/120 Carbopack B coated with 3% SP-1500 supplied by Supelco Inc. 1,3-Dichlorobenzene was analyzed on a 6-ft long, 1/8 in. i.d. stainless steel column packed with 100/120 Supelcoport coated with 3% SP-2250. The oven, detector, and injector temperatures were 110, 220, and 220°C, respectively. Peaks were integrated on an HP 3390A computing integrator.

The supernatant aqueous solutions were then analyzed for the surfactant using the classical methylene blue assay method (*32*). The amount of surfactant adsorbed on alumina was then determined by difference knowing the total added surfactant concentration.

RESULTS AND DISCUSSION

The adsorption of ionic surfactants on alumina is known to follow an S-shaped isotherm as shown in Fig. 2. The experimental isotherms for sodium dodecyl sulfate are shown in Fig. 3. Figures 4 gives the isotherm for DDBS. Three regions are clearly identifiable. Region I is the linear range of adsorption where Henry's law is shown to apply. In this region there is only very sparse coverage of the alumina surface. Region II is characterized by a very rapid incrase in adsorption and is known to be a result of a cooperative interaction between the surfactant hydrocarbon tails. The surface aggregates so formed are called hemimicelles (*10*). In Region III the adsorption increases only very slowly, eventually reaching a plateau above the CMC of the surfactant. Above the CMC the

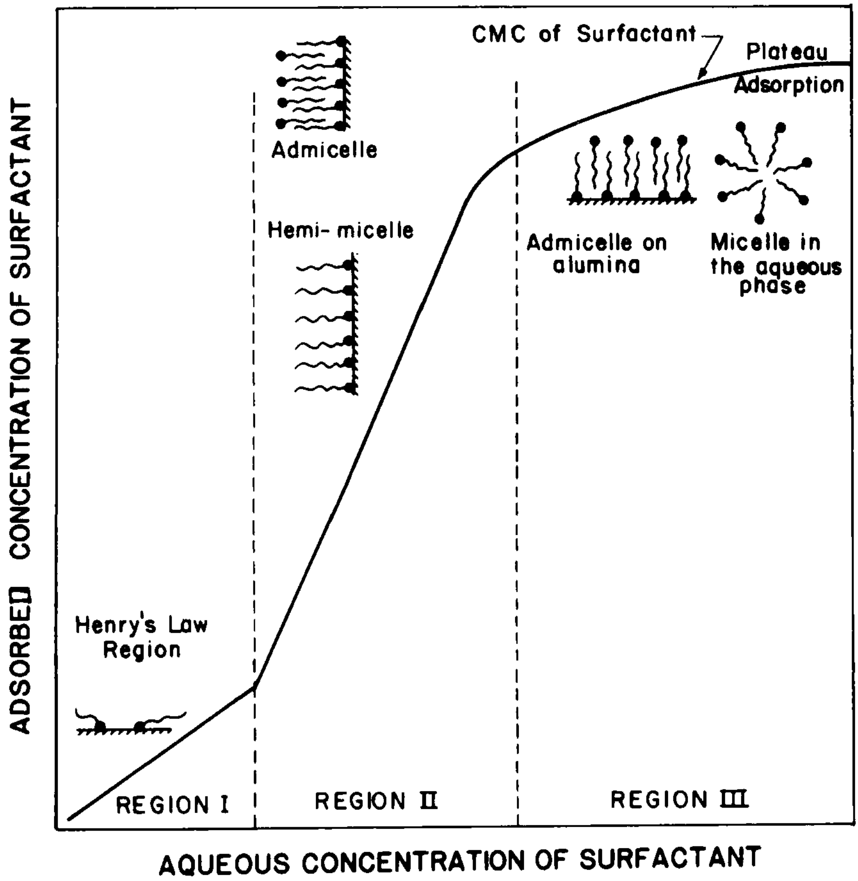


FIG. 2. A typical S-shaped isotherm for adsorption of sodium dodecylsulfate on alumina.

pseudophase separation model of micellization states that the monomeric concentration is constant and that the micelle concentration in the bulk aqueous phase increases linearly with added surfactant concentration. The adsorption of micelles on mineral surfaces is known to be minimal (*11*). Adsorption isotherms such as these are also observed for surfactants on colloids such as aluminum and ferric hydroxides that are commonly used in adsorbing colloid flotation for the removal of heavy metals from the aqueous phase (*12*). It is also known that as the concentration of the surfactant in Region II nears that of Region III, bi-

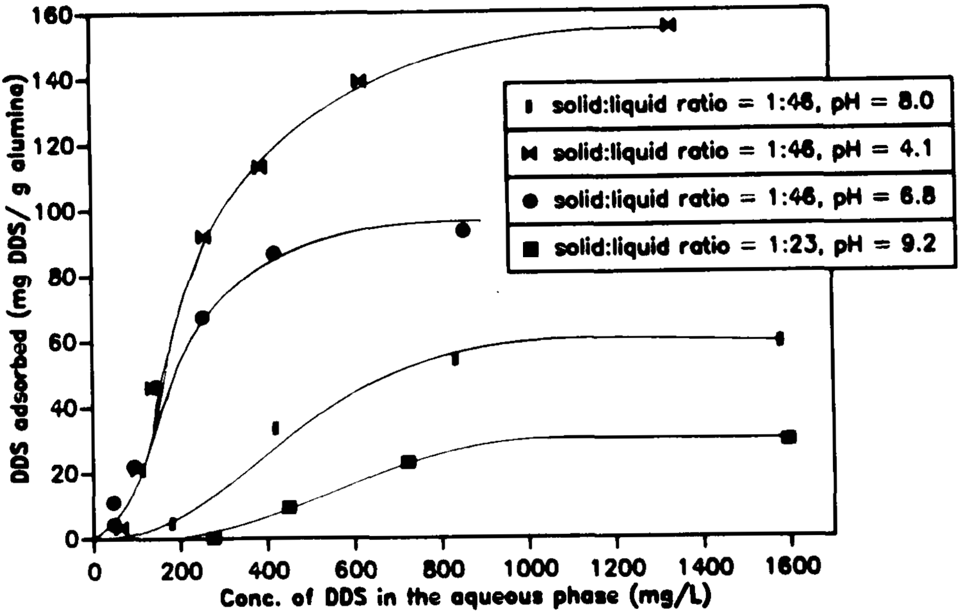


FIG. 3. Experimental adsorption isotherms for sodium dodecylsulfate on alumina at various pH values.

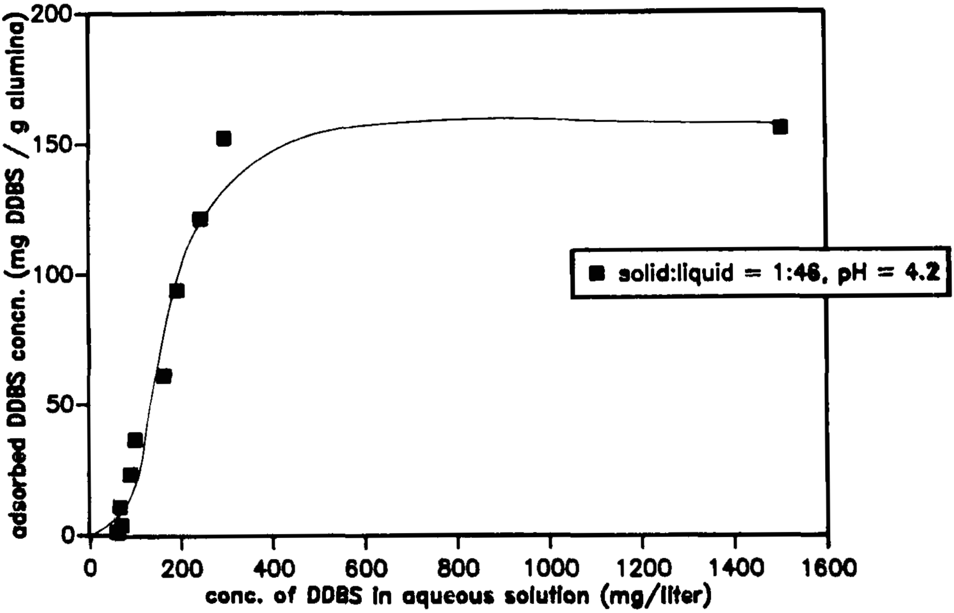


FIG. 4. Experimental adsorption isotherm for sodium dodecylbenzenesulfonate on alumina.

layered structures called "admicelles" are possible (*13*). It has also been suggested that both admicelles and hemimicelles are formed simultaneously on patches of adsorption sites (*14*). In a more recent work the same workers showed that under a wide range of conditions hemimicelles will form first without the simultaneous formation of the admicelles (*15*). Wilson and coworkers provided comprehensive theoretical investigations into the phase transitions occurring on the surfaces leading to hemimicelles and admicelles (*13*, *16*). Several experimental investigations have recently been reported that study the properties of the hemimicellar region. Wilson and co-workers (*17*, *18*) used NMR to show that the surfactants adsorbed as hemimicelles are more restricted in motion than in micelles. Somasundaran and coworkers (*19*) used ESR to study the hemimicellar structure. Others used fluorescence decay study of pyrene adsorbed in hemimicelles to show that the internal structure of hemimicelles is somewhat similar to that of bulk micelles, but of a higher microviscosity than the micellar interior, and that they are quite conducive to the incorporation of hydrophobic compounds such as pyrene (*20*, *21*). This property of hemimicelles was utilized by O'Rear and coworkers (*22*) to study the polymerization of styrene in hemimicelles and admicelles with possible use in the formation of uniform thin films on solid surfaces. More recently another interesting area called admicellar chromatography was reported (*23*) which also makes use of the solubilization capacity of these surfactant aggregates on alumina.

In the experimental adsorption isotherms of DDS and DDBS on alumina shown in Figs. 3 and 4, the three regions of adsorption discussed above are clearly evident. Notice that the equilibrium aqueous concentrations of DDS are smaller than the CMC (8 m*M* = 2312 mg/L) in these experiments, suggesting that under these conditions most of the surfactants exist as individual molecules with little or no micellar entities present. The adsorption is seen to be highly dependent on the pH of the solution. Since hydrogen (H^+) and hydroxyl (OH^-) ions are the potential determining ions on mineral oxides, there is an increase in surface potential as pH decreases. Therefore negatively charged surfactant ions are adsorbed more at low pH values due to increased interactions between the adsorbate and surface (*11*). As can be seen from Fig. 3, the plateau adsorption at pH 4.1 is approximately five times as large as at pH 9.2. It can also be seen that increasing pH leads to a larger aqueous surfactant concentration for the onset of the hemimicellar phase on alumina.

Under the conditions of adsorption shown in Figs. 3 and 4 we conducted partitioning experiments to determine the incorporation of VOCs in the hemimicelles. The equilibrium partitioning concept described here is based on a method previously used by Gossett (*24*) to obtain Henry's law constants for VOCs. The same method was used by Garbarini and Lion (*25*) to determine the sorption of VOCs on humic acid-coated alumina. Valsaraj and coworkers (*4*, *26*) used a variation of the same technique to obtain the partition constants for VOCs between aqueous and micellar phases.

Consider two identical closed systems, one containing alumina and a certain concentration of a VOC and the other containing the same amount of alumina and VOC but also containing a certain amount of surfactant adsorbed on the alumina to form hemimicelles. The aqueous volume in both caes should be the same. Then at equilibrium the following mass conservation equations are applicable to the two systems:

$$M_T = C_{l1}H_cV_g + C_{l1}V_l \tag{1}$$

$$M_T = C_{l2}H_cV_g + C_{l2}V_l + X \tag{2}$$

where M_T is the total mass of VOC added (grams), C_{l1} and C_{l2} are the equilibrium aqueous concentrations of VOCs in the two cases (grams/liter), V_g is the gas phase volume (liter), V_l is the aqueous phase volume (liter), and X is the amount of VOC incorporated into the hemimicelle (grams).

It is well known that alumina by itself and not subjected to any chemical pretreatment is a very poor adsorber of nonpolar VOCs (*25*, *27*, *28*). If adsorption of VOCs does occur at all on mineral oxides, it has been suggested that it can be only through chemisorption and has been shown to be quite negligible (*28*) unless the adsorbed VOCs are significantly polar in nature. In our experiments on control samples we observed no adsorption of the VOCs used in these experiments. We measured the vapor concentration of VOCs in two identical closed systems of equal volumes, one containing only VOC in water and the other containing both alumina and VOC, and found less than 3% difference in the vapor concentrations for chloroform. This experiment also proved that alumina does not contribute to any "salting-out" of the VOCs. We also used 0.05 *M* NaCl as a "swamping" electrolyte in all the experiments, and it was necessary to see if NaCl would contribute to any "salting-out" effects. Hence we conducted an equilibrium experiment where two bottles both containing 1.5 g alumina with 10 m*M* chloroform in 70 mL aqueous solution (one containing 0.1 *M* NaCl and the other 0.05 *M* NaCl) were equilibrated. The vapor concentrations in these two bottles were equivalent within the limits of analytical precision, supporting our premise that the electrolyte was acting as a "swamping" electrolyte. Hence the Henry's constant values in both Eqs. (1) and (2) are assumed to be the same as for an aqueous solution of VOC in equilibrium with its vapor.

If we define a linear partition constant for the VOC between the aqueous phase and the surfactant aggregate as K_h = (amount of VOC solubilized in the hemimicelle per gram of adsorbed surfactant)/(concentration of the VOC in the aqueous phase), then we can write

$$(X/MX_d) = K_h C_{eq} \tag{3}$$

where X = mass of VOC adsorbed (grams), M = mass of alumina employed (grams), X_d = amount of surfactant adsorbed (grams surfactant/gram alumina), and C_{eq} = equilibrium concentration of the VOC in the aqueous phase (grams/liter). The above definition of K_h is similar to the conventional definitions of distribution constants for solutes between two liquid phases or between a solid surface and a liquid phase. It is a valid definition only for low solute concentrations in the two phases. Then from Eqs. (1) and (2) we have

$$X = (V_l + H_c V_g)(C_T - C_{eq}) \tag{4}$$

where $C_T = C_{l1}$ = equilibrium VOC concentration in the aqueous phase of the system without hemimicelles on alumina and $C_{eq} = C_{l2}$ = equilibrium aqueous concentration of VOC in the system with hemimicelles on alumina. By substitution of Eq. (3) into Eq. (4) we have

$$(C_{g,t}/C_{g,eq}) = (C_T/C_{eq}) = K_h[MX_d/(V_l + H_c V_g)] + 1 \tag{5}$$

where $C_{g,t}$ and $C_{g,eq}$ are gas phase concentrations in equilibrium with C_T and C_{eq}, respectively. When gas chromatographic peak areas are linearly related to gas concentrations measured, then the gas concentrations may be replaced with the respective peak areas. Equation (5) shows that a plot of $(C_{g,t}/C_{g,eq})$ versus $[MX_d/(V_l + H_c V_g)]$ will give K_h as the slope and 1 as the intercept. It is clear that Eq. (5) and therefore this technique will be more sensitive for solutes with low H_c and large K_h values. A major advantage of this technique is that we need not know the absolute values of the total added VOC concentrations. This is a marked advantage over other techniques like solvent extraction or purge-and-trap analysis of the aqueous phase for determining the residual aqueous phase VOC concentrations and thereby obtaining the partition constants between the aqueous and solid phases. Effects such as the "solids effects," which are experimental artifacts resulting from incomplete separation of the phases, are therefore eliminated when the vapor phase measurements in closed systems are used (*25*).

Figure 5 gives the plot of $[MX_d/(V_l + H_cV_g)]$ versus $C_{g,t}/C_{g,eq}$ for the three VOCs investigated, viz., chloroform, benzene, and 1,3-dichlorobenzene in DDS hemimicelles. Figure 6 is the same plot for DDBS. It is clear that as the adsorbed surfactant concentration X_d (as hemimicelles on alumina) increases, the value of $C_{g,t}/C_{g,eq}$ increases linearly. In other words, $C_{g,eq}/C_{g,t}$ decreases with increasing X_d. This means that the vapor concentration of VOCs decreases with X_d, showing the facile partitioning of these compounds onto the hemimicelles formed on alumina. It is known that below the CMC the surfactant molecules by themselves do not affect the aqueous solubility or vapor concentration of VOCs in a closed system (*4*). This, coupled with our observation that alumina by itself also does not affect the vapor concentration of VOCs, clearly indicates that the observed reductions in vapor concentrations of the VOCs are solely due to the presence of surfactant aggregates on alumina.

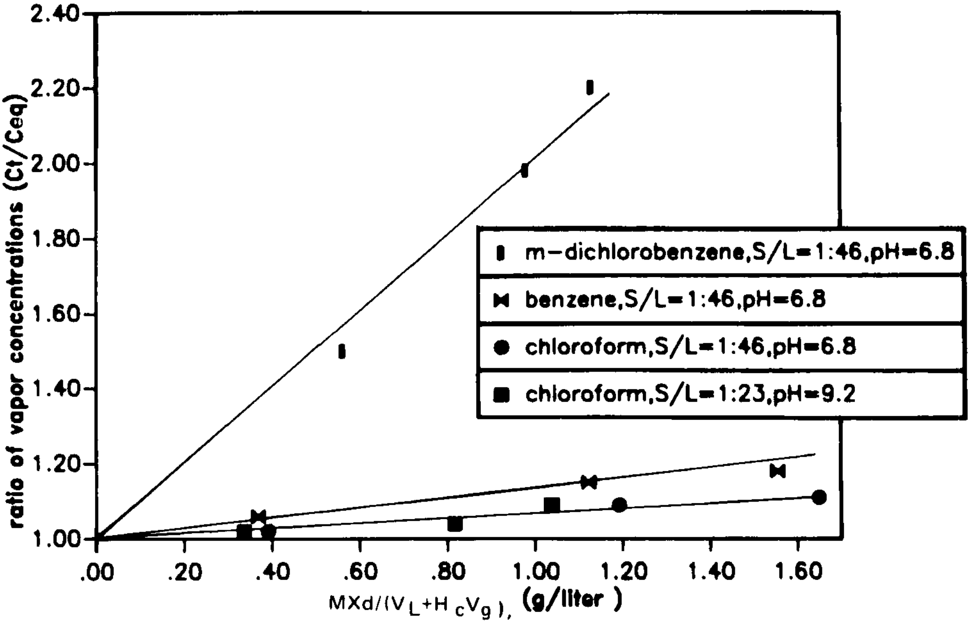


FIG. 5. Plot of vapor concentration ratios of VOC as a function of adsorbed DDS on alumina.

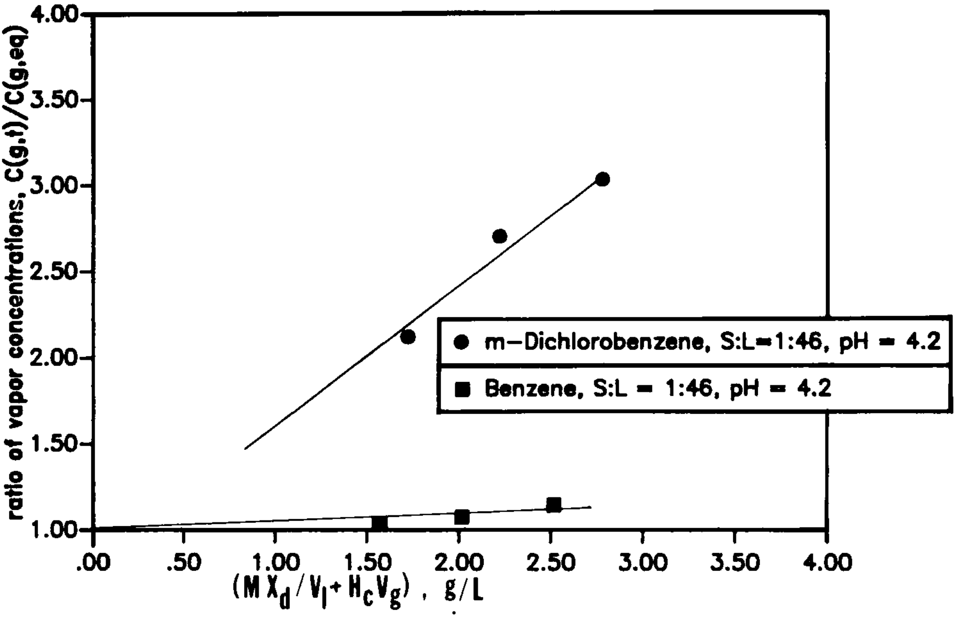


FIG. 6. Plot of vapor concentration ratios of VOC as a function of adsorbed DDBS on alumina.

The slopes of the lines are given in Table 1 along with other relevant properties of the VOCs. Notice that both the aqueous solubility and vapor pressure decrease as one goes from chloroform to 1,3-dichlorobenzene. The hydrophobicity as determined by their octanol–water partition constants follow the order 1,3-dichlorobenzene > benzene > chloroform. It can be seen that log K_h values also follow the same trend as shown in Fig. 7. The direct proportionality between log K_{ow} and log K_h is not surprising when we consider the fact that the driving force for the transfer of a hydrophobic molecule from water to octanol is the same as that for water to hemimicelles. In both cases it is the shearing off of an ordered layer of water molecules around the nonpolar solute that is responsible for the favorable transfer process (*29*). Similar relationships between K_{ow} and other partition constants such as sediment–water (*5*), micelle–water (*26, 31*), and dissolved organic matter–water (*30*) exist in the literature. It is interesting to note that the partition constants for the DDBS systems are slightly different from those for the DDS systems. This may be due to the different environments that the hydrophobic VOCs find themselves

TABLE 1
Pertinent Properties of VOCs

Property	Chloroform	Benzene	1,3-Dichlorobenzene
Molecular weight	119.5	78	147
Vapor pressure (mmHg)	158.1	95	2.3
Log S^a	−1.09	−1.64	−3.08
Log $K_{ow}{}^a$	1.93	2.13	3.48
K_h:[b]			
For DDS hemimicelles	76 ± 19	120 ± 5	1216 ± 70
For DDBS hemimicelles	—	110 ± 8	807 ± 60
$H_c{}^c$	0.170	0.230	0.136

[a] From Ref. *33*. S is in moles/liter. For compounds that are solids at room temperature, supercooled liquid solubilities are used as recommended in Ref. *33*.

[b] K_h expressed in liter/kilogram.

[c] Determined in our laboratory using EPICS as described in Ref. *24*.

in DDBS hemimicelles as compared to DDS hemimicelles. A similar trend was noticed for micelle-water partition constants (*4*). This also suggests that specific solute-surfactant interactions are to be considered in understanding the solubilization of VOCs in hemimicelles or micelles. This explains the difficulty in obtaining a single uniform correlation to predict the solubilization of hydrophobic compounds in hemimicelles or micelles (*26*). Since for nonpolar organic compounds K_{ow} is inversely proportional to molar solubility (S), the resultant log K_h–log S relationship shown in Fig. 7 is also not surprising. A similar relationship between S and micelle-water partition constants for the same compounds has been reported elsewhere (*26*).

Some of the compounds that are of environmental significance such as polychlorinated biphenyls (PCBs), polynuclear aromatics, chlorinated pesticides, dioxins, etc. have low vapor pressures and aqueous solubilities and large K_{ow} values. Such compounds may therefore be easily trapped in hemimicelles on alumina surfaces. Dechlorination reactions of PCBs in micellar media are reported to be much faster than in aqueous media (*7*). Photocatalysis on mineral oxide surfaces are also known to be faster than in aqueous media alone (*6*). It therefore seems feasible that dechlorination reactions may be facilitated by hemimicelles on alumina. This and other aspects of hemimicelle-mediated processes deserve careful study. Since neutral nonpolar molecules can be easily incorporated into hemimicelles, it seems possible to use the various spectroscopic tech-

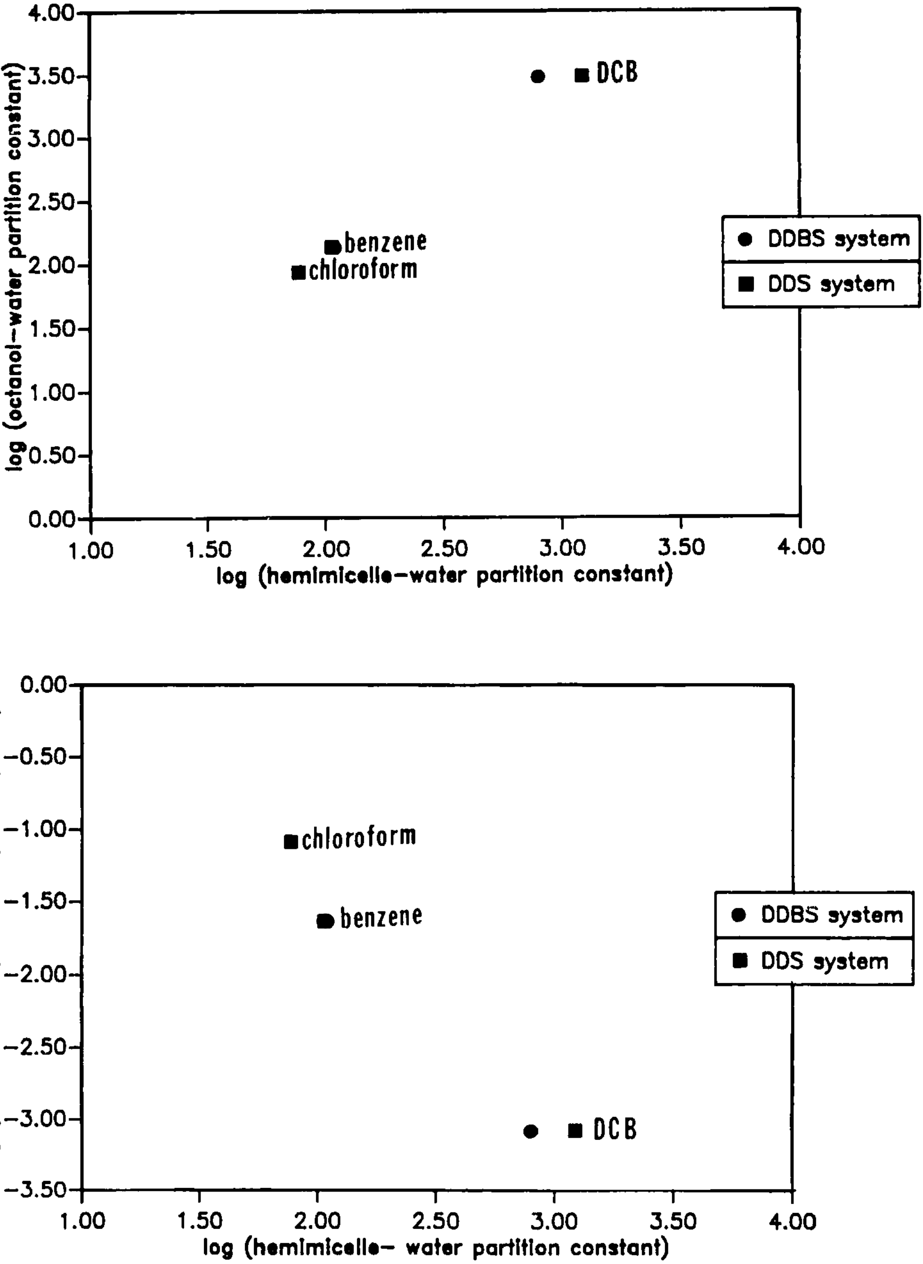


FIG. 7. Relationships between hemimicelle-water, octanol-water, and molar aqueous solubilities for hydrophobic VOCs.

niques to probe these solubilized molecules and thus indirectly study the surface aggregates without affecting their structure. Several of these aspects are being currently addressed in our laboratory.

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