⊕EPA ENVIRONMENTAL RESEARCH BRIEF

The Use of Cationic Surfactants to Modify Aquifer Materials to Reduce the Mobility of Hydrophobic Organic Compounds

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ABSTRACT

Cationic surfactants can be used to modify surfaces of soils and subsurface materials to promote sorption of hydrophobic organic compounds (HOC) and retard their migration. For example, cationic surfactants could be injected into an aquifer downgradient from a source of HOC contamination to provide a temporary barrier against migration. A possible side effect of such a treatment could be the mobilization of previously adsorbed metal ions through cation exchange with the cationic surfactant.

Batch and column experiments were performed to investigate these phenomena. The cationic surfactant was dodecylpyridinium (DP); the HOC were chlorobenzene homologs; competing metal ions were Pb^{2+}, Cd^{2+}, and Cu^{2+}; and sorbents were low-organic-carbon aquifer materials (Lula, EPA-12, Borden Sand) and pristine minerals (kaolinite, montmorillonite). The investigation covered three major topics: (i) adsorption of DP to particle surfaces; (ii) sorption of chlorobenzenes to DP-modified surfaces; and (iii) adsorption competition between DP and the metal ions.

The adsorption isotherms of DP were distinctly nonlinear, even at very low surface concentrations. The distribution of DP was strongly dependent on the solution concentrations of Na^+ and Ca^{2+}, but virtually independent of solution pH. A multisite adsorption model was developed to describe adsorption over a wide range of DP, NaCl, and $CaCl_2$ concentrations. Two types of adsorption reactions were found to be significant: exchange of DP with a alkali-metal cation, and adsorption of pyridinium with chloride counter-ion.

Distribution ratios of the chlorobenzenes varied nonlinearly with DP loading of the surface. The elution of chlorobenzenes from columns packed with DP-treated aquifer material showed significant retardation with only moderate amounts of DP on particle surfaces. A transport model based on results of the batch experiments and the local equilibrium assumption yields an acceptable approximation for the coelution of DP and HOC from the column. It is concluded that treatment of surfaces with cationic surfactants shows promise as a means of promoting HOC sorption in a variety of treatment processes.

A comparison of the adsorption isotherms of DP, Pb^{2+}, Cd^{2+}, Cu^{2+} shows that DP is adsorbed more strongly than the metal ions from solutions at pH 5.5 - 6.0. Competition experiments suggest that DP and the metal ions adsorb to different types of sites, and that competition becomes significant only when about half the CEC of the material is occupied by DP. These results suggest that adsorbed metal ions could not effectively be removed by washing aquifer material with DP, but that aquifer materials could be treated with DP to retard HOC without danger of mobilizing adsorbed metal ions.

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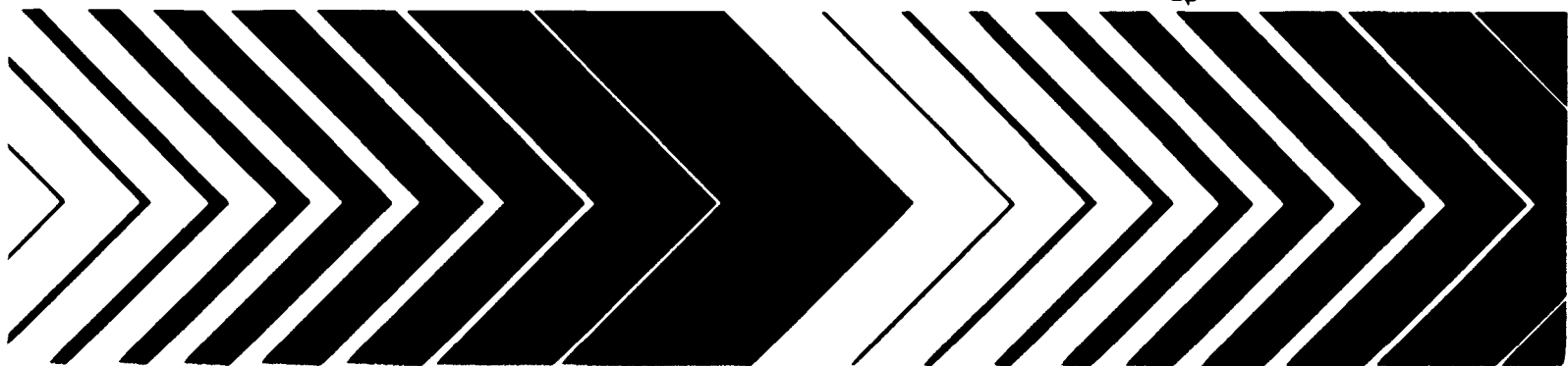   SUNY, Stony Brook, NY 11794-5000

INTRODUCTION

Cationic surfactants that enter the subsurface environment will modify the surfaces of soils and subsurface materials to promote sorption of hydrophobic organic compounds (HOC), and reduce

the mobility of the HOC in the subsurface environment. While this process will occur naturally as cationic surfactants enter the environment, this process might also be the basis for remedial action at contaminated sites. For example, cationic surfactants could be injected into an aquifer downgradient from a source of HOC contamination to provide a temporary barrier against migration. Alternatively they could be used in conjunction with in-situ bioremediation to eliminate the HOC contamination; the surfactant could retard a contaminant such as TCE long enough for a relatively slow process such as reductive dehalogenation to be effective. Related applications might include the control of vapor emissions from in-situ biofilters and the increase in retention time of HOC in slurry bioreactors.

A possible side effect of such a treatment could be the displacement of previously adsorbed metal cations through ion exchange with the cationic surfactant. Alternatively, the cationic surfactant could be considered as a means of accelerating desorption of metal cations as part of a soil cleaning treatment.

Thus, a wide range of questions on the environmental chemistry of cationic surfactants exist depending on whether the compounds are introduced as waste or as part of a treatment program, and whether the goal is to enhance or to retard the mobility of other pollutants, and whether the other pollutants behave more like metal ions or more like hydrophobic organic compounds. This study was undertaken to elucidate some these questions as a basis for management of cationic surfactants compounds in the environment.

We focus on batch and column experiments designed to examine the ability of cationic surfactants to modify the surface of a low organic carbon aquifer material to promote the sorption of HOC. Several questions were addressed: (i) will the cationic surfactant adsorb strongly enough that it will not itself migrate? (ii) will the cationic surfactant adsorb so strongly that it will be impossible to disperse it in the subsurface environment? (iii) how do major

cations (Na^+, Ca^{2+}) and pH affect adsorption of the cationic surfactant? (iv) will the cationic surfactants promote the sorption of the HOC to a sufficient degree? (v) how well can column behavior be predicted from batch behavior? (vi) is it possible to engineer a system to determine the amount of cationic surfactant that must be applied to obtain a preselected retardation of HOC? (vii) to what extent will the treatment of particle surfaces with cationic surfactants release adsorbed metal ions?

Although beyond the scope of this effort, several other issues would have to be considered before field application of cationic surfactants could be undertaken, including: the ultimate fate of the surfactant, the effect of the surfactant on the permeability of natural aquitards, the effect of the cationic surfactant on subsurface microorganisms (particularly if bioremediation were being considered), and the availability of cationic-surfactant-sorbed HOC for biological degradation.

METHODS

The study was carried out in three major steps: (i) study of adsorption of a cationic surfactant to particle surfaces (Brownawell et al., 1990); (ii) study of the sorption of chlorobenzenes to surfactant-modified surfaces (Wagner et al., 1994); and (iii) study of adsorption competition between the surfactant and the metal ions Pb^{2+}, Cd^{2+}, and Cu^{2+} (Westall and Chen, 1994). The original papers should be consulted for details about experimental procedures.

Materials

The cationic surfactant used in this study was dodecylpyridinium (DP), which was selected for the ease of analysis by UV spectrophotometry and its resistance to biodegradation in slurries of soils and subsurface materials; the structure of DP is shown in Figure 1. In a limited number of experiments, we have found that its behavior resembles that of other cationic surfactants. Additional
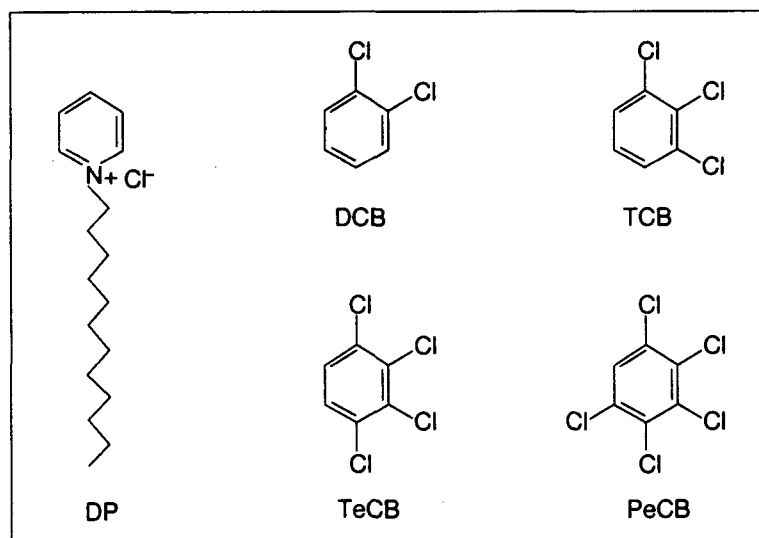

Figure 1. Structures of dodecylpyridinium chloride and chlorobenzene homologs.

criteria would have to be considered if field studies were planned. Labeled N-[1-^{14}C]dodecylpyridinium bromide was obtained from Pathfinder Laboratories, Inc., St. Louis, MO. The specific activity was 10.6 Ci/mol, and the purity of the label was greater than 99% as determined by HPLC with radioactivity detection. Solutions of DP used in this study were checked periodically for purity; no evidence of degradation was found. Unlabeled DP was purchased as the chloride monohydrate from Aldrich Chemical and used as received. The critical micelle concentrations (CMC) at 25°C in 0.01 and 0.1 M NaCl solutions are estimated from the data of Ford et al. (1966) as 13 and 6.3 mM, respectively.

The hydrophobic organic compounds were chlorobenzenes (Figure 1): 1,2-dichlorobenzene (DCB), 1,2,3-trichlorobenzene (TCB), 1,2,3,4-tetrachlorobenzene (TeCB), and pentachlorobenzene (PeCB). These compounds are moderately hydrophobic, with $3.4 < \log K_{ow} < 5.0$ (Miller et al., 1984).

Several low-organic-carbon aquifer materials and pristine minerals were used as sorbents (Table 1). The sorbent for the column experiments was Lula N6, a low-organic-carbon aquifer material, obtained from the R. S. Kerr Environmental Research Laboratory, U.S. EPA, Ada, Oklahoma. The material is essentially an iron oxide coated silica sand, with fraction of organic carbon, f_{oc}, of 0.2 g_c kg^{-1} (0.02%). The fraction that passed through a 250 μm sieve was used in all column experiments. Other sorbents were examined for comparison. A 74 - 210 μm fraction of aquifer material Borden sand (Bouchard et al., 1988; Fuller et al., 1987), isolated by dry-sieving, was used. EPA-12 soil (Hassett et al., 1980) was provided by Professor John J. Hassett of the University of Illinois. Georgia kaolin (KGa-1) and Wyoming Na-montmorillonite (SWy-1) (van Olphen et al., 1979) were obtained from Source Clays Repository at the University of Missouri. Before use in batch sorption experiments, each sorbent was washed several times to equilibrate the sorbent with the electrolyte and to reduce the amounts of suspended material that are not separated from the aqueous phase by centrifugation.

TABLE 1. SOME PROPERTIES OF THE SORBENTS USED IN THIS STUDY[a]

sorbent material	organic carbon, %	CEC, mmol/kg
kaolinite (KGa-1)	0.022	20[b]
Na-montmorillonite (SWy-1)	0.020	764[b]
Borden sand	0.026, 0.020[c]	7.0[d], 23[c]
Lula N6 aquifer material	0.021, 0.033[c]	90[c]
EPA-12 soil	2.12, 2.33[e]	135[e]

[a] Organic carbon contents were determined on a LECO carbon analyzer, unless otherwise referenced. Procedures for cation exchange capacity (CEC) determination are given in the references cited.
[b] van Olphen et al., 1979.
[c] Bouchard et al., 1988.
[d] Fuller and Davis, 1987.
[e] Hassett et al., 1980.

Procedures

Batch sorption experiments were carried out as described by Brownawell et al. (1990), Wagner et al. (1994), and Westall and Chen (1994). The concentration distribution ratio, D_c, is calculated from

$$D_c = C_i(s) / C_i(w) \qquad (1)$$

where $C_i(s)$ (μmol/kg) and $C_i(w)$ (μM) are the concentrations of the component i associated with the sorbent and in the water, respectively.

Column experiments were carried out as described by Wagner et al. (1994). The column, end fittings, tubing, and low dead-volume unions were stainless steel, which was found to be superior to a glass-teflon system in reducing sorption of these moderately hydrophobic compounds to surfaces of the apparatus.

RESULTS

Adsorption of DP to Particle Surfaces

Adsorption Isotherms of DP

Adsorption isotherms of DP at relatively high (mM) concentrations, on several different sorbents, are shown in Figure 2. The equilibrium concentrations of DP in solution were well below the critical micelle concentration (CMC) in all cases. The surface concentrations reach plateau levels in almost all cases. The plateau concentrations correspond closely, but not strictly, to the cation exchange capacities reported for the five sorbents (Table 1).

For high energy surfaces, plateau adsorption can occur at concentrations much below the CMC (Greenland and Quirk, 1962). When plateau adsorption occurs below the CMC, the possibility of multiple layer adsorption is more likely. Multiple layer adsorption has been suggested to interpret adsorption of cationic surfactants onto silica (Ter-Minassian-Saraga, 1966; Bijsterbosch, 1974), montmorillonite (Greenland and Quirk, 1962), and other clays (Malik et al., 1972; Ralston and Kitchener, 1975). While it is tempting to speculate about the orientation and structure of DP at the surface, the heterogeneity of the surface and the absence of additional data preclude any firm conclusions.

From the data in Figure 2, it appears that adsorption could be explained as a simple, virtually quantitative, ion-exchange reaction, with step-function isotherms. However, if the data are considered over a wider range of concentrations, it is apparent that the situation is more complicated. The logarithmic adsorption isotherms of DP on five different materials, over many orders of magnitude, are shown in Figure 3. From these data it is apparent that DP adsorption cannot be expressed as a simple reaction going to completion. Over a wide range of concentrations (below about 10-100 μM DP in solution), the isotherms conform to the Freundlich equation:

$$\log C_{DP}(s) = n \log C_{DP}(w) + \log K \qquad (2)$$

where $C_{DP}(s)$ is the amount of DP adsorbed to the surface, $C_{DP}(w)$ is the concentration of DP in solution, and K and n are constants. The values of n determined from the slopes of the isotherms in the low concentration region are approximately 0.6.
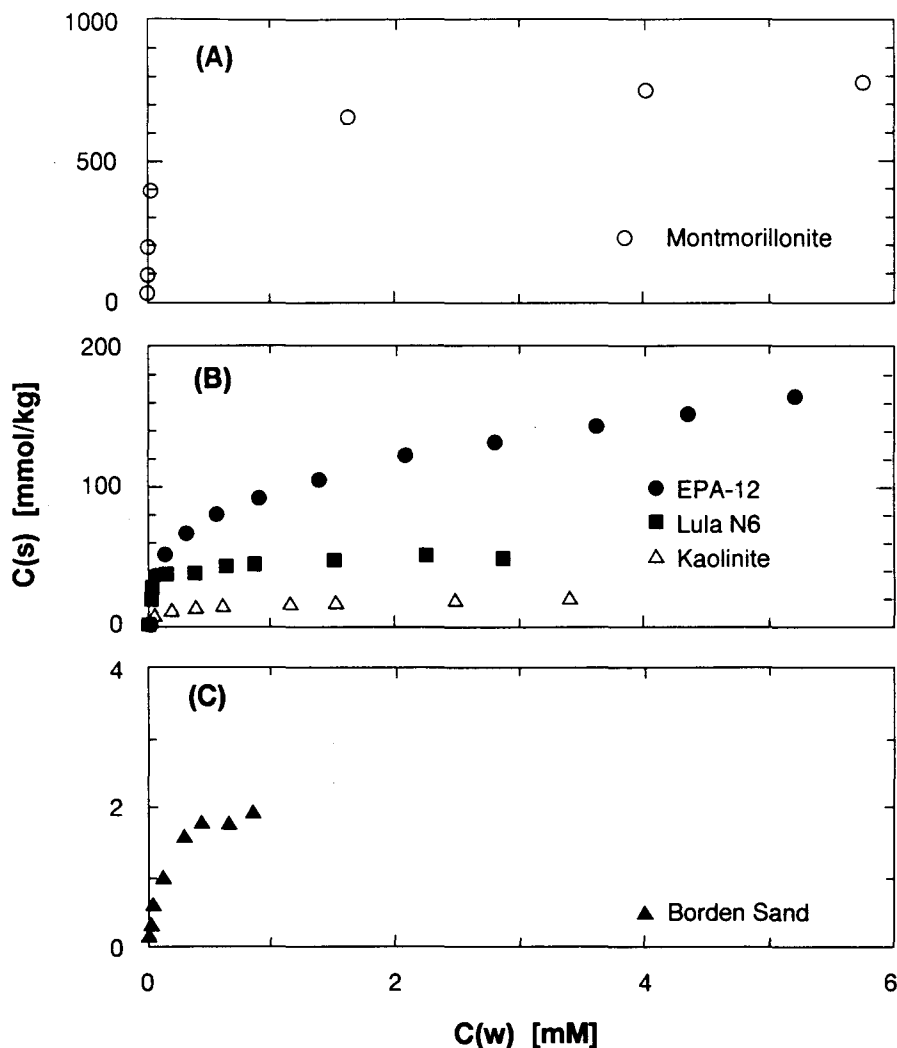
Figure 2. Adsorption isotherms of dodecylpyridinium on different materials. Data are from the high concentration range of Figure 3, plotted here on a linear scale. Note the correspondence between the plateaus of the adsorption isotherms and the cation-exchange capacities listed in Table 1. Range of pH values for the data in the isotherms: (A) montmorillonite, pH = 7.13-5.46; (B) kaolinite, pH = 5.39-4.72; soil EPA-12, pH = 7.43-7.00; Lula aquifer material, pH = 6.81-4.49; (C) Borden sand, pH = 9.39-9.02. Solutions contained 0.01 M Na$^+$; ratios of solids to liquids are given in the legend of Figure 3.

These low values of n indicate nonlinearity in the isotherms, but not the step-function that one perceives from Figure 2. (A linear isotherm is one in which the surface concentration is directly proportional to the solution concentration, i.e., n = 1 in Equation 1.) The nonlinearity extends to surface concentrations that are as low as 0.02% of the maximum surface coverage measured in the case of EPA-12 soil. As will be discussed, this nonlinearity is attributed to heterogeneity of adsorption sites.

The isotherms in Figure 3 exhibit no evidence of hemimicelle formation, which we define operationally as a region in the log-log isotherm with slope greater than one. Hemimicelle formation occurs at surfaces when cooperative hydrophobic interactions among adsorbed species dominates over repulsive and entropic

effects. The absence of an observable hemimicelle region in the isotherms is attributed to the heterogeneity of the materials and the electroneutrality of the ion-exchange reactions.

Effect of pH on Adsorption of DP

The effect of [H$^+$] on the adsorption of DP is shown in Figure 4. A very small dependence of D_c on pH was observed for the environmental sorbents; the slopes (Δ log D_c / (Δ log [H$^+$])) determined from linear regression of the data in Figure 4 were less than -0.05.

Two mechanisms through which pH can influence adsorption are (i) a change in surface potential from protonation-deprotonation
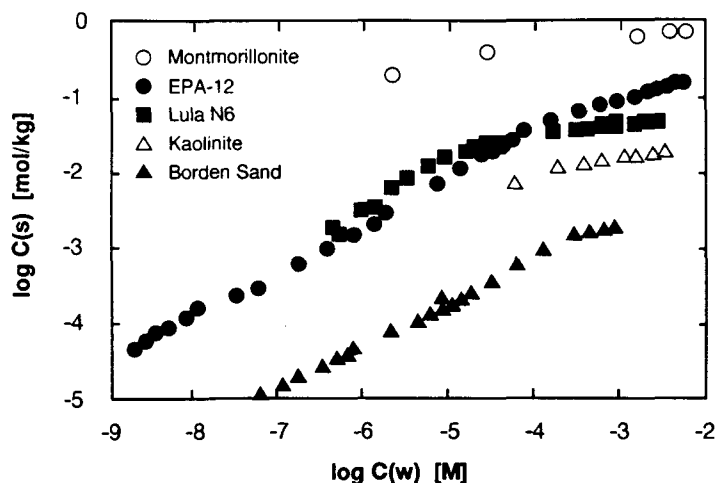
Figure 3.   Logarithmic adsorption isotherms of dodecylpyridinium on different materials. Montmorillonite, ratio of solids to liquids [$C_s(w)$] was 0.0050 kg/L; kaolinite $C_s(w)$ = 0.025; soil EPA-12, $C_s(w)$ = 0.025; Lula aquifer material, $C_s(w)$ = 0.0025; and Borden sand, $C_s(w)$ = 0.025 or 0.050 kg/L. Solutions contained 0.01 M Na^+.

of pH-dependent surface functional groups, or (ii) ion-exchange of H^+ for pyridinium. The data (Figure 4) indicate that both of these effects are weak.

Effect of Major Cations on Adsorption of DP

The effect of concentration and type of electrolyte on adsorption of DP was examined with two complementary types of data: (i) adsorption isotherms of DP from solutions with various concentrations of salts; and (ii) concentration distribution ratio of DP as a function of concentration of NaCl or $CaCl_2$, with a constant amount of DP in the system. In view of the nonlinearity of the isotherms, the first method is preferable for development of mechanistic models, while the second provides a quick estimate of the magnitude of the effect.

A number of experiments were performed with the sorbents and different inorganic salts at various concentrations. Here we present data for one representative system. Figure 5 shows the isotherms of DP on Lula aquifer material in the presence of 0.01 M NaCl, 0.1 M NaCl, and 0.001 M $CaCl_2$. The effect of the salt concentration was generally much greater than that of pH.

A comparison of the isotherms in NaCl shows that, at low concentrations of DP, an increase in the NaCl concentration decreases the adsorption by a nearly constant factor. This behavior is consistent with an ion-exchange mechanism. At high concentrations of DP, the isotherms merge and cross at surface concentrations that corresponds roughly to the CEC. This behavior is consistent with the predominance of adsorption of pyridinium-chloride at high concentrations of DP. Similar isotherms (not shown) were obtained for EPA-12, Borden sand, and kaolinite.

The effect of Ca^{2+} on the adsorption of DP on Lula aquifer material is generally stronger than that of Na^+, consistent with ion exchange. A solution of 0.001 M Ca^{2+} impedes adsorption of DP more effectively than 0.01 M Na^+, but less than 0.1 M Na^+.

Nonlinearity of Isotherms

All of the adsorption isotherms determined in this study were nonlinear, even at very low surface coverages of dodecylpyridinium. While the Freundlich isotherm can be used to represent these data empirically, it provides no mechanistic basis for evaluating competition effects, saturation effects, and comparison of adsorption energies for a homologous series of cationic surfactants. Thus the usefulness of the Freundlich isotherm is limited.

In order to derive a more useful description of adsorption data, it is necessary to consider the causes of nonlinearity: (i) non-uniformity of energies of adsorption sites, with saturation of high-energy sites; (ii) sorbate-sorbate interactions such as repulsive electrostatic interactions or cooperative chain-chain interactions, and (iii) experimental artifacts that stem from covariation of experimental conditions, such as changes of pH, major ion concentrations, or aggregation of particles, that accompany changes in cationic surfactant concentrations.

We interpret the nonlinearity of isotherms in these experiments primarily as the result of heterogeneity of sites. Particularly in the low-concentration regions of the isotherms, the changes in pH, concentrations of major ions in solution, and surface charge that accompanied adsorption of the cationic surfactant were too small to account for the isotherm nonlinearity. Thus, at low concentrations of cationic surfactant, heterogeneity of sites is the preferred explanation. At higher concentrations it is more difficult to exclude the influence of other processes on isotherm nonlinearity.

Model for DP Adsorption

The mechanistic models that were considered for these data were (i) multisite models, (ii) electrostatic models, and (iii) some combination of the two. Most of the phenomena observed in this study can be explained readily through the multisite model, with
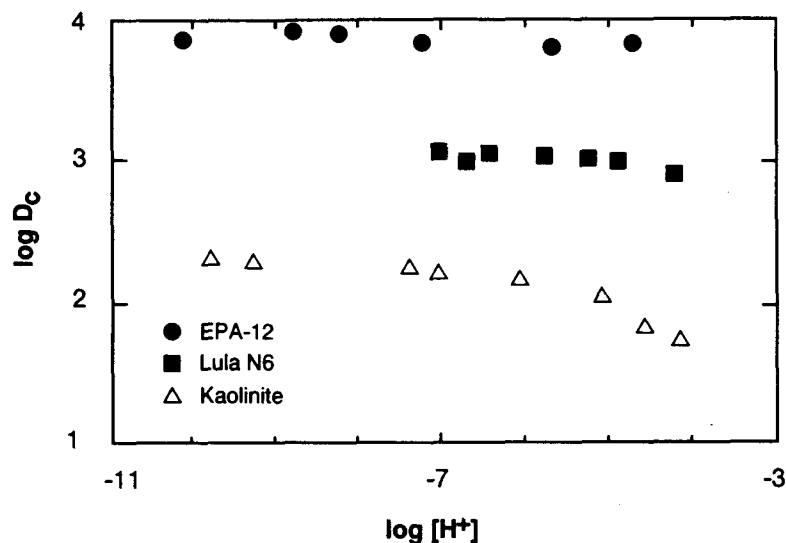
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Figure 4. Effect of log [H+] on the concentration distribution ratio, D_c, of dodecylpyridinium between aqueous solutions and selected sorbents. Sorbent concentrations (C_s(w)) were as follows: EPA-12, C_s(w) = 0.015 kg/L; Lula, C_s(w) = 0.0025; and kaolinite, C_s(w) = 0.0125. Solutions contained 0.01 M Na+. The amounts of dodecylpyridinium adsorbed (C_{DP}(s)) were nearly constant for EPA-12 and Lula sorbents: C_{DP}(s) = 0.20 and 29 μmol/g, respectively. C_{DP}(s) ranged from 7.6 to 15 μmol/g for kaolinite.
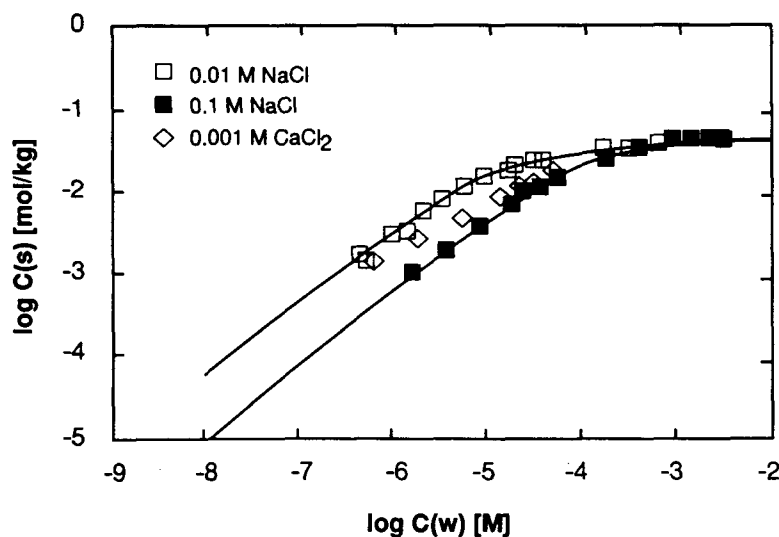

Figure 5. Logarithmic adsorption isotherms of dodecylpyridinium on Lula aquifer material from 0.1 M NaCl, 0.01 M NaCl, and 0.001 M $CaCl_2$. The ratio of solids to liquid was 0.0025 kg/L.

electroneutral reactions and no explicit electrostatic energy term. While this approach is obviously an approximation, it is consistent with a variety of observations, and it is conceptually very simple. Here the multisite approach is illustrated for the adsorption of DP. (In this example, effects of Na+, Ca^{2+}, and Cl- are omitted for simplicity; the full treatment is described by Brownawell et al., 1990). The nonlinear isotherm was modeled as a sum of Langmuir isotherms, with a discrete, regular distribution of log K's (Brownawell et al., 1990). DP is presumed to adsorb to each site

X_i according to the reaction

$$DP + X_i = DPX_i \qquad K_i \qquad (3)$$

for which the mass action equation is

$$[DP] \{X_i\} K_i = \{DPX_i\} \qquad (4)$$

6

where [DP] represents the concentration of species DP in solution (mol L^{-1}), and $\{DPX_i\}$ represents the concentration of species DP on the sorbent (mol kg^{-1}). The material balance equation for site i is:

$$T_i = \{X_i\} + \{DPX_i\} \qquad (5)$$

where T_i is the total amount of site i per mass of sorbent (mol kg^{-1}). Equations 4 and 5 exactly define a Langmuir isotherm. Then the total amount of DP adsorbed is taken as the sum over all types of sites i,

$$C_{DP}(s) = \Sigma \{DPX_i\} \qquad (6)$$

According to the log K spectrum approach, the values of log K_i were set to bracket the range of the data (i.e., log K_i = 2, 3, 4, 5, 6, 7 to span the range of - log C_{DP}(w)), and values of T_i were determined by FITEQL (Westall, 1982a, 1982b). The log K spectrum determined in this way for the DP-Lula-0.01 M CaCl$_2$ system is given in Table 2, and the isotherm calculated from this model is given as the solid line in Figure 6. As can be seen, the model yields an excellent representation of the experimental data. The advantage of this approach is that it offers a convenient parameterization of nonlinear isotherms that is consistent with general chemical equilibrium models.

Certainly this "discrete equilibrium-constant-spectrum" approach is subject to the criticism that a model can be fit to any set of data if enough adjustable parameters are used. Furthermore, there is some covariance among the values of the adjustable parameters;

TABLE 2. MULTI-LANGMUIR MODEL FOR DP ADSORPTION[a]

log K_I	T_I (mol/kg)
2	0
3	4.21 x 10^{-2}
4	1.91 x 10^{-2}
5	3.05 x 10^{-3}
6	8.77 x 10^{-4}
7	0

[a] Model defined by Equations 4-6 in text.

the values are not unique, but just one of an infinite number of sets that can be used to represent the data.

However, the advantages of this approach are significant, too. The practical advantage is that the effects of multiple interactions in complex systems can be represented in a way that is completely compatible with chemical equilibrium models used in environmental chemistry. An adsorption isotherm that conforms closely to the Freundlich equation over more than than six orders of magnitude range in C(w) can be described very well by conventional mass action and material balance equations; these equations have a
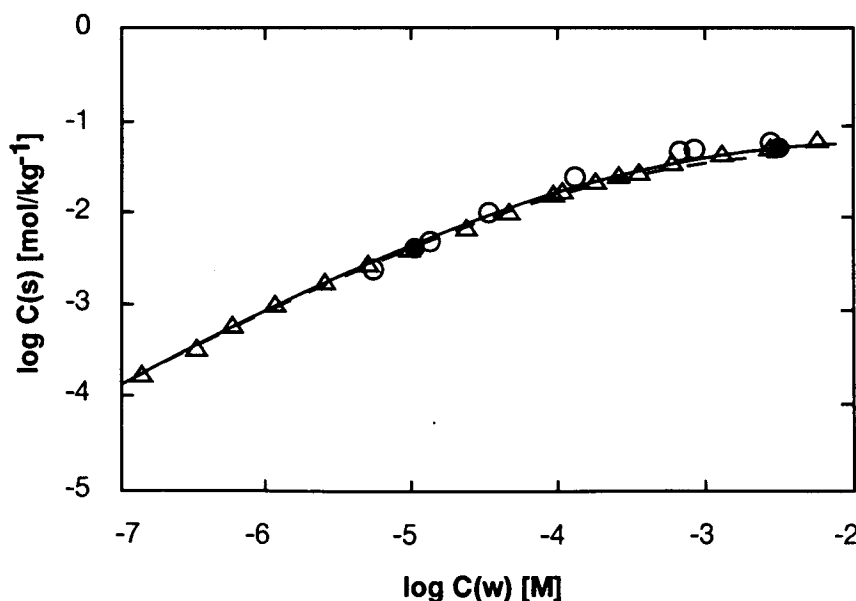

Figure 6.   Adsorption isotherm of dodecylpyridinium on Lula aquifer material (0.005 kg/L) in 0.01 M CaCl$_2$. (Δ) experiments conducted with ^{14}C-labeled DP and direct determination of DP in solution and on the sorbent; (o) experiments conducted with unlabeled DP and determination of DP in solution by UV spectrophotometry and DP on the sorbent by difference. The solid line is the isotherm calculated from the multi-Langmuir model (Table 2), and the broken line is the empirically adjusted isotherm used in the transport model in Figure 9. The two symbols (●) on the isotherm designate the DP concentration at which the Phase II experiment (10 μM, Figure 8) was carried out and the initial DP concentration for the Phase III experiment (3 mM, Figures 9 and 10).

mechanistic basis, which potentially could be used to understand the factors that influence adsorption.

Another advantage of such a model is that it provides a framework for evaluating quantitatively mechanisms that could be responsible for the phenomena that are observed experimentally, such as (i) reversal of effect of electrolyte concentration on isotherms near the CEC; (ii) lateral shift of isotherms with salt concentration far below the CEC; (iii) absence of pH effect; and (iv) relative effect of Na vs. Ca on the isotherms.

SORPTION OF CHLOROBENZENES TO DP-MODIFIED SURFACES

This work was carried out in three phases. First, in batch experiments, we determined the adsorption isotherm of DP on Lula aquifer material and investigated sorption of chlorobenzenes to the DP-treated aquifer material.

Next we examined the breakthrough of chlorobenzenes on columns containing the aquifer material with a uniform, time-invariant amount of DP on the surface. These conditions are not those that one would expect to encounter in field application, but they are useful in evaluating the applicability of data generated in batch experiments to column experiments and the validity of the local equilibrium assumption in these systems. To maintain the constant amount of DP on the sorbent, the solution flowing into the column always contained a constant low concentration (10 μM) of DP.

Finally we investigated the breakthrough of chlorobenzenes on columns that were initially uniformly coated with DP, but, when the chlorobenzene pulse was applied to the column, the supply of DP to the column was stopped, and the DP was allowed to desorb slowly as the chlorobenzenes passed through the column. This design is closer to that which would actually used in the field — a pulse of the cationic surfactant would be applied to treat the surfaces of aquifer particles, but the cationic surfactant would not be injected into the aquifer over extended periods.

Adsorption Isotherm of DP

The adsorption isotherm of DP on Lula aquifer material in 0.01 M $CaCl_2$ is shown in Figure 6 on a log-log scale. The isotherm is nonlinear. The slope of the log-log plot is approximately 0.6 in the low concentration range; on a linear scale (not shown), the isotherm has an almost step-function appearance. In the high concentration range, near the critical micelle concentration, the isotherm levels off at approximately the cation exchange capacity of the sorbent. The f_{oc} of untreated Lula is about 0.02%; near the plateau of the isotherm, the amount of DP on the surface is about 40 mmol/kg, or $f_{oc} \approx 1\%$. Thus, the f_{oc} of the sorbent can be increased by a factor of about 50 by loading with DP.

A significant feature of this isotherm is its nonlinearity: at 3 mM DP in solution, the distribution ratio of DP is approximately 10 L kg^{-1}, while at 10 μM DP in solution, the distribution ratio is approximately 5000 L kg^{-1}. Thus, the lower the concentration of DP in solution, the more tenaciously it adheres to the sorbent. This behavior is ideal for establishing absorbent barriers by injecting a pulse of cationic surfactant into the ground. At high concentrations the surfactant would be mobile and would disperse to cover a zone, while at low concentrations it would be virtually immobile and provide a coating to particles to retard migration of HOC.

Distribution of Chlorobenzenes on DP-treated Aquifer Material

The distribution ratios of the chlorobenzenes between the DP-treated aquifer material and 0.01 M $CaCl_2$ are shown in Figure 7 as a function of DP loading. The values of log K predicted for the HOC from K_{ow} (Miller et al., 1984) and f_{oc} by the equation of Schwarzenbach and Westall (1981) are lower than the values found here. This result indicates that the DP accommodates the chlorobenzenes much better than natural organic matter, per carbon atom. The correlation developed by Schwarzenbach and Westall (1981) included all of the compounds used in this study, and the sorbents were a variety of environmental materials including soils, sediments, aquifer materials and activated sludge. Third order polynomials were fit to these data for incorporation in the transport model of chlorobenzenes on DP-treated aquifer material (Wagner et al., 1994). The chlorobenzene distribution ratios presented in Figure 7 were determined from "one-point" isotherms, rather than the slopes of multipoint isotherms, that is, the linearity of the chlorobenzene isotherms was not verified experimentally in this study. Other studies (Smith and Jaffé, 1991; Smith et al., 1990; Boyd et al., 1988), have indicated that isotherms of HOC are linear for sorbents treated with cationic surfactants with long alkyl chains.

Breakthrough of Chlorobenzenes

The breakthrough curves of the chlorobenzenes through the untreated and treated aquifer material are shown in Figure 8. In these experiments, the DP on the surface was in equilibrium with 10 μM DP in the mobile phase, and the surface concentration did not vary. The interstitial volume was determined from the NO$_3^-$ breakthrough curves. Physical properties of the column are given in Table 3. Curves calculated from a model as well as experimental data are shown. Two approaches could be taken to determination of the adjustable parameters in this model: (i) use independently determined parameters from the batch experiments and the column experiment with a nonsorbing tracer, and compute "ab initio" breakthrough curves to be compared with the experimental data; or (ii) adjust the parameters in the model of the chlorobenzene breakthrough curves to optimize agreement with the experimental data, and then compare these parameter values with the independently determined ones. Since the data from the chlorobenzene breakthrough curves are as reliable as the data from the batch experiments, we have chosen the second approach.

The model of the breakthrough curves is the one-dimensional, advection-dispersion model for steady flow through a homogeneous porous medium with local equilibrium:

$$\frac{\partial C\,(z,t)}{\partial t} = \frac{D}{R}\,\frac{\partial^2 C\,(z,t)}{\partial z^2} - \frac{u}{R}\,\frac{\partial C\,(z,t)}{\partial z} \qquad (7)$$

where $C(z,t)$ is the concentration in the aqueous phase at time t and distance along the column z, D is the dispersion coefficient, R is the retardation factor, and u is the flow velocity. For all of these experiments, the apparent dispersion coefficient, D, was set to 0.0002 cm^2 s^{-1}; the value of D estimated from the nitrate breakthrough was 0.0003 ± 0.0001 cm^2 s^{-1}. The values of K determined from the breakthrough curves can be compared with those determined from batch experiments in Table 4; they are not significantly different. The solid lines in Figure 8 were calculated
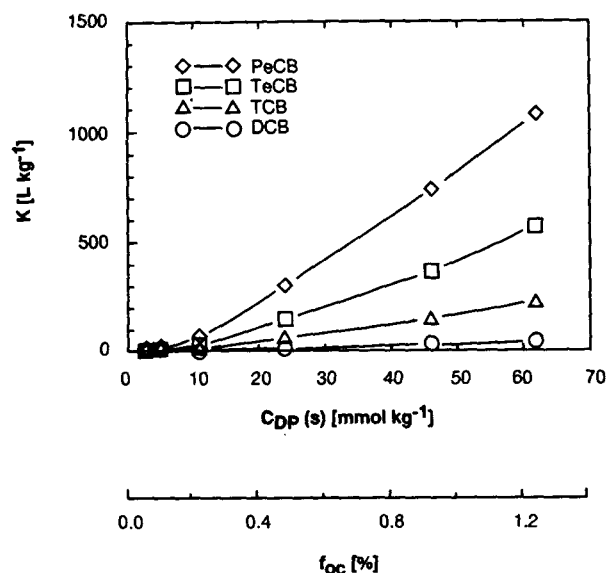
Figure 7. The partition constant of chlorobenzenes between 0.01 M $CaCl_2$ and Lula aquifer material (0.025 kg/L solid/solution ratio) with different loadings of DP.

TABLE 3. PHYSICAL PROPERTIES OF COLUMN PACKED WITH LULA AQUIFER MATERIAL

Symbol	Description	Experimental [a]	Model [b]	Units
Determined Directly				
L	column length	5.000 ± 0.001	5.00	cm
d_i	internal diameter	1.000 ± 0.001	1.00	cm
M_s	sorbent mass	6.84 ± 0.01	6.84	g
V_m	holdup volume	1.73 ± 0.14	1.71	mL
V_d	dead volume	0.14 ± 0.01	0.14	mL
F_c	flow rate	3.99 ± 0.03	3.99	mL h^{-1}
D	dispersion coefficient	0.0003 ± 0.0001	0.0002[c]	cm^2 s^{-1}
Derived				
V_i	interstitial volume $= V_m - V_d$	1.59 ± 0.14	1.57	mL
X	empty column volume $= 3.14^*(d_i/2)^{2*}L$	3.927 ± 0.008	3.927	mL
V_s	volume of sorbent $= X - V_i$	2.34 ± 0.14	2.36	mL
ε_i	porosity $= V_i/X$	0.40 ± 0.04	0.40	—
τ	residence time $= V_i/F_c{}^*3600$ s h^{-1}	1435 ± 120	1417	s
u	flow velocity $= L/\tau$	0.0035 ± 0.0003	0.003	cm s^{-1}
ρ_B	bulk density $= M_s/X$	1.742 ± 0.003	1.742	g mL^{-1}
ρ_s	sorbent density $= M_s/V_s$	2.92 ± 0.17	2.90	g mL^{-1}

[a] Estimated uncertainty in experimentally determined value is given.
[b] Values used in the models.
[c] As described in the text, several different values for D were used. D = 0.0002 for model of HOC breakthrough on untreated aquifer material and for model of HOC breakthrough on aquifer material equilibrated with 10 μM DP (Figure 8). D = 0.02 for DP transport (Figures 9 and 10). D = 0.002 for HOC transport through column with time-varying DP (Figure 10).

TABLE 4. DISTRIBUTION CONSTANTS, K, OF CHLOROBENZENES BETWEEN 0.01 M CaCl₂ AND LULA AQUIFER MATERIAL. AMOUNTS OF DP ON THE AQUIFER MATERIAL ARE INDICATED.

| | Untreated Sorbent | | DP-treated Sorbent [c] | |
	batch K [a] (L kg⁻¹)	column K [b] (L kg⁻¹)	batch K [a] (L kg⁻¹)	column K [b] (L kg⁻¹)
DCB	< 0.1 ± 0.5	0.2	0.6 ± 3	1.1
TCB	0.2 ± 0.3	0.7	3 ± 1	3.5
TeCB	2 ± 1	2.3	8 ± 3	7.9
PeCB	7 ± 3	9.0	25 ± 8	23

[a] Determined from data in Figure 7.
[b] Determined from data in Figure 8.
[c] {DP} = 4.3 mmol kg⁻¹
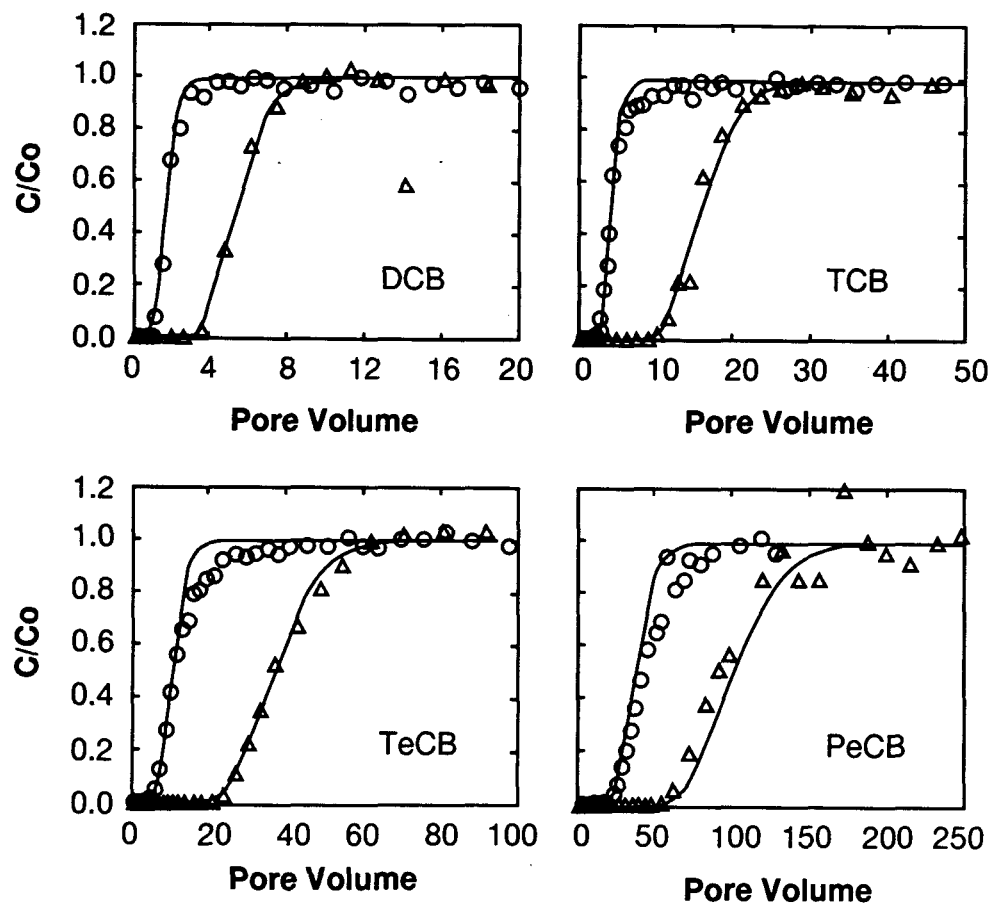
Figure 8. The breakthrough curves of the chlorobenzenes on (o) untreated Lula aquifer material and (Δ) Lula aquifer material equilibrated with 10 μM DP. The solid lines were calculated from a finite difference approximation to the advection dispersion equation, with the parameters in Table 3 and the partition constants of the chlorobenzenes defined by the data in Figure 7.

from this model (i.e., the solution to Equation 7 with parameters in Tables 3 and 4).

This experiment has important implications for both applications and theory. First note that the amount of DP adsorbed was only 4.3 mmol kg^{-1}; this amount is equivalent to a DP-f_{oc} of about 0.09% compared to the natural f_{oc} of 0.02%. As seen in Figure 7, much higher loadings are possible. Even at this low amount of DP, retardation factors for the HOC are approximately three times the retardation factor for HOC on untreated sorbent, as shown in Table 5.

TABLE 5. RETARDATION FACTORS, R[a], FOR HOC ON LULA AQUIFER MATERIAL AS CALCULATED FROM COLUMN K GIVEN IN TABLE 2.

	Untreated Sorbent	DP-treated Sorbent [b]
DCB	2	6
TCB	4	16
TeCB	11	35
PeCB	40	101

[a] $R = 1 + K \rho_s ((1-\epsilon_i) / \epsilon_i)$ where ρ_s and ϵ_i are as defined in Table 3.
[b] {DP} = 4.3 mmol kg^{-1}

Second, the model, which was based on the local equilibrium assumption and values of K's not significantly different from those determined in batch experiments, agrees well with the experimental data. This agreement indicates that a "particle concentration effect" is negligible, both for the DP and the chlorobenzenes, since the solid/liquid ratios in the batch experiments were 0.005 kg/L and 0.025 kg/L, and in the column experiment it was 4.35 kg/L, that is, over a factor of 1000 difference. We attribute this good agreement to the fact that we washed the materials used in the batch experiments thoroughly to remove materials that cannot be separated by centrifugation. Also the fact that the local equilibrium assumption seems to hold indicates that sorption of the chlorobenzenes is rapid compared to transport through the column.

Breakthrough of DP and Chlorobenzenes

Since the final phase of this part of the study deals with the sorption of chlorobenzenes onto aquifer material with a time-varying amount of DP, we discuss first our understanding of the time variation of DP on the column.

The experimental data for the breakthrough of 3mM DP and the elution of DP from a column containing Lula initially equilibrated with 3 mM DP are presented in Figure 9. The retardation factor calculated from integration of the breakthrough curve is 80 compared to 86 calculated from the batch isotherm. We feel that this agreement within 10% is good, considering the uncertainty introduced from factors such as the high concentrations of DP, the effect of DP on the surface charge and the packing of the particles, and the uncertainty in the interstitial volume.

Whereas the retardation factor agrees with the simple batch-based model, the shape of the breakthrough curve is impossible to explain in terms of a simple local-equilibrium model with the dispersion coefficient from the NO_3^- breakthrough curve. The low-dispersion local equilibrium model would predict a sharp, almost step-like, breakthrough curve (due to the convex isotherm) rather than the relatively broad wave that is observed. Moreover, an understanding of the mechanism of broadening is important since the distribution of DP along the length of the column depends on the mechanism, and the transport of the chlorobenzenes must depend to some degree on how the DP is distributed, since the curves in Figure 7 are not linear.

Among the many possibilities for explaining the breadth of the wave is a slow adsorption-desorption step, which results in greater dispersion. For solutes which follow a linear adsorption isotherm, it can be shown how a slow adsorption-desorption step leads to an increase in dispersion, which is directly proportional to the flow velocity (Baetslé, 1969; Giddings, 1991; Bales and Szecsody, 1985). Additional data, at different flow velocities, would allow us to substantiate this mechanism and its applicability to the nonlinear isotherms in this study. At this point, our objective is to have a plausible explanation for the shape of the breakthrough curve. This objective can be fulfilled by adjusting the apparent dispersion coefficient to 0.02 cm^2 s^{-1}, on the basis of slow adsorption-desorption kinetics, and modeling adsorption by the local equilibrium assumption according to the isotherm in Figure 6. It is worth noting that other more explicit kinetic models for explaining the breadth of the wave were tested, but were not as successful as the simple model presented here.

Although the desorption curve (Figure 9B) appears to approach $C/C_0 = 0$, integration of the elution curve reveals that, even after approximately 1000 pore volumes, about 16% of the original DP loading is still on the column. The nonlinearity of the isotherm ensures that as the concentration of DP decreases, it adheres more tenaciously to the column. The amount of DP remaining on the column is almost twice the amount of DP on the column during the experiment involving the breakthrough of chlorobenzenes on a column containing aquifer material with a uniform, time-invariant amount of DP on the surface as shown in Figure 8. Thus after 1000 pore volumes there is still enough DP on the column to retard the chlorobenzenes. This extensive tailing is that which is expected from the highly convex isotherm.

The DP adsorption isotherm in Figure 6, adjusted as shown for concentrations above 170 μM, was incorporated into the transport model previously described. The apparent dispersion coefficient for DP in the model was set to 0.02 cm^2 s^{-1}. Other model parameters are given in Table 3. The model so defined agrees well with the experimental data, as seen in Figure 9.

Sorption-Desorption of Chlorobenzenes

After the column was equilibrated with 3 mM DP, a pulse of chlorobenzenes in 0.01 M CaCl$_2$, without DP, was passed through the column, followed by 0.01 M CaCl$_2$. The elution histories are shown in Figure 10, along with the elution histories from the model, for which the parameters are given in Table 3. The model for the chlorobenzene breakthrough curves in Figure 10 is based on parameters that were determined in independent experiments (Figures 6-9). The only adjustable parameter determined form the data in Figure 10 was the dispersion coefficient of the chlorobenzenes in the column with varying DP. Additional
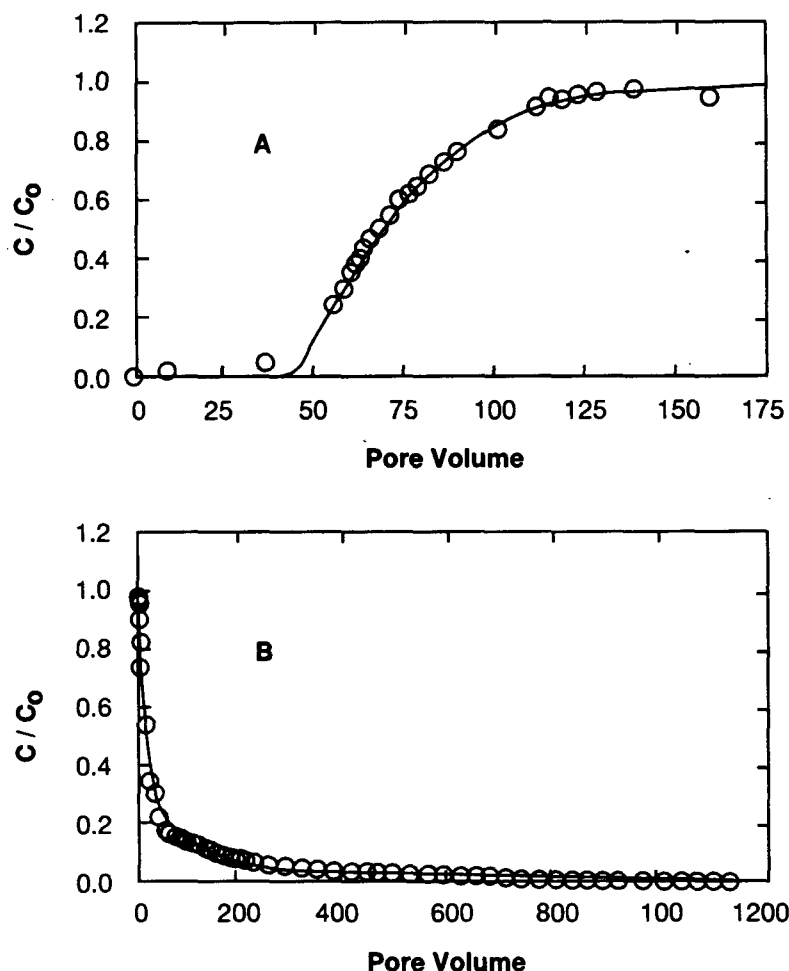
Figure 9. The breakthrough curve and desorption curve of 3 mM DP in 0.01 M CaCl$_2$. The solid line was calculated from a finite difference approximation to the advection dispersion model with the constants in Table 3 and the empirically adjusted adsorption isotherm depicted in Figure 6.

adjustable parameters were not introduced. Thus, the model used in Figure 10 was developed from the following data: (i) the amount of DP on the column as a function of time and distance was calculated from the advection-dispersion model with local equilibrium according to the batch isotherm in Figure 6 and the apparent dispersion coefficient determined from data in Figure 9; (ii) the partition coefficients of the chlorobenzenes were calculated for the amount of DP on the Lula and the third order polynomial derived from the data in Figure 7; (iii) sorption of the chlorobenzenes on the sorbent were assumed to be linear; (iv) the hold-up volume was determined from NO$_3^-$ breakthrough; and (v) the apparent dispersion coefficient for the chlorobenzenes was set to 0.002 cm^2 s^{-1} to fit the model to the data. The actual breakthrough curves were then calculated from the advection-dispersion model based on these parameters.

An interesting feature of Figure 10 is noted: the ratio of effluent concentration to influent concentration (C/C$_0$) for DCB is

appreciably greater than one. The model reproduces this feature as well. This phenomenon is attributed to a "preconcentrate and strip" mechanism: DCB is initially preconcentrated in a narrow zone on the column, and then it is stripped off the column as the DP itself elutes from the column.

We conclude that the simple local equilibrium model is successful in describing retention volumes in Figures 9 and 10, but that considerable liberty must be taken with the apparent dispersion coefficients to achieve agreement of the model with the data. However, the uncertainty about the treatment of dispersion does not invalidate the general conclusions presented here, but points out an area for further experimentation.

COMPETITION BETWEEN DP AND METAL IONS

Adsorption of cationic surfactants can displace adsorbed metal ions (Beveridge and Pickering, 1983; Bouchard et al., 1988). In
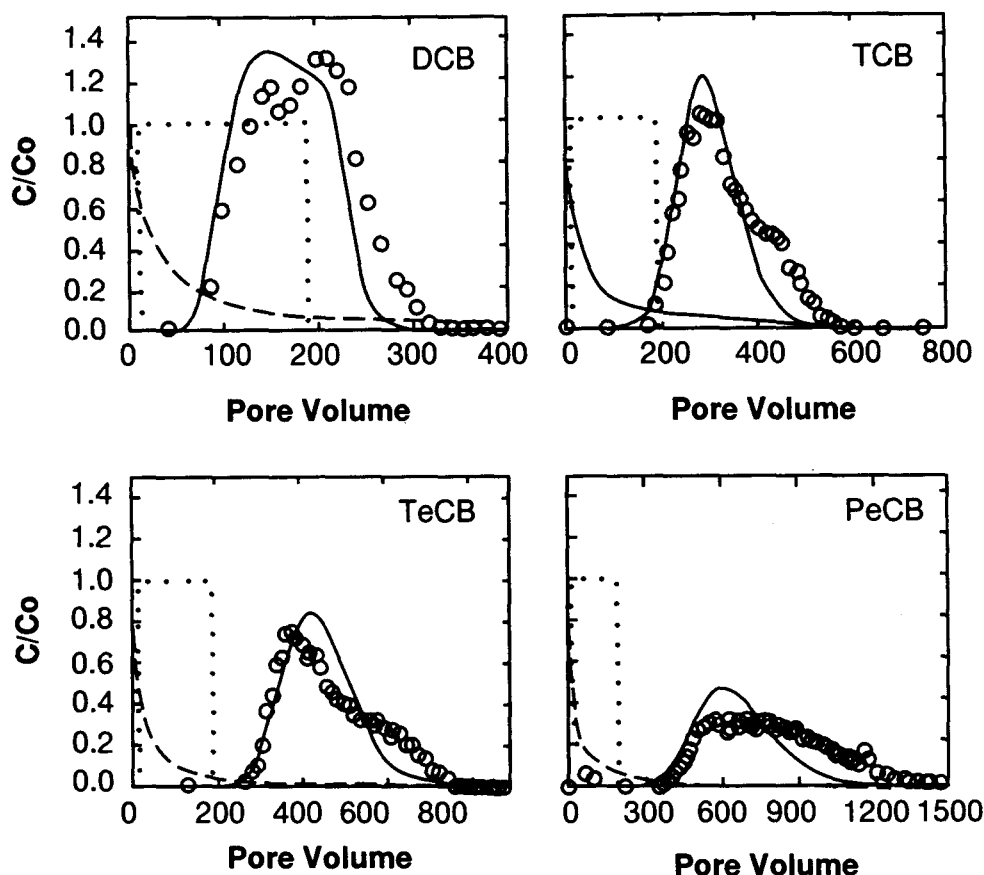
Figure 10. The breakthrough curves of the chlorobenzenes on a column of Lula aquifer material that was pre-equilibrated with 3 mM DP in 0.01 M CaCl$_2$, but, before the pulse containing the chlorobenzenes was applied to the column, the supply of DP to the column was stopped. The circles represent the concentration of the respective chlorobenzenes in the column effluent. The dashed line represents the concentration of DP in the column effluent (not the amount remaining on the column!), the dotted line represents the concentration of chlorobenzenes in the column influent, and the solid line represents the concentration of chlorobenzenes in the column effluent calculated from the finite difference model. The model is defined by the constants in Table 3 for the column, the adjusted isotherm for local equilibrium of DP (Figure 6) with dispersion coefficient of 0.02 cm^2 s^{-1}, the partition constants of the chlorobenzenes defined by the data in Figure 7.

this study we have investigated the effect of DP on adsorption of Pb(II), Cd(II), and Cu(II) on aquifer materials from Lula OK, Elizabeth City NC, and Cape Cod MA. The results of the study of Lula-DP-Cu(II) system, which illustrate the kinds of interactions that are to be expected, are presented here.

Adsorption Isotherms of DP and Cu(II) on Lula

Adsorption isotherms of DP in the absence of Cu(II), and of Cu(II) in the absence of DP, on Lula in 0.01 M NaCl are shown in Figure 11. Qualitatively it is seen that DP adsorbs more strongly than Cu(II) under the solution conditions given, pH $\approx$ 5.5 - 5.0 and 0.01 M NaCl.

The strongly nonlinear isotherms make it impossible to compare adsorption energies of Cu(II) and DP as single values of log K. As an alternative, one could compare apparent distribution ratios of

the sorbates at equal concentrations on the surface, at equal concentrations in solution, or at equal total concentrations in the system, depending upon the question of interest. For example, the distribution ratios for DP and Cu at concentrations of 10 μM in solution are log D$_{DP}$ = 3.2 L kg^{-1} and log D$_{Cu}$ = 2.2 L kg^{-1}. Thus, the DP and Cu(II) adsorb "moderately strongly" under the conditions of these experiments.

Dependence of adsorption on pH

The pH dependence of the distribution ratios of Cu(II) and DP are illustrated in Figure 12. The distribution of DP on Lula is effectively independent of pH over a relatively wide range, while that of Cu(II) appears to decrease slightly with increasing log [H$^+$]:
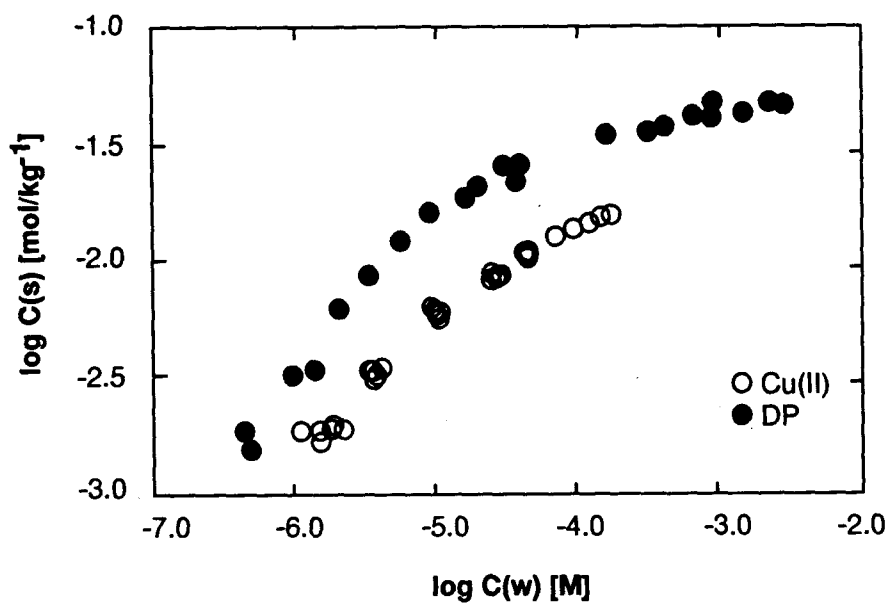
$$d \log D / d \log [H^+] \approx 0.25.$$

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Figure 11. Adsorption isotherms of Cu(II) (in the absence of dodecylpyridinium) and dodecylpyridinium (in the absence of Cu(II)) on Lula aquifer material (0.005 kg/L in 0.01 M NaCl). In the Cu(II) experiment, solution pH varied from about pH 5.6 at low concentrations of Cu(II) to about pH 4.9 at high concentrations of Cu(II).
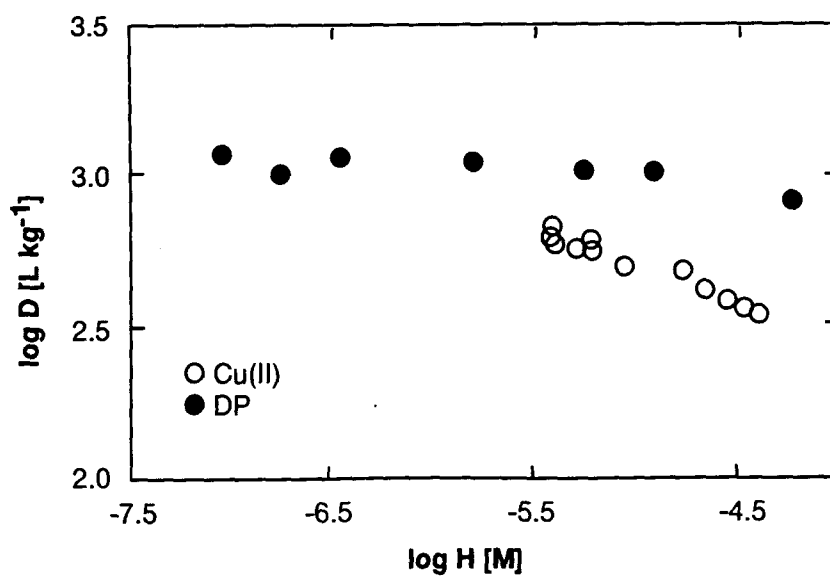

Figure 12. The pH dependence of the distribution ratio of Cu(II) (in the absence of dodecylpyridinium) and dodecylpyridinium (in the absence of Cu(II)), for adsorption onto Lula aquifer material (0.005 kg/L in 0.01 M NaCl). Total Cu(II) concentration was 40 µM in all experiments; total DP concentration was 40 µM in all experiments.

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Thus we expect that the data in Figure 11, which were obtained in batch experiments without strict pH control, were influenced slightly by this pH dependence of Cu adsorption. In these experiments, the pH decreased from pH ≈ 5.5 to pH ≈ 5.0 as the mildly acidic Cu(II) solution was added, presumably causing the value of log D to decrease by up to about 0.10 - 0.15 log unit. This change is large enough to be detected but not so large that it would grossly affect our conclusions if it were not considered explicitly in the data interpretation.

This weak pH dependence of Cu(II) resembles that expected for ion exchange of Cu(II) more than that expected for surface complexation. It is not unlikely that surface complexation of Cu(II) sets in at slightly higher pH values. However, hydrolysis and precipitation of Cu(II) also set in at higher pH values.

Comparison of effect of DP on Cu(II) with effect of Cu(II) on DP

The effects of DP on the adsorption isotherms of Cu(II) and the effects of Cu(II) on the adsorption isotherms of DP can be compared in Figures 13a and 13b. At first glance, it might appear that DP has a much stronger effect on Cu(II) than vice versa; however, it should be noted that the total concentrations of the competing DP are up to 1000 µM in Figure 13a, while the total concentrations of the competing Cu(II) are up to only 100 µM in Figure 13b. If one compares the isotherms with only up to 100 µM total concentration of competing ion, the differences are not so marked.

The series of Cu(II) isotherms obtained with various total concentrations of DP in the system illustrate that large amounts of DP in the system clearly suppress the adsorption of Cu(II). The "nominal" amounts of DP on the surface are 0, 9, 17, 37, and 42, mmol/kg, corresponding to T_{DP} in the system of 0, 50, 100, 400, and 1000 µM. The solution pH varied from about pH 5.6 at low concentrations of Cu(II) to about pH 4.9 at high concentrations of Cu(II).

The isotherms show essentially no effect of DP until about 9 mmol/kg DP (about 20% of the DP exchange capacity) is on the surface. Then the isotherms are flattened substantially by 17, 37, and 42 mmol/kg DP on the surface. The flattening of the isotherms seems to indicate some sort of saturation phenomenon: either DP adsorbs to a certain extent, leaving a certain number of sites free for Cu(II), or, DP adsorption alters the surface charge on the surface, effectively causing "electrostatic saturation". Electrophoretic mobility measurements (data not shown) are consistent with the latter explanation.

Total amount of DP and Cu(II) on the surface

Some insight into the nature of the competition between DP and Cu(II) can be gained from Figure 14, in which the amount of Cu(II) adsorbed is plotted against amount of DP on the surface, for several values of total Cu(II) (20, 40, 70, and 100 µM) and total DP (50, 100, 400, 1000 µM).

At low total concentration of both sorbates on the surface ($C_{Cu}(s)$, $C_{DP}(s) < 10$ mmol kg^{-1}), adsorption of the two species appears to be independent (i.e., at constant total Cu(II), the amount of Cu(II) on the surface seems relatively independent of the DP surface amount, and vice versa). Only at the point of 100 µM total Cu(II)

and 50 µM total DP are the values of $C_{DP}(s)$ and $C_{Cu}(s)$ shifted from their no-competition values, with the Cu(II) shifted more than the DP.

At higher concentrations on the surface, both $C_{DP}(s)$ and $C_{Cu}(s)$ are shifted from their no competition values, with the Cu(II) always shifted more than the DP. Ultimately the DP and Cu(II) on the surface fall along the line corresponding to the saturation of the 45 mmol kg^{-1} exchange capacity of the sorbent. It appears that the DP affects the Cu(II) more than the Cu(II) affects the DP.

From the standpoint of environmental management, probably the best way to summarize these data (Figures 11-14) is to say that the capacity of the Lula aquifer material for Cu(II) is reduced to 25 % of the initial value in the presence of 42 mmol/kg DP, etc. The nonlinearity of the isotherms makes it difficult to express the effects in terms of log D. Furthermore, it appears that another cationic surfactant that adsorbed more strongly than DP would accomplish the same mission at lower aqueous-phase concentrations.

From the standpoint of a mechanistic understanding of the competition, one could consider two basic mechanisms: (i) DP adsorbs much more intensely than Cu (i.e., effectively irreversibly), renders adsorption sites unavailable to Cu(II), and causes an effective reduction in capacity of the sorbent for Cu(II); or (ii) DP and Cu(II) compete through a classic mass-action material-balance mechanism, with or without electrostatic term. These mechanisms are discussed in more detail by Westall and Chen (1994).

SUMMARY

Large cationic surfactants, such as dodecylpyridinium, are strongly adsorbed to aquifer materials. Adsorption depends strongly on the concentration of major cations (e.g., Na$^+$, Ca^{2+}) in solution, but is almost independent of solution pH. The capacity for adsorption is close to the CEC of the sorbent; from a limited amount of data, it appears that the organic carbon content of the sorbent has a relatively minor effect on adsorption intensity and capacity.

The adsorption isotherms are distinctly nonlinear. Plotted on a linear scale, the isotherms have almost a step function appearance, suggesting that the adsorption reaction goes to completion and that the surfactant is effectively irreversibly bound; however, plotted on a logarithmic scale over several orders of magnitude, the isotherms reflect the equilibrium distribution that is observed in batch experiments on adsorption-desorption kinetics and column experiments. The isotherm data conform to the Freundlich equation $C(w)^n K = C(s)$, with a slope $n \approx 0.6$.

At high aqueous concentrations, the cationic surfactant adsorbs rather weakly, the isotherm leveling off at approximately the cation exchange capacity of the sorbent. At lower aqueous concentrations, it adheres more tenaciously to the sorbent. This behavior is consistent with the highly convex isotherm. This behavior is ideal for establishing absorbent barriers by injecting a pulse of cationic surfactant into the ground. At high concentrations the surfactant would be mobile and would disperse to cover a zone, while at low concentrations it would be immobile and provide a coating to particles to retard migration of HOC. The cationic surfactant significantly promotes the sorption of HOC to the aquifer material even with low amounts of surfactant on the surface of the aquifer material.
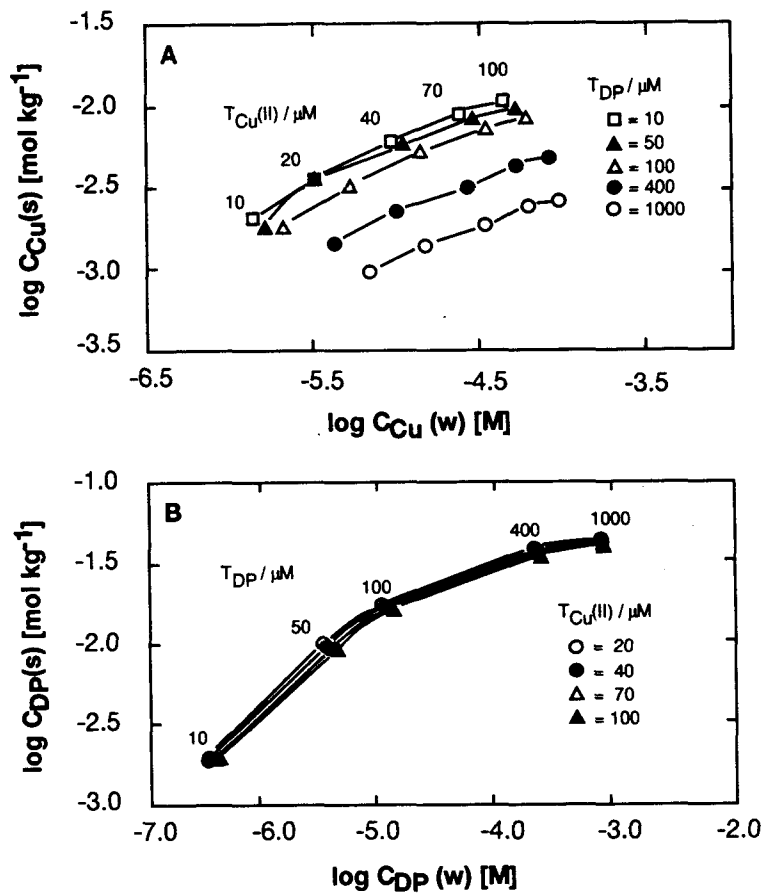
Figure 13. (A) Logarithmic adsorption isotherms of Cu(II) on Lula aquifer material (0.005 kg/L in 0.01 M NaCl) in the presence of DP. The "nominal" amounts of DP on the surface are 0, 9, 17, 37, and 42, mmol/kg, corresponding to T_{DP} in the system of 0, 50, 100, 400, and 1000 μM. The solution pH varied from about pH 5.6 at low concentrations of Cu(II) to about pH 4.9 at high concentrations of Cu(II). (B) Logarithmic adsorption isotherms of DP on Lula aquifer material (0.005 kg/L in 0.01 M NaCl) in the presence of Cu(II). The $T_{Cu(II)}$ in the system is 20, 40, 70, 100 μM, yielding "nominal" (i.e., in the absence of DP) amounts of Cu(II) on the surface of 2, 3, 6, 9, 11 mmol/kg. The solution pH varied from about pH 5.6 at low concentrations of Cu(II) to about pH 4.9 at high concentrations of Cu(II).
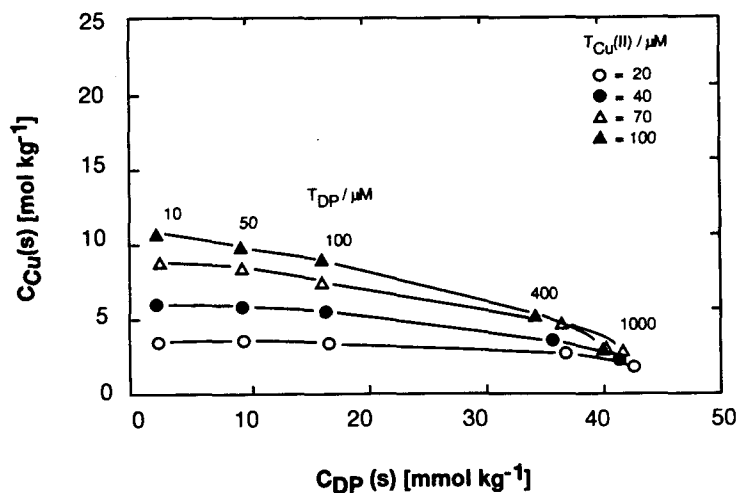
Figure 14. Amount of DP and Cu(II) on the surface of Lula aquifer material (0.005 kg/L in 0.01 M NaCl), with all possible combinations of T_{DP} in the system 0, 10, 50, 100, 400, 1000 μM and $T_{Cu(II)}$ in the system of 0, 20, 40, 70, 100 μM.

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A transport model based on the local equilibrium assumption and on results of batch experiments can be used to predict HOC column behavior reasonably well, although additional work on dispersion of the surfactant breakthrough curve is warranted. The agreement between batch and column experiments indicates that a "particle concentration effect" is negligible for the materials used in this study. Also the fact that the local equilibrium assumption seems to hold indicates that sorption of the HOC is rapid compared to transport through the column.

It may be possible to design a system that allows for limited dispersal of the cationic surfactant on injection and retardation of HOC in the region treated with the dispersed surfactant. To a first approximation, such a system can be designed by a model based on reversible adsorption of the cationic surfactant and on the local equilibrium assumption (for the materials used in this study).

There is relatively weak competition between DP and metal ions (Cu(II), Cd(II). Pb(II)) for adsorption sites on Lula aquifer material. From the standpoint of environmental management, probably the best way to summarize these results is to say that the capacity of the Lula aquifer material for Cu(II) is reduced to 25 % of the initial value in the presence of 42 mmol/kg DP, etc. The nonlinearity of the isotherms makes it difficult to express the effects in terms of log D. It appears that another cationic surfactant that adsorbed more strongly than DP would accomplish the same mission at lower aqueous-phase concentrations.

From the standpoint of a mechanistic understanding of the competition, one could consider two basic mechanisms: (i) DP adsorbs much more intensely than Cu (i.e., effectively irreversibly), renders adsorption sites unavailable to Cu(II), and causes an effective reduction in capacity of the sorbent for Cu(II); or (ii) DP and Cu(II) compete through a classic mass-action material-balance mechanism, with or without electrostatic term.

QUALITY ASSURANCE STATEMENT

DISCLAIMER

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