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RELATIONSHIPS BETWEEN MICELLE–WATER AND OCTANOL–WATER PARTITION CONSTANTS FOR HYDROPHOBIC ORGANICS OF ENVIRONMENTAL INTEREST

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Abstract—The partition constants between micelles of sodium dodecyl sulfate and water for eleven hydrophobic non-polar organics of environmental interest were correlated to their octanol–water partition constants, aqueous solubilities and total molecular surface areas. Octanol–water partition constant was found to be the best correlating parameter. Values of partition constants for micelles formed of dodecylbenzenesulfonate and hexadecyltrimethylammonium bromide surfactants were also correlated to the octanol–water partition constants. A possible practical application of the K_m–K_{ow} correlation to determine the micellar-mediated transport of hydrophobic organics in groundwater is illustrated.

Key words—micelle–water partition constants, octanol–water partition constants

INTRODUCTION

Surfactant micelles in aqueous solutions are capable of solubilizing non-polar hydrophobic compounds which are otherwise insoluble or only partly soluble in water (Attwood and Florence, 1983). This capacity for micelles is known to be as a result of their hydrocarbon-like interior (Tanford, 1980). The facile solubilization of aliphatic, aromatic and polycyclic aromatic halo- and hydrocarbons in micelles is due mainly to the incompatibility of these compounds with water molecules, i.e. their inability to compete with the strong hydrogen bonds between water molecules (Franks, 1983). This phenomenon first described by Frank and Evans (1945) is called the "hydrophobic interaction". Such interactions are the driving force for a variety of phenomena such as the adsorption of hydrophobic compounds by the organic matter of soils and sediments (Karickhoff *et al.*, 1979), partitioning into hydrocarbon solvents and sorption onto dissolved humic acid components in groundwater.

Micelles formed by ionic surfactants have an inner hydrocarbon layer, and outer ionic layer and an intermediate region termed the palisade layer. Hydrophobic solutes can remain dissolved in the hydrocarbon core, adsorbed on the ionic layer or sandwiched in the palisade layer. For most non-polar hydrophobic compounds, the locus of solubilization is the hydrocarbon core of the micelle (Attwood and Florence, 1983). Thus it is apparent that there should exist a correlation between the micelle–water partition constant (K_m) and other similar solvent–water partition constants for non-polar hydrophobic solutes. However, it is well known that the solubility of a hydrophobic solute in a micelle will be less than its solubility in a bulk hydrocarbon solvent owing to the large Laplace pressure acting across the curved micelle–water interface (Bolden *et al.*, 1983). The micellar solubilization of hydrophobic compounds can be treated both as a solute partitioning process with a partition constant, K_m, or as a simple binding process with a binding constant, K_b. These two are however linearly related, as was shown by Hinze (1987) and Attwood and Florence (1983).

A measure of the hydrophobicity of a solute is its octanol–water partition constant, K_{ow} (Chiou, 1981). Leo and Hansch (1971) and Helmer *et al.* (1968) used it as a reference standard in conjunction with Linear Free Energy Relationships (LFER). Numerous other investigators have used it successfully to predict the sediment–water and natural organic matter–water partition constants for hydrophobic solutes (Elzerman and Coates, 1987).

The relationship between non-ionic micelle–water and octanol–water partition constants were first investigated by Collett and Koo (1975) for a variety of para substituted benzoic acid derivatives in polysorbate 20 micelles. Subsequently Azaz and Donbrow (1976) showed that a correlation existed between octanol–water or heptane–water partition constants and micelle–water partition constants for a variety of phenolic compounds. Tomida *et al.* (1978) investigated similar relationships for 34 benzoic acid derivatives in polyoxyethylene lauryl ether micelles. For polar compounds such as described above, the

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solubilization behavior for a given system is difficult to predict because their interactions with the micelle depend on specific parameters unique to both the micelle and the solute such as charge, water content of the micelle etc. On the other hand, for neutral non-polar hydrophobic compounds which solubilize mostly in the hydrophobic core of the micelle, the relationship between K_m and K_{ow} would be more predictable.

There are numerous articles available in the literature relating to the micellar solubilization of non-polar or slightly polar hydrophobic chemicals. The solubilization of low molecular weight hydrocarbon solutes in various types of micelles have been reported (Bolden *et al.*, 1983; Wishnia, 1962; Abu-Hamdiyyah and Rahman, 1985, 1987; Almgren *et al.*, 1979). Most recently we reported the partition constants of low molecular weight chloromethanes between water and micelles of two anionic and one cationic surfactant (Valsaraj *et al.*, 1988). In that paper we also summarized a variety of applications in environmental chemistry that involved the utilization of micellar-enhanced solubilities of hydrophobic compounds. These aspects required the determination of K_m values. It would be convenient if one has a prescription to calculate these values from known parameters like K_{ow}, aqueous solubility of the hydrophobic compound and surfactant type. In this paper we extend the method described in our previous paper for the determination of K_m values for a few other compounds and along with available literature values for a few more compounds we relate K_m to K_{ow} and other hydrophobicity indicators.

EXPERIMENTAL

Materials

The surfactants used were sodium dodecylsulfate, DDS (Bio-Rad Labs), sodium dodecyl benzene sulfonate, DDBS (Sigma Chemical Co.) and hexadecyltrimethylammonium bromide, HTAB, (Eastman Kodak). In the case of hexadecyltrimethylammonium bromide, sodium chloride (EM Scientific) was used for ionic strength adjustment. The hydrophobic organics used were supplied by Fisher Scientific Co.

Method

The experimental determination of partition constants was carried out using the procedure of Equilibrium Partitioning in Closed Systems (EPICs) which was described in detail in our previous work (Valsaraj *et al.*, 1988). It is similar to the methods of Hayase and Hayano (1979) and Spink and Colgan (1983).

Briefly, experiments were conducted in glass hypovials (157 ml capacity) sealed with Teflon-lined rubber septa with aluminum crimp caps (Pierce Chemical Co.). Aqueous phase volume was 70 ml and headspace volume was 87 ml. Stock solutions of the hydrophobic compounds in water were prepared by overnight stirring. Appropriate amount of these stock solutions were added to vials with surfactant (82 mM in all cases) and vials without surfactant. These solutions were equilibrated in a water bath at 25°C prior to analysis of the gas phase by gas chromatography. The analytical procedure and data analysis were described in our previous work (Valsaraj *et al.*, 1988).

RESULTS AND DISCUSSION

The micelle–water partition constant (K_m) reported here is the ratio of mole fraction of the hydrophobic organic compound in the micellar phase (X_m) to its mole fraction in the aqueous phase (X_s). Values of K_m for the three low molecular weight chloromethanes, viz, methylene chloride, chloroform and carbon tetrachloride in DDS, DDBS and HTAB micelles were reported by us earlier and are reproduced from that work (Valsaraj *et al.*, 1988). Values of K_m for benzene, toluene, 1,3-dichlorobenzene and naphthalene in DDS micelles, benzene in DDBS micelles and in HTAB micelles were determined using EPICs. The values for 1-methylnaphthalene, biphenyl, anthracene and pyrene in DDS micelles were obtained from the literature (Almgren *et al.*, 1979; Hinze, 1987). All the above data are summarized in Table 1 along with the octanol–water partition constants, total molecular surface areas and aqueous solubilities.

Sodium dodecylsulfate is a common surfactant for which the values of K_m for alcohol, phenols and other polar compounds have been determined by several research groups. The micellar structure and properties for DDS have also been extensively studied and reported (Vold and Vold, 1983).

Table 1. Relevant parameters for selected hydrophobic organics

Compound	Molecular weight	Aqueous solubility* (mol l^{-1})	Molecular surface area* ($Å^2$)	log K'_{ow}§	log K_{ow}†	log K_m‡
Methylene chloride	84.9	1.197×10^{-1}	82	2.07	1.25	2.29
Chloroform	119.5	8.00×10^{-2}	99	2.78	1.96	2.83
Carbon tetrachloride	154	5.19×10^{-3}	119	3.65	2.83	3.44
Benzene	78	2.28×10^{-2}	99.8	2.95	2.13	3.04
Toluene	92	5.58×10^{-3}	127.9	3.51	2.69	3.22
m-Dichlorobenzene	147	8.36×10^{-4} (9.33×10^{-4})	144.7	4.30	3.48	3.88
Naphthalene	128.2	2.65×10^{-4} (8.32×10^{-4})	155.8	4.17	3.35	3.79
1-Methylnaphthalene	142.2	2.00×10^{-4} (2.04×10^{-4})	172.5	4.69	3.87	4.35(a)
Anthracene	178.2	4.09×10^{-7} (3.89×10^{-5})	200.0	5.36	4.54	5.09(a)
Pyrene	202.2	6.67×10^{-7} (5.75×10^{-6})	218.6	6.00	5.18	5.72(b)
Biphenyl	154.2	4.45×10^{-5} (1.32×10^{-4})	182.0	4.91	4.09	4.36(a)

*Mackay *et al.* (1982); values in parentheses are supercooled liquid solubilities (Chiou, 1981).
†Chiou (1981).
‡This work except (a) Almgren *et al.* (1979) and (b) Hinze (1987).
§K'_{ow} is the ratio on a mole fraction scale.

As noted in the Introduction, the micellar solubility of a hydrophobic compound is less than a similar bulk hydrocarbon solvent solubility due to the higher pressure (Laplace pressure) existing across the curved micelle–water interface. This pressure is given by $P_L = 2\gamma/r$ where γ is the interfacial tension across the micelle–water interface and r is the radius of the micelle.

Let us now obtain a theoretical relationship between K_{ow} and K_m. Consider the partitioning of a hydrophobic compound between the aqueous and octanol phases, for which we have, at equilibrium the condition that the solute chemical potentials ($\mu_i = \mu_i^\circ + RT \ln \tau_i X_i$) in the two phases be equal, so that

$$\tau_o^* X_o^* = \tau_w^* X_w^* \quad (1)$$

where τ_o^* and τ_w^* are the solute activity coefficients in the octanol and aqueous phases, respectively. X_o^* and X_w^* are the mole fractions in the respective phases. The asterisks denote that the two phases are mutually saturated with one another. For solutions that are dilute, $X = VC$ where C is the molar concentration of the solute and V is the molar volume of the solvent. Thus we can write equation (1) in terms of molar concentrations and obtain an expression for K_{ow} defined as C_o/C_w

$$K_{ow} = \frac{C_o}{C_w} = \frac{\tau_w^* V_w^*}{\tau_o^* V_o^*} \quad (2)$$

where V_w^* and V_o^* are the molar volumes of water saturated with octanol and octanol saturated with water, respectively.

The aqueous solubility of a solute may be considered as a partitioning of the solute between pure state in liquid form and saturated aqueous phase. Then equation (2) may be written as

$$S = \frac{1}{V_w \tau_w} \quad (3)$$

where the asterisks are omitted since no co-solvent is present and the solute is considered in its pure liquid form ($X_o = 1$) and consequently is at its standard state ($\tau_o = 1$).

Since the solubility of octanol in water is only 0.0045 M (Chiou, 1981), we can assume $V_w^* = V_w$, the molar volume of pure water. Then

$$K_{ow} = \frac{1}{SV_o^*} \frac{\tau_w^*}{\tau_w} \frac{1}{\tau_o^*}. \quad (4)$$

The factors τ_w^*/τ_w and $1/\tau_o^*$ are respectively corrections for the activities in the aqueous phase (due to octanol dissolution in water) and the octanol phase (due to octanol saturated with water). It has been argued that τ_w^* is indistinguishable from τ_w for most hydrophobic compounds, and that τ_o^* accounts for the majority of deviations from the ideal behavior (Curtis *et al.*, 1986). Thus we shall use

$$K_{ow} = \frac{1}{SV_o^*} \frac{1}{\tau_o^*}. \quad (5)$$

We now turn to the micelle–water distribution of the solute. Considering equality of chemical potentials for the solute in the two phases at equilibrium (Bolden *et al.*, 1983) we can obtain

$$\tau_w X_w = \tau_m X_m \exp(P_L v_A/RT) \quad (6)$$

where τ_w and τ_m are the solute activity coefficients in the aqueous and micellar phases respectively, X_w and X_m are the respective mole fractions. The exponential term is the Laplace pressure contribution to the solubility in the micelle. P_L represents the Laplace pressure acting across the curved micelle–water interface and v_A is the molar volume of the solute. The micelle–water distribution constant for the solute which is defined as the mol fraction ratio (X_m/X_w) is then given by

$$K_m = \frac{X_m}{X_w} = \frac{\tau_w}{\tau_m} \exp(-P_L v_A/RT) \quad (7)$$

Substituting for τ_w from equation (3) we have

$$K_m = \frac{1}{\tau_m} \frac{1}{SV_w} \exp(-P_L v_A/RT) \quad (8)$$

Assuming ideality of solute in the micellar phase, $\tau_m = 1$.

$$K_m = \frac{1}{SV_w} \exp(-P_L v_A/RT) \quad (9)$$

From (5) and (9) we have

$$K_m = K_{ow} \tau_o^* \frac{V_o^*}{V_w} \exp(-P_L v_A/RT) \quad (10)$$

Thus

$$\log K_m = \log K_{ow} + \log \tau_o^* + \log (V_o^*/V_w) - P_L v_A/2.303RT \quad (11)$$

The above equation is a general $K_{ow} - K_m$ correlation for solutes in any given micelle of Laplace pressure P_L. The nature and type of the micelle enters into the picture through the last term in the above equation.

Assuming ideality in the octanol phase, $\tau_o^* \to 1$ It is possible to correlate v_A to K_{ow} as shown in Fig. 1 and as described by Miller *et al.* (1985)

$$\log K_{ow} = 0.024\, v_A - 0.12. \quad (12)$$

Using (12) in (11) we have

$$\log K_m = (1.00 - 18.0\, P_L/RT) \log K_{ow} - 2.17\, P_L/RT + \log \frac{V_o^*}{V_w} \quad (13)$$

For sodium dodecylsulfate micelles, we have $P_L/RT = 7.8 \times 10^{-3}$ mol cm^{-3} where $P_L = 2\tau/r$, $\tau = 29$ ergs cm^{-2}, $r = 30 \times 10^{-8}$ cm, $R = 8.3 \times 10^7$ ergs (K mol^{-1}) and $T = 298$ K (Bolden *et al.*, 1983). Also $V_o^*/V_w = 120/18 = 6.67$ (Chiou, 1981).

Then

$$\log K_m = 0.858 \log K_{ow} + 0.807. \quad (14)$$

Thus a slope of 0.858 is predicted for $\log K_m$–$\log K_{ow}$

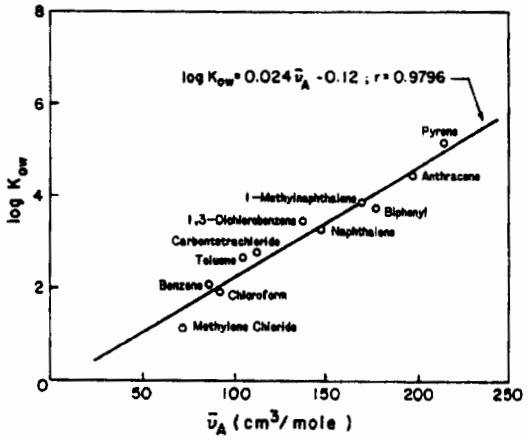

Fig. 1. Plot of log K_{ow} vs molar volume of hydrophobic compounds.

slope for micelles of sodium dodecylsulfate. Thus slopes can be predicted for other surfactant micelles, if the relevant parameters are known. It should be noted that K_m is a mole fraction ratio while K_{ow} is a concentration ratio.

In terms of mole fraction ratio for both micelle–water (K_m) and octanol–water (K^x_{ow}) partition constants we have

$$\log K_m = 0.858 \log K^x_{ow} - 0.017. \quad (15)$$

Thus we predict that $K_m < K^x_{ow}$. As explained earlier, this should be expected since solute solubility in micelles should be less than in octanol or a similar bulk solvent solubility.

For the eleven compounds given in Table 1, the experimental log K_m values for DDS micelles were plotted against log K_{ow} as shown in Fig. 2. A slope of 0.847 was obtained with a correlation coefficient of 0.9884. This slope should be compared with the 0.858 value obtained from equation (14). There is only a

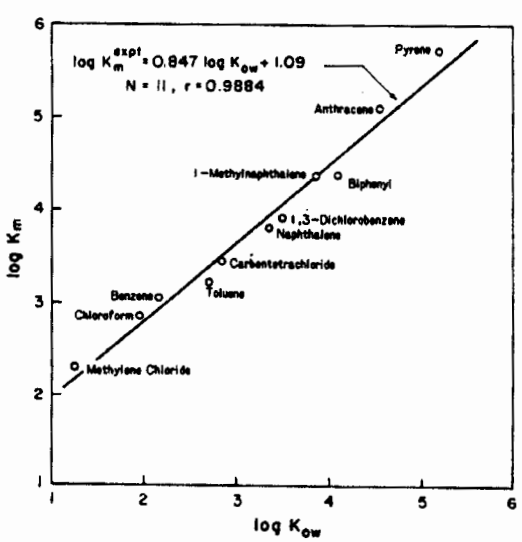

Fig. 2. Log K_{ow}–log K_m relationship for non-polar hydrophobic compounds in sodium dodecylsulfate micelles.

1.2% difference between experimental and theoretically predicted slopes for DDS micelles while there is a 35% difference in the intercept valves. The correlation between log K_m and log K_{ow} shown in Fig. 2 is excellent. The immediate question is how such an excellent correlation is obtained. The answer appears to be that the main driving force for water to octanol transfer of a hydrophobic molecule is the entropic change associated with the shearing off of an ordered water layer around these molecules (Helmer *et al.*, 1968); once in the octanol phase there is little restriction in the movement of the hydrophobic molecule and little or no reorientation is necessary (Tanford, 1980). The same driving force is responsible for the partitioning of a hydrophobic compound between the aqueous and micellar phases, albeit somewhat counteracted by the Laplace pressure acting across the micellar surface. Similar arguments have been put forward by Helmers *et al.* (1968) to explain the excellent correlation for the transfer of a variety of organics from water to a macromolecule like bovine serum albumin (BSA). Same arguments also apply to the partitioning of hydrophobic compounds between the aqueous medium and the organic matter (DOC) at sediment–water interfaces (Karickhoff *et al.*, 1979; Curtis *et al.*, 1986) and the capacity of humic acids to bind hydrophobics (Landrum *et al.*, 1984).

The value of the slope of linear free energy relationships such as these are said to be of importance in determining relative lipophilicity of the solvents considered (Leo and Hansch, 1971). If a particular solvent is more lipophilic than the reference solvent, the slope is > 1; if the sample solvent is less lipophilic than the reference solvent, the slope is < 1 (Leo and Hansch, 1971). The value of the slope is independent of the unit in which K_m is expressed, while the intercept value does depend on the units of K_{ow} and K_m and hence a general interpretation of the intercept value is difficult. The slope of 0.847 obtained in the present case for DDS micelles shows that the micellar phase is less lipophilic than the octanol phase as far as the partitioning of these non-polar hydrophobic organics are considered.

For a homologous series of surfactants, P_L decreases as the number of carbon atoms in the surfactant chain increases since the radius of the micelle increases. In other words the micellar solubility of a hydrophobic increases with increasing surfactant chain length. This has been verified by Bolden *et al.* (1983) for hydrocarbon gases.

The considerable success of the correlation of log K_m with log K_{ow} leads one to believe that other parameters which are closely related to K_{ow} should also be equally well capable of predicting log K_m.

An experimentally determined quantity is the aqueous solubility (ρ_m) which for neutral non-polar molecules is inversely related to log K_{ow} (Chiou, 1981). Figure 3 displays the relationship obtained between log K_m and log ρ_m where ρ_m is in mol l^{-1}. For

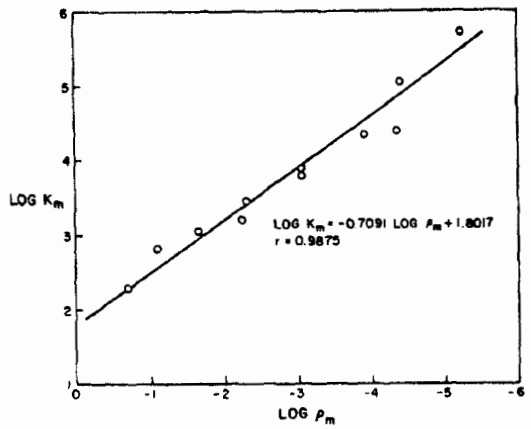

Fig. 3. Log K_m–log ρ_m relationship for non-polar hydrophobic compounds in sodium dodecylsulfate micelles where ρ_m is the aqueous molar solubility.

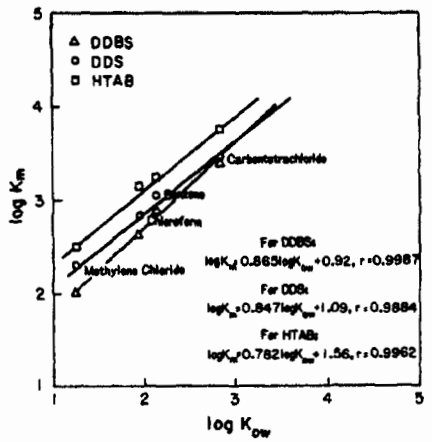

Fig. 5. Comparison of log K_m–log K_{ow} relationships for 4 hydrophobic compounds in sodium dodecylsulfate, sodium dodecylbenzenesulfate and hexadecyltrimethylammonium bromide micelles.

compounds that are solids at 25°C, the sub-cooled liquid solubilities as indicated in Table 1 were used. The correlation is not as good as one would expect. This may partly be due to the fact that experimental values of ρ_m for very slightly soluble compounds are in considerable error as has been noted by Sabljic (1987) in his attempts to correlate soil–water partition constants to aqueous solubility.

Another parameter which correlates well with K_{ow} is the solute molecular surface area, S_t. Solute molecular surface area for non-polar organics is also a measure of the hydrophobicity of a molecule (Valsaraj, 1988). The correlation between log K_m and S_t is given in Fig. 4. Although the correlation is not as good as one might expect, it appears that S_t is a satisfactory predictor of K_m.

Of all the three parameters considered, it appears that K_{ow} is the most satisfactory predictor of K_m.

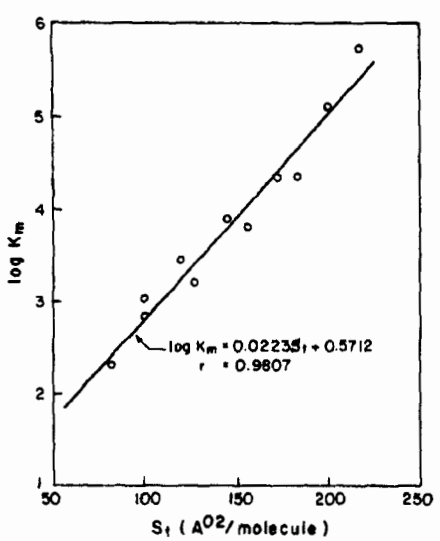

Fig. 4. Log K_m–S_t relationship for non-polar hydrophobic compounds in sodium dodecylsulfate micelles where S_t is the solute molecular surface area (square angstroms).

As a matter of comparison, Fig. 5 gives the log K_m–log K_{ow} correlation for three different surfactants. Only four compounds were considered, viz, CH_2Cl_2, $CHCl_3$, CCl_4 and C_6H_6. As expected, the slopes and intercepts for both DDS and DDBS surfactants agree closely. However, the values of K_m for HTAB surfactant are distinctly higher than for DDBS and DDS. Possible reasons for this were discussed in our previous work (Valsaraj *et al.*, 1988). The slope and intercept values are also significantly different from the other two micelles. Overall, one can conclude that for a specific surfactant, a specific correlation should be obtained. This is expected since specific surfactant–solute interactions are responsible for the solubilizing capacity of each type of surfactant micelle. Moreover, the site of solubilization of the same solute in different micelles may vary depending on such factors as the type of surfactant (ionic or non-ionic), chain length of the surfactant, the ionic groups of the surfactant molecule and type of micelle formed (e.g. spherical, rod-shaped or bilayered).

APPLICATION

We now illustrate a possible practical application of the K_m–K_{ow} correlation derived from our experiments for DDS micelles. It has been reported that linear alkyl sulfate surfactants present in groundwater facilitates the transport of hydrophobic compounds to distances far greater than predicted by simple retarded diffusion equations (Barber *et al.*, 1988; Enfield and Bengtsson, 1988). This situation as applied to the dissolved macromolecule-mediated transport of hydrophobic compounds in groundwater has been analyzed by Kan and Tomson (1986) who derived a modified retardation factor for the convective diffusion of hydrophobic organics. Their method can be utilized for surfactant micellar mediated transport of hydrophobic compounds in groundwater by replacing $10^{-6}\,K_{DOC}$[DOC] with

$K_m v_w[C\text{-CMC}]$ to derive the following equation for the retardation factor:

$$R = 1 + \frac{K_{oc}[\text{oc}](1-n)\rho/n}{1 + K_m v_w(C - \text{CMC})} \quad (16)$$

where

K_{oc} = partition constant for the hydrophobic compound between the soil (based on organic carbon content, oc) and water ($cm^3\,g^{-1}$)
oc = fractional organic carbon content of the soil (mass fraction)
n = porosity of soil
ρ = bulk soil density ($g\,cm^{-3}$)
K_m = partition constant for hydrophobic compound between the micellar and aqueous phases (mole fraction ratio)
v_w = molar volume of water ($1\,mol^{-1}$)
C = total concentration of surfactant ($mol\,l^{-1}$)
CMC = critical micellar concentration of the surfactant ($mol\,l^{-1}$)
$(C - \text{CMC})$ = concentration of micellar entities in the aqueous phase ($mol\,l^{-1}$).

There are several correlations in the literature between K_{oc} and K_{ow}, of which we use one of the most recent (Curtis *et al.*, 1986)

$$\log K_{oc} = 0.92 \log K_{ow} - 0.23. \quad (17)$$

For the value of K_m for DDS micelles we shall use the experimental correlation developed in the present work (Fig. 2)

$$\log K_m = 0.847 \log K_{ow} + 1.09. \quad (18)$$

Let us choose a soil with the following properties:

$$\rho = 2\,g\,cm^{-3}, n = 0.1 \text{ and oc} = 0.02.$$

Using these values along with equations (17) and (18) in (16) gives

$$R = 1 + \frac{0.21\,K_{ow}^{0.92}}{1 + 0.22\,K_{ow}^{0.847}[C - \text{CMC}]}. \quad (19)$$

It should be noted that equation (19) is only applicable when the surfactant concentration is above its CMC. Below the CMC, no micelles are available for transport. For DDS, the value of CMC is reported to be 0.008 M. Equation (19) can be used to predict the retardation factors for chemicals of various hydrophobicities for situations involving DDS concentrations >0.008 M. Figure 6 gives a plot of log R vs log K_{ow}. The plot for zero molar surfactant is the one obtained from the conventional retardation equation (Kan and Tomson, 1986) where only the advective diffusion limited by adsorption on soil is limiting the transport. Remarkable differences in retardation factors can be observed when the surfactant micelles are present. The reduction in the value of R amounts to an increase in the velocity of transport of the hydrophobic compound in groundwater. Below log K_{ow} of 1, micellar mediated transport is predicted to be negligible while for compounds with log $K_{ow} > 5$, the velocity of transport is predicted to be the same for a particular micellar concentration. These conclusions must be approached with caution since the derivation of equation (16) assumes that surfactant micelles do not adsorb onto the aquifer materials. Equations such as (19) may be obtained for micelles formed by any particular surfactant and can thus be used to predict the transport of hydrophobic contaminants in groundwater. Thus a knowledge of a K_m–K_{ow} relationship such as given in Fig. 2 becomes very useful. Experiments such as those of Kan and Tomson (1986) or Enfield and Bengtsson (1988) can be used to test the predictions of equation (19).

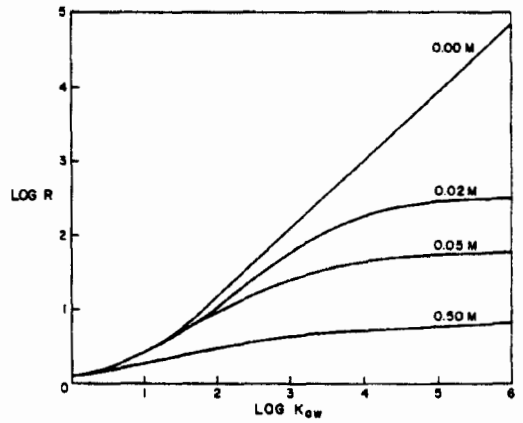

Fig. 6. Change in retardation factors for the transport of hydrophobic compounds in groundwater in the presence of sodium dodecylsulfate micelles.

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