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On the Estimations of Micelle-Water Partition Constants for Solutes from Their Octanol-Water Partition Constants, Normal Boiling Points, Aqueous Solubilities, and Group and Bond Contribution Schemes

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Abstract

Five different estimation procedures for micelle-water partition constants for organic solutes are discussed. The procedures are based on 1) knowledge of octanol-water partition constants for the solutes, 2) aqueous solubilities of the solutes, 3) normal boiling points of the solutes, 4) a bond contribution scheme, and 5) a group contribution scheme. Available data in the literature including our own are used in obtaining these correlations. Potential advantages and drawbacks of each of the methods are explored.

INTRODUCTION

Although there exists voluminous literature on the solubilization of organic compounds in micellar pseudophases in aqueous solutions, a satisfactory and comprehensive review of this ever-expanding area is still lacking. At the outset, we make it clear that this paper does not purport to achieve such a task. We wish to bring together a large set of disparate data

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on the partitioning of a variety of compounds between the aqueous and typical micellar phases with a view to inquiring as to whether there exists any reliable way of estimating these values by any of the estimation procedures normally used to obtain solvent-water partition constants.

Knowledge of micelle-water partition constants are of significance in many areas such as pharmaceutical applications, environmental applications, etc. In the realm of pharmaceutical applications, octanol-water systems have often been used as a model to resemble lipid-water partitioning of organic molecules (*1*). However, this practice has been criticized by some who suggest that micelles may be better systems to represent lipids. In the realm of environmental applications, there are a host of situations where micellar-enhanced aqueous phase solubilities of organic compounds are important. We had reviewed these in our earlier work (*2*), some of them being micellar-enhanced ultrafiltration for removal of organic compounds from aqueous phase (*3*), *in-situ* surfactant flushing of soils (*4*), solvent sublation using microgas dispersions (*5*), evaluation of contaminant transport by organic colloids in groundwater (*6*), etc. Thus the evaluation of the capability of micelles to solubilize other compounds and comparison with bulk solvents is an important area of research.

DISCUSSION

It is well substantiated in the literature that micelles formed by anionic, cationic, or nonionic surfactants all have the capability of solubilizing otherwise insoluble or partly soluble compounds in water (*7*). The reason for such a property for the micelles is the hydrocarbonlike core of these microstructures. Compounds that are hydrophobic and nonpolar are usually solubilized in the core region while those that are partly polar are found to reside in the palisade layer of the micelle. Ionic compounds tend to bind to the surface of the micelles. The driving force for the transfer of a hydrophobic compound from the aqueous to the micellar phase is the inability of the compound to compete effectively with the strong hydrogen bond forces between water molecules. This is the same driving force that is at work in the partitioning of a hydrophobic compound between a solvent, such as octanol, and water (K_{ow}). This is the same reasoning used to relate K_{ow} values to other partition constants such as between sediment-water (K_d) and dissolved organic matter-water(K_{doc}) partition constants for hydrophobic compounds. One is thus led to the conclusion that K_{ow} values must be linaerly related to micelle-water partition constants as well. Octanol-water systems are often chosen as the reference system in deriving many of the above linear free energy relationships since octanol serves as a "good" solvent satisfying several criteria such as: 1) octanol has been found to be a useful model system to describe nonspecific binding of solutes with biological macromolecules, 2) the largest number of measured partition coefficients for the widest variety of solute functional groups is available for this system, and 3) the balance of polar and nonpolar hydrocarbon chain in octanol presumably best simulates the fats and proteins in animals and plants.

In reality, any solvent which forms an immicible phase with water, but has a large solubility for hydrophobic compounds and satisfies some of the above criteria, can serve as a reference solvent. A pure nonpolar solvent such as hexane is also regarded by many as a good reference solvent.

The case of a micelle–water partitioning process for a solute is somewhat diferent from that of a partitioning process between two bulk solvents for the simple reason that the micellar phase is not a true separate phase but is considered a pseudophase. Since it is known that surfactants below their critical micellar concentration (cmc) do not show the ability to solubilize hydrophobic compounds, and only the microheterogeneous phase (micelles) formed above the cmc are capable of doing so, we are led to conclude that this so-called pseudophase has properties similar to those of a bulk solvent in equilibrium with the aqueous phase. However, unlike partitioning into a bulk solvent, there is an additional surface pressure effect (Laplace pressure) that tends to counteract the facile solubilization of compounds within micelles.

The various factors that influence micellar solubilization of compounds have been discussed by various authors (*7–10*). We have collected the values of partition constants for several organic compounds in two different micelles [an anionic surfactant (sodium dodecylsulfate) and a cationic surfactant (hexadecyl trimethyl ammoniumbromide)]. These values are shown in Table 1 and grouped according to the nature of the functional groups. There are a variety of methods used to obtain the values of partition constants. Examples are equilibrium partitioning in closed systems (*11*), direct vapor-phase measurements (*12*), direct gas solubility measurements (*39*), micellar chromatography (*10*), dissociation constant measurements for acidic molecules (*7*), direct determination of micellar solubilities (*48*), and spectroscopy techniques (*7*). In certain cases the authors have reported the partition constants as ratios of solute concentration in the micelle to the solute concentration in water, and in certain other cases they have reported the ratio of mole fractions in the two phases. The latter will be designated K_m and the former as P_m. The two constants are related through the molar volumes of the surfactant and

TABLE 1

Micelle–Water Partition Constants, Octnol–Water Partition Constants, Normal Boiling Points, and Aqueous Solubilities for Selected Hydrophobic Compounds[a]

			For DDS micelles			For HTAB micelles				
Compound	Log K_{ow}	Ref.	Log K_b	Log P_m	Ref.	Log K_b	Log P_m	Ref.	T_b (K)	Log S
			Aliphatic Halocarbons							
Methylene chloride	1.25	*31*	0.52	1.16	*11*	0.74	1.27	*11*	313.0	−0.92
Chloroform	1.96	*31*	1.08	1.72	*11*	1.40	1.93	*11*	334.3	−1.09
Carbon tetrachloride	2.83	*31*	1.68	2.33	*11*	1.99	2.52	*11*	349.9	−1.28
			Aromatic Hydrocarbons							
Benzene	2.13	*31*	1.29	1.93	*2*	2.19	2.72	*2*	353.2	−1.64
Toluene	2.69	*31*	1.47	2.11	*2*	—	—		383.8	−2.25
Naphthalene	3.35	*31*	2.05	2.69	*2*	3.18	3.71	*2*	491.1	−3.08
1-Methyl naphthalene	3.87	*31*	3.06	3.70	*30*	—	—		517.9	−3.69
Anthracene	4.54	*31*	3.81	4.45	*30*	4.64	5.17	*30*	613.1	−4.41
Biphenyl	4.09	*31*	3.07	3.71	*30*	3.85	4.38	*30*	528.0	−3.88
Pyrene	5.18	*31*	4.44	5.08	*30*	5.23	5.76	*30*	666	−5.24
p-Xylene	3.15	*31*	2.41	3.05	*30*	—	—		411.5	−2.73
Phenanthrene	4.46	*31*	3.84	4.48	*30*	4.57	5.10	*30*	613.0	−4.48
Perylene	6.50	*31*	5.44	6.08	*30*	5.65	6.19	*30*	673.0	−8.52
4-Bromo-*p*-terphenyl	—	—	4.98	5.62	*30*	—	—	—	—	—
			Aromatic Halocarbons							
m-Dichlorobenzene	3.48	*31*	2.13	2.77	*2*	—	—	—	446.0	−3.03
1-Bromonaphthalene	4.06	*31*	3.53	4.17	*30*	4.45	4.98	*30*	554.1	

				Aromatic Phenols						
Phenol	1.46	*32*	1.00	1.64	*13*	2.08	2.61	*33*	455	0.104
4-Methoxyphenol	1.34	*32*	1.17	1.81	*13*	—	—		516	
4-Ethoxyphenol	1.81	*32*	1.44	2.08	*13*	—	—		519	
4-Formylphenol	1.70	*32*	1.09	1.73	*13*	—	—		521	
4-Carboxymethylphenol	1.96	*32*	1.57	2.21	*7*	—	—		549	
4-Carboxyethylphenol	2.47	*32*	1.84	2.48	*7*	—	—		595	
4-Carboxypopylphenol	3.04	*32*	2.23	2.87	*7*	—	—		595	
4-Cuanophenol	1.60	*32*	1.17	1.81	*7*	—	—		552	
4-Nitrophenol	1.91	*32*	1.20	1.84	*7*	—	—		552	0.325
2-Carboxamidophenol	1.28	*32*	0.78	1.42	*7*	—	—		—	
3-Trifluoromethyl	2.95	*32*	2.11	2.75	*7*	—	—		451	
2-*N*-Phenylcarboxamidophenol	3.27	*32*	2.39	3.03	*7*	—	—			
1-Naphthol	2.98	*32*	2.25	2.89	*7*	—	—		561	
4-Methylphenol	1.92	*32*	1.38	2.02	*33*	2.34	2.87	*33*	474	−0.59
4-Ethylphenol	2.40	*32*	1.71	2.35	*34*	—	—		492	
				Aliphatic Alcohols						
1-Butanol	0.88	*32*	0.71	1.35	*12*	−0.30	0.50	*35*	390	−0.05
1-Pentanol	1.56	*32*	1.10	1.74	*12*	0.00	0.53	*35*	411	−0.61
1-Hexanol	2.03	*32*	1.60	2.24	*12*	0.57	1.00	*35*	430	−1.17
1-Heptanol	2.41	*32*	2.03	2.67	*12*	1.01	1.54	*35*	449	−1.73
1-Decanol	—	—	2.65	3.29	*34*	—	—		506	−3.41
				Aliphatic Hydrocarbons						
Methane	1.12	*23*	−0.004	0.64	*16*	0.19	0.72	*39*	111.5	−2.81
Ethane	1.78	*23*	0.77	1.41	*16*	0.92	1.46	*39*	184.4	−2.79
Propane	2.36	*23*	1.34	1.98	*16*	1.52	2.05	*39*	230.9	−2.85
Butane	2.92	*23*	2.03	2.67	*36*	—	—	—	272.5	−2.89
Pentane	3.62	*38*	2.46	3.10	*36*	—	—	—	309.1	−3.27
***n*-Hexane**	4.11	*38*	2.60	3.24	*37*	—	—	—	341.7	−3.95
Cyclohexane	3.44	*38*	1.73	2.37	*37*	—	—	—	353.7	−3.18

(continued)

TABLE 1 *(continued)*

			For DDS micelles			For HTAB micelles				
Compound	Log K_{ow}	Ref.	Log K_b	Log P_m	Ref.	Log K_b	Log P_m	Ref.	T_b (K)	Log S
			Aliphatic Amides							
Propionamide	−1.05	*32*	0.48	1.12	*34*	—	—	—	495.2	
Butyramide	−0.21	*32*	0.87	1.31	*34*	—	—	—	489.0	
Valeramide	0.73	*32*	0.98	1.62	*34*	—	—			
8-Valerolactam	—	—	0.67	1.31	*34*	—	—	—		
6-Caprolactam	−0.19	*32*	0.97	1.61	*34*	—	—	—		
4-Ethylparabem	—	—	2.11	2.76	*34*	—	—	—		
Benzocain	—	—	2.08	2.72	*34*	—	—	—		
Aniline	—	—	0.85	1.49	*41*	1.34	1.88	*41*		
p-Methylaniline	—	—	1.28	1.92	*41*	1.62	2.16	*41*		
			Aromatic Halophenols							
4-Fluorophenol	1.77	*32*	1.23	1.87	*33*	2.14	2.67	*33*	458.5	
4-Chlorophenol	2.44	*32*	1.48	2.12	*33*	2.84	3.37	*33*	492.7	−0.51
4-Bromophenol	2.59	*32*	1.78	2.42	*33*	2.96	3.49	*33*	511.0	−0.60
4-Iodophenol	2.91	*32*	2.15	2.79	*33*	3.11	3.64	*33*	520.6	
2,3,5,6-Tetrafluorophenol	2.64	*32*	1.93	2.57	*33*	2.37	2.90	*33*	413.0	
Pentafluorophenol	2.91	*32*	2.16	2.80	*33*	3.50	4.03	*33*	416.0	
3,5-Dichlorophenol	2.90	*32*	1.96	2.60	*33*	—	—	—	506.0	−2.57
2,3,5-Trichlorophenol	3.72	*32*	2.45	3.08	*33*	—	—	—	522.0	−1.91
2,3,4,5-Tetrachlorophenol	4.10	*32*	2.92	3.56	*33*	—	—	—	563.0	
Pentachlorophenol	5.01	*32*	3.37	4.01	*33*	—	—	—	583.0	−3.52
2,4,6-Tribromophenol	—	—	3.31	3.95	*34*	—	—	—	563.0	
2,4,6-Triiodophenol	—	—	4.35	4.99	*34*	—	—	—	689.1	
1-Naphthol	2.98	*33*	2.25	2.89	*34*	—	—	—	561.0	
4-Chloronaphthol	—	—	2.74	3.88	*34*	—	—	—	593.7	
6-Bromonaphthol	—	—	3.04	3.68	*34*	—	—	—	622.5	

Aromatic Phenols and Diols

2-Methylphenol	1.95	*33*	1.32	1.96	*40*	—	—	—	464.0	−0.485
3-Methylphenol	2.01	*33*	1.38	2.02	*40*	—	—	—	475.0	−0.588
4-Methylphenol	1.94	*33*	1.38	2.02	*40*	—	—	—	474.8	−0.653
2,3-Dimethylphenol	—	—	1.76	2.40	*40*	—	—	—	491.0	
2,4-Dimethylphenol	—	—	1.80	2.44	*40*	—	—	—	484.5	−1.25
2,5-Dimethylphenol	2.50	—	1.80	2.44	*40*	—	—	—	484.5	—
2,6-Dimethylphenol	2.36	*33*	1.76	2.40	*40*	—	—	—	476.0	
3,5-Dimethylphenol	2.35	*33*	1.80	2.44	*40*	—	—	—	492.5	−1.46
2,4,5-Trimethylphenol	—	—	2.09	2.73	*40*	—	—	—		
2,3,5,6-Tetramethylphenol	—	—	2.43	3.07	*40*	—	—	—		
Benzene-1,2-diol	0.80	*33*	0.80	1.44	*40*	—	—	—	518.5	1.73
4-Methylbenzene-1,2-diol	—	—	1.22	1.86	*40*	—	—	—	536.7	
4-Cyanobenzene-1,2-diol	—	—	0.81	1.45	*40*	—	—	—		
3-*i*-Propylbenzene-1,2-diol	—	—	1.71	2.35	*40*	—	—	—	543.0	
4-*t*-Butylbenzene-1,2-diol	—	—	1.99	2.63	*40*	—	—	—		
2-Methylbenzene-1,4-diol	—	—	0.68	1.32	*40*	—	—	—		
2-Chlorobenzene-1,4-diol	—	—	0.89	1.53	*40*	—	—	—		
2-Phenylbenzene-1,4-diol	—	—	1.66	2.30	*40*	—	—	—		
2-*t*-Butylbenzene-1,4-diol	—	—	1.75	2.39	*40*	—	—	—		
2,3,5-Trimethylbenzene-1,4-diol	—	—	1.09	1.73	*40*	—	—	—		

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[a] T_b values from refs. *26, 42,* and *44*; log S values from Refs. *31, 19, 24, 16,* and *45*. S is in mol/L.

water, with the assumption that the molar volume of a surfactant and water, with the assumption that the molar volume of a surfactant in the micelle is the same as that of a free surfactant monomer. Thus

$$P_m = C_m/C_w \qquad \text{and} \qquad K_m = X_m/X_w \tag{1}$$

where C_m = equilibrium solute concentration in the micelle (mol/L)
C_w = equilibrium solute concentration in the aqueous phase (mol/L)
X_m = mole fraction of solute in the micelle
X_w = mole fraction of solute in water

are related as

$$P_m = K_m \cdot (v_w/v_s) \tag{2}$$

where v_w and v_s are, respectively, the molar volumes of water and surfactant. In many other cases, authors have reported the so-called binding constant for solutes with micelles. In order to do so, they have considered the binding of solutes to micelles (solubilization within micelles) by a reaction scheme such as

$$\text{A} + \text{Mic} \rightleftharpoons \text{A-Mic} \tag{3}$$

characterized by an equilibrium binding constant,

$$K_b = \frac{[\text{A}-\text{Mic}]}{[\text{A}]_{\text{aq}}[\text{Mic}]} \tag{4}$$

where [A-Mic] is the concentration of solute associated with the micelle, $[\text{A}_{\text{aq}}]$ and [Mic] are the free aqueous concentration of uncomplexed A and the micelle, respectively. K_b is shown to be related to P_m as (*10*)

$$K_b = (P_m - 1)v_s \tag{5}$$

Many authors regard K_b to be more appropriate than P_m since the definition of K_b does not involve the assumption of a separate phase for the micelle. However, for many applications it is still very useful to adopt the pseudophase micellar model and obtain the values of P_m for various solutes. In Table 1 we give both K_b and P_m, and since they are both linearly related through Eq. (5), it makes no difference in utilizing either for further correlations. For our purposes we choose P_m as the correlating parameter.

The relationship between P_m and K_{ow} has been reported for a few selected compounds by several workers (*2, 13–15*). A general relationship between P_m and K_{ow} based on thermodynamic arguments was suggested by us earlier (*2*), based on earlier work by Bolden et al. (*16*) on the micellar solubilities of aliphatic hydrocarbon gases. The relationship was

$$\log P_m = \log K_{ow} + \log\left(\frac{v_o}{v_s}\right) - \frac{P_L v_A}{2.30\,RT} \tag{6}$$

where v_o is the molar volume of octanol, P_L is the Laplace pressure across the micelle, and v_A is the molar volume of the solubilized solute in the micelle. For a particular class of compounds, v_A has been shown to be also linearly related to $\log K_{ow}$ (*17*). Thus a particular group of compounds will obey a unique linear relationship between $\log P_m$ and $\log K_{ow}$:

$$\log P_m = a + b \log K_{ow} \tag{7}$$

That the above relationship holds is evident from Fig. 1. The values of the slopes and intercepts are given in Table 2. Certain specific trends are apparent. First, the slopes for DDS micelles vary only between 0.74 and 1.11 with amides excluded, and the intercept values vary between −0.13 and 1.40. The amides show a strange relationship, perhaps due to their unique nature of binding to the micelles. However, such abnormalities do not seem to have been addressed by the workers who reported these values (*34*). The values for HTAB micelles show b values between 0.79 and 1.07, while a values range from −0.47 to 0.94. Notice that the $\log P_m$ values are consistently higher for HTAB micelles than for DDS micelles. It is quite possible that because of the longer chain length of the HTAB molecule, and hence the larger size of the HTAB micelle, the Laplace pressure may be smaller and hence facilitate solubilization. The larger the micelle, the larger is the micellar volume which also may increase the amount of solubilizate in the micelle. It is also possible that the mechanism of binding of organic molecules will be different for cationic and anionic micelles. Compounds such as benzene, which are partly polarizable due to electron delocalization, may find it easier to bind to cationic micelles such as HTAB as compared to anionic micelles such as DDS. It is, however, interesting to point out that both highly polar as well as nonpolar compounds obey the $\log P_m$–$\log K_{ow}$ relationship, albeit differently.

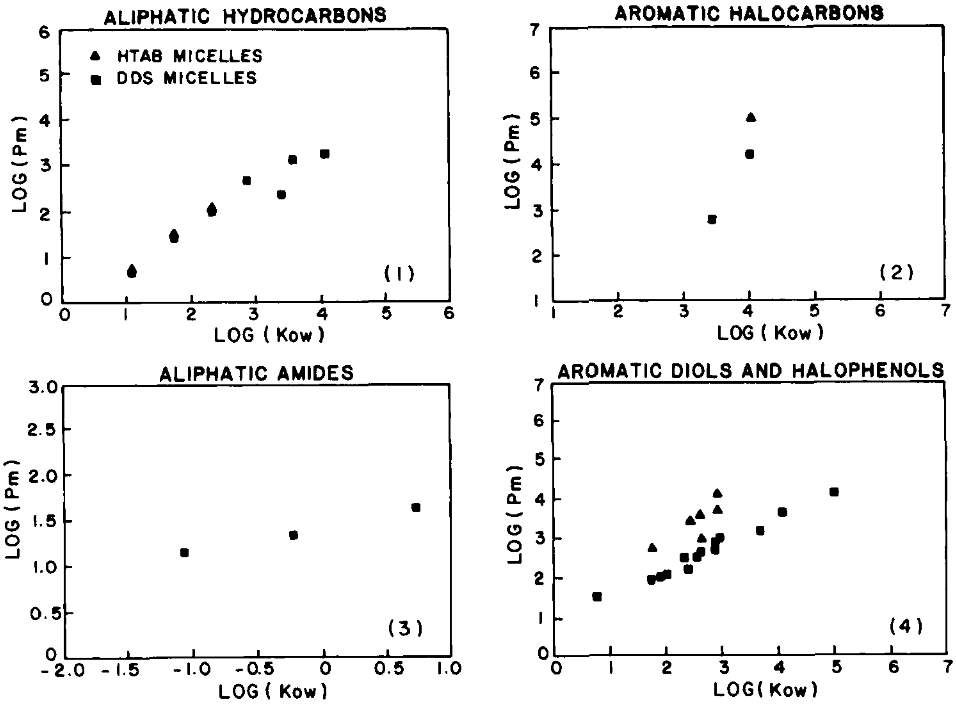

FIG. 1a. Plot of log P_m versus log K_{ow} for (1) aliphatic hydrocarbons, (2) aromatic halocarbons, (3) aliphatic amides, and (4) aromatic diols and halophenols.

The relationship for aliphatic hydrocarbons barely shows any difference for the two micelles, while for aliphatic alcohols the values for HTAB micelles are distinctly smaller than for DDS micelles. For all other compounds the HTAB micelles show higher values than DDS micelles. There are only a very few aromatic halocarbons for which values are available, and it appears that more work is needed here.

Some authors (*7*) have discussed the significance of the magnitudes of slopes and intercepts of log P_m–log K_{ow} relationships. They have suggested that the magnitude of the intercept is an indication of the site of solubilization of a molecule: the closer the value is to zero, the more the micellar environment resembles that of octanol. A negative intercept is identified with solubilization in the hydrocarbon core. Slopes of <1 show that it is easier to transfer a molecule from water to the micellar phase. Similar arguments were presented earlier by Helmer et al. (*18*) in relation

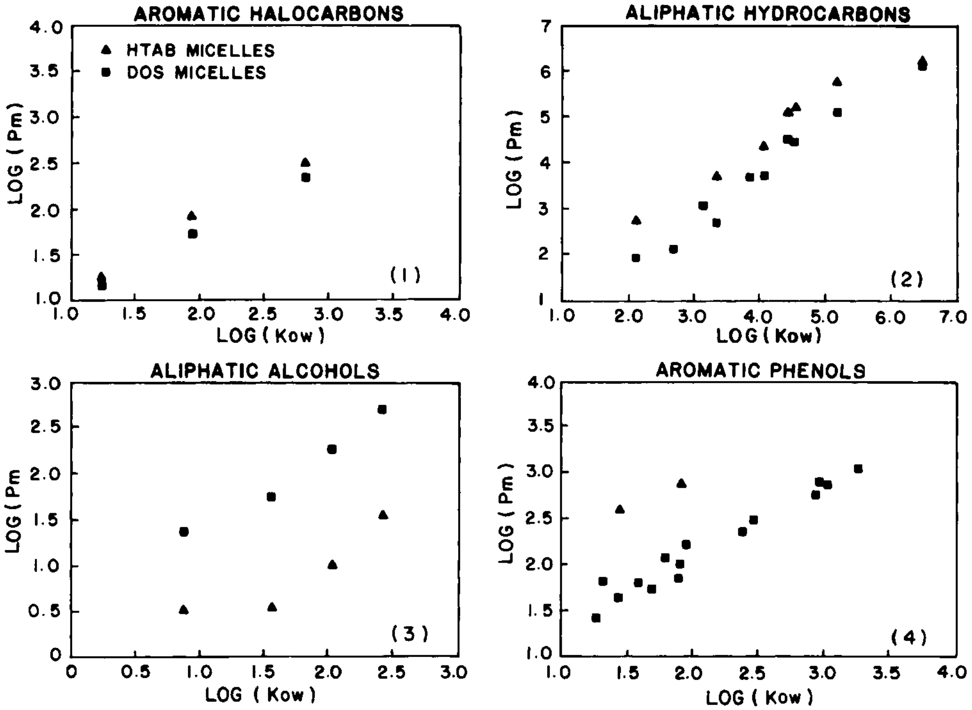

FIG. 1b. Plot of log P_m versus log K_{ow} for (1) aliphatic halocarbons, (2) aromatic hydrocarbons, (3) aliphatic alcohols, and (4) aromatic phenols.

to a comparision of the ease of transfer to molecules from water to octanol and water to a biological macromolecule (bovine serum albumin).

Can we define a single relationship for all compounds as are the cases for sediment-water and other solvent-water partition constants? It seems reasonable to expect such a relationship exists because, as already observed, the slopes of all the plots are fairly similar. Figure 2 for the DDS micelles of all compounds shows that this is reasonable. Fifty-seven compounds were included in the regression and, except for amides, they are closely bunched over seven orders of magnitude in log K_{ow}. The slope is 0.827, which is close to the expected value of 0.858 (*2*), and the correlation coefficient for regression is 0.9924. Similarly for the 26 compounds in HTAB micelles for which values are available; the regression gives a slightly higher slope of 1.101 with a correlation coefficient of 0.9917. In spite of the obvious variations between different groups of compounds, it

TABLE 2
Correlations between Log P_m and Log K_{ow}:
Log $P_m = a + b$ Log K_{ow}

Surfactant: DDS

Compound type	a	b	N	r
Aliphatic halocarbons	0.25	0.74	3	0.9994
Aliphatic alcohols	0.51	0.86	4	0.9864
Aliphatic amides	1.40	0.28	3	0.9945
Aromatic hydrocarbons	−0.66	1.11	9	0.9816
Aromatic phenols	0.59	0.75	13	0.9767
Aromatic halocarbons				
Aromatic halogenated phenols	0.76	0.66	9	0.9760
Aliphatic hydrocarbons	−0.13	0.84	7	0.9649

Surfactant: HTAB

Compound type	a	b	N	r
Aliphatic halocarbons	0.32	0.79	3	0.9959
Aliphatic alcohols	−0.52	0.86	4	0.9736
Aromatic hydrocarbons	0.42	1.02	6	0.9910
Aromatic halogenated phenols	0.94	0.95	6	0.8051
Aliphatic hydrocarbons	−0.47	1.07	3	0.996

is clear that there is a definite log P_m-log K_{ow} relationship for these compounds (Fig. 3).

One way of characterizing the relationship between the hydrophobicity of a molecule and the effects of substituent groups is to plot the micelle-water partition constant against Π, defined as log P_x − log P_H, where P_x is the octanol-water partition constant with substituant x on the molecule, and P_H that of the unsubstituted molecule. Figure 4 gives such a plot for chlorine substituents on the methane molecule, Fig. 5 for various substituents on the benzene molecule, Fig. 6 for various substituents on phenol, and Fig. 7 for substituents on naphthalene. Figure 4 clearly shows that replacement of H by Cl makes the methane molecule progressively more hydrophobic. The reason is quite obvious in that substitution by chlorine not only increases the molecular size but also makes the molecule less and less capable of H-bonding with water. The large decrease in entropy upon solubilization of these compounds in a pure aqueous phase drives them out of their aqueous environment into a less

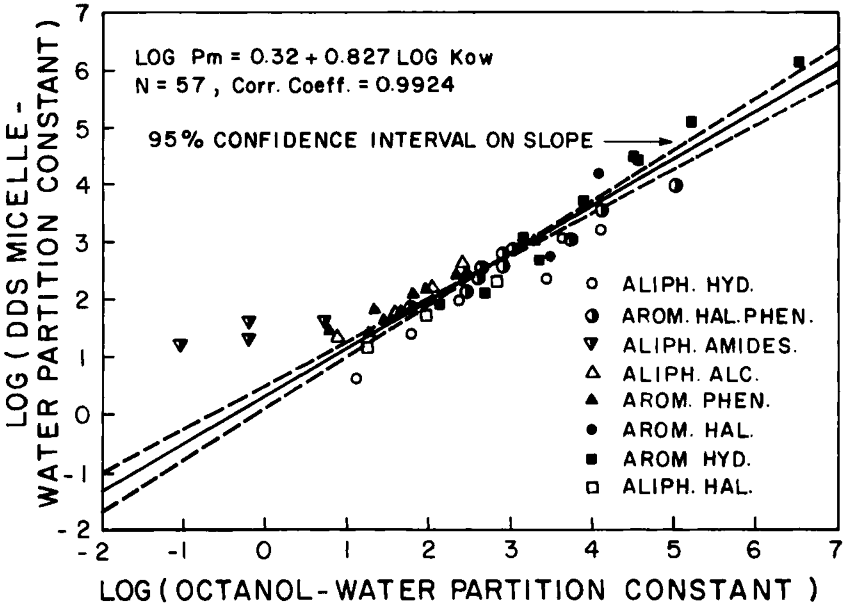

FIG. 2. Overall relationship between log P_m and log K_{ow} for DDS micelles.

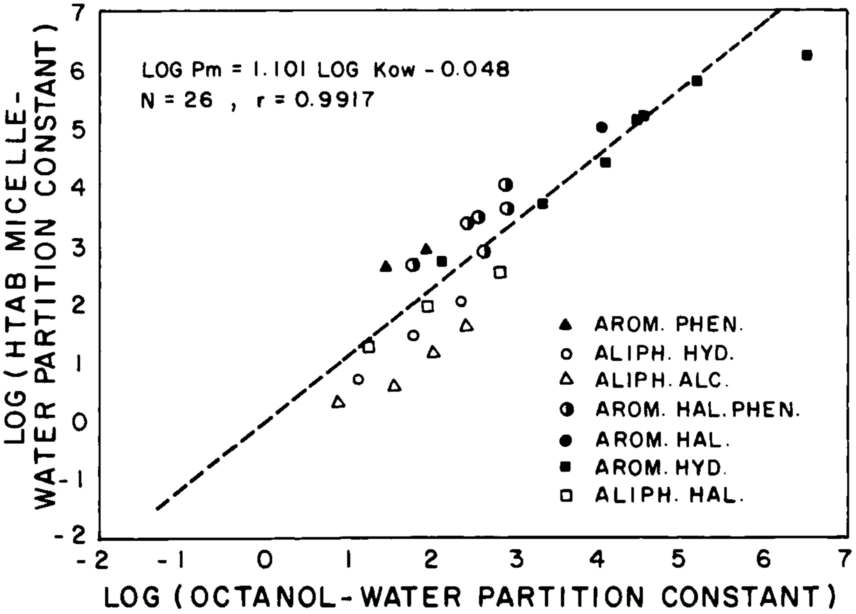

FIG. 3. Overall relationship between log P_m and log K_{ow} for HTAB micelles.

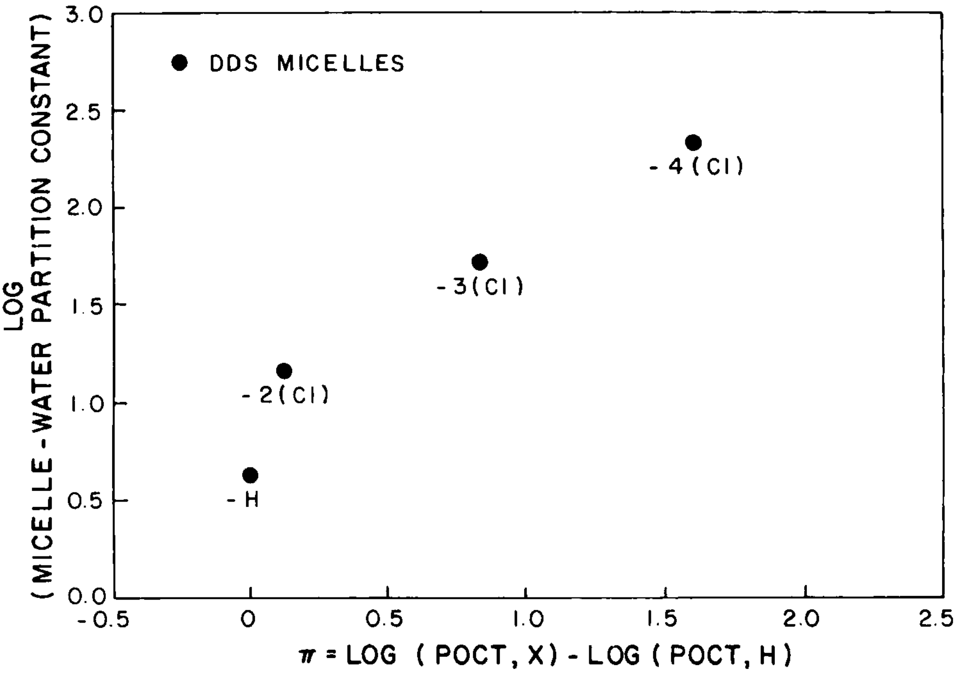

FIG. 4. Substituent effects on log P_m for chlorine substitution on methane.

polar environment such as the micellar interior. Similar arguments have been put forward for their accumulation by organic matter in sediments and soils, and by fish in water (*19*). Figure 5 shows that substitution of H on the benzene skeleton by bulkier groups such as $-CH_3$ and $-C_6H_5$ also leads to larger hydrophobicity for the compound, resulting in larger P_m values. On the other hand, substitution of an H by an OH group makes the molecule less hydrophobic than benzene itself, quite in line with our argument that compounds capable of H-bonding with solvent (water) molecules will have lower P_m values. It has also been suggested from experimental determinations of the interfacial activity of benzene and alkyl-substituted benzenes that progressive alkyl substitution on benzene certainly leads to a decrease in polarity [because the increasing nucleophilicity of alkyl groups makes the molecules move more and more toward the micellar interior from the micelle surface (*20, 21*)]. Pramauro et al.'s data (*13*) on substituted phenols were replotted as in Fig. 6, which shows that except for the $-OH$ and $-COONH_2$ groups, most other groups

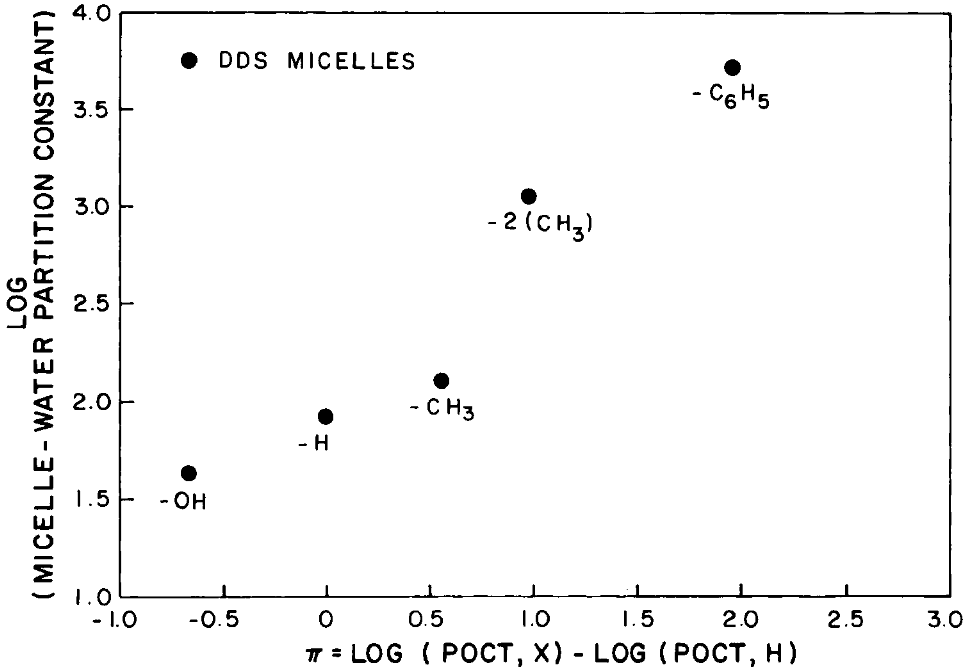

FIG. 5. Substituent effects on log P_m for benzene.

studied impart hydrophobicity to the phenol molecule. The trend seems to be that the hydrophobicity increases as F < Cl < Br < I, in accordance with the increasing nucleophilic nature of the substituents. Similarly, substitution of alkyl groups increases the hydrophobicity as $-CH_3 < -C_2H_5 < -C_3H_8$. The $-NO_2$ group on phenol was found to give it more hydrophobicity, and so does the $-CN$ group. Thus, even a molecule such as phenol, which is polar, can be made to be highly hydrophobic by appropriate substituent groups on the benzene skeleton, thus counteracting the tendency of the molecule to H-bond with water. It can be assumed that since such molecules have a hydrophilic group and a hydrophobic group, their location within the micelle will depend largely on the hydrophobic-hydrophilic balance imparted by these groups and in all likelihood will be solubilized in the palisade layer of the micelle. Figure 7 for naphthalene derivatives leads us to the same conclusion. Similar conclusions were drawn by others in ascertaining substituent effects on micelle-water partition constants for polar molecules such as substituted benzoic acid and acetanilide molecules between nonionic surfactants and water (*15, 22*).

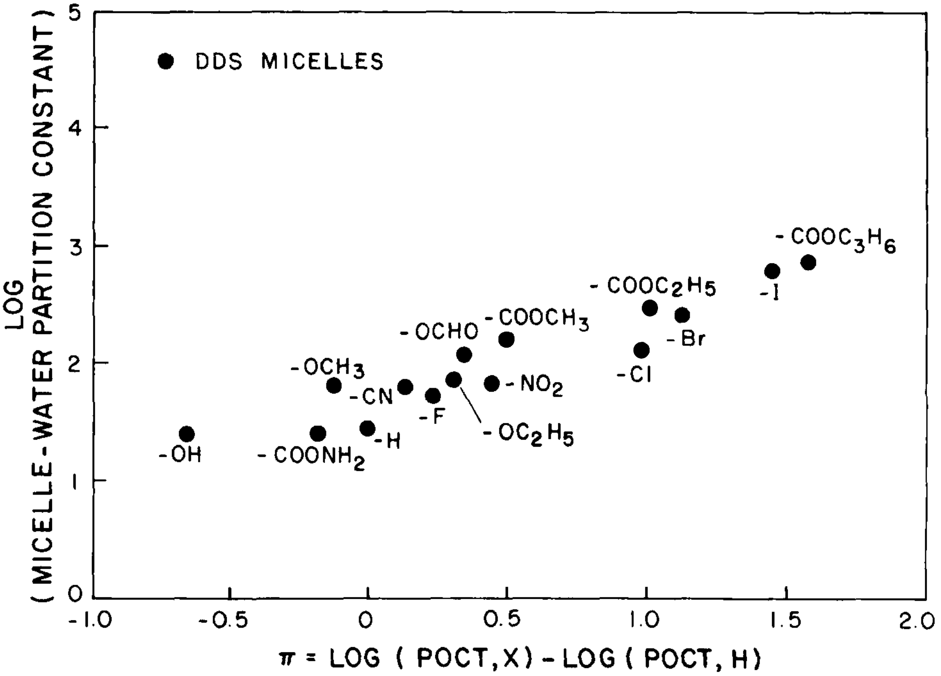

FIG. 6. Substitutent effects on log P_m for phenol.

It has been suggested by others that since octanol–water partition constants are inversely related to the aqueous solubility of compounds, S, there is a linear reltionship between log K_{ow} and log 1/S (*23*). For groups of compounds of similar properties and functional groups, this is even recommended as an estimation procedure for S if K_{ow} is known from literature compilations. Thus it seems logical to inquire as to whether P_m is also related to S. Figures 8 and 9 show plots of log P_m for DDS micelles versus log S for aliphatic and aromatic hydrocarbons, aliphatic halocarbons, alcohols, and aromatic phenols and halophenols. All compounds except aliphatic hydrocarbons of shorter chain length (<4) do show linear relationships between log P_m and log S. However, their slopes are widely different. McAuliffe (*24*) noted earlier that the aqueous solubilities of aliphatic hydrocarbons follow a linear behavior with solute molar volume only for compounds of 4 or more carbons atoms while those with <4 carbon atoms do not fit the linear behavior. Hence it seems appropriate to ex-

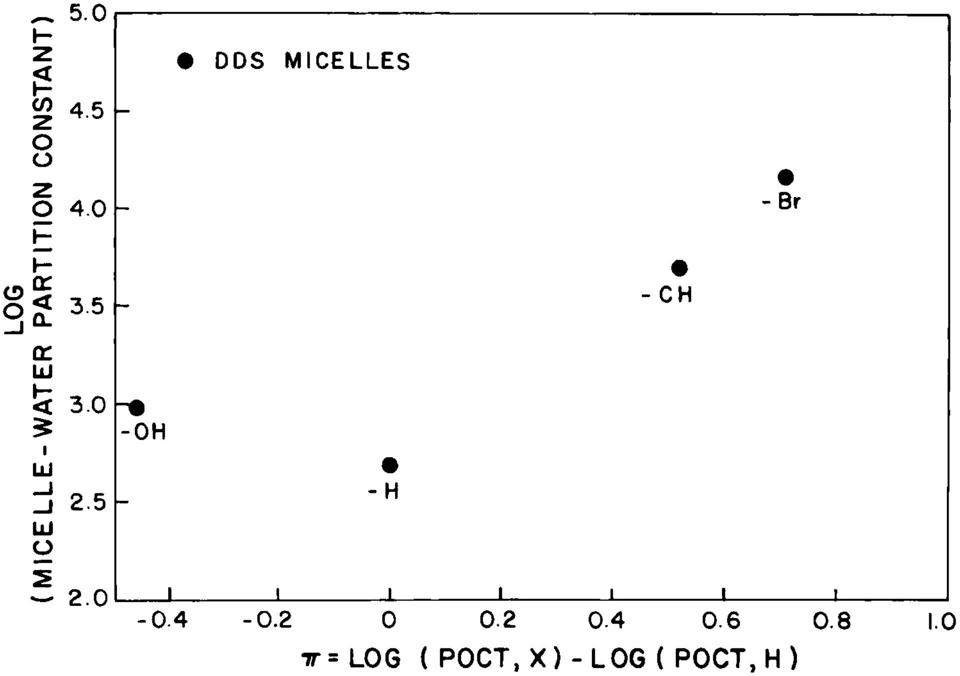

FIG. 7. Substituent effects on log P_m for naphthalene.

pect similar behavior for log P_m versus log S for aliphatic hydrocarbons. From what is observed in Figs. 8 and 9, it seems clear that molar solubility in the aqueous phase is a reasonable predictor of log P_m only for specific groups of compounds and that their slopes and intercepts will vary considerably. In using the molar solubilities in these correlations, we were careful to use the supercooled liquid solubilities for those compounds that are solids at room temperature.

It was suggested by Almgren et al. (*25*) that a good correlation between log P_m and the normal boiling points (T_b) of 11 aromatic hydrocarbons was possible for both anionic and cationic micelles. They also observed that a plot of log P_m versus T_b for various solutes in HTAB micelles gave a larger slope than for DDS micelles. They attributed this to some special binding characteristic of aromatic hydrocarbons to cationic micelles such as HTAB. A similar approach was therefore attempted for the various groups of compounds in Table 1. Figure 10 is such a plot, and the values of

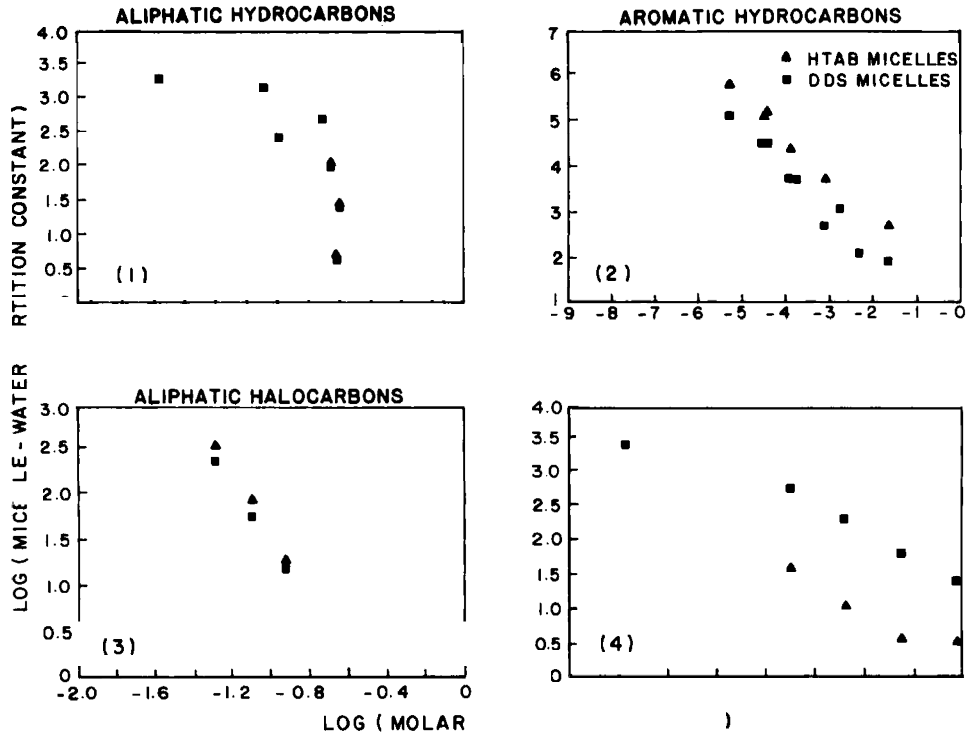

FIG. 8. Plot of log P_m versus log S for (1) aliphatic hydrocarbons, (2) aromatic hydrocarbons, (3) aliphatic halocarbons, and (4) aliphatic alcohols.

intercepts and slopes are given in Table 3. It is clear that each correlation is unique to a particular class of compounds. The slopes vary between 0.006 for aromatic phenols to 0.031 for aliphatic halocarbons. The degree of fit is, however, weak for aromtic phenols. Nevertheless, these relationships do show that T_b may be a good predictor of P_m values provided a larger data base is established for the various groups of compounds.

Two other methods of estimating P_m for a particular surfactant molecule are 1) a bond contribution scheme and 2) a group contribution scheme. Both of these methods are used by chemical engineers to estimate solubilities of solutes in solvents, liquid–liquid partition constants, and even solid–liquid partition constants (*26*). They depend on assigning energy contributions to each bond or each group by utilizing regressions upon a large set of experimental data. Such an approach was adopted for

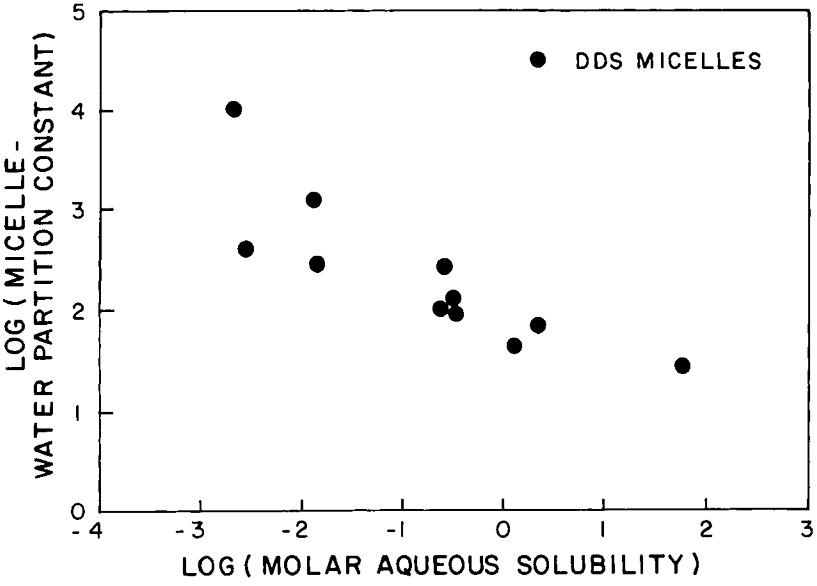

FIG. 9. Plot of log P_m versus log S for aromatic phenols and halophenols.

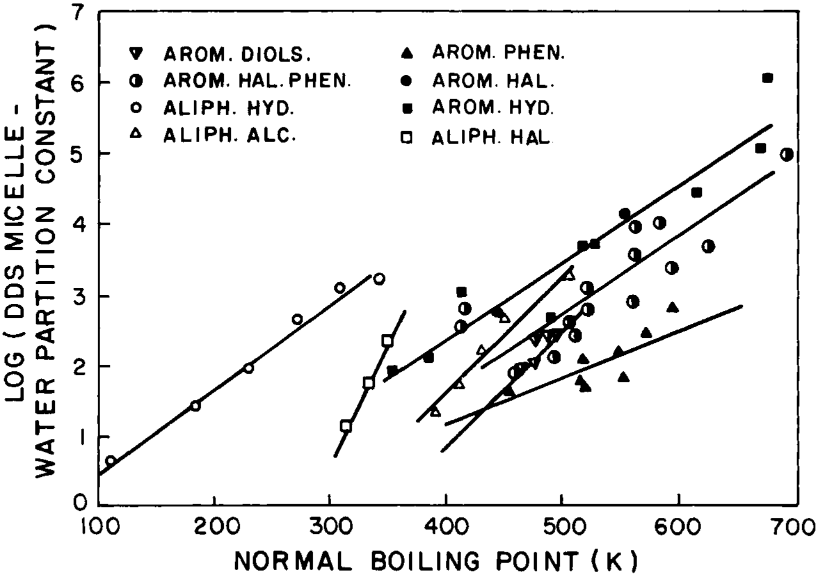

FIG. 10. Relationship between log P_m and T_b.

TABLE 3
Log P_m-T_b Relationship:
Log $P_m = a + bT_b$; DDS micelles

Compound type	a	b	N	r
Aliphatic halocarbons	−8.7	0.031	3	0.9936
Aromatic hydrocarbons	−2.0	0.011	10	0.9525
Aliphatic hydrocarbons	−0.7	0.012	6	0.9944
Aromatic halophenols	−1.7	0.009	16	0.8219
Aromatic phenols	−1.2	0.006	11	0.6053
Aliphatic alcohols	−5.2	0.017	5	0.9808
Aromatic diols	−6.8	0.019	8	0.8169

the 57 compounds for which micelle (DDS)-water partition constants were available, as in Table 1. The resulting bond contributions to the transfer free energy are given in Table 4 along with the results for the HTAB micelles obtained by regression on the 26 compounds for which data were reported in Table 1. By using the bond contribution scheme, the log P_m values for all 72 solutes in DDS micelles were recomputed and plotted in Fig. 11 as a parity plot. Except for the three highly substituted aromatic phenols (2,4,5-trimethylphenol, 2,3,5,6-tetramethylphenol, and 2,3,5-trimethylbenzene-1,4-diol), agreement between computed and experimental values is quite good. The bond contribution scheme we used was similar to the one reported by Hine and Mukerjee (*27*) for the estimation of air-water Henry's law constants for organic compounds. Certain groups such as cyano, nitro, and carbonyl were treated as atoms. Thus a C−CN bond implies the contribution of the C≡N triple bond, while H−CO includes half the contributions of C=O. Aromatic carbon is denoted by C_{ar}. A C_{ar}−H contribution does not include a C_{ar}=C_{ar} contribution; the latter was kept separate. As an example, the calculation of log P_m for naphthalene would proceed as follow:

Find the total free energy contribution to the transfer of a naphthalene molecule from water to a DDS micelle. From Table 4:

$$\Delta\mu^{\circ}_{tr} = 11[C_{ar}{=}C_{ar}] + 8[C_{ar}{-}H] = 11(0.11) + 8(-07.9) = -5.4\ \text{kcal/mol}$$

TABLE 4
Bond Contributions to $\Delta\mu^\circ_{tr}$ ($w \rightarrow m$), kcal/mol[a]

Bond	For DDS micelles	For HTAB micelles
C−H	−0.59	−0.65
C−C(chain)	0.65	0.89
C−C(ring)	0.39	
C−O	0.03	
C−F	−0.80	
C−Cl	−1.15	−1.29
C−N	−0.26	
O−H	0.00	
N−H	−0.13	
C−CO	−0.19	
$C_{ar}{\equiv}C_{ar}$	0.11	0.15
C_{ar}−H	−0.79	−1.04
C_{ar}−C	−0.19	
C_{ar}−O	−0.29	
C_{ar}−F	−1.24	−1.12
C_{ar}−Cl	−1.58	−2.07
C_{ar}−Br	−1.99	−2.23
C_{ar}−I	−2.49	−2.43
C_{ar}−CN	−2.03	
C_{ar}−CO	−0.86	
$C_{ar}-NO_2$	−1.20	

[a] CO group is considered a divalent atom, NH_2 and NO_2 groups are considered monovalent atoms.

$$\Delta\mu^\circ_{tr} = -RT \ln [55.5 P_m \bar{v}_s]$$

$$-5.14 = -1.98 \times 10^3 \times 298 \ln [55.5 P_m 0.227]$$

$$\therefore P_m = 481.8$$

$$\log P_m(\text{computed}) = 2.68 \text{ vs } \log P_m(\text{exptl}) = 2.69$$

As another example, the calculation of log P_m for phenol would be as follows:

$$\Delta\mu^\circ_{tr} = 6[C_{ar}{=}C_{ar}] + 5[C_{ar}{-}H] + 1(C_{ar}{-}OH)$$

$$= -3.58 \text{ kcal/mol}$$

$$P_m = 34.2$$

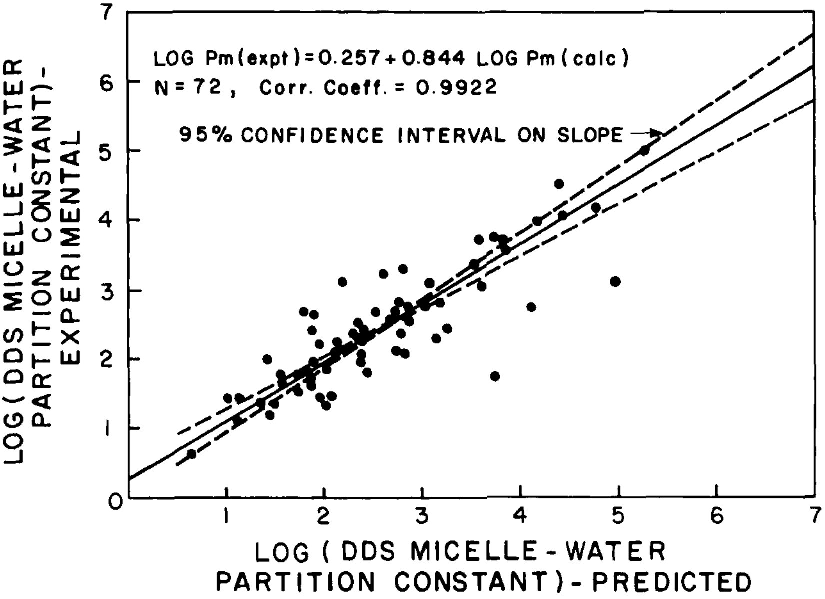

FIG. 11. Comparison of experimental and predicted log P_m values for DDS micelles using bond contribution scheme.

$$\log P_m(\text{computed}) = 1.54 \text{ vs } \log P_m(\text{exptl}) = 1.64$$

The correlation coefficient for Fig. 11 is 0.9922 with a slope of 0.844. The linear regression gives

$$\log P_m(\text{exptl}) = 0.257 + 0.844 \log P_m(\text{calcd})$$

$$N = 72, \qquad r = 0.9922$$

which should be considered good. One major inadequacy of a bond contribution scheme is that it does not take into consideration interactions between polar bonds. We also observed that the method underpredicted log P_m values for certain highly substituted compounds like 2,3,5,6-tetramethylphenol. The log P_m value for 2,3,5-trimethylbenzene-1,4-diol showed a maximum deviation of −2.02, which may be attributed to interaction between polar bonds.

As mentioned eariler, group contribution schemes enjoy a major advantage over bond contribution schemes because they take into account the interactions between different groups. Hine and Mukerjee (*27*) showed this to be especially true when using these schemes to estimate air-water partition constants. Smith et al. (*28*) recently reported a group contribution method to determine the micelle-water distribution constants. The method is based on the assumption that the free energy of transfer of a gaseous solute into the micellar interior [$\Delta G(g \rightarrow m)$] may be equated to the sum of the free energy of transfer of the solute from the ideal gas state into infinite dilution in water [$\Delta G(g \rightarrow w)$, obtained from the Henry's constant for the solute] and the free energy of transfer of solute from its solution at infinite dilution in water to the intramicellar solution, also at infinite dilution [$\Delta G(w \rightarrow m)$]. The authors suggested a group contribution scheme to calculate $\Delta G(g \rightarrow m)$ which, when combined with $\Delta G(g \rightarrow w)$, gives $\Delta G(w \rightarrow m)$ and hence the value of P_m. Thus only the solute structure and its Henry's constant are required to calculate P_m. *The scheme, though based on very limited data, seems useful in obtaining* P_m for those compounds for

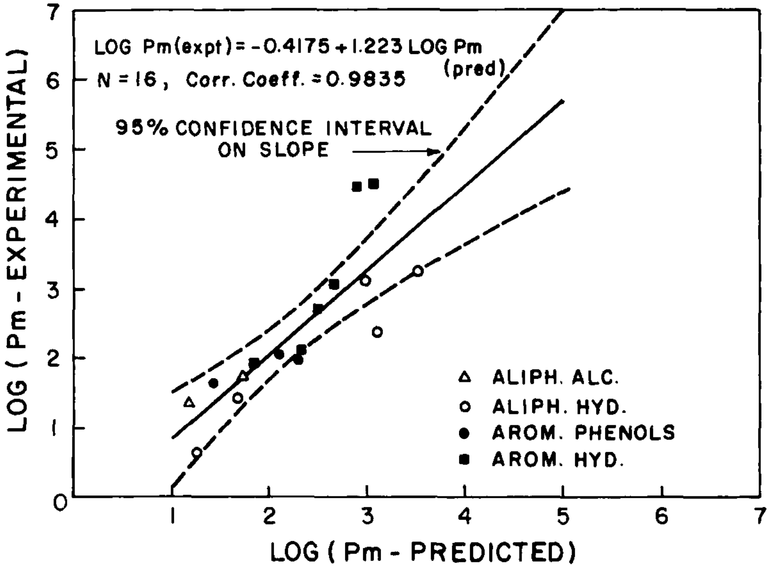

FIG. 12. Parity plot for log P_m (exptl) and log P_m (calcd) using a group contribution scheme.

which group contributions reported by the authors can be applied. We were able to apply this method to only 16 of the compounds in Table 1. The results are plotted in Fig. 12 as a parity plot and are tabulated in Table 5. A correlation coefficient of 0.9635 was obtained, and the slope was 1.223. Considering the fact that the method relies on limited data, the agreement is satisfactory. This method, however, suffers from one major drawback, and that is precise knowledge of Henry's constants, which for partly volatile compounds is difficult to obtain accurately.

In Table 6 we present the log P_m values for a typical compound, naphthalene, calculated by using the different estimation procedures narrated in this paper. One can observe that the percent deviations vary from −26.4 to +0.3. Considering the fact that experimental values show a considerable variation among different workers, as shown by several authors (*46, 47*), the observed deviations should be considered reasonable. Besides, when most authors report P_m values they fail to report the exact purity of the surfactants used; this can lead to considerable error in the

TABLE 5
Group Contribution Model of Smith et al. (*28*)

				Log P_m	
Compound	H_c	K' (from Smith et al., *28*)	$P_m = H_cK'$	calcd	exptl
Benzene	0.223	314	70.0	1.85	1.93
Naphthalene	0.017	18769	318.7	2.50	2.69
Toluene	0.275	765	210.4	2.32	2.11
1-Methylnaphthalene		44356			
Anthracene	7.24×10^{-4}	1.09×10^{6}	789.6	2.89	4.45
Phenanthrene	1.04×10^{-3}	1.09×10^{6}	1141.3	3.06	4.48
p-Xylene	0.257	1.81×10^{3}	465.2	2.67	3.05
Phenol	1.62×10^{-5}	1.70×10^{6}	27.65	1.44	1.64
2-Methylphenol	5.01×10^{-5}	4.03×10^{6}	202.05	2.30	1.96
4-Methylphenol	3.24×10^{-5}	4.03×10^{6}	130.57	2.11	2.02
Methane	28.18	0.657	18.52	1.27	0.64
Ethane	32.36	1.522	49.25	1.69	1.41
Pentane	51.28	19.69	1009.82	3.00	3.10
Hexane	74.13	46.06	3414.47	3.53	3.24
Cyclohexane	7.94	167.33	1329.15	3.12	2.37
1-Propanol	2.75×10^{-4}	1.89×10^{4}	5.20	0.71	
1-Butanol	3.47×10^{-4}	4.44×10^{4}	15.39	1.19	1.35
1-Pentanol	5.13×10^{-4}	1.04×10^{5}	53.13	1.73	1.74

TABLE 6
Comparison of the Various Estimation Procedures to Determine Log P_m for Naphthalene

Method of estimation	Equation used for Log P_m	Log P_m	% Deviation
Experimental	—	2.69	—
From log K_{ow}	$-0.66 + 1.11 \log K_{ow}$	3.06	−13.7
From S	—	3.00	−11.5
From T_b	$-2.0 + 0.011 \log T_b$	3.40	−26.4
From bond contribution	—	2.68	+0.3
From group contribution	—	2.50	+7.0

solubilities of solutes in micelles. Thus if one were to require the log P_m value for a particular compound of interest, ideally, one would prefer any one of the experimental techniques mentioned earlier. However, we do feel that any one of the estimation procedures, especially the one obtained using log K_{ow} (which, of course, is derived from the largest data base out of all the methods described here), would give a good estimate of log P_m.

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