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Water Solubility Enhancement of Phthalates by Cetyltrimethylammonium Bromide and β-Cyclodextrin

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Water solubility enhancements of six phthalates (five aliphatic phthalates and one phenyl phthalate) by cetyltrimethylammonium bromide (CTAB) and β-cyclodextrin (β-CD) were studied at 25 °C. The solubilities of these phthalates are remarkably enhanced by CTAB solutions above the critical micelle concentration (cmc). Only marginal enhancement of phthalate solubility was observed in solutions containing CTAB below its cmc and β-CD at low concentrations (less than 5 mM). The solubility enhancements of the phthalates are proportional to the added amount of CTAB and β-CD. Partition coefficients of the phthalates between monomeric CTAB surfactant and water (K_{MN}) and between CTAB micelle and water (K_{MC}) were estimated from the experimental data. The mechanisms of solubility enhancements by CTAB and β-CD were discussed. A log-linear equation was proposed and evaluated for the solubilization by CTAB below cmc, while the previously proposed linear partitioning model was questioned. The structures of the complexes formed between phthalates and β-CD were proposed, and the formation constants were estimated. The values of log K_{MC}, log K_{MN}, and log $K_{\beta\text{-CD}}$ of the phthalates were found to correlate linearly with the log K_{OW} of phthalates, with the exception of the solid phenyl phthalate.

Introduction

Phthalates are diesters of phthalic acid. Their physicochemical properties vary widely depending on the number of carbon atoms in the alkyl groups. As suitable plasticizers, phthalates exist in plastic materials of virtually every major product category, including construction, automobile, household products, apparel, toys, packaging, and medical products. Phthalates have been detected in soil, water, sediment, air, and animal and human tissues. Previous research has proved that phthalates can cause acute and chronic toxicity to many kinds of aquatic organisms.[1,2] They have also been suspected as an important type of endocrine-disrupting and potential genotoxic chemicals.[3−6]

Surfactants are also widespread in the environment. Their immense quantity of usage and special properties give rise to great concerns over their direct and indirect effects on the environment. Some surfactants are fungicidal and toxic to organisms.[7,8] On the other hand, they can affect the environmental behavior, such as aqueous solubility and speciation, of many pollutants of the highest concerns, such as polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), and many chlorinated pesticides, thus affecting their transport through groundwater and the efficiency of soil remediation.[9−11] In addition, because of the prohibition effect of some ionic surfactants on a microbe, the biodegradation of the pollutants could be greatly influenced.[12−14]

The ubiquity and immensity of phthalates and surfactants in the environment make it certain that they encounter each other in aquatic systems. The molecular interactions among surfactants, phthalates, and water are deemed to be highly complex and may alter the transport and fate of both pollutant classes as well as other coexisting pollutants in the environment. So far, however, little attention has been paid to such interactions, and we have found few data on the effect of surfactants on the environmental fate of phthalates.

The objective of this work was to investigate the effects of surfactants on the aqueous solubility of selected phthalates. Cetyltrimethylammonium bromide (CTAB), a widely used surfactant for industrial and research purposes, was chosen as a representative cationic surfactant. β-Cyclodextrin (β-CD), which has been used in the remediation of contaminated soil and groundwater because of its ability to form inclusion complexes with pollutants of low polarity,[15−17] was also chosen to compare with CTAB for the solubilization of phthalates.

Materials and Methods

Six phthalates were investigated. Their basic properties are summarized in Table 1, and their chemical structures are given in Figure 1. DMP, DEP, DIPP, and DBP are alkyl phthalates with ester groups at ortho positions of the benzyl ring, while the ester groups of *m*-DAP are at meta positions. DPhP is a phenyl phthalate with ester functional groups at ortho positions of the benzyl ring. DPhP is solid (powder) while the other five phthalates are liquid under normal conditions.

The purity of DIPP and DPhP used in this work were of analytical grade, and the other four phthalates had chromatographic purity (chromatographic fixation liquids). CTAB (analytical purity grade) and the phthalates were purchased from Shanghai Chemical Reagent Corp., Medicine Group of China. β-CD (>99% pure) was obtained from the Food Research Institute of Jiangsu Province, China. The structures of CTAB and β-CD are

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Table 1. Properties of Phthalates Used in This Study

							water solubility, mg L^{-1}	
phthalate	abbreviation	formula	MW	ML,[a] nm	mp, °C	log K_{OW}[17]	this study	ref 18
dimethyl *o*-phthalate	DMP	$C_{10}H_{10}O_4$	194.2	0.82	5.5	1.53	3500	2180−4320
diethyl *o*-phthalate	DEP	$C_{12}H_{14}O_4$	222.2	0.95	−40	2.35	804	680−1080
diisopropyl *o*-phthalate	DIPP	$C_{14}H_{18}O_4$	250.3	0.95		3.27[b]	167	108[b]
diallyl *m*-phthalate	*m*-DAP	$C_{14}H_{14}O_4$	246.2	1.38		4.15[c]	49	182
di-*n*-butyl *o*-phthalate	DBP	$C_{16}H_{22}O_4$	278.4	1.16	−35	4.57	10	11.2
diphenyl *o*-phthalate	DPhP	$C_{20}H_{14}O_4$	318.3	1.14	70−73	4.58[c]	3	3.04[d]

[a] Molecular length of the most stable molecular configuration calculated using Alchemy II.[19] [b] The data are for di-*n*-propyl *o*-phthalate. [c] Calculated by the Hansch and Leo fragment constant method using ClogP Internet computer program.[20] [d] Calculated by EPI Suite of EPA.[21]

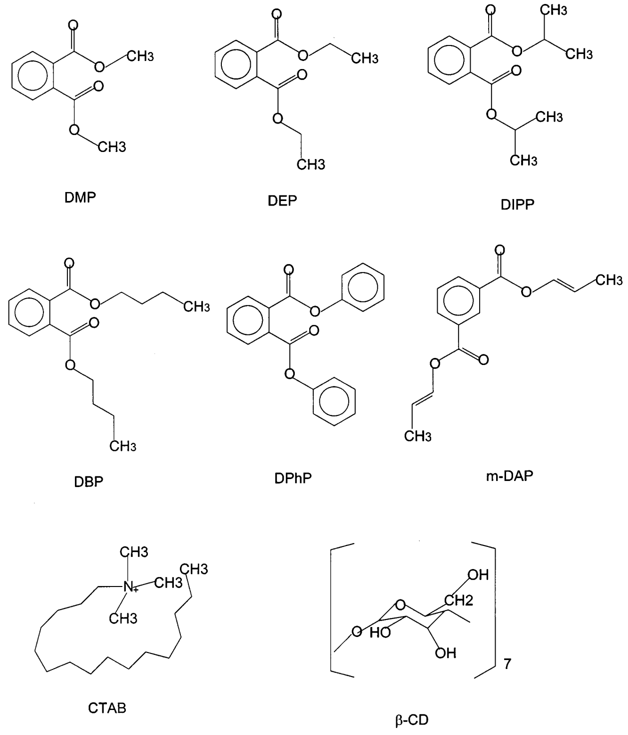


Figure 1. Structures of the chemicals used in this study.

also illustrated in Figure 1. Methanol used in this work was of analytical purity. Deionized water from a Millipore Reagent Water System was used in the preparation of all solutions.

Standard solutions of phthalates were prepared in a mixed solvent of methanol and water (50:50 in volume). Absorbance of the solutions was measured at 254 nm, using a UV−vis photospectrometer (model TU-1800PC, Beijing General Analytical Instrument Corp., China). CTAB and *β*-CD have zero absorbance at 254 nm and, therefore, did not interfere with the measurement of phthalates. All calibration curves had linear regression coefficients higher than 0.998.

Aqueous solutions of CTAB were prepared at concentrations below and above 361 mg L^{-1} (0.99 mM), its critical micelle concentration (cmc) reported previously.[10] The concentration ranged from 0.12 to 14.1 mM. A series of *β*-CD solutions, with concentrations ranging from 0.45 to 4.5 mM, were also prepared. Individual phthalate was added in slight surplus to 50 mL aqueous solutions with known concentrations of either CTAB or *β*-CD. The solutions were shaken for no less than 48 h in a swinging bed at 25 °C, followed by centrifugation at 3000 rpm for 30 min. The solubility of phthalate was determined by measuring the solution absorbance at 254 nm after being diluted with 50:50 methanol−water. Solubility of phthalates in pure water was measured in a similar procedure without CTAB or *β*-CD. All experiments were conducted in duplicate.

Results and Discussion

Solubilities of individual phthalates in pure water are given in Table 1. The experimental results of this work agree well with those reported in the literature. In the discussion below, the solubility enhancements are expressed by the ratio of the apparent solubility of phthalates in the aqueous solutions of CTAB or *β*-CD (S^*) to that in pure water (S_W). Table 2 summarizes the linear regression equations of observed solubility enhancement versus the amount of CTAB or *β*-CD added. Figures 2−4 illustrate the solubilization of phthalates by CTAB below cmc, CTAB above cmc, and *β*-CD, respectively.

Solubilization by CTAB below cmc. Most studies on solubilization use surfactant concentrations above the cmc. For surfactant solutions below cmc, the solubility of a solute is often considered equal to its solubility in pure water.[22] However, this may not be true for solutes that are sparsely soluble in water and highly sensitive to the change in solution composition. Chiou and Kile have reported the solubility enhancement of DDT, PCB, TCB, etc., by surfactants below cmc.[10,23,24] Ganeshalingham and co-workers have reported the PAH solubility enhancement by surfactants below cmc.[25] Solubility enhancement for phthalates was observed in this study. Figure 2 shows that the aqueous solubilities of all phthalates were enhanced by the presence of CTAB below its cmc.

A linear partition model was proposed for the solubilization by surfactants below cmc:[10]

$$S^*/S_W = 1 + K_{MN}C_S \tag{1}$$

where C_S is the added surfactant concentration and K_{MN} is the "monomer−water partition coefficient". This model has been used in environmental studies on hydrophobic organic compound (HOC) solubilization and sorption.[11,26] Values of K_{MN} determined from the slope of the linear regression of the experimental data are given in Table 3. The intercepts of the regression range from 0.96 to 1.02, very close to the theoretical value of unity as given in eq 1.

However, a close examination of the available experimental data on the solubilization of HOCs by surfactants below cmc seems to suggest a nonlinear pattern, as observed for DDT[10] and phthalates (see Figure 2). To explain the observed nonlinearity, Kile and Chiou proposed the idea of continuous aggregate formation, i.e., the existence of dimers, trimers, etc., in the aqueous phase.[10] Sun et al. proposed a "transitional zone"

Table 2. Linear Regression of Solubility Enhancements of Phthalates versus the Concentration of the Solubilizing Agents[a]

		phthalate					
		DMP	DEP	DIPP	*m*-DAP	DBP	DPhP
CTAB < cmc ($S^*/S_W = a + bC_S$)	a	0.999	1.018	1.007	0.972	0.965	0.96
	b	21.80	73.00	247.0	737.2	1028	300.5
	R^2	0.976	0.831	0.979	0.863	0.942	0.812
	F	162.7	19.67	186.5	25.20	64.97	17.28
CTAB < cmc [$\ln(S^*/S_W) = a + bC_S$]	a	−0.0006	0.017	0.0092	0.0009	0.0077	−0.033
	b	21.50	70.00	222.2	548.9	715.2	266.1
	R^2	0.977	0.823	0.976	0.904	0.973	0.838
	F	169.9	18.60	162.7	37.67	144.1	20.69
CTAB > cmc [$S^*/S_W = a + b(C_S - \text{cmc})$]	a	1.19	1.41	1.57	4.24	1.96	3.15
	b	86.06	189.8	767.1	1713	10943	5159
	R^2	0.991	0.996	0.999	0.996	0.999	0.999
β-CD ($S^*/S_W = a + bC_{\beta\text{-CD}}$)	a	1.08	0.96	0.99	1.02	1.06	1.50
	b	34.6	79.7	138.0	591.1	737.9	133.3
	R^2	0.972	0.947	0.997	0.998	0.997	0.911

[a] The unit of b is M^{-1}. F is the value of the F test, which is the ratio of regression mean square to error mean square, F = MSR/MSE.

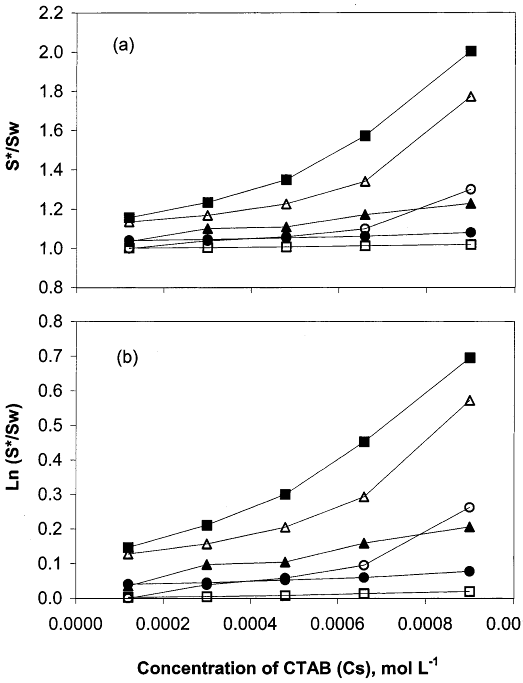


Figure 2. Solubility enhancement of phthalates by CTAB below cmc. Legend: □, DMP; ●, DEP; ▲, DIPP; △, *m*-DAP; ■, DBP; ○, DPhP.

Table 3. K_{MN}, K_{MC}, and $K_{\beta\text{-CD}}$ of Phthalates

phthalate	K_{MN}	K_{cmc}	K_{MC}	$K_{\beta\text{-CD}}$
DMP	21.8	1.02	86.1	91.8
DEP	73.0	1.10	189.8	102.5
DIPP	247.0	1.26	767.1	152.0
m-DAP	737.2	1.72	1,713	669.9
DBP	1028.0	2.05	10,943	757.9
DPhP	300.5	1.24	5,159	133.4

between monomers and micelles.[27] Conceptually, however, because monomers (and dimers, etc., if any) do not form phases which solute molecules could partition into, a partitioning mechanism may be fundamentally flawed.

Below cmc, surfactants exist as individual molecules, which possess both polar and nonpolar moieties. Such a structure is similar to those of a number of water-miscible cosolvents, such as low molecular mass alcohols and ketones which are known to promote the aqueous solubility of hydrophobic organic compounds. The major mechanism by which cosolvents work is the reduction in the hydrogen bond density of aqueous solutions.[22] Another mechanism, which may act to a lesser extent in dilute solutions, is the hydrophobic interaction between the nonpolar moiety of a cosolvent molecule and the solute. The effect of a disrupting hydrogen bond network of water on the solubility of HOCs appears to be a nonlinear function of cosolvent concentration. Rather, numerous experimental results indicated a roughly log-linear pattern of solubility enhancement; this forms the basis for the well-known log-linear model of Yalkowsky.[22]

To test the hypothesis that solubilization by surfactants below cmc increases in a log-linear manner with the amount of surfactant added, eq 2 is applied to our data:

$$\ln(S^*/S_W) = a + bC_S \tag{2}$$

In eq 2, a and b are regression constants. Ideally, $a = 0$ and b is the logarithm solubility enhancement, $\ln(S^*/S_W)$, by adding 1 M surfactant. It is important to note the fundamental differences between the widely used log-linear cosolvent model[22] and the empirical equation (2). The log-linear cosolvent model assumes an ideal solvent mixture; thus, the free energy of solute dissolution into the mixture is a linear combination of those into individual solvent components weighted by the volume fractions of the components in the mixed solvent. Such an assumption is not applicable to aqueous surfactant solutions.

As expected, the intercepts of eq 2 for phthalates are very close to zero, ranging from −0.03 (DPhP) to 0.017 (DEP) (see Table 2). In fact, the curves of DDT solubilization by a few Triton and Brij surfactants observed by Kile and Chiou[10] are also better represented by a log-linear equation than by a linear one, with the improvements being much more significant than those for the phthalates in CTAB systems. In water, Triton and Brij surfactants may be more molecularly heterogeneous than CTAB, as discussed by Kile and Chiou.[10] However, even for CTAB, which exists only as monomers,[10] a log-linear rather than a linear regression may be more explanatory on the nature of interactions between the surfactant monomers and the hydrophobic solute molecules.

More experimental data are needed to enable a rigorous investigation on the fundamental mechanisms of solubilization by surfactants below their cmc's. Apparent curvature still exists on most log-linear plots as

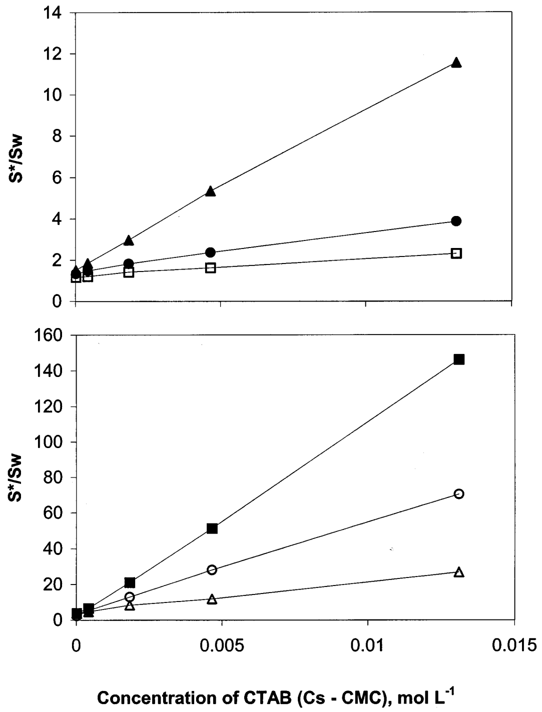


Figure 3. Solubility enhancement of phthalates by CTAB above cmc. Legend: □, DMP; ●, DEP; ▲, DIPP; △, *m*-DAP; ■, DBP; ○, DPhP.

shown in Figure 2b. In addition, the slopes of eqs 1 and 2 are close (see Table 2), and the statistics (*F* values, R^2) are similar. Indeed, the difference between mathematic functions $y = 1 + x$ and $y = e^x$ is small when x is small, making it difficult to compare the performance of eqs 1 and 2. In systems with low concentrations of either surfactant or cosolvent, it is highly possible that multiple mechanisms are operating, and the shift of their predominance depends on multiple variables such as the structures and properties of the solute and solubilizing agent(s), as well as the solution temperature. Banerjee and Yalkowsky presented a mechanistic interpretation for possibly linear solubilization in cosolvent–water systems for dilute cosolvent systems.[28] They propose that, in aqueous solutions which are in infinite dilution with respect to the cosolvent concentration, the solubilization of hydrophobic solutes is linearly proportional to the cosolvent fraction until this fraction is increased to a level high enough to initiate the overlap of the hydration shells of cosolvent molecules; after this point, the log-linear pattern appears. Compared with cosolvents on a molar basis, surfactants may have a higher capability of disrupting the hydrogen bond structure of water and stronger hydrophobic interactions with HOC solutesbecause of the larger size of their nonpolar moiety, or the "tail".[22] For extremely large molecules such as humic and fulvic acids which have molecular mass higher than the solute by orders of magnitude, partitioning is a logical mechanism of solubilization.[29] Whether the size of surfactant monomers or "multimers" is large enough to form phases as humic and fulvic acids do, thus make a partitioning theory authentic, is questionable.

Solubilization by CTAB above cmc. The solubility of all phthalates was dramatically enhanced when the CTAB concentration was increased above its cmc. The solubility enhancement is a linear function of the amount of CTAB in the micelles, as shown in Figure 3.

Above its cmc, CTAB congregates into micelles, which has a hydrophobic core and a hydrophilic mantle. Surfactant molecules in an amount equal to cmc are generally assumed as monomers in the aqueous solution.[10] This amount, however, is small compared with those in the pseudophase of micelles. Therefore, solubilization of phthalates is dominated by their partitioning into the core of the micelles. The solubility of a phthalate solute is the sum of those within and outside the micelles, with both portions reaching their respective concentration limits.

The partitioning of solute molecules in a micelle–water system can be approximated by the micelle–water partition coefficient K_{MC}, which is the ratio of concentrations or solubilities of the solute inside the micelles to that in water. Values of K_{MC} for individual phthalates in CTAB systems were estimated from the slope of linear regression of the experimental data. The independent variable of the regression is the concentration of micellar CTAB, i.e., the difference between C_S and cmc. Values of K_{MC} are summarized in Table 3.

$$\begin{aligned} S^*/S_W &= 1 + K_{MN}\text{cmc} + K_{MC}(C_S - \text{cmc}) \\ &= 1 + (K_{MN} - K_{MC})\text{cmc} + K_{MC}C_S \qquad (3) \end{aligned}$$

If this model works well, the intercept of the linear regression should be close to $1 + K_{MN}$cmc for each phthalate. This was found to be true with a relative error ranging from −3% to +32% for all of the phthalate solutes except *m*-DAP and DPhP. For these two solutes, the difference between the intercept of the empirical regression equation and $1 + K_{MN}$cmc is around 2, or a factor of 1.4.

Alternatively, if eq 2 is used for solubilization of CTAB in the amount equal to cmc, the overall solubilization of a solute by a surfactant above cmc may be estimated by eq 4,

$$\begin{aligned} S^*/S_W &= K_{cmc} + K_{MC}(C_S - \text{cmc}) \\ &= K_{cmc} - K_{MC}\text{cmc} + K_{MC}C_S \qquad (4) \end{aligned}$$

where K_{cmc} is defined for the purpose of this work as the ratio of the solute solubility in solutions with surfactant concentration equal to cmc (S^*_{cmc}) to that in pure water (S_W). Its value can be estimated with regression constants *a* and *b* determined by eq 2:

$$K_{cmc} = S^*_{cmc}/S_W = \exp[a + b(\text{cmc})] \qquad (5)$$

Values of K_{cmc} obtained using eq 5 are presented in Table 3. The values of K_{cmc} are very similar to those of $1 + K_{MN}$cmc, because both are derived from the same set of experimental data obtained below cmc.

Linear regressions between S^*/S_W and C_S − cmc generated regression coefficients R^2 greater than 0.99. These show the validity of the partitioning mechanism for the solubilization of CTAB above cmc. As mentioned above, however, the "experimental" intercept values obtained from fitting the data are generally higher than both "theoretical" intercepts $1 + K_{MN}$cmc of eq 3 and K_{cmc} of eq 4. Note that the values of both "theoretical" intercepts are, in fact, obtained empirically from the experimental data obtained from systems below cmc. Any errors in those systems may be transferred in the regressions for the cases above cmc. It is also possible that, in the micelle–monomer–water system above cmc, the contribution to solubilization by monomers (at cmc) may be different from that when they exist alone below cmc. That is, the presence of micelles may affect the state and behavior of the monomers, thus increasing the solubilizing capacity of the monomers. It is speculated that the degree of hydration of the monomers is decreased by the existence of micelles. As a result, the molecular interactions between monomer CTAB and solutes increase. *m*-DAP and DPhP, which are much different in molecular structure from the other four phthalates and are more hydrophobic, may benefit more by their solubilization in the micelle–monomer–water system. Further study is needed to confirm the phenomena and understand the mechanisms.

Solubilization by *β*-CD. *β*-CD is a cyclic oligosaccharide (seven glucose units) with a hydrophilic shell and a relatively nonpolar cavity. It has a shape of a truncated cone with a depth of 0.8 nm, with the diameters being 0.7 and 0.8 nm, respectively, at the two ends of the cone.[22] Organic solute molecules or its moiety with diameters less than that of the *β*-CD cavity can be encompassed in the cone, leading to inclusion complexation and the enhanced apparent aqueous solubility of the solute.

If a 1:1 inclusion complex is formed between solute S and *β*-CD, the reaction can be depicted as

$$\mathrm{S} + \beta\text{-CD} \leftrightarrow \beta\text{-CD}{-}\mathrm{S}$$

The equilibrium constant for this reaction is

$$\begin{aligned} K_{\beta\text{-CD}} &= [\beta\text{-CD}{-}\mathrm{S}]/[\mathrm{S}][\beta\text{-CD}] \\ &= [\beta\text{-CD}{-}\mathrm{S}]/[\mathrm{S}](C_{\beta\text{-CD}} - [\beta\text{-CD}{-}\mathrm{S}]) \end{aligned} \tag{6}$$

where [S], [*β*-CD], and [*β*-CD–S] are the equilibrium concentrations of the free solute, free *β*-CD, and the complex. $K_{\beta\text{-CD}}$ is the formation constant or stability constant of the *β*-CD–S complex, and $C_{\beta\text{-CD}}$ is the total concentration of *β*-CD added. For a solution in contact with a separate phase of solute, the concentration of the free solute molecules at equilibrium can be regarded as the aqueous solubility of the compounds, i.e., $[\mathrm{S}] = S_\mathrm{W}$.

The total aqueous concentration of the solute, S^*, includes both free and complexed species.

$$S^* = S_\mathrm{W} + [\beta\text{-CD}{-}\mathrm{S}] \tag{7}$$

Combining eqs 6 and 7 results in eq 8, which indicates a linear dependence of the apparent solute solubility on the added amount of *β*-CD:

$$S^* = S_\mathrm{W} + K_{\beta\text{-CD}} S_\mathrm{W} C_{\beta-\mathrm{CD}}/(1 + K_{\beta\text{-CD}} S_\mathrm{W}) \tag{8}$$

or

$$S^*/S_\mathrm{W} = 1 + K_{\beta\text{-CD}}/(1 + K_{\beta\text{-CD}} S_\mathrm{W}) C_{\beta\text{-CD}} \tag{9}$$

The experimental data are represented well by eq 9, with the intercept ranging between 0.9 and 1.5 and regression coefficient R^2 being above 0.9 for all six phthalates (see Table 2). Values of the complex formation constant, $K_{\beta\text{-CD}}$, can be deduced from the slope *b* of the regression equations:

$$K_{\beta\text{-CD}} = b/(1 - bS_\mathrm{W}) \tag{10}$$

The calculated $K_{\beta\text{-CD}}$ values are listed in Table 3. They are comparable to those reported by Murai et al.[16]

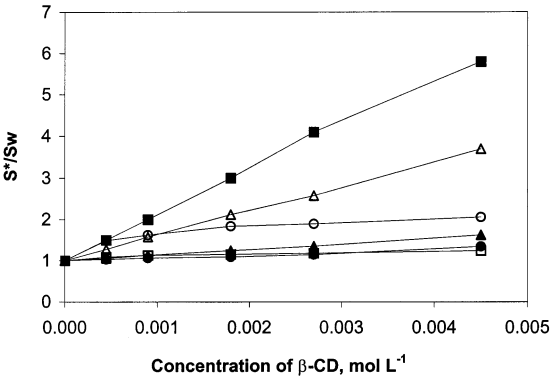
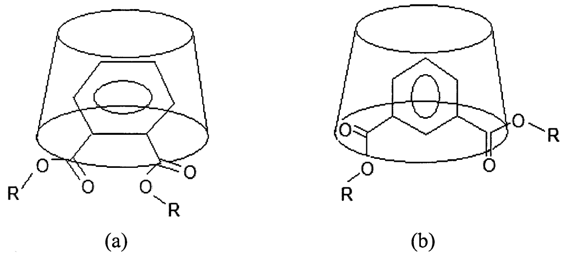


Figure 4. Solubility enhancement of phthalates by *β*-CD. Legend: □, DMP; ●, DEP; ▲, DIPP; △, *m*-DAP; ■, DBP; ○, DPhP.



(a) (b)

Figure 5. Most probable configurations of *β*-CD inclusion complexes with phthalates: (a) *o*-phthalates; (b) *m*-phthalates.

To understand the mechanism of solubilization by *β*-CD at the molecular level, computer program Alchemy[19] was used to obtain stable molecular configurations and measurements of these phthalates (see Figure 1 and Table 1). The lengths of the phthalates are larger than that of the *β*-CD cavity; thus, they can only achieve a partial entry into the cavity, leaving parts of molecules in water. In light of this picture, the interaction between the nonpolar cavity of *β*-CD and the solute is restricted to some extent depending on the molecular sizes of the solutes. Structures of phthalates by *β*-CD complexes are proposed in Figure 5. The aromatic rings of the phthalate molecules with a diameter of 0.54 nm are the moieties mostly likely to be enclosed in the *β*-CD cone, producing maximal contact with the hydrophobic cavity. The ester groups, on the other hand, extend into water because of their size and hydrophilic nature. The four oxygen atoms of the ester groups of the phthalates may also interact with the outer hydroxyl groups of *β*-CD to form hydrogen bonds.

Values of $K_{\beta\text{-CD}}$ are generally comparable with K_MN but significantly smaller than K_MC for the solutes used in this study with the exception of DMP (see Table 3). This means that, on a molar basis, *β*-CD is only about as efficient as CTAB monomers in enhancing the solubility of the phthalates. However, because *β*-CD, and especially some modified CD, can dissolve in water in much higher concentrations than CTAB monomers,[17] they are more practically useful in solubilizing sparsely soluble organic solutes. On the other hand, CTAB micelles are more powerful than *β*-CD. The difference lies in the different mechanisms involved: micelles form a separate phase which allows the solutes to partition, while the interactions between phthalate solutes and *β*-CD are bimolecular with the formation of a 1:1 complex. The relative solubilizing potential of CTAB and *β*-CD depends to some extent on the nature of the solutes, as will be discussed below.

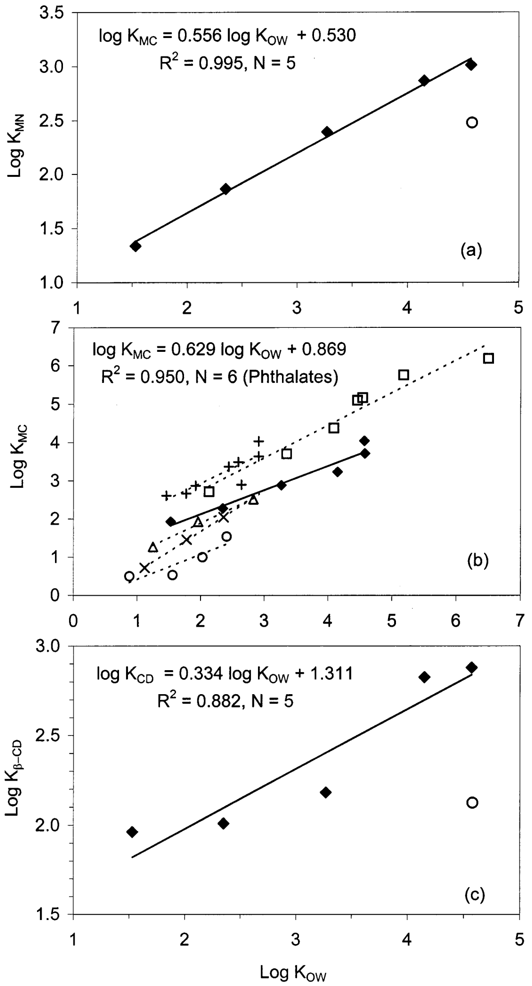


Figure 6. Correlation between K's and K_{OW}. The open circles in parts a and c are the outliers (DPhP) not included in the regressions. Legend for part b: ◆, phthalates (this study); ○, alcohols; +, halo- and methylphenols; ×, aliphatic hydrocarbons; □, aromatic hydrocarbons; △, aliphatic halocarbons. Data for all compounds other than phthalates are from ref 30.

Effect of the Solute Structure and Hydrophobicity. The extent of solubility enhancement by either CTAB or β-CD depends strongly on the properties of the solutes. Figure 6 illustrates the dependence of K_{MN}, K_{MC}, and $K_{\beta\text{-CD}}$ of the phthalates on the octanol−water partition coefficient K_{OW}. For alkyl phthalates, all K_{MN}, K_{MC}, and $K_{\beta\text{-CD}}$ increase linearly with increasing log K_{OW}. This suggests that, regardless of differences in mechanisms, the degree of solubilization increases as the solute hydrophobicity increases.

No previously published studies were found reporting the dependence of solubilization by surfactants below cmc on solute properties, probably because of the limited number of available data for such systems. For surfactant solutions above cmc, where the partition mechanism applies, the dependence of solubilization on the hydrophobicity of the solutes has been reported for various chemical groups of solutes. For CTAB, Valsaraj and Thibodeaux[30] reported correlations between log K_{MC} and log K_{OW} for various solutes, as illustrated by dashed lines in Figure 6b. The slope of a log K_{MC} vs log K_{OW} plot for phthalates is close to the one for aliphatic alcohols but lower than those for other classes of chemicals. It is possible that the slope is related to the polarity of the solutes, as demonstrated for a number of cosolvent systems with various solute groups.[31,32]

Similar to K_{MN} (Figure 6a), log $K_{\beta\text{-CD}}$ linearly related to log K_{OW} with the exception of DPhP (Figure 6c). However, the correlation is apparently weaker than those shown in parts a and b of Figure 6, with an R^2 of only 0.88 even with the outlier excluded. More importantly, the slope of the regression is much lower than those in CTAB systems, indicating a weaker dependence of the solubilization on solute hydrophobicity. As mentioned previously, the molecular sizes of the solutes and their orientation in the β-CD cavity are important factors besides hydrophobicity in determining the extent of solubilization by inclusive complexation. Therefore, although K_{MN} and K_{MC} of DEP are more than double those of DMP in CTAB solutions, the values of $K_{\beta\text{-CD}}$ for DMP and DEP are similar (see Table 3).

An obvious outlier in parts a and c of Figure 6 is DPhP. In both CTAB below cmc or β-CD systems used in this study, solubilization of DPhP is much lower than that for DBP, which has a similar K_{OW} value. DPhP is the most hydrophobic and the only solid phthalate used in this study. For solids, solubilization is a two-step process including melting and dissolution. The energy spent on melting often outweighs that for dissolution if the melting point temperature is high. Because the enthalpy of melting is an intrinsic property of the crystalline compound, a change in the solvent composition may affect only the enthalpy of dissolution. The limited solubility enhancements observed for DPhP seem to indicate the dominance of the melting process on the magnitude of its solubility. The melting process has no effect on the distribution of organic compounds between separate phases.[33] In solutions with CTAB above its cmc, the mechanism of solubilization is phase partitioning. This is the same for all organic solutes whether they are liquid or solid. Therefore, DPhP behaves “normally” according to its K_{OW}, as shown in Figure 6b.

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