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# The Solubility Behavior of Bisphenol A in the Presence of Surfactants

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The aqueous solubilities of bisphenol A (BPA) in water and water + surfactants have been determined at four different temperatures, 298.15 K, 303.15 K, 308.15 K, and 313.15 K. Results showed that the presence of a cationic surfactant cetyltrimethylammonium bromide (CTAB) caused a significant increase in the solubility of BPA, which increased linearly with the concentration of CTAB. When the anionic surfactants sodium dodecylbenzenesulfonate (SDBS) and dodecyl sodium sulfate (SDS) were added to the solutions, the minimum in the solubility of BPA was found at a lower concentration. However, when a certain concentration was exceeded, a most striking increase in solubility was observed. The sequence of solubility enhancement as a function of the critical micelle concentration is SDS > CTAB > SDBS at 298.15 K and negatively correlates to the hydrophilic lipophilic balance of the surfactants.

## Introduction

Bisphenol A (BPA), an alkylphenolic compound, is a principle monomer in the production of polycarbonates, epoxy resins, and other plastics. BPAs are suspected to enter rivers, streams, and surface waters in effluents from facilities that manufacture epoxy and polycarbonate plastics and elution from products containing BPA.[1,2] Exposure to BPA can affect the reproductive behavior, induce the vitellogenin yolk precursor, and even endanger the balance of ecosystems.[3] Therefore, BPA has been identified as an endocrine disrupting chemical by the U.S Environmental Protection Agency, and the World Wide Fund for Nature.[4,5]

Surfactants are also widely found in environment due to their applications in the fields of oil exploitation, synthetic detergents, printing, and dyeing and can coexist with BPA in contaminated surface water and groundwater systems. They have been found to affect the fate, transformation, and transportation of pollutants in the environment.[6] However, solubility data of BPA has only been reported in pure water, and there is no solubility data reported in surfactant solutions. Therefore, the aqueous solubility of BPA from water to surfactant + water systems is studied in this paper.

## Materials and Methods

***Materials.*** BPA, cetyltrimethylammonium bromide (CTAB), sodium dodecylbenzenesulfonate (SDBS), and dodecyl sodium sulfate (SDS) are all of analytical grade (Shanghai Chemical Reagent Co., China) with a purity of 99.9 %, 99.0 %, 99.5 %, and 99.5 %, respectively. The basic properties of the surfactants are shown in Table 1. Doubled distilled water, treated with ion-exchange resin before distillation, was used and its conductivity was $1.18 \cdot 10^{-4}$ $\mathrm{S \cdot m^{-1}}$.

***Solubility of BPA Measurement.*** Saturated solutions of BPA were obtained by the following procedures. A series of concentrations were prepared for each surfactant at levels above and below the critical micelle concentration (CMC). A slight excess amount of BPA was added to 15 mL of aqueous solution with a known concentration of surfactant. Then, the tubes were sealed with a tight-fitting ground stopper and Parafilm, followed by equilibration in a DZK-2 thermostated water bath (specially made by the Shanghai Jinghong Experimental Instrument Co. Ltd) at (298.15, 303.15, 308.15, and 313.15) K. The fluctuation in temperature was ± 0.05 K. The equilibrium time was selected on the basis of a condition test using the following procedure. The supernatant solution was analyzed by spectrophotometry after 3 to 4 days, and the operation was repeated at intervals of 3 to 4 days until there was no change of absorbance beyond the experimental error. After the condition test, the sealed glass tubes were not opened before determination of the solubility to avoid tiny effects of volume change of solution on the experimental results.

The maximum absorption peak of BPA had no shift when the surfactant concentration in solution was lower than 50 $\mathrm{mg \cdot L^{-1}}$. Therefore, an appropriate amount of supernatant was carefully withdrawn from each vessel and diluted with the appropriate ratio to maintain the surfactant concentration at 50 $\mathrm{mg \cdot L^{-1}}$ for the measurement of BPA at 276 nm using a PCS UV spectrophotometer (made by Shanghai Unico Co. Ltd). A BPA-free solution containing 50 $\mathrm{mg \cdot L^{-1}}$ of surfactant was used as the reference solution to correct the background UV absorption of each surfactant.[7,8]

Standard solutions of BPA for each surfactant were prepared, which contain the corresponding surfactant at 50 $\mathrm{mg \cdot L^{-1}}$. All calibration curves had linear regression coefficients higher than 0.995. The solubility measurements in all cases were independently repeated thrice for each surfactant composition, and the precision was within 0.3 %.

## Results and Discussions

The solubility of BPA with CTAB at concentrations extending from below CMC to far above CMC is represented in Table 2 As shown in Table 2, the solubility of BPA increased significantly over the whole range of CTAB concentrations. The solubility of BPA was increased from 381 $\mathrm{mg \cdot L^{-1}}$ in the absence of CTAB to 873 $\mathrm{mg \cdot L^{-1}}$ at a CTAB concentration of 800 $\mathrm{mg \cdot L^{-1}}$ at 298.15 K. The solubility ratio of BPA exhibited a linear relationship with the concentration of CTAB. A similar

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**Table 1. The Basic Properties of Surfactants**

| surfactant | abbreviation | chemical formula | MW | CMC[a] (mg·L$^{-1}$) | HLB[b] |
|---|---|---|---|---|---|
| cetyltrimethylammonium bromide | CTAB | $C_{16}H_{33}N(CH_3)_3{}^+Br^-$ | 364 | 361 | 13.1 |
| sodium dodecylbenzenesulfonate | SDBS | $C_{18}H_{29}NaO_3S$ | 348 | 500 | 10.6 |
| dodecyl sodium sulfate | SDS | $C_{12}H_{25}OSO_3{}^-Na^+$ | 288 | 2100 | 40 |

[a] CMC is the lowest concentration of surfactants when the surfactant solution begins to form the micelle. [b]HLB is an indicator of the relative affinity of a surfactant to partition between water and an oil phase.

**Table 2. The Solubility of BPA in Water and Water + CTAB**

| | *S* (mg·L$^{-1}$) | | | |
|---|---|---|---|---|
| CTAB (mg·L$^{-1}$) | 298.15 K | 303.15 K | 308.15 K | 313.15 K |
| 0 | 381 | 466 | 541 | 594 |
| 100 | 445 | 477 | 572 | 638 |
| 200 | 431 | 564 | 645 | 706 |
| 300 | 531 | 651 | 742 | 821 |
| 400 | 591 | 712 | 804 | 987 |
| 800 | 878 | 1058 | 1128 | 1295 |
| 1200 | 1182 | 1321 | 1425 | 1591 |
| 2000 | 1526 | 1818 | 1958 | 2261 |

**Table 3. The Solubility of BPA in Water and Water + SDBS**

| | *S* (mg·L$^{-1}$) | | | |
|---|---|---|---|---|
| SDBS (mg·L$^{-1}$) | 298.15 K | 303.15 K | 308.15 K | 313.15 K |
| 0 | 381 | 466 | 541 | 594 |
| 100 | 302 | 370 | 426 | 476 |
| 200 | 306 | 372 | 448 | 528 |
| 300 | 319 | 383 | 448 | 616 |
| 400 | 358 | 403 | 484 | 730 |
| 800 | 516 | 602 | 695 | 967 |
| 1200 | 640 | 738 | 830 | 1195 |
| 2000 | 882 | 998 | 1097 | 1681 |

**Table 4. The Solubility of BPA in Water and Water + SDS**

| | *S* (mg·L$^{-1}$) | | | |
|---|---|---|---|---|
| SDS (mg·L$^{-1}$) | 298.15 K | 303.15 K | 308.15 K | 313.15 K |
| 0 | 381 | 466 | 541 | 594 |
| 100 | 319 | 424 | 493 | 571 |
| 200 | 376 | 425 | 506 | 596 |
| 300 | 469 | 560 | 636 | 749 |
| 400 | 603 | 712 | 790 | 928 |
| 800 | 848 | 989 | 1105 | 1248 |
| 1200 | 1053 | 1303 | 1420 | 1548 |
| 2000 | 1511 | 1697 | 1814 | 1973 |

result has been observed for DDT in previous studies.[9] This is because the monomer below the CMC has polar and nonpolar components in its structure, and the micelle above the CMC of CTAB has a hydrophobic core and a hydrophilic mantle, both of which promote the aqueous solubility.[8,9]

Tables 3 and 4 show the solubility changes of BPA on addition of the surfactants SDBS and SDS, respectively. It can be seen from Tables 3 and 4 that the trend in solubility is not smooth and continuous in the presence of anionic surfactants. At lower concentration, the solubility decreases and the minimum solubility was found at around 100 mg·L$^{-1}$ for SDBS and SDS. However, when the concentration exceeds a certain value, the solubility increases and the increase in the solubility followed a log-linear behavior. There have been relatively few reports on the decrease in the solubility by the addition of surfactants. Although a clear explanation has never been made on this matter so far, the structure of the surfactants may need to be considered when their amount is not sufficient to provide homogeneous water−surfactant mixtures.[10,11,12]

Figure 1 illustrates the solubility enhancement of BPA as a function of the multiples of surfactant's CMC at 298.15 K. Above 0.2 CMC, the BPA solubility increased linearly with increasing surfactant concentration for all the surfactants used.

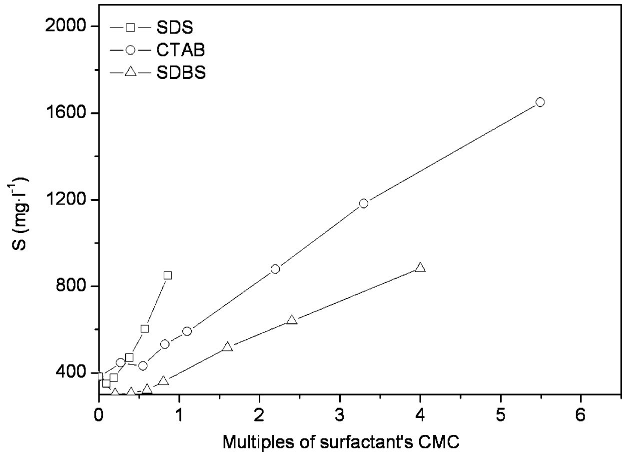

**Figure 1.** The solubility of BPA in different surfactant solutions at 298.15 K.

The order of increasing solubility enhancement of BPA is SDS > CTAB > SDBS. As shown in Table 1, SDS has higher hydrophilic lipophilic balance (HLB) values than SDS and CTAB. The difference in solubilizing ability among three surfactants could be attributed to the different HLB value. The HLB is an indicator of the relative affinity of a surfactant to partition between water and an oil phase. A surfactant with a higher HLB prefers the water phase and can significantly enhance the solubility of a compound with higher water solubility while a lower HLB value indicates preference for the oil phase. Because of the relatively high water solubility of BPA, the hydration effect of CTAB and SDBS should be less significant than that of SDS and thus interferes with the molecular interaction of the nonpolar hydrocarbon with BPA.[10,11,12] This is in accordance with the results of previous studies. The results of Doong indicate that SDS with a higher HLB has a more significant effect than TritonX-100 on benzene, chlorobenzene, and styrene solubilities. This clearly shows that the surfactant with a higher HLB is suitable for enhancing the solubility of high water solubility compounds in amending contaminated soil.

## Conclusion

From the above, we can draw the following conclusions: (1) the cationic surfactant CTAB significantly increases the aqueous solubility of BPA; (2) anionic surfactants SDBS and SDS lead to a minimum in the BPA aqueous solubility at low concentration; and (3) the order of increasing aqueous solubility enhancement of BPA is SDS > CTAB > SDBS due to the different HLB of surfactant and negatively correlates to the HLB.

## Literature Cited

(1) Stapher, C. A.; Dorn, P. B.; Kleka, G. M. A review of the environmental fate, effect and exposures of bisphenol A. *Chemosphere* **1998**, *36*, 2149−2173.

(2) Snyder, S. A.; Villeneuve, D. L.; Snyder, E. M.; Giesy, J.-P. Identification and quantification of estrogen receptor agonists in wastewater effluents. *Environ. Sci. Technol.* **2002**, *35*, 3620−3625.

(3) Howdeshell, K. A.; Peterman, P. H.; Judy, B. M. Bisphenol A is released from used polycarbonate animal cages into water at room temperature. *Environ. Health Perspect.* **2003**, *111*, 1180−1187.

(4) Krishnan, A. V.; Starhis, P.; Permuth, S. F. Bisphenol A: an estrogenic substance is released from polycarbonate flasks during autoclaving. *Endocrinology* **1993**, *132*, 2279 - 2286.

(5) Sun, W. L.; Ni, J. R.; Hao, P. P. Analysis of endocrine disruptors in water by solid phase extraction-liquid chromatography-ion trap mass/mass spectrometry. *J. Chin. Mass Spectrom. Soc.* **2005**, *26*, 222−226.

(6) Jia, L. Q.; Ou, Z. Q.; Yang, Z. Y. Ecological behavior of linear alkylbenzene sulfonate (LAS) in soil-plant systems. *Pedosphere*. **2005**, *15*, 216−224.

(7) Shen, X. Y.; Sun, Y. L.; Ma, Z. Y.; Zhang, P. Effects of mixed surfactants on the volatilization of naphthalene from aqueous solutions. *Environ. Pollut*. **2007**, *140*, 187−193.

(8) Song, W. L.; Li, A.; Xi, X. Q. Water solubility enhancement of phthalates by cetyltrimethylammonium bromide and $\beta$-cyclodextrin. *Ind. Eng. Chem. Data* **2003**, *42*, 949−955.

(9) Daniel, E. K.; Chiou, C. T. Water solubility enhancement of DDT and trichlorobenze by some surfactant below and above the micelle concentration. *Environ Sci. Technol*. **1989**, *23*, 832−838.

(10) Kohsaku, K.; Naohike, O.; Kyola, M.; Takeshi, F.; Yasuo, I. Solubilization behavior of a poorly soluble drug under combined use of surfactants and cosolvents. *Eur. J. Pharm. Sci*. **2006**, *28*, 7−14.

(11) Liu, J. C.; Chang, P. S. Solubility and adsorption behaviors of chlorophenols in the presence of surfactant. *Water Sci. Technol*. **1997**, *35*, 123−130.

(12) Doong, R. A.; Lei, W. G.; Chen, T. F.; Lee, C. Y. Effect of anionic and nonionic surfactants on sorption and micellar solubilization of monocyclic aromatic compounds. *Water Sci. Technol*. **1996**, *34*, 327−334.

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