EFFECTS OF PH ON THE WATER SOLUBILITY AND 1-OCTANOL PARTITION COEFFICIENT OF TETRABROMOBISPHENOL A

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Introduction

To predict the behaviour of tetrabromobisphenol A (TBBP-A), which has two phenolic groups, in the environment, it is necessary to know its physicochemical properties (water solubility (S_w), 1-octanol/water partition coefficient (K_{ow}), and Henry's law constant (H_w)). Although the S_w and K_{ow} of TBBP-A at a pH of about 3, that is, the non-ionic form, were measured in our previous work[1], those values are not useful for accurate prediction of its environmental distribution. The reason is that ionization of the phenolic group of TBBP-A is expected to begin in a solution pH of higher than 5.5, as shown in Fig. 1. This shows that TBBP-A may exist in both the ionic and non-ionic form in the environment and also that S_w and K_{ow} for a mixture of the ionic and non-ionic forms are more important.

In this study, the S_w and K_{ow} of TBBP-A in different aqueous solutions prepared by varying the solution pH were measured using the shake flask method to understand the properties of the ionic and non-ionic forms of TBBP-A. The effect of pH on S_w and K_{ow} was first revealed from the present experimental data. The pH effect and the environmental partition of TBBP-A were discussed through comparing the properties of TBBP-A with those of 2,4,6-tribromophenol (TBP), which has a phenolic group. In addition, the pH effect on S_w was represented using an analytical expression based on mass balance equation and the dissociation constants of the phenolic groups (K_{a1} and K_{a2}), to evaluate if these literature values[2] are reasonable.

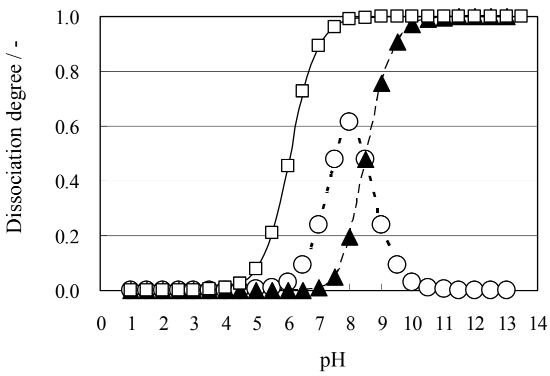

Fig. 1. Dissociation degree of TBBP-A and TBP versus solution pH. ○:monovalent anionic form of TBBP-A, ▲: divalent anionic form of TBBP-A, □: monovalent anionic from of TBP. pK_{a1} and pK_{a2} of TBBP-A were 7.5 and 8.5[2], respectively. pK_{a1} of TBP was 6.08[4].

Materials and Methods

TBBP-A (98%) was purchased from Sigma-Aldrich Corporation (Milwaukee, WI) and was used without further purification. Pure water (<0.1 $\mu S \cdot cm^{-1}$) was supplied by a Milli-RX 45 system (Millipore, Bedford, MA). A buffer solution for UV adsorption spectrometry[3] was used to measure the effect of pH on S_w and K_{ow}.

Measurement of S_w The experimental apparatus consisted of an equilibrium cell (50 mL amber glass flask), a thermostated water bath controlled to within ±0.05 °C, and a magnetic stirrer, as shown in Fig. 2a. An excess amount of solid TBBP-A was added to a buffer solution with the pH of interest in the equilibrium cell. After the cell was placed in the bath at 298.15 K, the solution was stirred until equilibrium was reached. At least 48 h of equilibration was allowed for each measurement. The aqueous sample was filtrated with a 0.45 μm syringe filter (Toyo Roshi Kaisha, Tokyo, Japan). The concentration of the filtrated sample, S_w, was determined using a Ubest DU700 spectrometer (Jasco, Tokyo, Japan). The initial pH value of the buffer ranged from 7.5 to 12.

Measurement of K_{ow} The experimental apparatus was basically the same as that for S_w measurement, as shown in Fig. 2b. The measurement procedure is briefly described as follows: water-saturated 1-octanol solution was prepared, and solid TBBP-A was then dissolved in the 1-octanol solution. The concentration was fixed at 1 $g \cdot L^{-1}$. 1-Octanol-saturated buffer solution was prepared by mixing a buffer solution with the pH of interest with 1-octanol. The initial pH value of the buffer was also similar to that for the S_w measurement. Then, 3 mL of the 1-octanol solution was added to 30 mL of the 1-octanol-saturated buffer solution in a 50 mL amber glass flask. The heterogeneous mixture was incubated for 4 h at 298.15 K and centrifuged for 10 min at 9,000×g using an MX-300 centrifuge (Tomy Seiko, Tokyo, Japan). The concentration in both phases was analyzed using the same method as for the S_w measurement. K_{ow} was determined using the ratio of the concentration in the 1-octanol phase to that in the aqueous phase.

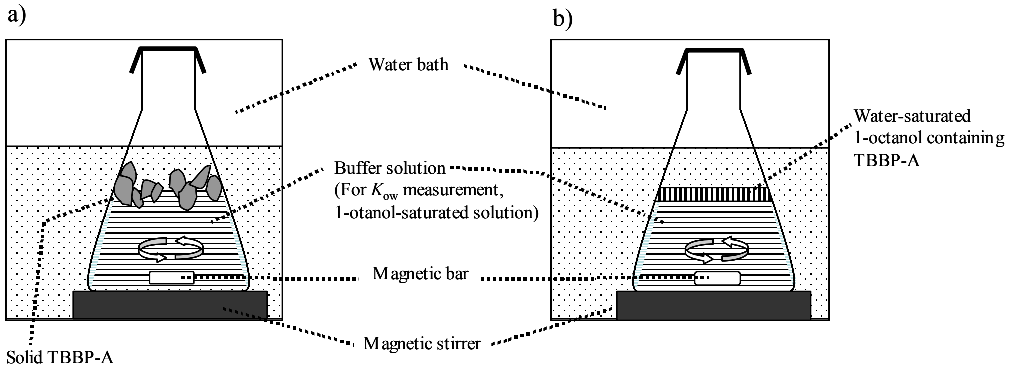

Fig. 2. Schematic diagram of apparatus used for water solubility (S_w) and 1-octanol/water partition coefficient (K_{ow}) measurements. a) S_w measurement by the shake flask method. b) K_{ow} measurement by the shake flask method.

Results and Discussion

S_w measurement The experimental results obtained in this S_w measurement and the S_w value of the non-ionic form obtained in our previous work[1] are summarized in Table 1. The S_w values are plotted as a function of the solution pH in Fig. 2. The S_w values above pH 7.5 increased significantly due to the ionization of phenolic group. The S_w value at pH 9.50 was 27,900 $mg \cdot L^{-1}$, the highest value of the present experimental data, and was higher than that at pH 3.05 (0.171 $mg \cdot L^{-1}$; S_w of the non-ionic form) by five orders of magnitude.

The dissociation curve of TBP and the S_w values of the non-ionic or ionic form of TBP reported in our previous work[3] are shown in Figs.1 and 3, respectively. Although the S_w of non-ionic form of TBBP-A was significantly different from that of TBP, the highest S_w value of the former was almost equal to that of the latter (31,100 mg·L^{-1}). This indicates that S_w of divalent anionic TBBP-A is almost the same as that of monovalent anionic TBP. However, the S_w increment, the ratio of S_w of a mixture of ionic and non-ionic forms to S_w of non-ionic form, in the case of the dissociation degree of about 50% (at pH 7.5 = pK_{a1}) for TBBP-A was about 10-fold higher than that for TBP (at pH 6.08 = pK_{a1}). Since the S_w increments for chlorinated phenols in that case ranged from about 1.5 to 2.5[5], we consider that the pK_{a1} and pK_{a2} values of TBBP-A used in this work are overestimated.

As an environmental characteristic, the leaching potential of TBBP-A to the aquatic environment at near neutral pH is lower than that of TBP by two or more orders of magnitude. However, it should be noted that there is no difference in the leaching potential over pH 9.5 between TBBP-A and TBP. Such high pH water is sometimes observed in a landfill containing incineration residues[6].

K_{ow} measurement The measured K_{ow} values at pH 7.5 to 12 and the value of the non-ionic form reported in our previous work[1] are listed in Table 2. Plots of log K_{ow} versus solution pH are shown in Fig. 4. Contrary to the S_w results, it can be seen in the figure that log K_{ow} decreased significantly from 6.53 to –1.22 between pH 3 and 12. The reason for this decrease is that the concentration of the ionic form with a high S_w value increased, as shown in Fig. 3. Above pH 10, however, the log K_{ow} decrement was smaller.

From the comparison with TBP, the K_{ow} value of TBBP-A was 10- or 100-fold higher than that of TBP below pH 9. There is a positive linear correlation between the log bioconcentration factor or log organic-carbon sorption coefficient and log K_{ow}. TBBP-A is thus expected to be more bioaccumulative and concentrated in soil and sediment compared to TBP within the pH range of 3 to 9. In contrast, beyond pH 9 to a highly basic condition, the log K_{ow} value of TBBP-A was lower than that of TBP by one to two orders of magnitude. Under such pH conditions, the log K_{ow} value of TBBP-A was negative, while that of TBP was positive. Hence, TBBP-A has a tendency to partition from aquatic biota, soil, and sediment to water, whereas TBP does not exhibit such a tendency. This is the only major difference between TBP and TBBP-A in partitioning characteristics.

Evaluation of pK_{a1} and pK_{a2} To examine whether the literature values of pK_{a1} and pK_{a2}[2] are resonable, pH-S_w profile of TBBP-A was represented by the Henderson-Hasselbalch equation with the literature values. The eqation is as follows;

$$S_w = S_w^o \left[1 + 10^{(\mathrm{pH}-\mathrm{p}K_{a1})} + 10^{(2\mathrm{pH}-\mathrm{p}K_{a1}-\mathrm{p}K_{a2})}\right] \quad (1)$$

Where, S^o_w denotes water solubility of the non-ionic form. The calculated results could not represent the experimental data, as shown in Fig. 3. Therefore, we concluded that the literature values were not reasonable. In this study, the pK_{a1} and pK_{a2} values were newly determined by minimizing the deviation between the calculated and experimental values. The determined pK_{a1} and pK_{a2} values were 6.79 and 7.06, respectively. As shown in Fig. 3, the new values can express the experimental data, and thus are considered to be reasonable.

Table 1. pH Effect on Water Solubility (S_w) of TBBP-A at 298K

pH	3.05	7.56	7.99	8.48	8.91	9.50
S_w / mg•L^{-1}	0.171±0.004*	4.15±0.36	30.5±1.8	228±6	1510±60	27900±400

±: standard deviation. *: S_w of non-ionic form[1].

Table 2. pH Effect on 1-Octanol/Water Partition Coefficient (log K_{ow}) of TBBP-A at 298K

pH	3.05	7.53	8.12	9.18	10.19	10.95	11.83
logK_{ow} / -	6.53±0.12*	4.75±0.07	3.00±0.03	1.25±0.01	-0.293±0.020	-0.769±0.023	-1.22±0.00

±: standard deviation. *: K_{ow} of non-ionic form[1].

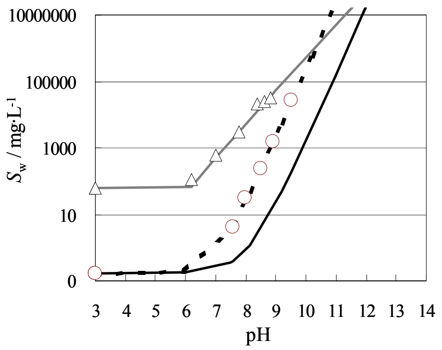

Fig. 3. Effect of solution pH on S_w of TBBP-A and TBP at 298 K. Open circles: experimental data for TBBP-A; open triangles: experimental data for TBP[3]; solid line: calculation for TBBP-A by Eq 1 using pK_{a1} = 7.5[2] and pK_{a2} = 8.5[2]; dashed line: calculation for TBBP-A by Eq 1 using pK_{a1} = 6.79 and pK_{a2} = 7.06; gray line: calculation for TBP by the Henderson-Hasselbalch equation using pK_{a1} = 6.08[4].

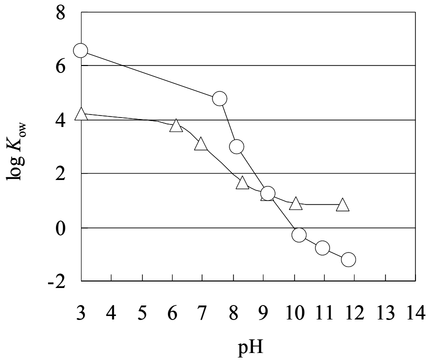

Fig. 4. Effect of solution pH on log K_{ow} of TBBP-A and TBP at 298 K. Open circles: experimental data for TBBP-A; open triangles: experimental data for TBP[3].

References

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