Measurements of Water Solubilities and 1-Octanol/Water Partition Coefficients and Estimations of Henry's Law Constants for Brominated Benzenes

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The water solubilities (S_w) at various temperatures from 283 K to 308 K and 1-octanol/water partition coefficients (K_{ow}) for four brominated benzenes (1,4-dibromobenzene, 1,2,4-tribromobenzene, 1,2,4,5-tetrabromobenzene, and hexabromobenzene) were measured by either the generator-column or the shake-flask method and the high-performance liquid chromatography method, respectively. These solubility data revealed not only the temperature dependence of S_w, in the form of the enthalpy of solution ($\Delta_{sol}H$), but also the effect of bromine substitution on S_w and $\Delta_{sol}H$. To estimate the activity coefficients (γ_w) of the brominated benzenes in water from the present S_w data, enthalpies of fusion and melting points for those compounds were measured with a differential scanning calorimeter. Henry's Law constants (H_w) of the brominated benzenes were derived assuming that the obtained γ_w represented the infinite dilution activity coefficients (γ_w^∞). Some physicochemical characteristics of brominated benzenes were also suggested by comparing the data in this study with that of chlorinated benzenes in the past studies.

Introduction

Brominated benzenes (BBzs) as raw materials have several industrial uses. Examples include hexabromobenzene as a brominated flame retardant (BFR) in the plastics and electric manufactured goods and 1,4-dibromobenzene as an intermediate in the synthesis of drugs and liquid crystal materials. On the other hand, brominated benzenes may be released into the environment during the combustion of solid wastes containing various BFRs.[1–2] Recently, toxic effects of some BBzs have been observed.[3–4] In Japan, 1,4-dibromobenzene has specifically been registered as a designated chemical that is suspected to be toxic. To understand the behavior of BBzs in the environment, their physicochemical properties such as water solubility (S_w), 1-octanol/water partition coefficient (K_{ow}), and Henry's Law constant (H_w) are required.[5] Unfortunately, the amount and reliability of the experimental values of S_w and K_{ow} data does not allow for a prediction of environmental behavior, and experimental H_w data is not available. In the absence of these physicochemical data, however, the infinite dilution activity coefficient in water can be used to estimate S_w and H_w via thermodynamic relationships.[6–7]

In this work, S_w and K_{ow} for four selected BBzs (1,4-dibromobenzene, 1,2,4-tribrombenzene, 1,2,4,5-tetrabromobenzene, and hexabromobenzene) were measured by the generator-column or shake-flask method and the high-performance liquid chromatography (HPLC) method, respectively. The experimental temperature for S_w ranged from 283 K to 308 K to determine the temperature dependence of S_w for the BBzs. In addition, the activity coefficients (γ_w) of these compounds in water were deter-

mined from the S_w values by using enthalpies of fusion and melting points measured with a differential scanning calorimeter. The present γ_w data was used to estimate H_w for the BBzs. On the baiss of the results of these experiments, some characteristics of BBzs were discussed.

Experimental Section

Materials. The following brominated benzenes were used in this study: 1,4-dibromobenzene (1,4-D2BBz) 97%, 1,2,4-tribromobenezene (1,2,4-T3BBz) 98%, 1,2,4,5-tetabromobenzene (1,2,4,5-T4BBz) 97%, and hexabromobenzene (H6BBz) 98%. All compounds were purchased from Sigma-Aldrich Corporation (Milwaukee, WI) and were used without further purification. Pure water ($<0.1~\mu S\cdot cm^{-1}$) was supplied by Milli-RX 45 (Millipore, Bedford, MA).

Apparatus and Procedure. The apparatus and procedures used in this study were similar to our previously reported method.[8] For water solubility, two methods were used on the basis of solubility value. In accord with EPA Test Guidelines,[9] in the case of a water solubility higher than 10 mg/L, the shake-flask method was used. For a water solubility lower than 10 mg/L, the generator-column method was used. For K_{ow}, an indirect HPLC method was used.

Shake-Flask Method. As described in our previous work,[10] the experimental apparatus was made up of an equilibrium cell (a 50-mL amber glass flask), a thermostated water bath, and a magnetic stirrer. The temperature of the bath was kept constant within ±0.05 K from 283 K to 308 K. An excess amount of the solute of interest was added to pure water in the equilibrium cell, and the aqueous solution was then stirred until equilibrium was reached. The aqueous phase was filtered using a 1.0 μm glass filter (Whatmann, Clifton, NJ) and then analyzed by a Waters Associate Separation Module 2695 HPLC system with a Model 2487 variable-wavelength UV detector (Wa-

Table 1. Operating Conditions for HPLC Analysis in S_w Measurement of BBzs

	mobile phase composition	mobile phase condition	flow rate of mobile phase/mL·min^{-1}	UV detector λ/nm
1,4-dibromobenzene	methanol/water (80/20)	isocratic	1	226
1,2,4-tribromobenzene	methanol/water (85/15)	isocratic	1	227
1,2,4,5-tetrabromobenzene	methanol/water (90/10)	isocratic	1	231
hexabromobenzene	methanol/water (90/10)	isocratic	1	232
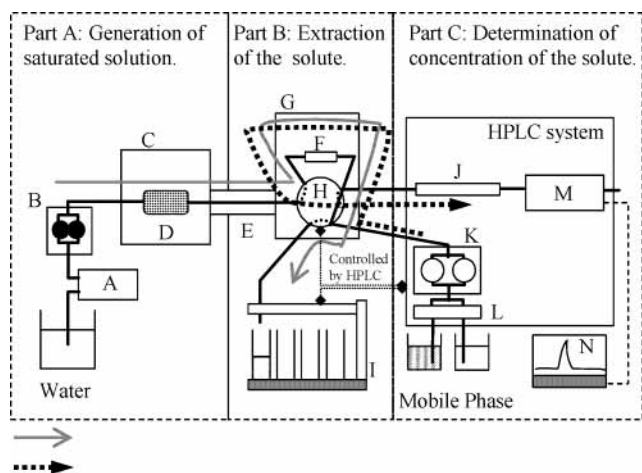
Figure 1. Schematic diagram of apparatus used for the DCCLC method. A, degassor; B, dual plunger pump; C, thermostated water bath; D, generator column; E, thermostated tape heater; F, extractor column; G, thermostated air oven; H, two-position six-port switching valve; I, fraction collector; J, analytical column; K, HPLC pump; L, HPLC degassor; M, UV detector; N, integrator.

ters Associates, Milford). The analytical column was a 3.9 × 300-mm μ-Bondapack C18 column (Waters Associates, Milford, MA). The analytical condition is summarized in Table 1. For the conversion from molarity to mole fraction, the density of the liquid phase was measured using an Anton Paar DMA 35N density meter (Anton Paar, Graz, Austria). For the determination of S_w at each temperature, three flasks were used, and 3−4 equilibrium samples were collected for each flask.

Generator-Column Method. A direct-coupled column-linked chromatographic technique (DCCLC) was used as the generator column method. A schematic of the apparatus is shown in Figure 1. This method consists of three primary steps: (1) the generation of a saturated solution, (2) sample extraction and injection by two-position six-port switching valve with an extractor column, and (3) the determination of the solute concentration by HPLC. Since the details of the apparatus and procedure were explained in our previous work,[8] we will provide only a brief description of the experimental procedures and conditions here. The generator column consists of a 4.5 × 250-mm stainless column packed with 60−80 mesh glass beads coated with sample compound. The weight ratio of the solid to glass beads ranged from 1 to 2%. Pure water was pumped through the generator column in a temperature-controlled water bath (within ±0.05 K) at a flow rate of 1.0 mL/min. A 20-mm extractor column (Sentry Symmetry C18; Waters Associates, Milford, MA) was used to extract the solute from the saturated solution. After pumping the HPLC mobile phase through the extraction column, the extracted solute was injected into an analytical column. Consequently, S_w was calculated from the result of HPLC analysis, and the weight of the eluted solution passed through the extraction column. The HPLC system used in this method is the same as in the shake-flask method. The details of the HPLC analysis condition are summarized in Table 1. For the determination of S_w at each temperature, three generator

columns were used, and 6−9 equilibrium samples were collected for each generator column. It should be noted that all light sources were blocked out to prevent photochemical decomposition of samples during sample preparation. In solubility measurements higher than 1 mg/L, the six-port valve with the extractor column was not used. In other words, the saturated solution eluted from the generator column was collected with an HPLC sample vial and then analyzed by HPLC.

HPLC Method. According to the Organization for Economic Cooperation and Development Guideline for Testing of Chemicals,[11] the 1-octanol/water partition coefficient (K_{ow}) of BBzs was indirectly determined by measuring the retention time (t_R) of BBzs in fixed HPLC conditions (column and mobile phase (water/methanol = 25/75)). First, the t_R of standard samples with a log K_{ow} value between 2.84 and 5.73, such as chlorinated benzenes with 1−6 chlorines, was measured and then converted to the capacity factor (k) as follows

$$k = \frac{t_R - t_0}{t_0} \qquad (1)$$

where t_0 denotes the dead time of the column under the same HPLC condition as the t_R measurement of the standards. By plotting log K_{ow} vs log k for all reference standards, the following linear relationship between log K_{ow} and log k was obtained

$$\log K_{ow} = a \log k + b \qquad (2)$$

where a and b are fitting parameters. Next, t_R values of BBzs were measured under the same HPLC conditions. For the log K_{ow} determination, three t_R measurements were carried out. The log K_{ow} values were then determined by substituting the k values from measured t_R into eq 2.

Results and Discussion

Water Solubility. The reliability of the generator-column method has been examined by measuring the water solubilities of phenanthrene and anthracene under various temperature conditions and comparing them with the literature data in our previous paper.[8] The temperatures in the present experiment were fixed at 283 K, 298 K, and 308 K. Experimental S_w values and standard deviations for the BBzs are summarized in Table 2. The chromatographic errors in the S_w determination for BBzs except for H6BBz ranged from ±0.1% to ±0.5%. From the fact that the S_w deviation for 1,2,4-T3BBz was larger than that for 1,2,4,5-T4BBz, the dynamic-link method reduces the operating error. In the case of H6BBz, the chromatographic error was ±1.4% and higher than the others due to dealing with much lower concentration. In addition, longer extraction time results in increasing the operating error. The result of H6BBz also indicates that the DCCLC method provides more accurate values with a higher S_w value. The values of S_w at 298 K ranged from 17.0 mg/L for 1,4-dibromobenzene to 1.10×10^{-4} mg/L for hexabromobenzene, clearly showing a significant decrease in water solubility with increasing bromine substitution. Although

Table 2. Water Solubilities (S_w) from 283 K to 308 K in This Study and Literature Values at 298 K

compounds	S_w (283 K) mg·L^{-1}	S_w (298 K) mg·L^{-1}	S_w (308 K) mg·L^{-1}	S_w (lit,298 K) mg·L^{-1}	ref
1,4-dibromobenzene	9.91 ± 0.10	17.0 ± 0.2	24.6 ± 0.2	20.0	10
1,2,4-tribromobenzene	3.67 ± 0.07	7.21 ± 0.10	11.0 ± 0.21	9.97	11
1,2,4,5-tetrabromobenzene	0.0186 ± 0.0002	0.0435 ± 0.0006	0.0778 ± 0.0002	0.0412	11
hexabromobenzene (10^4)	0.472 ± 0.031	1.10 ± 0.05	2.32 ± 0.08	1.6, 30	10, 12

Table 3. Physicochemical Properties for BBzs Presented in this Study and Literature Values

BBzs	1,4-dibromobenzene	1,2,4-tribromobenzene	1,2,4,5-tetrabromobenzene	hexabromobenzene
S_w at 298 K/mol·L^{-1}	7.23 ± 0.08 × 10^{-5}	2.29 ± 0.03 × 10^{-5}	1.11 ± 0.02 × 10^{-7}	2.00 ± 0.09 × 10^{-10}
$\Delta_{sol}H$/kJ·mol^{-1}	26.2 ± 0.7	31.9 ± 0.2	41.3 ± 1.2	45.6 ± 4.7
α in eq 4	1.06 ± 0.27	2.19 ± 0.10	0.681 ± 0.49	−3.85 ± 1.9
T_m/K	357.7 ± 0.5	317.0 ± 0.5	454.5 ± 0.5	598.8 ± 0.5
$\Delta_{fus}H$/kJ·mol^{-1}	18.6 ± 0.9	17.9 ± 0.9	24.4 ± 1.2	24.6 ± 1.2
$\Delta_{mix}H$/kJ·mol^{-1}	7.60 ± 1.1	14.0 ± 0.9	16.9 ± 1.7	21.0 ± 2.2
log K_{ow}	3.62 ± 0.08	4.32 ± 0.08	5.00 ± 0.08	6.07 ± 0.08
log K_{ow} (lit)[12]	3.79	4.66[a]	5.13	6.07
log γ_w at 298 K	5.34 ± 0.23	6.20 ± 0.08	7.23 ± 0.61	9.28 ± 0.90
$p^{o,S}$ at 298 K (lit)[12]/Pa	7.67	0.731[a]	0.0417[a]	2.17 × 10^{-6} [a]
vapor pressure of subcooled liquid $p^{o,L}$ at 298 K/Pa	26.7	1.12	1.23	3.17 × 10^{-4}
H_w at 298 K/Pa·m^3·mol^{-1}	106	31.9	376	10.8
H_w at 298 K (lit)[12] Pa·m^3·mol^{-1}	90.5[a]	34.6[a]	13.8[a]	2.85[a]

[a] Estimated value.

the reliability of the literature data[12−15] could not be precisely evaluated by lack of the uncertainty of the literature data, the present results were in relatively good agreement with the literature values with the exception of Tittlemier et al.'s value for hexabromobenzene.[14] This was also the only value that was significantly outside the linear relationship obtained by the QSPR (Quantitative-Structure-Property Relationship) plot of the subcooled water solubility, which is calculated from S_w, vs the Le Bas molar volume.[15] For this reason, we consider our value to be reasonable.

The temperature dependence of S_w for BBzs was also investigated. For all BBzs, S_w increased at higher temperature. This demonstrates that the solubility of BBzs is an endothermal process. To quantitatively evaluate the temperature effect on S_w, a plot of the log of S_w vs reciprocal temperature $1/T$, namely, a van't Hoff plot, was examined. The slope of this plot is related to the enthalpy of solution, $\Delta_{sol}H$, as expressed in eq 3

$$\frac{d \ln S_w}{d \, 1/T} = -\frac{\Delta_{sol}H}{R} \tag{3}$$

where R denotes the ideal gas constant. If $\Delta_{sol}H$ is approximated as a constant from 283 to 308 K, the value of $\Delta_{sol}H$ can be determined by a least-squares fit to the integrated form of eq 3 as follows

$$\ln S_w = -\frac{\Delta_{sol}H}{RT} + \alpha \tag{4}$$

where α is a constant. Values of $\Delta_{sol}H$ are given in Table 3. BBzs with higher levels of bromine substitution have higher $\Delta_{sol}H$ values.

1-Octanol/Water Partition Coefficient. From the capacity-factor (k) data of the six reference compounds (chlorobenzene, 1,4-dichlorobenzene, 1,2,4-trichlorobenzene, 1,2,4,5-tetrachlorobenzene, pentachlorobenzene, and hexachlorobenzene), the constants a and b in eq 2 were determined as follows: $a = 2.764 ± 0.180$, $b = 3.092 ± 0.144$, $r = 0.996$. On the basis of an excellent correlation between the values of these reference compounds, log K_{ow} values of the BBzs were determined using these param-

eters, as listed in Table 3. The errors in the t_R measurements for BBzs were with ±0.2%, and then the error propagation via eq 2 for each BBz was less than 0.01 as an absolute value. Therefore, the uncertainty of log K_{ow} was mainly due to the correlation of the standard chemicals. For comparison, Table 3 also shows the literature values for log K_{ow} for the BBzs.[12] K_{ow} increased with an increase in bromine content. On the basis of the good agreement between our experimental data and the literature data[12] (within 0.17 log units), we believe that the present K_{ow} data obtained using the HPLC method are reasonable. Since an experimental value for 1,2,4-T3BBz is not available, this study provides a reliable experimental value for 1,2,4-T3BBz.

Determination of the Activity Coefficient in Water and Enthalpy Analysis. To determine the activity coefficient (γ_w) of the BBzs in water, the melting point (T_m) and enthalpy of fusion ($\Delta_{fus}H$) were measured with a SII DSC 6200 differential scanning calorimeter (Seiko Instruments, Chiba, Japan). Experimental values of T_m and $\Delta_{fus}H$ are summarized in Table 3. The $\Delta_{fus}H$ values ranged from 17.9 kJ/mol to 24.6 kJ/mol. By assuming that the isobaric heat capacity of a solid is approximately equal to that of its subcooled liquid, γ_w is derived from the water solubility, T_m, and $\Delta_{fus}H$ as follows[16]

$$\gamma_w = \frac{1}{x_i} \exp\left[-\frac{\Delta_{fus}H}{RT_m}\left(\frac{T_m}{T} - 1\right)\right] \tag{5}$$

Where x_i denotes the water solubility in units of mole fraction. By substituting the measured $\Delta_{fus}H$, T_m, and x_i values into eq 5, γ_w of each compound was determined at various temperatures. The calculated results are given in Table 4. γ_w increased by approximately 1 order of magnitude with each additional bromine added to the molecule.

The observed $\Delta_{sol}H$ and $\Delta_{fus}H$ values were used for enthalpy analysis. $\Delta_{mix}H$ was calculated from $\Delta_{sol}H - \Delta_{fus}H$. As shown in Table 3, BBzs with higher bromine content had higher $\Delta_{mix}H$ values. This indicates that increasing the level of bromine substitution lead to an increase in repulsive molecular interactions between the BBz and water. This is responsible for the higher $\Delta_{sol}H$

Table 4. Activity Coefficients (γ_w) in Water for BBzs

| compounds	log γ_w		
	283 K	298 K	308 K
1,4-dibromobenzene	5.41 ± 0.30	5.34 ± 0.23	5.29 ± 0.18
1,2,4-tribromobenzene	6.33 ± 0.15	6.20 ± 0.08	6.11 ± 0.04
1,2,4,5-tetrabromobenzene	7.37 ± 0.71	7.23 ± 0.61	7.11 ± 0.55
Hexabromobenzenes	9.42 ± 1.00	9.28 ± 0.90	9.09 ± 0.84
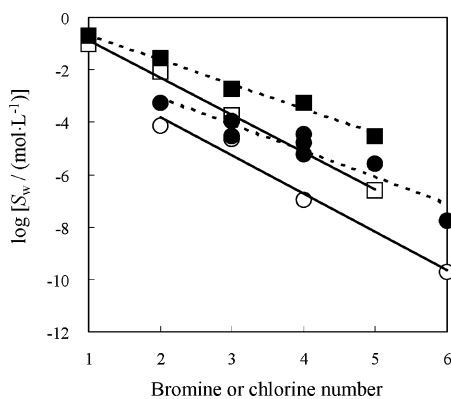
Figure 2. Effect of halogen content on water solubility (S_w) of halogenated benzenes and phenols. ○, brominated benzenes (this work); ●, chlorinated benzenes;[15] □, brominatd phenols;[8] ■, chlorinated phenols.[18] Solid lines, brominated benzenes and phenols. Dotted lines, chlorinated benzenes and phenols. Chlorinated benzenes: 1,4-dichlorobenzene, 1,2,3-trichlorobenzene, 1,3,5-trichlorobenzene, 1,2,3,5-tetrachlorobenzene, 1,2,4,5-tetrachlorobenzene, pentachlorobenzene, hexachlorobenzene. S_w values of CBzs are selected values by Mackey et al.[15]

values for BBzs with more bromines. In addition, the $\Delta_{mix}H$ value is useful for estimating γ_w at a given temperature between 283 K and 308 K. In fact, the variation of ln γ_w with the reciprocal temperature values was almost equal to $\Delta_{mix}H/R$.

Estimation of Henry's Law Constant. Regardless of the point of saturation, γ_w of a solute can be regarded as the infinite dilution activity coefficient γ_w^∞ if the solution is sufficiently dilute. By substituting the vapor pressure of the subcooled liquid of pure compound i ($p_i^{o,L}$) and γ_w^∞ into eq 6, Henry's Law constant (H_w) can be derived

$$H_w = (18.015 \times 10^{-6})\gamma_w^\infty p_i^{o,L} =$$
$$(18.015 \times 10^{-6})\gamma_w^\infty p_i^{o,S} \exp\left(\frac{\Delta_{fus}H}{RT_m}\left(\frac{T_m}{T} - 1\right)\right) \quad (6)$$

where $p_i^{o,S}$ and the exponential term denote the vapor pressure of the solid and the liquid–solid fugacity ratio of the pure compound,[16] respectively. This fugacity ratio is derived based on the approximation that the difference of isobaric heat capacity between subcooled liquid and solid is negligible. From the assumption that the obtained γ_w values can be regarded as γ_w^∞, H_w values of the BBzs at 298 K were calculated using the literature $p_i^{o,S}$ values[12] and the $\Delta_{fus}H$ and T_m values measured in this study. The $p_i^{o,S}$ data, except for 1,4-D2BBz, were estimated values. The γ_w^∞-derived H_w values are summarized in Table 3, and compared with H_w estimated by Howard and Meylan.[12] The present H_w values, except for 1,2,4,5-T4BBz, were in relatively good aggrement with the literature data. It is possible that the $p_i^{o,S}$ value of 1,2,4,5-T4BBz (0.0417 Pa) used in this study is an overestimate, since its extrapolated value (0.0027 Pa) from experimental data[17] is lower than the literature value by 1 order of magnitude. Therefore, the H_w value of 1,2,4,5-T4BBz is expected to range from 10 to 100 Pa·m³·mol⁻¹.
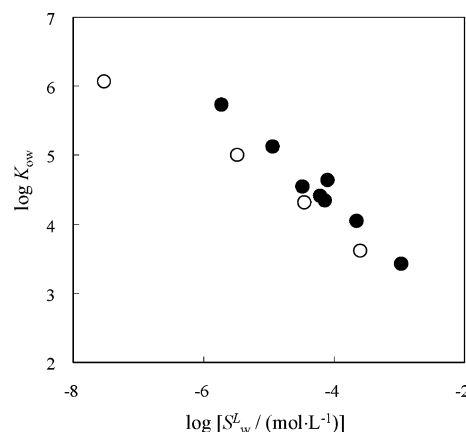
Figure 3. Plot of log 1-octanol/water partition coefficient (K_{ow}) vs log subcooled water solubility (S_w^L) for BBzs and CBzs. ○, BBzs (this work); ●, CBzs.[12,15] CBzs: 1,4-dichlorobenzene, 1,2,3-trichlorobenzene, 1,3,5-trichlorobenzene, 1,2,3,5-tetrachlorobenzene, 1,2,4,5-tetrachlorobenzene, pentachlorobenzene, hexachlorobenzene.
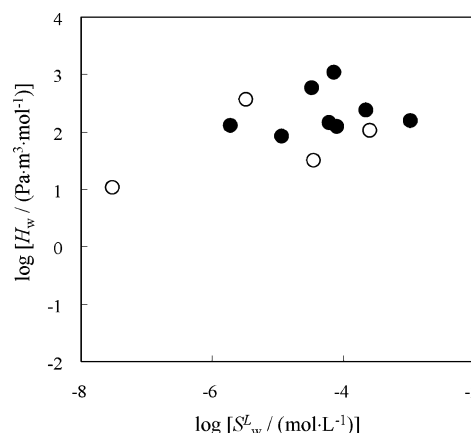
Figure 4. Plot of log Henry's Law constant (H_w) as a function of log subcooled water solubility (S_w^L) for BBzs and chlorinated benzenes CBzs. ○, BBzs (this work); ●, CBzs.[15] CBzs: 1,4-dichlorobenzene, 1,2,3-trichlorobenzene, 1,3,5-trichlorobenzene, 1,2,3,5-tetrachlorobenzene, 1,2,4,5-tetrachlorobenzene, pentachlorobenzene, hexachlorobenzene.

Overall Characteristics of BBzs. By comparing our results with the physicochemical data of chlorinated benzenes (CBzs),[12,15] some overall characteristics of BBzs can be described. In Figure 2, S_w data for brominated and chlorinated benzenes at 298 K are plotted as a function of halogen substitution number. Similar to our previous report[8] on the effects of halogen content on S_w of phenols, the substitution effects of bromine are more intense than that of chlorine. The variation of S_w of BBzs is −1.47 log units per one bromine substitution, while that of CBzs is −1.02 log units per one chlorine. Ths difference is almost equal to that for halogenated phenols, as shown in Figure 2.

Log K_{ow} values are plotted vs the log of subcooled water solubility S_w^L, which is equal to $1/(\gamma_w V_w)$, where V_w is the molar volume of water, in Figure 3. At the same S_w^L value, or the same γ_w value, the log K_{ow} value for the CBzs is higher than that for the BBzs. Since log K_{ow} values are approximately equal to the ratio of γ_w^∞ to the infinite dilution activity coefficient in n-octanol (γ_o^∞), this difference between CBzs and BBzs may be due to the lower γ_o^∞ values of CBzs compared with those of BBzs. In addition, this figure indicates that γ_o^∞ for BBzs significantly increases with an increase in bromine substitution. If this was not

so, the difference in log K_{ow} values between CBzs and BBzs with higher halogen contents could not increase.

H_w values were also compared, as shown in Figure 4. When the vapor pressure of 1,2,4,5-T4BBz is considered to be an overestimated value as described above, H_w values for BBzs are lower than those for CBzs for the same S^L_w values. In terms of an environmental characteristic, this shows that the distribution of BBzs from the aqueous phase to air is weaker than that of CBzs at the same solubility level.

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