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Volatility of Low-Henry's Constant Contaminants in Water

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The volatilization rate of low-Henry's constant contaminants (less than about 2 m^3 Pa/mol) from water to the atmosphere was studied, together with the water volatilization rate, using tracer compounds under various mixing conditions. 1-Butanol, 1-pentanol, 1-hexanol, and 1-heptanol were used as the tracer compounds. The volatilization rates of these compounds and water were controlled by a mass-transfer process in the gas phase. The measured parameter was the ratio of the volatilization rate constant of a tracer(i) to that of water, $K_v^{(i)}/K_v^{(H_2O)}$. The obtained ratios agreed with those estimated theoretically. The volatilization rate constant of low-Henry's constant contaminant(i) in environmental water, $K_{v(env)}^{(i)}$, can be estimated by multiplying the ratio, $K_v^{(i)}/K_v^{(H_2O)}$, by the environmental value of $K_{v(env)}^{(H_2O)}$.

The volatilization of contaminants (such as pesticides) from water bodies to the atmosphere can be an important environmental pathway for certain contaminants. The rate equation for the volatilization of a contaminant, i, in water to the atmosphere is given by Eq. 1:

$$-dC_L^{(i)}/dt = K_v^{(i)}(C_L^{(i)} - p^{(i)}/H^{(i)}), \qquad (1)$$

where C_L is the concentration of the contaminant in water; t is the time; K_v is the volatilization rate constant; p is the partial pressure of the contaminant in the atmosphere; and H is Henry's constant. The ratio of the volatilization rate constant of a contaminant(i) to the oxygen-reaeration rate constant, $K_v^{(i)}/K_v^{(O_2)}$, has been experimentally determined[1–10] as a parameter for the volatility of contaminants in water. Mackay and Leinonen[11] suggested that the volatilization rate of the volatilized compound is controlled by a mass transfer in the aqueous phase when Henry's constant is greater than about 400 m^3 Pa/mol. However, it is controlled by a mass transfer in the gas phase when Henry's constant is less than about 2 m^3 Pa/mol. In the former case ($H \geq 400$ m^3 Pa/mol), the ratio $K_v^{(i)}/K_v^{(O_2)}$ remains constant, independent of the mixing conditions and the temperature. If the ratio is available, the volatilization rate constant of the contaminant in environmental water, $K_{v(env)}^{(i)}$, can be estimated by multiplying the ratio by the environmental value of $K_{v(env)}^{(O_2)}$. However, the parameter for the volatility in the latter case ($H \leq 2$ m^3 Pa/mol) has been little investigated. Pesticides such as DDT, dieldrin, lindane, parathion, and chlordane correspond to a low-Henry's constant contaminant as an environmental interest, and their pesticide volatilizations from water to the atmosphere have been reported.[9,12–15]

In this work, the volatilization rate of the contaminant which is controlled by a mass transfer in the gas phase was simultaneously measured along with the water volatilization rate, instead of the oxygen reaeration rate. The ratio $K_v^{(i)}/K_v^{(H_2O)}$ was investigated as the parameter for the volatility of low-Henry's constant contaminants in water. As the tracer compounds for the low-Henry's constant contaminants, 1-butanol (H=0.84 m^3 Pa/mol at 298 K), 1-pentanol (H=1.0), 1-hexanol (H=1.3), and 1-heptanol (H=1.6)[16] were used since the concentrations of these compounds and water could be continuously monitored.

Experimental

A schematic diagram of the experimental apparatus is shown in Fig. 1. A dilute aqueous solution of 1-butanol (the tracer for volatilization) which was dissolved into distilled water was prepared in a volatilization vessel (V in Fig. 1), and was then stirred at a constant agitation speed by means of a magnetic stirrer. The vessel was maintained at a constant temperature using the outside-jacket of the vessel. Nitrogen was made to flow through the space above the aqueous solution at a constant rate. The dissolved 1-butanol was volatilized together with the water into the flowing nitrogen as a vapor. The 1-butanol and water concentrations vaporized in the nitrogen were continuously measured by means of a photo-ionization detector (PID in Fig. 1, model PI-101, HNU System, INC., U. S. A.) and a humidity meter (HD in Fig. 1), respectively. The volatilization-rate constant of 1-butanol, $K_v^{(BuOH)}$, was

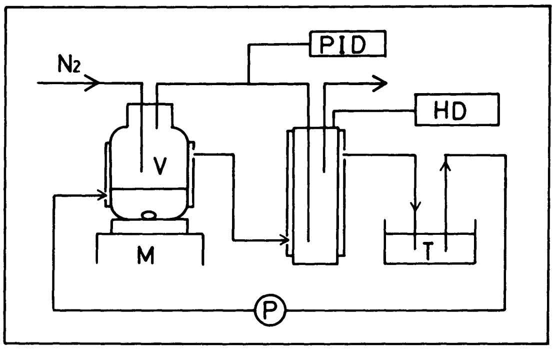

Fig. 1. Schematic diagram of experimental apparatus. V: Volatilization vessel, M: magnetic stirrer, P: pump, T: thermostat, PID: photo-ionization detector, HD: humidity meter.

determined by fitting the concentration data to an integral form of Eq. 1 as $p^{(i)}=0$. That of water, $K_V^{(H_2O)}$, was determined from Eq. 2 using the volatilization rate of water vapor, $F^{(H_2O)}$.

$$K_V^{(H_2O)} = F^{(H_2O)}/(C_{SG}-C_G)V_L, \qquad (2)$$

where C_{SG} is the saturated water concentration at the water surface; C_G is the water-vapor concentration in the gas phase; and V_L is the volume of the aqueous solution (0.10 dm^3 in this work).

The same techniques were also used to determine the volatilization-rate constant for 1-pentanol, 1-hexanol, and 1-heptanol with that of water at 298 K.

Results and Discussion

The volatilization-rate constant of 1-butanol, $K_V^{(BuOH)}$, was not affected by the concentration over a range from 0.01 to 0.1 mol dm^{-3}, as was to be expected from Eq. 1. The effects of turbulence in the aqueous phase, which depends on the agitation speed, on $K_V^{(BuOH)}$ and $K_V^{(H_2O)}$ were negligibly small (Fig. 2). On the other hand, both volatilizationrate constants increased with an increase of turbulence in the gas phase, which depends on the nitrogen flow rate, as shown in Fig. 3. In Fig. 4, the values of $K_V^{(BuOH)}$ and $K_V^{(H_2O)}$ are linearly related with a slope of 1.1×10^{-4} ($=K_V^{(BuOH)}/K_V^{(H_2O)}$) at 298 K. Fig. 5 shows the temperature effect on the ratio, $K_V^{(BuOH)}/K_V^{(H_2O)}$, in a temperature range from 288 to 303 K.

From the above data it can be seen that the volatilization rates of both 1-butanol and water were much more affected by turbulence in the gas phase than by that in the aqueous phase. Also, the ratio is highly dependent on temperature. Consequently, the results indicate that the volatilization rates of 1-butanol and water are controlled by a mass-transfer

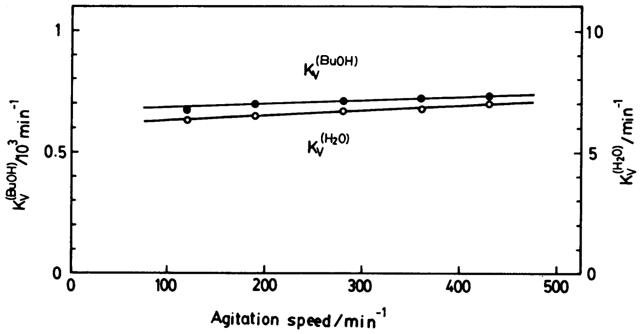

Fig. 2. Effects of turbulence in the aqueous phase (the agitation speed) on $K_V^{(BuOH)}$ and $K_V^{(H_2O)}$ at 298 K. Nitrogen flow rate: 2.0 dm^3 min^{-1}, 1-butanol concentration: 0.05 mol dm^{-3}.

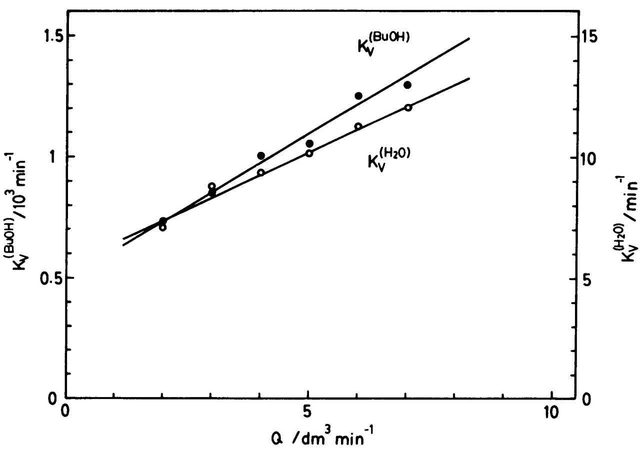

Fig. 3. Effects of turbulence in the gas phase (the nitrogen flow rate) on $K_V^{(BuOH)}$ and $K_V^{(H_2O)}$ at 298 K. Agitation speed: 430 min^{-1}, 1-butanol concentration: 0.05 mol dm^{-1}.

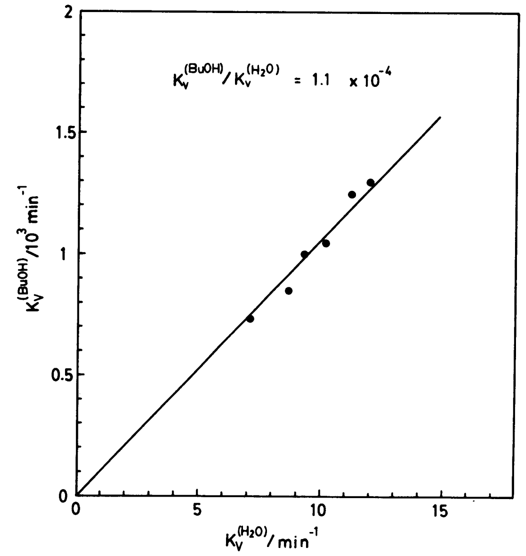

Fig. 4. Relationship between $K_V^{(BuOH)}$ and $K_V^{(H_2O)}$ at 298 K.

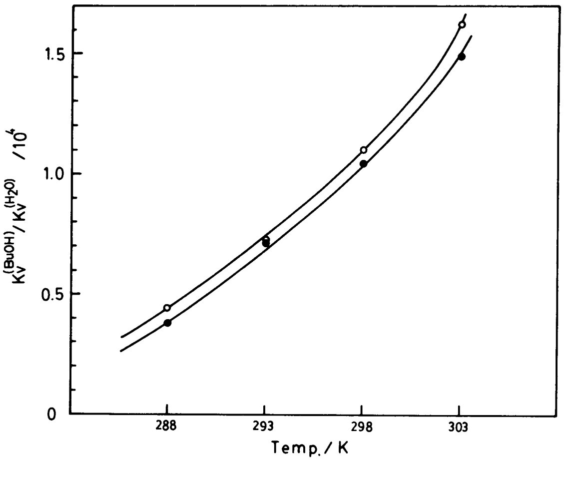

Fig. 5. Effect of temperature on $K_V^{(BuOH)}/K_V^{(H_2O)}$. 1-Butanol concentration: 0.05 mol dm^{-3}, ●: measured, ○: estimated.

in the gas phase, supporting the suggestion of Mackay and Leinonen.[11] Therefore, it is concluded that most of the resistance to these mass-transfer rates lies in the gas-phase boundary layer; thus, the ratio can be theoretically estimated from Eq. 3 since the resistance in the aqueous phase can be neglected.

$$
\begin{aligned}
K_v^{(i)}/K_v^{(H_2O)} &= (H^{(i)}/RT)k_G^{(i)}a/k_G^{(H_2O)}a \\
&= (H^{(i)}/RT)(D_G^{(i)}/D_G^{(H_2O)})^n \qquad (3)
\end{aligned}
$$

where k_G is the mass-transfer coefficient in the gas phase; a is the interfacial contact area per liquid volume which corresponds to the reciprocal of the depth of water;[3] D_G is the diffusivity in the gas phase; R is the gas constant; and T is the absolute temperature. The value of n is suggested to be 1 and 2/3 according to the classical theory of the two-film mass-transfer model[17] and the analogy of Chilton and Colburn[18,19] ((Sherwood numbers)$\propto$(Schmidt numbers)$^{1/3}$), respectively. Experimentally, the values of n so far reported are in the range from 0.5 to 1.[20] Using Eq. 3, the ratio $K_v^{(BuOH)}/K_v^{(H_2O)}$ is estimated to be 1.2×10^{-4} for $n=1$ or 2.0×10^{-4} for $n=0.5$ at 298 K. In Fig. 5, the estimated ratios were obtained for $n=1$ in the temperature range 288 to 303 K. The diffusivities in the gas phase in Eq. 3 were calculated from the equation of Fuller *et al.*,[21] suggesting that the diffusivity is proportional to $T^{1.75}$. The good agreement of the measured values with the estimated values indicated that the estimated values for $n=1$ were better than those for $n=0.5$.

Table 1. The values of $K_v^{(i)}/K_v^{(H_2O)}$ measured and estimated, and of $D_G^{(i)}$ at 298 K

Tracer (i)	$D_G^{(i)}$/cm² s⁻¹	$K_v^{(i)}/K_v^{(H_2O)}\times10^4$	
		Measured	Estimated ($n=1$—0.5)
1-Butanol	0.0899	1.1±0.2	1.2—2.0
1-Pentanol	0.0807	1.6±0.2	1.3—2.3
1-Hexanol	0.0739	2.0±0.2	1.6—2.9
1-Heptanol	0.0684	1.9±0.2	1.8—3.4

Table 1 shows the measured and estimated ratios, $K_v^{(i)}/K_v^{(H_2O)}$, for 1-pentanol, 1-hexanol, and 1-heptanol with 1-butanol at 298 K. These results indicate the effective estimation of Eq. 3 in the n value range from 0.5 to 1. Therefore, Eq. 3 would give an "order of magnitude" estimation for the volatility of low-Henry's constant contaminants such as the pesticides. Table 2 shows the volatilization-rate constants, $K_{v(ocean)}^{(i)}$, and half-lives, $\tau^{(i)}$, of low- and high-Henry's constant contaminants in the ocean. The mass-transfer rates between the ocean and the atomosphere were reviewed in terms of the gas- and liquid-phase mass-transfer coefficients by Liss and Slater.[22] They suggested that the values of the gas- and liquid-phase mass-transfer coefficients were typically 30 m/h ($=k_{G(ocean)}^{(H_2O)}$) for water and 0.2 m/h ($=k_{L(ocean)}^{(O_2)}$) for oxygen, respectively. Hence, the relations of $K_{v(ocean)}^{(H_2O)}=k_{G(ocean)}^{(H_2O)}/L$ and $K_{v(ocean)}^{(O_2)}=k_{L(ocean)}^{(O_2)}/L$ in the ocean are held for the volatilization and reaeration rate constants, respectively, where L is the water depth. In Table 2, the volatilization-rate constant of the contaminant (i) in the ocean, $K_{v(ocean)}^{(i)}$, is estimated from Eq. 4 as the water depth $L=1$ m.

$$K_{v(ocean)}^{(i)} = K_{v(ocean)}^{(j)} \times (K_v^{(i)}/K_v^{(j)}) \qquad (4)$$

where j refers to water (H_2O) or oxygen (O_2). While, the half-life of the contaminant in the ocean, $\tau^{(i)}$, is given by Eq. 5.

$$\tau^{(i)} = 0.693/K_{v(ocean)}^{(i)} \qquad (5)$$

The values of $K_v^{(i)}/K_v^{(H_2O)}$ for DDT, dieldrin, α-HCH (α-hexachloro-cyclohexane), and DBP (dibutyl phthalate) in Table 2 were calculated from Eq. 3 using $H^{(i)}$ from the EPA compilation,[10] whereas the values of $K_v^{(i)}/K_v^{(O_2)}$ were experimentally obtained by Smith *et al.*[3] and Okouchi *et al.*[2] The volatilization rate of low-Henry's constant contaminants was very slow, compared with that of high-Henry's constant contaminants. However, the worldwide atmospheric distribution of pesticides such as DDT clearly indicates that the volatilization of pesticides from

Table 2. The volatilization rate constant, $K_{v(ocean)}^{(i)}$, and half-lives, $\tau^{(i)}$, of low- and high-Henry's constant contaminants in the ocean at 293—295 K as $L=1$ m

	Contaminant (i)	$H^{(i)}$/m³ Pa mol⁻¹	$K_v^{(i)}/K_v^{(H_2O)}$	$K_v^{(i)}/K_v^{(O_2)}$	$K_{v(ocean)}^{(i)}$/h⁻¹	$\tau^{(i)}$/h
low-Henry's constant $H^{(i)}<2$	DDT	0.36 —1.6	2.5×10^{-5}—1.1×10^{-4}		7.4×10^{-4}—3.3×10^{-3}	936—211
	Dieldrin	0.049—0.76	3.6×10^{-6}—5.6×10^{-5}		1.1×10^{-4}—1.7×10^{-3}	6383—412
	α-HCH[a)]	0.46 —0.78	4.2×10^{-5}—7.0×10^{-5}		1.2×10^{-3}—2.1×10^{-3}	556—328
	DBP[b)]	0.16	1.2×10^{-5}		3.7×10^{-4}	1852
	(1-Butanol)	0.49	7.2×10^{-5}		2.2×10^{-3}	321
high-Henry's constant $H^{(i)}>400$	benzene	445		0.56	0.11	6.2
	tetrachloromethane	2300		0.63	0.13	5.5
	mercury	992		0.94	0.19	3.7

a) α-Hexachlorocyclohexane, b) Dibutyl phthalate.

aquatic systems or soils (or both) is an important process because of their toxicities and persistences. The ratio, $K_v^{(i)}/K_v^{(H_2O)}$, suggested in this work would be used to estimate the volatilization rate of low-Henry's constant contaminants ($H \leq 2\ m^3\ Pa/mol$) from environmental water bodies and wastewater treatment facilities to the atmosphere.

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