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Gas Solubilities (CO_2, O_2, Ar, N_2, H_2, and He) in Liquid Chlorinated Methanes

Katsuhiro Shirono,[†] **Tatsumasa Morimatsu,**[‡] **and Fumio Takemura***[,†,‡]

National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki 305-8564, Japan, and Graduate School of Systems and Information Engineering, University of Tsukuba, Tsukuba, Ibaraki 305-8573, Japan

Gas solubilities (CO_2, O_2, Ar, H_2, N_2, and He) in two liquid chlorinated methanes (dichloromethane and chloroform) from 283.15 K to 323.15 K were determined by measuring the decrease in pressure due to absorption. For all gases except for CO_2, Henry's law constant decreased with increasing temperature in both solvents. The order of solubility of the gases was $CO_2 > O_2 > Ar > H_2 > N_2 > He$ in dichloromethane and $CO_2 > Ar > O_2 > H_2 > N_2 > He$ in chloroform. On the basis of the measurements, semiempirical correlations for the solubility in that temperature range were then determined. The measured solubility data were theoretically analyzed using the method proposed by Wilhelm and Battino (*J. Chem. Thermodyn.* **1971**, *3*, 379; *J. Chem. Thermodyn.* **1971**, *3*, 743). to reveal the molecular basis of the solubility. The resulting theoretical Lennerd-Jones (LJ) potential parameters for both liquids are higher than those for methane but lower than those for carbon tetrachloride. The theoretical analysis also revealed that (a) interaction between the nonpolar gases tested in this study and the solvent liquid depend mainly on the dispersion interaction between solvent molecules and gas molecules, despite a dipole moment in liquid dichloromethane and chloroform and (b) temperature dependence of Henry's law constant for CO_2 depends on the energetic effect, whereas that of the other gases (O_2, Ar, H_2, N_2, and He) depends on the entropic effect.

1. Introduction

Chlorocarbons, such as dichloromethane, chloroform, and carbon tetrachloride, are often used as polymer solvents in the fabrication of nano/microcapsules that have a biodegradable polymer shell,[1,2] due to the various characteristics of the chlorocarbons, such as high volatility, nonflammability, high recovery and reuse performance, and high solubility of polymers. These nano/microcapsules are expected to be an integral component in drug delivery systems (DDS) in medical and pharmaceutical applications. For example, hollow microspheres less than 5 μm in diameter with a polylactic-co-glycolic acid shell have been successfully tested as ultrasonic contrast agents.[3] These hollow capsules are typically fabricated using a solvent evaporation technique.[2] Takemura et al. recently developed a simple method to directly fabricate hollow microspheres covered with a biodegradable polymer by using microbubbles as templates.[4] In this method, microbubbles are generated in a dichloromethane solution of a biodegradable polymer by degassing the supersaturated dissolved gas into the solution. The gas solution/separation in liquid organic solvent is therefore a key process in bubble formation and, consequently, in the morphology of fabricated hollow microcapsules. Solubility data for various gases in different solvents over a wide temperature range are needed to design hollow microcapsules fabricated using the microbubble template method.

Solubility data for various gases in liquid carbon tetrachloride have been reported.[5,6] With increasing temperature in liquid carbon tetrachloride, the solubility of H_2, N_2, O_2, and CO increases, whereas that of CO_2 and SO_2, C_2H_2, C_2H_3, and C_2H_6 decreases.[5] The trend is the same for the solubility of these gases in acetone and benzene. The solubility of these gases in liquid carbon tetrachloride is small enough so that Henry's law can be applied. Semiempirical correlations have been used to calculate the Henry's law constant of H_2, N_2, O_2, and CO_2 at various temperatures.[6]

Detailed information about the solubility of gases in liquid carbon tetrachloride is readily available, whereas solubility data of gases in liquid dichloromethane and chloroform are currently limited. For example, IUPAC Solubility Data Series includes Ar, CO_2, H_2, and N_2 in chloroform and CO_2 in dichloromethane,[7] although, with the exception of CO_2 in chloroform, the temperature ranges are quite narrow; e.g., the solubilities of N_2 gas in $CHCl_3$ are given only for (20 to 25) °C. Compared with carbon tetrachloride, advantages of using dichloromethane and chloroform in the removal of solvent from product in certain applications such as microcapsules include easier handling and lower boiling temperature (39.8 °C for dichloromethane and 61.2 °C for chloroform, compared with 76.5 °C for carbon tetrachloride).

Solubility data of gases in liquid dichloromethane and chloroform are needed in the design of new polymer materials. In this study, first the solubilities of CO_2, O_2, Ar, N_2, H_2, and He gas in these two liquid chlorinated methanes from (283.15 to 323.15) K were determined by measuring the decrease in pressure due to absorption. On the basis of the measurements, semiempirical correlations for the solubility in that temperature range were then determined. Then the measured solubility data were theoretically analyzed to reveal the molecular basis of the solubility.

2. Experimental Apparatus and Method

Figure 1 shows a schematic of the experimental apparatus used to determine the solubilities of CO_2, O_2, Ar, N_2, H_2, and He gas in each of the two liquid chlorinated methanes (from

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* Corresponding author. E-mail: takemura.f@aist.go.jp. Tel.: +81-29-861-7207. Fax: +81-29-851-7523.

[†] National Institute of Advanced Industrial Science and Technology.

[‡] University of Tsukuba.

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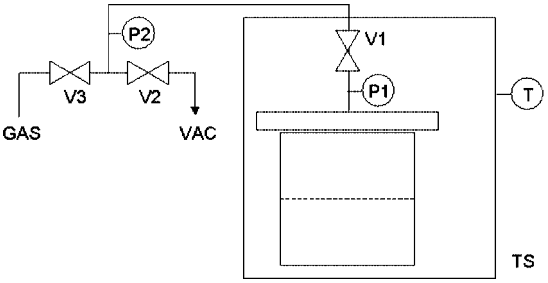

Figure 1. Scheme of experimental apparatus for solubility measurement. P1 is the barometer to measure P^{total} (AP-53A, Keyence, Japan); P2 is the barometer to measure $P_{\text{sat}}^{\text{ini}}$ (AP-V85, Keyence, Japan); TS is the thermostat (F25, Julabo, Germany); T is the thermometer; V1 to V3 are the valves; VAC is the vacuum pump; GAS is the gas cylinder.

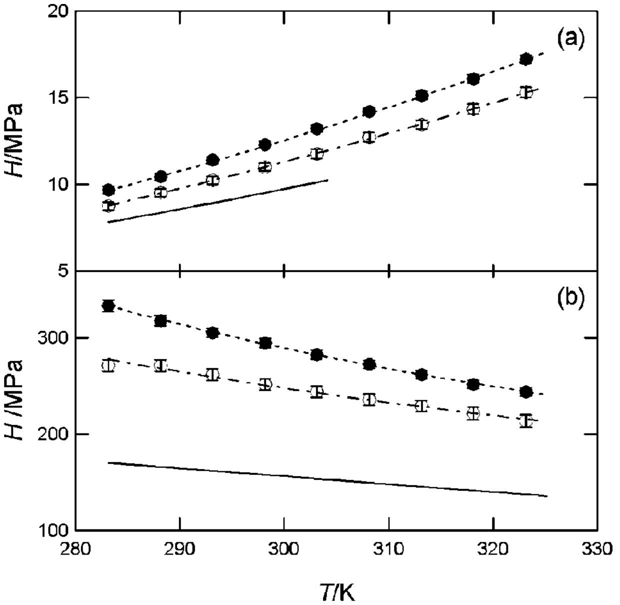

Figure 2. Henry's law constant *H*/MPa for (a) CO_2 and (b) N_2. ●, the measured *H*/MPa in liquid dichloromethane; ○, that in chloroform with error bars representing the standard uncertainty. •••, the fitted curve to the semiempirical equations in dichloromethane; -•-, that in chloroform; —, that in liquid carbon tetrachloride cited from ref 6.

298.15 K to 323.15 K) placed in a stainless steel vessel ($4.0 \cdot 10^{-2}$ m diameter and $6.0 \cdot 10^{-2}$ m high) by using a barometric method.[8] The total volume, V_T, was estimated to be $7.73 \cdot 10^{-5}$ m^3 by the geometrical measurement. The purities of gases were more than 99.9 %. Liquid dichloromethane and chloroform (Wako, Japan) with the purities of more than 99.9 % were used here as the solvents without any purification. The digital pressure indicators of AP-53A (Keyence, Japan), whose range and resolution are $(0 \text{ to } 1) \cdot 10^6$ Pa and $1 \cdot 10^3$ Pa, and AP-V85 (Keyence, Japan), whose range and resolution are $(0.0 \text{ to } 2.0) \cdot 10^5$ Pa and 10 Pa, respectively, were used. Both indicators were calibrated by using a barometer. AP-53A (P1) was used to measure the initial total pressure, $P_T^{\,i}/\text{Pa} = P_1^{\,\text{sat}} + P_2$, and the total pressure, P_T/Pa. AP-V85 (P2) was used to measure the initial vapor pressure, $P_1^{\,\text{sat,i}}$ /Pa. (Subscript 1 and 2 denote the solvent and the gas, respectively.) The water bath type of thermostat (Julabo, F25) was employed.

Pressure measurements were carried out using the following procedure. (1) Liquid solvent [$(6.0 \text{ to } 7.0) \cdot 10^{-2}$ kg of dichloromethane or $(6.5 \text{ to } 7.5) \cdot 10^{-2}$ kg of chloroform] was placed in the vessel (Figure 1), and then valves 1, 2, and 3 were closed. (2) Valves 1 and 2 were opened, and the liquid was degassed using a vacuum pump. Then valve 2 was closed, and the vessel was shaken. This degassing process was repeated several times. After $P_1^{\,\text{sat,i}}$ indicated the constant value, the mass of liquid solvent, Mn_T/g, was measured. (3) Valve 3 was quickly opened to introduce the gas, and then the initial total pressure, $P_T^{\,i}$, was measured. Here, $P_T^{\,i}$ is the sum of the initial partial pressure of dissolved gas, $P_2^{\,i}$/Pa and $P_1^{\,\text{sat,i}}$. (4) Valve 1 was closed, and the vessel was sinked in the thermostat at 323.15 K. (5) When the pressure reached a steady state at the set temperature, *T*, the pressure, P_T, was recorded. Then P_T was measured down to 283.15 K, reducing the temperature by every 5 K.

The measurement accuracy of the gas solubility is sensitive to T^i/K. Using the AP-V85, the standard uncertainty of the $P_1^{\,\text{sat,i}}$ measurement can be reduced to $1.0 \cdot 10^2$ Pa. The uncertainty of $1 \cdot 10^2$ Pa in $P_1^{\,\text{sat,i}}$ corresponds to that of (0.03 to 0.04) K in T^i. It is more accurate than the direct measurement of T^i by a thermocouple. Therefore, the initial temperature T^i was estimated by $P_1^{\,\text{sat,i}}$.

The volume of the vapor and liquid phases, V_V/m^3 and V_L/m^3, respectively, was not measured by direct observation but was calculated from the total volume of the vessel, V_T/m^3, the total mole number of the solvent, n_T/mol, and temperature, *T*, by using the following equation

$$V_T = \frac{RT}{P_1^{\,\text{sat}}} n_1^{\,V} + \frac{M_1}{\rho_1^{\,\text{sat}}} n_1^{\,L} \tag{1}$$

$$n_1 = n_1^{\,V} + n_1^{\,L} \tag{2}$$

where *R* (=8.31 J·K^{-1}·mol^{-1}) is the gas constant; M_1/(kg·mol^{-1}) is the molar weight of the liquid solvent [$(84.93 \text{ and } 119.4) \cdot 10^{-3}$ kg·mol^{-1} for dichloromethane and chloroform]; $P_1^{\,\text{sat}}$/Pa is the saturated pressure of gas; $\rho_1^{\,\text{sat}}$/(kg·m^{-3}) is the saturated liquid density at the set temperature *T*; and n_1/mol and n_2/mol are the mole numbers of liquid solvent and gas, respectively. Here, $P_1^{\,\text{sat}}$ was calculated from previously reported correlation equations,[9] and $\rho_1^{\,\text{sat}}$ was determined from $\rho_1^{\,\text{sat}}-T$ diagrams.[10] The Benedict−Webb−Rubin (BWR) equation[11] is often used for the equation of state when the system pressure is high. However, the ideal gas law was applied in our calculation because n_2 estimated by the BWR equation just differs 0.2 % from that estimated by the ideal gas law at maximum.

Then, the solubility of the gas was determined as follows. The moles of dissolved gas, $n_2^{\,L}$, were calculated by using the following equation

$$n_2^{\,L} = \frac{P_2^{\,i} V_V^{\,i}}{RT^i} - \frac{P_2 V_V}{RT} \tag{3}$$

where $P_2^{\,i}$ was calculated from the difference between $P_T^{\,i}$ and $P_1^{\,\text{sat,i}}$ and P_2/Pa is the partial pressure of the gas obtained by subtracting the saturated vapor pressure, $P_1^{\,\text{sat}}$, of the solvent from P_T. $V_V^{\,i}$/m^3 is the vapor volume at T^i, and V_V is the vapor volume at *T*.

The mole fraction of dissolved gas in solvent, *x*, is defined as

$$x = \frac{n_2^{\,L}}{n_1^{\,L} + n_2^{\,L}} \tag{4}$$

Then, Henry's law constant, *H*/Pa is

$$H = \frac{P_2}{x} \tag{5}$$

Based on preliminary experiments (data not shown), the measurement uncertainties of P_T, $P_T^{\,i}$, and $P_1^{\,\text{sat,i}}$, i.e., $u(P_T)$,

Table 1. Mole Fraction, at $P^* = 1.0 \cdot 10^5$ Pa, $x^*(= x \cdot P^*/P_2)$, of CO_2, O_2, Ar, N_2, He, and H_2 in Liquid Dichloromethane with the Ranges of the Measured Partial Pressure of the Gas, P_2/Pa

	$x^* \cdot 10^3$					
T/K	CO_2	O_2	Ar	N_2	H_2	He
283.15	10.3	0.529	0.482	0.300	0.153	0.0640
288.15	9.54	0.547	0.487	0.314	0.165	0.0645
293.15	8.77	0.561	0.502	0.327	0.175	0.0712
298.15	8.12	0.573	0.517	0.339	0.186	0.0778
303.15	7.56	0.587	0.531	0.353	0.201	0.0838
308.15	7.05	0.598	0.544	0.366	0.211	0.0909
313.15	6.61	0.613	0.558	0.381	0.222	0.104
318.15	6.22	0.625	0.572	0.397	0.232	0.109
323.15	5.82	0.645	0.584	0.410	0.242	0.117
$P_2 \cdot 10^6$/Pa	0.086 to 0.142	0.466 to 0.517	0.563 to 0.632	0.573 to 0.645	0.709 to 0.822	0.712 to 0.844

Table 2. Mole Fraction, at $P^* = 1.0 \cdot 10^5$ Pa, $x^*(= x \cdot P^*/P_2)$, of CO_2, O_2, Ar, N_2, He, and H_2 in Liquid Chloroform with the Ranges of the Measured Partial Pressure of the Gas, P_2/Pa

	$x^* \cdot 10^3$					
T/K	CO_2	O_2	Ar	N_2	H_2	He
283.15	11.4	0.703	0.765	0.367	0.179	0.0728
288.15	10.5	0.712	0.771	0.368	0.185	0.0789
293.15	9.76	0.723	0.789	0.382	0.199	0.0852
298.15	9.08	0.730	0.799	0.397	0.216	0.0942
303.15	8.48	0.742	0.809	0.409	0.230	0.102
308.15	7.84	0.752	0.817	0.425	0.243	0.110
313.15	7.46	0.764	0.826	0.437	0.260	0.119
318.15	6.97	0.776	0.840	0.451	0.273	0.127
323.15	6.52	0.785	0.847	0.467	0.287	0.136
$P_2 \cdot 10^6$/Pa	0.068 to 0.110	0.547 to 0.620	0.495 to 0.559	0.608 to 0.696	0.625 to 0.720	0.721 to 0.863

Table 3. Fitted Parameters H_0/MPa, A, and B for a Semi-Empirical Equation for Henry's Law Constant H at Temperature T/K, $\ln(H/H_0) = A(1 - 298.15/T) + B \ln(T/298.15)$, of CO_2, O_2, Ar, N_2, He, and H_2 in Liquid Dichloromethane and Chloroform from Temperature $T_L = 283.15$ K to $T_H = 323.15$ K

		CO_2	O_2	Ar	N_2	H_2	He
CH_2Cl_2	H_0	12.3(1)	176(1)	193(1)	294(2)	537(4)	1200(33)
	A	4.43(13)	−1.44(13)	−1.56(13)	−2.38(13)	−3.57(16)	−4.52(62)
	B	–	–	–	–	–	–
$CHCl_3$	H_0	11.0(1)	136(1)	125(1)	251(2)	465(8)	1070(39)
	A	4.25(18)	−0.86(20)	−0.80(12)	−1.95(21)	−3.78(40)	−4.87(89)
	B	–	–	–	–	–	–
CCl_4	H_0	9.51	84.4	74.15	230	314	933
	A	3.779	0.550	0.0741	4.087	−2.373	−3.02
	B	–	−0.554	–	−5.646	–	–
	T_H to T_L	283 to 304	273 to 334	248.15 to 373.15	280 to 334	273 to 334	282.71 to 318.13
	ref	6	6	7, 13 to 15	6	6	16

$u(P_T{}^i)$, and $u(P_1{}^{sat,i})$, were $1.4 \cdot 10^3$ Pa, $1.4 \cdot 10^3$ Pa, and $1.0 \cdot 10^2$ Pa, respectively. The uncertainty of H, $u(H)$, can be expressed as a function of $u(P_T)$, $u(P_T{}^i)$, and $u(P_1{}^{sat,i})$, i.e., $u^2(H) = (\partial H/\partial P_T)^2 u^2(P_T) + (\partial H/\partial P_T{}^i)^2 u^2(P_T{}^i) + (\partial H/\partial P_1{}^{sat,i})^2 u^2(P_1{}^{sat,i})$, because the uncertainties of the total volume, the temperature, and the other experimental factors can be neglected comparing with $u(P_T)$, $u(P_T{}^i)$, and $u(P_1{}^{sat,i})$.

The uncertainties of H for He gas reached about 10 % due to the low solubility of He gas. To decrease the uncertainty of H, the resolution of the pressure measurement must be improved.

3. Experimental Results

Tables 1 and 2 show the mole fraction at $P^* = 1.0 \cdot 10^5$ Pa, $x^*(= x \cdot P^*/P_2)$. In liquid dichloromethane, the solubility of CO_2 gas was the highest among the gases studied here, and the order of solubility was $CO_2 > O_2 > Ar > N_2 > H_2 > He$ at any temperature. In liquid chloroform, the order was $CO_2 > Ar > O_2 > N_2 > H_2 > He$ at any temperature. The order in liquid chloroform was the same as both that in liquid carbon tetrachloride found in the IUPAC Solubility Data Series[7] and that predicted from the theoretical equation proposed by Wilhelm and Battino.[12] The measured P_2 and x were then used to calculate H by using eq 5. The following commonly used semiempirical equation was used to correlate H as a function of temperature[6]

$$\ln(H/H_0) = A(1 - T_0/T) \tag{6}$$

where H_0 and A are fitting parameters and $T_0 = 298.15$ K. Table 3 shows H_0 and A for each gas in the liquid chlorinated hydrocarbons and shows those and the additional parameter B for the equation, $\ln(H/H_0) = A(1 - T_0/T) + B \ln(T/T_0)$, in liquid carbon tetrachloride.[6,7,13–16] Figures 2a and b show calculated H of CO_2 and N_2 gas for dichloromethane and chloroform with H previously reported for liquid carbon tetrachloride.[6,7,13–16] Error bars show the standard uncertainty. H for all the gases showed the following order: H in dichloromethane > H in chloroform (> H in carbon tetrachloride). Furthermore, with increasing temperature, H of O_2, Ar, H_2, N_2, and He decreased both in dichloromethane and chloroform as shown in Figure 2a, whereas H of CO_2 increased as shown in Figure 2b.

4. Discussion

We analyzed H by using the following method by Wilhelm and Battino.[12,17] In this method, the interactions of solvent liquid and sorbate gas are considered on the molecular scale, and H/Pa can be expressed as follows.

$$RT\ln(H/P_0) = G_c + G_i + RT\ln[(RT/V_1^0)/P_0] \quad (7)$$

where $V_1^0/\text{m}^3\cdot\text{mol}^{-1}$ is molar volume of solvent; P_0 (= $1.01325\cdot10^5$ Pa) is the constant to convert H/Pa into a dimensionless value; $G_c/(\text{J}\cdot\text{mol}^{-1})$ and $G_i/(\text{J}\cdot\text{mol}^{-1})$ are the partial molar Gibbs energies of cavity formation and interaction, respectively. The expression for G_c for a fluid of hard spheres was derived by Reiss et al.,[18] who obtained for pressures around atmospheric

$$G_c = RT\left[6\frac{y}{1-y}\left\{2\left(\frac{\sigma_{12}}{\sigma_1}\right)^2 - \frac{\sigma_{12}}{\sigma_1}\right\} + 18\left(\frac{y}{1-y}\right)^2\left\{\left(\frac{\sigma_{12}}{\sigma_1}\right)^2 - \frac{\sigma_{12}}{\sigma_1} + \frac{1}{4}\right\} - \ln(1-y)\right] \quad (8)$$

where $y = (\pi\sigma_1^3\rho)/6$ (unit less); ρ/m^{-3} is the molecular density N_A/V_1^0 of the fluid (N_A/mol^{-1} is Avogadro's constant); and σ_1/m is the Lennerd-Jones (LJ) diameter of a solvent molecule and $\sigma_{12} = (\sigma_1 + \sigma_2)/2$, in which σ_2/m is the LJ diameter of a gas molecule. σ_{12} corresponds to the LJ diameter between solvent and gas molecules. $G_i/(\text{J}\cdot\text{mol}^{-1})$ is approximated as the molar interaction energy $U_i/(\text{J}\cdot\text{mol}^{-1})$ of solute.[12,17] $U_i/(\text{J}\cdot\text{mol}^{-1})$ is decomposed into two terms, $U_{\text{disp}}/(\text{J}\cdot\text{mol}^{-1})$ and $U_{\text{ind}}/(\text{J}\cdot\text{mol}^{-1})$, where $U_{\text{disp}}/(\text{J}\cdot\text{mol}^{-1})$ is the dispersion energy and $U_{\text{ind}}/(\text{J}\cdot\text{mol}^{-1})$ is the induced energy.

$$G_i \approx U_i = U_{\text{disp}} + U_{\text{ind}} \approx \left[-\frac{32}{9}\pi\rho R(\varepsilon_1/k)^{1/2}(\varepsilon_2/k)^{1/2}\sigma_{12}^{\ 3}\right] + \left[-\frac{4}{3}\rho N_A\frac{\alpha_2\cdot10^{-6}\cdot(3.335\cdot10^{-30}\cdot\mu_1)^2}{\varepsilon_{\text{ele}}\sigma_{12}^{\ 3}}\right] \quad (9)$$

where U_{disp} and U_{ind} are the first and the second term of the equation, respectively. ε_1/J and ε_2/J are the absolute values of the depth of the LJ pair potential function between solvent molecules and gas molecules, respectively; μ_1/D is the dipole moment of the solvent (= 1.8 D for dichloromethane and 1.1 D for chloroform[9]); α_2/cm^3 is the polarizability of the solute; and $\varepsilon_{\text{ele}}/(\text{J}^{-1}\cdot\text{C}^2\cdot\text{m}^{-1})$ is the permittivity of a vacuum (= $8.854\cdot10^{-12}$ $\text{J}^{-1}\cdot\text{C}^2\cdot\text{m}^{-1}$). Here, $\sigma_1 = 4.51\cdot10^{-10}$ m for dichloromethane and $4.96\cdot10^{-10}$ m for chloroform, both of which were calculated from H for He at 298.15 K using the method by Wilhelm and Battino.[12] Substituting eq 8 and 9 into eq 7 yields the following expression for the dispersion energy, $U_{\text{disp}}/(\text{J}\cdot\text{mol}^{-1})$

$$U_{\text{disp}} = RT\ln(H/P_0) - G_c - U_{\text{ind}} - RT\ln[(RT/V_1^0)/P_0] \quad (10)$$

Figures 3a and b show U_{disp} calculated using eq 10 and show experimental results of H/MPa with respect to $\rho(\varepsilon_2/k)^{1/2}\sigma_{12}^{\ 3}/\text{K}^{1/2}$ in liquid dichloromethane and chloroform. For both liquids, a linear plot was obtained, and the slope of the line should be $32/9R\pi(\varepsilon_1/k)^{1/2}/(\text{J}\cdot\text{K}^{-1/2}\cdot\text{mol}^{-1})$ depending on eq 9. Here, based on a fitted line by using the least-squares method, $(\varepsilon_1/k) = 311$ K for dichloromethane and 409 K for chloroform. The literature reports $\sigma_1 = 5.36\cdot10^{-10}$ m and $\varepsilon_1/k = 528$ K for carbon tetrachloride and $\sigma_1 = 3.70\cdot10^{-10}$ m and $\varepsilon_1/k = 157$ K for methane molecules.[12] Both the estimated σ_1 and ε_1/k for dichloromethane and chloroform are larger than those for methane and less than those for carbon tetrachloride.

For all gases and temperature, $U_{\text{ind}}/U_i < 0.25$ in both dichloromethane and chloroform (e.g., at 298.15 K, $U_{\text{ind}}/U_i = 0.056$ and 0.014 for CO_2 gas in dichloromethane and chloroform, respectively). These results suggest that the potential induced by the dipole moment of dichloromethane or chloroform has relatively no effect on the interaction between gas and solvent and that the dispersion force is the dominant factor in the interaction between nonpolar gases, such as the gases investigated in this study.

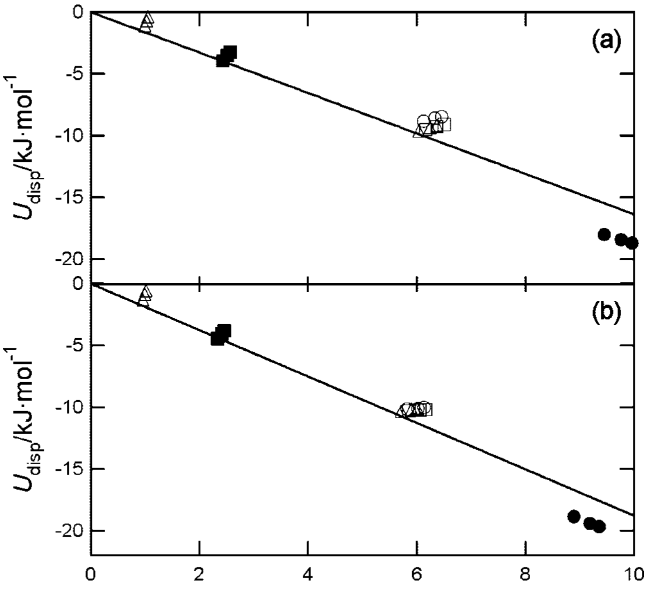

Figure 3. Estimated dispersion energies, $U_{\text{disp}}/\text{kj}\cdot\text{mol}^{-1}$ between gas molecules of (a) dichloromethane and (b) chloroform determined from measured Henry's law constant, H/Pa, with respect to $\rho(\varepsilon_2/k)^{1/2}\sigma_{12}^{\ 3}/\text{K}^{1/2}$ at 283.15 K, 298.51 K, and 323.15 K. ●, that for CO_2; □, O_2; ○, Ar; △, N_2; ■, H_2; ▲, He. ρ/m^{-3} is the molecular density of solvents: i.e., $N_A/V_1^0/\text{m}^3\cdot\text{mol}^{-1}$ where N_A is Avogadro's constant = $6.02\cdot10^{23}$ mol^{-1} and $V_1^0/\text{m}^3\cdot\text{mol}^{-1}$ is molar volume of liquid. ε_2/J is the absolute value of the depth of the LJ pair potential function between gas−gas molecules. k (=$1.38\cdot10^{-23}$ $\text{J}\cdot\text{K}^{-1}$) is the Boltzmann constant. σ_{12}/m is the LJ diameter between solvent−gas molecules.

Note that the measured H of O_2, Ar, N_2, H_2, and He decreases with increasing temperature, whereas the H calculated using eqs 7, 8, and 9 increases. This difference suggests that the entropic effect in G_i in eq 7 cannot be neglected, whereas it is neglected in eq 9. In contrast, with increasing temperature, the calculated H of CO_2 shows the same trend as the measured H of CO_2 for both solvents This suggests that the dispersion energy between CO_2−(dichloromethane or chloroform) is sufficiently high that the entropic effect is negligible. In conclusion, the temperature dependence of Henry's law constant for CO_2 depends primarily on the energetic effect, whereas that of the other gases (O_2, Ar, H_2, N_2, and He) depends primarily on the entropic effect.

5. Conclusions

Solubilities of gases (CO_2, O_2, Ar, H_2, N_2, and He) at a temperature range from (283.15 to 323.15) K in liquid dichloromethane and chloroform were determined by first measuring the decrease in pressure due to absorption and then estimating the gas solubility by using semiempirical correlations based on these measurements. Results revealed that, except for CO_2 gas, Henry's law constant decreased with increasing temperature in both liquids and that the order of the solubility of gases was $CO_2 > O_2 > \text{Ar} > H_2 > N_2 > \text{He}$ in dichloromethane and $CO_2 > \text{Ar} > O_2 > H_2 > N_2 > \text{He}$ in chloroform. Theoretical analysis of the solubility data using the method by Wilhelm and Battino[12,17] revealed the following three key points. (1) The resulting theoretical LJ potential parameters for both liquids are higher than those for methane but lower than those for carbon tetrachloride. (2) The dispersion interaction between solvent molecules and gas molecules is much stronger than the induced interaction for nonpolar gases in dichloromethane and chloroform, despite the dipole moment of these solvent liquids. (3) The temperature dependence of Henry's law constant for CO_2 depends on the energetic effect, whereas that of the other gases (O_2, Ar, H_2, N_2, and He) depends on the entropic effect.

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