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Thermodynamic and Magnetic Studies on the Formation of *gem*-Diol in an Aldehyde–Water Mixture

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A thermodynamic study on the formation of *gem*-diol in an aldehyde–water mixture was carried out by NMR measurements. The equilibrium constants for the formation of *gem*-diol were determined at 280.3—298.4 K. From the relationship between the equilibrium constant and the temperature, ΔH and ΔS were obtained to be $-20.4\ \text{kJ mol}^{-1}$ and $-101\ \text{J K}^{-1}\ \text{mol}^{-1}$ in the case of acetaldehyde, and $-22.9\ \text{kJ mol}^{-1}$ and $-110\ \text{J K}^{-1}\ \text{mol}^{-1}$ in the case of propionaldehyde, respectively. It is difficult to isolate the *gem*-diol from an aldehyde–water mixture. The diamagnetic susceptibility of *gem*-diol was estimated by measuring the susceptibilities of the aldehyde–water mixture at various molar ratios. The diamagnetic susceptibility was determined using Gouy's method. The diamagnetic susceptibilities of 1,1-ethanediol and 1,1-propanediol were $-39.1\times10^{-6}\ \text{cm}^3\ \text{mol}^{-1}$ and $-51.5\times10^{-6}\ \text{cm}^3\ \text{mol}^{-1}$ at 287 K, respectively.

It has been well-known that the aldehyde bound with water forms hydrated aldehyde consisting of *gem*-diol in aqueous solution.[1—11] It is difficult to isolate the *gem*-diol, though the presence of $-CH(OH)_2$ is considered to be one of the active intermediates in organic reactions. There have been many reports on studies for determining the enthalpy change for the formation of the *gem*-diol compound in a mixture of aldehyde and water.[2—5,7,10,11] The enthalpy changes for the acetaldehyde–water mixture were reported to be between -20.5 and $-36\ \text{kJ mol}^{-1}$, which were determined using different concentrations of acetaldehyde. For a thermodynamic determination, the activity should be used instead of the concentration. However, the enthalpy changes reported above were calculated from equilibrium constants obtained at various concentrations.

There has been no report on the diamagnetic susceptibilities of *gem*-diol, because free *gem*-diol is hardly separated, except for 2,2,2-trichloroacetaldehyde hydrate. We have reported that the diamagnetic susceptibility of the concerned compound can be determined by calculating the results on the diamagnetic susceptibilities of various mixtures according to Wiedemann's additive law.[12,13]

This paper presents the results on (1) equilibrium constants and enthalpy changes in the formation of hydrated aldehydes of acetaldehyde and propionaldehyde by NMR measurements and (2) the diamagnetic susceptibilities of *gem*-diol measured in a mixture.

Calculation

Equilibrium Constant of *gem*-Diol Formation. In the equilibrium of aldehyde bound to water to form *gem*-diol,

$$RCHO + H_2O \rightleftharpoons RCH(OH)_2,$$

the equilibrium constant (K) can be expressed by

$$K = \frac{a_D}{a_A \cdot a_W} = \frac{1}{\gamma} \cdot \frac{C_D}{C_A \cdot C_W}, \tag{1}$$

where a, C, and γ are the activity, concentration, and activity coefficient, and subscripts A, D, and W are aldehyde, *gem*-diol, and water, respectively. Let K_C be $K_C = C_D/(C_A \cdot C_W)$. The K_C's were obtained experimentally. The K in Eq. 1 could be determined from a calculation involving extrapolation at zero concentration of aldehyde, since $\gamma \to 1$ and in turn $K_C \to K$.

In Eqs. 2 and 3, $C_W{}^0$ is defined as the total concentration of free water and water bound with aldehyde in a mixture, and C_t is defined as the total concentration of free aldehyde and *gem*-diol:

$$C_W{}^0 = C_W + C_D, \tag{2}$$

$$C_t = C_A + C_D. \tag{3}$$

Let r be the ratio of C_D against C_A; then,

$$r = C_D/C_A = x_D/x_A, \tag{4}$$

where x is the molar fraction. All denotations are summarized in Table 1.

The C_t's are given based on the experimental conditions. Consequently, the K_C's can be calculated by the following equation in terms of C_t, x, and r:

Table 1. The Denotation of Concentration and Molar Fraction on Chemical Species

		H_2O	RCHO	$RCH(OH)_2$
Concentration	in preparation	$C_W{}^0$	C_t	0
	in mixture	C_W	C_A	C_D
Molar fraction	in preparation	$1-x$	x	0
	in mixture	x_W	x_A	x_D

$$K_C = r \Big/ C_t\left(\frac{1-x}{x} - \frac{r}{1+r}\right). \tag{5}$$

Diamagnetic Susceptibility. The observed diamagnetic susceptibility (χ_{obsd}) is a gram-diamagnetic susceptibility, which is replaced by the molar diamagnetic susceptibility (χ_{mix}). The molar diamagnetic susceptibilities of the aldehyde and water mixture were calculated by the following equations according to Wiedemann's additive law:[13]

$$\chi_{\mathrm{mix}} = (x_A m_A + x_D m_D + x_W m_W)\chi_{\mathrm{obsd}}, \tag{6}$$

$$\chi_{\mathrm{mix}} = x_A\chi_A + x_D\chi_D + x_W\chi_W, \tag{7}$$

where m, x, and χ are the molecular weight, molar fraction, and molar diamagnetic susceptibility; the subscripts, mix, A, D, and W, are mixture, free aldehyde, *gem*-diol, and water, respectively. From all equations with definitions, we obtain

$$x_A = \left(\frac{1}{1+r}\right) \Big/ \left(\frac{1}{x} - \frac{r}{1+r}\right), \tag{8}$$

$$x_D = \left(\frac{r}{1+r}\right) \Big/ \left(\frac{1}{x} - \frac{r}{1+r}\right). \tag{9}$$

The x's are determined by the experimental conditions, and the r's by a NMR measurement.

Materials and Method

Materials. Acetaldehyde, propionaldehyde, and 2,2,2-trichloroacetaldehyde hydrate were purchased as guaranteed grade or the best commercially available. Propionaldehyde was used after distillation.

Measuring Apparatus. A Varian NMR instrument (VXR-300) and a Varian (UNITY-INOVA) were used to measure the NMR spectra. The temperatures were measured by using a relationship between the temperature and the chemical shift difference between the methyl and hydroxy signals of methanol. The chemical shifts of the proton signal were measured with respect to tetramethylsilane as a standard, which is filled in a capillary tube inserted into the NMR tube. The molar ratio of *gem*-diol against aldehyde was obtained from the ratio of the signal area of two methyl signals: one for aldehyde and the other for *gem*-diol in case of the acetaldehyde–water system. In the same way, two methylene signals of aldehyde and *gem*-diol were adopted to calculate the molar ratio of *gem*-diol against aldehyde in the case of the propionaldehyde–water system. The pulse-repetition time is 5 s. This is longer than the relaxation time of the proton signal in ordinary organic compounds. Therefore, it is possible to determine the signal area, even supposing an experimental error.

The diamagnetic susceptibilities were measured by Gouy's method at 298.2±0.2 and 287.2±0.2 K in the same manner as described in previous papers.[12,14—16]

Results and Discussion

The Equilibrium of Aldehyde Bound to Water to Form *gem*-Diol. The chemical shift of *gem*-diol was identified from the NMR spectra. The methyl chemical shift (doublet) of free acetaldehyde and that of *gem*-diol appeared at 1.64 and 0.73 ppm, respectively, in the case that the molar fraction of total aldehyde (x) is 0.031 in aqueous solution at 287.5 K. From both areas of the methyl signal, r ($=[\mathrm{CH_3CH(OH)_2}]/[\mathrm{CH_3CHO}]$) was obtained. The relationship between r and x is shown in Fig. 1. The ratio of *gem*-diol seems to reach a constant by extrapolating the total aldehyde concentration to zero, and to increase at lower temperature.

The methylene chemical shift (quartet) of free propionaldehyde and that of *gem*-diol appeared at 1.96 and 0.99 ppm, respectively, in the case that the molar fraction of total aldehyde is 0.027 at 287.5 K. Figure 2 shows the relationship between r and x, which is similar to that in Fig. 1.

The Equilibrium Constants, ΔH and ΔS. A aqueous solutions of acetaldehyde and propionaldehyde with various molar fractions (x) were prepared, and the r's were determined from the NMR spectra. The K_C's were calculated according to Eq. 5 with r and x. The results are shown in

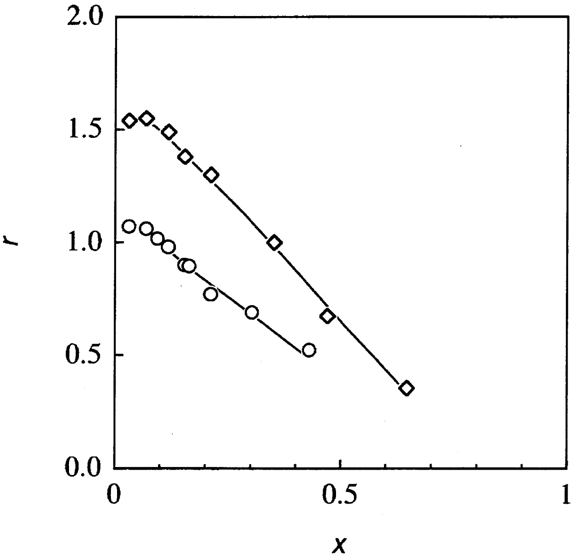

Fig. 1. The molar ratio of *gem*-diol to aldehyde in acetaldehyde–water mixture. ○: 298 K, ◇: 287 K.

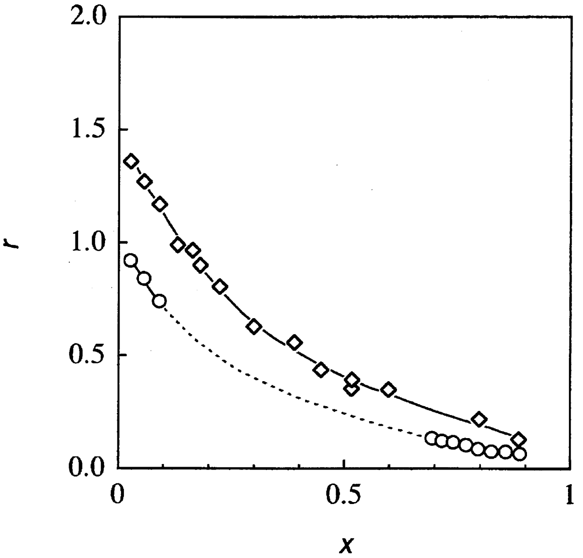

Fig. 2. The molar ratio of *gem*-diol to aldehyde in propionaldehyde–water mixture. ○: 298 K, ◇: 287 K.

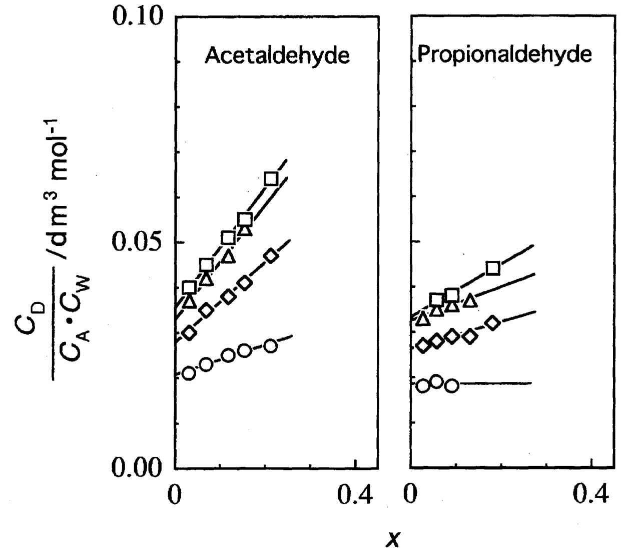

Fig. 3. The equilibrium constant for the formation of *gem*-diol in aldehyde–water mixture. □: 280.3 K, △: 281.5 K, ◇: 287.5 K, ○: 298.4 K.

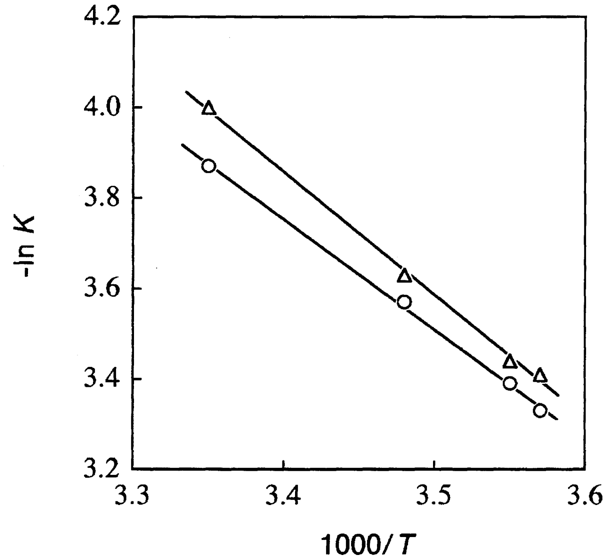

Fig. 4. The plots of $\ln K$ vs. $1/T$. ○: acetaldehyde–water mixture, △: propionaldehyde–water mixture.

Fig. 3. The K_C's decreased with decreasing the molar fraction of aldehyde. The concentration of aldehyde was used instead of the activity to calculate the K_C's. Therefore, the K_C's obtained by extrapolation to zero concentration of aldehyde and by $\gamma \rightarrow 1$ in Eq. 1 were considered as the equilibrium constant (K) for the formation of *gem*-diol.

The plots of K's vs. temperature fell on straight lines, as shown in Fig. 4. This fact indicates that an aqueous solution of aldehyde may consist of the equilibrium system of only $RCHO+H_2O \rightleftarrows RCH(OH)_2$. From the slope and the intercept of the lines, ΔH and ΔS were obtained. The results are summarized in Table 2.

Many authors[2—5,7,10,11] have reported various values of ΔH for the formation of *gem*-diol of acetaldehyde. The molar ratio in each report is different for the determination of ΔH. Kurz obtained $\Delta H = -23.5$ kJ mol^{-1} by the calorimetric method;[7] Ferino et al. reported -23.8 kJ mol^{-1}, but details were unclear;[11] -21 kJ mol^{-1} and -23 kJ mol^{-1} were obtained by a measurement of dehydration rate of *gem*-diol using $x = 0.004$—0.01 of acetaldehyde,[5] and by a spectrophotometric determination using $x < 0.002$;[10] -36 kJ mol^{-1} was obtained by a Raman spectrophotometric method using $x = 0.28$.[3] These results indicate that ΔH depends on x. On the other hand, -20.5 kJ mol^{-1} was reported using $x = 0.3$.[2] This result was obtained from the slope of the line in relationship between $\ln K$ vs. $1/T$ on the NMR data. The slope of the line was determined by using the least-squares method. However, we reexamined their data carefully and obtained -36 kJ mol^{-1} when we deleted some plots which were apart from the line obtained by the least-squares method. This -36 kJ mol^{-1} was in accord with the value obtained from Fig. 3 at $x = 0.3$. Figure 3 demonstrates that the respective value of ΔH can be calculated from the different molar ratio of aldehyde. As a conclusion, the K at zero concentration of aldehyde should be considered to be the equilibrium constant.

Diamagnetic Susceptibilities of Aldehyde–Water Mixtures. Acetaldehyde and propionaldehyde aqueous solutions containing various molar fractions of aldehyde were prepared for measurements of the diamagnetic susceptibilities. The results obtained at 298 K are shown in Fig. 5. The diamagnetic susceptibility of an acetaldehyde–water mixture could not be determined at higher than 0.5 of the molar ratio of acetaldehyde due to volatility. Since the boiling point of acetaldehyde is 294 K, the susceptibility of neat acetaldehyde

Table 2. The Thermodynamic Data for the Formation of *gem*-Diol in Aldehyde–Water Mixture

	Temperature	$C_D/(C_A \cdot C_W)$	$-\Delta H$	$-\Delta S$
	K	dm^{3}mol^{-1}	kJ mol^{-1}	J K^{-1} mol^{-1}
Acetaldehyde–Water	280.3	0.036	20.4	101
	281.5	0.034		
	287.5	0.028		
	298.4	0.021		
Propionaldehyde–Water	280.3	0.033	22.9	110
	281.5	0.032		
	287.5	0.026		
	298.4	0.018		

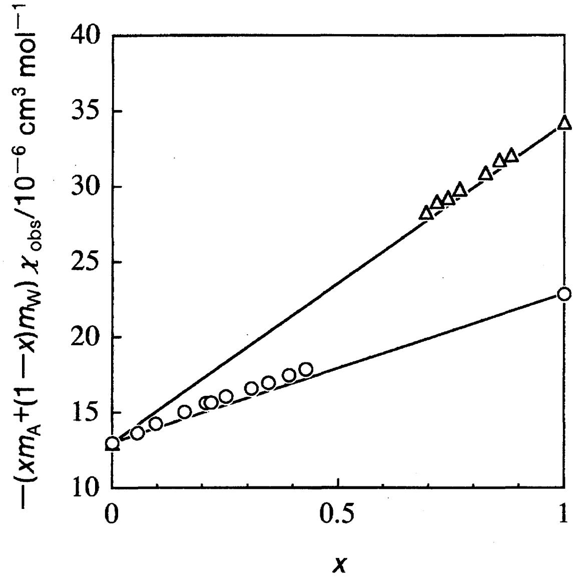

Fig. 5. The diamagnetic susceptibilities of aldehyde–water mixture at 298 K. ○: acetaldehyde, △: propionaldehyde.

could not be determined at 298 K. Therefore, the susceptibility of acetaldehyde was obtained by an estimation from a straight line which was drawn on plots of the susceptibility vs. carbon number of the alkyl group in various normal chained aldehydes, as shown in Fig. 6.[17] From the slope and the intercept of the straight line in Fig. 6, the diamagnetic susceptibilities of the CH_2 group and the CHO group were obtained to be -11.3×10^{-6} cm^3 mol^{-1} and -9.5×10^{-6} cm^3 mol^{-1}, respectively. From Fig. 6, the diamagnetic susceptibility of acetaldehyde was estimated to be -22.9×10^{-6} cm^3 mol^{-1}. This is in accord with -22.6×10^{-6} cm^3 mol^{-1} obtained at 293 K.

The diamagnetic susceptibilities of a propionaldehyde–water mixture at 298 K could not be determined at higher than 0.1 and lower than 0.65 of the molar ratio of propionaldehyde, because mutual dissolution could not occur in between propionaldehyde and water (dotted line in Fig. 2). Propionaldehyde dissolved in water mutually in the region of all molar ratios at 287 K. The results are shown in Fig. 7.

In both cases of aldehyde, plots appeared slightly above the lines, which are drawn according to Wiedemann's additive law on diamagnetic susceptibility of mixture. This fact suggested that *gem*-diol might be formed in the aldehyde–water mixture.

Diamagnetic Susceptibility of *gem*-Diol. The diamagnetic susceptibility of the aldehyde–water mixture was considered to consist of the sum of the susceptibilities of free aldehyde, water, and *gem*-diol. The susceptibilities of free aldehyde and water were obtained by a direct measurement. The ratio of *gem*-diol against free aldehyde (r) could be determined from the NMR spectra. Therefore, the diamagnetic susceptibility of *gem*-diol was obtained from a calculation with Eqs. 6, 7, 8, and 9.

In the case of the acetaldehyde–water mixture at 298 and 287 K, the experimental data, each molar fraction calculated, and the diamagnetic susceptibility of *gem*-diol are summarized in Table 3. The calculated susceptibility of *gem*-diol was almost constant in all regions of the molar fraction of aldehyde. The susceptibility of the acetaldehyde–water mixture was deduced to obey the Wiedemann's additive law while considering *gem*-diol.

In the case of the propionaldehyde–water mixture, the same results as for acetaldehyde were obtained, as shown in Table 4. The diamagnetic susceptibility of 1,1-propanediol, -51.5×10^{-6} cm^3 mol^{-1} at 287 K was nearly in accord with the sum of 1,1-ethanediol, -39.1×10^{-6} cm^3 mol^{-1} and methylene group, -11.3×10^{-6} cm^3 mol^{-1}. Since the susceptibility of 1,1-propanediol at 298 K was not determined experimentally, it was estimated to be -51.8×10^{-6} cm^3 mol^{-1} by adding -11.3×10^{-6} cm^3 mol^{-1} of the meth-

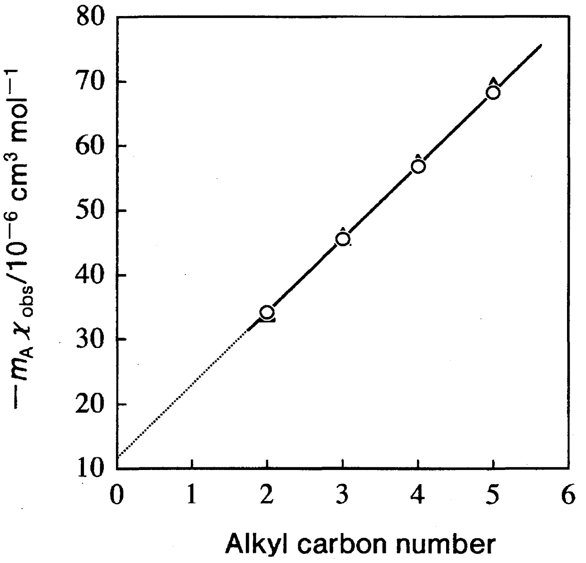

Fig. 6. The diamagnetic susceptibilities of aliphatic aldehyde at 298 K. ○: our data, △: reference data.[17]

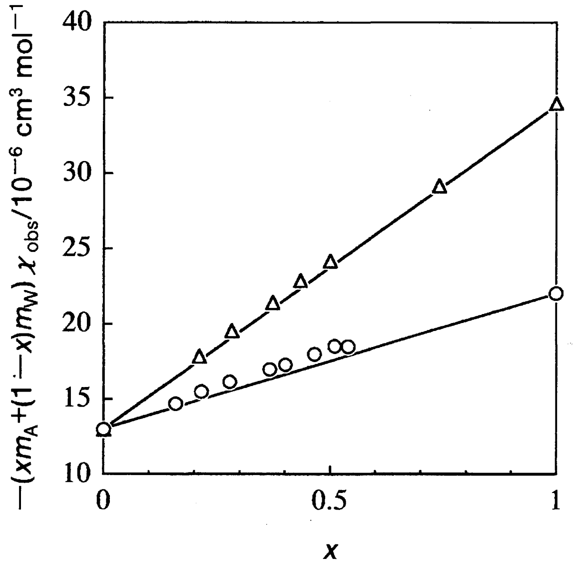

Fig. 7. The diamagnetic susceptibilities of aldehyde–water mixture at 287 K. ○: acetaldehyde, △: propionaldehyde.

Table 3. Estimation of Molar Diamagnetic Susceptibility of *gem*-Diol in Acetaldehyde–Water Mixture

x	r	x_A	x_D	$-\chi_{mix}$ 10^{-6} cm^3 mol^{-1}	$-\chi_D$ 10^{-6} cm^3 mol^{-1}
T=298 K					
0.220	0.80	0.135	0.108	17.3	40.7
0.253	0.76	0.162	0.122	18.0	41.1
0.309	0.67	0.211	0.143	18.9	40.1
0.347	0.62	0.247	0.153	19.6	40.1
0.392	0.56	0.292	0.164	20.4	40.5
0.429	0.52	0.330	0.172	20.9	40.4
					Average 40.5±0.5
T=287 K					
0.216	1.28	0.108	0.138	17.6	39.3
0.278	1.15	0.152	0.175	18.9	39.2
0.366	0.96	0.228	0.219	20.7	38.7
0.401	0.88	0.262	0.231	21.3	38.8
0.465	0.74	0.333	0.246	22.4	39.0
0.510	0.64	0.388	0.248	23.1	39.6
					Average 39.1±0.5

Table 4. Estimation of Molar Diamagnetic Susceptibility of *gem*-Diol in Propionaldehyde–Water Mixture at 287 K

x	r	x_A	x_D	$-\chi_{mix}$ 10^{-6} cm^3 mol^{-1}	$-\chi_D$ 10^{-6} cm^3 mol^{-1}
0.211	0.85	0.126	0.107	19.7	51.1
0.283	0.70	0.188	0.132	22.1	52.0
0.373	0.55	0.277	0.152	24.7	51.2
0.434	0.48	0.341	0.164	26.6	52.1
0.500	0.42	0.414	0.174	28.4	51.1
					Average 51.5±0.5

ylene group to -40.5×10^{-6} cm^3 mol^{-1} of 1,1-ethanediol.

From the diamagnetic susceptibilities of acetaldehyde (-22.9×10^{-6} cm^3 mol^{-1}) and the CHO group (-9.5×10^{-6} cm^3 mol^{-1}), we obtained -13.4×10^{-6} cm^3 mol^{-1} as the CH_3 group. In turn, from the diamagnetic susceptibilities of 1,1-ethanediol (-40.5×10^{-6} cm^3 mol^{-1}) and the CH_3 group, we obtained -27.1×10^{-6} cm^3 mol^{-1} as the $CH(OH)_2$ group. This is different from the sum (-22.5×10^{-6} cm^3 mol^{-1}) of the CHO group (-9.5×10^{-6} cm^3 mol^{-1}) and water (-13.0×10^{-6} cm^3 mol^{-1}).

The NMR spectra showed that the chemical shifts of CHO and $CH(OH)_2$ appeared at 9.75 and 5.26 ppm to the lower field from the tetramethylsilane signal. This result indicates that the shielding effect of $CH(OH)_2$ is larger than that of CHO. The shielding effect on the chemical shift is known to depend on the diamagnetic susceptibility. It is well-known that the chemical shift of the CHO group appears in the lower field caused by the diamagnetic anisotropic effect.[18] The CO double bond in the CHO group is considered to reduce the diamagnetic susceptibility. Consequently, the chemical shift of $CH(OH)_2$, of which the diamagnetic susceptibility is larger than CHO, appears at a higher field than that of CHO.

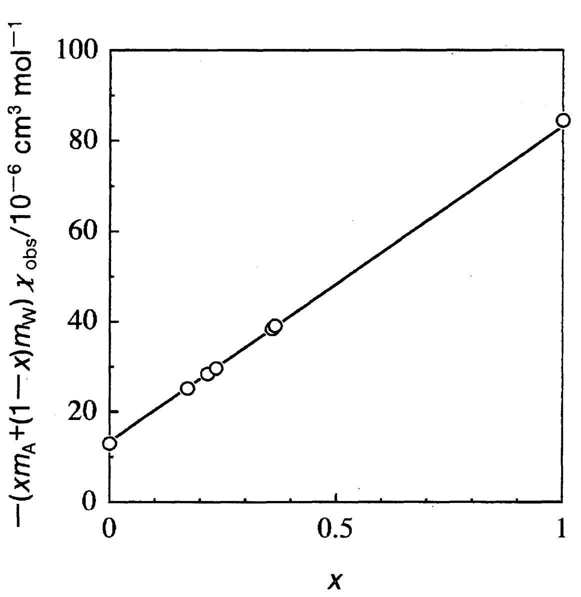

Fig. 8. The diamagnetic susceptibilities of 2,2,2-trichloroacetaldehyde–water mixture at 298 K.

Diamagnetic Susceptibility of 2,2,2-Trichloro-1,1-ethanediol Aqueous Solution. 2,2,2-Trichloroacetaldehyde hydrate is well-known to be a compound of *gem*-diol. The diamagnetic susceptibilities of an aqueous solution containing various molar ratios of 2,2,2-trichloroacetaldehyde are shown in Fig. 8. The plots fall on a straight line due to obeying Wiedemann's additive law. From the NMR spectra, only 2,2,2-trichloro-1,1-ethanediol was observed in water. The result, -83.9×10^{-6} cm^3 mol^{-1}, as shown in Fig. 8, is in accord with -84.4×10^{-6} cm^3 mol^{-1}, which was obtained by measuring a powder of 2,2,2-trichloroacetaldehyde hydrate.

The diamagnetic susceptibilities of chloroform and hydrogen were known to be -59.3×10^{-6} cm^3 mol^{-1} and -2.0×10^{-6} cm^3 mol^{-1},[17] respectively. The diamagnetic susceptibility of 2,2,2-trichloro-1,1-ethanediol was obtained to be -84.4×10^{-6} cm^3 mol^{-1} from a calculation using the following equation:

$$\chi[CCl_3CH(OH)_2] = \chi[HCCl_3] - \chi[H] + \chi[CH(OH)_2].$$

This is in accord with the experimental result. It is concluded that the diamagnetic susceptibility of the other *gem*-diol can be estimated by a calculation using -27.1×10^{-6} cm^3 mol^{-1} for the $CH(OH)_2$ group.

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