The Change of Diamagnetic Susceptibility and the Thermodynamic Data due to Hydrogen Bonding between 2-Propanol and Various Hydrogen Acceptors

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The diamagnetic susceptibility and the equilibrium constants were determined for systems of 2-propanol and various kinds of hydrogen acceptors. Acetone, methyl ethyl ketone, tetrahydrofuran, dimethyl sulfoxide, and *N*, *N*-dimethylacetamide were used as hydrogen acceptors. The diamagnetic susceptibility of 2-propanol without self-association was estimated to be -41.7×10^{-6} cm^3 mol^{-1} from the results for mixtures of 2-propanol and carbon tetrachloride. Then the sum of the diamagnetic susceptibilities of both a hydrogen acceptor and 2-propanol without self-association was calculated. From the differences between experimental results and calculated values, the changes of diamagnetic susceptibility ($\Delta\chi_M$) due to hydrogen bonding were estimated to be in the region of 9.0—13.5×10^{-6}cm^3 mol^{-1}. ΔH, ΔS, and ΔG due to hydrogen bonding were determined. $\Delta\chi_M$ seemed to be related to ΔS and ΔG. On the other hand, ΔH was -17.9—18.7 kJ mol^{-1}, and it seemed not to be related to $\Delta\chi_M$.

The change of diamagnetic susceptibility ($\Delta\chi$) decreases with increasing ΔG on the hydrolysis of organic phosphate including a high-energy phosphate bond to form the OH compound.[1] This result suggested that the change of diamagnetic susceptibility before and after hydrolysis might be equivalent to a situation change of the pair of electrons which formed a covalent bond. If so, such hydrogen bonding is suggested to be a suitable subject matter in order to deal with a situation change of the pair of electrons in place of hydrolysis. When the pair of nonbonding electrons formed a hydrogen bond, the freedom of electrons might be restricted by such bond formation. Consequently, the diamagnetic susceptibility of "pair of electrons" might change before and after the formation of hydrogen bond. There have been many papers concerning the changes of diamagnetic susceptibility due to the formation of hydrogen bonds in butanol, acetic acid, etc.[2—8] However, no paper has yet discussed the change of diamagnetic susceptibility in connection with the thermodynamic data. It is well known that ΔG, ΔH, and ΔS can be easily determined in the study of hydrogen bonding. The effect of solvation should be considered for the hydrogen bonding in solution. Therefore, it might not completely elucidate in the connection with thermodynamic data to change the diamagnetic susceptibility, but it was expected to obtain the result on above-described relationship.

One of the authors in this paper has already studied the hydrogen bonding of 2-propanol (2-PrOH) in order to determine the thermodynamic data by an NMR method.[9]

The purposes of this paper are to determine the changes of diamagnetic susceptibility due to hydrogen bonding of 2-PrOH to various hydrogen acceptors and to investigate the relationship between the thermodynamic data and the change of diamagnetic susceptibility.

Theory

The molar diamagnetic susceptibility of 2-PrOH monomer can be calculated according to Pascal's additive law.[10] This value calulated was in accord with the molar diamagnetic susceptibility of 2-PrOH in CCl_4 solution obtained experimentally. The self-association of 2-PrOH should be removed from the mixture of 2-PrOH and hydrogen acceptor before the determination of diamagnetic susceptibility. As shown in Fig. 1, we can draw a tangent line by extrapolation to zero 2-PrOH mole fraction in the 2-PrOH–CCl_4 system, and this tangent line is extended to 1 of 2-PrOH mole fraction. The value at 1 of 2-PrOH mole fraction was found to be in accord with the calculated one. Therefore, this value was considered to be the molar diamagnetic susceptibility of 2-PrOH monomer.

If there is no mutual interaction between 2-PrOH monomer and hydrogen acceptor, the diamagnetic susceptibility of the mixture must be in a linear relation

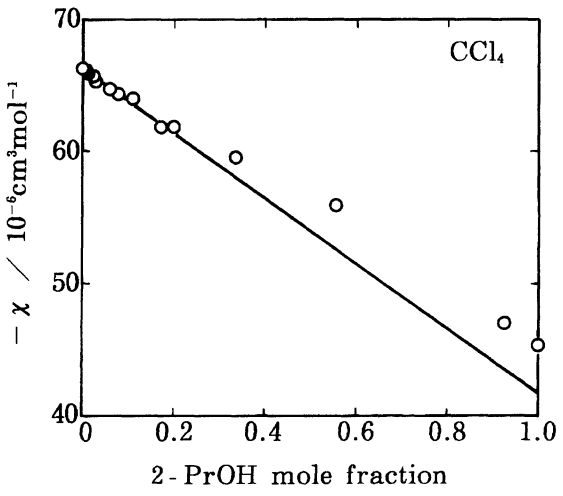

Fig. 1. The diamagnetic susceptibility of 2-PrOH–CCl_4 mixture.

with the mole fraction obtained as shown in Fig. 2 (a solid line using the diamagnetic susceptibility of 2-PrOH monomer). However, plots did not fall on a straight line. $\Delta\chi$ represents the difference between the plots and the straight line at the same mole fraction in Fig. 2.

Under the condition of [total 2−PrOH]≪[total hydrogen acceptor], almost all 2-PrOH can participate in hydrogen bonding with hydrogen acceptors. Then the concentration of 2-PrOH monomer might be low enough to neglect the self-association. Plots of $\Delta\chi$ divided by mole fraction (x) were extrapolated to $x\rightarrow 0$. The value at $x=0$ must be the difference between the diamagnetic susceptibility of 2-PrOH monomer–hydrogen acceptor complex and the sum of diamagnetic susceptibilities of 2-PrOH monomer and hydrogen acceptor. It should be equivalent to the change of diamagnetic susceptibility ($\Delta\chi_M$) of a pair of nonbonding electrons in the various hydrogen acceptors before and after hydrogen bonding:

$$\Delta\chi_M = \lim_{x\rightarrow 0} \frac{\Delta\chi}{x}. \quad (1)$$

The equilibrium constant, K, of hydrogen bonding was determined by the NMR method, using Eq. 2 under the condition of [total 2−PrOH]≪[total hydrogen acceptor] at each temperature as described in the previous paper.[9] In Eq. 2, A and, ν, ν_f, and ν_c denote the concentration of hydrogen acceptor, and the chemical shift of OH proton signal in every 2-PrOH sample solution, the chemical shift of OH proton signal of 2-PrOH monomer itself and that of 2-PrOH monomer-hydrogen acceptor complex.

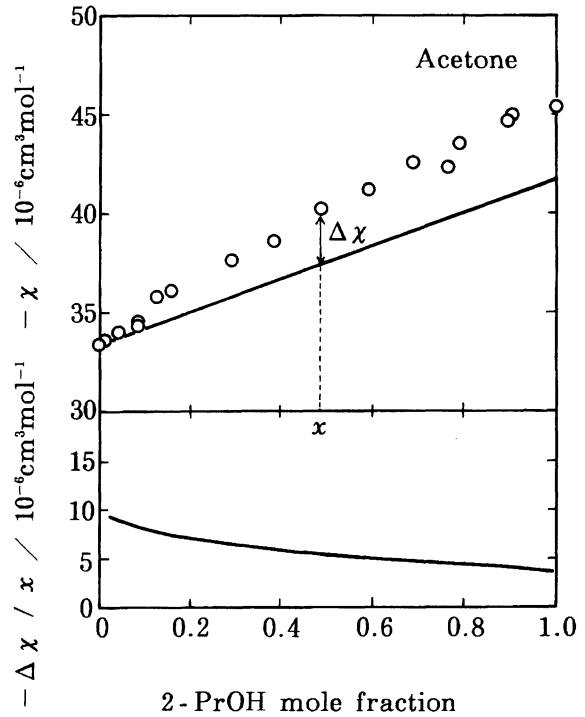

Fig. 2. The diamagnetic susceptibility of 2-PrOH–acetone mixture.

$$\frac{1}{\nu-\nu_f} = \frac{1}{K(\nu_c-\nu_f)A} + \frac{1}{\nu_c-\nu_f}. \quad (2)$$

Experimental

Reagents and Sample Solutions. Organic solvents such as *N,N*-dimethylacetamide (DMA), dimethyl sulfoxide (DMSO), acetone, and methyl ethyl ketone (MEK) including 2-PrOH used were purchased from Kanto Chemical Co., Inc. as guaranteed grade. Tetrahydrofuran (THF) was used after distillation. In order to avoid contamination by moisture during storage, a small amount of 0.3 nm molecular sieve was added in each solvent.

For the NMR chemical shift measurement, 0.04 mol dm^{-3} 2-PrOH in CCl_4 solution containing various concentrations of hydrogen acceptor was prepared. For the measurement of diamagnetic susceptibility, 2-PrOH was mixed with each hydrogen acceptor at various mole fractions. All sample solutions were prepared in a dry-box.

Equipments and Methods. The diamagnetic susceptibility was measured by Gouy's method, as described in a previous paper.[1,11] The temperature was kept constant at 25±1 °C.

A Varian NMR instrument VXR-300 was used for the NMR measurement. The OH proton signal of 2-PrOH was determined as the chemical shift from the proton signal of tetramethylsilane. In the NMR measurement, temperatures were estimated from the differences of chemical shifts between CH_3 and OH proton signal of methanol, according to the reference date already known.

Results

The Diamagnetic Susceptibility. The results for the magnetic susceptibility are shown in Figs. 2, 3, and 4. In all measurements, the experimental error was estimated to be within ±1%. The diamagnetic susceptibilities of 2-PrOH and hydrogen acceptors are shown in Table 1. The diamagnetic susceptibilities of 2-PrOH, acetone, MEK, DMA in Figs. 1, 2, and 3 were in accord with reference data.[12] There was no data reported on THF and DMSO. The solid lines at the top of Figs. 2, 3, and 4 were estimated from the sum of diamagnetic susceptibilities of 2-PrOH monomer and each hydrogen acceptor without hydrogen bonding. Results did not fall on solid line, due to hydrogen bonding. The values of $\Delta\chi/x$ were determined from the data in each figure (top). Plots of $\Delta\chi/x$ against x are shown by the lines at the bottom in the figures. $\Delta\chi_M$ was obtained by the extrapolation of this line to zero of 2-PrOH mole fraction. The experimental error was within ±5%. The result is summarized in the last column in Table 2.

The Hydrogen Bonding. ν_f Measurement: In order to determine the ν_f, we obtained the chemical shift of OH proton signal of 2-PrOH at 316 K to be 0.752, 0.763, and 0.823 ppm with respect to 0.0102, 0.0204, and 0.0511 mol dm^{-3} 2-PrOH in CCl_4. From the extrapolation to zero concentration of 2-PrOH, ν_f was estimated to be 0.747 ppm. In the previous paper, ν_f was 0.77 ppm.[9] This is because 0.025 mol dm^{-3} was then available as the measurable minimum concen-

Table 1. The Molar Diamagnetic Susceptibility of Various Compounds

Compound	Molar diamagnetic susceptibility / 10^{-6} cm^3 mol^{-1}		
	Present data	Reference data	Calculated data
2-Propanol	−45.3	−45.7—46.0	−41.7[a)]
N,*N*-Dimethylacetamide	−55.3	−55.8—56.1	
Dimethyl sulfoxide	−43.6		
Acetone	−33.4	−33.6—34.1	
Tetrahydrofuran	−50.4		
Methyl ethyl ketone	−45.5	−45.6	

a) This value is in accord with one estimated from 2-PrOH–CCl_4 system in Fig. 1.

Table 2. The Changes of Diamagnetic Susceptibility ($\Delta\chi_M$) and the Thermodynamic Data due to Hydrogen Bonding between 2-PrOH and Hydrogen Acceptor

Hydrogen acceptor	Temp / K	ν_c / ppm	K / dm^{-3} mol	$-\Delta H$ / kJ mol^{-1}	$-\Delta S$ / J K^{-1} mol^{-1}	$-\Delta G$ (25 °C) / kJ mol^{-1}	$-\Delta\chi_M$ / 10^{-6} cm^3 mol^{-1}
Dimethyl sulfoxide	288	4.06	6.07	18.3	49	3.86	13.5
	316	4.00	3.10				
N,*N*-Dimethylacetamide	288	4.35	4.16	18.3	52	2.92	13.5
	316	4.32	2.13				
Acetone	288	2.85	1.80	17.9	57	0.85	9.7
	316	2.78	0.93				
Tetrahydrofuran	288	3.15	1.48	18.7	62	0.33	9.3
	316	3.09	0.75				
Methyl ethyl kenote	288	2.99	1.46	18.7	62	0.31	9.0
	316	2.97	0.74				

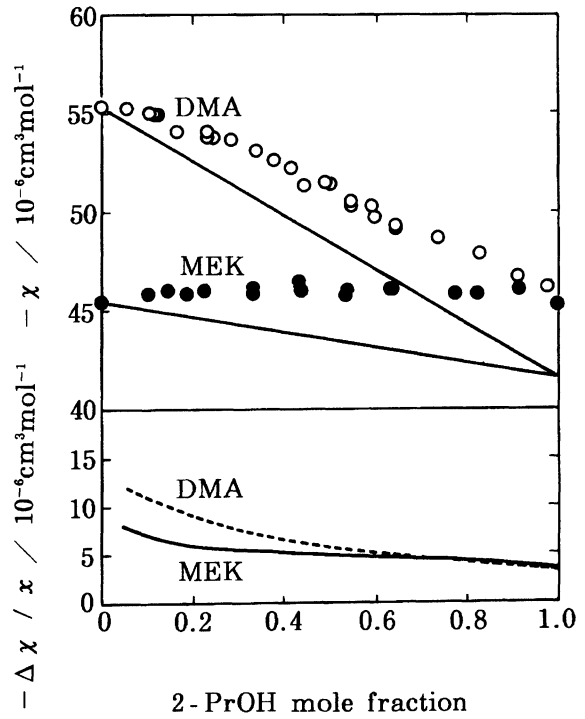

Fig. 3. The diamagnetic susceptibilities of 2-PrOH–*N*,*N*-dimethylacetamide mixture and 2-PrOH–methyl ethyl ketone mixture.

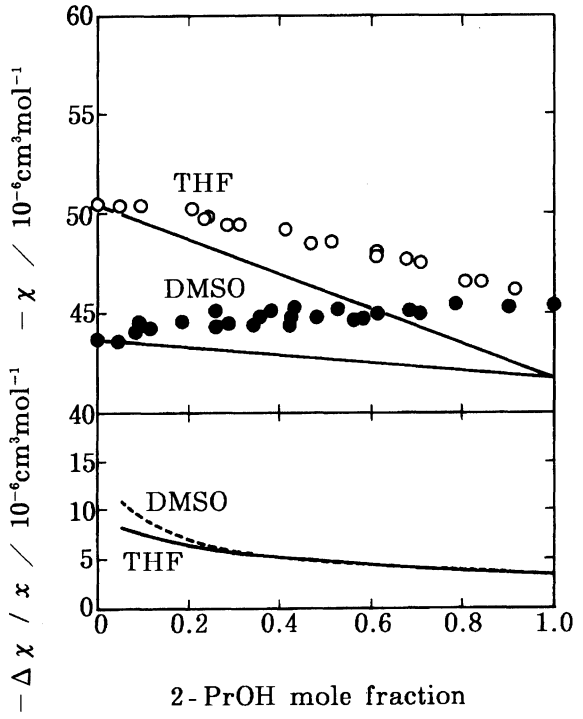

Fig. 4. The diamagnetic susceptibilities of 2-PrOH–dimethyl sulfoxide mixture and 2-PrOH–tetrahydrofuran mixture.

tration. We can now measure the OH proton signal to lower concentrations of 2-PrOH. Consequently, the data in this paper are thought to be more reliable for the OH proton signal of 2-PrOH monomer.

The Equilibrium Constants: The chemical shifts of OH proton signals of 2-PrOH were determined at 288 and 316 K using 0.04 mol dm^{-3} 2-PrOH in CCl_4 containing various concentrations of hydrogen acceptor. The OH proton signal was found to shift to lower field due to hydrogen bonding. The results are shown in Figs. 5 and 6 plotted according to Eq. 2. Plots fall on each straight line. The equilibrium constant, K and ν_c were obtained from the slope and the intercept of the straight line. The experimental error is estimated to be less than 1%. ΔH and ΔS were obtained by thermodynamic calculations. These results are summarized in Table 2.

Discussion

$\Delta\chi_M$ was in the region of (9.0—13.5)$\times 10^{-6}$ cm^3 mol^{-1}. The diamagnetic susceptibilities of every 2-PrOH-hydrogen acceptor complex were greater than that estimated under the condition of no mutual interaction between 2-PrOH monomer and hydrogen acceptor in the mixture. The changes of diamagnetic susceptibility have been reported in the cases of hydrogen bonding of acetic acid to dioxane or ethyl acetate.[5] In that case, the differences were much smaller. A similar result was reported on butanol hydrogen bonding to methyl isobutyl ketone.[6] It is suggested that the differences in both acetic acid and butanol cases might be greater than the results reported, if the diamagnetic susceptibility of mixture could be estimated by assuming the condition of neither self-association nor hydrogen bonding.

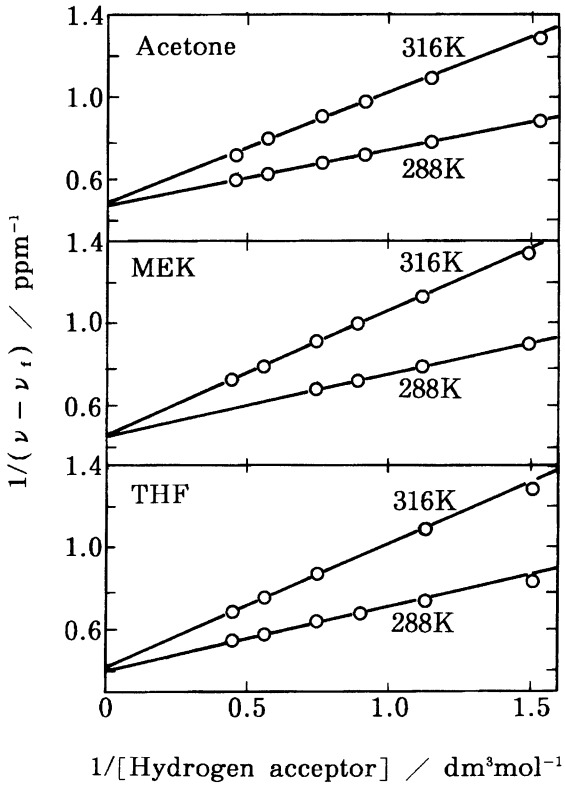

Fig. 5. Plots of $1/(\nu-\nu_f)$ vs. 1/[hydrogen acceptor] of acetone, tetrahydrofuran, and methyl ethyl ketone.

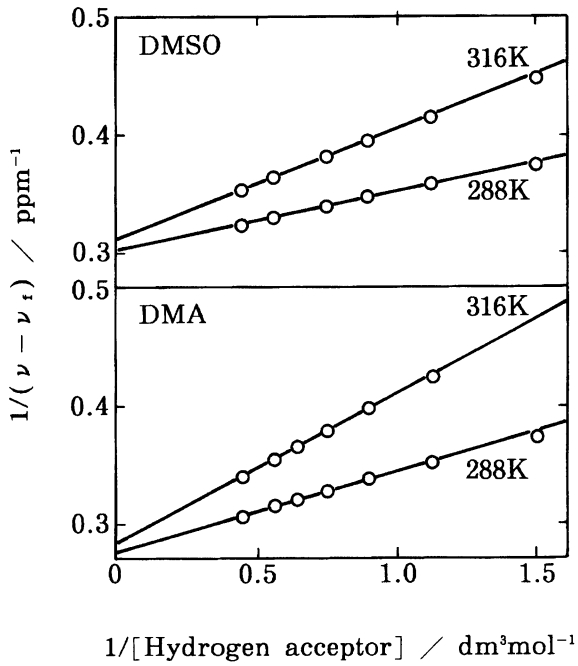

Fig. 6. Plots of $1/(\nu-\nu_f)$ vs. 1/[hydrogen acceptor] of dimethyl sulfoxide and *N*,*N*-dimethylacetamide.

The value of ΔH ($=-2.4$ kcal mol$^{-1}=-10.0$ kJ mol^{-1}) for the case of 2-PrOH–DMA system reported in the previous paper[9] was not in accord with the present one (-18.3 kJ mol^{-1}). This is because both ν_f and the concentration of 2-PrOH used in the present work are different from the values in the previous paper. The present result is more reliable.

In the case of organic phosphates,[1] only the relationship, between ΔG and $\Delta\chi$ was discussed. In this paper, both ΔH and ΔS were discussed in addition to

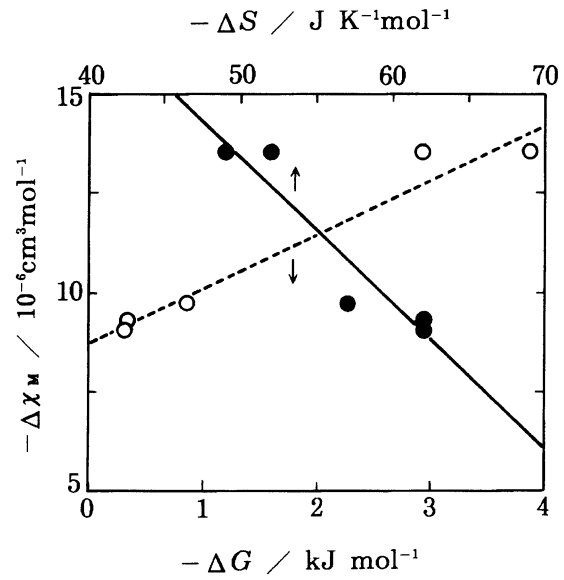

Fig. 7. Plots of $\Delta\chi_M$ against ΔG and ΔS.

ΔG. The relationship between the thermodynamic data and $\Delta\chi_M$ is shown in Fig. 7. $\Delta\chi_M$ seems to be related to ΔS and ΔG. On the other hand, $\Delta\chi_M$ seems not to be related to ΔH, of which the values are almost constant in Table 2. It seems that the pair of nonbonding electrons may get more freedom, and may be more susceptible to an external magnetic field. However, further investigation is necessary to confirm this speculation.

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