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Studies on the Proton Magnetic Resonance Spectra of Aliphatic Systems. VIII.[1] Complex Shift and Equilibrium Constant of Aliphatic Alcohol-Tris(dipivalomethanato)europium Complex in Solution

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1:1 Complex formation between Eu(DPM)$_3$ and aliphatic alcohol was confirmed under the condition of [Eu(DPM)$_3$]$\gtrsim$[ROH] in a dilute solution, where the concentrations of donor [ROH] and acceptor [Eu(DPM)$_3$] are below 0.02 M, respectively. Of the two parameters K_c and Δ_c estimated by the computer simulation of the equilibrium equation, the formers are solvent dependent, whereas the latters are not. Δ_{AD} and ΔG estimated from the solute-solvent interaction model are comparable with the 1:1 complex shift Δ_c and free energy obtained from the temperature dependence of K_c, and the infinite concentration shifts Δ_{ic} are also comparable with Δ_c.

Keywords——proton magnetic resonance; shift reagent; complex shift; equilibrium constant; thermodynamic parameter; solvent effect; infinite concentration shift; solution theory; solute-solvent interaction

Introduction

In the previous report,[1] the system aliphatic alcohol+Eu(DPM)$_3$ has been intensively studied as a typical weak interaction with the 1:1 complex formation in CCl$_4$. We extended here our work to discuss the induced paramagnetic shift under the view point of the chemical equilibrium, and the complex shifts and equilibrium constants were estimated by the simulation of the equilibrium equation under the condition of [ROH]$\lesssim$Eu(DPM)$_3$ in a few kinds of solvents. In addition, considering the role of the solvent occupying an overwhelming majority than the two solutes in solution, a modified Benesi-Hildebrand type equation derived from the solute-solvent interaction model[3] was introduced for the estimation of the 1:1 complex shift and the free energy of the complex formation. And, as another approach, the so-called infinite concentration shift Δ_{ic} was estimated from the linear relation between the succesive dilution shift *vs.* $C^{-2/3}$ of equimolar solution, where C means the molarity of the solute.

Experimental

Aliphatic alcohols used in this work were of the J.I.S. grade. They were dried over Linde molecular sieves 4A for some days before use. The shift reagent Eu(DPM)$_3$ purchased from Dojin Chemical Laboratories was sublimed under reduced pressure and stored over silica gel in a desiccator. Sample preparations were carried out in an air-conditioned room. All nuclear magnetic resonance (NMR) spectra were measured in a Hitachi R-22 type high resolution NMR spectrometer in CCl$_4$, CDCl$_3$, CH$_2$Cl$_2$(CD$_2$Cl$_2$) or cyclo-C$_6$H$_{12}$ containing 0.3% Me$_4$Si as an internal reference. Chemical shifts were measured using a frequency counter with an accuracy of ±1.0 Hz. The calibration of temperature was carried out by ethyleneglycol with an accuracy of ±1°. Experimental conditions are mentioned in the figures and tables.

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[1] Part VII: Y. Sasaki, H. Kawaki and Y. Okazaki, *Chem. Pharm. Bull.* (Tokyo), **23**, 2432 (1975).

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[3] *a*) J.M. Prausnitz, "Molecular Thermodynamics of Fluid-Phase Equilibria," Chapter 7, Prentice Hall, New Jersey, 1969; *c*) J. Homer and A.R. Dudley, *J.C.S. Faraday II*, **69**, 1955 (1973).

Results and Discussion

Determination of the Complex Shift and Equilibrium Constant

At an equilibrium of the 1 : 1 complex formation as Eq. 1,

$$A + D \rightleftarrows AD \tag{1}$$

and when the activity coefficients are approximated to 1, an equilibrium constant K_c is expressed as Eq. 2;

$$K_c = \frac{C_{AD}}{(C_A^\circ - C_{AD})(C_D^\circ - C_{AD})} \tag{2}$$

where C_A° and C_D° represent the initial concentrations of the donor [ROH] and acceptor[Eu(DPM)$_3$], and C_{AD} means an equilibrium concentration of the complex. In the NMR method, the calculated shift of the donor is shown as follows;

$$\Delta_{calc.} = \frac{C_{AD}}{C_D^\circ} \Delta_c \tag{3}$$

where $\Delta_{calc.}$ and Δ_c are equivalent to $\delta_{calc.} - \delta_D$ and $\delta_{AD} - \delta_D$ respectively.

$\Delta_{calc.}$ therefore is expressed as the function of K_c and Δ_c (*cf.* Eq. 4). Then we employed a simulation method to obtain the K_c and Δ_c, *i. e.* they are determined so as to give the best fit between $\Delta_{calc.}$ and $\Delta_{obs.}$[4]

TABLE I. Complex Shifts Δ_c (ppm) and Equilibrium Constants K_c(M^{-1}) estimated from Simulation Method of Equimolar Solution at 35° in CCl_4

	Δ_c (ppm)$^{a)}$				K_c (M^{-1})
	α	β	γ	δ	
n-C_3H_7OH	26.4	14.6	9.2		623±37
n-C_4H_9OH	28.3			5.2	818± 7
Iso-C_4H_9OH	27.0		10.4		608±70
s-C_4H_9OH		15.1	9.3		482± 4
t-C_4H_9OH		18.3			351

a) Error being within ±5%.

TABLE II. Complex Shifts Δ_c (ppm) and Equilibrium Constants K_c (M^{-1}) estimated from Simulation Method at 35°

		cyclohexane		CCl_4		$CDCl_3$		$CH_2Cl_2(CD_2Cl_2)$	
		Δ_c (ppm)$^{a)}$	K_c (M^{-1})$^{b)}$	Δ_c (ppm)$^{a)}$	K_c (M^{-1})$^{b)}$	Δ_c (ppm)$^{a)}$	K_c (M^{-1})$^{b)}$	Δ_c (ppm)$^{a)}$	K_c (M^{-1})$^{b)}$
n-C_4H_9OH	I	4.6	778	5.2	818	5.7	7.0	5.2	88
	II			5.0	781			5.4	138
Iso-C_4H_9OH	I	9.2	811	10.4	608	11.2	71	10.3	129
	II	9.0	979	9.1	674	11.5	79		
s-C_4H_9OH	I	9.7 *15.8	609	9.3 *15.1	482	10.1 *16.3	54	*16.8	104
	II	9.2 *14.9	802	*15.5	610	10.9 *15.5	88	10.2 *17.3	126
t-C_4H_9OH	I	18.2	571			20.4	44	21.8	44

I; $C_D^\circ = C_A^\circ = 0.002$—$0.02$ M, II, $C_D^\circ = 0.001$—0.007 M, $C_A^\circ = 0.002$—0.02 M.

a) Complex shifts of Me groups. *=α-Me groups. Error being within ±5%

b) Equilibrium constants estimated from Me groups. Error being within ±10%

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[4] Root mean square deviations were minimized by NEAC 2200 Model 500 computer at Osaka University Computer Center utilizing a library program DAVID.

$$\Delta_{\mathrm{calc.}} = \frac{\{K_c(C^\circ_A+C^\circ_D)+1\} - [\{K_c(C^\circ_A+C^\circ_D)+1\}^2 - 4K_c^2 C^\circ_A C^\circ_D]^{1/2}}{2K_c \cdot C^\circ_D}\,\Delta_c \qquad (4)$$

Δ_c and K_c obtained under the condition of [ROH]$\lesssim$[Eu(DPM)$_3$] in a few kinds of solvents were summarized in Tables I and II, and the calculated shifts successfully reproduced the observed values as shown in Fig. 1. As shown in Table II, Δ_c is solvent independent, whereas K_c decreases as the dielectric constant of solvent increases. The S values[1,5] formerly obtained from the slopes of linear relations between the induced shifts *vs.* molar ratio [Eu(DPM$_3$)]/[ROH] under the large excess of bases well reproduced the 1:1 complex shifts Δ_c (*cf.* Fig. 2) and provided the following Eq. 5.

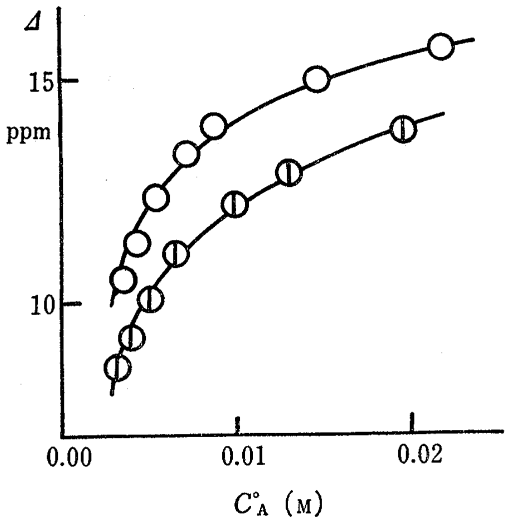

Fig. 1. Comparisons between $\Delta_{\mathrm{calc.}}$ and $\Delta_{\mathrm{obs.}}$ of t-C_4H_9OH at 35 °C in CCl_4

——=calculated curves, ○ and ⏀=experimental points of C°_A/C°_D=2.15 and 1.04, respectively.

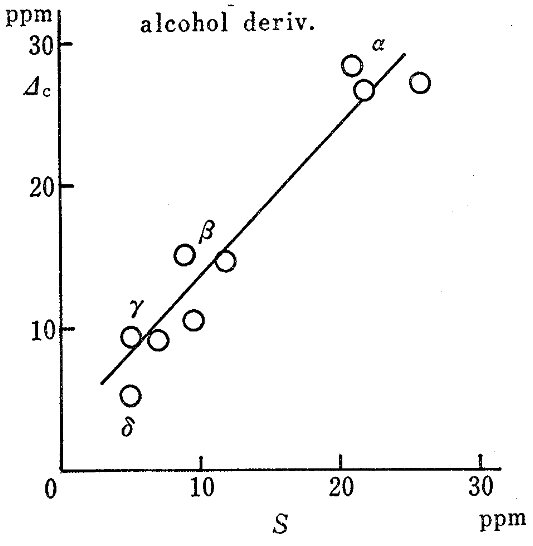

Fig. 2. Correlations between Complex Shifts Δ_c and Paramagnetic Shift Parameters S of each Proton of ROH (R=n-C_3H_7–, n-C_4H_9–, iso-C_4H_9–, s-C_4H_9– and t-C_4H_9–)

Eu(DPM)$_3$/Substrate$\lesssim$0.02
Substrate Concentration=0.2 M.

$$\Delta_c = 1.07\,S + 2.29 \qquad (5)$$

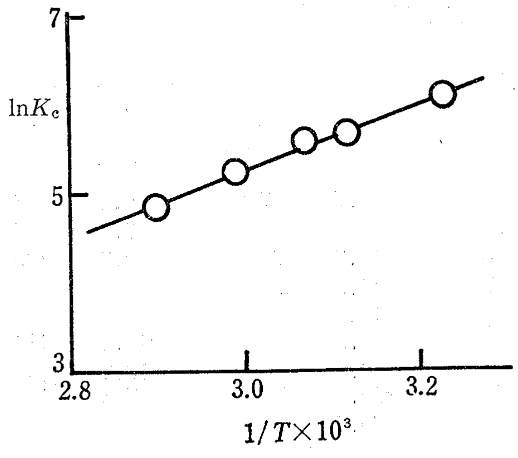

Fig. 3. Correlation between Equilibrium Constants K_c and $1/T$ of t-C_4H_9OH

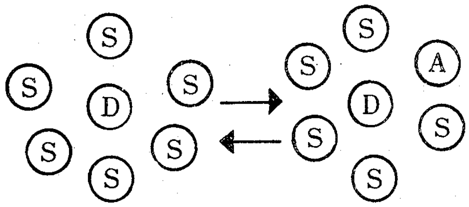

Fig. 4. Solute-Solvent Interaction Model

A=acceptor molecule, D=donor molecule, S=solvent molecule.

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5) G.V. Smith, W.A. Boyd, and C.C. Hinckley, *J. Am. Chem. Soc.*, **93**, 6319 (1971).

Estimation of Thermodynamic Parameter in CCl_4

Equilibrium constants K_c estimated by the above way at several temperatures afforded the linear relations between $\ln K_c$ *vs.* $1/T$ with positive slopes (*cf.* Fig. 3). These slopes and intercepts present the thermodynamic parameters ΔH and ΔS, the formers are of $-7\sim8$ kcal M^{-1} and the latters are ~-11 e.u. in this series, therefore free energies at 35° are of $-3\sim4$ kcal M^{-1}. These ΔH values are comparable with the order of ordinary hydrogen bonding.

Estimation of 1: 1 Complex Shift and Free Energy by Solute-Solvent Interaction Model

We marked so far only molalities of donor [ROH] and acceptor [Eu(DPM)$_3$], however, these two solutes are surrounded by an overwhelming majority of the solvent molecules. Now, we present a model shown in Fig. 4,[3] where the observed shift $\Delta_{\text{obs.}}$ of the donor [ROH] is expressed by Eq. 6, assuming that the induced shifts are proportional to the fractions of acceptor [Eu(DPM)$_3$] surrounded by the solvent molecules;

$$\Delta_{\text{obs.}} = \frac{kC_A^\circ x}{C_S + kC_A^\circ x}\Delta_{\text{AD}} \tag{6}$$

Rearrangement of the above equation gives

$$1/\Delta_{\text{obs.}} = \Delta_{\text{AD}}/kC_S \cdot 1/C_A^\circ x + 1/\Delta_{\text{AD}} \tag{7}$$

where C_S, k, x and Δ_{AD} represent the molarity of the solvent, Boltzmann factor, molar ratio of C_A°/C_D° and 1: 1 complex shift, respectively. Eq. 7 is an analogue of the Benesi-Hildebrand equation, and k or free energy ΔG and Δ_{AD} are all estimated from the linear relations between $1/\Delta_{\text{obs}}$. and $1/C_A^\circ\, x$ as shown in Fig. 5. Δ_{AD} obtained in this way coincides with Δ_c as shown in Fig. 6 and Eq. 8, and ΔG of ~-3 kcal M^{-1} is comparable with the free energy estimated from the temperature dependence of K_c.

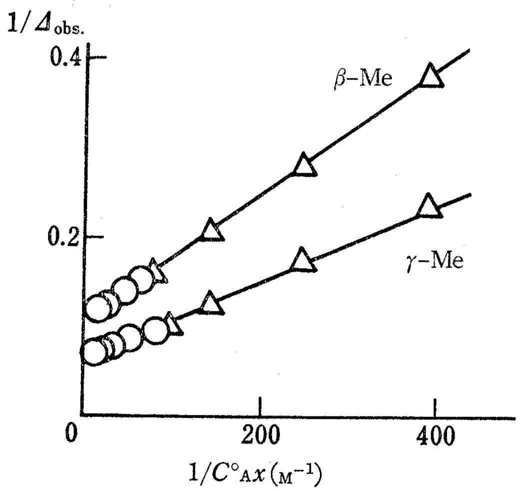

Fig. 5. Correlations between $1/\Delta_{\text{obs.}}$ and $1/C_A \cdot x$ of s-C_4H_9OH at 35° in CCl_4

$C_A^\circ = 0.003$—002 M, $x = C_A^\circ/C_D^\circ = 0.2$—3 (△), $x = 3$ (○).

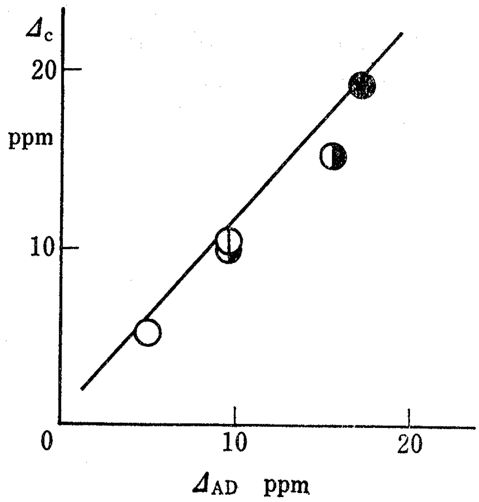

Fig. 6. Correlations between Complex Shifts Δ_c and Δ_{AD} of Me Groups

○ ⦶, ◑, and ● = n-, iso-, s- and t-C_4H_9OH, respectively.

$$\Delta_c = 1.09\,\Delta_{\text{AD}} + 0.47 \tag{8}$$

Thus, we conclude that this solute-solvent interaction model is effective to examine a weak interaction in solution.

Concentration Dependence of Dilution Shift of Equimolar Solution

From the linear relations between the dilution shifts and $(C_D^\circ)^{-2/3}$ of the equimolar solution as illustrated in Fig. 7, Eq. 9 is obtained[6]

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[6] Y. Sasaki, H. Fujiwara, H. Kawaki, and Y. Okazaki, *Chem. Pharm. Bull.* (Tokyo), **25**, 3177 (1977)

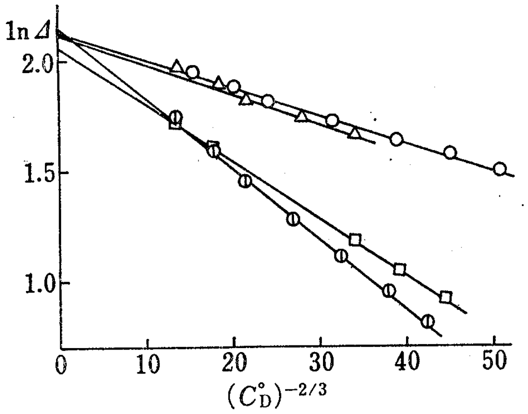

Fig. 7. Correlations between Successive Dilution Shifts of t-C_4H_9OH and $(C_D^\circ)^{-2/3}$

$C_A^\circ = C_D^\circ = 0.002$—0.02 M
Solvent; ○=cyclohexane, △=CCl_4, □=CH_2Cl_2, ⦶=$CDCl_3$.

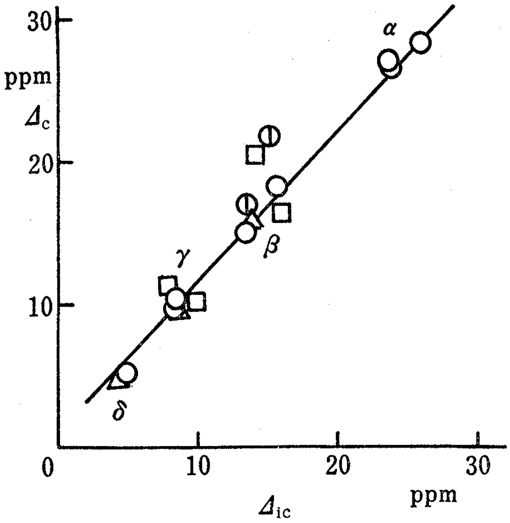

Fig. 8. Correlations between Complex Shifts $\varDelta_c$ and $\varDelta_{ic}$ of each Proton of ROH (R=n-C_3H_7–, n-C_4H_9–, iso-C_4H_9–, s-C_4H_9– and t-C_4H_9–)

Solvent; ○=CCl_4, △=cyclohexane, □=$CDCl_3$, ⦶=$CH_2Cl_2(CD_2Cl_2)$.

$$\ln \varDelta_c = B(C_D^\circ)^{-2/3} + \ln \varDelta_{ic} \qquad (9)$$

where B and $\varDelta_{ic}$ represent the slope and intercept. The infinite concentration shifts $\varDelta_{ic}$ thus obtained are also comparable with $\varDelta_c$ as shown in Fig. 8 and Eq. 10.

$$\varDelta_c = 1.05\varDelta_{ic} + 0.84 \qquad (10)$$