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Studies on the Proton Magnetic Resonance Spectra in Aliphatic Systems. VII.[1] Stoichiometry of Lewis Base and Tris (Dipivalomethanato)-europium Complex in Solution

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The induced paramagnetic shifts between Eu(DPM)$_3$ and aliphatic amines or alcohols were measured to the stoichiometry, *etc.*, with the following results.

1) The continuous variation and molar ratio methods showed a 1: 1 stoichiometry between Lewis base and Eu(DPM)$_3$ complex in CCl$_4$ solution.

2) The shift parameters $S_{0.01}$ and $S_{1.0}$ corresponded well with each other, and the chemical shifts of equimolar mixtures were of the same magnitudes as $S_{1.0}$.

3) The chemical shift differences of the 1: 1 mixture and free base at infinite dilution afforded linear relations between the slope 0.8 and $S_{0.01}$.

4) The induced paramagnetic shift parameters $S_{0.01}$ do not represent the so-called bound chemical shift Δ_B, but are measures of the equilibrium binding constants K_b of the 1: 1 complex formed between Lewis base and Eu(DPM)$_3$.

Introduction

Determination of stoichiometry in solution is an important step in quantitative elucidation of the induced paramagnetic shift between a Lewis base and Eu(DPM)$_3$. This paper reports results on this problem obtained by the continuous variation and molar ratio methods of nuclear magnetic resonance spectrometry.

Experimental

The Lewis bases used in this work were aliphatic amines and alcohols of the J.I.S. grade. They were dried over KOH pellets or molecular sieves for some days before use. The shift reagents Eu(DPM)$_3$ were purchased from Dojin Chemical Laboratories, and stored in a desiccator. Samples were taken in an air conditioned room. Nuclear magnetic resonance spectra were measured in a Hitachi R-22 type high resolution spectrometer in CCl$_4$ solution with Me$_4$Si as internal reference at an optional temperature. Chemical shifts were calibrated using a frequency counter.

Variable temperature experiments were carried out between ~70°—~40° with an external lock mode.

The concentrations of reagents used were as follows.

a. Molar ratio method with Eu(DPM)$_3$
   Concentration of base, 0.2 mole. Concentration of Eu(DPM)$_3$, 0.05—0.3 mole.

b. Continuous variation method with Eu(DPM)$_3$
   Total concentration, 0.4 mole. Concentration of base, 0.15—0.3 mole.

c. Variable temperature experiment
   sec-C$_4$H$_9$NH$_2$/Eu(DPM)$_3$ molar ratio=1/1.1
   n-C$_4$H$_9$NH$_2$/Eu(DPM)$_3$ molar ratio=1/0.02

Results and Discussion

Continuous Variation and Molar Ratio Methods

As shown in Figs. 1 and 2, the results obtained by these two methods suggest the formation of a 1: 1 complex between base and reagent in solution, in all cases except with triethylamine.

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[1] Part VI: Y. Sasaki, H. Kawaki and Y. Okazaki, *Chem. Pharm. Bull.* (Tokyo), 23, 1899 (1975).

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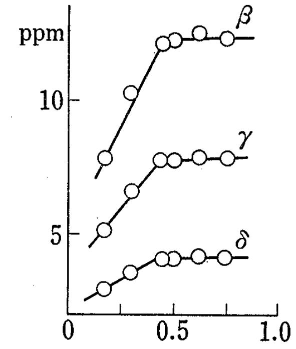

Fig. 1. Continuous Variation Method with n-$C_4H_9NH_2$+$Eu(DPM)_3$

total concentration=0.4 mole

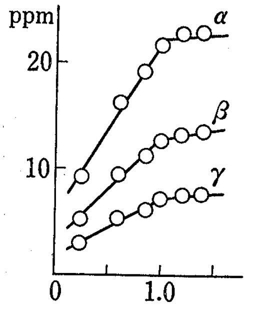

Fig. 2. Molar Ratio Method with *sec*-$C_4H_9NH_2$+$Eu(DPM)_3$

base concentration=0.2 mole

Formerly, it was concluded from the NMR time scale that complexed and free bases are in rapid equilibrium, and that only a time-averaged spectrum of the Lewis base can be observed.[3,4]

Accordingly, the separate signals of free and complexed species cannot be observed at the same time, and phenomenological treatment is necessary for examination of the chemical equilibrium.

In this work almost all the patterns obtained in the continuous variation, and molar ratio methods showed inflections with equimolar mixtures.

The induced shift parameters $S_{1.0}$ (*i.e.* estimated from the slopes at a reagent/substrate ratio of 1.0) corresponded well with the shift parameters $S_{0.01}$ reported in the previous paper[1] (*cf.* Fig. 3a—b and Table Ia—b).

Next, the infinite dilution shifts of 1:1 complexes were measured. As examples Fig. 5a and 5b show results on the infinite dilution signal patterns of n-$PrNH_2$ and n-PrOH and valuer for the chemical shift differences $\Delta\delta_{\text{inf.}}$ (*i.e.* the chemical shift differences between the 1:1 complex and free Lewis base at infinite dilution) are summarized in Table II.

These $\Delta\delta_{\text{inf.}}$ values for each position were linearly related with the $S_{0.01}$ values, as shown in Fig. 5.

The above experimental results can be summarized as follows:

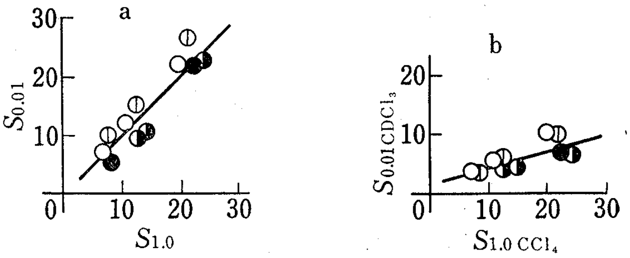

Fig. 3. (a) Correlations between $S_{0.01}$ and $S_{1.0}$ of Simple Aliphatic Alcohols in CCl_4
(b) Correlations between $S_{0.01}$ in $CDCl_3$ and $S_{1.0}$ in CCl_4 of Simple Aliphatic Alcohols

○: n-propyl alcohol
⦶: isobutyl alcohol
◑: *sec*-butyl alcohol
●: n-butyl alcohol

$$\begin{tikzcd} S_{0.01} \arrow[rr, leftrightarrow] \arrow[dr, leftrightarrow] & & S_{1.0} \arrow[dl, leftrightarrow] \\ & \text{Infite dilution shift} \\ & \Delta\delta_{\text{inf.}} & \end{tikzcd}$$

The correlations of $S_{0.01}$, $S_{1.0}$ and $\Delta\delta_{\text{inf}}$. in CCl_4 solution are as follows:

$$S_{0.01} = 1.02S_{1.0} - 0.52$$
$$S_{0.01} = 1.85\Delta\delta_{\text{inf.}} + 0.09$$
$$S_{1.0} = 1.91\Delta\delta_{\text{inf.}} - 0.17$$

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[3] D.R. Eaton, *J. Am. Chem. Soc.*, **87**, 3097 (1965).
[4] C.C. Hinckley, *J. Am. Chem. Soc.*, **91**, 5160 (1969).

Table Ia. Induced Paramagnetic Shift Parameters $S_{0.01}$ of Aliphatic Alcohols at 35° in CCl_4

	α	β	γ	δ
n-PrOH	21.8	11.8	7.1	
n-BuOH	21.1			5.0
iso-BuOH	25.9	14.8	9.6	
sec-BuOH	22.0	10.0 CH_2 9.0 Me	5.0	
neo-$C_5H_{11}OH$	11.4		4.3	

$S_{0.01}$=shift parameter at a $Eu(DPM)_3$/substrate molar ratio of 0.01
substrate concentration=0.2 mole

Table Ib. Induced Paramagnetic Shift Parameters $S_{1.0}$ of Aliphatic Alcohols at 35° in CCl_4

	α	β	γ	δ
n-PrOH	19.9	10.8	6.7	
n-BuOH	22.4	11.8	8.2	3.5
iso-BuOH	21.7	12.6	7.5	
sec-BuOH	24.5	14.3 CH_2 12.8 Me		

$S_{1.00}$=shift parameter at a $Eu(DPM)_3$/substrate molar ratio of 1.0
substrate concentration=0.2 mole

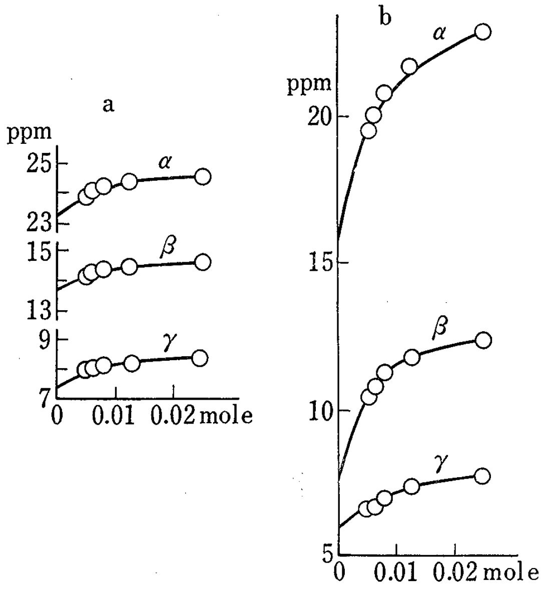

Fig. 4. (a) Infinite Dilution Shifts of Equimolar Mixtures of *n*-$C_3H_7NH_2$ and $Eu(DPM)_3$ in CCl_4
(b) Infinite Dilution Shifts of Equimolar Mixtures of *n*-C_3H_7OH and $Eu(DPM)_3$ in CCl_4

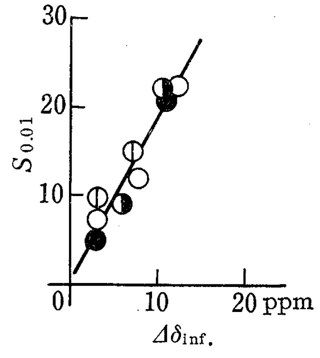

Fig. 5. Correlations between $S_{0.01}$ and Infinite Dilution Shift Difereces $\Delta\delta_{inf.}$ of Simple Aliphatic Alcohols in CCl_4

○: *n*-propyl alcohol
⦶: iso-butyl alcohol
◑: *sec*-butyl alcohol
●: *n*-butyl alcohol

Table II. Infinite Dilution Shift Differences $\Delta\delta_{\mathrm{inf.}}$ (ppm) of Equimolar Mixtures of Eu(DPM)$_3$ and Aliphatic Alcohols at 35° in CCl$_4$

	α	β	γ	δ
n-PrOH	12.0	7.7	3.3	
n-BuOH	10.7			3.3
iso-BuOH		7.0	3.3	
sec-BuOH	11.4	6.1 Me	3.5	

Thus the $S_{0.01}$ values seem to be good measures of the equlibrium binding constant K_b of the 1:1 complex formed between Eu(DPM)$_3$ and Lewis base in solution. However unfortunately, the $S_{0.01}$ (*i.e.* the induced shift parameter estimated from the slopes at a moler ratio of reagent/substrate of 0.01) do not represent the so-called bound chemical shift, ΔB from which the concentration fraction of the complex and the equilibrium binding constant K_b can be deduced.[5]

Variable Temperature Experiment

As shown in Figs. 6 and 7, variable temperature experiments afforded good linear relations of the positive slopes with $1/T\times10^3$, and variation in stoichiometry due to increase in temperature can be excluded in the temperature range used.

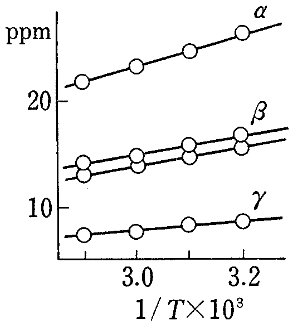

Fig. 6. Variable Temperature Experiments on *sec*-C$_4$H$_9$NH$_2$ in CCl$_4$

molar ratio of base/Eu(DPM)$_3$=1.1

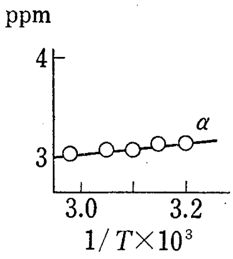

Fig. 7. Variable Temperature Experiments on *n*-C$_4$H$_9$NH$_2$ in CCl$_4$

molar ratio of base/Eu(DPM)$_3$=0.02

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[5] I. Amitage, G. Dunsmore, L.D. Hall and A.G. Marshall, *Can. J. Chem.*, **50**, 2119 (1972).