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Nuclear Magnetic Resonance Studies of Acid-Base Association in Solution. I. Thermodynamic Parameters of the Association between Lewis Bases and Tris(dipivalomethanato)europium

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The enthalpy and entropy of the association between tris(dipivalomethanato)europium and pyridine bases or aliphatic alcohols were determined in CCl_4. The parameters of the pyridine bases are comparable with those for the reactions of pyridine base+MeI reported Brown *et al.* This supports the validity of our results and suggests that the two systems have analogous modes of interaction in solution. The K_1 and Δ_1 values of the pyridine base+$Eu(DPM)_3$ series depend on ΔH and ΔS. For aliphatic alcohols, on the other hand, there is a clear correlation between K_1 and steric factors.

Keywords——^1H NMR; acid-base association; equilibrium constant; bound chemical shift; entropy; enthalpy; steric effect; pyridine base; aliphatic alcohol

Introduction

X-Ray crystallography of the complexes of 7-,[2,3] and 8-coordinated[4] tris(dipivalomethanato)europium, $Eu(DPM)_3$, with Lewis bases in the solid state has shown the former to produce capped triangular prisms and the latter to form square antiprismatic structures. However, the results for solid state complexes do not always coincide with those in solution. As regards the complexes of $Eu(DPM)_3$ in solution, the existence of 7-coordinated complexes has been supported by osmometry, ebulliometry and Job's method using the *f–f* absorption band of the $Ln(DPM)_3$ complex.[5a,b]

In our previous reportes,[6a,b] a 1:1 stoichiometry was confirmed between $Eu(DPM)_3$ and pyridine bases as well as aliphatic alcohols under various conditions: equimolar, a large excess of the base and a large excess of $Eu(DPM)_3$.

Both the bound chemical shift Δ_1 and the equilibrium constant K_1 of the 1:1 associate were also determined by curve fitting of the calculated and observed chemical shifts.

In this work, thermodynamic parameters were determined from the temperature dependence of K_1 of the association between $Eu(DPM)_3$ and a pyridine base or aliphatic alcohol. These parameters for the pyridine base+$Eu(DPM)_3$ series parallel those for the pyridine+MeI series,[7] and this result supports the validity of our experimental data. These thermodynamic data are discussed in terms of the substituent constants.

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1) *a) Kowakae 3-4-1, Higashi-Osaka, Osaka 577, Japan*; *b) Yamadakami 133-1, Suita, Osaka 565, Japan.*
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Experimental

Pyridine bases and aliphatic alcohols used in this study were of J.I.S. grade. They were dried over Linde molecular sieves 4A for several 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 preparation was carried out in a dry box. All NMR spectra were taken on a Hitachi R-22 high resolution nuclear magnetic resonance spectrometer in CCl$_4$ solution containing 0.3% Me$_4$Si as an internal reference, and signal position was determined with a frequency counter to within ± 1.0 Hz. Variable temperature experiments were carried out using a temperature control unit and the measurement temperature was calibrated using ethyleneglycol to within $\pm 1°$.

Results and Discussion

The K_1 values were determined at several temperatures,8) and the plots of lnK_1 *vs.* $1/T$ gave a straight line (*cf.* Fig. 1).

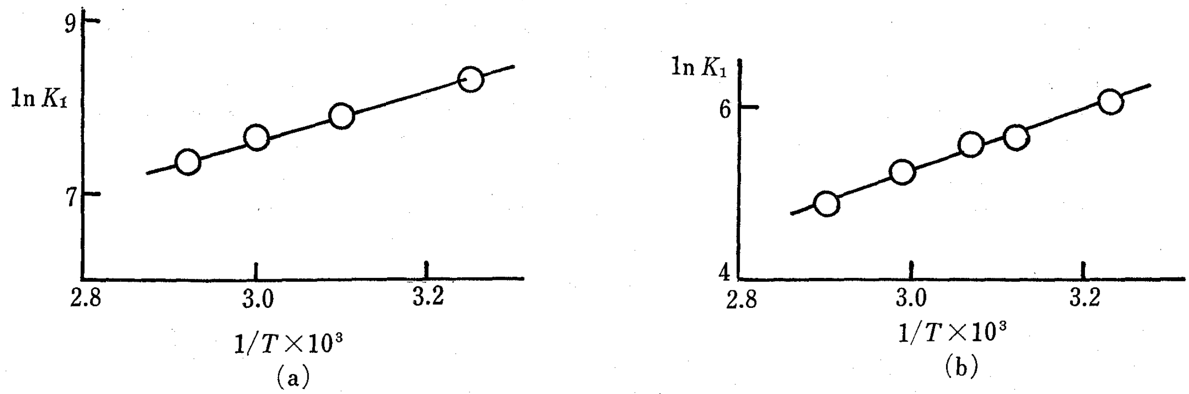

Fig. 1. Plots of lnK_1 *vs.* $1/T$ in CCl$_4$

(a) 3,5-diMe Py.+Eu (DPM)$_3$
(b) *t*-BuOH+Eu (DPM)$_3$
$C_A = C_B = \sim 2 \times 10^{-3} - 2 \times 10^{-2}$ M.

Both the enthalpy ΔH and entropy ΔS estimated in the usual way are summarized in Table I.

Plots of ΔH *vs.* ΔS were linear, and the so-called isoequilibrium temperature9*a*,*b*) was estimated to be 192°*K* (*cf.* Fig. 2).

As is well known, the europium complex has a temperature-dependent paramagnetic contribution of Eu^{3+}, so ΔH contains an effect of this term.

In the next step, we compared ΔH and ΔS (summarized in Table I) with $\Delta H^{\ne}$ and $\Delta S^{\ne}$ values determined for the reaction of pyridine base and MeI in nitrobenzene,7) Linear relations were found among these thermodynamic parameters (*cf.* Fig. 3).

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8) K_1 and Δ_1 were estimated by the following method.

$$\mathrm{A} + \mathrm{B} = \mathrm{AB} \tag{1}$$

$$\delta_{\mathrm{calcd}} = \delta_{\mathrm{B}} + \frac{1 + K_1(C_{\mathrm{A}} + C_{\mathrm{B}}) - \sqrt{[1 + K_1(C_{\mathrm{A}} + C_{\mathrm{B}})]^2 - 4K_1{}^2 C_{\mathrm{A}} C_{\mathrm{B}}}}{2K_1 C_{\mathrm{B}}} \Delta_1 \tag{2}$$

In Eq. (2), δ_{calcd} is the calculated shift of B, δ_{B} is the shift of B in the free state, $\Delta_1 = \delta_{\mathrm{AB}} - \delta_{\mathrm{B}}$, δ_{AB} is the shift of B in the associated state, C_{A} and C_{B} are the initial concentrations of A and B, and K_1 is the equilibrium constant. Based on the equilibrium of Eq. (1), root mean square deviations of the values calculated with Eq. (2) and observed shifts were minimized by the curve fitting method. This calculation was performed with a NEAC 2200 model 700 computer at the Osaka University Computer Center. A library program for the minimization of functions using derivatives was employed.

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Table I. ΔH and ΔS Values for the Association between Eu (DPM)$_3$ and Lewis Bases in CCl_4

	$-\Delta H$ (kcal/M)	$-\Delta S$ (e.u.)
2-Me Py.[a]	8.8	16.1
2-Et Py.	10.3	23.6
3-Me Py.	7.5	7.9
4-Me Py.	6.5	5.2
3,5-diMe Py.	7.4	7.3
n-PrOH	8.5	13.6
n-BuOH	8.3	12.8
iso-BuOH	8.1	12.1
sec-BuOH	8.1	12.4
t-BuOH	7.5	12.0

Error, within ±20%.

a) Py. = pyridine.

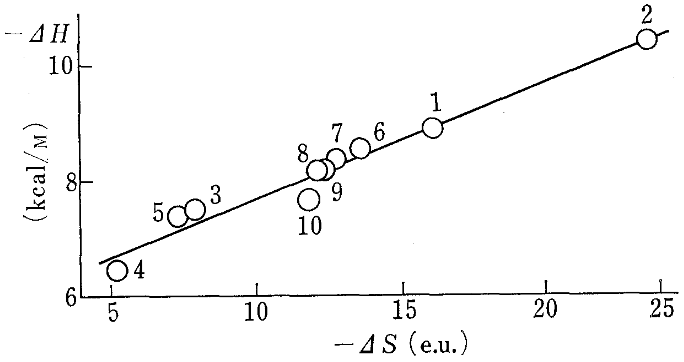
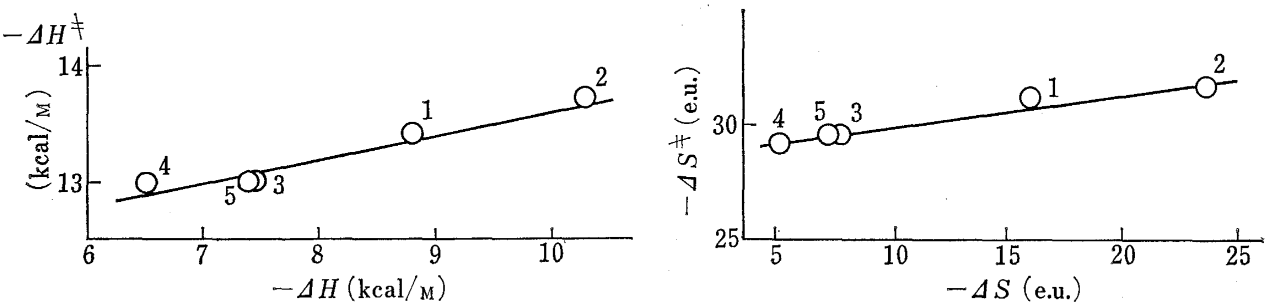


Fig. 2. Plots of ΔH *vs.* ΔS for the Association between Lewis bases and Eu (DPM)$_3$

1=2-Me Py., 2=2-Et Py., 3=3-Me Py., 4=4-Me Py., 5=3,5-diMe Py., 6=*n*-PrOH, 7=*n*-BuOH, 8=iso-BuOH, 9=*sec*-BuOH, and 10=*t*-BuOH.



(a)

(b)

Fig. 3. Plots of ΔH *vs.* $\Delta H^{\ddagger}$ (a), and of ΔS *vs.* $\Delta S^{\ddagger}$ (b) for Pyridine Bases 1=2-Me Py., 2=2-Et Py., 3=3-Me Py., 4=4-Me Py., and 5=3,5-diMe Py.

$\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$=enthalpy and entropy of the reaction of the pyridine base+MeI in $C_6H_5NO_2$7).

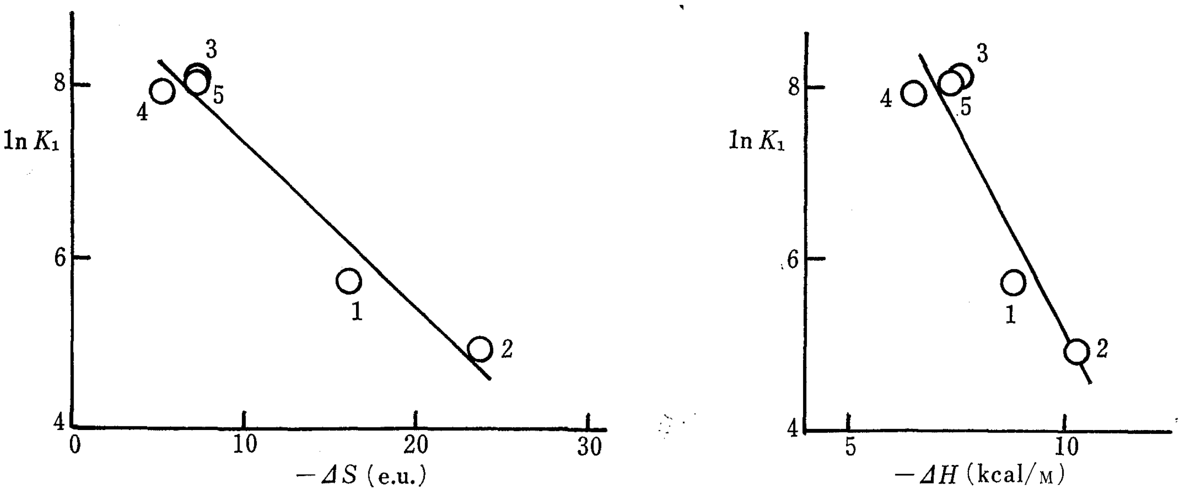


Fig. 4. Plots of $\ln K_1$ *vs.* ΔH and ΔS for Pyridine Base+Eu (DPM)$_3$

1=2-Me Py., 2=2-Et Py., 3=3-Me Py., 4=4-Me Py. and 5=3,5-diMe Py.

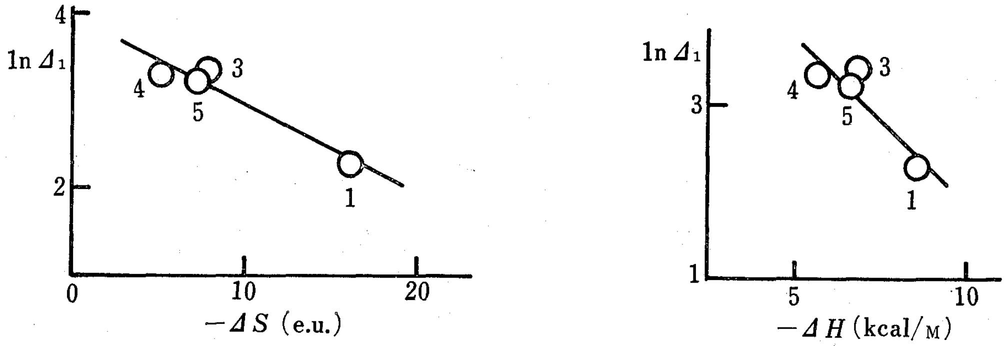


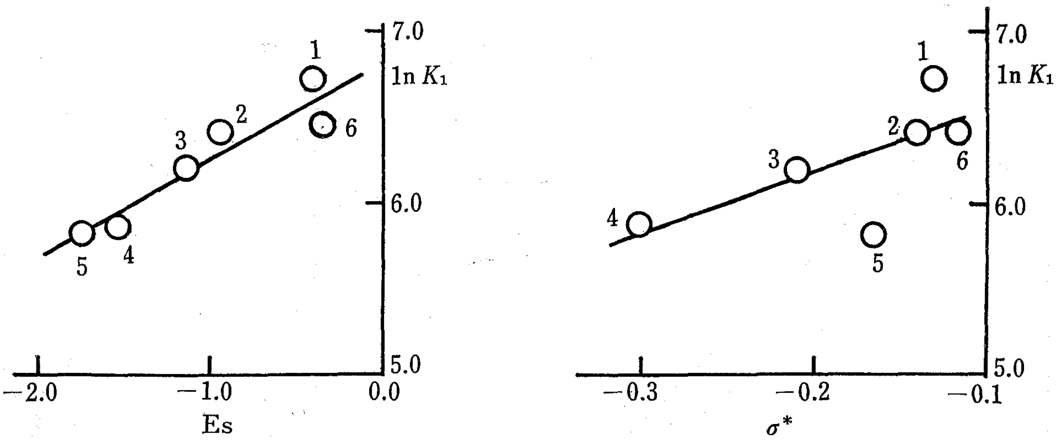
Fig. 5. Plots of $\ln\Delta_1$ *vs.* ΔH and ΔS for Pyridine Base+Eu $(DPM)_3$

1=2-Me Py., 3=3-Me Py., 4=4-Me Py. and 5=3,5-diMe Py.

Table II. Bound Chemical Shift Δ_1[a] (ppm) and Equilibrium Constant K_1[b] (M^{-1}) Values for Lewis Bases+Eu $(DPM)_3$ in CCl_4 at 35°

	Δ_1 (ppm)	K_1 (M^{-1})
Py.[c]	25.5	1389
2-Me Py.	9.7	308
3-Me Py.	28.1	3335
4-Me Py.	27.4	2737
3,5-diMe Py.	24.7	3210
n-PrOH	26.4	623
n-BuOH	28.3	818
iso-BuOH	27.0	608
sec-BuOH		482
t-BuOH		351
neo-PentylOH		338

[a] α-position with respect to N and O. Error, within ±5%.
[b] Error, within ±10%.
[c] Py.=pyridine.



(a)

(b)

Fig. 6. Plots of $\ln K_1$ *vs.* Steric Substituent Constant Es (a) and Polar Substituent Constant σ* (b) for ROH+Eu $(DPM)_3$

1=*n*-BuOH, 2=iso-BuOH, 3=*sec*-BuOH, 4=*t*-BuOH, 5=*neo*-PentylOH, and 6=*n*-PrOH.

This result suggests that the parameters determined in this work are reliable and that the pyridine base+MeI and pyridine base +Eu(DPM)$_3$ systems have analogous modes of interaction. As shown in Fig. 4 and 5, the K_1 and $\varDelta_1$ values summarized in Table II depend on $\varDelta H$ and $\varDelta S$.

On the other hand, for the aliphatic alcohol series, $\ln K_1$ correlated well with the steric substituent constant *Es* rather than with the polar substituent constant σ^*[10] (*cf.* Fig. 6).

This suggests that K_1 for the association between aliphatic alcohols and Eu(DPM)$_3$ is controlled mainly by steric factors, whereas this is not the case for the bound chemical shift $\varDelta_1$. It is probable that K_1 for aliphatic alcohols depends on the environment during the process of association, while $\varDelta_1$ depends on the structure of the associate.

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