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INFRARED SPECTROSCOPIC STUDIES ON THE SHIFT REAGENT-SUBSTRATE COMPLEXES

Minoru HIROTA and Soichi OTSUKA
Department of Applied Chemistry, Faculty of Engineering,
Yokohama National University, Minami-ku, Yokohama 233

The shift reagent-substrate complexes were studied by infrared spectroscopic methods. The composition of the Eu(dpm)$_3$-2-methyl-2-propanol complex was determined to be 1:1, and the enthalpy and the entropy of its formation were calculated from the temperature dependence of the intensities of the free and the complexed O-H bands of the alcohol. The ΔH and ΔS are -9.6 kcal·mol^{-1} and -21 cal·mol^{-1}·deg^{-1}, respectively.

Since the discovery by Hinckley,[1)] lanthanide shift reagents have been widely used to simplify the PMR spectra and also to determine the stereochemistry of many complex organic compounds.[2)] However, the properties of the shift reagent-substrate complexes have not been investigated very thoroughly. Thus, the shift reagent-substrate complexes were studied by infrared spectroscopic methods. As exemplified with other metal complexes, the coordination of metal affects the frequencies and the intensities of some vibrational modes of the substrate. Typical examples of the frequency changes observed are shown in the Table.

Table The Changes in Absorption Frequencies of Some Substrates Caused by the Complex Formation with Shift Reagents.

Substrate	Mode of Vibration	Solvent	Absorption Frequencies in cm^{-1}		
			Free Substrate	Complexed Substrate	
				with Eu(dpm)$_3$	with Eu(fod)$_3$
Dimethyl Sulfoxide	ν_{SO}	CS_2	1071	1035	----
Acetone	$\nu_{C=O}$	CCl_4	1718	1712	----
Pyridine N-Oxide	ν_{NO}	CS_2	1269,1277	1250(broad)	1250(broad)
2-Methyl-2-propanol	ν_{OH}	CCl_4	3619	3480	3520
Cyclohexanol	ν_{OH}	CCl_4	3623	----	3560
Aniline	ν_{NH}	CCl_4	3483,3396	3385,3308	3380,3310

Among these substrates, 2-methyl-2-propanol is very convenient in many ways to investigate the complex formation quantitatively. Firstly, its OH stretching band is symmetrical and well approximated by Lorentz function.3,4) Moreover, the OH band of the complexed species, which appears at about 3500 cm^{-1}, is isolated from that of the free species and is also symmetrical. Secondly, other absorptions of both the shift reagent and the substrate do not appear in the OH stretching region. Thus, the ternary mixture of $Eu(dpm)_3$-$(CH_3)_3COH$-CCl_4 is investigated quantitatively in order to determine the composition and the thermodynamic properties of the $Eu(dpm)_3$-alcohol complex.

$$Eu(dpm)_3 \;+\; n\cdot(CH_3)_3COH \rightleftharpoons Eu(dpm)_3\cdot[(CH_3)_3COH]_n$$

The OH absorption intensities of the free and the complexed species were determined for various concentrations of the alcohol(substrate, S) in the presence of the constant amount(R_t) of $Eu(dpm)_3$. From these intensity data, the concentrations of the free and the complexed alcohol([S] and S_b, respectively) were estimated, and the coordination ratio(n) of the substrate to the shift reagent was calculated from the slope and the intercept of the plot shown in Fig. 1 by using the following equation proposed by Scatchard.5)

$$\frac{S_b}{R_t[S]} = \frac{n}{K} - \frac{1}{K}\cdot\frac{S_b}{R_t}$$

The least squares calculation gives n = 0.92, which supports the existence of the 1:1 complex. The formation constant(K) of the complex is also obtained to be 348 at 20° C.

The temperature dependence measurement of the equilibrium constant gives the thermodynamic properties of the substrate-shift reagent complex. Thus the intensities of the OH bands were determined at various temperatures ranging between 20 and 40°C, and logarithms($\log_{10}K$) of the equilibrium constants obtained were plotted against the reciprocals of the absolute temperatures(1/T). From this plot illustrated in Fig. 2, the enthalpy and the entropy of the complex formation were calculated by the well-known procedure, and are shown to be -9.6 $kcal\cdot mol^{-1}$ and -21 $cal\cdot mol^{-1}\cdot deg^{-1}$, respectively. The thermodynamic quantities are similar to those of rather weak bimolecular complexes. However, the equilibrium is quite favorable to the shift reagent-substrate complex, and the shift reagent added reacts nearly quantitatively to form the complex under the conditions for the lanthanide induced shift(LIS) measurement of the PMR spectra.

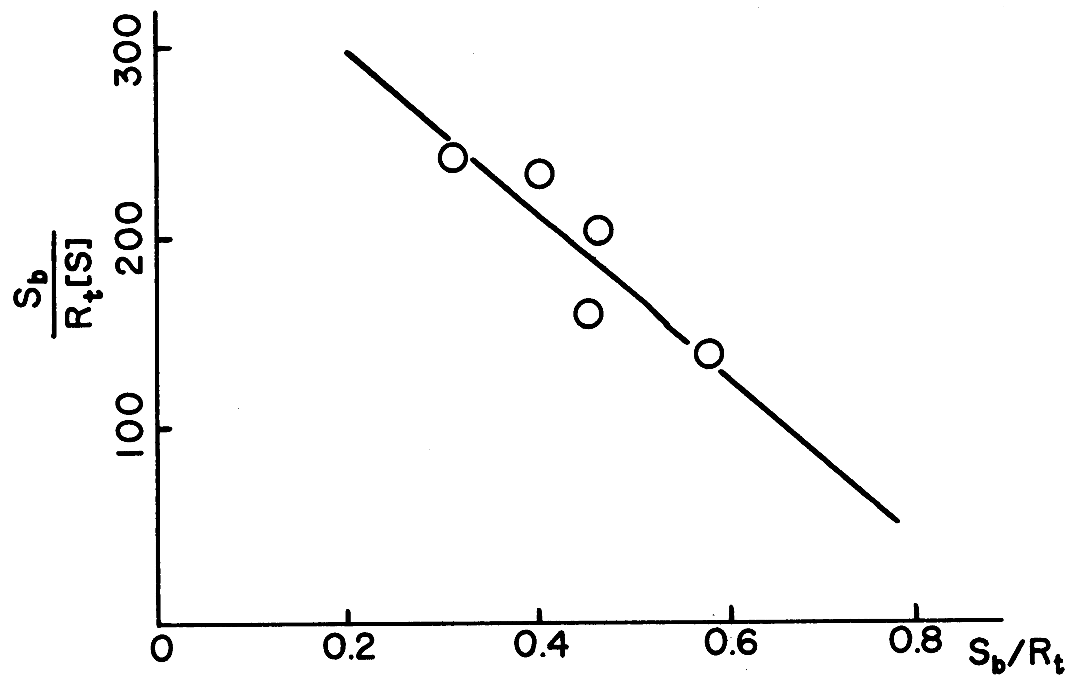

Fig.1 The Scatchard plot to obtain K and n. [R_t = 2.12 10^{-3} mol·l^{-1}, S_t = 2.04, 2.67, 3.29, 3.89, and 5.34 10^{-3} mol·l^{-1}]

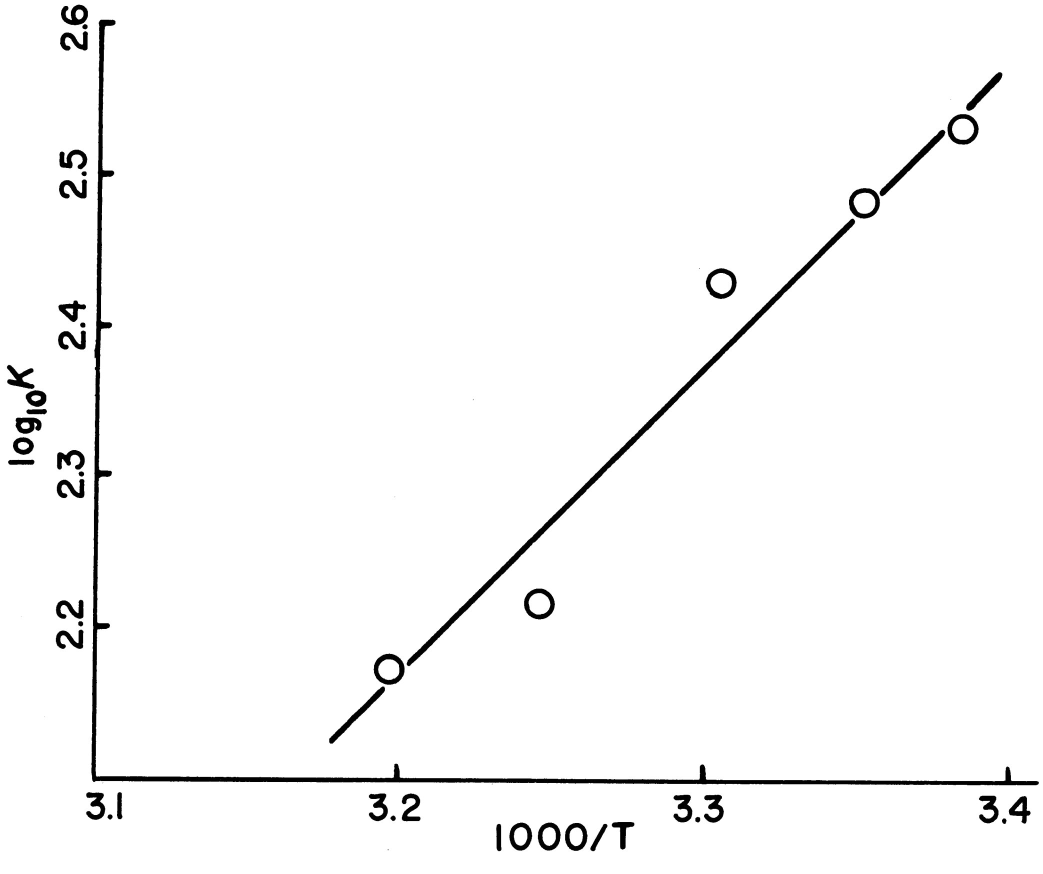

Fig. 2 The $\log_{10}K$ vs. 1/T plot.

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