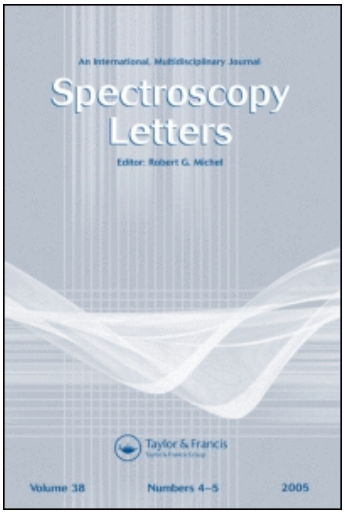

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A Quantitative Study of Effects of Rare Earth Chelates on NMR Chemical Shifts: I. Treatment of 1:1 Complexes and Chemical Shifts of the Pure Complexes

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A QUANTITATIVE STUDY OF EFFECTS OF RARE EARTH CHELATES ON NMR CHEMICAL SHIFTS: I. TREATMENT OF 1:1 COMPLEXES AND CHEMICAL SHIFTS OF THE PURE COMPLEXES

KEY WORDS: Chemical shifts, Rare earth chelates, Pure complexes

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INTRODUCTION

Recently several rare earth chelates have been found that induce large and dramatic chemical shifts when complexed with a ligand.[1] This is due to paramagnetic shielding, the mechanism of which is observed to be a pseudo-contact shift. In cases such as this involving dynamic equilibria where exchange of protons is rapid compared to observation time, the observed chemical shift represents an average environment determined by the time the proton nuclei spend at each site. The effective site of the complex is a lone pair donor such as the oxygen of a carbonyl group, alcohol, or ether, or the nitrogen of various nitrogen containing groups. The oxygen bearing compounds could theoretically form strong complexes with the added possibility of multiple complexes with chelates. The nitrogen bearing compounds of weak donor strength and containing only a lone pair would presumably form only the 1:1 complex.

The types of chelates used in this study were $Eu(DPM)_3$ [DPM] and $Eu(FOD)_3$ [FOD]. In the literature the FOD chelate has been reported to be a a "vastly superior" shift agent; although it is more soluble, its superiority is dependent upon one's purposes for employing it which will be discussed later. These rare earth chelates can be beneficial to NMR spectroscopy in several ways: (1) effectively reduce second order to first order spectra, (2) allow specific protons within a molecule to display unique chemical shifts in cases where they normally would not, and (3) can subject a molecule to an effectively much higher applied field.[2] The rare earth chelates though may suffer two severe limitations: (1) the limited solubility of the chelate, and (2) an effective solvent cannot contain a lone pair for it may be preferentially complexed.

The magnitude and direction of the shift is a function of the metal chelate used, the mole ratio of the chelate complex to ligand, the concentration of the solution, the temperature, the distance and geometry of the protons relative to the coordination site, and the basic strength of the donor.

DISCUSSION

Most studies to date have avoided a quantitative study concerning the mole ratio of chelate to ligand, the effect of temperature, and the effect of concentration on chemical shifts. This is largely due to two reasons. First, the interaction of the chelate and ligand involves up to four equilibria as shown below.

$$C + L \rightleftharpoons CL \qquad (1)$$

$$C + 2L \rightleftharpoons CL_2 \qquad (2)$$

$$2C + L \rightleftharpoons C_2L \qquad (3)$$

$$C_2 \rightleftharpoons 2C \qquad (4)$$

where C = rare earth chelate

L = ligand (bearing lone pair)

Thus, equilibrium constants for each class of functional groups must be determined in the presence of multiple equilibria unless conditions can be judiciously chosen to minimize the number of equilibria occurring to a significant extent. Secondly, the NMR data can best be interpreted with the knowledge of the chenical shift of the pure chelate-ligand complex, but the pure complex has not been obtained.

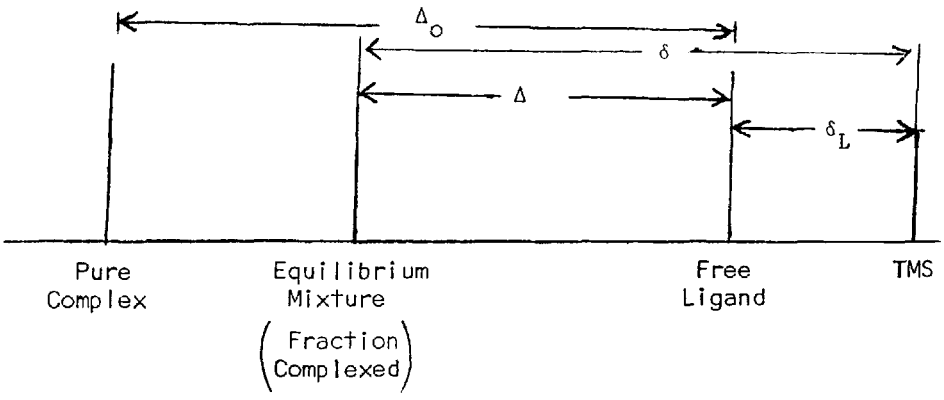
Typically, a plot of induced shift versus increasing chelate concentration tends to flatten and reach a limiting value at higher chelate concentrations. This maximum induced chemical shift has been interpreted in the literature[1] as being the chenical shift of the pure complex. However, our data indicate that this limiting chemical shift is not identical with the chemical shift of the pure complex, but rather is a limiting shift due to solubility limitations and possibly the effects of multiple equilibria. This must be apparent since the limiting shift obtained is a function of the initial ligand concentration.

Shown in Figure 1 are the definitions of the shift values which will be used subsequently. Δ is taken to represent the observed difference in chemical shift from the free ligand and the equilibrium mixture of complex and free ligand. Δ_o represents the hypothetical differential shift of the pure complex and the free ligand. The problem, as already mentioned, is that in order to treat these systems in a quantiative manner, one needs to know the chemical shift for the pure complex which has not been observed.

The observed chemical shift can be predicted with a knowledge of Δ_o, the chemical shift of the free ligand, and a knowledge of the fraction of these components present. The fraction of these components present will also give the equilibrium constant if one also has knowledge of what equilibria are occurring. The 1:1 equilbrium is shown in equation (1)

$$C + L \rightleftharpoons CL \qquad (1)$$

Figure 1
CHEMICAL SHIFTS



Δ_o = differential shift of the pure complex

Δ = differential shift of equilibrium mixture

Derivation of the equilibrium expression for the 1:1 complex follows:

$$\delta = P_L\delta_L + P_{CL}\delta_{CL}$$ where P = fraction of species present and δ = observed chemical shift

Since $P_L + P_{CL} = 1$

$$\therefore \delta = \delta_L(1-P_{CL}) + P_{CL}\delta_{CL}$$

upon rearranging: $\delta = \delta_L + P_{CL}(\delta_{CL}-\delta_L)$

Let $\Delta_o = \delta_{CL}-\delta_L$ and $\Delta = \delta-\delta_L$

$$P_{CL} = \frac{\delta-\delta_L}{\delta_{CL}-\delta_L} = \frac{\Delta}{\Delta_o} = \frac{[CL]}{[L]_o}$$

where $[L]_o$ = initial concentration of the ligand

$$K_{CL} = \frac{[CL]}{[C][L]}$$

$$\frac{\Delta}{\Delta_o} = \frac{[CL]}{[L]_o}$$

$$[CL] = \frac{\Delta[L]_o}{\Delta_o}$$

$$[L] = [L]_o - [CL] = [L]_o - \frac{\Delta[L]_o}{\Delta_o}$$

$$[C] = [C]_o - [CL] = [C]_o - \frac{\Delta[L]_o}{\Delta_o}$$

$$\therefore [C]_o = x[L]_o \text{ where } x = \text{mole ratio of } \frac{[C]_o}{[L]_o}$$

$$\frac{\frac{\Delta}{\Delta_o}[L]_o}{(x[L]_o - \frac{\Delta}{\Delta_o}[L]_o)([L]_o - \frac{\Delta}{\Delta_o}[L]_o)}$$

Upon rearrangement and simplification, one obtains equation (5), the equilibrium expression for the 1:1 complex:

$$\frac{1}{[L]_o K_{CL}} = x\left(\frac{\Delta_o}{\Delta} - 1\right) - 1 + \frac{\Delta}{\Delta_o} \qquad (5)$$

Equation (5) contains two unknowns, K_{CL}, the equilibrium constant, and Δ_o, the differential shift of the pure complex, and cannot be solved without a knowledge of one of the two. However, utilizing equation (5), two simultaneous equations can be written; upon simplification and rearrangement, equation (6) is obtained which is a quadratic expression with only one unknown, Δ_o:

$$x_1\left(\frac{\Delta_o}{\Delta_1} - 1\right) - 1 + \frac{\Delta_1}{\Delta_o} = x_2\left(\frac{\Delta_o}{\Delta_2} - 1\right) - 1 + \frac{\Delta_2}{\Delta_o}$$

$$\Delta_o^2\left(\frac{x_1}{\Delta_1} - \frac{x_2}{\Delta_2}\right) + \Delta_o(x_2 - x_1) = \Delta_2 - \Delta_1 \qquad (6)$$

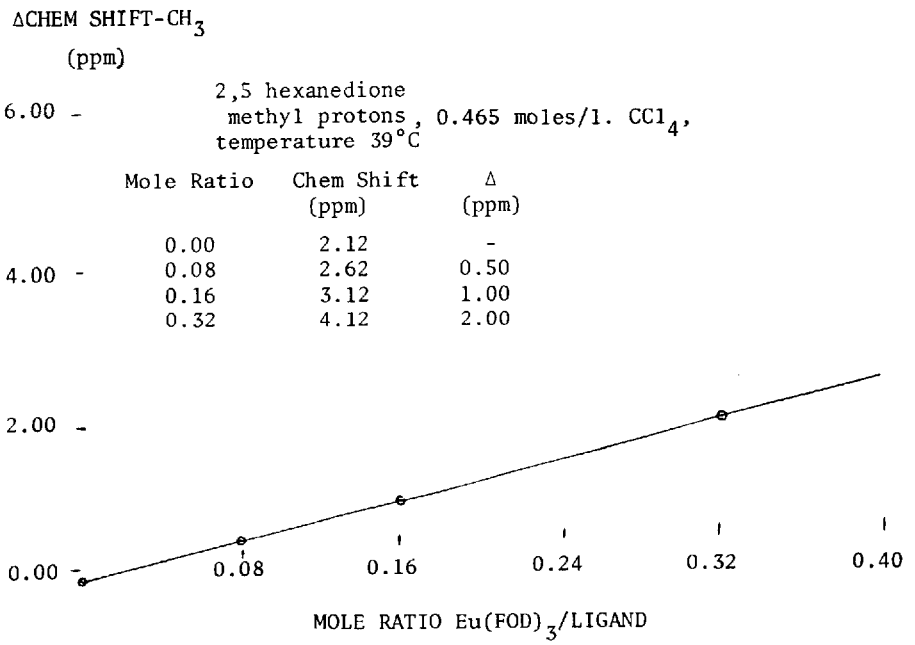
Therefore, if data is taken of the observed Δ as a function of the mole ratio of chelate to ligand at constant ligand concentration, equation (6) can be solved for Δ_o. Then armed with the value of Δ_o, the rest of the terms in equation (5) are known except K_{CL}, and equation (5) can now be solved for K_{CL}.

Figure 2 represents a plot of the methyl protons of 2,5 hexanedione. Data was generally taken at relatively low concentrations of ligands and chelates in an effort to minimize the occurrence of multiple equilibria.

Results shown in this figure are typical data for the observed incremental shift Δ as a function of mole ratio. It should be noted that the resulting plot appears to be linear and one is tempted to take the value of Δ_o as being identical with the value of the slope. This is not strictly correct for the following reasons, as mole ratio increases then: (1) activity coefficients may vary disproportionally, (2) additional equilibria may become more significant, and (3) the effects of solubility limitations may become more pronounced. However, in the limit, at low concentrations of chelate and ligand, the above considerations are minimized and the slope will be very close to, if not identical with, Δ_o.

Figure 2

CHEMICAL SHIFT VS. MOLE RATIO



RESULTS

Table 1 shows typical results for Δ_o obtained from the systems listed which include utilization of both DPM and FOD chelates at various ligand concentrations. The last column gives the standard deviations for mole ratios obtained from the least squares linear treatment of the data.

In all cases, the values for Δ_o given for these various functional groups are quite similar to the slopes reported by Sanders and Williams to which they refer as gradients.[3] It is also noteworthy that the Δ_o's as given are somewhat dependent on the ligand concentration, but even so, seem to be fairly characteristic of a given functional group. [Rabenstein studied normal alcohols C_2-C_7 and the average slope obtained was 22.8 ± 0.2.[4] Differences between his data and that presented here can easily be explained as being due to differences in ligand concentrations and

Table 1

TYPICAL DATA

Functional Group	Compound	Ligand Concentration[a]	Δ_o[b] DPM	FOD	Standard Deviation[c]
OH	n-decanol	0.522	20.0	20.5	0.01
		0.736	24.1	24.6	0.01
ROR	n-propylether	0.330	15.3		0.02
		0.700	17.6		0.06
R-C(=O)-R	acetone	0.706	12.2		0.04
		1.120		20.5	0.09
		1.430	13.4		0.01
R-C(=O)-C-C(=O)-R	2,5-hexanedione	0.465			
	CH_3			6.9	0.03
	CH_2			8.4	0.02
		0.982			
	CH_3			7.0	0.00
	CH_2		9.4	9.8	0.04

[a] moles per liter CCl_4

[b] ppm

[c] obtained from least squares fit of data

temperature.] An apparent anomaly to this statement can be seen in the Δ_o's listed for the 2,5 diketone, but it should be pointed out that the apparent low values for the Δ_o for the methyl group is low because the molecule is difunctional rather than monofunctional. Thus, the effective concentration of chelate per functional group is half that given by the mole ratio and consequently the value for Δ_o here is about half what would be expected. The Δ_o for the methylene group in this system is different from that of the methyl and this is easily explained since this shows that the methylene experiences some of the paramagnetic field of the chelate whether the chelate is complexing with the carbonyl which the methylene is α or β to and thus it would have a greater value for Δ_o.

An equilibrium constant of approximately 12 was obtained for the system acetone and FOD. This example appears to be in agreement with the magnitude of the equilibrium constants measured in a series of nitriles where the 1:1 complex predominated.[2] Constancy in the equilibrium constants for n-decanol and n-propylether were not obtained suggesting that these systems were not simply 1:1 complexes in the concentration range studied. Equilibrium constants for the hexanedione and difunctional groups in general are still under investigation.

The typical effect of temperature can be seen in Figure 3 showing the spectra of n-propyl ether. The resonance lines do shift somewhat, but rather slightly over the temperature range investigated (39°C-75°C). The resonance lines from the chelate itself also shift with temperature as would be expected.

The change in Δ as a function of temperature can be more easily seen in Figure 4 showing 2,5-hexanedione. This represents a plot of the incremental shift Δ as a function of temperature and a relatively linear response is obtained. The linearity of the lines indicates that ΔH^o, the

Figure 3

TEMPERATURE EFFECTS ON N-PROPYL ETHER

0.33 MOLES/LITER $Eu(DPM)_3$

0.08 MOLE RATIO CHELATE TO LIGAND

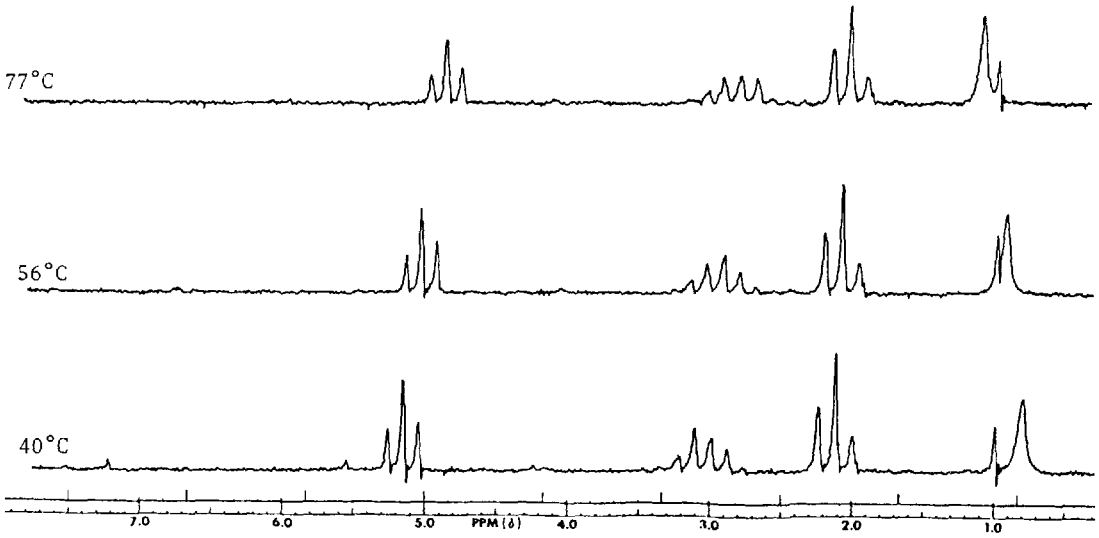
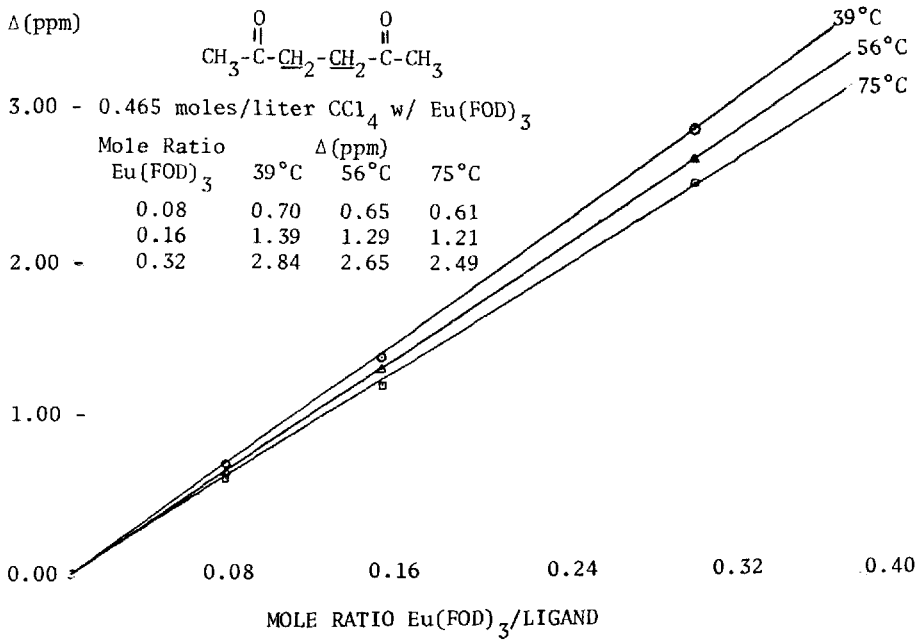


Figure 4

EFFECTS OF TEMPERATURE



standard enthalpy, is essentially constant over this temperature range, and also that there are no dramatic changes in the nature of multiple equilibria over this temperature range. The standard free energy (ΔG^o) can be obtained from K_{CL} and utilizing ΔH^o, the standard entropy (ΔS^o) can be obtained.

The application of shift agents to polymers appears to be a very promising area for study. The measurement of sequence distributions in polymers is very important, and with regard to NMR, is often limited by virtue of the fact that shifts due to different structures are not well enough resolved so that they can be properly assigned and their intensities accurately measured. The application of shift agents should be very beneficial in that greater shifts would be observed which would allow these lines to be resolved. Shown in Figure 5 is the spectra of polyvinyl acetate as a free ligand and then in the presence of DPM and FOD.

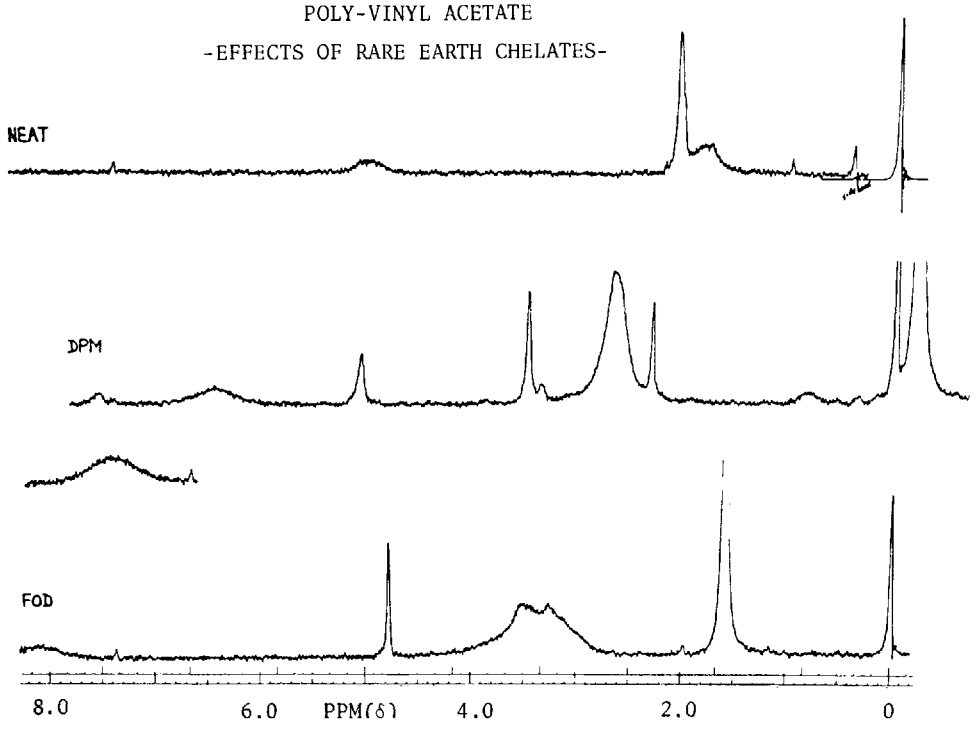
Several observations can be made, one is that the greater shift is in fact obtained with the FOD, but the DPM seems to be more discriminating to the structures and shows the resolutions of the overlapping region into two resonance areas much more clearly; thus there may be many occasions when the greater selectivity of the DPM might warrant its choice over the FOD chelate. This may be more important when steric factors may allow the DPM chelate to approach the functional group somewhat more closely than the FOD chelate and thereby induce a greater shift. The observed chemical shifts have been tentatively interpreted in terms of tactic structures, but a discussion of this is being deferred to a later paper.

As mentioned previously, the values for Δ_o do show a dependence on ligand concentration. Thus, if one plotted Δ_o versus ligand concentration and extrapolated to zero ligand concentration, the value Δ_o^o would be obtained as shown in Figure 6. Several noteworthy points are apparent.

Figure 5

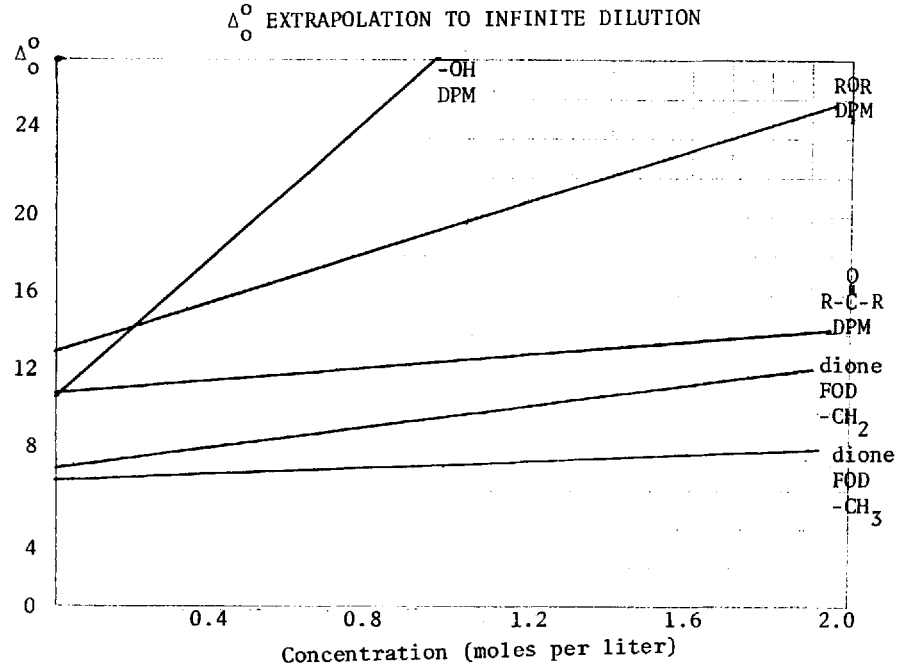
POLY-VINYL ACETATE

-EFFECTS OF RARE EARTH CHELATES-



One is that the Δ_o^o values for the alcohol, the ether, and the simple ketone all extrapolate back to the vicinity of 12 ppm. This would imply that the Δ_o^o value for the pure complex involving oxygen at infinite dilution is the same for all three species and is likely due to the 1:1 complex, and secondly, that the value 12 relates to the strength of the oxygen-chelate complex. Furthermore, this could be useful in determining the multiplicity of the equilibria occurring in any given system at any given ligand concentration. That is to say, that it would suggest that over the concentration range in which decanol was studied, it always occurred as at least a 2:1 complex. It is also interesting to note that twice the value for the Δ_o^o of the methyl group in the diketone is about equal to the Δ_o^o value for the methyl group in acetone.

Figure 6



EXPERIMENTAL

All spectra were taken on Varian A-60 or A-60A spectrometers. Probe temperature was 38.5 ± 1°C. Solvents used were $CDCl_3$ and CCl_4 with TMS used as an internal standard. The rare earth chelates were stored under anhydrous conditions prior to use. Most rare earth chelates were obtained from the Norell Chemical Company. All ligands were spectral grade reagents.

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