

LANTHANIDE-INDUCED CONTACT SHIFTS IN POLYGLYCOLDIMETHYLETERS
III TEMPERATURE DEPENDENCE OF THE SHIFTS⁺

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The idea of plotting lanthanide induced (LI) shifts versus the reciprocal of the temperature is based on the equations of McConnell and Robertson (1), that predict this 1/T dependence. Kurland and McGarvey (2) and Bleaney (3) recently pointed out that due to crystal field interactions an extra term should be added to the equations of McConnell and Robertson, which is proportional to 1/T². Bleaney also indicated that due to the isotropic Landé g factor for lanthanide ions the terms with 1/T are zero, and therefore LI shifts should be proportional to 1/T². For Sm³⁺ and Eu³⁺ effects of nearby excited states result in a 1/T dependence of the shifts.

In a number of experiments we investigated the temperature behaviour of 1 : 1 complexes of dimethoxyethane (DME) with Pr(FOD)₃ (4), Eu(FOD)₃ (4), Pr(DPM)₃ (5) and Eu(DPM)₃ (6).

Fig. 1 shows the least squares fit of the shifts for the CH₃ and the CH₂ protons of DME present in Pr(FOD)₃, DME (1 : 1), plotted versus 1/T². Good straight lines are obtained with small intercepts, the latter in agreement with the negligible contribution of the temperature independent paramagnetism (TIP) to the Pr³⁺ induced shifts (3). If the shifts are plotted versus 1/T curved plots are obtained, as found also by other authors (7, 8).

Fig. 2 shows the least squares fit of the shifts for the protons of DME present in Eu(FOD)₃, DME (1 : 1) plotted versus 1/T. Perfectly straight lines were obtained. The intercept for 1/T = 0 is large, in agreement with the expected large contribution of TIP to the Eu³⁺ induced shifts (3).

The shifts for the protons of DME present in Eu(DPM)₃, DME (1 : 1) and Pr(DPM)₃, DME (1 : 1) showed a similar temperature behaviour: the Eu³⁺ induced shifts were proportional to 1/T, the Pr³⁺ induced shifts to 1/T². At temperatures higher than 35°C small deviations from these plots arose, very probably due to the smaller complexation constant of DME to DPM complexes ($\approx 10^3$ l mol⁻¹) compared to FOD complexes ($\approx 10^5$ l mol⁻¹), which allows free DME to develop in solution at high temperatures.

⁺) Part I and part II appeared earlier in Tetrahedron Letters, 4863 (1971) and 2067 (1972), respectively.

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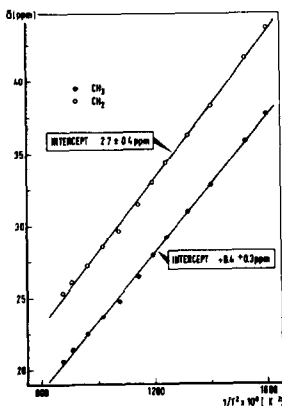


Fig. 1: Least squares fit of the shifts for the CH_3 and the CH_2 protons of DME present in a 1 : 1 mixture of $\text{Pr}(\text{FOD})_3$ and DME in CCl_4 ($[\text{Pr}(\text{FOD})_3] = 0.075 \text{ M}$), plotted versus $1/T^2$. Proton shifts are relative to those of non complexed DME.

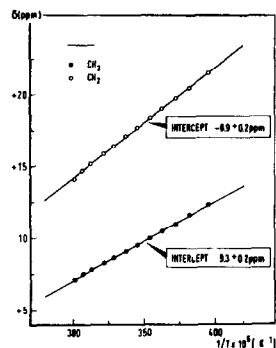


Fig. 2: Least squares fit of the shifts for the CH_3 and the CH_2 protons of DME present in a 1 : 1 mixture of $\text{Eu}(\text{FOD})_3$ and DME in CCl_4 ($[\text{Eu}(\text{FOD})_3] = 0.075 \text{ M}$), plotted versus $1/T$. Proton shifts are relative to those of non complexed DME.

These experimental results are in perfect agreement with Bleaney's theory (3) and forms additional proof for the correctness of this theory (9).

The experiments were performed on a Varian XL 100 spectrometer operating at 100 MHz. The temperatures were measured by means of a thermocouple, placed in the rotating sample tube and connected to an electronic temperature meter.

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