LETTERS TO THE EDITOR

ENERGY TRANSFER BETWEEN Tb³⁺ AND Eu³⁺ IN DMSO

ENERGY transfer processes have been extensively studied in glasses[1-3] crystals[4-6] and to a limited extent in solutions. Holloway and Kestigian[7] studied the quenching of Tb³⁺ by other rare earth ions (Nd³⁺, Ho³⁺ and Er³⁺) in aqueous chloride solutions and interpreted the results on the basis of a non-radiative transfer of energy from the fluorescent Tb³⁺ level to excited levels of the quencher ion through a dipole-dipole interaction. The radiationless transfer of energy from Tb³⁺ and Eu³⁺ to various rare earth ions in acetone and water was studied by Antipenko and Ermolaev[8]. The transfer rates were found to be slow in water as compared to acetone. Van Uitert et al.[9] studied the energy transfer between Tb³⁺ and Eu³⁺ in tungstates and the quenching of the $^5D_4$ state is attributed to the dipole-dipole interaction whereas quenching of the $^5D_3$ state is attributed to the dipole-quadrupole interaction. A preliminary study showed that the quenching of Tb³⁺ by Eu³⁺ in Dimethyl-sulphoxide (DMSO) obeys a Stern-Vomer law; however a diffusion limited dipole-dipole mechanism of energy transfer is suggested for Tb³⁺ → Nd³⁺ and Tb³⁺ → Ho³⁺ in DMSO[10]. The purpose of the present paper is to establish the mechanism of the energy transfer from Tb³⁺ to Eu³⁺ in DMSO.

The fluorescence yield of the rare earth ions in solutions depends strongly upon the solvent and it is found that the fluorescence yield is low in the protic solvents whereas it increases appreciably in the aprotic solvents e.g., $POCl_3$: $SnCl_4$, $POCl_3$: $ZrCl_4$[11-13]. It is found that the fluorescence yield of Tb³⁺ and Eu³⁺ increases in DMSO.

The chlorides of the rare earth ions were prepared by dissolving 99·9% pure oxides (Koch-Light Lab. Ltd., England) in HCl (G.R.) and by recrystallising the salts from the concentrated solutions. The $TbCl_3 \cdot 6H_2O$ and $EuCl_3 \cdot 6H_2O$ were dissolved in spectrograde DMSO and the samples were sealed immediately. Samples were excited by using 365 and 487 nm radiations from a xenon arc (150 W). The emission spectra were recorded Spex-1902 fluorolog having two double Czerny-Turner scanning monochromators each for excitation and emission. Detection is done with the help of single photon amplifier discriminator, S 20 response photomultiplier and a chart recorder.

Spectrum of Tb³⁺ in DMSO is shown in Fig. 1 (curve a). The emission peaks are at 4880 Å, 5440 Å, 5850 Å and 6220 Å originating from $^5D_4$ state but no

emission from $^5D_3$ state is observed. Curve (b) in Fig. 1 shows the emission spectrum of Eu³⁺ in DMSO with emission peaks at 5910 Å and 6140 Å originating from the lowest excited state (i.e., $^5D_0$ state) and curve (c) in the same figure presents a typical emission spectrum of a mixture of Tb³⁺ and Eu³⁺, showing a small enhancement of Eu³⁺ emission accompanied by the quenching of Tb³⁺ emission.
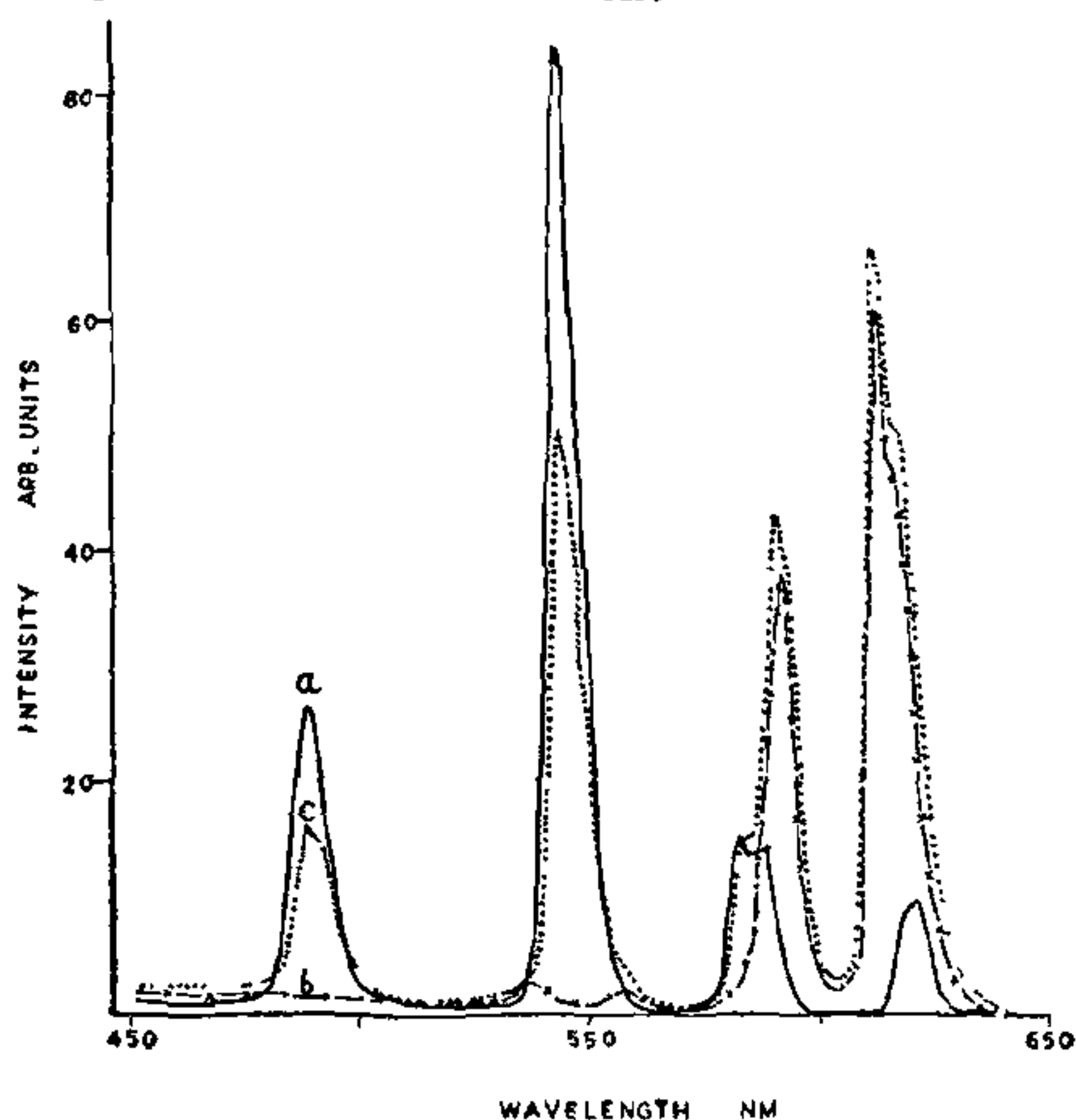

FIG. 1. Emission spectra of Tb³⁺ and Eu³⁺ in DMSO with excitation wavelength 365 nm (a) ——— ·1 M Tb³⁺, (b) — × — × — ·5 Eu³⁺ and (c) ···· ·1M Tb³⁺ + ·5M Eu³⁺.

The decay plots for $^5D_4 \rightarrow {}^7F_5$ transition have been taken and it is found that the decay curve of pure terbium in DMSO is a simple exponential with a lifetime 2·2 ms. As we introduce Eu³⁺ in this solution the decay time decreases and the decay curve remains exponential as shown in Fig. 2. The lifetime has been obtained from the slope of the decay curve.

Figure 3 shows the ratio of intensity of the donor without and with the acceptor versus concentration of the acceptor. The intensities were found out by measuring the peak intensity of 5440 Å emission. It can be seen that the emission intensity of Tb³⁺ decreases with the increase in the acceptor concentration. It is observed that the intensity of the Eu³⁺ increases with the increase in Tb³⁺ concentration whereas lifetime of the acceptor remains unchanged.

Under a multipolar energy transfer process[14]
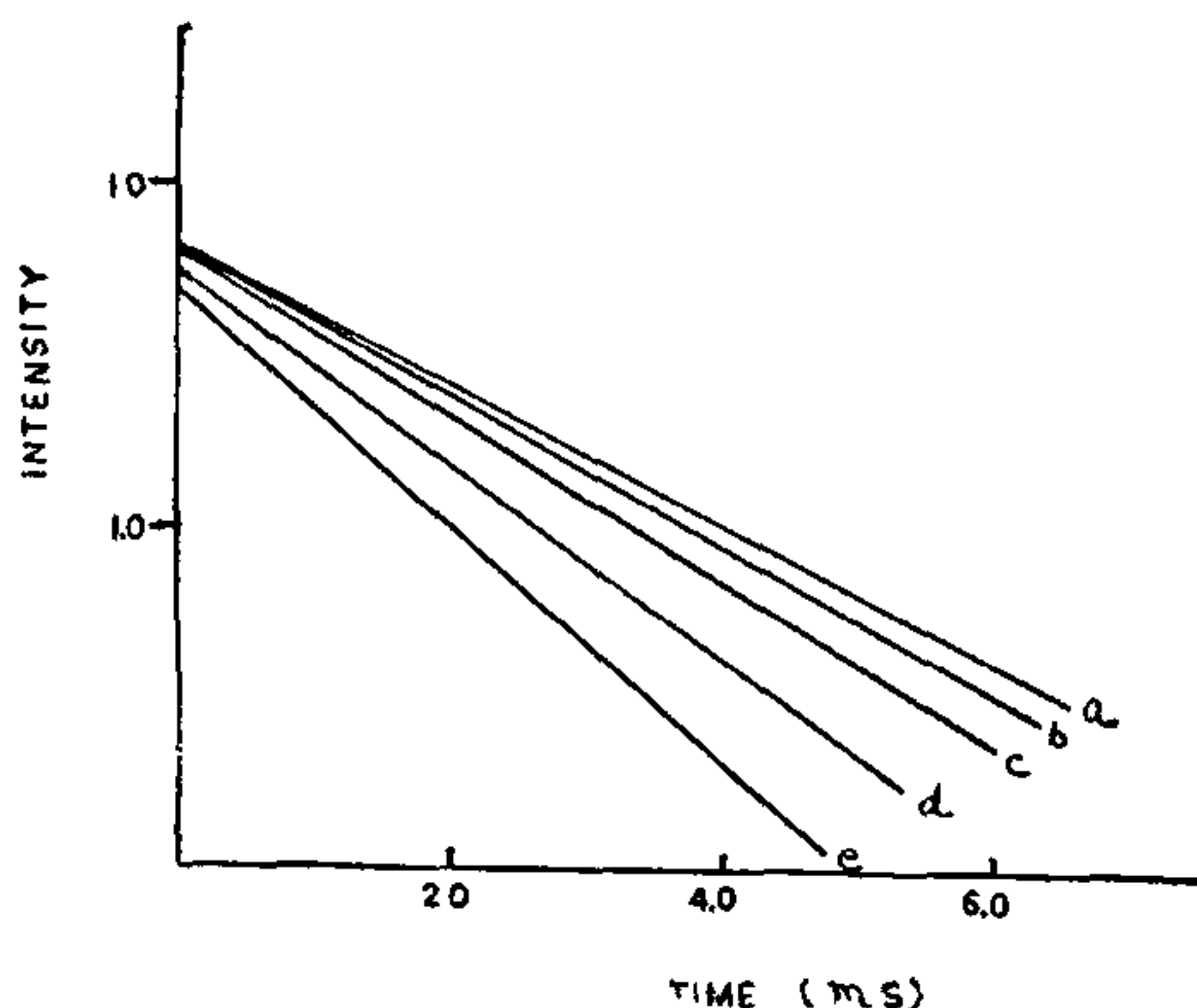
$$I_c = I_0 (1 + \beta C^{\theta/3})^{-1} \qquad (1)$$

FIG. 2. Decay plots of (a) ·02M Tb³⁺, (b) ·02M
Tb³⁺ + ·1 M Eu³⁺,   (c) ·02 M Tb³⁺ + ·25 M Eu³⁺,
(d) ·02 M Tb³⁺ + ·5 M Eu³⁺ and (e) ·02 M Tb³⁺
+ ·8 M Tb³⁺.

where I_0 and I_c are the intensities of the donor without and with the acceptor concentration C, β is the quenching coefficient and θ is the characteristic of the multipolar transfer having a vaue 6, 8 and 10 for dipole-dipole, dipole-quadrupole and qudrupole-quadrupole respectively. In case $7 = 3$, the equation describes the situation where dipole-dipole interaction is influenced by diffusion or collision takes place and the Stern-Volmer kinetics is obeyed.

$$I_c = I_0 (1 + Kq\,\tau_0 C)^{-1} \qquad (2)$$

where τ_0 is the lifetime of the pure donor and Kq is the rate constant of quenching.

In order to investigate the mechanism of the energy transfer process we have plotted the concentration of the acceptor C against I_0/I_c (Fig. 3). It gives a straight line which implies that the quenching of Tb³⁺ by Eu³⁺ is linearly dependent on the concentration of Eu³⁺ in agreement with equation (2) and hence obeys Stern-Volmer kinetics. From the slope of the straight line we obtain the value of Kq $\tau_0 = 2\cdot 2$. The lifetime of Tb³⁺ is $2\cdot 2$ ms so that Kq = 1×10^3 M⁻¹S⁻¹. This value is much lower from the value one would expect for a diffusion controlled process*. Similar results are observed by plotting τ_0/τ against the acceptor concentration (Fig. 4).

Eu³⁺ deactivates Tb³⁺ by the process

Tb³⁺ (⁵D₄) + Eu³⁺ (⁷F) — Tb³⁺ (⁷F) + Eu³⁺ (⁵D₀)

Since ⁷F₁ level is only 400 cm⁻¹ above the ⁷F₀ level it has a considerable population. The ⁷F₀ → ⁵D₀ and ⁷F₁ → ⁵D₁ transitions are electric dipole and

---

* The rate of a diffusion controlled pocess is given by Kd = 8RT/3000 η where R is the gas constant, T is the temperature and η is the viscosity. For DMSO ($\eta = 1\cdot 996$ CP) it's value is $\sim 10^1$ sec⁻¹.
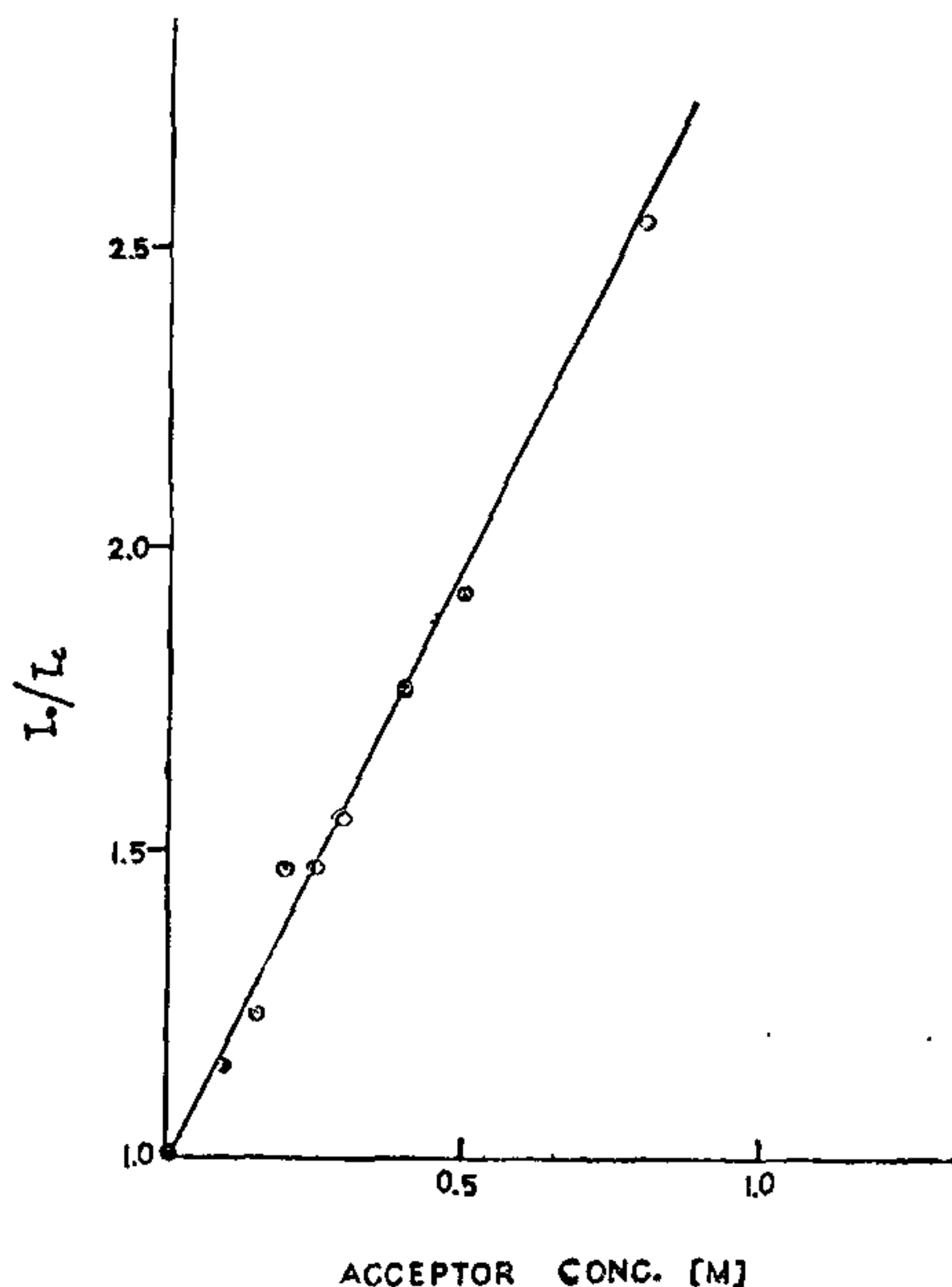

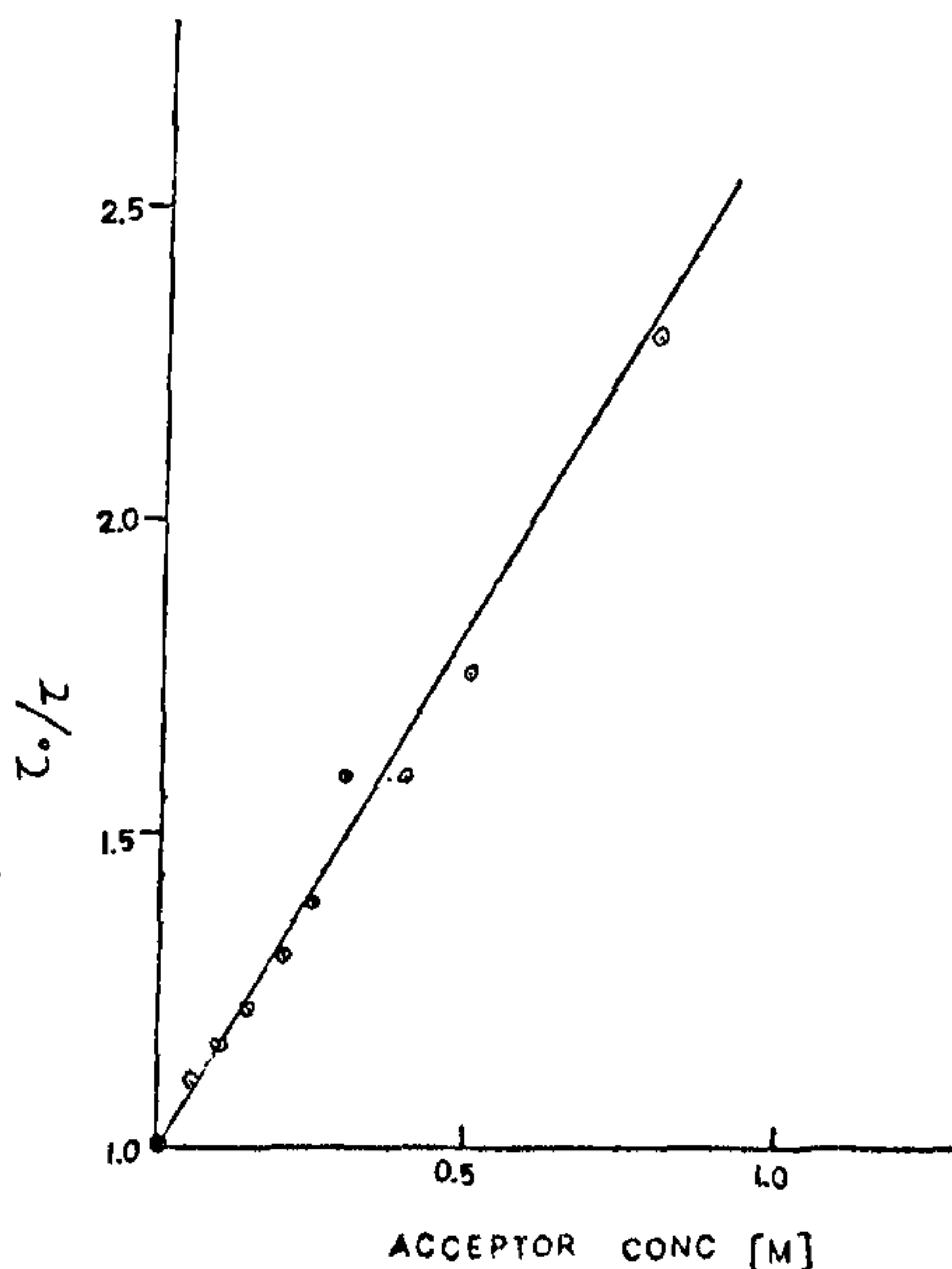FIG. 3. I_0/I_c (with (λ exc = 487 nm) *versus* europium concentration.

FIG. 4. τ_0/τ *versus* europium concentration.

$F_1 \rightarrow {}^5D_0$ is magnetic dipole transition. It has been shown by Dexter[15] that the participation of the magnetic dipole transition in energy transfer is negligible as compared to electric dipole transition. Thus, it is clear that the transfer occurs via mainly ${}^7F_0 \rightarrow {}^5D_0$ but this transition is only weakly allowed. From this, one would predict that such a transfer is short range and of the order of collision diameter.

The critical transfer distance for the excitation transfer probability and spontaneous deactivation probability is calculated from $C_0 = 3000/4\pi N R_0^3$ where C_0 is the critical concentration and N is the Avogadro's number[16]. The concentration at which $\tau = \tau_0/2$ corresponds to the critical concentration. Putting the values of C_0 and N R_0 is found to be 8.31 Å which is in agreement with the short range interaction. The present study however does not explain why only the $Tb^{3+} \rightarrow Eu^{3+}$ transfer in DMSO is r^{-6} dependent while $Tb^{3+} \rightarrow Ho^{3+}$ or Nd^{3+} transfers are r^{-6} dependent. Further work is in progress.

Author expresses sincere gratitude to Dr. D. D. Pant for the helpful discussions and C.S.I.R., New Delhi for financial assistance.

Department of Physics,   J. SHAH.
D.S.B. Constituent College,
Kumaun University,
Naini Tal 263 002 India, *June* 14, 1980.

1. Reisfeld, R., Greenberg, E. and Biron, E., *J. Solid State Chem.*, 1974, 9, 224.
2. — and Hoehm, L., *Ibid.*, 1972, 4, 417.
3. Pant, T. C., Bhatt, B. C. and Pant, D. D., *J. Lumin*, 1975, 10, 323.
4. Hirano, H. and Shiyonoya, S., *J. Phys. Soc., Japan*, 1971, 30, 1343.
5. Van Vitert, L. G., Dearborn, E. F. and Rubin, J. J., *J. Chem. Phys.*, 1966, 45, 1578.
6. Blasse, G. and Bril, A., *Ibid.*, 1967, 47, 1920.
7. Holloway, W. W. and Kestigian, M., *Ibid.*, 1967, 47, 1826.
8. Antipenko, B. M. and Ermolaev, V. L., *Opt. and Spectry.*, 1969, 26, 415.
9. Van Uitert, L. G., *J. Lumin.*, 1971, 4, 1.
10. Kandpal, H. C., Agarwal, A. K. and Tripathi, H. B., *Ibid.*, 1979, 20, 207.
11. Tokousbalides, P. and Chrysochoos, J., *J. Phys. Chem.*, 1973, 76, 3379.
12. Chrysochoos, J. and Evers, A., *Spectrosc. Lett.*, 1973, 6, 208.
13. Bhatt, B. C., Joshi, G. C. and Pant, D. D., *Indian J. Pure and Appl. Phys.*, 1973, 11, 226.
14. Van Uitert, L. G., *J. Electrochem. Soc.*, 1967, 114, 1048.
15. Dexter, D. L., *J. Chem. Phys.*, 1953, 21, 836.
16. Forster, Th., *Disc. Faraday Soc.*, 1959, 27, 7.

MECHANISM OF SUBSTITUTION OF AMINES INTO COBALT(III) AMINE COMPLEXES

ALTHOUGH substitution by anionic ligands into Co(III) amine complexes, has been a subject of investigation by many workers[1], mechanism of substitution by neutral species other than solvent molecules has not been studied extensively. We report here, the results of our studies of substitution by organic bases—piperidine (PIP), diethylamine (DEA), cyclohexylamine (CHA), n-butylamine (BuA) and benzylamine (BA)—into cis- and trans- $[CO (en)_2Cl_2]$ Cl and trans-$[Co (en)_2 Br_2]$ Br; in methanol. The products $[Co (en)_2 (base) X] X_2$ were characterised by their visible and IR spectra. Our observations indicate the operation of a conjugate base mechanism, Dcb (Langford-Gray nomenclature) in these reactions.

Experimental

The complexes were prepared by methods reported in literature[2]. The bases were dried with KOH and distilled before use. Analytically pure solvents were used without further purification. Dowex 50W-X8 resin in the acid form was used for ion exchange experiments.

Method

Reactions were followed conductometrically after mixing the appropriate volumes of complex and base solutions in a thermostated cell. The resistance was preset and the time required by the solutions to attain this value was noted. Complex concentrations were in the range 0·001 to 0·0015 M. The second order rate constants were graphically evaluated using a modified form of the equation suggested by Daniels et al[3].

Rate studies were made at four different temperatures in the range 10–35°C and activation parameters were calculated:

$$Ea \sim 100 \text{ kJ mol}^{-1};$$

$$\Delta S^{\#} \sim +82 \text{ to } +164 \text{ JK}^{-1} \text{ mol}^{-1};$$

$$\Delta G^{\#} \sim 65 \text{ kJ mol}^{-1}.$$

Results and Discussion

Table I gives the rate data at 25°C for substitution of bases into the complexes. It may be noted that the rates are in the order : PIP >DEA > CHA > BuA > BA. It may be of interest to note that the base strengths in water[4] are also in the same order. Values of the free energies of activation in the case of each complex for the substitution of the five bases are almost the same, indicative of an identical mechanism. The large positive entropies of activation observed suggest a dissociative activation process.