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Solvent and Temperature Effects on Fluorescence Emission of Europium β-Diketonates

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Abstract - The fluorescence intensity of the $^5D_0 \longrightarrow {}^7F_2$ transition of trivalent europium ion in differently substituted β-diketone chelates has been determined in solvents of different polarity over a wide range of temperatures.

Author

UNPUBLISHED PRELIMINARY DATA

INTRODUCTION

Characteristic intra 4f shell line fluorescence of trivalent rare earth ions is excited in certain organic complexes by irradiation with light absorbed only by the organic part of the compounds. The ionic fluorescence is the result of an intramolecular energy transfer from the broad absorbing organic ligand to the chelated metallic ion. The process involves (1) absorption from the ground singlet to excited singlet states, (2) intersystem crossing to the lowest triplet state, (3) transfer of energy to the rare earth ion, and (4) ionic fluorescence. Competing processes are the organic fluorescence, phosphorescence, and radiationless deactivation of the organic triplet and/or of the excited metallic ion. The individual steps and the over-all energy migration, as reflected in the fluorescence spectra, are strongly dependent on the surroundings, namely on the nearest neighbors, character of the metal-ligand bonds, resonance in the chelating rings, substituents attached to the chelate rings, temperature, and host. The present study is concerned with the effects of temperature and solvent on the fluorescence intensity.

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EXPERIMENTAL

The preparation and purification of the europium β-diketone chelates was reported previously[2,3]. Spectro grade chloroform, acetone, methanol, acetonitrile, toluene, ethyl acetate, and dimethylformamide were used. Reagent grade pyridine, diethyl ether, and tetralin were redistilled. 10^{-4} molar solutions of europium chelate in different solvents were poured in a clear quartz Dewer provided with a sensitive iron-constantan thermocouple, a cooling tube connected to a liquid nitrogen container, a heating coil, and a capillary tube, all immersed in the solution (Figure 1). The solutions were cooled with cold nitrogen and heated slowly with a nichrome spiral in a closed tube, stirring being performed by a fine stream of dry nitrogen through the capillary. Dry air was caused to circulate over the outside of the Dewar vessel to prevent moisture from condensing at low temperatures. The solutions were irradiated with two sources: the internal Hg vapor lamp in the Cary 14 spectrophotometer in front illumination and an external mercury lamp of 9W perpendicular on the sample-slit beam. The filter system for the excitation sources was described elsewhere[2,4]. The relative fluorescence intensity of the $^5D_0 \rightarrow {}^7F_2$ transition of europium ion was determined with the Cary 14 spectrophotometer employing the fluorescence attachment. Different slit-widths were used depending on the intensity and comparable values were found by extrapolation to 0.5 mm slit on a slit-width - relative intensity logarithmic diagram.

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(2) W. F. SAGER, N. FILIPESCU, and F. A. SERAFIN, J. Phys. Chem. (in press)

(3) N. McAVOY, N. FILIPESCU, M. R. KAGAN and F. A. SERAFIN, J. Phys. Chem. Solids 25, 461-8 (1964)

(4) N. FILIPESCU, W. F. SAGER, and F. A. SERAFIN, J. Phys. Chem. (in press)

RESULTS AND DISCUSSION

The following diketonates of europium have been investigated: dibenzoylmethide, benzoylacetonate, theonyltrifluoroacetonate, p-methoxydibenzoylmethide, di-p-methoxydibenzoylmethide, m-methoxydibenzoylmethide, and di-m-methoxydibenzoylmethide. The nitro substituted dibenzoylmethides and the aliphatic β-diketonates (acetylacetonate, trifluoroacetylacetonate, and hexafluoroacetylacetonate) of europium do not emit significantly in liquid solutions. The relative intensity of the $^5D_0 \rightarrow {}^7F_2$ transition has been determined over the freezing point - boiling point temperature range and the results are illustrated in Figures 2-8. In some of the solvents the chelates exhibited detectable fluorescence only in the solid frozen system. Solvent quenching of the ionic fluorescence in solution can take place at different stages of the intramolecular energy transfer. The excited singlet state of the ligand formed upon absorption has a relatively short lifetime ($\sim 10^{-8}$sec.) compared to the ^5D states of the ion ($\sim 10^{-3}$sec.) and the lowest triplet of the organic ligand (< 0.5 sec.). The probability of ligand triplet state quenching by the solvent is orders of magnitude higher than for the quenching of the excited singlet or ^5D europium states. This is substantiated by the total absence of phosphorescence (lowest triplet → ground singlet emission) from gadolinium chelates[2] in liquid solution in any solvent. It has been generally found that the radiationless conversion from the upper singlet to the triplet (intersystem crossing) occurs with about the same efficiency in ordinary liquid solutions as in solids and rigid solutions[5]. It is reasonable to assume that the excited singlet state deactivation by solvent quenching is negligible. A simplified scheme is:

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(5) (a) G. PORTER and M. WINDSOR, Proc. Roy. Soc. (London) A 245, 238 (1958); (b) L. J. HEIDT, "Photochemistry in the Liquid and Solid States", J. Wiley, N.Y., 1957

$^7FS_0 + h\nu \longrightarrow {}^7FS_1$	Organic absorption
$^7FS_1 \xrightarrow{k_1} {}^7FT$	Intersystem crossing
$^7FT \xrightarrow{k_2} {}^5DS_0$	Transfer of energy to the ion
$^7FT + (S) \xrightarrow{k_3} {}^7FS_0 + (S)$	Solvent quenching of the organic triplet
$^5DS_0 \xrightarrow{k_4} {}^7FS_0 + h\nu_f$	Ionic fluorescence
$^5DS_0 + (S) \xrightarrow{k_5} {}^7FS_0 + (S)$	Solvent quenching of the excited ion

Where ^7F - the ground state of the europium ion

S_0 - the ground state of the organic ligand (singlet)

S_1 - the first excited singlet state of the ligand

T - the lowest triplet state of the ligand

^5D - the excited state of the europium ion

(S)- solvent

ν and ν_f - the organic absorption and ionic emission frequencies respectively

If the concentrations are expressed in molecules/cc., and the absorption and emission intensities in quanta/cc./sec., in a stationary concentration:

$$\frac{I_f}{I_a} = \frac{1}{1 + \frac{k_5}{k_4} e^{-\frac{E_i}{RT}} + \frac{k_3}{k_4} e^{-\frac{E_t}{RT}} + \frac{k_3k_5}{k_2k_4} e^{-\frac{E_i-E_t}{RT}}} \qquad (1)$$

where E_i and E_t are the heats of activation of the quenching of the excited ion and the triplet state respectively[6]. If the solvent quenching of the ^5D ionic excited state is negligible compared to the triplet quenching ($k_5 \ll k_3$), then eq. (1) leads to:

$$\log_{10}\frac{I_a-I_f}{I_f} = \log_{10}\frac{k_3}{k_4} - \frac{E_t}{2.3RT} \qquad (2)$$

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(6) This is only an approximation where both E_i and E_t incorporate other paths of radiationless degradation of the excited ionic or organic triplet states such as intramolecular quenching by vibronic coupling to the ligand and changes in transition probabilities on solvent - chelate complex formation, which are not taken into consideration in the above discussion.

The data in Figures 2-8 could be used to evaluate E_t and $\log_{10}\frac{k_3}{k_4}$ in eq. (2), with I_a estimated from I_f at low temperatures. However, the calculated values would be only crude approximations because (1) the quantum efficiency is not unity even at low temperatures, (2) the curves do not tend to a common value for the relative intensity at low temperatures, and (3) E_t and $\log_{10}\frac{k_3}{k_4}$ in eq. (2) preserve only vaguely their meaning[6].

Two ways of solvent-chelate interaction affecting the fluorescence intensity are possible: complex formation and collisions. Both can take place in the same solvent. The collisional deactivation depends on temperature, steric effects, and quenching efficiency of collisions. The result is a degradation of energy from the excited chelate (triplet or ^5D) by conversion to vibrational or translational energy. The complex formation results from donor-acceptor bonding between the solvent and chelated ion and may go as far as to replace ligand groups in the case of solvents with high polarity. In general it is apparent that a higher fluorescence intensity is recorded at the same temperature for the same chelate in a solvent of higher dipole moment. Two effects may explain this behavior: (1) an increase in energy transfer from the ligand to the ion and/or an increase in the intra 4f radiative transition probability as a result of the new field introduced by the complexing solvent molecules, which is more powerful for the more polar solvents, and (2) a "cloud" formation around the ion by the polar solvent molecules, with a decrease in collisional quenching efficiency.

The negative temperature effects are explained by both the tendency to dissociate the solvent-chelate complex with removal of its positive effects and an increased number of collisions at elevated temperatures. The fact that the asymetrically substituted β-diketonates (benzoylacetonate and theonyltrifluoroacetonate) have a smaller temperature effect than the dibenzoylmethides indicate that the molecular field distortion introduced by the solvent molecules on complex formation is less significant than the perturbations introduced in the molecular field of the dibenzoylmethide chelates whose ionic emission decreases rapidly with the increase of temperature.

The fluorescence of europium in organic chelates has been subject for extensive investigations in connection with its use in liquid lasers.[7-9] The variation of the fluorescence intensity for the same chelate at the same temperature in different solvents is rather significant. By employing proper solvents, the need for extensive refrigeration of the laser cavity containing the chelate solution may diminish substantially. For example, the methanol-ethanol mixture employed for the europium benzoylacetonate laser[7] needs efficient cooling to -90°C to obtain a fluorescence intensity comparable with the one emitted by the same chelate at ambient temperature in dimethylformamide or acetone. Other factors such as line broadening and optical, chemical, and thermal properties of the host will have to be evaluated. The spectral distribution of energy in the fluorescence spectra of europium β-diketone chelates as a function of substituents was reported previously[4] and together with the present data will give an indication as to the selection of chelate-solvent pairs for laser applications. Mixtures of solvents cannot be disconsidered as potentially valuable liquid base hosts. Small amounts of a solvent with high polarity may accomplish both positive aspects - molecular field distortion through complex formation and "aggregate" arrangement - offering protection from collisional quenching. However, if ligand groups are displaced on solvation this would be detrimental to a laser, first because the "free" ligand would absorb at the same wavelength as the chelate thus decreasing the pumping efficiency and second because it will bring an undesired extra thermal energy in the cavity. Excessive absorption by the organic ligand has been the main reason for the use of small diameter laser cavities. To overcome "overabsorption" in chelate liquid lasers, mixtures of different chelates of the same ion, which absorb in adiacent spectral regions could be employed if the lasing transition ($^5D_0 \longrightarrow {}^7F_2$) in the chelates coincide. Probably

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(7) H. SAMELSON, A. LEMPICKI, V. A. BROPHY, and C. BRECHER, J. Chem. Phys. <u>40</u>, 2547 2553 (1964)

(8) H. WINSTON, O. J. MARSH, C. K. SUZUKI, and C. L. TELK, J. Chem. Phys. <u>39</u>, 267 (1963)

(9) E. T. SCHIMITSCHEK and E. G. K. SCHWARTZ, Nature <u>196</u>, 832 (1962); G. A. CROSBY J. Mol. Spectry. 8, 315 (1962)

even better results may be obtained by using "mixed" chelates, namely complexes grouping around the same ion various ligands able to absorb at different wavelengths. These mixed chelates would also present the advantage of a more distorted symmetry about the ion which will increase the intra 4f "forbidden" transition probabilities. Work along these lines is continued.

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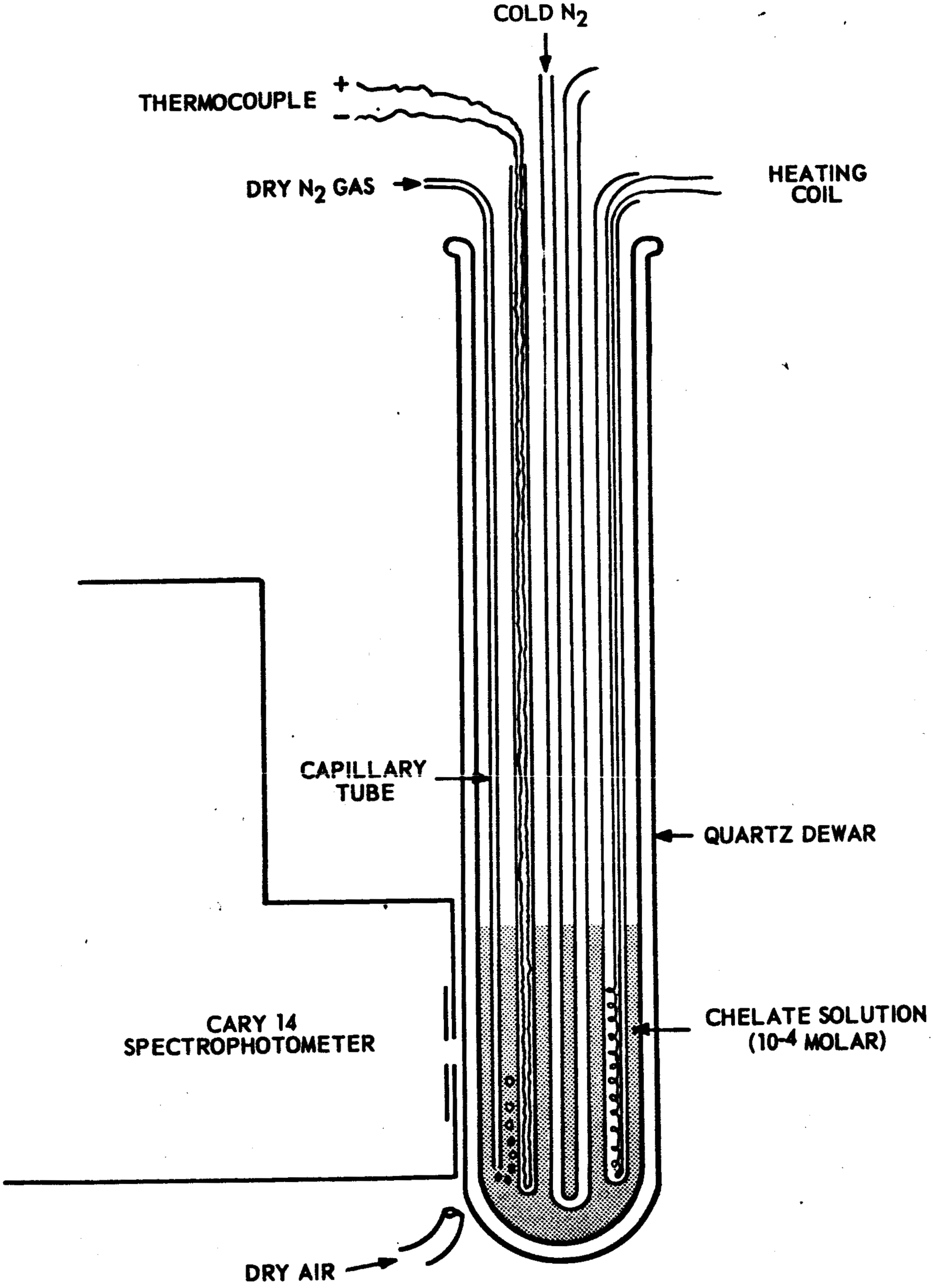

FIGURE 1

EXPERIMENTAL ARRANGEMENT

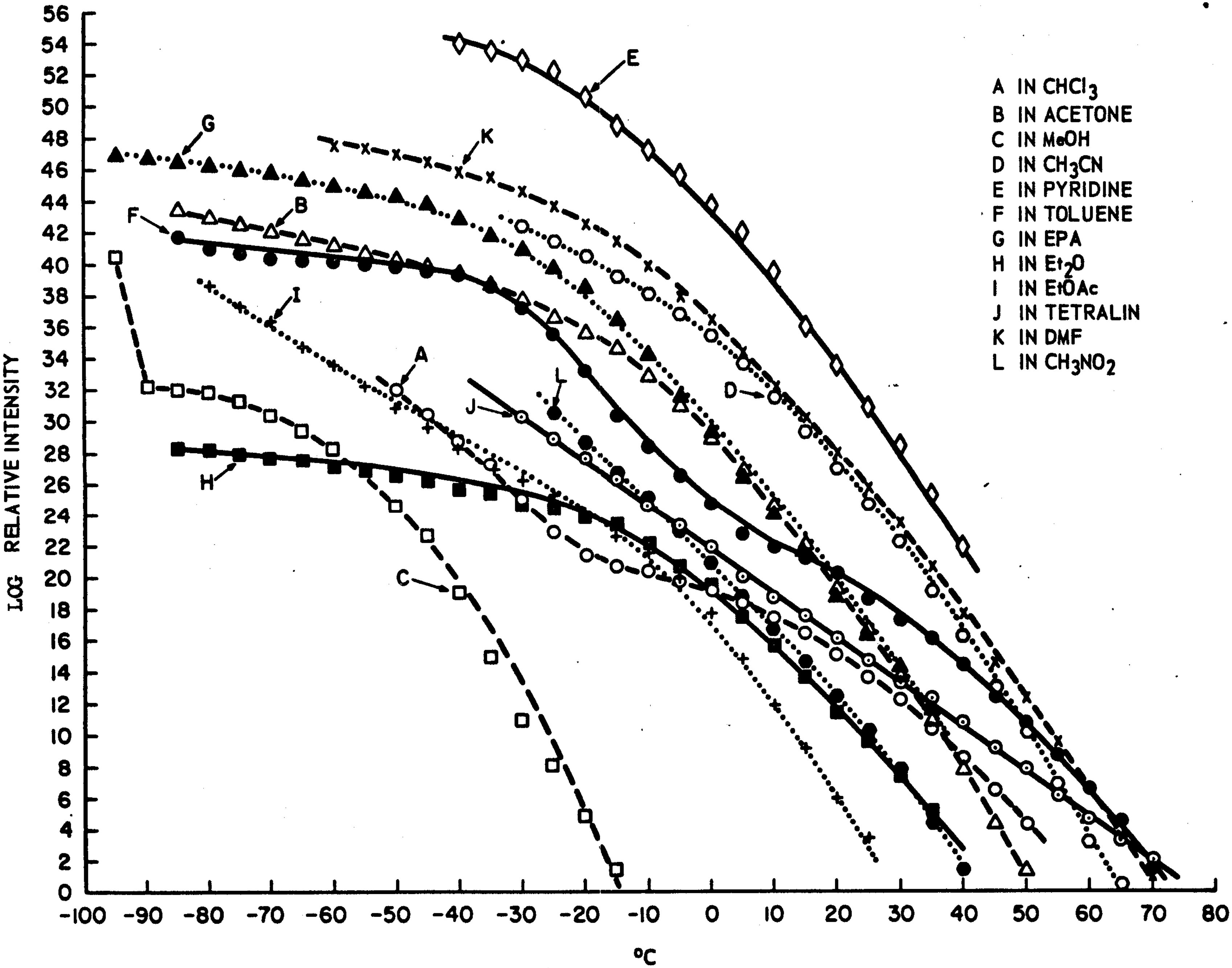

FIGURE 2

Europium dibenzoylmethide, 10^{-4} M, $^5D_0 \longrightarrow {}^7F_2$ line.

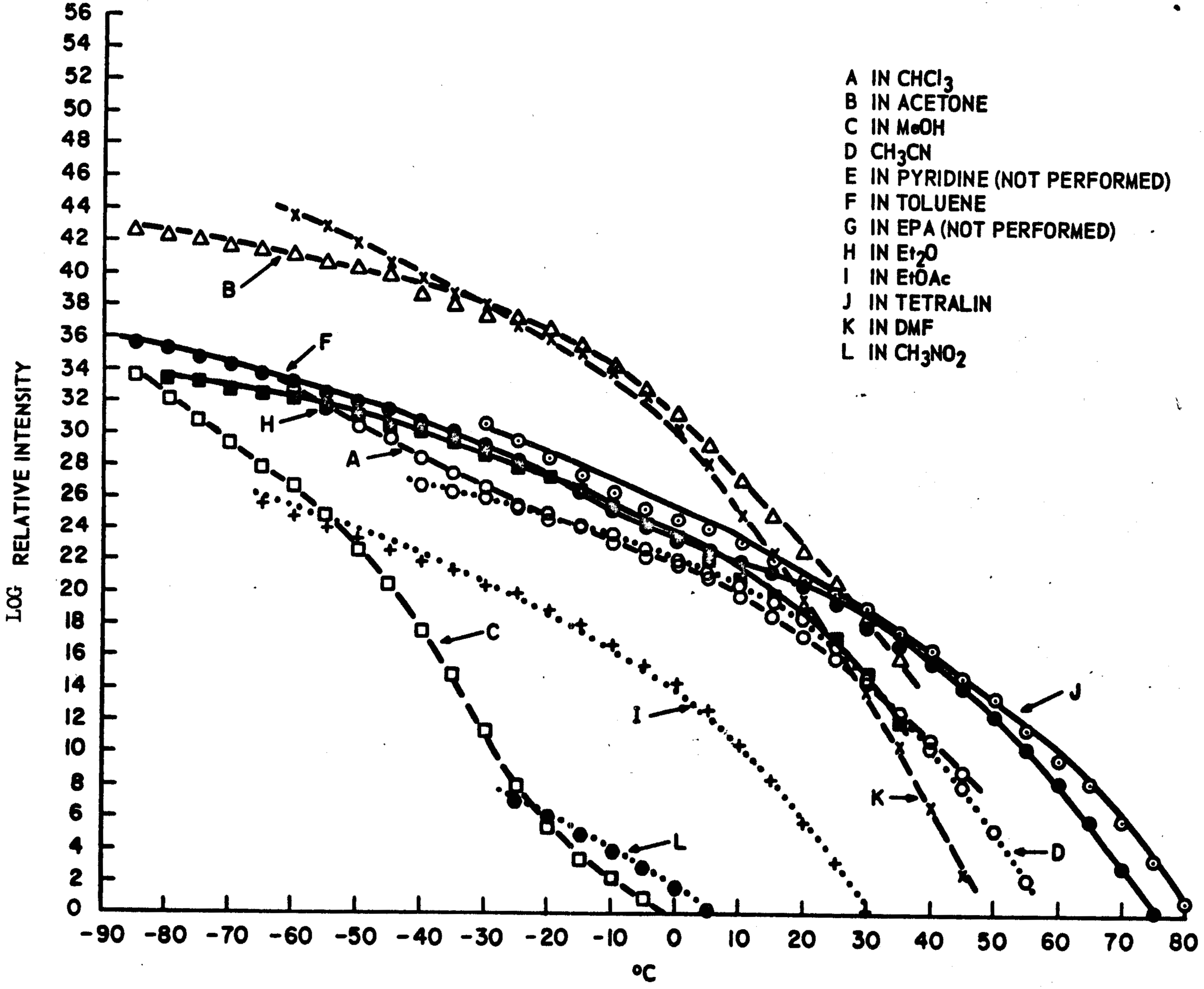

FIGURE 3

Europium benzoylacetonate, 10^{-4} M, $^5D_0 \longrightarrow {}^7F_2$ line.

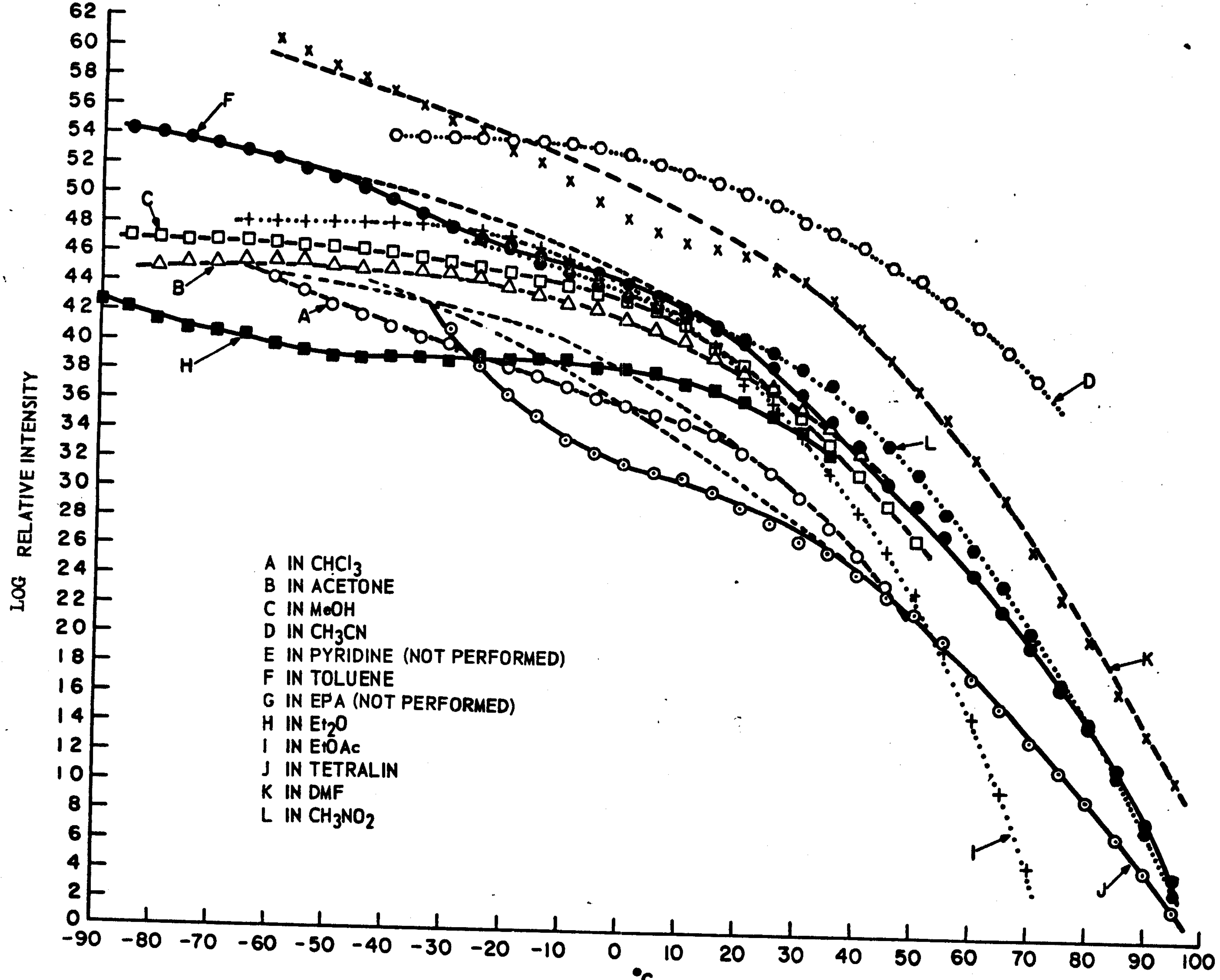

FIGURE 4. Europium theonyltrifluoroacetonate, 10^{-4} M, $^5D_0 \longrightarrow {}^7F_2$ line.

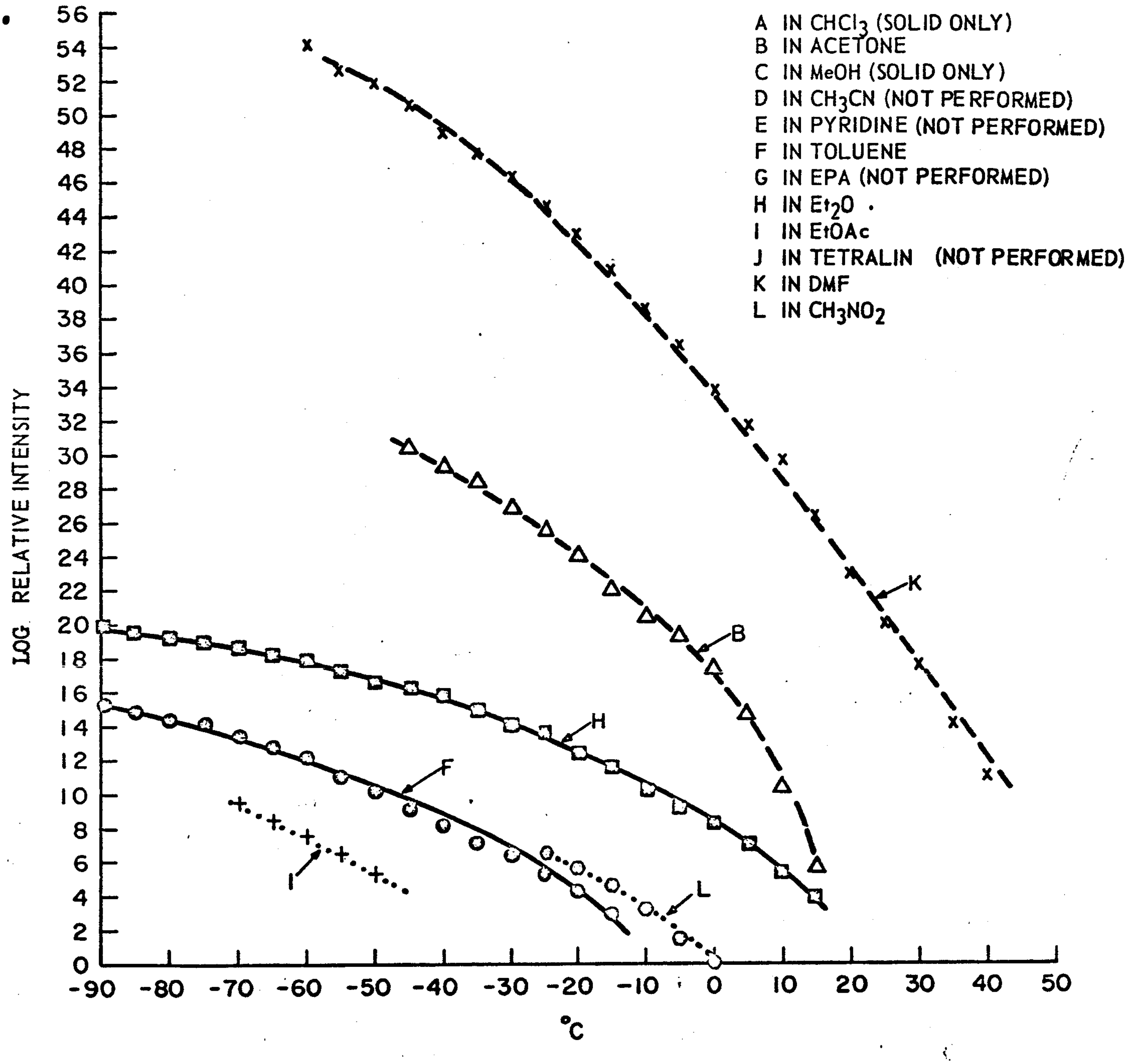

FIGURE 5. Europium p-methoxydibenzoylmethide, 10^{-4} M, $^5D_0 \longrightarrow {}^7F_2$ line.

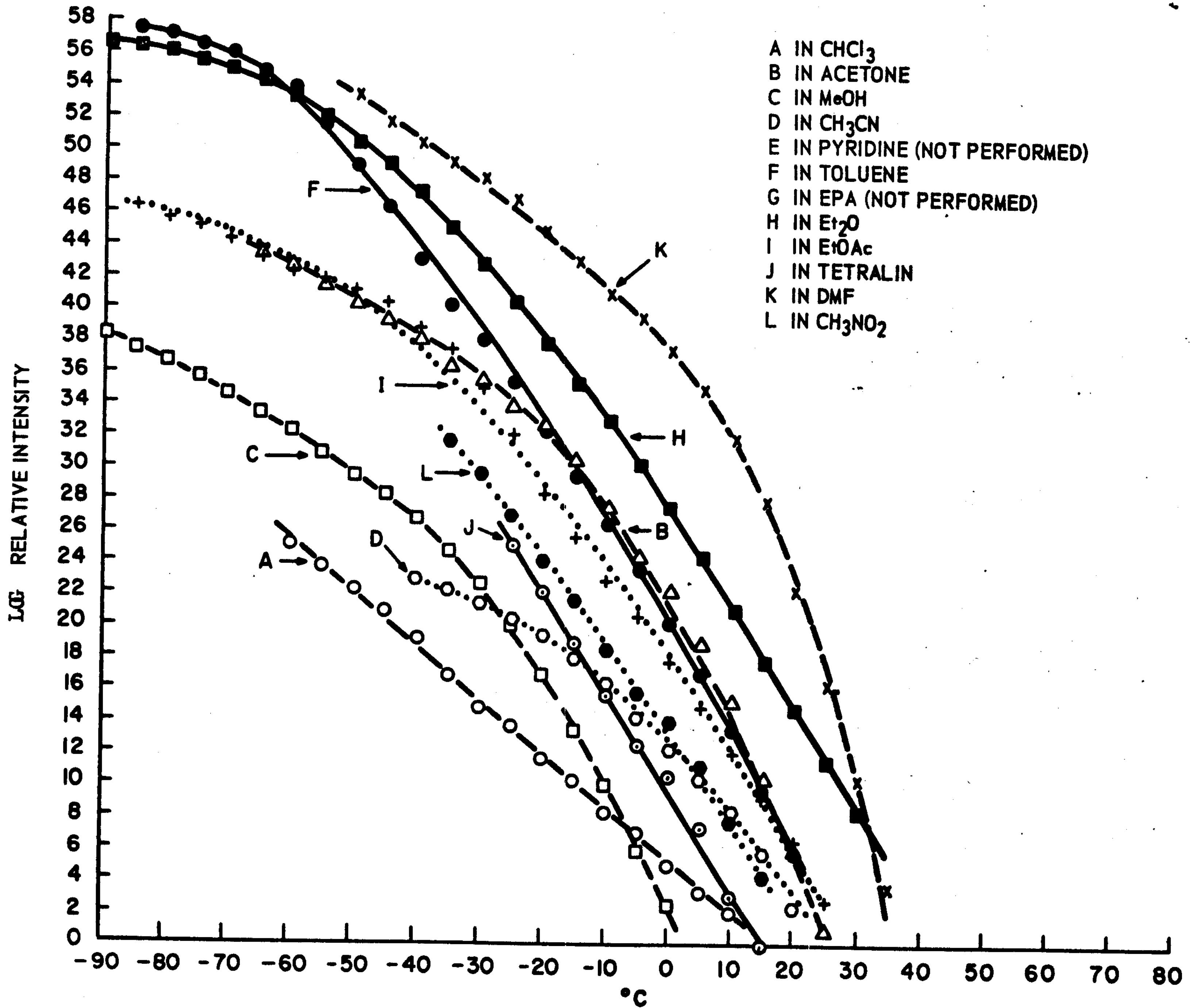

FIGURE 6. Europium di-p-methoxydibenzoylmethide, 10^{-4} M, $^5D_0 \rightarrow {}^7F_2$ line.

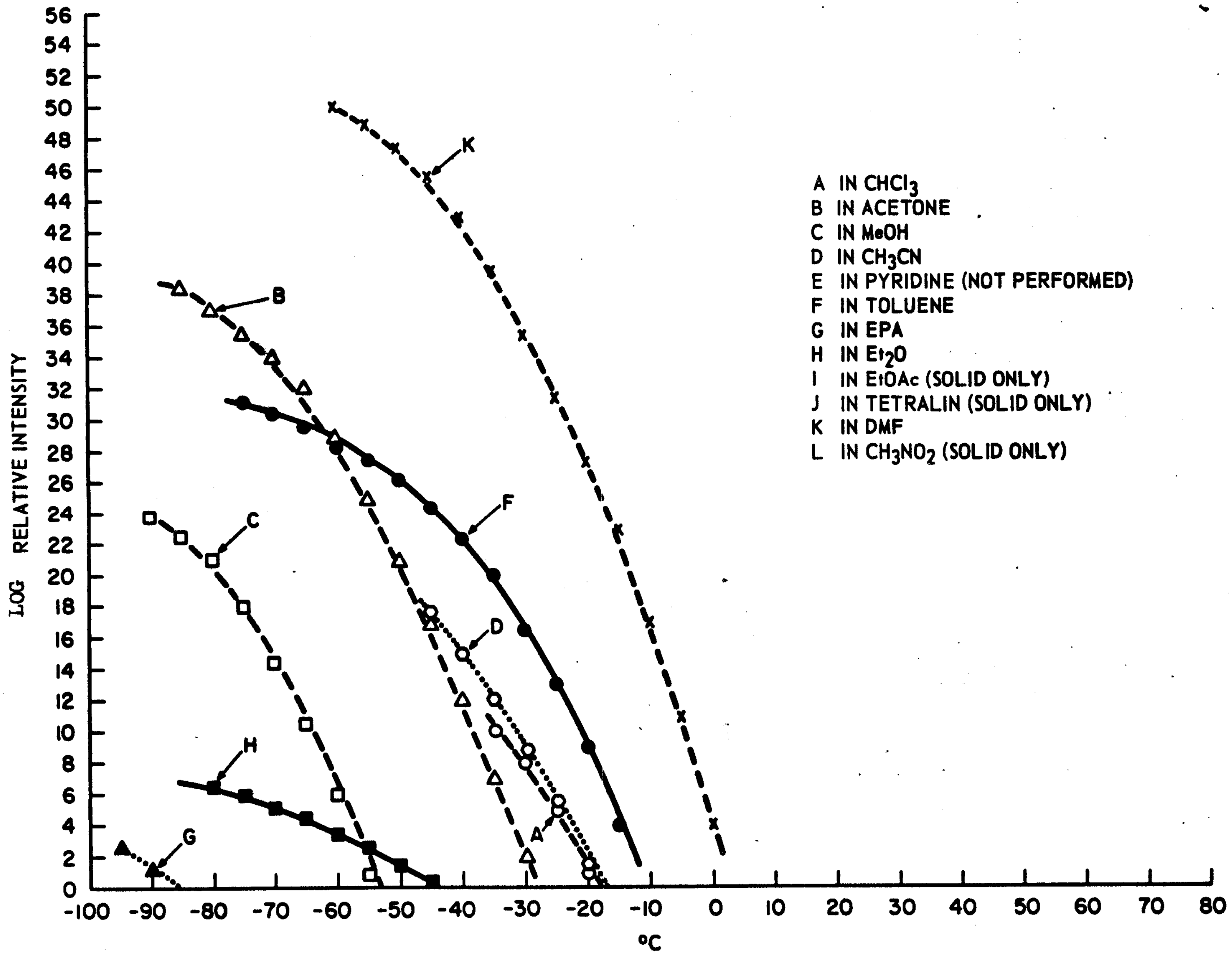

FIGURE 7. Europium m-methoxydibenzoylmethide, 10^{-4} M, $^5D_0 \rightarrow {}^7F_2$ line.

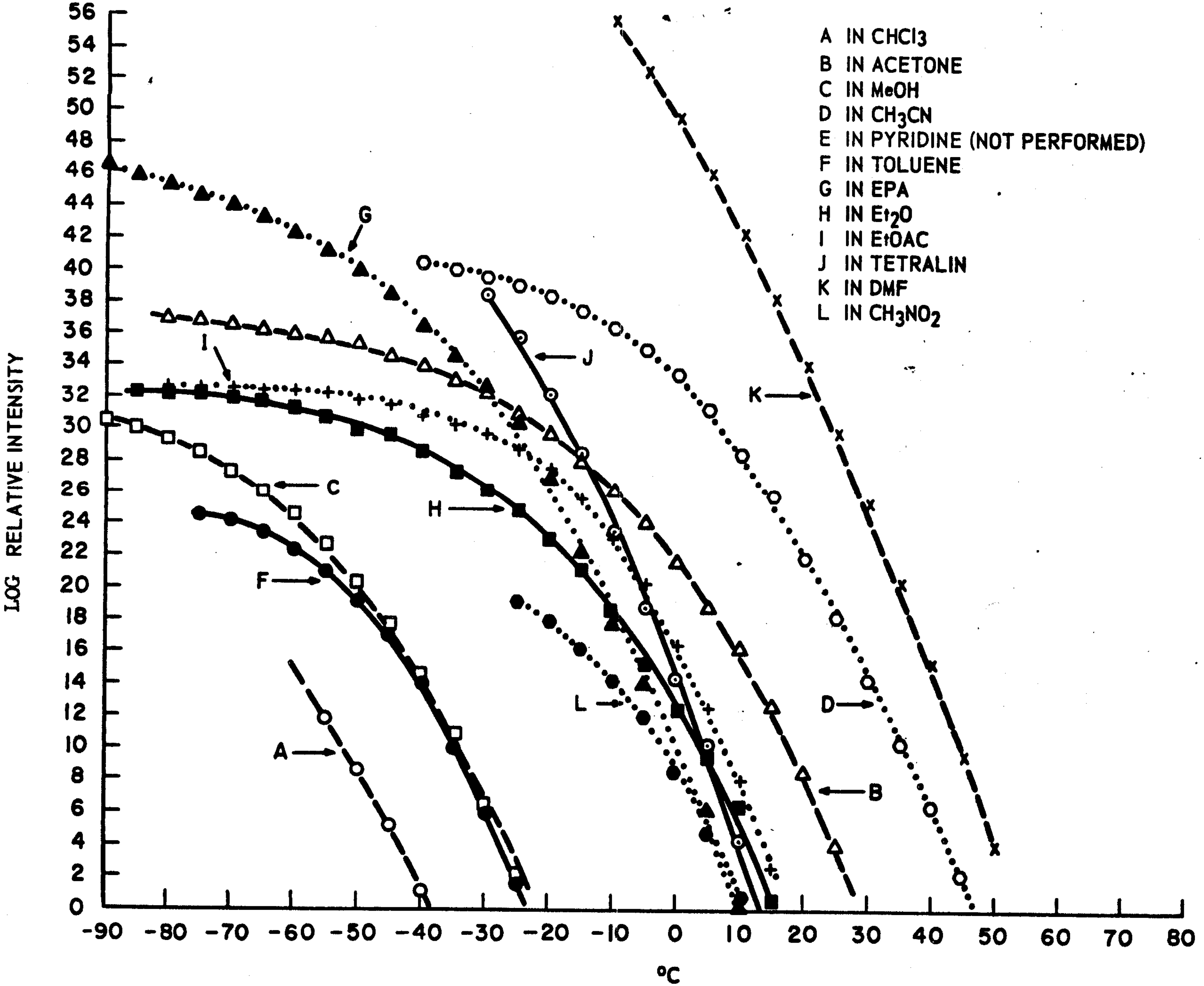

FIGURE 8. Europium di-m-methoxydibenzoylmethide, 10^{-4} M, $^5D_0 \longrightarrow {}^7F_2$ line.