

EFFECT OF SOLVENT ON THE POLARIZATION OF FLUORESCENCE OF ACRIDINE ORANGE

THE polarization of fluorescence of most of the dye solutions have been found to depend upon several factors, viz., viscosity of the solvent¹, migration of the excited state from the originally excited molecule to a neighbouring molecule², shape and size of the fluorescent molecule³, temperature, etc. Perrin's formula¹ giving a correlation between polarization and viscosity is not able to explain the effect of solvent on the polarization of fluorescence completely particularly when the viscosity is low. The present note deals with the observed variation in the fluorescence polarization in terms of the dipole-dipole interaction.

The polarization of fluorescence of acridine-orange (conc $\sim 2 \times 10^{-6}$ g/cc) has been measured at room temperature ($\sim 30^\circ\text{C}$) with an Amino Bowman spectrophotofluorometer. For solution in each solvent, the excitation and emission peaks were located and them polarization was calculated using the method of Azumi⁴. The effect of background and scattered light for each solvent was measured by using pure solvent in the cuvette. The contribution of this effect to the intensity of fluorescence was found to be less than 0.5%. The observed fluorescence intensity was accordingly corrected. The results obtained for polarization along with peak excitation and emission wavelengths are given in Table 1. The Table also includes the values of dipole moment and viscosity which are taken from standard Tables^{5,6}.

It is, therefore, likely that the observed variation in polarization is due to the dipole moment of the solvent. From the Table it is obvious that percentage polarization increases as the dipole moment increases. The effect can be explained as follows :

During the short interval of time in which the absorption of the excitation energy takes place, the dipole moment of the solute molecule under the influence of dipole-dipole interaction in the solvent cage of the surrounding solvent molecule remains unchanged. But the solute molecule gets enough time before a radiative transition takes place to reorient itself in the cage to get a new equilibrium state and this causes fluorescence depolarization. The Brownian rotation tends to destroy this equilibrium orientation and causes further depolarization. But the Brownian rotation is opposed by the dipole-dipole interaction between solvent-solute molecules which for a given solute depends on the dipole moment of the solvent. Thus this interaction tries to reduce the depolarization caused by the Brownian rotation. Therefore, the polarization is expected to be higher in a solvent with higher dipole movement. In the case of formamide and *n*-butanol, the viscosities are almost of the same order, percentage polarization is found to be higher in a solvent of higher dipole moment (formamide). Similarly for water and ethanol, ethanol and acetic anhydride, acetic anhydride and water, the percentage polarization is observed to be higher with increase of dipole moment. However, if the dipole-dipole interaction adds to the

Results

TABLE I

Solvent	Dipole moment	Viscosity η (CP)	λ_{ex} (nm)	λ_{em} (nm)	% P
Formamide	3.25	3.307	486	520	3.3
Water	2.3	1.002	490	520	3.2
Acetic anhydride	2.80	0.900	486	574	2.5
Ethanol	1.70	1.197	482	512	2.1
<i>n</i> -Butanol	1.67	2.900	482	510	2.2
Methanol	1.65	0.594	482	512	2.1

Discussion

From the above Table it is seen that the observed variation in polarization cannot be accounted for as viscosity effect alone because a plot of $1/P$ and $1/\eta$ (perrin plot) is not linear. Also as the concentration is low, the electromagnetic coupling of neighbouring molecules and its effect on depolarization due to energy migration is small. In any case, the concentration is the same in all the solvents and hence the variation in polarization cannot be explained only by energy migration.

Brownian rotation, the depolarization will further increase causing the percentage polarization to decrease with increasing dipole moment.

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THE CRYSTAL STRUCTURE OF MONOADIPATO TETRAAQUO NICKEL (II)

THE title compound $\text{Ni}(\text{C}_6\text{H}_8\text{O}_4) \cdot 4\text{H}_2\text{O}$ was studied in this laboratory to investigate hydrogen bonding in crystalline solids as also to study the oxygen ligands around the metal.

Synthesis—The compound was prepared by the reaction of stoichiometric amounts of adipic acid and nickel carbonate and crystals were grown out of water solution. The crystals were thin elongated and platelike in appearance.

Crystal Data—Monoclinic with $a = 11.70$, $b = 9.77$, $c = 4.75 \text{ \AA}$, $\beta = 99^\circ 19'$, space group $P2_1/a$, $D_{\text{obs}} = 1.70 \text{ g/cc}$, $D_{\text{cal}} = 1.71 \text{ g/cc}$, $Z = 2$. Reflections (670) were collected using single crystal Weissenberg photography. The intensities were estimated visually and the data processed applying usual corrections. The relative intensities were brought to approximate absolute scale by statistical method.

Structure determination and comments—The structure is solved by the heavy atom technique. The metal atoms occupy special positions of centres of symmetry. The acid residues also occupy centres of symmetry. The water molecules are in general position.

A view of the crystal structure down [001] is shown in Fig. 1. In the crystal there is a six-fold co-ordination around nickel with distances ranging from 2.06 to 2.11 \AA (shown by dotted lines). The structure is held together by ionic linkages and hydrogen bonds provided by the water molecules (shown by dashes and dots in the figure). The hydrogen bonds range from 2.65 to 2.96 \AA . Chains of adipate anions are linked *via* water molecules parallel to [100].

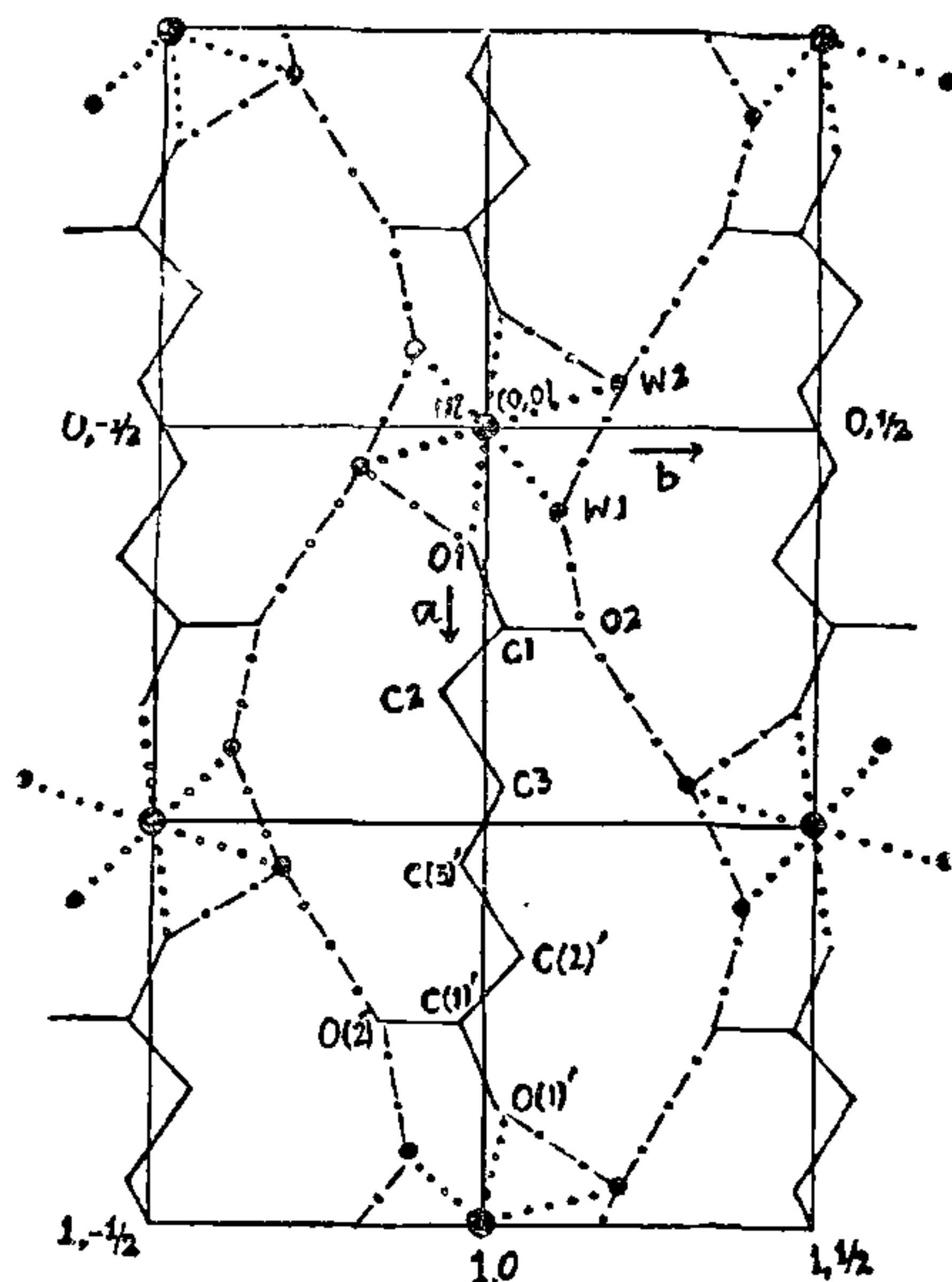


FIG. 1. The crystal structure down [001] axis.

Further work is in progress to locate the hydrogen atoms and to refine the positional and thermal parameters.

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FORMATION CONSTANTS AND THERMODYNAMIC PARAMETERS OF SOME POLY-HYDROXY PHENOLS

Experimental

ALL the chemicals used were of Analar quality. Polymetron model CL-41 pH-meter was used for pH-metric titrations. pH-metric titrations of free perchloric acid and perchloric acid with ligands, in aqueous medium, were carried out against standard caustic soda solution while maintaining the ionic strength at 0.1 M (sodium perchlorate).

Results and Discussion

The Irving-Rossotti method¹ was used for calculating \bar{n}_A values and the protonation constants $\log K_1^{H'}$ and $\log K_2^{H'}$ by half-integral method, as suggested by