

found to grow by spiral mechanism when the concentration of ammonium carbonate is between 1 M and 2 M. However above 2 M solution of ammonium carbonate, these crystals grow in spherulitic and dendritic form.

The growth steps starting from a single screw dislocation group can easily spread on the surface of the crystal as a continuous spiral or successive spirals. This is what we observe in Fig. 1. The formation of double spirals can be explained by assuming that the factors controlling the growth of the crystals might create local slip, with the result that two screw dislocations of opposite sign will be created at the two extremities of the slip. These screw dislocations will give rise to two spirals of opposite sign, which will ultimately form loops as observed in our investigation. Pits formed at the centre of the spirals represent the points of emergence of the dislocations.

Parts of the arms of the spirals are parallel to the respective edges of the rhombohedral face; this leads us to assume that the spiral belongs to calcite and not due to any foreign growth.

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#### HIGH RESOLUTION NMR STUDIES IN THE SOLUTION OF OXALIC ACID IN DIOXANE

RECENT ultrasonic studies<sup>1-3</sup> on oxalic acid and benzoic acid in dioxane solutions have shown that the adiabatic compressibility of the solution decreases with the increase of concentration, attains a minimum value and then increases with further increase of concentration of the carboxylic acid. The minimum adiabatic compressibility in the solution of oxalic acid in dioxane was observed at the mole fraction of

0.08. This has been interpreted as due to the formation of hydrogen bonds between monomer carboxylic acid and dioxane. The behaviour of the compressibility above the critical concentration has been explained as due to the formation of dimer hydrogen bonds among the carboxylic acid molecules in addition to the hydrogen bonds formed between monomer carboxylic acid and dioxane. High resolution NMR studies would provide a method of verifying the above hypothesis. If dimers are existing below the critical concentration, the chemical shifts should be large since the hydrogen bonds in dimers are stronger than hydrogen bonds between monomer and dioxane. Hence to obtain further confirmation on this aspect, the high resolution NMR chemical shift studies for proton signal in the solution of oxalic acid dihydrate in dioxane are carried out and the results are reported in this paper.

Chemically pure AR/BDH samples of dioxane and oxalic acid dihydrate were used in the study. The NMR spectra were recorded in Varian XL 100 NMR spectrometer in the concentration ranges 0.06 to 0.10 mole fraction of the acid. The RF field was kept sufficiently low to avoid saturation effects. The chemical shift for protons in these solutions is calculated with reference to CH<sub>2</sub> signal of dioxane<sup>4</sup> which occurs at 3.7 ppm. The chemical shift in the solution of oxalic acid dihydrate and dioxane has been plotted as function of concentration in Fig. 1. from which it can be seen that the downfield chemical shift initially increases with the increase of concentration and attains the maximum value at the mole fraction of 0.09 and then remains at the same value for higher concentrations.

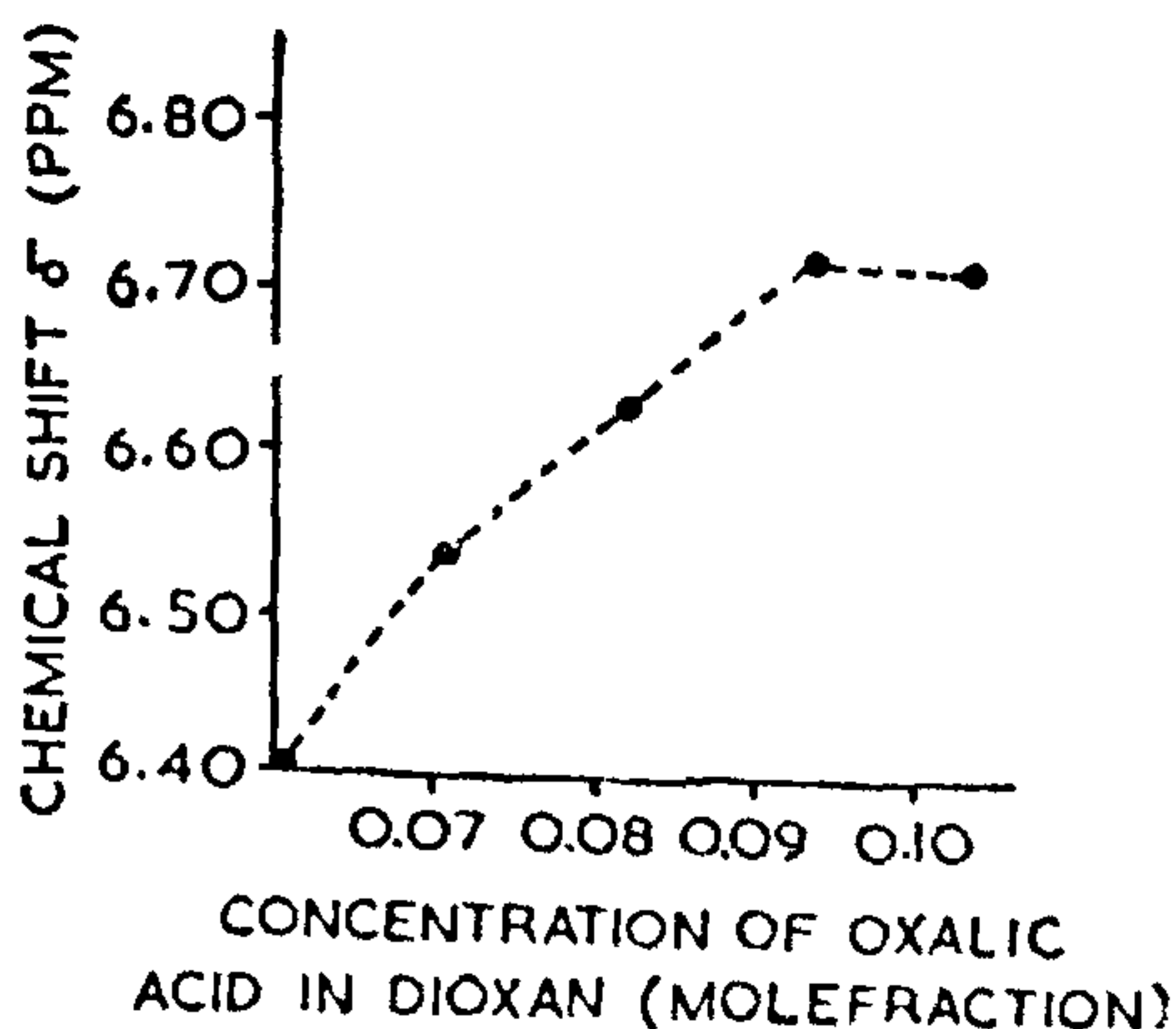


FIG. 1. Graph showing the variation of chemical shift as a function of concentration of oxalic acid in dioxane.

It is known that the proton chemical shift is an indication of the strength of hydrogen bonding in liquids<sup>5,6</sup>. The initial increase of the proton chemical shift, with concentration of oxalic acid in the present studies shows that the hydrogen bond strength increases with concentration and this is in conformity with our earlier studies by ultrasonic method<sup>1</sup>. The explanation that is usually offered is that solvent dioxane breaks the oxalic acid dihydrate into free water, and hydrogen bonds are formed between the monomer carboxylic acid and dioxane molecules. Since the carboxylic protons are highly electropositive, the formation of O-H...O hydrogen bonds of carboxylic acid monomer with dioxane molecules is favoured more than the hydrated water dioxane hydrogen bonds. The ultrasonic experiments conducted by adding proportionate amount of water (equivalent to water of hydration of oxalic acid) to dioxane support the above view. The proton chemical shift depends only on the strength of the hydrogen bonds but does not have any bearing on the nature of hydrogen bonds in the solution. If dimers were existing in the concentration range mentioned above, the proton chemical shift should be large and independent of the concentration of the oxalic acid. The present high resolution NMR study shows that the dimer carboxylic acid groups are not present to any significant extent as to influence the chemical shift in the concentration ranges 0.06 to 0.09 mole fraction.

The proton chemical shift above the concentration of 0.09 mole fraction of oxalic acid remains constant at the value of 6.74 ppm. with increase of concentration. The proton signal for carboxylic acid usually occurs in the range of 10-13 ppm<sup>7</sup>. In the present study, the chemical shift is in the range of 6.40 to 6.74 ppm. and this may be due to the rapid exchange of carboxylic acid protons with hydroxyl protons of hydrated water released by dioxane. The fact that the proton chemical shift attains the maximum value and remains constant above 0.09 mole fraction shows that dimers carboxylic acid are present in the solution above the critical concentration thereby confirming our earlier observations<sup>1</sup>. Once the formation of these dimers in the solution is favoured, the chemical shift should remain independent of concentration as the dimers are the strongest possible hydrogen bonds that are likely to be present in the solution. However one should observe an increase in the NMR signal strength with the increase of concentration above the critical concentration even though the chemical shift remains the same and such an increase in the NMR signal strength is observed in the present studies.

A comparison of the present high resolution NMR studies and our earlier ultrasonic studies in solution

of oxalic acid in dioxane shows that the observed critical concentration is slightly higher in NMR studies. This difference may be due to the exchange interaction between the carboxylic protons and water protons which does not probably affect the ultrasonic velocity to any significant extent.

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#### MORPHOLINE-4-CARBODITHIOATE AS A GRAVIMETRIC REAGENT FOR Zn(II), Cd(II) AND Hg(II)

MORPHOLINE-4-carbodithioate has been found to give white precipitate with Zn(II), Cd(II) and Hg(II) at pH 4.0-11.0. These metals have been estimated from their binary mixtures using ammonical EDTA as the masking agent. The sensitivity of reactions (in  $\mu\text{g/ml}$ ) has been found to follow the order  $\text{Zn} < \text{Cd} < \text{Hg}$ . Physico-chemical methods reveal 1 : 2 metal ligand ratio in all the three cases.

Metal complexes of various carbodithioates<sup>1-3</sup> have been widely studied with respect to their applications in various fields. Morpholine-4-carbodithioate of potassium has not yet been used as a gravimetric reagent for these metals, though Bayer and Ott<sup>4</sup> have reported it as a possible chelating agent. Brown *et al.*<sup>4</sup> have reported the bidentate behaviour