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PROPERTIES OF TGS AQUEOUS SOLUTION FOR CRYSTAL GROWTH

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A study has been made of the properties of triglycine sulfate (TGS) aqueous solution relevant to its use for single crystal growth. Measurements of the solubility, index of refraction, density, viscosity, diffusivity, and optical dispersion are presented and discussed. A knowledge of these properties is of importance for controlling and modeling the growth process and for obtaining high quality single crystals.

1. Introduction

Single crystals of triglycine sulfate $(NH_2CH_2COOH)_3(H_2SO_4)$ are grown from aqueous solution and are of interest because of their physical properties and their application as infrared detectors. As a pyroelectric material at temperatures below 49°C, TGS possesses an axis of spontaneous electrical polarization which is along the (010) crystallographic direction [1]. The electrical polarization is temperature dependent and it is this property which is utilized in fabricating thermal infrared detectors from single crystals. TGS undergoes a space group transformation from $P2_1$ to $P2_1/m$ at 49°C with a loss of both its pyroelectric and ferroelectric properties [2].

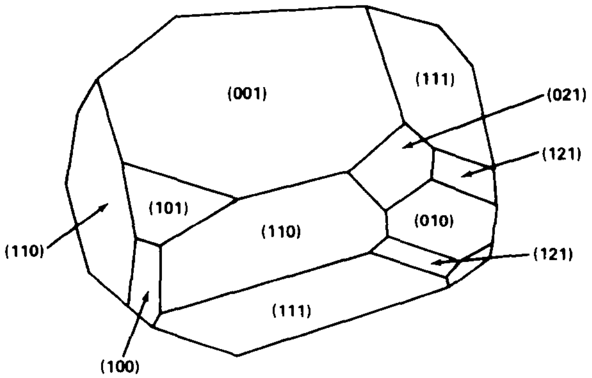

Fig. 1. Typical TGS crystal habit, illustrating various crystallographic directions. The polar axis is in the (010) direction, along the b-axis. The cleavage plane is perpendicular to the polar axis.

Fig. 1 shows a facetted TGS crystal and identifies various crystallographic directions. TGS has a monoclinic structure with $a = 9.41$ Å, $b = 12.63$ Å, $c = 5.73$ Å and $\beta = 110°23'$ [3–5]. It also possesses a natural cleavage plane which is perpendicular to the *b*-axis, which is the pyroelectric axis. Thus cleaved sections give proper orientation for use as infrared detectors.

In order to make a good quality detector, one with a low noise equivalent power (NEP) or high detectivity (D), a high quality single crystal must be used [6,7]. Common crystallographic defects such as inclusions and dislocations are believed to adversely affect the detectivity of TGS and determine its limits of sensitivity. In order to understand, control and model those aspects of the growth process which lead to high quality single crystals a study was made of the physical properties of the TGS growth solution [8,9].

2. Measurements and procedure

The first step in seeded solution crystal growth is to determine the solubility curve. The research literature contains much solubility data, however there is a wide spread of values in the data from different investigators. For this reason we carried out our own determination over the temperature

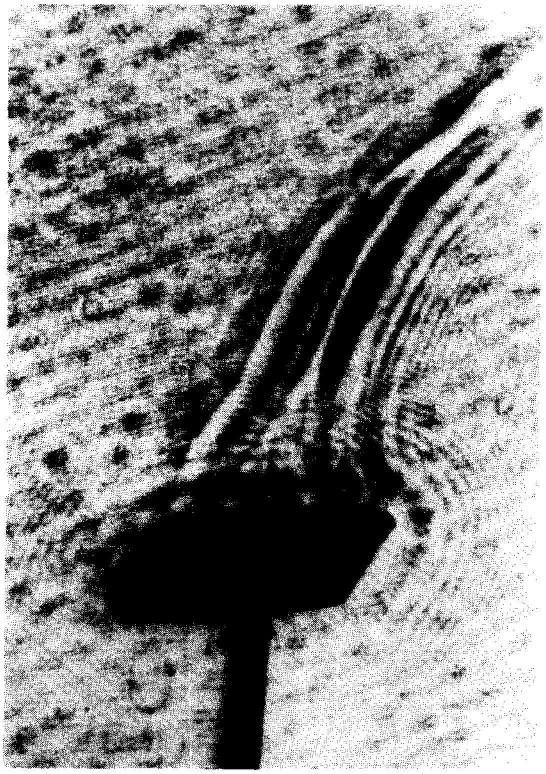

Fig. 2. Shadowgraph image of TGS crystal growing from solution illustrating growth plume.

range 25 to 50°C. The technique used was to accurately prepare solutions of specific concentrations, insert a seed crystal and then slowly adjust the temperature until the seed was in complete equilibrium with the solution and no growth or dissolution occurred. In some cases we constructed a shadowgraph image (fig. 2) of the seed crystal. These images very clearly delineated the presence of a growth or dissolution plume and was the best method for accurately determining the saturation temperature.

Fig. 3 shows the solubility curve for TGS. For comparison data of Brezina, Davey and White, and Nitsche are also shown [10–12]. The data from these three investigators was chosen for comparison because of the relative close agreement among themselves, while many other investigators have published data considerably different in value.

When an aqueous solution is made for crystal growth by weighing, mixing, and heating the components some water vapor is often driven off during the heating stage leading to an uncertainty in the final concentration. Also one would like to monitor the concentration at various times during a crystal growth run or to re-use a partially depleted solution. This requires the ability to determine the concentration of an existing solution.

We found that the index of refraction of a TGS solution is a sensitive indicator of its concentration [13,14]. The index of refraction of samples of known concentrations was measured. These measurements were made using an Abbe refractometer with a temperature controlled sample stage using light of $\lambda = 5893$ Å from a sodium vapor lamp. The temperature range over which the measurements were made was from 24 to 60°C and the concentrations were from 30 g TGS/100 cm^3 H_2O to 60 g TGS/100 cm^3 H_2O. One advantage of this method is that it only requires a sample volume of a few milliliters to make the measurement. Fig. 4 shows the index of refraction versus temperature. The saturation concentration and isoconcentration lines are also shown.

In some experiments it may be necessary to work with light of a wavelength different than the 5893 Å sodium light. For example, we have been using a HeNe laser of 6328 Å for schlieren and shadowgraph imaging of the growth process. Thus we need to determine the dispersion relationship. Measurements of the index of refraction were made on samples of TGS solutions of different concentrations and at different temperatures using both the sodium lamp and the HeNe laser. In all cases it was found that the value of the index of refraction was 0.0014 lower for the 6328 Å light. The dispersion is

$$\mathrm{d}N/\mathrm{d}\lambda = -3.2184 \times 10^{-6},$$

where $\mathrm{d}N$ is the change in index of refraction and $\mathrm{d}\lambda$ is the change in wavelength (Å). One can calculate the index of refraction at other wavelengths by using the two-constant form of Cauchy's equation

$$N_\lambda = A + B/\lambda^2,$$

where

$$B = \frac{\lambda^3}{2}\frac{\mathrm{d}N}{\mathrm{d}\lambda} = 366216.$$

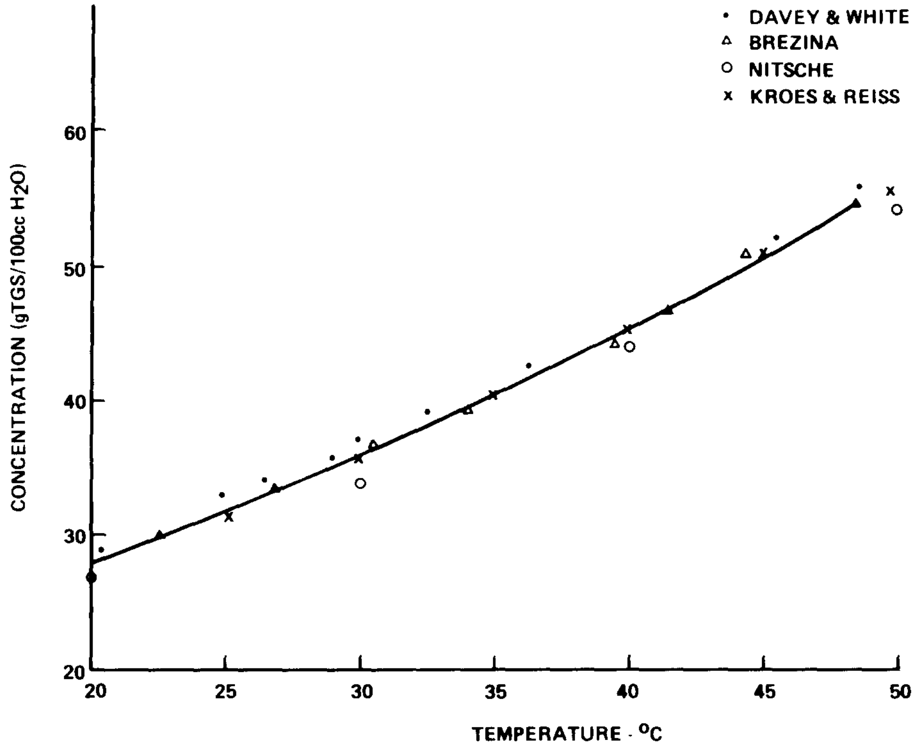

Fig. 3. Solubility curve for Aqueous TGS solution.

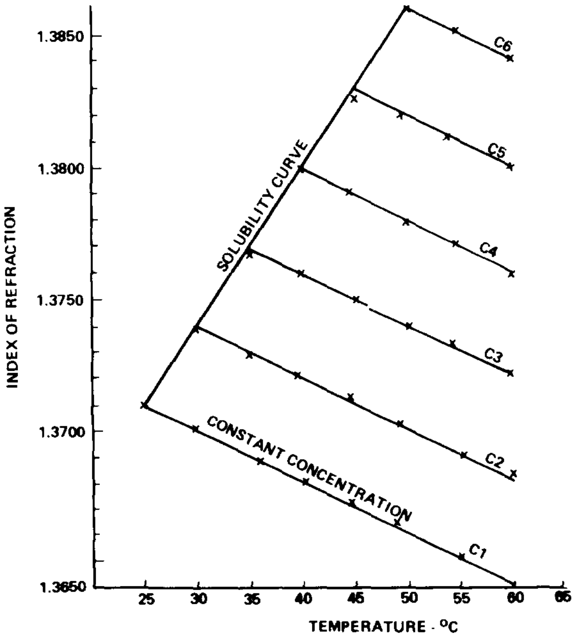

Fig. 4. Variation of the index of refraction with temperature and concentration of TGS solutions.

The constant A for a given solution concentration and temperature can be gotten from the data in fig. 4. For greater accuracy over a wider range of wavelengths the above procedure could be ex-

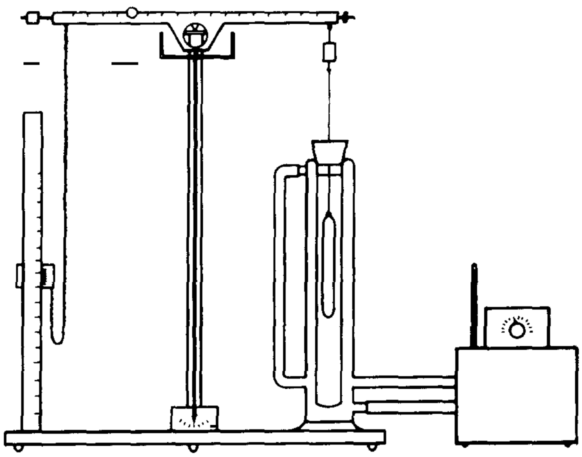

Fig. 5. Apparatus for measuring the density versus temperature at various concentrations of TGS solutions.

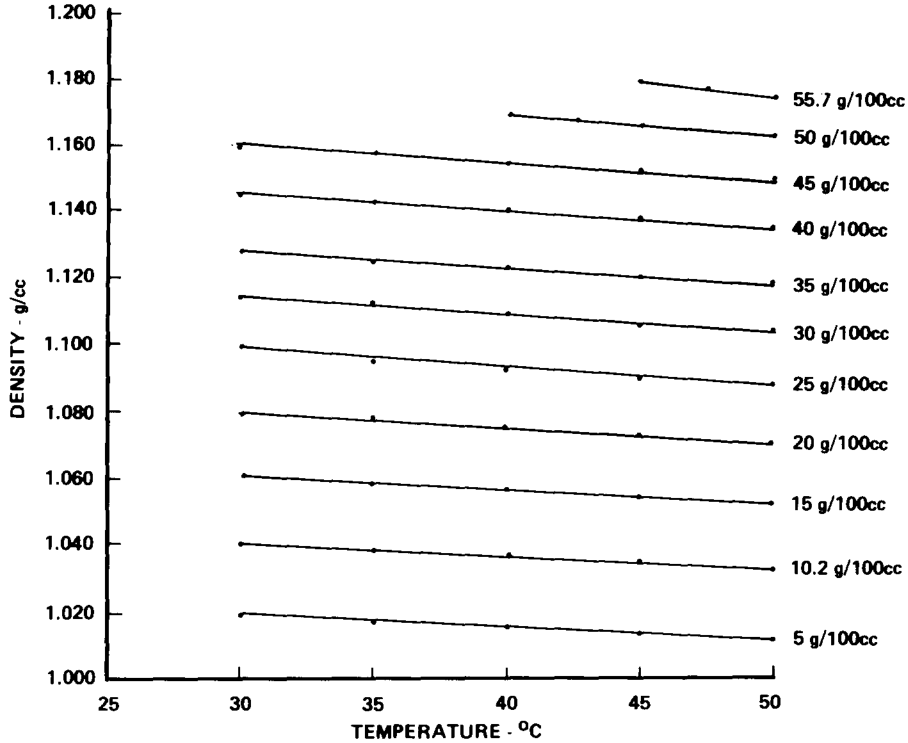

Fig. 6. Density of TGS solutions versus temperature.

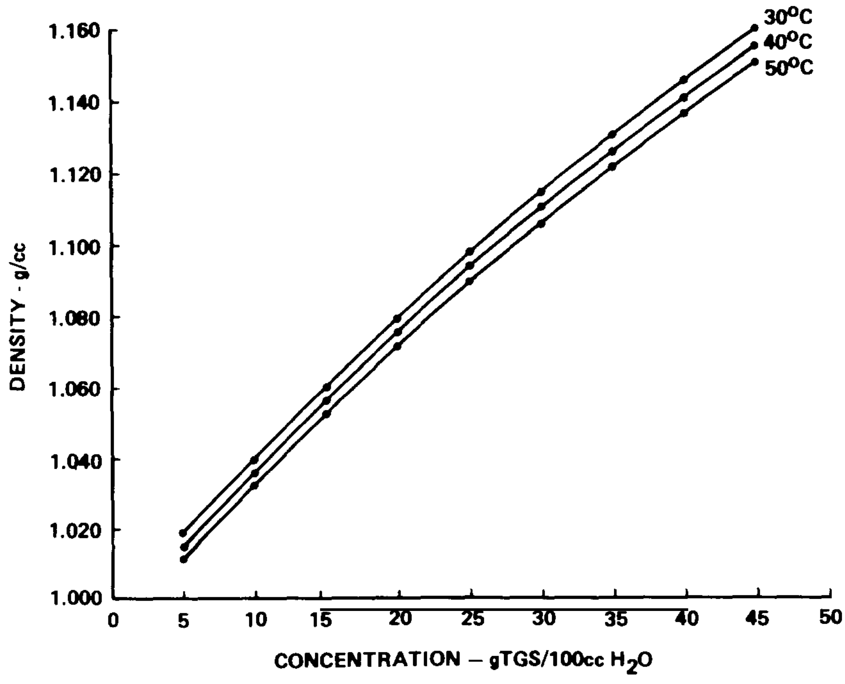

Fig. 7. Density of TGS solutions versus concentration measured at 30°C, 40°C and 50°C.

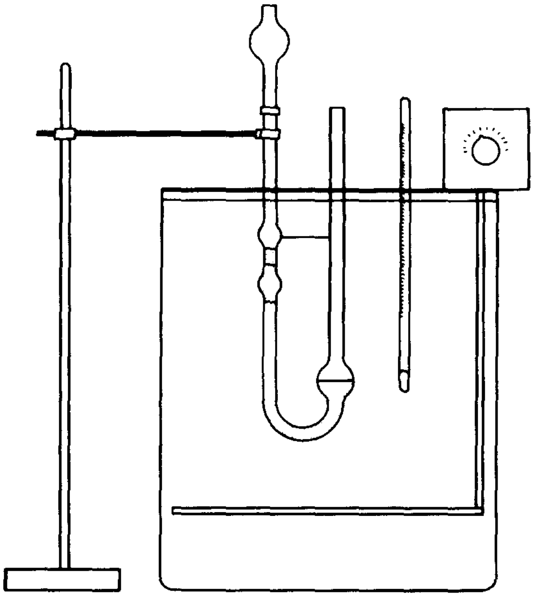

Fig. 8. Apparatus used to measure viscosity of TGS solutions.

tended using measurements at three different wavelengths and applying the three-constant Cauchy equation

$$N_\lambda = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4}.$$

In analysing optical images of the growth process the significant optical parameter is N, the index of refraction. However, in relating this to fluid dynamic equations which model fluid flow and mass transport one needs to convert from the index of refraction, N, to the mass density, ρ. Hence a series of measurements was made to determine the density as a function of concentration and temperature. The measurements were made using a chain balance and glass specific gravity plummet (fig. 5) capable of measurements to ± 0.0001 g/ml. A temperature controlled glass cell controlled to $\pm 0.1°C$ was used to contain the solution and measurements were made over the

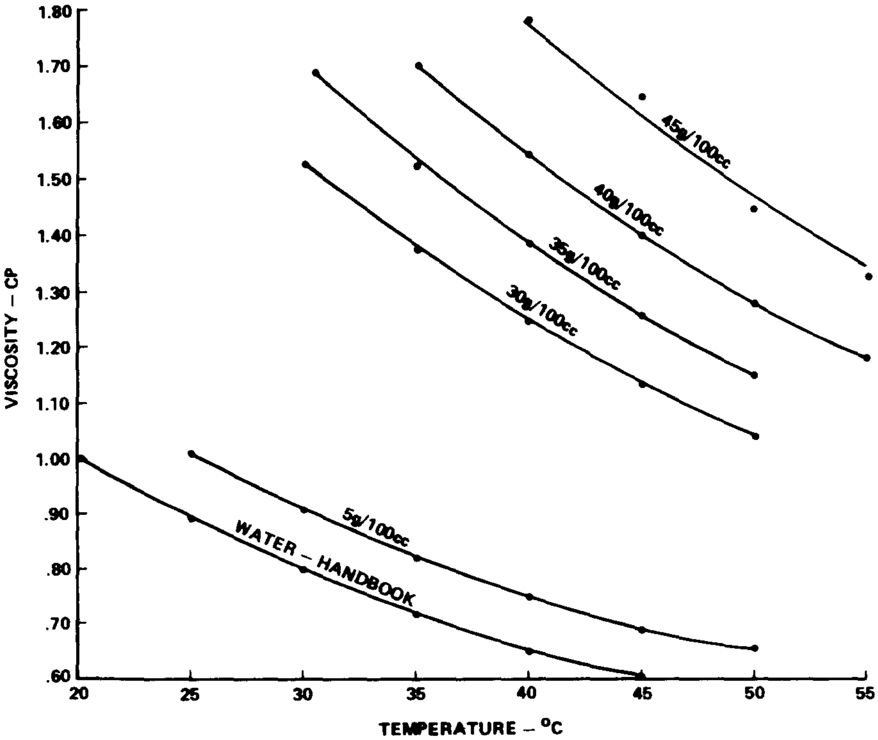

Fig. 9. Viscosity of TGS solutions versus temperature.

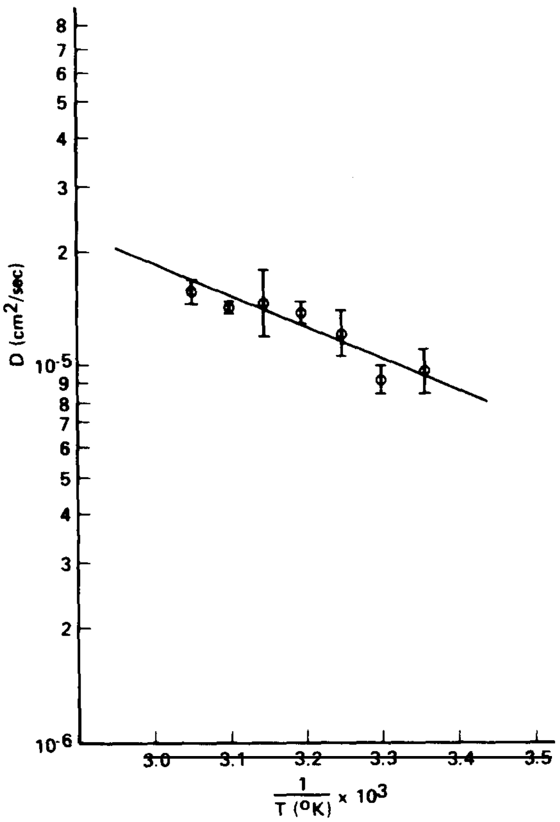

Fig. 10. Diffusion coefficient of TGS in water as a function of the reciprocal of temperature.

range 24 to 50°C. Figs. 6 and 7 show the concentration and temperature dependence of the density.

Another parameter used in modeling fluid flow is viscosity. It relates momentum transfer to fluid shear by the relationship $\tau = -\mu \mathrm{d}v/\mathrm{d}y$. The viscosity was measured for concentrations of 5 g TGS/100 cm^3 H_2O to 45 g TGS/100 cm^3 H_2O over a temperature range of 20 to 55°C using a Ubbelohde viscometer immersed in a temperature controlled water bath (fig. 8). Viscosity is determed by measuring the time required to draw a known volume of fluid through a capillary with a constant pressure difference across the fluid column. Fig. 9 shows the viscosity as a function of temperature for various concentrations. Water is included as a reference.

In order to calculate the growth rate of a single crystal from solution it is necessary to know the mass diffusion coefficient. As a crystal grows from solution a concentration depletion layer forms around the crystal. New solute must be transported from the bulk solution across the depletion layer to the crystal–liquid interface for continued growth. The concentration gradient is the driving force and mass diffusion the mechanism governing this mass transport. The mass diffusion of TGS in water was measured using a two-chamber glass cell. A solution of TGS was allowed to diffuse from the bottom chamber through a porous glass frit into the upper chamber which initially contained pure water. The diffusion cell was immersed in a thermal controlled water bath controlled to ±0.01°C. Fig. 10 shows the diffusion coefficient of TGS in water as a function of the reciprocal of temperature.

3. Summary

A study has been carried out to measure properties of a TGS aqueous solution relevant to its use for single crystal growth. The data from the solubility curve will suffice to start growing fair quality single crystals. However in order to mathematically model the growth process other solution parameters as presented in this paper are also necessary. To study the dynamics of the growth process using optical techniques such as schlieren, shadowgraph or interferometry requires a detailed knowledge of the optical index of refraction and how it is related to temperature and concentration changes as well as density. Using the index of refraction to determine the solution concentration enables one to monitor in real time the concentration in a crystal growth apparatus and gives one the flexibility of making adjustments in the temperature to keep a constant degree of supersaturation to maintain a constant growth rate.

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