CHAPTER IV

EXPERIMENTAL DETAILS

(A) Sample Preparation

This section contains a brief description of the nature of the NaCl:Tl samples used in the present investigations. Microcrystalline samples were prepared by the usual method of crystallization from aqueous solution. These samples were studied in as-received condition and after various thermal and mechanical pretreatments. The base material used was "specpure" NaCl supplied by Johnson, Matthey and Co., London, which according to the manufacturers, is spectroscopically pure. Investigations were also carried out on NaCl:Tl solution. For this purpose the base material used was analar grade BDH sodium chloride which was certified to have a purity of 99.9%. According to the manufacturers, the maximum probable impurities are insoluble matter 3×10^{-3} %, free acid (HCl) 1.8×10^{-3} %, free alkali 0.05 ml. N/1 %, bromide and iodide (Br) 5×10^{-3} %, ferrocynide $[Fe(CN_6)]$ 1×10^{-4} %, nitrate (NO_3) 5×10^{-4} %, phosphate (PO_4) 5×10^{-4} %, sulphate (SO_4) 2×10^{-3} %, ammonium (NH_4) 5×10^{-4} %, arsenic (As) 4×10^{-5} %, Barium (Ba) 1×10^{-3} %, calcium group and magnesium (Ca) 4×10^{-3} %, iron (Fe) 3×10^{-4} %, heavy metals (Pb) 5×10^{-4} % and potassium (K) 1×10^{-2} %.

In both the above cases the impurity used was thallium added in the form of salt, viz. TlCl, which was supplied by E. Merck, Germany.

Extreme care was taken in regard to the cleanliness and purity while preparing and handling the samples. All the surfaces which were to come in contact with the phosphor were cleaned by washing soda and kept in running water for an hour. The surfaces were then kept in contact with concentrated hydrochloric acid and nitric acid for 24 hours, to remove contamination or stray elements. Finally the surfaces were kept in contact with boiling distilled water for nearly two hours and then dried thoroughly in an oven.

To prepare microcrystalline samples of NaCl:Tl by crystallization from aqueous solution, the weighed quantity of sodium chloride was dissolved in double distilled demineralized water and the weight of the impurity as determined by the molar calculation was added to the solution. Subsequently the solution was heated slowly on a hot plate, until the excess of water was completely driven out. Microcrystals were collected, dried at about 40°C, powdered and mixed homogeneously.

The specimens thus prepared are designated "as-received" samples. The concentration of the impurity (Tl) in representative lot was determined by the spectrophotometric analysis. The 214 nm absorption band of Tl^+ in water solution was utilized for this purpose. Thallium concentration in these samples varied in the range of 10^{-4}, 10^{-3}, 10^{-2} and 10^{-1} m.f.

The specimens thus prepared from aqueous solutions were studied after subjecting them to thermal and mechanical treatments. In the thermal treatment, powder NaCl:Tl specimen, was enclosed in evacuated and sealed tube made of pyrex glass. The sealed capsule was kept in a muffle furnace maintained at about 500°C for about 24 hours. At the end of 24 hours, the capsule was removed from the furnace and kept on a massive iron block, maintained at room temperature and quenched rapidly by a blast of cold air. The rate of cooling for such sample was on an average 80°C per minute. Such samples are termed as "annealed and quenched specimens".

The specimens were also prepared by melting the mixture of sodium chloride and thallous chloride powder and quenching the melt to room temperature. The known

weight of TlCl powder as determined by the molar calculation, was placed at the bottom of a cleaned platinum crucible. The requisite amount of NaCl powder was placed on its top. The platinum crucible with the mixture was then placed inside the muffle furnace. The temperature of the furnace was adjusted till above the melting point of NaCl (801°C). The molten mass in crucible was subsequently poured onto a silica dish maintained at room temperature. The massive, compact, poly crystalline specimen thus obtained was powdered and mixed homogeneously. These specimens are designated as "melt and quenched specimens".

Mechanical treatment was given to all the above specimens. The polycrystalline specimens of a suitable quantity were compressed to tablets in a stainless steel press using a mechanical vice. The average size of the tablet was about 1.0 cm in diameter and 0.1 cm in thickness. The pressure under which the specimens were compressed was around 2000 Kg/cm^2.

Measurements were also made on the excitation and emission spectra of TlCl powder of saturated

NaCl-solution with varying amounts of TlCl dissolved in it and of aqueous TlCl-solution of various concentrations.

(B) Instrumentation

The excitation and emission spectra in the present work were examined by means of Aminco-Bowman Spectrophotofluorometer supplied by American Instrument Co., Inc. It consists of an optical unit, photomultiplier, microphotometer and a power supply. The optical unit includes an electrical panel, Xenon lamp with housing and blower, two monochromators, two slit holders (installed in monochromators), sample compartment, photomultiplier housing with manually operated rotary slit turret, and filter holder with shutter control. The Xenon lamp power is supplied from D.C. power supply, and the sweep power circuit is energized by a mercury battery contained within the optical unit.

(a) Principles of Operation and Description:

The dispersion of light from the Xenon lamp is carried out by the excitation monochromator (grating type) into monochromatic radiation incident on the

sample. Emitted light from the sample is dispersed by a similar monochromator into monochromatic radiation incident on the photomultiplier. The light is then transformed to a weak electrical signal and fed to the photometer where it is amplified. The photometer output is indicated on the self-contained meter. This output signal is connected to a strip-chart recorder.

The gratings are oscillated by motor-driven cams to which are coupled graduated discs for visual observation and adjustment of wavelength. Provision is also made to adjust the wavelength manually. Spring loaded arms follow the continuous cam rotation and oscillate the gratings. The maximum and minimum angular positions of the gratings correspond to the high and low points of the cams and to the maximum and minimum wavelength of the monochromators namely, 800 and 200 nm respectively. The recorder could be started and stopped at any desired wavelength reading on the graduated scale. As the motor-driven cam moves with uniform speed, the intermediate wavelength values between two extreme readings on the chart could be determined by equally dividing the linear distance between two end points into

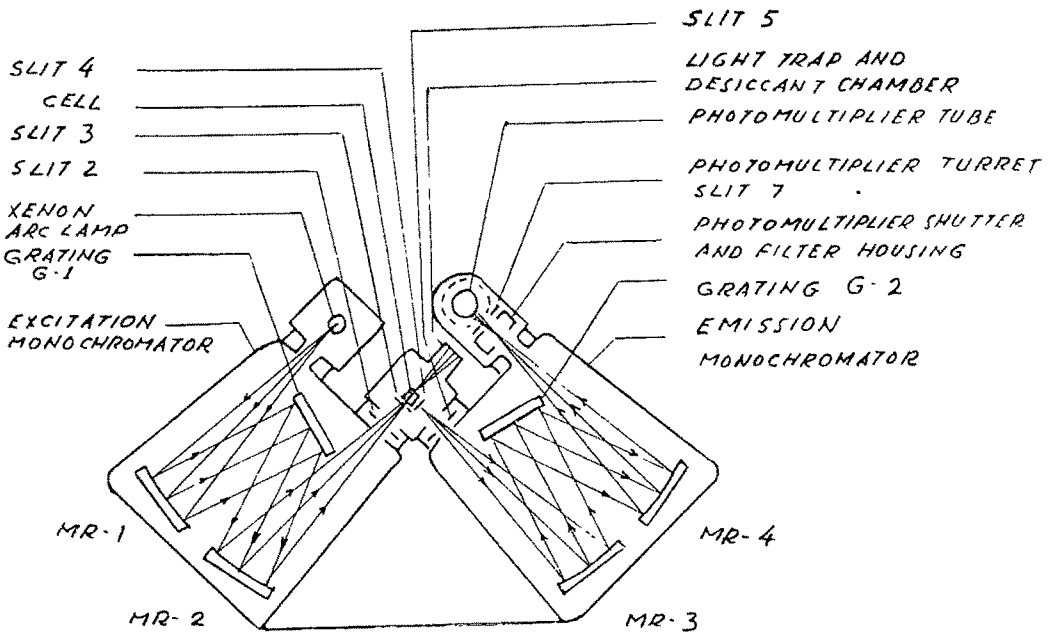
the number of wavelengths involved in the corresponding range. The peak position of an excitation or an emission peak read from the chart was found to be coinciding with the position of the corresponding peak as observed by the manual operation of the graduated disc.

(b) Optical Unit:

Properties of the mounting of grating monochromators are discussed fully in two articles by W.G. Fastie[78]. It incorporates two grating monochromators of the basic type first described by Ebert[79]. The schematic diagram of the optical system is shown in Fig. I which illustrates the following:

(i) The excitation monochromator selects light of monochromatic wavelength from the xenon arc lamp and focusses it on the sample holder. The light emitted from the sample is received by the emission monochromator and directed on the photomultiplier tube.

(ii) Both the monochromators are optically identical except for a difference in "blaze" wavelength between the two gratings. The excitation grating is blazed at 300 nm (1st order) to strengthen the output from the



OPTICAL UNIT SHOWING POSITION OF SLITS

FIG. I

Xenon lamp which decreases below 400 nm. The emission grating is blazed at 500 nm (1st order) to improve the response to the emission at wavelength from 400 - 600 nm.

(iii) The xenon arc lamp, located at the focus of the spherical mirror, MR-1 (vide fig.I), produces a continuous spectrum peaking at 400 nm and again at 900 nm (beyond the range of the instrument). Light from the lamp, indicated by the three rays, strikes MR-1 which renders it parallel and directs it to the plane grating. Dispersed light from the grating is redirected to the second mirror MR-2 (identical with MR-1) which focusses a monochromatic image of the lamp on the centre of the sample holder. The magnification of system is unity resulting in an image equal in size to the Xenon arc (1.8 mm wide by 3.5 mm high). Emitted light from the sample is similarly dispersed by the emission monochromator and imaged on the photomultiplier slit. Five slit positions are provided in the optical unit. Slits 2 and 3 determine the band-width and the resolution for excitation spectra whereas slits 5 and 4 decide the band-width and the resolution in the case of emission spectra. Photo-multiplier slit turret (7) controls the intensity. A

convenient arrangement of the slits was found out by trial and this arrangement remained unchanged throughout all the measurements, thereby keeping the band-width and resolution constant.

A certain amount of scatter is always present in varying degree in any optical instrument. This is especially true for instruments which measure fluorescence. In the design of the equipment presently being used, though the scatter has been reduced to a practical minimum, a certain amount of scatter exists. Thus one observes scatter or reflection peaks whenever the excitation and emission wavelengths are equal. Due to unlimited second order light from the gratings a noticeable amount of apparently spurious signal will frequently be present at high wavelengths. For example, if emission is maximum at 300 nm, there will be some indication at 600 nm. This spurious indication should be ignored, since it will usually not interfere with the shape of the peaks (both excitation and emission spectra). It can be eliminated with the use of suitable optical filters. Thus whether a given peak is genuine or not can be verified by the use of appropriate optical filters.

(iv) A dessicant chamber mounted on the sample housing of the spectrophotofluorometer performs two functions (1) serves as a light trap for the excitation wavelength and (2) prevents condensation on the cell window or sample, especially under conditions of high humidity. For liquid sample, cells made of fused quartz are used. Care is taken not to touch the sides of the cell. The solid sample is fixed on the sample holder with the help of a non-fluorescent grease, and placed diagonally in the sample compartment such that the sample faces the excitation and emission monochromator slits. The position is adjusted in such a way that it gives the maximum emission. The sample holder is made of ebonite whose surface was covered with black paper which did not show any excitation or emission peaks without the phosphor.

(c) Photomultiplier and Microphotometer:

This assembly essentially consists of a light sensitive photomultiplier tube with associated circuitry and an amplifier which responds to the

small current produced by the photomultiplier tube and registers the amplified current on a microphotometer. The photometer sensitivity is controlled by the meter-multiplier switch and sensitivity knob. Coarse adjustments are made with meter-multiplier switch which reduces the meter readings in steps of 1,3,10,30, 100,300,1000. Fine adjustments are made with the sensitivity knob which continuously adjusts the recorder output signal, together with the meter readings over a range of 3.5 to 1. The photomultiplier tube used in this setup is IP21 with S4 spectral response.

(d) Procedure for Obtaining Excitation and Emission Spectra:

Excitation spectra are obtained by recording the luminescence intensity at fixed wavelength as a function of the wavelength of the exciting source, whereas emission spectra are records of the spectral distribution of luminescence at fixed excitation wavelength.

(1) After inserting the sample in the sample chamber the photomultiplier shutter was opened.

(2) The emission monochromator wavelength disc was then allowed to rotate slowly with the help of slow-fast control.

(3) The photometer was set for high sensitivity. Subsequently, the excitation wavelength disc was changed manually in steps of 20 nm at the completion of each emission scan until a maximum was indicated on the photometer.

(4) When the excitation wavelength was located, the emission scan was stopped and the emission wavelength was adjusted for maximum emission indicated on the meter.

(5) The excitation wavelength disc was again adjusted until a new maximum on-scale meter reading was obtained.

Knowing the excitation peak wavelength, and placing the excitation monochromator wavelength disc at the above value, the emission spectrum was recorded. Knowing the emission peak wavelength, the emission monochromator wavelength disc was kept at the above value, and excitation

spectrum was recorded. During the above procedure the sensitivity was adjusted with the help of meter-multiplier, so that the photometer reading was within the range of the meter.

Whenever the instrument was switched on for measurements a warm-up period of about half an hour was given for stability. The excitation and emission spectra were recorded immediately one after another to avoid the effect of voltage fluctuations. These fluctuations were kept to a minimum with the help of a voltage stabilizer.

For the sake of convinience the speed of chart recorder was kept at 5 sec/inch for recording the excitation spectra and 10 sec/inch for recording the emission spectra.