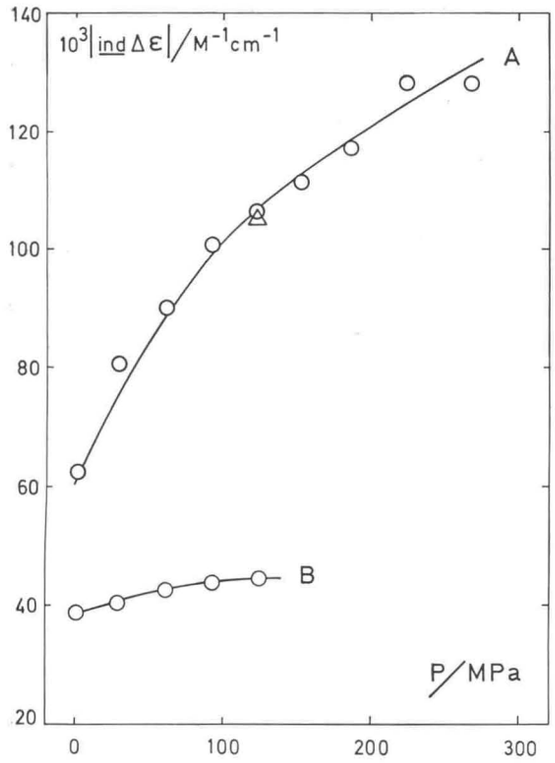

Fig. 3. The effect of high pressure on the magnitude of the induced circular dichroism of (A) *trans*-azobenzene and (B) ethylene trithiocarbonate dissolved in (−)-bornyl acetate measured in a JASCO J20 dichrometer. The value represented by the triangle was taken during depressurization.

and in all subsequent handling of the pressurized cell the optical path was examined *only* by means of a dental mirror and never by direct sighting. When the desired pressure had been locked in, the pressure in the Carver press was released, the rod was removed and the pressurized cell transferred to the optical bench in the circular dichrometer sample compartment.

It was convenient to have the Carver press located in a corner of the laboratory close to the sample compartment of the dichrometer, so that during transfer of the cell to and from the press exposure of personnel to alignment with the optical windows while under pressure was completely avoided.

The standard needle valve of the press was replaced by a micrometer needle valve to permit more delicate pressure adjustments. The bottom pressing face was provided with a special slotted holder for accurate positioning of the cell. A piece of 1/2 inch plexiglass was bolted to the front vertical surfaces of that face as a safety shield which could be extended to completely cover the gap between the press faces.

Depressurization and recovery of the solution

If a lower pressure was required the hydraulic fluid in the press was slowly released by means of the micrometer valve while the top screw of the cell was simultaneously slowly loosened by hand. This procedure ensured that a sudden drop of hydraulic pressure would not permit instantaneous release of the locked-in pressure in the cell.

When the internal pressure had been reduced to atmospheric the cell was opened by removing one of the window pistons by means of a double screw puller tool designed on the principle of a wine bottle opener. The complete disassembly and recovery of the cuvette and the spectroscopic solution could then be performed in a conventional way. The cuvette was carefully washed free of the pressure-transmitting fluid, first while mounted in the holder and then after removal from the holder using water for glycerol and chloroform for silicone oil. A check was thus possible whether readings at atmospheric pressure were the same before and after pressurization.

Calibration of the cell

The pressure calibration of the high pressure cell was based on the known compression of water [12] using water-filled piezometers with mercury seals as described by Andersson [13]. The calibration curve giving the relation between press-gauge readings and pressure inside the cell is shown in Fig. 2.

Typical performance of the apparatus

The effect of high pressure on the magnitude of circular dichroism induced in the achiral solutes *trans*-azobenzene and ethylene trithiocarbonate when dissolved in the chiral solvent (−)-bornyl acetate is shown in Fig. 3 as an example of the use of the high pressure dichrometer cell. These experiments will be discussed in a separate publication.

Spectral scans at intermediate pressures generally showed no significant differences between ascending and descending pressurization sequences (Fig. 3).

It is obvious from these data that circular dichroism experiments may be performed on solutions while under pressures up to at least 300 MPa without loss of sensitivity or accuracy.

Acknowledgements

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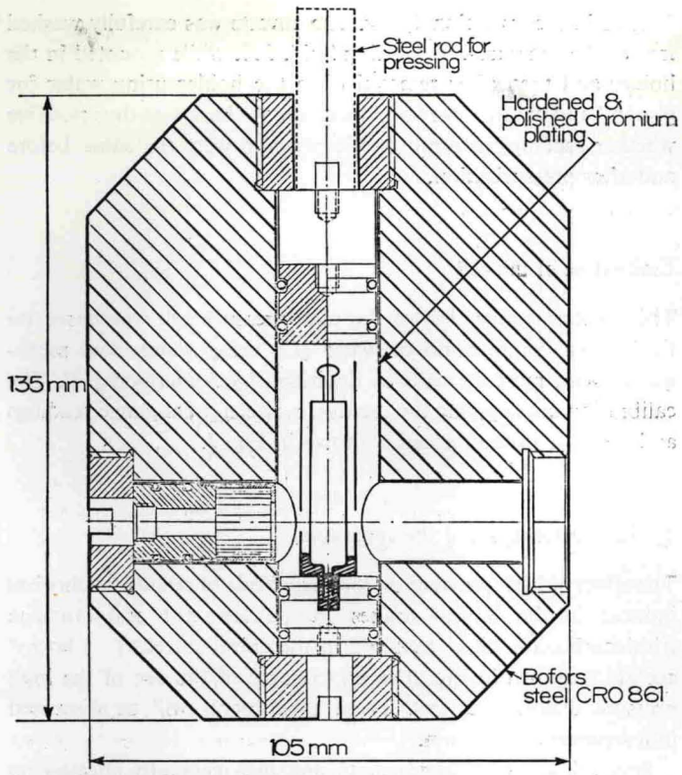

Fig. 1. High pressure circular dichrometer cell. In the vertical channel are shown from bottom to top: bottom supporting-screw, bottom piston, stainless steel cuvette holder with mercury pool, rectangular quartz optical cuvette with mercury seal, top piston, plunger, top pressure-locking-screw with central hole, and steel rod for pressing. In the horizontal optical channel from the left are shown: window-piston-supporting-screw, window piston, and quartz optical window inside window cap; the right hand window channel is empty.

1. *Mercury seal.* A 1 × 1 cm fused silica rectangular cuvette was fabricated from stock square fused quartz tubing (Vitro Dynamics, Inc., Rockaway, N. J.) drawn down to a short neck with a 0.12 mm diameter opening as shown in Fig. 1. A length of quartz rod terminating in a 4 mm diam. ball was fused to the closed end to serve as a handle. The cuvette was filled completely from a hypodermic syringe with the solution under study and was then inverted in a pool of mercury held in the bottom of the narrow cylindrical cavity of the stainless steel cuvette holder (Fig. 1). The cuvette was held down in the mercury by a pin across the top of the steel holder. After immersion of the cuvette and holder in the pressure-transmitting fluid increasing pressure on the fluid forced mercury into the cuvette as the volume of the solution decreased and this process was reversed during depressurization.

2. *Silicone oil seal.* For aqueous solutions, particularly of biological materials and other substances reactive toward mercury, the solution was placed in a standard rectangular silica (Suprasil) spectrophotometer cuvette, $l = 1.00$ or 0.100 cm, which was then sealed with a layer of silicone oil (*vide infra*) and then one of paraffin wax as described by Williams [10]. With organic solvents such as propylene carbonate which are insoluble in and more dense than the silicone oil [11], the head space of the cuvette was completely filled with silicone oil. The filled cuvette, in upright position, was placed in a cylindrical brass cup provided with lateral holes for the optical path. Cup and cuvette were then immersed in the silicone oil inside the pressure vessel. Experiments showed that diffusion of solutes across the silicone oil/solvent interface was negligibly slow even for solutes readily soluble in the silicone oil.

For some organic solvents, e.g. bornyl acetate, the density of the solution increased less rapidly with pressure than that of the silicone oil and at a certain applied pressure, e.g. 50–75 MPa, a density inversion occurred and the solution escaped from the cuvette into the upper part of the HP vessel. This occurrence was always readily evident as a sudden change in light transmission through the cell.

3. *Teflon membrane seal.* A more laborious technique was to confine the solution by a thin Teflon membrane stretched across the mouth of the cuvette. The membrane was clamped to the neck of the cuvette by means of a heat shrunk tube of Teflon.

Assembling and pressurizing the cell

The windows were sealed to the optically flat surfaces of the window pistons by means of an extremely thin layer of grease (Singer Sewing Machine Company) originally applied to the outer rim of the piston surface by means of a toothpick. It is essential to minimize the quantity of grease applied. The retaining caps, lined with Teflon washers, were then screwed onto the pistons to prevent slippage of the windows in further handling. The window and bottom pistons, complete with neoprene ○-rings, were inserted into the appropriate openings in the pressure vessel by means of handles screwed into their outer ends. A rotary motion during insertion under hand pressure prevented bunching or cutting of the ○-rings. The handles were unscrewed and the supporting screws were turned home against the pistons.

With the pressure vessel in the upright position the sealed cuvette, filled with the solution under test and fastened into its stainless steel holder, was lowered into the HP vessel and aligned in the optical path through the pressure windows. The pressure-transmitting fluid (silicone oil, $HOSiMe_2(OSiMe_2)_nOSiMe_2OH$, Aldrich Chemical Company, for melting and boiling point apparatus, Cat. No. 14, 615-3, or glycerol, Fisher spectroanalyzed, Cat. No. G-153) was run in, covering the cuvette in its holder and filling the sample cavity to within 22 mm of bottom of the threaded top hole. The pressure vessel was transferred to a plastic bell jar and the jar evacuated to remove air from the sample cavity. The top piston was then inserted and the assembly completed as previously described [7]. The assembled cell was placed vertically in the Carver press and pressurized. During pressurization

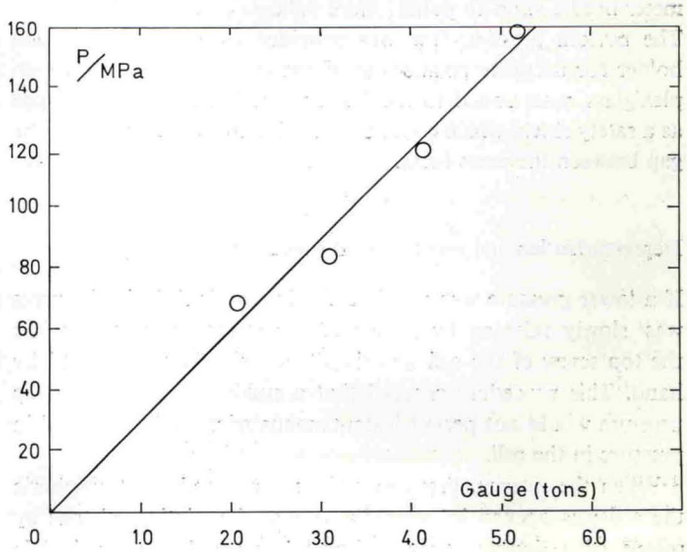

Fig. 2. Pressure calibration of the circular dichrometer cell based on the compression of water showing P vs. gauge readings.

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A Circular Dichrometer Cell Permitting Measurement of Optical Activity of Liquids while under High Pressure

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Abstract

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Details of the design, construction, and operation of a portable dichrometer cell for measuring optical activity of liquids while under pressures up to 300 MPa are described. The construction and mounting of the optical windows obviated interference from pressure-created birefringence. Three new methods for flexibly sealing the internal optical cuvettes are presented which permit wide variation in the chemical constitution of solutions to be studied. Both ascending and descending pressure regimes may be followed. The performance of the cell is illustrated with examples of the effect of high pressure on the magnitude of the induced circular dichroism of achiral solutes in chiral solvents.

Introduction

Attempts to measure optical rotation of solutions under pressure by polarimetry date back to W. C. Röntgen [1] and were frustrated by the large and variable birefringence created by pressure in the optical windows [2, 3]. Gill and Glogovsky [4] solved this problem by placing both polarizer and analyzer within the high pressure vessel but measurements were then restricted to a single change of setting of the analyzer actuated magnetically from outside the pressure vessel. Nevertheless they were able to show that up to 1 000 atm the rotation of a sucrose solution was insensitive to pressure while the rotation of a ribonuclease solution increased markedly thus suggesting that the results reflected changes of molecular conformation in solution.

The advent of the recording circular dichrometer in 1960 [5] provided a convenient and sensitive spectrophotometric method for measuring optical rotatory power in the visible and near ultraviolet spectral regions and initiated rapid advances in this field of molecular physics. Circular dichroism (CD), the differential absorption of left- and right-circularly polarized light, $(\varepsilon_L - \varepsilon_R) = \Delta\varepsilon$, is not subject to interference from stray birefringence to the same extent as rotation [6] and hence it occurred to us that combination of an appropriately modified high pressure optical cell of the type described by Claesson and coworkers [7] with a commerically produced circular dichrometer should permit measurement of optical activity of solutions while the hydrostatic pressure and the temperature were varied over convenient ranges. These experiments were successful and were described in a preliminary publication [8]. Here we give details of further development of the circular dichrometer cell and techniques for measurement of circular dichroism at pressures up to 300 MPa.

The HPCD experiments provide quantitative information on solute-solvent interactions and we have applied the technique to studies of the intermolecularly induced optical activity generated in achiral solutes by chiral solvents, the mutarotation of aqueous solutions, and the racemization of atropoisomers, and these will be described in subsequent publications.

The high pressure vessel

The general philosophy of design and operation of the optical cell were retained as described previously [7] with modifications introduced to accomodate the requirements of the circular dichroism experiment. In this design the high pressure vessel is filled with a pressure-transmitting fluid (glycerol or silicone oil) and the top piston is pressed down by a steel rod passing through a central hole in the upper supporting screw by means of a small hydraulic press. When the desired pressure in the cell has been reached it is locked in by turning the top screw down against the top piston. The cell can now be removed from the press and placed in any convenient instrument for performing measurements under pressure.

1. The pressure vessel was given a decahedral configuration (Fig. 1) such that it was free-standing on any one of its sides. This design feature greatly assisted manipulation during emptying, cleaning, and filling and also permitted positioning of the vessel in either a vertical or horizontal plane in the light beam.

2. The windows. The synthetic sapphire windows used in the HP optical cell for isotropic absorption spectroscopy were unsuitable for use in the circular dichrometer since the crystal structure would cause scrambling of the polarization of the transmitted light [9] and they were replaced by windows made from fused quartz (Suprasil I, Heraeus, Germany). The unsupported area method to mount the windows used in the previous design proved to be suitable also for these more sensitive measurements. However, to minimize lens effects due to the high pressure rather thick windows were used even at moderate pressures. The windows had a diameter of 15 mm and rested on the inner optically flat steel surface of the window piston where the opening for the light beam (the unsupported area) was 6 mm in diameter. The window thickness mostly used was 12 mm, but also 10 mm and 6 mm functioned well up to pressures of about 200 MPa.

Optical cuvettes

The fused quartz cuvettes require a flexible seal separating the solution under study from the pressure-transmitting fluid and equalizing the pressures inside and outside the cuvette. In addition to the previously described piston seals [7] three other closures were developed to avoid impurities introduced by certain solvents acting on the ○-rings.