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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.