A DIFFERENTIAL REFRACTOMETER*

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ABSTRACT

The differential refractometer here presented is designed on the principle of light refraction at two liquid interfaces. A collimated beam of monochromatic light (436 mμ or 546 mμ) is passed through a hollow glass cell of square cross-section filled with solution and immersed in an outer cell of solvent, so that the diagonal was along the light beam. The separation of the slit images formed by a lens of long focal length from the rays passing through two halves of the square cell is determined by a reading microscope to 10^{-3} cm. The width of the image is reduced by two pairs of double slits put before the lens to give three very bright interference fringes at the image of slit. The refractometer has a sensitivity of $\Delta n = 2.5 \times 10^{-6}$. The dn/dc data for some solutions of high polymers and organic compounds of interest to light scattering work are given.

For successful measurement, attention is called to the following remarks:

(1) Due to large value of dn/dt for most organic liquids, the fluctuation and temperature difference between the solution cell and the solvent cell should not exceed 0.005°C.

(2) The cell should be so designed as to avoid distilling the solvent into the solution during measurement.

(3) Sucrose solution in water is preferred as the standard solution to calibrate the apparatus.

Light scattering has been widely used in recent years for the determination of molecular weight and molecular extension of linear macromolecules in solution. In the evaluation of molecular weight from scattering intensity or turbidity data, the value for the refractive index increment dn/dc of the solution is needed, and $M \propto (dn/dc)^{-2}$. The range of concentrations encountered in light scattering is usually below 10^{-2} g/ml, while the value of dn/dc mostly falls in the order of 0.1, so the difference in refractive indeces, Δn, between the solution and the solvent is of the order of 10^{-3}. If a precision of $\pm 1\%$ is attempted for the value of dn/dc, Δn has to be determined to within 10^{-5}. An ordinary refractometer obviously will not serve the purpose.

Differential refractometers based on the refraction of rays through the boundary surface of two liquids have been known for some time[1]. Since the development of light scattering technique in polymer research, many designs have appeared in literature[2-7]. The apparatus usually makes use of

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a collimated monochromatic beam of light from a narrow slit source to pass through a triangular or dimond-shaped cell filled with solution and put in an outer cell filled with solvent. The deflection of the light ray is a measure of Δn. The image lens usually has a long focal length and the displacement of the image is read by means of a reading microscope. Multi-reflecting mirrors[3] or autocollimation[7] were used in some designs in order to shorten the physical dimension of the refractometer. Cecil and Ogston[5] introduced double slits in front of the image lens to reduce the width of the enlarged image of the slit into interference fringes, while Schulz, Bodmann and Cantow[6] used a photomultiplier to get the intensity profile of the image. Both were aimed at a more precise measurement of image displacement. Korösy[8] designed a refracting cell in which the differences in the refractive indices among the solution, a reference standard and the solvent can be compared simultanuously. Caplan[9] determined $\Delta n^2/\Delta c$ directly after the design of Hallwachs[10].

The differential refractometer here presented (Fig. 1) is similar in design to that described by Cecil and Ogston[5]. However, the refracting cell of

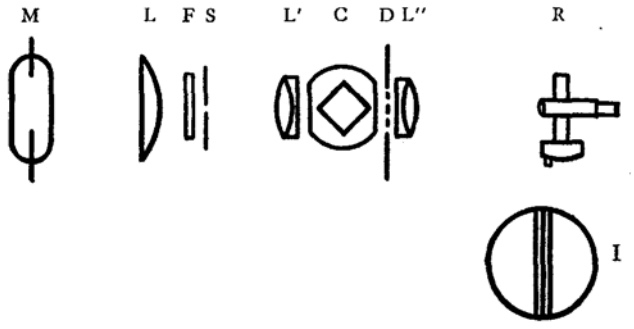

Fig. 1. The differential refractometer (top view, schematic).
M, Hg vapour lamp; L, condensing lens; F, filter; S, slit; L', collimating lens; C, refracting cell; D, double slits; L'', image lens; R, travelling microscope; I, interference fringes seen in the microscope.

the latter appeared not suitable for working with organic solvents, owing to the climbing of the liquid over the partition glass separating the solution from the solvent. A solution cell of square cross section was finally adopted with its diagonal put in the direction of the light beam. The rays passing through the two halves of the square cell would deviate in opposite sense causing a separation of images formed by a lens of long focal length (100 cm). Two pairs of double slits were put before the lens. The opening and spacing of the double slits were all 1 mm wide, and the two pairs were separated by 7 mm. Three very bright interference fringes were observed so that the image displacement Δd could be measured to within 1×10^{-3} cm by a travelling microscope. The angle of deflection for a ray passing through a prism of apex angle A is given by[2].

$$\alpha = 2(\Delta n) \tan A/2 .$$

The separation of two images from the square cell will be

$$\Delta d = 2f \sin \alpha \doteq f \Delta n ,$$

where f is the focal length of the lens. For $f \doteq 100$ cm, $\Delta n/\Delta d \doteq 2.5 \times 10^{-3}$/cm and so the sensitivity of the differential refractometer here described is $\Delta n = 2.5 \times 10^{-6}$.

Most organic liquids have a temperature coefficient of the refractive index about $3.5—5.5 \times 10^{-4}/°C$, and consequently fluctuations and temperature difference between the solution cell and the solvent cell should not exceed 0.005°C. The square cell used by the authors was made of glass while the solvent cell was made of gold-plated brass with glass windows for the light beam. The difference in the thermal conductivities of brass and glass presented great difficulties to meet the temperature requirement, so that the separation of images appeared unstable. The trouble was finally solved by operating the instrument in a temperature-controlled room at 25 ±0.2°C. The solution, the solvent and the refracting cell were let stand in the room for 3—4 hours to attain thermal equilibrium before a measurement was attempted. Then stable readings were obtained within 20—30 minutes.

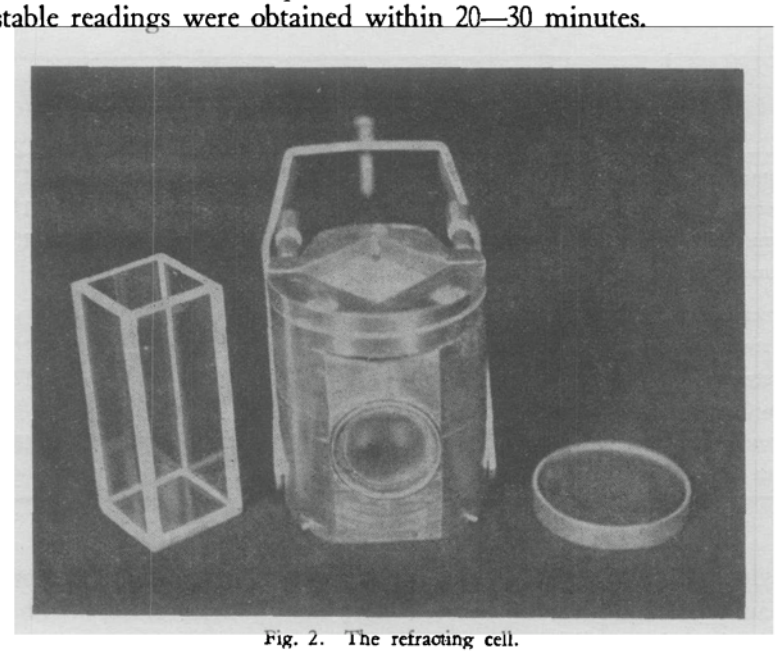

Fig. 2. The refracting cell.

Although the difference in vapour pressure between the solution and the solvent is very small in the range of concentrations used, the distilling effect in the refracting cell was still observable, causing a gradual decrease of the image separation during measurement. Therefore a brass cover which could be

screwed tight with polyethylene packing against the cell was provided (Fig. 2). The distilling effect was then greatly suppressed. The unstable image shifts mentioned in literature[3] are believed to be the result of distilling effect and temperature fluctuation.

Aqueous solutions of sucrose, NaCl and KCl have often been used for the calibration of differential refractometers. A closer inspection of the values of $\Delta n/\Delta c$ recorded in literature[11] revealed that those for NaCl and KCl are not quite constant in the range of concentrations used. The present authors suggest that sucrose solutions are to be recommended as calibration standard which have a constant value of $\Delta n/\Delta c=0.143$ (λ 546 mμ)[12] for concentrations up to 5 g/100 ml. The instrument constant thus obtained for the differential refractometer here described is $\Delta n/\Delta d=2.513\times10^{-3}$/cm.

The differential refractometer has been used to determine dn/dc of some solutions of high polymers and organic compounds of interest to light scattering work as recorded in Table 1. The values of dn/dc for polymethyl-

Table 1

Results of Measurement, 25°C

Substance	Solvent	dn/dc(observed)		dn/dc(literature)		Ref.
		5461Å	4358Å	5461Å	4358Å	
Polymethylmethacrylate	acetone	0.128_1	0.129_5	0.129_8	0.131_8	[13]
Polymethylmethacrylate	acetone	——	——	0.134	0.137	[14]
Polymethylmethacrylate	acetone	——	——	0.125	——	[15]
Polymethylmethacrylate	methyl acetate	0.126_1	0.128_8	——	——	——
Polycetylmethacrylate	heptane	$0.11\frac{1}{2}$	0.116_4	——	——	——
Polystyrene	benzene	0.106_1	0.110	——	0.118	[16]
Polystyrene	benzene	——	——	0.106	——	[17]
Octa-phenyl-cyclo-tetrasilane	benzene	0.213_7	0.233_5	——	——	——
Sucrose octaacetate	methanol	0.109_2	0.111_2	——	0.114	[18]
Hevea rubber	heptane	0.173_1	0.182_8	——	——	——

methacrylate in acetone found in literature vary considerably according to various authors. The value reported here agrees most closely with that of Cantow and Bodmann[13].

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