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Interference Method for the Determination of Refractive Indices and Birefringence of Liquid Crystals

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A new interference method for the determination of refractive indices and birefringence as functions of the wavelength is proposed. Application of a spectrophotometer and a specially constructed interferometer makes the measurements easier and enables the determination of refractive indices over a broad spectral region.

1 INTRODUCTION

The need for refractive index measurements occurs frequently in pure science and numerous technical applications. Knowledge of the refractive index values, and especially their dispersion, plays an important role in the study of intermolecular interactions. These parameters are also useful in designing technical devices in which liquid crystals are applied. However, the determination of the refractive indices of liquid crystals presents certain difficulties. Routine refractive methods currently applied to crystals and isotropic liquids, cannot be applied directly to liquid crystals. The optical anisotropy of liquid crystals excludes the use of all methods developed for isotropic liquids, whereas the necessity of an accurate orientation of the optical axis of the crystal against the refracting angle of the prism limits the application of the conventional methods used for crystals. In unoriented samples, one can determine the refractive index of the ordinary ray, but the determination of the refractive index of the extraordinary ray is more difficult because of the blurring of the boundary in the refractometer telescope. When using a prism refractometer, one can actually stimulate the orientation of the liquid crystal by means of a special treatment of the prism plane; this is, however, not always possible and one comes up against some difficulties when checking the results of such liquid crystal orientation. Taking all these facts into consideration, the interference method based on measuring the distance between the fringes of equal inclination¹ or measuring the wavelength of maximum light intensity² seems to be more useful. This latter variant of the refractometric method proposed by Wright² is very convenient because it enables us to perform measurements as a function of the wavelength. There are, however, some inconveniencies in the Wright method, due to the limit of interferometer length, the tedious nature of the determination of the maximum interference fringe positions, and, finally, the possibility to determine the refractive index only in such materials in which it differs considerably from that of glass.

In the method proposed by us, the inconveniencies mentioned above are largely eliminated by a specially constructed interferometer and the application of a spectrophotometer acting simultaneously as monochromator, detector, and recorder with a linear wavenumber scale.

2 PRINCIPLE OF MEASUREMENT

When a parallel beam is incident on two plane parallel semi-transmitting mirrors, the rays multi-reflected at the mirror surfaces interfere mutually. The light transmitted through such a system, provided the incident beam is perpendicular to the mirrors, will have maximum intensity when the distance between the mirrors d amounts to a multi-half wavelength of the light passing through the interferometer, i.e. when:

$$N\frac{\lambda}{2n} = d \tag{1}$$

where N is an integer, n the refractive index of the medium placed between the mirrors, and λ the light wavelength in vacuum. By increasing the light wavelength, one obtains successive maximum of light intensity when:

$$(N-1)\frac{\lambda'}{2n'}=d\tag{2}$$

where n' is the refractive index at the wavelength λ' . The interval (λ, λ') is in practice very small, so that the approximation n = n' is quite good. Thus, by Eqs (1) and (2), one has:

$$\frac{1}{\lambda} - \frac{1}{\lambda'} = \frac{1}{2dn} \tag{3}$$

Introducing the wavenumbers $v = 1/\lambda$ and $v' = 1/\lambda'$, one has the following equation:

$$\Delta v = \frac{1}{2nd} \tag{4}$$

where $\Delta v = v - v'$. By measuring Δv one can determine either the thickness of the interferometer d, if the refractive index is known, or the refractive index, if the thickness d is known. Hence, measurements of two Δv values, one for the medium for which the refractive index is known, and one for the medium investigated, allow us to determine the thickness d and the refractive index in question. When air is used as a medium of known refractive index (n = 1) and the appropriate distance between fringes (constant for the whole spectrum) is Δv_0 , then:

$$n = \frac{\Delta v_0}{\Delta v} \tag{5}$$

A similar procedure can be applied in order to determine the birefringence of a liquid crystal $\Delta n = n_e - n_0$ i.e. the difference in refractive indices for the extraordinary and ordinary rays. If the uniformly oriented liquid crystal sample is placed between crossed polarizers, there is interference of the ordinary and extraordinary rays, and the intensity of the light passing through the system will be maximal when:

$$\Delta n \cdot d = N\lambda \tag{6}$$

Following the above mentioned procedure, one obtains:

$$\Delta n = \frac{1}{d\Delta v} \tag{7}$$

where Δv is the distance between two successive interference fringes. As in the case of the refractive index, one can assume that the birefringence is the same for the any two successive fringes. This requirement can in all cases be met, even for samples with strong dispersion, provided the interferometer thickness d is large enough.

3 THE APPARATUS

In order to measure the dispersion of refractive indices, the interferometer, shown in cross-section in Figure 1, was constructed. The interferometer consists of two metal plates (1) and (2), adjustable by means of screws (6) and nuts (7). At the centre of the metal plates, two rings (3) and (4) are placed as glass plate (5) holders. The opposite faces of the glass plates are coated

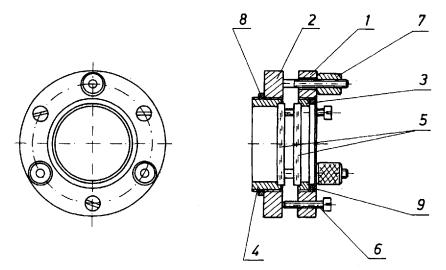


FIGURE 1 Cross-section of the interferometer.

with semi-transmitting metal layers and rubbed in one direction to stimulate liquid crystal orientation. To adjust the distance between the glass plates, the ring (4) is fixed by means of fine-pitch thread. The ring (3) can be rotated in order to adjust the cracks parallel on the surfaces of both mirrors. The nuts (8) and (9) hold the rings (3) and (4). Before the measurement, the glass plates have to be adjusted parallel to each other, and this can be achieved by means of the screws (6) and nuts (7). In the properly adjusted interferometer, the fringes of equal inclination vanish and the whole surface has identical colour when observed in a perpendicular incident beam of white light. The interferometer thus adjusted was placed in the path of one beam of a ultra-violet and visible UV/VIS Zeiss spectrophotometer and the interferometer transmission versus wavenumber was recorded.

Typical fringes recorded by means of this spectrophotometer are shown in Figure 2. Application of the spectrophotometer makes the measurement very convenient since fringe scanning and recording are automatic. Moreover, the recording is performed in a linear wavenumber scale, thus eliminating tedious calculations.

On determining Δv_0 , the liquid crystal was introduced into the interferometer. The homogeneity of the sample orientation was checked previous to measurement. The interferometer construction permits us to use a polarisation microscope for this purpose. In order to determine both refractive indices of the liquid crystal under study, measurements must be carried out in polarised light. The refractive indices of the extraordinary ray n_e and ordinary

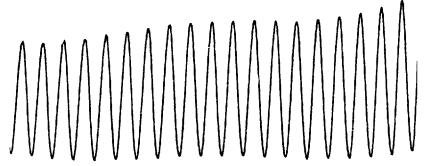


FIGURE 2 Interference fringes, recorded spectrophotometrically.

ray n_0 can be determined from Eq. (5) taking the distance between fringes $\Delta \nu$ measured when the optical axis of the liquid crystal is parallel and perpendicular to the plane of light wave oscillations, respectively. In birefringence measurements the sample is placed between the polarizer and analyzer, so that the orientation direction of the liquid crystal molecules subtends an angle of 45° with the polarisation planes of the polarizer and analyzer. As an example, the interference fringe record obtained in this way for *p*-methoxy-benzylidene-*p*-*n*-butylaniline (MBBA) is shown in Figure 3.

We determined the refractive indices and birefringence of MBBA by the above method. The values obtained are in agreement with those of other authors. The birefringence Δn measured at 22°C, is shown in Figure 4. The anomalously large value of Δn in the short-wave region of the spectrum is due to the strong dichroic absorption band, detected spectrophotometrically.

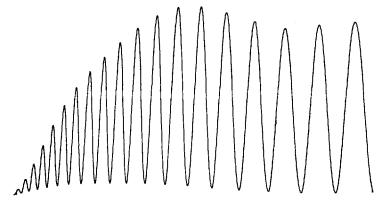


FIGURE 3 Interference fringes, recorded when determining the birefringence of MBBA.

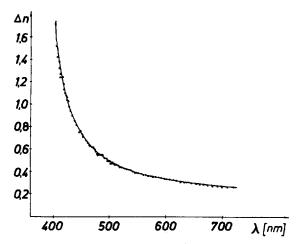


FIGURE 4 Birefringence of MBBA in the visible region of the spectrum.

4 ACCURACY OF MEASUREMENT

The experimental error depends mainly on the accuracy with which the distance between the fringes is determined, and this is limited by the accuracy of the spectrophotometer wavenumber scale. In our calculations, we use the mean value of Δv for many fringes depending on the interferometer thickness and liquid crystal dispersion.

To check the accuracy of the above described interference method, the refractive index of paraffin oil was also measured by means of a PR-2 Zeiss Refractometer. An accuracy of ± 0.005 was achieved in the visible region.

5 CONCLUSIONS

The interference method described above is especially useful for the determination of refractive index dispersion and birefringence because one can obtain an almost continuous change of their values as a function of the light wavelength. The interferometer construction enables a special treatment of the mirror surfaces in order to stimulate liquid crystal orientation and to check this orientation under a polarisation microscope.

The present method counts among the rare procedures enabling to carry out measurements in the invisible region of the spectrum. Application of the spectrophotometer renders the measurements easier, enhances their accuracy and, due to the high detector sensitivity, permits some measurements on the slope of the absorption bands.

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