Pakistan J. Sci. Ind. Res., Vol. 30, No. 6, June 1987

A MODIFIED TECHNIQUE FOR REFRACTIVE INDEX INCREMENT MEASUREMENTS FOR CETYLTRIMETHYL AMMONIUM BROMIDE SOLUTIONS USING AN INTERFERENCE REFRACTOMETER

Anwar Ejaz Beg

Department of Pharmaceutics, Faculty of Pharmacy, University of Karachi, Karachi-32

(Received June 26, 1985; revised April 2, 1987)

A modified technique for the measurement of refractive index increments on detergent solutions using an interferometer is presented in this paper. The study is being carried out on various concentrations of cetyltrimethyl ammonium bromide (CTAB) in absence and presence of 10^{-4}M, 10^{-3}M, 0.1M potassium bromide at pH ranging between 8.0 and 9.2. The technique was applied on two known values of refractive index increments for an anionic surfactant which agreed well with the published ones.

Key words: Refractive index increment; Rayleigh interferometer; Surfactant solution.

INTRODUCTION

In recent years, several interferometers have been developed [1-5] having wide applications in optical diffraction techniques, solar magnetic and volocity – field measurements, fundamental physics etc.

An interesting and important use of interferometers is the accurate measurement of refractive index increments which in terms of surfactant and added salt molalities arise simply and directly from the older Prins-Hermans [6], Mysels [7], Princen and Mysels [8] and Mysels and Princen [9] (PHMP) theories, still reliable for estimating molecular weights of surfactant micelles. Recent advancement and approach in the field of Rayleigh scattering and its application in anisotropic/nonrigid molecules again requires an accurate estimation of this parameter [10-13].

Specific refractive index increments of 158 natural and synthetic polymers in pure and mixed solvents are available in literature [14-15], where the influence of various physical factors on refractive index increments are discussed. This discussion is quite useful for those involved in the measurement or use of refractive index increment of a polymer. Unfortunately the published data appear to be very incomplete even for the polymers listed and particularly for biopolymers. The method available for the measurement is also somewhat complicated and time-consuming. This paper describes an easy and modified technique for the determination of the increments for CTAB solutions where the precision in the refractive index increments is somewhat better than 0.4 %.

EXPERIMENTAL

Refractive index increments for various CTAB solutions were determined at 546 nm with a Rayleigh-Haber-Lowe interferometer (manufactured by Aus Jena Germany (DDR). The instrument was first calibrated using the data of Kruis [16] for KCl solutions as interpolated by Stamm [17]. This calibration procedure has been described by Emerson and Holtzer [18] and Aranow [19]. Measurements were made in calibrated 2 cm cells at 30^{o} between pH 8.0 and 9.2 in a non-buffer system as well as in Delory and King's carbonate-bicarbonate buffer [20] at pH 9.2 only. The pH in the non-buffer system was maintained by sodium hydroxide alone.

The two compartments of the cell were filled with the reference liquid, and after temperature equilibration, adjusted to bring the interference fringes of the upper half into coincidence with those of the lower half, using white light to match the dark zero-order bands. The white light source was then replaced by 546 nm monochromatic light and the coincidence of the bands finely adjusted. (The initial zero-order band match cannot be made with monochromatic light as all bands then appear equivalent). The position of the compensator was then noted from the finely divided micrometer drum (γo). The compartment of the cell in line with the adjustable plate was then filled with the sample solution to be measured. This displaced the upper fringe pattern due to the difference in refractive index from that of the reference liquid. The bands were brought back to approximate coincidence with the lower system using white light and the final adjustment again made at 546 nm. The new micrometer reading was taken as 'γ_1'. The compensator was then screwed back to a position 'γ_2' whilst counting the number of interference bands past the lower reference band (a). (Position 'γ_2' is that of the nearest whole band to position 'γ_0'). From $\frac{\gamma_1 - \gamma_2}{(a)}$, the mean band width 'd' was calculated and hence the exact number of bands 'N' displaced by the sample solution was obtained from :

$$N = \frac{\gamma_2 - \gamma_1}{d} + (a) \qquad \ldots\ldots\ldots\ldots (1)$$

After substituting the value of "d" in equation (1), the same equation could be written in the reduced form :

$$N = \frac{(\gamma_1 - \gamma_2)}{\gamma_1 - \gamma_2} \times (a) \qquad \ldots\ldots\ldots (2)$$

(Equation 1 is a modified form of what has been described by Weissberger (21) and is simplified in this form by the author).

RESULTS AND DISCUSSION

Although the working as well as the mechanism of the instrument has been discussed by Weissberger [21], yet it has been slightly modified here in the light of the procedure adopted in this study. Therefore, the description of the instrument in its modified form will be presented first in this section which will then be followed by the results obtained on the instrument.

The interferometer used in this study is based on the principle that two beams of light, derived from the same small source each passing through a different liquid held in a two compartment cell, can be arranged to produce an interference pattern. If a transparent substance of refractive index 'μ' is placed in the path of one beam and an equal length of another substance with a different refractive index 'μ_0' in the path of the other beam, there is a displacement of the interference pattern or bands. The interferometer provides a method of obtaining the difference in refractive index ($\mu - \mu_0$), by measuring the shift in position of the interference bands. The main features of the instrument are shown diagramatically in Fig. 1. Light from a 'high intensity source' passes throuh a narrow vertical slit 'A' and is collimated by an achromatic object lens 'B'. The collimated beam falls on a plate in which there are two narrow vertical apertures 'C'. Light emerges from these as twin parallel beams of coherent light; the upper halves of these beams pass through the liquids to be compared, the lower halves through a reference compartment containing air, against which fringe differences are measured.

The upper halves of the beams enter a two-compartment E-shaped cell ('D' and 'E'), which contains the liquids to be compared. The beams emerge to fall on two thin glass plates 'K' and 'L', each inclined to the optical axis. These plates form the compensator. The plate 'K' is fixed at about 45° to the optical axis, the plate 'L' rotates about a horizontal axis perpendicular to the optical path and by doing so varies the thickness of glass which that particular beam has to traverse. Light from the compartment 'D' with the known liquid passes through the fixed plate 'K', light from the other compartment 'E' with the liquid under examination passes through the moveable plate 'L'. The position of the fringes formed by the beams can be altered by rotating the moveable plate; *this movement or band shifts,* is the basis of the refractive index increment measurement.

The lower halves of the beams pass through a glass prism 'H' which is inclined to the optical path. This prism removes optical obstructions such as the cell-walls, etc. and brings the lower beams adjacent to the upper beams but separated from them by a sharp dividing line. The fringes formed by the lower beams are immoveable under all conditions and provide the reference system by which fringe shifts in the upper half are measured.

The upper and lower beams, now adjacent, are focused by an "achromatic objective lens" 'Q' and the image is observed with the cylindrical eyepiece 'R'.

Since the refractive index increments on surfactants in aqueous electrolyte solutions are used to determine the molecular weights of charged micelles [6, 22] therefore part of the trouble may arise in the use of incorrect refractive

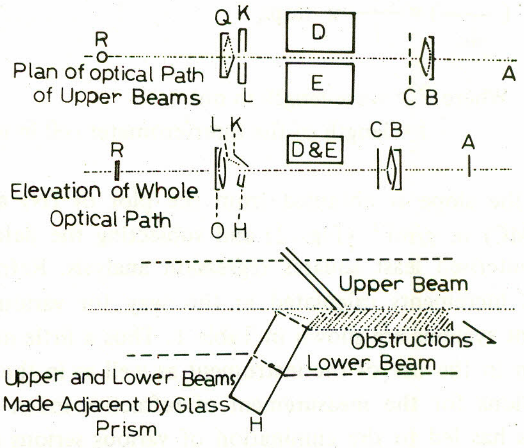

Fig. 1. Diagram of the optical path of the rayleigh interference refractometer.

index gradients in the calculation of reliable micellar weights as reported earlier [23]. Consequently it is necessary that the accuracy of any developed or modified technique should be known. For the same reason the modified technique in this study was applied on sodium dodecyl sulphate solutions at 21° in presence of 0.1M NaCl at 546 and 589 nm wave-length. The values obtained for the increments are 0.117076 and 0.116782 ml/g respectively which agree quite well with the published values of 0.1171 and 0.1168 ml/g at 546 and 589 nm respectively [24].

The number of bands (N) obtained for each surfactant system in this study were then plotted against ΔC i.e. (C-CMC) in $g.ml^{-1}$ on a linear scale, which gave straight lines. 'C' stands for a particular concentration of CTAB and 'CMC' is the critical micelle concentration of the surfactant in that system. For this study the CMC of CTAB at 30° was measured by surface tension, light scattering and bromide ion activity methods. Values of CMC under various sets of condition obtained by these techniques have been discussed earlier [25].

A typical plot of 'N' versus ΔC is shown in Fig. 2. All the determinations were carried out three times and the average of three readings for (N) was plotted. The Bartlett test was applied to these three replicate experiments. Calculated and tabulated X^2 test values at the 5% ($P = 0.05$) probability level were 0.139 and 9.025 respectively. The low values of X^2 calc. than X^2 tab. indicates that the result obtained from the three replicate experiments are reproducible and assumed to be indistinguishable at the stated level. The refractive index increment (dn/dc) were calculated from equation 3 which is a modified form and has been derived from various basic equations described by Weissberger [21].

$$\left(\frac{dn}{dc}\right) = \frac{\gamma}{1} \times \text{slope} \qquad \ldots\ldots\ldots(3)$$

Where γ = wave-length in nm
1 = length of the interferometer cell in nm

and the slope is obtained from the plot of (N) against (C-CMC) in g/ml^{-1} (Fig. 2) and subjecting the data to a computerised least squares regression analysis. Refractive index increments calculated in this way for various surfactant systems are shown in Table 1. Thus a little modification in the use of the instrument as well as in the basic equations for the measurement of refractive index increments has led to the elimination of various serious errors such as the "dispersion effect" without using any "rotating chamber" difficulty in the accurate location of the ρ-order band, "overlapping" with monochromatic light etc. which are generally described in literature for different types of interferometer [3, 5, 21].

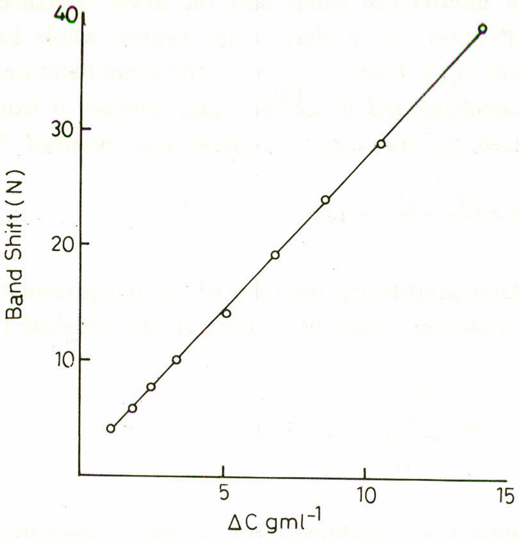

Fig. 2. Band shift against ΔC for CTAB in water at pH 9.2 and 30°C in the determination of (dn/dc) at 546 nm.

Table 1. Calculated values of refractive index increments for CTAB (between the concentration range of 1×10^{-4} M and 4×10^{-2} M) at 30°C and 546 nm.
(+ = Present and – = Absent)

System			Refractive index increment	
pH.	Buffer	KBr	dn/dc $g\ ml^{-1}$	dn/dc $moles\ ml^{-1}$
Water alone	–	–	0.143884	0.052441
8.0	–	–	0.143884	0.052441
8.6	–	–	0.143887	0.052449
9.2	–	–	0.143886	0.052447
8.0	–	10^{-4}M	0.143974	0.052498
8.6	–	10^{-4}M	0.143974	0.052498
9.2	–	10^{-4}M	0.143977	0.052504
8.0	–	10^{-3}M	0.144301	0.052587
8.6	–	10^{-3}M	0.144301	0.052587
9.2	–	10^{-3}M	0.144304	0.052594
8.0	–	0.1M	0.145015	0.052992
8.6	–	0.1M	0.145015	0.052992
9.2	–	0.1M	0.145019	0.053000
9.2	+	–	0.144399	0.052629
9.2	+	10^{-4}M	0.144500	0.052680
9.2	+	10^{-3}M	0.144701	0.052771
9.2	+	0.1M	0.146998	0.053951

The data shown in Table (1) indicate that the pH in the range of 8.0 and 9.2 under similar experimental condition has no significant effect on the increments. Again, differences in refractive index between pairs of solutions at different surfactant concentrations above the CMC are found to be constant within experimental error. This is due to the fact that the concentration of surfactant monomers remains approximately constant in the concentration region of interest i.e. above the CMC [22, 26], the contribution of monomers to the refractive index increment will cancel out and the increment is that for the micelle. The data shown in Table 1 further indicate that potassium bromide has a significant but steady effect on refractive index increments. The values of increment gradually increase with increase in the concentration of potassium bromide. At the concentration of 0.1M electrolyte in the presence of buffer the refractive index increment for CTAB becomes sufficiently high which correlates with the earlier studies on light-scattering and viscosity [27, 28] for CTAB solutions where a marked change in micelle structure on the addition of 0.1M potassium bromide in buffer was proposed.

REFERENCES

1. D. Balzarini and P. Palffy-Muhoray, Liq. Cryst. Ordered Fluids, **4**, 531 (1984).
2. O. Gehre, Int. J. Infrared Millimeter Waves, **5**, 369 (1984).
3. H. Rauch, J. Phys. Colloq., **C3**, 197 (1984).
4. H.E.L.G. Schweigart, Gov. Rep. Announce Index, U.S.), **84** (4), 155 (1984).
5. Jan O. Stenflo, Appl. Opt., **23**, 1267 (1984).
6. W. Prins and J.J. Hermans, Proc. Kon. Ned. Akad. Van. Wetensch., **B59**, 162 (1956).
7. K.J. Mysels, J. Colloid Sci., **10**, 507 (1955).
8. L.H. Princen and K.J. Mysels, *Ibid.*, **12**, 594 (1957).
9. K.J. Mysels and L.H. Princen, J. Phys. Chem., **63**, 1696 (1959).
10. G. Fytas and C.H. Wang, J. Am. Chem. Soc., **106**, 4392 (1984).
11. G. Fytas, J. Chem. Phys., **80**, 3774 (1984).
12. G. Fytas, J. Mol. Liq., **28**, 95 (1984).
13. R. Vilhjalmsson, J. Koeppen and W. Mueller-Warmuth, Mol. Phys. **51**, 1357 (1984).
14. M.B. Huglin, J. Appl. Polymer Sci., **9**, 3963 (1965).
15. *Ibid.*, p. 4003.
16. A. Kruis, Z. Physik. Chem. (Frankfurt), **B34**, 13 (1936).
17. R.F. Stamm, J. Opt. Soc. Am., **40**, 788 (1950).
18. M.F. Emerson and A. Holtzer, J. Phys. Chem., **69**, 3718 (1965).
19. R.H. Aranow, *Ibid.*, **67**, 556 (1963).
20. "Documenta Geigy", Scientific Tables, (Geigy Pharmaceutical Co. Ltd., Manchester, U.K., 1962). 6th ed..
21. A. Weissberger, *Technique of Organic Chemistry*, Part II (Interescience Publishers Ltd., London. 1140-1271, 1960). Vol. I.
22. P.J. Debye, Ann. N.Y. Acad. Sci., **51**, 575 (1949).
23. E.W. Anacker and H.M. Ghose, J.Am. Chem. Soc., **90**, 3161 (1968).
24. H.F. Huisman, Proc. Kon. Ned. Akad. Van. Wetensch., **B67**, 388 (1964).
25. A.E. Beg, B.J. Meakin and D.J.G. Davies, Pakistan J. Sci. Ind. Res., **22**, 283 (1979).
26. P.J. Debye, J. Phys. Colloid Chem., **53**, 1 (1949).
27. A.E. Beg., B.J. Meakin and D.J.G. Davies, Karachi Univ. J. Sc., **8**, 17 (1980).
28. A.E. Beg, B.J. Meakin and D.J.G. Davies, Pakistan J. Sci. Ind. Res., **22**, 277 (1979).