Dispersion Effects in White Light Interferometry

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A micromanometer, which has been used to measure very small osmotic pressures interferometrically, has been devised at this institute¹. An interferometer of the Rayleigh type² has been constructed, designed in the ordinary way with two glassplates, which can be tilted, thus changing the optical path for either light beam. Differences in optical path in this apparatus arise from the light beams passing through liquid layers of different thickness, and these differences are compensated by glass in the original design of the apparatus. Furthermore, it is often convenient to use white light sources (see below). Two disadvantages arise from these facts:

1. The range of measurement is rather limited, as the glass plates for practical reasons cannot be made large enough to compensate for a level difference of more than about 1 mm.
2. The difference in the relative optical dispersions of glass and liquid gives rise to a systematic error which in many cases is considerable.

In view of these drawbacks a new type of compensating arrangement, a liquid compensator, was provided, making it possible to measure osmotic pressures up to 25 mm H₂O and to compensate for the greater part of the differences in optical path with liquid.* In this way the range of measurement has been extended and the dispersion effect almost eliminated at the same time. A certain compensation by means of the glass plates is convenient, however. This paper gives an account of the theoretical background of this dispersion effect, as well as of some experiments carried out in order to obtain the corrections to be made when white light is used.

* Compensation by means of liquid for the determination of refractive index differences between solvent and solution has earlier been described by Borgesius, A. H. *Ann. Physik (Wiedemann)* 54 (1895) 222.

Suppose the two interfering light beams pass through two liquid layers, for which the difference of level is l . The difference in optical path due to l is compensated by tilting the glass plate in one of the beams; let p be the change in optical path due to this movement and N_λ the corresponding number of fringes of wave-length λ . The refractive indices of liquid and glass for wave-length λ are denoted by n^l and n^g respectively. For monochromatic light of wave-length λ the following relation holds:

$$l(n^l - 1) = p = N_\lambda \lambda \quad (1)$$

The number of fringes N_λ being known, l can be computed for any liquid with known n^l *. This is the basic idea behind the determination of osmotic pressure by this method. N_λ can be determined using a monochromatic light source. It will be realized, however, that when a monochromatic source is used it is impossible to differentiate between one fringe and another, so a white light source is very often to be preferred since it is then unnecessary to follow the movement of the fringes. But the difference in the relative dispersions of glass and liquid gives rise to a shift $(N'_\lambda - N_\lambda)$ of the achromatic fringe, a systematic error mentioned above. This effect has been theoretically studied by Adams ³, who has also given practical applications of the theory ⁴. Assuming the following approximation of the Cauchy dispersion formula

$$n = A + \frac{B}{\lambda^2} \quad (2)$$

and using the condition that at the centre of the achromatic fringe the change of phase with respect to wave-length λ shall be a minimum, he derives the following equation [(11) in Adams's paper ³] for this shift $(N'_\lambda - N_\lambda)$:

$$N'_\lambda - N_\lambda = \frac{2}{\lambda^3} (B_1 - B_2) l + \frac{dp}{d\lambda} \quad (3)$$

Applied in the present case, where $N'_\lambda = N_s$, $B_1 = B^l$, $B_2 = 0$ and $p = p_s$, the index s referring to white light, (3) gives

$$N_s - N_\lambda = N_t = \frac{2}{\lambda^3} \left[B^l l - B^g \frac{dp_s}{dn} \right] \quad (4)$$

This means that the monochromatic fringe is displaced fewer wave-lengths than the achromatic one, *i.e.* (1) becomes

$$l(n^l - 1) = (N_s - N_t) \lambda \quad (5)$$

* or n^l for a known l .

The value of l obtained from the uncorrected equation is called l_s , and is defined by

$$l_s(n^i - 1) = p_s = N_s \lambda \quad (6)$$

Combining (5) and (6), we get

$$\frac{l}{l_s} = 1 - \frac{N_t}{N_s} = 1 - \frac{2}{\lambda^3} \left[B^i \frac{l}{N_s} - B^e \frac{1}{N_s} \frac{dp_s}{dn} \right] \quad (7)$$

or

$$\frac{l}{l_s} = 1 - \frac{2}{\lambda^2} \left[B^i \frac{l}{p_s} - B^e \frac{1}{p_s} \frac{dp_s}{dn} \right] \quad (8)$$

Furthermore, (2) gives

$$B = \frac{n_F - n_C}{\frac{1}{\lambda_F^2} - \frac{1}{\lambda_C^2}} \quad (9)$$

Put

$$\frac{1}{p_s} \frac{dp_s}{dn} = P \quad (10)$$

Finally, for $\lambda = \lambda_D$,

$$\frac{l_s}{l} = K_1 \frac{n_F^i - n_C^i}{n_D^i - 1} + K_2 \quad (11)$$

where

$$K_1 = \frac{1}{\frac{\lambda_D^2}{2} \left[\frac{1}{\lambda_F^2} - \frac{1}{\lambda_C^2} \right] + P(n_F^e - n_C^e)} \quad (12)$$

$$K_2 = \frac{\lambda_D^2}{2} \left[\frac{1}{\lambda_F^2} - \frac{1}{\lambda_C^2} \right] K_1 \quad (13)$$

In the case where $\Delta n = n_1 - n_2$, the change of the refractive index between a solution 1 and solvent 2, is measured in white light in a cuvette of length l , according to (3) we obtain

$$\frac{\Delta n_s}{\Delta n} = K_1 \frac{\nu_1 - \nu_2}{\Delta n} + K_2 \quad (14)$$

where ν_1 and ν_2 are the dispersions $n_F - n_C$ for the solution and solvent respectively.

Fig. 1.

P is a function of the angle of incidence at the compensating glass plate and is easily expressed in terms of this angle. Using (3) and (8) in Adams's paper ³, we obtain

$$P(\theta) = 2n^s \frac{\frac{1}{\sqrt{H + \sin 2\theta}} - \frac{1}{\sqrt{H + \sin 2\theta_0}}}{\sqrt{H + \sin 2\theta} - \cos\theta - \sin\theta - \sqrt{H + \sin 2\theta_0} + \cos\theta_0 + \sin\theta_0} \quad (15)$$

$(45^\circ + \theta)$ being the angle of incidence and $H = 2(n^s)^2 - 1$. The initial position of the plate, θ_0 , is in our case about 35° , whereas in Adams's case $\theta_0 = 0$. For $5^\circ < \theta < 35^\circ$, i.e. the interval in which θ varies in our case, $P(\theta)$ is a monotone function varying very slowly. As a matter of fact

$$1.12 < P(\theta) < 1.24. \quad (16)$$

(For the glass plate used $n^s = 1.5163$ and $n_F^s - n_C^s = 0.0080$.) Consequently,

Table 1 (Cyclohexane). *SR* is calibrated in λ_D between the screw readings 25.00—0.00. 25.00 is fringe No. 0 — 0.00 is fringe No. 820.

Reading on <i>LC</i> mm	Reading on <i>SR</i> mm	Average value <i>SR</i>	Fringe No.	N_s No. of λ_D
0.0	1.78 .75 .75 .77	1.76	738.3	
0.5	11.11 .08 .11 .09	11.10	371.1	367.2
1.0	24.64 .67 .65 .66	24.65	7.0	364.1
1.0	1.44 .42 .42 .42	1.42	753.8	
1.5	10.66 .65 .63 .63	10.64	386.9	366.9
2.0	23.89 .91 .90 .89	23.90	22.3	364.6
2.0	1.93 .91 .92 .92	1.92	730.9	
2.5	11.31 .30 .28 .28	11.29	364.6	366.3
3.0	24.98 25.00 .00 24.99	24.99	0.2	364.6

3.0	1.45 .43 .46 .43	1.44	752.8	
3.5	10.65 .66 .64 .67	10.65	386.6	366.2
4.0	23.93 .94 .96 .93	23.94	21.5	365.1
4.0	1.88 .88 .88 .89	1.88	732.8	
4.5	11.25 .26 .24 .26	11.25	366.0	366.8
5.0	24.89 .89 .90 .90	24.90	2.0	364.0

Average value $N_s = 365.6 \pm 0.4$
 $l_s = (0.510 \pm 0.001)$ mm.

it is obviously justifiable to consider K_1 and K_2 as approximately constant, and the theory thus predicts the correction factor $\frac{l_s}{l}$ to be a linear function of the relative optical dispersion $\frac{n_F^l - n_C^l}{n_D^l - 1}$ of the liquid according to (11).

A brief description of the experimental arrangement and the method of measuring will be given. It is intended that the details of the apparatus will be discussed in a later publication. Fig. 1 shows the principal features of the apparatus used. The optical path through the compensating plates of glass P_1 and P_2 can be varied by moving the micrometer screws SR and SL , the screw reading being calibrated in number N_s of fringes of wave-length λ_D , D referring to the D -line ($\lambda_D = 589.3$ m μ). SR covers $820 \lambda_D$, corresponding to about 1 mm of most liquids. The liquid compensator LC is essentially a micrometer screw threaded in an outer tube filled with liquid. The pitch of the

thread is 0.5 mm and has been accurately determined (see below). M is a vessel, the two halves of which are in communication with the two halves of the osmotic cell. M is consequently the vessel where the osmotic pressure is measured. It can be used separate from the cell by replacing the connecting tubes from the cell by tightening arrangements, and as a matter of fact it has been used in this way during this investigation. The difference in liquid level has been changed in accordance with the position of the LC screw; it has proved to be advantageous to use LC in discrete steps, e.g. every turn of the screw i.e. every 0.5 mm. The bottoms of the screw and tube in LC , as well as M , consist of optically plain glass plates. LC contains the same liquid as M .

For the study of the dispersion effect the liquid layer of known thickness l to be compensated by glass was obtained by using LC ; M has been used separately as mentioned before. The distance l , equivalent to the rise of the LC screw (Fig. 1), was measured interferometrically as follows. The central achromatic fringe (white light) was moved by SR (SL being fixed meanwhile) until it coincides with the cross-wire CW of the ocular. The optical path of the left-hand beam was increased by turning the LC screw (l mm rise of the screw). The achromatic fringe was again brought into coincidence by moving SR . The difference between the two readings on SR gives the change in optical path due to the movement of the LC screw. This determination gives N_s , and consequently l_s .

The optical path on the left was increased by turning the LC screw in 0.5 mm steps, cross-wire settings being made for every turn as described. As the range of SR corresponds to about 1 mm liquid in most cases (except for large n^i), measurements for two positions of LC could generally be performed without changing the liquid level in M . In this way l_s was determined for $l = 0.500 \pm 0.002^*$, the pitch of the thread being calibrated by means of a microcomparator. The LC screw is made with about the same precision as the one in the comparator used. The value of l_s (and N_s), as well as l , is the average of the first ten turns of the screw. l_s was determined for ten liquids, mainly common solvents selected to cover a wide range of dispersion. As both n_D^i and $(n_F^i - n_C^i)$ were measured (with a Zeiss Abbe-Refractometer Model G) for each liquid, no special efforts were made to purify the liquids. The purest available substances were of course used. All measurements were carried out at $25.00^\circ \pm 0.01$.

To give an idea of the accuracy in the N_s determination, a series of measurements on one of the liquids (*cyclohexane*) is given (Table 1). The accuracy in

* The deviation is in all cases computed as $\sqrt{\frac{\sum \Delta_i^2}{n(n-1)}}$.

Fig. 2.

the determination is obviously about ± 0.001 mm. It should be observed from Table 1 that every second N_s value is smaller than the preceding one, due to the fact that P is not a real constant. The average is computed from all the determinations, however. Table 2 is a survey of the most pertinent experimental results, and Fig. 2 shows graphically $\frac{l_s}{l}$ as a function of the relative dispersion $\frac{n_F^l - n_C^l}{n_D^l - 1}$. Within the limits of experimental error, a straight line is obtained in agreement with the theoretical findings. The slope of the

Table 2.

Liquid	N_s	n_D^l	$n_F^l - n_C^l$	$\frac{n_F^l - n_C^l}{n_D^l - 1} \cdot 10^2$	$\frac{l_s}{l}$
Methanol	281.3	1.3262	0.00486	1.46	1.016
Cyclohexane	365.6	1.4222	0.00703	1.66	1.021
Water	288.8	1.3321	0.00570	1.72	1.025
Carbon tetrachloride	398.4	1.4571	0.00842	1.84	1.028
Chloroform	382.0	1.4388	0.00840	1.91	1.026
Acetylene dichloride	392.7	1.4421	0.01117	2.53	1.047
Toluene	445.5	1.4933	0.01567	3.18	1.064
Benzene	450.8	1.4975	0.01609	3.23	1.067
Styrene	504.7	1.5442	0.02349	4.32	1.093
Carbon disulphide	597.3	1.6234	0.03369	5.39	1.130

line, K_1 , and the intercept K_2 [(12) and (13)] have been computed by the method of least squares, giving

$$K_1 = 2.84 \pm 0.07 \text{ and } K_2 = 0.974 \pm 0.002$$

The corresponding values of P are

$$P = 2.5 \pm 1.1 \text{ and } P = 1.13 \pm 0.08$$

It is obvious that (12) does not give a reliable value for P . The uncertainty in the value from (13) is considerably less, and the value is furthermore in fair agreement with the theoretical value (16).

The correction to be made in the determination of l can be obtained from Fig. 2 for any liquid with known dispersion. These corrections are obviously in most cases very large, but as will be seen, can be determined very accurately. They are essential in many other applications of white light interferometry where large differences in optical path have to be compensated [*cf.* (14)]. Chromatography with interferometric recording is just one example that may be mentioned.

SUMMARY

A Rayleigh interferometer with a white light source has been used to measure the thickness of liquid layers. Differences in optical path due to the passage of one of the light beams through liquid has been compensated by glass. The effects arising from the difference in the relative optical dispersion of liquid and glass have been studied. The correction factors have been determined and plotted in a diagram against the relative optical dispersion of the liquid. This diagram gives the correction for any liquid with known dispersion. The theory developed on this subject has been verified within the limits of experimental error.

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