A Method for Measuring Interdiffusion Coefficients in Liquids by Wave-front-shearing Interferometry

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A new method for measuring interdiffusion coefficients in transparent liquids is presented. By using a diffusion vessel made of fused quartz with optically flat surfaces perpendicular to the optic axis it is possible to follow the complete concentration distribution with a wave-front-shearing interferometer during the diffusion process.

It has been shown[1–3] that interdiffusion coefficients in liquids can be measured precisely and conveniently by means of wave-front-shearing interferometry. We shall show here that by using a cell of a new type the whole profiles of the optical path distribution and not only the optical path gradient can be observed throughout the diffusion process.

The diffusion cell, made of fused quartz, is shown in Figure 1. The front and rear surfaces of the quartz piece were polished to interferometric quality and covered by optical quartz windows. The windows were pressed against the cell by the evacuated light ports with the force of a pneumatic pressure mechanism. The evacuated light ports make it possible to apply the present method to measurements of interdiffusion coefficients of molten salts at high temperature[2, 4].

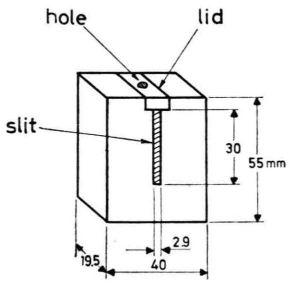

Fig. 1. Diffusion cell made of quartz Herasil III.

The Variable Shearing Interferometer[5] was employed in this case as a beamsplitter, shearing the light horizontally by approximately 6 mm.

In order to test the arrangement experimentally the interdiffusion coefficient of potassium chloride in pure water was measured with this method. A small crystal (0.95 mg) of potassium chloride was dropped to the bottom of the diffusion cell in order to initiate the diffusing process[1]. In this case the optical path through the solution as a function of the distance x from the bottom of the cell and time t is given by[2]

$$R(x,t) = R_0 + (\partial\mu/\partial c)\, M(\pi D t)^{-1/2} \exp\{-x^2/\sigma^2\} \tag{1}$$

where R_0 is the optical path through the solvent, M is the total amount of the diffusing substance supplied to the bottom divided by the cell width perpendicular to the optical axis. $(\partial\mu/\partial c)$ is the concentration dependence of the refractive index of the solution, D is the interdiffusion coefficient and $\sigma^2 = 4\,D\,t$. If the dimensions of the cell are properly chosen, no indication of a deviation from this mathematical description has ever been observed.

If the shearing in the horizontal direction is greater than the cell-width, the optical path difference between the interfering rays becomes

$$\Delta R(x,t) = R(x,t) - R_q + \Delta R_{\text{int}} \tag{2}$$

where R_q is the optical path through the quartz wall and ΔR_{int} is the path difference introduced by the interferometer. Thus for every point in the interferogram one gets

$$\Delta R(x,t) = m\,\lambda \tag{3}$$

where λ is the wave-length of the incident light and m is the order of interference. Taking

$$A = (\partial\mu/\partial c)\, M(\pi D t)^{-1/2}$$

the fringes corresponding to the destructive or constructive interference appear at positions x_n given

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by

$$A \exp\{-x_n^2/\sigma^2\} = (n+\varepsilon)\,\lambda \tag{4}$$

where $n = 1, 2, 3, \ldots$ and $-1 < \varepsilon < 1$. Equation (4) can be transformed to

$$\ln(n+\varepsilon) = \ln B - x_n^2/\sigma^2 \tag{5}$$

where $B = A/\lambda$.

By plotting $\ln(n+\varepsilon)$ versus x_n^2 one can determine the values of σ^2 and $\ln B$ at a given time t. The points ought to lie on a straight line with some random fluctuations caused by errors from e. g. the fringe localisations. This makes it possible to calculate ε, σ^2 and B numerically by varying ε from 1 to -1 and searching for the best fit of the points to the straight line.

In our investigation 18 interferograms obtained at different times from one particular experiment were evaluated. Three of them are shown in Figure 2. The highest black fringe corresponds to the destructive interference of the lowest order as long as the diffusing substance has not altered the concentration in the upper part of the cell. In Fig. 3 four plots of $\ln(n+\varepsilon)$ versus x_n^2 for four different ε are shown. This clearly indicates how sensitive the evaluation is to a proper choice of ε.

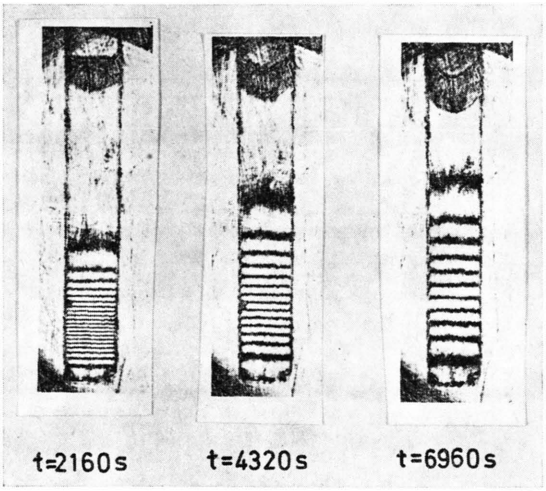

Fig. 2. Interferograms of a diffusion process initiated by dropping a 0.95 mg crystal of potassium chloride into pure water. Only one of the two pictures obtained with a 6 mm horizontal shear is presented here.

Having obtained a number of σ^2 values from the interferograms of one experiment, the diffusion coefficient is calculated from a plot of σ^2 versus $4\,t$ (Figure 4). The slope of this plot gives the diffusion coefficient and the intercept gives the zero-time correction. Once the diffusion coefficient is determined it is possible to return to the calculations of the individual σ^2-values and obtain the concentration dependence of the refractive index $(\partial\mu/\partial c)$.

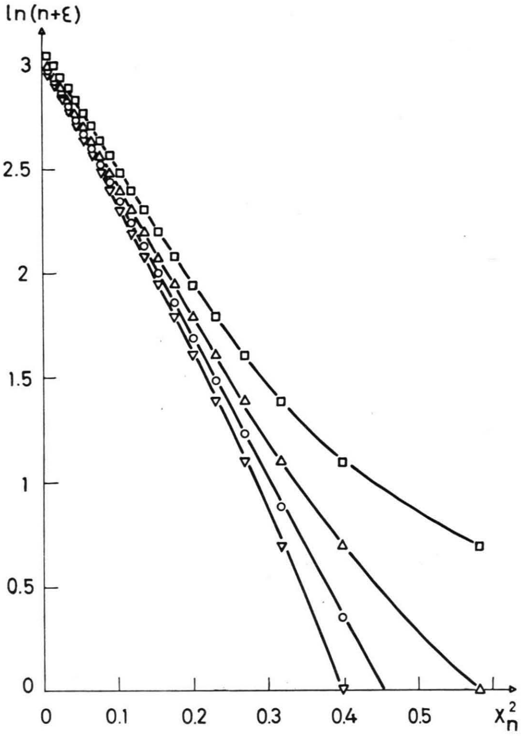

Fig. 3. The dependence of $\ln(n+\varepsilon)$ on x_n^2 for various values of ε. □: $\varepsilon=0.99$, △: $\varepsilon=0$, ○: $\varepsilon=-0.58$, ▽: $\varepsilon=-0.99$. The data are obtained from the interferogram recorded at the time $t=2160$ sec.

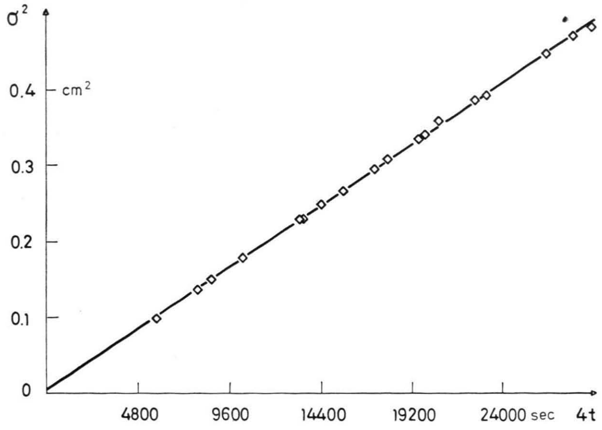

Fig. 4. The plot of σ^2 versus $4\,t$. The intercept of the fitted line gives the zero-time correction and the slope of this plot gives the diffusion coefficient.

From the present experiment, the diffusion coefficient of potassium chloride diffusing in pure water is calculated to be $(1.668 \pm 0.009) \times 10^{-5}$ cm²/sec at 20 °C which compares favorably with the value 1.667×10^{-5} cm²/sec at the mean concentration 0.05 mole/l at 20 °C by Lamm[6], 1.689×10^{-5} cm²/sec at 0.011 mole/l and 20 °C by Harned and Nutall[7] and 1.64×10^{-5} cm²/sec at 0.06 mole/l and 20.6 °C by Gustafsson, Wallin and Arvidsson[1]. The concentration at the inflexion point $x = (2\,D\,t)^{-1/2}$ does never exceed 0.04 mole/l after the recording of the first interferogram. This concentration should be compared with the higher one necessary when recording the optical path gradient.

The calculated value of $(\partial \mu / \partial c)$ is (0.132 ± 0.004) cm³/g for the wave-length $\lambda = 6328$ Å which is in a good agreement with values presented by Longsworth[8] for $\lambda = 5461$ Å.

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[1] S. E. Gustafsson, L.-E. Wallin, and T. E. G. Arvidsson, Z. Naturforsch. **23 a,** 1261 [1968].

[2] S. E. Gustafsson in Abstracst of Gothenburg Dissertations in Science **12,** 1969.

[3] T. E. G. Arvidsson, S.-Å. Afsenius, and S. E. Gustafsson, J. Chem. Phys. **53,** 2621 [1970].

[4] S. E. Gustafsson, N.-O. Halling, and R. A. E. Kjellander, Z. Naturforsch. **23 a,** 44 [1968].

[5] S. E. Gustafsson and E. Karawacki, The design of two shearing interferometers for studying the refractive index distribution near opaque boundaries (to be published).

[6] O. Lamm, Nova Acta Reg. Sci. Uppsala **IV,** 10(6) [1937].

[7] H. S. Harned and R. L. Nutall, J. Amer. Chem. Soc. **71,** 1460 [1949].

[8] L. G. Longsworth, in: The Structure of Electrolytic Solutions, p. 194, W. J. Hamer, Ed., John Wiley & Sons, Inc., New York 1959.