

Piezo-optic Behavior of Water and Carbon Tetrachloride under High Pressure*

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A new interferometric method of measuring Δn , the variation of refractive index of liquids with pressure, to 14 kbar is described. The results obtained on Δn versus pressure up to the freezing point of water and carbon tetrachloride at room temperature are presented and discussed.

The refractive index of liquids at high pressures has been studied by a number of workers¹⁻³ up to a maximum pressure of 1.5 kbar only. We have now designed and constructed a suitable liquid-cell interferometer for insertion in a high-pressure optical vessel⁴ so that it is possible to carry out precision interferometric measurements on the piezo-optic properties of various liquids, up to a maximum pressure of 14 kbar.

The liquid-cell interferometer consists of a stainless-steel body connected to a polyurethane bag containing the liquid under study. The optical components of the interferometer consist of a suitably silvered optical flat, a plano-convex lens, and a vitreous silica spacer between the optical flat and the lens; these components are properly aligned so that localized Newtonian fringes can be obtained between the optical flat and the convex side of the lens with the spacer and the liquid in between. The spacer for this interferometer was fabricated from vitreous silica, but before fabrication the large block of vitreous silica itself was used to determine its second- and third-order elastic constants. With this information and a knowledge of the pressure in the system as read by a precision Heise gauge or manganin gauge the thickness of the spacer of the interferometer at any pressure could be evaluated to within $\pm 0.1\%$. As the pressure in the system is increased, the flexibility of the polyurethane bag containing the fluid under study allows the optical interferometer to be filled with the liquid at all pressures. The maximum amount of

liquid necessary for these measurements is only about 3 cm³. The temperature of liquids inside the pressure vessel during the experiments was maintained to within 0.1°C and thus corrections for thermal fluctuations are not needed.

As the pressure in the system is increased, the refractive index of the liquid in the interferometer as well as the thickness of the spacer are altered with consequent shift of the interference fringes across a fiducial mark on the optical flat of the interferometer. The change in refractive index Δn of the liquid could be evaluated with the help of the usual interference formula. Such a computational procedure implies the following two assumptions: (i) The radius of curvature of the lens is not changed significantly by the change in pressure, and (ii) the thickness of the spacer is the same as the true thickness of the interferometer at the fiducial mark. Since the radius of the plano-convex lens of the interferometer is very large (~ 10 m) and since the pressure change in any one measurement and the consequent computation involved never exceeded 50 bar, the above assumptions are considered to be valid and the consequent errors involved are considered to be negligible.

Table I presents typical results obtained on water and carbon tetrachloride at 25°C. In both cases the maximum pressures stated were determined by the freezing of liquid at 25°C at these pressures. The number of fringes observed to shift with increasing pressure matched, to within a fractional fringe, the number of fringes shifted

TABLE I. Variation of the refractive index of liquids with pressure at $T = 25^\circ\text{C}$.

Liquid	λ (Å)	n	Max. pressure (kbar)	Total no. of fringes shifted	Δn
Water	5893	1.3325	11.03 \pm 0.01	370	0.0821 \pm 0.0001
CCl ₄	5461	1.4600	1.94 \pm 0.01	324	0.0671 \pm 0.0001

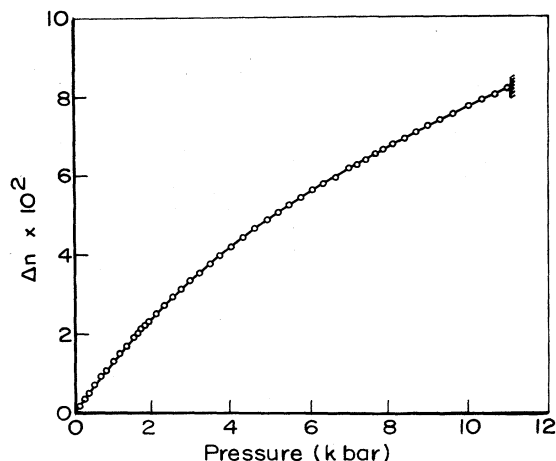


FIG. 1. Variation of refractive index of water with pressure at $T = 25^\circ\text{C}$.

on release of pressure, provided the high-pressure freezing point is not reached during the excursion. The table gives the values of the refractive indices, n , of these liquids at atmospheric pressure and also the total measured change Δn in the refractive indices of the liquids.

Figure 1 shows the variation of refractive index of water with pressure in one of many identical runs. The corresponding figure for carbon tetrachloride is similar to Fig. 1 and hence is not shown here. In the case of water, a total of 370 fringes were found to shift from atmospheric pressure to a maximum pressure of 11.03 kbar, at which point the water froze to ice VI. It is seen from Fig. 1 that the refractive index increases nonlinearly with pressure, particularly at high pressures. At low pressures the results obtained on dn/dP are in excellent agreement with those of Waxler and Weir³ and Rosen² who have also carried out similar measurements on water and CCl_4 . With use of the P - V data of Gibson and Loeffler⁵ and the usual Tait equation,⁶ the change in volume and hence the Lagrangian strain η , at different pressures, were evaluated for both liquids. The Lagrangian strain $\eta = [(1 + \Delta t/t_0)^2 - 1]/2$ is related to the volume strain by the relation $\Delta V/V_0 = 3\eta + \frac{3}{2}\eta^2$. Figures 2 and 3 represent Δn as a function of η , the Lagrangian strain so evaluated. It is seen that the nonlinearity is very much reduced compared to that in Fig. 1. It may be recalled that in the case of solids^{4,7} it was found that the change in refractive index was exactly linear with Lagrangian strain, even though in some cases the total volume strain was as

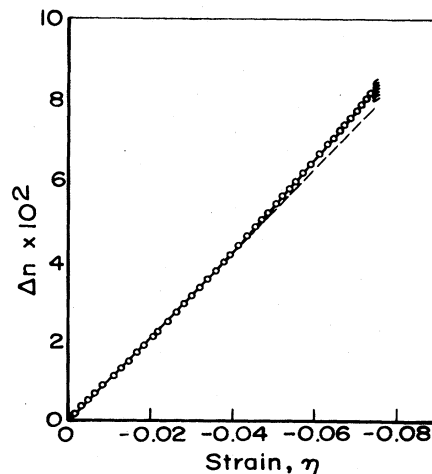


FIG. 2. Variation of refractive index of water with Lagrangian strain.

large as 9% (for which $\eta \approx 3\%$) provided such measurements are not carried out near the absorption edge. From Figs. 2 and 3 it is seen the carbon tetrachloride does exhibit such a linear relationship throughout its liquid phase. However, a slight nonlinearity in the Δn - η relationship for water can be noticed above about 4.4% strain. This nonlinearity can very well arise from either the failure of the Tait equation at such large pressures, or errors in the P - V experimental data, or a combination of both. In fact, MacDonald⁸ in a recent review of the experimental and analytical equations of state concludes that "even the combination of the best data on water apparently available and the use of better statistical analysis

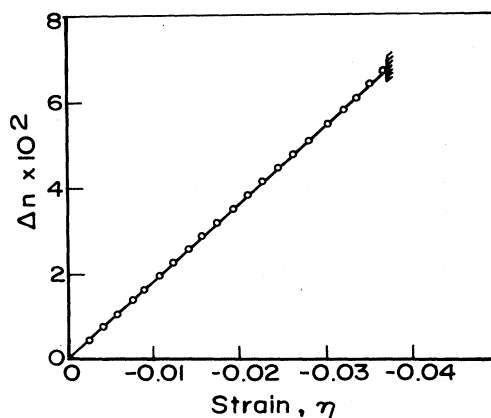


FIG. 3. Variation of refractive index of CCl_4 with Lagrangian strain.

methods than have been employed before does not yet allow one to obtain highly accurate values of K_0' (the pressure coefficient of isothermal bulk modulus at $P=0$) and only an order of magnitude estimate of the K_0'' parameter seems currently possible."

It may be possible to use the present interferometric method of measuring Δn , as a function of pressure, to yield the true isothermal P - V data of liquids. Of course, this is based on the assumption that Δn versus η is linear. As mentioned earlier, such a linear relationship is found to be valid in the case of the high-band-gap inorganic solids where there is a considerable amount of overlap of the electronic wave functions of neighboring ions. In the case of liquids where the intermolecular distances are much larger than in the solid state, it is expected that Δn will be linear with Lagrangian throughout the entire range of pressure during which the material is in the liquid state. The present type of measurements can verify this conjecture and if proved correct this method will enable one to arrive at the true P - V relationship for the liquids. Furthermore, it may be possible to verify the validity of the various theories⁹⁻¹⁰ (both empirical as well as fundamental) that have been proposed for the correct equation of state of liquids as well as to improve our understanding of the concept of free volume and structure of liquids.

From an analysis of the data available up to that time on various liquids and crystals, Waxler, Weir, and Schamp¹¹ concluded that for both liquids and solids under hydrostatic pressure a change in density produces two competing effects—a change in the polarization field and a change

in the polarizability of the individual oscillator; in the liquids the first effect is dominant in view of their large compressibility, whereas in the case of crystals the second effect can often be dominant. In general, the present measurements confirm these conclusions. The exact numerical values of the various piezo-optic coefficients and their implications will be discussed elsewhere.

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