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Variation of hypersound velocity in the isotropic phase of liquid crystal mixtures

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The hypersound velocity in a series of binary mixtures containing the constituents 4-*n*-pentyl-4′-cyanobiphenyl and 4-cyano-4′(2-methyl)butoxybiphenyl has been measured using Brillouin scattering techniques. Measurements have been made in the isotropic phase of the mixtures over the temperature range 30°C to 80°C. A simple theory for the observed velocity variations is proposed and compared with the experimental data. Agreement is found to be excellent over the temperature range studied.

The study of Brillouin scattered light allows the accurate determination of the hypersound velocity in both solids and liquids. This velocity, together with appropriate theory, permits the measurement of elastic constants and thereby provides an understanding of the elastic behaviour of the material. Studies with samples of pure liquid crystal compounds have led to the direct observation of second sound in the smectic A phase of 4-methylbutyl-4′-[MBA]cinnamate [1] and its inference in thin films of 4-*n*-octyl-4′-cyanobiphenyl [2]. Measurements on thin films in the nematic phase have highlighted the anisotropy of this phase [3] and added to the understanding of this anisotropy through the theory developed by Lui [4]. Here we report the application of Brillouin scattering techniques to the study of mixtures of liquid crystals. In our preliminary experiments discussed here the liquid crystal mixtures were prepared from stable cyanobiphenyl compounds obtained from BDH Chemicals. These were studied in their isotropic phase to establish the general behaviour of such mixtures.

In order to obtain measurable variations in the velocities with concentration it was found necessary to prepare mixtures of compounds whose individual hypersound velocities, at any given temperature, are widely different. The two compounds 4-cyano-4′(2-methyl)butoxybiphenyl (C15) and 4-*n*-pentyl-4′-cyanobiphenyl (5CB) were chosen for this reason. C15 is a cholesteric biphenyl having a virtual cholesteric to isotropic transition at 10°C whilst pure 5CB is a nematogen with a nematic–isotropic transition at 35·3°C. Small amounts of C15 are often added to the mixtures used in nematic displays to avoid regions of reverse twist. At 40°C their hypersound velocities, which are in the region of 1650 ms^{-1}, differ by about 8 per cent, the difference falling to 5 per cent at 70°C.

The hypersound velocity in the mixtures of 5CB and C15 of different compositions was measured as a function of temperature. From these measurements the variation

of velocity with mixture composition at fixed temperatures was deduced. The experimental data obtained have been compared to that expected by theory and good agreement found.

The 90°-scattering experiments were performed using an argon–ion laser (λ = 488 nm), Burleigh triple-pass Fabry–Perot interferometer (plate separation of 10·17 mm) and low noise photon counting equipment built in the department. The experimental arrangement has been described elsewhere [5]. Thin samples of the order of 100 μm thickness were fabricated by sandwiching the liquid crystal mixture between parallel glass plates. With mixtures containing more than a few per cent of C15 it was not possible to obtain uniformly aligned samples below the isotropic to nematic transition temperature. We therefore limited our investigation in these mixtures to the isotropic phase in the temperature range 30°C to 80°C. The samples were mounted on a heating stage and their temperature stabilized to better than $\pm$0·02°C. Sample temperature was determined directly using a very thin calibrated copper–constantan thermocouple inserted into the sample cell. The hypersound velocity was calculated from the Brillouin shift by fitting the Brillouin spectra obtained to the theoretically expected intensity profile [6]. This procedure enabled the hypersound velocity to be measured to $\pm 3\,\mathrm{ms}^{-1}$.

In figure 1 we show the variation of velocity with temperature for pure 5CB, pure C15, and a 50 per cent/50 per cent mixture by weight. The dot size indicates the

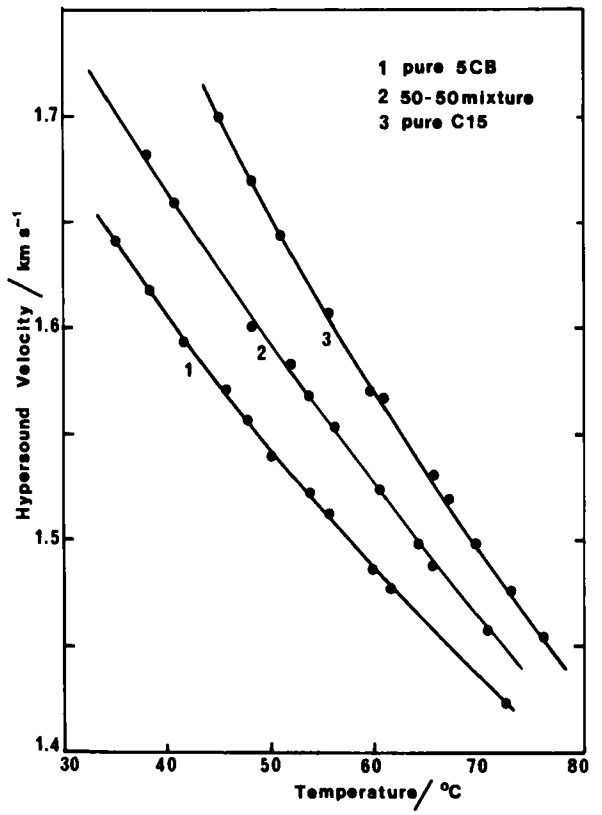

Figure 1. The temperature dependence of the hypersound velocity in 5CB, C15 and a mixture of the two compounds containing 50 per cent of 5CB by weight.

experimental error on each data point. In every case, as expected, the velocity is seen to decrease smoothly with increasing temperature. The small scatter in the experimental data is within the experimental error for each point. For simple isotropic liquids the bulk modulus, K, of the material and hypersound velocity, v, are linked by the relationship

$$K = \varrho v^2,$$

where ϱ is the density of the material. Using density values obtained from Dunmur and Miller [7] the bulk modulus of 5CB was found to be $2{\cdot}59 \pm 0{\cdot}01 \times 10^9\,\mathrm{Nm}^{-1}$ at 40°C and to decrease linearly to $2{\cdot}18 \pm 0{\cdot}01 \times 10^9\,\mathrm{Nm}^{-1}$ at 60°C.

Our experimental data for several mixtures are presented in figure 2 where the hypersound velocity is shown as a function of the percentage by weight, x, of 5CB present in each mixture. For each temperature at which measurements were made, the same behaviour was observed. There is a small but non-linear reduction in v as the concentration of 5CB is increased. We expect this reduction to reflect the variation of the effective bulk modulus, K_m, for the mixture. If this is the case, to a first approximation, the value of K_m would be expected to be an average value weighted by the concentration of each component present. The solid lines drawn through the

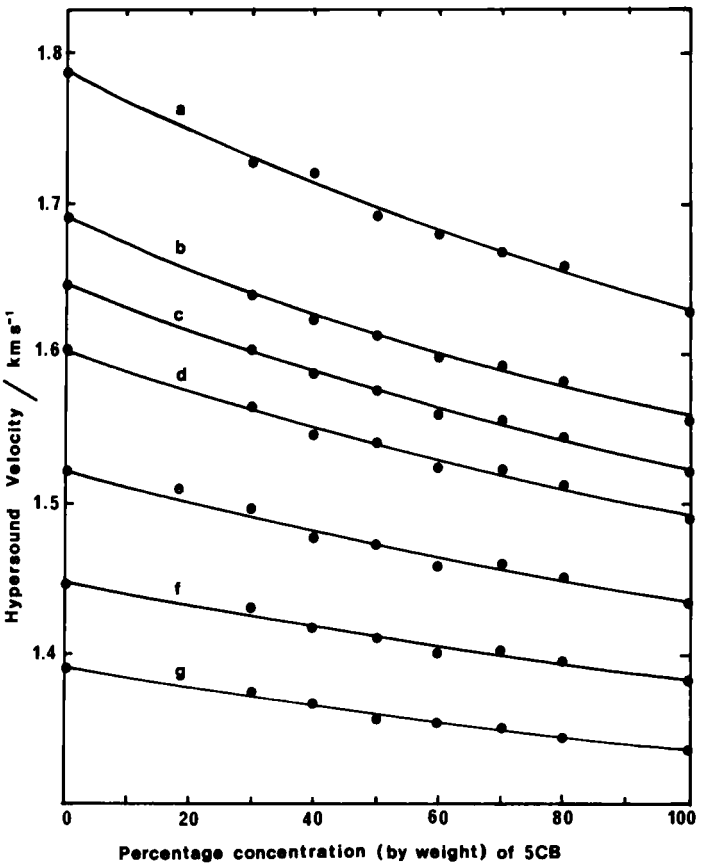

Figure 2. Variation of the hypersound velocity with concentration of 5CB present in a mixture of 5CB and C15. Curves (*a*) to (*g*) are for the temperatures 30°C, 40°C, 45°C, 50°C, 60°C, 70°C and 80°C respectively.

experimental data in figure 2 represent a best fit to the first order theory outlined and indicates remarkable agreement.

For a mixture the hypersound velocity would be given by (K_m/ϱ_m) where ϱ_m is the density of the mixture. The mixture density can be obtained from the densities of the individual components and simple thermodynamics enables one to relate K_m to the individual bulk moduli of the components. Consider a mixture of two components with a total volume V. The individual components occupy volume V_1 and V_2 such that

$$V = V_1 + V_2.$$

If the component in a volume V suffers a small volume change dV due to a pressure fluctuation dP then

$$dV = -V\,dP/K,$$

where K is the component's bulk modulus. For the mixture therefore we may write

$$dV = -\left[\frac{V_1}{K_1} + \frac{V_2}{K_2}\right]dP \tag{1}$$

and hence the effective bulk modulus may be written as

$$K_m = \frac{K_1(1 + V_1/V_2)}{1 + K_1V_2/K_2V_1}. \tag{2}$$

With the weight percentage x of component 1 present in the mixture, component densities ϱ_1, ϱ_2 and their ratio, ϱ_1/ϱ_2 $(= R)$ we have

$$\left.\begin{aligned} \frac{V_1}{V_2} &= \frac{x}{(1-x)R}, \\ \varrho_m &= \frac{\varrho_1}{x + R(1-x)}. \end{aligned}\right\} \tag{3}$$

Combining equations (2) and (3) we are able to express the hypersound velocity v for a mixture as a function of weight per cent x of component 1 at a fixed temperature in terms of the velocities v_1 and v_2 for pure 5CB and C15 respectively,

$$v = \frac{v_1v_2[x + (100 - x)R]}{[xv_2^2 + (100 - x)R^2v_1^2]^{1/2}}. \tag{4}$$

This expression for v was used in the least squares fit to the experimental data given in figure 2 where the solid line indicates the fit obtained. Agreement between theory and experiment is very good over the temperature range studied. The density ratio R was used as the single fitting parameter and good fits were obtained for each temperature with a value for R of $0{\cdot}93 \pm 0{\cdot}01$. This quantity appears to be independent of temperature.

Using the published data [7] for the densities of the cyanobiphenyls (nCB) the rate of change of density with temperature for the isotropic phases of these compounds with n, lying in the range 5 to 9, was found to be the same within experimental error. For mixtures of these compounds then we would expect to observe a temperature independent value for R and strongly argues that the requirement on R of our fitting is not unreasonable.

To compare our fitted value of R with experiment we have measured the density of C15 at 35°C using a simple capillary tube method. The value obtained for the

density was $1{\cdot}09 \pm 0{\cdot}01\,g\,cm^{-3}$. The density of 5CB in the isotropic phase, close to the nematic transition, is quoted as $1{\cdot}009\,g\,cm^{-3}$ [7]. These two density values give an expected ratio R equal to $0{\cdot}93 \pm 0{\cdot}01$, in excellent agreement with our fitting parameter.

In conclusion therefore we find that the behaviour of the hypersound velocity for liquid crystal mixtures in their isotropic phase agrees with that expected on the basis of a simple model. This treats the liquid mixture as having independent constituents even though they mix thoroughly, and predicts the simple averaging noted in their macroscopic properties. It would be pertinent to observe the behaviour of nematic mixtures as they pass through the isotropic to nematic transition. To achieve this the essential requirements for a successful experiment are that the individual components of the mixture have a large velocity difference and that the samples may be aligned in the nematic phase. Unfortunately the later constraint was not possible with the mixtures used here. We are currently searching for compounds which satisfy these criteria to extend our studies into the nematic phase.

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