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A CRITICAL ANALYSIS OF THE USE OF THE ULTRASONIC INTERFEROMETER FOR VELOCITY MEASUREMENTS IN LIQUIDS.

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1. INTRODUCTION.

It may be argued that the Curies' discovery of the piezoelectricity of quartz in 1880[1] was the first step towards our utilization of ultrasonic waves as an investigative tool or an agent for change. However it was over twenty years later, in 1906 that Lee De Forest introduced the triode valve that permitted amplification of electrical systems, and led to the widespread development of devices for radio. This technology was also utilised for driving and detecting signals from piezoelectric elements. Although Langevin [2] appears to have been the first to design an ultrasonic instrument in 1918, the interferometric apparatus produced by Pierce in 1925 [3] appears to have been one of the very first scientific ultrasonic instruments. Its application to gases appears to have been extended shortly afterwards to liquids by Hubbard and Loomis [4,5]

The 1930's were years of intense activity in ultrasonic science, with several groups using and identifying improved versions of the interferometer for new applications. Thus Pielemeier [6] and Klein & Hershberger [7] describe its application to the measurement of absorption, and Swanson [8] to a determination of the pressure coefficient of velocity. Hubbard's group identified relatively quickly the possibilities of measuring the compressibility of liquids [9] and of solutes in solution [10]. Some of the earliest Indian work was that of Parthasarathy [11,12] who extended his interest to velocity measurements in liquid mixtures [13].

Since that time there has been considerable activity in the field of molecular acoustics as a number of texts [14-17, for example] give evidence. The interferometer has tended to be the instrument of choice, and although improved versions or analyses are of current interest [18,19] it represents an instrument which is relatively simple to construct (and therefore economic) but capable of quite high precision. Its commercial availability appears surprisingly, to be relatively rare, such devices being most easily available in India. Based on this local industry, and perhaps following the historical lead given by Parthasarathy, there are a significant number of laboratories in the sub-continent whose main efforts are devoted to exploiting the use of interferometric velocity measurements in liquids.

ULTRASONIC INTERFEROMETER.

The published contributions in this area exhibit a wide range of quoted accuracy for the measurements. The extreme range appears to be from 0.01% [20] to 0.2% [21, 22], with 0.1% being typical. The disparity of these quoted values suggested that it would be appropriate to attempt to provide some systematic discussion to define what may realistically be achieved, and what is necessary to achieve it, so that all the laboratories concerned may strive to achieve uniformly high standards in their measurements. The present paper represents the first stages in such a critical analysis. However before discussing the technique it is important to give a brief outline of the nature of the chemical information that is extracted from the ultrasonic velocity measurements.

2. CHEMICAL INFORMATION FROM ULTRASONIC VELOCITY.

There appear to be no substantial review articles or texts devoted solely to a discussion of ultrasonic velocity measurements and their value. This may be due in part to the fact that structural information or information on molecular processes is more easily determined from the measurement of absorption than from the velocity dispersion. Although the latter is an inevitable companion of the former, it is numerically often too small to permit easy measurement. Probably the most comprehensive account for non-electrolytes is that of Sette [23]. He points out that the main initial use for sound velocity measurements was in connection with measurements of density, which permitted evaluation of the adiabatic compressibility and thus the ratio of the specific heats if the isothermal compressibility had been determined by static measurements.

However the early interest in this area, and particularly the work of Schaaffs [15], led to the identification of intimate relations between the values of the sound velocity and the chemical or structural characteristics of the liquid. As a result of this sound velocity has become a primary quantity in the molecular theory of liquids. Thus, for example, assuming Van der Waal's equation for a liquid, but allowing the parameters a, b (which are taken to be constants for gases) to be functions of density, ρ and temperature, T we have:

$$\left[p + \frac{\rho^2}{M^2}\, a(T,\rho)\right]\left[\frac{M}{\rho} - b(T,\rho)\right] = RT \quad \ldots\ldots\ldots (1)$$

using $c^2 = \gamma \frac{dp}{d\rho}$ where c is the speed of sound, the molecular radius, which is related to b can be evaluated as:

$$r_m = \frac{3}{16\pi N_A} \frac{M}{\rho} \left[1 - \frac{RT\gamma}{Mc^2}\left(\sqrt{1 + \frac{1}{3}\frac{Mc^2}{\gamma RT}} - 1\right)\right] \quad \ldots\ldots\ldots(2)$$

where N_A is Avogadro's number, and M is the molecular weight. The values of r_m obtained from (2) agree well, for a number of molecules, with those obtained by other methods. For the value of the velocity, Schaaffs obtained:

$$c^2 = \frac{\gamma RT}{M}\left[\frac{\frac{1}{3}}{(1 - \frac{b}{V})^2} - \frac{2}{(1 - \frac{b}{V})}\right]^{\frac{1}{2}} \quad \ldots\ldots\ldots(3)$$

Since the value of b can be found by the addition of atomic terms in the molecule the calculation of a theoretical value of c would appear to be possible for comparison with the experimental values. This is not, in practice, usually feasible because the ratio of specific heats is not known as priori, and because small errors in b give rise to large errors in c, from equation (3). Nevertheless equation (3) has proved valuable in providing a basis for some of the empirical rules developed by Parthasarathy between velocity, molecular weight, density and molecular size.

The majority of recent interest has centred on the use of ultrasonic velocity measurements in the investigation of solute: solvent interactions, such as hydration [24] and mechanisms of association and dissociation. Whereas it is possible to provide some theoretical approaches to ultrasonic propagation in pure liquids, in a solution or a liquid binary mixture this is not generally possible. Thus the sound velocity in such a mixture is a function of composition and the form of the function depends on the nature and strength of the interactions between the molecules - whether of the same or differing types. While it is an advantage that sound velocity measurements can be used as a probe of these interactions (albeit non-specific), the disadvantage is that the information obtained can only fuel hypotheses which require independent assessment and validation.

In order to investigate these interactions more specifically, a number of parameters are derived from the velocity and density

measurements, some of them based on semi-empirical analyses. Dewan et al [25] has detailed many of the approaches used. Some of the most common parameters are, however, the following:

1. The apparent molal compressibility, ϕ_k:

$$\phi_K = \frac{1000}{C\rho_2}(\rho_2\beta_1 + \beta_2\rho_1) + \frac{\beta_2 M_2}{\rho_2}$$

where ρ_1,β_1 and ρ_2,β_2 are parameters for the solvent and solute respectively. This is a measure of the total compressibility of one litre of solution containing C gm moles of a solute of molecular weight M_2

2. The intermolecular free length, L_f:

$L_f = K\sqrt{\beta}$ where K is Jacobson's constant.

This is temperature dependent and differs from van der Waal's radius in that it does not include the atomic radii.

3. The available volume, V_a:

$$V_a = V\left(1 - \frac{C}{C_\infty}\right)$$

where V is the molar volume of the solvent and $C_\infty = 1600\text{m s}^{-1}$.

4. The molar sound velocity, R:

$$R = \frac{\bar{M}}{\rho}C^{\frac{1}{3}} \quad \text{where} \quad \bar{M} = \frac{n_1M_1 + n_2M_2}{n_1 + n_2}$$

with n_1,M_1 and n_2,M_2 being the mole fractions and molecular weights of the solvent and solute respectively. ρ is the density of the solution.

5. The solvation number, S_n:

$$S_n = \frac{n_1}{n_2}\left(1 - \frac{c\beta_1}{n_1 c_2 \beta_2}\right)$$

This gives the number of layers of the solvent molecules surrounding the solute molecules.

3. THE INTERFEROMETER.

There are a number of designs of interferometer but the basic elements are essentially common. The essence of the device is the cavity in which standing waves are established by a continuously-excited transmitting transducer at one end. Although a second transducer may be used at the other end [19], it is more usual to place a reflector there. The key to the measurement is the establishment of standing waves in the cavity. This may be achieved by changing the frequency of the transmitted waves or by adjusting the length, ℓ, of the cavity. However for accurate measurements [19] a high Q is required, so the latter is the system of choice.

The main reason that interferometers are popular for precision velocity measurements is that rather than measuring time and distance for pulse travel, both of which may involve significant uncertainties, the interferometer measures frequency and wavelength. As a continuous wave instrument the frequency is relatively easy to measure to one part in 10^6 or 10^7. Thus the main errors come in relation to the determination of the wavelength. Again two main methods appear to be used. In the fixed path interferometer, having adjusted the length of the cavity for resonance, the wavelength is measured by some independent means. A probe inserted into the cavity to determine the positions of the standing wave maxima was one of the early procedures, while for optically transparent liquids, optical methods based on the transmission of light perpendicular to the direction of propagation of the sound-waves have been described. These include both a 'shadowgraph' [26] and the use of the standing wave as a diffraction grating [18].

By far the most popular procedure, however, is the use of the variable path interferometer. In this the reflector is moved relative to the transmitting transducer. Whenever the spacing of the reflector and transducer is such that standing waves occur, the load impedance of the transducer passes through a maximum, and the current driving it through a minimum. If plane waves are assumed

in the cavity, the spacing of these current minima is half a wavelength.

4. ERRORS OF MEASUREMENT.

The essential causes of uncertainty in the measurement of the wavelength, and thus, of the speed of sound in the liquid concerned, arise from limitations on temperature control, on the measurement of the spacing of the standing wave positions and from a lack of planarity in the propagating waves.

4.1 Temperature control.

Using the figure for water of a change in the speed of sound (1480m s^{-1} at room temperature) of 3m s^{-1} per degree celsius, it is easy to estimate the significance of the temperature control needed. For the ±0.2% accuracy quoted above, the temperature control must be better than ±1·C; for 0.01% accuracy, it must be better than ±0.05·C.

4.2 Measurement of spacing of resonances.

In general the methods for measuring distances accurately have an absolute error associated with them for a given range of distances measured. It is clearly advantageous to optimise this. A micrometer, for example, may give an accuracy of 1um over a distance of 2.5cm, ie 0.004%. The increasing demands of interferometric optics and micromachining have led to the commercial availability of linear measurement devices with a quoted precision of 0.1um, a bidirectional repeatability of 0.5um, and an accuracy of 1um per 100mm. Thus the precision is 1 part in 10^6, but in practice the identification of an extremum in a parameter such as the transducer driving current will, in the first instance (unless extreme care is taken), require a bidirectional approach; and will then be limited by the sensitivity with which the position of the extremum can be identified. Thus overall for the distance measurement, the accuracy figure given above, ie. 0.001% is probably optimistic, but represents a reasonable limit to what can be achieved in terms of distance measurement.

4.3 Lack of planarity of wavefronts.

The fundamental problems in most ultrasonic measurement systems arise firstly from the fact that the transducers used are always diffractive, and therefore do not emit plane-waves, and secondly from the fact that experimental techniques for determining exactly how a given transducer is vibrating are not yet well developed [27]. There are several interrelated factors in the choice of the size of the transducer and the frequency at which it operates. As far as the distance measurement is concerned, clearly a reasonable number (say a few tens) of minima should be counted, but the

accuracy of the determination of the spacing of the minima, expressed as a percentage, will be essentially that of the distance measurement. Increasing the frequency to decrease the wavelength has no major advantage and may lead to a blurring of the minima due to increased absorption, (unless of course, the purpose of the measurements is to determine the velocity dispersion). With a wavelength of the order of 0.5mm at 3MHz, clearly the low megahertz frequencies appear most appropriate.

In some circumstances the cost or availability of the liquids to be examined requires the minimisation of the sample volume. For this a fixed path interferometer may be best. For an ideal circular transducer of radius a working with a wavelength in the liquid to be measured of λ, the beam is collimated for a distance from the transducer of about a^2/λ (the Fresnel region) and then diverges (the Fraumhofer region). Extension of the measurement region to the far field, where the wavefronts become more closely plane requires a significant increase in cavity diameter. Even if financial constraints allow this, it is not always advisable due to the problems of maintaining close temperature control over a large volume.

Reflections from the side walls of the cavity were recognized at an early stage as a source of 'satellite' extrema. These can also be caused by an incorrect orientation of the reflector. Good absorbers tend to be good thermal insulators so is advisable to minimise the sound incident on the side walls. A cavity diameter of approximately 1.5 x the transducer diameter appears to be considered adequate. The higher the frequency, the longer is the Fresnel region. Using a frequency of 3MHz and a crystal radius of 7mm, the Fresnel region extends to an axial distance of 98mm.

One of the effects of the complex interference patterns in the Fresnel region is to move the positions of the wavefronts relative to their plane wave positions. It is possible to apply a 'diffraction correction' for this phenomenon if the vibration pattern of the transducer is known. Not only is there such a 'near-field' for the transducer, the reflector will also generate one, and these two patterns depend upon the radius of the source and reflector in relation to the wavelength. There are relatively few experimental investigations of these diffraction corrections. That by Subrahmanyam et al [28] shows the ideal theory to give the correct dependence on λ, and D (the axial distance) but to underestimate the actual errors by a factor of 3.2. These authors give the correction (the apparent relative excess velocity) as:

$$\frac{\Delta C}{C} = 3.2\lambda^{\frac{3}{2}}/4\pi^2 a D^{\frac{1}{2}}$$

It is not clear whether the diffractive nature of the reflector was included in their theoretical analysis. However some of the observed difference may well have come from the non-ideal behaviour of the transducer. Chivers et al [29] have shown that the effective radius of a transducer is usually less than its ideal value, that it is frequency dependent, and often exhibits marked variations in the vicinity of its natural frequency. This effect is unlikely to account for more than half of the discrepancy observed by Subrahmanyam et al.

Inserting the figures given earlier into the above expression, we find:

$$\frac{\Delta C}{C} = 0.00058 \quad at \quad D = 50mm$$
$$= 0.00041 \quad at \quad D = 100mm$$

Thus the diffraction correction is of the order of 0.005%. The theoretical value was 0.00018 at 50mm, ie 0.02%. In the worst case the difference between these (0.03%) may be attributed to non-ideality of the transducer.

5. CONCLUSION.

The analysis given above has not been extended to provide an optimal measurement situation. However it is clear that distance measurement should not be the limiting factor in the accuracy of ultrasonic interferometric determination of velocity. The major factor appears to come from the diffraction from the transducer. In the example cited, if no diffraction correction at all was applied, 0.05% would represent the most optimistic assessment. If an ideal correction was applied this might drop to 0.03%. If the effective radius of the transducer was determined, this might drop further but the use of the effective radius in this context still needs validation before a reliable numerical assessment of the errors could be made. It appears that the claim of 0.01% accuracy in the literature is rather optimistic at the present time.

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