ULTRA-SONIC VELOCITIES IN SOLUTIONS*

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1. Introductory

Falkenhagen and Bachem\(^1\) have determined the ultra-sonic velocities in aqueous solutions of a few electrolytes and non-electrolytes. Parthasarathy\(^2\) has carried out experiments for the determination of the ultra-sonic velocities in some binary liquid mixtures. Werner Schaafls\(^3\) has investigated the ultra-sonic velocities in liquid mixtures and solutions and has thereby deduced the sound velocity even in the solid from values obtained for its solutions. Such determinations lead us to a knowledge of the adiabatic compressibilities of the solutions and of the mixtures. In the present investigation, an attempt has been made to find the variation of the ultra-sonic velocity and hence of the compressibility with concentration in solutions of naphthalene in organic liquids—both polar and non-polar. The free volume of naphthalene has also been estimated. Comparison is made of the sound velocity in naphthalene with that obtained by extrapolation by Schaafls.\(^3\) The justification for this extrapolation however is discussed.

2. Experimental

A convenient method of measuring ultra-sonic velocities has already been described.\(^4\) Earlier experiments indicated the unsuitability of fibre and ebonite as insulating materials in the design of crystal holders as both of them were subject to serious breakdown in insulation after having been in contact with organic solutions for some time. In the final design of the crystal holder (Fig. 1) ivory has been employed with success. The quartz crystal 'Q' is held between two brass discs D\(_1\) and D\(_2\) supported from the two opposite faces of the thick ivory block B. The lower disc D\(_2\) has a

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circular hole cut out of it to enable the piezo-quartz to set up stationary vibrations in the liquid. Between the perforated disc and the piezo-quartz is placed a thin tin foil for establishing good electrical contact. The pressure on the crystal can be adjusted to any required magnitude by rotating the knurled head H which actuates a spiral spring situated in the hollow screw S. The crystal holder is introduced into an optically worked containing vessel so that only the bottom half of the crystal is immersed under the liquid. This reduces the di-electric loss as well as the conduction loss, if any, in the solution. The four faces of the glass vessel are completely covered by dark paper except for two small circular holes on opposite faces to allow the passage of light.

The optical arrangement is the same as in one of the methods previously described. Light from a mercury arc lamp is condensed on the crossed slits of a Hilger constant deviation spectrograph. After collimation, the parallel beam is diffracted by the ultra-sonic waves in the liquid and the spectrum of this diffracted pattern is photographed.

Q — Quartz Crystal
C — Split Stator Condenser 250 μF each section.
H.F.C. — High frequency choke. Frequency 4000 to 8000 KHz.

The quartz crystal is set in vibration by connecting it across the split-stator variable condenser of the tank circuit of an oscillator employing two RCA 830B tubes in push-pull. The diagram of connections of the oscillator used to excite the quartz crystal is shown in Fig. 2. To ensure that stationary waves of constant frequency are generated in the various solutions,
a precision wavemeter is employed and no detectable variation of frequency from solution to solution under constant experimental conditions is noticed.

If the ultra-sonic frequency of the vibrating quartz is maintained constant, and if \( v_0 \) is the velocity of sound in the pure liquid and \( v_c \) that in the solution of a concentration of \( c \) moles per litre, then

\[
\frac{v_c}{v_0} = \frac{d_0}{d_c},
\]

where the \( d' \)s are the displacements of the lines of the same order diffracted by the sound wave from the central undiffracted line of the same optical wavelength \( \lambda \). By measuring the ratio \( d_0/d_c \) for lines of different optical wavelengths like \( \lambda \lambda 5790, 5770, 5461, 4358 \) and \( 4047 \, \text{Å} \), an accurate value of \( v_c/v_0 \) can be estimated. After determining the densities of the solutions, the variations in their adiabatic compressibilities can be determined. If \( \beta \) is the coefficient of adiabatic compressibility of the pure liquid, and \( \rho \) its density, then it can be shown that for a solution,

\[
-\frac{\Delta \beta}{\beta} = 2 \frac{\Delta v}{v} + \frac{\Delta \rho}{\rho}
\]

where \( \Delta \beta, \Delta \rho \) and \( \Delta v \) are the changes in the compressibility, the density and the ultra-sonic velocity respectively in the solution from the corresponding quantities in the pure liquid.

3. Naphthalene Solutions

For a known concentration of a solution of naphthalene in a liquid, the mean value of \( v_c/v_0 \) is calculated for a number of optical wavelengths. The procedure is repeated for other concentrations and similarly for solutions in different solvents. Fig. 3 illustrates in a striking manner the variation of \( \cdot d' \) with concentration for the naphthalene-chloroform solution for \( \lambda \lambda 5770, 5461 \) and \( 4358 \, \text{Å} \). In Table I below, values of \( \frac{\Delta v}{v} \) and \( \frac{\Delta \rho}{\rho} \) obtained with solutions of various concentrations of naphthalene in toluene, benzene, chloroform and carbon tetrachloride are given. The computed values of \( \frac{\Delta \beta}{\beta} \) are also entered.
### Table I

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Concentration in moles per litre $n_s$</th>
<th>$\Delta \nu_% / \nu$</th>
<th>$\Delta \rho_% / \rho$</th>
<th>$-\Delta \beta_% / \beta$</th>
<th>Free volume of naphthalene $C_{10}H_8 ,(\nu_f)$ in c.c./c.c.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene $(C_6H_5CH_3)$</td>
<td>0.74</td>
<td>16</td>
<td>18</td>
<td>50</td>
<td>0.09</td>
</tr>
<tr>
<td></td>
<td>1.68</td>
<td>38</td>
<td>41</td>
<td>117</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.10</td>
<td>48</td>
<td>52</td>
<td>148</td>
<td></td>
</tr>
<tr>
<td>Benzene $(C_6H_6)$</td>
<td>1.0</td>
<td>28</td>
<td>22</td>
<td>78</td>
<td>0.09</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>55</td>
<td>44</td>
<td>154</td>
<td></td>
</tr>
<tr>
<td>Chloroform $(CHCl_3)$</td>
<td>1.0</td>
<td>51</td>
<td>-37</td>
<td>65</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>75</td>
<td>-53</td>
<td>97</td>
<td>0.13</td>
</tr>
<tr>
<td></td>
<td>2.5</td>
<td>127</td>
<td>-92</td>
<td>162</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.0</td>
<td>153</td>
<td>-111</td>
<td>195</td>
<td></td>
</tr>
<tr>
<td>Carbon tetrachloride $(CCl_4)$</td>
<td>0.75</td>
<td>45</td>
<td>-33</td>
<td>57</td>
<td>0.09</td>
</tr>
<tr>
<td></td>
<td>1.75</td>
<td>106</td>
<td>-77</td>
<td>135</td>
<td></td>
</tr>
</tbody>
</table>

### 4. Free Volume of Naphthalene

Kincaid and Eyring\(^5\) have estimated the free volumes of various liquids from different view-points. It is possible to have some idea of the free volume of a solid if data as regards the variation of compressibility with concentration of its solution in a liquid are available.

Let us associate each gram molecule of the liquid with a free volume $\nu_l$ and of the solid with $\nu_s$. If we further assume that the total volume of a litre of solution is equal to the sum of the volumes of the pure liquid and of the solute comprising it—an assumption justifiable on the basis of the observed linear relation between density and concentration—then the change in free volume of the solution per unit free volume of the pure liquid is

$$\frac{n_l \, \nu_l + n_s \, \nu_s - N \, \nu_l}{N \, \nu_l}.$$
where $n_l$ and $n_s$ are the number of gram molecules of the liquid and of the solute in a litre of the solution and $N$ the number of gram molecules of the pure liquid per litre.

If the free volume ($v_f$) in one c.c. of pure liquid is assumed to vary under external (P) and internal (K) pressures according to the relation

$$v_f (P + K) = \text{constant},$$

it can be shown that for small changes in external pressure, the compressibility of the liquid varies directly as its free volume. We can therefore write

$$\frac{\Delta \beta}{\beta} = \frac{n_l}{N} + \frac{n_s v_s}{N v_f} - 1$$

As

$$\frac{n_l M_l}{\rho_l} + \frac{n_s M_s}{\rho_s} = 1000,$$

where $M_l$ and $M_s$ are the molecular weights of the liquid and of the solute respectively, it can be shown that

$$-\frac{1}{n_s} \frac{\Delta \beta}{\beta} = \frac{1}{N} \left[ \frac{V_s}{V_f} - v_s \right] = \frac{V_s}{1000} - \frac{v_s}{v_f} \frac{V_f}{1000}$$

where $V_s$ and $V_f$ are the molar volumes of the solute and of the liquid respectively. Equation (3) shows that the slope of the $\left( -\frac{\Delta \beta}{\beta} \text{ vs. } n_s \right)$ line for any solution is approximately constant so long as the same solute is used and equal to $\frac{V_s}{1000}$ if the free volume of the solute is negligible compared with that of the liquid. The departure from the slope $\frac{V_s}{1000}$ is a measure of the ratio $v_s/v_f$. Fig. 4 shows four such curves for naphthalene. As $-\frac{1}{n_s} \frac{\Delta \beta}{\beta}$ can be experimentally determined, $v_s/v_f$ is given by

$$\frac{v_s}{v_f} = \frac{1}{V_f} \left[ V_s - 1000 \frac{\Delta \beta}{\beta} \right].$$

The last column in Table I gives the values of the free volume in c.c. per c.c. ($v_f$) of naphthalene as calculated from (4) and based on the free volume per c.c. of toluene, benzene, chloroform and carbon tetrachloride as estimated by Kincaid and Eyring. While the agreement is not very good, it is felt that it is satisfactory if we bear in mind the nature of the assumptions made in the derivation of equation (4) as well as in the estimation of free volumes of the liquid by Kincaid and Eyring.
5. Ultra-sonic Velocity in Naphthalene

Werner Schaaffs has claimed that the ultra-sonic velocity of a solid solute could be determined by assuming that the velocity varies linearly with the percentage by weight of the solute in solution. Dissolving naphthalene in five different liquids—of which only benzene and carbon tetrachloride have been commonly employed by Schaaffs and ourselves—, he has estimated the ultra-sonic velocity in naphthalene at 20° C. as 1570 metres per second, while the individual values differ from 1540 to 1622 m./sec.

Employing the results obtained with the four solutions here studied, the mean velocity in naphthalene at 25° C. is found to be 1554 m./sec. as indicated in Table II below (vide Fig. 5).
TABLE II

<table>
<thead>
<tr>
<th>Solute</th>
<th>Solvent</th>
<th>Extrapolated velocity in solute in m./sec.</th>
<th>Mean value m./sec.</th>
<th>Schaffs' value m./sec.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naphthalene (C_{10}H_{8})</td>
<td>C_6H_6</td>
<td>1550</td>
<td></td>
<td>1550</td>
</tr>
<tr>
<td></td>
<td>CHCl_3</td>
<td>1540</td>
<td></td>
<td>1554</td>
</tr>
<tr>
<td></td>
<td>CCl_4</td>
<td>1570</td>
<td>1554</td>
<td></td>
</tr>
<tr>
<td></td>
<td>C_6H_6CH_3</td>
<td>1555</td>
<td></td>
<td>1580</td>
</tr>
</tbody>
</table>

If the extrapolation method advocated by Schaffs is accepted, the agreement of our results with his values is remarkably good. In none of
the liquids, however, in which naphthalene has been dissolved, has it been possible to obtain a solution stronger than 3 molar concentration per litre of solution corresponding to 30% by weight of naphthalene. Therefore, a linear or nearly linear extrapolation between 30% and 100% from values obtained up to 30% only for deducing the velocity in naphthalene seems to have little justification, in spite of the concordance between the calculated values as obtained from solutions using different solvents. The agreement merely indicates that the value so obtained is a characteristic of the state of the solute in solution rather than of the solid solute in bulk; it is likely that the velocity refers to naphthalene at 20° C. in a hypothetical liquid state having only bulk modulus and no rigidity at that temperature, resembling a condensed gaseous state.

As a support for this computed value of velocity in naphthalene, Schaaffs has determined the velocity in molten naphthalene at 100° C. as 1276 m./secs. This result by itself cannot however lend support to the computed sound velocity of 1570 m./sec. at 20° C. in naphthalene; for the acoustic velocity has been observed by Zwicky and others, to vary abruptly from the solid to the liquid state. It has been shown, for instance, that the velocity, for longitudinal sound waves, in solid metals is about twice as great as the velocity in the liquid state. If therefore, the velocity of sound in naphthalene at 100° C. is 1276 m./sec., the velocity in the liquid near its melting point (80° C.) should be greater by at least 100 m./sec. Consequently, it is doubtful whether at 20° C., the velocity in naphthalene could be as low as 1570 m./sec.; it is felt that this velocity should exceed 2000 m./sec. This point can be settled only by a direct determination of the sound velocity in naphthalene at 20° C. If thereby, it is established that the extrapolated value gives the sound velocity in the solute at temperatures when it can only be in the solid state, this indirect and new method of finding the acoustic velocity in soluble substances can be utilised in cases where a direct method is practically not possible.

In conclusion we desire to thank Prof. A Venkat Rao Telang, for his kind encouragement.

REFERENCES

Fig. 3.—Ultrasonic diffraction patterns (a) in pure chloroform, (b) in chloroform solution containing 3 moles of naphthalene per litre.