ULTRASONIC VELOCITIES IN SOME ORGANIC LIQUIDS—PART II.

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1. Introduction.

In a paper appearing in the Proceedings of the Indian Academy of Sciences,
Vol. II, p. 497 (1935), the author gave determinations of ultrasonic velocities in 52 organic liquids. It was thought that it would be of interest to find out the velocities in some related groups of organic liquids. In the present paper, results of both ultrasonic velocities and adiabatic compressibilities are given for di-esters, for the xylenes and for two bases, quinoline and o-toluidine.

The complete experimental arrangement has been described in the earlier paper.*

In these experiments, the liquids which were distilled, were contained in a cubic glass cell of 100 c.c. capacity, bigger than the vessel used previously. They were all of the purest stock, from Kahlbaum or Merck or Dr. Schukardt or de Haen.

The frequency employed for the vibration was $7.37 \times 10^6$ cycles per second. The temperatures at which the determinations were made, are noted against each liquid.

2. Results.

The following table contains the results of determinations of ultrasonic velocities in 14 organic liquids. The last column gives the calculated adiabatic compressibilities from the known acoustic velocities.

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* In a private communication to the author, Professor J. C. Hubbard has explained the two points raised in the earlier paper on page 504.
**Table I. Ultrasonic velocities at $7.37 \times 10^6$ cycles/second.**

<table>
<thead>
<tr>
<th>Liquids</th>
<th>Chemical Formula</th>
<th>Temp. in °C</th>
<th>Wavelength of sound in mms.</th>
<th>Velocity of sound in meters per second</th>
<th>Adiabatic compressibility $\beta_0 \times 10^6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$-Xylene</td>
<td>C$_6$H$_4$(CH$_3$)$_2$</td>
<td>22°</td>
<td>0.1834</td>
<td>1352</td>
<td>62.4</td>
</tr>
<tr>
<td>m-Xylene</td>
<td>''</td>
<td>22°</td>
<td>0.1800</td>
<td>1328</td>
<td>65.9</td>
</tr>
<tr>
<td>p-Xylene</td>
<td>''</td>
<td>22°</td>
<td>0.1805</td>
<td>1330</td>
<td>65.9</td>
</tr>
<tr>
<td>Diethyl oxalic ester</td>
<td>COO·C$_2$H$_5$</td>
<td>22°</td>
<td>0.1888</td>
<td>1392</td>
<td>48.0</td>
</tr>
<tr>
<td></td>
<td>COO·C$_2$H$_5$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diethyl malonic ester</td>
<td>CH$_2$(\text{COO}\cdot\text{C}_2\text{H}_5)</td>
<td>22°</td>
<td>0.1879</td>
<td>1386</td>
<td>49.6</td>
</tr>
<tr>
<td>Diethyl succinic ester</td>
<td>CH$_2$(\text{COOC}_2\text{H}_5)</td>
<td>22°</td>
<td>0.1869</td>
<td>1378</td>
<td>50.7</td>
</tr>
<tr>
<td>Diethyl adipic ester</td>
<td>CH$_2$(\text{COOC}_2\text{H}_5)</td>
<td>22°</td>
<td>0.1866</td>
<td>1376</td>
<td>52.7</td>
</tr>
<tr>
<td>Diglycollic ester</td>
<td>CH$_2$(\text{COOC}_2\text{H}_5)</td>
<td>22°</td>
<td>0.1947</td>
<td>1435</td>
<td>43.9</td>
</tr>
<tr>
<td>Thiodiglycollic ester</td>
<td>S(\text{COOC}_2\text{H}_5)</td>
<td>22°(5)</td>
<td>0.1966</td>
<td>1449</td>
<td>41.7</td>
</tr>
<tr>
<td>Methyl adipate</td>
<td>CH$_3$(\text{CH}_2\text{COO}\cdot\text{CH}_3)</td>
<td>21°(8)</td>
<td>0.1994</td>
<td>1469</td>
<td>43.9</td>
</tr>
</tbody>
</table>
**Ultrasonic Velocities in some Organic Liquids—II**

**TABLE I—(contd.)**

<table>
<thead>
<tr>
<th>Liquids</th>
<th>Chemical Formula</th>
<th>Temp. in °C</th>
<th>Wavelength of sound in mms.</th>
<th>Velocity of sound in meters per second</th>
<th>Adiabatic compressibility $\beta \phi \times 10^4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone dicarboxylic ester</td>
<td>$\text{CO}_2\text{CH}_2\cdot\text{COO}\cdot\text{C}_2\text{H}_5$</td>
<td>$22^\circ.5$</td>
<td>0.1828</td>
<td>1348</td>
<td>50.7</td>
</tr>
<tr>
<td>Quinoline</td>
<td></td>
<td>$22^\circ$</td>
<td>0.2228</td>
<td>1643</td>
<td>34.0</td>
</tr>
<tr>
<td>o-Toluidine</td>
<td></td>
<td>$22^\circ.5$</td>
<td>0.2265</td>
<td>1669</td>
<td>36.1</td>
</tr>
<tr>
<td>Methyl hexaline</td>
<td>$\text{C}<em>6\text{H}</em>{10}(\text{CH}_3)(\text{OH})$</td>
<td>$22^\circ$</td>
<td>0.1936</td>
<td>1428</td>
<td>53.7</td>
</tr>
</tbody>
</table>

Of the liquids studied here, data of previous determinations are available only for four liquids. We give below, in Table II, values for comparison with those obtained earlier.

**TABLE II.**

*Velocities in meters/second.*

<table>
<thead>
<tr>
<th>Liquids</th>
<th>Audio range from I. C. T.</th>
<th>R. Bär. Freq. about $7.5 \times 10^6$ c./s.</th>
<th>Author Freq. $7.37 \times 10^6$ c./s.</th>
</tr>
</thead>
<tbody>
<tr>
<td>o-Xylene</td>
<td>—</td>
<td>1345 at 21° C.</td>
<td>1352 at 22° C.</td>
</tr>
<tr>
<td>m-Xylene</td>
<td>—</td>
<td>1330 at 21° C.</td>
<td>1328 ,, ,,</td>
</tr>
<tr>
<td>p-Xylene</td>
<td>—</td>
<td>1333</td>
<td>1330 ,, ,,</td>
</tr>
<tr>
<td>o-Toluidine</td>
<td>1645 at 21° C.</td>
<td>—</td>
<td>1669 ,, 22°.5 C.</td>
</tr>
<tr>
<td>m-Toluidine</td>
<td>1602.4 at 21°.6 C.</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>
R. Bär's results are taken from a paper by him appearing in *Helv. Phys. Acta* 1933, 6, 578; while for the audio range, the value for o-toluidine is taken from the *International Critical Tables*. The velocity for m-xylene has already been given in the earlier paper. The results are in good agreement.

3. Discussion.

Remarks of a general kind were made in the earlier paper, of the relation between sound velocities and chemical constitution. We shall, however, go more elaborately in this paper.

The xylenes: The sound velocity in the ortho-compound is higher than in the other two xylenes which have approximately the same velocities. Substitution in the ortho position favours greater sound velocity. Even for the toluidines, ortho has the higher velocity (see Table II).

The di-esters (ethyl): In the series, oxalic, malonic, succinic and adipic esters, the sound velocity decreases with increasing weights of the radical. The same effect was noticed in the earlier paper, on the ethyl esters of formic, acetic, propionic and butyric acids. In the latter group, ethyl formate has a velocity of 1263 m./s., those for the remaining compounds being 1187, 1185 and 1171 m./s. respectively. This is quite the reverse of what obtains in hydrocarbons and alcohols; the sound velocity increasing with the length of the chain.

Ethyl and methyl adipates: Introduction of a methyl radical instead of an ethyl radical in an ester, enhances the sound velocity. That this is true can be seen from the earlier results also, given below:

<table>
<thead>
<tr>
<th>Liquids</th>
<th>Velocity of sound in meters/second</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethyl adipate</td>
<td>1376</td>
</tr>
<tr>
<td>Methyl ,,</td>
<td>1469</td>
</tr>
<tr>
<td>Ethyl acetate</td>
<td>1187</td>
</tr>
<tr>
<td>Methyl ,,</td>
<td>1211</td>
</tr>
<tr>
<td>Ethyl propionate</td>
<td>1185</td>
</tr>
<tr>
<td>Methyl ,,</td>
<td>1215</td>
</tr>
</tbody>
</table>
In all the cases above given, even though the length of the chain increases, by the introduction of an ethyl in place of a methyl radical, there is a decided diminution in velocity. Variations in density alone cannot account for this anomaly.

*Thio- and di-glycollic esters:* In the thio-compound an atom of sulphur replaces an atom of oxygen in the diglycollic ester. The velocity is enhanced in the thioglycollic ester. But it was observed in the earlier paper that the introduction of a heavy atom usually lowered the sound velocity; cf. carbon tetrachloride and chloroform; methylene chloride and methylene bromide. When we find that the esters behave differently from alcohols or hydrocarbons in the matter of velocity of sound, and when we know that we are now dealing with these two esters, it is not difficult to understand why it should be so.

*o-toluidine and quinoline:* The ultrasonic velocity in o-toluidine is much higher than that for toluene, but nearer to that of aniline; to which it is related, being less by about 15 meters. Quinoline, another base, has a velocity higher than that for either pyridine or benzene. Bases usually show higher sound velocities than the corresponding hydrocarbons.

The author thanks Sir C. V. Raman, Kt., for his interest in the work.

*Summary.*

The paper contains determinations of ultrasonic velocities in 14 organic liquids, some of them being di-esters, by the method of diffraction of light by high frequency sound waves. Included are also adiabatic compressibilities for these compounds, calculated therefrom.