Chapter - 3

THEORETICAL ASPECTS
3.1 Introduction

Various acoustic parameters such as ultrasonic velocity \((u)\), adiabatic compressibility \((\beta_a)\), Wada constant \((W)\), specific acoustic impedance \((z)\), viscosity \((\eta)\), fluidity \((\phi)\), relaxation time \((\tau)\), intermolecular free length \((L_f)\), classical absorption coefficient \((\alpha/\rho^2)\), relaxation strength \((r)\) and relative association \((R_A)\) are evaluated for polymer mixtures at different frequencies and temperatures. Various theoretical relations regarding ultrasonic velocity and molecular interaction properties have been established. The propagation velocity of ultrasonic waves have been used as a support in studying properties of liquid and polymer solutions based on molecular interaction theory.

3.2 Acoustic Parameters

i) The ultrasonic velocity of a liquid is defined as, partial derivative of pressure \(P\) with respect to density \(\rho\) under adiabatic conditions.

The ultrasonic velocity \((u)\) is given by,

\[
\begin{align*}
u^2 &= \left(\frac{\delta P}{\delta \rho}\right)_a
\end{align*}
\]
Also \[
\frac{1}{u^2} = \frac{1}{\rho} \frac{1}{\rho} \left( \frac{d\rho}{\delta P} \right) a
\]

\[
\frac{1}{u^2} = \rho \cdot \beta_u
\]

\[
\beta_u = \frac{1}{u^2 \rho}
\]

Similarly, the ultrasonic velocity of liquid\(^{1,3,11,14}\) is given by

\[
u = f \cdot \lambda
\]

where, \(\beta_u\) = adiabatic compressibility

\(f\) = frequency of ultrasonic waves.

\(\lambda\) = wavelength of ultrasonic waves.

Unit: cm/sec.

Values of 'u' show an increase with increase in temperature. Such a trend seems apparently associated with the peculiar liquid structure of water. Generally, the propagation velocity of ultrasound in normal liquids falls off with increase in temperature. \(u\) varies in the system with solute concentration. The factor apparently responsible for such a behaviour may be the presence of weak interactions.

Ultrasonic velocity is related to intermolecular free length. As the free length decreases due to the increase in concentration, the ultrasonic velocity has to increase and vice-versa.
ii) **Adiabatic Compressibility** \((\beta_a)\) is defined as the partial derivative of volume \(v\) with respect to pressure \(P\) under adiabatic conditions.

\[
\beta_a = - \left( \frac{\delta v}{\delta \rho} \right)_a
\]

The adiabatic compressibility\(^1,3,4,6,11-14\) can be estimated from the measurements of ultrasonic speed \(u\) and density \([\rho = 1/v]\) from the relation,

\[
\beta_a = \frac{1}{\rho \ u^2}
\]

where, \(\rho\) – density of liquid
\(u\) – velocity

Unit : \(\text{cm}^2/\text{dyne}\)

The increase in \(\beta_a\) may be due to departure of solvent interactions. When solvent molecules come between the solute molecules the latter become more mobile and separate. In such a case, adiabatic compressibility should decrease on dilution in the absence of any specific interaction such as compound formation. The decrease of \(\beta_a\) leads to the conclusion that specific interactions are absent in the mixtures.

The bulkier complex containing molecules will naturally exhibit greater \(\eta, z\) than individual molecules giving rise to maximum in \(\eta\) and \(z\). Similarly, the adiabatic compressibility decreases with bulkier molecules resulting in a minimum in \(\beta_a\).
iii) **Intmolecular Free Length (L_F):**

Jacobson pointed out that as temperature is increased, liquid expands as a whole and the available volume (V_a) in between molecules increases while the actual volume occupied by the molecules remains unchanged. On investigating a very large number of liquids at various temperatures, Jacobson has given an expression for free length\(^{1,3,9,11,13}\) as,

\[
L_F = \frac{k}{\rho^{\frac{1}{2}} u}
\]

\[
\therefore L_F = k \beta_a^{\frac{1}{2}}
\]

Since \(\beta_a = \frac{1}{\rho u^2}\)

where 'k' is temperature dependent constant and \(u\) and \(\rho\) are ultrasonic velocity and density of the liquid respectively. \(\beta_a\) – adiabatic compressibility of liquid. Unit of \(L_F\) is \(A^o\)

Intmolecular free length increase hence, the decrease in velocity. This indicates that there is a weaker and weaker interaction between the ion and solvent molecules, suggesting a structure promoting behaviour of added metals. Intmolecular free length is a predominant factor in determining the variation of ultrasonic velocity in liquids and their solutions.

The intermolecular free length decreases with increase in concentration of the solute. This is suggestive of solute – solvent interactions in the mixture.

Increase in concentration leads to decrease in gap between two species and which is referred by intermolecular free length \((L_F)\), i.e. with the
increase in concentration, intermolecular free length \( (L_f) \) has to decrease. It may be stated that density and intermolecular free length are inversely related.

iv) **Specific Acoustic Impedance \( (z) \):** The Specific acoustic impedance\(^{1,6-12}\) is the product of ultrasonic velocity \( (u) \) and density of liquid \( (\rho) \).

\[
\therefore \quad z = u \rho
\]

Unit: dyne-s / cm\(^3\)

The acoustic impedance gives the characteristics of the medium that is nearly similar to electrical impedance. If there is no variation in the impedance within the material then there is no reflection.

Specific acoustic impedance is found to be almost reciprocal of \( \beta_a \). The increase in \( z \) with the concentration is due to interaction between solute and solvent molecules, which increases the intermolecular distance, making relatively wider gap between the molecules.

v) **Wada Constant \( (W) \):** Wada suggested a constant called Wada constant \( (W) \), which gives the relation between density and adiabatic compressibility of liquid.

\[
W = \rho \cdot (\beta_a)^{1/7}
\]

where, \( \rho \) – density of liquid

\( \beta_a \) – adiabatic compressibility of liquid

Unit: gm. dyne\(^{-1}\).cm\(^{-1}\)
vi)  **Viscosity (η)** :-

The absolute viscosity of liquid\(^{3,5,7-10,14}\) is given by,

\[ \eta = \frac{\eta_1 \cdot \rho \cdot t}{\rho_1 \cdot t_1} \]

where,

- \(\eta_1\) – Viscosity of water, which is taken as 0.01 poise.
- \(\rho_1\) – Density of H\(_2\)O which is taken as 1 gm/c.c.
- \(t_1\) – Time of flow of H\(_2\)O between two marks on Ostwald’s viscometer tube.
- \(\eta\) – Viscosity of polymer mixture
- \(\rho\) – Density of polymer mixture
- \(t\) – Time of flow of polymer mixture between two marks on Ostwald’s viscometer tube.

Unit : poise.

vii) **Fluidity (ϕ)** :- The reciprocal of coefficient of viscosity of liquid is called fluidity.

\[ \therefore \quad \phi = \frac{1}{\eta} \]

where,

- \(\eta\) – Viscosity of liquid

Unit of \(\phi\) : poise\(^{-1}\)

viii) **Relaxation time (τ)** :- According to Frenkel, in liquid individual atoms and molecules are bound to equilibrium positions so that motion through it is highly restricted and equilibrium position of the molecules is not fixed. As the
time passes, the individual molecule may accumulate sufficient energy to pass to a neighbouring equilibrium position overcoming a potential barrier in the process. Thus a relaxation time can be defined as,

\[ \tau = A \exp(\Delta W / RT) \]

where, \( \Delta W \) – Activation energy.

In the absence of external force, these barrier jumps are random and no flow results. However, if an external applied force (such as in a sound wave) lost for a long time compared with \( \tau \), many molecules get enough energy to cross the barrier and flow results.

The following relation for relaxation time\(^4,6\)

\[ \tau = \frac{4 \pi^2 \eta}{3 \rho u^2} \]

Or

\[ \tau = \frac{4 \pi^2 \eta \beta_a}{3} \quad \text{Since} \quad \beta_a = \frac{1}{\rho u^2} \]

where, \( \eta \) – coefficient of viscosity of liquid
\( \beta_a \) – adiabatic compressibility of liquid
\( \rho \) – density of liquid
\( u \) – velocity

Unit : Sec.

ix) Classical Absorption Coefficient \((\alpha/l^2)\) :- Shah et al calculated classical absorption coefficient for poly 4,4-cyclohexylidene diphenylene in chlorinated
solvent and explained results on the basis of solute-solvent interaction. To find out classical absorption coefficient\textsuperscript{6-10}, the relation is

\[
\frac{\alpha}{f^2} = \frac{8 \pi^2 \eta}{3 \rho u^3}
\]

Or

\[
\frac{\alpha}{f^2} = \frac{8 \pi^2 \eta \beta_a}{3}
\]

Or

\[
\frac{\alpha}{f^2} = 2 \tau \quad \text{since} \quad \tau = \frac{4 \pi^2 \eta \beta_a}{3}
\]

where, \( \eta \) – coefficient of viscosity of liquid
\( \beta_a \) – adiabatic compressibility of liquid
\( \tau \) – relaxation time
Unit : \( \text{sec}^2 \cdot \text{cm}^{-1} \)

\textit{x) Relative Association (}\( R_A \textit{)}

The relative association\textsuperscript{11,12} is influenced either by breaking up of the solvent molecules on addition of electrolyte or by the solvation of ions that are simultaneously present. \( R_A \) increases with increase in concentration due to increase in \( L_F \) and increase in electrostatic attraction.

\[
R_A = \frac{\rho}{\rho_0} \left( \frac{u_0}{u} \right)^{1/3}
\]
Where, \( \rho \) – Density of polymer solution
\( u \) – Velocity of polymer solution
\( \rho_o \) – Density of solvent THF (\( \rho_o = 0.89 \text{ gm/c.c.} \))
\( u_o \) – Velocity of THF (\( u_o = 127000 \text{ cm/sec} \))

Unit : Dimensionless.

xi) Relaxation Strength (r)

The results of polymer are interpreted in terms of molecular interactions with the help of a acoustic parameter called relaxation strength\(^{15-17}\). Increase in relaxation strength suggests predominance of solute-solute interactions whereas decrease in relaxation strength values are also due to solute-solute interactions.

The relaxation strength\(^7-10\) is given by

\[
r = 1 - \left( \frac{u}{u_\alpha} \right)^2
\]

where, \( u_\alpha = 1.6 \times 10^5 \text{ cm/sec.} \)
\( u \) – Velocity of polymer solution.

Unit : Dimensionless.
### 3.3 Experimental and Literature Values of Ultrasonic Velocity for Different Liquids

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Liquid</th>
<th>Experimental Value m/s</th>
<th>Literature Value m/s</th>
<th>% Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Acetone</td>
<td>1169.7</td>
<td>1170.0</td>
<td>0.05</td>
</tr>
<tr>
<td>2.</td>
<td>Benzene</td>
<td>1295.6</td>
<td>1295.0</td>
<td>0.04</td>
</tr>
<tr>
<td>3.</td>
<td>Carbon tetrachloride</td>
<td>930.5</td>
<td>930.0</td>
<td>0.05</td>
</tr>
</tbody>
</table>

### 3.4 Ultrasonic Velocity of THF

Frequency : 3 MHz

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Temp. °C</th>
<th>Temp. K</th>
<th>Ultrasonic velocity Experimental cm/s</th>
<th>Ultrasonic velocity Literature cm/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>30</td>
<td>303</td>
<td>125500</td>
<td></td>
</tr>
<tr>
<td>2.</td>
<td>35</td>
<td>308</td>
<td>124500</td>
<td></td>
</tr>
<tr>
<td>3.</td>
<td>40</td>
<td>313</td>
<td>121800</td>
<td>126300</td>
</tr>
<tr>
<td>4.</td>
<td>45</td>
<td>318</td>
<td>120600</td>
<td></td>
</tr>
</tbody>
</table>
### 3.5 Experimental and Literature Values for THF

Frequency : 2 MHz

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Parameter</th>
<th>Temp. K</th>
<th>Experimental Value</th>
<th>Literature Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Density (ρ)</td>
<td>303</td>
<td>0.9144 gm/cc</td>
<td>0.8815 gm/cc</td>
</tr>
<tr>
<td>2.</td>
<td>Viscosity (η)</td>
<td>303</td>
<td>0.8117 x 10⁻² poise</td>
<td>0.4335 x 10⁻² poise</td>
</tr>
<tr>
<td>3.</td>
<td>Ultrasonic Velocity (u')</td>
<td>303</td>
<td>134000 cm/s (at 2 MHz)</td>
<td>126420 cm/s (at 3 MHz)</td>
</tr>
<tr>
<td>4.</td>
<td>Adiabatic Compressibility (β_a)</td>
<td>303</td>
<td>0.60905 x 10⁻¹₂ cm²/dyne (at 2 MHz)</td>
<td>0.4063 x 10⁻¹² sec (at 3 MHz)</td>
</tr>
<tr>
<td>5.</td>
<td>Relaxation Time (τ)</td>
<td>303</td>
<td>0.65916 x 10⁻¹² sec (at 2 MHz)</td>
<td>0.6343 x 0⁻¹⁶ sec²/cm (at 3 MHz)</td>
</tr>
<tr>
<td>6.</td>
<td>Classical Absorption Coefficient (α/π²)</td>
<td>303</td>
<td>0.9712 x 10⁻¹⁶ sec³/cm (at 2 MHz)</td>
<td>0.9712 x 10⁻¹⁶ sec³/cm (at 2 MHz)</td>
</tr>
<tr>
<td>7.</td>
<td>Wada Constant (W)</td>
<td>303</td>
<td>0.0317 gm dyne⁻¹ cm⁻¹ (at 2 MHz)</td>
<td>0.0317 gm dyne⁻¹ cm⁻¹ (at 2 MHz)</td>
</tr>
<tr>
<td>8.</td>
<td>Intermolecular Free Length (L_F)</td>
<td>303</td>
<td>0.4924 A° (at 2 MHz)</td>
<td>0.4924 A° (at 2 MHz)</td>
</tr>
<tr>
<td>9.</td>
<td>Fluidity (φ)</td>
<td>303</td>
<td>123.198 poise⁻¹ (at 2 MHz)</td>
<td>123.198 poise⁻¹ (at 2 MHz)</td>
</tr>
<tr>
<td>10.</td>
<td>Relaxation Strength (r)</td>
<td>303</td>
<td>0.2985 (at 2 MHz)</td>
<td>0.2985 (at 2 MHz)</td>
</tr>
<tr>
<td>11.</td>
<td>Specific Acoustic Impedance (z)</td>
<td>303</td>
<td>122529.6 gm cm⁻¹ sec⁻¹ (at 2 MHz)</td>
<td>122529.6 gm cm⁻¹ sec⁻¹ (at 2 MHz)</td>
</tr>
</tbody>
</table>

The results agree fairly well with the reported values.
3.6 References


