HSP for biomedical polymers - application of inverse gas chromatography

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Solubility parameter

Biomedical field

- pharmacy
- dentine bonding systems
- polymer miscibility/solubility
- biological materials
- technique of mixture separation on the individual components
- chromatographed substance is divided between the mobile phase (gas/liquid) and stationary phase (solid, liquid)
- components of the mixture interact with the stationary phase with a different strength and with different speed migrate along the column - separation of the mixture
• a stationary phase (investigated material) is immobilized within a column,
• probes (test solutes) of known physicochemical properties are injected and passed through the column with mobile phase,
• the retention time of probes reflects interactions between the test solute and stationary phase (investigated material)
• retention parameters are used for calculation of different thermodynamic parameters - materials characteristics

IGC- applications

- Surface energy
- Acid/base functionality of surfaces
- Adsorption isotherms
- Solubility parameter
- Glass transition and crystallinity of polymer stationary phases
Solubility parameter/IGC

- The Flory-Huggins interaction parameter

\[
\chi_{1,2} = \chi_H + \chi_s
\]

\[
\chi_{1,2} = \left(\frac{V_1}{RT}\right)\left(\delta_1 - \delta_2\right)^2 + \chi_s
\]

\[
\chi = \ln\left(\frac{273.15 R}{p^0_1 V_g M_1}\right) - \frac{p^0_1}{RT}\left(B_{11} - V_1\right) + \ln\left(\frac{\rho_1}{\rho_2}\right) - \left(1 - \frac{V_1}{V_2}\right)
\]
Solubility parameter/IGC

- Smidsrod and Guillet

\[
\frac{\delta_1^2}{RT} - \frac{\chi_{(1,2)i}^\infty}{V_i^0} = \left( \frac{2\delta_2}{RT} \right) \delta_1 - \left( \frac{\delta_2^2}{RT} + \frac{\chi_{si}^\infty}{V_i^0} \right)
\]

Solubility parameter can be calculated from:

- the slope \[\frac{2\delta_2}{RT}\]
- the intercept \[\left( \frac{\delta_2^2}{RT} + \frac{\chi_{si}^\infty}{V_i^0} \right)\]
\[ \delta_T^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \]

\[ \delta_d = \frac{m_{n-alkanes} \times RT}{2} \]
\[ \delta_p = \frac{(m_1 - m_{n-alkanes}) \times RT}{2} \]
\[ \delta_h = \frac{(m_2 - m_{n-alkanes}) \times RT}{2} \]

\( m_1 \) - value of the slope for aromatic hydrocarbons, ketones, 1-nitropropane

\( m_2 \) - value of the slope for alcohols and pyridine
# Test solute selection

<table>
<thead>
<tr>
<th>Test solute</th>
<th>$\delta_p$ [MPa]^{1/2}</th>
<th>$\delta_h$ [MPa]^{1/2}</th>
<th>ratio $\delta_p / \delta_h$</th>
<th>ratio $\delta_h / \delta_p$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Data 1*</td>
<td>Data 2*</td>
<td>Data 1*</td>
<td>Data 2*</td>
</tr>
<tr>
<td>acetonitrile</td>
<td>11.1</td>
<td>18</td>
<td>19.6</td>
<td>6.1</td>
</tr>
<tr>
<td>toluene</td>
<td>8.0</td>
<td>1.4</td>
<td>1.6</td>
<td>2.0</td>
</tr>
<tr>
<td>1,2-dichloroethane</td>
<td>11.2</td>
<td>8.2</td>
<td>9.1</td>
<td>0.4</td>
</tr>
<tr>
<td>butan-2-one</td>
<td>9.5</td>
<td>9.0</td>
<td>9.5</td>
<td>5.1</td>
</tr>
<tr>
<td>ethanol</td>
<td>11.2</td>
<td>8.8</td>
<td>20</td>
<td>19.4</td>
</tr>
<tr>
<td>propan-1-ol</td>
<td>10.5</td>
<td>6.8</td>
<td>17.7</td>
<td>17.4</td>
</tr>
<tr>
<td>butan-1-ol</td>
<td>10.0</td>
<td>5.7</td>
<td>15.4</td>
<td>15.8</td>
</tr>
<tr>
<td>1,4-dioxane</td>
<td>10.1</td>
<td>1.8</td>
<td>7.0</td>
<td>7.4</td>
</tr>
<tr>
<td>chloroform</td>
<td>13.7</td>
<td>3.1</td>
<td>6.3</td>
<td>5.7</td>
</tr>
</tbody>
</table>

Hansen/ Flory-Huggins interaction parameter

- Lindvig et al. proposed to use the modified Hansen relationship correlating experimentally determined values of the Flory-Huggins interaction parameter and the differences between HSP values of the examined material and respective test solutes:

\[
\chi = \alpha \frac{V_1}{RT} \left( (\delta_{1,d} - \delta_{2,d})^2 + 0.25(\delta_{1,p} - \delta_{2,p})^2 + 0.25(\delta_{1,hb} - \delta_{2,hb})^2 \right)
\]
Lindvig/ABV procedure

- Experimental \( \chi^{\infty}_{1,2} \) data for series test solutes were taken to calculate HSP parameters of the examined material by finding of minimum of the function:

\[
G^2 = \frac{4 \chi^{\infty}_{12}RT}{\alpha V_1} \left( (\varepsilon_{1,d} - \varepsilon_{2,d})^2 + (\delta_{1,p} - \delta_{2,p})^2 + (\delta_{1,p} - \delta_{2,p})^2 \right)
\]

where: \( \varepsilon_{1,d} = 2\delta_{1,d} \)

Optimization was carried out in two ways:

- **OPT_A** taking into account the difference \(- \left( G^2_{\text{exp}} - G^2_{\text{act}} \right)^2 \)

- **OPT_B** taking into account the difference \(- \left( \frac{G^2_{\text{exp}} - G^2_{\text{act}}}{\min(G^2_{\text{act}})} \right) \)
Experimental

- Biopolymers

- poly(ε-caprolactone) (PCL)  
  Mw = 70 000-90 000

- poly(ethylene glycol) (PEG)  
  Mw = 10 000

- polylactide (PLA)
Experimental

<table>
<thead>
<tr>
<th>Test solutes</th>
</tr>
</thead>
<tbody>
<tr>
<td>dispersive - (n-alkanes)</td>
</tr>
<tr>
<td>polar - acetonitrile, toluene, 2-butanone, 2-pentanone, 1,2-dichloroethane, 1-nitropropane</td>
</tr>
<tr>
<td>hydrogen bonding – ethanol, 1-propanol, 1-butanol, 1,4-dioxane, pyridine</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Solid support</th>
<th>Chromosorb P AW / DMDCS 100/120 mesh</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass column</td>
<td>30 cm length, 2 mm i.d.</td>
</tr>
<tr>
<td>Loading of the column</td>
<td>20% of liquid stationary phase</td>
</tr>
<tr>
<td>Carrier gas</td>
<td>Helium, flow 10 ml/min</td>
</tr>
<tr>
<td>Temperature of measurements</td>
<td>75°C</td>
</tr>
<tr>
<td>Temperature of detector</td>
<td>180°C</td>
</tr>
</tbody>
</table>

**Equipment** - SEA (Surface Energy Analyzer, Surface Measurement System Ltd., UK) equipped with a flame ionization detector, FID.
Results

Results

The solubility parameter of blood components*

<table>
<thead>
<tr>
<th>Blood component</th>
<th>Solubility parameter (MPa)$^{1/2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cholesterol and esters</td>
<td>17.2-17.6</td>
</tr>
<tr>
<td>Triglycerides</td>
<td>16.4-17.0</td>
</tr>
<tr>
<td>Lipid-soluble vitamins</td>
<td>17.6-22.3</td>
</tr>
<tr>
<td>Phospholipids</td>
<td>&gt;32</td>
</tr>
</tbody>
</table>

Conclusions

- Inverse gas chromatography is useful in HSP determination for biopolymers.
- The Hansen solubility parameters data vary depending on the procedure of calculation – important test solutes selection.
- The value of the total solubility parameter for all biopolymers is higher than value obtained from the Guillet procedure.
- The values of dispersive component for all the materials are very close, but slight differences are observed for the polar and the hydrogen bonding components.
- PEG addition to the PCL-PLA mixture influenced the hydrogen bonding ability of PCL/PLA/PEG blend (what is evidenced by using HSP) and the increase of the hydrophilicity of such system.
Thank you for your attention