Self-assembly mechanism of 1,3:2,4-dibenzylidene-D-sorbitol in ethanol fuel

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Abstract
The self-assembly or the gelation behavior of low molecular weight gelator 1,3:2,4-dibenzylidene-D-sorbitol (DBS) in the ethanol fuel is investigated for the application of gel propellant rockets. The gelation behavior of DBS in the ethanol fuel is predicted using three component Hansen solubility parameters (HSPs). From the HSP calculations, the gelation of ethanol is predominant when $\delta$ was in the range $26.10 \leq \delta \leq 26.42 \text{ MPa}^{0.5}$. The gelation time ($t_{gel}$) is found to decrease with increase in the concentration of DMSO ($C_{DMSO}$) up to $C_{DMSO} < 9 \text{ wt.\%}$. However, further increase in $C_{DMSO}$ increased $t_{gel}$ due to the hindering effect of DMSO on self-assembly of DBS. From the molecular interaction studies, the self-assembly of DBS in the ethanol fuel is due to the interplay between intra- and intermolecular hydrogen bonding between DBS and ethanol mixture and a shift of 30 cm$^{-1}$ in the –OH peak towards intramolecular band is observed with increase in the $C_{DMSO}$. Finally, from the microstructure analysis, the presence of nano-fibrillar 3D network is confirmed using scanning electron microscopy.

Keywords: Ethanol gel, dibenzylidene-D-sorbitol, hydrogen bonding, nanofbrils, gel propellant

1. Introduction
Gels are colloidal materials which demonstrate continuous flow behavior of liquids when subjected to shear and solid-like behavior upon storage or rest. In recent years, there has been a surge of academic interest in transforming liquid fuels such as kerosene, ethanol, JP-8 and so on, to gel materials as a potential candidate for the gel propulsion systems. Many gel fuels are based on polymers, which are either chemically or physically cross-linked to generate three-dimensional solid-like network or inorganic gellants such as fumed silica where the backbone of cross-linking is hydrogen bonding [1-3]. However, in recent years, low-molecular-weight gelator (LMWG) molecules that transform into the 3D fibrous network via self-assembly, and the fibers tangle each other to form a nanofibrillar network in the entire volume of the solvent, which is of particular interest [4-7]. Unlike polymeric gellants, the network formed by LMWG is commonly thermoreversible, giving rise to tunable and responsive nanostructured gel material on a wide applications. Interestingly, one such LMWG reported in the literature is 1,3:2,4-dibenzylidene-D-sorbitol (DBS). DBS is a butterfly-shaped molecule with a hydroxylated center and benzyl groups on either side and is capable of gelling many organic solvents such as alcohols, polymers, and hydrocarbons at low concentration [8]. The non-covalent self-assembly of DBS molecules results in the formation of the nanofibrous 3D network, which entraps the liquid solvent within the network to form the gels.
In the present study, we report the self-assembly mechanism (gel formation) of LMW organogelator 1,3:2,4-dibenzylidene-D-sorbitol (DBS) in eco-friendly ethanol fuel for rocket application. The framework of DBS gelation in ethanol is predicted using Hansen solubility parameter. The molecular interaction studies using Fourier transform infrared (FTIR) spectroscopy is used to determine the effect of concentration of DBS in the formation of hydrogen bond between DBS and ethanol. Finally, the three-dimensional microstructure formed by the self-assembling of DBS in ethanol is investigated using a scanning electron microscope.

2. Experimental Section

2.1. Materials

Base fuel ethanol (CAS No. 64-17-5), organic solvent dimethyl sulfoxide (DMSO; CAS No. 67-68-5) were obtained from Sigma-Aldrich Co., 1,3:2,4-dibenzylidene-D-sorbitol (DBS; CAS No. 32647-67-9) was supplied as a white crystalline powder by Milliken chemicals. All the aforementioned materials were used without further modification.

2.2. Sample preparations

The preparation of ethanol gel involves two steps: First, a predefined amount of DBS as a gelling agent was dissolved in DMSO solvent to make a gellant stock solution. Secondly, the required amount of gellant stock solution was added to the defined quantity of ethanol. The solution was thoroughly mixed using magnetic stirrer for ~1 minute at 1000 rpm and stored at room temperature to complete the self-assembly or gelation process. The gelation time ($t_{gel}$) was defined as the relative time when the mixture was taken off from the impeller ($t = 0$) and formation of complete gel by passing the vial inversion test, i.e., a sample was termed as a gel if it held its own weight in the inverted vial. Table 1 details the composition of test samples employed in the study.

2.3. Fuel characterization

The molecular interactions of DBS with ethanol was studied using Fourier Transform Infrared (FTIR) spectroscopy using ThermoFisher Nicolet iS50 spectrometer. Attenuated Total Reflection (ATR)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Concentration (wt.%)</th>
<th>$t_{gel}$ (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ethanol</td>
<td>DMSO</td>
</tr>
<tr>
<td>Et10</td>
<td>94</td>
<td>05.0</td>
</tr>
<tr>
<td>Et20</td>
<td>89</td>
<td>09.0</td>
</tr>
<tr>
<td>Et25</td>
<td>86</td>
<td>11.5</td>
</tr>
<tr>
<td>Et30</td>
<td>83</td>
<td>14.0</td>
</tr>
<tr>
<td>Et40</td>
<td>77</td>
<td>19.0</td>
</tr>
</tbody>
</table>
sampling technique was used to determine the absorbance spectra in the range of 4000-400 cm⁻¹ at room temperature for all the samples. The morphology or the microstructure of the gel samples was observed using a field emission scanning electron microscope (FESEM; Hitachi SU8320). The sample was spread into a thin film of 1 mm thickness on a glass substrate and dried in a vacuum for a week at 25 °C. Finally, the samples were attached to an SEM holder and then coated with Osmium for 15 seconds to increase the conduction and to reduce the sample charging.

3. Results and discussion

3.1. Calculation of Hansen solubility parameters (HSP)

In the present study, the self-assembly-induced gelation behavior of low molecular weight gelator, DBS was demonstrated in the ethanol fuel. DBS is a butterfly-shaped molecule with the hydroxylated center and two aromatic rings on either side [8]. It self-assembles into strong gels in various organic and inorganic solvents at lower concentrations (<5 wt.%) [9]. The self-assembly of DBS into nanofibril three-dimensional network has been shown to occur via a combination of intra- and intermolecular hydrogen bonding and π-stacking. The ability of DBS to form a gel or a solution in a given solvent can be predicted by comparing the HSPs of DBS and the solvent. The HSPs quantitatively determined the cohesive energy density δ of a species through three weak interactions: van der Waals or dispersive interactions (δ_D), dipole-dipole or polar interactions (δ_P), and hydrogen-bonding interactions (δ_H) excluding induced dipoles, metallic bonds, and electrostatic interactions. The HSPs of DBS were empirically determined to be (δ_D, δ_P, δ_H) = (15.9, 3.9, 18.3) (in MPa⁰.⁵). The solvents that falls close to this point in 3D Hansen space were found to be a good solvent for DBS, i.e., it is incapable of gelling these solvent. Conversely, DBS is insoluble in the solvent whose HSPs falls far away from the origin in 3D Hansen space, and the gelation spectra lies between the soluble and insoluble region in Hansen space. It was found that ethanol forms gels with DBS as the HSPs of ethanol (15.8, 8.8, 19.4) lies in the gel spectra in Hansen space [9]. The Hansen solubility parameters for the ethanol-DBS system were estimated by the linear interpolation based on HSPs of pure ethanol, DMSO and their volume fraction (∅). The components in the HSP was calculated using,

\[ \delta = \sqrt{\delta_D^2 + \delta_P^2 + \delta_H^2} \]  

For the solvent mixtures (ethanol and DMSO), the solubility parameter (δ_i^mix) was calculated using Eq. 2:

\[ \delta_i^\text{mix} = \delta_i^E \phi_E + \delta_i^\text{DMSO} \phi_{\text{DMSO}} \]  

where δ_i^mix corresponds to the cohesive energy of ethanol-DMSO mixture and i represents individual components in Hansen solubility parameter.
Table 2. Hansen solubility parameters of the ethanol gel samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\delta_D$ (MPa$^{0.5}$)</th>
<th>$\delta_P$ (MPa$^{0.5}$)</th>
<th>$\delta_H$ (MPa$^{0.5}$)</th>
<th>$\delta$ (MPa$^{0.5}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Et10</td>
<td>15.90</td>
<td>9.07</td>
<td>19.06</td>
<td>26.42</td>
</tr>
<tr>
<td>Et20</td>
<td>15.97</td>
<td>9.31</td>
<td>18.77</td>
<td>26.35</td>
</tr>
<tr>
<td>Et25</td>
<td>16.02</td>
<td>9.47</td>
<td>18.60</td>
<td>26.30</td>
</tr>
<tr>
<td>Et30</td>
<td>16.08</td>
<td>9.63</td>
<td>18.38</td>
<td>26.26</td>
</tr>
<tr>
<td>Et40</td>
<td>16.31</td>
<td>10.30</td>
<td>17.58</td>
<td>26.10</td>
</tr>
</tbody>
</table>

Table 2 summaries the HSPs of the ethanol gel system. The polar interaction parameter ($\delta_P$) and hydrogen-bonding parameter ($\delta_H$) for ethanol gel are in the range of $9.07 \leq \delta_P \leq 10.3 \text{ MPa}^{0.5}$ and $17.58 \leq \delta_H \leq 19.06 \text{ MPa}^{0.5}$ respectively. The dispersive interaction ($\delta_D$) parameter lies in the range of $15.9 \leq \delta_D \leq 16.31 \text{ MPa}^{0.5}$ while, $\delta$ lies in the narrow range of $26.10 \leq \delta \leq 26.42 \text{ MPa}^{0.5}$. It is observed from the Fig. 1 that the gelation time is largely affected by the concentration of DMSO ($C_{DMSO}$) in the ethanol-DMSO mixture. For instance, $t_{gel}$ was decreased 36 times when $C_{DMSO}$ increased by about 44%. However, further increase in $C_{DMSO}$, i.e., $C_{DMSO} > 10$ wt.% increased $t_{gel}$ indicating that increase in $C_{DMSO}$ in the ethanol-DMSO mixture inhibits the self-assembling of DBS which supports the previous findings by Diehn et.al. [9]. So, an optimum concentration of DBS in DMSO is required for the self-assembly of DBS in ethanol fuel.

3.2. Molecular interaction study

FTIR spectra were used to investigate the molecular interaction and the hydrogen bonding ability of DBS with the solvent mixtures. Fig. 2 shows the FTIR spectra of neat DBS sample. The absorption peak was observed at wavelength ranges from 400 to 4000 cm$^{-1}$. The DBS intermolecular hydrogen bond (OH band) appear in the range of 3200-3550 cm$^{-1}$, and an intramolecular hydrogen bond appear in the range of 3400-3590 cm$^{-1}$ [10]. As seen from the Fig. 2, a clear peak at 3210 cm$^{-1}$ for -OH group were found for DBS.

![Fig. 1. Correlation of gelation time ($t_{gel}$) with Hansen parameters for ethanol gels.](image)
Fig. 2. FTIR spectra of DBS gelator.

Fig. 3 shows the FTIR spectra of ethanol gel system with the varying amount of DBS and DMSO. The FTIR spectra of the samples show an -OH stretching vibrations in the range of 3310 to 3340 cm$^{-1}$, -CH stretching vibrations peak at 2970 cm$^{-1}$, -CO peak at 1650 cm$^{-1}$, -CH deformation peak at 1380 cm$^{-1}$, -CO stretching vibration of ethanol at 1050 cm$^{-1}$, -C-C peak at 879 cm$^{-1}$, and -C-C deform peak at 613 to 638 cm$^{-1}$. FTIR spectra further reveal that there were no new chemical/covalent bonds formed during the gelation of ethanol. From the spectra, the intensity and the bandwidth of absorption peak attributed to the OH band (observed in the range 3640 to 3040 cm$^{-1}$) clearly decreased with respect to the increasing amount of DBS and DMSO. This is mainly due to the decrease in concentration of ethanol in the gel system. A definite conclusion from the intensity of OH band cannot be drawn because; the absorption peak was formed due to the overlapping of OH group in DBS, DMSO, and ethanol. However, when the concentration of DBS was increased by 3 wt.%, a slight shift of 30 cm$^{-1}$ in the –OH peak towards intramolecular band was observed (see Fig. 3 (inset)). This is mainly due to the hydroxyl group in the DBS molecule tend to form intramolecular hydrogen bonds with the surrounding ethanol fuel and is primarily driven by the polarity of the solvent mixture.

Fig. 3. FTIR spectra of ethanol gel samples. Inset shows –OH band region of the samples.
3.3. Microstructure of the ethanol gel

The nano-fibrillar 3D network formed by DBS in the ethanol was investigated using the scanning electron microscope (SEM). The presence of fibrous network was revealed from the SEM image for all the gel samples. Fig. 4 shows the SEM images of xerogels with varying $C_{DMSO}$ and $C_{DBS}$ respectively. The nanofibrillar network of DBS exhibited a ‘ropelike’ helical fibre aggregate in all the samples except Et40 where a ‘non-uniform web-like’ structures was observed. As the $C_{DMSO}$ and $C_{DBS}$ increased in the mixture, the self-assembly/gelation of DBS was prominent which supports the findings of molecular interaction studies. This concludes that a minimum required concentration of DBS along with DMSO ($5 \leq C_{DMSO} \leq 19$ wt.%) should be in the ethanol fuel for the self-assembly of DBS.

4. Conclusion

In the present study, self-assembly or the gelation behavior of low molecular weight gelator 1,3:2,4-dibenzylidene-D-sorbitol (DBS) in the ethanol fuel was investigated in detail. The gelation behavior of DBS in the ethanol fuel was predicted using three component Hansen solubility parameters (HSPs). From the HSP calculations, we observed that the gelation was predominant in the fuel when $\delta$ was in the range $26.10 \leq \delta \leq 26.42 \text{MPa}^{0.5}$. The gelation time ($t_{gel}$) was found to decrease with increase in the concentration of DMSO ($C_{DMSO}$) up to $C_{DMSO} < 9$ wt.%. However, further increase in $C_{DMSO}$ increased $t_{gel}$ due to the hindering effect of DMSO on self-assembly of DBS. From the molecular interaction studies, the self-assembly of DBS in the ethanol fuel was due to the interplay between intra- and intermolecular hydrogen bonding between DBS and ethanol mixture and a shift of $30$ cm$^{-1}$ in the –OH peak towards intramolecular band was observed with increase in the $C_{DBS}$. Finally, from the microstructure analysis, the presence of nano-fibrillar 3D network was confirmed using scanning electron microscopy.

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References


