The use of Heat Flow Calorimetry to Study Nitrocellulose Dissolution in Various Solvents

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Background

- Compatibility with solvents
  - *Not possible at elevated temperatures (traditional tests) – boiling / evaporation*
- Conventional ampoule HFC at ambient temperatures possible
  - *Small initial heat flow lost due to system perturbations when introducing calorimeter cells*
  - *Require Time zero heat flows to investigate dissolution and compatibility*
- HFC with titration cell
  - *Heat flows when the solvent is injected onto the solid sample*
- HFC with solution calorimeter
  - *Heat flows when the sample is dropped into bulk solvent*
Scope

- Initial investigation of processing and analysis solvents on nitrocellulose (11.8% Nitrogen; dried and IPA wet)
  - MEK
  - THF
  - Acetone
  - Toluene

- Comparison of titration and solution calorimetry HFC experiments using TA Instruments TAM III
Titration Experiments Methodology

- Used with nanocalorimeter reference cell
- Investigation of initial contact. Solvent added to nitrocellulose
- 10 mg nitrocellulose
- 5 x 50 µl aliquots of solvent titrated at 45 min intervals

![Titration Cell]

- Canula for solvent delivery
- Stirring impeller for liquid samples - removed for NC work
Titration Experiments - MEK

- MEK added to empty ampoule
- Large energy from evaporation reducing if IPA present in the headspace.

Exotherm about two thirds the size compared to NC experiment

Endotherm due to MEK evaporation

Initial exotherm immediately followed by larger endotherm

Energy of evaporation reduced by absorption into nitrocellulose.

- MEK added to nitrocellulose
- IPA aids MEK dissolution
- Initial energy from interaction reducing on subsequent additions
Titration Experiments: THF – MEK Comparison

THF preferentially evaporates (lower $\Delta H_v$ than MEK).

MEK greater affinity for NC than THF – small initial exotherm

<table>
<thead>
<tr>
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<th>Heat Flow Peak Area (mJ) (Dry / IPA Wet)</th>
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<tbody>
<tr>
<td>MEK Blank</td>
<td>-455 / -319</td>
</tr>
<tr>
<td>MEK - NC</td>
<td>-221 / -22.6</td>
</tr>
<tr>
<td>THF Blank</td>
<td>-912 / -369</td>
</tr>
<tr>
<td>THF - NC</td>
<td>-146 / -180</td>
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• THF $\Delta H_v = 32 \text{ kJmol}^{-1}$ – Literature
• THF evaporation into 1ml:
  • Theoretically 1.24J
  • Measured 0.9J
• Errors in cell volume and small heat losses
Titration Experiments

- Energy of evaporation much larger than energy of interaction with nitrocellulose for both solvents
- MEK interaction with nitrocellulose occurs before evaporation. THF interaction occurs during evaporation
  - Larger evaporation heat flow for THF
- Difference between the energy of evaporation for solvent blank and energy of evaporation with nitrocellulose present may be considered as the energy of interaction between the solvent and nitrocellulose
  - For THF and a 10mg dry NC sample:
    \((-146 + 912) \times 100 \text{ Jg}^{-1}\) \(\rightarrow\) 76.6 Jg\(^{-1}\)
  - More complicated for MEK due to the initial exotherm
Solution Calorimetry Methodology

- 3 x 20mg nitrocellulose pellets
- 15 ml solvent
- Pellets are injected into the solvent (45 min intervals), fall apart and release the nitrocellulose

**Pellets**
- Casing parts
- Assembled
- Opened to show NC

**Calorimeter Cell**
- Insertion port for pellet
- Empty
- Full
Solution Calorimetry - Dry NC

- Solvent system at equilibrium prior to introduction of nitrocellulose samples
  - No evaporation effects on heat flow
  - Realistic assessment of solvent interaction heat flows
- For THF, cumulative heat comparable to energy of interaction established in titration experiments
  - THF – Dry NC; 76.6Jg⁻¹
- However, not comparable for MEK
  - MEK – Dry NC; 25.4Jg⁻¹

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<tr>
<th>Solvent</th>
<th>Cumulative Heat / Jg⁻¹</th>
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<tbody>
<tr>
<td></td>
<td>1</td>
</tr>
<tr>
<td>THF</td>
<td>75.5</td>
</tr>
<tr>
<td>MEK</td>
<td>41.2</td>
</tr>
<tr>
<td>Acetone</td>
<td>22.3</td>
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<tr>
<td>Toluene</td>
<td>5.4</td>
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</tbody>
</table>
Solution Calorimetry - IPA Wet NC

- Cumulative heats in IPA wet nitrocellulose lower for THF, MEK and Toluene but comparable to dry nitrocellulose for Acetone
- For THF, cumulative heat comparable to titration energy of interaction (18.9Jg\(^{-1}\))
- No dissolution occurs in Toluene, pellets fail to open; negative heat flow due to slow IPA evaporation?
  - Pellet removed from Toluene and opened
Conclusions

- Measurement of solvent evaporation energy undertaken.
  - THF measured value is comparable to literature
- Heat flow for the interaction of solvents and nitrocellulose at the time of mixing has been measured.
  - Measured energies are significantly lower than energy of evaporation
  - Interaction of MEK seems to be more complicated than THF
- Further work needed to understand very small heat losses in the system
- Future work on other solvents will help to inform appropriate compatibility criteria for the assessment of solvents with energetic materials
Acknowledgements

Thanks to Dr Dave Scott for technical discussion

Questions ?

Comments ?