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

Alan Macdonald
alan.f.macdonald@awe.co.uk
www.awe.co.uk

Jenny Roberts
jenny.roberts@awe.co.uk

Background

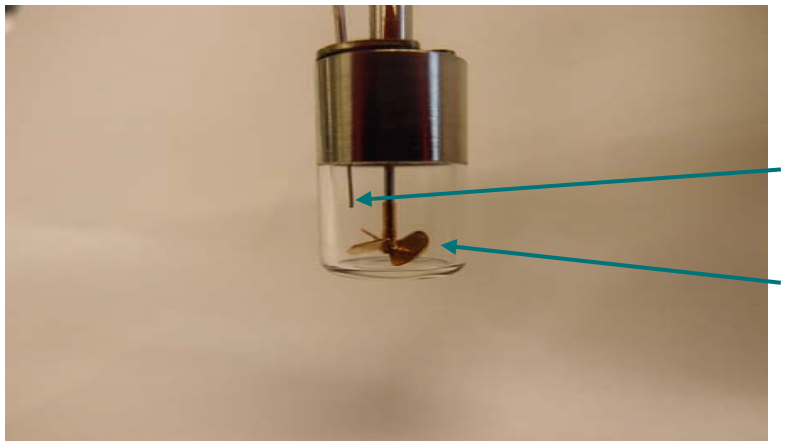
- Compatibility with solvents
  - *Not possible at elevated temperatures (traditional tests) – boiling / evaporation*
- Conventional ampoule HFC at ambient temperatures possible
  - *Small initial heat flow lost due to system perturbations when introducing calorimeter cells*
  - *Require Time zero heat 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

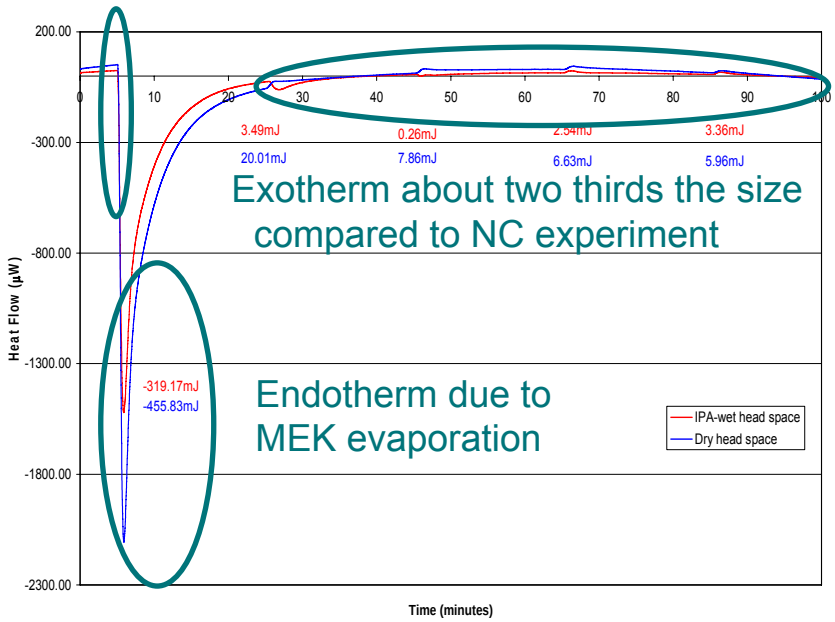


Titration Cell

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

Titration Experiments - MEK

No exotherm

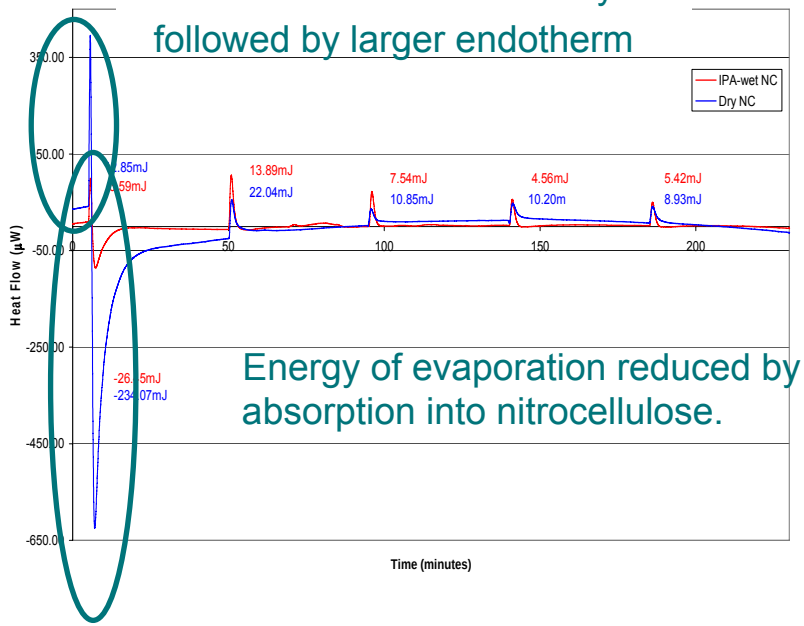


Exotherm about two thirds the size compared to NC experiment

Endotherm due to MEK evaporation

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

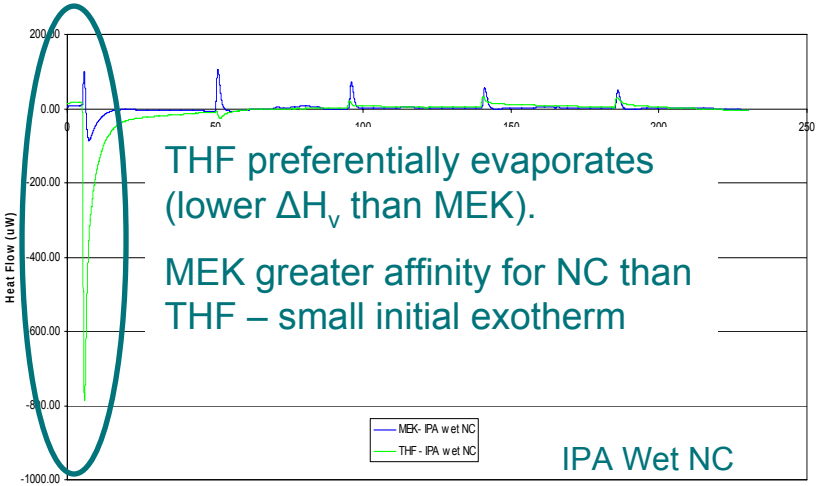
Initial exotherm immediately followed by larger endotherm

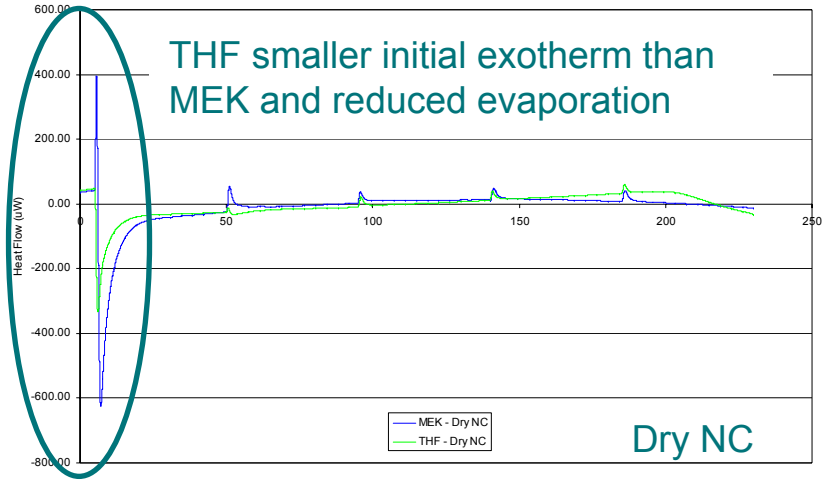


Energy of evaporation reduced by absorption into nitrocellulose.

- MEK added to nitrocellulose
- IPA aids MEK dissolution
- Initial energy from interaction reducing on subsequent additions

Titration Experiments: THF – MEK Comparison





	Heat Flow Peak Area (mJ) (Dry / IPA Wet)
MEK Blank	-455 / -319
MEK - NC	-221 / -22.6
THF Blank	-912 / -369
THF - NC	-146 / -180

- THF $\Delta Hv = 32\ kJmol^{-1}$ – 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 that 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:

  $(-146 + 912) * 100\ Jg^{-1} \longrightarrow 76.6Jg^{-1}$

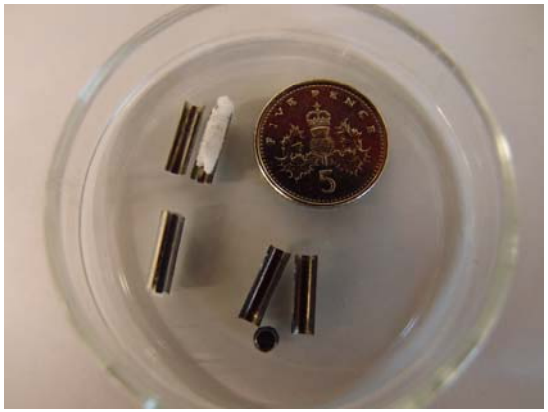
  - More complicated for MEK due to the initial exotherm

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

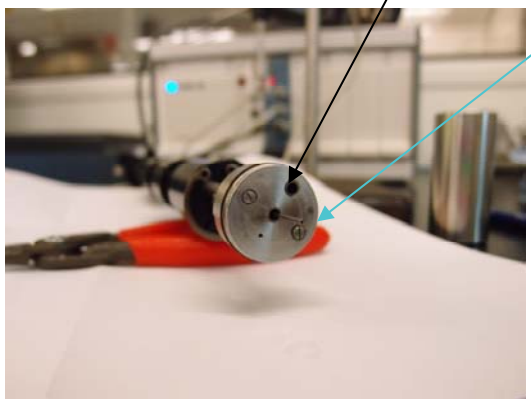
- Casing parts
- Assembled
- Opened to show NC

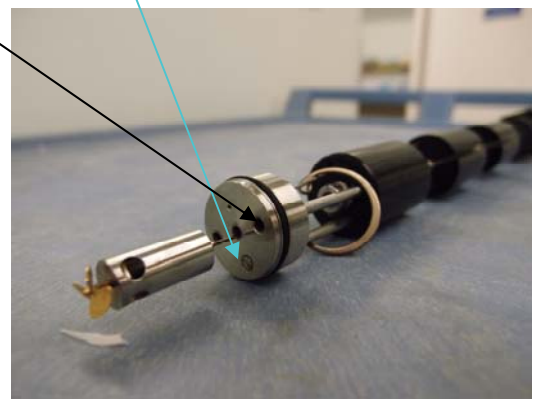


Calorimeter Cell

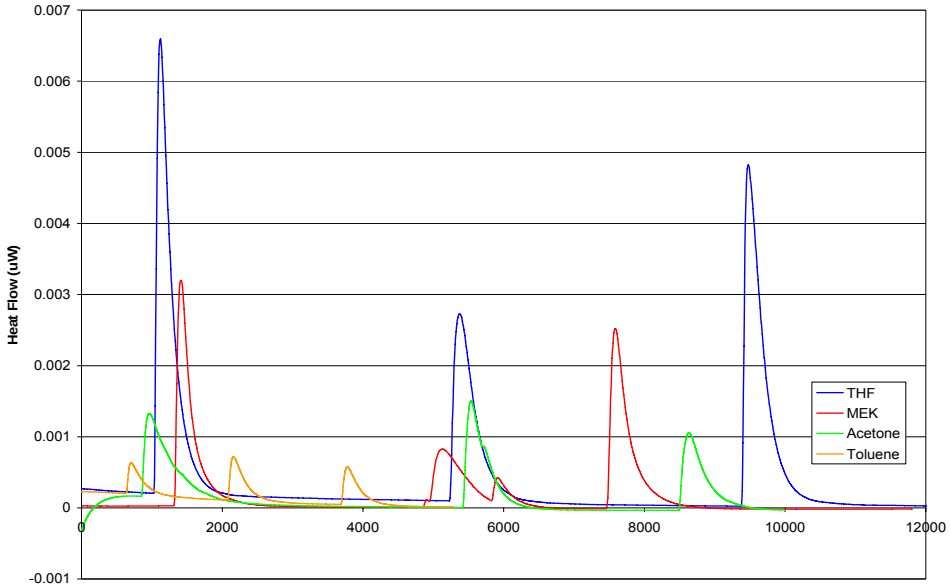
- Insertion port for pellet

Empty Full





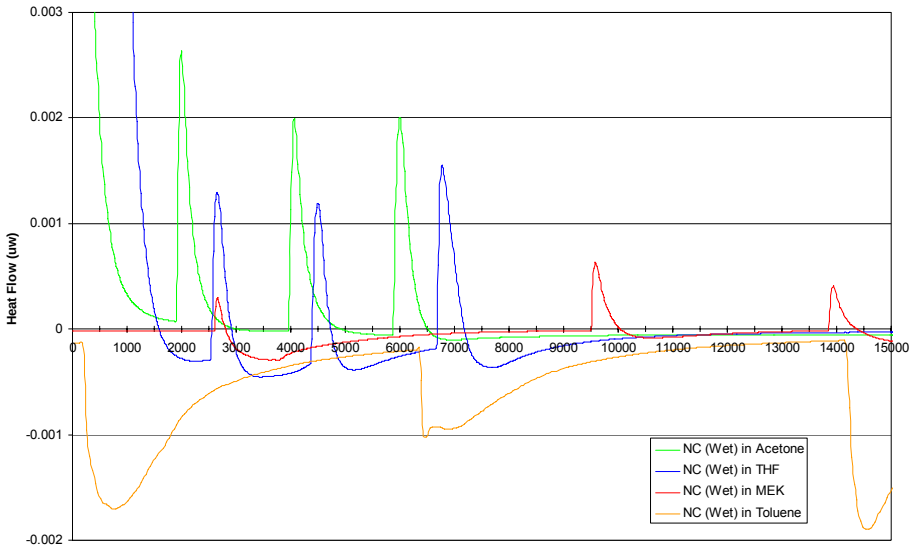
Solution Calorimetry - Dry NC



	Cumulative Heat / Jg-1			
	1	**2**	**3**	**Av**
THF	75.5	47.2	75.7	75.6
MEK	41.2	25.6	41.6	41.4
Acetone	22.3	21.5	18.6	20.8
Toluene	5.4	7.7	4.2	5.8

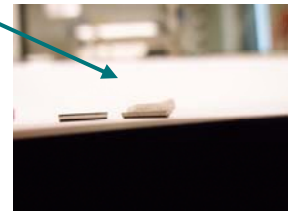
- Solvent system at equilibrium prior to introduction of nitrocellulose samples
  - No evaporation effects on heat flow
  - Realistic assessment of solvent interaction heat flows
- For THF, cumulative heat comparable to energy of interaction established in titration experiments
  - THF – Dry NC; 76.6Jg^{-1}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

Solution Calorimetry - IPA Wet NC



	Cumulative Heat / Jg-1			
	1	**2**	**3**	**Av**
THF	13.3	13.2	18.5	15.0
MEK	0.96	4.93	2.76	2.88
Acetone	27.3	28.9	18.7	24.9
Toluene	-152	-68.1	-96.4	-105

- 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 that energy of evaporation
  - Interaction of MEK seems to be more complicated that 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 ?