Supplementary Information
for

Non-ionic Surfactant Self-assembly in Calcium Nitrate Tetrahydrate and Related Salts

Yashfeen Zahid [a], Yizhen Li [b], Ömer Dag [c,d], Gregory Warr [b], Cemal Albayrak [b,e,*]

[a] Sustainable Environment and Energy Systems, Middle East Technical University Northern Cyprus Campus, Kalkanlı, Güzelyurt, via Mersin 10, Türkiye

[b] School of Chemistry and University of Sydney Nano Institute, The University of Sydney, Sydney, NSW 2006, Australia

[c] Department of Chemistry, Bilkent University, 06800 Ankara, Türkiye

[d] UNAM — National Nanotechnology Research Center and Institute of Materials Science and Nanotechnology, Bilkent University, 06800, Ankara, Turkey

[e] Chemistry Group, Middle East Technical University Northern Cyprus Campus, Kalkanlı, Güzelyurt, via Mersin 10, Turkey

* Corresponding author. Email address: cemal.albayrak@sydney.edu.au

Note on ATR-IR Spectra of Nitrates

The υ(NO) stretching band shows some response to LLC formation. Free nitrates in aqueous solutions have a broad band at around 1400 cm^{-1}, which splits into two bands at 1320 and 1411 cm^{-1} (with a splitting of ~90 cm^{-1}) for molten $Ca(NO_3)_2$, and 1321 cm^{-1} and 1414 cm^{-1} (with a splitting of ~90 cm^{-1}) in $Ca(NO_3)_2$-$C_{12}E_{10}$. The splitting is known to arise from strong interactions (*i.e.* covalent coordination or ion-pairs), which reduce the symmetry of the ion, from D_{3h} to C_{2v}, and splits the doubly degenerate **E** mode into two bands.[1,2] The degree of splitting is directly proportional to the strength of the interaction between metal centre and nitrate. This interaction is weaker in alkali and alkaline earth metals because of the lack of low-lying d-orbitals and lower charge.[3] The degree of splitting in $Ca(NO_3)_2 \cdot 4H_2O$–$C_{12}E_{10}$ system corresponds to monodentate or weaker bridging bidentate coordination.[4]

There are two bending modes of free nitrate which are found at 825 and 719 cm^{-1}. Both of them are again sensitive to perturbation and the latter is also a doubly degenerate mode.[2] The doubly degenerate E mode of 719 cm^{-1} band, which is related to D_{3h} symmetry, splits into A_1 and B_1 modes upon perturbation.[2] The splitting of the 719 cm^{-1} band is smaller compared to the stretching mode and also one of the resultant modes, related to B_1 symmetry, although it is IR active, may not be visible in infrared spectrum.[2] 719 cm^{-1} band shifts to higher energy (743 cm^{-1} in 7.2M calcium nitrate) upon perturbation and it is also attributed as an indicator of contact ion pairs.[1] This band is found at 736 cm^{-1} in $Ca(NO_3)_2$-$C_{12}E_{10}$ sample, and at 744 cm^{-1} in molten CaN sample. Additionally, earlier studies show that 825 cm^{-1} band shifts to 820 cm^{-1} with increasing concentration and perturbation.[1,2] This band is found at 823cm^{-1} in $Ca(NO_3)_2$-$C_{12}E_{10}$ sample and 818 cm^{-1} in molten calcium nitrate, which means that nitrates are more free in the LC medium. Finally, the symmetric stretching of nitrate (ν_1) is also found at the same frequency in both samples. The analysis of these four bands (two stretching and two

bending modes) show that nitrate is perturbed more in molten $Ca(NO_3)_2$ compared to $Ca(NO_3)_2$-$C_{12}E_{10}$ system.

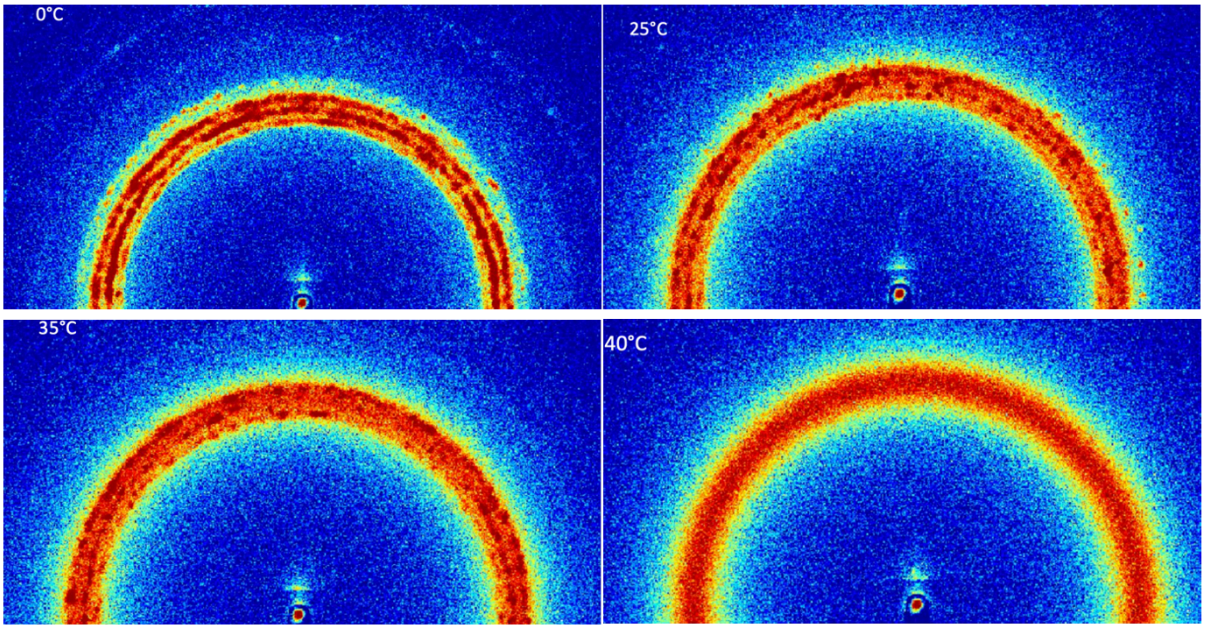


Figure S1-1. 2D-SAXS patterns of sample with 6.0 salt/surfactant mole ratio at different temperatures.

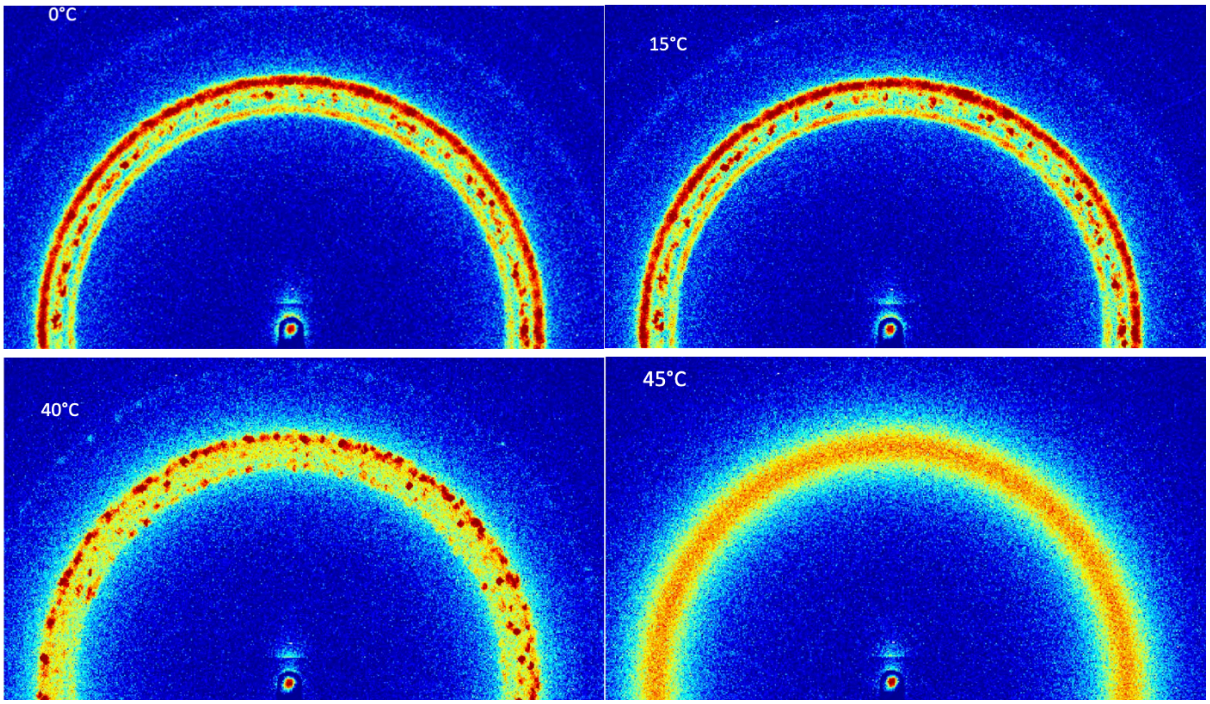


Figure S1-2. 2D-SAXS patterns of sample with 5.5 salt/surfactant mole ratio at different temperatures. Note that the spots for rings at lower temperatures.

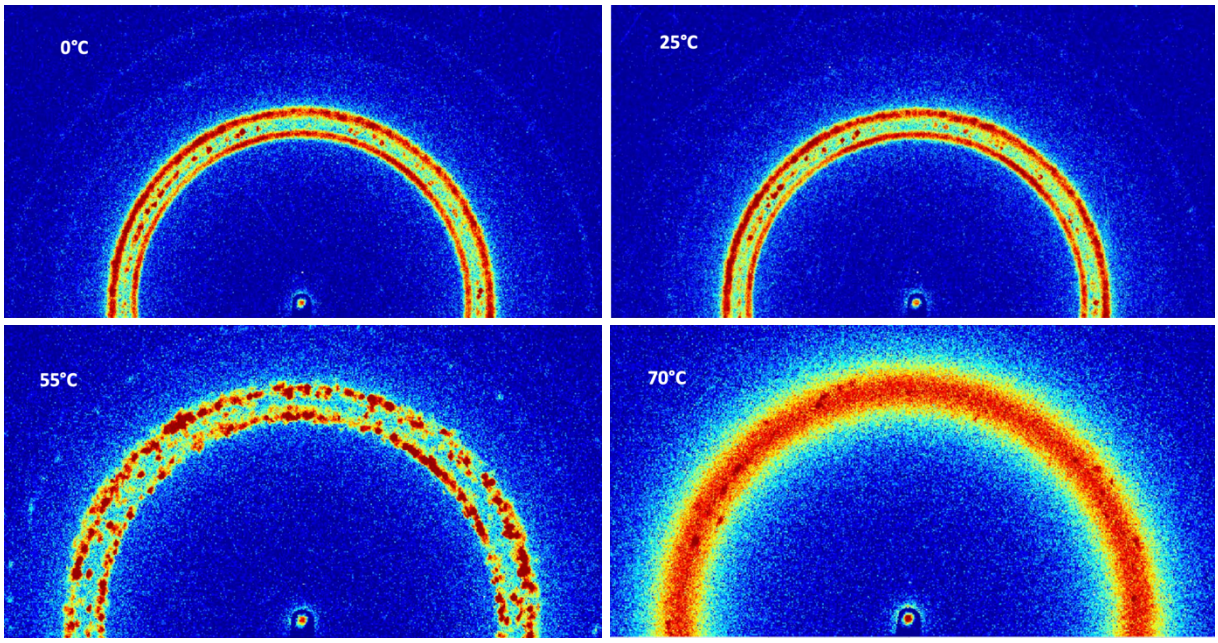
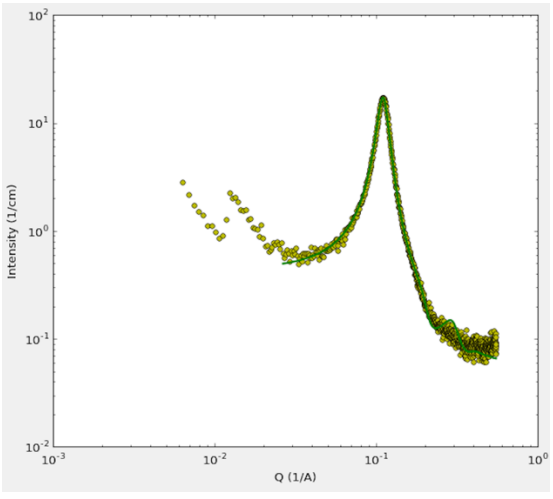


Figure S1-3. 2D-SAXS patterns of sample with 4.5 salt/surfactant mole ratio at different temperatures. Note that the spots for rings at lower temperatures.



Model Parameters

Parameter	Value			Min	Max	[Units]
☑ scale	1.4654	+/-	0.41962	0.0	inf	
☑ background	0.061143	+/-	0.040162	-inf	inf	1/cm
☑ radius	20.113	+/-	2.0638	0.0	inf	Ang
☑ thickness	11.212	+/-	2.08	0.0	inf	Ang
☐ sld_core	1.0			-inf	inf	1e-6/Ang^2
☑ sld_shell	5.8572	+/-	0.44317	-inf	inf	1e-6/Ang^2
☐ sld_solvent	6.0			-inf	inf	1e-6/Ang^2
☑ volfraction	0.48795	+/-	0.0038072	0.0	0.74	

Figure S1-4. Graph showing the fit for the SAXS pattern of a micellar sample at 77 wt.% $Ca(NO_3)_2$ with a core-shell particle model function, performed with the *SAXSview* program (left). Parameters that are used in the model (right).

XRD Patterns

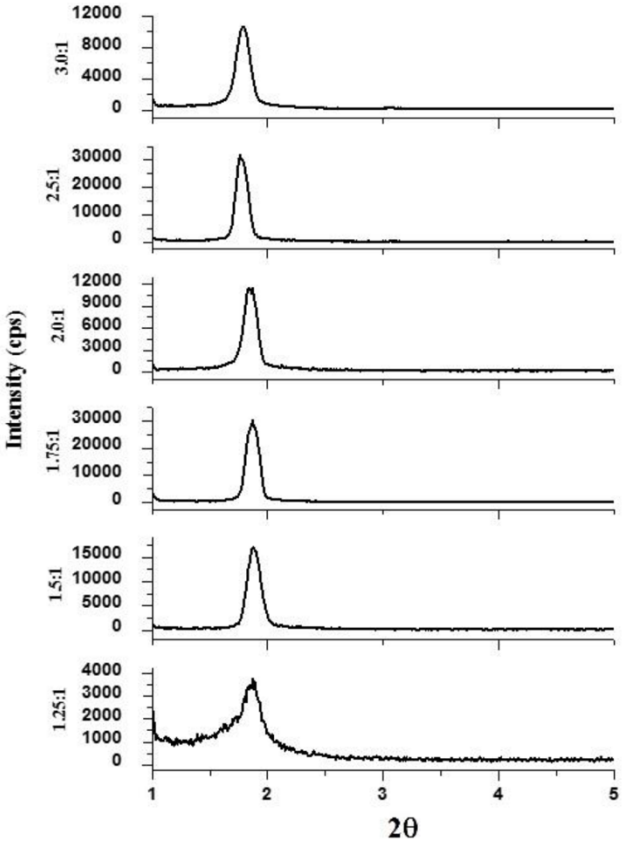


Figure S2-1. XRD Patterns of $[Ca(NO_3)_2.4H_2O]$-$C_{12}EO_{10}$ from 1.25:1 to 3.0:1 mole ratios

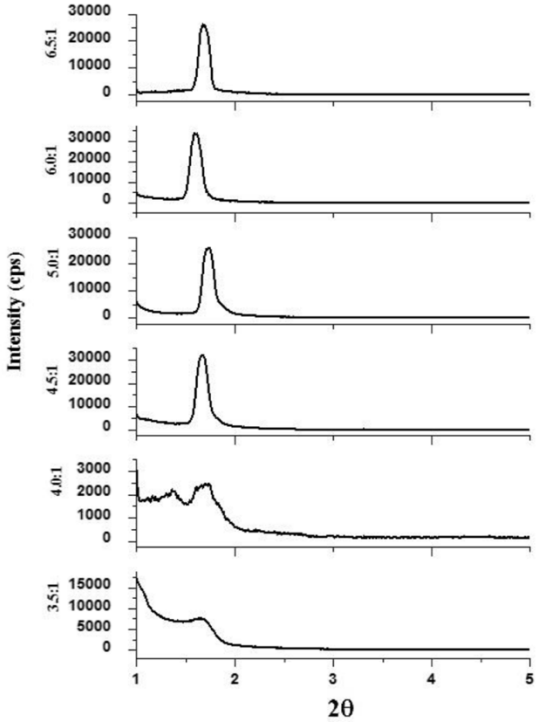


Figure S2-2. XRD Patterns of $[Ca(NO_3)_2.4H_2O]$-$C_{12}EO_{10}$ from 3.5:1 to 6.5:1 mole ratios

DSC thermographs

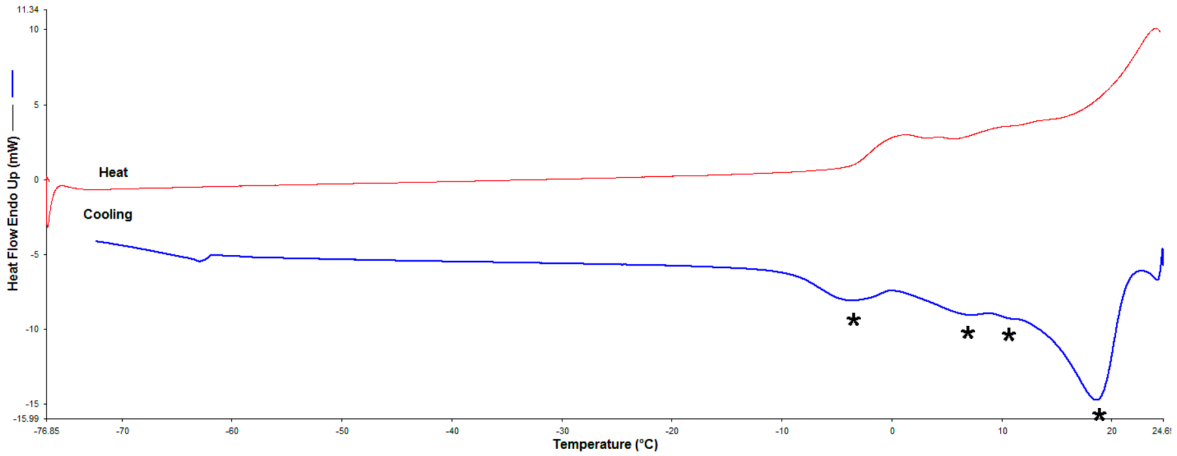


Figure S3-1. *DSC Thermogram for pure surfactant.*

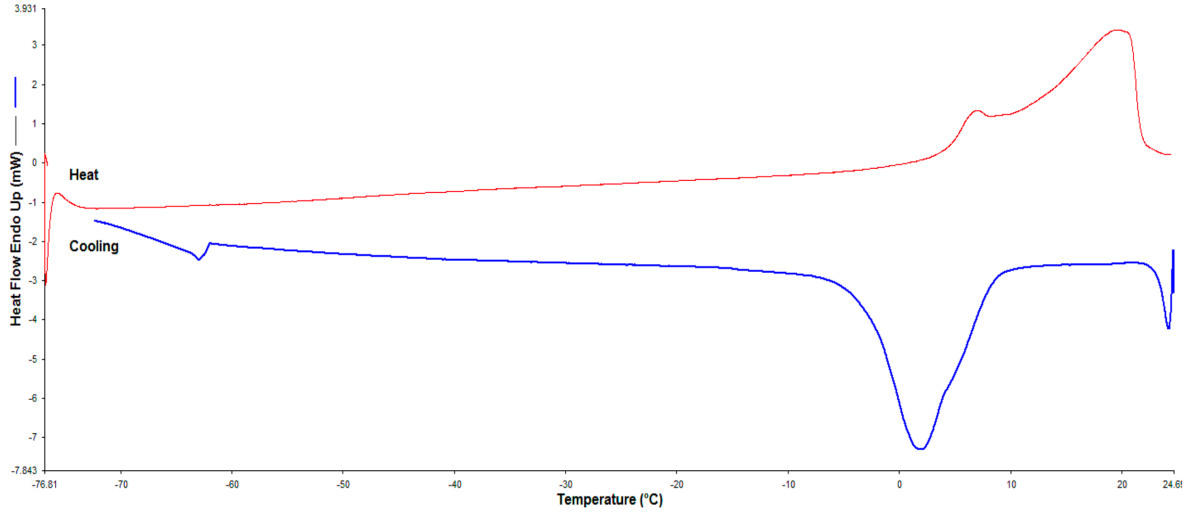


Figure S3-2. *DSC Thermogram for 0.3:1 mole ratio (11 wt. % of CaN)*

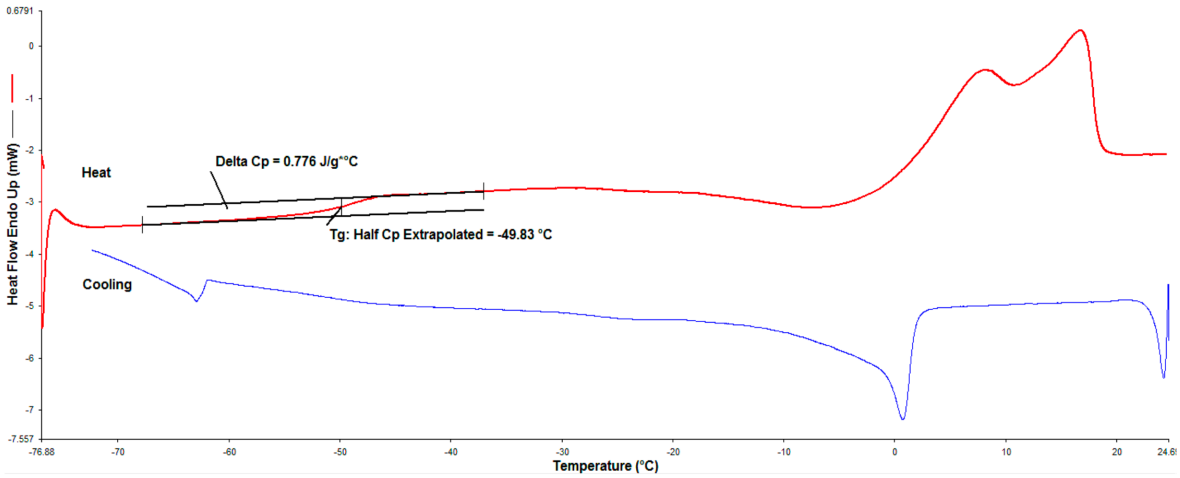


Figure S3-3. DSC Thermogram for 0.6:1 mole ratio (19 wt. % of CaN)

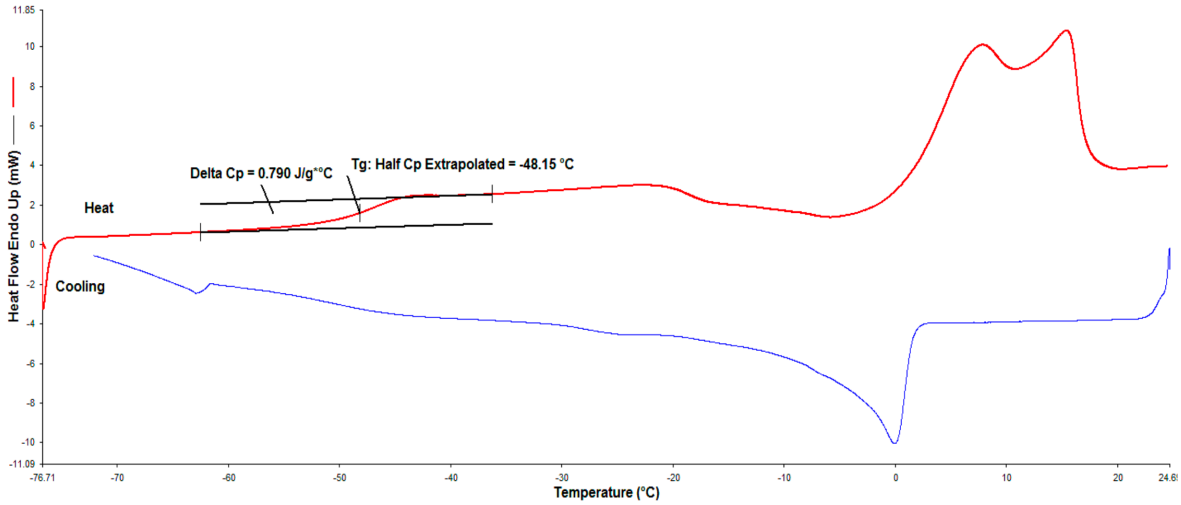


Figure S3-4. DSC Thermogram for 1.0:1 mole ratio (27 wt. % of CaN)

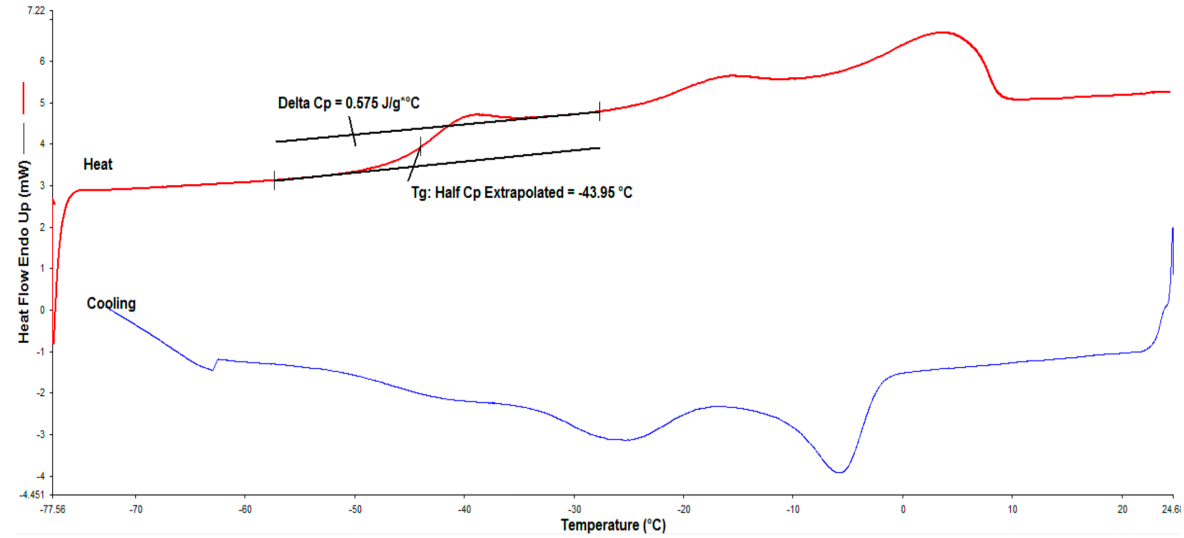


Figure S3-5. DSC Thermogram for 1.25:1 mole ratio (31 wt. % of CaN)

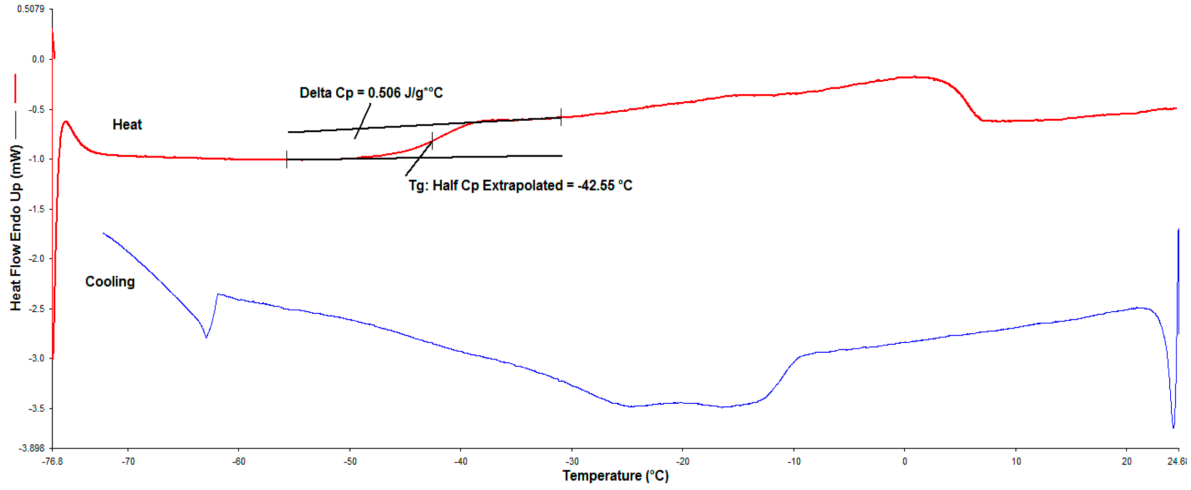


Figure S3-6. DSC Thermogram for 1.5:1 mole ratio (37 wt. % of CaN)

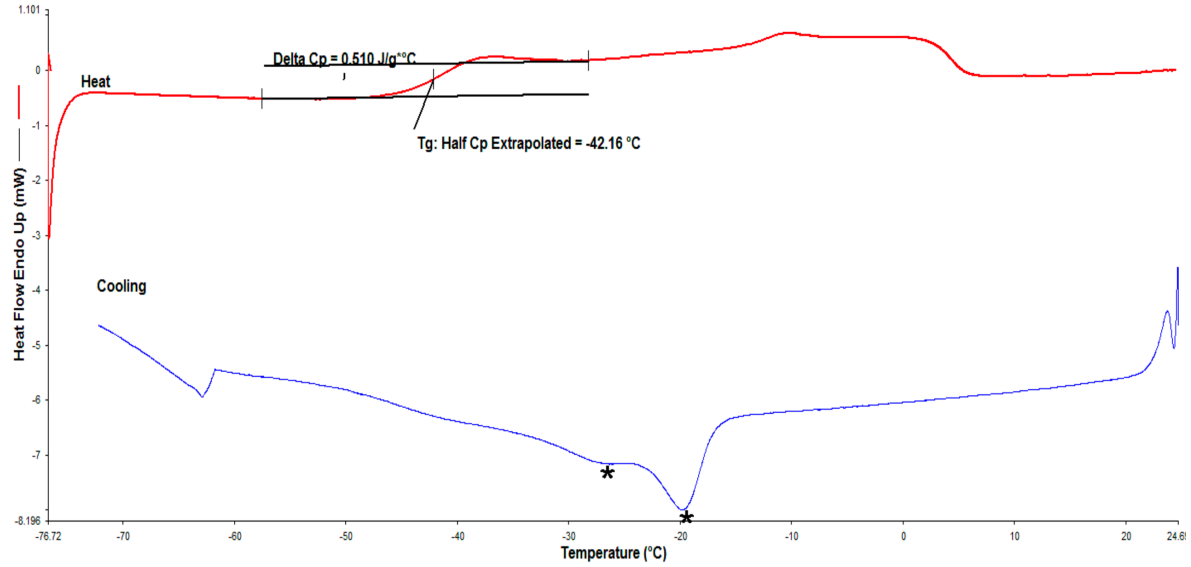


Figure S3-7. DSC Thermogram for 1.75:1 mole ratio (40 wt. % of CaN)

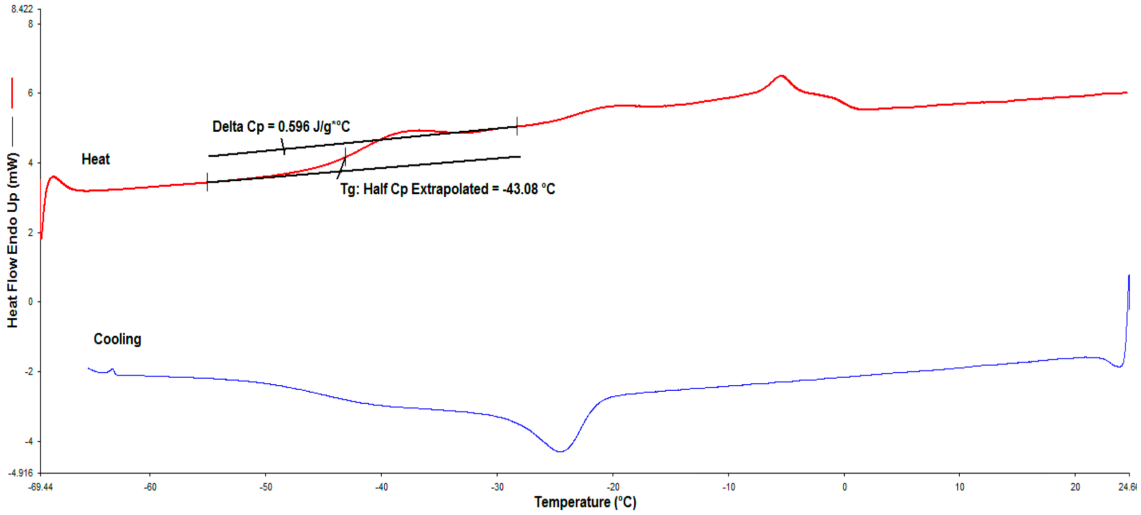


Figure S3-8. DSC Thermogram for 2.0:1 mole ratio (43 wt. % of CaN)

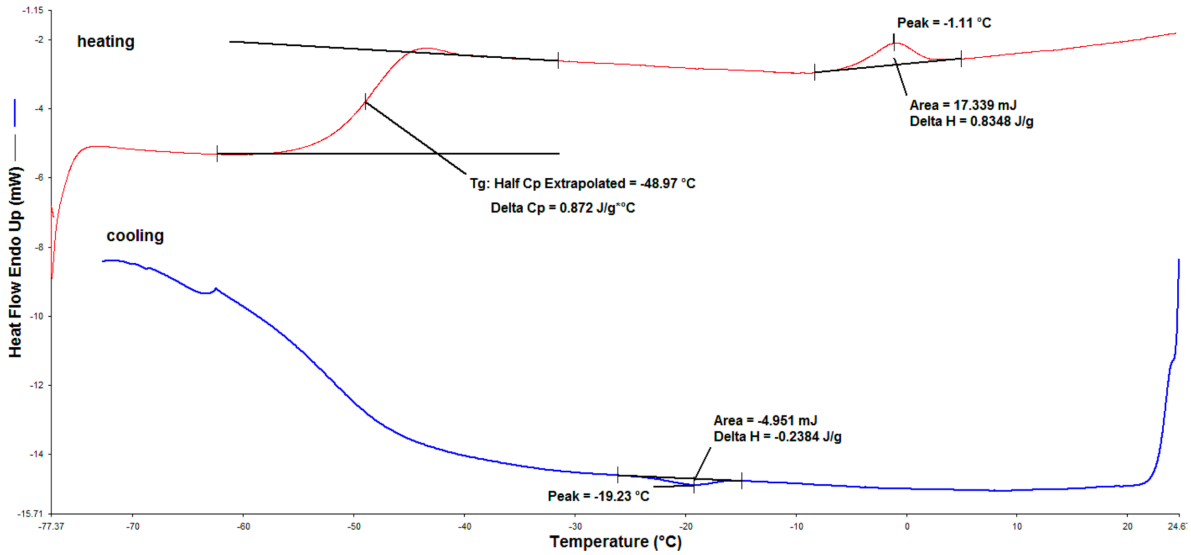


Figure S3-9. DSC Thermogram for 2.5:1 mole ratio (49 wt. % of CaN)

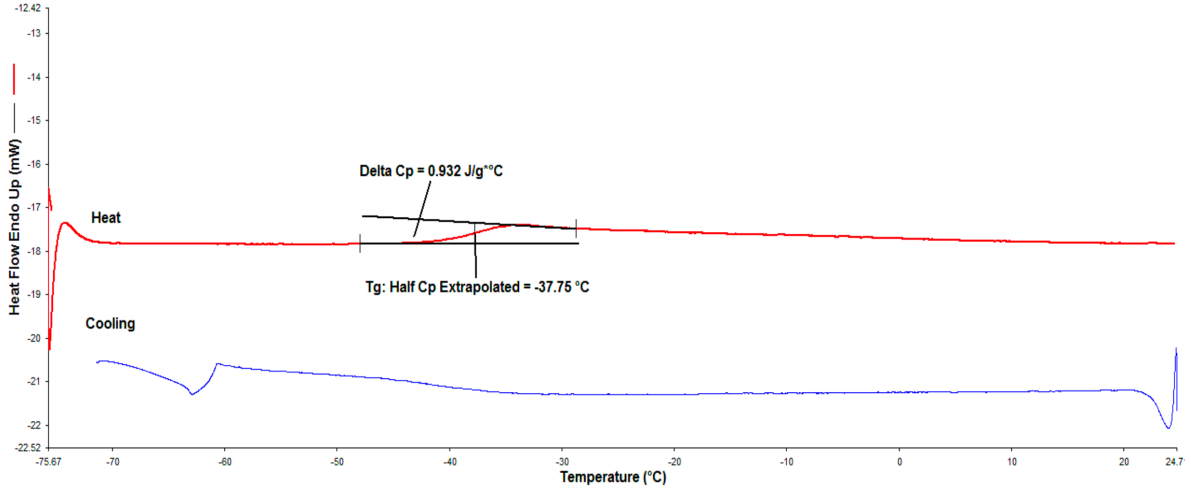


Figure S3-10. DSC Thermogram for 3.0:1 mole ratio (53 wt. % of CaN*)*

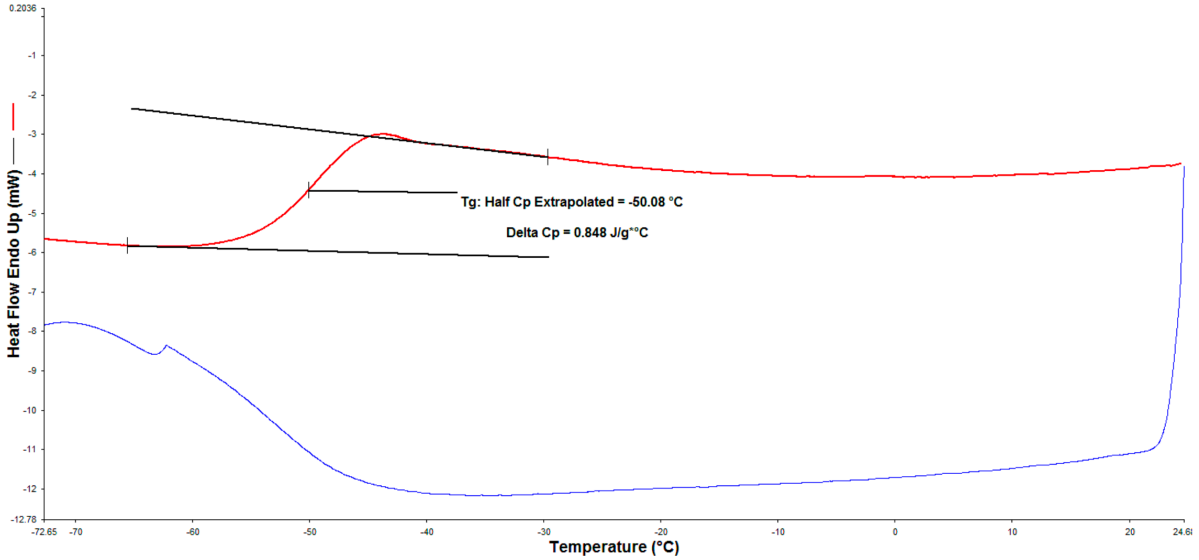


Figure S3-11. DSC Thermogram for 3.5:1 mole ratio (55 wt. % of CaN)

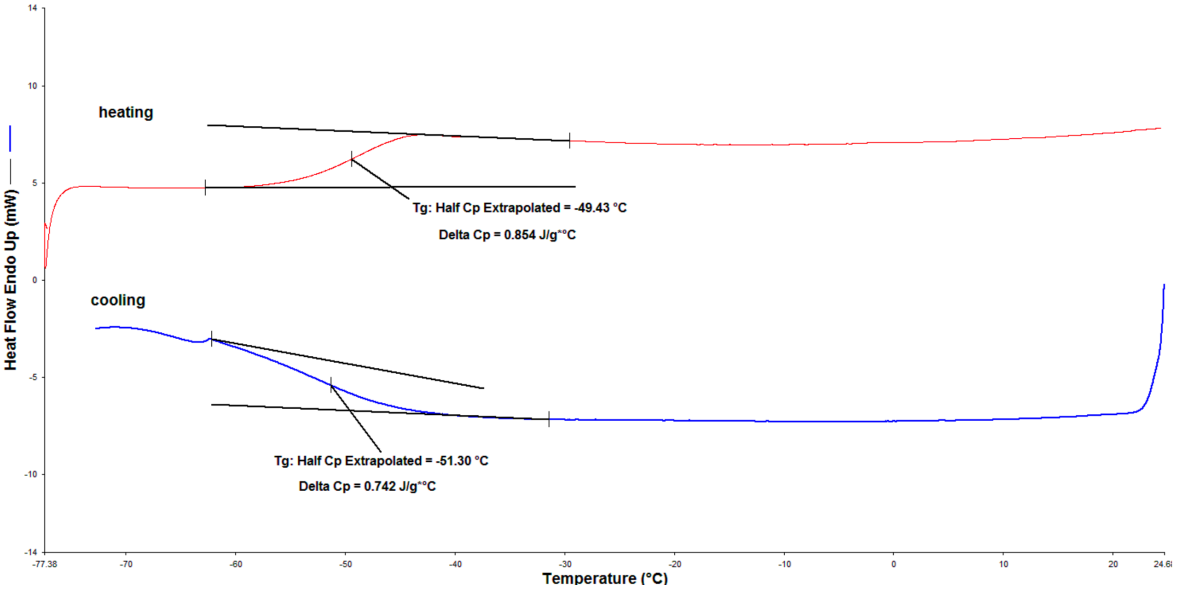


Figure S3-12. DSC Thermogram for 4.0:1 mole ratio (60 wt. % of CaN)

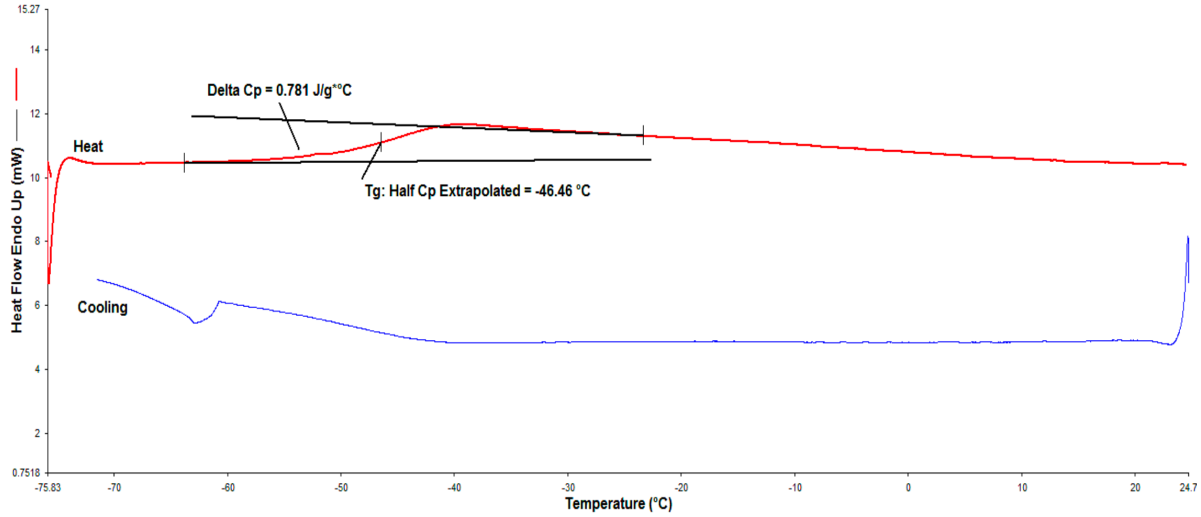


Figure S3-13. DSC Thermogram for 4.5:1 mole ratio (63 wt. % of CaN)

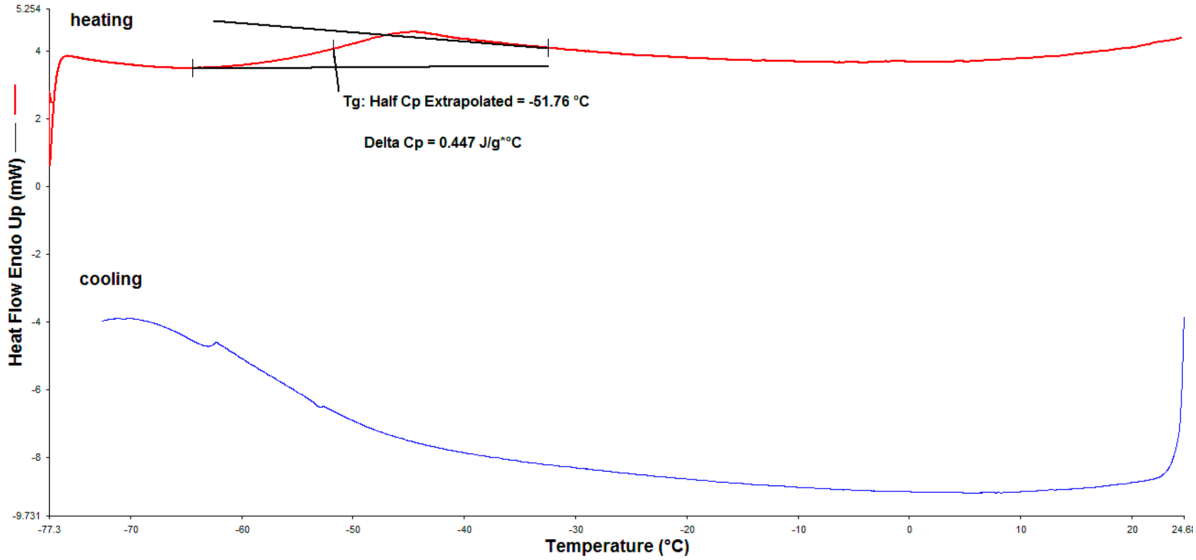


Figure S3-14. DSC Thermogram for 5.0:1 mole ratio (65 wt. % of CaN)

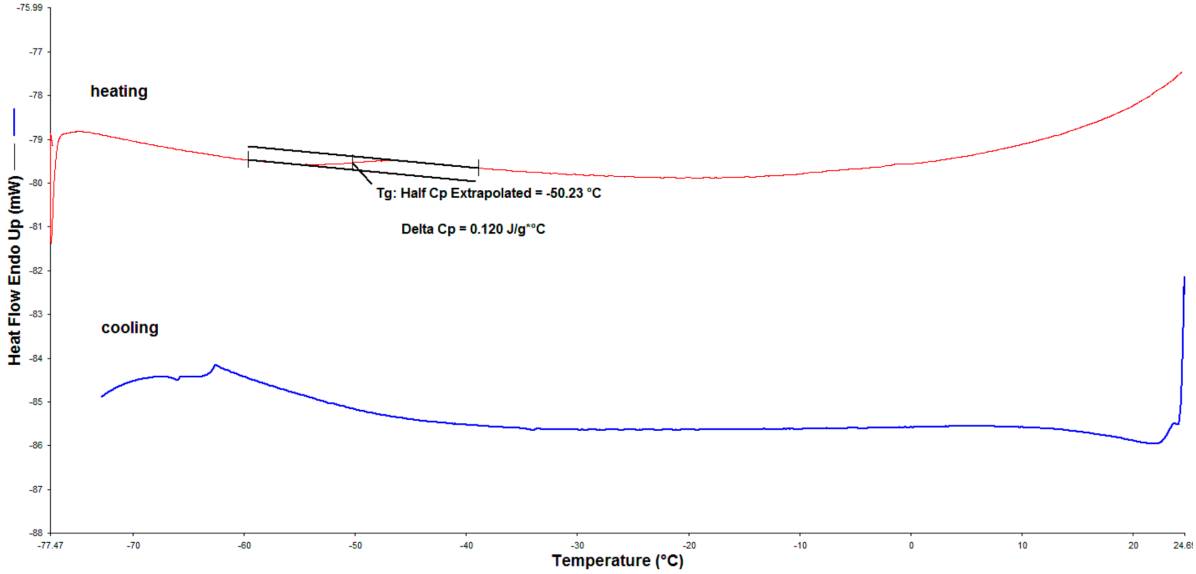


Figure S3-15. *DSC Thermogram for 6.0:1 mole ratio (68 wt. % of CaN)*

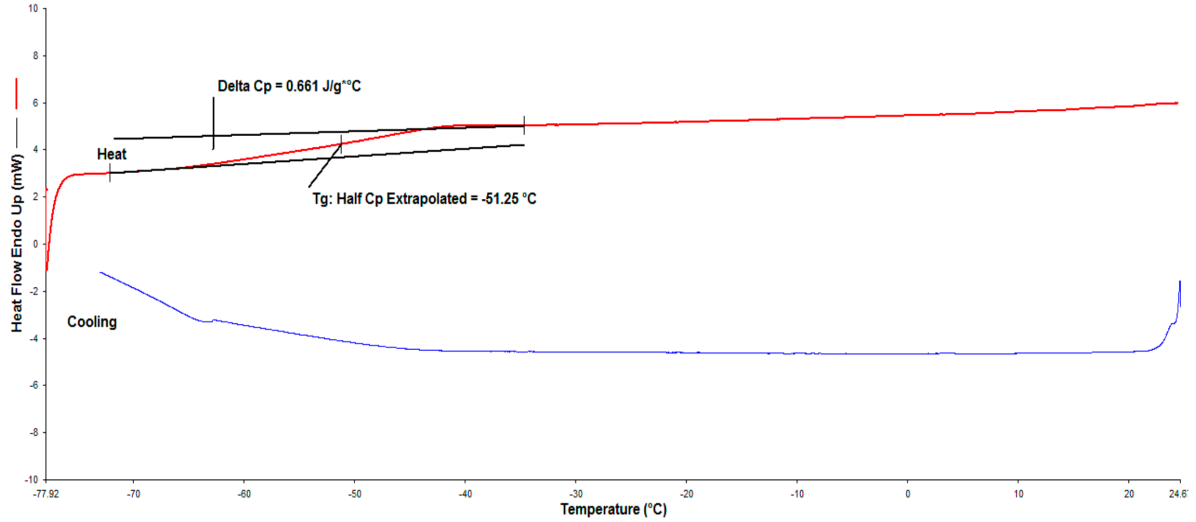


Figure S3-16. *DSC Thermogram for 6.5:1 mole ratio (71 wt. % of CaN)*

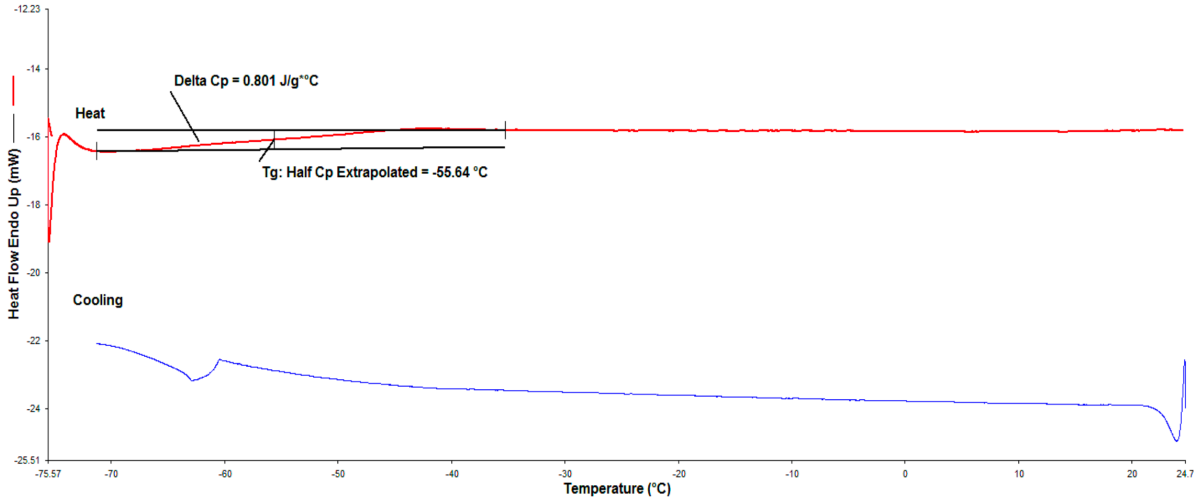


Figure S3-17. DSC Thermogram for 7.0:1 mole ratio (73 wt. % of CaN)

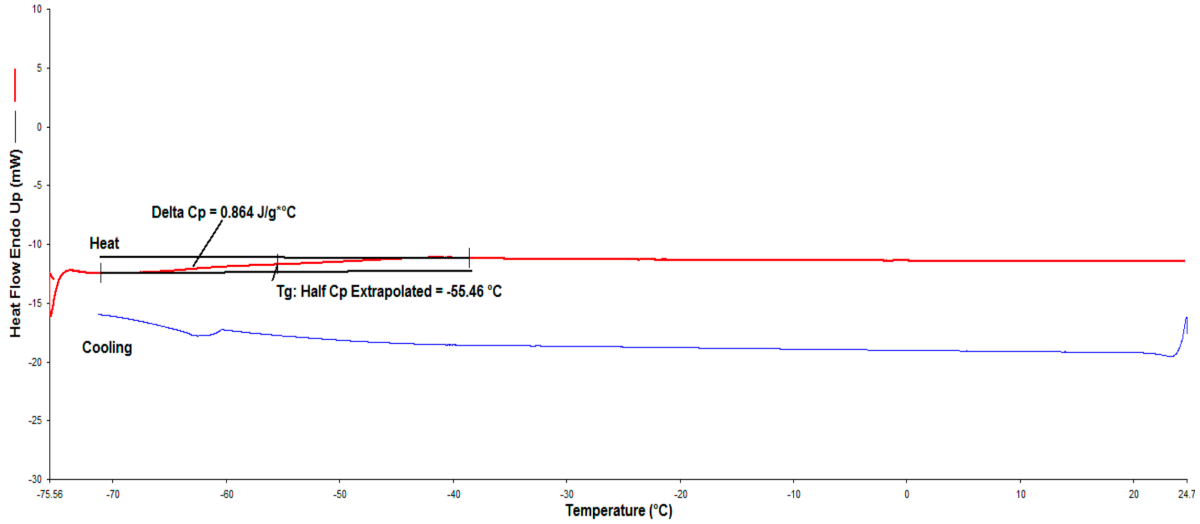


Figure S3-18. DSC Thermogram for 8.0:1 mole ratio (75 wt. % of CaN)

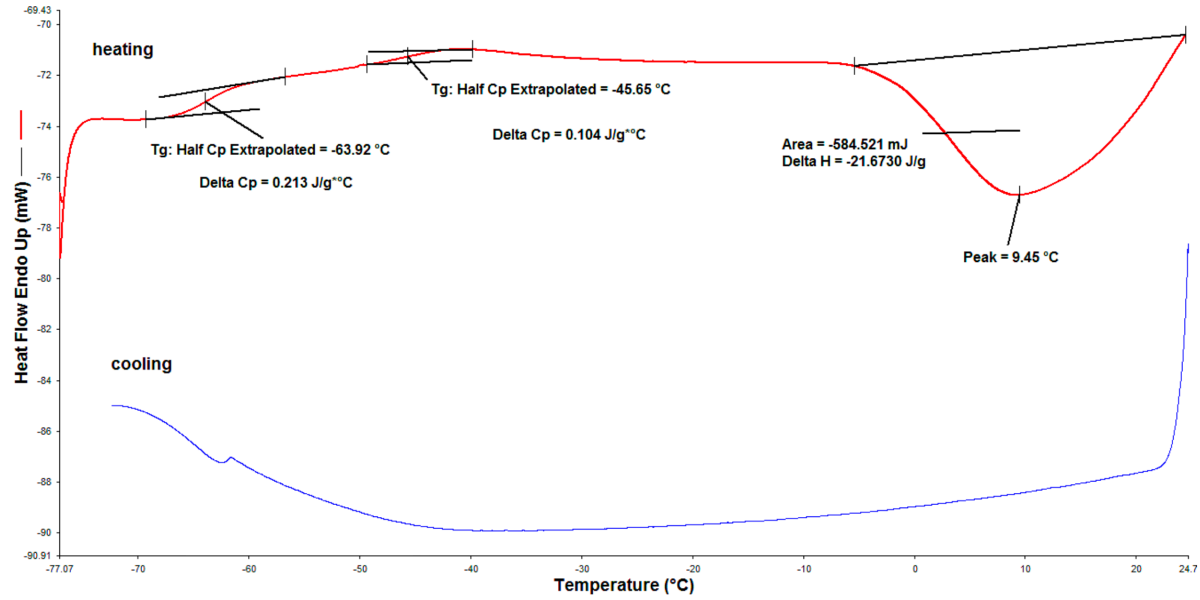


Figure S3-19. DSC Thermogram for 10.0:1 mole ratio (78 wt. % of CaN)

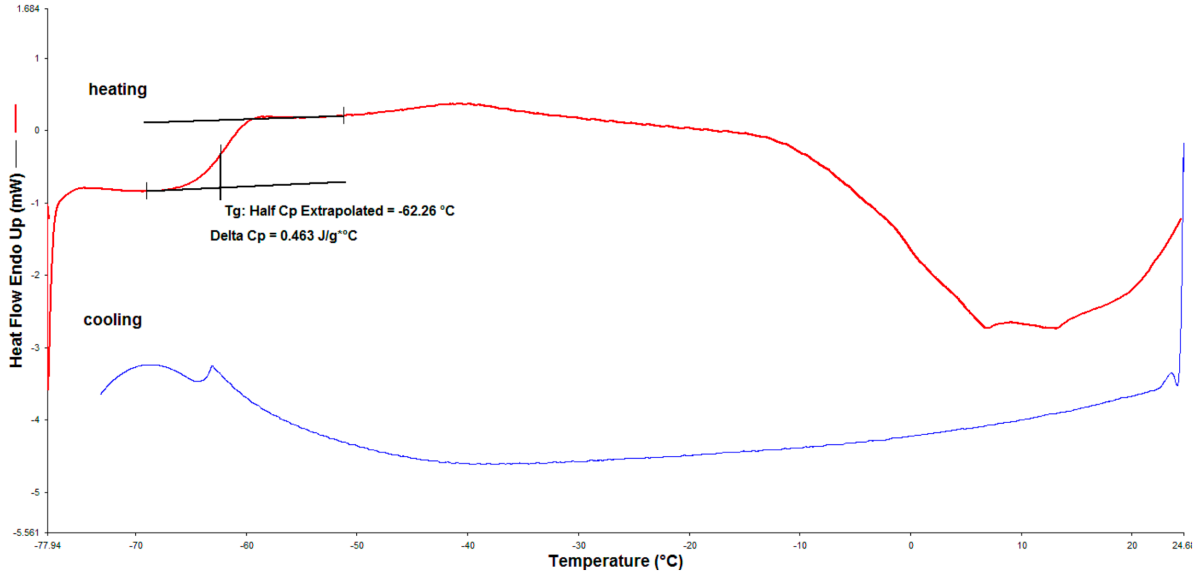


Figure S3-20. DSC Thermogram for 15.0:1 mole ratio (85 wt. % of CaN)

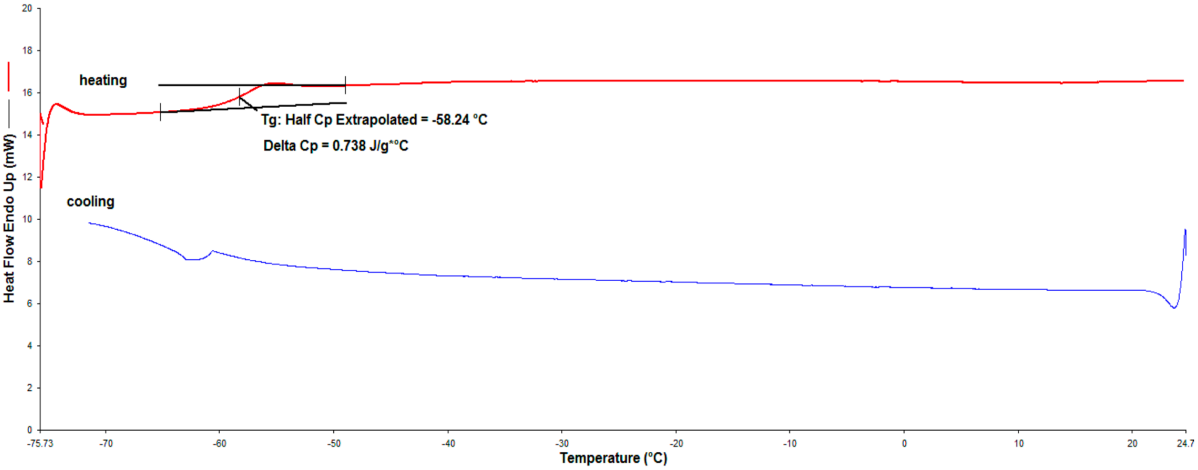


Figure S3-21. DSC Thermogram for 30.0:1 mole ratio (92 wt. % of CaN)

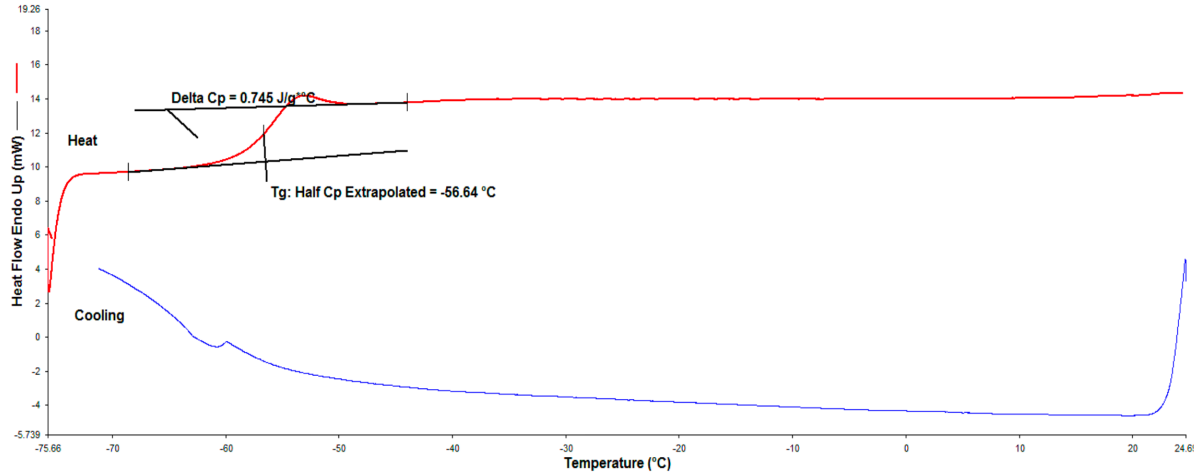


Figure S3-22. DSC Thermogram for 50.0:1 mole ratio (95 wt. % of CaN)

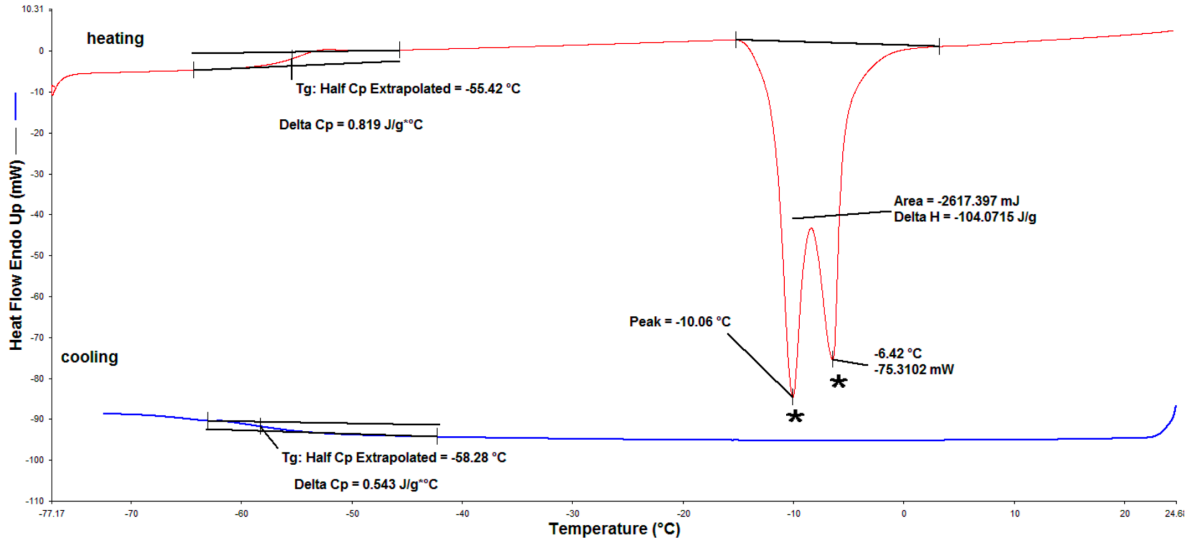


Figure S3-23. DSC Thermogram for molten of CaN

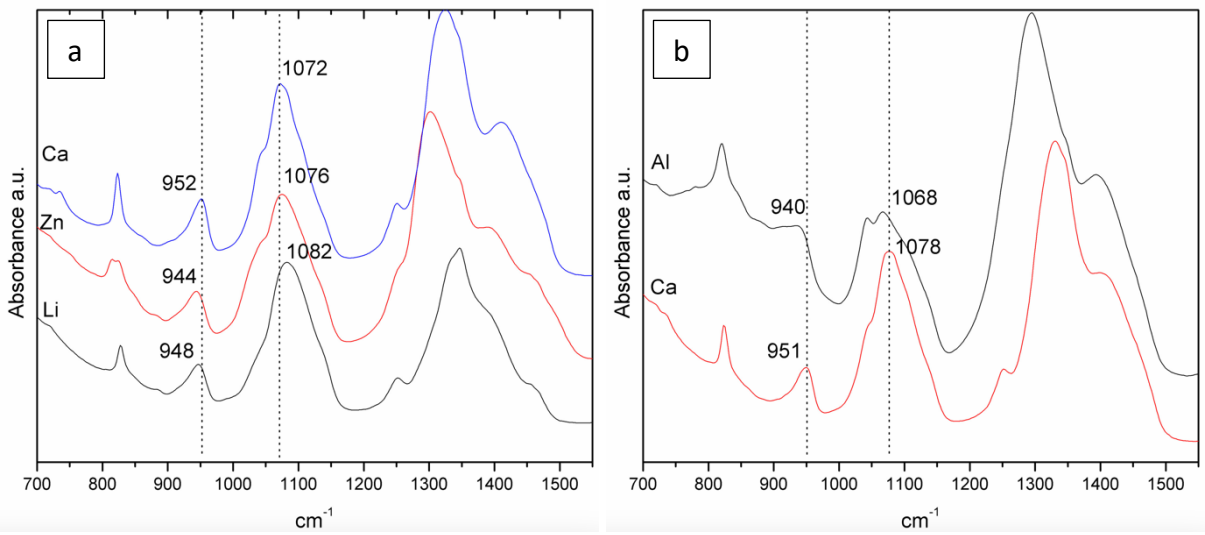


Figure S4. ATR-FTIR spectra of the samples at fixed water/salt mole ratio: **a.** $3LiNO_3$-$18H_2O$-$C_{12}E_{10}$, $3Ca(NO_3)_2$-$18H_2O$-$C_{12}E_{10}$, $3Zn(NO_3)_2$-$18H_2O$-$C_{12}E_{10}$ **b.** $3Ca(NO_3)_2$-$27H_2O$-$C_{12}E_{10}$ and $3Al(NO_3)_3$-$27H_2O$-$C_{12}E_{10}$.

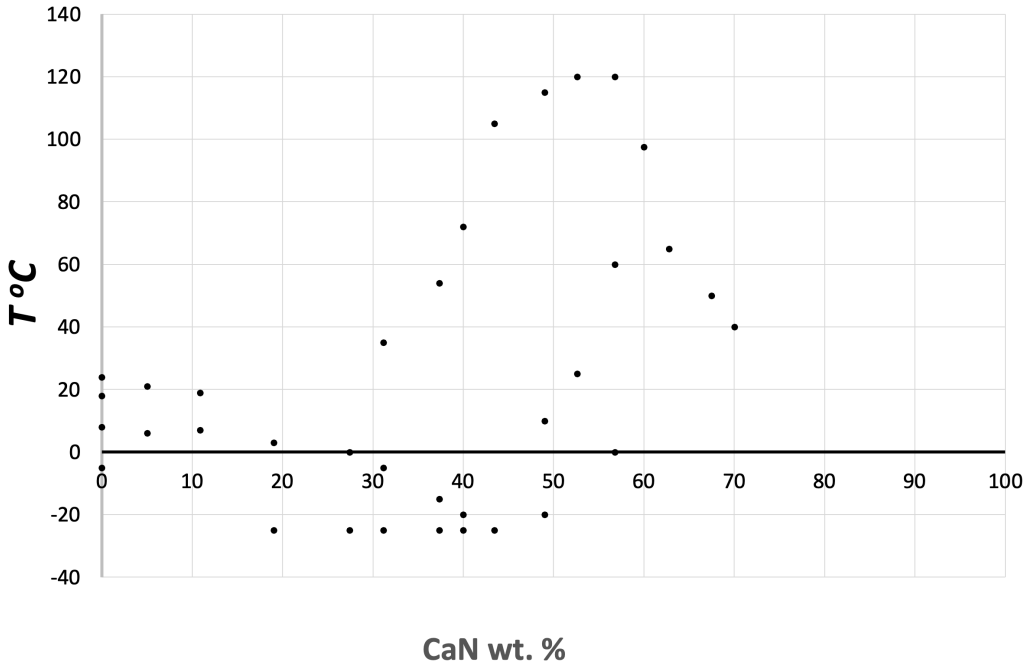


Figure S5. Data points of the phase diagram.

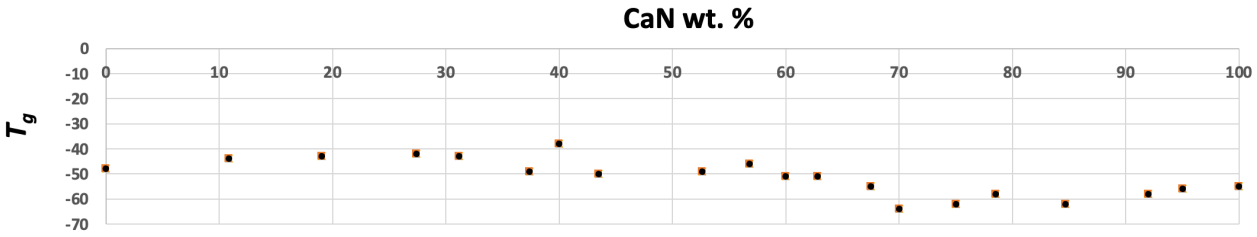


Figure S6. Glass formation temperatures obtained by DSC.

References

1. Irish, D. E. & Davis, A. R. Interactions in aqueous alkali metal nitrate solutions. *Can. J. Chem.* **46**, 943–951 (1968).

2. Irish, D. E. & Walrafen, G. E. Raman and Infrared Spectral Studies of Aqueous Calcium Nitrate Solutions. *The Journal of Chemical Physics* **46**, 378–384 (2004).

3. Çelik, Ö. & Dag, Ö. A New Lyotropic Liquid Crystalline System: Oligo(ethylene oxide) Surfactants with [M(H2O)n]Xm Transition Metal Complexes. *Angewandte Chemie International Edition* **40**, 3799–3803 (2001).

4. Curtis, N. F. & Curtis, Y. M. Some Nitrato-Amine Nickel(II) Compounds with Monodentate and Bidentate Nitrate Ions. *Inorg. Chem.* **4**, 804–809 (1965).