Specac

Application Note

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Phase Behaviour of Stearic Acid-Triethanolamine Soap on the Specac Heated Puck for Quest:

A Literature Replication Study

Specac Heated Puck and Quest

Inside: Investigate the thermotropic behaviour of acid-soap mixtures.

Introduction

The Quest ATR Heated Puck is an accessory for temperature-controlled experiments such as thermotropic phase change in materials and chemical systems. As a proof of performance, we have chosen a past study to replicate. Pudney *et al.* reported an ATR study of the phase behaviour of stearic acid-triethanolamine soap, from 0-100% neutralization of the acid [1]. Such compounds are commercially important and in widespread use in the soap industry.

In their work Pudney *et al.* were able to construct a phase behavior diagram from the 20 sample concentrations they had analyzed. At 85% acid neutralization the authors reported that the CH_2 stretching vibrations decreased in intensity, shifted in position, and broadened upon heating. In this application note, we will look to replicate their findings for 85% acid neutralization.

The heated puck enables the ATR study of the temperature induced behavior of liquids, small solids and powders.

- Heat liquid and solid samples up to 110 °C.
- Accurate, stable temperature measurement via 4-wire RTD sensor.
- Superior physical and chemical robustness provided by monolithic diamond ATR crystals.
- Setting and logging temperature made simple by PC software and compact USB interface.
- Retrofits to all Quest family accessories.

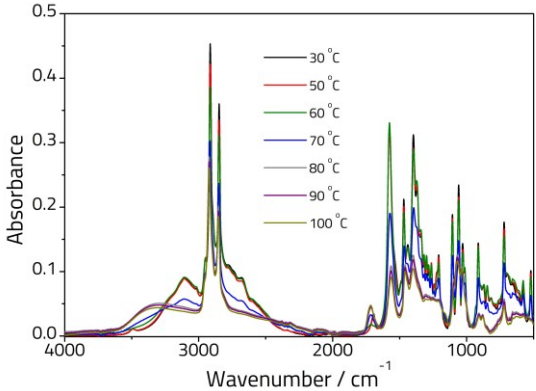


Figure 1: Selected FTIR spectra as the Acid-Soap is heated from 30-100 ° C.

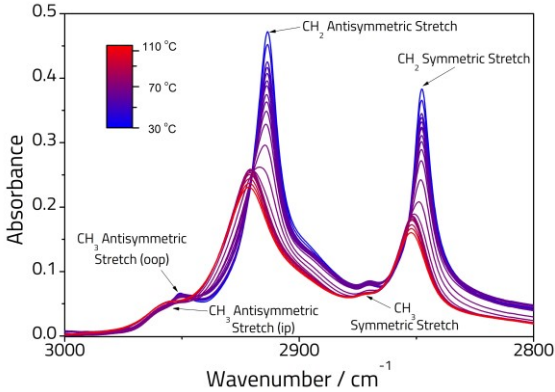


Figure 2: Alkyl CH stretching region, showing the effect of temperature on this region. Compare to Fig. 5 in [1]. Assignments are based on [1].

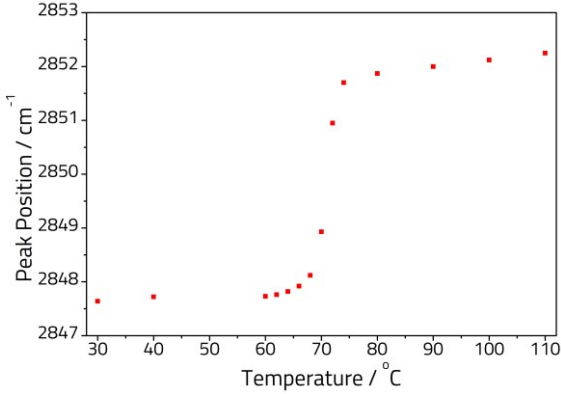


Figure 3: CH_2 symmetric stretch peak position variation with temperature, showing the thermotropic behaviour. Compare to Fig 6 in [1].

Experimental

Stearic acid (SA) and triethanolamine (TEA) were obtained from the same source as reported in the literature. SA was melted at 80 °C and then TEA was added drop-wise with stirring until a molar ratio of 100:85 SA:TEA was achieved. The temperature of the mixture was increased to 90 °C to ensure a homogenous blend. The solution was cooled to room temperature, ground in a pestle and mortar to form a fine powder and then left for 1 week.

An automated program was built in our spectrometer software using the command line functionality of the Specac USB Temperature Controller software. This allowed the spectrometer to control the temperature of the accessory directly. At each temperature step (30-110 °C) the accessory was heated to the target temperature and then held for 20 minutes to allow the system to equilibrate. To account for temperature induced variation in the diamond phonon bands a blank spectrum was recorded at each temperature step relative to a background recorded at 27 °C. The experiment was then repeated, this time with samples of the SA/TEA soap powder pressed against the surface of the diamond using the Quest ATR's pre-set 40 lb. load tower. Data were then processed by subtracting from each SA/TEA spectrum the blank spectrum recorded at the same temperature. Given the long duration of the experiment, further processing was used to remove the $H_2O_{(g)}$ and CO_2 features in the spectra. A purge gas generator could also be fitted to spectrometer and the purge port on the Quest to mitigate this.

Results and Discussion

Figure 1 shows selected spectra at various temperatures. As the temperature increases the overall intensity of the spectrum decreases. In the black trace (30 °C) two broad peaks are observed between 2500-3000 cm^{-1} (underlying the CH stretch features) and 3000-3500 cm^{-1}. These are tentatively assigned to the un-neutralized SA OH peak and to the soap TEA OH groups. Upon heating, these features merge into a single asymmetrical feature between 2000-3500 cm^{-1}.

The flat region around *ca.* 2000 cm^{-1} demonstrates the high degree of temperature reproducibility and the efficiency of spectral subtraction of the diamond phonon modes. This method of processing proves superior to the use of a background recorded at the specified temperature and

and used days later, owing to variation in the spectrometer alignment. This variation is cancelled by referencing first to a background recorded on the same day and then subtracting the diamond phonon features.

Figure 2 shows the alkyl CH stretching region and is comparable to Fig. 5 in [1]. As the temperature is increased the peak position shifts to higher frequency. As the sample melts the peaks also broaden due to a more disordered state in the chemical environment. The spectra show a good correlation to the literature reference.

Figure 3 plots the variation of the peak position of the CH_2 stretching frequency with temperature. A direct comparison with the work of Pudney *et al.* (Fig. 6 in [1]) shows that at low temperature there is a small discrepancy in peak position (~0.8 cm^{-1}). This could be due to spectrometer variation, or due to differences in the peak position algorithm used. The overall trend of the graph shows a good match to the graph in [1]. Both plots show the peak shifting slowly from *ca.* 64 to 70 °C, corresponding to a multiphase system. Above 70 °C the peak frequency rapidly increases in both experiments corresponding to the transition to a liquid crystal phase. The phase transition from liquid crystal to liquid was determined using the peak ratio I_{1301}/I_{1276}, and again our results (Appendix B) are comparable to the literature, with a phase transition above 90 °C.

Conclusions

We have shown that the Quest ATR Heated Puck, allied to the functionality of the Temperature Controller software, is a powerful system for collecting high quality spectra at a range of temperatures. Direct spectrometer control allowed the experiment to be fully automated except for sample loading.

Detailed analysis of the temperature induced changes in the spectra can be used to obtain insights into the phase behavior of mixtures such as the soaps described here. Finally, use of blank spectra to control for changes in the diamond phonon mode changes proved superior to the use of a blank temperature background and is strongly recommended.

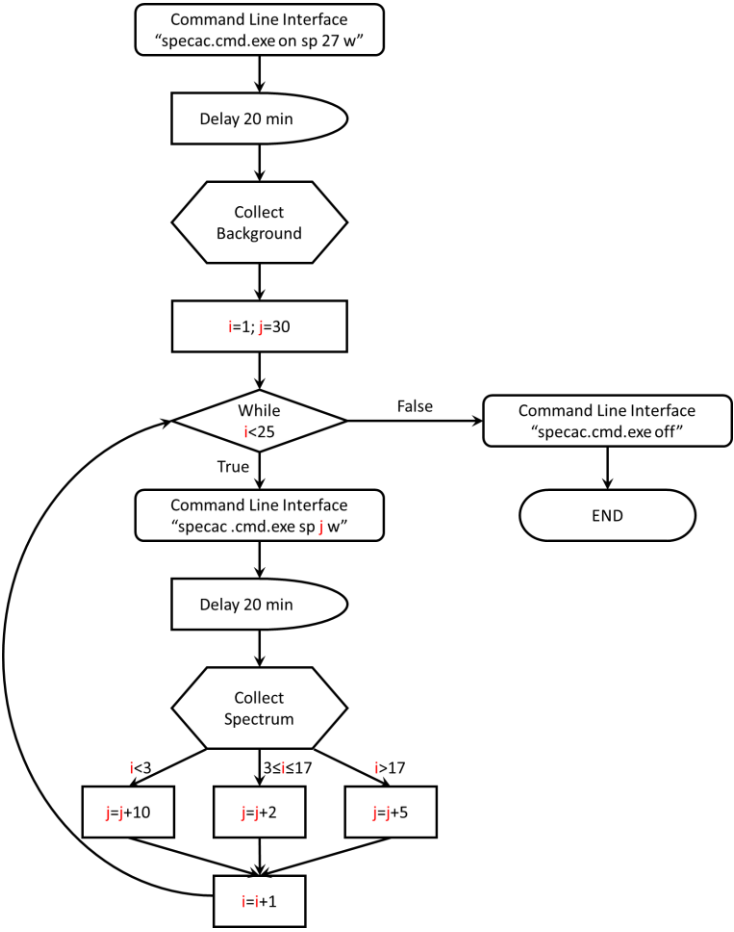
References

[1] Pudney P.D.A., Zhu S., Mutch K., *Phys. Chem. Chem. Phys.*, **11**, (2009), 5010–5018. DOI: 10.1039/b819582j

Appendix A

The exact method for programming your spectrometer will vary according to your equipment manufacturers software. A generic flow diagram is provided below to illustrate one potential setup for this. Some additional external coding may be necessary.

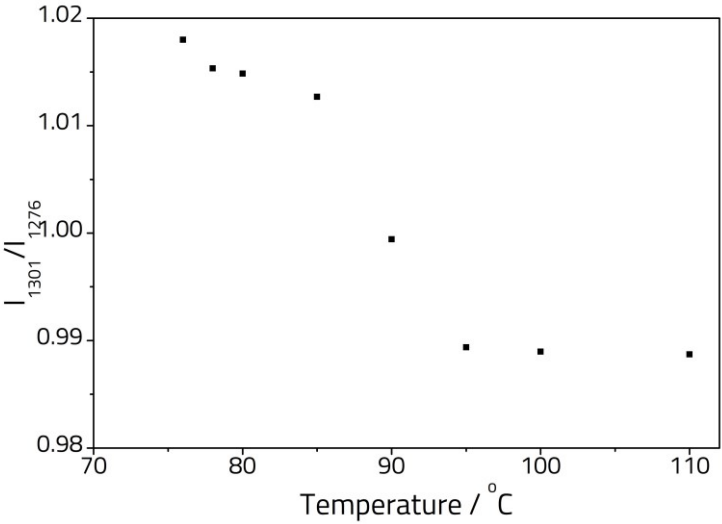
Contact your Specac Sales Representative for further information and assistance.



Flow diagram showing an illustration of an automated spectrometer program using the "Specac.cmd.exe" CLI interface to control the USB Temperature controller

Appendix B

In order to determine the temperature of the third transition from liquid crystal to liquid Pudney *et al.* examined the intensity of the CH_2 wagging vibrations, plotting the intensity of the 1301 cm^{-1} band against the intensity of the band at 1276 cm^{-1}. At lower temperatures this region is obscured by other bands, however above 76 ºC these bands can be examined directly. These results show a near perfect corelation to the paper data, confirming the performance of the heated puck.



Intensity of the band at 1301 cm^{-1} relative to the band at 1276 cm^{-1}, showing the transition from liquid crystal to liquid phase.

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