Frustrated paraffin phase transitions

Frederick G. Haibach* and Suzanne K. Schreyer*

Chemometrics and Applications Engineering, Polychromix Inc., 30 Upton Dr, Wilmington MA, 01810 USA. E-mail: fhaibach@polychromix.com, schreyer@polychromix.com

Introduction

Phase states are important in many industries, i.e. food, pharmaceutical, forestry and incidental in many other applications of near infrared (NIR) spectroscopy.^{1,2} Fundamental understanding of phase states and their affect on NIR spectra is needed. In this study we provide an overview of the results that may be achieved using a portable NIR spectroscopy system on paraffin systems *in situ*. Paraffins, despite their simple molecular structure have a broad variety of crystalline phases.³ Microencapsulation frustrates crystallisation and melting, especially when the interior is rough, and the number of molecules in the microcapsule approaches a countable number at the small end of the distribution (about 10⁶). We present results of quantitative analyses of the solid/liquid phase change transitions applied to microencapsulated materials, for phase change monitoring of this microencapsulated material embedded in gypsum.

NIR spectroscopy is a very sensitive probe of molecular environment. The symmetry and confinement imposed by crystalline structures alters both the dipole moment and energies of molecular vibrations.⁴ The vibrational energies of higher quanta are more sensitive to the anharmonic components of the vibrational potential energy surface than are other kinds of vibrational spectroscopy.

Experimental

Samples of BASF Micronal DS 5001⁵ as a free-flowing powder and immobilised in a gypsum matrix at ~30% by weight, were measured using a PHAZIRTM 1624 between 3°C and 60°C. The spectral response is explored using spectral differences and the PCA mode of Polychromix MGTM 1.63. The transition temperature associated with phase change occurs at ~26°C.³

Three sets of experiments were performed; on pure micronal powder, in CaSO₄ hemihydrate and on CaSO₄ dihydrate. BASF Micronal DS 5001XTM free flowing powder was placed in three glass vials for replicate measurements. Spectra were collected over a temperature range between 3°C and 60°C. Replicate spectra were also collected as the Micronal cooled from a high of 60°C to room temperature, as well as heated from a low of 3°C to room temperature. BASF Micronal was mixed at 30% (w/w) with DAP Plaster of Paris (primarily CaSO₄· ½ H₂O), resulting in powder mixtures. The same temperature ramping and spectral collection as in experiment 1 was performed. The plaster mixture from experiment 2 was mixed with water (1 part water : 2 parts plaster mixture). The gypsum mixture was left to dry, forming $CaSO_4 \cdot 2 H_2O$. The resulting plaster was then used in the same temperature ramping and spectral collection as for experiment 1. All spectra were preprocessed using Savitsky–Golay smoothing (1st derivative, three-point smooth of a 2nd order derivative), and range normalisation. This removes baseline effects.

Results and discussion

Micronal powder results

The resulting preprocessed spectra for the pure Micronal powder over the temperature range from 3° C to 60° C are shown below. Peak regions corresponding to the CH stretch clearly show the differentiation due to the associated phase changes with temperature. The phase change can be clearly seen in Figure 1a.

The phase change diagram was made using the pseudo-scores of the first latent variable, from PLSR analysis. As shown, there is a concomitant rise in scores at the transition temperature. On either side of the transition temperature, there is a relatively stable crystallisation state, as shown in the plateau regions. The phase change is not instantaneous, but occurs over a 3°C to effect the phase change.

Micronal-gypsum powder results

The combination of 30% Micronal in the hemihydrate gave similar results to the pure Micronal. The preprocessed spectra show the differentiation in the CH peaks due to shifts in crystallisation of the paraffins. These changes are primarily due to CH groups seen at 1700 nm and 2260 nm regions. A notable change from the pure spectra is the peak at 1921 nm due to waters of hydration from calcium sulfate hemihydrate (CaSO₄· $\frac{1}{2}$ H₂O). Figure 1b, derived from the scores of the first PLS latent variable again shows the transition between the two crystallisation states. In this case, as this is just a 30% (w/w) mixtures, in the hemihydrate, the transition is observed over 10°C and has shifted lower by approximately 3°C. However, the phases are still differentiated.

Gypsum mixture

The final example is the gypsum mixture after the hemihydrate was further hydrated and allowed to set. The preprocessing of the spectra was similar to the two previous examples, however, the effects of the water peak were removed by restricting wavelengths to (1600–1825 nm, 2145–2305 nm). Therefore only the relevant and useful CH regions were used in the PLS analysis. Figure 1c, constructed from the scores, is similar to that obtained from the mixture only. Again, there is an approximate 10°C change observed between the two phases, and a similar 3°C lowering in transition temperature is observed.

An analysis of PCA scores from the same data (not shown) shows a remarkably clearer picture of the phase transition. This indicates that the assumption of the presence of only a single phase-state at low temperatures in the two-point PLS model applied to this data is useful, but has limited validity. More sophisticated modelling is needed.



Figure 1. Phase diagrams of Micronal as expressed in PLS scores. (a) neat Micronal, (b) 30% w/w in CaSO₄· $\frac{1}{2}$ H₂O and (c) 20% w/w in CaSO₄·2 H₂O.

Conclusions

NIR has high sensitivity to the phase-state of many materials, and when these materials change phase-state with temperature the effects can be profound. The transitions appear are easy to calibrate for, unless the phase diagram is complex. Complexity in phase-state often arises in nearly pure materials, or when confinement occurs. Traditionally, these types of interactions have been studied using XRD, DSC and solid state NMR. NIR spectroscopy provides a useful complement.

For teaching, this system is easy to reproduce and analysis of the spectra is straightforward at the simplest level. The basic tools required are a temperature-controlled oven, NIR spectrometer, sample and Excel. There is additional underlying complexity that could be identified and characterized with further experimentation.

Acknowledgments

The authors wish to thank Dr Stephan Altmann of BASF for discussion and the Micronal[™] samples.

References

- 1. E. Dufour, G. Mazerolles, M.F. Devaux, G. Dubozb, M.H. Duployer and N. Mouhous Riou, *Int. Dairy* J. 10, 81 (2000).
- 2. D. Bertrand and C.N.G. Scotter, Appl. Spectrosc. 46, 1420 (1992).
- 3. H. Chung, S.Y. Choi, J. Choo and Y. Lee, Bulletin-Korean Chemical Society 25, 647–651 (2004).
- D.H. Igo and P. Chen, "Vibrational Spectroscopy of Solid-State Forms—Applications and Examples", in *Applications of Vibrational Spectroscopy in Pharmaceutical Research and Development*, Ed by D.E. Pivonka, J. Chalmers and P. Griffiths. Wiley, Chichester, UK (2007).
- 5. BASF Press Release, www.basf.com/group/pressrelease/P-05-369 (2005).