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Iso-activity Analysis of Phenol Crystals

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An iso-activity is essentially the inverse of an isotherm. It records the equilibrium uptake at different temperatures and constant vapor concentration. A combination of Raman Spectroscopy and Dynamic Vapour Sorption (DVS) iso-activity analysis has been used to study Phenol crystals.

Introduction

Sorption isotherms describe the amount of vapour adsorbed or desorbed at different equilibrium concentrations (partial pressures) and at a constant temperature. The shape of a sorption isotherm depends on the interaction between the vapour molecules and the solid sample at various concentrations and constant temperature, which allows for conclusions regarding the sorption mechanism. An iso-activity however, is essentially the inverse of an isotherm i.e. an iso-activity records the equilibrium uptake at different temperatures and constant concentration. Iso-activities, like isotherms, reveal a lot of information about the interactions occurring between a vapour and a solid. For example, diffusion constants measured at the same partial pressure but at different temperatures allow the determination of the activation energy of diffusion.

This paper describes the combination of Raman spectroscopy and Dynamic Vapour Sorption (DVS) analysis to study phenol crystals between 10 - 50°C and at 0% RH. At ambient temperatures, pure phenol is a white crystalline solid with a melting point of 40.91°C [1]; however, the melting point of phenol is quoted variously by different sources within a 40 - 43°C range [2]. The problem in determining an accurate melting point lies probably in the difficulty of getting the phenol absolutely dry. The crystals are often wet and discoloured, and sublime readily at room conditions; that is, solid phenol crystals have a high vapour pressure at these conditions [3]. Phenols are important raw materials in the production of plastics, adhesives, paints, varnishes, dyes, weed killers, drugs (phenolphthalein, salicylic acid, phenyl salicylate), surfactants, and odoriferous substances [1].

Method

DVS studies were performed on phenol supplied by Aldrich (purity > 99.5%). A sample size of 41 mg was analysed on a DVS automated moisture sorption instrument. The iso-activity test was then performed to investigate the melting point of phenol. The DVS iso-activity analysis records the equilibrium uptake at different temperatures and at constant % partial pressure; i.e. keeping the equilibrium vapour uptake constant whilst varying the sample temperature. For the iso-activity test the sample was exposed to temperatures from 10 to 50°C, with step increments of 1.0°C.

Raman spectra were acquired at different temperatures using the iRaman BWS415 instrument from BWTek. This instrument is connected via a specially designed adaptors which allow fibre optic probes to be coupled to the system. The adaptors accommodate probes with a diameter of 12mm. Therefore, a wide range of commercial Raman and NIR spectrometer models to be interfaced with the DVS Advantage which would allow the capability of taking Raman spectra of the sample *in situ*. For these experiments a laser of wavelength of 785 nm was used. Each spectrum is a mean value of 5 number of scans at a 100% laser power collected with an integration time of 30 seconds. Spectra were collected at the end of a temperature step increment. In addition, *in-situ* video images were collected at the end of each temperature step using the microscope option of the DVS-Advantage. Images were used to confirm visible changes in the sample.

Results

In Figure 1, the red curve, plotted on the left y-axis, shows a typical plot of the net percent change in mass of phenol (based on dry mass) versus time. The blue line, plotted on the right y-axis, traces the step-wise and controlled requested temperature. The continuous decrease in mass of the sample during the experiment is due first to sublimation (when still solid) or to vaporization (liquid) of phenol. Because the DVS instrument maintains a constant flow of fresh air around the sample, the rate of sublimation of phenol depends only on its sublimation vapor pressure, not being negatively affected by any build-up of phenol vapours around the sample [4].

From the iso-activity plot it can be observed that the volatilization rate of phenol is greater in the liquid state than in the solid state. This is graphically explained by the green dotted tangent lines drawn to the iso-activity plot in Figure 1: The absolute value of their slopes constantly increases positively as the vaporization rate of phenol increases due to the temperature changes.

From Figure 1, the melting point of phenol cannot be readily obtained. However, the change of phase temperature can be confirmed from the video images shown in Figure 2. Figure 2a shows the sample at the start of the experiment. Here, the sample is in a crystalline solid state. There is little visible change in the sample below 35°C. However, at and above 35°C, there is a distinct change in the visible appearance of the sample, depicted in Figures 2b and 2c. Figure 2d shows the sample at 40°C, just below its melting point, and still in the solid state. At 41°C, as shown in Figure 2e, the sample is already in the liquid state. This observable change from Figure 2d to Figure 2e confirms that phenol melts at some point between 40 and 41°C, as reported in the literature [2].

Raman spectra of Phenol, especially in the solid state, are in good agreement with previously published data [5]. The spectra collected between 20 - 45ºC (Figure 3) show a significant change at 40ºC, which is in good agreement with the DVS video images confirming the melting point transition of phenol. Spectra from 1 to 3 are essentially the same, confirming that no phase change has occurred in this range. However, spectrum 4 is already different from the previous three, with some of the characteristic peaks observed at lower temperatures not being resolved by the instrument. This may signal the onset of a phase change. Spectrum 5, obtained at 45ºC, contains no peaks that can be attributed to those observed in the solid state. This shows that phenol molecules are already in a different environment as in the solid state.

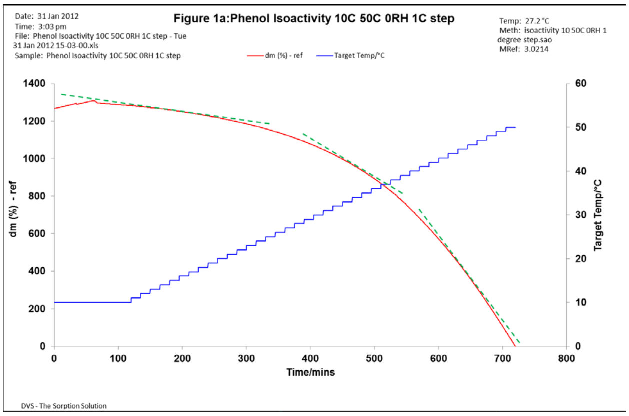

Figure 1. red: Phenol iso-activity between 10-50°C at 0% RH; blue: controlled step-wise temperature increments; green: tangent lines to the iso-activity plot showing an increase in the vaporisation rate as their absolute slope increases.

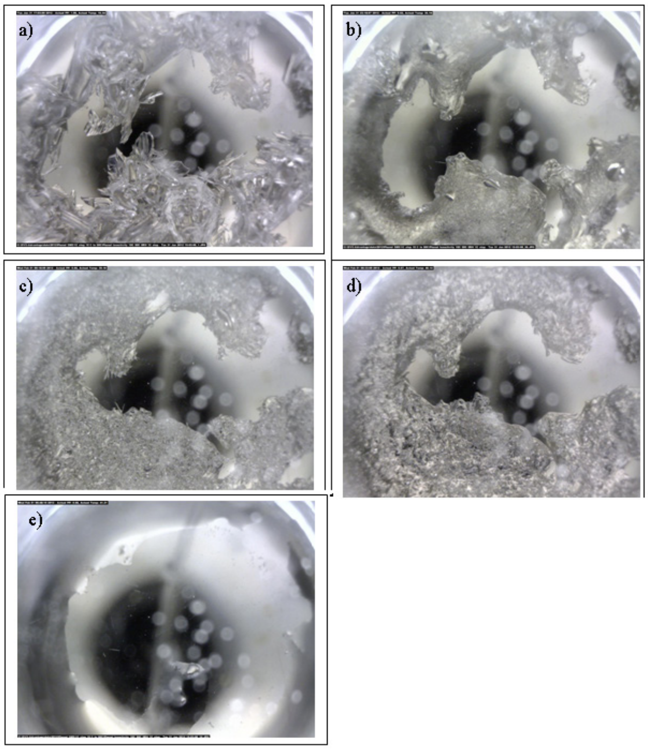

Figure 2. DVS microscope images of the Phenol at 0% RH. The conditions at which these images were collected are as follows: a) 10ºC, b)35ºC, c)39 ºC, d)40ºC and e)41ºC

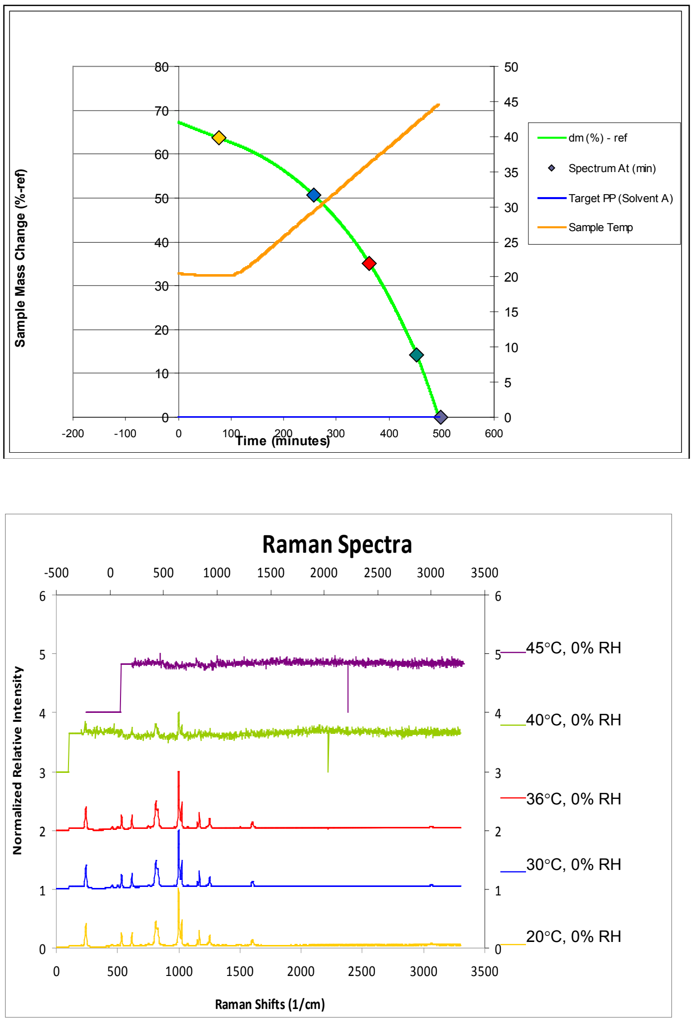

Figure 3. DVS a) Iso-activity between 10-50°C at 0% RH b) Raman spectra for Phenol crystals

Conclusion

This study demonstrates the power and flexibility of the DVS instrument to characterize the physical and chemical properties of solid materials. The iso-activity ramping experiment combined with the video images in DVS and the Raman spectra acquired in situ gave a crystallization point of Phenol which agrees very well with the literature value.

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