*Project 16**: Stochastic features of nucleation* Date: **20/08/10**	Author: **Donal Mealey** Strand: **Particle Engineering** Institute: University of Limerick

Title: Variations in the nucleation points observed during metastable zone width experiments

Principal Focus: The aim of this study was to capture the randomness associated with nucleation. This was examined by measuring the metastable zone width of the non polymorphic compound salicylic acid in a number of pure solvent systems during a constant cooling crystallization.

Experimental:

A visual method was developed to detect nucleation in a large number of samples simultaneously whilst controlling factors such as cooling rate, agitation, and temperature accurately.

1. Approx 250ml saturated solution of salicylic acid in pure solvent was prepared from solubility data (Nordstrom and Rasmuson 2006)
2. This solution was maintained at 5^0C above the saturation temperature for 24 hours and then divided into ten tubes of 20ml volume.
3. The tubes were sealed and left for a further 24 hours at 5^0C above the saturation temperature with 200rpm agitation.
4. Cooling crystallization experiments were conducted where the bath temperature was monitored and dropped at -10^0C/hour while agitation remained at 200rpm.
5. A video recorder in was used to detect nucleation in each tube and the temperature of nucleation was noted.
6. This could then be related to the solubility curves for the given solution (Nordstrom and Rasmuson 2006) and the supersaturation necessary for nucleation to occur could be calculated.
7. Once all tubes had nucleated the bath temperature was increased to 5^0C above the saturation temperature for 24 hours and the cooling cycle was repeated until at least 100 nucleation temperatures were generated for each system.

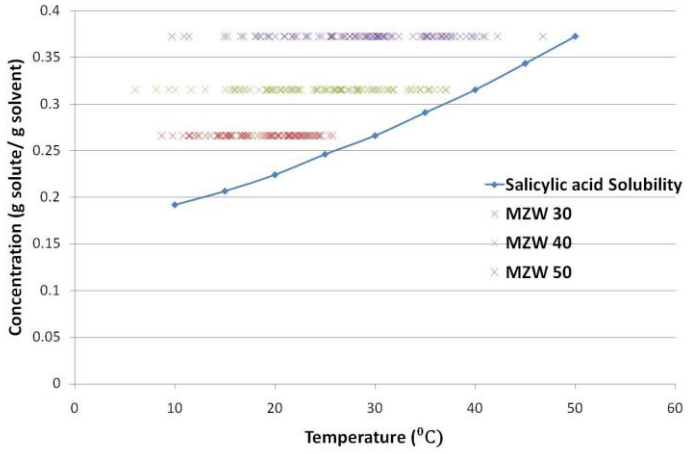

Figure 1: Metastable zone width data of saturated solutions of salicylic acid in ethyl acetate at three different temperatures of 30, 40, and 50 ⁰C. At least 100 samples are shown for each starting saturation temperature.

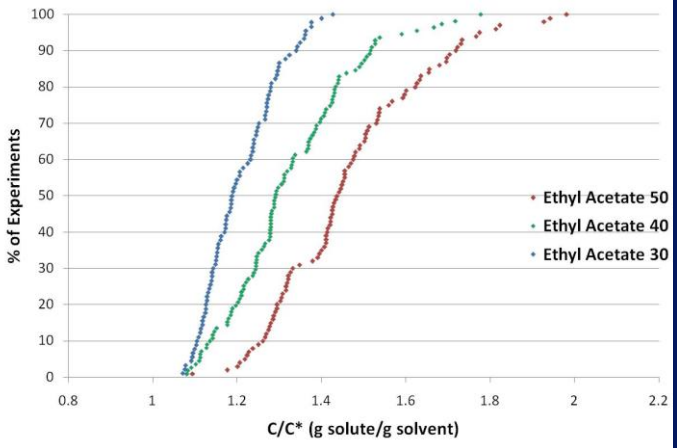

Figure 2: Cumulative critical supersaturation distribution for solutions of salicylic acid in ethyl acetate saturated at three different temperatures of 30, 40, or 50 ⁰C.

Discussion:

A large range of nucleation temperatures were detected for identical solutions undergoing cooling crystallization at a set cooling rate of -10^0C/min and agitation of 200rpm, as seen in figure 1. The supersaturations at which nucleation occurred at for each solution are plotted in figure 2. The stochastic nature of nucleation is evident here from the very wide range of nucleation supersaturations and temperatures seen for each system.

So far metastable zone width experiments have been conducted on salicylic acid in four different pure solvent systems, all giving large variations in the nucleation points.

Future Work:

It is intended to examine the metastable zone width of salicylic acid in a number of other pure solvent systems and to compare the nucleation data in order to try to explain the specific interaction the solvent has with the solvent molecules. Further possibilities exist in a new representation of the metastable zone by a region defined by the probability of nucleation as opposed to the current boundary line currently in use. Studying nucleation in terms of induction time experiments is also planned to gain further control over the experimental conditions and provide more insight into the stochastic nature of nucleation.

References:

Nordstrom, F. L. and Rasmuson, A. C. (2006) 'Solubility and Melting Properties of Salicylic Acid', Journal of Chemical & Engineering Data, 51(5), 1668-1671.