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CELLULAR MONOTECTIC MODEL SOLIDIFICATION

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Semi-annual Report

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Cellular Monotectic Model Solidification

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by Dr. William F. Kaukler UAH

Introduction:

This report summarizes the most recent experiments and results from this project. As the work is near completion, a brief compilation of points will be made as a more detailed report will soon be made that spells out everything.

Since the last report, more experiments were run, succinonitrile was purified to a superior level of purity, the phase diagram for succinonitrile and glycerol was filled out (figure 1) and considerable data was analysed on the growth morphologies that allowed a stability diagram (figure 2) to be prepared.

Experiments:

Great success was obtained for the fractional recrystallization purification of sn method I developed. The melting point of the best twice recrystallized sn was not raised by following with double distillation. This was tested using the Differential Scanning Calorimeter in Frazier's lab. The peak shape on melting was also proving that double distillation after double recrystallization did not improve the quality.

From the first series of runs made with hypermonotectic sn-glycerol, it was found that thinner cells were needed for the

satisfactory suppression of the worm morphology so that coupled growth of the two phase interface could proceed and to do so even under constitutional breakdown conditions. Special care was taken to manufacture as thin a cell as possible. The cells were dissected and measurements of the cell gap thickness were made. Now with very thin cells, although the micrographs have low contrast as a result, the desired cellular structures are readily formed. Originally, it was thought necessary to purposely inoculate the alloy in order to induce cell formation. This was to be done to otherwise pure original constituents. As it appeared that self-degredation of the solution with time and heat occurred, unknown impurities may have developed. The constitutional undercooling of these hypermonotectic alloys will still occur because of the excess solute in the solution. Monotectic freezing will occur, but rejection of excess glycerol into the L_1 phase will lead to constitutional undercooling, in theory. The attempt to grow the alloy inoculated with the orange-colored azobenzene, was a failure. The azobenzene did not significantly segregate to make the interface colored into clear solid and orange liquid as expected. I could expect this because experiments showed the azobenzene has a higher affinity for the glycerol than the sn. The inclusion of the azobenzene did not significantly alter the growth morphology, although measurements were not made to test this.

It seemed that the approach to cellular breakdown solely from excess solute was the best one. The stability diagram will

bear this out (probably). To fine tune this approach some measurements are needed to determine more accurately the planar to cellular transition for two hypermonotectic compositions. This will allow the appropriate equations to be used and see which mechanism is expected (Hellawell or Parr). The two compositions are needed to determine if the cellular to planar transition is indeed composition dependent. This should lead to a sloped line delineating the planar-cellular transition points at various compositions. The best compositions to try will be 8 and 16 weight per cent glycerol. The reasons more detailed measurements of this transition have not been made is simply that the study was one or cellular growth and not planar.

The collection of micrographs, when laid out by G/R, show that the cell size relationship can also be obtained. This series of measurements will be done to round out the study and make the final paper more of a study of cellular monotectic interfaces rather than of mechanism determination for alignment. The graphic tablet and computer will serve this measurement well.

Arrangements have been made with Frank Szofran to perform FTIR analysis on grown cells in order to see if segregation occurs and is so, by how much. This work will need scheduling with other users. It will help in the analysis of planar-cellular transitions and the theories for cell formation in monotectic systems. I have the absorption curve for sn and should easily find the one for glycerol. The instrument may be

sensitive enough to show the decomposition products in the cell.

Theory:

Diagrams to differentiate the two mechanisms for particle alignment were prepared. These are shown in figures 3 and 4. They do not illustrate the results obtained experimentally. Enhanced photographs and another diagram will be used to show our results. The results are not definitive for the case where large liquid particles could be pushed and subsequently undergo Rayleigh breakdown into aligned spheres. In order to see if this could happen, the particle pushing theories have been developed. The results, although not reproducible with the literature values will help when properly refined. The tests of the theories do not match the literature because the data used in the literature only fits the model they propose. A general model does not exist as yet. Also, and more importantly, the data in the models were for dense, solid particles generally of a metal type. In our case, the viscosities and thermal conductivities are not metal-like at all. The best models work with metallic spheres pushed by an organic solid. This way, specific thermal and interfacial conditions are set. These models do not have applicability to our systems either the organic or the metal monotectic. The Kaukler model may be the easiest to prove useful, but to extend the model to include gravity effects may take more time.

In an effort to develop the models for our organic system,

considerable time was spent collecting the raw data for the system and developing the solution parameters from the pure component parameters. This is not easily done for viscosities or diffusion coefficients for organics. It may be easier to measure the solution viscosity for a couple of points and fit the solution models to those points. This may not take much time and is important to the study.

Calculations were made to calibrate the gradient stage thermal gradients that develop in the cell for different growth rates and thermal inputs to the hot and cold blocks. This analysis was needed to obtain the proper G for the G/R analysis that is crucial to this study. Little mathematical analysis could be performed and would consume more time than is appropriate for this short project. The thermal characterization will also permit prediction of operating conditions other than those that have been used to date. Thus, if growth at higher rates would be desired, for example, a steeper gradient could be employed to stabilize the interface. This is important in the determination of the planar to cellular transition since the long times of growing at low speeds needed for planar growth can accelerate solution decomposition. Higher rates should make decomposition a smaller problem. Note however that higher rates also mean that diffusion rate sensitivity could also play a part in the analysis. This opens up a new question about what rate of growth can sustain cell growth at low gradients. There may be a need to try very low G and high R but still have the same

G/R in further experiments.

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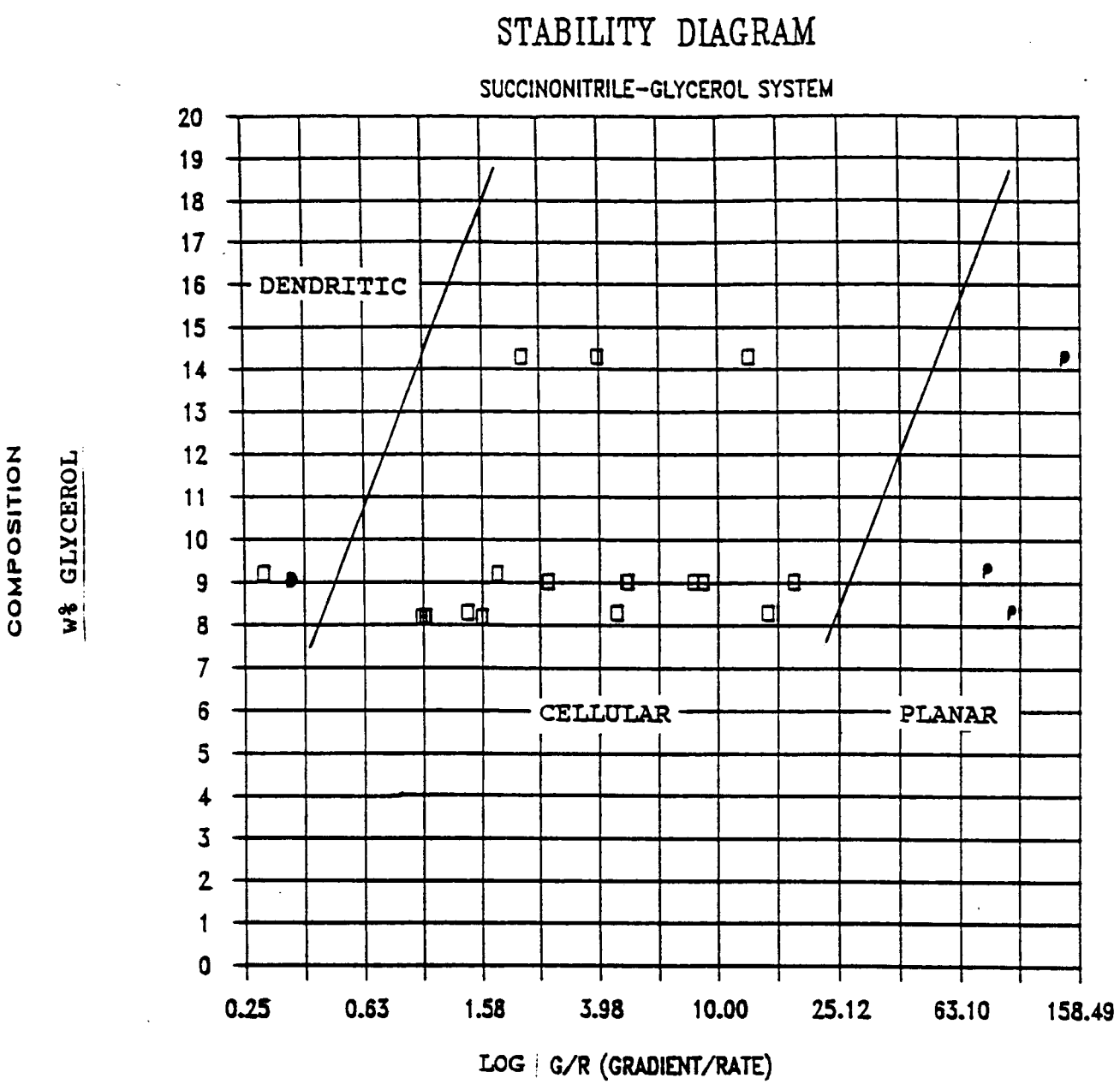
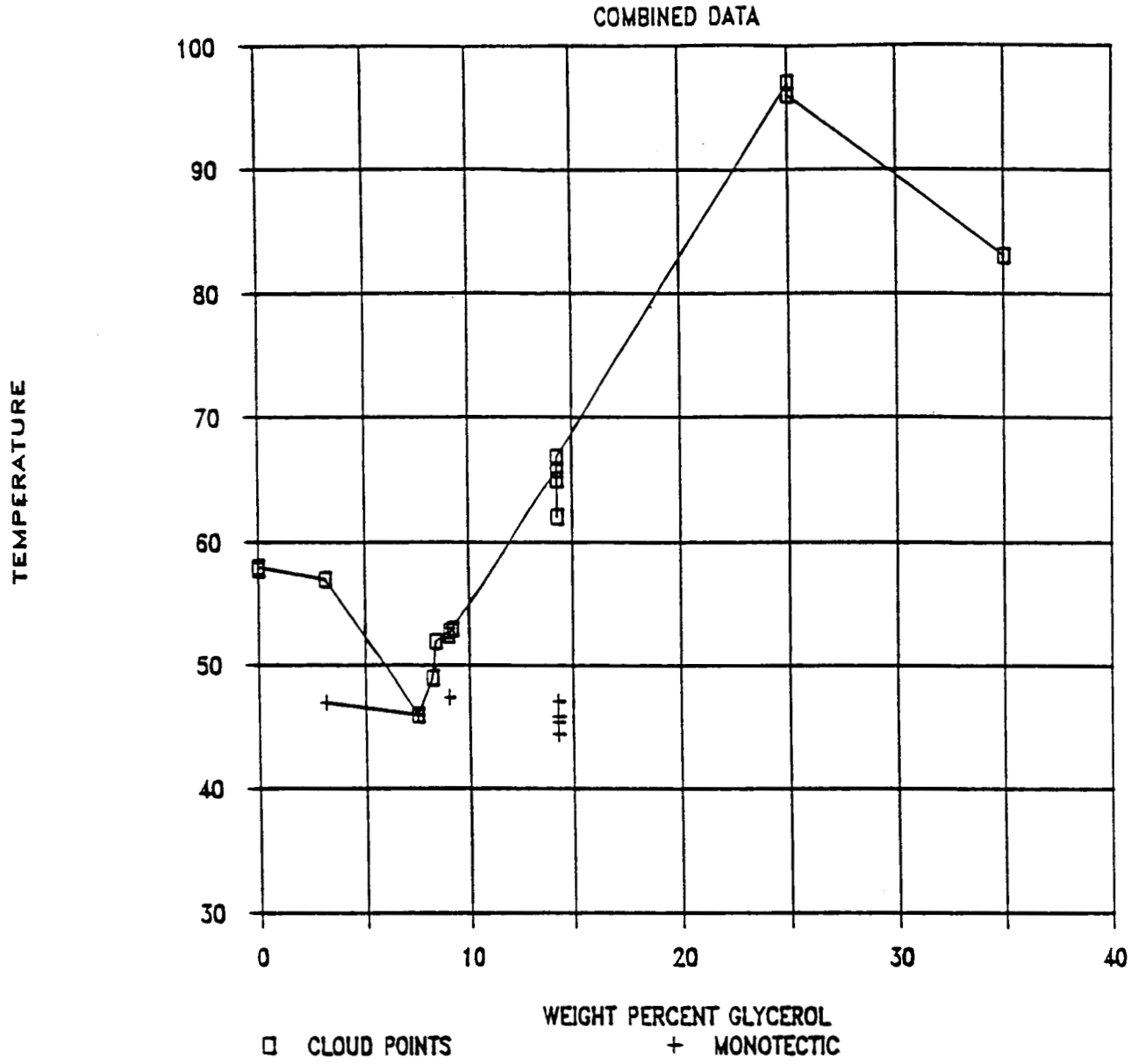

STABILITY DIAGRAM
SUCCINONITRILE-GLYCEROL SYSTEM
COMPOSITION
w% GLYCEROL
20
19
18
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
DENDRITIC
CELLULAR
PLANAR
0.25
0.63
1.58
3.98
10.00
25.12
63.10
158.49
LOG G/R (GRADIENT/RATE)

SUCCINONITRILE-GLYCEROL PHASE DIAGRAM



Monotectic Liquid
Cell
Cell
Parr et al Mechanism
Hellawell's Mechanism