DETERMINATION OF SATURATION AND FREEZING POINT CURVES FOR DIAZONIUM SALT SOLUTIONS – USING IN SITU INFRARED SPECTROSCOPY

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A significant number of incidents have been attributed to the rapid decomposition of inadvertently isolated solid diazonium salts. Studies were initiated to determine the process boundaries beyond which precipitation of these salts from solution may occur. In a previous study in this laboratory, it was demonstrated that the crystallization of diazonium salts could be observed by monitoring the infra-red absorption spectra using a Mettler-Toledo (ASI) ReactIR. The reactor parameters are controlled utilizing the RC1 Reaction Calorimeter. A decrease in the IR absorption at a frequency unique to the diazonium salt indicates a decrease in concentration as the diazonium salt precipitates from solution or increases as other salts precipitate or ice formation occurs. This experimental technique has now been refined to give more accurate saturation curves for the diazonium solutions. It can also be used in systems where more that one salt can precipitate or to produce freezing curves for the solutions. The transition temperature is determined by slowly reheating the solution at a controlled rate. A break in the curve for the plot of absorbance vs. temperature is taken to be the saturation temperature or freezing point for that concentration.

Keywords: decomposition, diazonium salts, crystallization, saturation curves, freezing curves

Introduction

Solid diazonium salts can be shock or friction sensitive. Inadvertent isolation of the solid salt in filters and transfer lines has lead to serious incidents including fatalities. In order to prevent isolation of the salts, the properties of these solutions must be understood.

To study the physical properties of diazonium solutions, a method was needed to accurately determine the temperature below which the solutions become saturated. This analysis is often complicated by the fact that the solutions can super-saturate, other salts may be co-precipitating, and solid by-products may be formed in the synthesis reaction.

Previous experiments, solutions of diazonium salts containing a nitro group were cooled to approximately −20°C and a nitro band in the IR was observed. A decrease in the absorbance of was used to indicate that the diazonium salt had precipitated. In a series nearly 20 experiments, the data from just one experiment was consistent with diazonium precipitation. Recently this technique has been modified and its usefulness can be illustrated in some screening experiments recently started on 2-nitrobenzenediazonium bisulfate.
Observation of coprecipitation of diazonium and sulfate salts.

As the diazonium solution is cooled, an exotherm is seen when the temperature reaches 3°C as evidenced by the sharp increase in Tr–Ta. As the solution cools only a small increase in power to the agitator (Rt) is seen. When the temperature reaches −10°C, a second exotherm is seen along with a sharp increase in Rt.

With higher concentrations of sulfuric acid, a different result is seen. Sulfate precipitates at a lower temperature (−4°C). The solution was cooled to −10°C and held for two hours. At this point a very small amount of diazonium crystals were added to the slurry. After the addition of the crystals, a very small exotherm is observed along with a decrease in the absorption of the nitro band.

Examination of the IR data helps to explain the data. With the first exotherm, a decrease is seen in the intensity of the sulfate band while a small increase is seen in the intensity of the nitro band absorption. This indicates that a sulfate salt is precipitating. With the second exotherm, both the nitro and the sulfate bands increase in intensity. This, along with the large increase in Rt, indicates that the aqueous solution freezing.

The slurry was then slowly warmed until all salts had dissolved. Plots of absorbance vs. temperature for the sulfate and nitro bands are shown below. The break in the curve for the nitro band at −3.2°C gives the diazonium salt saturation temperature. A break in the sulfate curve indicates that the sulfate is all dissolved at 1°C.

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Work with this diazonium salt is still in progress. In these screening experiments, the warming rates were typically 0.1 to 0.2°C min⁻¹. Better resolution can be obtained with slower ramp rates. In the experiments below rates of 0.02 to 0.05°C were used.

**Saturation curve for a diazonium salt**

Again the diazonium salt in these experiments contained a nitro group providing a strong band to use as an IR handle. In these experiments a reaction mass was cooled until precipitation of the diazonium salt was indicated by the sharp decrease in the nitro band. After precipitation was observed the reaction mass was warmed at 0.05°C.

An absorbance vs. temperature curve is plotted for the slow warming phase of the experiment.

From a series of experiments, a saturation temperature vs. diazonium concentration curve can be generated.

**Freezing point curve**

An example of a freezing point curve is shown below. In this case, −30°C brine is used to cool the synthesis reaction. On occasion, a bag filter in the transfer line would blind during transfer. Washing the filter with water to the bag filter would clear the filter. These test were conducted to see if this diazonium salts could precipitate.

The reaction mass was cooled until an increase in the absorbance of the nitro band and a large increase in Rt indicated the solution was beginning to freeze. The reaction mass was then warmed at 0.04°C min⁻¹.

In this case, the freezing point can be obtained from a plot of absorbance vs. temperature for the warming phase of the experiment.
Using the techniques described above, a curve was generated that predicts the freezing point based on the mole fraction of water in the solution. The mole fraction of water can be calculated using the diazonium chloride and hydrochloric acid assays of the solutions, and then assuming that an equal molar amount of sodium chloride is produced in the reaction.

No indication of precipitation of a diazonium salt was observed with this series of experiments, however the possibility of super-saturation has not yet been completely excluded in this system. Our current theory is that the blinding of the filter is most likely due to ice crystals that melt when the filter is washed with water.

Conclusion

The combination of in-situ infrared spectroscopy with the RC1 calorimeter is a useful tool to investigate the properties of diazonium solutions and qualitatively identify the precipitate. Diazonium salts have a tendency to form super-saturated solutions. The possibility that the higher concentrations of 2-nitrobenzene diazonium chloride solutions are super-saturated has not yet been excluded.

The only way to insure that there is no crystalline diazonium salt will be present is to remain above the saturation temperature.

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