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**A Visual Cell for Measuring the
Solubility of Prograde Soluble
Salts in Water at High
Temperatures and Pressures**

Robert C. Moore
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MANAGED BY
MARTIN MARIETTA ENERGY SYSTEMS, INC.
FOR THE UNITED STATES
DEPARTMENT OF ENERGY

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CHEMICAL AND ANALYTICAL SCIENCES DIVISION

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SOLUBLE SALTS IN WATER AT HIGH TEMPERATURES AND PRESSURES

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A VISUAL CELL FOR MEASURING THE SOLUBILITY OF PROGRADE SOLUBLE SALTS IN WATER AT HIGH TEMPERATURES AND PRESSURES

Robert C. Moore, John M. Simonson, and Robert E. Mesmer

ABSTRACT

An apparatus has been constructed for measuring the solubility of prograde soluble salts in water at high temperatures and pressures. The apparatus consists of a visually accessible cell thermostated in a rocking furnace. The apparatus allows for rapid, accurate solubility measurements for temperatures over 650 K and pressures up to 170 bars. The cell was constructed of platinum with sapphire windows and gold seals for corrosion resistance. A 3x telescope is used to observe the phase change in the cell. A key feature of the cell is the ability to control the system pressure. A section of small bore platinum tubing is used to connect the cell to an external pressure source. The tubing can remain open to the pressure source or be sealed off during a measurement. To minimize equilibration times, the entire apparatus was mounted to a rocking frame which can operate in the horizontal or vertical position. The apparatus was tested by measuring the solubility of NaCl in water at temperatures between 345 and 516 K at saturation pressure. The results are in good agreement with existing literature values.

INTRODUCTION

High temperature, high pressure solubility measurements of salts in water are needed for geochemical models and geothermal, fossil fuel, and nuclear power plant operation. However, solubility measurements of prograde soluble salts are experimentally difficult. With a few exceptions, very little high temperature solubility data exist for prograde soluble compounds. The conventional method of measuring solubility, direct sampling of a saturated solution held at constant temperature and pressure, is impractical because of precipitation of salt in the sample lines and sample vessel.

Early studies of prograde soluble compounds used novel approaches for obtaining solubility data. For example, Waldech et al.(1) developed a bomb with an internal needle valve and sample container for direct sampling. The technique was very tedious and time consuming because the apparatus had to be cooled to room temperature, disassembled, and flushed for analysis for each data point. More recently, other techniques, such as isopiestic studies(2) and the synthetic method(3), have been used. Isopiestic methods are based on the principle that two solutions of non-volatile solutes will distill from one to the other until their concentrations are such that the solutions have equal vapor pressure.(2) Major drawbacks of this method are the time required for equilibrium to be reached is typically long, particularly at low temperatures, and an in situ weighing is required. The synthetic method entails the preparation of a solution of known composition and the visual determination of the temperature at which a phase transition has occurred. The solution is typically sealed in a Pyrex or silica tube, and rocked or vibrated in a variable temperature furnace with an observation slit. (3) The accuracy of the measurement depends on the ability to detect the last trace of dissolving solid, accurate knowledge of the weight of salt and water, and the sensitivity of temperature control.(2) The technique has been used in this laboratory for more than 25 years

for determining solubility, liquid-liquid immiscibility, and studying critical phenomenon. (3,5-11) The major drawbacks of the method are the inability to work at pressures other than the saturation vapor pressure of the solution and dissolution of the silica cell when working with alkaline solutions.(4)

In this work, a rocking visual apparatus has been built for measuring the solubility of pure salts and salt mixtures in water. The visual cell is constructed entirely of platinum with gold seals and sapphire windows for corrosion resistance. A key feature of the apparatus is the ability to control the system pressure. A section of platinum tubing is used to connect the cell to an external pressure source. The visual cell has been tested by measuring the solubility of NaCl in water at seven different temperatures between 345 and 516 K. The solubility of this compound at high temperatures is well known.(4,13) The apparatus has been tested to temperatures over 650 K and pressures up to 170 bars. The technique is relatively fast when compared with other methods and can provide accurate data for salts that exhibit a strong positive temperature dependence of solubility.

DESCRIPTION OF APPARATUS

Figure 1 is photograph of the visual cell components in an exploded view. The main component is the platinum body piece. This piece is approximately 2.55 cm long with a volume of 0.25 cc. Sapphire windows, 0.64 cm thick, (ESCO products, Oak Ridge, NJ) are sealed to each end of the cell body using gold washers seated inside the cell. The washers were made from 8 mil gold sheet and are annealed before each use. The two additional gold washers shown in the photo are placed between the windows and follower pieces to prevent breakage of the windows.

A schematic diagram of the assembled cell is shown in figure 2. The s.s. enclosure containing the cell is held together with four 1/4" dia. bolts. The pressurization line is connected to the cell body using a platinum ferrule gold soldered to the line. A

FIG. 1. Photograph of visual cell for measuring solubility of prograde soluble salts. Body piece is constructed of platinum with an internal volume of 0.25 cc. Phase changes are observed through sapphire windows sealed in place at each end with gold washers. Additional gold washers are placed between follower pieces and windows to prevent breakage of windows. Body piece is constructed of 316 s.s.

FIG. 2. Schematic diagram of assembled visual cell. Platinum pressurization line is sealed to platinum cell body with platinum ferrel gold soldered to line.

1/16" dia. hole was drilled through the s.s. shell and into the platinum body approximately 1/10 " deep for use as a thermowell.

The visual cell assembly was mounted inside a Marshall tube furnace (1.5' long with a 2.5" bore) attached to a rocking frame to provide mixing in the cell and minimize equilibration times. The apparatus is shown in figure 3. The visual cell was mounted to an aluminum strip using two 1/4" dia. bolts. The entire assembly was then secured in the tube furnace. The furnace was mounted on an aluminum plate connected to a rocking motor. At one end of the plate, a Specwell 3x telescope was mounted for viewing the cell contents.

A variable intensity light was mounted at the other end of the plate. Two glass cylinders were placed on each side of the cell to provide a clear viewing path. Blanket ceramic insulation was packed around the glass tubes to hold them in place and reduce heat losses. Between observations of the cell contents, pieces of insulation were used to seal the ends of the furnace. A Barber-Colman 560 temperature controller was used to control the furnace temperature to ± 1 degree.

The entire assembly can be rocked through 45 degrees in the horizontal or vertical position. Typically, the cell was rocked in the horizontal position between observations, and the cell contents were viewed while the apparatus was locked in the vertical position. In this position, salt crystals would collect on the bottom cell window and could be easily seen.

PERFORMANCE

Experimental Materials and Procedure

Water purified using a Barnstead NANOpure Ultrapure Water System was used. NaCl was purchased from Fisher Scientific. The NaCl was > 99.9% pure and was used after drying overnight at 433 K in a vacuum oven.

The cell was charged with salt and solvent gravimetrically

FIG. 3. Rocking Frame/Visual Cell for measuring salt solubility. Furnace can be rocked in vertical or horizontal position. 3x telescope is used to view phase change in visual cell.

with a precision of 0.0001 g. Salt solubility was determined by observing the phase change while increasing the cell temperature. The cell was rocked in between observations to minimize equilibration time. Typically, the temperature was rapidly increased until only a small amount of solid remained. Near the phase change the temperature was slowly increased at a rate of approximately 1 degree per 15 minutes. A typical measurement could be taken and repeated in a single day. Measurements were repeated for every solubility point.

Results and Discussion

The results from the solubility measurements for sodium chloride are given in table I. Since values were determined at the saturation pressure of the solutions, the pressurization line was not needed and was removed during these measurements. The values have been corrected to take into account water saturating the vapor space of the cell. The vapor space was estimated to be one-half of the total cell volume (0.125 cc), based on visually observing the liquid level in the cell while in the horizontal position. In the correction procedure, vapor densities, activity coefficients, and osmotic coefficients were calculated using the correlations of Archer.(12) At temperatures less than approximately 450 K the correction to the data is less than 1 percent and considered within the experimental uncertainty of the measurements. For higher temperatures, the correction becomes more significant. At the highest experimental temperature of 516 K, the correction amounts to approximately 3 percent of the gravimetrically determined concentration.

The estimated accuracy of the temperature measurements is ± 1 K. This value is based on the accuracy of temperature control and the reproducibility of the measurements. The accuracy of this method depends strongly on the temperature dependency of the salt solubility. For NaCl, large increases in solubility coincide with relatively small temperature changes.

Table I. Solubility of NaCl in water measured with a rocking visual cell. Values have been corrected for water in vapor space of cell.

Temperature (K)	NaCl Solubility (molality)
345	6.49
392	6.83
442	7.60
443	7.53
472	7.94
495	8.30
516	8.79

Figure 4 is a plot of the experimental data along with literature data from Linke and Seidell(4) and Lui and Lindsay(13). The literature data from Linke and Seidell represent a compilation from several sources. The lines drawn through the literature data represent polynomial fits and are only presented to guide the eye. For all of the experimental values, there is good agreement with literature values. Higher temperature runs for NaCl will be performed at a later date. However, the correction to the data for vapor phase saturation at such temperatures may limit the accuracy of the data.

In addition to the solubility measurements for NaCl, the cell was tested to temperatures over 700 K and pressures in excess of 170 bars. Because of thermal expansion at the higher temperatures (> 520 K), the cell end caps had to be tightened periodically as the temperature was increased. However, there were no indications of any leaks even after more than 8 hours of operation at high temperatures.

The sapphire windows have also been tested at high temperature with alkaline solutions. Experiments at temperatures below 530 K indicated no observable dissolution. At temperatures between 530 and 650 K, the windows showed some signs of dissolution. Earlier experiments with quartz windows indicated severe dissolution at high temperatures.

For experiments performed at pressures other than saturation conditions, there were concerns over condensation of solvent inside the pressurization line. Therefore, a method to seal off the line after pressurization of the cell was devised. A 1/32 " OD line was used to connect the cell to a 1/16" OD line connected to a pressure source. A small piece of gold was placed inside the tubing next to the opening of the 1/32 " tubing. After pressurizing the cell, a torch was used to heat the outside of the tubing and melt the gold sealing the inner tube. This technique worked very well and will be examined further in future experiments.

In addition to solubility measurements, the cell can be used for studying liquid-liquid immiscibility, critical phenomenon, and

FIG. 4. Solubility data for NaCl in water measured with rocking visual apparatus plotted along with literature data. Measurements performed at saturation conditions. All values have been corrected for saturation of vapor phase with solvent. Polynomials fit to literature data are to guide the eye only.

solid phase changes. Additionally, the cell may be easily modified for flow type experiments. Two HIP type ports are already present in the s.s. enclosure piece.

CONCLUSIONS

A rocking visual cell has been built capable of measuring rapidly the solubility of salts in water at high temperature and pressure. The apparatus is particularly useful for measuring the solubility of prograde soluble salts where other methods are unsuitable. The cell can be operated to temperatures over 650 K at pressures to 170 bars. The accuracy of the technique depends on the temperature dependence of the salt solubility. For the NaCl-water system, data were obtained between 345 and 516 K. The results are in good agreement with literature values. Measurements taken with this apparatus must be corrected to account for saturation of the vapor space in the cell with the solvent. For water, this correction is very small for temperatures below 450 K, but becomes significant at higher temperatures.

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