Experimental determination of the PVTX properties of aqueous solutions at elevated temperatures and pressures using synthethic fluid inclusions: H₂O-NaCl as an example

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Abstract: The Synthetic Fluid Inclusion Technique provides a new and relatively simple experimental procedure for determining the Pressure-Volume-Temperature-Composition (PVTX) properties of aqueous solutions at elevated temperatures and pressures. With this technique, samples of the fluid(s) are isolated in quartz (SiO_2) at elevated temperatures and pressures and maintained for later laboratory study. Application of the Synthetic Fluid Inclusion Technique to determine isochores, critical properties, freezing-point depression, NaCl solubility, and liquid-vapor and liquid-solid phase equilibria in the H_2O-NaCl system over a wide range of PTX conditions is described.

INTRODUCTION

The past decade has seen a renewed interest in the PVTX and thermodynamic properties of aqueous solutions at elevated temperatures and pressures, particularly at P-T conditions in the vicinity of the critical point. This interest has been driven by activities in diverse fields, including the discovery of salt-rich supercritical brines emanating from submarine hydrothermal systems (1), development of techniques for the destruction of hazardous chemical wastes using supercritical water oxidation processes (2), engineering and industrial applications which require information on aqueous solutions at elevated temperatures and pressures (3), and improved thermodynamic models for aqueous solutions which require basic experimental data both for model development and testing (4).

Experimental studies of the PVTX properties of aqueous solutions at P-T conditions near and beyond the critical point of water have been hampered by numerous problems, including corrosion of the autoclave and the inability to obtain samples at elevated P-T conditions, particularly for solutions containing high concentrations of salts or volatile components. Recently, Bodnar and Sterner (5-8) described an experimental technique for sampling and isolating aqueous solutions at high temperatures and pressures by trapping a small amount of the solution as a fluid inclusion in quartz (SiO_2). The Synthetic Fluid Inclusion Technique (SFIT) has been tested and proven to be an effective means of studying the PVTX behavior of aqueous solutions over a very wide range of pressure, temperature, and composition conditions. In this paper, application of the Synthetic Fluid Inclusion Technique to experimental determination of the PVTX properties of the system H_2O-NaCl is described.

THE SYNTHETIC FLUID INCLUSION TECHNIQUE

The Synthetic Fluid Inclusion Technique has been described in detail elsewhere (5, 6), and will only be summarized here. With SFIT, samples of the fluid are trapped by healing fractures in quartz at a known elevated temperature and pressure. Cylinders of quartz ~2-3 cm long and 4 mm in diameter are cut from Brazilian quartz that contains no natural fluid or solid inclusions. The quartz cores are heated to ~350°C and removed from the oven and immediately immersed in cold, distilled water. The instantaneous drop in temperature causes thermal cracking of the quartz, producing abundant closely-spaced fractures that extend from the edge into the core approximately one-half of the core radius. The fractured cores are removed from the distilled water and placed into a vacuum oven at ~110°C to remove any water that entered the fractures during quenching. After drying, the cores are stored in a vacuum desiccator until needed for experiments.

To conduct a synthetic fluid inclusion experiment, a fractured quartz core is placed into a platinum capsule along with the solution of interest and the capsule is sealed with an arc-welder. The capsule, containing the core and solution of known composition, is then placed into a high pressure autoclave and heated to experimental conditions. The pressure inside of the vessel, and inside of the flexible-walled capsule, is maintained and controlled by pumping water into the vessel using high-pressure liquid pumps. The temperature during the experiment is monitored using thermocouples placed in the vessel, and pressure is monitored using transducers and/or Bourdon-tube gauges.

During the experiment at elevated temperature and pressure, some of the solution loaded into the capsule enters the fractures in the quartz and causes the fractures to partially heal through dissolution and re-precipitation processes. As a result, small amounts of the solution become isolated in the partially healed fracture. These isolated pockets of solution are referred to as fluid inclusions. Natural fluid inclusions are ubiquitous in rocks and minerals from a variety of geologic environments (9), and have been used for decades by geoscientists to infer formation temperatures and pressures of minerals and compositions of fluids present during their formation. Previous determinations of PVTX properties of aqueous solutions using synthetic fluid inclusions (5, 8, 10-13) have confirmed that the density and composition of the fluid trapped in the inclusions are representative of the bulk fluid present in the capsule at the conditions of trapping, and that the density and bulk composition do not change during quenching to ambient conditions.

Following quenching of the sample and removal of the capsule from the pressure vessel, the quartz core containing partially healed fractures decorated by fluid inclusions is cut into disks approximately 0.25 to 0.50 mm thick and polished on both sides. The disks are examined under the microscope and fluid inclusions suitable for microthermometric analysis are selected. Most often the inclusions range in size from less than one µm to several tens of µm in diameter. Inclusions less than ~2-3 µm are generally too small to study, and inclusions larger than ~50 µm are rare. When observed at room temperature, the inclusions generally contain two or more phases (Fig. 1). Note, however, that the inclusions originally trapped a single, homogeneous fluid phase at the P-T formation conditions, and the multiple phases observed at room temperature are the result of phase changes that have occurred under isochoric conditions during cooling. With the SFIT, the inclusions are reheated (or cooled) in the laboratory using a heating/cooling stage mounted on a petrographic microscope, and the temperatures at which the various phase changes occur during heating and cooling are recorded. The measured temperatures of phase changes, and an understanding of the nature of the phases that are appearing or disappearing at each temperature, provide the basic information needed to determine PVTX properties of aqueous solutions using the SFIT.

A pure water or low salinity aqueous fluid inclusion usually contains two phases at room temperature - a liquid phase and a vapor bubble that is essentially a vacuum (Fig 1A, B). The relative sizes of the liquid and vapor phases reflects the density of the inclusion, with higher density inclusions having smaller vapor bubbles and *vice versa*. When liquid-rich inclusions are heated in the fluid inclusion stage, the inclusion follows the liquid-vapor curve for the solution in the inclusion (Fig. 2). During heating, the vapor bubble decreases in size and eventually disappears at a temperature referred to as the *homogenization temperature*, abbreviated as *"Th"* in the fluid inclusion literature (Fig. 2). With further heating, the one phase inclusion follows the isochore through the one phase liquid field (Fig. 2). Note that for an inclusion having a bulk density less than the critical density (vapor-rich inclusion; Fig. 1B), the vapor bubble increases in size during heating from room temperature and completely fills the inclusion at the homogenization temperature. With further heating this inclusion follows an isochore through the one phase vapor field.

Aqueous inclusions having higher salinities and those containing additional volatile components, such as CO_2, may nucleate more than two phases during cooling from formation conditions. At room temperature these inclusions may contain various solid phases such as halite or sylvite (Fig. 1D-F) or additional fluid phases such as liquid and/or vapor CO_2 (Fig. 1C, F). The temperatures of disappearance of these various phases during heating provides information on phase relations in these systems, and the temperature at which the last two phases homogenize provides one point along the isochore. The known formation temperature and pressure conditions define a second point along the isochore.
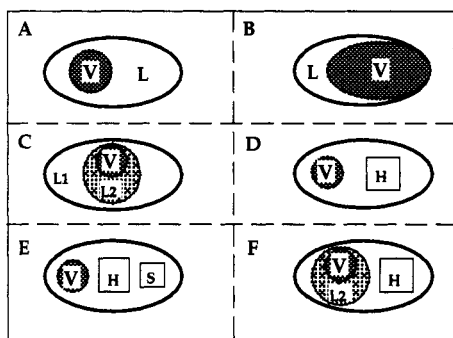

Fig. 1. Room temperature phase relations of typical fluid inclusions in the H_2O-"salt"-CO_2 system. **(A)**. Two-phase, low-salinity liquid-rich inclusion; **(B)**. Two-phase, low-salinity, vapor-rich inclusion; **(C)**. H_2O-CO_2 inclusion containing liquid H_2O (L1), liquid CO_2 (L2), and CO_2 vapor (V); **(D)**. High-salinity, halite-bearing (H) inclusion; **(E)**. High-salinity inclusion with halite (H) and sylvite (S); **(F)**. H_2O-$NaCl$-CO_2 inclusion with liquid (L2) and vapor (V) CO_2, halite (H) and liquid water saturated in $NaCl$ and CO_2.
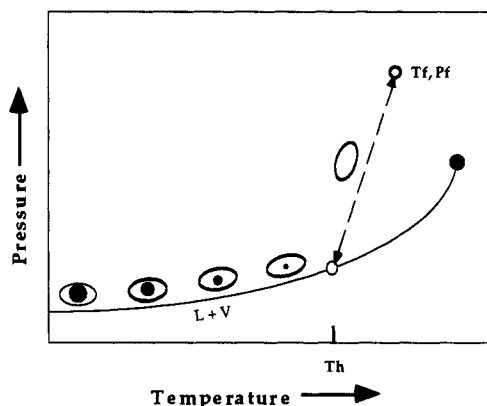
Fig. 2. Behavior of a low-salinity, liquid-rich aqueous inclusion during cooling from the formation T & P (Tf, Pf) to room temperature. During cooling the inclusion follows the isochore (dashed line) through the one-phase liquid field until it intersects the liquid-vapor curve (L + V). At this point the inclusion nucleates a vapor bubble and follows the liquid-vapor curve with continued cooling. In the heating/cooling stage, this process is reversed and the temperature of homogenization (Th) is measured.

VOLUMETRIC PROPERTIES

Experimental data on PVT properties of aqueous solutions are fundamental to understanding the behavior of natural solutions deep within the Earth. Moreover, volumetric properties of aqueous solutions, and the pressure and temperature derivatives of these properties, are critical to the development of thermodynamic models for aqueous solutions. Unfortunately, the experimental data base for PVT properties of aqueous solutions is very limited, and most published studies cover only very narrow ranges in PTX conditions. This lack of data is related to the difficulty of obtaining such data, and to the expensive and sophisticated laboratory equipment needed for such studies. Recently, however, Bodnar and Sterner (8) showed that the SFIT provides relatively accurate PVT data for aqueous solutions over a broad range of PTX conditions.

The procedure used to obtain PVT data using the SFIT is as follows. For a given composition, fluid inclusions are trapped at various temperatures and pressures covering the range of P-T conditions over which information is sought (Fig. 3). Then the homogenization temperatures of the inclusions are measured using a heating stage, and a line in P-T space connecting the original formation conditions (Pf, Tf; Fig. 1) with the temperature (Th; Fig. 1) and pressure at homogenization define a line of constant volume or isochore. This procedure assumes that the isochores are straight lines in P-T space, and this assumption is generally valid over P-T ranges of several kilobars and several hundred degrees Celsius.

The SFIT has been used to determine the isochores for H_2O-NaCl solutions over the range 0-50 wt.% NaCl, T≤800°C and P≤6 kbars. Figure 3 shows the P-T points at which synthetic fluid inclusions were trapped for each composition, and Fig. 4 shows smoothed isochores for a composition of 20 wt.% NaCl. It is important to note that the SFIT can be used to define the location in P-T space of a line of constant volume (isochore), but does not provide the density or molar volume for the isochore. In order to obtain volumetric data for aqueous solutions using SFIT, the density of the solution at some point along the isochore must be known. Fortunately, densities of many aqueous solutions are known along their vapor-saturation curves. Because fluid inclusions homogenize along the vapor-saturation curves, these data may be used to obtain the densities at any point along the isochores, i.e., at P-T conditions in the one-phase liquid field.
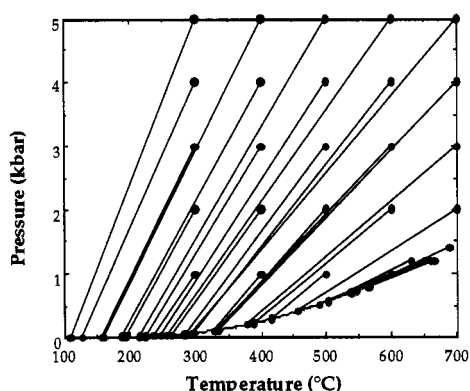

Fig. 3. P-T grid points at which synthetic fluid inclusions were trapped to obtain PVT data for the system H_2O-NaCl. A line connecting each P-T trapping condition with the measured homogenization temperature (lower solid dot along the L-V curve) defines the isochore.
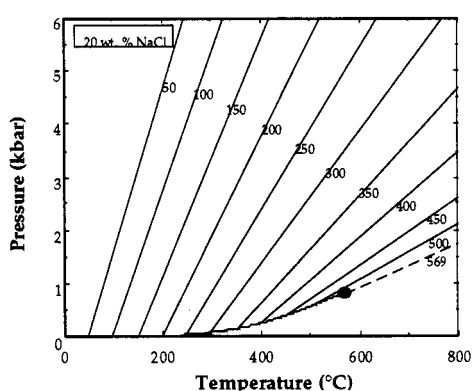
Fig. 4. Smoothed isochores for an H_2O-NaCl solution containing 20 wt.% NaCl. Numbers along each isochore represent the homogenization temperature corresponding to the isochore. The dashed isochore represents the critical isochore.

CRITICAL PROPERTIES

The recognition of supercritical fluids emanating from submarine hydrothermal systems as well as emerging supercritical water oxidation technology for destruction of hazardous wastes has generated considerable interest in the physical and thermodynamic properties of aqueous solutions in the vicinity of the critical point. Moreover, the large absolute values in the magnitudes of derivatives of thermodynamic and transport properties of fluids in the vicinity of the critical point has important implications for mass and energy transport in natural hydrothermal systems (14).

The Synthetic Fluid Inclusion Technique provides a simple means of determining the critical properties of aqueous solutions, and has been used to determine critical properties for H_2O-NaCl (15) and H_2O-$CaCl_2$ (16) solutions. As noted above, fluid inclusions that are liquid-rich at room temperature (i.e., have a density > critical density; Fig. 1A) homogenize by shrinking and disappearance of the vapor bubble during heating to homogenization (Fig. 5). Conversely, vapor-rich inclusions (i.e., have a density < critical density; Fig. 1B) homogenize by expansion of the vapor bubble to fill the inclusion at homogenization (Fig. 5). Inclusions with the critical density display neither expansion or shrinking of the bubble during heating. Rather, the meniscus between the liquid and vapor phases becomes less distinct during heating as the densities of liquid and vapor approach each other, and the inclusions homogenize by fading of the meniscus at the homogenization temperature, which is also the critical temperature. So, by trapping synthetic fluid inclusions at various P-T conditions and noting both the mode (i.e., to the liquid phase, to the vapor phase, or by critical behavior) and temperature of homogenization, the critical temperature is easily determined. Additionally, if two different P-T trapping conditions both show critical behavior, then both of these points must lie along the critical isochore. A straight line drawn through these two points and extrapolated to the common measured critical homogenization temperature defines the critical pressure. Using this technique, Knight and Bodnar (15) determined the critical temperatures, pressures, and the slopes of the critical isochores for H_2O-NaCl solutions having salinities from 0-30 wt.% NaCl. The relationship between salinity and critical temperature for this system is shown on Fig. 6.

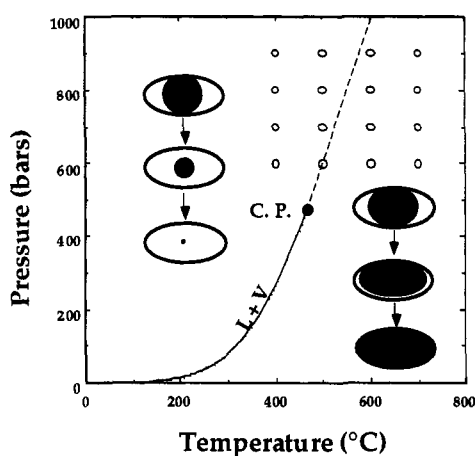

Temperature (°C)

Salinity (wt. % NaCl)

Fig. 5. Schematic representation of the technique for determining the critical properties of aqueous solutions using synthetic fluid inclusions.
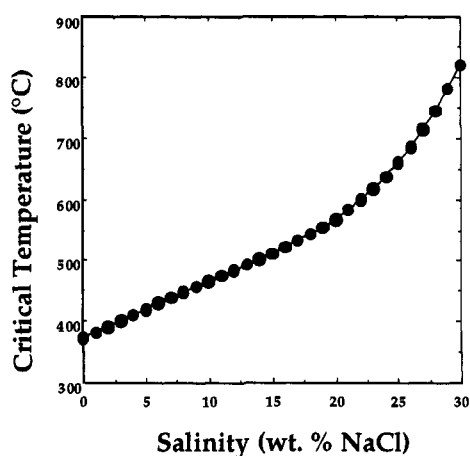
Fig. 6. Relationship between salinity and critical temperature for H_2O-NaCl solutions. Data from Knight and Bodnar (15).

PHASE EQUILIBRIA

One of the most important applications of the SFIT is the determination of phase equilibrium properties of aqueous solutions at elevated temperatures and pressures. In the determination of volumetric properties of aqueous solutions using SFIT, inclusions are trapped in the one-phase field, each inclusion traps a single, homogeneous fluid, and the composition of the fluid in the inclusions is known. However, if the inclusions are trapped in an immiscibility field containing two or more phases, which may be solid, liquid or vapor, only the bulk composition loaded into the capsule is known, and the compositions of individual inclusions are *not* known. Moreover, it is possible that some or all of the inclusions may trap more than one phase. So, in order to use SFIT to determine the phase relations of aqueous systems, it is necessary to be able to determine the compositions of the inclusions independently and to be able to identify inclusions that may have trapped more than one phase.

The SFIT has been used to determine liquid-vapor phase relations in the H_2O-NaCl system (10). First, it was necessary to have a means of determining the compositions of the resulting liquid-rich and vapor-rich inclusions trapped in the two-phase field. This was accomplished by determining the relationship between the amount of NaCl in solution and the temperatures of ice-melting and halite-dissolution. Synthetic fluid inclusions having known salinities ranging from 0 to about 80 wt.% NaCl were trapped in the one-phase field, i.e., at temperatures and pressures well outside of the region of immiscibility. Inclusions containing less than about 23 wt.% NaCl are undersaturated in halite at room temperature and remain so during cooling to temperatures below the eutectic for the H_2O-NaCl system (-21.21°C). So, by measuring the ice-melting temperature for these inclusions, the freezing-point-depression as a function of salinity was defined (Fig. 7). Inclusions having salinities greater than about 26 wt.% NaCl become saturated in halite during cooling from trapping conditions. Thus, at room temperature these inclusions contain, in addition to liquid and vapor phases, a crystal of halite (Fig. 1D). Synthetic fluid inclusions containing various salinities were trapped, and the temperature of dissolution of halite was measured to define the relationship between NaCl solubility and temperature (Fig. 8). Using data shown on Figs. 7 and 8, the salinity of any inclusion in the H_2O-NaCl system can be determined from either its freezing-point-depression or halite dissolution temperature.
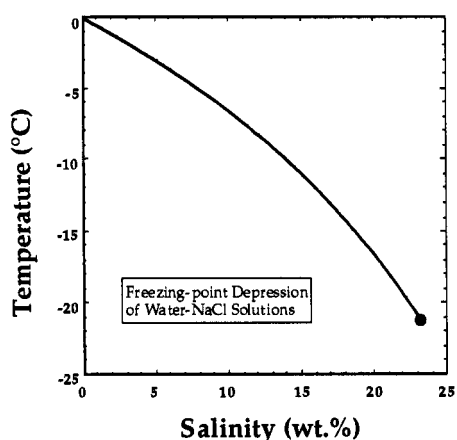

Fig. 7. Freezing-point depression of H_2O-NaCl solutions calculated using equations in Bodnar (17). The filled circle represents the eutectic point (-21.21°C, 23.18 wt.% NaCl).
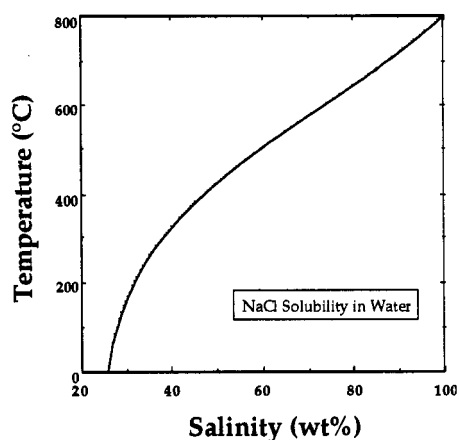
Fig. 8. Solubility of NaCl in water as a function of temperature. Calculated using equations in Bodnar et al. (18).

Liquid-vapor phase equilibria in the H_2O-NaCl system were determined to 1000°C and about 1500 bars using synthetic fluid inclusions (10). A low to moderate salinity (5-20 wt.% NaCl) solution was loaded into each capsule and the inclusions were formed at various P-T conditions. The inclusions were then observed using a petrographic microscope equipped with a heating/cooling stage. If all of the inclusions within a given sample displayed identical phase relations at room temperature, and if the ice-melting temperatures of all the inclusions were the same and corresponded to a salinity equal to the salinity of the solution originally loaded into the capsule, then the inclusions were trapped in the one-phase field for that particular composition. However, if the inclusion population showed variable phase relations at room temperature, with some inclusions containing halite crystals and relatively small vapor bubbles (Fig. 1D), while others contain only liquid and vapor with the vapor bubble occupying most of the inclusion volume (Fig. 1B), the inclusions must have been trapped in the two-phase (liquid + vapor) field. Ideally, each inclusion would trap only a single phase, either the liquid or the vapor present at formation conditions. In practice, however, many inclusions trap some of each phase. The vapor-rich inclusions almost always trap some small amount of liquid, owing to the fact that the liquid phase is the continuous phase that wets the fracture walls. Inclusions that trap dominantly liquid rarely trap any of the vapor phase present.

If petrographic examination suggests two populations of inclusions, indicating formation in the two-phase (liquid + vapor) field, the compositions of the liquid and vapor phases that were in equilibrium at formation conditions are obtained by measuring the ice-melting temperature of the liquid in the vapor-rich inclusions, and by measuring the halite dissolution temperature in the liquid-rich, halite-bearing inclusions, and referring these data to the previously determined freezing-point-depression (Fig. 7) and halite solubility (Fig. 8) relationships. An example of such determinations for synthetic fluid inclusions trapped in the two-phase field at 1000 bars and various temperatures from 650° to 1000°C is shown on Fig. 9. Note that the range in salinities determined for the vapor-rich inclusions is much larger than that for the coexisting liquid-rich, halite-bearing inclusions, consistent with trapping of small amounts of liquid in the dominantly vapor-rich inclusions.
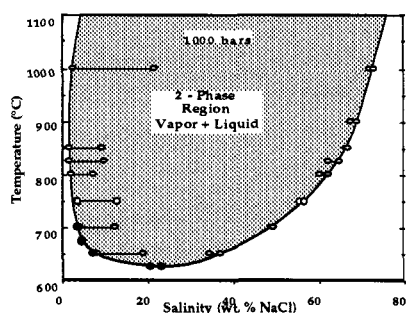

Fig. 9. Liquid-vapor phase relations for H_2O-NaCl at 1000 bars determined using synthetic fluid inclusions. Open circles (from Bodnar et al. (10)) represent the minimum and maximum salinities determined for the vapor (left limb) and liquid (right limb) compositions at each temperature. Filled circles from Sourirajan and Kennedy (19).
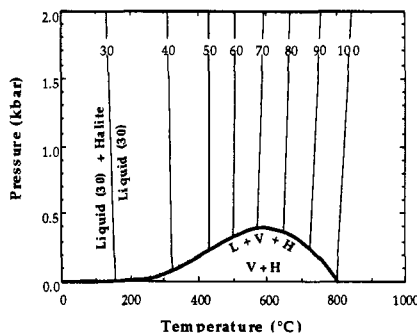
Fig. 10. Solid-liquid equilibria in the H_2O-NaCl system determined using synthetic fluid inclusions. Each sub-vertical liquidus line represents equilibrium between a liquid phase having the indicated salinity (in wt.% NaCl) and halite. Data from Bodnar (20).

Synthetic fluid inclusions have also been used successfully to determine solid-liquid equilibria in the H_2O-NaCl system (19). The SFIT data have been combined with results of other workers to develop a single model to predict the slopes of the liquidi (Fig. 10) as well as the isochores for high-salinity brines in both the one-phase liquid and the two-phase (liquid + solid) fields. These results have been used to constrain P-T histories of shallow hydrothermal systems associated with silicic plutons (19).

ACKNOWLEDGMENTS

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