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Phase diagram of salt–water system determined by TG-DTA

Keiichi Endoh, Hiroshi Suga*

Research Institute for Science and Technology, Kinki University Kowakae 3-4-1, Higashi-Osaka 577-8502, Japan

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Abstract

Thermogravimetry (TG) and differential thermal analysis (DTA) techniques were used to determine the solid-solution equilibrium curve between certain inorganic salts and water. The rate of evaporation of water through a pin hole of an aluminum pan, containing a small amount of aqueous solution of the salt, was measured by TG and DTA. A slight change in the rate was found to occur when the solution crosses the solubility curve. The composition and temperature at which the vaporization rate changed were determined by differentiating the TG curve with respect to time and then comparing with the literature value. The solubilities of NaCl, KCl, and Na_2SO_4 crystals into water were determined rapidly with the accuracy of ±1% for a small amount of sample solution. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Thermal analysis; Thermogravimetry; Solubility; Salt in water

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1. Introduction

Thermal analysis is the oldest and, perhaps, still the most popular method for detecting phase changes occurring in single and multi-component system through the observation of heat effects associated with the processes [1–4]. The method quickly determines the freezing point, eutectic point, peritectic point, etc. in single and binary systems. Most of the phase diagrams have been constructed in this way [5]. One equilibrium curve that is difficult to determine by the heating or cooling procedure is the solubility equilibrium of some inorganic salts with their saturated solutions. For example, the solubility of NaCl crystal into water does not change much with temperature. Thus, the solubility curve lies almost vertically in the *T*–*x* phase diagram. This behavior may arise from large differences in the cohesive energies, hence in their fusion temperatures of both substances. In such a case, the solubility is determined as a function of temperature in a separate experiment and the solubility equilibrium curve is connected to the freezing curves of water and aqueous solutions to construct the entire phase diagram. The determination of solubility requires, however, tedious and time-consuming operations as well as a large amount of sample.

A new method for determining the solubility using the TG method for a small amount of sample is proposed here. A sample solution of a known concentration encased in an aluminum pan is heated. The sample pan has a small pin hole at the top. Mass reduction due to evaporation of water from the solution is recorded by a TG apparatus. As the temperature is raised, the evaporation rate of water increases, and the composition of the solution changes simultaneously. The process is continued until the aqueous

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*Corresponding author. Tel.: +81-6-6721-2332; fax: +81-6-6721-2353; e-mail: suga@cc.kindai.ac.jp

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solution crosses the solubility curve, at which some changes in the vaporization process can be expected. In fact, a slight change in the evaporation rate was observed in the derivative of the TG curve, as will be described later. The composition of the solution at the moment can be calculated from the change in the mass of the solution. The solubility at the temperature was found to agree reasonably with the literature data. Changes in the initial concentration of the sample solution or in the size of pin hole provide the variation of solubility with temperature.

2. Experimental

In order to test the validity of this method, three kinds of well-studied salt that were chosen. Optical grade NaCl, KCl, and reagent grade $Na_2SO_4{\cdot}10H_2O$ crystals were purchased from Aldrich. Each salt was purified by recrystallization using distilled water. Purified $Na_2SO_4{\cdot}10H_2O$ crystals were carefully dehydrated by evacuation. The sample crystals were kept in a desiccator over a silica gel. A sample solution of a definite concentration was prepared gravimetrically. About 5 mg of the aqueous solution were put into a sealed-type DSC pan by a syringe. A small hole of the order of 0.5 mm in diameter was opened by a pin at the top of the lid, and the sample pan was placed in the TG-DTA apparatus, Rigaku Denki TG 8101D, which has facilities of computer manipulation to take derivatives of each of the TG and DTA curves with respect to time, hence with respect to temperature under the condition of a constant heating rate. An empty sample pan was used as the reference. In order to obtain a stationary vaporization, all the measurements were carried out under a constant flow of dry N_2 gas at a rate of $50\,cm^3\,min^{-1}$. Heating rates in the range between 0.5 and $2\,K\,min^{-1}$ were used.

The change that the sample undergoes during warming is drawn schematically in Fig. 1. The concentration C_{NaCl} is expressed in mass% of the salt. The initial sample condition is marked by A. As the temperature is raised, the solution becomes gradually concentrated due to the evaporation of water through the pin hole. Finally, the solution crosses the solubility curve at the point C and goes into two-phase coexistence region until all the water evaporates off from the sample pan. Measurement of the remaining mass can be used to test the correctness of the initial concentration of the solution. A possible mass reduction of the sample solution during the experimental setup is confirmed to be too small to affect the result beyond the claimed accuracy.

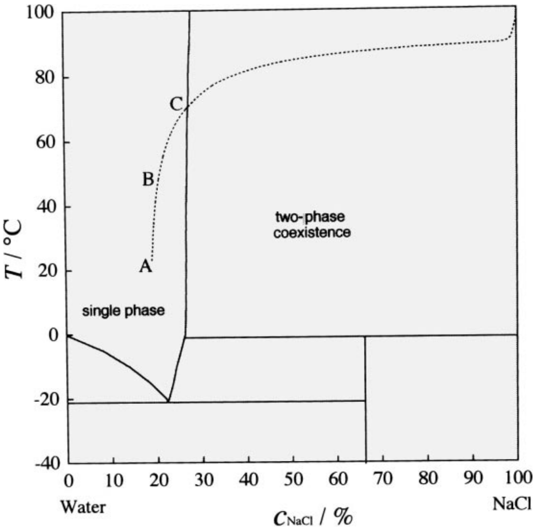

Fig. 1. Phase diagram of the NaCl–H_2O system and the principle of determining the solubility equilibrium curve by the TG method.

A quasi-isothermal experiment is also possible. The sample is rapidly heated up to ca. 340 K and held at that temperature. Isothermal evaporation of the water shifts the composition of the solution to the right side of the phase diagram. Essentially the same effect is observed when the solution crosses the solubility curve.

3. Results and discussion

A typical experimental result for an aqueous NaCl solution is shown in Fig. 2. This represents TG and DTA curves along with their derivative curves plotted as a function of temperature. The latter two are designated as DTG (dm/dt) and DDTA ($d\Delta T/dt$). The experiment was performed at a heating rate of $1\,K\,min^{-1}$. As the temperature is raised, the increased vapor pressure of water enhances the evaporation rate. The vapor-pressure increase with temperature is partly compensated by the increasing vapor-pressure depression arising from increased salt concentration of the solution. The total mass seems to decrease smoothly

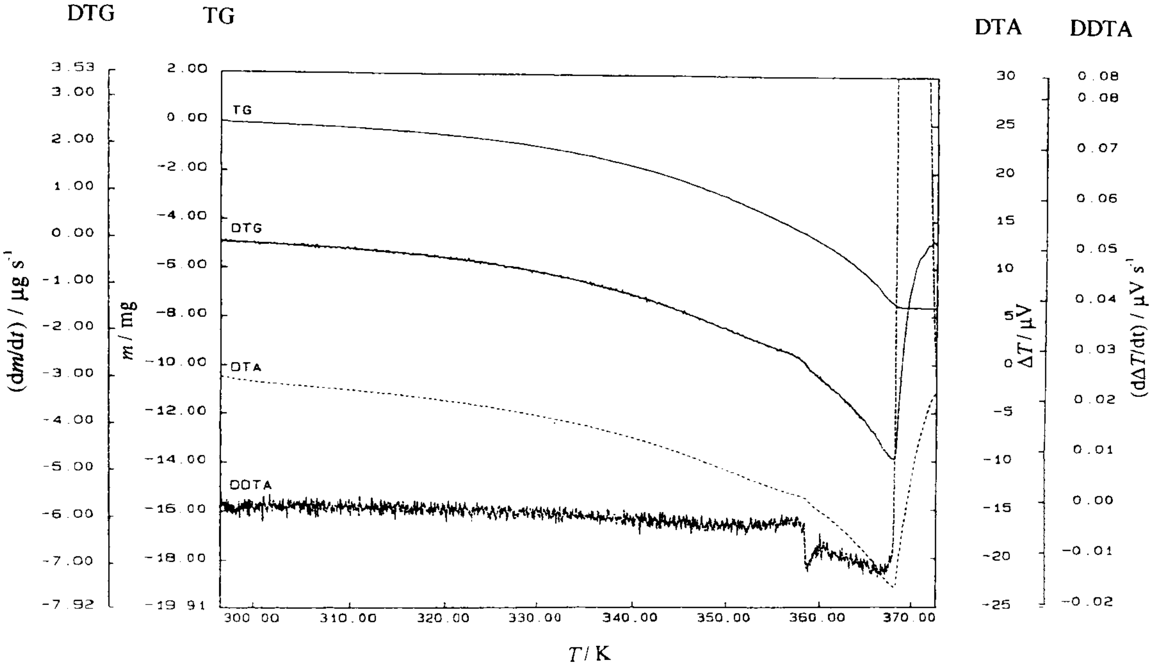

Fig. 2. Typical TG-DTA curves along with their derivative (DTG-DDTA) curves of NaCl aqueous solution in a pin-holed pan.

with temperature, but the corresponding DTG curve exhibits an anomalous behavior at a particular temperature region before all the water evaporates off from the pan. At the same time, DTA and DDTA curves show irregular behavior in the same temperature region.

The DTG curve is drawn in Fig. 3 in a magnified scale. The vaporization rate is slightly decreased at point T_1 and then starts to recover the original rate at point T_2. Calculation of the composition of the solution at point T_1 by the TG data shows that the point corresponds closely to the literature value of the solubility at this temperature. What does the change in the evaporation rate mean during a continuous heating of a solution? It is hard to imagine that the vaporization mechanism of the solution would change on passing through the equilibrium curve from an unsaturated to a supersaturated region. When an aqueous NaCl solution contained in a beaker is heated slowly, the formation of a thin film of NaCl crystallites takes place on the surface of the solution when the concentration of the salt reaches a certain value. Nucleation starts at the surface because the surface temperature is lower than those of any remaining parts of the solution owing to the high enthalpy of vaporization of water. The crystallites are probably floating because of the surface tension and inclusion of air. The filmy crystallites grow in their size and thickness until

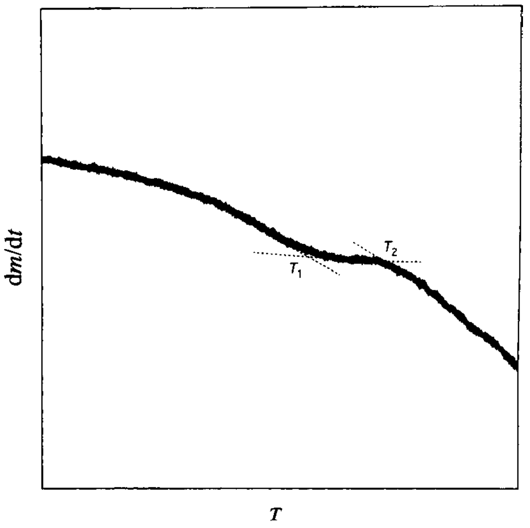

Fig. 3. Magnified DTG curve of NaCl aqueous solution and determination of solubility equilibrium temperature T_1.

they fall down to the bottom of the container. Thereafter, the crystallization proceeds only at the bottom and no new filmy crystallites appear at the surface.

The situation will be similar in a miniaturized sample of the present experiment. Surface temperature of the solution is always lower than the average temperature even though the heat conduction by the aluminum pan lowers the temperature gradient in the solution to some extent. At the temperature T_1, formation of filmy crystallites at the surface partly prevents the evaporation of water and, therefore, lower the rate of mass reduction. The effect will stop at T_2 when the crystallites fall down from the surface and the rate of mass reduction of the sample recovers the original value. The DTA and DDTA curves agree well with this picture. The heat effect is almost entirely due to the enthalpy of vaporization of water. A small heat effect of crystallization will be overruled by the enthalpy of vaporization.

The temperature distribution inside the solution is difficult to estimate even in the stationary state. A higher heating rate will induce a turbulent convection flow in the solution. In addition, the effect of supersaturation of the salt makes the problem intractable. The determination of any equilibrium properties from a dynamic experiment would not, therefore, be easy from any theoretical analysis. Thus, it is necessary to determine experimentally a relation between the temperature T_1 and the concentration of the solution.

Fig. 4 shows the solubility data of NaCl, determined experimentally in this way. The value T_1 can be changed either by modifying the initial concentration of solution or by changing the size of the pin hole. The full line in the figure was taken from literature. The symbols ▲, •, × correspond to data taken at heating rates of 0.5, 1, and 2 K min^{-1}, respectively. Obviously, a slow heating rate is desirable for realizing the thermal equilibrium, but the determination of T_1 as the intersection of the two extrapolated curves becomes ambiguous due to poor signal-to-noise ratio. The mass-reduction rate of the order of 2 μg s^{-1} seems to be most appropriate to give a good turning point T_1. Rapid heating will much disturb the equilibrium state by inducing undesirable gradients in concentration and temperature within the solution. Thus, the heating rate of 1 K min^{-1} gives the most precise and reliable data under the present experimental conditions. All the data taken at 0.5 and 1 K min^{-1} agree with the literature data [6] within ±1%.

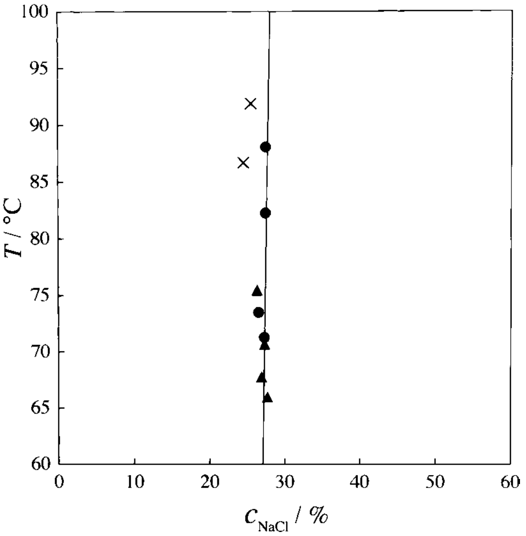

Fig. 4. Solubility of NaCl in water (in mass%) as a function of temperature.

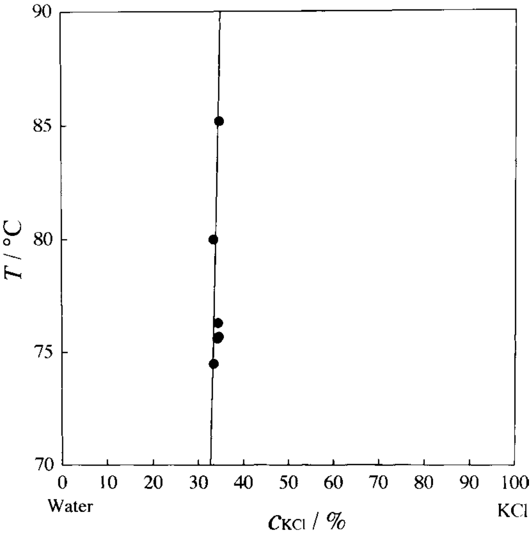

Fig. 5. Solubility of KCl into water (in mass %) as a function of temperature.

Figs. 5 and 6 show the data for KCl and Na_2SO_4. The data were taken at the heating rate of 1 K min^{-1}. Again, the full lines in the figures were taken from literature [6] with the concentration of salt in mass%. Sodium sulfate was chosen to test the effect of super-

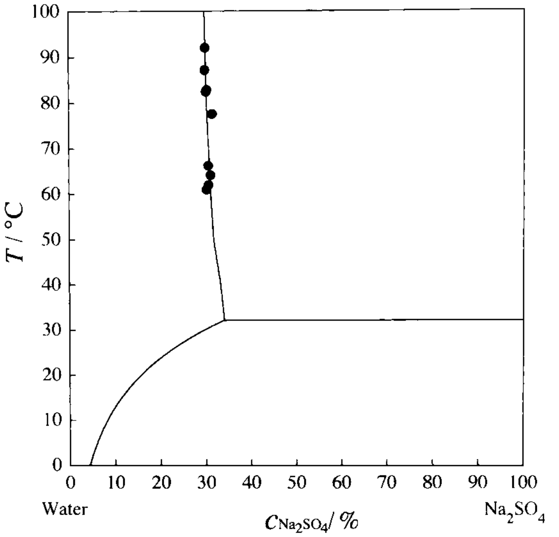

Fig. 6. Solubility of Na_2SO_4 into water (in mass %) as a function of temperature.

saturation. Inorganic salts with different sizes of cations and anions are generally prone to supersaturate. Both these results are satisfactory in view of the reasonable accuracy and rapidity of the determination.

One of the problems in the present experiment is the quality of the employed semi-microbalance. The accuracy of data is limited by the determination of concentration through the mass measurement for a small amount of sample solution. About 60% of the present error comes from the mass measurement. Use of a microbalance will surely improve the obtained result. Thus, a possible mass loss during the set up of a sample pan can be detected and should be corrected for. Anyway, further investigations on various kinds of salt are necessary in order to confirm the validity of this new method for a wide range of salts.

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