

# Solubility and metastable zone width of aqueous sodium dichromate dihydrate solutions in the presence of sodium chromate additive



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## ARTICLE INFO

### Article history:

Received 29 March 2016

Received in revised form

29 August 2016

Accepted 5 September 2016

Communicated by Dr. T.F. Kuech

Available online 5 September 2016

### Keywords:

A1. Metastable zone width

A1. Solubility

A1. Nucleation kinetics

A2. Crystallization

A3. Sodium dichromate dihydrate

## ABSTRACT

Solubility and metastable zone width (MSZW) of aqueous sodium dichromate solutions in different concentration of sodium chromate were studied experimentally by the polythermal method using a turbidity monitoring technique. The effects of cooling rate  $R$ , saturation temperature  $T_0$  of sodium dichromate and concentration  $c_1$  of sodium chromate on the MSZW were studied. The results show that the MSZW widens with increasing cooling rate  $R$  but it narrows with increasing saturation temperature  $T_0$  of sodium dichromate and concentration  $c_1$  of sodium chromate. The experimental data were analyzed by using an equation, based on the classical three-dimensional nucleation theory, relating MSZW with cooling rate  $R$ .

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## 1. Introduction

Crystallization as an important technique in chemical industry serves the dual purposes of separation and purification of the chemical products [1,2]. The primary goal of crystallization is obtain crystals with high purity, optimum particle size distribution and ideal morphology [3,4]. To achieve this goal, the operating conditions should be optimized and controlled within the metastable zone throughout the crystallization process [5,6]. Metastable zone, which represents the interval between solubility and supersolubility curves, is considered as the critical nucleation parameter in industrial crystallization [3,7]. As required for the design, control and optimization of the process of crystallization, various factors affecting the values of metastable zone width (MSZW) of numerous compounds have been investigated during the last four decades [8]. Moreover, the MSZW data and the relations between MSZW and parameters such as cooling rate  $R$  are used to understand the processes associated with nucleation mechanisms [6,9]. Recently, Sangwal's group has proposed the novel equation of three-dimensional nucleation theory to explain the nucleation mechanism and physical basis of MSZW of solute-solvent systems [10–12].

During the last years, Wang and his coworkers have investigated the MSZW of sodium dichromate dihydrate from aqueous solutions and discussed the experimental data of the relationship of maximum supercooling  $\Delta T_{\max}$  on cooling rate  $R$  and saturation temperature  $T_0$  using the recently advanced approaches [13]. However, until now no study of impurities on the MSZW of sodium dichromate dihydrate has been carried out by the traditional polythermal method. In this paper, the MSZW of sodium dichromate dihydrate in different composition of sodium chromate solution has been determined by turbidity technology. The effects of cooling rate, saturation temperature, mass fraction of sodium chromate on the solubility and MSZW of sodium dichromate dihydrate have been investigated. The novel equation of three-dimensional nucleation theory was suggested to study the nucleation kinetics.

## 2. Experimental

### 2.1. Materials and apparatus

Sodium dichromate dihydrate (Tianjin Paisen Technology Corporation) has been recrystallized twice from aqueous solution before using in experiments. Deionized water (Resistivity: more than  $18.25 \text{ M}\Omega \text{ cm}$ ) was obtained from a water purification system (UPT – II – 20T, Chengdu Ultrapure Technology Co., Ltd). The solubility and MSZW of sodium dichromate dihydrate were

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measured by a CrystalSCAN PolyBlock with four parallel reactors (E1061, United Kingdom He., Ltd). As each reactor has independent control systems, turbidity and temperature sensors, it can carry out the experiment independently and offers the measurement of MSZW for same or different samples simultaneously. The accuracy of the temperature sensor was 0.1 K. Precise temperature control was introduced along with refrigerated/heating circulators (FP50-HL, Julabo Technology Co., Ltd). The products containing hydrates crystallized from sodium chromate solution were identified by X-ray diffractometer (X'Pert PRO, 2006 PANalytical).

## 2.2. Solubility and metastable zone width measurements

The solubility and MSZW of sodium dichromate dihydrate were measured by polythermal method using turbidity monitoring technology. Certain mass of sodium chromate and sodium dichromate were weighed to the crystallizer. Then deionized water was weighed and transferred to the crystallizer to guarantee the total amount of mixture was 80 g. In the process of measurement, the stirring rate was fixed with 450 rpm. At first, the temperature was raised for about 10 K above the dissolution temperature and held constant for 15 min to ensure that all of the nuclei were fully dissolved. Then the solution was cooled with a settled cooling rate until crystallites appeared. Finally, the mixture was kept 10 K below the nucleation temperature for 15 min and then was heated at the same constant rate until all the crystallites appeared. Five different cooling/heating rates of 55, 45, 35, 25, 15 K h<sup>-1</sup> were performed for all the measurements. The temperatures of disappearance and appearance of crystallites were recorded as  $T_{dis}$  and  $T_{nuc}$ , respectively. The saturation temperature  $T_0$ , which is defined as the temperature of dissolution at an infinitely slow rate [5,14], can be obtained by extrapolating of the curve of dissolution temperature ( $T_{dis}$ ) against the heating rate [15]. For each measurement, a set of at least two experiments was performed in parallel reactors to verify the reproducibility of the process and each data point represents a mean value of these measurements. The values of metastable zone width  $\Delta T_{max}$  were calculated from the difference between the saturation temperature  $T_0$  and the nucleation temperature  $T_{nuc}$ , i.e.  $\Delta T_{max} = T_0 - T_{nuc}$ .

## 3. Results and discussion

### 3.1. XRD analysis

Powder X-ray diffraction (XRD) has been used to identify the crystal composition obtained by crystallization from the solution during the process of MSZW measurement. The pure sodium dichromate dihydrate pattern obtained from the PDF card (Reference code: 00-022-1366) has been showed in Fig. 1a. Fig. 1b–e shows XRD patterns of the solid phase crystallized from aqueous solutions containing 2.66, 5.06, 7.91 and 10.05 wt% of sodium chromate, respectively. From the positions of peaks of XRD patterns in Fig. 1, all solids crystallized from sodium chromate solutions in our experiment were identified as sodium dichromate dihydrate.

### 3.2. Solubility of sodium dichromate

The dependence of solubility  $s$  (or  $c^*$ ) of sodium dichromate on temperature  $T_0$  in water containing different concentrations of sodium chromate is shown in Fig. 2. These results show that the solubility of sodium dichromate decreases significantly with the increasing sodium chromate concentration  $w$  and decreasing saturation temperature  $T_0$ . Compared with the data in pure aqueous solution [13], sodium chromate has a great salt-out effect on the solubility of sodium dichromate.

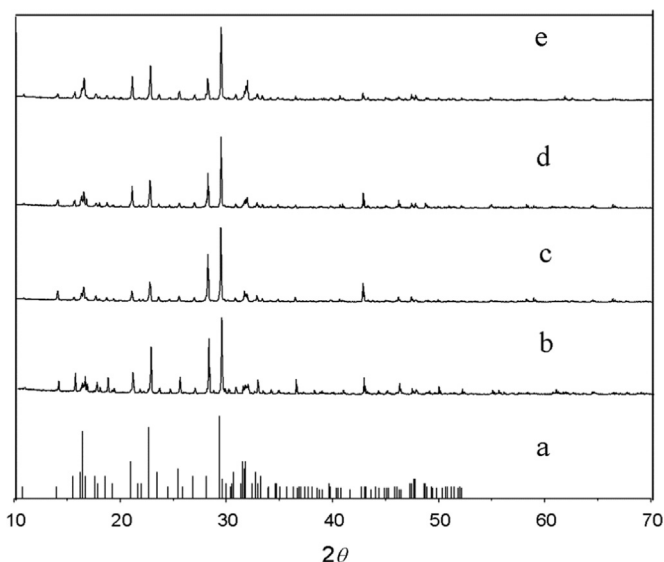


Fig. 1. XRD patterns of crystallized product in the presence of sodium chromate additive of different concentrations: (a) no additive, (b) 2.66%, (c) 5.06%, (d) 7.91%, and (e) 10.05%.

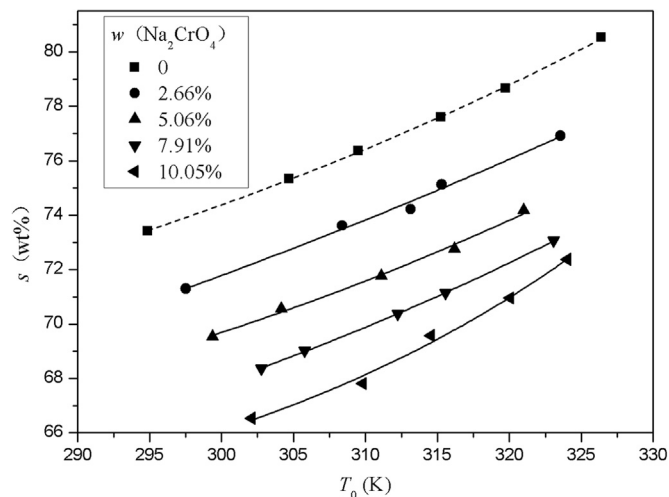


Fig. 2. Solubility  $s$  (mass fraction) of sodium dichromate as a function of temperature  $T_0$  in the presence of different concentration of sodium chromate in water.

The above experimented solubility data of sodium dichromate in solutions containing different concentration of sodium chromate were analyzed using Van't Hoff equation:

$$\ln c^* = -\frac{\Delta H_d}{R_G T_0} + \frac{\Delta S_d}{R_G} \quad (1)$$

where  $c^*$  solubility, expressed in mole fraction, of sodium dichromate,  $\Delta H_d$  is the dissolution enthalpy,  $\Delta S_d$  is the dissolution entropy,  $R_G$  is the gas constant, and  $T_0$  is the saturation temperature. The dependence of  $\ln c^*$  on  $T_0^{-1}$  for sodium dichromate at different concentration of sodium chromate is shown in Fig. 3. The best-fit plots of the data are drawn with the values of  $\Delta H_d$  and  $\Delta S_d$  listed in Table 1. It may be seen from Table 1 that for all additive concentrations  $\Delta H_d > 0$ , which proves the dissolution of sodium dichromate in water containing sodium chromate additive is an endothermic process.

### 3.3. MSZW of sodium dichromate dihydrate

The metastable zone widths of sodium dichromate dihydrate at

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