

Antisolvent crystallization of aqueous ammonium dihydrogen phosphate solutions by addition of methanol

Keshra Sangwal^a, Ewa Mielniczek-Brzóska^{b,*}

^a Department of Applied Physics, Lublin University of Technology, ul. Nadbystrzycka 38, 20-618 Lublin, Poland

^b Institute of Chemistry, Environment Protection and Biotechnology, Jan Długosz University of Częstochowa, ul. Armii Krajowej 13/15, 42-200 Częstochowa, Poland

ARTICLE INFO

Article history:

Received 28 April 2016

Received in revised form

1 July 2016

Accepted 22 July 2016

Communicated by S. Veessler

Available online 25 July 2016

Keywords:

A1. Antisolvent crystallization

A1. Metastable zone width

A1. Kinetics

B1. Ammonium dihydrogen phosphate

ABSTRACT

Experimental results of antisolvent crystallization of ammonium dihydrogen phosphate from their aqueous solutions saturated at 30 °C by addition of methanol at preselected feeding rate R_A , studied by *in situ* measurements of laser beam intensity I transmitted through solutions and their temperature T as functions of feeding time t for methanol at rate R_A , are described and discussed. It was found that (1) measurement of temperature of solutions during antisolvent feeding is more informative and is more reliable than transmitted laser beam intensity measurements, (2) there are two regions of methanol feeding durations involving endothermic reactions and one region involving exothermic reactions, (3) the data of metastable zone width determined from the values of maximum antisolvent content Δx_{\max} calculated from methanol feeding duration are reliable when the temperature difference $\Delta T = T_s - T_w$, where T_s and T_w are temperatures of solution and water, respectively, for theoretical analysis, (4) rates $\Delta T/\Delta t$ of linear changes in temperatures of solution and water with methanol feeding time t increases with feeding rate R_A , and (5) the maximum changes ΔT_{\max} in the temperature of solution and water are related to antisolvent content Δx associated with their appearance. It is argued that feeding of antisolvent methanol to saturated solutions or water leads to chemical reactions with evolution of heat.

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1. Introduction

There has been a constant interest in the study of antisolvent crystallization of a variety of materials in chemical and pharmaceutical industries. One of the problems associated with antisolvent crystallization of different materials is the measurement of metastable zone width of their solutions saturated at known temperatures in suitable solvents by generating supersaturation by feeding antisolvents to the solutions at well defined rates. The maximum antisolvent composition added to the solution saturated at a given temperature defines the metastable zone width (MSZW) and is a measure of the maximum value of supersaturation necessary for spontaneous occurrence of nucleation generated by the antisolvent. For the detection of the nucleation stage during antisolvent crystallization, sophisticated techniques such as focussed-beam reflectance measurements (FBRM) [1–3] and attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy [2] have been used successfully but other techniques based on turbidity probe [4], ultrasound probe [5] and

transmission of laser light through the solution [6] have also been proposed. Studies have also been devoted to the theoretical explanation of the relationship between metastable zone width in antisolvent crystallization, antisolvent feeding rate and solution stirring [2,7,8].

Recently, the authors [9] investigated processes of antisolvent crystallization occurring in aqueous ammonium dihydrogen phosphate (ADP) solutions saturated at 303.15 K, using a indigenously designed experimental setup, by *in situ* measurements of their temperature T and laser beam intensity I transmitted through them during feeding of antisolvent acetone at different rates. An important finding of this study was that the temperature of saturated solution does not remain constant during the feeding of the antisolvent. A direct consequence of a change in solution temperature is that its density also changes, resulting in changes in the concentration of particles serving as transport and scattering centers in the solution. Therefore, all techniques based on transport and scattering properties of particles in the solutions are likely to give incorrect measurements. However, in the studies on antisolvent crystallization of materials using different techniques it has always been assumed that the solution temperature during an experiment remains unchanged.

* Corresponding author.

E-mail address: e.mielniczek@ajd.czest.pl (E. Mielniczek-Brzóska).

The generation of supersaturation in a solution of a known solute concentration by addition of an antisolvent is considered to occur by changes in the concentration of solute in the solution at a particular temperature. However, all types of changes in solution temperature during antisolvent crystallization shed doubt whether our understanding of creation of supersaturation is correct and whether different techniques for measurements of MSZW in the solutions are reliable. In view of temperature changes observed in initially saturated solutions of solutes during antisolvent crystallization, investigations devoted to the understanding of processes involved in changes in solute concentration and creation of supersaturation for crystallization are desired. The present study is an attempt in this direction, where processes associated with the antisolvent crystallization of ammonium dihydrogen phosphate (ADP) from their aqueous solutions saturated at 30 °C by addition of methanol at preselected feeding rate are described and discussed. As in our previous study [9], crystallization was followed by *in situ* measurements of laser beam intensity I transmitted through solutions and their temperature T as functions of feeding time t for methanol at rate R_A .

2. Experimental procedure

Fig. 1 shows schematically the experimental arrangement for measurements of transmitted laser beam intensity I and temperature T of solution during antisolvent crystallization. Details of the experimental setup and the procedure used for measurements have been described earlier [9].

The experimental setup consists of the following main components: a double-walled crystallizer of 300-ml capacity cylindrical base (80 mm high and 68 mm internal diameter) having an inverted funnel-shaped top (about 30 mm high) with a neck (internal diameter of about 40 mm) closed by an air-tight Teflon cork, an external thermostating arrangement, maintaining a constant temperature to control temperature in the crystallizer by circulating water in its outer jacket, a green light diode laser (power 5 mW, wavelength 532 nm; Spectra-Laser, Opole, Poland), a laser

power meter to register power of the laser beam transmitted through the solution (meter range 0–10 mW; measurement accuracy 0.01 mW) connected to computer 1, and a temperature meter (P795 with Pt-100 sensor; Dostman Electronic GmbH, Wertheim-Reichplzheim, Germany; measurement accuracy 0.01 K) connected to computer 2, an antisolvent feeding arrangement, a magnetic stirrer with predefined rotation rate and a mechanical stirrer. The Teflon cork has three holes such that the mechanical stirrer passes through the center of the Teflon cork whereas the temperature sensor and the antisolvent feeding tube (internal diameter 0.8 mm) running through a glass pipe of internal diameter of 3 mm were about 6 mm away on its either sides. A peristaltic pump with appropriate tubing is used for antisolvent feeding at predefined rates. The glass tube supplying the antisolvent to the solution was parallel to the glass rod of the mechanical stirrer at a distance of about 10 mm and its terminal was always kept about 10 mm above the solution level.

The thermostatic system for controlling temperature of water circulating in the outer jacket around the crystallizer consists of a Julabo thermostat (model Julabo 4 (High Tech)), with an auxiliary home-made cooling module. The Julabo thermostat is connected to a computer and Julabo Easy Temp Professional program enables to attain the predefined temperature (set point) of 30 °C of the circulating water, equal to that of aqueous saturated ADP solutions, and maintain it constant, with an accuracy of ± 0.01 °C. Irrespective of the antisolvent feeding rate R_A , which leads to different changes in the solution (or water) temperature T in the crystallizer during an experiment by feeding of the antisolvent with time t at different rates R_A , the auxiliary cooling module maintained this accuracy of ± 0.01 °C in temperature control in all experiments. Temperature in the crystallizer and in the thermostatic system was monitored both before the beginning as well as during antisolvent feeding. The Julabo thermostat circulated water in the outer jacket at a constant rate of 4 dm³/min.

The bore of the glass tube for supplying antisolvent was used to fill the crystallizer with solution by inserting a funnel into it and to remove the used solution or solvent mixture contained in the crystallizer and to clean it after completion of measurements in an experimental run. For a crystallization run 220 ml of freshly prepared solutions saturated at 303.15 K, with the solubility data reported by Söhnel and Novotný [10], from double-distilled water and analytical grade ADP (Chempur, Piekary Śląskie, Poland) were used. After an initial homogenization of the solution for 15 min at 303.15 K, it was slowly cooled down to the saturation temperature of 303.15 K and finally maintained at this temperature for a period of 30 min using a stirring rates of 100 revolutions per minute for both magnetic and mechanical stirrers. Thereafter arrangements for acquisition of data of transmitted laser beam intensity I and solution temperature T were set up simultaneously. Due precautions were taken to align laser beam through the solution and to situate the temperature sensor in the solution. After the registration of the transmitted laser beam intensity I and solution temperature T for 4 min, feeding of the antisolvent at a pre-selected rate R_A was commenced. Analytical-grade methanol (Chempur, Piekary Śląskie, Poland) was used as antisolvent. Feeding of methanol to the saturated ADP solutions was interrupted after the temperature increase in the crystallizer reached its maximum value.

The effect of addition of the antisolvent on aqueous ADP solutions during crystallization was also compared with that on pure water. For this purpose data of laser beam intensity I and temperature T of pure water in the crystallizer as a function of feeding time t of the antisolvent at the selected rates R_A were recorded following the above procedure.

It should be mentioned that small differences in the initial values of the laser beam intensity I of saturated solutions were

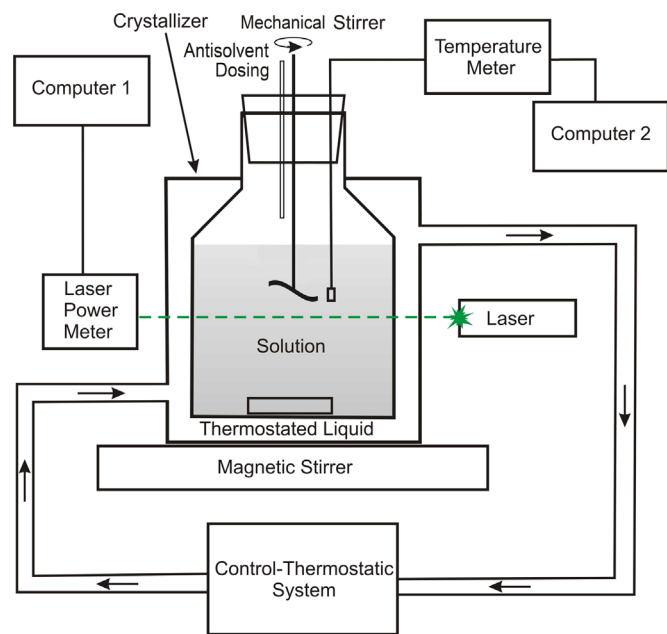


Fig. 1. Schematic illustration of experimental arrangement for measurement of transmitted laser beam intensity I and temperature T of solution during antisolvent crystallization. Different parts are indicated. Crystallizer dimensions are not drawn according to scale.

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