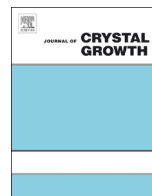




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Effect of sample volume on the metastable zone width of potassium nitrate aqueous solutions



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ABSTRACT

Results of an experimental study of the effect of sample volume on the metastable zone width of pure unstirred potassium nitrate aqueous solutions investigated as functions of cooling rate R and saturation temperature T_0 of the solution by the polythermal method are described and discussed. The metastable zone width was measured as the maximum undercooling ΔT_{\max} during the cooling of 4 and 100 mL solutions at constant predefined rates between 5 and 40 K/h by registering changes in the intensity of transmitted light using the UV–vis spectrophotometer and observation of visible nuclei by the visual method, respectively. The experimental data of the maximum undercooling ΔT_{\max} corresponding to saturation temperature T_0 for the two investigated volumes as a function of cooling rate R were analyzed by employing self-consistent Nývlt-like approach and an approach based on the classical three-dimensional nucleation theory. The results suggest that the dependence of the value of the metastable zone width of unstirred solutions on their volume is associated with the diffusion processes in the solution.

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1. Introduction

The efficiency of crystallization processes, such as separation and purification of industrial chemicals and control of the shape and size of final crystalline products, is intimately connected with the metastable zone width (MSZW) of the liquid phase. The MSZW of a solution saturated at temperature T_0 is usually determined experimentally by the polythermal method [1,2]. The method is based on the measurement of the maximum supercooling ΔT_{\max} which the solution can withstand before the detection of crystallites by a particular experimental technique in the solution volume at temperature T_c during its cooling at a constant rate R . MSZW is the temperature difference $\Delta T_{\max} = T_0 - T_c$. Since the size of crystallites is related to the formation of three-dimensional nuclei in the liquid volume and their subsequent growth to a size detectable by the observation technique for crystallization, MSZW of a solid–solvent system depends on a variety of factors such as saturation temperature, solvent used for preparation of supersaturated solutions, presence of impurities dissolved in the solution, presence of crystalline seeds in the solution, solution stirring, cooling rate of solution from saturation temperature, technique for the detection of crystallites and solution volume.

The solution volume encountered in crystallization varies from liters contained in flasks and crystallizers [1,2] down to the size of emulsion droplets measuring a few hundred micrometers [3].

Therefore, among the various factors affecting the value of MSZW of solutions, the effect of sample volume has been poorly investigated experimentally [4]. Kozíšek et al. [3] studied theoretically the conditions for the formation of the first nuclei by homogeneous and heterogeneous nucleation from supercooled melt and supersaturated solution, and found that critical supercooling or supersaturation for nucleation increases with decreasing volume of the mother phase. Kashchiev [5] showed that the volume dependence of this critical supercooling or supersaturation can be explained by the classical nucleation theory.

Kadam et al. [4] studied the metastable zone width for paracetamol from stirred 1 mL and 1 L aqueous solution samples. These authors found that the value of MSZW for 1 mL sample was not reproducible, thereby showing stochastic nature, but its value for 1 L sample was reproducible and deterministic. Using stochastic and deterministic models, Kubota [6] discussed theoretically the dependence of MSZW and induction period on sample volume. He found that the average values of both stochastic MSZW and induction period decrease with an increase in sample volume, whereas the deterministic MSZW and induction period remain unchanged. However, until now there are sparse experimental data on the volume dependence of metastable zone width to refute or corroborate the above findings.

The aim of the present work is two-fold: (1) to investigate experimentally the metastable zone width of KNO_3 in 4 and 100 mL unstirred aqueous solutions using the polythermal method and to analyze the experimental $\Delta T_{\max}(T_0)$ data for different cooling rates R using self-consistent Nývlt-like [7] and three-dimensional nucleation theory-based approaches [8], and (2) to discuss the cause

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(s) of the dependence of MSZW on sample volume for unstirred solutions.

2. Experimental

Measurements of ΔT_{\max} of KNO_3 aqueous solutions in 4 and 100 mL volumes were made by recording absorbance of light in UV–vis spectrophotometer (Helios Zeta) and visual observation of appearance of crystallites in the solution volume with the naked eye, respectively. For measurements of ΔT_{\max} , known volumes of the solutions corresponding to saturation temperatures between 40 and 70 °C were prepared from analytical grade KNO_3 (Chempur, Piekary Śląskie, Poland) and double-distilled water. For preparing a solution saturated at a predefined temperature the solubility data reported by Söhnel and Novotný [9] were used. Appropriate amounts of KNO_3 were dissolved in water with stirring and heating the solution to a temperature much higher than the saturation temperature T_0 . Depending on the method of measurement of MSZW, the solution was then transferred to cuvette placed in spectrophotometer cell or to 150 mL flat-bottomed flask placed in a water bath. During transfer of the solution to the cuvette and the flask, their temperature was 7–8 °C higher than T_0 . The temperature was controlled with an accuracy of $\pm 0.1^\circ\text{C}$ using Julabo thermostat.

Before starting the procedure of cooling, solutions contained in the spectrophotometer cuvette as well as in the flask were first thermostated for about 30 min. In the case of measurement of MSZW in the spectrophotometer cuvette, the solution was cooled at a predefined rate R and absorbance A of light of wavelength 380 nm, measured in arbitrary units (a.u.), by the solution and solution temperature T was registered simultaneously as a function of time (P795 with Pt-100 sensor; Dostman Electronic GmbH, Wertheim-Reichplzheim, Germany). From the recorded data of these two dependences, plots of absorbance A against solution temperature were constructed. Examples of such plots are shown in Fig. 1 for solutions saturated at different temperatures T_0 and cooling rates R . In Fig. 1a, T_c is the temperature when absorbance suddenly increases due to the onset of crystallization from a practically steady value from T_0 , whereas the temperature difference $\Delta T_{\max} = T_0 - T_c$ is the value of the MSZW obtained at different R for the solution saturated at T_0 . Similarly, 100 mL solutions, saturated at T_0 , contained in flat-bottomed flasks were cooled at different rates R and the temperature T_c corresponding to the appearance of the first crystallites was noted. Again the temperature difference $\Delta T_{\max} = T_0 - T_c$ is the MSZW.

3. Results and discussion

Fig. 2 shows the ΔT_{\max} data measured for 4 and 100 mL solutions saturated at different T_0 as a function of cooling rate R .

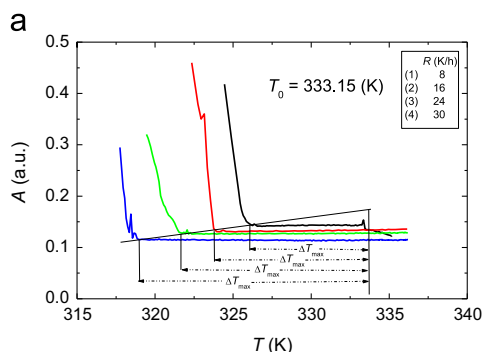


Fig. 1. Plots of absorbance A of KNO_3 aqueous solution on solution temperature T for different cooling rates R : (a) solution saturated at $T_0 = 60^\circ\text{C}$, and (b) solutions saturated at three different temperatures. Solution volume $V = 4$ mL.

It may be seen from the figure that the value of MSZW for both 4 and 100 mL KNO_3 aqueous solutions increases with an increase in solution saturation T_0 and cooling rate R . These observations are similar to those reported before for a variety of solute–solvent systems [7,8,10]. From the figure one also notes that the maximum dispersion in the value of ΔT_{\max} for the two volumes of the solutions is less than $\pm 20\%$ in the studied range of cooling rate R and saturation temperature T_0 , and does not appear to be significantly related to the solution volume. However, for all solutions saturated at different T_0 , the average value of ΔT_{\max} measured in 100 mL solutions at a given R is higher than that measured in 4 mL solutions. The former observation of large dispersion both in 4 and 100 mL solutions suggests that the nucleation process in these solution volumes is essentially stochastic. The latter observation of a higher value of MSZW in larger volume is contrary to the prediction of classical nucleation theory [3,5] and stochastic model [6]. However, some influence of the difference in the method used for the detection initial stage of crystallization on the higher values of MSZW in larger volume cannot be excluded.

The dependence of ΔT_{\max} on solution volume may be due to the heterogeneous nucleation or changes in temperature in the crystallizer. Since the solutions for the measurements in both volumes of 4 and 100 mL are identical regarding the purity of chemicals, it is unlikely that heterogeneous nucleation results in volume dependence of ΔT_{\max} during a particular cooling rate R . However, minor differences in the values of ΔT_{\max} for our two volumes are possible due to small delay in reaching the instantaneous nucleation in large solution volume but these changes in ΔT_{\max} lie within experimental errors. Below we use two different

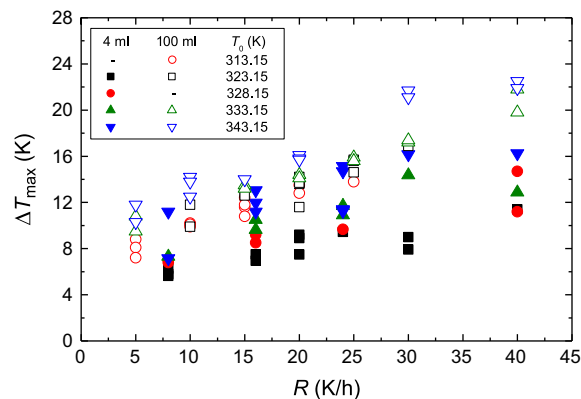


Fig. 2. Dependence of maximum undercooling ΔT_{\max} obtained from absorbance and visual data on cooling rate R for solutions saturated at different temperatures T_0 . Solution volumes $V = 4$ mL and 100 mL.

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