Journal of Crystal Growth xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Journal of Crystal Growth

journal homepage: www.elsevier.com/locate/jcrysgro

Reprint of: Effects of solution degassing on solubility, crystal growth and dissolution–Case study: Salicylic acid in methanol

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ARTICLE INFO

Communicated by T.F. Kuech

Keywords:
Solubility
Dissolution
Growth from solutions
Dissolved gases
Salicylic acid

ABSTRACT

The influence of dissolved gases on the crystallization parameter solubility, MZW, growth and dissolution rates was investigated experimentally using degassed and non-degassed (air-saturated) solutions. The results of this study show that degassing has no effect on the solubility curve of the used model substance salicylic acid (SA) in methanol (MeOH). This reveals in the assumption that a thermodynamic effect of dissolved gases can be excluded. Growth rates were measured by means of a desupersaturation method and the results indicate that the growth rates of SA are not affected by degassing. The results of the dissolution rate measurements reveal a distinct decrease in dissolution rates for non-degassed solutions compared to degassed solutions, especially, at low temperature (10 °C).

To explain this phenomenon the gas solubility, represented by oxygen, in MeOH in dependence on the SA concentration was estimated by means of Hansen Solubility Parameters (HSP) [1]. It was found that the oxygen solubility decreases with increasing SA content which explains the inhibition of crystal dissolution in non-degassed solution compared to degassed solution. Moreover, this kind of 'drowing-out' mechanism would not appear in growth rate measurements, where indeed no effect of degassing could be observed.

1. Introduction

In crystallization processes variations in the experimental conditions are known to influence solubility, growth or dissolution rates. Some of these effects are well known and of general consideration, like pH value. Even though, there are many possibilities to adjust the pH, e.g. by the use of buffers, there are cases where adjusting pH is more difficult, as in of case is the sea water desalination. There, the release of dissolved carbon dioxide leads to a pH increase. Consequently, the solubility of dissolved salts, e.g. calcium carbonate, decreases and crust formation in pipes and crystallizers occur [2].

Another, but for industrial applications less meaningful effect of dissolved gases on the crystallization was observed by Waldschmidt et al. [3]. They described that dissolved gases are able to increase or decrease the growth rates of ciclopirox depending on the type of gas [3]. Apart from that, the influence of dissolved gases is hardly reported on in literature, yet [4].

The aim of this study is, therefore, to investigate the influence of dissolved gases on the crystallization parameters solubility curve, metastable zone width (MZW), growth and dissolution rates using salicylic acid (SA) as model substance and methanol (MeOH) as solvent for this case study.

The approach of investigating the influence of dissolved gases by removing them makes it necessary to consider them as part of the model system. To simplify the considerations a three-component-system SA-MeOH-oxygen is assumed. Oxygen was chosen as third component because it is expected to show a very similar behavior as nitrogen and there are well investigated data for solubility predictions available [5] using the model of Hansen Solubility Parameters (HSP) [1].

2. Materials and methods

2.1. Degassing

Solutions were degassed using the degasser DE01 (by M2-Automation, Berlin, Germany) which contains a gas permeable membrane tube in a vacuum cell with defined pressure (Fig. 1). When the prepared solution is pumped slowly (max. 1 mL min^{-1}) through this tube the dissolved gases are removed from the solution. A pressure of 300 mbar in the vacuum cell was used and, according to Henry's law [6], the gas content of the solution could be reduced to 30% of its saturation amount at 1 bar. Solubility values for oxygen and nitrogen in MeOH depending on the temperature can be found in Table 1. All

DOI of original article: http://dx.doi.org/10.1016/j.jcrysgro.2016.11.037
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http://dx.doi.org/10.1016/j.jcrysgro.2017.03.046
Received 18 July 2016; Received in revised form 28 October 2016; Accepted 7 November 2016

Nomenclature

SA	salicylic acid
MeOH	methanol
HSP	Hansen solubility parameter
MZW	metastable zone width
Non-deg.	non-degassed
Sat. curve	saturation curve

Symbols

mbar	millibar
°C	degree celsius
%	percent
mL	milliliter
min	minutes
h	hour
g	gram
E	energy
J	Joule
V	molar volume
MPa	mega pascal
3D	three-dimensional
x	mole fraction
T	temperature
c	concentration

Greek symbols

δ	Hansen solubility parameter
ϕ	volume fraction

Sub- and superscripts

δ_D	dispersion interactions
δ_P	dipole interactions
δ_H	hydrogen bonding interactions
L_{gas}	Volume of gas in liter
L_{MeOH}	Volume of methanol in liter
K h^{-1}	Kevlin per hour
cm^3 mol^{-1}	cubic centimeter per mol
R_a	distance of the HSP of two components in a three dimensional diagram
x_{O2}	mole fraction of oxygen
m s^{-1}	meter per second

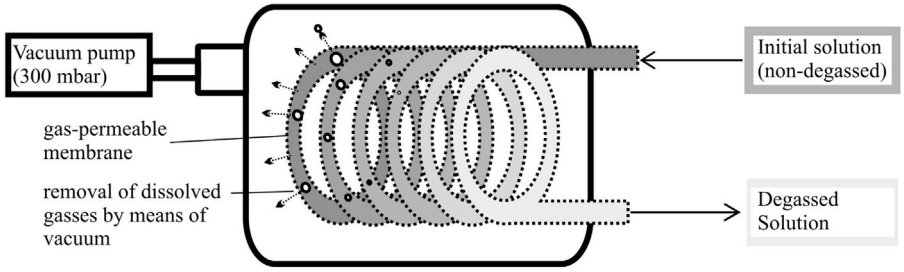

Fig. 1. Scheme of degassing unit. Gases are removed from the initial solution by means of vacuum (300 mbar) through a gas permeable membrane.

experiments were run using both degassed and non-degassed solutions.

Since the thermodynamics depend decisively on the pressure all experiments were performed under normal pressure. This means that it cannot be avoided that over time the gases above the solution dissolve again. In order to handle this issue solutions were degassed for 1.5 h before each experiment which was started immediately after the degassing procedure.

2.2. Solubility curve by means of saturation method

In this experimental study two methods were used to determine the solubility of SA in MeOH. The first method is based on measuring the mass fraction of SA in a saturated SA solution and will be termed 'saturation method'. The second used method was based on an US method and will be described in details below.

In order to determine the solubility curve of SA in MeOH by means of the saturation method saturated solutions of SA in MeOH were prepared. Therefore, supersaturated solutions were filled into 2 mL plastic tubes and cooled to the aimed temperature (5, 10, 15, 20, 25, 30 °C). After 15 min seed crystals were added and the tubes were kept at constant temperature for 1 h and shaken each 15 min. It was found that this period was long enough to ensure desupersaturation of the solutions and, thus, reach a saturated solution. Afterwards, the supernatant solution was removed carefully and its concentration was measured by means of a refractometer against external calibration. The procedure is depicted schematically in Fig. 2.

2.3. Solubility and MZW from US method

As mentioned above a second method for solubility determination based on an ultrasonic probe (LiquiSonic, Magdeburg, Germany) was applied (Fig. 3a). It should be pointed out that this US probe transfers only negligible amounts of energy to the solution. While common power US probes transmit at least 100 W the used device (including control unit) consumes max. 6 W. The measurement principle (Fig. 3b) is based on determining the US velocity in the solution by measuring the time the signal needs to pass the gap between both plates of the probe. Since the US velocity depends on temperature, density and adiabatic compressibility this technique can be used to register online changes of the solutions' concentration [8].

Table 1
Solubility data for oxygen and nitrogen in MeOH are given in volume fractions (φ) expressed by volume of dissolvable gas [L] per 1 L MeOH. Based on literature data for saturation solubility [7] the amount of oxygen and nitrogen that will be left in solution after degassing at 300 mbar was calculated.

Temperature [°C]	Oxygen		Nitrogen	
	Saturation solubility [7]	Amount after degassing	Saturation solubility [7]	Amount after degassing
−25	0.243	0.072	0.144	0.042
0	0.245	0.072	0.153	0.045
25	0.248	0.073	0.165	0.049
50	0.255	0.076	0.177	0.052