Solubility of ammonium oxalate in water–acetone mixtures and metastable zone width of their solutions

Keshra Sangwal [a,*], *Ewa Mielniczek-Brzóska* [b], *Sylwia Barylska* [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*

ABSTRACT

Experimental results on the solubility c of ammonium oxalate in mixed water–acetone solvents containing acetone content $x < 0.55$ by weight at different saturation temperature T are presented and discussed using the theory of regular solutions. It was found that: (1) the dependence of the solubility c of ammonium oxalate in solutions of different mixed water–acetone solvents on temperature T follows an Arrhenius-type relation, (2) the dependence of c on acetone content x at different temperature T follows the relation: $\ln(c + \delta) = a - bx$, where the parameters a and b are measures of deviation of a solution from ideality and the correction factor δ is related to the activity coefficient f_a of the solution, which decreases with an increase in c, and (3) the dependence of the solubility c of ammonium oxalate in solutions of different compositions x of water–acetone mixtures is related to the dielectric constant ε^* of the solvent mixture, following the relation $\ln c = C + C_1 \varepsilon^*$, where C and C_1 are related to the parameters a and b, respectively. Study of the metastable zone width, defined as maximum undercooling ΔT_{max} a solution saturated at a particular temperature T can withstand, of some selected solutions of mixed water–acetone solvents at different T revealed that ΔT_{max} decreases with an increase in antisolvent content x. The results are discussed using the self-consistent Nývlt-like approach.

© 2013 The Institution of Chemical Engineers. Published by Elsevier B.V. All rights reserved.

Keywords: Ammonium oxalate; Antisolvent crystallization; Metastable zone width; Mixed water–acetone solvents; Regular solutions; Solubility

1. Introduction

Crystallization from solutions plays a key role in the separation and purification of industrial chemicals and the control of the shape and size of final crystalline products. The efficiency of these processes is determined by the nucleation of crystals and their development in the supersaturated solution, and is intimately connected with the solubility of the crystallizing material in a given solvent and the metastable zone width of the resulting solution. The metastable width of a solution is the region of solute concentration higher than that of the solubility concentration at a given temperature of the solution in which the supersaturated solution does not nucleate spontaneously.

Crystallization of a solid mass dissolved in a pure or mixed solvent can occur when supersaturation is created in the solution, which can be achieved by several methods. Among these different methods, methods based on change in temperature and solvent composition are commonly used in industrial crystallization.

Solubility of most materials increases with increasing temperature. Therefore, cooling of the solution of a solute saturated at a given temperature T and pressure can be used to create supersaturation in the solution. At a given temperature, the solubility of a solute in different solvents is different. Therefore, the solubility of a solute in the solution can also be changed at a particular temperature by mixing two different miscible solvents in various proportions. In these cases, supersaturation in the saturated solution of a solute in a solvent is generated by mixing another miscible solvent, usually called antisolvent or nonsolvent in which the solute is insoluble or poorly soluble. The rate of creation of supersaturation

---

is controlled by controlling the rate of cooling of a solution at a constant rate or the rate of addition of miscible antisolvent.

Investigation of metastable zone width of various solute–solvent systems has been a field of intensive research activity for over four decades (Nývlt et al., 1985; Mullin, 2001). Polythermal method is commonly used for the investigation of metastable zone width of solutions. In this method, the solution is cooled at a constant cooling rate from saturation temperature T to a temperature T_{lim} when visible crystals appear in the solution. The temperature difference $(T - T_{lim})$ is taken as the metastable zone width of the solution saturated at temperature T. Metastable zone width can also be measured by the isothermal method. In this method, a solution saturated at temperature T contained in some vessel is rapidly cooled down to a predefined temperature, and the time elapsed from cooling to the first appearance of change in the state of the solution is measured. However, when spontaneous nucleation occurs immediately after attaining the preset temperature, the temperature difference between saturation and preset temperatures may be taken as the metastable zone width of the solution. Since 2008 several papers have been devoted to the understanding of the effect of various experimental factors on the metastable zone width by these methods. These recent developments in the understanding of metastable zone width of solute–solvent systems have been reviewed recently (Sangwal, 2011).

Antisolvent crystallization is widely used in chemical and pharmaceutical industries for materials whose temperature coefficient of solubility is low and which are unstable at high temperatures. However, our understanding of the metastable zone width in antisolvent crystallization is relatively poor (O'Grady et al., 2007; Kubota, 2008; Sangwal, 2010a). Theoretical interpretation of the metastable zone width in these systems is based on the assumption that the solubility c of a solute in solvent–antisolvent mixture decreases linearly with an increase in antisolvent composition x (O'Grady et al., 2007; Kubota, 2008). Contrary to the above assumption, the dependence of the experimental solubility of different compounds on antisolvent–solvent composition is found to be nonlinear (Sangwal, 2010a). Therefore, for a better understanding of the metastable zone width of solvent–antisolvent systems it is necessary to investigate the nature of the solubility of inorganic, organic and semiorganic compounds on solvent–antisolvent composition and saturation temperature of the solutions in such systems.

The main purpose of the present study was to obtain experimental results on the solubility of ammonium oxalate (AO) as a function of water–acetone composition at different saturation temperature and to analyze these data using the theory of regular solutions. The other aim was to study the metastable zone width of some selected solutions of water–acetone mixtures as a function of saturated temperature. AO was chosen for the study because the authors have investigated before the metastability of this compound in aqueous solutions (Sangwal and Mielniczek-Brzóska, 2004; Sangwal and Wójcik, 2009).

2. Experimental

For the preparation of solutions demineralized water, analytical grade ammonium oxalate monohydrate, $(NH_4)_2C_2O_4 \cdot H_2O$ (with the following impurities: 0.015% SO_4, 0.001% Cl, 0.001% Pb, and 0.0005% Fe), analytical grade acetone (containing 0.05% CH_3OH and C_2H_5OH, 0.002% CH_3COOH, 0.002% HCOH and

0.001% NH_3) were used. Both ammonium oxalate monohydrate and acetone were produced by Chempur, Piekary Śląskie (Poland).

The first step was to prepare a series of water–acetone solutions containing different acetone content (i.e. 4, 8.0, 12.2, 16.4, 20.8, 25.2, 29.8, 34.5, 39.2, 44.1, 49.1 and 54.2 wt%) in the solvent mixture. Different solvent mixtures were then saturated with ammonium oxalate at the following temperatures: 25, 30, 35, 40, 45, 50 and 60 °C. Appropriate amounts of ammonium oxalate salt in small portions were successively poured to these solvent mixtures contained in 250 ml flat-bottomed flasks, sealed tightly to avoid solvent evaporation and maintained at the predefined temperature with ±0.01 K accuracy in a commercial Julabo MV–4 thermostat over different durations. During the saturation of the solutions they were systematically stirred to assist the dissolution of the added salt. A period of 24 h was found to be sufficient to achieve saturated solutions of ammonium oxalate in the mixed water–acetone solvents.

After the saturation of a solution, AO content in the solution saturated at a particular temperature was determined by the standard manganometric method involving titration of oxalate ions against permanganate solution (Pataki and Zapp, 1980; Skoog et al., 2007). For this purpose, 1 cm³ of the solution was withdrawn from the flask, diluted with water to 10 cm³, acidified with 1 M H_2SO_4, heated to a temperature of about 70 °C and titrated against $KMnO_4$ to estimate oxalate content in the sample. From three measurements of the oxalate content estimated for a solution saturated at a given temperature, the solubility of AO was determined. The remaining parts of the saturated solutions were used for the study of their metastable zone width. Solubility data for AO in pure water at different temperature was taken from Söhnel and Novotny (1985).

The metastable zone width of solutions saturated at different particular temperatures was carried out by the polythermal method based on cooling them at a constant cooling rate R of 6 K/h. An arrangement consisting of Julabo thermostat steared by a computer equipped with the computer program EasyTEMP enabled to cool the solution at the constant cooling rate. In an experiment, the temperature of the thermostat with flasks containing AO solutions was first kept 3–5 K higher than the saturation temperature T for 15–20 min, and then the solution temperature was lowered at the above cooling rate. The temperature at which first nuclei were observed with the naked eye in a flask was taken as the maximum temperature T_{lim} for solution metastability. From the values of saturation temperature T and maximum nucleation temperature T_{lim}, the metastable zone width defined by the temperature difference $\Delta T_{max} = T - T_{lim}$ was calculated.

3. Solubility of AO in water–acetone mixtures

3.1. Resumé of different theoretical expressions

The temperature dependence of solubility c, usually expressed in mole fraction, of a solute in a solvent forming ideal solution is given by (Hildebrand and Scott, 1962; Mullin, 2001)

$$\ln c = A^* - \frac{\Delta H_m}{R_G T}, \tag{1}$$