



METASTABLE ZONE WIDTH MEASUREMENT OF ADIPIC ACID-WATER SOLUTIONS

MEDICIÓN DEL ANCHO DE LA ZONA METAESTABLE DE SOLUCIONES DE ÁCIDO ADÍPICO-AGUA

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Abstract

The metastable zone width of adipic acid-water solutions has been determined in a temperature range from 293.15 to 328.15 K and cooling rates from 1 to 30 K·h⁻¹ by means of the conventional polythermal method, using a laser diffraction technique. In addition, it is proposed an alternative method for estimating the metastable zone width based on the solution density measured online. The apparent nucleation order is evaluated using the Nývlt equation. Experimental results showed that initial composition and cooling rate had significant effects on the metastable zone width. An increment in cooling rate increased the metastable zone width and an increment in initial composition decreased the metastable zone width. On the other hand, it was found that online density measurements could be used as an alternate method for estimating the metastable zone width. The comparison of metastable zone width obtained with both methods produced an average difference of 6.75 %. Finally, the apparent nucleation order calculated was 4.3 which is closed to the value 4.2 reported in the literature.

Keywords: crystallization, density, nucleation order, polythermal method, supersaturation.

Resumen

El ancho de la zona metaestable de soluciones de ácido adípico-agua ha sido determinado en el intervalo de temperatura de 293.15 a 328.15 K y velocidades de enfriamiento de 1 a 30 K h⁻¹ empleando el método politérmico convencional y una técnica de difracción de rayos láser. Además se propone un método alternativo para estimar el ancho de la zona metaestable basado en mediciones de densidad en línea. El orden de nucleación aparente es evaluado usando la ecuación de Nývlt. Los resultados experimentales mostraron que la composición inicial y la velocidad de enfriamiento tienen un efecto significativo en el ancho de la zona metaestable. Un incremento en la velocidad de enfriamiento aumenta el ancho de la zona metaestable y un incremento en la composición inicial disminuye el ancho de la zona metaestable. Por otra parte, se encontró que las mediciones de la densidad pueden ser usadas como un método alternativo para estimar el ancho de la zona metaestable. La comparación del ancho de la zona metaestable obtenidas con ambos métodos produjeron una diferencia promedio del 6.75 %. Finalmente, el orden de nucleación aparente calculado fue de 4.3, que resulta muy cercano al valor de 4.2 reportado en la literatura.

Palabras clave: cristalización, densidad, método politérmico, orden de nucleación, supersaturación.

1 Introduction

Adipic acid is the most useful dicarboxylic acid used in the reaction of salt-forming, esterification, acylation and polycondensation with diamines or dihydric alcohols. It is the main precursor in the synthesis of nylon-6,6, polyurethane and plasticizers. Besides, it also used in the production of high-

grade lubricating oil, food additives, intermediates of medicine, controlling reagents of perfume, plastic foamer, coating, adhesive, insecticide and dyestuff. However, adipic acid is produced mainly by a nitric acid oxidation of cyclohexanone and/or cyclohexanol. This process leads to nitrous oxide (N₂O) as a

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stoichiometric waste product and it may be generating global warming and ozone depletion. Sato *et al.* (1998) proposed a green route to produce adipic acid by oxidation of ciclohexanone with H_2O_2 in an aqueous solution. The reaction product is normally cooled and crystallized as adipic acid almost pure (>99%). Investigation of this new route is important specially the crystallization step. The evaluation of the metastable zone properties of the adipic acid is required for the design and operation of a crystallization process because such property generally affects other customer acceptance criteria, such as good performance, high purity, final product appearance, ability to flow and dissolution rate (Quintana-Hernandez *et al.*, 2005; Costa-Caline *et al.*, 2005; Trifkovic *et al.*, 2009; Titiz-Sargut and Ulrich, 2002). The final crystal size distribution (CSD) is strongly influenced by the supersaturation profile; therefore, it is essential to operate the crystallizer at the optimum supersaturation level with respect to the final desired properties (Trifkovic *et al.*, 2009; O'Grady *et al.*, 2007). Operating the crystallizer at high supersaturation results in the production of a large number of nuclei that compete with seeds and reduce the overall crystal size. In addition, it makes the subsequent solid-liquid separation more difficult. On the other hand, operating the crystallizer close to the saturation limit reduces the growth rate as well as the economical process feasibility. Therefore, it is important to define an operation zone for optimal crystallizers performance (Titiz-Sargut and Ulrich, 2003).

Theoretically, nucleation should initiate when solute concentration is larger than the saturation value (Mersmann, 1996). However, nucleation does not occur instantly, and solute remains in solution until a sufficiently high level of supersaturation is generated to induce spontaneous nucleation. This supersaturation defines what is called the metastable zone width. The metastable zone width has been considered as the maximum supercooling or supersaturation allowed for stable operation without spontaneous nucleation in a crystallizer, besides an essential parameter for development of optimization and control of crystallization process (Sangwal, 2009). The metastable zone width has two limits, the lower one is determined by the saturation temperature and the upper one is determined by the temperature at which the first crystals are detected (Kadam *et al.*, 2011; Kadam *et al.*, 2012).

The metastable zone width is a complex and not fully understood function of the cooling, nucleation

and growth rates, as well as process conditions, such as stirring speed, saturation temperature, presence of impurities dissolved in the solution, solvent used for preparation of supersaturated solutions, and the detection technique used (Titiz-Sargut and Ulrich, 2003). Several investigators have determined the metastable zone width of various compounds in different solvents (Sangwal, 2009; Kadal, *et al.*, 2011; Kashchiev and Van Rosmalen, 2003; Sangwal, 2011; Jiaoyu *et al.*, 2012). They have used conventional polythermal method in which the appearance of the first nuclei is detected while the solution is cooled at a constant rate. Nývlt (1968) proposed an equation for calculating nucleation rate as function of concentration difference or temperature difference. He included an empirical power-law relationship with quantities like nucleation constant and nucleation order and assumed that the solubility coefficient does not depend on saturation temperature. Nývlt's equation is frequently used for the study of nucleation kinetics by the polythermal method. On the other hand, several studies have been devoted to the understanding of the effect of various experimental factors on the metastable zone width and have tried to include these factors into mathematical models. Costa-Calaine *et al.* (2005) considered a nucleation mechanism including primary and a secondary nucleation as well as agglomeration of two particles. Sangwal (2009) included the classical theory of three-dimensional nucleation. His equation is function of solid-liquid interfacial energy, spherical nuclei collision factor, Boltzmann constant and the temperature of spontaneous nucleation. Kashchiev *et al.* (2010) analyzed the negative effects of impurities on nucleation rates caused by physically blocking of active sites. Kubota (2008, 2010) derived an equation, similar to Nývlt's but considering the number density of accumulated primary nuclei approaching a fixed value. Kim and Mersmann (2001) attempted to predict metastable zone width for seeded and unseeded systems at various cooling rates and compositions. They found a good agreement for some systems. Unfortunately, there are still no generally reliable mathematical models for calculating the metastable zone width and in many cases experimental determination is still necessary. In this work, the metastable zone width of adipic acid-water solutions is experimentally measured following the polythermal method in a temperature range from (293.15 to 328.15) K and cooling rates from (1 to 30) $K \cdot h^{-1}$.

2 Methodology

2.1 Materials and apparatus

Adipic acid (CAS No. 124-04-9, 99.6% w/w, W201103, Sigma-Aldrich) and tri-distilled water (Ecopura, Queretaro, Mexico) were used in all experiments. A crystallization system Pignat (Pilot Unit # 9312122, Pignat, France) was used. The system included a stainless steel 3-liter crystallizer with four vertical baffles equally distributed and agitated by a stirrer Janke & Kunkel (RW20DZM Model, range from 80 to 900 rpm). The solution temperature was measured with a thermocouple 900 FJ type. The cooling flow rate was controlled by a thermostat (LAUDA RP1800, Lauda-Königshofen, Germany) that allows to establish working profiles for cooling, heating or pumping. Peristaltic pumps (Easy-Load Masterflex Model 77201-62) helped to circulate the solution through a densitometer (mpDs 2000, Anton Paar GmbH, Austria) and a particle size analyzer Mastersizer S (Malvern Instruments Ltd UK) with a measuring range from 0.01E-06 to 800E-06 m. Temperature, density and crystal size distribution were read and stored on line with a data acquisition system cDAQ 9401 (National Instruments, USA). Figure 1 shows schematically the experimental setup for measuring the metastable zone width.

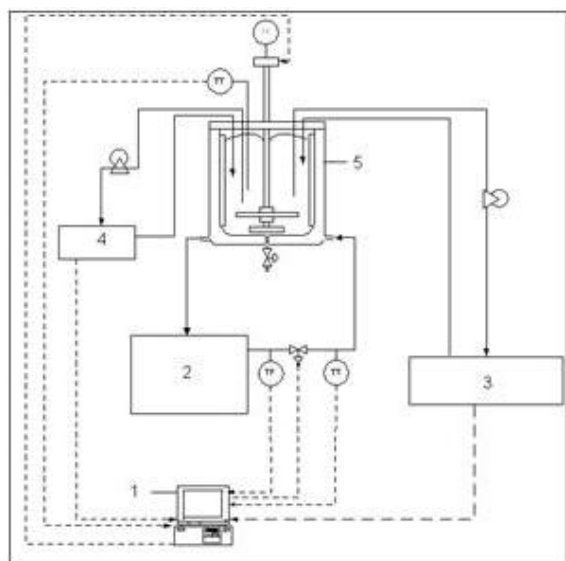


Fig. 1. Apparatus for experimental evaluation of metastable zone width: 1, PC processing system; 2, programmable thermostatic bath; 3, masterizer; 4, densitometer; 5, crystallizer.

2.2 Experimental procedure

For all experiments, 2.5 liters of saturated mixtures of adipic acid were prepared in triplicate at 293.15 K, 298.15 K, 303.15 K, 308.15 K, 313.15 K, 318.15 K, 323.15 K and 328.15 K using the saturation concentration reported by Zhibo *et al.* (2009). The solutions were heated 15 K above the saturation temperature to dissolve all crystals and left unsaturated 30 minutes before cooling. Hot solutions were circulated through a circuit that included the crystallizer, the densitometer and the particle size analyzer. Agitation rate for all runs was constant at a rate of 300 rpm. Density and CSD were measured continuously and stored every 30 and 60 seconds respectively. Hot solutions were cooled at a rate of 1, 5, 10, 15, 20, 25 and 30 K·h⁻¹. The metastable temperature, T_{exp} , was established when the first visible nucleus was detected by the Mastersizer and later compared to the estimated values obtained from the changes in density due to the presence of crystals in the solution. A detailed explanation of all experiments was previously published by Díaz-Pérez (2011).

2.3 Proposed alternative method

The proposed method is based on comparisons of the density of solution containing crystals and solutions free of crystals. The experimental procedure in this method is similar to the one used by the conventional polythermal method. Saturated solutions are prepared at the different experimental conditions, heated 15 K above saturation temperatures and then cooled at a constant rate. The main difference between the polythermal and the proposed methods is that instead of recording the temperature at which the first nuclei appear, an analysis of the variation of density as function of temperature and concentration is performed. The density of a homogeneous solution, with constant concentration, changes smoothly with temperature. If the solution is continuously cooled and crystals begin to appear then the solution concentration decreases and density changes abruptly. These changes in the solution density allow us to perform a mathematical analysis to determine the metastable zone width. The analysis begins with the collection of temperature and density data online for each of the experimental conditions. This information is used to develop models for estimating the density as function of temperature and concentration. The comparison of experimental and estimated densities generates an

Table 1. Uncertainties of measurements estimated for this study.

Property	estimated uncertainty
Temperature	± 0.05 K
Solubility	± 0.05 mol of 100 kg of H ₂ O
Density	± 0.05 kg·m ⁻³
nucleus size	$\pm 0.25E-06$ m

error function that allows us to establish the point at which crystals begin to appear in the solution. When the solution is free of crystals the error magnitude falls within the limits of uncertainty (experimental and model), but when the crystals appear, the error grows rapidly. Experimental data obtained at the cooling rate of 1 K·h⁻¹ was used to prove this alternative method. Estimates of uncertainty values for this study were evaluated and summarized in Table 1.

2.4 Evaluation of apparent nucleation order and nucleation rate constant

The evaluation of the apparent nucleation order and the nucleation rate constant was done using the equation established by Nývlt (1968). Ec. (1) relates the maximum temperature difference ΔT_{max} between saturation temperature and temperature of nucleation events and the cooling rate R at a constant stirring rate. The equation is expressed as follows:

$$\log(\Delta T_{max}) = \frac{1-m}{m} \log\left(\frac{dc^*}{dT}\right) - \frac{1}{m} \log(k_1) + \frac{1}{m} \log(R) \quad (1)$$

where R is the cooling rate, k_1 is a constant related to the nucleation rate, dc^*/dT is the slope of the solubility as function of temperature at the saturation temperature and m is the apparent nucleation order.

3 Results and discussion

3.1 Unsaturated zone

The triplicate experimental results of density as function of temperature were averaged for each of the eight different saturation conditions and plotted as shown in Fig. (2). The data in the unsaturated region show a close to linear relation between density and temperature at high concentrations and a quadratic relation at low concentrations. We decided to use a quadratic model, Eq. (2), for all eight experimental saturation conditions. Table 2 presents the regression

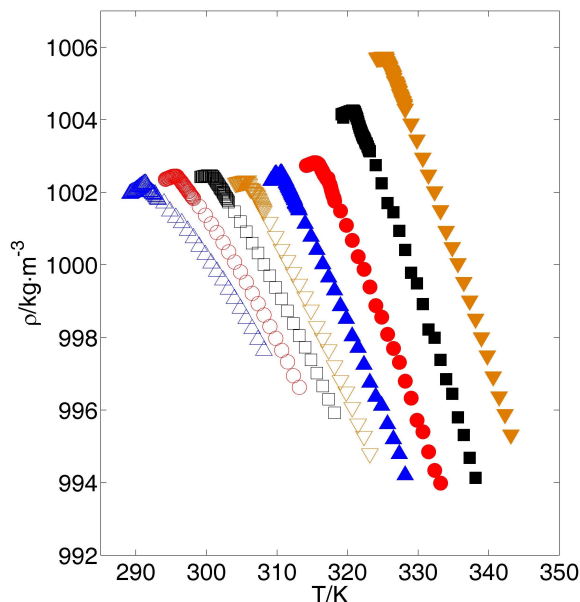


Figure 2. Adipic acid-water solution densities, ρ , as function of temperature T for solutions with initial concentration (mol·kg⁻¹). Δ , 0.1253; \circ , 0.1572; \square , 0.1979; ∇ , 0.2539; \blacktriangle , 0.3318; \bullet , 0.4382; \blacksquare , 0.5798; \blacktriangledown , 0.7631

coefficients; a_2 , a_1 , and a_0 ; the asymptotic standard error and R-squared for each experimental condition.

$$\rho/\text{kgm}^{-1} = a_2T^2 + a_1T + a_0 \quad (2)$$

3.2 Metastable zone

Fig. (3) shows the average maximum supercooling, ΔT_{max} , at the different initial compositions as function of cooling rates. Each ΔT_{max} was calculated as the difference between the saturation temperature and the temperatures at which the first crystals were detected by the Mastersizer (T_{exp}). The results showed that metastable zone width for the adipic acid - water system becomes narrower when the initial concentration is increased. The principal reason for this effect is generated by the higher saturation temperature. The diffusion and transfer rate of solute increase because of the larger number of molecular collision favoring nucleation phenomena. In the same way, the metastable zone width becomes narrower when cooling rate is decreased. Since the supersaturated solution has enough time for nucleation at slow cooling rates, the crystallization temperature will be higher favoring again the nucleation phenomena. The metastable zone width range was from 2.20 K to 2.85 K with an average

Table 2. Regression coefficients, a's, for evaluation of density at different experimental saturation temperatures

T_{sat}/K	$C_{sat}/mol \cdot kg^{-1}$	Parameter Name	Parameter Estimate	Asymptotic Standard Error	R^2
293.15	0.1253	a_2	-5.7622E-03	1.4909E-04	0.9996
		a_1	3.1846E+00	8.9335E-02	
		a_0	5.6346E+02	1.3380E+01	
298.15	0.1572	a_2	-5.2005E-03	2.9403E-05	0.9999
		a_1	2.8315E+00	1.7976E-02	
		a_0	6.1992E+02	2.7468E+00	
303.15	0.1979	a_2	-4.0076E-03	2.1848E-05	0.9999
		a_1	2.1022E+00	1.3573E-02	
		a_0	7.3275E+02	2.1076E+00	
308.15	0.2539	a_2	-3.7656E-03	1.0902E-04	0.9998
		a_1	1.9353E+00	6.8862E-02	
		a_0	7.6267E+02	1.0873E+01	
313.15	0.3318	a_2	-2.2317E-03	1.5125E-04	0.9994
		a_1	9.5099E-01	9.7050E-02	
		a_0	9.2259E+02	1.5565E+01	
318.15	0.4382	a_2	-4.9759E-03	1.7708E-04	0.9996
		a_1	2.7108E+00	1.1535E-01	
		a_0	6.4303E+02	1.8782E+01	
323.15	0.5798	a_2	-6.0839E-03	2.2421E-04	0.9996
		a_1	3.4239E+00	1.4830E-01	
		a_0	5.3200E+02	2.4519E+01	
328.15	0.7631	a_2	-3.9187E-03	8.3005E-05	0.9999
		a_1	2.0298E+00	5.5594E-02	
		a_0	7.6023E+02	9.3068E+00	

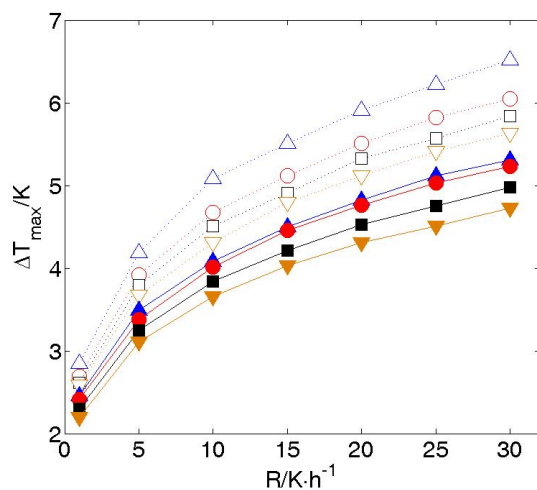


Fig. 3. Maximum supercooling as function of cooling rates for solutions with initial concentration (mol·kg⁻¹). Δ , 0.1253; \circ , 0.1572; \square , 0.1979; ∇ , 0.2539; \blacktriangle , 0.3318; \cdot , 0.4382; \blacksquare , 0.5798; \blacktriangledown , 0.7631.

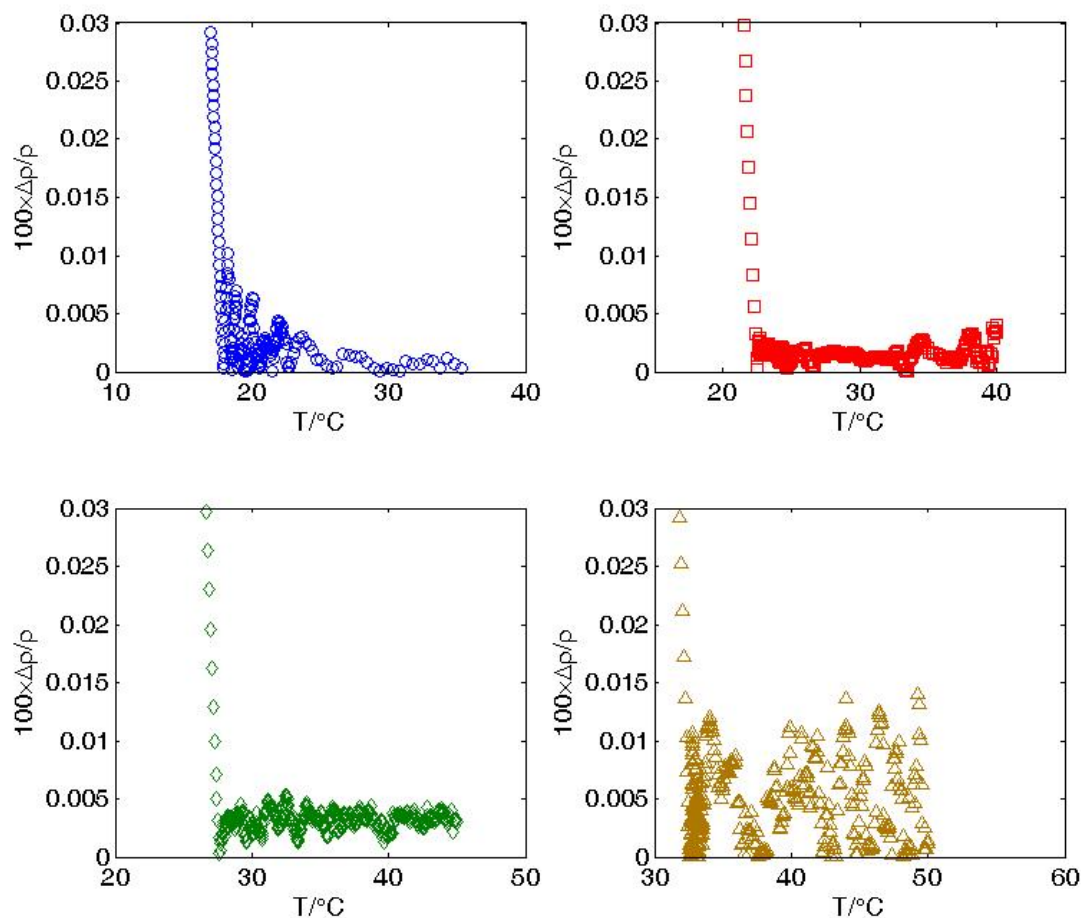


Fig. 4. Fractional deviations $\Delta\rho = \rho(exp) - \rho(calc)$ of the experimental density $\rho(exp)$ during the cooling process of mixtures with initial concentration ($\text{mol}\cdot\text{kg}^{-1}$). \circ , 0.1253; \square , 0.1572; \diamond , 0.1979; \triangle , 0.2539.

Table 3. Metastable zone width for the adipic acid-water system evaluated with the experimental polythermal method (ΔT_{exp}) and estimated with the proposed density analysis method (ΔT_{calc}) at a cooling rate of $1 \text{ K}\cdot\text{h}^{-1}$.

T_{satu}/K	$\Delta T_{exp}/\text{K}$	$\Delta T_{calc}/\text{K}$	%Error
293.15	2.85	2.94	3.16
298.15	2.69	2.77	2.97
303.15	2.61	2.85	9.19
308.15	2.59	2.83	9.27
313.15	2.46	2.67	8.54
318.15	2.41	2.64	9.54
323.15	2.30	2.44	5.91
328.15	2.20	2.32	5.32

6.52 K with an average of 5.54 K for a cooling rate of $30 \text{ K}\cdot\text{h}^{-1}$.

On the other hand, the comparison of experimental and estimated densities at temperatures above the saturation temperature produced a small relative error. When the solution was cooled at a temperature below the saturation temperature and crystals appeared the difference between the estimated and the experimental densities quickly increased and the relative error became bigger than the experimental error. Figs (4)-(5) present the percentage average relative error, $100\Delta\rho/\rho$, for all saturation concentrations at a cooling rate of $1 \text{ K}\cdot\text{h}^{-1}$. The pictures showed that in all runs the error remained small before crystals appeared in the mixture and increased quickly after crystals appeared. This fact was used to propose that the last

of 2.51 K for the cooling rate of $1 \text{ K}\cdot\text{h}^{-1}$ and 4.73 K to

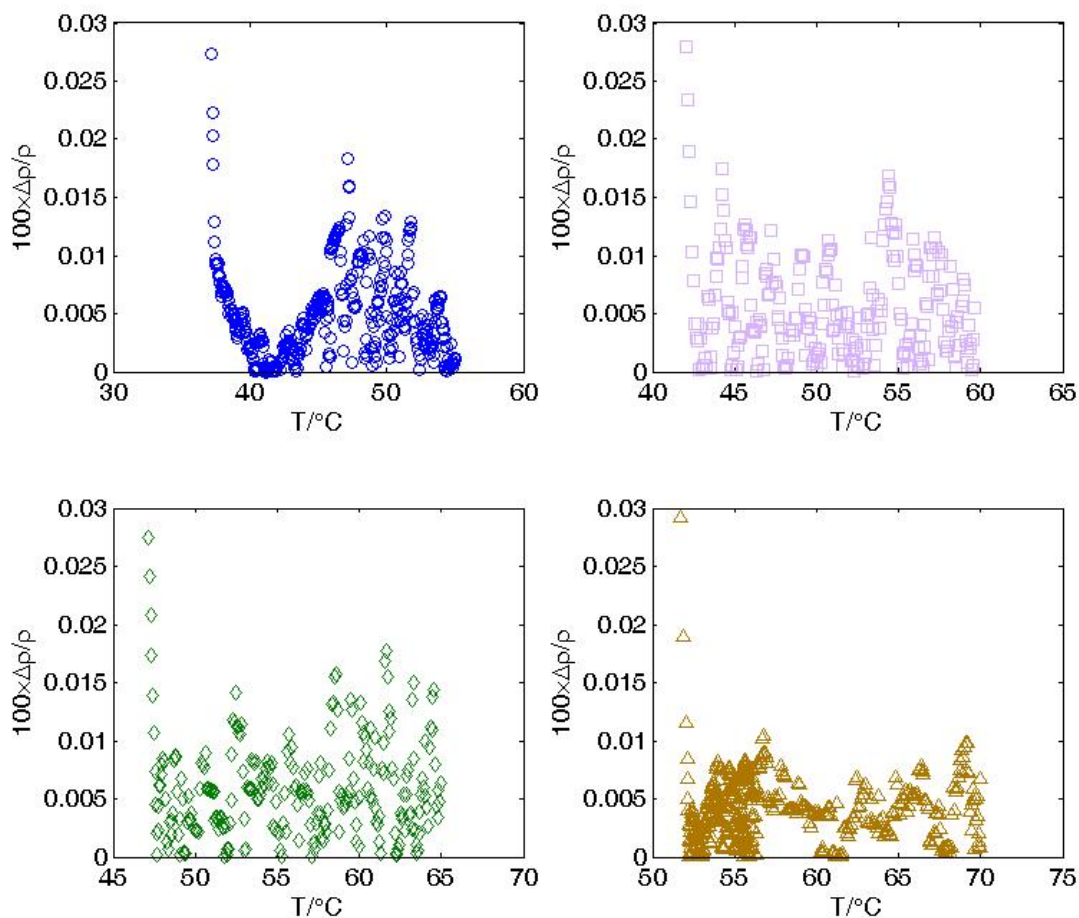


Fig. 5. Fractional deviations $\Delta\rho = \rho(exp) - \rho(calc)$ of the experimental density $\rho(exp)$ during the cooling process of mixtures with initial concentration (mol·kg⁻¹). \circ , 0.3318; \square , 0.4382; \diamond , 0.5798; \triangle , 0.7631.

achieved temperature before the gap appeared it would be considered as the limit of the estimated metastable zone. Table 3 shows the values of ΔT_{max} obtained with the polythermal method and the estimations made with the density model.

For all the experiments, the calculated metastable zone width values were larger than those determined by the polythermal method with an average difference of 6.75%. These differences could be explained on the basis of the densitometer sensibility. At the time the first crystals appeared the overall solid mass was not enough to produce a detectable change in the measured density; that is actually a disadvantage of our alternative method for the estimation of the metastable zone width. On the other hand, a clear advantage of our alternative approach is

the relative simplicity for taking the experimental measurements without introducing significant errors in the estimation; it is in fact much easier to measure densities than detecting the first appearance of crystals through the Mastersizer (as required in the polythermal method).

Fig. (6) shows the limits of the metastable zone width (concentration as function of temperature) obtained with a cubic correlating equation, Eq (3). The lines are reproduced by the correlation models and the symbols represent the experimental data of this work (upper limit, nucleation concentration at a cooling rates of 1 K·h⁻¹ and 30 K·h⁻¹) and the information reported by Zhibo *et al.* (2009) (lower limit, saturation concentration). The coefficients of Eq. (3) are given in Table 4.

Table 4. Regression parameters c 's, for evaluation of nucleation concentration, C_{nucl} , and saturation concentration,

Parameter	C_{sat}		$C_{sat}/\text{mol}\cdot\text{kg}^{-1}$
	$C_{nucl}/\text{mol}\cdot\text{kg}^{-1}$		
	Cooling rate 1 $\text{K}\cdot\text{h}^{-1}$	Cooling rate 10 $\text{K}\cdot\text{h}^{-1}$	
c_3	8.1524E-06	7.4158E-06	8.8040E-06
c_2	-7.0496E-03	-6.3234E-03	-7.7000E-03
c_1	2.0376E00	1.8025E00	2.2506E00
c_0	-1.9674E02	-1.7175E02	-2.1978E02
R^2	0.9999	0.9999	0.9999

 Table 5. Nucleation equation of adipic acid in water at different solubilities ($\text{mol}\cdot\text{kg}^{-1}$).

C_{sat}	Nucleation equation	R^2
0.1253	$\log(\Delta T_{max}) = 0.4552 + 0.2436\log(R)$	0.9993
0.1572	$\log(\Delta T_{max}) = 0.4286 + 0.2396\log(R)$	0.9998
0.1979	$\log(\Delta T_{max}) = 0.4159 + 0.2367\log(R)$	0.9997
0.2539	$\log(\Delta T_{max}) = 0.4096 + 0.2298\log(R)$	0.9991
0.3318	$\log(\Delta T_{max}) = 0.3876 + 0.2272\log(R)$	0.9992
0.4382	$\log(\Delta T_{max}) = 0.3768 + 0.2303\log(R)$	0.9984
0.5798	$\log(\Delta T_{max}) = 0.3583 + 0.2275\log(R)$	0.9993
0.7631	$\log(\Delta T_{max}) = 0.3397 + 0.2254\log(R)$	0.9995

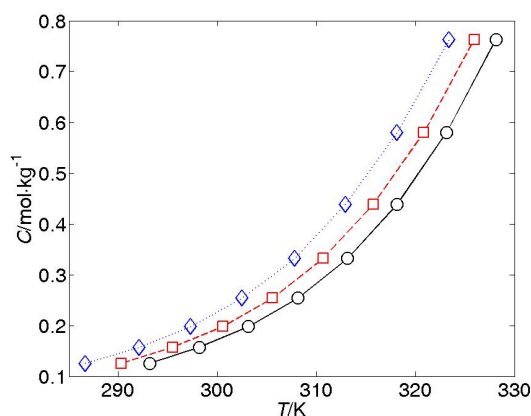


Fig. 6. Metastable zone width for the adipic acid-water system. \diamond , metastable zone width nucleation limit at a cooling rate of 30 K h^{-1} ; \square , metastable zone width nucleation limit at a cooling rate of 1 K h^{-1} ; \circ , metastable zone width limit at saturation concentration.

$$C = c_3T^3 + c_2T^2 + c_1T + c_0 \quad (3)$$

3.3 Apparent nucleation order

Fig. (7) shows the plot of $\log(\Delta T_{max})$ as function of $\log R$. It may be seen that the resulting lines are basically straight and parallel and they may be represented as:

$$\log(\Delta T_{max}) = C_1 + C_2 \log(R) \quad (4)$$

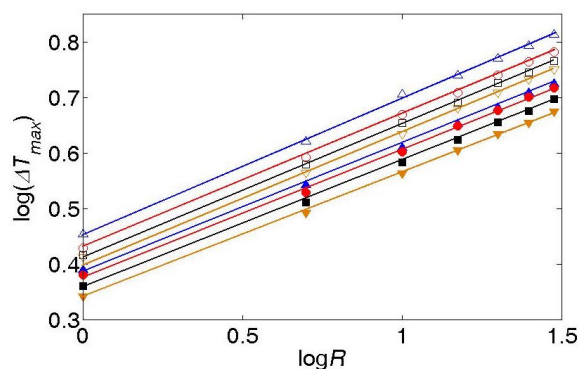


Fig. 7. Relationship between $\log(\Delta T_{max})$ and $\log(R)$ at initial compositions ($\text{mol}\cdot\text{kg}^{-1}$). \triangle , 0.1253; \circ , 0.1572; \square , 0.1979; ∇ , 0.2539; \blacktriangle , 0.3318; \bullet , 0.4382; \blacksquare , 0.5798; \blacktriangledown , 0.7631.

A comparison of these lines with the Nývlt equation suggests that the first two term of Nývlt equation may be combined as C_1 and the value C_2 represents the inverse of the apparent nucleation order. A linear regression for each set of values generate the coefficients C_1 and C_2 presented in Table 5. The overall coefficients of Nývlt equation were obtained carrying out a multiple linear regression. The apparent nucleation order m was 4.3011 ± 0.0406 , which is closed to the value 4.2 reported in the literature by Liu (1991). The obtained value for k_1 was 1.0777 ± 0.0583 .

Conclusions

The results obtained with the polythermal method showed that the metastable zone width for the adipic acid-water system decreases with increasing initial composition and increases with increasing cooling rates. In addition, it was found that online density measurements could be used as an alternate method for estimating the metastable zone width. The proposed method confirmed the variation of the metastable zone width as function of the initial concentration. A comparison of the metastable zone width obtained with both methods produced an average difference of 6.75 %. Finally, the calculated apparent nucleation order is in good agreement with the value reported in the literature.

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