

## Supersaturation dependence of glycine polymorphism using laser-induced nucleation, sonocrystallization and nucleation by mechanical shock

Yao Liu, Mees van den Berg and Andrew J. Alexander\*

*School of Chemistry, University of Edinburgh, David Brewster Road,  
Edinburgh, Scotland, EH9 3FJ*

### Supporting Information

#### 1. Aqueous solubility of glycine

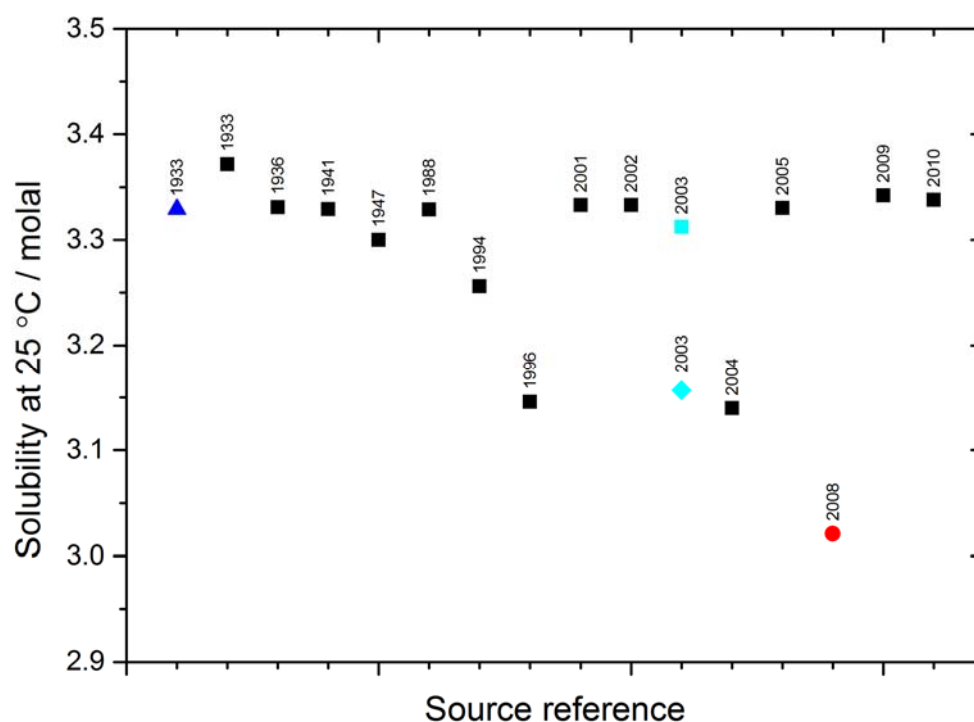
In Fig. S1 we plot the solubility in molality (moles of glycine solute per kg of water) at 25 °C, calculated from various sources. Note that we have not conducted an exhaustive survey. The solubility data of Yang et al. (2008) appear to be anomalously low in comparison to data from other sources (red circle in Fig. S1).<sup>1</sup> The data plotted are from actual measurements at this temperature except for Park et al. (2003),<sup>2</sup> where we have used quadratic fits to obtain the values. We note that the data of Park et al. (tabulated as wt% in that work) have been incorrectly plotted in Fig. 1 of ref. 1.

Where not specified, it was assumed that the solution was in equilibrium with  $\alpha$ -glycine, as this is the form most often obtained by spontaneous nucleation. Sources agree that the solubility of  $\gamma$ -glycine is lower than that of  $\alpha$ -glycine at 25 °C.<sup>1,2</sup> The data for Gude et al. (1996)<sup>3</sup> and Ferreira et al. (2004)<sup>4</sup> are remarkably close to the value for  $\gamma$ -glycine observed by Park et al. (cyan diamond in Fig. S1), so it is possible that these measurements were made with solutions in equilibrium with  $\gamma$ -glycine.

The solubility data we have used in our work was that of Dalton et al. (1933) [blue triangle in Fig. S1],<sup>5</sup> which we prefer due to the quality of the measurements and agreement with other data sources over a range of temperatures. Clair et al. used the solubility data of Yang et al. to determine supersaturations.<sup>1,6</sup> We calculated the solubilities from Yang et al. at 17 °C (using 2-point linear interpolation) as  $C_{\text{sat}} = 2.48 \text{ mol kg}^{-1}$  for  $\alpha$ -glycine and  $C_{\text{sat}} = 2.21 \text{ mol kg}^{-1}$  for  $\gamma$ -glycine. It should be noted that  $S$  in Fig. 6 of Clair et al. (fraction of samples nucleated) were calculated relative to the  $\gamma$  polymorph; and  $S$  in Fig. 10 (distribution of polymorphs obtained) were calculated relative to the  $\alpha$  polymorph.

We calculated the solubility for  $\alpha$ -glycine at 17 °C as  $C_{\text{sat}} = 2.82 \text{ mol kg}^{-1}$  from Dalton et al. Note that this value is 12% higher than that of Yang et al. Using the concentration data in Fig. 6-

16 (fraction of samples nucleated) and Fig. 6-39 (distribution of polymorphs obtained) of Clair's thesis,<sup>7</sup> we calculated  $S$  using Dalton's value for  $C_{\text{sat}}$ . The resulting  $S$  values were used in the present article to facilitate comparison. For convenience, the adjusted values are listed in Tables S1–S2.



**Fig. S1.** Aqueous solubility of glycine in molality at 25 °C from various sources. Points highlighted are the source used in the present work (blue triangle), the value for  $\alpha$ -glycine value of Yang et al.<sup>1</sup> (red circle), and the values for  $\alpha$ -glycine (cyan square) and  $\gamma$ -glycine (cyan diamond) of Park et al.<sup>2</sup> The sources from left to right are Dalton (1933),<sup>5</sup> Dunn (1933),<sup>8</sup> Cohn (1936),<sup>9</sup> Seidell (1941),<sup>10</sup> Mason (1947),<sup>11</sup> Talukdar (1988),<sup>12</sup> Eyseltova (1994),<sup>13</sup> Gude (1996),<sup>3</sup> Islam (2001),<sup>14</sup> Ramasami (2002),<sup>15</sup> Park (2003),<sup>2</sup> Ferreira (2004),<sup>4</sup> Yi (2005),<sup>16</sup> Yang (2008),<sup>1</sup> Venkatesu (2009),<sup>17</sup> El-Dossoki (2010).<sup>18</sup>

Concentration / g kg <sup>-1</sup>	Supersaturation (S) [Yang et al.]	Supersaturation (S) [Dalton et al.]
205	1.22	0.97
224	1.33	1.06
242	1.44	1.15
261	1.55	1.23
280	1.66	1.32

**Table S1.** Concentrations taken from Fig. 6-16 of Clair,<sup>7</sup> and the corresponding supersaturations using the solubility at 17 °C for  $\gamma$ -glycine of Yang et al.<sup>1</sup> (as plotted in Fig. 6 of Clair et al.<sup>6</sup>) versus the solubility at 17 °C for  $\alpha$ -glycine of Dalton et al.<sup>5</sup> (as plotted in Fig. 1(a) of the present work).

Concentration / g kg <sup>-1</sup>	Supersaturation (S) [Yang et al.]	Supersaturation (S) [Dalton et al.]
251	1.35	1.19
263	1.41	1.24
268	1.44	1.27
274	1.47	1.30
280	1.51	1.32
285	1.53	1.35
291	1.56	1.38
297	1.60	1.40

**Table S2.** Concentrations taken from Fig. 6-39 of Clair,<sup>7</sup> and the corresponding supersaturations using the solubility at 17 °C for  $\alpha$ -glycine of Yang et al.<sup>1</sup> (as plotted in Fig. 10 of Clair et al.<sup>6</sup>) versus the solubility at 17 °C for  $\alpha$ -glycine of Dalton et al.<sup>5</sup> (as used plotted in Fig. 2(a) of the present work).

## 2. Analysis of glycine polymorphs

Glycine powder was analysed using powder X-ray diffraction (pXRD, Bruker D2 PHASER) and attenuated total-reflectance infrared spectroscopy (ATR-FTIR, Perkin Elmer UATR Two). X-ray Cu K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ), a current of 10 mA, a voltage of 30 kV and a temperature of 20–25 °C were used. Data were collected from  $2\theta = 5$  to  $40^\circ$  in steps of  $0.036^\circ$  with 0.35 s per step. FTIR spectra were recorded in the range 500–4000  $\text{cm}^{-1}$ . Polymorphs were distinguished by comparing the intensities of doublet peaks at 892 and 909  $\text{cm}^{-1}$  for  $\alpha$  glycine and 889 and 928  $\text{cm}^{-1}$  for  $\gamma$  glycine.

## 3. Tables of data

Tables S3 to S5 contain numbers of samples exposed and corresponding counts of products.

<b>Supersaturation (S)</b>	<b>Number of samples exposed (N)</b>	<b>Number of samples nucleated (n)</b>	<b>Number of samples producing only <math>\gamma</math> glycine (<math>n_g</math>)</b>
1.4	98	20	4*
1.45	50	15	14
1.5	91	54	54
1.6	32	28	27
1.7	12	12	12

**Table S3.** Number of samples exposed to NPLIN and the resulting counts of products. (\*) Note that for  $S = 1.4$  it was found that 4 samples produced  $\gamma$  glycine, 9 produced  $\alpha$  glycine, 6 samples produced mixtures of  $\alpha$  and  $\gamma$  glycine. The fractions of  $\gamma$ -glycine in the mixed samples were determined to be 0.99, 0.87, 0.81, 0.43, 0.42 and 0.30.

<b>Supersaturation (S)</b>	<b>Number of samples exposed (N)</b>	<b>Number of samples nucleated (n)</b>	<b>Number of samples producing only <math>\gamma</math> glycine (<math>n_g</math>)</b>
1.4	67	43	9
1.5	52	38	17
1.6	48	23	16
1.7	46	34	27

**Table S4.** Number of samples exposed to sonocrystallization and the resulting counts of products.

<b>Supersaturation (S)</b>	<b>Number of samples exposed (N)</b>	<b>Number of samples nucleated (n)</b>	<b>Number of samples producing only <math>\gamma</math> glycine (<math>n_g</math>)</b>
1.4	15	11	3
1.5	15	12	7
1.6	10	9	8
1.7	8	8	8

**Table S5.** Number of samples exposed to mechanical shock and the resulting counts of products.

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