The effect of carboxylic acids on glycine polymorphism, salt and co-crystal formation. A comparison of different crystallisation techniques.

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Supplementary materials

1. Viscosities* of solvents used

Solvent	Viscosity (cP)
Acetone	0,36
Ethyl alcohol	1,1
THF	0,55
1,4-dioxane	1,37

* http://macro.lsu.edu/HowTo/solvents/viscosity.htm

We suppose that the differences in viscosities is not of great importance as compared to differences of miscibility of this solvents with glycine water solution.

2. The results of experiments on anti-solvent presipitation of water solutions with stoichiometric amounts of α-glycine and carboxylic acids.

2.1 Acetone as antisolvent

1 run

	Products			
Dicarboxylic acid	The polymorphs of glycine (%)			Salt
	α	β	γ	
Oxalic acid (dihydrate)	-	-	15	bis(Glycinium) oxalate - 85%
Malonic acid	-	95	5	-
Succinic acid	20	80	-	-
Maleic acid	-	100	-	-
Glutaric acid	33	67	-	-
L-malic acid	-	100	-	-

2 run

	Products			
Dicarboxylic acid	The polymorphs of glycine (%)			Salt
	α	β	γ	
Oxalic acid (dihydrate)	-	-	68	bis(Glycinium) oxalate — 32%
Malonic acid	-	100	-	-
Succinic acid	-	100	-	-
Maleic acid	-	100	-	-
Glutaric acid	100	-	-	-
L-malic acid	-	100	-	-

3 run

	Products			
Dicarboxylic acid	The polymorphs of glycine (%)			Salt
	α	β	γ	
Oxalic acid (dihydrate)	-	-	-	bis(Glycinium) oxalate — 100%
Malonic acid	-	16	84	-
Succinic acid	1	99	-	-
Maleic acid	-	99	1	-
Glutaric acid	10	90	-	-
L-malic acid	-	100	-	-

2.2 THF as antisolvent

1 run

	Products			
Dicarboxylic acid	The polymorphs of glycine (%)			Salt
	α	β	γ	
Oxalic acid (dihydrate)	-	-	-	bis(Glycinium) oxalate - 100%
Malonic acid	-	-	100	-
Succinic acid	100	-	-	-
Maleic acid	100	-	-	-
Glutaric acid	100	-	-	-
L-malic acid	30	-	70	-

2 run

	Products			
Dicarboxylic acid	The polymorphs of glycine (%)			Salt
	α	β	γ	
Oxalic acid (dihydrate)	-	-	85	bis(Glycinium) oxalate — 15%
Malonic acid	1	99	-	-
Succinic acid	1	99	-	-
Maleic acid	-	100	-	-
Glutaric acid	-	100	-	-
L-malic acid	-	100	-	-

3 run

	Products			
Dicarboxylic acid	The polymorphs of glycine (%)			Salt
	α	β	γ	
Oxalic acid (dihydrate)	-	-	70	bis(Glycinium) oxalate — 30%
Malonic acid	40	60	-	-
Succinic acid	5	95	-	-
Maleic acid	1	99	-	-
Glutaric acid	14	86	-	-
L-malic acid	1	99	-	-

3. pH values of the solutions

Typical pH measured in freshly prepared glycine water solutions with 1-40 percent adding of carboxylic acid

Carboxylic acid	pH
Oxalic	4.2 — 2.0
Malonic	4.6 — 2.8
Maleic	4.6 — 2.4
L-malic	4.6 — 3.0
Glutaric	4.7 — 3.5

Any amounts of glutaric acid didn't lead to crystallisation of γ-glycine regardless the identical pH values compared to other carboxylic acids.
As an extra experiment we prepare glycine water solutions with 5 and 10 molar percent of hydrochloric acid resulting in crystallisation of mixtures of α- and γ-glycine in the case of 5 percent addition (respective pH was about 3.5) and crystallisation of γ-glycine when 10 percent added (respective pH was about 3.3).