Korean J. Chem. Eng., 34(9), 2445-2450 (2017)
DOI: 10.1007/s11814-017-0158-2

pISSN: 0256-1115
eISSN: 1975-7220

Crystallization of glycine in water/saturated fatty acid emulsions

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(*Received 11 February 2017 • accepted 3 June 2017*)

Abstract−It was found that carbon chain length of fatty acids strongly affects polymorphic selection in the cooling crystallization of glycine from water/saturated fatty acid emulsions. Two-dimensional packing density of saturated fatty acid head groups, which is inversely proportional to the number of carbon atoms, was shown to be responsible for polymorphic selection of glycine: γ-glycine was obtained from the emulsions of hexanoic acid and octanoic acid, whereas α-glycine was found to crystallize from the emulsions of dodecanoic acid, tetradecanoic acid, hexadecanoic acid and octadecanoic acid. Those results indicate that molecular structure of γ-glycine is only well matched with molecular structure of head groups of hexanoic acid and octanoic acid at the interface of the emulsion, and thus such molecular interface provides the preferential site for the organization of γ-form crystal structure from the liquid-like cluster of glycine.

Keywords: Glycine, Polymorph, Fatty Acid

INTRODUCTION

Glycine with three modifications (α, β and γ-form) in ambient condition is the simplest amino acid widely used in nutritional supplements and animal feedstuffs [1,2]. Glycine is not only one of inhibitory neurotransmitters in central nervous system, especially in spinal cord, but also a required co-agonist for an excitatory neurotransmitter facilitated at a N-methyl-D-aspartate (NMDA) glutamatergic receptors [3,4]. Therefore, exogenous glycine is widely used for control of neuronal activity misbalance between inhibitory and excitatory [5]. In addition, administration of a suitable amount of glycine is effective in mediation for a number of nervous diseases and problems such as unsatisfactory sleep, ischaemic stroke, peripheral nerve injury, schizophrenia, and so on [6-9].

Over 80% of solid-phase organic compounds have multiple crystalline forms, and about 50% of those including glycine have more than two forms of polymorphic modifications [10,11]. Polymorphic composition affects physicochemical properties such as solubility, dissolution rate, density, heat capacity, melting point, crystal morphology, and so on [12]. In case of active pharmaceutical ingredients, in particular, different solid-state forms can lead to different bioavailability and pharmacological activity [13]. For this reason, once a new drug is launched, the U.S. Food and Drug Administration requires characterization of the stable form of polymorphs and also requires pharmaceutical manufacturers to control the crystallization of drugs so that the desired polymorph is consistently produced [14,15].

In recent years, effects of glycine polymorphs on pharmacological activities have been extensively investigated by Boldyrev et al. [5,16-18]. They reported that γ-glycine has much higher pharmacological potency for mediation of negative behavioral symptoms of schizophrenia compared with α-glycine on the basis of their in vivo rat study [16,17]. Their in vitro experiments in which glycine was applied directly on hippocampal neuron cells showed that γ-form developed a modulating influence on NMDA channel more slowly compared with α-form [5]. This prolonged effect of γ-glycine may be demanded for the mediation of schizophrenia. Furthermore, they confirmed that γ-glycine has stronger inhibitory effect on an olfactory bulb compared with α-glycine in the in vivo rat study on intranasal delivery of manganese hydroxide nanoparticles [18]. Such results highlight the importance of separation and purification process of γ-glycine.

γ-Glycine at aqueous solution is known to be thermodynamically stable at room temperature, but α- and γ-glycine mixture is abundant in most commercial glycine powders because α-form is selectively crystallized from neutral water [11]. Many strategies have been proposed to obtain γ-glycine such as crystallization from highly acidic or basic aqueous solution, crystallization in small-sized crystallizing medium, crystallization with tailor-made impurities which inhibit crystallization of both α- and β-glycine, and crystallization under the irradiation with intense polarized laser light, direct-current electric field, or ultrasound [19-26]. However, these methods can induce pH control problem, usage of harmful chemicals or uneconomical processes.

Recently, it has been reported that stable γ-glycine can be obtained from neutral water/oleic acid emulsion due to complementary interactions between the carboxyl head group of oleic acid and the NH_3^+ group of (001) face of γ-glycine [27]. Here, oleic acid, the major component of olive and soybean oils, is not harmful to humans. However, *cis*-double bond of oleic acid of hydrocarbon chain induces auto-oxidation of oleic acid [28] and subsequent difficulty of solvent reuse, i.e., oxidized oleic acid exerts a deleterious effect on reproducibility. We performed experiments on batch cooling crystallization of glycine from water/saturated fatty acid

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Table 1. Saturated fatty acids used in the present work

IUPAC name	Common name	Molecular formula
Octadecanoic acid	Stearic acid	$C_{18}H_{36}O_2$
Hexadecanoic acid	Palmitic acid	$C_{16}H_{32}O_2$
Tetradecanoic acid	Myristic acid	$C_{14}H_{28}O_2$
Dodecanoic acid	Lauric acid	$C_{12}H_{24}O_2$
Decanoic acid	Capric acid	$C_{10}H_{20}O_2$
Octanoic acid	Caprylic acid	$C_8H_{16}O_2$
Hexanoic acid	Caproic acid	$C_6H_{12}O_2$

emulsions for the production of γ-glycine without auto-oxidation of fatty acids.

EXPERIMENTAL

1. Materials

Raw glycine used in the present work (>99%, Tokyo Chemical Industry, Japan) was α-form. Saturated fatty acids (>98%, Tokyo Chemical Industry, Japan) used were summarized in Table 1 with International Union of Pure and Applied Chemistry (IUPAC) name, common name, and molecular formula. The triple-distilled water was used as a solvent.

2. Batch Cooling Crystallization

Batch cooling crystallizations and solubility measurements were performed using a 500 mL jacketed glass crystallizer. Solution was stirred by a Teflon-coated two straight blade impeller at a 300 rpm. At 85 °C, solubility of α-glycine in water measured by a gravimetric method is 0.654 g/g water, whereas fatty acid cannot dissolve glycine [27]. At this temperature, a saturated aqueous solution of α-glycine was prepared and mixed with fatty acid (60 wt% on a solute free basis) and then kept at 95 °C for 1 h for the stabilization of the emulsion. Batch cooling crystallization was conducted to 70 °C at a constant cooling rate of 10 °C/h. This cooling rate was reported as a proper condition for the production of γ-glycine for a cooling crystallization from water/oleic acid emulsion [27].

3. Characterization of Glycine Polymorph

Crystal structure of glycine was characterized by a powder X-ray diffractometer (PXRD) (MiniFlex, Rigaku, Tokyo, Japan) operated at 30 kV and 15 mA with graphite monochromatized Cu Kα radiation (λ=1.5418 Å). PXRD patterns were collected using a rotating flat-plate sample holder over the 2θ range from 10° to 40° with a step size of 0.02° and a scanning rate of 1.0°/min under ambient conditions. Typical peaks of PXRD pattern representing α- and γ-glycine are at 2θ of around 29.8° and 25.3°, respectively [27].

RESULTS AND DISCUSSION

1. Effect of Hydrocarbon Chain of Fatty Acids on Crystallization of Glycine

Zwitterions of α-glycine interact by hydrogen bonds in double antiparallel layers, and these double layers form relatively weak interactions. However, zwitterions of γ-glycine form polar helixes interacting with each other in a polar network consisting of NH_3^+-rich (001) face and COO^--rich (00$\bar{1}$) face [11]. As mentioned, the (001) face of γ-glycine has strong affinity with the head group of fatty acid [27]. An effective surface area of a pocket site on (001) face of γ-glycine is 42.13 Å^2/pocket, which was calculated as the area of a triangle of three molecules with lattice parameters of a γ-glycine (a=b=6.975 Å; c=5.473 Å; α=β=90°; γ=120°; Z=3, space group $P3_2$) [29]. Therefore, to induce γ-glycine nuclei at the fatty acid/water interface, two-dimensional effective surface area of the fatty acid head group at the interface should be in good agreement with 42.14 Å^2, i.e., one molecule of fatty acid per roughly 42.14 Å^2 at the interface. Such lattice matching concept has been known as one of significant factors in the selection of crystalline substrates for polymorphic control by heterogeneous nucleation [30].

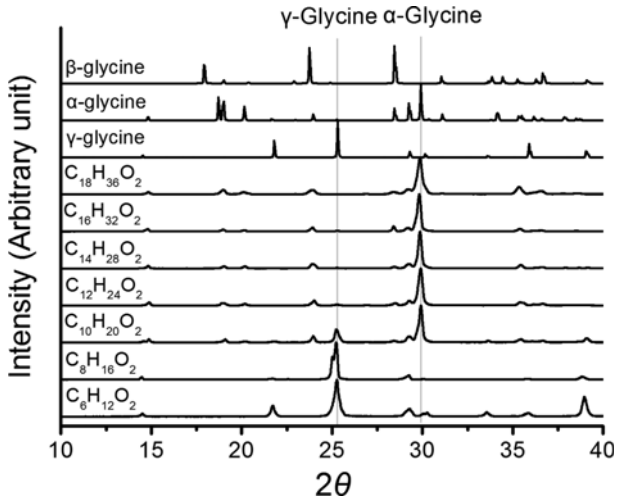

Fig. 1. Normalized PXRD patterns of glycine crystals obtained by cooling crystallization from the emulsions of neutral water/saturated fatty acids. α-, β- and γ-glycine indicate theoretical PXRD patterns. Two vertical lines indicate major peak positions of α- and γ-polymorphs.

Fig. 1 shows the theoretical and experimental PXRD patterns of glycine crystals obtained from neutral water/saturated fatty acid emulsions. In this figure, the theoretical PXRD pattern of each polymorph was simulated by using Materials Studio (Accelrys, version 5.5, USA). It was found that γ-glycine crystals were obtained from emulsions comprised of hexanoic and octanoic acids (number of carbon atoms is 6 and 8, respectively). From the water/decanoic acid emulsion (number of carbon atoms: 10), mixture of α- and γ-glycine was produced. Only α-glycine was obtained from emulsions comprised of dodecanoic, tetradecanoic, hexadecanoic, and octadecanoic acids (number of carbon atoms is 12, 14, 16, and 18, respectively). From those results, it may be concluded that the two-dimensional arrangement of head groups of hexanoic and octanoic acids is well matched with the surface structure of (001) face of γ-glycine, as illustrated in Fig. 2(a).

It has been reported that the packing density of head group of saturated fatty acids in their monolayer increases with increasing carbon number of hydrocarbon chain due to van der Waals interaction between the hydrocarbon chains [31]. These experimental results may be extended to the interface of water/fatty acid emul-

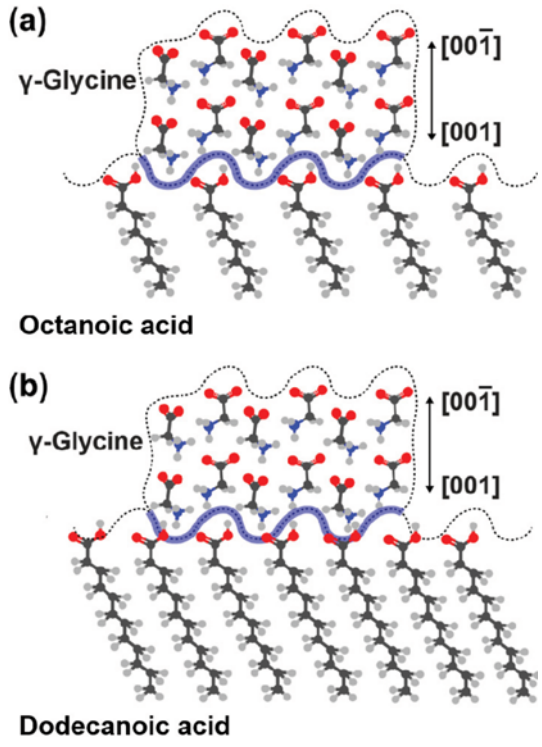

Fig. 2. Schematic diagram of arrangement of γ-glycine cluster at molecular layer of the fatty acids: (a) octanoic acid and (b) dodecanoic acid. Colors of atom: carbon (dark grey), nitrogen (blue), oxygen (red), and hydrogen (light grey). Broad blue curves indicate the (001) surface of γ-glycine.

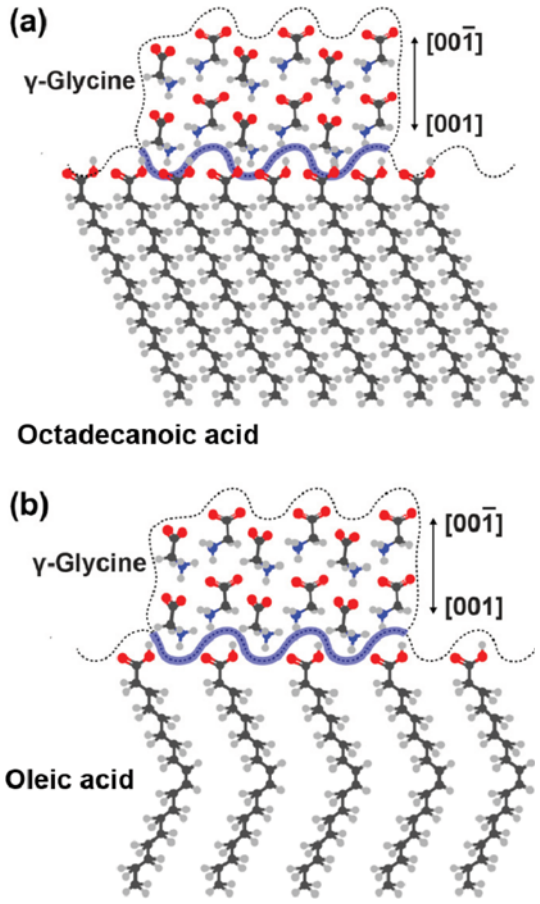

Fig. 3. Schematic diagram of molecular arrangements of γ-glycine cluster and molecular layer of (a) octadecanoic acid and (b) oleic acid at their interface with water.

sions. Therefore, as illustrated in Fig. 2(b), the effective surface area may decrease with increasing number of carbon atoms, and the two-dimensional arrangement of those fatty acids does not match with the (001) face of γ-glycine. Therefore, only α-forms are shown to be generated in those emulsions.

Furthermore, γ-glycine crystal can be obtained from the emulsion of water and oleic acid that is an unsaturated fatty acid when the similar experimental conditions (saturation temperature and cooling profile) are employed. According to the pressure/surface area relationship of saturated and unsaturated fatty acid monolayers, packing density of head group of an unsaturated fatty acid is larger than saturated fatty acid with the same number of carbon atoms due to the *cis*-double bond in the hydrocarbon chain [32]. The number of carbon atoms of oleic acid is the same as that of stearic acid, but oleic acid has a *cis*-double bond in the hydrocarbon chain. This *cis*-double bond induces bending of the hydrocarbon tail, and thus packing density of head group of oleic acid is larger than that of stearic acid [32]. As a result, the molecular interface of head groups of oleic acid seems to be a preferential site for the selective nucleation of γ-glycine similar to those by hexanoic acid and octanoic acid: their molecular packing of carboxyl head groups is looser than that comprised of stearic acid, as illustrated in Fig. 3.

2. Nucleation Mechanism of γ-Glycine at the Interface

Classical nucleation theory and two-step nucleation theory are widely used to explain nucleation mechanism [33]. The former describes the free energy change for the growing cluster as sum of the free energy change for the bulk phase transformation and the free energy change for the formation of a surface without consideration of effect of lattice organization of cluster for nucleation. On the other hand, the latter describes the nucleation process as a combination process of growing of amorphous dense cluster and the subsequent lattice organization to crystal structure. In classical nucleation theory, polymorphic selections at the water/oil interface are explained by the cluster capture model [34]. The cluster capture model states that if a certain interface were energetically and geometrically more favorable with clusters of a certain polymorphic form compared with other forms, then the interface might preferentially capture clusters of a certain form (not molecules). Here, it was assumed that growing cluster has the same crystal structure to that of fully developed crystal.

Chattopadhyay et al. investigated the size and fractal structure change of glycine cluster through small angle X-ray scattering experiments during cooling crystallization of glycine [35]. They reported that size of glycine cluster increases steadily to a maximum value of 4.24 Å, and then decreases to 4.02 Å with a fractal structure transformation from mass fractal to surface fractal. They stated that it is an evidence of two-step nucleation of glycine. Harano et al. reported the real time observation of a heterogeneous nucle-

ation of 1,3,5-tris(4-bromophenyl)benzene crystal at a solid substrate by single-molecule real-time transmission electron microscopy [36]. They observed that an amorphous dense liquid-like cluster of those molecules is formed initially and then subsequently ordered crystal is formed. This is a two-step nucleation process. Therefore, in the present work, it is a possible interpretation that molecular layer of head groups of hexanoic and octanoic acids provides the preferential site for the organization of ordered γ-glycine structure from the amorphous liquid-like cluster of glycine, not classical nucleation theory.

3. Morphology of Glycine Crystals

Fig. 4 shows optical microphotographs of glycine crystals obtained from the various emulsions. As can be seen from Fig. 4(a), γ-glycine crystals obtained from water/octanoic acid emulsion have a conical shape with a sharp tip of COO^--rich $(00\bar{1})$ face and a broad terminus of NH_3^+-rich (001) face. However, in Fig. 4(d), glycine crystals obtained from the water/oleic acid emulsion have much larger aspect ratio compared with those obtained from the emulsion with octanoic acid. It may be caused by different degree of supersaturation during cooling crystallization. Han et al. reported that the $(00\bar{1})$ face of γ-glycine can be grown only at high supersaturation, because water molecules are strongly adsorbed on the COO^- rich $(00\bar{1})$ face of γ-glycine [37].

As can be seen from Fig. 4(c), α-glycine obtained from a water/dodecanoic acid emulsion has a prismatic morphology with longer [010] direction and shorter [001] direction. In the cooling crystal-

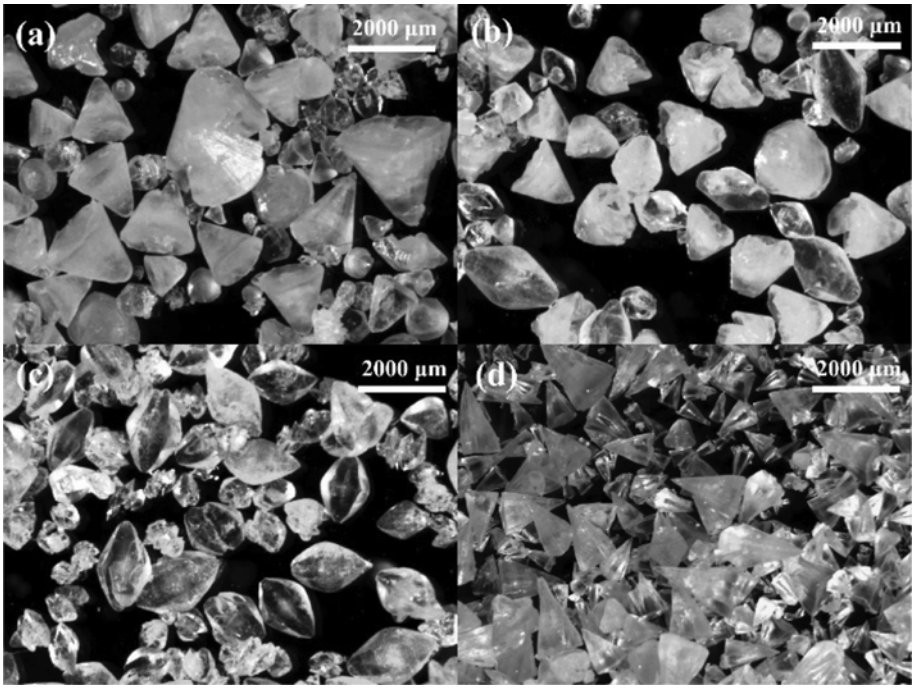

Fig. 4. Optical microphotographs of glycine crystals obtained from neutral aqueous glycine solution/fatty acids emulsion: (a) octanoic acid, (b) decanoic acid, (c) dodecanoic acid, and (d) oleic acid.

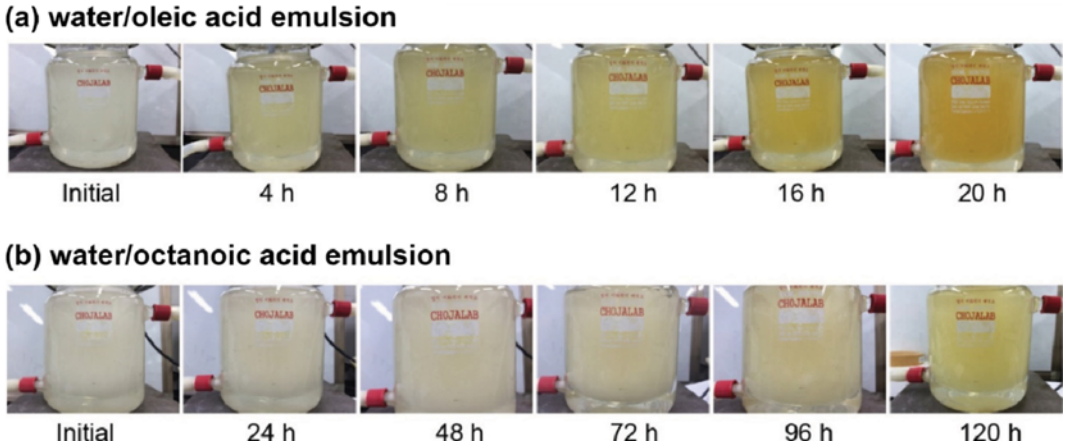

Fig. 5. Photographs of (a) aqueous glycine solution/oleic acid emulsion and (b) aqueous glycine solution/octanoic acid emulsion with aging time at 85 °C.

lization of glycine from water/decanoic acid emulsion, mixture of prism-like α- and conical γ-glycine was obtained (Fig. 4(b)).

4. Effect of Auto-oxidation of Fatty Acid on Glycine Crystallization

Unsaturated fatty acids, including oleic acid, undergo a chemical change by auto-oxidation due to cleavage of double bond during a free radical reaction [38]. As a result, hydroxy, keto, or epoxy groups are formed at the site of double bond [39,40]. Auto-oxidation induces color change of water/fatty acid emulsion from colorless to pale yellow, and finally to brown. As shown in Fig. 5, due to auto-oxidation reaction of oleic acid, the color change of water/oleic acid emulsion is remarkably faster than that of water/octanoic acid emulsion. Although octanoic acid is a saturated fatty acid, some impurities, which may be some unsaturated fatty acids, induce weak oxidation [41]. The auto-oxidation of fatty acid should influence the two-dimensional arrangement of the fatty acid/water interface and thus affect polymorphic selection during crystallization. Since functional groups containing oxygen are hydrophilic, oxidized fatty acids have more than two hydrophilic sites. A part between carboxyl head group and functional group containing oxygen formed by auto-oxidation lies flat on the surface on the water for an oxidized *cis*-unsaturated fatty acids [42]. Therefore, two-dimensional packing of fatty acid head groups in the emulsion with oxidized oleic acid could be loose compared with that before the auto-oxidation.

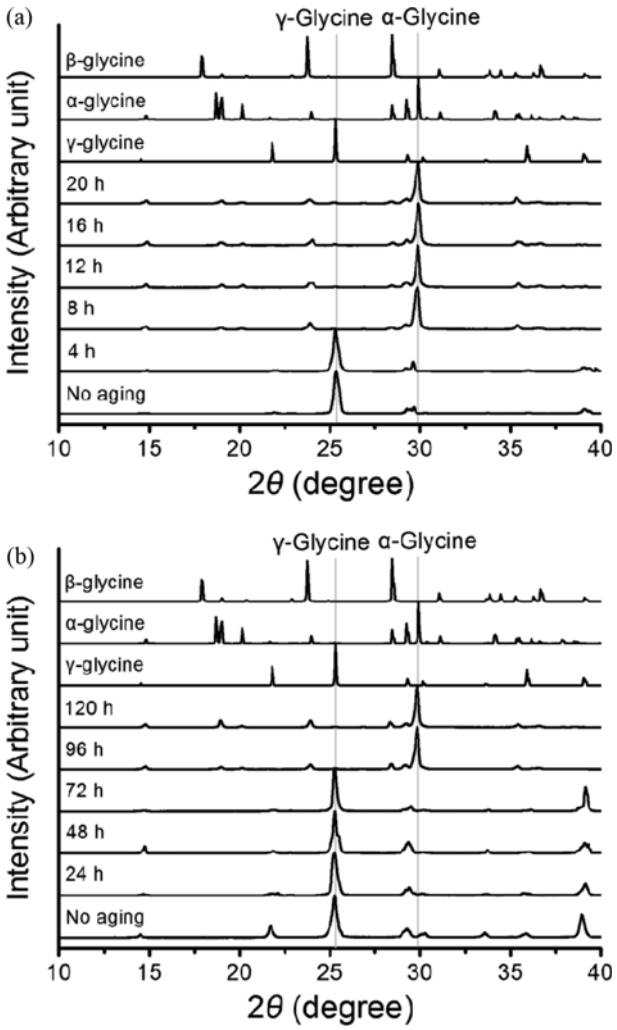

Fig. 6. PXRD patterns of glycine obtained from (a) aqueous glycine solution/oleic acid emulsion and (b) aqueous glycine solution/octanoic acid emulsion by batch cooling crystallization at 85 °C. α-, β- and γ-glycine indicate theoretical PXRD patterns. Two vertical lines indicate major peak positions of α- and γ-polymorphs.

Fig. 6 shows effect of aging time on glycine polymorphs of the process at 85 °C. In case of aqueous glycine solution/oleic acid emulsion, γ-glycine is obtained when aging time is shorter than 8 h. However, when aging time is longer than 8 h, α-glycine is obtained. It indicates that chemical change of oleic acid by auto-oxidation induces lattice mismatching between γ-glycine and the water/fatty acid interface. Such tendency was also observed for a water/octanoic acid emulsion. However, oxidation rate is shown to be remarkably slow compared to that in a water/oleic acid emulsion and γ-glycine was obtained even at the aging time of 72 h. Therefore, saturated fatty acids are recommended for the crystallization of γ-glycine in terms of solvent recycling.

CONCLUSION

Cooling crystallization of glycine from the neutral water/saturated fatty acid emulsions was carried out. γ-Glycine crystals were successfully obtained from the emulsions with hexanoic and octanoic acids, whereas only α-glycine was observed to crystallize from fat-ty acids with number of carbon atoms larger than 12. Those results suggest that emulsions with hexanoic and octanoic acids provide A preferential environment for the nucleation of γ-glycine. However, emulsions with other fatty acids are not suitable for the nucleation of γ-glycine, since packing density of the carboxyl head groups of a saturated fatty acid increases with the length of hydrocarbon chain. Unsaturated fatty acid such as oleic acid was also found to produce γ-glycine by the similar reason given to hexanoic and octanoic acids due to bending of cis-double bonding in hydro-carbon chain. However, in case of water/oleic acid emulsion, fast auto-oxidation, which has a deleterious effect on production of γ-glycine, was clearly observed. Therefore, water/saturated fatty acid emulsions with very slow auto-oxidation are recommended for an economic production of γ-glycine.

REFERENCES

1. I. González-Martín, N. Álvarez-García and J. M. González-Cabrera, *Talanta*, **69**, 706 (2006).
2. A. A. Jackson, R. L. Dunn and M. C. Marchand, *Clin. Sci.*, **103**, 633 (2002).
3. S. Roseth and F. Fonnum, *Neurosci. Lett.*, **183**, 62 (1995).
4. J. W. Johnson and P. Ascher, *Nature*, **325**, 529 (1987).
5. I. A. Malakhin, A. F. Achkasov, A. S. Ratushnyak, T. A. Zapara, A. L. Markel, E. V. Boldyreva and V. V. Boldyrev, *Dokl. Biol. Sci.*, **444**, 157 (2012).
6. W. Yamadera, K. Inagawa, S. Chiba, M. Bannai, M. Takahashi and K. Nakayama, *Sleep Biol. Rhythms.*, **5**, 126 (2007).

7. B. Baltazar-Rendon, K. Padilla-Martin, A. Gonzalez-Maciel, A. Nuño-Licona, R. Uribe-Escamilla, A. Hernandez-Romero, A. Ramos and A. Alfaro-Rodriguez, *Ulus. Travma. Acil. Cerrahi. Derg.*, **15**, 103 (2009).
8. D. Babić and R. Babić, *Psychiatr. Danub.*, **21**, 376 (2009).
9. E. I. Gusev, V. I. Skvortsova, S. A. Dambinova, K. S. Raevskiy, A. A. Alekseev, V. G. Bashkatova, A. V. Kovalenko, V. S. Kudrin and E. V. Yakovleva, *Cerebrovasc. Dis.*, **10**, 49 (2000).
10. G. P. Stahly, *Cryst. Growth Des.*, **7**, 1007 (2007).
11. Y. Iitaka, *Acta Cryst.*, **14**, 1 (1961).
12. J. Chen, B. Sarma, J. M. B. Evans and A. S. Myerson, *Cryst. Growth Des.*, **11**, 887 (2011).
13. Y. Kobayashi, S. Ito, S. Itai and K. Yamamoto, *Int. J. Pharm.*, **193**, 137 (2000).
14. A. J. Alvarez, A. Singh and A. S. Myerson, *Cryst. Growth Des.*, **9**, 4181 (2009).
15. X. He, J. G. Stowell, K. R. Morris, R. R. Pfeiffer, H. Li, G. P. Stahly and S. R. Byrn, *Cryst. Growth Des.*, **1**, 305 (2001).
16. A. L. Markel, A. F. Achkasov, O. I. Prokudina, T. A. Alekhina, E. V. Boldyreva and V. V. Boldyrev, *Dokl. Biochem. Biophys.*, **434**, 235 (2010).
17. A. L. Markel, A. F. Achkasov, T. A. Alekhina, O. I. Prokudina, M. A. Ryazanova, T. N. Ukolova, V. M. Efimov, E. V. Boldyreva and V. V. Boldyrev, *Pharmacol. Biochem. Be.*, **98**, 234 (2011).
18. A. F. Achkasov, E. V. Boldyreva, V. I. Bukhtiyarov, T. A. Zapara, E. A. Losev, M. P. Moshkin, A. S. Ratushnyak, A. V. Romashchenko, S. Y. Troitskii and V. V. Boldyrev, *Dokl. Biochem. Biophys.*, **454**, 6 (2014).
19. I. Weissbuch, L. Leiserowitz and M. Lahav, *Adv. Mater.*, **6**, 952 (1994).
20. J. Yano, H. Füredi-Milhofer, E. Wachtel and N. Garti, *Langmuir*, **16**, 10005 (2000).
21. J. Zaccaro, J. Matic, A. S. Myerson and B. A. Garetz, *Cryst. Growth Des.*, **1**, 5 (2001).
22. J. Aber, S. Arnold, B. Garetz and A. Myerson, *Phys. Rev. Ltt.*, **94**, 145503 (2005).
23. G. He, V. Bhamidi, S. R. Wilson, R. B. H. Tan, P. J. A. Kenis and C. F. Zukoski, *Cryst. Growth Des.*, **6**, 1746 (2006).
24. M. Louhi-Kultanen, M. Karjalainen, J. Rantanen, M. Huhtanen and J. Kallas, *Int. J. Pharm.*, **320**, 23 (2006).
25. T. Rungsimanon, K.-I. Yuyama, T. Sugiyama, H. Masuhara, N. Tohnai and M. Miyata, *J. Phys. Chem. Lett.*, **1**, 599 (2010).
26. E. A. Losev, M. A. Mikhailenko, A. F. Achkasov and E. V. Boldyreva, *New J. Chem.*, **37**, 1973 (2013).
27. J.-W. Kim, H.-M. Shim, J.-E. Lee and K.-K. Koo, *Cryst. Growth Des.*, **12**, 4739 (2012).
28. R. T. Holman and O. C. Elmer, *J. Am. Oil Chem. Soc.*, **24**, 127 (1947).
29. Å. Kvick, W. M. Canning, T. F. Koetzle and G. J. B. Williams, *Acta Cryst.*, **B36**, 115 (1980).
30. K. Chadwick, A. Myerson and B. Trout, *Cryst. Eng. Comm.*, **13**, 6625 (2011).
31. G. C. Nutting and W. D. Harkins, *J. Am. Chem. Soc.*, **61**, 1180 (1939).
32. K. Hąc-Wydro and P. Wydro, *Chem. Phys. Lip.*, **150**, 66 (2007).
33. D. Erdemir, A. Y. Lee and A. S. Myerson, *Acc. Chem. Res.*, **42**, 621 (2009).
34. K. Allen, R. J. Davey, E. Ferrari, C. Towler, G. J. Tiddy, M. O. Jones and R. G. Pritchard, *Cryst. Growth Des.*, **2**, 523 (2002).
35. S. Chattopadhyay, D. Erdemir, J. M. B. Evans, J. Ilavsky, H. Amenitsch, C. U. Segre and A. S. Myerson, *Cryst. Growth Des.*, **5**, 523 (2005).
36. K. Harano, T. Homma, Y. Niimi, M. Koshino, K. Suenaga, L. Leibler and E. Nakamura, *Nat. Mater.*, **11**, 877 (2012).
37. G. Han, S. K. Poornachary, P. S. Chow and R. B. H. Tan, *Cryst. Growth Des.*, **10**, 4883 (2010).
38. F. E. Deatherage and H. A. Mattill, *Ind. Eng. Chem.*, **31**, 1425 (1939).
39. W. E. Neff and W. C. Byrdwell, *J. Chromatogr. A*, **818**, 169 (1998).
40. N. A. Porter, S. E. Caldwell and K. A. Mills, *Lipids*, **30**, 277 (1995).
41. T. Riisom, R. J. Sims and J. A. Fioriti, *J. Am. Oil Chem. Soc.*, **57**, 354 (1980).
42. V. Lorraine Schneider, R. T. Holman and G. O. Burr, *J. Phys. Chem.*, **53**, 1016 (1949).