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POLYMORPHISM OF GLYCINE
Thermodynamic aspects.
Part I. Relative stability of the polymorphs

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Abstract

The contribution summarizes the results of a systematic study of the three glycine polymorphs (α, β, γ-forms), including: *i*) the controlled crystallization of a desirable form, *ii*) a comparative calorimetric study of the three forms in the temperature range between 5 K and the sublimation temperatures (≈500 K).

Keywords: calorimetry, glycine, heat capacity, polymorphs

Introduction

One of the important problems of solid state chemistry, materials science, pharmaceutical science is the problem of polymorphism. The problem has several aspects: 1) to find experimentally and/or to predict theoretically all the possible polymorphs of a given compound; 2) to range the experimentally known and/or the predicted polymorphs with respect to their thermodynamic stability, their free energies of formation, etc.; 3) to find experimentally and/or to predict, which of the polymorphs will be formed under particular experimental conditions, and to control the formation of the desired polymorph [1–3]. The three aspects are closely interrelated, but the relative stability of the polymorphs and the preferable growth of a particular polymorph in real experiments do not necessarily correlate directly. This is a reason, why much confusion and contradictory statements can be found in the literature even for seemingly simple and repeatedly studied systems. Glycine, NH_2CH_2COOH, can provide an example.

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Three crystalline polymorphs were described for glycine: two monoclinic (α, s.gr. $P2_1/n$, and β, s.gr. $P2_1$) and one trigonal (γ, s.gr. $P3_1$). The three polymorphs differ in the way how $^{+}NH_3–CH_2–COO^{-}$ zwitter-ions are linked together via a hydrogen-bonds network. In the α-polymorph zwitter-ions are linked by hydrogen bonds in double antiparallel layers, the interactions between these double layers being purely van der Waals. In the β-polymorph individual parallel polar layers are linked by hydrogen bonds in a three-dimensional network. In the γ-polymorph zwitter-ions form polar helixes linked with each other in a three-dimensional polar network [4–23].

There are many publications describing the formation of a particular polymorph under various experimental conditions, starting from the early papers and until very recent reports [4–32]. Still, the data on the conditions of crystallization of a particular polymorph are often contradictory and poorly reproducible. There is also no common opinion on the relative stability of the polymorphs, on the thermodynamic parameters and on the conditions of the transformations of one polymorph into another. Most conclusions on the relative stability of the polymorphs were made on the basis of the crystallization and storage experiments, and this is obviously not sufficient. Thermodynamic data, first of all – derived from the calorimetric measurements in a wide range of temperatures, are required to solve the problem. It is very strange, but in most of the publications on the thermodynamic properties of crystalline glycine there was no indication on the structure of the sample investigated. Specific heat, heat of combustion, heat of dissolution, lattice energy, etc., were referred to 'glycine' in general, not to the specific (α or β or γ) polymorph. This makes a comparison of the data published in different papers (and the discrepancies between the results of different authors) very problematic. The rare data obtained for pure, clearly defined polymorphs are also contradictory [14, 21, 33–41].

In 2000 we have initiated a project aimed at systematic comparative studies of the three polymorphs of glycine, combining structural, thermodynamic, kinetic studies at variable experimental conditions [22, 23, 31, 32, 42–45]. The objectives of this work were 1) to develop procedures of obtaining reproducibly pure polymorphs; 2) to measure their heat capacities in a wide range of temperatures, in order to determine, which of the polymorphs is stable at normal conditions and which are metastable; 3) to find conditions, under which a particular polymorph transforms into another one, and to determine the thermodynamic parameters characterizing these phase transformations. The first part of this contribution addresses problems 1 and 2; the second part [46] – problem 3.

Experimental

We tested the chemicals 'glycine' received from different chemical companies: Soyuzkhimreaktiv (Russia); ICN Biomedicals (1-800-854-0530 [56-40-6]); Merck (104201); Riedel-de Haen (Sigma-Aldrich Laborchemikalien GmbH). Neither company indicates crystalline polymorph of glycine. Usually, the reagents contain mixture of two polymorphs (α and γ). The polymorph content in different chemicals ranges from α with admixture of γ to γ with admixture of α. Pure polymorphs for

thermoanalytical experiments were obtained by special procedures described in the next Sections.

The samples were characterized by means of X-ray powder diffraction (GADDS D8, Bruker, for powders; Stadi-4, Stoe, Darmstadt, for single crystals). Calorimetric measurements were performed using DSC-111 (Setaram), DSC-204 (Netzsch), DSC-30 (Mettler) in the temperature range 140–500 K, and a low-temperature adiabatic calorimetric system working over the temperature range of 4.2–320 K [47, 48]. Sublimation was studied using TG-209 (Netzsch). Details of the experiments were described elsewhere [22, 23, 31, 43–45].

Crystallization of the polymorphs

α–Polymorph was described in the literature to crystallize spontaneously under almost any experimental conditions – as the main polymorph from pure aqueous solutions [5–7, 9, 11, 15–18, 20, 21, 24–30]. Crystallization of γ-polymorph from acid and base water solutions (with additives of acetic acid or ammonia, correspondingly) was reported in [4, 10, 14, 18, 19, 21, 25]. γ-polymorph was observed to grow preferentially from heavy water solutions [14], from aqueous solutions irradiated with intense nanosecond pulses of near-infrared laser light [29, 30], and also from solutions with additives of compounds that inhibit the growth of α-glycine, such as, for example, hexafluoravaline [24–27]. The data on the crystallization of β-glycine are limited. This polymorph was first observed in 1905 [4], cell parameters were measured by Bernal [5], Hengstenberg and Lenel [6], Ksanda and Tunell [8]; later the structure was solved and analyzed by Iitaka [12, 13]. According to [4, 5, 8, 12, 13, 18, 21], ethanol should be used, in order to precipitate this form from a saturated water solution.

In our own experiments we have found that the reality is more complicated than described in the literature. The three forms of glycine usually crystallized simultaneously from the same solution, that is they can be classified as concomitant polymorphs [49]. Previously, Bernal has also mentioned that several polymorphs of glycine could be found in the same preparation [5]. We have obtained the α-form as an admixture to the β- and the γ-polymorphs as a result of crystallization from water solutions with additives of ethanol, ammonia, or acetic acid. At the same time, crystals of the γ- and the β-polymorphs were found as admixtures also in the samples crystallized from pure water and containing the α-polymorph as the main product [31, 32].

The γ-polymorph crystallized from pure aqueous solutions containing small 'nuclei' of γ-glycine, or freshly prepared by dissolving a sample of α-glycine with even a small admixture of γ-glycine. Actually, the success of crystallizing the γ-polymorph seemed to depend much more on the presence of the seeds of this polymorph in the powder used for preparing a saturated solution, than on the solvent used. If we took very pure α-glycine (no admixtures of the γ-form in the sample), then only the α-form crystallized also from the solutions with acid or base additives of acetic acid or ammonia [32]. As was already mentioned in the Experimental, the chemicals sold by different companies, and even the chemicals sold by the same company but from different packages, usually differ in the ratio of the α- and the γ-forms. This may be a

reason, why the literature data on the crystallization of the γ-glycine are not always reproducible.

We could not precipitate the pure β-polymorph using ethanol, as was described in the literature [4, 5, 8, 12, 13, 18, 21]. A mixture of the α- and the β-forms was obtained instead. We have developed another technique, allowing us to obtain reproducibly large amounts of the β-form [31, 32]. A commercial sample of glycine (which is usually a mixture of the α- and the γ-forms) was solved in a 1:2 mixture of water and glacial acetic acid and kept standing for at least 3 days. If the solution was used as freshly prepared, a large admixture of the α-form was formed during subsequent crystallization. Sometimes, if the starting powder sample contained the γ-polymorph, the γ-polymorph was obtained also on crystallization from the freshly prepared solution. The longer the solution was stored, the higher was the yield of the β-polymorph during the subsequent crystallization. After a long enough storage of the solution it was filtered, then acetone was added and the solution was filtered under vacuum immediately after it became turbid. The cotton-like precipitate contained small needle-shaped crystals (about 1 mm long and 0.05 mm in diameter). One crystallization allowed us to obtain about 1 g of pure β-polymorph. This amount was enough to carry out low-temperature heat capacity measurements (see next Section). Larger single crystals suitable for single crystal X-ray diffraction could be obtained by crystallization from a 2:1 mixture of acetic acid and water by slow evaporation, if a small crystal of β-polymorph was used as a nucleus.

Calorimetric measurements

Having worked out the procedures of obtaining pure samples of desirable glycine polymorphs in amounts sufficient for calorimetric studies, we could proceed with calorimetric measurements in a wide temperature range from 5 to 500 K. The values of heat capacity were close for all the three polymorphs; in the temperature range 100–200 K the differences between them did not exceed 3%. At ambient temperature (298.15 K) the heat capacity C_p for the α-form was equal to 99.2 J mol^{-1} K^{-1}, the heat capacity for the γ-form – to 96.0 J mol^{-1} K^{-1} [45]. At the temperatures above 300 K, the values of heat capacity decreased in the order α>β>γ [45]. The heat capacity of the β-form was about 1% lower than that of the α-form [31]. The discrepancy in the values of heat capacity published in several earlier publications for 'glycine' [34–36] could be explained assuming that different polymorphs were studied (α in [34], γ in [36]).

At about 10 K, the heat capacity of the γ-form was about 26% larger than that of the α-form. A phase transition of the piezoelectric nature can be supposed to take place in this temperature region (Fig. 1) [45]. For the β-polymorph, the reversible changes in the heat capacity at about 250 K also indicate at a previously unknown phase transition, presumably of the piezoelectric nature (Fig. 2). The study of this phase transition by spectroscopic and diffraction techniques is in progress.

According to our data, the α- and the γ-polymorphs of glycine sublime at rather low temperatures (Fig. 3). This is in agreement with the results of [27], in which sublimation was used for crystal growth of the α-form, and does not confirm the state-

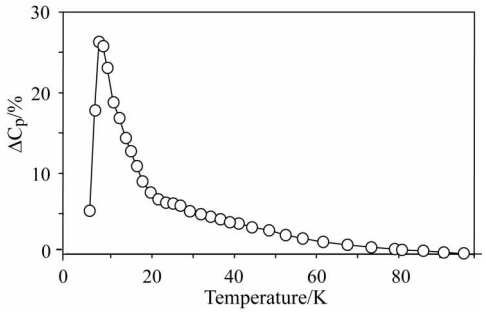

Fig. 1 The difference in the low-temperature heat capacity C_p of the α- and the γ-polymorphs of glycine

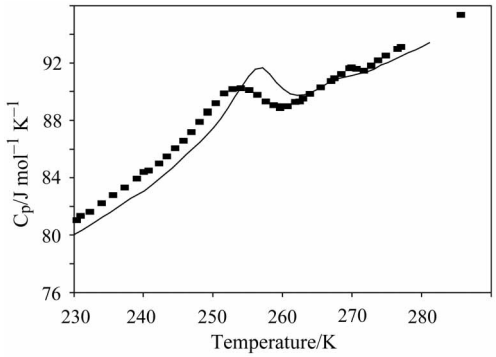

Fig. 2 The heat capacity of the β-polymorph of glycine in the temperature range of a reversible low-temperature phase transition: squares – adiabatic vacuum calorimetry, solid line – DSC

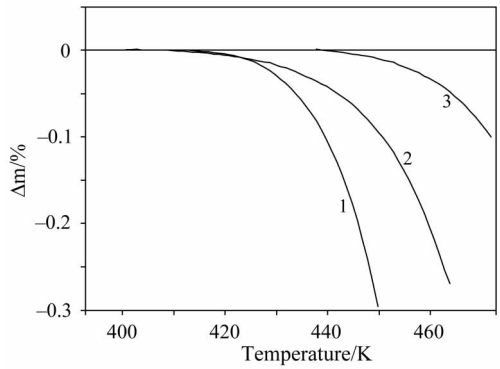

Fig. 3 The mass loss due to the sublimation of the α-glycine at different heating rates: 1 – 0.1 K min^{-1}, 2 – 0.5 K min^{-1}, 3 – 2 K min^{-1}

ment published in [21], that the β-glycine is the only form of glycine, for which the sublimation could be observed, in the range 483–513 K. In [21], the β-glycine was also reported to be stable on heating up to its melting point at about 523 K. In all our experiments, on the contrary, the maximum temperature, at which the existence of

the β-form was at all possible (about 340 K), was much lower than the temperature, at which any noticeable sublimation could be observed. The temperature, at which the noticeable sublimation was observed, strongly depended on the heating rate (Fig. 3). The effective activation energy of sublimation of the α-glycine was estimated to be about 135 kJ mol^{-1} (the average value, the values in the range 124–152 kJ mol^{-1} could be obtained, depending on the heating rate and the model used for the data processing). The sublimation of the γ-glycine is observed close to the temperatures of its transformation into the α-form (Part 2 [46]), but it is still possible to speak of the sublimation of the γ-form parallel to this transformation. Sublimation was accompanied by partial decomposition of the samples. This could be concluded from the color change from white to grey already after a 1–2 % mass loss. At the same time, the elemental chemical analysis and the X-ray powder diffraction were not sensitive enough to reveal any impurity phases in the samples after their partial sublimation. Sublimation was shown to be a self-accelerating process.

Discussion

The values of the heat capacity of all the three polymorphs at ambient temperature are about 100 J mol^{-1} K^{-1}. This is only 40% of the value predicted by the classic theory (250 J mol^{-1} K^{-1}=3Rm, R – the universal gas constant, m – the number of atoms in the molecule). The low value of the heat capacity corresponds to a high value of the characteristic Debye temperature, T_D, which, in turn, correlates with the bond energies in the solid. At the same time, glycine sublimes very easily at relatively low temperatures (below 470 K), and this means that the bonds between the zwitter-ions may be broken rather easily. The complementary measurements of the heat capacity and of the sublimation prove that the bond energies in the glycine zwitter-ions are much higher than the energies of relatively weak interactions between the zwitter-ions in the crystal structure. The properties of the glycine crystals can be expected as an intermediate between those of molecular and ionic crystals, since the interactions between the zwitter-ions include not only hydrogen bonds, but also strong dipole-dipole interactions. For example, the compressibility of glycine is intermediate between that of ionic salts and molecular crystals [50].

The variable temperature measurements of the heat capacity of the glycine polymorphs made it possible to calculate the thermodynamic parameters, to estimate the order of relative stability of the polymorphs, and to calculate the changes in the enthalpy and the Gibbs free energy for the transitions between the polymorphs [45]. The order of the stability of the glycine polymorphs at ambient temperature was shown to be γ>α>β. At 298.15 K, ΔG for the α- and the γ-forms was estimated as about 160 J mol^{-1}, predicting that the γ→α transition is thermodynamically forbidden at this temperature, whereas the reverse α→γ transition should be allowed [45]. At temperatures high enough, the γ-form becomes less stable than the α-form, and one can expect the γ→α transformation on heating, what is really the case (Part 2 [46]).

In many of the previously published papers the α-polymorph was supposed to be the most stable form, since i) it is most easily obtained, ii) its transformation into the

γ-form was not observed (the only two exceptions being the publication [28], in which a moisture-mediated α→γ transformation was described, and the publication [14], in which it was mentioned, that for deuterated α-glycine (powder) the transformation from the α- to the γ-form has actually been observed at room temperature). Our study has confirmed the hypothesis of Iitaka [14], and of Sakai *et al*. [28], that 'the γ-form may be a stable form at least at room temperature'. The order of stability γ>α>β at ambient conditions found from our measurements correlates with the order of changes in the lattice energies calculated in [21] from the measured heats of dissolution of the three polymorphs in water. At the same time, the same order in the lattice energy remains at the elevated temperatures, although the order of stability changes to α>γ> β.

The differences in the lattice energies of the glycine polymorphs are related to the differences in the weak intermolecular interactions. Therefore the heats of transitions between the polymorphs are rather low, and therefore the metastable forms can be obtained rather easily and can be preserved for a long time if the barriers required for a structural reorganization are much larger than the small potential energy gain resulting from the transformation. The relative stability of the polymorphs does not correlate directly with the easiness of their crystallization. The crystallization conditions, the structure of solution, and, first of all, the presence of pre-nuclei determine, which polymorph will grow. To induce crystallization of the β- or γ-polymorphs of glycine it is necessary to destroy the dimers present in glycine solution [51], which direct the crystallization towards the formation of the α-form. This can be achieved by applying electric field, by changing solvents, by adding specially selected impurities. If the formation of the dimers in solution, and, hence, the growth of the α-polymorph, is inhibited, then the stable γ-polymorph grows under crystallization conditions closer to the equilibrium (slow crystallization), whereas very quick precipitation gives the β-polymorph. It is also very important to exclude the presence of nuclei of undesirable polymorphs, and to introduce the nuclei of desirable polymorphs as precursors [52]. The fact that ageing of solutions is important for further crystallization can indicate that the clusters of glycine zwitter-ions in the solution keep memory of their organization in the crystals prior to the dissolution. This effect was described previously for several other compounds [2, 53]. For α-glycine, atomic-force microscopy (AFM) experiments on the growth and dissolution of single crystals have shown that a lower limit to the step size on the (010) glycine face is close to the thickness of the hydrogen-bonded bilayer, that is the dissolution of α-glycine seems to proceed with preservation of dimers in solution. Diffraction data used together with the results of the in situ AFM measurements of glycine dissolution and growth in a complementary manner allow one to conclude that glycine leaves or docks to the crystal surface as cyclic hydrogen-bonded dimers [54–56]. One can suppose the clusters of glycine zwitter-ions keeping memory of the parent crystal structure to remain in solutions also after the dissolution of the γ-form. Since the chemicals used for the crystallization of glycine polymorphs never contain the β-form, but, generally, a mixture of the α- and the γ-forms in different ratios, these two forms are also most easily crystallized from freshly prepared solutions – the γ-form if the formation of dimers is prevented, the α-form – if not.

Isothermal cross-seeding experiments of suspensions with several polymorphs followed by monitoring the relaxation of the system are often applied to check the relative stability of the different forms [1, 3]. In the case of the polymorphs of glycine this procedure does not work well and gives poorly reproducible results. The reason is in the small difference in the stability of the three polymorphs, and in the strong effect of the structure of solution on the crystallization. The calorimetric experiments have proven to be really the best tool to range the glycine polymorphs according to their stability as solids, independently from the interactions with solvent.

Conclusions

The γ-polymorph is the most stable form at ambient conditions, although the α-form crystallizes much more readily at ambient conditions, and although the α-form (with rare exceptions) was not observed to transform into the γ-form at ambient conditions. With increasing temperature, the order of stability inverts, the α-form becomes the most stable one above ~440 K, and a gamma→alfa polymorph transition is observed when heating the γ-form. On subsequent cooling, the α-form does not transform back to the γ-form, presumably due to kinetic reasons. The β-form is obviously metastable at all temperatures.

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