# GLYCINE SULFATES AND SELENATES

Jitka EYSSELTOVÁ, Martin MOHYLA and Marie TOMÁŠKOVÁ
*Department of Inorganic Chemistry,*
*Charles University, 128 40 Prague 2, The Czech Republic*

Received September 15, 1992
Accepted November 16, 1992

Solubility isotherms in the glycine–$H_2SO_4$–$H_2O$ system at 25 °C and in the glycine–$H_2SeO_4$–$H_2O$ system at 0 °C and 25 °C are presented. Based on these isotherms, the literature data on preparation of glycine sulfates and selenates are evaluated critically.

After the discovery of the ferroelectric activity of triglycine sulfate[1], glycine sulfates–triglycine sulfate (TGS) $(NH_2CH_2COOH)_3 \, . \, H_2SO_4$ and diglycine sulfate (DGS) $(NH_2CH_2COOH)_2 \, . \, H_2SO_4$ – and isomorphous selenates have been studied frequently[2 – 7]. All these compounds are prepared from aqueous solutions either isothermally or by slow cooling. Quite surprisingly, the reports on the growth of the individual sulfates and selenates show controversy regarding the composition of the starting solutions. No agreement can be even found in the data on hydration of DGS. The literature data are summarized in Table I. Similar uncertainty may be stated in the case of the temperature dependence of solubility of congruently soluble TGS in $H_2O$, where the curves of Davey and White[8], Nitsche[9], Březina[10] and Konstantinova[4] differ mutually in ca 10%.

This paper tries to solve all these problems by the most complete and thermodynamically consistent way – presenting the phase diagrams in relevant part of the glycine–$H_2SO_4$–$H_2O$ and glycine–$H_2SeO_4$–$H_2O$ systems.

## EXPERIMENTAL

All chemicals employed were the commercial substances of p. a. purity unless stated otherwise. Glycine was a product of Reanal, Budapest, sulfuric acid of Lachema, Brno and selenic acid was used in the form of the solution containing 25 g/ml at 20 °C (BDH). For the investigation of the $H_2SeO_4$-rich region of the glycine–$H_2SeO_4$–$H_2O$ system, selenic acid was synthesized by oxidation of metallic Se (Lachema, Brno) by $H_2O_2$ (pure, Lachema, Brno), neutralization of the product with $MgCO_3$ (Lachema, Brno) and following ion exchange.

Computerized balance method[11] was used to study the solubility. Theoretical backround and experimental technique of this method are identical with those of geometric-analytical method for the study of solubility in multicomponent salt systems[12]. It means, the relative mass of the equilibrium solid phase is measured in a set of experimental points covering the composition diagram in ternary system consisting of two salt components and water. In the method employed, a menu of solubility

TABLE I
Literature data on preparation of glycine sulfates

| Source | Triglycine sulfate |  | Diglycine sulfate |  |
|---|---|---|---|---|
|  | molar ratio $H_2SO_4$ : gly | pH | molar ratio $H_2SO_4$ : gly | pH |
| Whips[2] | 2 : 1; 3 : 1 | not given | 1 : 1 | not given |
| Wood, Holden[3] | nothing given |  | 2 : 1 | not given |
| Konstantinova[4] | 3 : 1 | not given | nothing given |  |
| Dominiguez[5] | 1 : 1; 2 : 1; 3 : 1 | $pH > 1.9$ | not given | $1.9 > pH > 1$ |
| Szczepanska[6] | not given | $2.2 > pH > 1$ | not given | $1 > pH$ |
| Pandya, Vyas[7] | 4.2 : 1; 7 : 1 | $2.5 > pH > 1.5$ | 2 : 1 | $1 > pH > 0.5$ |

curves is calculated on assumption of existence of equilibrium solid phases of different composition. After that, the choice of the real solubility curve is made in such a way, that the general laws of physico-chemical analysis are met.

The equilibration time for selenate system was 12 – 14 days, for sulfate system depended very strongly on the viscosity of saturated solutions and varied from two weeks to 3 – 4 months. Reaching of the equilibrium was checked by measurement of the refractive index of saturated solutions. The composition of invariant points of the systems was checked analytically. Glycine was analyzed after mineralization of the sample with the use of Conway method[13]. Sulfuric and selenic acids were determined by titration with 0.1 M NaOH.

In the glycine–$H_2SO_4$–$H_2O$ system, pH of saturated solutions was measured using the apparatus of Radiometer, Copenhagen.

The temperature dependence of TGS solubility was measured using a balance method modified for the investigation of binary systems salt–water. The idea of the method is like this: two phase complexes having the solid phase and its saturated solution in different mass ratios are prepared at each temperature. After equilibrization, the relative mass of the equilibrium solid phase is found. If we adapt the diagram of relative mass of the equilibrium solid phase against composition[12] for binary systems, it may be proven easily that the solubility may be found as the composition at which the line connecting the figurative points under consideration intersects the composition axis. The method makes it possible not only to find the solubility, but also to make qualified conclusions about the hydration of the equilibrium solid phase at the temperature of the experiment[14].

## RESULTS AND DISCUSSION

Solubility diagram in the glycine–$H_2SO_4$–$H_2O$ system at 25 °C is depicted on Fig. 1. In the glycine–$H_2SeO_4$–$H_2O$ system at 25 °C (Fig. 2), metastable crystallization field of DGSe was observed. Therefore, the solubility diagram in the system at 0 °C was studied (Fig. 3). The liquid phase composition at the invariant points of the systems are given in Table II.

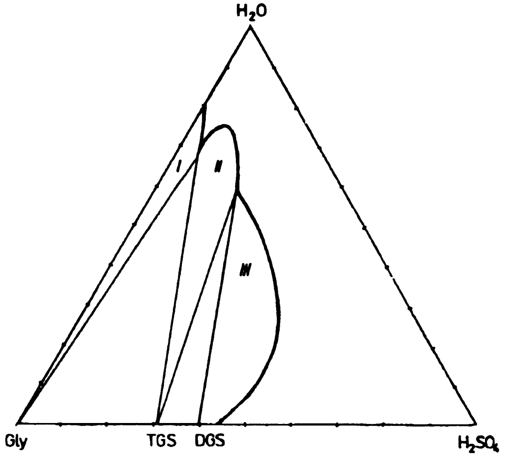

FIG. 1
Solubility in the glycine–$H_2SO_4$–$H_2O$ system at 25 °C

The solubility diagram in the glycine–$H_2SO_4$–$H_2O$ system at 25 °C indicates that, in addition to glycine (crystallization field *I*), congruently soluble triglycine sulfate (crystallization field *II*) and incongruently soluble diglycine sulfate (crystallization field *III*) are formed.

In the glycine–$H_2SeO_4$–$H_2O$ system at 25 °C (Fig. 2), in addition to glycine only congruently soluble triglycine selenate has a crystallization field. However, congruently soluble diglycine selenate crystallized in this system as a metastable solid phase. This fact makes it possible to explain the lack of precise information on synthetic experiments in the system under consideration under laboratory conditions.

To avoid the occurence of metastable equilibria, the solubility diagram in the glycine–$H_2SeO_4$–$H_2O$ system at 0 °C was investigated (Fig. 3). Under these conditions, the system resembles the analogous sulfate system. In addition to glycine (crystal-

TABLE II
Liquid phase composition (wt.%) at the invariant points of the systems

| Temperature, °C | Equilibrium solid phases | Glycine | Acid |
|---|---|---|---|
| 25 | glycine + TGS | 27.5 | 5.50 |
| 25 | TGS + DGS | 23.0 | 18.0 |
| 25 | glycine + TGSe | 28.3 | 14.0 |
| 25[a] | glycine + DGSe | 30.2 | 15.6 |
| 0 | glycine + TGSe | 31.1 | 16.9 |
| 0 | TGSe + DGSe | 24.6 | 17.8 |

[a] This is a metastable invariant point.

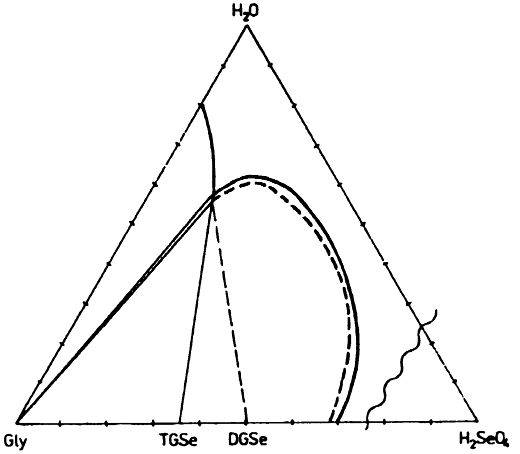

FIG. 2
Solubility in the glycine–$H_2SeO_4$–$H_2O$ system at 25 °C. Stable solubility curve (full line), metastable solubility curve (dashed line)

lization field *I*) triglycine selenate (crystallization field *II*) and diglycine selenate (crystallization field *III*) crystallize, both of them being congruently soluble. In both Fig. 2 and Fig. 3, only the part of the solubility diagram depicting the crystallization fields of glycine-containing solid phases is included. The determination of the shape of the crystallization field of $H_2SeO_4$ is connected with considerable experimental difficulties and the field is irrelevant as far the conditions of crystallization of glycine selenates are concerned.

On the basis of the solubility diagrams, the optimum conditions for synthesis of individual glycine sulfates and selenates were found. These conditions are summarized in Table III.

In synthesis of triglycine and diglycine sulfate, it is the composition of the starting solution that represents the main condition to be followed. On the other hand, in syn-

TABLE III
Optimum conditions for crystallization of glycine sulfates and selenates

| Compound | Molar ratio glycine : acid : water | *T*, °C |
|---|---|---|
| $(NH_2CH_2COOH)_3 . H_2SO_4$ | 1 : 3 : 8 | 25 |
| $(NH_2CH_2COOH)_2 . H_2SO_4$ | 1 : 1.3 : 5.6 | 25 |
| $(NH_2CH_2COOH)_3 . H_2SeO_4$ | 1 : 3 : 4 | 0 |
| $(NH_2CH_2COOH)_2 . H_2SeO_4$ | 1 : 2 : 3 | 0 |

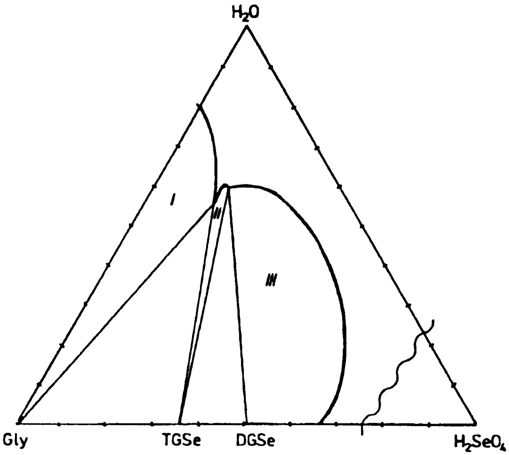

FIG. 3
Solubility in the glycine–$H_2SO_4$–$H_2O$ system at 0 °C

thesis of triglycine and diglycine selenates main role is played by the temperature. These facts make it possible to explain the discussable statements in the literature satisfactorily as follows.

Thus Hiltzer et al.[15] report the diglycine selenate "as a by-product in the product of growing TGSe". As far these authors mention no special measures concerning temperature control, crystallization at laboratory temperature is probable, by which the occurence of both TGSe and DGSe is possible.

As far the contradicting data on preparation of glycine sulfates (Table I) are concerned, the solubility diagram seems to prove the results of Whips et al.[2]. As the boundary pH value separating the existence areas of TGS and DGS we found pH 1.8. This value is close to that reported by Dominguez et al.[5] (pH 1.9). However, the data of Dominguez[5] on the composition of the starting solution as well as on hydration of DGS are wrong. No evidence of monohydrate of DGS was found in the solubility diagram at 25 °C. Both the controversary data on the existence area of DGS and the description of this compound as monohydrate (of which even the X-ray crystal structure study has been reported[16]) may be explained with the aid of the shape of the solubility branch of DGS in the solubility diagram under consideration. As it may be seen in Fig. 1, DGS is incongruently soluble and its solubility branch falls steeply with respect to the $H_2SO_4$ axis, being even convex with respect to the $H_2O$ axis. Besides, both density and viscosity of saturated solutions having $w_{H_2O} < 20$ wt.% are high and the time required for equilibration extremely long (3 – 4 months). All these facts make mistakes during preparative investigation of glycine sulfates quite probable.

We have found the following temperature dependence of the solubility of TGS:

| Temperature, °C | 25 | 35 | 40 | 45 | 50 |
|---|---|---|---|---|---|
| TGS, wt.% | 33.4 | 39.5 | 44.2 | 47.8 | 51.0 |

These data are very close to those of Nitsche[9]. Exact comparison with the measurements of other authors is not possible, because they use g TGS/100 $cm^3$ $H_2O$ as concentration unit. Based on graphical comparison made by Kroes and Reiss[16] we may say, that the data of Davey and White[8], Březina[10] and Kroes and Reiss[16] seem to be too high in 5 – 10 rel.%.

## REFERENCES

1. Matthias B. T., Miller C. E., Remeika J. P.: Phys. Rev. *104*, 849 (1956).
2. Whips P. W., Coster R. S., Bye K. L.: J. Mater. Sci. *7*, 1476 (1972).
3. Wood E. A., Holden A. N.: Acta Crystallogr. *10*, 145 (1957).
4. Konstantinova V. P., Silvestrova I. M., Aleksandrov K. S.: Kristallografiya *4*, 69 (1959).
5. Dominiguez E., Jimenez B., Mendiola J., Vivas E.: J. Mater. Sci. *7*, 363 (1972).
6. Szczepanska L.: Krist. Tech. *11*, 285 (1976).
7. Pandya G. R., Vyas D. D.: J. Cryst. Growth *50*, 870 (1980).

8. Davey R. J., White E. A. D.: J. Cryst. Growth *30*, 125 (1975).
9. Nitsche R.: Helv. Phys. Acta *31*, 306 (1958).
10. Březina B.: Mater. Res. Bull. *6*, 401 (1971).
11. Eysseltová J., Mička Z., Walzelová M.: Chem. Papers *46*, 218 (1992).
12. Eysseltová J., Kovářová B.: Chem. Papers *39*, 607 (1985).
13. Barthová J., Sofrová D., Tichá M.: *Základní praktikum z biochemie*, p. 61. Charles University, Prague 1984.
14. Eysseltová J.: Unpublished results.
15. Hilczer B., Szczepanska L., Baran J., Lukaszewicz K., Olejnik S.: Krist. Tech. *8*, K 23 (1973).
16. Kroes R. L., Reiss D.: J. Cryst. Growth *69*, 414 (1984).

Translated by the author (J. E.).