

SOLUBILITY IN THE GLYCINE–H₃BO₃–H₂O SYSTEM

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Solubility isotherms in the title system were measured at 0, 25, 50, and 70 °C. Regression straight line equations interrelating the solubilities of boric acid and glycine were derived. The activity of water in saturated solutions of the system at 25 °C was determined by vapour pressure measurements.

In contrast to other systems consisting of glycine, an inorganic oxygen-containing acid and water (e.g.^{1,2}), formation of compounds is unlikely in the glycine–boric acid–water system. This assumption is consistent with the magnitude of the acid dissociation constants of boric acid and glycine ($5.8 \cdot 10^{-10}$ and $4.8 \cdot 10^{-3}$, respectively). The glycine–H₃BO₃–H₂O system has been studied at 25 °C by Skvortsov and coworkers³. As expected, the solubility diagram is eutonic type, the eutonic solution composition being 62.13 wt.% H₃BO₃, 22.43 wt.% glycine and 14.44 wt.% water. The authors also fitted the solubility of boric acid in glycine solutions by a linear equation in the form

$$w_{\text{H}_3\text{BO}_3} = 0.034 w_{\text{gly}} + 5.66, \quad (1)$$

where *w*'s are the solubilities in wt.% (gly is glycine). However, the solubility of glycine at 25 °C, 29.42 wt.%, is substantially higher than as reported in the literature⁴, and also about 10 wt.% higher than as obtained by our research team previously^{1,2}.

The aim of the present work was to obtain solubility isotherms of the title system at 0, 25, 50 and 70 °C and to address the problem of possible interactions between the components. In addition, the applicability of vapour pressure osmometry to the determination of the water vapour pressure over the saturated solutions of the system was tested.

EXPERIMENTAL

Glycine (pure) was obtained from Merck. All other chemicals were reagent grade products of Lachema, Brno.

As in our previous work², the solubility was determined by using the computerized balance method¹. The equilibration time at 0, 25, 50 and 70 °C was 12, 6, 4 and 2 days, respectively. For the equilibrium solid phase separation at 50 and 70 °C, the apparatus was coated with a thermally insulating material.

Water activity was determined by measuring the water vapour pressure over saturated solutions, using a Knauer model 1978 vapour pressure osmometer. The instrument was calibrated with a set of KCl solutions, the concentration dependence of a_w in them was taken from ref.⁵.

RESULTS AND DISCUSSION

The composition data of the saturated solutions in the glycine–boric acid–water system at 0, 25, 50 and 70 °C are given in Table I, the corresponding segment of the curve of simultaneous crystallization of glycine and boric acid is shown in Fig. 1. In analogy to the equation obtained by Skvortsov and coworkers³, the coefficients in the linear equations

$$w_{\text{H}_3\text{BO}_3} = a w_{\text{gly}} + b \quad (2)$$

for the crystallization branches of boric acid, and

$$w_{\text{gly}} = a' w_{\text{H}_3\text{BO}_3} + b' \quad (3)$$

for the crystallization branches of glycine were calculated by the standard least squares method. The values of the coefficients, along with the characteristics of the fit, are given in Table II. This table displays interesting temperature dependence of the con-

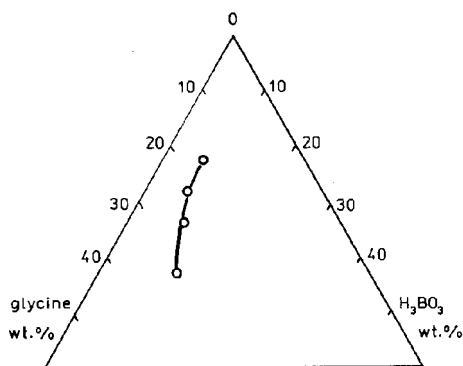


FIG. 1
Curve of simultaneous crystallization of glycine and boric acid in the glycine– H_3BO_3 – H_2O system over the temperature region of 0 – 70 °C

stant a : while positive a values (salting-in) are found at 0 and 25 °C, the boric acid content is constant along the solubility branch at 50 °C, and a negative a value indicating salting-out is observed at 70 °C. The temperature dependence of the constant a' is less straightforward but an overall tendency to a decrease with increasing temperature is apparent. The constants b and b' have the physical meaning of solubilities of boric acid and glycine, respectively. Their values agree with tabulated data^{4,6} within the mean error given in Table II.

Salting-in can be generally regarded as an indication of some interaction of the components. The temperature dependence of the constants a and a' as described above

TABLE I
Solubility in the glycine–H₃BO₃–H₂O system

| Saturated solution, wt.% | | | Solid phase | Saturated solution, wt.% | | | Solid phase |
|--------------------------|--------------------------------|------------------|--|--------------------------|--------------------------------|------------------|--|
| Glycine | H ₃ BO ₃ | H ₂ O | | Glycine | H ₃ BO ₃ | H ₂ O | |
| 0 °C | | | | 50 °C | | | |
| 0.00 | 3.54 | 96.46 | H ₃ BO ₃ | 0.00 | 9.15 | 90.85 | H ₃ BO ₃ |
| 7.65 | 3.92 | 88.43 | H ₃ BO ₃ | 9.07 | 9.20 | 81.73 | H ₃ BO ₃ |
| 10.62 | 4.57 | 84.81 | H ₃ BO ₃ | 19.18 | 9.08 | 71.74 | H ₃ BO ₃ |
| 10.58 | 5.36 | 84.06 | H ₃ BO ₃ | 18.51 | 9.47 | 72.02 | H ₃ BO ₃ |
| 15.80 | 6.30 | 77.90 | H ₃ BO ₃ + glycine | 24.74 | 9.00 | 66.26 | H ₃ BO ₃ + glycine |
| 15.30 | 3.63 | 81.07 | glycine | 25.96 | 6.43 | 67.61 | glycine |
| 13.35 | 2.51 | 84.13 | glycine | 25.10 | 4.38 | 70.52 | glycine |
| 14.15 | 0.00 | 85.85 | glycine | 25.38 | 2.18 | 72.44 | glycine |
| | | | | 25.39 | 0.00 | 74.61 | glycine |
| 25 °C | | | | 70 °C | | | |
| 0.00 | 5.56 | 94.44 | H ₃ BO ₃ | 0.00 | 15.68 | 84.33 | H ₃ BO ₃ |
| 10.62 | 4.57 | 84.81 | H ₃ BO ₃ | 12.82 | 13.25 | 73.93 | H ₃ BO ₃ |
| 18.58 | 5.61 | 75.81 | H ₃ BO ₃ | 17.18 | 12.46 | 70.36 | H ₃ BO ₃ |
| 17.25 | 5.60 | 77.15 | H ₃ BO ₃ | 21.05 | 12.90 | 66.05 | H ₃ BO ₃ |
| 21.62 | 6.70 | 71.60 | H ₃ BO ₃ + glycine | 27.22 | 11.66 | 61.12 | H ₃ BO ₃ |
| 20.72 | 6.89 | 72.39 | glycine | 30.41 | 12.49 | 57.10 | H ₃ BO ₃ + glycine |
| 20.07 | 4.61 | 75.32 | glycine | 29.47 | 10.73 | 59.79 | glycine |
| 19.50 | 2.33 | 78.17 | glycine | 30.12 | 9.98 | 59.90 | glycine |
| 19.64 | 0.00 | 80.36 | glycine | 29.64 | 4.60 | 65.77 | glycine |
| | | | | 30.09 | 0.00 | 69.91 | glycine |

seems to indicate that a weak interaction between glycine and boric acid exists in the system at low temperatures, but it grows weaker as the temperature is increased, to be completely absent at 70 °C. Data concerning the water vapour pressure over the saturated solutions and the activity of water in them are given in Table III. The activity of

TABLE II

The coefficients of the Eqs (2) and (3)

| $T, ^\circ\text{C}$ | a | b wt. % | a' | b' wt. % | Mean relative error, % | Regression sum of squares |
|---------------------|---------|--------------|---------|---------------|---------------------------|------------------------------|
| 0 | 0.1731 | 3.19 | – | – | 9.5 | 0.94 |
| 25 | 0.0412 | 5.03 | – | – | 9.4 | 1.70 |
| 50 | 0.0000 | 9.12 | – | – | 1.3 | 0.12 |
| 70 | –0.1136 | 15.1 | – | – | 3.9 | 1.83 |
| 0 | – | – | 0.3097 | 13.7 | 7.8 | 5.72 |
| 25 | – | – | 0.2477 | 19.3 | 2.0 | 0.91 |
| 50 | – | – | –0.0364 | 25.5 | 0.9 | 0.29 |
| 70 | – | – | 0.0000 | 29.9 | 1.0 | 0.59 |

TABLE III

Water vapour pressure and water activity in saturated solutions of the glycine– H_3BO_3 – H_2O system at 25 °C

| Saturated solution composition | | | $p_{\text{H}_2\text{O}}, \text{kPa}$ | a_w |
|--------------------------------|-----------------------------------|--|--------------------------------------|-------|
| glycine mol/kg | H_3BO_3 mol/kg | H_2O mol/100 mol solute | | |
| 0.000 | 0.952 | 5 830 | 3.114 | 0.983 |
| 1.668 | 0.872 | 2 182 | 3.038 | 0.959 |
| 2.978 | 1.174 | 1 335 | 3.013 | 0.951 |
| 3.265 | 1.197 | 1 243 | 2.968 | 0.937 |
| 4.018 | 1.512 | 1 006 | 2.937 | 0.927 |
| 3.813 | 1.539 | 1 039 | 2.943 | 0.929 |
| 3.550 | 0.990 | 1 223 | 2.971 | 0.938 |
| 3.323 | 0.482 | 1 462 | 2.990 | 0.943 |
| 3.256 | 0.000 | 1 704 | 3.013 | 0.951 |

water and water concentration along the solubility isotherm at 25 °C is shown in Fig. 2, which clearly demonstrates an interrelation of the above variables. Similar observations have been made for other aqueous systems as well⁷.

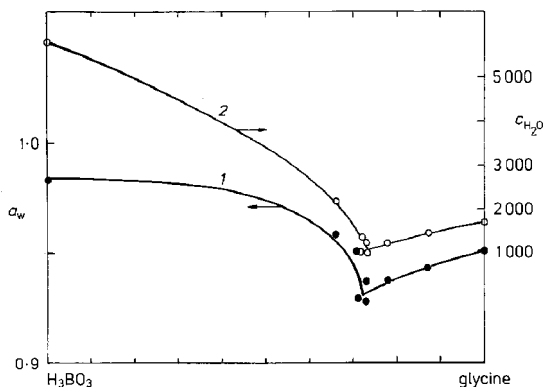


FIG. 2
Activity of water (1) and water concentration (2) ($c_{\text{H}_2\text{O}}$, mol/100 mol solute) in saturated solutions of the glycine– H_3BO_3 – H_2O system at 25 °C

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