Supplementary information

On the concomitant crystallization of amino acid crystals upon dissolution of some amino acid salt crystals

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Content:

Phase diagram calculation of the glutamic acid – sodium hydroxide system

If sodium hydroxide is added to a glutamic acid solution, several other compounds as compared to the hydrochloric systems play a role. An additional compound monosodium glutamate monohydrate as well as the occurrence of two-fold ionized glutamic acid must be considered. Again, molarities instead of activities are used in the calculations. Further, we neglect the presence of the crystal water in the monosodium glutamate crystals. The calculations are based on $[OH^-]$, rather than $[H_3O^+]$; this gives a more clear insight. Values of the various constants used for the calculation are given in table SI-1.

Table SI-1: Input parameters used for the calculation of the glutamic acid /NaOH phase diagram

Input parameters	**Value**
K_{b1} [S1]	$6.46 \cdot 10^{11}$ M^{-1}
K_{b2} [S1]	$5.62 \cdot 10^{9}$ M^{-1}
K_{b3} [S1]	$2.14 \cdot 10^{3}$ M^{-1}
K_w	$0.68 \cdot 10^{-14}$ M^2
Solubility A; $[A_{tot,0}]$ **	0.0558 M
Solubility NaA ***	2.54 M

*Concentrations and equilibria are expressed in terms of molarities, M.
**Average of refs. [S2] and [S3]
***Average of [S4], [S5], [S6].
**** $K_b = K_a/K_w$

SI-1 Equilibria and triple point values

The equilibria involved in the glutamic acid – sodium hydroxide system are:

$[A^+] + [OH^-] \leftrightarrow [A]$; $$\frac{[A]}{[A^+][OH^-]} = K_{b1} \quad (1)$$

$[A] + [OH^-] \leftrightarrow [A^-]$; $$\frac{[A^-]}{[A][OH^-]} = K_{b2} \quad (2)$$

$[A^-] + [OH^-] \leftrightarrow [A^{2-}]$; $$\frac{[A^{2-}]}{[A^-][OH^-]} = K_{b3} \quad (3)$$

$$2[H_2O] \leftrightarrow [H_3O^+] + [OH^-]; \qquad [H_3O^+][OH^-] = K_w \tag{4}$$

$$[A] \leftrightarrow A_{solid} \qquad [A_{slb}] = K_A \tag{5}$$

$$[A^-] + [Na^+] \leftrightarrow \mathrm{NaA}_{solid} \qquad [A^-][Na^+] = K_{NaA} \tag{6}$$

The first step in the computation of the phase diagram is calculating the solubility of the neutral species, $[A_{slb}]$ in contact with solid amino acid in water. This is done in the main text and gives $K_A = 0.0470$.

The second step is deriving the solubility constant K_{NaA}, using the experimental concentration, $[NaA]_{\mathrm{sat}}$, of a saturated sodium glutamate solution. This can be computed by (numerically) solving equations (2), (3), (4) and (6) including the charge neutrality condition

$$[Na^+] + [H_3O^+] = [A^-] + 2[A^{2-}] + [OH^-] \ , \tag{7}$$

and considering the facts that

$$[A_{tot}] = [A] + [A^-] + [A^{2-}], \tag{8}$$

and the sodium is completely ionized

$$[Na^+] = [A_{tot}] = [NaA]_{\mathrm{sat}} \tag{9}$$

This gives the equilibrium constant K_{NaA} , which is given in table SI-2. It is assumed that the concentration of A^+ can be neglected in a saturated NaA solution.

Table SI-2: Calculated parameters for the glutamic acid /NaOH system

Calculated parameters/concentrations	**Value**
$[A_{\mathrm{slb}}] = K_A$	0.0470 M
$K_{\mathrm{NaA}} = [A^-][Na^+]$	6.43 M^2
$[A_{\mathrm{tot,trip}}]$	2.582 M
$[Na^+]_{\mathrm{trip}}$	2.536 M
$[OH\text{-}]_{\mathrm{trip}}$	$6.5 \cdot 10^{-9}$ M

At the triple point of the glutamic acid - NaOH phase diagram, solid amino acid and solid monosodium glutamate are in equilibrium with the aqueous solution. Using the equilibrium constants, K_A *and* K_{NaA}, the six concentrations $[A]$, $[A^-]$, $[A^{2-}]$, $[H_3O^+]$, $[OH^-]$ and $[Na^+]$ at this point can be calculated by numerically solving the set of six equations (2), (3) (4), (5), (6) and (7). From these values the total amino acid concentration in the solution at the triple point, $[A_{tot}]$, readily follows from equation (8). Results are given in table SI-2.

SI-2 Constructing the phase diagrams

Fig. SI-1 shows the calculated phase diagram of the system the glutamic acid /NaOH.

The L - $L+A_s$ boundary line is calculated by solving the set of equations (2), (3), (4), (5), (7) and (8) for $[A_{tot}]$as a function of $[Na^+]$, which as a consequence of its complete ionization is identical to the total amount of NaOH added to the system. Here, A = glutamic acid (Glu).

If amino acid is added to a solution corresponding with the triple point, the composition of the solution does not change and only solid amino acid is formed. This implies a vertical $L+A_s$ – $L+A_s+NaA_s$ line starting from the triple point. Similarly, if monosodium glutamate is added to a triple point solution, only solid NaA_s is formed. Therefore, in the phase diagram the $L+A_s+NaA_s$ – $L+NaA_s$ boundary is a straight line with slope one, starting from the triple point.

The L – $L+ACl_s$ border line is calculated by solving the set of equations (2), (3), (4), (6), (7) and (8) for $[A_{tot}]$ as a function of $[Na^+]$ (= $NaOH_{added}$).

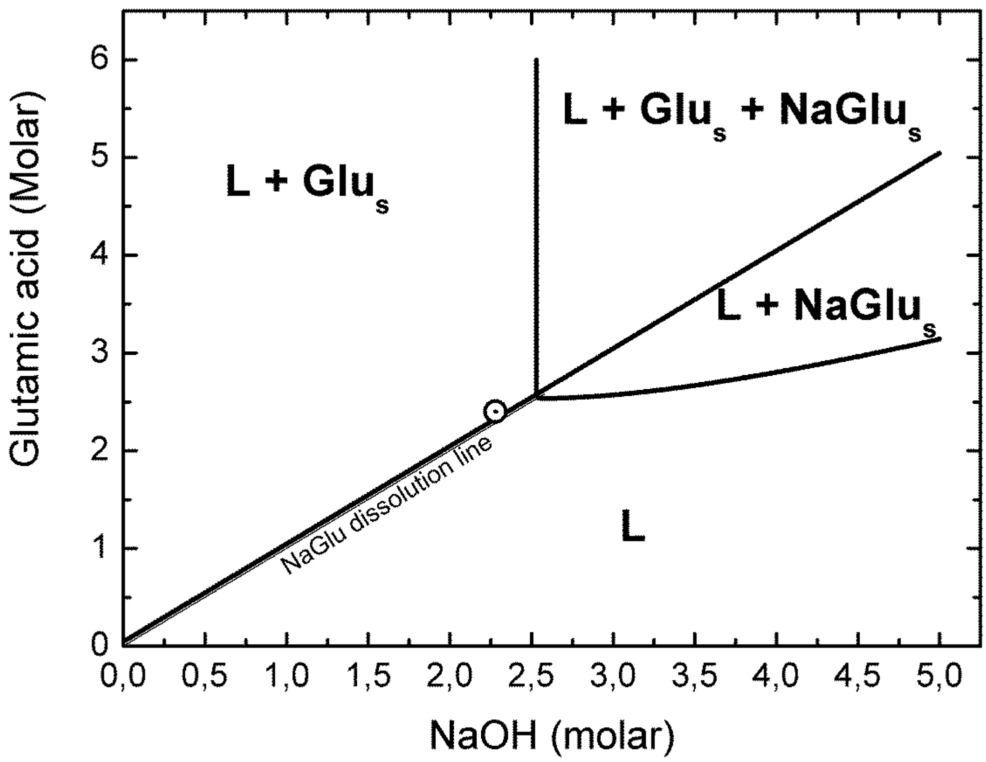

Fig. SI-1. Calculated phase diagram of the system glutamic acid/NaOH. The thin line nearly coinciding with, but always below, the L – $L+Glu_s$ boundary line is the sodium glutamate dissolution line; the experimental triple point is indicated by the center point circle.

References

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