Supplementary Information

Study on the solid-liquid equilibrium and thermodynamic model of L-phenylalanine +L-tryptophan + water system

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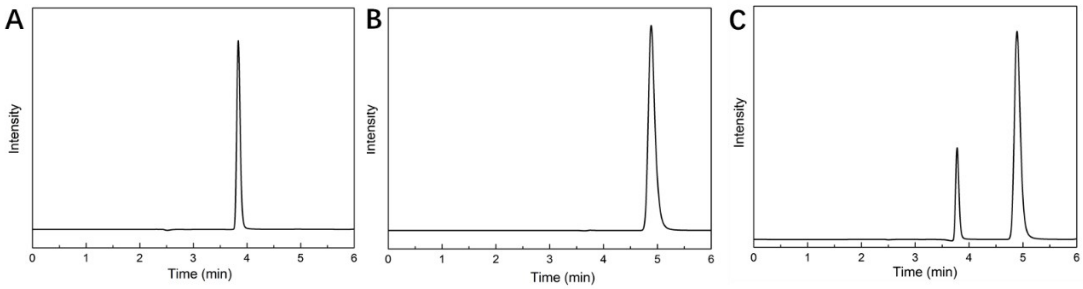

Figure S1. Liquid chromatography of amino acids. L-phenylalanine aqueous solution (A); L-tryptophan aqueous solution (B); L-phenylalanine + L-tryptophan aqueous solution (C).

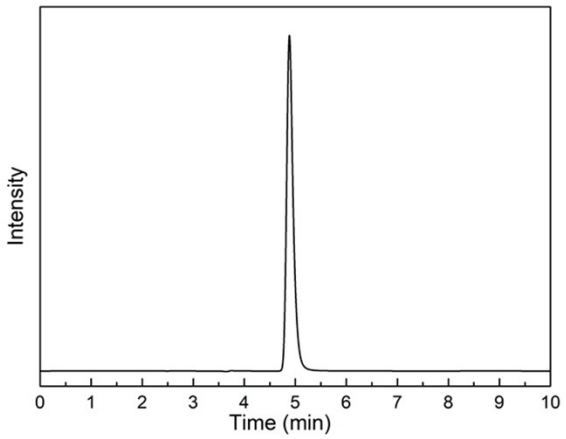

Figure S2. Liquid chromatography of the solid phases 1.

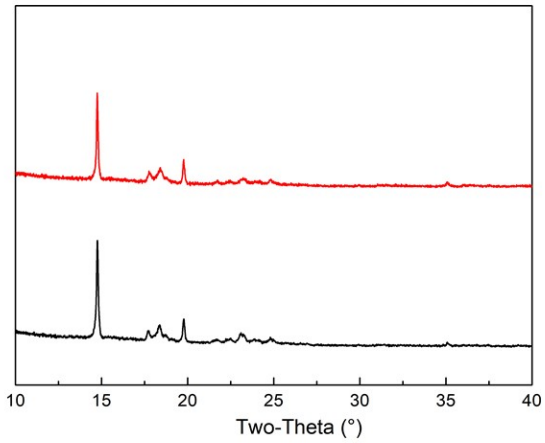

Figure S3. XRD pattern of wet residue (black line) and pure L-tryptophan (red line).

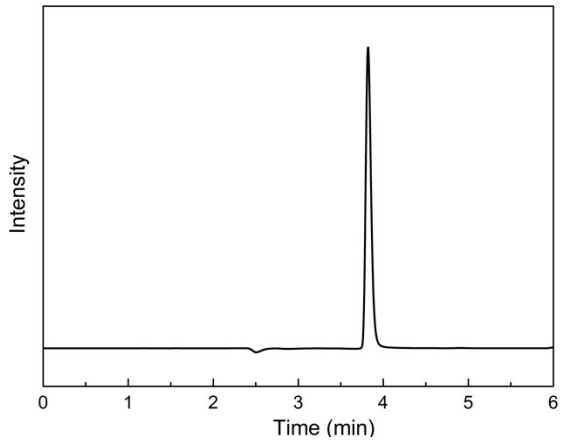

Figure S4. Liquid chromatography of the solid phases 2.

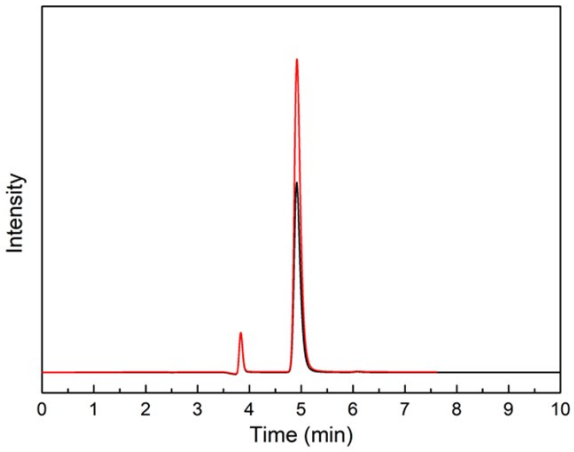

Figure S5. Liquid chromatogram of the supernatant at point E (red line) and D (black line).

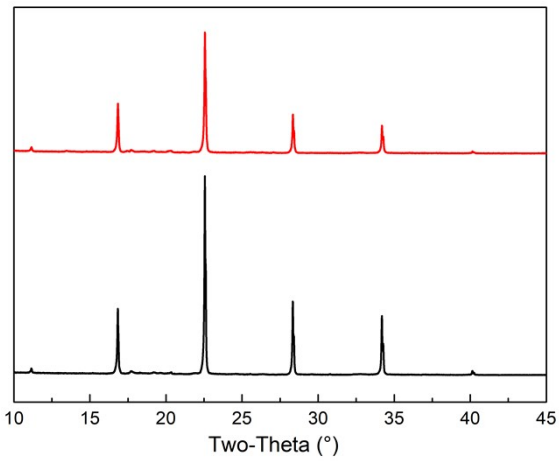

Figure S6. XRD pattern of wet residue (black line) and pure L-phenylalanine (red line).

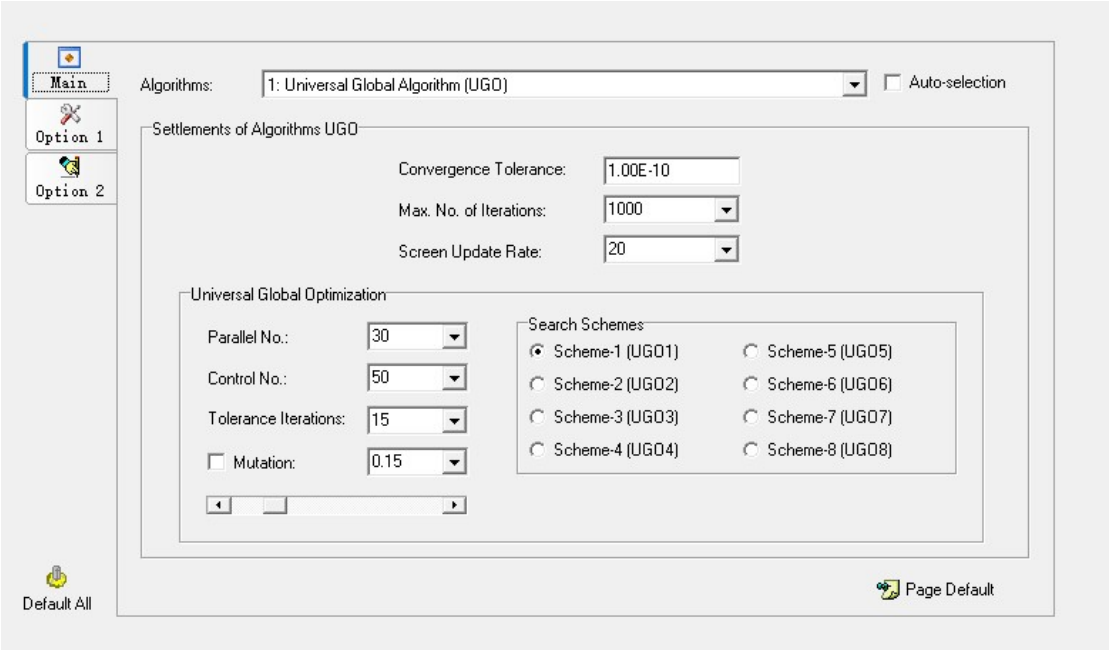

Figure S6. Calculation algorithm Settings.

```
Variable tp,ma,mb,lnr;
Parameter  at12,bt12,at12a,bt12a; // ,k1,k2
Constant k2=0.5,
pd11=    -0.0511550689218954,
pd12=   1.10536853197906 ,
pd13=   -634.853403850243   ;
ConstStr  pd1=pd11*tp+pd12*tp^0.5+pd13/tp,
          p12=at12*tp+bt12*tp^k1,  //+ct12/tp
          p12a=at12a*tp+bt12a*tp^k1; //+ct12a/tp
Function lnr=pd1+(p12*mb+p12a*mb^k2 );
```

Figure S7. The calculation code of the correlation procedure for the precipitation of L-phenylalanine from ternary system.

```
Variable tp,ma,mb,lnr;
Parameter  at12,bt12,at12a,bt12a; // ,k1,k2
Constant k2=0.5,
pd11=    0.00662618986028544,
pd12=   -0.355918425585242 ,
pd13=   1319.44610441873   ;
ConstStr  pd1=pd11*tp+pd12*tp^0.5+pd13/tp,
          p12=at12*tp+bt12*tp^k1,  //+ct12/tp
          p12a=at12a*tp+bt12a*tp^k1; //+ct12a/tp
Function lnr=pd1+(p12*mb+p12a*mb^k2 );
```

Figure S8. The calculation code of the correlation procedure for the precipitation of L-tryptophan from ternary system.

```
Variable t,lnr;
Function lnr=p1*t+p2*t^0.5+p3/t;
```

Figure S9. The calculation code of the correlation procedure for the binary system.

Table S1 Primary experimental data used to calculate amino acid liquid phase mass fraction by HPLC.

T/K	L-phenylalanine (g/100 g H_2O)	L-tryptophan (g/100 g H_2O)
278.15 K	0.0000	0.9343
278.15 K	0.2356	0.9513
278.15 K	0.4060	0.9580
278.15 K	0.6581	0.9937
278.15 K	0.8050	0.9574
278.15 K	1.0718	0.9411
278.15 K	1.3068	0.9920
278.15 K	1.4937	0.9900
278.15 K	1.8938	0.9846
278.15 K	2.0635	0.9780
278.15 K	2.2919	0.8154
278.15 K	2.3316	0.3102
278.15 K	2.3475	0.4568
278.15 K	2.3586	0.5776
278.15 K	2.3669	0.7244
278.15 K	2.4532	0.0000
288.15 K	0.0000	1.2721
288.15 K	0.0972	1.1918
288.15 K	0.5280	1.2227
288.15 K	0.7856	1.2146
288.15 K	0.9993	1.2255
288.15 K	1.4848	1.2372
288.15 K	1.5576	1.2405
288.15 K	1.9144	1.2394
288.15 K	2.2623	1.2539
288.15 K	2.3719	1.2212
288.15 K	2.5279	0.7146
288.15 K	2.5316	1.0592
288.15 K	2.5357	0.5265
288.15 K	2.5462	0.4005
288.15 K	2.5932	0.0000
288.15 K	2.5782	0.1331
288.15 K	2.5808	0.2861
288.15 K	2.5850	0.7261
288.15 K	2.5909	0.3534
288.15 K	2.6112	0.9541
288.15 K	2.6221	0.6268

298.15 K	0.0000	1.2909
298.15 K	0.4783	1.1412
298.15 K	0.7888	1.2987
298.15 K	1.0623	1.2896
298.15 K	1.1324	1.2923
298.15 K	1.3779	1.2560
298.15 K	1.8813	1.2723
298.15 K	1.9797	1.2973
298.15 K	2.1513	1.2336
298.15 K	2.2353	1.2254
298.15 K	2.5643	1.3345
298.15 K	2.7532	0.8548
298.15 K	2.8509	0.5292
298.15 K	2.8946	0.2263
298.15 K	2.9168	0.0000
308.15 K	0.0000	1.6832
308.15 K	0.2457	1.5758
308.15 K	0.5749	1.4807
308.15 K	0.5979	1.5697
308.15 K	0.7061	1.5682
308.15 K	0.9418	1.5614
308.15 K	1.0915	1.5351
308.15 K	1.4565	1.6189
308.15 K	1.4907	1.5378
308.15 K	1.7575	1.5418
308.15 K	1.8966	1.5543
308.15 K	2.0863	1.5752
308.15 K	2.2532	1.5426
308.15 K	2.4164	1.5738
308.15 K	2.5966	1.5596
308.15 K	2.8148	1.5765
308.15 K	3.0180	1.5853
308.15 K	3.0974	1.5929
308.15 K	3.3940	1.3011
308.15 K	3.4082	1.6081
308.15 K	3.4651	0.6808
308.15 K	3.5681	0.0000
308.15 K	3.4721	0.5453
308.15 K	3.4840	0.3480
308.15 K	3.5022	0.9563
308.15 K	3.5257	1.2017
308.15 K	3.5225	0.7009
308.15 K	3.5658	0.1514

308.15 K	3.6221	0.8822
318.15 K	0.0000	2.0367
318.15 K	0.2831	1.9598
318.15 K	0.6748	1.9190
318.15 K	0.9387	1.9497
318.15 K	1.1118	1.9220
318.15 K	1.2164	1.8719
318.15 K	1.5343	1.9277
318.15 K	2.0161	1.9922
318.15 K	2.8852	1.9321
318.15 K	3.1016	1.9440
318.15 K	3.3634	1.9188
318.15 K	3.5024	1.8842
318.15 K	3.8191	1.9868
318.15 K	3.8346	1.2906
318.15 K	4.2066	0.0000
318.15 K	4.1321	0.6090
318.15 K	4.1839	0.3752
318.15 K	4.2202	1.1066

Uncertainty Analysis

According to the principle of solid-liquid equilibrium and experimental method, the main items leading to the error of mass fractions measurement include temperature and reagent purity. The Law of Error propagation is given in the following equation:

$$u_c(y) = \sqrt{\sum_{i=1}^{N} (\frac{\partial f}{\partial x_i})^2 u^2(x_i) + 2\sum_{i=1}^{N-1} \sum_{j=i+1}^{N} (\frac{\partial f}{\partial x_i})(\frac{\partial f}{\partial x_i}) u(x_i, x_j)} \quad \text{(S1)}$$

where y is the output variable, x_i is the input variables, f refers to the function that relates the input and output variables, $u_c(y)$ refers to the combined standard uncertainty of the output variable y and $u(x_i)$ is the combined standard uncertainty of the input variable x_i and $u(x_i,x_j)$ refers to covariance between two input variables x_i and x_j.

(1) Temperature uncertainty

The measurement uncertainty $u_{x,T}$ was calculated by following equation:

$$u_c(T) = \sqrt{u_{T,m}^2 + u_{T,a}^2} \quad \text{(S2)}$$

$u_{T,m}$, $u_{T,a}$ are the uncertainties of measurement and apparatus, respectively. The measurement uncertainty $u_{T,m}$ was calculated by following equation:

$$u_{T,m} = \sqrt{\frac{1}{n(n-1)} \sum_{i=1}^{n} (T_i - \overline{T})^2} \quad \text{(S3)}$$

where T_i is the measured value at time i, $\overline{T}$ is the average of all measured values, and n is the number of independent replications. The measurement of temperature was repeated at least three times, and the measurement uncertainty would be:

$$u_{T,m} = \sqrt{\frac{0.05^2 + 0.03^2 + 0.01^2}{3*2}} = 0.024kPa \quad \text{(S4)}$$

The apparatus uncertainty $u_{T,a}$ was calculated by:

$$u_{T,a} = \frac{e_a}{k_c} \quad \text{(S5)}$$

where e_a is apparatus error, and k_c is the confidence coefficient, which is assumed to $\sqrt{3}$ when the distribution of e_a is rectangular. As a result, $u_{T,a}$ was calculated by:

$$u_{T,a} = \frac{0.07}{\sqrt{3}} = 0.040kPa \quad \text{(S6)}$$

As a result, the temperature uncertainty u(T) was calculated to be:

$$u_c(T) = \sqrt{0.024^2 + 0.040^2} = 0.05K \quad \text{(S7)}$$

(2) Composition uncertainty

The measurement uncertainty $u_{x,r}$ was calculated by following equation:

$$\frac{u_c(w)}{w} = \sqrt{(\frac{u_{w,T}}{T})^2 + \sum (\frac{u_{w,r}}{r})^2} \quad \text{(S8)}$$

where T and r represent temperature and reagent purity, $u_{w,T}$ and $u_{w,r}$ are relevant uncertainties.

For example, for the mixture L-tryptophan + L-phenylalanine + H_2O at 278.15 K in Table 3, the mass fraction is 0.00986.

The measurement uncertainty $u_{w,T}$ was calculated by following equation:

$$\frac{u_{w,T}}{T} = \frac{0.05K}{278.15K} = 1.80e-04 \quad \text{(S9)}$$

The measurement uncertainty $u_{w,r}$ was calculated by following equation:

$$\sum (\frac{u_{w,r}}{r})^2 = (\frac{0.0003}{\sqrt{3} * 0.9997})^2 + (\frac{0.0004}{\sqrt{3} * 0.9996})^2 = 8.36e-06 \quad \text{(S10)}$$

The overall uncertainty of the composition measurement was:

$$\frac{u_c(w)}{w} = \sqrt{(\frac{u_{w,T}}{T})^2 + \sum (\frac{u_{w,r}}{r})^2} = 2.89e-04 \quad \text{(S11)}$$

$$u_c(w) = 0.003$$