

Solubilities of L-Cystine, L-Tyrosine, L-Leucine, and Glycine in Their Water Solutions

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The solubilities of four amino acids, L-cystine, L-tyrosine, L-leucine, and glycine, in aqueous solutions containing another amino acid have been measured at 298.15 K, 308.15 K, and 318.15 K. In aqueous solutions containing L-cystine and L-tyrosine, which have a low solubility, the solubility of the other amino acids is similar to that in pure water except for L-cystine in water + L-tyrosine. On the other hand, compared to their solubilities in pure water, in aqueous solutions containing glycine, which is quite soluble, a large variation in the solubilities of all the amino acids can be seen. Considerable variations in the solubility of L-cystine or L-tyrosine are observed in aqueous solutions containing L-leucine.

1. Introduction

Since their isolation in the second half of the 19th century, the physical chemical properties of amino acids have been studied, not only because of their value as basic elements in all forms of life but also for their importance in industrial processes.

To use them in industrial processes as constituents of pharmaceutical products or food additives, many amino acids must be extracted from mixtures that could be obtained, for example, from the hydrolyzation of protein-containing materials (such as horns, hair, wool, etc.) or from fermentation broths. Fractional crystallization or other separation methods, such as chromatographic methods, are suitable for purification processes; all these methods can benefit from an understanding of the behavior of solubility, which is basic to the design and optimization of such processes.

A lot of research has already been carried out on the solubility of amino acids in single solvents (Carta and Tola, 1996; Gatewood and Rousseau, 1994; Fasman, 1976; Needham et al., 1971) and in mixtures of two solvents (Day and Lahiri, 1992; Orella and Kirwan 1989, 1991; Mozaki and Tanford, 1963, 1965; Gekko, 1981; Gekko and Koga, 1984), as well as on their properties as amphoteric and ionic substances (Carta, 1998; Cohn et al., 1939). However, the fact that both in protein hydrolysis and fermentation broths the desired amino acids are always in solution together with other amino acids may affect their solubility. So the investigation of the solubilities of amino acids in binary mixtures of water with other amino acids is a further step in the representation of the complex mechanisms behind the separation of solid amino acids from liquid solutions.

In this work the solubility of an amino acid in aqueous solutions containing known concentrations of another amino acid is studied. Three methods were used to evaluate the quantity dissolved at saturation. Densities of the initial and of the saturated solutions with the added amino acid at (298.15, 308.15, and 318.15) K have been measured.

2. Experimental Procedure

Solutions were prepared by dissolving known masses (balance Mettler Toledo model AB104; accuracy, 10^{-3} g) of

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Table 1. Possible Mixtures of Solution + Added Amino Acid and Methods of Analysis Used (C = L-Cystine; T = L-Tyrosine; L = L-Leucine; G = Glycine; HPLC = Reverse Phase Chromatography; AA = Ion Exchange Chromatography; DMM = Dry Mass Method)

| solution | added amino acid and method of analysis | | | |
|-----------|---|--------|-------|-------|
| | C | T | L | G |
| water + C | | × HPLC | × DMM | × DMM |
| water + T | × HPLC | | × DMM | × DMM |
| water + L | × HPLC | × HPLC | | × DMM |
| water + G | × AA | × HPLC | × DMM | |

L-cystine, L-tyrosine, L-leucine, and glycine (Aldrich Chemie, 99%) in water plus for HPLC (Carlo Erba RS). These amino acids were used without further purification. Excess amounts of amino acid other than the one used in the preparation of these solutions were added to the solutions of L-cystine, L-tyrosine, L-leucine, and glycine. Table 1 shows the different combinations used. For example, excesses of solid L-tyrosine, L-leucine, and glycine were added to a water + L-cystine solution.

The amount of solid amino acid added was about three times that required to saturate pure water at the same temperature. The solutions were placed in flasks with magnetic stirrers, thermostated in a water bath with a thermostat (TR12, Carlo Erba), and shaken with a magnetic drive agitator (AG/215, Carlo Erba) for 48 h at a constant temperature of (298.15 ± 0.1) K, (308.15 ± 0.1) K, and (318.15 ± 0.1) K. After 48 h when the samples had reached equilibrium, as shown in a previous study (Carta and Tola, 1996), the agitation was stopped and the amino acid in excess of the amount required to saturate the solution was decanted off. Three samples of about 3 mL of the clear liquid were taken and filtered (with Whatman paper no. 52) at the equilibrium temperature. The experiment was repeated three times to give nine analyses.

The samples were analyzed using three different methods (i.e. dry mass, reverse-phase chromatography, and ion-exchange chromatography) depending on the amino acid pairs.

Dry Mass Method. The method used by Jin and Chao (1992) and Needham et al. (1971) was used when the added

Table 2. Measured Density [$\text{kg}\cdot\text{dm}^{-3}$] Values for the Various Solutions Water + Glycine (C = L-Cystine; T = L-Tyrosine; L = L-Leucine; G = Glycine)

| (a) Water + Glycine | | | | | | | |
|---------------------|--------------|---|--|--|--|--|---------------|
| added AA | T/K | $C_G = 0.13$ $\text{mol}\cdot\text{dm}^{-3}$ | $C_G = 0.400$ $\text{mol}\cdot\text{dm}^{-3}$ | $C_G = 0.667$ $\text{mol}\cdot\text{dm}^{-3}$ | $C_G = 1.000$ $\text{mol}\cdot\text{dm}^{-3}$ | $C_G = 1.333$ $\text{mol}\cdot\text{dm}^{-3}$ | at saturation |
| none | 298.15 | 1.0014 | 1.0051 | 1.0179 | 1.0281 | 1.0379 | 1.0718 |
| | 308.15 | 0.9984 | 1.0064 | 1.0143 | 1.0238 | 1.0335 | 1.0582 |
| | 318.15 | 0.9945 | 1.0030 | 1.0111 | 1.0088 | 1.0185 | 1.0317 |
| C | 298.15 | 1.0013 | 1.0050 | 1.0178 | | | |
| | 308.15 | 0.9983 | 1.0066 | 1.0149 | | | |
| | 318.15 | 0.9947 | 1.0030 | 1.0111 | | | |
| T | 298.15 | | | 1.0181 | 1.0284 | 1.0386 | |
| | 308.15 | | | 1.0145 | 1.0243 | 1.0344 | |
| | 318.15 | | | 0.9991 | 1.0089 | 1.0186 | |
| L | 298.15 | | | 1.0209 | 1.0307 | 1.0406 | |
| | 308.15 | | | 1.0176 | 1.0269 | 1.0366 | |
| | 318.15 | | | 1.0137 | 1.0231 | 1.0332 | |

| (b) Water + L-Leucine | | | | | | |
|-----------------------|--------------|--|--|--|---------------|--|
| added AA | T/K | $C_L = 0.038$ $\text{mol}\cdot\text{dm}^{-3}$ | $C_L = 0.076$ $\text{mol}\cdot\text{dm}^{-3}$ | $C_L = 0.114$ $\text{mol}\cdot\text{dm}^{-3}$ | at saturation | |
| none | 298.15 | 0.9979 | 0.9989 | 0.9997 | 1.0012 | |
| | 308.15 | 0.9949 | 0.9960 | 0.9968 | 0.9991 | |
| | 318.15 | 0.9912 | 0.9922 | 0.9993 | 0.9982 | |
| C | 298.15 | 0.9979 | 0.9989 | 0.9998 | | |
| | 308.15 | 0.9950 | 0.9961 | 0.9968 | | |
| | 318.15 | 0.9912 | 0.9922 | 0.9930 | | |
| T | 298.15 | 0.9981 | 0.9991 | 1.0001 | | |
| | 308.15 | 0.9951 | 0.9961 | 0.9969 | | |
| | 318.15 | 0.9914 | 0.9923 | 0.9931 | | |
| G | 298.15 | 1.0776 | 1.0787 | 1.0790 | | |
| | 308.15 | 1.0888 | 1.0890 | 1.0896 | | |
| | 318.15 | 1.0994 | 1.0993 | 1.1003 | | |

| (c) Water + L-Tyrosine | | | | | |
|------------------------|--------------|---|---|---|---------------|
| added AA | T/K | $C_T = 0.000552$ $\text{mol}\cdot\text{dm}^{-3}$ | $C_T = 0.001105$ $\text{mol}\cdot\text{dm}^{-3}$ | $C_T = 0.001656$ $\text{mol}\cdot\text{dm}^{-3}$ | at saturation |
| none | 298.15 | 0.9971 | 0.9971 | 0.9972 | 0.9973 |
| | 308.15 | 0.9942 | 0.9942 | 0.9943 | 0.9944 |
| | 318.15 | 0.9904 | 0.9904 | 0.9905 | 0.9906 |
| C | 298.15 | 0.9971 | 0.9971 | 0.9972 | |
| | 308.15 | 0.9942 | 0.9942 | 0.9943 | |
| | 318.15 | 0.9904 | 0.9904 | 0.9905 | |
| L | 298.15 | 1.0010 | 1.0010 | 1.0011 | |
| | 308.15 | 0.9981 | 0.9982 | 0.9982 | |
| | 318.15 | 0.9945 | 0.9946 | 0.9947 | |
| G | 298.15 | 1.0783 | 1.0786 | 1.0797 | |
| | 308.15 | 1.0897 | 1.0902 | 1.0911 | |
| | 318.15 | 1.0947 | 1.0948 | 1.0947 | |

| (d) Water + L-Cystine | | | | | |
|-----------------------|--------------|---|---|---|---------------|
| added AA | T/K | $C_C = 0.000167$ $\text{mol}\cdot\text{dm}^{-3}$ | $C_C = 0.000250$ $\text{mol}\cdot\text{dm}^{-3}$ | $C_C = 0.000417$ $\text{mol}\cdot\text{dm}^{-3}$ | at saturation |
| none | 298.15 | 0.9970 | 0.9970 | 0.9972 | 0.9972 |
| | 308.15 | 0.9942 | 0.9943 | 0.9943 | 0.9944 |
| | 318.15 | 0.9906 | 0.9906 | 0.9907 | 0.9908 |
| T | 298.15 | 0.9971 | 0.9971 | 0.9972 | |
| | 308.15 | 0.9943 | 0.9943 | 0.9944 | |
| | 318.15 | 0.9906 | 0.9906 | 0.9906 | |
| L | 298.15 | 1.0008 | 1.0009 | 1.0009 | |
| | 308.15 | 0.9981 | 0.9981 | 1.0027 | |
| | 318.15 | 0.9944 | 0.9944 | 1.0051 | |
| G | 298.15 | 1.0767 | 1.0773 | 1.0779 | |
| | 308.15 | 1.0889 | 1.0874 | 1.0871 | |
| | 318.15 | 1.0967 | 1.0983 | 1.0999 | |

solid amino acid was L-leucine or glycine. About 2 mL of the filtered sample was withdrawn with an automatic pipet and placed in a preweighed sample bottle, where its mass was determined. The volume was calculated from density values obtained with a tube vibrating densimeter (DMA 602, Anton Paar K. G.). Parts a–d of Table 2 give the measured densities. The sample was placed in an oven (GGT, Turin) and evaporated to dryness at (333.15 ± 0.5) K and atmospheric pressure and its mass determined. The

evaporation temperature was chosen to allow rapid evaporation without decomposition or loss of liquid due to splashing.

The estimated uncertainties in the solubility values for glycine and L-leucine in the presence of L-tyrosine was $\pm 2.5 \times 10^{-4}$ and $\pm 5.0 \times 10^{-4}$ $\text{mol}\cdot\text{dm}^{-3}$.

Reverse-Phase Chromatography (High-Pressure Liquid Chromatography). This method was used to analyze the solubility of L-cystine and L-tyrosine in the solutions,

Table 3. Retention Times of the Four Amino Acids in the Column Used for HPLC Analysis

| amino acid | retention time/min | amino acid | retention time/min |
|------------|--------------------|------------|--------------------|
| glycine | 2.02–2.03 | L-leucine | 4.8–4.9 |
| L-cystine | 2.01–2.02 | L-tyrosine | 4.3–4.4 |

Table 4. Buffer Solutions Used for Sample Preparation and Analysis for the Amino Acid Analyzer

| components (all ACS Aldrich chemicals) | dilution buffer pH 2.2 | buffer 1 pH 2.85 | buffer 2 pH 3.10 |
|--|------------------------|----------------------|---------------------|
| citric salt (trilithium salt hydrate; 99%) | 18.8 g | 18.8 g | 14.099 g |
| hydrochloric acid; 37% | 13.5 cm ³ | 13.0 cm ³ | 9.0 cm ³ |
| phenol (loose crystals; 99%) | 0.5 g | 0.5 g | 0.5 g |

except those containing glycine with L-cystine as an added amino acid. The chromatographic apparatus (1050 series, Hewlett-Packard with autoinjector) was used with a column (25 cm length, 4 mm i.d.) packed with 5 μ m sized octosilica particles (Lichrosphere 100 RP-8). The effluent from the column was detected by a multiple wavelength UV adsorption detector. The detection was set at 210 nm to avoid any interference from the mobile phase (buffer solution, 1×10^{-6} M CH₃COOH and 2×10^{-5} M CH₃COONa). The results were processed with an automatic integrator (3396/6 Hewlett-Packard).

Before processing for HPLC, the filtered samples were diluted with water in a 1:4 ratio to avoid precipitation from the saturated solution. When necessary, further dilution with water was made to bring the amino acid concentrations lower than 3000 ppm (a higher value may lead to column damage). All dilutions were made by mass (the density values reported in Table 2a–d were used to obtain the volumes).

The retention times of the four amino acids at a flow rate of 1.0 cm³·s⁻¹ with standard solutions prepared for the amino acid pairs are shown in Table 3.

Reproducibility was determined by analyzing two samples containing known amounts of L-cystine and L-tyrosine, respectively. Each sample was injected 7 times, giving an uncertainty of $\pm 1.4 \times 10^{-5}$ mol·dm⁻³ for the samples containing L-cystine and $\pm 3.8 \times 10^{-5}$ mol·dm⁻³ for those containing L-tyrosine.

Ion Exchange Chromatography (Amino Acid Analyzer). This method was used to determine the solubility of L-cystine in solutions containing glycine. In fact, since the amino acid pair, L-cystine and glycine, shows almost the same retention times on the HPLC column, the separation could not be carried out. Thus an automatic amino acid analyzer (Carlo Erba 2A30) based on ion-exchange chromatography was used.

The filtered samples were diluted, with an automatic micropipet, in a 1:50 ratio using the dilution buffer (Table 3). This solution was centrifuged at 13 000 rpm (Micro Centaur centrifuge) for 600 s to eliminate all microparticles. A 50 μ L aliquot of the solution was then automatically injected into the column (SS16, 12 \times 0.46 cm, packed with 4 g of the resin 3AR/IC/6/10, Fisons Instruments) where the cation bound the resin. An oxygen-free ninhydrin reagent [20 g of ninhydrin (Sigma Chemicals) dissolved in 750 cm³ of ethylene glycol monomethyl (Sigma) + 250 cm³ of a sodium acetate buffer at pH 5.51] was then pumped through the column at 3.33×10^{-1} cm³·s⁻¹ and 4.67×10^{-1} cm³·s⁻¹, respectively, for 1860 s. The column was kept at (318.15 \pm 0.1) K by its jacketed dry heating system. An amount of 4.67×10^{-1} cm³·s⁻¹ of buffer 2 (Table 4) was then flowed through the column for 1200 s at (333.15 \pm

Table 5. Solubilities of L-Tyrosine; L-Leucine, and Glycine in Solutions Containing L-Cystine at Concentration C_C [Subscripts, T = L-Tyrosine, L = L-Leucine, G = Glycine]^a

| T/K | C _C $\times 10^6$ / (mol·dm ⁻³) | added amino acid/(mol·dm ⁻³) | | |
|--------|--|--|------------------------------|----------------|
| | | C _T $\times 10^4$ | C _L $\times 10^3$ | C _G |
| 298.15 | 0 | 28.0* | 177.2* | 2.741* |
| 298.15 | 167 | 28.6 | 175.9 | 2.745 |
| 298.15 | 200 | 28.6 | 175.4 | 2.743 |
| 298.15 | 250 | 28.8 | 175.1 | 2.741 |
| 298.15 | 360 | 29.1 | 174.0 | 2.747 |
| 298.15 | 471 | 29.2 | 173.3 | 2.748 |
| 308.15 | 0 | 38.0 | 190.7 | 3.106 |
| 308.15 | 167 | 38.1 | 187.6 | 3.108 |
| 308.15 | 200 | 38.2 | 186.9 | 3.112 |
| 308.15 | 250 | 38.2 | 185.8 | 3.111 |
| 308.15 | 360 | 38.2 | 184.1 | 3.108 |
| 308.15 | 471 | 38.3 | 183.1 | 3.103 |
| 318.15 | 0 | 50.5 | 204.1 | 3.538 |
| 318.15 | 167 | 51.0 | 202.2 | 3.531 |
| 318.15 | 200 | 51.1 | 201.6 | 3.531 |
| 318.15 | 250 | 51.2 | 200.8 | 3.531 |
| 318.15 | 360 | 51.6 | 199.4 | 3.530 |
| 318.15 | 471 | 51.8 | 198.1 | 3.529 |

^a Values marked with an asterisk are from Carta and Tola (1996).

0.1) K. The length of the elution was checked before using test samples, and it was found that both amino acids eluted within this time. The column effluent was sent to a reactor chamber (15 m PTFE coil, 1.6 \times 0.3 mm) immersed in an oil bath at 393.15 K, where the amino acid reacts with the ninhydrin to form colored complexes, which were identified by a photometric analysis performed at 440 nm and 570 nm using a tungsten lamp (12 V, 15 W).

The results were sent to a computer and processed using the package Carlo Erba Chrom-Card Version 1.1.

Reproducibility, obtained by using a sample containing 2.915×10^{-4} mol·dm⁻³ of L-cystine and prepared following the same procedure as that used for the samples, was very poor due to the large dilution that must be applied to the samples. Reproducibility was $\pm 7.0 \times 10^{-5}$ mol·dm⁻³.

3. Results and Discussion

Tables 5–8 give the solubilities of the amino acid in solutions of known concentrations of L-cystine, L-tyrosine, L-leucine, and glycine. Solutions containing glycine were made at five different concentrations (1.333, 1.000, 0.667, 0.400, and 0.133) mol·dm⁻³. When the added amino acid was L-cystine, it was not possible to use the solution containing 1.333 mol·dm⁻³ of glycine, since the samples could not be diluted to give a final solution with concentrations of both amino acids detectable by the amino acid analyzer. Solutions containing L-leucine were prepared with the following concentrations: (0.0366, 0.0561, 0.0763, 0.0959, and 0.1145) mol·dm⁻³; while those containing L-cystine and L-tyrosine were prepared with (0.000 167, 0.000 25, 0.000 36, 0.000 471 and 0.000 552, 0.000 82, 0.001 127, 0.001 422, 0.001 657) mol·dm⁻³.

The addition of L-leucine and glycine to water modifies significantly its electric properties. Because of the small amount of L-cystine and L-tyrosine that can be dissolved, the electric properties of these two amino acid solutions are about equal to that of pure water. For this reason we expect a large change in the solubility of the amino acids dissolved in solutions containing L-leucine and glycine compared to their solubility in pure water, and a small effect or no effect at all in the solutions containing L-cystine and L-tyrosine.

Table 6. Solubilities of L-Cystine, L-Leucine, and Glycine in Master Solutions Containing L-Tyrosine at Concentration C_T [Subscripts, C = L-Cystine, L = L-Leucine, G = Glycine]^a

| <i>T</i> /K | $C_T \times 10^6 / (\text{mol} \cdot \text{dm}^{-3})$ | added amino acid/(mol·dm ⁻³) | | |
|-------------|---|--|-------------------|--------|
| | | $C_C \times 10^5$ | $C_L \times 10^3$ | C_G |
| 298.15 | 0 | 69.1* | 177.2* | 2.741* |
| 298.15 | 552 | 70.0 | 176.8 | 2.720 |
| 298.15 | 820 | 71.9 | 176.6 | 2.707 |
| 298.15 | 1127 | 73.2 | 176.5 | 2.707 |
| 298.15 | 1422 | 74.0 | 176.1 | 2.704 |
| 298.15 | 1657 | 74.8 | 176.3 | 2.705 |
| 308.15 | 0 | 71.0 | 190.7 | 3.106 |
| 308.15 | 552 | 82.1 | 188.5 | 3.074 |
| 308.15 | 820 | 87.1 | 192.4 | 3.101 |
| 308.15 | 1127 | 92.2 | 189.2 | 3.091 |
| 308.15 | 1422 | 98.0 | 188.2 | 3.076 |
| 308.15 | 1657 | 104.0 | 188.1 | 3.082 |
| 318.15 | 0 | 85.0 | 204.1 | 3.538 |
| 318.15 | 552 | 97.0 | 203.3 | 3.587 |
| 318.15 | 820 | 102.1 | 200.3 | 3.542 |
| 318.15 | 1127 | 110.9 | 201.5 | 3.521 |
| 318.15 | 1422 | 115.8 | 204.8 | 3.531 |
| 318.15 | 1657 | 122.1 | 201.4 | 3.531 |

^aValues marked with an asterisk are from Carta and Tola (1996).

Table 7. Solubilities of L-Cystine, L-Tyrosine, and Glycine in Master Solutions Containing L-Leucine at Concentration C_L [Subscripts, C = L-Cystine, T = L-Tyrosine, G = Glycine]^a

| <i>T</i> /K | $C_L \times 10^4 / (\text{mol} \cdot \text{dm}^{-3})$ | added amino acid/mol·dm ⁻³ | | |
|-------------|---|---------------------------------------|-------------------|--------|
| | | $C_C \times 10^5$ | $C_T \times 10^4$ | C_G |
| 298.15 | 0 | 69.1* | 28.0* | 2.741* |
| 298.15 | 366 | 82.0 | 28.1 | 2.732 |
| 298.15 | 561 | 88.2 | 28.2 | 2.728 |
| 298.15 | 763 | 94.8 | 28.3 | 2.725 |
| 298.15 | 959 | 101.2 | 28.4 | 2.721 |
| 298.15 | 1145 | 109.2 | 28.5 | 2.718 |
| 308.15 | 0 | 71.0 | 38.0 | 3.106 |
| 308.15 | 366 | 89.9 | 39.3 | 3.131 |
| 308.15 | 561 | 101.7 | 39.5 | 3.126 |
| 308.15 | 763 | 112.6 | 39.8 | 3.121 |
| 308.15 | 959 | 125.1 | 40.1 | 3.117 |
| 308.15 | 1145 | 137.8 | 40.3 | 3.112 |
| 318.15 | 0 | 85.0 | 50.5 | 3.538 |
| 318.15 | 366 | 132.0 | 52.2 | 3.520 |
| 318.15 | 561 | 160.0 | 52.7 | 3.513 |
| 318.15 | 763 | 190.0 | 53.1 | 3.506 |
| 318.15 | 959 | 214.0 | 53.6 | 3.499 |
| 318.15 | 1145 | 241.0 | 54.1 | 3.493 |

^aValues marked with an asterisk are from Carta and Tola (1996).

The data are presented in terms of the slope of the straight line

$$\left[\frac{S^i}{S_W^i} - 1 \right] = q \frac{C^M}{S_W^M} \quad (1)$$

where C^M is the concentration of the amino acid used to make the solution and S_W^M the solubility of this amino acid in pure water. S^i and S_W^i are the solubility of the added amino acid "i" in the solution and in pure water, respectively.

The q values were obtained by linear regression of the experimental data. The values obtained are reported in Table 9.

In solutions containing L-cystine, no changes were observed in the solubility of the added amino acids compared to their solubility in pure water. In fact the values

Table 8. Solubilities of L-Cystine, L-Tyrosine, and L-Leucine in Master Solutions Containing Glycine at Concentration C_G [Subscripts C = L-Cystine, T = L-Tyrosine, L = L-Leucine]^a

| <i>T</i> /K | $C_G / (\text{mol} \cdot \text{dm}^{-3})$ | added amino acid/(mol·dm ⁻³) | | |
|-------------|---|--|-------------------|-------------------|
| | | $C_C \times 10^5$ | $C_T \times 10^4$ | $C_L \times 10^3$ |
| 298.15 | 0 | 69.1* | 28.0* | 177.2* |
| 298.15 | 0.133 | 67.6 | 28.7 | 172.5 |
| 298.15 | 0.400 | 65.8 | 30.1 | 159.3 |
| 298.15 | 0.667 | 63.8 | 31.4 | 147.5 |
| 298.15 | 1.000 | 61.6 | 33.1 | 135.9 |
| 298.15 | 1.333 | | 34.8 | 126.6 |
| 308.15 | 0 | 71.0 | 38.0 | 190.7 |
| 308.15 | 0.133 | 69.2 | 38.5 | 184.9 |
| 308.15 | 0.400 | 66.6 | 40.9 | 174.3 |
| 308.15 | 0.667 | 64.5 | 42.9 | 160.1 |
| 308.15 | 1.000 | 62.5 | 44.9 | 146.3 |
| 308.15 | 1.333 | | 46.2 | 136.8 |
| 318.15 | 0 | 85.0 | 50.5 | 204.1 |
| 318.15 | 0.133 | 82.2 | 51.6 | 204.4 |
| 318.15 | 0.400 | 78.9 | 53.8 | 187.6 |
| 318.15 | 0.667 | 76.7 | 56.2 | 176.5 |
| 318.15 | 1.000 | 74.2 | 59.1 | 163.7 |
| 318.15 | 1.333 | | 61.9 | 146.7 |

Table 9. q Values of the Straight Line $[(S^i/S_W^i) - 1] = q (C^M/S_W^M)$

| solutions | <i>T</i> /K | added amino acid | | | |
|--------------------|-------------|------------------|------------|-----------|---------|
| | | L-cystine | L-tyrosine | L-leucine | glycine |
| water + L-cystine | 298.15 | | 0.08 | -0.03 | 0.00 |
| | 308.15 | | 0.01 | -0.07 | 0.00 |
| | 318.15 | | 0.05 | 0.05 | 0.00 |
| water + L-tyrosine | 298.15 | 0.14 | | -0.01 | -0.03 |
| | 308.15 | 1.04 | | -0.03 | -0.02 |
| | 318.15 | 1.32 | | -0.10 | 0.02 |
| water + L-leucine | 298.15 | 0.87 | 0.03 | | -0.01 |
| | 308.15 | 1.52 | 0.11 | | 0.01 |
| | 318.15 | 3.25 | 0.13 | | -0.03 |
| water + glycine | 298.15 | -0.28 | 0.50 | -0.59 | |
| | 308.15 | -0.34 | 0.52 | -0.67 | |
| | 318.15 | -0.38 | 0.60 | -0.80 | |

of the constant q reported in Table 9 at (298.15, 308.15, and 318.15) K are close to zero.

In the solution containing L-tyrosine, changes in the solubilities occur only when the added amino acid is L-cystine. For these solutions, positive q values show that the solubility of the added amino acid increases as the concentration of L-tyrosine in water increases. The solubility of L-leucine or glycine are the same in L-tyrosine-containing solutions as in pure water.

The solubility of glycine or L-tyrosine in L-leucine solutions is similar to that in water. In fact, for these solutions, the values close to zero taken from the constant q highlighted the poor effect of L-leucine on the solubility of L-tyrosine and glycine. When L-cystine is added to the water + L-leucine solution, its solubility is considerably different from that in pure water. At 318.15 K, as the concentration of L-leucine rises from 0.00 to 0.11 mol·dm⁻³, the amount of L-cystine that can be dissolved increases from 8.5×10^{-4} to 24.1×10^{-4} mol·dm⁻³.

In solutions containing glycine that show the largest differences in electric properties compared to pure water, the solubilities of all the added amino acids show significant changes. The solubility of L-cystine and L-leucine decrease while that of L-tyrosine increases.

4. Conclusions

The uncertainties related to the use of the amino acid analyzer to analyze the L-cystine–glycine system are due to the need for diluting the original sample in a 1:50 ratio.

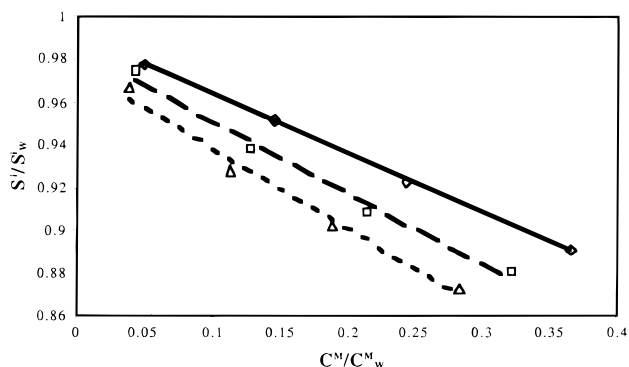


Figure 1. Straight lines S/S_w^i vs C^M/S_w^M for the system water-glycine-L-cystine at (298.15, 308.15, and 318.15) K (\diamond , data at 298.15 K; —, least-squares straight line at 298.15 K; \square , data at 308.15 K; — —, least-squares straight line at 308.15 K; \triangle , data at 318.15 K; - - -, least-squares straight line at 318.15 K).

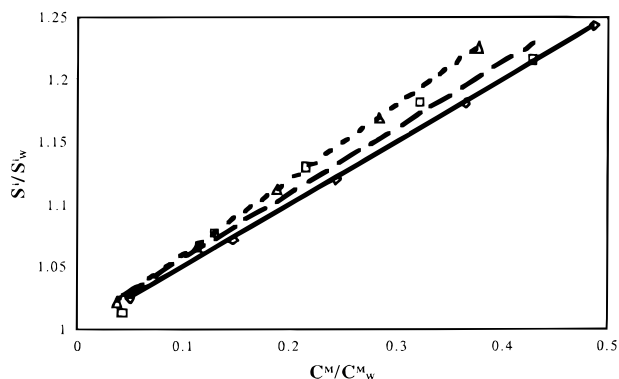


Figure 2. Straight lines S/S_w^i vs C^M/S_w^M for the system water-glycine-L-tyrosine at (298.15, 308.15, and 318.15) K (\diamond , data at 298.15 K; —, least-squares straight line at 298.15 K; \square , data at 308.15 K; — —, least-squares straight line at 308.15 K; \triangle , data at 318.15 K; - - -, least-squares straight line at 318.15 K).

This leads to a poor confidence in the solubility figures presented here for L-cystine in water + glycine. Therefore, even if the tendency to reduce the solubility of L-cystine as the amount of dissolved glycine increases is assumed to be correct, the reported values may also vary a great deal. For example at $C^M/S_w^M = 0.3648$, S/S_w^i can vary from 1 to 0.79 and the value of q reported in Table 9 from 0 to 0.57.

Figures 1–3 show S/S_w^i vs C^M/S_w^M at (298.15, 308.15, and 318.15) K respectively for the water-glycine-L-cystine, water-glycine-L-tyrosine, and water-glycine-L-leucine systems. As can be seen, the rise in temperature increases the effect of the solvent on the solubilities of the added amino acids. In fact on increasing the temperature, the absolute values of the slope of the straight lines in Figures 1–3 rise. This points out that as the temperature of the solution rises, increases in the concentration of the amino acids used to make the solutions cause larger variations in the solubility of the added amino acid.

This conclusion can also be drawn for the solubilities of L-cystine and L-tyrosine in solutions containing L-tyrosine and L-leucine.

For the other examined systems, i.e., water-L-cystine-L-tyrosine, water-L-cystine-L-leucine, water-L-cystine-glycine, water-L-tyrosine-L-leucine, water-L-tyrosine-glycine, and water-L-leucine-glycine, as the temperature

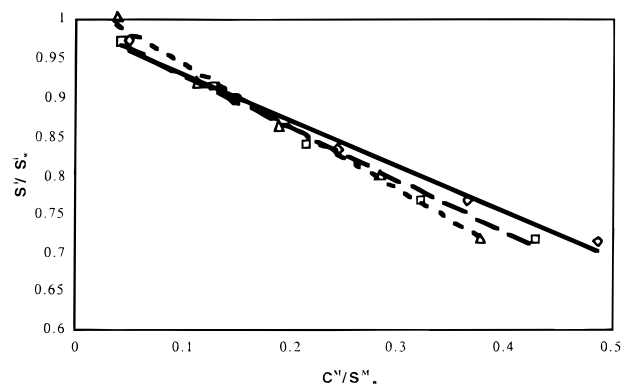


Figure 3. Straight lines S/S_w^i vs C^M/S_w^M for the system water-glycine-L-leucine at (298.15, 308.15, and 318.15) K (\diamond , data at 298.15 K; —, least-squares straight line at 298.15 K; \square , data at 308.15 K; — —, least-squares straight line at 308.15 K; \triangle , data at 318.15 K; - - -, least-squares straight line at 318.15 K).

risers, the concentration of the amino acid used to prepare the solution has no effect on the increase in solubility.

Furthermore, considering the large number of combinations possible, a model able to give an “a priori” evaluation of the solubilities of amino acids in mixtures must be developed. These results are therefore useful, since they contribute to give the basis needed to develop a theory.

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