THE EFFECT OF THE ALCOHOL CONTENT ON THE SOLUBILITY OF AMINO ACIDS IN AQUEOUS SOLUTION

Luísa A. Ferreira and Simão P. Pinho

Laboratory of Separation and Reaction Engineering, Departamento de Tecnologia Química, Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5301-857 Bragança, Portugal

Eugénia A. Macedo

Laboratory of Separation and Reaction Engineering, Departamento de Engenharia Química, Faculdade de Engenharia da Universidade do Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal

SUMMARY

The solubility of the most simple α-amino acid, glycine, was measured in the temperature range between 25 and 60°C for the aqueous system of ethanol and at 25 °C for the aqueous system of 1-propanol. Theoretical work was essentially focused on the application of the excess solubility approach with conventional thermodynamic models such as the Margules and Wilson equations. The simple three suffix Margules model, with only one parameter to be estimated, gave the best results, with an average absolute deviation of 3.8%.

INTRODUCTION

The physical chemical properties of amino acids have been a very important studied subject, not only because they are the basic building blocks of proteins and peptides but also for their importance in industrial processes, particularly for pharmaceutical and food industries.

Recent advances of the biochemical industry draw much attention to the development of more sophisticated and efficient processes for separation, concentration, and purification of these valuable biochemicals due to their high cost in comparison to the total manufacture cost.

However, the choice of a suitable separating agent and the operating conditions to perform the separation of amino acids is limited since they can denaturise. Thus, the development of thermodynamic models for the description of the phase behaviour of amino acids in different kind of mixtures is fundamental for the design of suitable separation processes.

EXPERIMENTAL WORK

Chemicals

In all experiments double-ionized water was used. Glycine, 99.7% purity, ethanol and 1-propanol, 99.8% purity were supplied by Merck and used as received.

Method

The analytical gravimetric method was chosen to perform the measurements [1]. The method consists in the preparation of a saturated solution at constant temperature. The equilibrium cell is charged with know weighted amounts of all components and to reach the solution equilibrium conditions, stirring is promoted for at least 48 hours. Then the solution is allowed to settle for 4 hours before sampling. After the slow evaporation of the solvent, samples are weighted and the process is repeated until a constant value is achieved. Each experimental point is an average of at least three different measurements with high reproducibility.

Figures 1a and 1b compare the experimental results measured in this work with literature data [2, 3, 4]. As expected, the solubility of glycine increases with the temperature and decreases, at constant temperature, with the increasing alcohol concentration. Figure 1b shows that for small concentrations of ethanol the solubility diminish greatly while for larger amounts of alcohol this effect is much less pronounced. The analytical method proved to be very successful; the results obtained show high agreement with the previous published values, either with temperature or solvent composition.

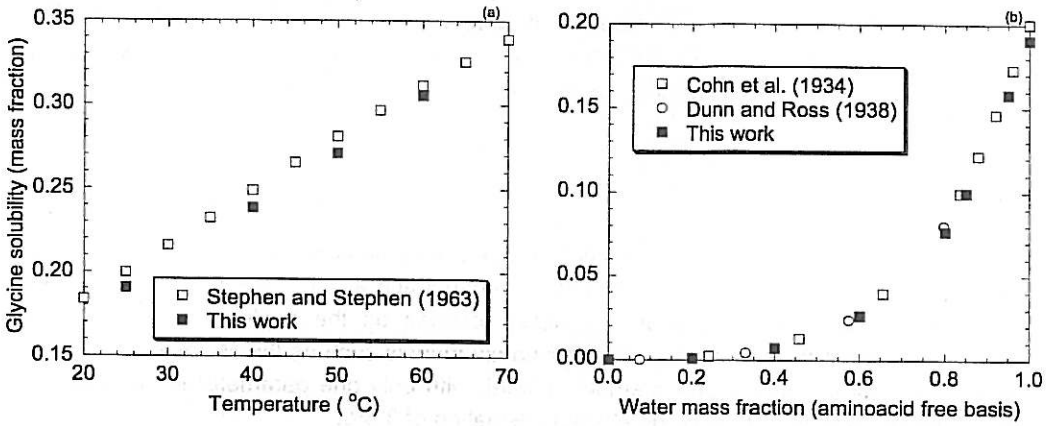

Figure 1. Comparison of the measured solubility data with the values reported in the literature: (a) water-glycine at different temperatures (b) water-ethanol-glycine at 25 °C.

MODEL DEVELOPMENT

The switch of the solvent from water to an alcohol has a drastic effect on the solubility of amino acids. With the evaluation of the relative solubility it becomes easier to understand and characterize the influence of the various agents on the solubility.

The excess solubility (x_3^E) of a solute in a mixed solvent solution can be defined as [5]:

$$\ln x_3^E \equiv \ln \frac{x_{3,mix}}{x_3^0} + x_2 \ln \frac{x_3^0}{x_3^a} \tag{1}$$

where $x_{3,mix}$, x_3^0 and x_3^a are, respectively, the solute mole fractions in the mixed solvent, aqueous and alcohol saturated solutions, and x_2 is the mole fraction of the alcohol.

Choosing the standard state of the solute as pure fused amino acid at the system temperature and pressure, the chemical potential of the solute at the standard state is independent of the solvent composition. Thus, the relative solubility (x_3/x_3^0) varies inversely with the activity coefficient of the solute:

$$x_3 / x_3^0 = \gamma_3^0 / \gamma_3 \tag{2}$$

being γ_3^0 and γ_3 respectively, the activity coefficients of the amino acid in saturated solutions of water or for some general solvent composition. Therefore, the change in the relative solubility reflects a change in the activity coefficient of the solute as the composition of the solvent is modified.

Several methods can be employed in order to correlate the activity coefficients. To model the solubilities of amino acid in aqueous-alcohol solutions, Orella and Kirwan [5] used an excess solubility approach in combination with the Margules, Wilson and NRTL equations. Due to its simplicity and the quality of the results achieved, in this work, only the results obtained with the three suffix Margules model are presented.

Combining the expression for the activity coefficient of the amino acid using the Margules equation [6] with equation (1) it is possible to derive, after some simplifications, the following expression for the excess solubility:

$$\ln x_3^E = -A_{3s}x_1'x_2' + 2A_{12}x_1'x_2'^2 + 2A_{21}x_1'^2x_2' \quad (3)$$

where x_1' and x_2' are the mole faction of water and alcohol in amino acid free basis, respectively, A_{12} and A_{21} are the Margules binary solvent-solvent interaction parameters -available in the Dechema Chemistry Data Series [7]- and A_{3s}, which is the only parameter left to be estimated, accounts for the interactions between the amino acid and the solvent.

RESULTS AND DISCUSSION

For each system the A_{3s} parameter was estimated minimizing the following objective function:

$$Fob = \sum \left[\frac{\left(x_3/x_3^0\right)^{calc} - \left(x_3/x_3^0\right)^{exp}}{\left(x_3/x_3^0\right)^{exp}} \right]^2 \quad (4)$$

where the superscripts exp and calc refer to the experimental and calculated relative solubility. For the system water-ethanol-glycine the solubility data at 25, 50 and 60 °C were used to estimate the parameters A_{3s}^0 and A_{3s}^t of the temperature dependence introduced according to:

$$A_{3s} = A_{3s}^0 + A_{3s}^t(T - 298.15) \quad (5)$$

and T is the absolute temperature. As can be seen from figure 2a the results are very good, with an average absolute deviation (AAD) of 2.8%. This figure also shows the values of the estimated parameters and the fitted curve for the dependence of the parameters A_{12} and A_{21} with the temperature [7]. Concerning the correlation of the solubility data of the system water-1-propanol-glycine the results, presented in figure 2b, are good, with AAD around 6.7%.

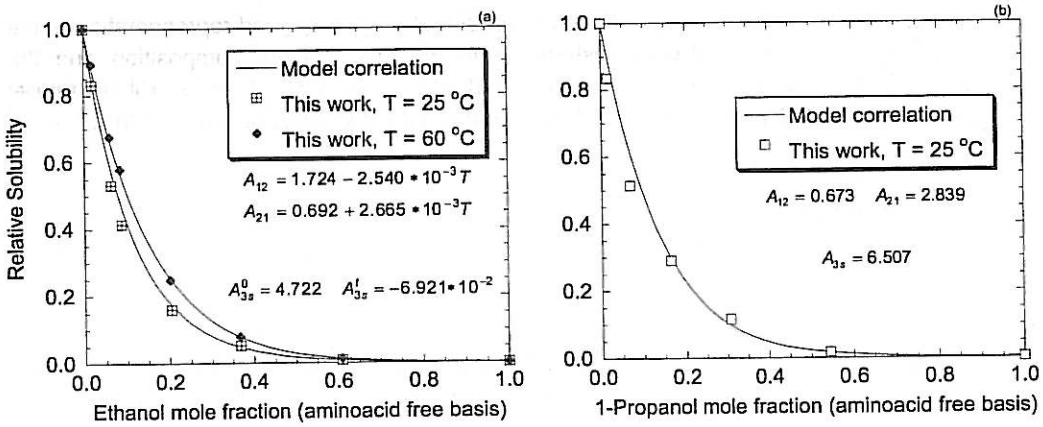

Figure 2. Comparison between model correlation and experimental data: (a) water-ethanol-glycine (b) water-1-propanol-glycine.

A very important feature of any model is its predictive ability. In this way, data not included in the correlation process were used to evaluate the prediction capabilities of this methodology. The results are very promising since the average absolute deviation found were 4.1% and 3.4% respectively for the data measured in this work at 40 °C and for the data published by Dunn and Ross [4] at 65 °C. The good quality of the predictions can be seen in figures 3a and 3b.

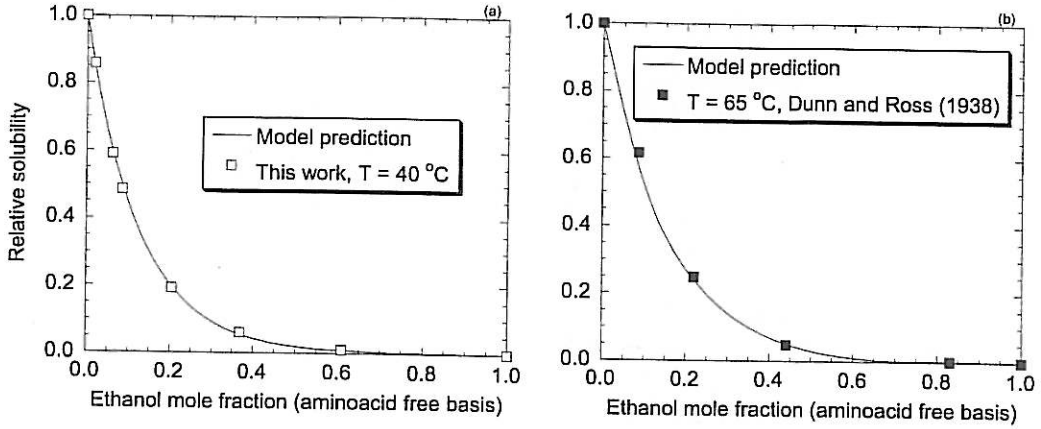

Figure 3. Comparison between model predictions and the experimental data for the water-ethanol-glycine: (a) 40 °C (b) 65 °C.

Despite the high quality of the modelling work the results are, so far, restricted to the solubility of glycine in water-alcohol solvents. To overcome this limitation the representation of solubility of L-alanine, L-isoleucine and L-phenylalanine in water-1-propanol solvents at 25 °C was also studied. Orella and Kirwan [5] concluded the best model to correlate that solubility data is the Wilson model with AAD of 15%. Using the Margules equation, which needs a smaller number of parameters to be estimated, a correlation with AAD of 11.4% was found for the studied systems.

CONCLUSIONS

The Margules model and the excess solubility approach allow a very good representation of the solubility of glycine in water-alcohol systems, both with the solvent composition and the temperature. The global AAD for correlation and prediction is 3.8%. Results will be further extended and evaluated as long as new experimental data measured are available for some other amino acids.

ACKNOWLEDGMENT

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