Fluid Phase Equilibria 459 (2018) 158–169

Contents lists available at ScienceDirect

Fluid Phase Equilibria

journal homepage: www.elsevier.com/locate/fluid

Modelling the effects of ethanol on the solubility of the proteinogenic amino acids with the NRTL, Gude and Jouyban-Acree models

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ARTICLE INFO

Article history:
Received 14 June 2017
Received in revised form
31 October 2017
Accepted 28 November 2017
Available online 5 December 2017

Keywords:
Thermodynamics
Aqueous-solutions
Equilibria
Organic solvents
Excess solubility

ABSTRACT

The addition of organic solvents, such as ethanol, to molecules in solution is an effective process for crystallization and is used in industrial settings (i.e. pharmaceutical production, downstream processing, etc.). In this study, we use solubility data of all proteinogenic α-amino acids in binary ethanol/water systems to model their excess solubility. We use the empirical and regressive models of Gude and NRTL and the predictive Jouyban-Acree model. Based on the results, we hypothesize that amino acids that are spherical and lack a reactive side chain show little or no excess solubility. Being rod-like and/or having a reactive side chain leads to a positive excess solubility in a mixed solvent of ethanol and water. The empirical and regressed models, NRTL and Gude, fit the data well and the predictive Jouyban-Acree model, not originally intended to be used for small molecules, is less accurate but offers insights into the thermodynamic properties of the amino acids.

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1. Introduction

In the future, products that are currently being produced using non-renewable resources (e.g. plastics, pharmaceuticals and fine chemicals) could be made from bio-based sources, such as proteins and α-amino acids [1–3]. One of the challenges in this line of research, is to find a way to separate α-amino acids from industrial residues so that the production of bio-based products can begin. This research is applicable to the industrial challenges of separating amino acids from solution.

Industrial residues can be used as a feedstock for the extraction of amino acids and other biomolecules. When amino acids are extracted, they need to be separated from aqueous solution. Currently, the most common method of separating many amino acids from solution is by using industrial chromatography. An alternative to chromatography could be to crystallize the amino acids using an anti-solvent, such as ethanol.

The structure of every amino acid contains a carboxyl group attached to an α-carbon. This α-carbon is also attached to an amino group. The amino acids studied in this article are α-amino acids, which all have side chains also attached to the α-carbon. The exception is glycine which does not have a side chain. The side chains of α-amino acids include aliphatic groups, aromatic and non-aromatic rings, hydroxyl groups, sulphur and charged groups (e.g. a second carboxyl group, lysyl group, guanidinium group). The amino and carboxyl groups attached to the α-carbon will be charged at a pH that is not the isoelectric point. At the isoelectric point, the amino acid has a neutral charge and is called a zwitterion. All measurements in this manuscript were taken at the isoelectric point.

There has been some research on the solubility of α-amino acids in mixtures of alcohol and water [4–7]. Basic solubility measurements were reported and subsequent research focused on calculating the partition coefficients of the solubility of these α-amino acids and their phase behavior [8]. Recently, complete and reliable data has been published on the solubility of α-amino acids in ethanol/water systems and mixtures of α-amino acids.

Many models have been proposed to model the solubility of amino acids in aqueous solution. These models include calculating partition coefficients [11], using regressed coefficients [12], examining non-ideality [13], measuring and modelling activity

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https://doi.org/10.1016/j.fluid.2017.11.036
0378-3812/© 2017 Published by Elsevier B.V.

coefficients [14–17], activities [18] and applying a modification of the Wilson model [19]. Other models have been applied to model the solubility of amino acids in salt solutions [20–27]. Only a few models have been proposed to describe the solubility of α-amino acids in ethanol/water systems, but these manuscripts focus on a single model and only a few α-amino acids [28–30]. This article will model all proteinogenic α-amino acids using solubility data that is available in the literature.

We use three models that represent two different modelling approaches. Of these three, two of the models use regressed parameters. The models that we use that have regressed parameters are the Gude model and the Non-Random Two Liquid (NRTL) model. While models that use regressed parameters have in general given excellent results, they do not explain what thermodynamic properties of the molecules lead to their results. The third model that we use is the Jouyban-Acree model, which is a predictive model. Predictive solubility models are based on thermodynamic properties of the molecules that they are modelling. While the thermodynamic properties of the molecules explain the results of the predictive models, predictive models have been less accurate than regressed models.

Using the different approaches allows conclusions to be made on whether the predictive model (Jouban-Acree) provides sufficient accuracy to model amino acid solubility or if a regressed model (Gude or NRTL) should be used. Other solubility models [31–36] were considered for this article, but due to their complexity were left out in favour of models with fewer variables.

The Gude [12] and NRTL [54] models were chosen in this research for their accuracy in the literature and the minimum number of parameters they use. Both the NRTL and Gude models furthermore acknowledge the lattice and therefore entropic nature of liquids, first investigated by Flory [37] and Huggins [38]. The Gude model has one parameter that is regressed to fit the data and the NRTL has two parameters that are regressed to fit the data. For this reason, it is expected that the NRTL model will have a lower error. However, it is preferential to use a regressive model with the least number of regressed parameters. In the case where both models have similar errors, the Gude model could be used.

While the Gude and NRTL models will be accurate, in comparison, the Jouyban-Acree model is predictive and based on the bonds and forces of the molecules being modelled. The version of the Jouyban-Acree model that is used in this research has nine regressed constants. These constants are used in conjunction with Hansen solubility parameters, which are based on physical chemistry group contribution data. While the Jouyban-Acree model uses more parameters than the Gude and NRTL models, the parameters are predictive, not regressed. The Jouyban-Acree model has been shown to perform well with relatively large pharmaceutical solutes in ternary systems [39]. A version of this model with regressed parameters has been applied to only a few amino acids in ternary solution, but no α-amino acids in water and ethanol mixtures, with the exception of glycine [40]. We use the Jouyban-Acree model without regressed parameters in this research in order to evaluate the use of group contribution data to amino acid solubility models. In the future, data from this work could contribute to refining the non-regressed Jouyban-Acree parameters for amino acids.

2. Theory

2.1. Thermodynamic modelling of excess solubility

The addition of organic solvents, e.g. ethanol, to aqueous solutions of amino acids lowers the solubility of the amino acid solutes. This allows for precipitation and crystallization. The solubility of the amino acids is often lowered by organic solvents by more than 1000 times its solubility in water alone. Industrial applications using organic solvents can only be designed when this effect on the solubility is understood. This presents a challenge for chemical engineers in modelling their solubility.

Data is taken from the literature [4–7] and modelled with two empirical and regressive models and with one predictive model. The two empirical and regressive models are the Gude [12] and NRTL [41–45] models and the semi-empirical and predictive model is the Jouyban-Acree model [46–50].

In order to effectively compare the performance of the models, excess solubility has been chosen as the output of the model. This decision aligns with literature [51,52] in the specific case of binary solvent mixtures. Excess solubility, represented by the mole fraction x_{aa}^{E}, can be calculated using equation (1).

$$\ln x_{aa}^{E} \equiv ln\, x_{aa,\,mix} - \sum_{i=1}^{N} x_i' \ln x_{aa,i} \tag{1}$$

in which case $x_{aa,\,mix}$ and $x_{aa,i}$ are the mole fractions of the amino acid solute *(aa)* in a mixed solvent and pure solvent, *i*, respectively. The mole fraction of the solvent *i* without the solute is denoted by x_i'.

When assuming a pure solvent phase as a standard state, such as in this research, at standard system pressure and temperature, the chemical potential of the solute is not dependent on the solvent composition. Therefore, the excess solubility can be rewritten as:

$$\ln x_{aa}^{E} \equiv -\, ln\, \gamma_{aa,\,mix} + \sum_{i=1}^{N} x_i' \ln \gamma_{aa,i} \tag{2}$$

where the dimensionless activity coefficients of the solute in saturated solutions of the mixed solvent and pure solvent are represented by $\gamma_{aa,\,mix}$ and $\gamma_{aa,i}$.

Cohn and Edsall [53] noted that the solubility of the solute in these systems is low. Therefore, it can be assumed that the solute is infinitely dilute and approximated as:

$$\ln x_{aa}^{E} \equiv -\, ln\, \gamma_{aa,\,mix}^{\infty} + \sum_{i=1}^{N} x_i' ln\, \gamma_{aa,\,i}^{\infty} \tag{3}$$

2.2. Gude model

Gude [6] developed a simplified equation to model the solubility of amino acids in mixed solvents. This model uses 2 constants. The constant for the interaction between the solvents, $A_{j,i}$, was set to 1.55 for ethanol/water in the work of Gude and is applied in this work. The constant for the interaction between the amino acid and the solvent mixture, $C_{j,i,aa}$, is specific to each amino acid. This interaction parameter, $C_{j,i,aa}$ (mol·L^{-1}), is constant for the system and found by fitting the model to the data. Equation (4) describes the model:

$$\ln x_{aa}^{E} \equiv ln\, r' - \sum_{j=1}^{N} x_j' ln\, r_j + r_{aa}\left(\frac{1}{r'} - \sum_{j} \frac{x_j'}{r_j}\right) + \sum_{j}\sum_{i}\left[A_{j,i} x_j' x_i' (1 + C_{j,i,aa})\right] \tag{4}$$

where subscripts *j* and *i* relate to solvents and subscript *aa* relates to the solute. The values of the UNIFAC variable r were set at 0.92 for water and 2.11 for ethanol and calculated individually for the amino

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