Effect of alcohol on the solubility of amino acid in water

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ABSTRACT

In a previous work, the parameters of the statistical associating fluid theory (SAFT) equation of state for amino acids were determined by using the method developed. The solubility of amino acids in water was modeled. In this work, the SAFT equation of state has been applied to describe the solubility of amino acids in aqueous alcohol solutions. The systems include DL-alanine/ethanol/water, glycine/ethanol/water, DL-valine/ethanol/water, DL-serine/ethanol/water, glycine/1-propanol/water, glycine/2-propanol/water, L-alanine/2-propanol/water, L-leucine/ethanol/water. Binary interaction parameters between amino acid and alcohol are needed by the SAFT model to get good modeling results.

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1. Introduction

Amino acids are of commercial importance in industrial processes, they can be utilized as food additives and constituents of pharmaceutical products. The purification of amino acids can be performed by crystallization from aqueous solution, or by the use of a multicomponent extraction system. Usually, optimized mixtures rather than single component solvents are demanded. The choice of a suitable separating agent and the operating conditions to perform the separation of amino acids is of extreme importance. The solubility is the key property that should be known for the recovery and separation of amino and for the rational design of downstream separation equipment [1]. Solid–liquid equilibria in mixed solvent systems are phenomena that must be dealt with to obtain solubility data. For ternary or higher systems of amino acids, equilibrium is difficult to establish in solid–liquid systems, and equilibrium data are relatively lacking. Developing a modeling approach is necessary to have a knowledge of phase equilibria for the multicomponent systems.

The thermodynamic models, such as Wilson, UNIFAC, and NRTL equations, have been applied to describe phase behavior for systems containing amino acids [2–4]. However, for considering the effect of pressure on the amino acid solubility and the modeling of density of aqueous amino acid solutions, this type of model cannot be applied. In this work, we are intended to use equations of state to model the solubility of amino acid in mixed solvent. There are some predictive equations of state, for example the statistical associating

fluid theory (SAFT) [5,6], perturbed hard-sphere-chain (PHSC) [7], hard-sphere-chain fluids (HSCF) [8]. In the previous work [9–11], by taking advantage of the method developed for determining the SAFT parameters for amino acids, the SAFT equation of state [12] has been applied to describe the solubility of amino acid in aqueous solutions. The objective of this work is to apply the SAFT equation of state to describe the amino acid solubility in alcohol solutions. The results will be useful in the rational design and optimization of industrial processes.

2. Statistical associating fluid theory equation of state

The SAFT equation of state we have applied is the version of Huang and Radosz [12]. The general expression for the Helmholtz energy is given by

$$a^{\text{res}} = a^{\text{seg}} + a^{\text{chain}} + a^{\text{assoc}} \tag{1}$$

$$\frac{a^{\text{seg}}}{RT} = m \left(\frac{4\eta - 3\eta^2}{(1-\eta)^2} + \sum_i \sum_j D_{ij} \left[\frac{u}{kT} \right]^i \left[\frac{\eta}{\tau} \right]^j \right) \tag{2}$$

$$\frac{a^{\text{chain}}}{RT} = (1-m) \ln \frac{1 - 0.5\eta}{(1-\eta)^3} \tag{3}$$

$$\frac{a^{\text{assoc}}}{RT} = \sum_A \left[\ln X^A - \frac{X^A}{2} \right] + \frac{1}{2} M \tag{4}$$

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Nomenclature

a	Helmholtz energy
D_{ij}	square-well energy constants
$g(d)^{hs}$	hard sphere distribution function
k	Boltzmann constant
K_{12}	binary interaction parameter for u/k between i and j
m	SAFT parameter, segment number
N_{AV}	Avogadro's number
N^{ass}	number of association sites on a molecule
P	pressure
R	gas constant
T	temperature
u/k	temperature-dependent dispersion energy of interaction between segments (K)
u^0/k	SAFT parameter, temperature-independent dispersion energy of interaction between segments (K)
X	mole fraction
X^A	mole fraction of molecules not bonded at site A

Greek letters

Δ^{AB}	strength interaction between sites A and B
ε^{AB}/k	SAFT parameter, association energy interaction between sites A and B
κ^{AB}	SAFT parameter, volume of interaction between sites A and B
η	reduced density
ρ	density
τ	constant, $\sqrt{2}\pi/6$
υ^{00}	SAFT parameter, temperature-independent segment volume (cm^3/mol)

The mole fraction of molecules not bonded at site A is expressed as

$$X^A = \left[1 + N_{AV} \sum_B \rho X^B \Delta^{AB} \right]^{-1} \tag{5}$$

where Δ^{AB}, the association strength, is expressed as

$$\Delta^{AB} = g(d)^{hs} \left[\exp\left(\frac{\varepsilon^{AB}}{kT} - 1 \right) (\sigma^3 \kappa^{AB}) \right] \tag{6}$$

In the above expressions, the reduced density is calculated by

$$\eta = \tau \rho m \upsilon^{00} \left[1 - C \exp\left[\frac{-3u^0}{kT} \right] \right]^3 \tag{7}$$

and the temperature-dependent dispersion energy of interaction between segments, u/k, is expressed as

$$\frac{u}{k} = \frac{u^0}{k} \left[1 + \frac{e}{kT} \right] \tag{8}$$

C and e/k are constants set to 0.12 and 10.0, respectively. For oxygen and carbon dioxide, e/k are set to 0 and 40, respectively.

For each fluid, three parameters are needed for a non-associating component, segment number, m, segment volume, υ^{00}, and segment–segment interaction energy, u^0/k. And two additional parameters are needed for an associating component, the association energy ε^{AB}/k and volume κ^{AB}.

Table 1
The parameters of the SAFT equation of state

Substance	m	u/k (K)	υ^{00} (cm^3/mol)	ε^{AB} (K)	κ^{AB}	N^{ass}
DL–Alanine[a]	2.582	176.335	12.0	4147.86	0.056	3
Glycine[a]	2.865	161.162	8.0	4055.48	0.065	3
DL–Valine[a]	2.203	197.446	22.0	4806.18	0.022	3
Leucine	2.866	218.789	19.0	5053.87	0.057	2
DL–Serine	3.034	227.788	12.0	7134.12	0.0035	2
Water[b]	1.165	194.29	8.0	3229	0.052	3
Ethanol[c]	2.457	213.48	12.0	2759	0.0292	2
1-Proppanol[c]	3.240	225.68	12.0	2619	0.01968	2
2-Propanol[c]	3.249	202.94	12.0	2670	0.02095	2

[a] From Ref. [11].
[b] From Ref. [9].
[c] From Ref. [12].

For mixtures, the following mixing rule (9) is used

$$\frac{u}{k} = \frac{\sum_i \sum_j X_i X_j m_i m_j [u_{ij}/kT](\upsilon^0)_{ij}}{\sum_i \sum_j X_i X_j m_i m_j (\upsilon^0)_{ij}} \tag{9}$$

where

$$(\upsilon^0)_{ij} = \left[\frac{1}{2} \left[(\upsilon^0)_i^{1/3} + (\upsilon^0)_j^{1/3} \right] \right]^3 \tag{10}$$

$$\frac{u_{ij}}{k} = (1 - k_{ij}^{dis}) \left(\frac{u_i}{k} \frac{u_j}{k} \right)^{1/2} \tag{11}$$

3. Modeling of amino acid solubility in water/alcohol solutions

In the previous work [11], for describing amino acids, five parameters required by the SAFT model, namely, the segment number m, segment volume υ^{00}, and segment–segment interaction energy u^0/k, association energy ε^{AB}/k, and association volume κ^{AB}, were determined by using the method developed [9]. The SAFT parameters are listed in Table 1.

The solubility of amino acid in aqueous alcohol solutions can be calculated using the following equation [13]:

$$\ln\left(\frac{f_i^s}{f_i^l} \right) = -\frac{\Delta H_i^{sl}}{RT} \left(1 - \frac{T}{T_{mi}} \right) + \frac{\Delta C_{P_i}^{sl}}{R} \left(\frac{T_{mi}}{T} - 1 \right) + \frac{\Delta C_{P_i}^{sl}}{R} \ln \frac{T}{T_{mi}} \tag{12}$$

where T_{mi} is the melting temperature of species i, ΔH_i^{sl} the enthalpy change of melting, and $\Delta C_{P_i}^{sl}$ is the heat capacity change of melting. For most amino acids, due to decomposition before reaching melting temperature, ΔH_i^{sl}, T_{mi} and $\Delta C_{P_i}^{sl}$ are not measurable. ΔH_i^{sl}, T_{mi} and $\Delta C_{P_i}^{sl}$ are taken as constants, they are determined by solubility data. f_i^s/f_i^l is expressed by the SAFT model [12]. The solubility constants ΔH_i^{sl}, T_{mi} and $\Delta C_{P_i}^{sl}$ of Eq. (12) are listed in Table 2 [11].

Table 2
Solubility constants of amino acids in water

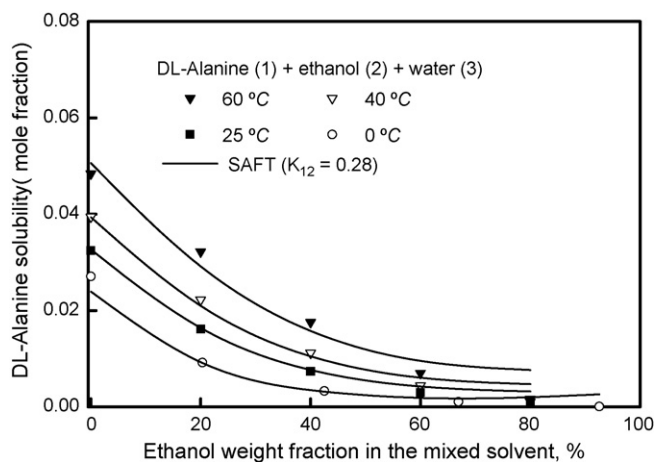| Amino acid	ΔH_i^{sl} (J/mol)	T_{mI} (K)	$\Delta C_{P_i}^{sl}$ (J/(mol K))
DL-Valine	71684.60	567.15	212.71
Glycine	13708.99	688.28	0.000
DL-Alanine	30702.21	618.29	60.44
DL-Serine	26873.17	586.70	34.12
L-Leucine	76586.02	610.15	224.26

Fig. 1. Solubility of DL-alanine in water/ethanol solutions at different temperatures. The symbols represent experimental data from Ref. [14], the lines are calculated by SAFT.
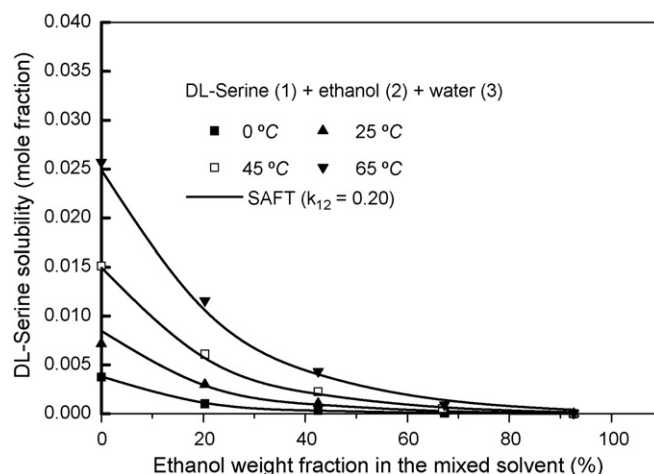

Fig. 3. Solubility of DL-serine in water/ethanol solution at different temperatures. The symbols represent experimental data from Ref. [14], the lines are calculated by SAFT.

4. Results and discussion

Figs. 1 and 2 show the solubility of DL-alanine and glycine in water/ethanol solutions at different temperatures. The solubility of glycine and DL-alanine increases with the temperature. The solubility of amino acid in pure ethanol is significant lower than that in pure water. At constant temperature, the solubility decreases with the increasing ethanol concentration. The decrease of the solubility is much more pronounced at low-ethanol concentrations than at high-ethanol concentrations. The significant low solubility of amino acids in pure ethanol makes the modeling at high-alcohol concentrations very difficult. With a binary interaction parameter between amino acid and ethanol, the SAFT model can have good modeling results at the ethanol concentrations lower than 70% on a weigh basis. Fig. 3 shows the solubility of DL-serine in water/ethanol solutions. As can be observed, with a binary interaction parameter, the SAFT equation of state can give a quite good description of equilibrium data for all the ethanol composition range at different temperatures. As shown in Fig. 4, for the description of the solubilities of DL-valine in water/ethanol solutions, a function of binary interaction parameter is required by SAFT. However, the temperature-dependent function can not presents good results for the ethanol concentration higher than 60%. Fig. 5 shows
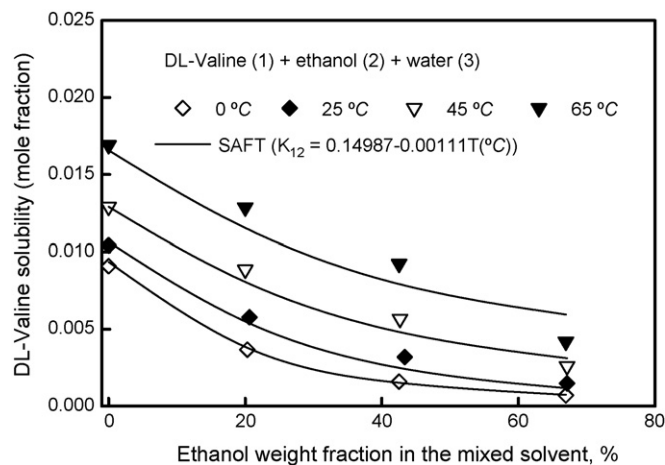

Fig. 4. Solubility of DL-valine in water/ethanol solutions at different temperatures. The symbols represent experimental data from Ref. [14], the lines are calculated by SAFT.
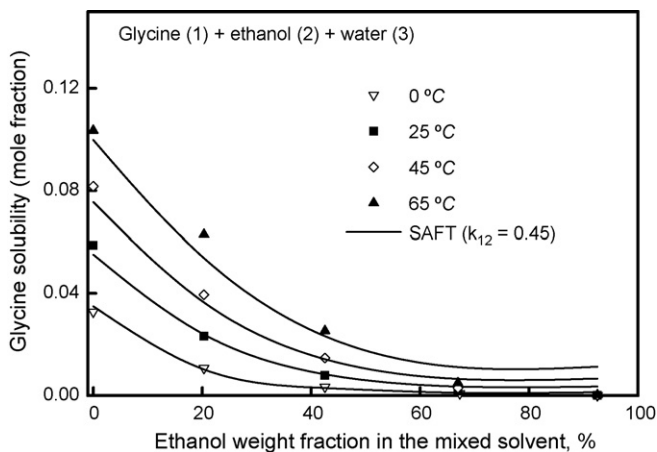

Fig. 2. Solubility of glycine in water/ethanol solutions at different temperatures. The symbols represent experimental data from Ref. [14], the lines are calculated by SAFT.
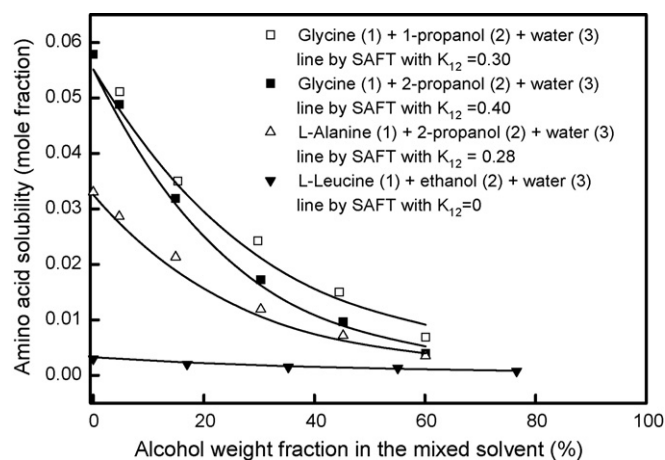

Fig. 5. Amino acid solubility in water/alcohol solutions at 25 °C. The symbols represent experimental data from Refs. [15,16], the lines are calculated by SAFT.

the solubilities of glycine in water/1-propanol solutions, glycine in water/2-propanol solutions, L-alanine in water/2-propanol solutions, and L-leucine in water/ethanol solutions at 25 °C. As can be seen, with binary interaction parameters, the SAFT model can describe the solubiliteis of glycine and L-alanine with good results at alcohol concentrations lower than 60%. The solubility of L-leucine is predicted well by SAFT without using binary interaction parameter.

5. Conclusions

The SAFT equation of state has been applied to describe the solubility of amino acids in the alcohol solutions. The systems include DL-alanine/ethanol/water, glycine/ethanol/water, DL-valine/ethanol/water, DL-serine/ethanol/water, glycine/1-propanol/water, glycine/2-propanol/water, L-alanine/2-propanol/water, L-leucine/ethanol/water. Binary interaction parameters between amino acid and alcohol are needed by the SAFT model to get good modeling results.

Acknowledgements

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