P 33 MODELING OF PHASE EQUILIBRIA OF AMINO ACIDS MIXTURES USING THE A-UNIFAC MODEL

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The group-contribution with association UNIFAC method (A-UNIFAC) was initially proposed by Mengarelli *et al.* [1]. It results from the addition of a third contribution, which quantifies the association forces, to the traditional combinatorial and residual UNIFAC contributions, as it was done by Fu *et al.* [2] for the UNIQUAC model. The association term is based on Wertheim's theory [3] for fluids with highly directed attractive forces and it follows the group contribution approach proposed by Gros *et al.* [4] for the GCA-EoS equation. More recently, the parameters table was extended to several cross-associating mixtures containing alcohols, water, carboxylic acids, esters, alkanes and aromatic hydrocarbons [5].

The group-contribution nature of this association term allows its application to highly associated mixtures, for which experimental information is scarce or not available. In the present work, an extended UNIFAC group contribution model is used to calculate activity coefficients in solutions containing additionally amines or amino acids, by explicitly taking into account hydrogen bonding in these mixtures. In aqueous neutral solutions, amino acids are mainly present as zwitterions. In this way, charges in amino acids can be modelled by considering them as electron-donor and electron-acceptor sites. One amino-acid association group is defined to account for their self-association. Additionally, cross-association between the amino acid and the hydroxyl association groups is considered.

After defining which associating groups are present in the mixture, the association contributions for the activity coefficient can be obtained from the energy of Helmholtz of association. The original expressions for the association contribution to the activity coefficients involve the calculation of derivatives of the fraction of non-bonded sites X^{A_k} [6]. More recently, some researchers [7,8] have presented and discussed a simpler but equivalent mathematical expression that does not include any derivative of X^{A_k}. The general expressions that result from applying this much simpler mathematical approach to the group-contribution association expressions are presented.

Satisfactory results for the calculation of activity coefficients and solubilities of several amino acids are obtained.

References

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