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Contents

PLENARY LECTURES

ORAL PRESENTATIONS: ADVANCING THE CHEMICAL AND BIOLOGICAL ENGINEERING FUNDAMENTALS

Solubility of multifunctional associating molecules: measurements and thermodynamic modeling

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Introduction

Numerous molecules in the pharmaceutical, food and chemical industries present complex chemical structures with different functional group substitutions. Many of these groups such as amine, carboxyl and hydroxyl can form hydrogen bonds. To adequately describe the phase equilibria of these complex chemicals, models able to take into account association effects are required. Still, for model development and evaluation, experimental data on some representative systems are needed. In this work, new experimental measurements and literature data were combined to develop a methodology to model the phase equilibria of phenolic acids using the Cubic-plus-Association (CPA) equation of state. A comparison with the UNIQUAC activity coefficient model is also presented. Within the different classes of multifunctional associating molecules, phenolic compounds, due to their chemical and biological importance, are among the most important. Apart from being starting materials for many chemical syntheses, there is also huge evidence that some phenolic compounds have beneficial effects on human health.

Experimental

Solid-liquid equilibria of hydroxybenzoic acids such as gallic, salicylic, syringic and protocatechuic acids and phenilpropenoic acids such as trans-cinnamic, ferulic, coumaric and caffeic acids were measured from 288 K up to 323 K using the analytical shake-flask and a synthetic DSC methods. Particular attention was given to aqueous solubilities. Besides solubility data, the melting properties (fusion enthalpies and temperatures) were also determined by DSC. The corresponding pH of the saturated aqueous solutions as well as the acid dissociation constants were determined by potentiometry with a glass electrode.

Modeling

An activity coefficient model, the modified UNIQUAC proposed by Peres and Macedo (Peres and Macedo, 1996) and an equation of state, the CPA EoS (F. L. Mota, 2008) were evaluated for modeling the measured data, neglecting the heat capacity term in the general solid-liquid equilibria relation (Prausnitz et al., 1999).

As both the solutes and the solvent can associate (self and cross-association is present in these mixtures), the CPA EoS was also adopted in this work. As the studied phenolic acids are multifunctional associating molecules, a new methodology was proposed to take into account the different associating groups as well as their repetitions and ring positions in the chemical structure. Values for the associating energies and volumes of the acid groups will also be proposed. Different mixture results will be used to demonstrate the reliability of the proposed model.

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