

524a Totally Predictive Models for Supercritical Fluid Extraction of Natural Products

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Cubic equations of state (EOS) have been extensively utilized for the estimations of compositions under phase equilibria because the algorithm requires minimal amount of species data, such as the critical properties. Over the last two decades, several excess free energy (GE) models have been incorporated into the EOS algorithms to relax the limitations of the conventional van der Waals mixing rule on modeling the pressure effects of excess free energy of solutions. Consequently, a new family of mixing rules has been developed. When a group contribution model, such as UNIFAC or UNIQUAC, is adopted for the estimation of excess free energy, the combined EOS / GE model becomes a powerful, totally predictive approach for the estimation of compositions under phase equilibria as it eliminated the necessity of critical properties.

High molecular weight plant materials often decompose before they reach the critical conditions. Consequently, EOS / GE / group contribution models are uniquely attractive to the extraction of natural products. The excess free energies predicted by these state-of-the-arts algorithms are usually based on the UNIFAC parameters at low pressures, their applications at high pressures, such as extraction by supercritical fluids, have drawn attentions only recently due to its potentially large application in pharmaceutical and food industries.

To selectively extract large quantities of natural products by supercritical fluids, we systematically examined the various EOS / GE / group contribution models reported in the literature; these include the HVO model (Huron and Vidal, 1979), MHV2 model (Dahl et al., 1991), LCVM model (Boukouvalas et al., 1994; Yakoumis et al., 1996), WS model (Wang and Sandler, 1993, 1995), and HVOS model (Orbey and Sandler, 1998). A library of PC-based programs has been developed. The dissolutions of naphthalene in supercritical carbon dioxide at various temperatures and pressures were used as the model system. It was found that the interaction parameters in the UNIFAC model reported for low-pressure systems have to be experimentally corrected for high-pressure systems. We will demonstrate that each of mixing rules reviewed here is successful at selected temperatures, but the HVO and WS models that were developed based on infinite pressure give the best results without such corrections. Our study also illustrate that there are rooms for theoretical development in the future.