PREDICTION OF PHASE EQUILIBRIUM OF AQUEOUS TWO-PHASE SYSTEMS
WATER + POLY(ETHYLENE GLYCOL) + SALT

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Abstract
Liquid-liquid extraction by aqueous two-phase systems of the type polymer-salt has been increasing importance in the separation of biomolecules. The thermodynamic behavior of these systems is extremely difficult to model, due to the size differences between the smaller molecules and the polymer. Several activity coefficient models have been proposed, including the combinatorial and free volume effects in one term. This work uses the Elbro-FV model as the combinatorial-free volume contribution of the UNIFAC-Dortmund group contribution model. New group interaction energy parameters for this model have been determined using reported data on the systems water + poly(ethylene glycol) [PEG4000] + salt, where the salts were potassium phosphate and sodium sulfate.

1. Introduction
Liquid-liquid extraction has been increasing importance in biochemical engineering as a result of the development of aqueous two-phase systems for purification and isolation of macromolecules, such as proteins or antibiotics. This process has a lower cost compared with traditional biomolecules separations, due to use of traditional equipment of extraction and the small number of stages. According to Kula (1990), aqueous two-phase systems are formed spontaneously when a solution of two hydrophilic components is mixed and a certain concentration is exceeded. Aqueous two-phase systems consist in two polymers [e.g., poly(ethylene glycol) and dextran] or one polymer and one isotropic salt [poly(ethylene glycol) and phosphates, citrates or sulfates] in water. It is possible to have an extremely selective separation of substances using aqueous two-phase systems; they provide a gentle and protective environment for biological material, since both phases are composed primarily of water. Aqueous two-phase systems of the type polymer-salt have several advantages over the type polymer-polymer: larger relative size of the drops, larger density differences, larger selectivity, smaller viscosity and smaller cost; besides, systems with two polymers are more difficult to adapt to industrial scale due to high viscosity and high cost (Franco et al., 1996). However, the thermodynamic behavior of the polymer-salt systems is more complicated.

This work uses the Elbro-FV model as the combinatorial-free volume contribution of the UNIFAC-Dortmund group contribution model. New group interaction energy parameters for this model have been determined using reported data on the systems water + poly(ethylene glycol) [PEG4000] + salt, where the salts were potassium phosphate and sodium sulfate.

2. Thermodynamic Models
There are several models for the calculation of activity coefficients. Some of them are empirical, as those by Margules and Van Laar; others use the local composition concept, as Wilson (1964) and NRTL (Renon and Prausnitz, 1968); others have a more theoretical basis, as UNIQUAC (Abrams and Prausnitz, 1975); finally, some use the group contribution method, such as ASOG (Derr and Deal, 1969; Kojima and Tochigi, 1979) and UNIFAC (Fredenslund et al., 1975, 1977).

The group contribution concept was introduced by Langmuir (1925) and treats a mixture not as a mixture of components, but as a mixture of functional groups. In this way, the properties of the mixture can be determined by adding the individual contributions of each one of the groups that constitute it.

The advantage of this method is that it allows to represent a very big amount of mixtures with a much smaller amount of groups. The disadvantage is the admitted additivity hypothesis, since it is considered that the presence of another groups in the mixture does not affect the contribution of the other ones. The calculation of the activity coefficient through of that method is expressed by two parts: a combinatorial one, considered an enthalpic contribution and a residual one, considered as an entropic contribution. A review of group contribution methods for phase equilibrium calculations have been made by Aznar et al. (1997). However, polymeric solutions need another contribution, named free volume. The concept of free volume is not yet fully understood and several formulas have been proposed for its mathematical interpretation. Free volume ($V_f$) is normally defined as the volume available to the center of mass of a single molecule. The most well-known mathematical expression is the simple one proposed by Bondi (1968):