MOLECULAR SOLVENT DESIGN AND NEAR CRITICAL SOLVENTS OPTIMIZATION WITH ECOFAC

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***Abstract*— In this work an efficient analysis tool for separation process design and property predictions is presented. ECOFAC can estimate pure compound and solution properties, specially some of environmental interest, generate the best potential solvents for a specific liquid-liquid extraction or extractive distillation problem through molecular design, or find the optimal operating conditions for a given supercritical extraction process.**

***Keywords*— Separation Processes, Solvents, Molecular Design, ECOFAC, Supercritical.**

I. INTRODUCTION

The computer aided solvent design problem requires different methodologies for liquid solvents and for near critical or supercritical solvents. In the liquid solvents problem there is a great universe of solvent candidates and their selection and evaluation should be made in an efficient way. When dealing with near critical solvents, the solvent choices are few but the operating conditions for its application should be optimized. The use of the same group contribution methods for both property predictions and rigorous process simulation gives also a wide applicability to the computer aided solvent design.

The selection of a liquid solvent can be made testing promising solvent candidates obtained by inspection of component data bases or the properties can be specified and solvent candidates that meet the required properties are generated by molecular design. This is known as the inverse solvent selection problem (Gani and Brignole, 1983) and requires the use of group contribution methods based on UNIFAC or similar group definitions for the prediction of solution properties. The inverse problem has found applications in a great number of product design problems, however the stability of the generated compounds and the quality of the physical property predictions based on group contribution methods have been overlooked in most cases. Pretel *et al.* (1994) proposed three basic types of group valences, with increasing degree of electronegativity for the feasibility analysis of linear structures. However, this characterization of the group combination properties failed when applied to branched as oposed to linear molecular structures (Cismondi and Brignole, 2001)

On the other hand, chemical processes with supercritical fluids have received increasing interest during the past decade. Experimental data are scarce and difficult to obtain and there is still much research to be done on near critical fluid property prediction, rigorous unit simulations and synthesis and optimum design of these processes (Diaz *et al.*, 2000a).

In this work we present ECOFAC, a set of computer libraries based on group contribution methods for process and property prediction calculations.

II. LIQUID SOLVENTS

The solvent molecular design that ECOFAC performs in a Liquid-liquid extraction or Extractive Distillation problem is based on an upgraded version of the program MOLDES (Pretel *et al.*, 1994). The molecular synthesis has been extended to branched solvent structures with the introduction of new feasibility criteria and rules. In addition, a new characterization of group combination properties had to be made (Cismondi and Brignole, 2001). The formulation of robust feasibility criteria for the synthesis of the branched structures requires in some cases not only the characterization of the group free attachments but also of its internal bonds. When the internal and free bonds are taken into account, only two bond status: K (electronegative) and J (neutral) are required to define the combination properties. The revision of UNIFAC group combination properties is presented in Table 1.

The new synthesis concept is: *each J group cannot be attached to more than one K group* and the associated feasibility criteria obtained (Cismondi and Brignole, 2001) are shown in Table 2.

The larger number of free attachments (NFA) of the branched intermediate structures greatly increases the size of the synthesis problem in comparison to the synthesis of linear structures. To reduce the problem size, an efficient algorithm based on the concept of metha groups (groups with equivalent combination properties) has been implemented. The ECOFAC computer program executes the following steps:

1. Definition of the desired product property constraints and performance index;
2. Selection of the set of intermediate and terminal groups in an interactive way;
3. Synthesis of *feasible* metha- Intermediate Molecu-