

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 opposed to linear molecular structures (Cismondi and Brignole, 2001)

On the other hand, chemical processes with super-

critical 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-

Table 1. Revision of the combination properties of UNIFAC groups

Combination Properties		Groups			
(M,1)	(CH ₃)				
(J,2)	(CH ₂)				
(J,3)	(CH)				
(J,4)	(C)				
(J,2) (K,1)	(CH ₂ Cl)	(CH ₂ NH ₂)	(CH ₂ CN)	(CH ₂ SH)	
(J,3) (K,1)	(CHCl)	(CHNH ₂)	(HCON(CH ₂) ₂)		
(J,4) (K,1)	(CCl)	(CF)			
(J,2) (K,2)	(CH ₂ CO)	(CH ₂ COO)	(CH ₂ O)	(CH ₂ NH)	
	(CONHCH ₂)	(CONCH ₂ CH ₂)	(FCH ₂ O)	(CH ₂ S)	
	(C ₂ H ₄ O ₂)				
(J,3) (K,2)	(CH-O)	(CHNH)	(CON(CH ₂) ₂)	(CHS)	
(J,2) (K,3)	(CH ₂ N)				
(K,1)	(CH ₂ =CH)	(OH)	(CH ₃ CO)	(CHO)	
	(CH ₃ COO)	(HCOO)	(CH ₃ O)	(CH ₃ NH)	
	(C ₂ H ₄ N)	(COOH)	(CHCl ₂)	(CCl ₃)	
	(CH ₂ NO ₂)	(I)	(Br)	(CH=C)	
	Cl-(C=C)	(SiH ₃)	(CCl ₂ F)	(HCCIF)	
	(CClF ₂)	(C ₂ H ₅ O ₂)	(CH ₃ S)	(C ₄ H ₃ S)	
	(CONH ₂)	(CONHCH ₃)	(CON(CH ₃) ₂)	(CF ₃)	
(K,2)	(CH=CH)	(CH ₂ =C)	(CH ₃ N)	(C ₃ H ₃ N)	
	(CCl ₂)	(CHNO ₂)	(C=C)	(COO)	
	(SiH ₂)	(SiH ₂ O)	(C ₄ H ₂ S)	(CF ₂)	
(K,3)	(CH=C)	(SiH)	(SiHO)		
(K,4)	(C=C)	(Si)	(SiO)		
(I,1)	(ACH)	(ACF)			
(H,1)	(ACCH ₃)	(ACOH)	(ACNH ₂)	(ACCl)	
	(ACNO ₂)				
(K,1) (H,1)	(AC)	(ACCOO)			
(J,2) (K,1) (H,1)	(ACCH ₂)				
(J,3) (K,1) (H,1)	(ACCH)				

lar Structures (IMS) using the metha-groups that corresponds to those selected. Then, each metha-IMS is replaced by all different possible combinations of the selected real groups to form "true" IMSs.

- In a similar way pre - Final Molecular Structures (FMS) are obtained by adding (NFA - 2) terminal groups to each IMS.
- Screening of the pre-FMSs according to the physical property constraints.
- Termination of FMSs by adding to each accepted pre-FMS different combinations of two terminal groups that preserve their molecular feasibility.
- Screening of the synthesized FMSs according to the physical constraints.

Table 2. General feasibility criteria for molecular structures

	$K \leq NJF$	$K > NJF$
Non cyclic structures	$K \leq J$	$2K \leq J + NJF$
Cyclic structures	$K \leq J$	$2K \leq J + NJF$
$J = 0$	-----	$K \leq 1$

The remaining products are ranked in accordance with molecular complexity and performance index, indicating the predicted product properties.

It should be pointed out that between steps 3-4, 4-5 and 6-7 the synthesis procedure eliminates all intermediate and final structures with unknown binary interaction parameters, reducing in this way the size of the combinatorial problem and the computing time. In any case the synthesis program runs in a very short time in a standard PC, as is shown in the example of Tables 3 and 4 for separation of benzene from hexane, which runs in less than one minute.

Table 3. A case of solvent design: separation of benzene from hexane.

Problem Definition	
Component to be recovered	(ACH) 6
Principal comp. in raffinate	(CH ₃) 2 (CH ₂) 4
Separation type	L-L Extraction
Operation temperature	320 K
Interm. groups selected	(C) (CH) (CH ₂) (DMF-2)
Terminal groups selected	(CH ₃) (CH ₂ =CH) (OH) (CHO) (CH ₃ COO) (HCOO) (CH ₂ CN) (CH ₂ SH)
Problem constraints	
Minimum Selectivity for pre-FMS [wt]	1.00
Maximum Solvent Loss for pre-FMS [wt %]	8.00
Minimum Selectivity [wt]	6.00
Minimum Solvent Power [wt %]	20.00
Maximum Solvent Loss [wt %]	4.00
Minimum Distribution Coefficient [wt]	0.60
Maximum Molecular Weight	260.0

Table 4. Results of the synthesis procedure

Number of metha – intermediate structures generated	255
Number or intermediate structures generated	255
Number of metha – pre final solvents	1664
Number of pre-final solvents	25595
- Pre –final solvents rejected by MW restriction	16247
- Pre –final solvents rejected by lack of binary parameters	4156
- Pre –final solvents evaluated	5192
Number of accepted pre-final solvents	4622
Number of metha-final solvents generated	4638
Number of final solvents generated	42436
- Solvents rejected by MW restriction	21887
- Solvents rejected by lack of binary parameters	10846
- Solvents evaluated	9703
Number of final solvents that satisfy all physical constraints	742
Best Solvents	Selectivity S. Power S. Loss Distr. Coef.
(CH ₃) ₁ (CH ₂) ₁ (CH) ₁ (CHO) ₂	10.04 71.96 3.10 1.21
(CH ₃) ₂ (CH ₂) ₃ (CH) ₃ (CH ₃ COO) ₁ (HCOO) ₂	7.68 64.87 2.10 1.10
(CH ₃) ₄ (CH) ₅ (CHO) ₂ (HCOO) ₁	6.29 63.60 2.59 1.07
(CH ₃) ₁ (CH ₂) ₂ (CH) ₁ (CHO) ₁ (HCOO) ₁	6.85 62.54 3.17 1.06
(CH ₃) ₃ (CH ₂) ₁ (CH) ₄ (CHO) ₁ (CH ₃ COO) ₁ (HCOO) ₁	6.85 61.92 3.46 1.05
(CH ₂) ₈ (CH) ₁ (CHO) ₁ (HCOO) ₂	6.46 60.90 1.63 1.03
(CH ₃) ₂ (CH ₂) ₁ (CH) ₃ (CH ₃ COO) ₂ (HCOO) ₁	8.45 60.83 3.37 1.03
(CH ₃) ₁ (CH ₂) ₄ (C) ₁ (HCOO) ₂ (CH ₂ SH) ₁	6.03 60.60 3.14 1.02
(CH ₃) ₁ (CH ₂) ₁ (CH) ₂ (CH ₂ =CH) ₁ (CHO) ₁ (HCOO) ₁	6.51 58.04 3.34 0.98

III. NEAR CRITICAL SOLVENTS

Each specific supercritical fluid process must be analyzed as a special case in detail. Different processes such as oxychemicals recovery and dehydration from aqueous solutions (Gros *et al.*, 1998; Diaz *et al.*, 2000b), gas antisolvent crystallization (Amaro *et al.*, 2000), separation of fatty acid alkyl esters (Diaz *et al.*, 2000b), vegetable oil purification (Espinosa *et al.*, 2000a; Diaz *et al.*, 2000b), deterpenation of citrus oil (Espinosa *et al.*, 2000b) or fractionation of fish oil fatty acid ethyl esters (Espinosa *et al.*, 2000c) have been studied in our group with ECOFAC.

ECOFAC describes the high-pressure phase equilibrium behavior with the GCA-EOS model. The original GC-EOS model (Skjold-Jorgensen, 1988) was proposed to study gas solubilities in nonideal mixtures at high pressures and takes into account only repulsive and dispersive interactions. Its capability has been extended (Gros *et al.*, 1997) to treat associating systems in mixtures of water and alcohols with non polar gases, like propane or CO₂. An upgraded version of the GCA-EOS model has been developed for the correlation and simulation of vegetable oils and derivatives processing with near critical fluids (Bottini *et al.*, 1999).

The determination of operating conditions for different supercritical processes are solved as Nonlinear Programming (NLP) problems. Equality constraints represent the process mathematical model and they are solved within a sequential process simulator. This program includes rigorous models for a high-pressure multistage extractor (Kehat and Ghitis, 1981), low and high-pressure distillation columns (Naphtali and Sandholm,

1971), and a multiphase flash (Michelsen, 1982). Inequality constraints include process specifications, operating bounds and bounds on potential units.

The optimization program interacts with a rigorous sequential modular process simulator in a black box way and non-linear programming problems are solved with OPT (Biegler and Cuthrell, 1985).

Some examples of “solvent design” for supercritical process are given below. Figure 1 shows an example of removal of pollutants from Palm Kernel oil, using propane as a near critical solvent. The results clearly indicate that there is an optimum operating pressure that minimizes solvent requirement keeping the solvent loss below the maximum value (Espinosa *et al.*, 2000a).

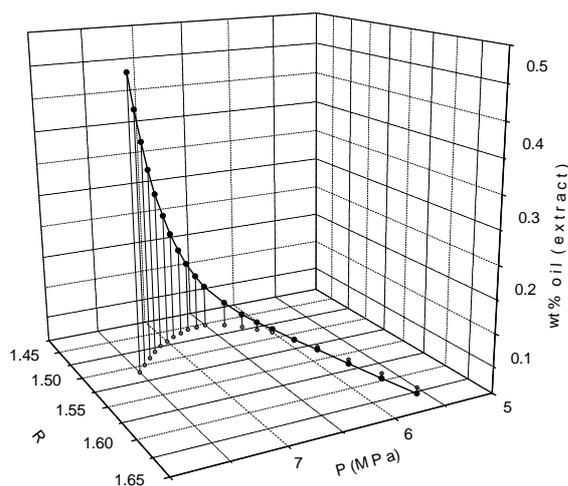
The optimum conditions for the operation (countercurrent and with reflux) for a destraction (high pressure distillation with a near critical gas as an entrainer) for the deterpenation of citrus oils are presented in Table 5 (Espinosa *et al.*, 2000b).

Table 5: Optimal operating conditions for countercurrent extraction with external reflux.

Variable	NLP Optimum
Extractor Pressure (bar)	95.00
Extractor Temperature (K)	333.15
Separator Temperature (K)	273.15
Reflux Ratio	0.54
Solvent Flowrate (Kmol/h)	82.45
Linalool in Raffinate, CO ₂ free (% molar)	99.00
Linalool Recovery (%)	93.37
Limonene in Sep. Bottom (% molar)	98.52
Limonene Recovery (%)	97.65
CO ₂ in Sep. Vapor (% molar)	99.99

In this case the optimum pressure is a compromise between solvent power of the near critical gas and the operation in the two phase region required to make possible the separation.

Fig. 1. Effect of operating pressure on the Propane-feed weight ratio and oil loss in the removal of hexane from palm kernel oil at 390.15 330.15 K (1 wt % of hexane in feed; 5 ppm of hexane in raffinate. R: solvent to feed weight ratio).



IV. PROPERTY PREDICTIONS

ECOFAC uses correlations derived previously (Pretel *et al.*, 1992) to estimate pure compound properties. The analysis of solvents and products from an environmental point of view also requires the knowledge or prediction of solution properties like solubility in water, Henry constants in aqueous solutions or partition coefficients in different systems. Especially the n-octanol/water partition coefficient of a solute have received a great industrial and legal interest in recent years. ECOFAC can perform these calculations using the LLE and VLE UNIFAC parameter tables, which has been discussed recently (Kuramochi *et al.*, 1998; Derawi *et al.*, 2001), and also using the "gamma infinite dilution" UNIFAC (Bastos *et al.*, 1988).

Table 6: Predictions of the logarithm of the n-octanol-water partition coefficient ($\log K_{ow}$) for some n-alkylbenzenes.

Compound	Sherblom et al. (1992)	UNIFAC LV	UNIFAC LL
n-decylbenzene	7.38	6.63	7.03
n-undecylbenzene	8.14	7.07	7.51
n-dodecylbenzene	8.65	7.50	7.98
n-tridecylbenzene	9.36	7.94	8.46
n-tetradecylbenzene	9.95	8.37	8.92

Predictions of the $\log K_{ow}$ with the LV and LL UNIFAC tables have been already reported in the literature for some n-alkanes, 1-alkanols, carboxylic acids,

aldehydes and ketones (Derawi *et al.*, 2001). In addition, we have tested the infinite dilution table, finding the highest deviations in this case for the families already mentioned. This is due to the high solubilities of most of these organic compounds in n-octanol, and in some cases also in water. In Table 6, ECOFAC predictions of $\log K_{ow}$ using the LV and LL tables are compared to the values reported by Sherblom *et al.* (1992) for Alkylbenzenes.

V. CONCLUSIONS

In the present work the ECOFAC approach for the solvent selection problem has been introduced. A procedure for the synthesis of branched molecular structures has been developed based on the use of metha groups and new characterization of the combination properties of the UNIFAC groups. A strategy for reducing the size of the combinatorial synthesis problem is presented. The evaluation of supercritical solvents based on rigorous simulation of the separation units is demonstrated by the optimization of the operation conditions for the determination of citrus oil and the removal of contaminants from natural oils. The possibilities of property prediction calculations using ECOFAC have been exemplified with the n-octanol-water partition coefficient.

NOTATION

J Number of J groups.

K Number of K groups.

NFA Number of free attachments in the intermediate structure.

NJF Number of J free attachments after combination of J groups only.

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REFERENCES

- Amaro, D., G. Mabe, G., M. Zabaloy and E. A. Brignole. "Gas Antisolvent Crystallization of Organic Salts from Aqueous Solutions", *J. Supercritical Fluids*, **17**, 249-258 (2000).
- Bastos, J.C., M.E.Soaes and A.G.Medina. "Infinite dilution Activity Coefficients Predicted by UNIFAC Group Contribution", *Ind. Eng. Chem. Res.*, **27**, 1269-1277 (1988).
- Biegler, L. and Cuthrell, J. "Improved Infeasible Path Optimization for Sequential Modular Simulators.II: The Optimization Algorithm", *Comp. Chem. Eng.* **9**, 257-267 (1985).
- Bottini, S., T. Fornari and E. A. Brignole. "Phase Equilibrium modeling of triglycerides with near critical solvents", *Fluid Phase Equilibria*, **158-160**, 211-218 (1999).

- Cismondi, M. and E. A. Brignole. "ECOFAC.Computer Aided Solvent Design and Evaluation in Environmental Problems", *Computer Aided Process Engineering*, **9**, 375-380 (2001)..
- Derawi, S.O.; G.M. Kontogeorgis and E.H. Stenby. "Application of group contribution models to the calculation of the octanol-water partition coefficient", *Ind. Eng. Chem. Res.* **40**, 434-443 (2001).
- Diaz, S., S. Espinosa and E. A. Brignole. "Modeling and Simulation Tools for Supercritical Fluid Processes", *Computer Aided Process Engineering*, **8**, 319-324 (2000a).
- Diaz, S., H. Gros and E. A. Brignole. "Thermodynamic Modeling, Synthesis and Optimization of Extraction – Dehydration Processes", *Comp. Chem. Eng.*, **24**, **9**, 2069-2080 (2000b).
- Espinosa, S., Bottini, S. and E. A. Brignole. "Process Analysis and Phase Equilibria for the Removal of Chemicals from Fatty Oils Using Near Critical Solvents", *Ind. Eng. Chem. Res.*, **39**, 3024-3032 (2000a).
- Espinosa, S., S. Diaz and E. A. Brignole. "Optimal Design of Supercritical Fluid Processes", *Comp. Chem. Eng.*, **24**, 2/7, 1301-1307 (2000b).
- Espinosa, S., S. Diaz and E. A. Brignole. "Biomolecules Supercritical Extraction. Process Simulation and Optimization", *Proceedings AIChE Annual Meeting*, Los Angeles, USA (2000c).
- Gani, R. and E. A. Brignole. Molecular design of solvents for liquid extraction based on UNIFAC. *Fluid Phase Equilibria*, **13**, 331-340 (1983).
- Gros, H.; S. Bottini and E. A. Brignole. "High Pressure Phase Equilibrium Modeling of Mixtures containing Associating compounds and Gases", *Fluid Phase Equilibria*, **139**, 75-87 (1997).
- Gros, H., S. Diaz and E. A. Brignole "Process Synthesis and Optimization of Near Critical Separations of Aqueous Azeotropic Mixtures", *J. Supercritical Fluids*. **12**, 69-84 (1998).
- Kehat, E. and B. Ghitis. "Simulation of an extraction column", *Comp. Chem. Eng.*, **5**, 171-180 (1988).
- Kuramochi, H.; H. Noritomi, D. Hoshino, S. Kato and K. Nagahama. "Application of UNIFAC models to partition coefficients of biochemicals between water and n-octanol or n-butanol", *Fluid Phase Equilibria*, **144**, 87-95 (1998).
- Michelsen, M.. "The isothermal flash problem. Part II: phase split calculations", *Fluid Phase Equilibria*. **9**, 21-40 (1982).
- Naphtali, L. and Sandholm. "Multicomponent separation calculations by linearization", *AIChE J.*, **17**, 148-153 (1971).
- Pretel, E., P.Lopez, A.Mengarelli and E.Brignole. "Prediction of physical properties for molecular design of solvents", *Latin American Applied Research*. **22**, 187-194 (1992).
- Pretel, E., P.Araya López, S. B.Bottini and E .A. Brignole. "Computer aided molecular design of solvents for separation processes", *AIChE Journal*, **40**, **8**, 1349-1360 (1994).
- Sherblom, P.M., Gschwend, P.M. and Eganhouse, R.P.. "Aqueous solubilities, vapor pressures, and 1-Octanol-Water partition coefficients for C9-C14 linear alkylbenzenes", *J. Chem. Eng. Data*, **37**, 394-399 (1992).
- Skjold-Jorgensen, S. "Group Contribution Equation of State (GC-EOS): a Predictive Method for Phase Equilibrium Computations over Wide Ranges of Temperatures and Pressures up to 30 Mpa", *Ind. Eng. Chem. Res.*, **27**, 110-118 (1988).

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