# Computer-Aided Molecular Design of Solvents for Separation Processes

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*The search for potential solvents for liquid extraction and extractive distillation is carried out through a group contribution molecular design of solvents (MOLDES) approach. A set of submolecular groups (UNIFAC) is used for the synthesis of molecular structures with desired solvent properties. Submolecular group combination (linking) properties are characterized to ensure the chemical feasibility of the MOLDES generated molecular structures. The size of the combinatorial problem posed by the molecular synthesis procedure is reduced by group selection and by imposing physical and molecular constraints at different stages. Criteria are developed for solvent evaluation and the reliability of the VLE and the LLE UNIFAC parameter tables for solvent screening are compared with experimental data for the recovery of oxychemicals by liquid extraction from dilute aqueous solutions.*

## Introduction

The usual approach for separation processes solvent selection is to examine several compounds with respect to primary solvent properties: distribution coefficients, selectivities, solvent losses, and so on. For example, Kollerup and Daugulis (1985) have built an extensive solvent database to carry out more efficiently the screening of solvents for the extraction of ethanol from water. Cockrem et al. (1989) have proposed an improved strategy for the selection of extraction solvents to recover chemicals from dilute aqueous solutions. In both works the evaluation of activity coefficient derived solvent properties is computed by UNIFAC (Fredenslund et al., 1975) with LLE parameter tables.

A different application of the UNIFAC group contribution approach has been taken by Gani and Brignole (1983) and Brignole et al. (1986): molecular design of solvents (MOLDES). MOLDES performs the solvent selection problem, synthesizing molecular structures with the desired solvent properties from a set of UNIFAC groups. One of the main features of the proposed methodology is that the search for solvents is not limited to a predefined set of compounds. On the basis of UNIFAC groups, a great number of molecular structures can be explored and their properties readily evaluated. More recently, Joback and Stephanopoulos (1989), Gani et al. (1991), and Porter et al. (1991) have presented new applications of the computer-aided molecular design approach. Joback and Stephanopoulos (1989) have presented an efficient methodology to reduce the problem size when the desired properties are pure component properties. Brignole et al. (1986) and Gani et al. (1991) have developed group characterization methods to ensure the synthesis of feasible solvent structures. Naser and Fournier (1991) have presented a synthesis method using continuous optimization that generates an optimum extracting molecule. In the present work, the MOLDES procedure is further developed and solvent evaluation criteria for liquid-liquid extraction and extractive distillation are presented.

The prediction of solvent properties requires the selection of UNIFAC LLE or VLE parameter tables (Magnussen et al., 1981; Tiegs et al., 1987) according to the separation problem at hand. The selection of solvents for liquid extraction is somehow limited because the LLE parameter table has not been revised and extended since original publication. Therefore, in the present work the application of the VLE parameter table to the selection of liquid extraction solvents is also investigated. In addition, the reliability of the MOLDES approach to solvent selection is studied for the particular problem of the recovery of oxygenated organic chemicals from aqueous solutions. A comparison of MOLDES results against experimentally based solvent selections is made.

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**Table 1. Type of UNIFAC Groups and Synthesis Structures**

| Type of Compound | Intermediate Groups | Terminal Groups | IMSs | SMSs |
|---|---|---|---|---|
| Aliphatic | $(CH_2)$<br>$(CH_2COO)$<br>$(CHCL)$<br>$(CHCO)$ | $(CH_3)$<br>$(OH)$ | $-(CH_2)_3-$<br>$-(CH_2)_4-(CH_2COO)-$<br>$-(CH_2)_3-(CHCL)-$ | $(CH_3)-(CH_2)_3-(OH)$<br>$(CH_3)-(CH_2)_4-(CH_2COO)-(CH_3)$<br>$(CH_3)-(CH_2)_3-(CHCL)-(CH_3)$<br>$(CH_3)-(CH_2)_3-(CHCL)-(OH)$ |
| Aromatic | $(ACH)$<br>$(ACCH_2)$<br>$(ACCH)$ | $(CH_3)$<br>$(CH_3COO)$ | $(ACH)_5(ACCH_2)-$<br>$(ACH)_5(ACCH)<$ | $(ACH_5)(ACCH_2)-(CH_3COO)$<br>$(CH_3)$<br>$(ACH)_5(ACCH)<$<br>$(CH_3)$ |
| Cyclic | $(CH_2)$<br>$(CH)$ | $(CH_3)$<br>$(CH_3CO)$<br>$(COOH)$ | $(CH_2)_2(CH)-$ | $(CH_2)_2(CH)-(CH_3)$<br>$(CH_2)_2(CH)-(CH_3CO)$<br>$(CH_2)_2(CH)-(COOH)$ |

## Molecular Design of Solvents

### *Computer strategy of molecular synthesis*

The computer-aided synthesis follows the combinatorial method developed by Brignole (1985). The selected molecular groups are combined, considering all possible chemical structures, which are then screened by evaluating their chemical feasibility and primary solvent properties. The combinatorial nature of the synthesis procedure leads to an efficient strategy for reducing the problem size:

(A) Selection of a set of molecular groups for the synthesis (intermediate and terminal groups).

(B) Synthesis of intermediate molecular structures (IMSs) by the combination of intermediate groups.

(C) Synthesis of solvent molecular structures (SMSs) by the combination of IMSs with terminal groups.

A SMS is a potential solvent unit which satisfies chemical feasibility criteria and the primary solvent property restrictions imposed by the specific separation problem. It is composed of an IMS and one or more terminal groups. An IMS is formed by a chain of two or more intermediate groups joined by means of their free attachments and satisfies the intermediate chemical feasibility criteria and solvent property restrictions. The intermediate groups have two or more free attachments, while the terminal groups have only one free attachment. Table 1 gives examples of intermediate and terminal groups, and of IMSs and SMSs obtained.

### *Reduction in the combinatorial problem size*

In order to obtain acceptable computational times and memory requirements, the reduction of the combinatorial problem is systematically carried out during the three stages of the synthesis strategy.

*Selection of Groups.* The number of selected groups fixes the size of the combinatorial problem. Therefore, the first step is to reduce the number of participating groups, without losing variety of generated compounds. The reduction in the number of groups is based on the following criteria:

(a) *Interaction Parameters Availability.* The prediction of solvent properties requires the availability of UNIFAC binary parameters. Therefore, the first criterion for the selection of groups is the availability of binary parameters for the synthesis groups with those of the feed mixture compounds. Details of 39 groups and 18 compounds can be found in the LLE UNIFAC parameter table and of 82 groups and 26 compounds in the VLE UNIFAC parameter table. However, the lack of binary information limits the range of applications of MOLDES, but reduces the combinatorial size of the problem to manageable dimensions. The MOLDES computer algorithm checks group parameter availability for the synthesis groups taking into account:

- Group structure of the compounds to be separated;
- Type of structures to be generated (that is, aliphatic, aromatic, mixed-aliphatic, cyclic or others); and
- Solvent properties to be calculated.

(b) *Elimination of Structural and Functional Isomers.* For a given UNIFAC main group, the binary interaction parameters are the same irrespective of the group valence. Thus, in the case of aliphatic or mixed aliphatic compound synthesis, a significant reduction in the number of groups is achieved by selecting only groups with a maximum total valence of two. A further reduction is achieved by eliminating from among the single valence groups those that lead to functional isomers.

(c) *Elimination of Groups that Affect the Chemical or Physical State of the Solvents.* Groups that lead to solvents with corrosion properties, chemical reactivity, or chemical instability must be avoided. Furthermore, it is important to study the effect of different groups on the physical state, solid or liquid, of the solvent at the process temperature. For example, in the selection of groups for the generation of aromatic solvents, the following considerations are taken:

- Ortho/para directing and activating groups (for example, $(ACNH_2)$, $(ACCH_3)$) usually form liquid compounds with up to three substitutions in the aromatic ring;
- Meta directing and deactivating groups (for example, $(ACNO_2)$) with three substitutions form solid compounds;
- Ortho/para directing and deactivating groups (for example, (ACCl)), form liquid compounds with up to three substitutions in the aromatic ring; and
- (ACOH) and (ACOOH) structures form solid compounds.

### *Feasibility of the molecular structures*

In the computation of thermodynamic and physical properties of mixtures by group contribution methods, the mixture molecules are decomposed into groups and the group com-

**Table 2. Attachment Type Characterization of UNIFAC Groups**

| Type of Attachments | | Groups | | | |
|---|---|---|---|---|---|
| $(M,1)$ | | $(CH_3)$ | | | |
| $(J,2)$ | | $(CH_2)$ | | | |
| $(L,1)$ | | $(CH_2CL)$ | | | |
| $(L,2)$ | | $(CHCL)$ | | | |
| $(K,1)$ | | $(CH_2=CH)$ | $(OH)$ | $(CH_3CO)$ | $(CHO)$ |
| | | $(CH_3COO)$ | $(HCOO)$ | $(CH_3O)$ | $(CH_2NH_2)$ |
| | | $(CH_3NH)$ | $(C_5H_4N)$ | $(CH_2CN)$ | $(COOH)$ |
| | | $(CHCL_2)$ | $(CCL_3)$ | $(CH_2NO_2)$ | $(CH_2SH)$ |
| | | (I) | (BR) | $(CH\equiv C)$ | CL-$(C=C)$ |
| | | $(SIH_3)$ | | | |
| $(K,2)$ | | $(CH=CH)$ | $(CH_2=C)$ | $(CH_3N)$ | $(C_5H_3N)$ |
| | | $(CCL_2)$ | $(CHNO_2)$ | $(C\equiv C)$ | (DMF-2) |
| | | (COO) | $(SIH_2)$ | $(SIH_2O)$ | |
| $(K,1)$ | $(L,1)$ | $(CH_2CO)$ | $(CH_2COO)$ | $(CH_2O)$ | $(CHNH_2)$ |
| | | $(CH_2NH)$ | $(FCH_2O)$ | | |
| $(I,1)$ | | (ACH) | (ACF) | | |
| $(H,1)$ | | $(ACCH_3)$ | (ACOH) | $(ACNH_2)$ | (ACCL) |
| | | $(ACNO_2)$ | | | |
| $(H,1)$ | $(M,1)$ | $(ACCH_2)$ | | | |
| $(H,1)$ | $(J,2)$ | (ACCH) | | | |

$(i,j)$: ordered pair where $j$ is the number of $i$ attachments in a given group.

position of each component is obtained. No information is required about the group combination (linking) properties. However, for the inverse problem of generating molecular structures, the combination properties of the group free attachments should be analyzed in detail. The combination properties are stated mainly to satisfy two criteria: to obtain chemically feasible structures and to avoid proximity effects that could lead to unreliable UNIFAC predictions.

Four types of attachments were defined by Brignole (1985) for nonaromatic groups:

$K$ = severely restricted attachment such as OH
$L$ = partially restricted attachment such as $CH_2Cl$
$M$ = unrestricted carbon attachment in linear dual valence or single valence groups such as $CH_3$
$J$ = unrestricted carbon attachment in "radial" dual valence groups, $CH_2$.

The synthesis of aromatic compounds requires the introduction of two new attachments:

$I$ = aromatic carbon ring attachment such as ACH
$H$ = substituted aromatic carbon ring attachment such as ACCl

Types $M$ and $J$ attachments are extended to aromatic groups as follows:

$M$ = unrestricted attachment in a carbon linked to an aromatic carbon such as $ACCH_2$
$J$ = unrestricted attachment in a "radial" carbon linked to an aromatic carbon, such as ACCH

**Table 3. Feasibility Criteria for IMSs and SMSs**

| Type of Compound | IMSs | | SMSs | |
|---|---|---|---|---|
| Aliphatic | $\hat{k} \leq \hat{m} + \hat{j}/2 + 2$ | (1) | $\hat{k} \leq \hat{m} + \hat{j}/2$ | (3) |
| Aromatic | $\hat{i} + \hat{h} = 6$,<br>$\hat{h} \leq 2$ or $\hat{h} \leq 3$ | (2) | Eq. 2 | |
| Aliphatic-aromatic | Eqs. 1 and 2 | | Eqs. 2 and 3 | |
| Cyclic | — | | Eq. 1 | |

$\hat{h}$, $\hat{i}$, $\hat{j}$, $\hat{k}$, $\hat{l}$, or $\hat{m}$: number of attachments of type $H$, $I$, $J$, $K$, $L$, or $M$.

The attachment types of the UNIFAC groups are shown in Table 2. Groups were taken from the LLE and the VLE UNIFAC parameter tables as defined respectively by Magnussen et al. (1981) and Tiegs et al. (1987). Aliphatic groups with more than two free attachments were excluded because of the group selection criteria explained above. The attachment types are indicated as ordered pairs $(i, j)$, where $i$ is the type of attachment and $j$ the number of $i$ attachments present in a given group. The valence of the aromatic carbon attachment has been defined to be one, for example, the characterization of the group (ACH) is $(I, 1)$. The combination properties of a given group can be changed by modifying its attachment types. For instance, proximity effects between polar groups can be avoided by changing the type of a particular attachment from $L$ to $K$.

The combination rules for the synthesis of paraffinic, aromatic, and cyclic solvents are:

(R1) Type $K$ attachments can only be combined with unrestricted carbon attachments

(R2) Type $L$ attachments can be combined with $L$, $M$, or $J$ attachments

(R3) Type $J$ attachment changes to $L$ after its combination with a type $K$ attachment

(R4) Aromatic rings are built only with type $I$ and $H$ attachments.

The set of groups that makes up a molecular structure should have a number of unrestricted carbon attachments equal to or greater than the number of $K$ (severely restricted) attachments. If this condition is satisfied, there is no restriction in the combination of the remaining attachments. Table 3 shows the feasibility criteria that IMSs and SMSs must satisfy, according to the nature of the generated compounds. Only single ring aromatic structures are considered in the synthesis procedure.

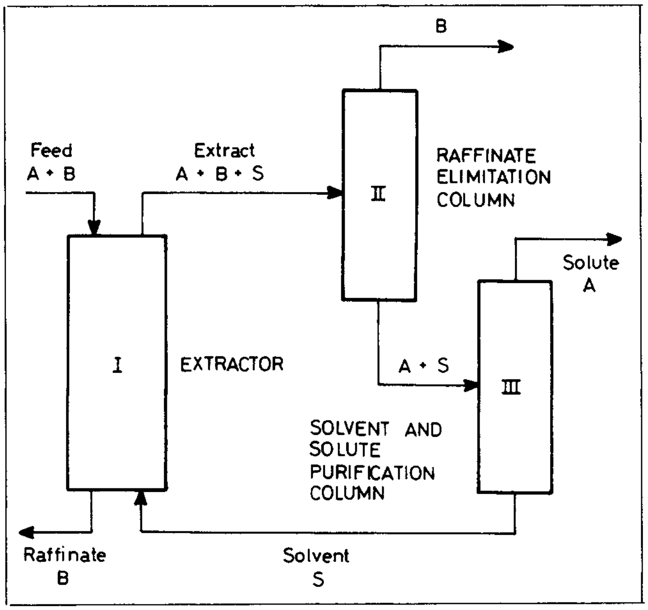

**Figure 1. Typical cycle for the extraction of a dilute solute.**

(A) Solute feed component; (B) main feed component; (S) solvent.

Besides, a maximum of two or three groups of type *H* (substituted) are allowed. When dealing with mixed aliphatic-aromatic solvents, the feasibility conditions required for both types of structures should be met.

### *Solvent evaluation*

The MOLDES approach requires the screening of a large number of potential solvents by the evaluation of specific solvent properties. In this regard, it is necessary to consider all the separating operations involved in the separation process at hand. For instance, in liquid extraction there are many possible process scheme arrangements. The scheme shown in Figure 1 is typical for the extraction of a dilute component. This scheme has three steps: extraction, separation of the raffinate from the extract by distillation, and solute removal from the top and solvent recovery from the bottom of a second distillation column. Therefore, in dealing with dilute solutions, the solute/solvent volatilities should be much greater than one, and the solvent solubilities in the raffinate should be very low. The volatility restriction can be relaxed if solvents with high distribution coefficients can be found. Cockrem et al. (1989) have shown that the dominant solvent properties for this family of separation problems are the solute distribution coefficient and the solvent solubility in the raffinate (solvent loss). The size of the extractor and the amount of solvent to be circulated are inversely proportional to the value of the distribution coefficient. Cockrem et al. (1989) also show that low solvent solubility in the raffinate determines raffinate-extract immiscibility, and it is an indication of good solvent selectivity. High solvent selectivity is required to reduce the cost of solute recovery from the extract. The solute-solvent relative volatility is another important solvent property when the solute purification is carried out by distillation. To avoid azeotrope formation and to insure high relative volatility for the solute-solvent pair, a minimum normal boiling point difference of 30 to 50 K can be specified. Finally, another important extraction property is the difference in density between the solvent and the raffinate.

MOLDES evaluates the potentiality of solvents for liquid extraction by calculating the properties shown in Table 4. Estimates of the solvent selectivity, solvent power, solute distribution coefficient, and solvent loss are readily obtained from UNIFAC, based on the predictions of infinite dilution activity coefficients. Pure component properties like normal boiling points and densities can be estimated by group contribution methods. Details of these methods are given elsewhere (Pretel et al., 1992; Reid et al., 1987). In Table 4, certain properties marked are evaluated for both IMSs and SMSs, while the others are only evaluated for SMSs.

A typical extractive distillation process is shown in Figure 2. This process has two steps: the extractive distillation column

**Table 4. MOLDES Property Estimates for Solvent Evaluation**

| Liquid-liquid Extraction | | Extractive Distillation | |
|---|---|---|---|
| Property | Estimate | Property | Estimate |
| Solvent Selectivity[†] | $\beta=\frac{\gamma^\infty_{B,S}}{\gamma^\infty_{A,S}}\frac{MW_A}{MW_B}$ | Relative Volatility[†] | $\alpha_{B,A}=\frac{\gamma^\infty_{B,S}P^S_B}{\gamma^\infty_{A,S}P^S_A}$ |
| Solvent Power | $Sp=\frac{1}{\gamma^\infty_{A,S}}\frac{MW_A}{MW_S}$ | Solvent Power[†] | $Sp=\frac{1}{\gamma^\infty_{A,S}}\frac{MW_A}{MW_S}$ |
| Solute Distribution Coefficient | $m=\frac{\gamma^\infty_{A,B}}{\gamma^\infty_{A,S}}\frac{MW_B}{MW_S}$ | Minimum Solvent Molar Fraction to Break the Azeotrope | $x_{ms},\ \alpha_{B,A}\vert_{x_{ms}}=1.0$ |
| Solvent Loss[†] | $Sl=\frac{1}{\gamma^\infty_{S,B}}\frac{MW_S}{MW_B}$ | Phase Stability Criterion | $\gamma_{S,\text{aze.}}x_{ms}\leq 1.0$* |
| Solvent Boiling Point | $Tb_S$: Pretel et al. (1992) | Solvent Boiling Point | $Tb_S$: Pretel et al. (1992) |
| Density | $\rho_S$: Le Bas and Schroeder methods (Reid et al., 1987) | Performance Index | $PI=\frac{\alpha_{B,A}}{MW_S x_{ms}}$ ** |

*The phase stability criterion is evaluated at $x_{ms}$ in an azeotropic mixture of *A* and *B*. This criterion is not applied for nonazeotropic mixtures.

**$x_{ms}=1.0$ when *A* and *B* do not form azeotrope.

[†] These properties are evaluated for both IMSs and SMSs, while the others are evaluated only for SMSs.

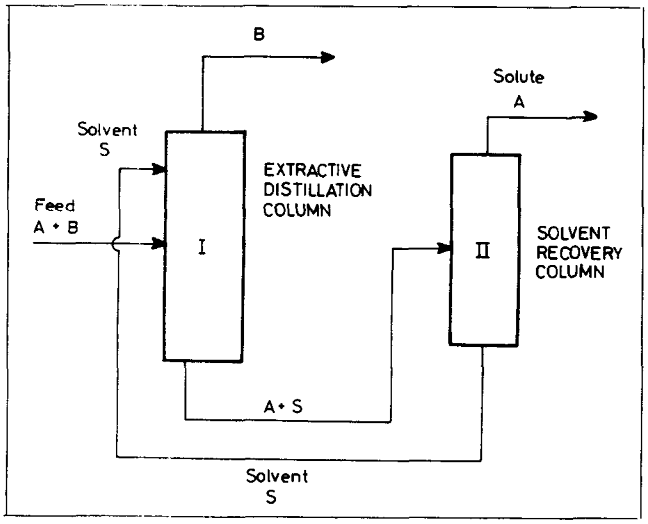

**Figure 2. Typical extractive distillation cycle.**
(A) Solute feed component; (B) feed component; (S) solvent.

which recovers the solute component and the solvent from the bottom, and the solvent recovery column which obtains the purified solute as distillate and the solvent from the bottom. The primary solvent properties are the increase in the relative volatility between the mixture components at infinite dilution in the solvent, the normal boiling point difference between the solute and the solvent, and the amount of solvent required to break the azeotrope, in the case of an azeotropic feed mixture. If $A$ represents the solute, $B$ the other component in the feed, and $S$ the solvent, there are two possibilities for the variation of the relative volatility with composition: $\alpha_{B,A}$ is less than one either at $x_A = 0$ or at $x_B = 0$. Accordingly, the minimum solvent molar fraction $x_{ms}$ that makes $\alpha_{B,A} = 1.0$ at $x_A = 0$ for the first case or at $x_B = 0$ for the second, can be found. Another important constraint is imposed by the fact that the solvent must be completely miscible in the mixture at the desired concentration range. In the case of an azeotropic feed mixture, solvent and feed miscibility is investigated on the basis of the phase stability criterion proposed by Michelsen (1982) and shown in Table 4. This criterion is evaluated at $x_{ms}$ in an azeotropic mixture of $A$ and $B$. Furthermore, the feed concentration should be considered in selecting the component to be removed from the top of the extractive distillation column. This choice determines the nature of the solvents to be generated with the purpose of increasing or decreasing the $\alpha_{B,A}$ of the feed mixture.

MOLDES estimates of the increase in relative volatility and of other solvent properties are calculated from UNIFAC according to Table 4. The ranking of solvents for extractive distillation is obtained through the computation of a performance index $PI$ for each solvent. This index is directly proportional to the $B/A$ relative volatility at infinite dilution ($\alpha_{B,A}$) in the solvent, divided by the product of the minimum solvent molar fraction necessary to break the azeotrope ($x_{ms}$) and the solvent molecular weight ($MW_S$). When feed mixtures do not form an azeotrope, $PI$ is obtained directly by the ratio of relative volatility to solvent molecular weight.

### *Computer program*

A user friendly computer program incorporating all the features described above and supported by VLE and LLE UNIFAC parameter tables has been developed. The program executes the following steps:

(1) *Definition of the Separation Problem.* This includes separating operation (liquid extraction or extractive distillation), compounds to be separated, and required solvent properties (constraints).

(2) *Selection of Intermediate and Terminal Solvent Groups.* The program selects, in an interactive way, a subset of intermediate and terminal groups for which interaction parameters with the feed component groups are available.

(3) *IMS Synthesis.* This includes a combination of intermediate groups to form the IMSs and rejection of all structures in which there are groups with unknown binary interaction parameters, and structure screening according to chemical feasibility and solvent properties.

(4) *SMS Synthesis.* This includes IMSs and terminal group combination and rejection of all structures in which there are groups with unknown binary interaction parameters, and structure screening according to chemical feasibility and solvent properties.

(5) *SMS Ordering in Terms of the Specific Separation Problem Constraints.* Solvents for liquid extraction are ranked in order of decreasing distribution coefficients, and solvents for extraction distillation are ranked in order of decreasing performance index (PI). Furthermore, for both separating operations, solvents are ranked in order of increasing degrees of molecular complexity.

## Liquid Extraction and UNIFAC Parameter Tables

In the present work MOLDES is applied to study the recovery of oxygenated organic compounds from dilute aqueous solutions. The primary solvent properties are estimated on the basis of the infinite dilution activity coefficients of the components involved, according to Table 4. In order to study the applicability of the LLE and the VLE parameter tables, MOLDES predictions of solute distribution coefficients are compared with experimental data obtained at dilute but finite solute concentrations.

The binary interaction parameters from the LLE parameter table (Magnussen et al., 1981) were adjusted to obtain a good fit of a mixture concentration objective function. A poor quality in the predictions of solute distribution coefficients has been reported by Gupte and Danner (1987). Besides, the LLE parameter table has not been revised or extended since its original publication. There are only 39 groups in this table, against more than 100 in the original UNIFAC VLE parameter table and its revisions (Gmehling et al., 1982; Macedo et al., 1983; Tiegs et al., 1987; Hansen et al., 1991). On the above discussion, it seems natural to study the application of the VLE parameter tables to the molecular design of solvents for liquid-liquid extraction.

Predictions of the distribution coefficients of potential solvents for the recovery of ethanol from aqueous solutions are compared with experimental data in Tables 5 and 6. It should be noted that MOLDES predictions are based on water/solvent activity coefficient ratios at infinite dilution, while experi-

Table 5. Experimental (Roddy, 1981; Roddy and Coleman, 1981; Sorensen and Arlt, 1980) and UNIFAC Predicted Values of Solute Distribution Coefficients for the Extraction of Ethanol from Water at $T = 298.0$ K and $P = 101.3$ kPa

| | *m* (Molar Basis) | | |
|---|---|---|---|
| Solvent | UNIFAC VLE | UNIFAC LLE | Exp. |
| Hexanoic acid | 6.89 | 3.73 | 7.22 |
| Octanoic acid | 6.67 | 3.30 | 4.86 |
| 3-Phenyl propanol | 6.14 | 5.56 | 4.84 |
| Methyl isobutyl ketone | 3.08 | 2.42 | 2.84 |
| Butyl acetate | 2.34 | 3.01 | 2.51 |
| Isopropyl ether | 0.92 | 1.49 | 1.55 |
| Diethylbenzene | 0.67 | 0.604 | 0.18 |
| Hexane | 0.28 | 0.73 | 0.06 |

Table 6. Experimental (Roddy, 1981) and UNIFAC Predicted Values of Ethanol Distribution Coefficients in Normal and Branched Alcohols for the Extraction of Ethanol from Water at $T = 298.0$ K and $P = 101.3$ kPa

| | *m* (Molar Basis) | | |
|---|---|---|---|
| Solvent | UNIFAC VLE | UNIFAC LLE | Exp. |
| 2,7-Dimethyl 5-pentanol | 6.7 | 6.1 | 4.6 |
| 1-Octanol | 6.6 | 5.2 | 4.4 |
| 2-Ethyl 1-hexanol | 6.6 | 5.4 | 4.2 |
| 2,2-Dimethyl 3-octanol | 6.3 | 5.1 | 3.3 |
| 3,7-Dimethyl 3-octanol | 6.3 | 5.2 | 4.3 |
| 1-Tridecanol | 2.8 | 6.0 | 4.9 |

mental data have been measured at dilute but finite ethanol concentrations. Besides, the distribution coefficients of associating solutes change significantly with concentration in the dilute region. With these observations in mind, the agreement between predicted and experimental ethanol distribution coefficients is reasonable for oxygenated organic solvents. However, the predictions of distribution coefficients are poor for paraffinic or aromatic solvents, like hexane or toluene, in agreement with the findings of Gupte and Danner (1987). Table 6 shows the predicted distribution coefficients for branched alcohols and the experimental data obtained by Roddy (1981). Both parameter tables give reasonable agreement with the experimental values. However, the experimental data show a significant effect of branching on the distribution coefficient, whereas the UNIFAC predictions are almost constant for the different isomers considered. These results justify MOLDES synthesis procedure of generating linear chain molecules without branching.

Solvent property predictions for the extraction of acetic, propanoic, and acrylic acids are shown in Table 7. The agreement with experimental data is reasonable for the extraction of acetic and propanoic acids with alcohol, ester, ether, paraffinic, and aromatic solvents. However, in the case of acrylic acid, while the VLE parameter table gives poor results for diisopropyl ether, the LLE parameter table grossly under predicts distribution coefficients for alcohol, ether, and ketone

Table 7. Experimental (Sorensen and Arlt, 1980) and UNIFAC Predicted Values of Distribution Coefficients for the Extraction of Organic Acids from Water at $T = 298.0$ K and $P = 101.3$ kPa

| Solvent | | *m* (Molar Basis) | | |
|---|---|---|---|---|
| | | Acetic | Propanoic | Acrylic |
| 2-Ethyl 1-hexanol | (Exp.) | 2.74 | 15.0 | 11.0 |
| | (UNIFAC VLE) | 3.95 | 12.2 | 9.3 |
| | (UNIFAC LLE) | 3.52 | 10.5 | 1.6 |
| 1-Hexanol | (Exp.) | | 13.5 | 13.2 |
| | (UNIFAC VLE) | | 10.7 | 8.8 |
| | (UNIFAC LLE) | | 9.7 | 1.5 |
| Pentyl Acetate | (Exp.) | 2.2 | 8.5 | |
| | (UNIFAC VLE) | 1.29 | 4.2 | |
| | (UNIFAC LLE) | 5.14 | 8.5 | |
| Isopropyl acetate | (Exp.) | | | 11.0 |
| | (UNIFAC VLE) | | | 5.1 |
| | (UNIFAC LLE) | | | * |
| 4-Methyl 2-Pentanone | (Exp.) | 2.8 | 15.0 | 12.0 |
| | (UNIFAC VLE) | 2.4 | 7.8 | 7.6 |
| | (UNIFAC LLE) | 2.5 | 7.5 | 1.3 |
| Diisopropyl ether | (Exp.) | 1.5 | 9.0 | 9.0 |
| | (UNIFAC VLE) | 1.1 | 5.4 | 2.0 |
| | (UNIFAC LLE) | 2.8 | 9.4 | 1.8 |
| Toluene | (Exp.) | 0.28 | 2.5 | 1.8 |
| | (UNIFAC VLE) | 0.51 | 1.6 | 1.7 |
| | (UNIFAC LLE) | 0.787 | 2.9 | 0.8 |
| *n*-Hexane | (Exp.) | 0.10 | 1.4 | 0.8 |
| | (UNIFAC VLE) | 0.1 | 1.0 | 0.81 |
| | (UNIFAC LLE) | 0.32 | 4.3 | 0.64 |

* Unrealistic predictions.

**Table 8. Experimental (Sorensen and Arlt, 1980) and UNIFAC Predicted Values of Distribution Coefficients for the Extraction of Phenol from Water at $T = 298.0$ K and $P = 101.3$ kPa**

| Solvent | $m$ (Molar Basis) | | |
|---|---|---|---|
| | UNIFAC VLE | UNIFAC LLE | Exp. |
| $n$-Octanol | 109.5 | 42.5 | 347.0 |
| $n$-Butyl acetate | 67.5 | * | 525.0 |
| Isopentyl acetate | 57.7 | * | 250.0 |
| Methyl isobutyl ketone | 48.3 | * | 200.0 |
| Benzene | 1.3 | 11.4 | 5.6 |

* Unrealistic predictions.

solvents and over predicts the distribution coefficients for esters. These results indicate the need of revising the values of the interaction parameters between the ($CH_2 = CH$) group with (OH), ($CH_2COO$), ($CH_2CO$), ($CH_2O$), and ($H_2O$) from the LLE parameter table.

The results for the phenol extraction from water are shown in Table 8. Even though the trend of solvent power is again correctly predicted using the VLE parameter table, the numerical predictions are poor. Unrealistic predictions of distribution coefficients for ketones and esters are obtained with the LLE parameter table. Table 9 shows the predictions for the extraction of furfural. Furfural, as well as phenol, alcohols, and acids, shows a great variation of distribution coefficient with concentration in the diluted region. Taking this effect into account, the predictions obtained with the VLE parameter table are acceptable.

The comparison of experimental distribution coefficients with predictions based on both parameter tables, justifies the selection of the VLE parameter table as a more reliable source of predictions for MOLDES solvent screening. Furthermore, the VLE parameter table has been continuously updated and has a greater number of groups. However, the results of the present study indicate the need of upgrading the UNIFAC method to improve the solvent property predictions for the extraction of solvating or associating organic compounds from aqueous solutions.

## MOLDES Application to Liquid Extraction from Aqueous Solutions

### *Ethanol*

**Table 9. Experimental (Sorensen and Arlt, 1980) and UNIFAC Predicted Values of Distribution Coefficients for the Extraction of Furfural from Water at $T = 298.0$ K and $P = 101.3$ kPa**

| Solvent | $m$ (Molar Basis) | | |
|---|---|---|---|
| | UNIFAC VLE | UNIFAC LLE | Exp. |
| $n$-Butylacetate | 25.0 | 21.7 | 45.7 |
| 2,4-Dimethyl 4-heptanona | 22.5 | 13.0 | 38.2 |
| Benzene | 33.3 | 48.5 | 21.0–55.0 |
| Ethyl benzoate | 61.0 | 66.0 | 40.4 |
| Butanoic acid, 3-oxo ethyl ester | 47.0 | 34.5 | 12.0–40.0 |

**Table 10. MOLDES Solvent Selection for the Recovery of Alcohols from Aqueous Solutions at $T = 298.0$ K Using the VLE UNIFAC Parameter Table**

| Solvent | $m$ (Weight Basis) | |
|---|---|---|
| | Ethanol | Butanol |
| Phenylethanol | 0.90 | 6.7 |
| (3-Phenyl 1-propanol) | (0.64)* | |
| Nonanol | 0.81 | 6.4 |
| (1-Nonanol) | (0.72)* | |
| Dipropyl pyridine | 0.62 | 5.6 |
| Phenyl acetic acid | 0.76 | 4.9 |
| Nonanoic acid | 0.74 | 6.1 |
| ($n$-Octanoic acid) | (0.60)* | |
| Hydroxy heptyl acetate | 0.76 | 5.7 |
| Dipentyl amine | 0.56 | 5.1 |
| Phenylpropanone | 0.36 | 2.8 |

* Experimental data (Roddy, 1981; Munson and King, 1984).

The extraction of ethanol from aqueous solutions has been a problem of great interest in recent years. For most solvents, the relative affinity between water and ethanol leads to low values of distribution coefficients and selectivities. A ranking of solvents obtained by MOLDES is shown in Table 10 and a typical output of MOLDES is given in Table 11. The best solvents are alcohols (aromatic or paraffinic), alkyl substituted pyridines, and paraffinic acids. The solvents have a molecular weight of around 150, in order to reduce the solvent loss and to avoid the formation of azeotropes with ethanol. The predictions agree with the experimental results obtained by Roddy (1981), Munson and King (1984), and Egan et al. (1988). Roddy studied the distribution coefficients for 40 solvents and found that triisobutylphosphate, 3-phenyl 1-propanol, and 1-octanol were the three solvents with the greatest weight distribution coefficients. Munson and King reported data for 31 solvents and found that isophorone, 1-nonanol, and $n$-octanoic acid were the best in this regard. MOLDES selects phenylethanol, 1-nonanol, dipropyl pyridine, phenyl acetic acid, and nonanoic acid as the best solvents. MOLDES synthesis procedure based on UNIFAC groups is not able to generate isophorone or alkylphosphate compounds. For the purpose of comparison, experimental distribution coefficients for the MOLDES selected solvents or data for the closest homologous compounds are also shown in Table 10. For this type of separations the best paraffinic or mixed paraffinic-aromatic solvents have a single amine or oxygenated group linked to a paraffinic or mixed paraffinic-aromatic backbone. The functional group enhances the solubility of the alcohol through a solvation effect and the hydrophobic aromatic-paraffinic backbone gives high ethanol/water selectivity and low solvent loss.

The effect of the solvent property constraints on solvent screening for ethanol recovery is illustrated in Figure 3 for several solvent families: alcohol, diols, carboxylic acids, aromatic acids, and alkyl amines. This example was run with the following restrictions:

$$\beta \geq 7.0 \text{ wt./wt.}, \tag{4a}$$

$$Tb_S - Tb_{\text{ethanol}} \geq 50.0 \text{ K}, \tag{4b}$$

$$m \geq 1.0 \text{ wt./wt.}, \tag{4c}$$

Table 11. Typical Output of MOLDES for the Ethanol/Water Separation Problem at $T = 298.0$ K Using the VLE UNIFAC Parameter Table

| $\beta$ (wt./wt.) | $Sp$ (wt. %) | $Sl$ (wt. %) | $MW_S$ | $Tb_S$ (K) | $\rho_S$ (g/cm$^3$) | $m$ (wt./wt.) |
|---|---|---|---|---|---|---|
| *Solvents with one Functional Group* | | | | | | |
| 1** $(CH_2)$ 8 $(CH_3)$ 1 (OH) 1 | | | | | | |
| 13.48 | 27.07 | 0.902E-01 | 144.0 | 494.3 | 0.70 | 0.808 |
| 2** $(CH_2)$ 2 $(C_5H_3N)$ 1 $(CH_3)$ 2 | | | | | | |
| 6.69 | 26.18 | 0.255E+00 | 135.0 | 457.6 | 0.74 | 0.781 |
| 4** $(CH_2)$ 5 $(CHNH_2)$ 1 $(CH_3)$ 2 | | | | | | |
| 6.50 | 25.24 | 0.228E+00 | 129.0 | 426.4 | 0.66 | 0.753 |
| 5** $(CH_2)$ 7 $(CH_3)$ 1 (COOH) 1 | | | | | | |
| 10.50 | 24.85 | 0.198E+00 | 158.0 | 537.2 | 0.75 | 0.741 |
| 8** $(CH_2)$ 3 $(C_5H_3N)$ 1 $(CH_3)$ 2 | | | | | | |
| 6.75 | 23.18 | 0.933E-01 | 149.0 | 477.0 | 0.74 | 0.691 |
| 10** $(CH_2)$ 8 $(CH_3)$ 1 (COOH) 1 | | | | | | |
| 11.08 | 22.21 | 0.751E-01 | 172.0 | 556.0 | 0.74 | 0.663 |
| *Solvents with Two Functional Groups* | | | | | | |
| 3** $(CH_2)$ 6 $(CH_2COO)$ 1 $(CH_3)$ 1 (OH) 1 | | | | | | |
| 6.44 | 25.65 | 0.681E+00 | 174.0 | 539.8 | 0.80 | 0.765 |
| 7** $(CH_2)$ 6 $(CH_2CO)$ 1 $(CH_3)$ 1 (COOH) 1 | | | | | | |
| 6.41 | 23.46 | 0.744E+00 | 186.0 | 609.2 | 0.78 | 0.700 |
| 9** $(CH_2)$ 2 $(C_5H_3N)$ 2 $(CH_3)$ 2 | | | | | | |
| 5.27 | 22.98 | 0.948E-01 | 212.0 | 577.3 | 0.79 | 0.686 |
| 23** $(CH_2)$ 4 $(CH_2CO)$ 2 $(CH_3)$ 2 | | | | | | |
| 12.33 | 13.04 | 0.300E+00 | 170.0 | 545.3 | 0.74 | 0.389 |
| 30** $(CH_2)$ 4 $(CH_2CO)$ 1 $(CH_2COO)$ 1 $(CH_3)$ 2 | | | | | | |
| 7.22 | 11.55 | 0.156E+00 | 186.0 | 536.3 | 0.79 | 0.345 |

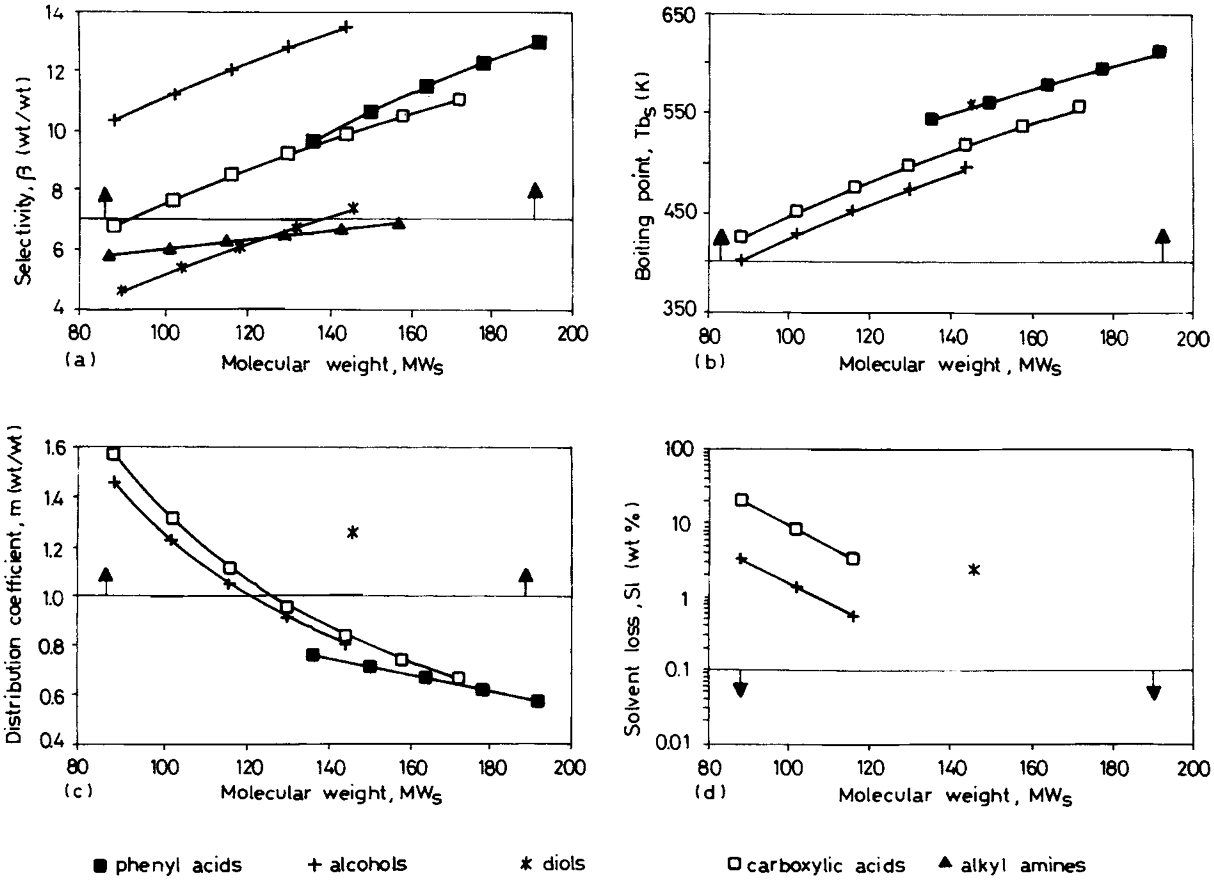

**Figure 3. MOLDES solvent screening for the ethanol/water separation problem.**

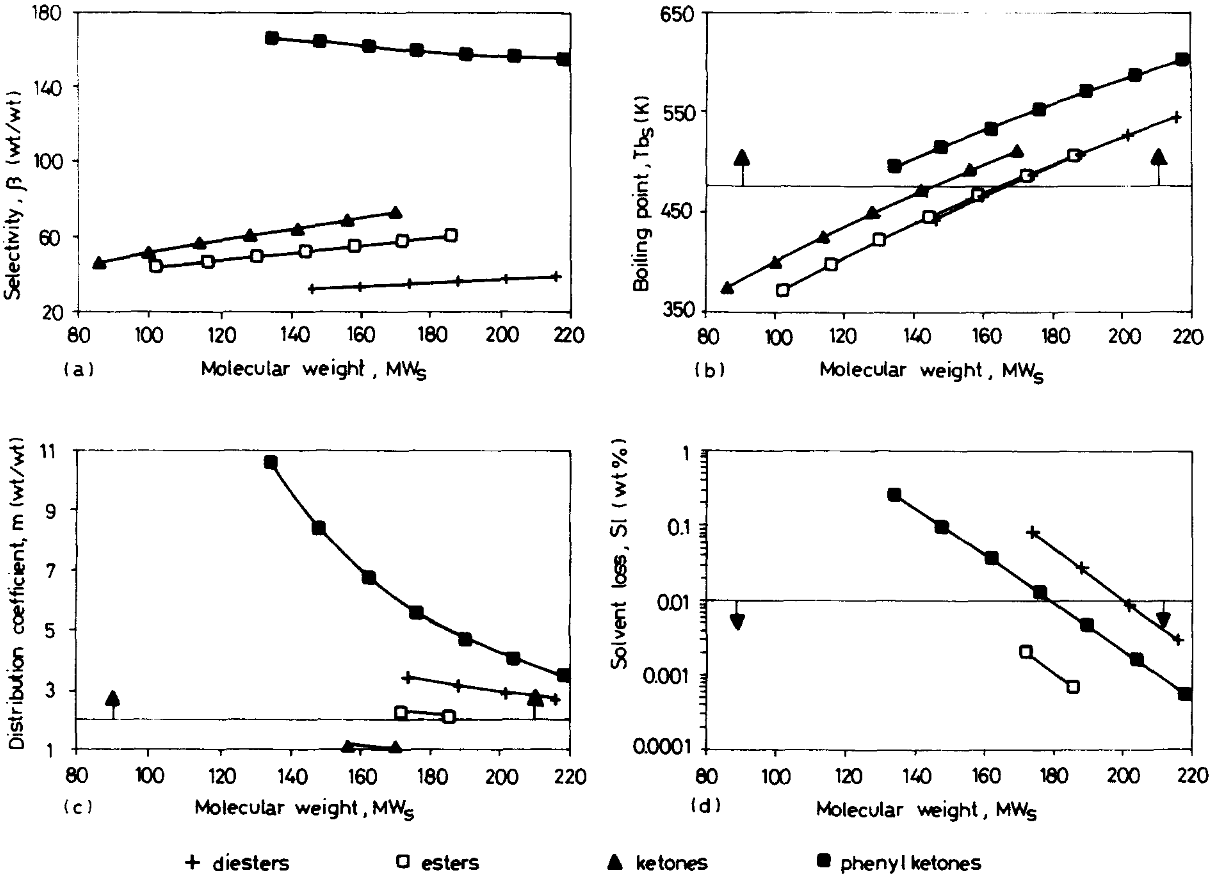

Figure 4. MOLDES solvent screening for the furfural/water separation problem.

$$SI \leq 0.1 \text{ wt. \%}. \tag{4d}$$

Figure 3a shows that the low selectivities of alkyl amines, and diols exclude these families as potential solvents. Figure 3b shows that all the remaining solvents satisfy the $Tb_S$ restriction. Furthermore, in Figure 3c it can be seen that the requirement of a distribution coefficient greater than 1.0 rejects all solvents with a molecular weight above 140. Finally, Figure 3d shows that none of the solvents meet the solvent loss restriction. Therefore, no solvents are found that satisfy the selectivity, distribution coefficient, and solvent lost restrictions for this separation. This result is in agreement with the fact that *there is no successful commercial application of liquid extraction to the recovery of ethanol from water.*

**Table 12. MOLDES Solvent Selection for the Recovery of Organic Acids from Aqueous Solutions Using the VLE UNIFAC Parameter Table at $T = 298.0$ K**

| | *m* (Weight Basis) | | |
|---|---|---|---|
| Solvent | Acetic | Propanoic | Acrylic |
| Dipropyl pyridine | 2.03 | | |
| 1-Nonanol | 0.5 | 1.4 | 1.2 |
| Decanoic acid | 0.29 | 0.83 | 0.74 |
| Decanone | 0.25 | 0.87 | 0.94 |
| Methyl benzyl ether | 0.21 | 0.60 | 0.68 |
| Benzyl acetate | 0.16 | 0.42 | 0.56 |
| Hydroxy octyl acetate | 0.52 | | 1.4 |

### *Butanol*

In the case of n-butanol it is possible to find solvents that meet the constraints given by Eqs. 4a to 4d, because compounds with greater $MW_S$ satisfy the solvent lost restriction. The ranking of solvents is similar to that of ethanol, and it is shown in Table 10. The distribution coefficients are one order of magnitude larger than those for ethanol. These results were obtained following the physical property restrictions suggested by Cockrem et al. (1989). These authors verified the applicability of UNIFAC for this separation problem. MOLDES selects phenylethanol, nonanol, and nonanoic acid as the best solvents. This selection agrees with the solvent functional groups and paraffinic chain lengths recommended by Cockrem et al. It is noteworthy that in their study, as well as in MOLDES, other solvent properties as solvent losses and differences in solute/solvent boiling points were also taken into account.

### *Furfural*

The effect of the solvent property constraints on solvent selection is shown in Figure 4 for the extraction of furfural from aqueous solutions. The following restrictions were imposed for solvent screening:

$$\beta \geq 20.0 \text{ wt./wt.}, \tag{5a}$$

$$Tb_S - Tb_{\text{furfural}} \geq 30.0 \text{ K}, \tag{5b}$$

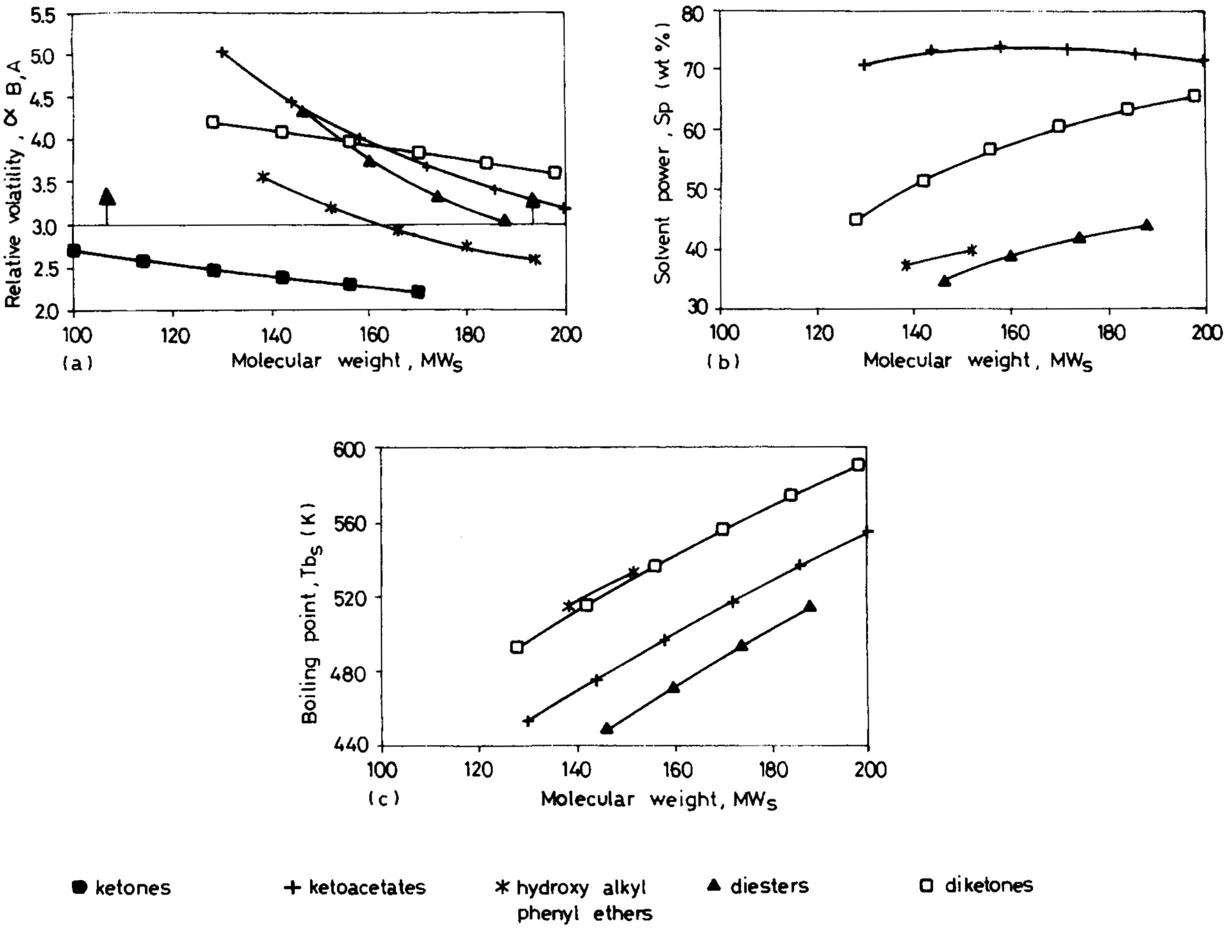

**Figure 5. MOLDES solvent screening for the toluene/methylcyclohexane separation problem.**

$$m \geq 2.0 \text{ wt./wt.,} \tag{5c}$$

$$Sl \leq 0.01 \text{ wt. \%.} \tag{5d}$$

For this separation problem there are many potential solvents available with good selectivity, high distribution coefficients and low solvent losses (Aly et al., 1983).

### *Organic acids*

Table 12 shows the MOLDES selected solvents for the extraction of organic acids from water according to the following restrictions:

$$\beta \geq 7.0 \text{ wt./wt.,} \tag{6a}$$

$$Tb_S - Tb_{\text{acid}} \geq 30.0 \text{ K,} \tag{6b}$$

$$m \geq 0.15 \text{ wt./wt.,} \tag{6c}$$

$$Sl \leq 0.3 \text{ wt. \%.} \tag{6d}$$

MOLDES selected monofunctional solvents are alkyl substituted pyridines, higher alcohols, acids, ketones, and mixed paraffinic-aromatic esters. Polyfunctional solvents like hydroxyoctyl acetate are usually rejected because they exhibit low selectivity and high solvent losses. This selection should be regarded as tentative given the limitations of UNIFAC predictions for these mixtures, as was previously discussed. Experimental data are not available for the solvents that meet all physical restrictions.

### *MOLDES performance*

In the synthesis of paraffinic solvents for the extraction of ethanol from water using 15 groups, MOLDES selects 206 IMSs among 7,569 possible combinations and it then generates 73 SMSs (final solvents) from 3,040 final possible combinations. The computing time for this example was less than 90 s in a 286 personal computer. These results indicate that even though more powerful synthesis procedures are being proposed, they cannot match the simple combinatorial-partition approach. The main reason for this is that the combinatorial problem is still manageable due to lack of completeness of binary information in the VLE or LLE parameter tables.

## MOLDES Application to Extractive Distillation

The application of MOLDES to extractive distillation is illustrated for two separation problems.

**Table 13. MOLDES Solvent Selection for the Extractive Distillation of Toluene from Methylcyclohexane at $T=383.8$ K and $P=101.3$ kPa**

| Solvent | $\alpha_{B,A}$ | $\alpha^*_{B,A\,\mathrm{exp}}$ | $Sp$ (wt. %) | $PI\times100$ |
|---|---|---|---|---|
| $n$-Methylpirrolidone | 6.26 | | 78.47 | 63.1 |
| Nitrobenzene | 7.33 | 2.60 | 77.34 | 59.6 |
| 2-Nitrotoluene | 5.56 | 2.55 | 48.68 | 40.6 |
| Ethyl Aceto Acetate | 5.03 | 2.80 | 70.74 | 38.7 |
| Morpholine | 3.13 | | 24.5 | 35.9 |
| 2,4-Hexanedione | 3.91 | | 57.48 | 34.3 |
| Phenol | 3.21 | 2.95 | 46.53 | 34.1 |
| Acetophenone | 3.31 | 2.68 | 58.76 | 27.6 |
| Ethylene glycol diacetate | 4.36 | 3.10 | 34.63 | 23.5 |
| Furfural | 2.18 | 3.35 | 23.06 | 22.7 |
| 1-Hydroxy ethyl phenyl ether | 3.20 | | 39.57 | 21.1 |

$A$ = toluene
$B$ = methylcyclohexane
* = Experimental data (Berg, 1983).

### *Toluene from methylcyclohexane*

The toluene/methylcyclohexane separation has been studied by Berg (1983). MOLDES results for this problem are shown in Figure 5 for several families of potential solvents. The following restrictions were imposed for solvent screening:

$$\alpha_{\mathrm{methylcyc/toluene}} \geq 3.0, \tag{7a}$$

$$Sp \geq 30.0 \text{ wt. \%}, \tag{7b}$$

$$Tb_S - Tb_{\mathrm{toluene}} \geq 50 \text{ K}. \tag{7c}$$

Not all the solvents meet the increase in relative volatility restriction as it is shown in Figure 5a, but all the remaining solvents satisfy the solvent power constraint as it is shown in Figure 5b. Finally, the solvents that satisfy the boiling point restriction are shown in Figure 5c. Ketoacetates, diesters, diketones, and hydroxyl alkyl phenyl ethers are among the MOLDES selected solvents. Monofunctional solvents like ketones in Figure 5a are rejected due to their low effect on the increase of relative volatilities. Table 13 shows some of the solvents in Figure 5c, together with other MOLDES selected solvents and experimental relative volatilities reported by Berg. Some industrial solvents like $n$-methylpirrolidone and morpholine are also included. These solvents are represented as single groups in the VLE UNIFAC parameter table. A direct comparison between experimental and predicted relative volatility values is not possible, because the values reported by Berg are average relative volatility values obtained from a laboratory distillation unit working at total reflux, with a solvent concentration around 50%, and the predicted values are at infinite dilution. However, MOLDES methodology leads to a set of solvents recommended in the literature and generates also new solvent alternatives.

**Table 14. MOLDES Solvent Selection for the Extractive Distillation of $n$-Propyl Acetate from $n$-Propyl Alcohol at $T=368.0$ K and $P=101.3$ kPa**

| Solvent | $\alpha_{B,A}$ | $\alpha^*_{B,A\,\mathrm{exp}}$ | $Sp$ (wt. %) | $x_{ms}$ | $PI\times100$ |
|---|---|---|---|---|---|
| Ethylbenzene | 5.40 | 4.23 | 80.60 | 35.9 | 14.20 |
| Nonene | 4.64 | | 46.45 | 35.7 | 10.31 |
| $n$-Decane | 5.26 | 4.63 | 35.70 | 37.6 | 9.84 |
| Chlorobenzene | 3.71 | 4.70 | 86.00 | 33.7 | 9.78 |
| Decalin | 4.64 | 4.63 | 42.60 | 34.1 | 9.71 |
| Chloroctane | 4.95 | | 47.11 | 34.8 | 9.57 |
| Xylene | 3.95 | 4.37 | 67.10 | 40.9 | 9.10 |
| Dichlorobenzene | 3.10 | 4.79 | 60.93 | 30.6 | 6.89 |
| Mesitylene | 2.32 | 4.24 | 35.70 | 47.8 | 4.05 |

$A$ = $n$-propyl acetate
$B$ = $n$-propyl alcohol
* = Experimental data (Cepeda and Resa, 1984).

**Table 15. MOLDES Solvent Selection for the Extractive Distillation of $n$-Propyl Alcohol from $n$-Propyl Acetate at $T=368.0$ K and $P=101.3$ kPa**

| Solvent | $\alpha_{B,A}$ | $Sp$ (wt. %) | $x_{ms}$ | $PI\times100$ |
|---|---|---|---|---|
| Ethylene glycol | 3.54 | 56.23 | 50.7 | 11.27 |
| Dihydroxy propyl ether | 2.17 | 50.19 | 37.7 | 4.29 |

$A$ = $n$-propyl alcohol
$B$ = $n$-propyl acetate

### *N-propyl acetate from n-propyl alcohol*

The separation of $n$-propyl acetate from $n$-propyl alcohol was experimentally studied by Cepeda and Resa (1984). In this separation problem, the $n$-propyl acetate forms an azeotrope with the $n$-propyl alcohol ($x_{\mathrm{acetate}}=0.38$, $T_{\mathrm{aze}}=368$ K). Selected solvents should increase the relative volatility of the feed mixture and break the azeotrope. The same restrictions as in the previous example were taken (Eqs. 7a to 7c) for the MOLDES synthesis problem. The best solvents are shown in Table 14 together with experimental relative volatility values obtained by Cepeda and Resa. Now, a very important property is added: the minimum solvent molar fraction necessary to break the azeotrope ($x_{ms}$).

From the solvents in Table 14, chlorobenzene, chloroctane, and dichlorobenzene must be discarded because of their instability and toxicity. Ethylbenzene, nonene, $n$-decane, and xylenes appear to be the most attractive solvents. Cepeda and Resa recommended the use of xylenes and saturated hydrocarbons with more than 9 carbon atoms.

If the reverse problem is studied, that is, if propyl alcohol is the solute of the extractive distillation, a few solvents that meet all restrictions are synthesized that will meet all restrictions. Table 15 shows the properties of the best two solvents that would carry out this separation.

## Conclusions

The combinatorial-partition strategy for solvent synthesis has been extended to include aromatic and mixed aromatic-paraffinic compounds with low computing times for problems involving less than 15 groups. The problem of recovery of organic oxygenated solutes from aqueous solutions has been studied in order to compare MOLDES predictions with experimental information. Reasonable results have been obtained for all systems with the exception of the extraction of acrylic acid and phenol, when using the LLE parameter table. The use of the UNIFAC VLE parameter table for liquid extraction processes gives better or comparable results than the LLE parameter. The VLE table increases the range of application of MOLDES and the reliability of the solvent screening process. The selection of the solvent property constraints has been discussed for liquid extraction and extractive distillation and the effect of solvent constraints on solvent screening has been illustrated.

MOLDES solvent selections are based on UNIFAC group contribution predictions. Even though this predictive method has been extensively used, it is considered only as a first approximation for the estimation of solution properties. In this regard, MOLDES provides a procedure for a systematic search of a list of solvents, but with the limitations of parameter availability and prediction capability of UNIFAC.

## Notation

$\hat{h}, \hat{i}, \hat{j}, \hat{k}, \hat{l}, \hat{m}$ = number of attachments of type $H$, $I$, $J$, $K$, $L$, or $M$
$m$ = solute distribution coefficient
$MW$ = molecular weight
$P$ = pressure
$P^s$ = saturation pressure
$PI$ = solvent performance index for extractive distillation
$Sl$ = solvent loss
$Sp$ = solvent power
$T$ = temperature
$Tb$ = normal boiling point
$x$ = molar fraction
$x_{ms}$ = minimum solvent molar fraction to break the azeotrope

### *Greek letters*

$\alpha$ = relative volatility
$\beta$ = solvent selectivity
$\gamma^{\infty}_{i,j}$ = infinite dilution activity coefficient of compound $i$ in compound $j$
$\gamma_{S,\mathrm{aze.}}$ = activity coefficient of solvent evaluated at $x_{ms}$ in an azeotropic mixture of $A$ and $B$
$\rho$ = density

### *Subscripts*

$A$ = solute feed compound
$B$ = feed compound
$S$ = solvent

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