Application of CAMD in Separating Hydrocarbons by Extractive Distillation

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The solvent is the core of extractive distillation, and a suitable solvent plays an important role in the economical design of extractive distillation. Computer-aided molecular design (CAMD) has been applied to rapidly screen the solvents for separating hydrocarbons by extractive distillation. The systems of propane/propylene, n-butane/1-butene, and n-heptane/benzene, respectively, as the representatives of C3, C4, and C6 hydrocarbons were investigated, and the potential solvents were selected by means of CAMD. The designed results were further proven by experiments and process simulation. The mechanism for separating hydrocarbons by extractive distillation is based on the different fluidities of the electron cloud of C—C (no double bond), C═C (one double bond), and ACH (aromatic carbon ring) bonds and thus different interactions between solvent and hydrocarbon molecules. To improve the separation ability of the main solvent, one strategy is to add some additive that can form hydrogen bonding with the main solvent to make into a mixture. © 2005 American Institute of Chemical Engineers *AIChE J,* 51: 3114–3121, 2005

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Introduction

Extractive distillation is commonly applied for separating hydrocarbons with close boiling points, such as C4, C5, and C6 mixtures and so on.[1-3] In extractive distillation, an additional solvent (entrainer or separating agent) is used to alter the relative volatility of the components to be separated. In this way, it is possible to obtain one pure component at the top of one column and the other, together with the solvent at the bottom, which may then be easily separated in a secondary distillation column because of the high boiling point of the solvent. The solvent does not need to be vaporized in the extractive distillation process.

It is known that the solvent is the core of extractive distillation, and a suitable solvent plays an important role in the economical design of extractive distillation. However, it is tiresome to choose the best solvent from thousands of different substances for a given system through experiments. The computer-aided molecular design (CAMD) developed in the 1980s may break new ground in this aspect by largely reducing the amount of experimental work.[4-15] The application of CAMD in chemical engineering is mostly based on the UNIFAC group contribution. Incalculable molecules would be formulated by simply joining UNIFAC groups, if they were without any constraint. In accordance with certain combination rules, however, the size of the combinatorial problem can be greatly reduced and only then are the chemically feasible molecules generated. Furthermore, in terms of given target properties, the desired molecules are screened from chemically feasible molecules. The groups of UNIFAC provide building blocks for assembling molecules. CAMD is essentially the inverse of property prediction by group contribution. Given a set of desirable properties, it is proposed to find a combination of structural groups satisfying the property specifications. In most

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cases more than one solution is produced. Thus, a screening is needed because only one of the alternatives may be chosen for the specified problem. Moreover, such factors as corrosion, prices, source, azeotrope, and so on should be taken into consideration. Of course, this procedure is performed after CAMD.

Many studies have been done in such unit operations as gas absorption, liquid–liquid, and so on. However, the application of CAMD in exploring the separation mechanism of hydrocarbons by extractive distillation has rarely been systematically reported. In this work, CAMD is applied for screening the solvents of extractive distillation, and some common and important systems in industry are investigated.

CAMD Program

CAMD is conducted in the following four steps.

Step 1: group sorting and preselection

Groups are the basis of CAMD and molecular design makes full use of the group concept raised by Franklin,[16] which is built on the UNIFAC groups. The groups must be systematically ordered to facilitate their use. We adopt the approach proposed by Gani et al.[17-19] to sort the groups. That is, a certain group is characterized by the number of attachments present in a given group (or the valence number of the group) and the degree of difficulty that the group combines other groups (or the type of attachment). If a group belongs to several different classes, it means that this group takes on different types of characterization in different molecules.

The attachment types are indicated as ordered pairs (i, j), where i is the type of attachment and j is the number of i attachments. Five types of attachments are put forwarded for nonaromatic groups:

N = single molecules as a group having no attachment with other groups, such as H_2O
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, such as CH_2

For aromatic molecules, two new attachments are introduced:

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:

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

The chemically feasible molecules will be generated from the characterized UNIFAC groups in terms of combination rules. Not all of the UNIFAC groups need to be used in CAMD for extractive distillation. The groups may be prescreened according to the criteria: availability of binary parameters for the synthesis group and elimination of unsteady, corrosive, toxic compounds. For instance, some groups, that is, Cl^- and F^-, may cause corrosion to the equipment and must be avoided in the extractive distillation process.

Step 2: combination of groups

The greatest difficulty in CAMD is assembling groups into one molecule. To generate chemically stable molecules, the assembly must fit to the following rules:

- The chemical valence of a molecule must be zero.
- The neighborhood effect of groups must be avoided. Fortunately, many researchers[17-20] have discussed this rule from different perspectives and given the corresponding restriction conditions. Their work is helpful for us to program CAMD.
- In general, a molecule is composed of not more than eight groups and the polar groups cannot number more than three. The groups in a molecule must accord with the following attachment criterion: $K \leq M + J/2 + 2$ for aliphatic compounds; $I + H = 6$, $H \leq 2$, or $H \leq 3$ for aromatic compounds. For aliphatic–aromatic compounds these restrictions must be satisfied simultaneously; otherwise, this molecule is unsteady under normal conditions.
- The group parameters and group interaction parameters must be known in advance. We have collected a set of parameters for 109 subgroups and 51 main groups based on the original UNIFAC model. Some parameters directly come from literature values[21-25] based on the original UNIFAC model, whereas others are obtained by transformation from the modified UNIFAC model.[26-30] In total about 1200 binary interaction parameters of UNIFAC groups are present. The properties concerned can be calculated by using these parameters.

The combination procedure is carried out in such a manner that the only combinations considered are those resulting in the generation of chemically feasible structures. The combinations from a preselected number of groups and testing for their chemical feasibility take place simultaneously.

Step 3: prediction of target properties

For CAMD for extractive distillation, such properties as relative volatility at infinite dilution (α_{ij}^{∞}), selectivity at infinite dilution (S_{ij}^{∞}), solubility capacity (SP), molecular weight (MW), and boiling point (T_b) are important. Specification of the problem type identifies the corresponding target properties. Because not all of the target properties are computable, it is convenient to classify them as explicit target properties and implicit target properties. Prediction methods for explicit target properties are available and can be implemented automatically by computer. Prediction methods for implicit properties are not presently available and thus a combination of experience, information from the open references, and experiments are needed to determine them. The prediction methods for explicit properties are given in Table 1, where γ_i^{∞} is the activity coefficient of component i at finite dilution, P_i^0 is saturated pressure, and MW is molecular weight.

On the other hand, a databank of pure components—constituting the physical properties of about 500 compounds, such as molecular weight, normal boiling point, critical properties, vapor pressure constants in Antoine equation, ideal gas heat capacity, and the like—is also set up. If target properties can be sought in the databank, the values from the databank (not from calculation) are regarded as the ultimate results.

Step 4: sort order and selection of potential solvents

As we know, relative volatility (which is consistent with selectivity) is the most important among all the explicit prop-

Table 1. Explicit Properties Estimation for Screening Solvents

Property	Method
Relative volatility at infinite dilution[20,31]	$\alpha_{ij}^{\infty} = \frac{\gamma_i^{\infty} P_i^0}{\gamma_j^{\infty} P_j^0}$
Selectivity at infinite dilution[20,31]	$S_{ij}^{\infty} = \frac{\gamma_i^{\infty}}{\gamma_j^{\infty}}$
Solubility capacity[20]	$SP = \frac{1}{\gamma_i^{\infty}} \frac{MW_i}{MW_s}$
Molecular weight	Pure component data bank or by adding group parameters[32]
Normal boiling point	Pure component data bank or by adding group parameters[32–34]
Critical properties	Pure component data bank or Joback method[32,33]
Vapor pressure	Antoine equation or Riedel equation[32,33]
Azeotropic judgment	By drawing the curves of x (mole fraction in the liquid phase)–y (mole fraction in the vapor phase) to judge

erties. The solvent with the highest relative volatility is always considered to be the most promising solvent for a given separation task. For this reason, solvents are ranked in order of decreasing relative volatility (or selectivity). Moreover, azeotropic judgment is carried out in this step by calling the dew point subroutine. Its role is to determine whether the solvent can form azeotropes with the components to be separated and at which concentration. Because it takes extended CPU time to draw an x–y curve for each solvent and component to be separated, this function is set in the end applying to the potential solvents.

In extractive distillation it is necessary to evaluate such implicit properties as toxicity, cost, stability, and material source. The solvents that do not satisfy the requirement of implicit properties are crossed out from the order. The remaining solvents ranked in the front are possible to be the potential solvents we seek.

CAMD has been programmed with Visual Basic for Windows. This program can provide much important information for extractive distillation. CAMD is an easy-to-use software with a user-friendly interface. One with only slight knowledge of extractive distillation can become familiar with it within a short time. A flow diagram of CAMD program is illustrated in Figure 1. For the solvent mixture, one is the main solvent, the other is the additive. In CAMD, the first step is to find the main solvent; when the basic solvent is determined, the next step is to find the additive in the same way as single solvent.

Case Studies

The systems of propane/propylene, *n*-butane/1-butene, and *n*-heptane/benzene are investigated because they are commonly encountered in industry and may be separated by extractive distillation.[3]

The separation mechanism for separating hydrocarbons by extractive distillation is based on the different fluidities of the electron cloud of C—C (no double bond), C═C (one double bond), and ACH (aromatic carbon ring) bonds. The greater the fluidity, the easier can the group be polarized by the polar solvent. The fluidity of the electron cloud of C═C (or ACH) bond is greater than that of the C—C bond so that propane (or *n*-butane, *n*-heptane) is brought out as a light component and propylene (or 1-butene, benzene) as a heavy component (although the boiling point of *n*-heptane is higher than that of benzene). That is, propane (or *n*-butane, *n*-heptane) would be obtained as the overhead product in extractive distillation column, which is propylene (or 1-butene, benzene) and the solvent, the bottom product.

The system of n-heptane and benzene

It is assumed that *n*-heptane and benzene are taken on as the representatives of nonaromatics and aromatics, respectively, because aromatics and nonaromatics are mainly composed of them and their separation mechanism is consistent. Extractive distillation is used here for the separation of *n*-heptane and benzene, and the solvents are screened by means of CAMD. The restrictions for solvents in CAMD are listed as follows:

- Preselected group types: CH_3, CH_2, CH_3COO, CH_3CO, COOH, OH, CH_2CN, CH_2NH_2, ACH, $ACCH_3$, $ACNH_2$, ACOH, H_2O, CH_3OH, $(CH_2OH)_2$, acetonitrile (ACN), *N,N*-dimethylformamide (DMF), *N*-methyl-2-pyrrolidone (NMP), morpholine (Morph), furfural, dimethyl sulfoxide (DMSO)
- Expected group number: 1–6
- Maximum molecular weight: 150
- Minimum boiling point: 323.15 K
- Maximum boiling point: 503.15 K
- Temperature: 303.15 K
- Minimum relative volatility at infinite dilution: 5.0
- Minimum solubility capacity: 0.10

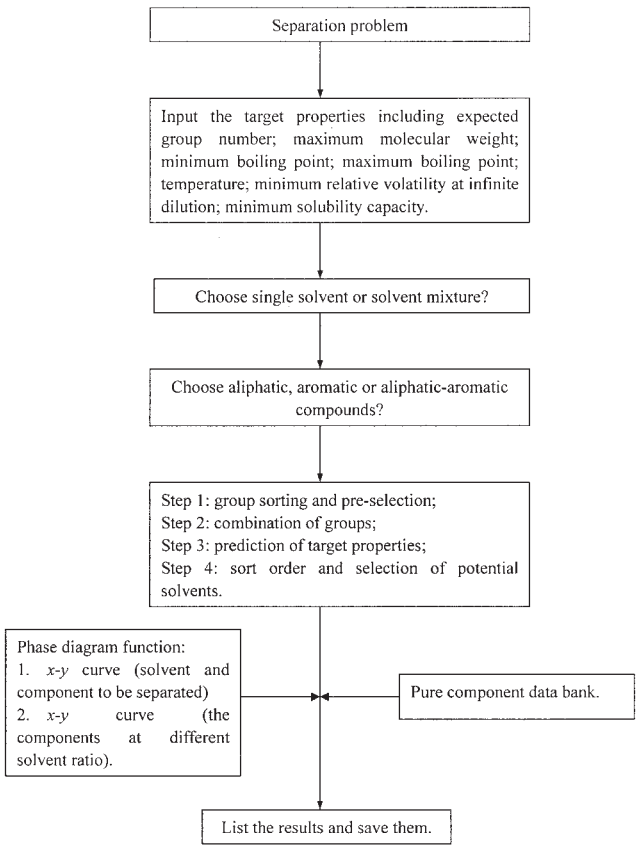

Figure 1. CAMD program.

Table 2. Results of CAMD for the Separation of *n*-Heptane (1) and Benzene (2) at $T = 303.15$ K

No.	Molecular Structure	MW	T_b (K)	α_{12}^{∞}	S_{12}^{∞}	SP	Azeotropic Judgment	
							1 and Solvent	2 and Solvent
1	DMSO	78.1	462.2	9.782	19.938	0.318	yes	no
2	CH_2CN—CH_2CN	80.0	495.3	8.759	17.853	0.312	yes	no
3	CH_3COO—CH_2—CH_2CN	113.0	474.3	7.026	14.321	0.354	no	no
4	DMF	73.1	426.15	5.767	11.754	0.686	yes	no
5	CH_2NH_2—CH_2CN	70.0	442.9	5.604	11.422	0.468	yes	no
6	NMP	99.1	477.2	5.552	11.317	0.756	no	no
7	CH_2NH_2—CH_2—COOH	89.0	486.3	5.242	10.685	0.543	no	no
8	ACN	41.0	354.8	5.134	10.465	0.621	yes	yes
9	CH_3COO—CH_2—CH_2—CH_2CN	127.0	497.2	5.086	10.366	0.417	no	no
10	OH—CH_2—CH_2CN	71.0	462.5	5.067	10.328	0.210	yes	no

By means of CAMD, the design results are obtained and listed in order of decreasing relative volatility at infinite dilution as shown in Table 2. Note that molecules 3, 5, 7, 9, and 10 are bought in chemical markets only with difficulty (or bought only at very expensive prices). From this perspective, they are excluded as the potential solvents. Furthermore, after considering such implicit properties as toxic (excluding molecules 2 and 4), boiling point (excluding molecule 8), and chemical stability (excluding molecule 1), only molecule 6, NMP, remains. NMP has many outstanding advantages as the solvent, such as nontoxicity, noninjurious, facility of ecological treatment, and high separation ability.

The reliability of NMP as a solvent has already been verified by our experiments.[2] However, CAMD goes a step further to provide a theoretical foundation for the selection of NMP. This also indicates that the designed results from CAMD are acceptable in this regard.

Process simulation of the separation of *n*-heptane and benzene by extractive distillation was made with PRO/II software. The process consisted of extractive distillation column with 30 theoretical plates and a solvent recovery column with 15 theoretical plates. The feeding mixture was composed of 45.0 wt % *n*-heptane and 55.0 wt % benzene with a flow rate 100 kg/h, and the feed/solvent volume ratio was 1:3. The extractive distillation column was operated at pressure 101 kPa and reflux ratio 0.5, whereas the solvent recovery column was operated at pressure 10 kPa and reflux ratio 1.0. When the concentration of benzene reached 99.5 wt % at the top of solvent recovery column, the yield ratio of benzene was 94.2%.

The system of propane (1)/propylene (2)

Because most of the propylene comes from pyrolysis gases, the separation of propylene in ethylene projects has great commercial significance. In ethylene projects, propylene is purified from a mixture mainly composed of propylene and propane. It is known that the pure-component boiling points are very close over a large range of pressure. However, in industry they are currently separated by ordinary distillation at pressures of 1910–2000 kPa with the number of theoretical trays at about 120 and reflux ratio up to 15–20. Extractive distillation is here used for the separation of propane and propylene, and the solvents are screened by means of CAMD. The restrictions for solvents in CAMD are listed as follows:

- Preselected group types: CH_3, CH_2, CH_3COO, CH_3CO, COOH, OH, CH_2CN, CH_2NH_2, H_2O, CH_3OH, $(CH_2OH)_2$, acetonitrile (ACN), *N,N*-dimethylformamide (DMF), *N*-methyl-2-pyrrolidone (NMP), morpholine (Morph), furfural
- Expected group number: 1–6
- Maximum molecular weight: 150
- Minimum boiling point: 323.15 K
- Maximum boiling point: 503.15 K
- Temperature: 303.15 K
- Minimum relative volatility at infinite dilution: 1.45
- Minimum solubility capacity: 0.10
- For the additive added to a main solvent, its concentration is 10% in mass fraction

By means of CAMD, the design results are obtained and listed in order of decreasing relative volatility at infinite dilution as shown in Table 3. It seems that for single solvent, the solvent with molecular structure of CH_2CN—CH_2CN (no. 1) has the largest relative volatility of propane to propylene, although it has strong toxicity. Therefore, ACN (no. 2) is regarded as the potential solvent. For the solvent mixture, the separation ability of the mixture of ACN and water (10 wt %) is a little lower than that of the mixture of NMP and water (10 wt %). However, the boiling point of NMP ($T_b = 477.2$ K) is much higher than that of ACN ($T_b = 354.8$ K). The extractive distillation process must be operated at high pressures because of the low boiling points of propane and propylene, which easily leads to decomposition of NMP. On the other hand, the separation ability of the mixture of ACN and water is higher than that of single ACN. Therefore, it may be advisable to select the mixture of ACN and water as the solvent for separating propane and propylene. One must be extremely cautious in the process design because ACN tends to hydrolyze, which contributes to the loss of ACN and corrosion of equipment during production.

The experimental results obtained by the methods of inert gas stripping and gas chromatography are also given in parentheses in Table 3. Details of the apparatus and experimental procedure used in this work have been described in a previous publication.[35] It can be seen that the mixture of ACN and water can apparently improve the relative volatility of propane to propylene, and α_{12}^{∞} is far away from unity. It is generally thought that because $\alpha_{12}^{\infty} > 1.20$, extractive distillation could be adopted for separating the components with close boiling points or forming azeotropes. From an economic perspective, the use of the solvent with the highest relative volatility will always give the lowest total annual cost of extractive distillation process.

Table 3. Results of CAMD for the Separation of Propane (1) and Propylene (2) at $T = 303.15$ K

No.	Molecular Structure	MW	T_b (K)	α_{12}^{∞}	S_{12}^{∞}	SP	Azeotropic Judgment: 1 and Solvent	Azeotropic Judgment: 2 and Solvent
Single solvent								
1	$CH_2CN—CH_2CN$	80.0	495.3	1.802	2.172	0.142	no	no
2	ACN	41.0	354.8	1.704 (1.620)	2.055	0.267	no	no
3	$CH_3COO—CH_2—CH_2NH_2$	103.0	421.9	1.634	1.970	0.451	no	no
4	$CH_3COO—CH_2—CH_2CN$	113.0	474.3	1.629	1.964	0.149	no	no
5	NMP	99.1	477.2	1.620	1.954	0.241	no	no
6	$CH_3CO—CH_2—CH_2NH_2$	87.0	417.5	1.576	1.900	0.406	no	no
7	$CH_3CO—CH_2—CH_2CN$	97.0	470.0	1.542	1.859	0.170	no	no
8	$CH_3COO—CH_2—CH_2—CH_2CN$	127.0	497.2	1.523	1.836	0.181	no	no
9	$CH_3COO—CH_2—CH_2—CH_2NH_2$	117.0	444.8	1.505	1.815	0.456	no	no
10	$CH_3CO—CH_2—CH_2—CH_2NH_2$	101.0	440.4	1.486	1.791	0.420	no	no
11	$CH_2NH_2—CH_2CN$	70.0	442.9	1.484	1.790	0.187	no	no
12	$CH_3CO—CH_2—CH_2—COOCH_3$	130.0	449.0	1.480	1.784	0.190	no	no
13	$CH_3COO—CH_2—CH_2—COOCH_3$	146.0	453.3	1.468	1.770	0.182	no	no
14	$CH_3CO—CH_2—CH_2—CH_2CN$	111.0	492.8	1.458	1.758	0.197	no	no
Additive added to ACN to make into a mixture (10 wt %)								
15	H_2O	18.0	373.2	1.846 (1.750)	2.226	0.248	no	no
Additive added to NMP to make into a mixture (10 wt %)								
16	H_2O	18.0	373.2	1.969	2.374	0.175	no	no

Process simulations of the separation of propane and propylene by ordinary distillation and by extractive distillation with the mixture of ACN and water as the solvent were respectively made with PRO/II software. The ordinary distillation column was operated at pressure 1910 kPa and reflux ratio 15.0 with 120 theoretical plates. The extractive distillation process consisted of four sections: extractive distillation column with 50 theoretical plates; stripping column with 10 theoretical plates; water scrubber column with 10 theoretical plates; and solvent recovery column with 20 theoretical plates. In the case of the feeding composition of propylene 82.0 wt %, feed rate 32,000 kg/h, production rate 26,500 kg/h, and molar composition of product propylene $\geq$ 99.3%, the extractive distillation process saved 13.2% reboiler load, 79.1% condenser load, and 25% theoretical plates when compared to ordinary distillation process.

The system of n-butane (1)/1-butene (2)

In the production of ethylene and/or propylene by pyrolysis of liquefied petroleum gas or naphtha, C4 mixtures are produced. In general, C4 mixtures mainly contain *n*-butane, isobutane, isobutene, 1-butene, *trans*-2-butene, *cis*-2-butene, 1,3-butadiene, and vinylacetylene (VAC). Earlier, we paid more attention to extracting 1,3-butadiene, which is an important raw material, from C4 mixtures. However, among the residua, *n*-butene (that is, the mixture of 1-butene, *trans*-2-butene, and *cis*-2-butene) is able to be used as one monomer of synthesizing polymers and one reactant of producing acetone by reacting with water. Isobutene can be selectively combined with methanol to make methyl *tert*-butyl ether (MTBE). Unfortunately, the separation of butane and butene has rarely been studied. Similarly, extractive distillation is here used for the separation of butane and butene, and the solvents are screened by means of CAMD. *n*-Butane and 1-butene are regarded as the key components. The restrictions for solvents in CAMD are the same as in the system of propane (1)/propylene (2).

By means of CAMD, the design results are obtained and listed in order of decreasing relative volatility at infinite dilution as shown in Table 4. For the solvent mixture, after such factors as source, toxic, and miscibility are taken into consideration, the first potential solvent is the mixture of ACN and water that are totally miscible, whereas the second potential solvent is the mixture of ACN and ethylenediamine (no. 18) that are also totally miscible.

Process simulation of the separation of *n*-butane and 1-butene by extractive distillation with the mixture of ACN and water as the solvent was performed with PRO/II software. The process consisted of extractive distillation column with 70 theoretical plates and solvent recovery column with 30 theoretical plates. The feeding mixture was composed of 6.1 wt % *n*-butane and 93.9 wt % 1-butene with a flow rate 2450 kg/h, and the feed/solvent mass ratio was 1:10. The extractive distillation column was operated at pressure 500 kPa and reflux ratio 5.0, whereas the solvent recovery column was operated at pressure 450 kPa and reflux ratio 4.0. When the concentration of 1-butene reached 99.0 wt % at the top of solvent recovery column, the yield ratio of 1-butene was above 95.0%.

Table 5 gives the number of molecules assembled with two to six groups from eight kinds of different groups (excluding molecular groups) for single solvents. It shows that if without any constraint, incalculable molecules would be formulated. After the constraints of steps 2 and 3 in CAMD, however, the number of chemically feasible molecules is greatly reduced, and thus the potential solvents can be rapidly screened.

Thermodynamic Analysis

By comparison of Tables 3 and 4, it is found that from numbers 1 to 13 the solvents screened by CAMD and their order in both systems is consistent. The reason may be explained by the similar molecular structure of C3 and C4 hydrocarbons (a difference of only one carbon chain) and the same separation mechanism.

The experimental results obtained by inert gas stripping and gas chromatography are also given in parentheses in Table 4. However, it is found that the mixture of ACN and ethylenedi-

Table 4. Results of CAMD for the Separation of Butane (1) and Butene (2) at $T = 303.15$ K

No.	Molecular Structure	MW	T_b (K)	α_{12}^{∞}	S_{12}^{∞}	SP	Azeotropic Judgment: 1 and Solvent	Azeotropic Judgment: 2 and Solvent
Single solvent								
1	$CH_2CN—CH_2CN$	80.0	495.3	1.780	2.172	0.111	no	no
2	ACN	41.0	354.8	1.684 (1.696)	2.055	0.238	no	no
3	$CH_3COO—CH_2—CH_2NH_2$	103.0	421.9	1.614	1.970	0.477	no	no
4	$CH_3COO—CH_2—CH_2CN$	113.0	474.3	1.609	1.964	0.122	no	no
5	NMP	99.1	477.2	1.601	1.954	0.225	no	no
6	$CH_3CO—CH_2—CH_2NH_2$	87.0	417.5	1.557	1.901	0.414	no	no
7	$CH_3CO—CH_2—CH_2CN$	97.0	470.0	1.524	1.859	0.143	no	no
8	$CH_3COO—CH_2—CH_2—CH_2CN$	127.0	497.2	1.505	1.836	0.157	no	no
9	$CH_3COO—CH_2—CH_2—CH_2NH_2$	117.0	444.8	1.487	1.815	0.491	no	no
10	$CH_3CO—CH_2—CH_2—CH_2NH_2$	101.0	440.4	1.468	1.791	0.437	no	no
11	$CH_2NH_2—CH_2CN$	70.0	442.9	1.466	1.790	0.161	no	no
12	$CH_3CO—CH_2—CH_2—COOCH_3$	130.0	449.0	1.462	1.784	0.168	no	no
13	$CH_3COO—CH_2—CH_2—COOCH_3$	146.0	453.3	1.451	1.770	0.161	no	no
Additive added to ACN to make into a mixture (10 wt %)								
14	H_2O	18.0	373.2	1.824 (1.880)	2.226	0.209	no	no
15	$CH_2CN—CH_2CN$	80.0	495.3	1.692	2.065	0.223	no	no
16	$OH—CH_2—CH_2CN$	71.0	462.5	1.649	2.012	0.219	no	no
17	$CH_3—CH_2—CH_2—CH_2—CH_3COO$	116.0	399.2	1.640 (1.725)	2.002	0.245	no	no
18	$CH_3CO—CH_2—CH_3$	72.0	352.8	1.631 (1.707)	1.990	0.251	no	no
19	$CH_2NH_2—CH_2NH_2$	60.0	390.4	1.626 (1.787)	1.984	0.238	no	no
20	CH_3OH	32.0	337.8	1.610	1.965	0.242	no	no
21	$OH—CH_2—CH_2NH_2$	61.0	443.5	1.607	1.961	0.225	no	no
22	$CH_3—CH_2—OH$	46.0	351.5	1.579 (1.713)	1.927	0.250	no	no
Additive added to NMP to make into a mixture (10 wt %)								
23	H_2O	18.0	373.2	1.945	2.374	0.139	no	no

amine also can give rise to higher relative volatility than single ACN or single ethylenediamine.

Why do the mixtures of ACN and water and that of ACN and ethylenediamine show good separation ability? This may be explained from Prausnitz and Anderson's solution thermodynamics.[36,37]

For the hydrocarbons to be separated by extractive distillation, selectivity (which is consistent with relative volatility) is related to the various energy terms leading to the desired nonideality of solution, which is the basis of extractive distillation, and can be expressed as

$$RT \ln S_{23} = [\delta_{1p}^2(V_2 - V_3)] + [V_2(\delta_{1n} - \delta_2)^2 - V_3(\delta_{1n} - \delta_3)^2] + [2V_3\xi_{13} - 2V_2\xi_{12}] \quad (1)$$

where subscripts 1 to 3 represent solvent, the light component, and the heavy component to be separated by extractive distillation, respectively; V is the molar volume, δ is Hansen's solubility parameter; and ξ is induction energy per unit volume.

The three bracketed terms in Eq. 1 show, respectively, the separate contributions of physical force to the selectivity, that is, the polar effect, the dispersion effect, and the inductive effect of the solvent. It is convenient to rewrite as

$$RT \ln S_{23} = P + D + I \quad (2)$$

where $P = \delta_{1p}^2(V_2 - V_3)$, $D = V_2(\delta_{1n} - \delta_2)^2 - V_3(\delta_{1n} - \delta_3)^2$, and $I = 2V_3\xi_{13} - 2V_2\xi_{12}$.

In general, the polar term P is considerably larger than the sum of D and I. Thus, Eq. 2 becomes

$$RT \ln S_{23} = \delta_{1p}^2(V_2 - V_3) \quad (3)$$

Equation 3 not only shows the effect of molecular size but also predicts that when one separates hydrocarbons of different molar volumes, the selectivity is sensitive to the polar solubility parameter. This indicates that the effectiveness of a solvent depends on its polarity, which should be large, and on its molar volume, which should be small.

In Tables 2–4, most of the solvents screened by CAMD are of two polar functional groups, showing high polarity. In addition, the influence of molar volume is investigated for the separation of *n*-butane (1) and 1-butene (2) with the solvents whose molecular structures are R—C≡N. It is assumed that the polar functional group C≡N is kept constant, but the carbon number in the R group changes. In this case the change of carbon number with relative volatility of *n*-butane to 1-butene at infinite dilution is shown in Figure 2. It can be seen that as the carbon number increases, the relative volatility decreases. This confirms that the solvent with high polarity and small molar volume will be desirable to produce a much higher relative volatility.

Table 5. Number of Molecules Assembled with Two to Six Groups from Eight Kinds of Different Groups (Excluding Molecular Groups) for Single Solvents

	Case 1	Case 2	Case 3
Without any constraint	2994	2994	2994
After step 2	112	112	112
After step 3	6	12	11

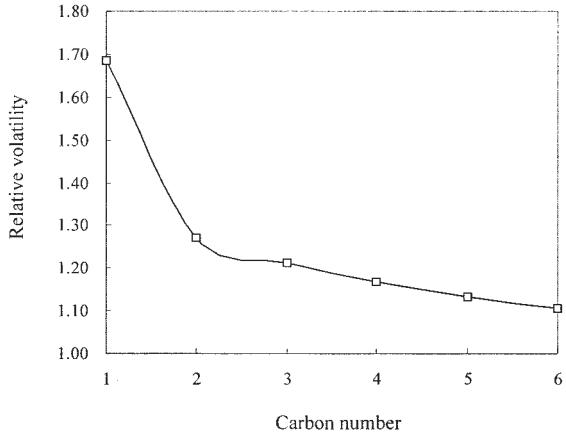

Figure 2. Influence of carbon number on relative volatility of *n*-butane to 1-butene at infinite dilution for the solvents whose molecular structures are R—C≡N: R = $C_nH_{2[infi]n+1}$ (*n* carbon number = 1, 2, 3, 4, 5, 6).

Besides, for a given separation task, the term $(V_2 - V_3)$ in Eq. 3 cannot be changed. For the components with similar molecular structures this value is even small. Therefore, to improve the relative volatility, the only way is to increase δ_{1p}, which can be fulfilled by introducing an additive into the main solvent. The schematic representation of the molecular interaction among main solvent (ACN), additive (water or ethylenediamine), and hydrocarbon is illustrated in Figure 3.

It is conceivable that hydrogen bonding is formed between molecules of ACN and ethylenediamine (or water) because ACN is a hydrogen bond acceptor and ethylenediamine (or water) is a hydrogen bond donor. This would result in the improvement of δ_{1p} by a transfer of electron cloud and thus intensify the interaction between the main solvent and the hydrocarbon. Therefore, relative volatility will increase in terms of Eq. 3. To verify this analysis, a set of inert gas stripping and gas chromatography equipment has been built to measure the relative volatility of *n*-butane (1) to 1-butene (2). The experimental results at different additive concentrations in the mixture of ACN and ethylenediamine are shown in Figure 4. It can be seen that the mixture of ACN and ethylenediamine performs more satisfactorily than single ACN.

Conclusions

CAMD has been programmed to screen the solvents for separating hydrocarbons by extractive distillation. The systems of propane/propylene, *n*-butane/1-butene, and *n*-heptane/benzene are investigated because they are commonly met in industry and may be separated by extractive distillation. By means of CAMD, it is found that for the separation of propane and propylene, the final potential solvent is ACN (no hydrolysis) or the mixture of ACN and water (hydrolysis); for the separation of *n*-butane and 1-butene, the final potential solvent is ACN (no hydrolysis) or the mixture of ACN and water (hydrolysis), although the mixture of ACN and ethylenediamine (no hydrolysis) also shows high separation ability; for the separation of *n*-heptane and benzene, the final potential solvent is NMP.

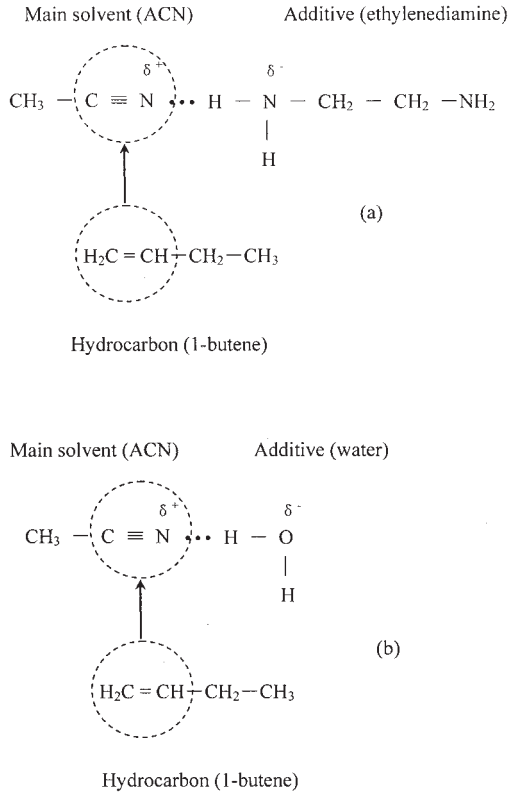

Figure 3. Molecular interaction among main solvent, additive, and hydrocarbon.

(a) ACN (main solvent), water (additive), and 1-butene system; (b) ACN (main solvent), ethylenediamine (additive), and 1-butene system.

For separating hydrocarbons by extractive distillation, the separation mechanism is consistent based on the different fluidities of electron cloud of hydrocarbon molecules. The solvent with high polarity and small molar volume will be desirable. To improve the separation ability of the main solvent, one

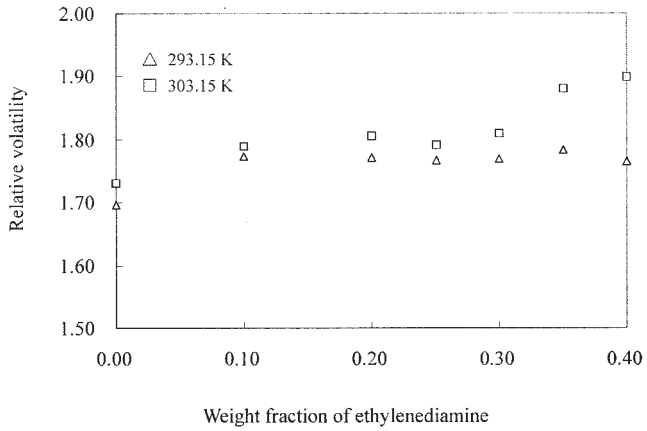

Figure 4. Influence of concentration of ethylenediamine in the mixture on relative volatility of *n*-butane to 1-butene at infinite dilution at 293.15 and 303.15 K.

strategy is to add some additive that can form hydrogen bonding with the main solvent to make into a mixture.

In this work the solvents of extractive distillation are restricted only to liquid solvents. In fact, so far they have been developed to include inorganic salts, polymers, and ionic liquids. Unfortunately, the group parameters of polymer and ionic liquid are vacant in the parameter table except that there are a few group parameters for inorganic salts. Even for liquid solvents, there are still about 54% of the UNIFAC group interaction parameters missing because experimental data are needed to fill them. This is where CAMD is limited. For the development of calculation techniques, it is thought that, besides the efforts to blend the computation methods of target properties with the screening of potential solvents and replenish the group parameters, were CAMD combined with other software (such as Excel, PRO/II, ASPEN PLUS), its functions would become stronger and the designed results would be more reliable.

Acknowledgments

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