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CONTENTS

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ABSTRACT

Extractive distillation is more and more commonly applied in industry, and becomes an important separation method in chemical engineering. This paper provides an in-depth review for extractive distillation. Separation sequence of the columns, combination with other separation processes, tray configuration and operation policy are included in process of extractive distillation. Since the solvent plays an important role in the

design of extractive distillation, such conventional and novel separating agents as solid salt, liquid solvent, the combination of liquid solvent and solid salt, and ionic liquid are concerned. The prominent characteristics of extractive distillation is that one new solvent with high boiling-point, i.e. separating agent, is added to the components to be separated, so as to increase their relative volatility. Selection of a suitable solvent is fundamental to ensure an effective and economical design. CAMD as a useful tool is applied for screening the solvents and thus reducing the experimental work. Theories from molecular thermodynamics, which can interpret the microscale mechanism of selecting the solvents, are also collected. To accurately describe the extractive distillation process, mathematical model is necessary. There are two types of mathematical models to simulate extractive distillation process, i.e. equilibrium (EQ) stage model and non-equilibrium (NEQ) stage model. The EQ stage model as an old method is widely used, but the NEQ stage model should be pay more attention. In the end comparison of extractive distillation and adsorption distillation, both of which belong to special distillation suitable for separating close boiling point or azeotropic components, is done, and it is shown that extractive distillation is more advantageous.

Key Words: Extractive distillation; Process; Solvent; Experiment technique; CAMD; Theory; Mathematic model.

1. INTRODUCTION

Extractive distillation is commonly applied in industry, and is becoming a more and more important separation method in petrochemical engineering. The product scale in industrial equipment is diverse, from several kilotons (column diameter about 0.5m) to hundred kilotons (column diameter about 2.5m) per year. It is mainly used in the following cases (Berg, 1983; Duan, 1978; Ewanchyna and Ambridge, 1958; Hafslund, 1969; Hilal et al., 2002). One application is separating hydrocarbons with close boiling point, such as C4, C5, C6 mixtures and so on, the other is the separation of mixtures which exhibit an azeotrope, such as alcohol/water, acetic acid/water, acetone/methanol, methanol/ methyl acetate, ethanol/ethyl acetate, acetone/ethyl ether and so on.

In extractive distillation, an additional solvent, i.e. 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 be separated easily in a secondary distillation column, due to a high boiling point of the solvent. The solvent doesn't need to be vaporized in the extractive

distillation process. However, in azeotropic distillation, which is also often used for the separation of close boiling point or azeotropic mixtures, both the solvent and components must be vaporized into the top of an azeotropic distillation column. Moreover, the amount of azeotropic solvent is usually large, which leads to large energy consumption compared to extractive distillation. For this reason, extractive distillation is more attractive than azeotropic distillation (Sucksmith, 1982). In recent years, an interesting special distillation method, i.e. adsorption distillation, has been proposed and in this work is compared with extractive distillation (See chapter 8).

The ease of separation of a given mixture with key components i and j is given by the relative volatility:

$$\alpha_{ij} = \frac{y_i/x_i}{y_j/x_j} = \frac{\gamma_i P_i^0}{\gamma_j P_j^0} \tag{1}$$

where x is molar fraction in the liquid phase, y is molar fraction in the vapor phase, γ is the activity coefficient, and P_i^0 is the pure component vapor pressure.

The solvent is introduced to change the relative volatility as far away from one as possible. Since the ratio of P_i^0/P_j^0 is constant for small temperature changes, the only way that the relative volatility is affected is by introducing a solvent which changes the ratio γ_i/γ_j. This ratio, in the presence of the solvent, is called selectivity S_{ij}:

$$S_{ij} = \left(\frac{\gamma_i}{\gamma_j}\right)_s \tag{2}$$

In some cases a significant change in operating pressure, and hence temperature, changes a_{ij} enough to eliminate an azeotrope.

Besides altering the relative volatility, the solvent should also be easily separated from the distillation products, that is, high boiling point difference between the solvent and the components to be separated is desirable. Other criteria, e.g. corrosion, prices, sources, etc. should also be taken into consideration. However, the relative volatility (which is consistent with selectivity) is the most important. When solvents are ranked in the order of relative volatility (or selectivity), the solvent with the highest relative volatility is always considered to be the most promising solvent for a given separation task. This may indicate that, from the viewpoint of economic consideration, the use of the solvent with the highest relative volatility (or selectivity) will always give the lowest total annual cost (TAC) of the extractive distillation process (Momoh, 1991). The economic evaluations were carried out by using many different solvents for separating three different binary mixtures: 2-methyl-butene/isoprene (Mixture A), n-butane/

trans-2-butene (Mixture B), and n-hexane/benzene (Mixture C). For each case a complete design and costing of the process was done by using cost estimating computer programs. Figures 1, 2, and 3 show, respectively, the ranking of solvent selectivity at infinite dilution with the TAC of extractive distillation process for separating 2-methyl-butene/isoprene, n-butane/trans-2-butene, and n-hexane/benzene mixtures for the various potential solvents.

It can be seen from Figures 1, 2, and 3 that as the solvent selectivity increases, in general, the total annual cost of the extractive distillation decreases. However, as selectivity increases to a high value, the matching of selectivity with the TAC is not perfect, which suggests how good or accurate the use of selectivity as a basis for screening solvents. Anyway, it indicates that the solvent with the highest selectivity has a potential as the best solvent.

Berg (1969) classified the liquid solvents into five groups according to their potential for forming hydrogen bonds. However, it is found by much experience that Class I and Class II, which are a highly hydrogen bonded liquids, are successful solvents in most cases.

Class I: Liquids capable of forming three dimensional networks of strong hydrogen bonds, e.g. water, glycol, glycerol, amino alcohols, hydroxylamine, hydroxyacids, polyphenols, amides, etc. Compounds such as nitromethane and acetonitrile also form three dimensional hydrogen bond networks, but the bonds are much weaker than those involving OH and NH groups. Therefore, these types of compounds are placed in Class II.

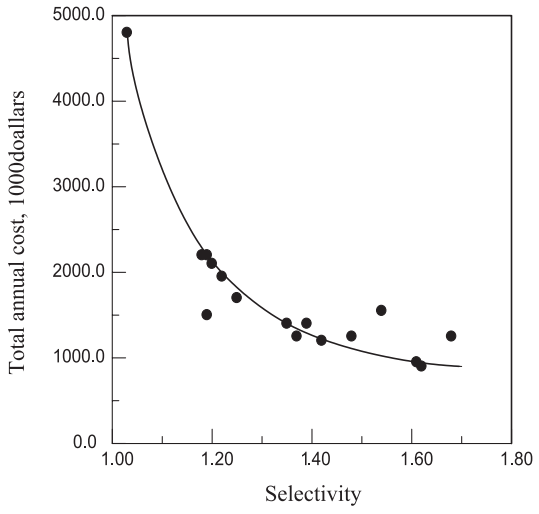

Figure 1. The effect of solvent selectivity on the total annual cost of an extractive distillation operation (2-methyl-1-butene/isoprene); adapted from Momoh (1991).

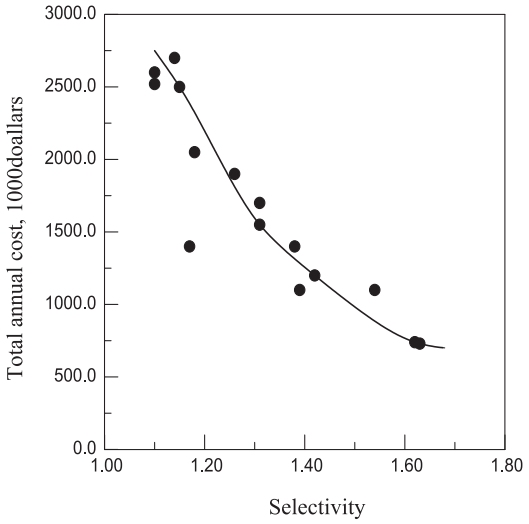

Figure 2. The effect of solvent selectivity on the total annual cost of an extractive distillation operation (n-butane/trans-2-butene); adapted from Momoh (1991).

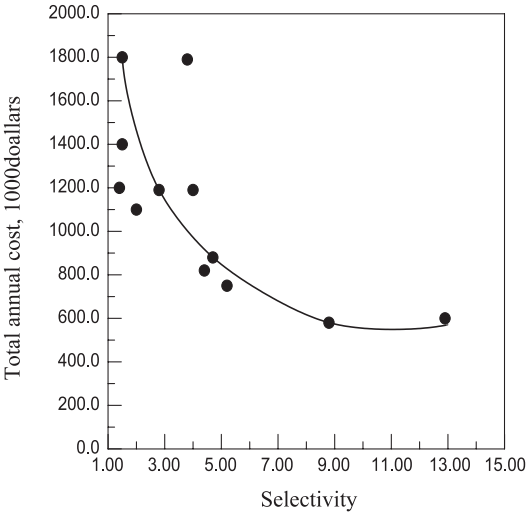

Figure 3. The effect of solvent selectivity on the total annual cost of an extractive distillation operation (n-hexane/benzene); adapted from Momoh (1991).

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Table 1. Examples of the single liquid solvents commonly used in the extractive distillation.

No.	Components to be separated	Solvents as the separating agents
1	Alcohol (ethanol, isopropanol, tert-butanol) and water	Ethylene glycol
2	Acetic acid and water	Tributylamine
3	Acetone and methanol	Water, ethylene glycol
4	Methanol/ methyl acetate	Water
5	Propylene and propane	ACN
6	C4 hydrocarbons	Acetone, ACN (acetonitrile), DMF (N,N-dimethylformamide), NMP (N-methyl-2-pyrrolidone), NFM (N-formylmorpholine)
7	Alcohol (ethanol, isopropanol) and water	DMF
8	C5 hydrocarbons	DMF
9	Aromatics and non-aromatics	DMF, NMP, NFM

Class II: Other liquids composed of molecules containing both active hydrogen atoms and donor atoms (oxygen, nitrogen and fluorine), e.g. alcohols, acids, phenols, primary and secondary amines, oximes, nitro-compounds with alpha-hydrogen atoms, nitriles with alpha-hydrogen atoms, ammonia, hydrazine, hydrogen fluoride, hydrogen cyanide, etc.

Table 1 illustrates some examples of the single liquid solvents commonly used in the extractive distillation (Min et al., 2002; Shealy et al., 1987; Wu et al., 1988), and proves the idea of Berg to be reliable.

For simplification, it is noted herein that the words ''separating agents'' and ''solvents'' are confused and have the same meaning in what follows.

2. PROCESS OF EXTRACTIVE DISTILLATION

In this section, process of extractive distillation is discussed from four aspects: column sequence, combination with other separation processes, tray configuration and operation policy, which is indispensable in the process design.

2.1. Column Sequence

In general, for a two-component system the extractive distillation process is made up of two columns, i.e. an extractive distillation column

and a solvent recovery column. The two column process is diagrammed in Figure 4 where components A and B to be separated are respectively obtained from the top of two columns, and the solvent S is recovered in the solvent recovery column and recycled (Chen at al., 2003; Lei et al., 2002a).

For a multi-component system, the arrangement of column sequence may be complicated, but is developed from the above two column process. An interesting example is for the separation of C4 mixture (Bannister and Buck, 1969; Barba et al., 1978; Coogler, 1967; King and Mondria, 1967; Klein and Weitz, 1968; Takao, 1966, 1979).

Among C4 mixture (butane, butene-1, trans-butylene-2, cis-butylene-2, 1,3-butadiene and vinylacetylene (VAC)), 1,3-butadiene is a basic organic raw material. In industry, 1,3-butadiene is usually separated from C4 mixtures by extractive distillation with the solvent acetronitile (ACN). On the basis of the two column process, the extractive distillation process for separating 1,3-butadiene is designed. Accordingly, the process designed is in the following sequence: extractive distillation (column 1) – solvent recovery (column 2) – extractive distillation (column 3) – solvent recovery (column 4), and is illustrated in Figure 5. In this case, butane and butene are regarded as one part and used for fuel.

In Figure 5 the feedstock flows into the extractive distillation column 1. The solvent S enters the top sections of columns 1 and 3. The mixtures of butane and butene are escaped from the top of column 1 while VAC from the top of column 4. The product, 1,3-butadiene, is obtained from the top of column 3. The solvent S is recovered in columns 2 and 4 and

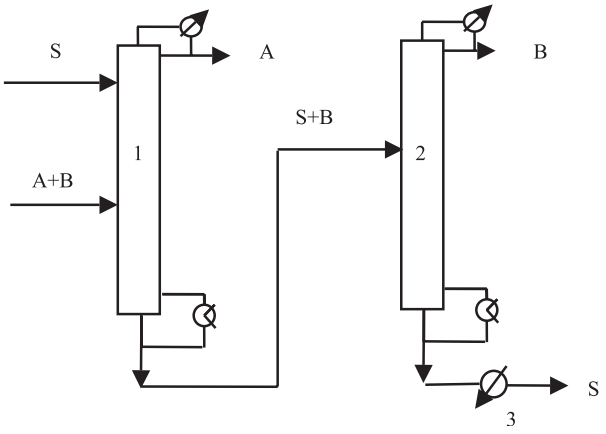

Figure 4. The two column process for extractive distillation. 1. Extractive distillation column; 2. solvent recovery column; 3. heat exchanger.

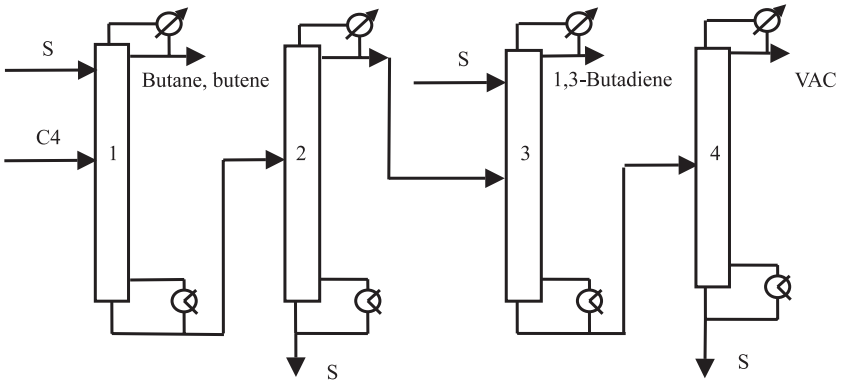

Figure 5. The extractive distillation process designed for separating C4 mixture.

recycled. It can be seen that column 2 is unnecessary and can be eliminated because the solvent is still needed in the following column 3 and need not be separated. At the same time, much energy is consumed because butadiene-1,3 goes through the unnecessarily repeated evaporation and condensation. The current process for separating C4 mixture with ACN is shown in Figure 6.

The product, 1,3-butadiene is obtained from the top of column 2. Alkyne hydrocarbons mainly containing VAC and drawn out through stream SL1, are removed from flash column 3. But SL2 stream is also returned

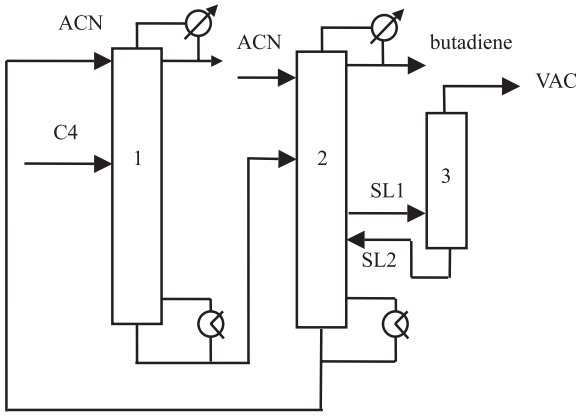

Figure 6. The current process of extractive distillation with ACN method for separating C4 mixture; adapted from Lei et al. (2002b).

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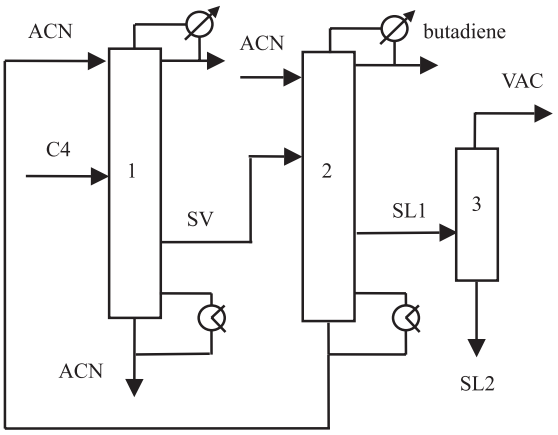

Figure 7. The optimum process of extractive distillation with ACN method for separating C4 mixture. 1. The first extractive distillation column; 2. the second extractive distillation column; 3. flash column; adapted from Lei et al. (2002b).

into column 2. This is to say that column 2 and column 3 are thermally coupled. However, there exists an obvious disadvantage in the current extractive distillation process, that is, the liquid load is very high in the lower section of column 2, which has negative influence on the tray efficiency and decreasing production capacity of 1,3-butadiene. It is the current case that the demand for 1,3-butadiene goes up gradually year by year. Moreover, the thermal coupling between columns 2 and 3 leads to the difficulty in operation and control.

To solve this problem, a new optimization process was put forward as shown in Figure 7. The vapor stream SV is drawn from the lower section of the first extractive distillation column 1 into the second extractive distillation column 2. SL1 mainly containing ACN and alkyne hydrocarbons is flashed in column 3, and the solvent coming from SL2 is recycled. It can be seen that the thermal coupling in the optimization process is eliminated and operation and control would be more convenient.

By simulation it is found that the liquid load in the lower section of the second extractive distillation column 2 is effectively decreased from 52,000kg/hr to 12,000kg/hr, about 77.0% of the original process, under the same production capacity of 1,3-butadiene 5200kg/hr (Lei et al., 2002b). In other words, this demonstrates that it is possible to farther increase the yield of butadiene on the basis of old equipment.

On the other hand, the comparison of heat duties on reboilers Q_R and condensers Q_C for Figure 5 to Figure 7 is done and listed in Table 2, where

Table 2. The comparison of heat duties of three processes.

	The figure 5 process		The figure 6 process		The figure 7 process	
No.	Q_C	Q_R	Q_C	Q_R	Q_C	Q_R
Column1	1161.5	2936.3	1161.5	2936.3	1163.6	4693.0
Column 2	1183.3	1984.7	1122.6	2545.1	1122.3	1178.0
Column 3	1122.0	1728.1	0.0	0.0	0.0	0.0
Total duty	3466.8	6649.1	2284.1	5481.4	2285.9	5871.0

the heat duties on reboilers and condensers are neglected in the column of separating VAC and solvent due to the very much smaller values than those of other columns.

It can be seen from Table 2 that heat duties on reboilers Q_R and condensers Q_C are the greatest in the Figure 5 process, and those are approximately equal in the Figures 6 and 7 processes, where 1,3-butadiene goes through the minimum number of evaporation and condensation. Therefore, it indicates that the Figure 7 process is the best from the aspects of equipment investment, energy consumption and production capacity.

However, in the past we only paid more attention on extracting 1,3-butadiene from C4 mixture. Indeed 1,3-butadiene is an important raw material, which is used for the preparation of synthetic rubber, e.g. the copolymers of butadiene and styrene. But it is a pity that the residual C4 mixture has always been burned as fuel. Until recently, many plants require the residual C4 mixture to be utilized more reasonably. Among the residua, n-butene (i.e. 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) (Eldridge, 1993; Ren et al., 1998; Safarik and Eldridge, 1998; Wang et al., 1999). Butane is still used as fuel. Therefore, the residual C4 mixture can be used in many respects, not only as fuel. Only are the useful C4 components separated from mixtures, the reasonable utilization is possible.

C4 mixture can be divided into four parts: butane (n-butane and isobutane), butene (n-butene, isobutene), 1,3-butadiene and VAC. N-butene and isobutene are regarded as one part, which is based on the consideration that isobutene is easy to be removed from n-butene by reacting with methanol. Those four parts have different fluidity of electron cloud, the sequence being butane < butene < 1,3-butadiene < VAC. Therefore, the interaction force between the polar solvent and C4 mixture is different, and the corresponding

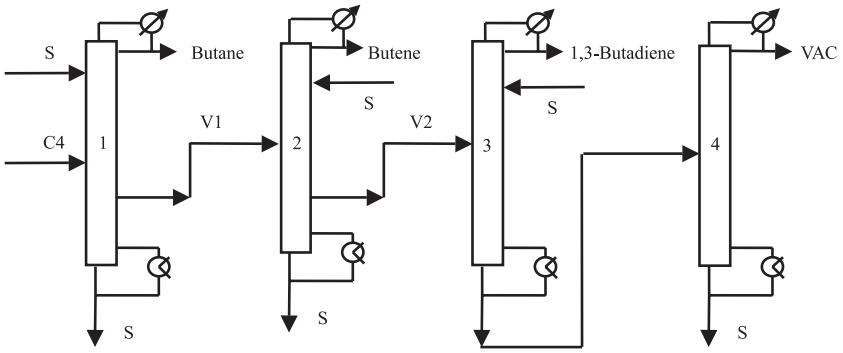

Figure 8. A new process for separating butane, butene, 1,3-butadiene and VAC.

order is that butane < butene < 1,3-butadiene < VAC. Thus C4 mixture can be separated in series by extractive distillation.

In terms of the above optimization process of separating 1,3-butadiene from C4 mixtures, it is straightforward to have a new process for separating butane, butene,1,3-butadiene and VAC in series, which is diagrammed in Figure 8.

It is evident that the new process has the advantages in equipment investment, energy consumption and production capacity. That is to say, for the very complicated separation of C4 mixture, we can still deduce the most optimum process step by step from the simplest two column process of extractive distillation as shown in Figure 4.

2.2. Combination with Other Separation Processes

As is said in the 1st chapter, extractive distillation is used more often than azeotropic distillation because of low energy consumption and flexible selection of the possible solvents. However, anything has its defects, and extractive distillation is not exceptive. For instance, comparing with azeotropic distillation, extractive distillation can't obtain a very high purity of product because the solvent coming from the bottom of solvent recovery column more or less contains a little impurity which influences the separation effect. Moreover, comparing with liquid–liquid extraction, extractive distillation consumes much more energy. So it is advisable to combine extractive distillation with another separation process such as azeotropic distillation, liquid–liquid extraction and so on.

2.2.1. Combination of Extractive Distillation and Azeotropic Distillation

Extractive distillation can't obtain a very high purity of product, but consumes less energy; however, azeotropic distillation can obtain a very high purity of product, but consumes much more energy. Therefore, a separation method, i.e. the combination of extractive distillation and azeotropic distillation is proposed (Lei et al., 1999), which eliminates the disadvantages of both extractive distillation and azeotropic distillation, and retains the advantages of them. This method has been used for the separation of 2-propanol (IPA) and water while the high purity of 2-propanol over 99.8%wt is required. The process of this method is diagrammed in Figure 9, where column 1, column 2, column 3 and column 4 are extractive distillation column, solvent recovery column (separating agent S_1 for extractive distillation), azeotropic distillation column and solvent recovery column (separating agent S_2 for azeotropic distillation), respectively.

This process is designed according to the sequence, firstly extractive distillation which ensures low energy consumption, and then azeotropic distillation which ensures high purity of 2-propanol as product. But this sequence can't be in reverse. Otherwise, high purity of 2-propanol can't be obtained.

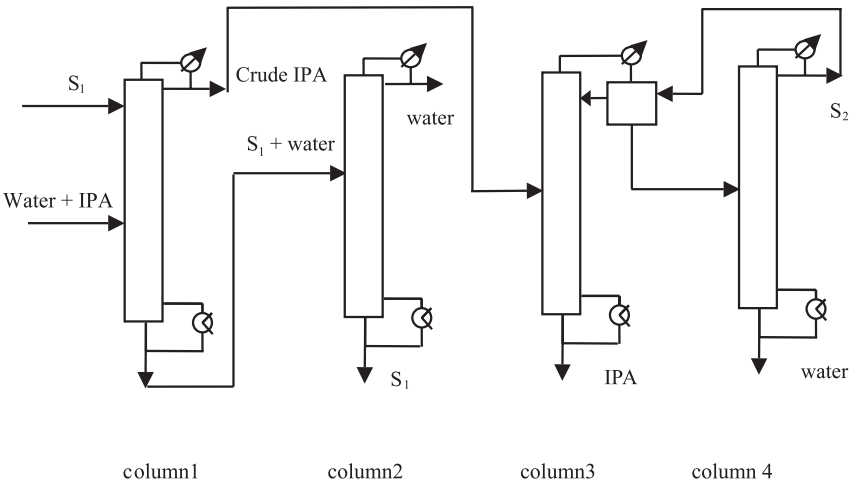

Figure 9. The process of the combination of extractive distillation and azeotropic distillation.

In addition, the energy consumption of this process is greater than that of extractive distillation, but less than that of extractive distillation. So it is concluded that this process is especially suitable for separations requiring high purity of product. For instance, in the case of separating acetic acid and water, the concentration of acetic acid in water below 20ppm is required in industry.

2.2.2. Combination of Extractive Distillation and Liquid–Liquid Extraction

This method has been sucessfully used for the recovery of benzene and toluene from pyrolysis hydrogenation gasoline fraction (Tian et al., 2001a; Wang et al., 2002). The mixture of benzene and toluene is firstly separated into two parts, i.e. one mainly containng benzene and the other mainly containing toluene. Then the rich-benzene mixture is dealt with by extractive distillation, while the rich-toluene mixture is dealt with by liquid–liquid extraction. The solvent used in these two processes is the same, sulfolane.

The reason why extractive distillation is selected for the separation of the rich-benzene mixture is that its boiling-point is lower than that of rich-toluene mixture, and thus the boiling-point difference between the rich-benzene mixture and the solvent is great enough, which facilitates the solvent recovery. However, the boiling-point difference between the rich-toluene mixture and the solvent is relatively small, which may not accord with the solvent criteria. Therefore, it is wise to select liquid–liquid extraction for the separation of the rich-toluene mixture.

The practical result from the Aromatics Plant of Yangzi Petrochemical Company with a capacity of 360kt a year showed that the the freezing point of benzene obtained by this method was 5.48°C, the sulfur content in benzene was less than 0.5 μg/g, and the non-aromatics content in toluene was less than 1000 μg/g. The recovery yield of benzene and toluene was 99.9% and 99.1% respectively. This proves that the combination of extractive distillation and liquid–liquid extraction is effective for the recovery of benzene and toluene from pyrolysis hydrogenation gasoline fraction.

2.3. Tray Configuration

One prominent characteristics of extractive distillation is that the solvent ratio (namely the mass ratio of solvent and feed) is very high, generally 5–8, which restricts increasing capacity. Accordingly, the liquid load is very large in the extractive distillation column, but the vapor load is relatively small. So when we design the extractive distillation column, more attention should be paid on the channels of passing liquid phase.

In most cases, either tray column or packed column can be adopted. However, if the extractive distillation column is operated under the middle or even high pressure such as the separation of C3, C4 and C5 mixtures, or if the components to be separated are easy to polymerize such as the separation of C5 mixture, then it is better to choose tray column. Herein, two types of plate trays used in the extractive distillation column are introduced (Department of Chemical Engineering, 1975; Duan et al., 1997; Research group on trays, 1977; Lei et al., 2002b; Li et al., 2001; Li and Zhang, 2001; Peng et al., 1996; Song et al., 2001).

Under the middle or even high pressure, the plate trays, especially double overflow trays, are generally used as internal fittings. Both double overflow valve trays and double overflow slant-hole trays have ever been adopted. However, it is reported that, if double overflow valve trays are replaced by double overflow slant-hole trays in a column for separating propane and propylene, the feeds to be treated are raised above 50% with a tray efficiency similar to or higher than that of the valve trays and an energy save of 10% by decreasing pressure drop to about 1/3 of the original.

Slant-hole trays, very excellent and extensively applied in the industry, has opposite stagger arrangement of slant-holes, which causes rational flowing of vapor and liquid phases, level blowing of vapor, permission of a large vapor speed, no mutual interference, steady liquid level and high efficiency of trays. On the basis of studying and analyzing the columns with multiple downcomer (MD) trays, a new-type multi-overflow compound slant-hole trays were invented, which adopt the downcomer similar to MD trays. The number of downcomers used is not too many, but only two. The downcomer has the feature of simple structure, longer flowing distance of liquid, higher capacity of column and high efficiency of trays. The configuration of the double overflow slant-hole trays is illustrated in the reference (Lei et al., 2002b). In terms of the vapor and liquid load of the extractive distillation column, the tray parameters are obtained by a computer program for tray design. Of course, it should be mentioned that the designed values are within the range of normal operation condition.

In the case that the components to be separated are easy to polymerize, the big-hole sieve trays are desirable. For instances, for the separation of the C5 mixture, the key components being pentene and isoprene, it is well-known that the polymerization reactions among unsaturated hydrocarbons take place, and influence the normal operation of the column while the conventional valve trays are employed. However, in this case the big-hole sieve trays with the hole diameter of 10–15mm are effective because the holes with large diameter prevent the trays from jam due to the formation of polymer. In addition, this type of trays eliminates the gradient of liquid layer and causes the rational flowing of vapor and liquid phases on the tray,

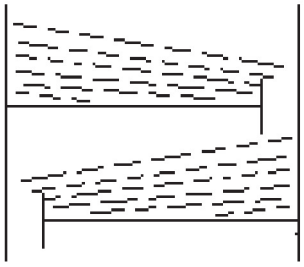

Figure 10. The gradient of liquid layer on the traditional trays.

with the help of directed holes arranged for decreasing the radial mix and bubble promoter installed in the outlet of the downcomer.

Figures 10 and 11 illustrate the gradient of liquid layer on the traditional trays and the improved gradient of liquid layer on the big-hole sieve trays, respectively. Figure 12 shows the flowing direction of liquid phases on the big-hole sieve trays. This manifests that the flowing of liquid phases on the big-hole sieve tray is indeed rational.

2.4. Operation Policy

We know that the simplest extractive distillation process is made up of two columns, i.e. an extractive distillation column and a solvent recovery column. Herein, we call it two column process. However, at some times (not often), only one column, which is either as extractive distillation

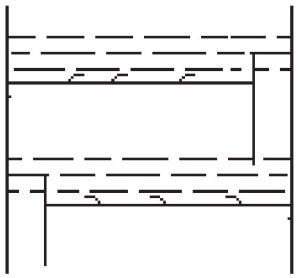

Figure 11. The gradient of liquid layer on the big-hole trays.

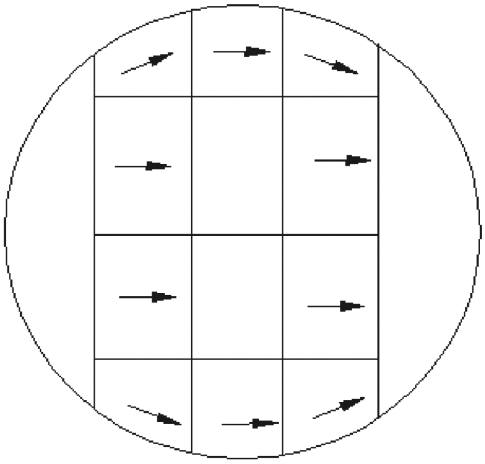

Figure 12. The flowing direction of liquid phases on the big-hole trays. *(Go to www.dekker.com to view this figure in color.)*

column or as solvent recovery column, is employed in the extractive distillation process. Herein, we call it single column process.

2.4.1. Two Column Process

For extractive distillation, two column process is often adopted. The two column process can be operated either in the batch way or in the continual way. In the continual way, two columns are operated at the same time, while in the batch way, there is still one column left no run.

Frankly speaking, we like the continual way rather than the batch way because the batch operation is tedious and the production efficiency is very low. However, the reason why the batch way is carried out comes from the solvent recovery column. Due to the very high boiling point of the solvent, the solvent recovery column has to be operated at vacuum pressure in order to decrease the temperature of the bottom and thus prevent the solvent from decomposition. Moreover, at some time there may be a strict requirement for the purity of the recycled solvent. All these lead to the difficulty of the continual operation in the solvent recovery column. But a strategy to solve them is by decreasing the boiling point of the solvent and canceling the vacuum system (See the 3rd chapter).

However, in the fine chemical engineering, the batch way is often used. Although it is complicated, the amount of treated feed is yet not many.

2.4.2. Single Column Process

For the single column process, there are two situations: batch mode and semi-continuous mode (Bai et al., 2001; Cui et al., 2002; Lang et al., 1994; Milani, 1999; Mujtaba, 1999; Safrit et al., 1995). In the batch mode, the solvent is charged in the reboiler with the feed mixture at the beginning of operation. Therefore, it limits the amount of feed mixture which can be processed as the reboiler has a limited capacity. This increases the number of batches to be processed in a campaign mode operation. In this mode, finding the optimum feed charge to solvent ratio is an important factor to maximize the productivity.

In the semi-continuous mode, the solvent is fed to the column in a semi-continuous fashion at some point of the column. There can be two strategies in this mode of operation as far as charging of the initial feed mixture is concerned.

1. Full charge. In this strategy the feed mixture is charged in the reboiler to its maximum capacity at the beginning of operation. For a given condenser vapor load, if the reflux ratio and the solvent feed rate are not carefully controlled, the column will be flooded.
2. Fractional charge. ''Full charge'' is not a suitable option to achieve the required product specifications for many azeotropic mixtures in a given sized column, operating even at the maximum reflux ratio, because the amount of solvent required in such separations is more than those that the column can accommodate without flooding. Mujtaba, (1999) proposed a fractional feed charge strategy for this type of mixture. In this strategy the feed mixture is charged to a certain fraction of the maximum capacity. The column can operate at a reflux ratio greater than maximum reflux ratio for some period until the reboiler level reaches to its maximum capacity.

However, it can be easily deduced that for batch mode and semi-continuous mode, the latter is more promising because this mode can deal with much more products in the same column. A complete batch extractive distillation of semi-continuous mode consists of the following steps:

1. Operation under total reflux without solvent feeding.
2. Operation under total reflux with solvent feeding. For decreasing the concentration of the less volatile component (LVC) in the distillate, this step is not absolutely necessary because the first part

of the distillate containing too much of the LVC can be recycled to the next charge.

3. Operation under finite reflux ratio with solvent feeding (production of the more volatile component (MVC)).
4. Operation under finite reflux ratio without solvent-feeding (separation of the LVC from the solvent). Before the start of the production of LVC an off-cut can be taken.

It should be noted that the holdup on the reboiler must not exceed the maximum capacity at any time within the entire operation period to avoid column flooding.

Many researchers focus on exploring the semi-continuous mode in such aspects as simulations, improving equipment with external middle vessel and so on, among which batch extractive distillation with external idle vessel is an interesting topic. The typical process and apparatus are diagrammed in Figure 13.

In one example, the packed column with a 38mm diameter was composed of three parts, i.e. scrubbing section, rectifying section and stripping section. The scrubbing section was packed to a height of 150mm with 2.5×2.5 Dixon rings, and the rectifying and stripping were, respectively, packed to a height of 500mm with 2.5×2.5 Dixon rings. The external

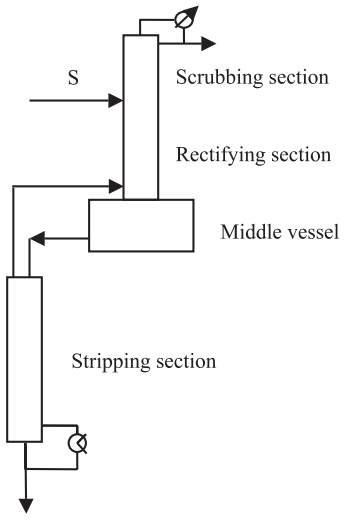

Figure 13. Single column process with an external middle vessel.

middle vessel is a 2000ml agitated flat bottom flask. The materials to be separated were charged to the middle vessel. The liquid flow from the middle vessel to the stripping section was controlled by an electric-magnetic device. The column was operated under the following steps:

1. Operation under total reflux without solvent feeding;
2. Operation under total reflux with solvent feeding;
3. Operation under finite reflux ratio and total reboiler ratio with solvent feeding (production of the more volatile component from the top of the column, while no production of solvent from the bottom);
4. Operation under finite reflux ratio and finite reboiler ratio with solvent feeding (production of more volatile component from the top and solvent from the bottom of the column simultaneously);
5. Operation under finite reflux ratio and finite reboiler ratio without solvent feeding (production of slop cut or less volatile component from the top while solvent from the bottom);
6. When the less volatile component or solvent in the middle vessel reaches the required purity or there is only a little liquid in the middle vessel, the operation is stopped.

The operation and simulation of this process, i.e. extractive distillation in a batch column with a middle vessel, is very complex, but it has many advantages such as flexibility, multi-component separation in one column and so on. It is especially suitable for the batch extractive distillation with large solvent ratio. However, when the boiling point of solvent is very high while the boiling point of the components to be separated are low, it is inconvenient to use the column, since the reboiler needs a high temperature heat resource.

3. SOLVENT OF EXTRACTIVE DISTILLATION

The two factors that influence the extractive distillation process are separation process and solvents (or separation agents). Assuming that the separation process is determined, the task is to select the basic solvent with high separation ability. When a basic solvent is found, this solvent should be further optimized to improve the separation ability and to decrease the solvent ratio and liquid load of the extractive distillation column.

The solvent is the core of extractive distillation. It is well-known that selection of the most suitable solvent plays an important role in the economical design of extractive distillation. Excellent solvents should at least

decrease the solvent ratio and the liquid load of the extractive distillation column, and make the operation easily implemented. Up to date, there are four kinds of solvents used in extractive distillation, i.e. solid salt, liquid solvent, the combination of liquid solvent and solid salt, and ionic liquid, which are discussed in detail later.

3.1. Extractive Distillation with Solid Salt

3.1.1. The Definition of Extractive Distillation with Solid Salt

In certain systems where solubility permits, it is feasible to use a solid salt dissolved into the liquid phase, rather than a liquid additive, as the separating agent for extractive distillation. The extractive distillation process in which the solid salt is used as the separating agent is called extractive distillation with solid salt. However, herein, the ionic liquids are not included in the solid salts although they are a kind of salts. Ionic liquid as a special separating agent will be discussed in what follows.

The so-called ''salt effect in vapor-liquid equilibrium (VLE)'' refers to the ability of a solid salt which has been dissolved into a liquid phase consisting of two or more volatile components to alter the composition of the equilibrium vapor without itself being present in the vapor. The feed component in which the equilibrium vapor is enhanced is said to have been ''salted out'' by the salt, while the other feed component is ''salted in.'' This phenomenon can be described by the following equation which is known as Setschenow equation and expresses the solubility of a non-electrolyte in a solid salt solution with low salt concentration (Johnson and Furter, 1960).

$$\log \frac{c_0}{c} = k_s c_s \tag{3}$$

In the above equation, c_0 is the solubility in pure solvent, c the solubility in a salt solution of concentration c_s, and k_s is the salting coefficient which has a characteristic value for a given salt-non-electrolyte pair. A positive value of k_s corresponds to salting out ($c_0 > c$); if k_s is negative, salting in is observed ($c_0 < c$).

3.1.2. The Process of Extractive Distillation with Salt

The process of extractive distillation with salt is somewhat different from the process shown in Figure 4 in the 2nd chapter, in that the salt is not recovered by means of distillation. Anyway, any extractive distillation process can be taken on as consisting of one extractive distillation column

and one solvent recovery equipment, sometimes maybe not distillation column (Barba et al., 1985; Furter, 1992; Furter, 1993).

Figure 14 demonstrates a typical flowsheet for salt-effect extractive distillation. The solid salt, which must be soluble to some extent in both feed components, is fed at the top of the column by dissolving it at a steady state into the boiling reflux just prior to entering the column. The solid salt, being nonvolatile, flows entirely downward in the column, residing solely in the liquid phase. Therefore, no scrubbing section is required above the situation of feeding separating agent to strip agent from the overhead product. Recovery of the salt from the bottom product for recycle is by either full or partial drying, rather than by the subsequent distillation operation for recovering the liquid separating agents.

Several variations on the Figure 14 process are possible. For example, an azeotrope-containing system could be separated by first taking it almost to the azeotrope by ordinary distillation without adding any separating agent, then across the former azeotrope point by extractive distillation with solid salt present, usually containing a little components to be separated,

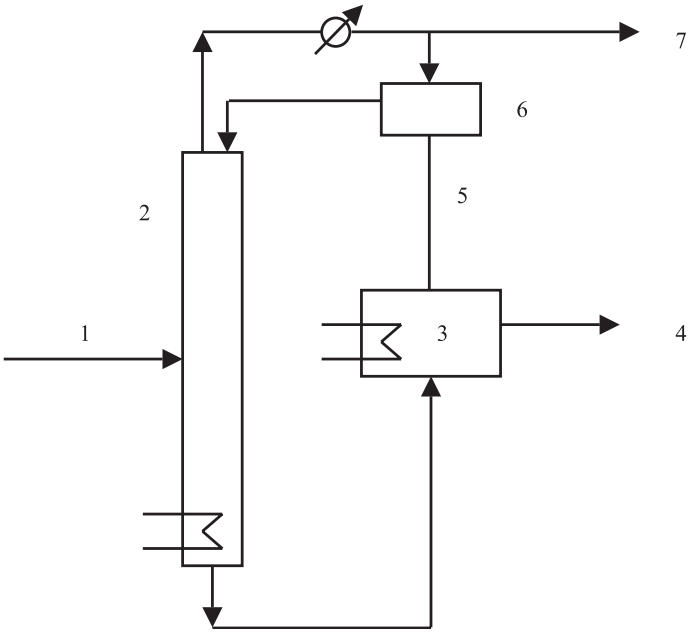

Figure 14. One flowsheet of extractive distillation with salt. 1-feed stream; 2-extractive distillation column; 3-salt recovery equipment; 4-bottom product; 5-the salt recovered; 6-reflux tank; 7-overhead product.

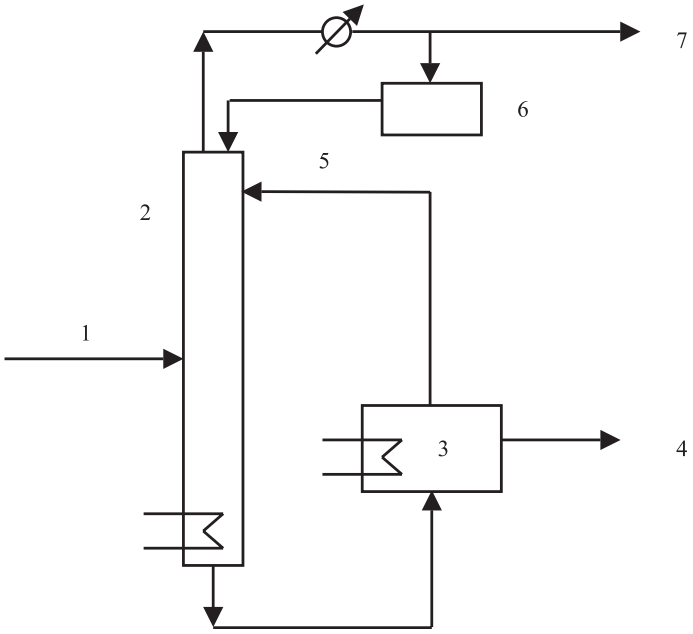

Figure 15. One flowsheet of extractive distillation with salt. 1-feed stream; 2-extractive distillation column; 3-evaporation tank; 4-bottom product; 5-salt solution; 6-reflux tank; 7-overhead product.

and then to final purity by further distillation without solid salt. The solid salt is generally recovered by evaporation.

In this case, the flowsheet of extractive distillation with salt is shown in Figure 15. One advantage of this process is that the salt isn't difficult to be recovered, only by evaporation, and thus the process is convenient to operate.

3.1.3. Case Studies

Separation of Ethanol and Water

Ethanol is a basic chemical material and solvent used in the production of many chemicals and intermediates. Especially in the recent year, ethanol is paid more attention because it is an excellent alternative fuel and has a virtually limitless potential for growth. However, ethanol are usually diluted and required to be separated from water. It is known that ethanol forms azeotrope with water, and can not be extracted to a high concentration from the aqueous solutions by ordinary distillation methods.

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A process known as HIAG (Holz Industrie Acetien Geselleschaft), licensed by DEGUSSA and based on patents registered by Adolph Gorhan, employed extractive distillation using a 70/30 mixture of potassium and sodium acetates as the separating agent, and produced above 99.8% ethanol completely free of separating agent directly from the top of the column (Furter, 1992; Furter, 1993).

The separation of ethanol and water is the most important application of extractive distillation with solid salt. The influence of various salts on the relative volatility of ethanol and water was investigated by Duan et al. (Duan et al., 1980; Lei et al., 1982; Zhang et al., 1984), and the results are listed in Table 3, where the volume ratio of the azeotropic ethanol-water solution and the separating agent is 1.0, and the concentration of salt is 0.2g (salt)/ml (solvent).

It can be seen from Table 3 that the higher the valence of metal ion is, the more obvious the salt effect is. That is to say, $AlCl_3 > CaCl_2 > NaCl_2$; $Al(NO_3)_3 > Cu(NO_3)_2 > KNO_3$. Besides, the effects of acidic roots are different, in an order of $Ac^- > Cl^- > NO^-_3$.

Separation of Isopropanol and Water

Azeotropic distillation with benzene as the entrainer is also a conventional process for the isopropanol-water separation. The Ishikawajima-Harima Heavy industries (IHI) company in Japan has developed a process for isopropanol production from aqueous solution using the solid salt, calcium chloride, as the azeotrope-breaking agent. In a 7300 tonnes per year

Table 3. The influence of various solid salts and liquid solvents on the relative volatility of ethanol and water.

No.	Separating agent	Relative volatility
1	No.	1.01
2	Ethylene glycol	1.85
3	Calcium chloride saturated	3.13
4	Potassium acetate	4.05
5	Ethylene glycol+NaCl	2.31
6	Ethylene glycol+$CaCl_2$	2.56
7	Ethylene glycol+$SrCl_2$	2.60
8	Ethylene glycol+$AlCl_3$	4.15
9	Ethylene glycol+KNO_3	1.90
10	Ethylene glycol+$Cu(NO_3)_2$	2.35
11	Ethylene glycol+$Al(NO_3)_3$	2.87
12	Ethylene glycol+CH_3COOK	2.40
13	Ethylene glycol+K_2CO_3	2.60

plant, IHI reported a capital cost of only 56%, and an energy requirement of only 45%, of those for the benzene process (Furter, 1992; Furter, 1993).

Separation of Nitric Acid and Water

A process in North America using extractive distillation by salt effect is the production of nitric acid from aqueous solution using a solid salt, magnesium nitrate as the separating agent. Hercules Inc. has been operating such plants since 1957, and reports lower capital costs and lower overall operating costs than for the conventional extractive distillation process which uses a liquid solvent, sulfuric acid, as the separating agent (Furter, 1992; Furter, 1993).

3.1.4. The Advantages and Disadvantages of Extractive Distillation with Solid Salt

In systems where solubility considerations permit their use, solid salt as the separating agents can have major advantages. The ions of a solid salt are typically capable of causing much large effects than the molecules of a liquid agent, both in the strength of attractive forces they can exert on feed component molecules, and in the degree of selectivity exerted. This means that the salt has a good separation ability and in the extractive distillation process, the solvent ratio is much smaller than that of the liquid solvent (discussed in the next section), which leads to high production capacity and low energy consumption. Moreover, since solid salt is not volatile, it can't be entrained into the product. At the same time, no salt vapor is inhaled by operators.

However, it is a pity that in industrial operation, when solid salt is used, dissolution, reuse and transport of salt is quite a problem. The concurrent jam and erosion limit the industrial value of extractive distillation with solid salt. That is why the technique, extractive distillation with solid salt, is not widely used in the industry.

3.2. Extractive Distillation with Liquid Solvent

3.2.1. The Definition of Extractive Distillation with Liquid Solvent

Like the extractive distillation with solid salt, in certain systems where solubility permits, it is feasible to use a liquid solvent dissolved into the liquid phase, rather than salt, as the separating agent for extractive distillation. Therefore, the extractive distillation process in which the liquid solvent

is used as the separating agent is called extractive distillation with liquid solvent. However, herein, the ionic liquids are not included in the liquid solvents although they are in the liquid phase from room temperature to higher temperature. The contents about ionic liquid as a special separating agent will be discussed later.

3.2.2. The Process of Extractive Distillation with Liquid Solvent

See Figure 4 in the 2nd chapter (the process of extractive distillation with liquid solvent).

3.2.3. Case Studies

Reactive Extractive Distillation

There are many examples for extractive distillation with a single liquid solvent as the separating agent, as shown in Table 1 in the 1st chapter. Herein, this example is concerned with the separation of acetic acid and water by reactive extractive distillation in which chemical reaction is involved.

Acetic acid is an important raw material in the chemical industries. But in the production of acetic acid, it often exists with much water. Because a high-purity of acetic acid is needed in industry, the problem of separating acetic acid and water is an urgent thing. By now, there are three methods commonly used for this separation, i.e. ordinary distillation, azetropic distillation and extractive distillation (Berg, 1987; Berg, 1992; Dil et al., 1993; Golob et al., 1981; Helsel, 1977; Ma and Sun, 1997). Although ordinary distillation is simple and easy to be operated, its energy consumption is large and a lot of trays are required. The number of trays for azeotropic distillation is fewer than that for ordinary distillation. But the amount of azeotropic agent is great, which leads to much energy consumption because the azeotropic agents must be vaporized in the column. However, in the extractive distillation process the separating agents are not vaporized and thus the energy consumption is relatively little. Therefore, extractive distillation is an attractive method for separating acetic acid and water, and has been studied by Berg, (1987, 1992).

The reported separating agents in extractive distillation are sulfolane, adiponitrile, pelargonic acid, heptanoic acid, isophorone, neodecanoic acid, acetophenone, nitrobenzene and so on. It is evident that the interaction between acetic acid or water and these separating agents is mainly physical force including the van der Waals bonding and hydrogen bonding.

However, a new term, complex extractive distillation, has been put forward, and a single solvent, tributylamine, is selected as the separating agent.

If we select the solvent, tributylamine (b.p. 213.5°C), as the separating agent, then the following reversible chemical reaction may take place:

$$HAc + R_3N \rightleftharpoons R_3NH^+ \cdot {}^-OOCCH_3$$

where HAc, R_3N and $R_3NH^+ \cdot {}^-OOCCH_3$ represent acetic acid, tributylamine and the salt formed by reaction, respectively. This reaction may be reversible because weak acid (acetic acid) and weak base (tributylamine) are used as reactants. That is, for the extractive distillation process the forward reaction occurs in the extractive distillation column and the reverse reaction occurs in the solvent recovery column. Therefore, this new separation method is different from traditional extractive distillation with liquid solvent, and based on the reversible chemical interaction between weak acid (acetic acid) and weak base (separating agent). So we call it reactive extractive distillation.

A new substance, $R_3NH^+ \cdot {}^-OOCCH_3$, is produced in this reaction, which can be verified by infrared spectra (IR) technique. It can be seen from the IR diagrams that a new characteristic peak in the range of $1550cm^{-1}$ to $1600cm^{-1}$ appears in the mixture of acetic acid and tributylamine, and is assigned to the carboxylic-salt function group, —COO^-. This indicates that chemical reaction between HAc and R_3N indeed takes place.

On the other hand, this chemical reaction is reversible, which can be verified by mass chromatogram (MS) technique. Two peaks denoting acetic acid and tributylamine respectively, can be found for the mixture of acetic acid 10%wt and tributylamine 90%wt.

So it indicates that HAc, R_3N and the product produced by them can all be detected by the combination of IR and MS techniques. In general, the reaction rate between weak acid and weak base is very quick. So the chemical reaction between HAc and R_3N may be reversible. The further proof of reversible reaction is supported by calculating the chemical equilibrium constant.

In order to verify the effect of tributylamine as the separating agent, the vapor liquid equilibrium (VLE) was measured by experiment. Figure 16 shows the equilibrium data for the ternary system of water (1) + acetic acid (2) + tributylamine (3), plotted on a tributylamin free basis. It may be observed that the solvent, tributylamin, enhances the relative volatility of water to acetic acid in such a way that the composition of the more volatile component (water) is higher in the liquid than in the vapor phase. The reason may be that the interaction forces between acetic acid and tributylamin molecules are stronger than those between water and tributylamin molecules because in the former reversible chemical reaction takes place. That is, water would be obtained as the overhead product in the extractive distillation column, being acetic acid and the solvent, tributylamin, the bottom product.

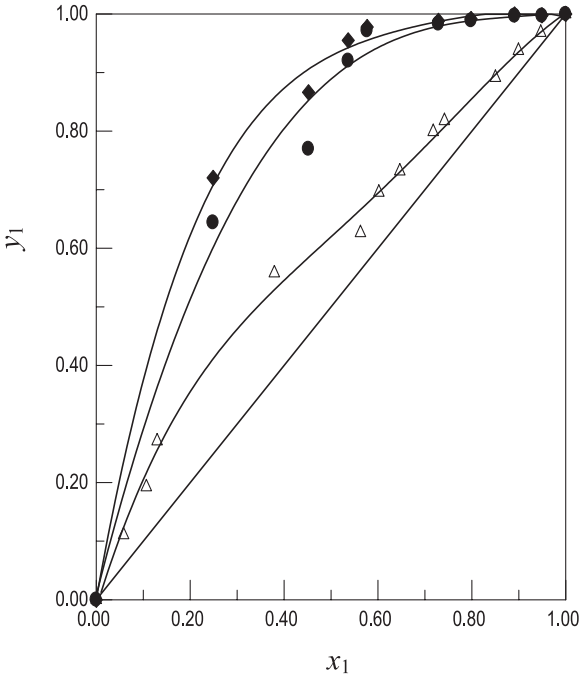

Figure 16. VLE curves on the solvent free basis for the ternary system of water (1) + acetic acid (2) + tributylamine (3) at 101.33 kPa. ◆—solvent/feed volume ratio 2:1; ●—solvent/feed volume ratio 1:1; △—no solvent.

By analyzing the reaction system, it is found that the new group –NH is formed and the old group –OH is disappeared during the reaction. This reaction is exothermic and the heat generated can be obtained from the reference (Ma and Sun, 1997), i.e. $-2.17\text{kJ}\cdot\text{mol}^{-1}$. In addition, the ionization constant PK_a of acetic acid and tributylamine at 25°C can be found from the reference (Chen, 1997), i.e. 4.76 and 10.87 respectively. Therefore, the chemical equilibrium constant at 25°C can be deduced, and thus the relation of chemical equilibrium constant with temperature is expressed by the following equation.

$$K_p = \frac{C_{salt}^2}{C_{HAc}C_{R_3N}} = \exp\left(-4.6284 + \frac{261.01}{T}\right) \tag{4}$$

where T is the absolute temperature (K), and C is the mole concentration (kmol/m^3).

It is found that chemical equilibrium constant is small, about 0.02 under the operation condition of the extractive distillation column. This

means that this reaction is reversible, and the chemical interaction between acetic acid and tributylamine is weak.

In terms of the mechanism of reactive extractive distillation, the following criteria should be satisfied to ensure that this method can be implemented.

1. The chemical reaction is reversible. The reaction product (here as $R_3NH^+ \cdot {}^-OOCCH_3$) is used as carrier to carry the separated materials back and forth.
2. One of the reactants (here as acetic acid) is a low boiling-point component. It can be easily removed by distillation so that the separating agent (here as tributylamine) is able to be regenerated and recycled.
3. There are no other side reactions between the separating agent and the component to be separated. Otherwise, the separation process will be complicated and some extra equipment may be added, which results in no economy of this technique.

It is obvious that the system consisting of water, acetic acid and tributylamine, meets these requirements. So it seems to be advisable to separate water and acetic acid by complex extractive distillation. However, it should be cautious that one solvent with a tri-amine R_3N, not di-amine R_2NH or mono-amine RNH_2, can be selected as the separating agent because the reaction between solvent with two or single amine groups and acetic acid is irreversible, and some amides will be produced.

The Mixture of Liquid Solvents

Compared with the single solvent, the mixture of the liquid solvents as the separating agents is complicated and interesting. However, in most cases, the number of the liquid solvents in the mixture is just two. According to the aims of adding one solvent to another, it can be divided into two categories: increasing separation ability and decreasing the boiling point of the mixture.

Increasing Separation Ability. As we know, selection of the most suitable solvent plays an important role in the economical design of extractive distillation. Moreover, the most important factor in selecting the solvents is relative volatility. Increasing separation ability of the solvent means increasing the relative volatility of the components to be separated. That is to say, when one basic solvent is given, it is better to find the additive to make into a mixture to improve the relative volatility, and thus to decrease the solvent ratio and liquid load of the extractive distillation column.

It has been verified by many examples that adding a little solvent (additive) to one basic solvent will increase the separation ability.

For example, adding small amounts of water has improved the separation ability of acetonitrile (ACN) in separating C4 mixture (Chemical Engineering Department of Zhejiang University, 1973; Lu, 1977). Some results are listed in Table 4, where the subscript (1–13) represents n-butane, isobutane, isobutene, 1-butene, trans-2-butene, propadiene, cis-2-butene, 1,3-butadiene, 1,2-butadiene, methyl acetylene, butyne-1, butyne-2 and vinylacetylene (VAC) respectively, and the numbers, 100%, 80%,70% are the solvent weight fraction in the mixture of the solvent and C4.

It can be seen from Table 1 that adding a little water to ACN indeed increases the relative volatilities of α_{18}, α_{28}, α_{38}, α_{48}, α_{58}, α_{68} and α_{78} in which 1,3-butadiene is as the heavy component, and decreases the relative volatilities of α_{98}, $\alpha_{10,8}$, $\alpha_{11,8}$, $\alpha_{12,8}$ and $\alpha_{13,8}$ in which 1,3-butadiene is as the light component. So the mixture of water and ACN can enhance the separation ability. However, ACN is blended with water to separate C4 mixture with the defect that ACN is prone to hydrolyze, which leads to equipment corrosion and operation difficulty. From this viewpoint, it is thought that water is not the best additive. Which additive is the best? This question will be answered in the 5th chapter.

Other examples in which the second additive is added to improve the separation ability of the original solvent are illustrated in Tables 5 and 6 for separating cyclopentane (1)/2,2-dimethylbutane (2) and n-pentane (1)/1-pentene (2), respectively. In Table 5, NMP, CHOL and NMEP stand for N-methyl-2-pyrrolidone, cyclohexanol and N-(β-mercaptoethyl)-2-pyrrolidone, respectively (Brown and Lee, 1990; Cui et al., 2001; Lee and Brown, 1990).

Table 4. The relative volatility of C4 mixture to 1,3-butadiene at 50°C.

	ACN			ACN + 5 %wt water			ACN + 10%wt water		
	100%	80%	70%	100%	80%	70%	100%	80%	70%
α_{18}	3.01	2.63	2.42	3.46	2.94	2.66	3.64	3.11	2.75
α_{28}	4.19	3.66	3.37	4.95	4.11	3.72	5.40	4.35	3.82
α_{38}	1.92	1.79	1.72	2.01	1.84	1.75	2.09	1.89	1.78
α_{48}	1.92	1.79	1.72	2.01	1.84	1.75	2.09	1.89	1.78
α_{58}	1.59	1.48	1.42	1.59	1.54	1.46	1.78	1.58	1.49
α_{68}	2.09	2.14	2.17	1.97	2.04	2.08	1.88	1.97	2.02
α_{78}	1.45	1.35	1.30	1.48	1.36	1.30	1.51	1.37	1.30
α_{88}	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
α_{98}	0.731	0.720	0.712	0.750	0.733	0.722	0.755	0.738	0.728
$\alpha_{10,8}$	1.00	1.09	1.16	0.947	1.060	1.130	0.897	1.050	1.120
$\alpha_{11,8}$	0.481	0.499	0.508	0.456	0.478	0.490	0.435	0.462	0.476
$\alpha_{12,8}$	0.296	0.303	0.308	0.278	0.288	0.293	0.267	0.279	0.287
$\alpha_{13,8}$	0.389	0.413	0.430	0.364	0.400	0.414	0.344	0.379	0.403

Table 5. Relative volatility α_{12} of the mixture of the solvents for separating cyclopentane (1) and 2,2-dimethylbutane (2).

No.	Solvent/feed mass ratio	Mixture of the solvents	α_{12}
1	3:1	NMEP	1.28
2	3:1	A: NMEP+CHOL	1.40
3	3:1	B: NMEP+CHOL	1.42
4	3:1	C: NMEP+NMP	1.32
5	5:1	NMEP	1.48
6	5:1	CHOL	1.32
7	5:1	NMP	1.37
8	5:1	A: NMEP+CHOL	1.64
9	5:1	B: NMEP+CHOL	1.57
10	5:1	C: NMEP+NMP	1.54
11	7:1	NMEP	1.71
12	7:1	CHOL	1.26
13	7:1	NMP	1.33
14	7:1	A: NMEP+CHOL	1.70
15	7:1	B: NMEP+CHOL	1.64
16	7:1	C: NMEP+NMP	1.74

Adapted from Cui et al. (2001).

Decreasing Boiling Point. In general, the solvent has a much higher boiling point than the components to be separated in order to ensure the complete recovery of the solvent. It indicates that at the bottom of the solvent recovery column, a water stream with a higher temperature than the

Table 6. Selectivity S_{12} of the mixture of the solvents for separating n-pentane (1) and 1-pentene (2).

	Mixture of the solvents		Concentration	
No.	A	B	Volume fraction of B,%	S_{12}
1	Methyl cellosolve	Nitromethane	0	1.69
2	Methyl cellosolve	Nitromethane	5	1.70
3	Methyl cellosolve	Nitromethane	100	2.49
4	Pyridine	Butyrolactone	0	1.60
5	Pyridine	Butyrolactone	32.1	1.79
6	Pyridine	Butyrolactone	100	2.17
7	Ethyl methyl ketone	Butyrolactone	0	1.62
8	Ethyl methyl ketone	Butyrolactone	50	1.79
9	Ethyl methyl ketone	Butyrolactone	100	2.17

Adapted from Cui et al. (2001).

Table 7. The examples of the mixture of the solvents for decreasing the boiling point.

No.	Systems	Mixture of the solvents
1	C4 hydrocarbons	ACN + water
2	Aromatics and non-aromatics	NMP + water
3	Benzene and non-aromatics	NFM + an additive

boiling point of the solvent is needed to heat the solvent to reach its boiling point at normal pressure. That means much energy with high level has to be consumed. If the solvent recovery column is operated at below normal pressure, the degree of vacuum pressure must not be too high due to the restriction of the temperature of condensing water at the top. Therefore, the best strategy is to find the suitable additive to make into a mixture to decrease the boiling point. It is evident that the boiling point of the additive is relatively lower than the basic solvent, but higher than the components to be separated. Table 7 illustrates the examples of the mixture of the solvents, in which the function of the additive is to decrease the boiling point (Tian et al., 2001b; Zhu et al., 2002).

However, one question arises, that is, the separation ability of the mixture of the solvents may decline. The fact is that, at some time, the separation ability of the mixture of the solvents is improved as the example of Table 4, where the mixture of ACN and water not only improves the separation ability, but also decreases the boiling point. At other time, the separation ability of the mixture of the solvents indeed declines, but not obviously. The reason is that as the temperature decreases, there is a positive effect on the separation ability of the mixture of the solvents. The temperature effect on selectivity is given by

$$\frac{d(\lg S_{12}^0)}{d(1/T)} = \frac{L_1^0 - L_2^0}{2.303R} \tag{5}$$

where L_i^0 is partial molar heat of solution, component at infinite dilution in the solvent, T is the absolute temperature (K), and R is gas constant (8.314J/(mol K)).

It can be obtained that $\lg S_{12}^0$ is proportional to the reciprocal absolute temperature. This means that although the separation ability of the additive is weaker than that of the basic solvent, the relatively low boiling point of the mixture of the solvents in some degrees offsets the negative influence of the separation ability of the additive, which leads to no apparent decrease of the separation ability of the mixture of the solvents. That is one reason why some researchers are willing to improve the solvent by decreasing the boiling point.

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In addition, the mixture of the solvents can raise the yield ratio of the product. Zhu et al. studied an extractive distillation process for recovering high purity of benzene from pyrolysis gasoline. The selected solvent is the mixture of N-formylmorpholine (NFM) and an additive. When the weight fraction of the additive is in the range of 5%–20%, the yield ratio of benzene increases from 99.0% to 99.8% and the bottom temperature of the solvent recovery column is less than 190°C.

3.2.4. The Advantages and Disadvantages of Extractive Distillation with Liquid Solvent

In most cases, the solvent and feed mass ratio (i.e. solvent ratio) in the extractive distillation with liquid solvents is very high, up to 5–8. For example, for the separation of C4 hydrocarbon using N,N-dimethylformamide (DMF) or acetonitrile (ACN) as the solvents, the solvent ratio is 7–8 in industry, which leads to much consumption of energy. However, in systems where solubility considerations permit their use, the separation ability of the solid salts is much greater than that of the liquid solvents, and thus the solvent ratio is generally low. The reason why extractive distillation with liquid solvent is more widely used in industry rather than extractive distillation with solid salt is that there is no problems of dissolution, reuse and transport for the liquid solvent because it is in the liquid phase under the operation condition of extractive distillation process. In a word, the advantages of extractive distillation with liquid solvent predominate over its disadvantages. On the contrary, the disadvantages of extractive distillation with solid salt predominate over its advantages.

3.3. Extractive Distillation with the Combination of Liquid Solvent and Solid Salt

3.3.1. The Definition of Extractive Distillation with Liquid Solvent and Solid Salt

Like the extractive distillation with solid salt or liquid solvent, in certain systems where solubility permits, it is feasible to use a combination of liquid solvent and solid salt dissolved into the liquid phase, rather than only salt or liquid solvent, as the separating agent for extractive distillation. Therefore, the extractive distillation process in which the combination of liquid solvent and solid salt is used as the separating agent is called extractive distillation with the combination of liquid solvent and solid salt.

3.3.2. The Process of Extractive Distillation with the Combination of Liquid Solvent and Solid Salt

See Figure 4 in the 1st chapter (the process of extractive distillation with liquid solvent). That is to say, the processes of extractive distillation with liquid solvent and with the combination of liquid solvent and solid salt, are the same.

3.3.3. Case Studies

Extractive distillation witxh the combination of liquid solvent and solid salt as the separating agent is a new process for producing high-purity products. This process integrates the advantages of liquid solvent (easy operation) and solid salt (high separation ability). In industrial operation, when only salt is used, dissolution, reuse and transport of solid salt is quite a problem. The concurrent jam and erosion limits the industrial value of extractive distillation with solid salt only. However, the mixture of liquid solvent and solid salt can avoid the defects and realize continual production in industry.

Extractive distillation with the combination of liquid solvent and solid salt can be suitable either for the separation of polar systems or for the separation of non-polar systems, which are mentioned afterwards, respectively.

Herein, we select aqueous alcohol solutions, i.e., ethanol/water and isopropanol/water as the representatives of polar systems and C4 mixture as the representatives of non-polar systems. It is known that both anhydrous alcohol and 1,3-butadiene are basic chemical raw materials. Anhydrous alcohol is not only used as chemical reagent and organic solvent, but also used as the raw material of many important chemical products and intermediates; 1,3-Butadiene mainly comes from C4 mixture and is utilized for the synthesis of polymers on a large scale. It is reported (Lei et al., 2002a,c,d) that the systems of aqueous alcohol and C4 mixture are able to be separated by extractive distillation. Because these two materials are very important in industry, the separation of them by extractive distillation is interesting.

Separation of the Systems of Ethanol/Water and Isopropanol/Water

Firstly the equilibrium data of the ethanol (1)-water (2) system, which corresponded well with the reference data (Gmehling and Onken, 1977), were measured. It is verified that the experimental apparatus was reliable. Then the measurements were respectively made for the system ethanol (1)-water (2)-ethylene glycol (solvent/feed volume ratio is 1:1) and the system ethanol (1)-water (2)-ethylene glycol-$CaCl_2$ (solvent/feed volume ratio is 1:1 and the concentration of salt is 0.1g/ml solvent) at normal pressure.

On the other hand, measurements were also made for the system of isopropanol (1)/water (2)/ ethylene glycol/ glycollic potassium at normal

pressure (Lei et al., 2002a). Isopropanol (1)/ water (2) and the mixture of ethylene glycol and glycollic potassium were blended with the feed/solvent volume ratio of 1:1. The mixture of ethylene glycol and glycollic potassium were prepared from ethylene glycol and potassium hydroxide with the weight ratio 5:1 and 4:1 respectively. During preparation, the mixture of ethylene glycol and potassium hydroxide were fed into a distillation column and the water produced was removed. Afterwards, the experimental VLE data were measured.

The experimental results from both systems show that under the same liquid composition the mole fraction of alcohol in the vapor phase with salt is higher than that without salt. It means that adding salt to ethylene glycol is advisable for improving the separation ability of the solvent with alcohol separated as a light component and water as a heavy component.

Separation of C4 Mixture

When acetonitrile (ACN) is regarded as an basic solvent, organic solvents including water and salts will be added to it (Lei et al., 2002d). The aim is to find the effect of them on α_{aj}^{∞} in the solvent ACN. Among organic solvents, water and ethylenediamine are better additives than other solvents. However, it is found that a little of solid salt added to ACN can effectively improve the relative volatility and the effect of solid salt is close to water and stronger than ethylenediamine. But in the former time ACN was mixed with water to separate C4 mixture with the defect that ACN is prone to hydrolyze, which leads to equipment corrosion and operation difficulty.

On the other hand, N,N-dimethylformamide (DMF) is another solvent commonly used to separate C4 mixture. Due to the same reason as ACN, DMF is used as a single solvent. It is expected to modify it with solid salt. Many substances are strongly soluble in DMF including many kinds of solid salts. The influence of solid salts and organic additives on the separation ability of DMF is tested (Lei et al., 2002c,d). The same phenomenon exists as with ACN. Salts added to DMF also improve the relative volatilities of C4 to some extent, and at the same concentration the effect of the salts is more apparent than that of organic solvents. Moreover, if some factors such as relative volatilities, price, erosion, source and so on are considered, the salts NaSCN and KSCN are the best additives.

3.3.4. The Advantages and Disadvantages of Extractive Distillation with the Combination of Liquid Solvent and Solid Salt

As said above, extractive distillation with the combination of liquid solvent and solid salt as the separating agent integrates the advantages of liquid solvent (easy operation) and solid salt (high separation ability). From the above discussion, we know that whether it is of separating polar systems

or non-polar systems, extractive distillation with the combination of liquid solvent and solid salt may be feasible. So it is concluded that extractive distillation with the combination of liquid solvent and solid salt is a promising separation method. If we meet with the problems about extractive distillation in the future, it is wise to try to solve it by adding solid salt.

Unfortunately, many solid salts are corrosive to the equipment and easies to decompose at high temperature. In some cases the kinds of solid salts that we can select are small. An economic calculation must be made in determining the final salts. The benefit from adding salts in the production should exceed the price of salts and other charges.

On the other hand, since the amount of solid salts added to the liquid solvents is often small, the role of solid salts in improving the separation ability is doomed to be limited. Besides, liquid solvents are volatile, which inevitably pollutes the top product of the extractive distillation column. Accordingly, new separating agents should be explored to avoid these problems brought out by liquid solvent and solid salt.

3.4. Extractive Distillation with Ionic Liquid

3.4.1. The Definition of Extractive Distillation with Ionic Liquid

Like the extractive distillation with solid salt or liquid solvent or the combination, in certain systems where solubility permits, it is feasible to use an ionic liquid dissolved into the liquid phase, rather than only salts or liquid solvents, as the separating agent for extractive distillation. Therefore, the extractive distillation process in which ionic liquid is used as the separating agent is called extractive distillation with ionic liquid.

Then, what are ionic liquids? Ionic liquids are salts consisting entirely of ions, which exist in the liquid state at ambient temperature, i.e. they are salts that do not normally need to be melted by means of an external heat source.

Ionic liquids are often used in the chemical reaction (Gordon, 2001; Gregory and Mahdi, 2002; Hagiwara and Ito, 2000; Olivier, 1999; Welton, 1999; Zhao et al., 2002). The cases of applications on the separation process are a few, especially rarely reported on the extractive distillation (only one patent found) (Arlt et al., 2001).

Ionic liquids are called ''green'' solvents. When they are used in the extractive distillation, the ''green'' is brought out in the following aspects:

1. Negligible vapor pressure, which means that ionic liquids don't pollute the product at the top of the column. However, when the liquid solvent or the combination of liquid solvent and solid salt is used as the separating agent, the solvent may be entrained more or less into the product. In the case of strict restriction for the

impurity of the product, it is advisable to use ionic liquids as the separating agents.

2. A wide liquid range of about 300°C with a melting point around room temperature. This temperature range in most cases corresponds with the operation condition of the extractive distillation.
3. A wide range of materials including inorganic, organic and even polymeric materials are soluble in ionic liquids, which ensures that the ionic liquids have an enough solubility for the components to be separated, and can play a role in increasing the relative volatility in the liquid phase.
4. Potential to be reused and recycled. Due to their non-volatility, ionic liquids are easy to be recovered from the components to be separated, and the simplest way is by evaporation in a tank.
5. Many ionic liquids are high thermal and chemical stability with or without water under the operation temperature of extractive distillation. However, some excellent liquid solvents, which are commonly used until now, such as acetontrile (ACN), dimethylformamide (DMF), N-methyl-pyrrolidone (NMP), etc., are not thermal and chemical stability with or without water, and are easy to be decomposed.

The most common ionic liquids in use are those with alkylammonium, alkylphosophonium, N-alkylpyridinium, and N, N-dialkylimidazolium cations. However, much more ionic liquids are synthesized based on 1,3-dialkylimidazolium cations with 1-butyl-3-methylimidazolium $[bmim]^+$-being probably the most common cation (See Figure 17). The most common anions are $[PF_6]^-$, $[BF_4]^-$, $[SbF_6]^-$, $[CF_3SO_3]^-$, $[CuCl_2]^-$, $[AlCl_4]^-$, $[AlBr_4]^-$, $[AlI_4]^-$, $[AlCl_3Et]^-$, $[NO_3]^-$, $[NO_2]^-$ and $[SO_4]^{2-}$. Ionic liquids of this type have displayed the useful combination of low melting point, along with high thermal and chemical stability necessary for extractive distillation process.

The most widely used methodology in the synthesis of ionic liquids is metathesis of a halide salt of the organic cation with a group 1 or ammonium

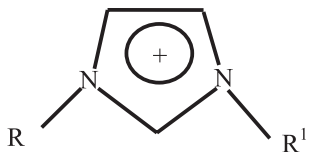

Figure 17. Typical 1-alkyl-3-methylimidazolium cations and the abbreviations used to refer to them. R = Me, R^1 = Et: $[emim]^+$; R = Me, R^1 = n-Bu: $[bmim]^+$; R = Me, R^1 = n-hexyl: $[hmim]^+$; R = Me, R^1 = n-octyl: $[omim]^+$.

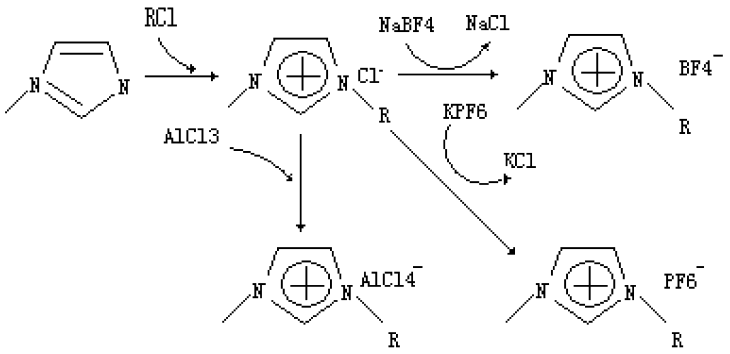

Figure 18. One synthesis route for ionic liquids.

salt containing the desired anion. Alternatively, the halide salt of the organic cation may be reacted with a Lewis acid. Figure 18 illustrates a synthesis route, in which synthesis of one ionic liquid may be carried out under an inert atmosphere because such substances as $AlCl_3$, $[AlCl_4]^-$ are sensitive to air and moisture.

3.4.2. The Process of Extractive Distillation with Ionic Liquid

The process of extractive distillation with ionic liquid may be same to the process of extractive distillation with solid salt (See Figures 14 and 15).

3.4.3. Case Study

Extractive distillation with ionic liquid as the separating agent is a very new process for producing high-purity products. This process integrates the advantages of liquid solvent (easy operation) and solid salt (high separation ability). But compared with extractive distillation with the combination of liquid solvent and solid salt, it has no problem of entrainment of the solvent into the top product of the column.

Extractive distillation with ionic liquids can be suitable either for the separation of polar systems or for the separation of non-polar systems. The following polar and non-polar systems have been investigated (Arlt et al., 2001): ethanol/water, acetone/methanol, water/acetic acid, tetrahydrofuran (THF)/water and cyclohexane/benzene. It is found that the separation effect is very apparent for these systems when the corresponding ionic liquids are used. However, it is cautious that the suitable ionic liquid should have enough solubility for the given components to be separated. The reason

Table 8. Vapor-liquid equilibrium data of cyclohexane (1) and toluene (2) at normal pressure, temperature T/K, liquid phase x_1, and vapor phase y_1, mole fraction for all cases, solvent/feed volume ratio is 1:1.

No.	T/°C	x_1	x_2	y_1	y_2
① No separating agent					
1	97.3	0.1267	0.8733	0.2468	0.7532
2	99.3	0.2614	0.7386	0.4488	0.5512
3	96.0	0.3534	0.6466	0.5852	0.4148
4	89.0	0.5021	0.4979	0.7167	0.2833
5	89.1	0.6516	0.3484	0.7604	0.2396
6	88.9	0.7738	0.2262	0.8336	0.1664
② $[AlCl4]^-$ as the anion					
1	105.5	0.1267	0.8733	0.2989	0.7011
2	98.0	0.2614	0.7386	0.5592	0.4408
3	94.0	0.3534	0.6466	0.6608	0.3392
4	86.8	0.5021	0.4979	0.7644	0.2356
5	86.0	0.6516	0.3484	0.8541	0.1459
6	81.6	0.7738	0.2262	0.8819	0.1181
③ $[BF_4]^-$ as the anion					
1	88.2	0.5021	0.4979	0.6876	0.3124
④ $[PF_6]^-$ as the anion but ionic liquid is in the aqueous solution					
1	90.6	0.5021	0.4979	0.5756	0.4244

why ionic liquid can greatly raise the relative volatility is the same as that of using solid salt, that is, due to the salt effect.

Recently, we measured the equilibrium data of the cyclohexane (1)-toluene (2) system in which three kinds of ionic liquids are selected as the separating agents. Ionic liquids were prepared according to the synthesis route shown in Figure 18, and $[bmim]^+$was the cation. Their molecular structures have been verified by HNMR technique. The experimental VLE data at normal pressure are listed in Table 8, in which the mole fractions are on solvent free basis.

As shown in Table 8, among three kinds of ionic liquids, $[bmim]^+[AlCl4]^-$, $[bmim]^+[BF_4]^-$ and $[bmim]^+[PF_6]^-$, the ionic liquid of $[bmim]^+[AlCl4]^-$ is best for separating cyclohexane and toluene because in the case of same liquid composition ($x_1 = 0.5021$, $x_2 = 0.4979$) the corresponding vapor composition of cyclohexane is the greatest. This means that in this case the relative volatility of cyclohexane to toluene is also the largest. Moreover, it can be seen that under the same liquid composition the relative volatility of cyclohexane to toluene, when the ionic liquid of $[bmim]^+[AlCl4]^-$ is used as the separating agent, is apparently larger than

when no separating agent is used. Since cyclohexane and toluene can be regarded as the representatives of aromatics and non-aromatics, the ionic liquid of $[bmim]^+[AlCl4]^-$ should be a potential solvent for separating aromatics and non-aromatics.

3.4.4. The Advantages and Disadvantages of Extractive Distillation with Ionic Liquid

As said above, extractive distillation with ionic liquids as the separating agent, like the combination of liquid solvent and solid salt, integrates the advantages of liquid solvent (easy operation) and solid salt (high separation ability). Whether it is of separating polar systems or non-polar systems, extractive distillation with ionic liquids may be feasible. So it is concluded that extractive distillation with ionic liquid is another promising separation method besides extractive distillation with the combination of liquids solvent and solid salt.

Unfortunately, extractive distillation with ionic liquid as the separating agents has some disadvantages, that is, it often takes much time to prepare ionic liquid and the prices of the materials used for synthesizing ionic liquid are somewhat expensive. These disadvantages may hold back the wide application of this technique in industry, even if the advantages of this technique are very attractive.

4. EXPERIMENT TECHNIQUE OF EXTRACTIVE DISTILLATION

The expressions of selectivity and relative volatility are given in Eqs. 1 and 2, respectively. Since the activity coefficients depend on the phase compositions, and the role of the solvent tends to increase with an increase in its concentration, it is common practice to consider the situation of infinite dilution. Then the definition of selectivity at infinite dilution becomes, from Eq. 2:

$$S_{ij}^{\infty} = \left(\frac{\gamma_i^{\infty}}{\gamma_j^{\infty}}\right) \tag{6}$$

which also represents the maximum selectivity.

A relation analogous to Eq. 6 holds for the relativity volatility, that is,

$$\alpha_{ij}^{\infty} = \frac{\gamma_i^{\infty} P_i^0}{\gamma_j^{\infty} P_j^0} \tag{7}$$

which also represents the maximum relativity volatility.

In order to evaluate the possible separating agents, the goal of the experimental technique is to obtain the value of selectivity, or relativity volatility, or activity coefficient from which selectivity and relativity volatility can be deduced, at infinite dilution.

These values may be found in some certain data banks. But it is a common situation that the systems concerned are not included. In this case, we have to rely on the experiments. There are four experimental methods to obtain selectivity, or relativity volatility, or activity coefficient at infinite dilution, i.e. direct method, gas-liquid chromatography method, ebulliometry method, and inert gas stripping and gas chromatography method.

4.1. Direct Method

This is an older method, involving extrapolation of classical vapor-liquid equilibrium (VLE) data (Ellis and Jonah, 1962; Hilmi et al., 1970). By plotting experimental data in the form of versus liquid composition (x) and extrapolating the curve to $x = 0$, the activity coefficient at infinite dilution γ^{∞} is deduced. Therefore, it is required that all of the VLE at total concentration should be measured, which leads to much time consumption and getting inaccurate results.

There are many famous experimental instruments to measure the VLE at normal or vacuum pressure (Beatriz et al., 2000; Furter, 1992; Furter, 1993; Jose et al., 1999; Jose et al., 2001). One kind of experimental instruments such as Rose still, Othmer still and their modifications can be bought in the market. The common characteristics of these instruments are that they belong to recycling vapor-liquid equilibrium still and the data under boiling, isobaric conditions are measured. Each experiment is done for each data.

Another kind of experimental instruments to measure the VLE at normal or vacuum pressure (Wu et al., 1988), such as Stage-Muller dynamic still and so on, are used to obtain the data under isothermal condition. Each experiment is done for each data.

In the recent year, one important experimental instrument, i.e. HSGC (Headspace-gas chromatography) method, to measure the VLE at normal or vacuum pressure has been developed to obtain the data under isothermal condition. Each experiment is done for many data.

In the references (Fawzi et al., 2000; Seiler et al., 2002a,b), this method is introduced. It combines a headspace sampler and a GC (gas chromatograph) in order to determine the composition of a vapor phase. Samples of different liquid (10ml) are filled into vials (capacity 20ml) and sealed with air-tight septa. To ensure thermodynamic equilibrium, the vials are mixed at equilibrium temperature for 24h and then transferred into the headspace oven. Inside the oven of the headspace sampler, the system is

mixed by an agitation mode and equilibrated again for another 5h. A pneumatically-driven thermostated headspace sampler takes a sample of approximately 0.05g out of the vials' vapor phase in equilibrium with the liquid phase. A specially designed sample interface delivers the sample to the GC column of the GC.

The HSGC method is the most promising direct method, and can finish the VLE measurement in a relatively short time. But it is a pity that the drawback of extrapolating the experimental data can't be overcome yet.

However, if the VLE at high pressure is required for the studied system such as C3, C4 hydrocarbons, direct method may be very tedious and difficult, and is better to be replaced by other methods such as gas-liquid chromatography method, and inert gas stripping and gas chromatography method.

4.2. Gas-Liquid Chromatography Method

This method is commonly used for determining experiments values of γ^{∞}. It involves measuring the retention behavior of a solute in an inert carrier gas stream passing through a column containing a solvent-coated solid support (Donohue et al., 1985; Thomas et al., 1982; Vega et al., 1997).

The equation used in calculating $\gamma^{\infty}1$ is:

$$\gamma_2^{\infty} = \frac{RT\phi_2 Z_m \exp(-V_2{}^{\infty}P/RT)n_1}{\phi_2^s P_2^s (V_R - V_m)} \tag{8}$$

where Z_m is compressibility of he mixture, ϕ_2 is vapor-phase fugacity coefficient of solute, V_R is retention volume of solute, V_m is volume of the mobile phase, V_2^{∞} is molar volume of solute at infinite dilution, and n_1 is moles of solvent on the column. This relation assumes that equilibrium is achieved throughout the column, that the solute is sufficiently dilute to be within the Henry's law region, and that the packing is inert relative to the solvent and the solute.

There are several advantages in using the gas-liquid chromatography method. Firstly, it is the method that γ^{∞} may be found directly. Secondly, commercially available equipment can be used and the techniques are well established. Further, although solvent purity is crucial, solute purity is not critical as separation is achieved by the chromatograph. Finally, the method is quick on the condition that the solvent is determined beforehand. Up to 30 data points may be measured in the course of a day's run. Conventional static technique in the direct method may take hours or days to obtain one or two limiting activity coefficients, and even the ebulliometric method to be discussed afterwards, can measure only four values in a day's run with existing equipment.

However, the most apparent defect of this method is that, when one solute system has been given and different solvents are to be evaluated, the column packing should be made once for each solvent. We know that the preparation of the column packing is a very tedious work and the time consumed is not endurable.

The minor defects of this method are encountered when solvents nearly as volatile as the solutes are used. The stripping of solvent from the column packing introduces impurities into the carrier gas and thus reduces the sensitivity of the detector. This means that many solutes can't be detected in certain volatile solvents.

4.3. Ebulliometric Method

Ebulliometric method is a rapid and robust method of measuring pressure-temperature-liquid mole fraction (*PTx*) data (Olson, 1989; Qian et al., 1981). *PTx* data are measured in an ebulliometer which is a one-stage total reflux boiler equipped with a vapor-lift pump to spray slugs of equilibrated liquid and vapor upon a thermometer well. The advantages of ebulliometric method are:

1. Degassing is not required.
2. Equipment is simple, inexpensive, and straightforward to use.
3. Data can be measured rapidly.
4. Either *Px* or *Tx* data can be measured.

For a binary system, the procedure is to measure $\left(\frac{\partial T}{\partial x}\right)_P$ in a twin-ebulliometer (differential) arrangement where a pure component is charged to both ebulliometers and small amounts of the second component are added to one ebulliometer. Activity coefficient at infinite dilution γ^{∞} is deduced by extrapolating $\left(\frac{\partial T}{\partial x}\right)_{x=0}$, which leads to getting inaccurate results. One expression of γ^{∞} is written as,

$$\gamma_1^{\infty} = \frac{P}{P_1^0}\left[1 - \left(\frac{\Delta H^V}{RT^2}\right)\left(\frac{dT}{dx_1}\right)_{x_1=0}\right] \tag{9}$$

where

$$\left(\frac{dT}{dx_1}\right)_{x_1=0} = T_1 - T_2 + \left(\frac{\Delta T}{x_1 x_2}\right)_{x_1=0}$$

$\Delta T = T - x_1T_1 - x_2T_2$, P is the total pressure, P_1^0 is the saturated pressure of solute 1, T is the absolute temperature, R is gas constant, and ΔH^v is the evaporation latent heat of solute 1.

When solute 1 is added into the solvent S, the concentration of solute 1, x_1, is determined. Only if the boiling point different of the mixture is measured, then the activity coefficient can be calculated from Eq. 9. Moreover, if solute 1 is in the very dilution, then it is reasonable to think that the activity coefficient may be γ_1^∞.

For extractive distillation, a ternary system, consisting of solvent S, components A and B to be separated, are encountered while one solvent S is evaluated. In this case selectivity, or relative volatility at infinite dilution in solvent S, can be obtained by carrying out two γ^∞ (γ_A^∞, γ_B^∞) experiments. From this viewpoint, ebulliometric method is somewhat tedious.

4.4. Inert Gas Stripping and Gas Chromatography Method

Leroi et al. (Leroi et al., 1977) proposed a new method to measure γ^∞, S^∞ and α^∞, i.e. the combination of inert gas stripping and gas chromatography method, which has the merits of a high level of accuracy and reproducibility (Chen et al., 1988; Duhem and Vidal, 1978). One schematic diagram of the experimental apparatus is depicted in the reference (Lei et al., 2002d). The principle of the method is based on the variation of the vapor phase composition when the highly diluted components of the liquid mixture, controlled to be below 0.01mol/l, are stripped from the solution by a constant flow of inert nitrogen gas with a flow rate 20ml/min. In the stripping cell, the outlet gas flow is in equilibrium with the liquid phase, and gas is injected into the gas chromatograph by means of a six-way valve at periodic intervals. The peak areas of solutes are recorded by the integrating meter.

The most important part in this method is the equilibrium cell. One modification to the structure proposed by Lei involves enlarging the gas-liquid interface and increasing the contact time between gas and liquid phases by means of a spiral path. Two similar cells, a presaturation cel and a stripping cell, are used. The configuration of the modified equilibrium cell is described in the reference (Lei et al., 2002d). The relative volatility can be obtained by this method in a shorter time than by other methods.

According to the experimental principle we can derive the relationship of activity coefficient γ_i^∞ at infinite dilution. It is given by the following equation:

$$\gamma_i^\infty = \frac{NRT}{DP_i^0 t} \ln \frac{A_0}{A} \tag{10}$$

where N is the total number of mole of solvent in the dilution cell at time t, and A_0 and A are respectively the original peak areas of the solute and the peak area at intervals of the time t.

For extractive distillation, we usually take on the selectivity or relative volatility at infinite dilution as the standard of evaluating the solvent. The selectivity S_{ij}^{∞} and the relative volatility α_{ij}^{∞} at infinite dilution are respectively given by the following equations:

$$S_{ij}^{\infty} = \frac{\gamma_i^{\infty}}{\gamma_j^{\infty}} = \frac{\ln(A_{i0}/A_i)P_j^0}{\ln(A_{j0}/A_j)P_i^0} \tag{11}$$

$$\alpha_{ij}^{\infty} = \frac{\gamma_i^{\infty}P_i^0}{\gamma_j^{\infty}P_j^0} = \frac{\ln(A_{i0}/A_i)}{\ln(A_{j0}/A_j)} \tag{12}$$

It is evident that the selectivity S_{ij}^{∞} and the relative volatility α_{ij}^{∞} are coordinate in evaluating the separation ability of the solvent. For the sake of simplicity, it is better to select α_{ij}^{∞}. Comparing with γ_i^{∞}, the data of α_{ij}^{∞} is easy to be obtained accurately because it needn't measure N and t which perhaps bring some extra errors in the experiment. Thus if the peak area A of the solute at different time is known, α_{ij}^{∞} is able to be calculated according to Eq. 12 in which only the peak area A is required. It has been verified by Lei (Lei et al., 2002d) that the results obtained by this method are reliable, and very suitable for the evaluation of different solvents.

The comparison of gas-liquid chromatography method (method 1) and inert gas stripping and gas chromatography method (method 2) for separating C4 mixture with ACN and DMF is given in Table 9 (Chemical Engineering Department of Zhejiang University, 1973; Lei et al., 2002d), where we use the subscript (1–5) for butane, 1-butene, 2-trans-butene, 2-cis-butene and 1,3-butadiene respectively. It can be seen that the difference between these two methods is below 15%.

It is concluded by comparison of these four methods that inert gas stripping and gas chromatography method should be firstly recommended,

Table 9. The comparison of gas-liquid chromatography method (method 1) and inert gas stripping gas chromatography method (method 2).

	ACN(20°C)			DMF(50°C)		
	Method 1	Method 2	Deviation %	Method 1	Method 2	Deviation %
α_{15}^{∞}	3.48	3.82	9.44	3.82	3.32	13.09
α_{25}^{∞}	2.13	2.11	0.01	2.40	2.12	11.67
α_{35}^{∞}	–	1.81	–	1.94	1.79	7.73
α_{45}^{∞}	1.47	1.63	10.88	1.65	1.61	2.42

secondly the HSGC technique in the direct method and finally gas-liquid chromatography method. However, it is hard to find the references about ebulliometric method in the recent year.

5. CAMD OF EXTRACTIVE DISTILLATION

It is tiresome to choose the best solvent from thousands of different substances for a given system through experiments only. There are some methods to pre-select the possible solvents by calculation, such as Pierotti-Deal-Derr method, Parachor method, Weimer-Prausnitz method, and CAMD, among which CAMD is both the recent development and the most important, and has completely replaced other calculation methods for screening solvents.

5.1. CAMD for Screening Solvents

CAMD (computer-aided molecular design) is developed in the 1980's and widely used in such unit operations as gas absorption, liquid–liquid extraction, extractive distillation and so on (Churi and Achenie, 1996; Harper et al., 1999; Hostrup et al., 1999; Joback and Stephanopoulos, 1995; Marcoulaki and Kokossis, 1998; Mavrovouniotis, 1998; Meniai et al., 1998; Ourique and Telles, 1998; Pistikopoulos and Stefanis, 1998; Raman and Maranas, 1998; Sinha et al., 1999; Venkatasubramanian et al., 1995). CAMD breaks new way in selecting the possible solvents by largely reducing experiments. The application of CAMD in chemical engineering is mostly based on the UNIFAC group contribution (Franklin, 1949; Gmehling et al., 1982; Jorgensen et al., 1979; Macedo et al., 1983). Incalculable feasible molecules will be formulated by UNIFAC groups in accordance with certain rules, but in terms of given target properties, the desired molecules are screened by computers. The groups of UNIFAC provide building blocks for assembling molecules. CAMD is essential 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 specification. In most cases, more than one solution is produced. Thus, a screening is needed since only one of the alternatives must be chosen for the specified problem. At this point, factors such as corrosion, prices, source, etc. should be taken into consideration. Of course, it is a procedure after CAMD.

The solvents are divided into three parts, liquid solvents, solid salt and ionic liquid which can be designed respectively by CAMD.

5.1.1. CAMD of Liquid Solvents

Procedure of CAMD for the Liquid Solvents

The UNIFAC groups are used as building blocks for the synthesis of liquid solvents. CAMD for liquid solvents is conducted in the following four steps (Gani and Brignole, 1983; Gani and Fredenslund, 1993; Gani et al., 1991; Joback and Reid, 1987; Lei et al., 2002e; Pretel et al., 1994; Reid et al., 1987): group sorting and pre-selection, combination of groups, prediction of target properties, final selection of solvents.

In the procedure, both explicit properties and implicit properties are considered. Explicit properties can be computed according to the thermodynamic method. But relative volatility among them is the key to extractive distillation. For this reason, compounds are ordered by the values of their relative volatility. For CAMD for extractive distillation, implicit properties such as toxicity, cost, stability and material source are important. The compounds that do not satisfy the implicit properties are crossed out from the order. The remaining compounds ranked in front of the order are the objects of the best possible solvents we seek. As a result, by CAMD, the work to search for the best solvents is reduced. The final solvents will be tested with only a minimum number of experiments.

Program of CAMD for the Liquid Solvents

Many CAMD algorithms have been proposed. These may be broadly classified as interactive, combinatorial, knowledge-based and mathematical programming methods. Recently, a new method, genetic algorithm, is put forward, which retains the efficiency of mathematical programming while still perform well in difficult search spaces.

In our work, CAMD for extractive distillation has been programmed with Visual Basic for Windows. This program is a combinatorial method, and can provide much information necessary for the extractive distillation. CAMD is an easy-to-use software with user friendly interface. One with a little knowledge of extractive distillation can become familiar with it in a few hours.

Application of CAMD for the Liquid Solvents

Separation of C4 Mixture with ACN. Extractive distillation is widely used in purification of 1,3-butadiene from C4 mixture. ACN is a frequently used basic solvents and is inconvenient to be completely replaced by other solvents to enhance the relative volatility of C4 mixture. Therefore, water is usually added to ACN as a cosolvent. But the mixed

ACN has a disadvantage, that is, it tends to give rise to hydrolysis, which contributes to the loss of ACN and corrosion of equipment during production. So, a more efficient additive is required to substitute water.

2-Butene and 1,3-butadiene are key components in C4 separation because their separation is difficult. So, it is reasonable to only consider 2-butene and 1,3-butadiene as the representative of C4 mixture for solvent evaluation.

CAMD for this separation has been performed on a PC (Pentium 2 286MHz) (Lei et al., 2002e). Water that has ever been used as the additive (Bannister and Buck, 1969; Coogler, 1967) is sought, which indicates that the designed result are reliable to some degree. After considering such implicit properties as toxicity, boiling point, chemical stability and hydrolysis, the molecules, (H2O), (CH_3 $3CH_2$ CH_3COO), (CH_3 CH_2 CH_3 CO), ($2CH_2NH_2$) and (CH_3 CH_2 OH), are regarded as the possible additives.

The additives generated by CAMD are tested by experiments, and it proved that water and ethylenediamine are good potential additives of ACN of all liquid solvents. Therefore, if we consider the hydrolysis influence of ACN, ethylenediamine is the best substance as liquid solvent that is added to ACN.

Thus, by means of the tool, CAMD, we can find the best additive, ethylenediamine, from a great number of liquid solvents with only a few experiments. It is shown that CAMD can effectively decrease the amounts of experiments and help researchers to explore the useful substances in a short time.

Separation of Aromatics and Non-aromatics. In industry the methods for separating aromatics and non-aromatics are liquid–liquid extraction and extractive distillation (Liu et al., 1995; Rawat and Gulati, 1981; Wardencki and Tameesh, 1981; Zheng et al., 1997). Liquid–liquid extraction as an old method is almost replaced by extractive distillation in most cases. It is assumed that cyclohexane and benzene are taken on as the representation of aromatics and non-aromatics respectively because they are the key components in the separation process. In order to find the potential solvents, CAMD for this separation is used (Yang et al., 2001). The restriction for the solvents are listed in the following order.

1. Maximum molecular weight: 240
2. Minimum boiling point: 383.15K
3. Maximum boiling point: 553.15K
4. Maximum melting point: 278.15K
5. Minimum selectivity at infinite dilution: 3.0
6. Maximum activity coefficient of component i at infinite dilution in solvent ($\gamma_{i,s}^{\infty}$): 12

7. Maximum activity coefficient of solvent at infinite dilution in component i ($\gamma_{s,j}^{\infty}$):

$$\frac{P_i^0}{P_s^0}$$

By means of CAMD, No.1, NMP, and No.2, DMF, are regarded as the potential solvents. Fortunately, both solvents have ever been reported as the solvents (Liu et al., 1995; Rawat and Gulati, 1981; Wardencki and Tameesh, 1981; Zheng et al., 1997). So in means that the result of CAMD are reliable in this case.

Braam (Braam and Izak, 2000) also studied this system by causing CAMD and found that aniline is the possible best solvent, resulting in a relative volatility of 2.65 (UNIFAC) with cyclohexane in the distillate. The only solvent not to result in a higher relative volatility is acetonyl acetone which has a higher boiling point than aniline. However, it happened that NMP is common for both cases in separating aromatics and non-aromatics. Unfortunately, DMF as a commonly used solvent is neglected by Braam. The reason may be that DMF forms minimum boiling point azeotropes with non-aromatic hydrocarbons with 6–8 carbon atoms (i.e, cyclohexane and heptane) (Cesar et al., 1997), which causes solvent losses with the distillate. In order to decrease the solvent losses, the addition of steam to the distillation column above the solvent feed has been recommended. Steam breaks the DMF-hydrocarbons azeotrope, and DMF entrained by the distillate can be recovered by washing it with water or ion exchange. So the post-treatment after extractive distillation is somewhat complicated, which contributes to no economics of the whole process.

Separation of Ethanol and Water. The mixture forms a minimum-boiling azeotrope, and extractive distillation may be used as an alternative to azeotropic and pressure-swing distillation. The solvent given in the reference for this system is ethylene glycol (Lei et al., 2002d). This solvent will allow the recovery of ethanol in the distillate with a predicted relative volatility of 2.54 (UNIFAC). In contrast to this, the first solvent generated by CAMD for this system, hexachlorobutadiene, is predicted to cause a relative volatility more than 3 times this value. This solvent was tested and performed very well (Braam and Izak, 2000).

Solvents were also generated to reverse the relative volatility of the system to facilitate the recovery of water in the distillate. In this case, the best solvent calculated by CAMD is dodecane. The reason may be that water and dodecane can form azeotrope. So this type of distillation should be the

combination of azeotropic distillation and extractive distillation. However, no solvents could be found in the reference for this separation.

Other Systems. The systems of acetone/methanol, ethanol/ethyl acetate and methanol/methyl acetate, have been studied by Braam by using CAMD (Braam and Izak, 2000). For separating acetone and methanol, dimethyl sulfoxide (DMSO), generated by CAMD, is found to be the best alternative to water that is commonly used in industry; for separating ethanol and ethyl acetate, diethylene glycol and DMSO, generated by CAMD, were tested by experiments to be potential alternatives; for separating methanol and methyl acetate, tetrachloroethylene, generated by CAMD, was tested and found to perform very well. Therefore, it is suggested that tetrachloroethylene should replace 2-methoxy ethanol which is now used as the industrial solvent. However, it is known that tetrachloroethylene is toxic, which doesn't conform to the requirement of implicit properties. From this viewpoint, tetrachloroethylene is toxic, which doesn't conform to the requirement of implicit properties. Form this viewpoint, tetrachloroethylene isn't the best as the solvent.

5.1.2. CAMD of Solid Salts

Procedure of CAMD for the Solid Salts

There is only one reference with regard to the work of CAMD for solid salts despite the frequent use of solid salts as separating agents in chemical engineering (Lei et al., 2002e), say nothing of ionic liquid. With the development of extractive distillation, the extractive distillation with the combination of liquid solvent and solid salts is becoming more and more applied in industry. Therefore, it is interesting to consider the salting effect in regard to CAMD.

As a simplified presumption, a salt is thought to be composed of one positive ion and one negative ion which are regarded as the groups of salts. It is consequently easy to assemble the ions into molecules in the same way as liquid solvents. These ions are collected and listed Table 10. In the procedure of CAMD, the combination rule is simply that the chemical valence of a salt must be zero, which impossible to lead to combination explosion because most molecules are composed of just two groups, one positive ion and the other negative ion. Therefore, both liquid solvents and solid salts can be designed in one CAMD program, and this goes further step in the application of CAMD.

The key of CAMD for solid salts is the selection of an appropriate thermodynamic method to obtain the target properties. However, the thermodynamic method for solids salts is very scare and inaccurate. That is where the limitation of CAMD for solid salts lie.

Table 10. Ions of CAMD for solid salts.

Ions	Groups			
Cation	Li^+	Na^+	K^+	Rb^+
	Cs^+	Ag^+	NH_4^+	Cu^+
	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}
	Be^{2+}	Fe^{2+}	Zn^{2+}	Cu^{2+}
	Al^{3+}	Fe^{3+}		
Anion	OH^-	F^-	Cl^-	Br^-
	I^-	SCN^-	NO_3^-	NO_2^-
	CH_3COO^-	ClO_4^-	BF_4^-	

Adapted from Lei et al. (2002e).

Application of CAMD for the Solid Salts

There is only one example reported in the reference (Lei et al., 2002e), i.e. the system of ACN/C4. CAMD for this separation has been performed on a PC (Pentium 2 286 MHz). The constraints for the system of ACN/C4 include pre-selected group type number, expected group number, temperature, minimum infinite dilute relative volatility, concentration of additive and key components. Moreover, the salts must meet the requirement of implicit properties, e.g. chemical stability, oxidation, material source, price factor and solubility in ACN, etc. These factors taken in, the solid salts NaSCN and KSCN are excellent additives. On the basis of CAMD, some experiments are performed to investigate the effect of solid salts.

Simulation of extractive distillation process for ACN and ACN/NaSCN with a 10wt% salt concentration is carried out. The results show that the required solvent flowrate decreases 11.8% and much energy is saved in the extractive distillation column when solid salt is added. Therefore, the mixture of ACN and solid salt performs more satisfactorily than a single ACN solvent. Apart from this, the mixture has no problem about dissolution, reuse and transport of salt, which is often brought on by using a single salt.

5.1.3. CAMD of Ionic Liquids

It is a pity that by now, there is no report of CAMD for ionic liquids. From the 3rd chapter, we know that ionic liquids may become potential excellent separating agents in extractive distillation. So CAMD for ionic liquids is a very interesting topic.

Since ionic liquid is still a kind of salt, the program of CAMD for ionic liquids should be similar to that for solid salts. Likewise, an ionic liquid can

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be assumed to be composed of one positive ion and one negative ion, which are regarded as the groups of salts. It is consequently easy to assemble the ions into molecules. In the procedure of CAMD, the combination rule for ionic liquids is also same to that for solid salts. So it indicates that CAMD for ionic liquids, solid salts and liquid solvents, can be placed in a same program, which facilitates the exploitation and use of CAMD.

These ions are collected and listed in Table 11, where *R* is alkyl (Zhao et al., 2002).

The key of CAMD for ionic liquids is the selection of an appropriate thermodynamic method to obtain the target properties. For extractive distillation, the most important of all the explicit properties is the activity coefficient, which can be used to calculate relative volatility or selectivity, and thus evaluate the possible ionic liquids.

Today, there are two methods commonly used for predicting activity coefficient, i.e. UNIFAC (UNIQUAC functional group activity coefficient) model and MOSCED (modified separation of cohesive energy density) model. The UNIFAC model is the most widely used, and based on the contributions of the constituent groups in a molecule. Since the first version of UNIFAC, several revisions and extensions have been proposed to improve the prediction of activity coefficient. The MOSCED model is an extension of regular solution theory to mixtures that contain polar and hydrogen bonding components. The cohesive energy density is separated into dispersion forces, dipole forced, and hydrogen bonding with small corrections made for asymmetry. However, it is very possible that group parameters of the selected ionic liquid can't be found in the present limited parameter table of UNIFAC and MOSCED models. In this case, COSMO-RS (Conductor-like Screening Model for Real Solvents) model is selected and used as an alternative to UNIFAC and MOSCED models (Gmehling, 1998; Thomas and Eckert, 1984).

Table 11. Typical cation/anion combinations in ionic liquids.

Cations	Anions	Coordination ability of anions
Alkylammonium, Alkylphosophonium, N-alkylpyridinium, N-dialkylimidazolium	$[BF_4]^-$, $[PF_6]^-$, $[SbF_6]^-$, $[CF_3SO_3]^-$, $[CUCl_2]^-$, N, $[AlCl_4]^-$, $[AlBr_4]^-$, $[AlI_4]^-$, $[AlCl_3Et]^-$, $[NO_3]^-$, $[NO_2]^-$, $[SO_4]^{2-}$	Weak (neutral)
PR_4^+, SR_4^+, NR_4^+	$[Cu_2Cl_3]^-$, $[Cu_3Cl_4]^-$, $[Al_2Cl_7]^-$, $[Al_3Cl_{10}]^-$	None (acidic)

COSMO-RS model is a novel and efficient method for the priori prediction of thermophysical data of liquids, and has been developed since 1994 (Klamt, 1995; Klamt and Eckert, 2000; Klamt et al., 1998). It is based on unimolecular quantum chemical calculations that provide the necessary information for the evaluation of molecular interactions in liquids. It can be applied to nearly any system for which no group parameters are available in the UNIFAC and MOSCED models. Moreover, COSMO-RS model is open for a large number of qualitative improvements and functional extensions. A correction for misfit charge interactions will improve the accuracy of the electrostatic part and enable calculations for ions.

In COSMO-RS model, the activity coefficient of component i is related with chemical potential and given as follows:

$$\gamma_i = \exp\left(\frac{\mu_i - \mu_i^0}{RT}\right) \tag{13}$$

where μ_i is the chemical potential of component i in the mixture, μ_i^0 the chemical potential in the pure liquid substance, T the absolute temperature and R gas constant. The chemical potential can be solved by using the exact equation resulting from statistical thermodynamics.

Therefore, it is possible to select the potential ionic liquid by means of CAMD. However, it is known that the ionic liquids must meet the requirement of implicit properties that can't be obtained by calculation. In this case it is better to set up a data bank of commonly used ionic liquids. Table 12 shows some implicit properties of commonly used ionic liquids (Zhao et al., 2002), which can be input into the CAMD program for screening ionic liquids. By combination of explicit and implicit properties, it is believed that the best ionic liquid can be found by CAMD.

5.2. Other Methods for Screening Solvents

5.2.1. Pierotti-Deal-Derr Method

Apart from CAMD, the potential solvents may be evaluated by other prediction methods. Pierrotti-Deal-Derr method is one of those methods (Duan, 1978) that can be used to predict the activity coefficient at infinite dilution and thus deduce relative volatility at infinite dilution, the most important explicit property in extractive distillation.

Activity coefficients at infinite dilution are correlated to the number of carbon atoms of the solute and solvent (n_1 and n_2). For the members of

Table 12. Some implicit properties of commonly used ionic liquids.

Ionic liquid[a]	x[b]	Color (with impurities)	Density (g/ml)	Liquid temperature (°C)		Solubility in common solvents[c]							
				Lowest	Highest	Water	Methanol	Acetone	Chloroform	Petroleum ether	Hexane	Acetic anhydride	Toluene
[bmim]BF_4		Light yellow	1.320	−48.96	399.20	s	s	s	s	i	i	i	i
[bmim]PF_6		Light yellow	1.510	13.50	388.34	i	s	s	s	i	i	s	i
[bmim]Cl/$AlCl_3$	0.50	Light brown	1.421	−88.69	263.10	r	r	s	s	i	i	s	s
	0.55	Light brown	1.456	−94.44	286.59	r	r	s	s	i	i	s	s
	0.60	Light brown	1.481	−95.87	316.34	r	r	s	s	i	i	s	s
[emim]Br/$AlCl_3$	0.50	Purplish black	1.575	13.61	272.51	r	r	s	i	i	i	s	i
	0.55	Brownish black	1.656	6.45	294.02	r	r	s	i	i	i	s	i
	0.60	Brownish black	1.995	−19.08	345.34	r	r	s	i	i	i	s	i
[emimi]PF_6		Yellow	1.426	2.71	304.65	i	i	s	s	i	i	s	i
N-butylpyridine/$AlCl_3$	0.50	Yellow	1.412	18.80	240.00	r	r	s	i	i	i	s	s
	0.55	Brownish yellow	1.430	33.73	245.39	r	r	s	i	i	i	s	s
	0.60	Brownish yellow	1.497	18.11	260.2	r	r	s	i	i	i	s	s
$(CH_3)_3NHCl$/$2AlCl_3$	0.66	Brownish yellow	1.621	−67.90	80.25	r	r	s	i	i	i	s	s

[a][bmim] = 1-butyl-3-methylimidazolium, [emim] = 1-ethyl-3-methylimidazolium.
[b]Apparent mole fraction of $AlCl_3$.
[c]s: soluble; i: insoluble; r: may react with each other.
Adapted from Zhao et al. (2002).

homologous series $H(CH_2)_{n1}X_1$ (solute) in the members of the homologous series $H(CH_2)_{n2}Y_2$:

$$\lg \gamma_1^{\infty} = A_{12} + \frac{F_2}{n_2} + B_2 \frac{n_1}{n_2} + \frac{C_1}{n_1} + D_0(n_1 - n_2)^2 \tag{14}$$

where the constants are functions of temperature, B_2 and F_2 are functions of the solvent series, C_1 is a function of the solute series, A_{12} is a function of both, and D_0 is independent of both.

For zero members of a series, e.g. water for alcohol, no infinite value for γ^{∞} is obtained. Instead, by convention, any terms containing an n for the zeromember are incorporated in the corresponding coefficient. So for n-alcohols in water:

$$\lg \gamma_1^{\infty} = K + B_2 n_1 + C_1/n_1 \tag{15}$$

Notice that the term $D_0(n_1 - n_2)^2$ is incorporated into the K constant because D_0 is smaller than the other coefficients by a factor of 1000. Therefore, this term is insignificant. In Eq. 15 only K is a function of the solute and solvent. B_2 is always the same when water is the solvent and C_1 is the same for n-alcohol solutes. This is shown better from the following homologous series in water at 100°C.

$$\text{n-Alcohols: } \lg \gamma_1^{\infty} = -0.420 + 0.517 n_1 + \frac{0.230}{n_1} \tag{16}$$

$$\text{n-Aldehydes: } \lg \gamma_1^{\infty} = -0.650 + 0.517 n_1 + \frac{0.320}{n_1} \tag{17}$$

where the coefficient B is the same in both cases.

5.2.2. Parachor Method

Activity coefficients at infinite dilution are obtained from the following relationship:

$$\lg \gamma_1^{\infty} = \frac{1}{2.303RT}[U_1^{1/2} - CU_2^{1/2}]^2 \tag{18}$$

$$U_i = \Delta H_i^v - RT \tag{19}$$

where U_i is potential energy of component i, ΔH_i^V is enthalpy of evaporation, C is a constant, a function of temperature, the parachor ratio of the two components, and the number of carbon atoms in the solute and solvent molecules, T is the absolute temperature, and R is gas constant. About the same variety of systems covered in the Pierrotti-Deal-Derr method, is covered in this approach.

5.2.3. Weimer-Prausnitz Method

Starting with the Hildebrand-Schatchard model for non-polar mixtures, Weimer and Prausnitz developed an expression for evaluating values of hydrocarbons in polar solvents:

$$RT \ln \gamma_2^{\infty} = V_2[(\lambda_1 - \lambda_2)^2 + \tau_1^2 - 2\psi_{12}] + RT\left[\ln \frac{V_2}{V_1} + 1 - \frac{V_2}{V_1}\right] \quad (20)$$

where V_i is the molar volume of pure component i, λ_i is the non-polar solubility parameter, τ_i is the polar solubility parameter, T is the absolute temperature, and R is gas constant. The subscript 1 represents the polar solvent and subscript 2 is the hydrocarbon solute with

$$\psi_{12} = k\tau_1^2 \quad (21)$$

Later Helpinstill and Van Winkle suggested that Eq. 20 is improved by considering the small polar solubility parameter of the hydrocarbon (olefins and aromatics):

$$RT \ln \gamma_2^{\infty} = V_2[(\lambda_1 - \lambda_2)^2 + (\tau_1 - \tau_2)^2 - 2\psi_{12}] + RT\left[\ln \frac{V_2}{V_1} + 1 - \frac{V_2}{V_1}\right] \quad (22)$$

$$\psi_{12} = k(\tau_1 - \tau_2)^2 \quad (23)$$

For saturated hydrocarbons,

$$\psi_{12} = 0.399(\tau_1 - \tau_2)^2 \quad (24)$$

For unsaturated hydrocarbons,

$$\psi_{12} = 0.388(\tau_1 - \tau_2)^2 \quad (25)$$

For aromatics,

$$\psi_{12} = 0.447(\tau_1 - \tau_2)^2 \quad (26)$$

The term ψ_{12} corresponds to the induction energy between the polar and non-polar components. Since no chemical effects are included, the correlation should not be used for solvents showing strong hydrogen bonding.

It is evident that the parameters of these three methods are incomplete, which leads to their very limited application in extractive distillation. So these methods are rarely reported in the recent references.

However, CAMD based on group contribution methods is very desirable. By means of CAMD, the experiment working is greatly decreased in a

search for the best solvents. CAMD as a useful tool plays an important role in finding the solvent and shortening the search time. It is believed that with the development of CAMD, it would be possible to be extended and applied in many more fields.

6. THEORY OF EXTRACTIVE DISTILLATION

Until now, there are two theories related to extractive distillation, i.e. Prausnitz and Anderson theory which gives semi-quantitative explanations, and Scaled Particle Theory which gives complete quantitative results. The two theories provide a molecular basis for explaining why some solvents can increase the relative volatility of the components to be separated, and more selective than others.

6.1. Prausnitz and Anderson Theory

Separation of hydrocarbon mixtures by extractive distillation has been practiced industrially for many years, even though there has been only limited understanding of the fundamental phase equilibria which forms the thermodynamic basis of this operation. In general, it is known that the addition of polar solvents to hydrocarbon mixture results in increased volatilities of paraffins relative to naphthenes, olefins, diolefins and alkynes, and in increased volatilities of naphthenes relative to aromatics. Therefore, the addition of a polar solvent enables facile separation by distillation of certain mixtures which otherwise can only be separated with difficulty. The Prausnitz and Anderson theory (Prausnitz and Anderson, 1961) tries to explain the solvent selectivity in extractive distillation of hydrocarbons from the viewpoint of molecular thermodynamics and intermolecular forces. The interaction forces between the solvent and the component are broadly divided into two types, i.e. physical force and chemical force. The true state in the solution is undoubtedly a hybrid of these two forces.

6.1.1. Physical Force

The selectivity 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 in such a manner.

$$RT \ln S_{23} = [\delta_{1p}^2(V_2 - V_3)] + [V_2(\delta_{1n} - \delta_2)^2 - V_3(\delta_{1n} - \delta_3)^2] + [2V_3\xi_{13} - 2V_2\xi_{12}] \quad (27)$$

where subscripts 1–3 represent solvent, the light component and the heavy component to be separated by extractive distillation, respectively, and V_i is the molar volume of component i.

The three bracketed terms in Eq. 27 show, respectively, the separate contributions of physical force to the selectivity, i.e. the polar effect, the dispersion effect and the inductive effect of the solvent. It is convenient to rewrite Eq. 1 as

$$RT \ln S_{23} = P + D + I \tag{28}$$

where

$$P = \delta_{1p}^2 (V_2 - V_3)$$

$$D = V_2(\delta_{1n} - \delta_2)^2 - V_3(\delta_{1n} - \delta_3)^2$$

$$I = 2V_3\xi_{13} - 2V_2\xi_{12}$$

It is found that the polar term P is considerably larger than the sum of D and I, and frequently very much larger. Thus, Eq. 28 becomes

$$RT \ln S_{23} = \delta_{1p}^2 (V_2 - V_3) \tag{29}$$

Of course in the special case where components 2 and 3 are identical in size, the polar term vanishes. This means that the physical force can't play a role in separating hydrocarbon mixture. In this case, the chemical force is dominant, and can be used to explain the separation phenomena, as is discussed in the following text.

Eq. 29 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. It indicates that the effectiveness of a solvent depends on its polarity, which should be large, and on its molar volume, which should be small.

One example of separating C4 mixture is given to illustrate the physical force. It is known that the order of the molar volume of C4 mixture is in the following

Butane > butene > butadiene > butyne

According to Eq. 29, the order of volatilities of C4 mixture is in the same following

Butane > butene > butadiene > butyne

However, in order to have a much higher selectivity, the polar solubility parameter of the solvents should be as great as possible. That is why

Table 13. The solvents for separating ethane and ethylene.

	Dipole moment	Relative volatility	Selectivity
Solvents	μ(debyes)	α_{12}^{∞}	S_{12}^{∞}
Toluene	1.23	0.84	0.83
Xylene	o-1.47	0.90	0.89
	m-1.13		
	p-0		
Tetrahydrofuran	5.70	0.97	0.96
Butyl acetate	6.14	0.95	0.94
Ethyl acetate	6.27	1.01	1.00
Pyridine	7.44	1.02	1.01
Acetone	8.97	1.08	1.07
ACN	11.47	1.24	1.23
DMF	12.88	1.20	1.19
Dimethyl sulfoxide	13.34	1.19	1.18
NMP	13.64	1.14	1.13

Adapted from Yi et al. (2001).

such solvents as ACN, DMF and NMP with high polarity and small molar volume, are used for this separation.

Another example is concerned with the separation of ethane (1) and ethylene (2) by extractive distillation (Yi et al., 2001). The experimental results are listed in Table 13, in which the solvent polarity is characterized by dipole moment. It can be seen from Table 13 that with the increase of dipole moment, relative volatility and selectivity at infinite dilution also approximately rise, which is consistent with the Prausnitz and Anderson theory.

6.1.2. Chemical Force

For components of identical size, solvent polarity is not useful and selectivity on the basis of a physical effect is not promising. For such cases selectivity must be based on chemical force which will selectively increase the interaction between the solvent and the components. However, separation of components of identical size is very rare.

The chemical viewpoint of solutions considers that nonideality in solution arises because of association and solvate. In accordance with this concept, the true species in solution are loosely bonded aggregates consisting of two (or more) molecules of the same species (association) or of

different species (solvate). That is to say, the solvent and the component can form complexes. Such complexes are believed to be the result of acid-base interactions following the Lewis definitions that a base is an electron donor and that an acid is an electron accepter.

For example, for the separation of C4 hydrocarbons, the fluidity of electron cloud is different for the group C–C (no double-bond), C═C (only one double-bond), C═C–C═C (two double-bonds), C≡C (one trinary-bond), and in the following order

$$C - C < C = C < C = C - C = C < C{\equiv}C$$

The greater the fluidity is, the easier the group is to be polarized. Accordingly, the basicity of C4 hydrocarbons is in the same order

$$C - C < C = C < C = C - C = C < C{\equiv}C$$

which means that the chemical force between solvent and butyne is the greatest, while it is the smallest between solvent and butane.

So the volatilities of C4 hydrocarbons are in the following order

$$\text{Butane} > \text{butane} > \text{butadiene} > \text{butyne}$$

which is consistent with the conclusion resulting from experiment.

A schematic diagram of complex formation between DMF and cis-2-butene is given in Figure 19.

In fact, in the solution physical and chemical forces exist at the same time. Just in some cases one is predominant, and the other is minor.

The limitation of this theory is that it is only suitable for the separation of non-polar systems. However, in extractive distillation, polar-polar and non-polar –polar systems are often met, and at this time the molecular interaction may be more complicated. But the idea of physical and chemical

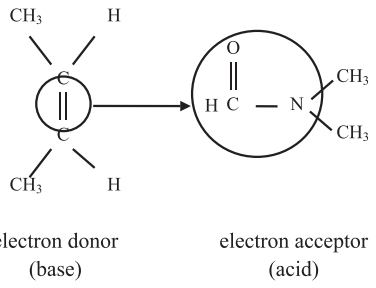

Figure 19. Schematic diagram of chemical interaction (arrow shows donation of electrons.)

forces is valuable and may be adopted. For instance, for the separation of acetic acid and water with tributylamine as the separating agent by extractive distillation, the chemical force between acetic acid and tributylamine is very strong and has been verified by IR and GC-MS techniques (See Chapter 3, 3.2.3 Case studies).

6.2. Scaled Particle Theory

6.2.1. The Relationship of Salt Effect and Relative Volatility at Infinite Dilution

Due to the unique advantages, extractive distillation with the combination of liquid solvent and solid salt as an advanced technique has been received more attention. However, selection of solid salt needs theoretical guidance. In this case, scaled particle theory is recommended to apply for extractive distillation, and tries to interpret the effect of solid salt on extractive distillation. Moreover, it provides a theoretical support for optimizing the solvents when needed.

Nowadays there are many theories (Li, 1988; Masterton and Lee, 1970; Pierotti, 1976; Shoor and Gubbins, 1969) about salt effect such as the electrostatic theory of Debye-McAulay in dilute electrolyte solutions, internal pressure theory of McDevit-Long, salt effect nature of Huangziqing, electrolyte solution theory of Pitzer and scaled particle theory, in which the first four theories require the experimental data to correlate or make some simplification with a little accuracy or have no wide range to apply. But the scaled particle theory, which is deduced from thermodynamics and statistical physics, has defined physical meaning, and the required molecular parameters are readily available. Especially, in the recent years, the study of scaled particle theory has been farther developed. But, first of all, scaled particle theory can be applied to extractive distillation with the combination of liquid solvent and solid salt. Therefore, it is reasonable to deal with salt effect of extractive distillation with this theory.

The relationship of salting coefficients and relative volatilities at infinite dilution can be deduced and expressed as follows

$$\frac{a_s^{\infty}}{a_0^{\infty}} = 10^{(k_{s1}-k_{s2})c_s} \tag{30}$$

where a_s^{∞} and a_0^{∞} represent relative volatilities at infinite dilution with salt and no salt.

Eq. 30 constructs a bridge between microscale and macroscale. Even if the calculated salting coefficients are not accurate due to the current

limitation of scaled particle theory, it is not difficult to judge the magnitude of k_{s1} and k_{s2} by the conventional solution knowledge and decide whether it is advantageous to improve the relative volatilities with salt. From Eq. 30, it concludes that if $k_{s1} > k_{s2}$ with low salt concentration the relative volatilities of components to be separated will be increased by adding salt, and the more great the difference between k_{s1} and k_{s2}, the more apparent the effect of improving relative volatility.

Four systems DMF/C4, ACN/C3, ethylene glycol/ethanol/water and ethylene glycol/acetone/methanol are investigated (Lei et al., 2002f; Liao et al., 2001). As to the first two non-polar solutes systems, the non-electrolytes bring out salting-out in the solutions. But for the final two polar solutes systems, the effect is salting-in.

For separating non-polar system, e.g. DMF/C4 and ACN/C3, the relative volatilities at infinite dilution calculated by scaled particle theory correspond well with experimental values. The reason may be that C4 and C3 are non-polar components and the sizes of them are not large, which lead to the accurate results. It is of interest to compare the relative contribution of the three terms k_α, k_β; and k_γ to the salting coefficient, k_s. It is noted that k_γ is small. Therefore, the salting coefficients k_s mainly depends upon the relative magnitudes of k_α and k_β.

However, for separating polar systems, salt coefficients are not easy to be accurately calculated in terms of scaled particle theory. But it does not influence our analysis on whether it is advantageous to add salt to a system because in most cases, it is not difficult for us to qualitatively judge the relative magnitude of salt coefficient of each component. But in the past the interpretation of the phenomena is very vague (Duan et al., 1980; Lei et al., 1982; Zhang et al., 1984; Zhao et al., 1989, 1992).

Although the application of scaled particle theory to the calculation of salt effect has the great advantages that the required molecular parameters are readily available, it is limited in some degrees. For polar solutes, scaled particle theory can only provide qualitative analysis according to Eq. 30. The reason may be that the hydrogen bonding between polar solutes and polar solvent is very complicated and greater than van der Waals bonding. By now, only van der Waals bonding is considered in scaled particle theory. So it is normal that quantitative calculation for polar solutes is very difficult and inaccurate. We know any theory has its own deficiency, but we believe that with the development of scaled particle theory, the problem will be solved one day.

Anyway, scaled particle theory is extended to solve the problem of extractive distillation with the combination of solvent and salt, and will promote the development of extractive distillation that is always an important separation method.

7. MATHEMATIC MODEL OF EXTRACTIVE DISTILLATION

For design of distillation process, two types of modeling approaches have been developed: the equilibrium (EQ) stage model and the non-equilibrium (NEQ) stage model. The most difference between these two models is that the mass and heat transfer rates should be considered in every tray in the NEQ stage model. For extractive distillation, the process can be simulated either by EQ stage model or by NEQ stage model.

7.1. EQ Stage Model

7.1.1. Model Equations

The schematic diagrams of a tray column for EQ stage model are shown in Figure 20. In general, the assumptions adopted are the following (Komatsu, 1977; Komatsu and Holland, 1977; Jelinek and Hlavacek, 1976):

1. Operation reaches steady state;
2. System reaches mechanical equilibrium in every tray;
3. The vapor and liquid bulks are mixed perfectly and assumed to be at thermodynamic equilibrium;
4. Heat of mixing can be neglected;
5. Reactions take place in the liquid phase; if reactions take place in the vapor phase, the actual vapor compositions are replaced by transformed superficial compositions.

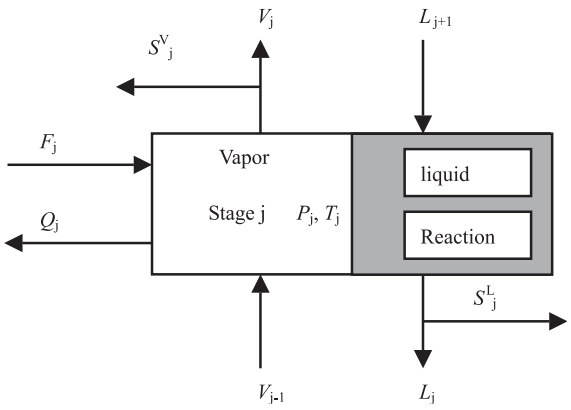

Figure 20. Schematic representation of an EQ stage.

6. The condenser and reboiler are considered as an equilibrium tray;
7. If the catalyst is used, then the amount of catalyst in each tray of reaction section is equal;
8. If the catalyst is used, then the influence of catalyst on the mass and energy balance is neglected because the catalyst concentration in the liquid phase is often low.

The equations that model EQ stages are known as the MESHR equations. MESHR is an acronym referring to the different types of equation. The M equations are the material balance equations. The total material balance takes the form

$$\frac{dM_j}{dt} = V_{j+1} + L_{j-1} + F_j - (1 + r_j^V)V_j - (1 + r_j^L)L_j + \sum_{k=1}^{r}\sum_{i=1}^{c} v_{i,k}R_{k,j}\varepsilon_j \tag{31}$$

where F, V, L are feed, vapor and liquid flowrates, respectively, t is time, $R_{\mathrm{k,j}}$ is reaction rate, $v_{i,k}$ is the stoichiometric coefficient of component i in reaction k, ε is reaction volume or amount of catalyst, and M_j is the hold-up on stage j. With very few exceptions, M_j is considered to be the hold-up only of the liquid phase. It is more important to include the hold-up of the vapor phase at higher pressures. The component material balance (neglecting the vapor hold-up) is

$$\frac{dM_j x_{i,j}}{dt} = V_{j+1}y_{i,j+1} + L_{j-1}x_{i,j-1} + F_j z_{i,j} - (1 + r_j^V)V_j y_{i,j} - (1 + r_j^L)L_j x_{i,j} + \sum_{k=1}^{r} v_{i,k}R_{k,j}\varepsilon_j \tag{32}$$

where x, y are mole fraction in the liquid and vapor phase, respective.

In the material balance equations given above r_j is the ratio of sidestream flow to interstage flow:

$$r_j^V = S_j^V/V_j,\ r_j^L = S_j^L/L_j \tag{33}$$

The E equations are the phase equilibrium relations

$$y_{i,j} = K_{i,j}x_{i,j} \tag{34}$$

where $k_{i,j}$ is chemical equilibrium constant. The S equations are the summation equations

$$\sum_{i=1}^{c} x_{i,j} = 1, \sum_{i=1}^{c} y_{i,j} = 1 \tag{35}$$

The enthalpy balance is given by

$$\frac{dM_jH_j}{dt} = V_{j+1}H_{j+1}^V + L_{j-1}H_{j-1}^L + F_jH_j^F - (1 + r_j^V)V_jH_j^V - (1 + r_j^L)L_jH_j^L - Q_j \tag{36}$$

where H is molar enthalpy, and Q is heat duty.

There is no need to take separate account in Eq. 36 of the heat generated due to chemical reaction since the computed enthalpies include the heats of formation.

The R equations are the reaction rate equations. For the reactive extractive distillation it is known that chemical reaction is reversible, and the reaction rate is assumed to be zero. That is to say, the chemical equilibrium is reached in every tray.

Under steady-state conditions all of the time derivatives in the MESH equations are equal to zero. Newton's method (or a variant thereof) for solving all of the independent equations simultaneously is an approach nowadays widely used. But other methods also frequently appear, e.g. the relaxation method. In this method the MESH equations are written in unsteady-state form and are integrated numerically until the steady-state solution has been found, is used to solve the above equations.

7.1.2. Case Studies

EQ stage model is used for the process simulation of extractive distillation, and can obtain the necessary information for various purposes. In what follows we discuss the steady state of extractive distillation and extractive distillation with chemical reaction (i.e. reactive extractive distillation) in the EQ stage model. It would be nearly impossible to cite every paper about the EQ stage model, but we try to be comprehensive in our coverage.

Steady State Analysis

Analysis of operation state is still a topic of considerable interest in the distillation community. Especially in the catalytic distillation process the non-linearity phenomena are very prominent, and multiple steady state is easy to appear.

For the separation of C4 mixture by extractive distillation with DMF, the operation state is analyzed by changing the feeding location of solvent, which

is a sensitive parameter. The feeding location of solvent into the extractive distillation column for recovering butane is variable, but other operating conditions are kept constant. The relation of the top molar composition of butane with the feeding stage of solvent is shown in Figure 21 (the stage is numbered from the top to the bottom). When the solvent is fed in the vicinity of No.20 stage, the composition change is very abrupt and two operation states (OS) are found. However, only No.1 operation state (OS) is desirable because in this case the top molar composition of butane is much higher.

Similarly, only the feeding location of solvent into the extractive distillation column for recovering 1,3-butadiene is variable, but other operating conditions are kept constant. In this case the top molar composition of 1,3-butadiene is stable because the amount of vinylacetylene (VAC) is so small that the 1,3-butadiene composition is not affected. The function of this column is to remove VAC from 1,3-butadiene, so the change of the bottom flowrate of VAC should be obvious. The relation of the bottom flowrate of VAC (kmol/h) with the feeding stage of solvent S is shown in Figure 22 (the stage is numbered from the top to the bottom). It can be seen from Figure 22 that when solvent S is fed in the vicinity of No.30 stage, two operation states are also found. However, only No.1 operation state is

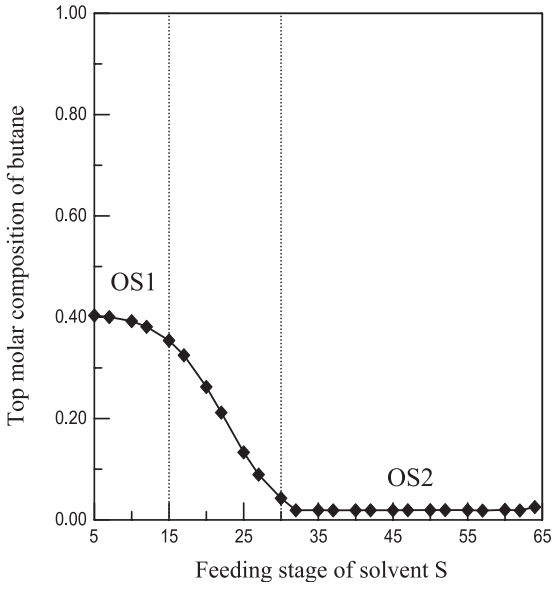

Figure 21. The relation of the top composition of butane with the feeding stage of solvent S in the extractive distillation column.

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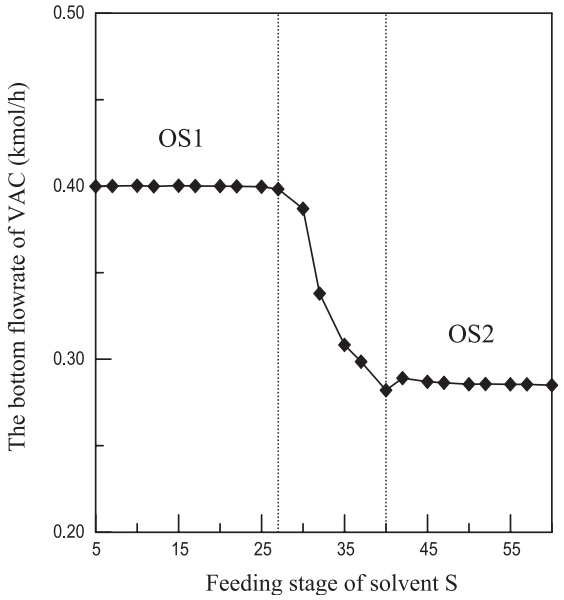

Figure 22. The relation of the bottom flowrate of VAC with the feeding stage of solvent in the extractive distillation column.

desirable because in this case the amount of VAC removed from 1,3-butadiene is greater.

Therefore, by using of EQ stage model, we can find which operation state is the best or the worst.

Reactive Extractive Distillation

In the EQ stage model, if there exists no chemical reaction, the independent equations are simplified, only solving MESH equations. However, for reactive extractive distillation, EQ stage model is somewhat complicated, especially when there exist more than one chemical reactions. Separation of acetic acid and water with tributylamine as the separating agent is just the case.

As mentioned in the front, the following reversible chemical reaction may take place:

$$HAc + R_3N \rightleftharpoons R_3NH^+ \cdot {}^-OOCCH_3$$

where HAc, R_3N and $R_3NH^+ \cdot {}^-OOCCH_3$ represent acetic acid, tributylamine and the salt formed by the reaction, respectively.

The chemical equilibrium constant K_p at 25°C can be deduced, and thus the relation of chemical equilibrium constant with temperature is expressed by Eq. 4.

On the other hand, it is known that aggregation of acetic acid molecules in the vapor phases occurs. If only aggregation of two molecules is considered, the following reversible chemical reaction may take place:

$$2A_1 \rightleftharpoons A_2$$

where A_1 is the monomer of acetic acid, and A_2 is the dimer of acetic acid.

In this case, the chemical equilibrium constant K_{A_2} is written,

$$K_{A_2} = \frac{\eta^V_{A_2}}{P(\eta^V_{A_1})^2} \tag{37}$$

where η is the superficial molecular number in the vapor phase.

In addition, K_{A_2}, the function of temperature, can also be calculated by the following empirical equation (Shi et al., 1999a,b),

$$\lg K_{A_2} = \varepsilon_{A_2} + \omega_{A_2}/T \tag{38}$$

where $\varepsilon_{A_2} = -10.4205$, $\omega_{A_2} = 3166$.

The key in the simulation of extractive distillation process is the selection of an accurate VLE model to solve the EQ stage model of the column. In general, the Wilson, NRTL and UNIQUAC equations, which are suitable for systems composed of many components and can deduce the multi-components system from binary systems, are used.

Although the VLE data can be obtained by experiments and then correlated by the iterative solution using the maximum likelihood regression, the interaction parameters of the VLE model may be various under different assumptions. Table 14 shows the interaction parameters of Wilson,

Table 14. Interaction parameters of Wilson, NRTL and UNIQUAC equations for the system of water (1) and acetic acid (2) (unit: J/mol).

Equation	A_{12}	A_{21}	Δy_1
1. Not considering two-molecule aggregation			
Wilson	3766.34	−3301.3	0.0204
NRTL ($\alpha = 0.47$)	87.86	363.04	0.0205
UNIQUAC	−2882.96	4149.57	0.0241
2. Considering two-molecule aggregation			
Wilson	3566.01	−818.99	0.0164
NRTL ($\alpha = 0.47$)	2861.58	−120.11	0.0164
UNIQUAC	−1553.11	2321.62	0.0185

Table 15. Interaction parameters of Wilson, NRTL and UNIQUAC equations for the system of water (1) and tributylamine (2) (unit: J/mol).

Equation	A_{12}	A_{21}	Δy_1
Wilson	16425.00	22378.10	0.0213
NRTL ($\alpha = 0.3$)	9245.76	2940.54	0.0202
UNIQUAC	791.39	302.74	0.0191

NRTL and UNIQUAC equations for the system of water (1) and acetic acid (2) under two cases: considering two-molecule aggregation and not, respectively; Table 15 shows the interaction parameters of Wilson, NRTL and UNIQUAC equations for the system of water (1) and tributylamine (2); Table 16 shows the interaction parameters of Wilson, NRTL and UNIQUAC equations for the system of acetic acid (1) and tributylamine (2) under three cases: not considering two-molecule aggregation and reversible chemical reaction, only considering reversible chemical reaction, and considering two-molecule aggregation and reversible chemical reaction at the same time, respectively.

In these tables, an average deviation Δy_1 is calculated as,

$$\text{Average deviation} = \frac{\sum_{i=\text{t}}^{N} |\Delta y|}{N}$$

where N is the times of experiments.

Table 16. Interaction parameters of Wilson, NRTL and UNIQUAC equations for the system of acetic acid (1) and tributylamine (2) (unit: J/mol).

Equation	A_{12}	A_{21}	Δy_1
1. Not considering two-molecule aggregation and reversible chemical reaction			
Wilson	7373.29	−3558.84	0.1158
NRTL ($\alpha = 0.2$)	−1553.97	5263.68	0.1160
UNIQUAC	−1707.19	4830.12	0.1156
2. Only considering reversible chemical reaction			
Wilson	7550.79	−3478.02	0.1182
NRTL ($\alpha = 0.2$)	346.69	3413.18	0.1181
UNIQUAC	−1551.01	4697.44	0.1200
3. Considering two-molecule aggregation and reversible chemical reaction simultaneously			
Wilson	8731.21	−2265.00	0.0580
NRTL ($\alpha = 0.2$)	1496.1	4118.9	0.0596
UNIQUAC	−1505.47	5463.82	0.0552

Table 17. The comparison of the experimental and calculated values.

	T_{top}/°C				Water concentration at the top, wt%			
No.	Exp.	EQ1	EQ2	EQ3	Exp.	EQ1	EQ2	EQ3
1	99.9	99.7	99.5	99.7	99.74	96.20	96.30	96.46
2	100.2	99.8	99.9	99.6	99.81	94.09	92.10	97.51
3	99.6	100.0	99.5	99.7	99.77	98.78	99.30	96.08
4	99.9	100.5	99.8	99.5	99.86	94.73	94.77	98.55

It can be seen from Table 14 that the difference of interaction parameters between two cases is somewhat obvious, but the average deviation in both cases is small enough. The reason may be that the activity coefficients of water and acetic acid are not apparently changed at the total concentration, and the interaction parameters of the VLE models can be well correlated. Even so, it manifests that the influence of two-molecule aggregation on the interaction parameters can't be ignored.

In Table 16, the difference of interaction parameters among three cases is also somewhat obvious. Moreover, the average deviation in the third case is small enough. The reason may be that this case is approximate to the actual situation, and the VLE model can accurately describe the real activity coefficients. Besides, it manifests that the influence of both two-molecule aggregation and reversible chemical reaction on the interaction parameters can't be ignored.

By using of EQ stage model, the extractive distillation process of separating water and acetic acid is simulated. In the simulation, three cases are concerned, i.e. ①. not considering two-molecule aggregation and reversible chemical reaction (EQ1 model); ②. only considering reversible chemical reaction (EQ2 model); ③. considering two-molecule aggregation and reversible chemical reaction simultaneously (EQ3 model).

The experimental data, as well as the calculated results from the EQ stage models (EQ1, EQ2 and EQ3 models), are listed in Table 17. It is shown that the values of EQ3 model are closer to experimental results than those of EQ1 and EQ2 models. That means that EQ3 model reflects the real state of the system of water/acetic acid/ tributylamine more accurately.

In order to further investigate the difference among EQ1, EQ2 and EQ3 models, the composition and temperature distributions along the extractive distillation column under the same operation condition are given in Tables 18 and 19, where subscripts 1, 2 ,3 and 4 represent water, acetic acid, tributylamine and salt produced by the reaction, respectively. The tray

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Table 18. The composition distribution along the extractive distillation column for the EQ1, EQ2 and EQ3 models.

	x_1			X_2			x_3			x_4		
No.	EQ1	EQ2	EQ3	EQ1	EQ2	EQ3	EQ1	EQ2	EQ3	EQ1	EQ2	EQ3
1	0.0004	0.0002	0.0	0.4970	0.4762	0.4906	0.5029	0.4904	0.4769	0.0	0.0331	0.0326
2	0.0029	0.0015	0.0	0.8910	0.8736	0.7917	0.1058	0.1013	0.1775	0.0	0.0235	0.0308
3	0.0068	0.0036	0.0	0.9350	0.9266	0.8419	0.0582	0.0552	0.1318	0.0	0.0145	0.0263
5	0.0301	0.0164	0.0	0.9168	0.9142	0.8577	0.0531	0.0549	0.1177	0.0	0.0145	0.0245
7	0.1200	0.0680	0.0	0.8270	0.8580	0.8584	0.0530	0.0590	0.1169	0.0	0.0149	0.0246
9	0.3430	0.2268	0.0012	0.6015	0.7046	0.8569	0.0553	0.0556	0.1178	0.0	0.0130	0.0242
11	0.6184	0.4690	0.0474	0.3255	0.4562	0.8133	0.0561	0.0638	0.1152	0.0	0.0108	0.0241
13	0.4862	0.5194	0.1237	0.3006	0.3512	0.5910	0.2133	0.1164	0.2411	0.0	0.0129	0.0441
15	0.4885	0.6162	0.1617	0.3061	0.2759	0.5971	0.2054	0.0981	0.2149	0.0	0.0098	0.0263
17	0.6334	0.6576	0.1619	0.2318	0.2096	0.5430	0.1348	0.1224	0.2607	0.0	0.0104	0.0344
19	0.6612	0.6618	0.1486	0.2029	0.2091	0.5256	0.1359	0.1205	0.3008	0.0	0.0086	0.0250
21	0.7236	0.7523	0.2890	0.1386	0.1274	0.3986	0.1378	0.1145	0.2927	0.0	0.0058	0.0196
23	0.7939	0.7414	0.8163	0.0722	0.0688	0.0925	0.1340	0.1870	0.0874	0.0	0.0028	0.0038
24	0.8717	0.8570	0.8705	0.0328	0.0321	0.0348	0.0955	0.1093	0.0930	0.0	0.0016	0.0018
25	0.9730	0.9721	0.9680	0.0115	0.0112	0.0106	0.0155	0.0166	0.0213	0.0	0.0001	0.0

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Table 19. The temperature distribution along the extractive distillation column for the EQ1, EQ2 and EQ3 models.

	T/K		
No.	EQ1	EQ2	EQ3
1	404.83	404.90	424.45
2	393.75	393.71	420.07
3	392.51	392.37	419.40
5	391.41	391.26	419.19
7	388.34	388.14	419.18
9	382.65	382.43	418.97
11	377.76	377.65	411.03
13	378.06	376.89	395.89
15	378.73	376.62	394.63
17	376.89	375.60	392.60
19	376.44	375.62	393.41
21	376.44	374.16	384.81
23	374.12	373.22	374.53
24	373.30	372.88	373.36
25	372.84	372.69	372.83

is numbered from the bottom to the top. It can be seen from Table 18 that the calculated results of EQ1 model correspond well with those of EQ2 model on a large part of trays. However, in the vicinity of the tray feeding the mixture of acetic acid and water, i.e. from No. 9 to No.15, the difference of liquid composition distribution is enlarged, which may be due to the relatively great influence of the feed mixture on the chemical reaction between acetic acid and tributylamine. But the difference of the composition and temperature distributions between EQ3 model and EQ1 (or EQ2) model is evident. This indicates that the influence of two-molecule aggregation is more obvious than that of reversible chemical reaction. Anyway, EQ3 model is more suitable for the design and optimization of extractive distillation process than EQ1 and EQ2 models.

On the other hand, the effect of the solvent, tributylamine, on the separation of water and acetic acid, can be verified by simulation. It can be seen from Table 17 that water composition at the bottom of the extractive distillation column is nearly equal to zero. That is to say, the mixture of water and acetic acid can be effectively separated by extractive distillation with tributylamine as the separating agent.

7.2. NEQ Stage Model

The NEQ stage model for extractive distillation should follow the philosophy of rate-based models for conventional distillation. Unfortunately, it has been rarely reported on the NEQ stage model for extractive distillation. The reason may be that extractive distillation is a special distillation mode, and building an NEQ stage model for a distillation process is not as straightforward as it is for the EQ stage model. If the chemical reaction is involved, we need to simply add an equation to take account of the effect of chemical reaction on a tray or section of packing. As we know, the NEQ stage model is more complicated than the EQ stage model. In the NEQ stage model, the design information on the column configuration must be specified so that mass transfer coefficients, interfacial areas, liquid holdups, etc. can be calculated. Therefore, for any new invented configuration of the column, many experiments have to be done in advance to obtain the necessary model parameters. Evidently, it is too tedious, and much time will be spent on the design of extractive distillation process. Fortunately, as pointed out by Lee and Dudukovic (Lee and Dudukovic, 1998), a close agreement between the predictions of the EQ and NEQ stage models can be found if the tray efficiency or HETP (height equal to a theoretical plate) is known. So the EQ stage model is widely used in extractive distillation.

The model equations of NEQ stage for extractive distillation are similar to those for reaction distillation (Baur et al., 2000, 2001; Higler et al., 1999a,b; Lei et al., 2003; Taylor and Krishna, 2000). Though sophisticated NEQ stage model is available readily, detailed information on the hydrodynamics and mass transfer parameters for the various hardware configurations is woefully lacking in the open reference. Moreover, such information may have vital consequences for the calculated results of the distillation column. There is a crying need for research in this area. It is perhaps worth noting here that modern tools of computational fluid dynamics could be invaluable in developing better insights into hydrodynamics and mass transfer in the distillation column. But the computing time may be greatly prolonged.

In the field of reaction distillation (RD), recent NEQ modeling works have exposed the limitations of EQ stage model for final design and for the development of control strategies. NEQ stage model has been used for commercial RD plant design and simulation. Thus, it is conjecturable that NEQ stage model would be widely applied in extractive distillation, and EQ stage model only has its place for preliminary design. The research on NEQ stage model for extractive distillation should be strengthened in the near future.

But both in the EQ stage model and in the NEQ stage model, the thermodynamic and physical properties are required. Moreover in the NEQ

stage model the mass and energy transfer models are also necessary. Interested readers can refer to the references (Kooijman and Taylor, 1991; Krishna and Wesselingh, 1997; Reid et al., 1987; Seader and Henley, 1998; Tong, 1996).

8. COMPARISON OF EXTRACTIVE DISTILLATION AND ADSORPTION DISTILLATION

Adsorption distillation as a new separation method seems attractive and in this work is compared with traditional extractive distillation. The system of ethanol and water is selected because ethanol is a basic chemical material and solvent used in the production of many chemicals and intermediates. Especially in the recent year, ethanol is paid more attention because it is an excellent alternative fuel and has a virtually limitless potential for growth.

8.1. Definition of Adsorption Distillation

There are two kinds called adsorption distillation. One has presently been proposed by Abu Al-Rub (Fahmi et al., 1999; Fawzi et al., 2000). It involves replacement of the inert packing material in packed-bed distillation column by an active packing material. The active packing materials used by Abu Al-Rub for separating ethanol and water are 3Å or 4Å molecular sieves, which are thought to be able to alter the VLE of ethanol and water considerably.

On the other hand, we think that some ion-exchange resins can be assumed to be composed of one anion which has generally large molecular weight and one cation which is generally a single metal ion. Since salt effect may plays a role in raising the relative volatility of ethanol to water, ion-exchange resins can also be selected as the packing material in the adsorption distillation column. In this work we only discuss this kind of adsorption distillation.

Another kind of adsorption distillation has been put forward by Cheng et al (1999a,b). It doesn't involve replacement of internals of distillation. Tiny solid particles are used as the adsorption agent, and blended with liquid phase in the column. The enhancement of gas-liquid mass transport by the tiny solid particles has been proved, and the mechanism model is proposed. However, when adding solid particles to liquid phase, the packed column is prone to be jammed. From this viewpoint, the tray column is more suitable for this kind of adsorption distillation. Even so, it is difficult

to run the distillation column because the solid particles are accumulated after a long stay. With regard to this content, the interested readers can refer to the references.

The comparison of adsorption distillation and extractive distillation for separating ethanol and water is very interesting because adsorption distillation is an attractive ''new'' technique and extractive distillation is an ''old'' technique. The most commonly used separating agents in the extractive distillation are ethylene glycol, the mixture of ethylene glycol and one salt, $CaCl_2$ and N, N-dimethylformamide (DMF) (Lei et al., 2002d, Shealy et al., 1987).

The comparison of azeotropic distillation and extractive distillation has been made in the 1st chapter. Today, azeotropic distillation is almost replaced by extractive distillation for separating ethanol and water.

8.2. Process Experiment

The experimental flow sheet of extractive distillation process with two columns (extractive distillation column and solvent recovery column) has been established in the laboratory and is shown in Figure 23. The extractive distillation column was composed of three sections, (I)rectifying section of 30mm (diameter) × 800mm (height), (II)stripping section of 30mm (diameter) × 400mm (height) and (III)scrubbing section of 30mm (diameter) × 150mm (height). The solvent recovery column was composed of two sections, (I)rectifying section of 30mm (diameter) × 650mm (height) and

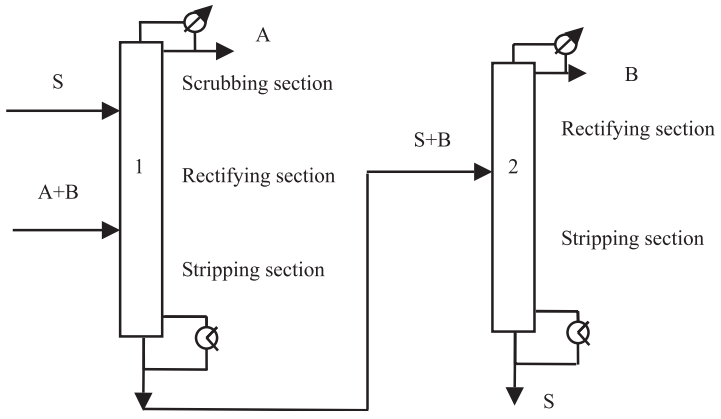

Figure 23. The two column process for extractive distillation. 1. Extractive distillation column; 2. solvent recovery column.

(II)stripping section of 30mm (diameter) × 300mm (height). The two columns were packed by a type of ring-shape packing with the size of 4mm (width) × 4mm (height). The theoretical plates are determined by use of the system of n-heptane and methylcyclohexane at infinite reflux, having 18 theoretical plates (including reboiler and condenser) for extractive distillation column and 14 theoretical plates (including reboiler and condenser) for solvent recovery column.

In the extractive distillation process experiment, the mixture of ethylene glycol and $CaCl_2$ was used as the separating agent. The reagents, ethylene glycol and $CaCl_2$, were of analytical purity, and purchased from the Beijing Chemical Reagents Shop, Beijing, PRC. Composition analyses of the samples withdrawn from the top of extractive distillation column were done by a gas chromatography (type Shimadzu GC-14B) equipped with a thermal conductivity detector. Porapark Q was used as the fixed agent of the column packing, and hydrogen as the carrier gas. The column packing was 160°C and the detector 160°C. The data were dealt with by a SC 1100 workstation. In terms of peak area of the components, the sample compositions could be deduced.

The experimental results of extractive distillation column are given in Table 20, where the feed concentration is ethanol of 0.3576 mole fraction and water of 0.6424 mole fraction. It is shown that high-purity ethanol (above 99.0%wt), up to 0.9835 mole fraction (almost 99.5%wt), is obtained under low solvent/feed volume ratio 2.0 and low reflux ratio 0.5, which means that the mixture of ethylene glycol and $CaCl_2$ is effective for the separation of ethanol and water by extractive distillation.

In order to test the effect of molecular sieves and ion-exchange resins on the separation of ethanol and water in the adsorption distillation column, a set of experimental apparatus was established and shown in Figure 24. The column was composed of two sections, (I) 30mm (diameter) × 600mm (height) and (II) 30mm (diameter) × 600mm (height). The first section was firstly filled with stainless steel ring-shape packing with the size of 3mm width and 3mm height, then filled with 3 Å sphere-shape molecular sieves with

Table 20. Experimental results of extractive distillation column.

No.	Solvent/feed volume ratio	Reflux ratio	T_{top}/K	The top composition	
				x_1 (ethanol)	x_2 (water)
1	0.5	0.5	351.1	0.8506	0.1494
2	1.0	0.5	351.1	0.9674	0.0326
3	2.0	0.5	351.1	0.9835	0.0165

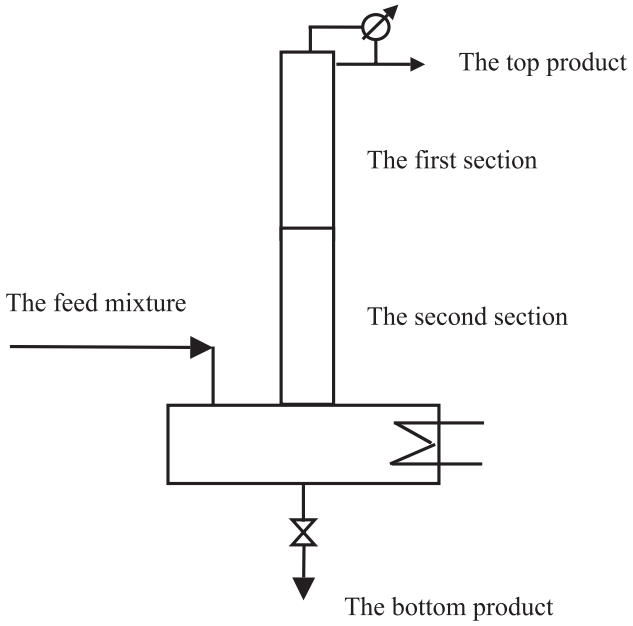

Figure 24. The experimental apparatus used for separating ethanol and water by adsorption distillation.

the diameter of 4–6mm, and finally filled with ion-exchange resins (the type is D072 Styrene-DVB, and composed of the anion RSO_3^- and the cation Na^+.) with the diameter of 1.20–1.30mm. The second section was always filled with stainless steel ring-shape packing with the size of 3mm width and 3mm height in both experiments. In the beginning the feed mixture entered into the bottom tin with 2500ml. Then the batch distillation column started to run. In the experiment it was assumed that the bottom and top concentration was keep constant because the operation time was not too long and concentration change in the bottom tin was negligible.

The organic solvents, ethanol, was of analytical purity. Ethanol and 3 Å molecular sieves were purchased from the Beijing Chemical Reagents Shop, Beijing, PRC. Ion-exchange resins were purchased from the Chemical Plant of Nankai University. Water was purified with ion-exchange resins. Composition analyses of the samples withdrawn from the top and bottom were done by a gas chromatography (type GC4000A) equipped with a thermal conductivity detector. Porapark Q was used as the fixed agent of the column packing, and hydrogen as the carrier gas. The column packing was 160°C and the detector 160°C. The data were dealt with by a BF9202

Table 21. The experimental results of adsorption distillation.

The top of the column			The bottom of the column		
T/K	x_1	x_2	*T*/K	x_1	x_2
No separating agent					
354.15	0.8057	0.1943	355.55	0.5930	0.4070
354.15	0.8063	0.1937	355.55	0.5940	0.4060
Molecular sieves					
354.55	0.8463	0.1537	356.05	0.5093	0.4907
354.55	0.8443	0.1557	356.35	0.5163	0.4837
Ion-exchange resins					
354.25	0.8205	0.1795	356.05	0.5093	0.4907
354.25	0.8183	0.1817	356.35	0.5163	0.4837

workstation. In terms of peak area of the components, the sample compositions could be deduced.

Under the infinite reflux condition, the experimental results are given in Table 21, where x_1 and x_2 are molar fraction of ethanol and water in the liquid phase, respectively, and T is temperature (K). The fresh molecular sieves and ion-exchange resins are used and not replaced during the operation.

It can be seen from the above that the enhancement of molecular sieves and ion-exchange resins on the separation of ethanol and water is very limited, and high-purity ethanol (above 99.0%wt) can not be obtained, at most up to 0.8463 mole fraction (94.8%wt) and 0.8205 mole fraction (93.8%wt) respectively in the case study. Therefore, although adsorption distillation, in which the solid separating agent is used and the operation process is simple, may be attractive, it seems to be unfeasible in the actual distillation process.

8.3. VLE Experiment

In order to further compare the separation effect of different separating agents used in adsorption distillation and extractive distillation, a typical recycling Vapor–liquid equilibrium cell having the volume 60ml, was utilized to measure the VLE of aqueous ethanol system. Salt and the solvent ethylene glycol were blended with the solvent/feed volume ratio 1:1 and the concentration of salt was 0.1g (salt)/ml (solvent). In the cell the mixture with about 40ml was heated to boil at normal pressure. One hour later, the desired phase equilibrium was achieved. At that time, small samples in the vapor and liquid phases were removed by transfer pipet with 1ml in order to make the equilibrium not to be destroyed.

Firstly we measured the equilibrium data of the ethanol (1)-water (2) system which corresponded well with the reference data. It is verified that the experimental apparatus was reliable. Then the measurements were respectively made for the system ethanol (1)-water (2)-ethylene glycol (solvent/feed volume ratio is 1:1), and the system ethanol (1)-water (2)-ethylene glycol-$CaCl_2$ (solvent/feed volume ratio is 1:1 and the concentration of salt is 0.1g/ml solvent) at 1 atm. The experimental VLE data are plotted in Figure 25 where the mole fractions are on solvent free basis, along with the results from the references with 4 Å molecular sieves as the separating agent.

It can be seen from the above figure that the separation effect of molecular sieves on ethanol and water is much less than that of ethylene glycol and the mixture of ethylene glycol and $CaCl_2$. Moreover, the separation ability of the mixture of ethylene glycol and $CaCl_2$ is higher than that of single ethylene glycol, which shows that it is an effective way to improve ethylene glycol by adding a little of salt.

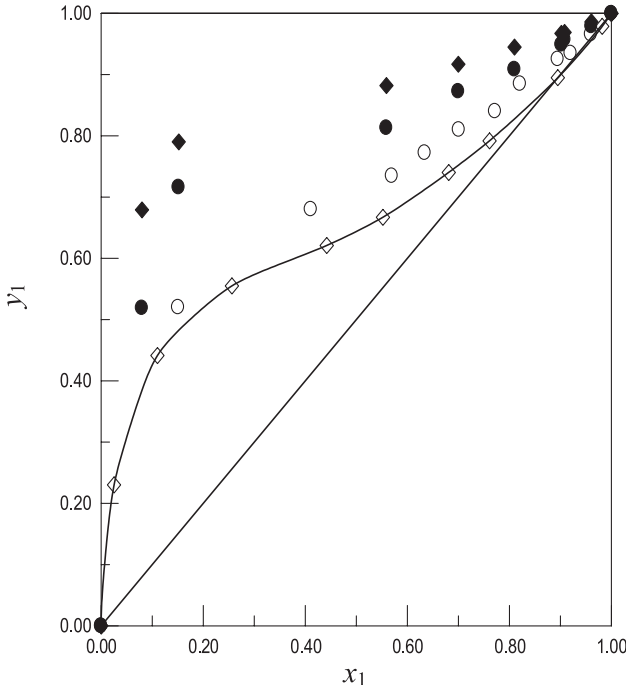

Figure 25. VLE of ethanol and water at 1 atm for different separating agent. ◆—ethanol (1)-water (2)-ethylene glycol-$CaCl_2$; ●—ethanol (1)-water (2)-ethylene glycol; ○—ethanol (1)-water (2)—300g of 4 Å molecular sieves; ◇—ethanol (1)-water (2).

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On the other hand, it is well-known that the mixture of ethanol and water is very difficult to be separated when the mole fraction of ethanol in the liquid phase is over 0.895. However, the VLE change in the presence of molecular sieves is not apparent especially when the mole fraction of ethanol in the liquid phase is in the range of 0.895–1.0. An important experimental operation condition should also be mentioned when measuring VLE of the ethanol-water-molecular sieves system. That is, ''fresh'' molecular sieves were used for each run. It indicates that only dehydrated molecular sieves can raise the relative volatility of ethanol to water and the used ''old'' molecular sieves have little effect on this separation if not dehydrated in time. However, it is a pity that the actual operation condition in the adsorption distillation column is quite different from that in the VLE experiment. When molecular sieves are selected as active packing materials for separating ethanol and water in the column, high-purity ethanol is not anticipated because molecular sieves may be quick to be saturated by water. That is why we obtained the result in the process experiment of adsorption distillation. To obtain high-purity ethanol as in the extractive distillation process, the molecular sieves should be constantly regenerated. It is very tedious to often unload and load the molecular sieves from the column. Moreover, much energy and equipment cost will be consumed in the process of regenerating molecular sieves. Thus, we think that molecular sieves are not good separating agent for adsorption distillation. The same applies for ion-exchange resins.

N, N-dimethylformamide (DMF) is also reported as the separating agent for separating ethanol and water (Shealy et al., 1987). In this work DMF is improved by adding a little of salt to make into a mixture. If some factors such as solubility, price, erosion, source and so on are considered, the salt NaSCN is the prospective additive. The separation ability of DMF, the mixture of DMF and NaSCN, ethylene glycol and ion-exchange resins are compared when the composition of feed mixture in the VLE cell is ethanol of 0.7861 mole fraction and water of 0.2139 mole fraction. The result is given in Table 22, where the solvent/feed volume ratio is 1.0.

It is well-known that relative volatility provides a useful index for selection of suitable separating agent. Relative volatility is defined as follows:

$$\alpha_{12} = \frac{y_1 x_2}{y_2 x_1} \tag{39}$$

Obviously, α_{12} larger than unity is desired. Thus, the following conclusions can be drawn from Table 22:

1. Adding a little of salt to DMF can improve the relative volatility of ethanol to water.

Table 22. Relative volatility of different separating agent for separating ethanol and water.

The separating agent	Relative volatility α_{12}
No separating agent	1.05
DMF	1.31
The mixture of DMF and NaSCN (0.10gNaSCD/ml DMF)	1.63
The mixture of DMF and NaSCN (0.20gNaSCD/ml DMF)	2.08
Ethylene glycol	2.23
Ion-exchange resins	1.16

2. The separation ability of ethylene glycol is greater than that of single DMF, and approximate to the mixture of DMF and NaSCN (0.20gNaSCD/ml DMF).
3. The separation ability of ion-exchange resins is lest among the separating agents. It is not advisable that ion-exchange resins are used for separating agent for the separation of ethanol and water. The reason may be that the molecular weight of ion-exchange resins is so high that the amount of function group $Na^+$is very little and can not apparently influence the relative volatility of ethanol to water.

Therefore, by combining the results of Figure 25 and Table 22, it is evident that the best separating agent is the mixture of ethylene glycol and $CaCl_2$, and the corresponding separation process is extractive distillation.

So, the separation technique using active packing materials for separating ethanol and water seems very attractive, but can not replace common extractive distillation process by now because molecular sieves and ion-exchange resins as solid separating agent are much more difficult to be regenerated than liquid separating agent, and the separation effect is also less than that of the separating agents currently used in the extractive distillation process.

9. CONCLUDING REMARKS

Since the solvent is the core of extractive distillation, more attention should be paid on the selection of the potential solvent. The procedure of selecting solvents is composed of two steps: calculation screening and experimental screening. The main method of calculation screening is CAMD, by which the amount of experiment work is greatly reduced.

However, until now, CAMD has been largely used for the search of liquid solvents, and the application on the solid salt is very few. The main reason may be that the quantitative calculation of salt effect is difficult and the thermodynamic method is incomplete. But the solid salt as one part of the solvent (e.g. combination of the liquid solvent and solid salt), is becoming more and more applied in industry. Moreover, it is a pity that by now CAMD for ionic liquids is completely blank. Ionic liquids with many unique advantages are a kind of special solvent in extractive distillation. We believe that with the development of CAMD, more studies would be concerned with ionic liquids. However, CAMD is limited by the accuracy of the group contribution methods that are used. The availability of accurate parameters for these methods is of crucial importance.

There are four methods for experimental screening, among which inert gas stripping and gas chromatography method is more promising. It is advisable that the potential solvents are first worked out by CAMD, and then tested by experiments.

Frankly speaking, the theories of extractive distillation is very scarce, let alone their accuracy. The Prausnitz and Anderson theory is based on semi-quantitative explanations, and the quantitative calculation is very difficult. Even so, this theory is only suitable for the hydrocarbon systems. Scaled particle theory constructs a bridge between microscale and macroscale. This theory can quantitatively calculate the salt effect and thus deduce relative volatilities at infinite dilution with salt. However, it is limited for polar solutes. The reason may be that only van der Waals bonding is currently considered in the scaled particle theory, and the hydrogen bonding between polar solutes and polar solvent is very complicated and greater than van der Waals bonding. But the scaled particle theory can provide qualitative analysis for polar solutes. Even so, this theory is only suitable for extractive distillation with the combination of solvent and salt. Anyway, the scaled particle theory is relatively perfect in extractive distillation.

Two types of modeling approaches, i.e. EQ and NEQ stage models, can be used for the design of extractive distillation process. The EQ stage model is mature and can be found in many references on extractive distillation or other special distillations. NEQ stage model is rarely reported in open references on extractive distillation, although it is widely used in other special distillation such as RD. The reason may be that extractive distillation is a special distillation mode, and building an NEQ model for a distillation process is not as straightforward as it is for the EQ stage model. However, in the field of reaction distillation (RD), recent NEQ modeling works have exposed the limitations of EQ stage model for final design and for the development of control strategies, which is never mentioned in extractive distillation. It may be due to the weaker non-linearity of modeling equations

in extractive distillation than in RD. Only in reactive extractive distillation is chemical reaction involved. Even in reactive extractive distillation, the chemical equilibrium constant is small in order to ensure that the solvent is easy to be recovered in the solvent recovery column. Therefore, the influence of chemical reaction on modeling equations is relatively not remarkable.

Since adsorption distillation is an attractive new separation method, the comparison of it and extractive distillation is an interesting work. However, by process and VLE experiments, it is found that the separation technique using active packing materials for separating ethanol and water can't replace common extractive distillation. This shows that extractive distillation is still a promising and challenging separation method, and more advantageous than both adsorption distillation and azeotropic distillation in the field of special distillations.

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