

CHAPTER II

LITERATURE REVIEW

2.1 Azeotrope

An azeotrope or azeotropic mixture is usually occurred in several steps of downstream processes, especially the separation processes in the petrochemical, chemical and biochemical fields (Roughton *et al.*, 2012). Nowadays, the separation of azeotropic mixtures is the most challenging work for a chemical engineer (Earle *et al.*, 2006). One simple example of azeotropic separation is the distillation of water and alcohol system since alcohol is one of the biofuels currently widely used as alternative energy fuels.

2.1.1 General Definition

Azeotrope, ancient Greek word (a-zeo-tropikos) that translates as “to boil unchanged”, expressed that the vapor composition has the same as the liquid and the equilibrium constants for all of the species are unity, sometimes called “constant boiling mixtures” (Widagdo *et al.*, 1996). The azeotrope is a mixture of at least two different components which cannot be easily separated by a simple distillation because of their thermodynamic properties and non-ideal details (Hadler *et al.*, 2009). If the low relative volatility of mixture is nearly the azeotrope, it generally names “close-boiling mixtures” (Hernández, 2013). For example, a well-known one is ethanol/water azeotrope at ethanol 95.63%wt and water 4.37%wt or equivalent to mole fraction 0.8943 (Wankat, 2006, Kulajanpeng, 2014).

2.1.2 Thermodynamic Explanation

In vapor-liquid equilibrium, an equilibrium constant equation (K_i) is as follows:

$$K_i \equiv \frac{y_i}{x_i} = \frac{y_i^* f_i^*}{\phi_i^* P} \quad (2.1)$$

where, y_i is the mole fractions of species i in the vapor at equilibrium.
 x_i is the mole fractions of species i in the liquid at equilibrium.
 γ_i^L is the activity coefficient of species i in the liquid phase.
 ϕ_i^V is the fugacity coefficient of species i in the vapor phase.
 f_i^L is the pure-liquid fugacity of species i in the vapor phase.
 P is the total pressure of all species in system at equilibrium.

If the deviation of the activity coefficient (γ_i^L) in the liquid phase is apart from unity (ideal), it is expressed as a non-ideal mixture. At low to moderate pressure, $\phi_i^V = 1$ and $f_i^L = P_i^S$, then Equation 2.1 is rearranged to Equation 2.2.

$$K_i \equiv \frac{y_i}{x_i} = \gamma_i^L \frac{P_i^S}{P} \quad (2.2)$$

where, P_i^S is the saturated vapor pressure of species i at equilibrium.

If the deviation is negative ($\gamma < 1$), it appears the maximum boiling azeotrope. On the other hand, The minimum boiling azeotrope has the positive deviation ($\gamma > 1$) (Widagdo *et al.*, 1996). Under isothermal conditions, the maximum boiling azeotrope (negative azeotrope) shows the total pressure higher than the vapor pressure of each components and the minimum boiling azeotrope (positive azeotrope) shows vice versa (Hadler *et al.*, 2009).

To sum up, homogeneous azeotropic systems are covered in two types: minimum boiling and maximum boiling azeotropes. Figure 2.1 illustrates the same characteristic behavior in term of x - y plot at constant temperature. The minimum boiling behavior is encountered considerably more often than the maximum boiling type in systems normally of interest to engineers (Balzhiser *et al.*, 1972).

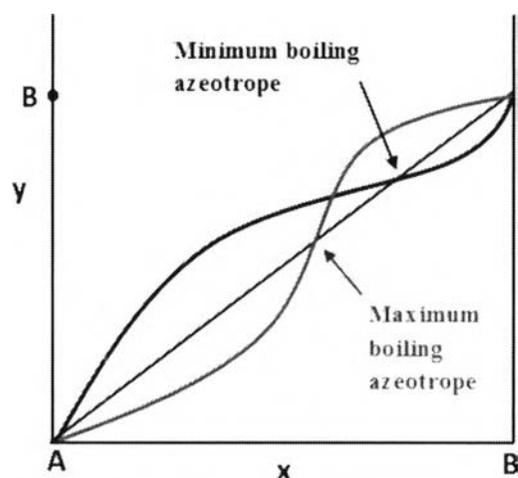


Figure 2.1 Liquid-vapor equilibrium for azeotrope (Balzhiser *et al.*, 1972).

If the deviation is very large ($\gamma > 4$), two phases are occurred and heterogeneous azeotrope are formed at equilibrium (Widagdo *et al.*, 1996). For a homogeneous azeotrope, the mixture boils at this composition as shown in Figure 2.2a when $x_1 = x_{1, azeo} = y_1$. For the heterogeneous azeotrope in Figure 2.2b, the mixture also boils at this composition when $x_1 = x_{1, azeo} = y_1$ and appears the vapor-liquid envelope overlapping with liquid-liquid envelope (Widagdo *et al.*, 1996).

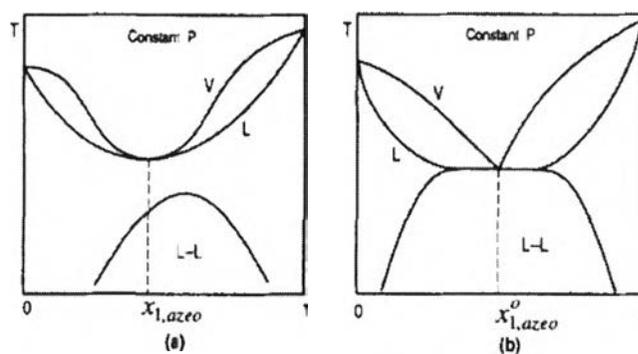


Figure 2.2 Two phase diagram at constant pressure. (a) homogeneous azeotrope; (b) heterogeneous azeotrope (Widagdo *et al.*, 1996).

In complex system, it might occur positive-negative azeotrope or called the saddle azeotrope by Swietoslowski (1963). For instance, the ternary mixtures of the acetone, chloroform and methanol in Figure 2.3 as shown a hyperbolic point (saddle point) at 57.6°C between the maximum and minimum boiling points at atmospheric pressure (Ngema, 2010).

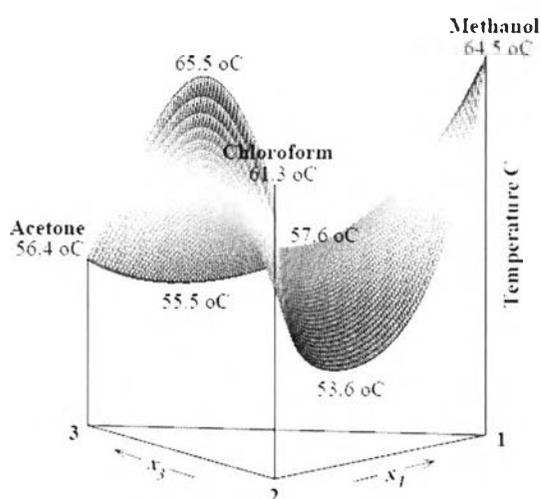


Figure 2.3 Saddle azeotropes in ternary mixtures of acetone, chloroform and methanol at atmospheric pressure (Ngema, 2010).

2.1.2.1 Minimum Boiling or Positive Azeotrope

This azeotropic system exhibits a positive deviation from ideal behavior and a minimum boiling point in Figure 2.4 (Kiva *et al.*, 2003). A well-known one is ethanol/water azeotrope at ethanol 95.63%wt and water 4.37%wt or equivalent to mole fraction 0.8943. The boiling temperature of each individual component is higher than the azeotropic point. For example, the azeotrope normally boils at 78.2°C, water at 100 °C and ethanol at 78.4 °C (Halder, 2009).

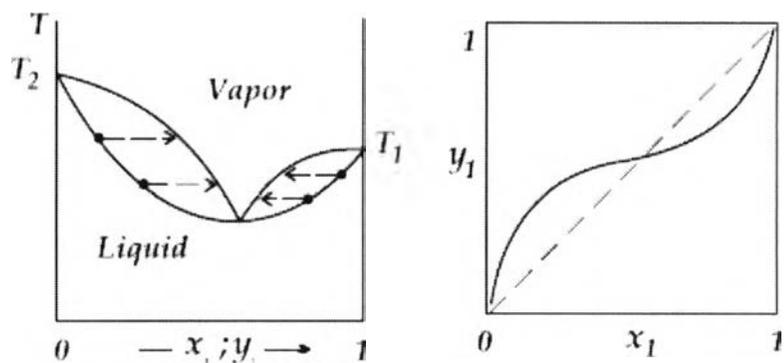


Figure 2.4 Vapor-liquid equilibrium of minimum boiling or positive azeotrope. Left: Temperature and Composition diagram. Right: Composition diagram (Kiva *et al.*, 2003).

2.1.2.2 Maximum Boiling or Negative Azeotrope

This azeotropic system exhibits a negative deviation from ideal behavior and a maximum boiling point in Figure 2.5 (Kiva *et al.*, 2003). An example is hydrochloric acid 20.2%wt and water 79.8%wt. The boiling temperature of each individual component is lower than the azeotropic point. For example, the azeotrope normally boils at 110°C , water at 100°C and hydrogen chloride at -84°C (Hadler *et al.*, 2009).

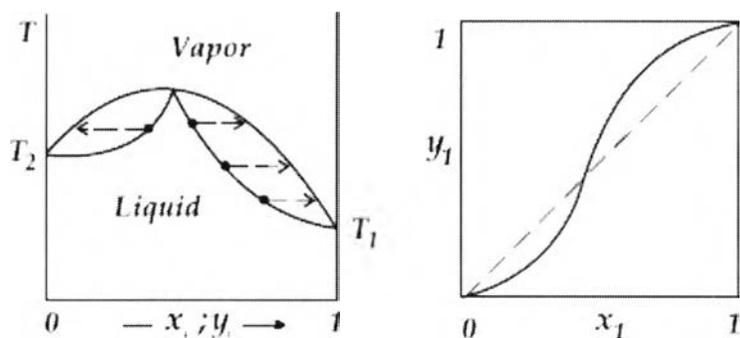


Figure 2.5 Vapor-liquid equilibrium of maximum boiling or negative azeotrope. Left: Temperature and Composition diagram. Right: Composition diagram (Kiva *et al.*, 2003).

2.1.2.3 Homogeneous and Heterogeneous Azeotrope

An azeotrope can be either a homogeneous or heterogeneous azeotrope. Mostly 90 percent of all azeotropes are homogeneous, containing a single phase and completely miscible mixtures. Beyond that, the immiscible mixtures are called heterogeneous (Kulajanpeng, 2014). The common examples of homogeneous and heterogeneous azeotrope are collected in Table 2.1 (Martínez Reina *et al.*, 2012, Kulajanpeng, 2014).

Table 2.1 Types of common azeotropes (Martínez Reina *et al.*, 2012, Kulajanpeng, 2014).

Component 1	Component 2	Type
Aqueous system		
Water + Alcohols		
Water	Ethanol	Homogeneous
Water	1-Propanol	Homogeneous
Water	1-Butanol	Heterogeneous
Water + Tetrahydrofuran		
Water	Tetrahydrofuran	Homogeneous
Non-aqueous system		
Alcohols + Aliphatic Hydrocarbons		
Methanol	heptane	Homogeneous
Ethanol	hexane	Homogeneous
Ethanol	heptane	Heterogeneous
Aromatic + Aliphatic/Cyclic Hydrocarbons		
Benzene	Hexane	Homogeneous
Benzene	Cyclohexane	Homogeneous

2.1.3 Physiochemical Explanation

To describe about the balance between intermolecular forces of the azeotropic mixtures, the deviation from ideal behavior is proposed and divided into three groups (Hilmen, 2000):

2.1.3.1 *Positive Deviation*

The components are too apart together because the attractive force of difference molecules is higher than identical molecules. This phenomenon forms the minimum-boiling azeotrope.

2.1.3.2 *Negative Deviation*

The components are too closed together. The attractive force of different molecules is lower than identical molecules. This phenomenon forms the maximum-boiling azeotrope.

2.1.3.3 *Ideal Mixture*

The attractive forces between different and identical molecules are equal.

2.2 **Separation Processes of Azeotropic Mixtures**

Since the separation of azeotropic mixtures by a basic distillation is impossibly done. Many potentially alternative processes are occurred, for example, adsorption, extraction, membranes and advanced distillations (e.g. azeotropic, extractive and pressure swig distillation) (Pereiro *et al.*, 2012).

However, the distillation is the most common process selected more than the other ones because of saving the total costs and energy consumption (Julka *et al.*, 2009). The azeotropic separation of seven different distillation are presented by Hilmen (2000):

2.2.1 Homogeneous Azeotropic Distillation

The azeotropic mixtures are completely miscible with volatile entrainers into one phase and released out at the top of column

2.2.2 Heterogeneous Azeotropic Distillation

The azeotropic mixtures are partially miscible or immiscible with entrainers into two liquid phases but the distillation are combined two systems between the separation column and decanter.

2.2.3 Extractive Distillation

The high boiling entrainer (higher than the individual components) is fed closely the top of the column to change the relative volatility of azeotropic mixture and select one of components in order to separate the mixture out each other. Next column separates again at the bottom for recycling the high boiling entrainer.

2.2.4 Reactive or Catalytic Distillation

The azeotropic mixtures are destroyed by chemical reactions and catalysts.

2.2.5 Distillations Using Solid Salts

Solid salts dissolve in azeotropic mixtures and then change the relative volatility until the separation occurs. An example is the dehydration of ethanol using potassium acetate solution.

2.2.6 Pressure-Swing Distillation

At least two columns are operated to break azeotropic mixtures by sharply increasing or decreasing the pressure in each column without the addition of any entrainers.

2.2.7 Membrane-Distillation Hybrids (Pervaporation)

This separation uses membranes to separate the heterogeneous azeotropic mixtures by absorbing and diffusing techniques.

At the beginning, an azeotropic distillation was always performed for a while but later unacceptable because of the large amount of required entrainers and the large energy requirement. To compare the overall efficiency, the extractive distillation is more attractive (Sucksmith, 1982, Lei *et al.*, 2003). After that, this technique uses the heavy chemicals added (entrainer) to interact with one of the components in the azeotropic mixtures (target component) and then extracts the target component by changing their relative volatilities (Pereiro *et al.*, 2012).

2.3 Extractive Distillation

At the present, the extractive distillation becomes the most efficient and the common process selected to separate several azeotropic mixtures. The extractive column and a solvent recovery column are composed in the process as shown in Figure 2.6 (Lei *et al.*, 2005). The non-volatile solvent entrainer is fed close to the top of the extractive column and then mixed with two reactants (A and B) in the feed stream to attract one component of the mixtures. The lower boiling point component is released at the top of column whereas the entrainer and the higher boiling point is released at the bottom of the column and finally recovered in solvent recovery columns (Lei *et al.*, 2005).

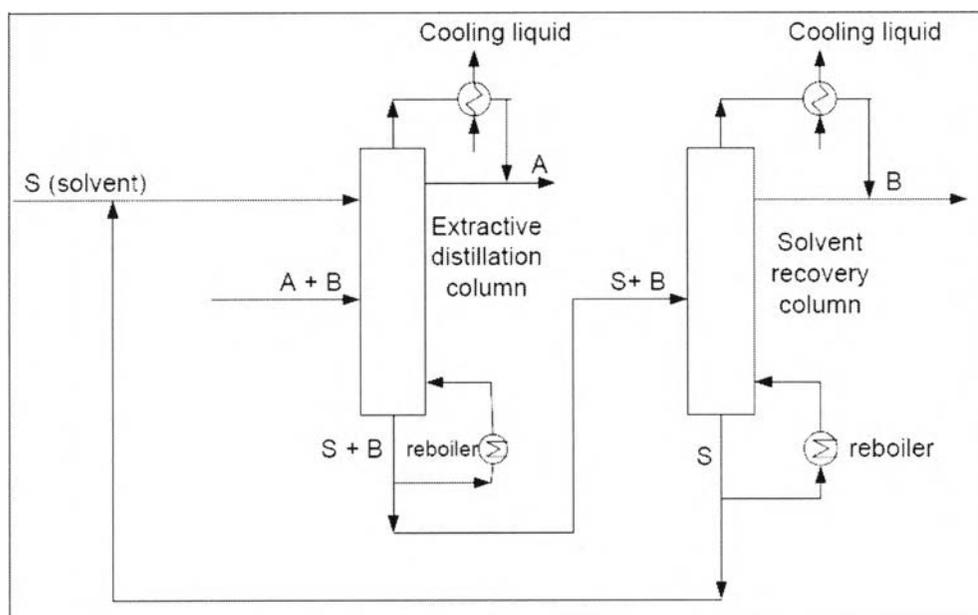


Figure 2.6 Process of extractive distillation (Zhigang *et al.*, 2005).

The calculation of theoretical stages in the column and the selection of the suitable entrainers are mainly influenced to the quality of product. Besides, the appropriate feed location of reactants and entrainers are also considered to maintain good separation in each column. (Lei *et al.*, 2005).

2.3.1 Condition of Separation in Distillation

The appropriate condition of separation in distillation is important to precisely design the distillation column (Kulajanpeng, 2014). A relative volatility is one parameter influenced to the calculation of the number of theoretical stages (Kulajanpeng, 2014). For a binary system at the azeotropic point, the ratio of the K_i -factors in each component is valid for homogenous systems by using the simplified equation 2.3 (Kulajanpeng, 2014).

$$\alpha_{12} \equiv \frac{K_1}{K_2} = \frac{y_1/x_1}{y_2/x_2} = \frac{\gamma_1 P_1^S}{\gamma_2 P_2^S} \quad (2.3)$$

where, x is mole fraction in the liquid phase.

y is mole fraction in the vapor phase.

γ is the activity coefficient.

P_i^S is the saturated vapor pressure.

If the relative volatility changes, other parameters are also affected (Ngema, 2010). The separation is impossible by a basic distillation because the relative volatility equals unity expressed the infinite number of theoretical stages (Lide, 2001). If the relative volatility of two components (α_{12}) are deviated from each other, it is easier to be separated in homogeneous azeotropes. Typically, conventional distillation becomes uneconomical when $0.95 < \alpha_{12} < 1.05$ (Ngema, 2010). To conclude, the efficiency of separation does not only depend on the suitable condition but the suitable entrainer is also necessary factor to consider.

2.3.2 Selective Solvents (Liquid/Solid) as Entrainers

Most of selective solvents as entrainers comprise of simply organic compounds. However, the entrainers should provide the most efficient separation and the least effect on environmental impacts as listed below (Hilmen, 2000):

- High selectivity
- High thermal and chemical stability
- Non-toxic

- Non-corrosive
- Low boiling point
- Low viscosity

A high selectivity indicates a quality of product and a high capability to separate azeotropic mixtures. The boiling point of entrainers should be lower than the pure components in the liquid phase. If the suitable entrainers are found, the next step is the optimization of energy requirement in the separation process (Hilmen, 2000). Up to date, there are four types of entrainers used in extractive distillation such as solid salt, liquid solvent, hyperbranched polymers and ionic liquids (Hilmen, 2000, Seiler *et al.*, 2004).

2.3.2.1 Solid Salt

A solid salt is dissolved into azeotropic mixtures and it affects the composition in the vapor-liquid equilibrium (VLE) (Hilmen, 2000). A schematic of this technique is shown in Figure 2.7 (Lei *et al.*, 2005). One drawback of using solid salt as entrainer is the difficulty in the recycle process (Hilmen, 2000).

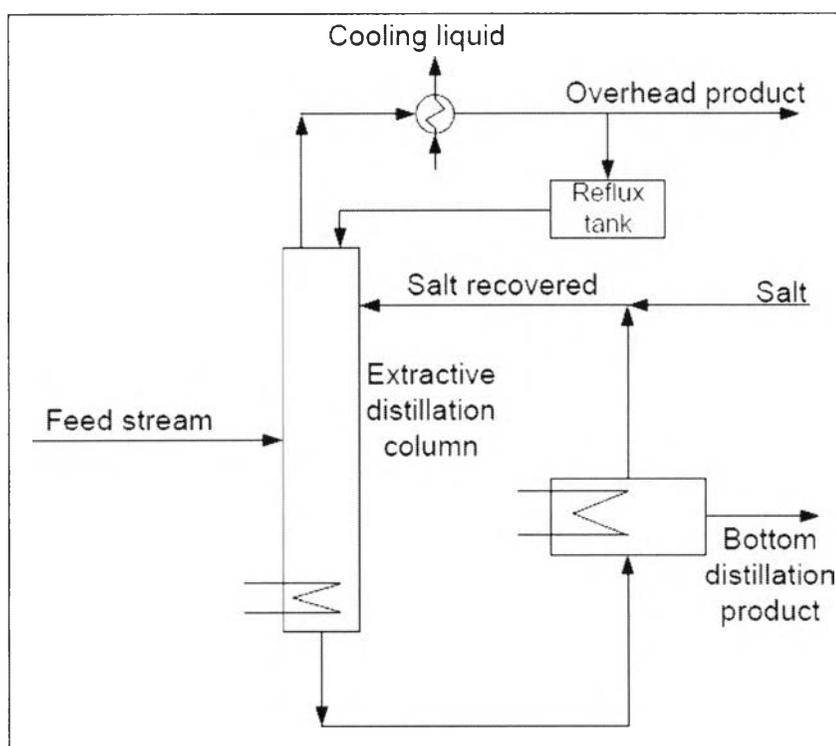


Figure 2.7 Extractive distillation with salt (Lei *et al.*, 2005).

2.3.2.2 *Liquid Solvent*

This technique is the same approach as using solid salt but easier soluble in azeotropic mixture. They are provided in two purposes: to increase the efficiency of separation and to reduce the boiling point by adjusting the relative volatility of the mixtures and the recycle ratio (Lei *et al.*, 2005).

2.3.3.3 *Hyperbranched Polymers (HyPol)*

HyPol (Seiler *et al.*, 2004) or dendrimers (Inoue, 2000) are used as entrainers in the extractive distillation. Their structure and properties are accurately modified but the complicated synthesis is unsuccessful to apply in worldwide industries (Seiler *et al.*, 2004).

In the past, various solid salts, liquid solvents and HyPol are previously used as conventional entrainers (Lei *et al.*, 2003). Unfortunately, volatile organic compound (VOC) emissions and high energy requirement are their crucial drawbacks (Li *et al.*, 2009, Kulajanpeng, 2014). A number of environmental issues and economic aspects are more increasingly influenced on how to select the suitable entrainer (Momoh, 1991, Kerton *et al.*, 2013). To create the eco-friendly innovative compounds, “Ionic liquids” are the promising entrainers with simpler synthesis from simple anion, cation and alkyl chain (on cation) (Rogers *et al.*, 2002, Zhao *et al.*, 2005).

2.3.3.4 *Ionic Liquids (ILs)*

“Ionic liquids” are currently only used in a pilot plant and not commercial to apply in large scale mainly due to their global price. Owing to their outstanding structures and properties, ionic liquids have demonstrated promising selectivity and solubility as entrainers in the extractive distillation. These have promoted ionic liquids to become the alternative replacements instead of conventional entrainers absolutely (Pereiro *et al.*, 2012). More details of ionic liquids are described as follows.

2.4 Ionic Liquids (ILs)

2.4.1 Definition of ILs

ILs are normally combined ions from an organic salts and an inorganic salt together, traditionally known as molten salts. (Kulajanpeng, 2014). Several synonym names have been used in the scientific literature e.g. room temperature ionic liquid (RTIL), ambient temperature ILs, non-aqueous ionic liquid (NAIL), molten organic salt, fused organic salt, low molting salt, neoteric solvent, green solvent, and designer solvent (Kulajanpeng, 2014).

2.4.2 Structure of ILs

Most common ILs are comprised of the alkyl chain on cation, cation and anion (Brennecke *et al.*, 2001). Some examples of these components are listed below.

2.4.2.1 *Cation*

Imidazolium [IM], Pyridinium [PY], etc.

2.4.2.2 *Anion*

Hexafluorophosphate [PF₆]⁻, Tetrafluoroborate [BF₄]⁻, etc.

2.4.2.1 *Alkyl Chain (On cation)*

Alkyl, Alkenyl, Methoxy, etc.

Figure 2.8 shows some well-known anions and cations of ILs (Hansmeier, 2010).

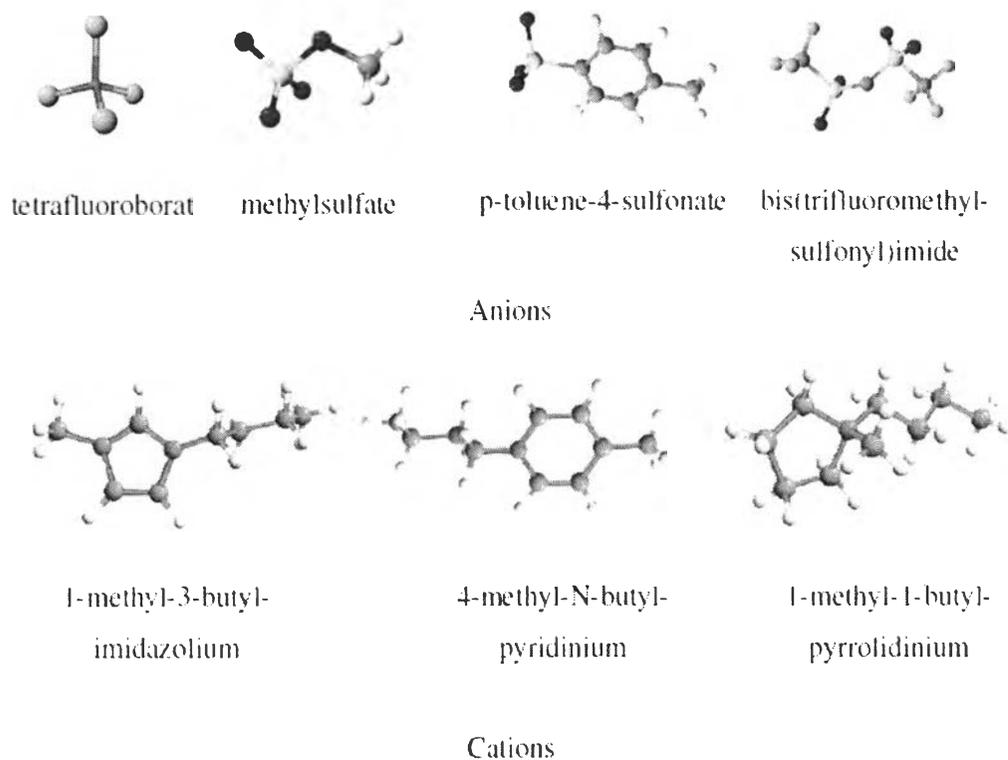


Figure 2.8 Well-known anions and cations of ILs (Hansmeier, 2010).

2.4.3 Properties of ILs

In general, ILs have non-flammability, chemical and thermal stability at higher temperature than conventional entrainers (Zhao *et al.*, 2005). ILs are initially formed by simple cation, anion and alkyl chain (on cation) that make the diversity of thermo physical properties, solubility and miscibility (Zhao *et al.*, 2005). Numerous properties are able to be determined by group contribution (GC) methods such as densities, critical properties (Valderrama *et al.*, 2008) and vapor-liquid equilibrium (VLE) (Roughton *et al.*, 2012). As a result, ILs can be designed to precisely be soluble in specific solvent, hence, they are called “designer solvents” (Marsh *et al.*, 2004). More details of group contribution (GC) are described in section 2.5.

2.4.4 Use and Application of ILs

Through a century, ILs have recently been acceptable and more attractive in chemical fields (Pereiro *et al.*, 2012). The multifunctional of ILs can be mainly applied for solvents, separation, heat storage, electroelastic materials, analytics, lubricant & additives, liquid crystal, and electrolytes as shown in Figure 2.9 (Shukla *et al.*, 2013). In areas of separations, ILs is commonly used as entrainers in extractive distillation and extraction (Shukla *et al.*, 2013).

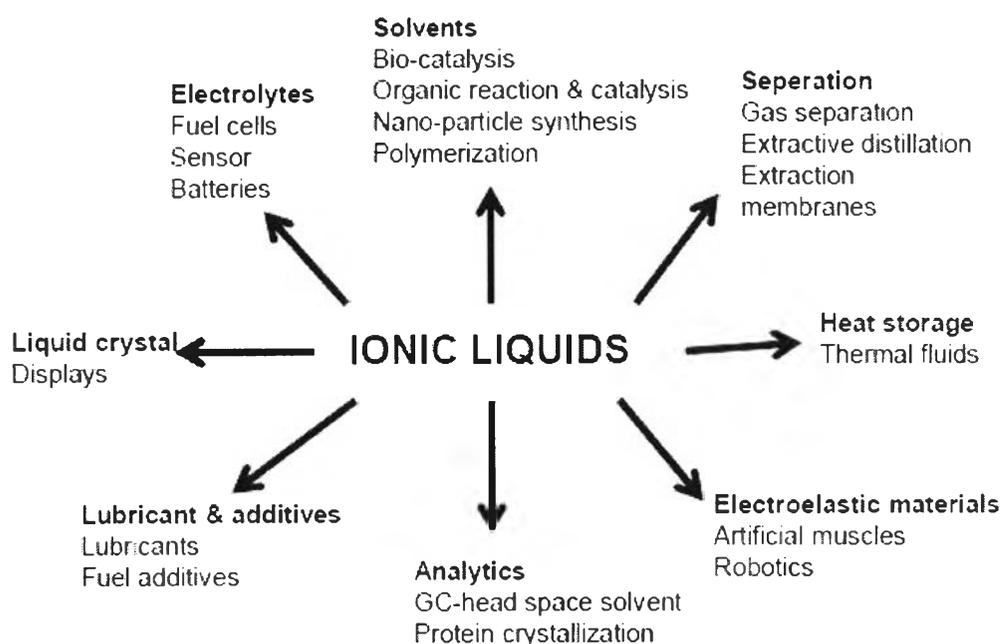


Figure 2.9 Applications of ILs (Shukla *et al.*, 2013).

2.4.5 ILs as Entrainers

Nowadays, ILs are potential candidates as entrainers in the extractive distillation of azeotropic mixtures due to their outstanding structures and properties such as non-volatility, non-flammability, chemical and thermal stability (Marsh *et al.*, 2004). For chemical engineers, they have become well-known as “green solvents” entrainers (Rogers *et al.*, 2002). Furthermore, the properties of ILs can be designed accurately by switching between anions, cations and alkyl chain (on cation)

(Roughton *et al.*, 2012). A large number of publications of different azeotropes has been studied with ILs as entrainers as illustrated in Figure 2.10 (Pereiro *et al.*, 2012).

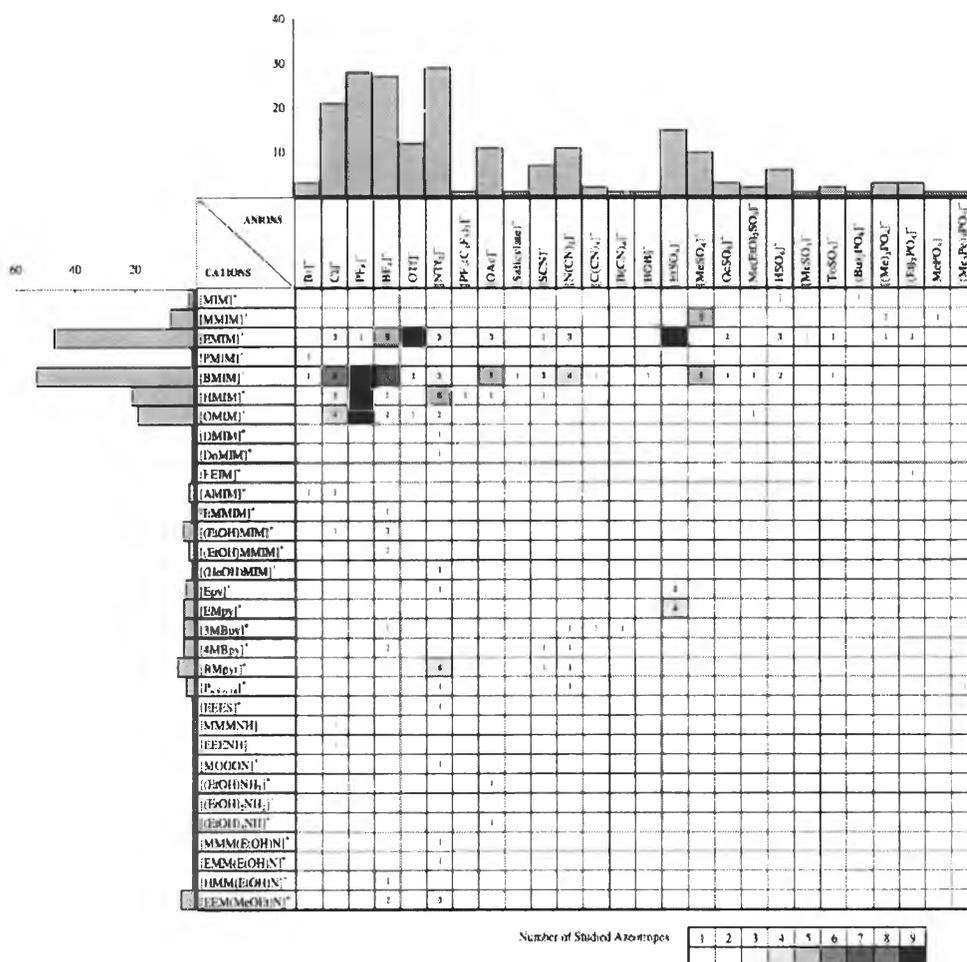


Figure 2.10 Matching of ions to be ILs and the different colors show the number of studied azeotropes (Pereiro *et al.*, 2012).

In this work, azeotropic mixtures can be divided into aqueous and non-aqueous azeotropic systems. Some examples of these mixtures are listed below.

2.4.5.1 ILs Used in Aqueous Systems

- Water + Alcohols system

The study of this system is important in several chemical, foods, pharmaceutical and petrochemical industries e.g. biofuel production, fuel additive, beverage fermentation, drugs, cosmetics and hydration of ethylene in downstream processes (Pereiro *et al.*, 2012). For instance, the strong attraction between ethanol and water makes the big problem to purify the product. The separation of ethanol and water is a challenging task.

To begin, the solid salts are commonly used as entrainers e.g. potassium acetate and calcium chloride. Unfortunately, the soluble limitation of salts and deteriorated equipments in column are the major obstacles (Zhao *et al.*, 2006). The use of liquid solvents can avoid these problems and conventional organic solvents are used as entrainers e.g. sulpholane, dimethylsulphoxide (DMSO) and N-methylpyrrolidone (NMP) but the outcomes are not satisfied. For ILs, it shows the best results and the most acceptable performance for separating. Table 2.2 lists the common ILs as entrainers used in the extractive distillation (Pereiro *et al.*, 2012).

Table 2.2 ILs used in (Water + Alcohol) system (Pereiro *et al.*, 2012)

Azeotrope	ILs
Water + Ethanol	[EMIM][OAc], [EMIM][OTf], [EMIM][EtSO ₄], [EMIM][BF ₄], [BMIM][OTf], [BMIM][Br], [BMIM][Cl], [BMIM][BF ₄], [EMIM][DCA], [MMIM][DMP]
Water + 1-propanol	[EMIM][OTf], [EMIM][BF ₄]
Water + 2-propanol	[EMIM][EtSO ₄], [EMIM][OAc], [EMIM][BF ₄], [BMIM][BF ₄], [BMIM][OAc], [HMIM][BTI]
Water + 1-butanol	[HMIM][BTI], [BMIM][PF ₆]

Other alcohols, which contain longer hydrocarbon chain than ethanol, have been applied in diverse industries, for instance, 1-propanol (i.e. used as solvent), 2-propanol (i.e. used in drugs, furnitures, cosmetics and foods industries), 1-butanol (i.e. used in plastics, fibers, electronics and perfumes industries) (Dürre, 2011, Pereiro *et al.*, 2012). Nevertheless, the functional alcohol groups are soluble in water due to the affinity of OH group towards water. Up to now, table 2.2 lists the common ILs as entrainers used in the extractive distillation (Pereiro *et al.*, 2012).

- Water + Ether system

One of the common aqueous azeotropic systems is the water and tetrahydrofuran (THF) mixture. It is generally used in pharmacy, chemical intermediate products and textile industry (e.g. polyester and polyurethane) (Pruckmayr *et al.*, 1996, Müller, 2000, Pereiro *et al.*, 2012). Table 2.3 lists the common ILs as entrainers used in extractive distillation and liquid–liquid extraction (Pereiro *et al.*, 2012).

Table 2.3 ILs used in (Water + Ether) system (Pereiro *et al.*, 2012)

Azeotrope	ILs
Water + THF	[EMIM][BF ₄], [EMIM][Cl], [BMIM][BF ₄], [BMIM][Cl]

2.4.6.2 ILs used in Non-Aqueous Systems

- Alcohols + Aliphatic hydrocarbons system

In petroleum and petrochemical fields, the alcohols + aliphatic hydrocarbons systems are the most interesting and challenging to study e.g. methanol + heptane and ethanol + hexane and ethanol + heptane mixtures (Pereiro *et al.*, 2012). Table 2.4 lists the common ILs as entrainers used in the extractive distillation (Pereiro *et al.*, 2012).

Table 2.4 ILs used in (Alcohols + Aliphatic hydrocarbons) system (Pereiro *et al.*, 2012).

Azeotrope	ILs
Methanol + Heptane	[OMIM][Cl]
Ethanol + Hexane	[EMIM][BF ₄], [OMIM][BF ₄] [HMIM][PF ₆], [BMIM][MeSO ₄]
Ethanol + Heptane	[EMIM][EtSO ₄]

- Aromatics + Aliphatic hydrocarbons System

In petroleum refinery, the reformat gasoline should be qualified by separating aromatic and aliphatic hydrocarbons from each other. Normally, reformat gasoline has high aromatic contents approximately 90%wt, which are used mostly in petrochemical products. Conventional entrainers used in this system are ethylene glycols (EG), N-methylpyrrolidone (NMP) and sulfolane (Pereiro *et al.*, 2012). However, they are uneconomical and hazardous to environment (Meindersma *et al.*, 2010). At the present, ILs are acceptable in several separations Table 2.5 lists the common ILs as entrainers used in the extractive distillation (Pereiro *et al.*, 2012).

Table 2.5 ILs used in (Aromatics + Aliphatic hydrocarbons) system (Pereiro *et al.*, 2012)

Azeotrope	ILs
Benzene + Hexane	[EMIM][DCA], [EMIM][SCN], [EMIM][EtSO ₄], [BMIM][MeSO ₄], [HMIM][BTI],[OMIM][BTI], [BMPY][BTI], [BMIM][BTI], [EMIM][BTI], [MMIM][BTI], [E3S][BTI], [BMPYR][TCB]

Table 2.5 ILs used in (Aromatics + Aliphatic hydrocarbons) system (Continued)
(Pereiro *et al.*, 2012)

Azeotrope	ILs
Benzene + Heptane	[EMIM][EtSO ₄], [BMIM][BF ₄], [BMIM][SCN], [BMIM][PF ₆], [HMIM][BF ₄], [HMIM][PF ₆]

- Aromatics + Cyclic hydrocarbons system

The research group of González *et al.* (2010) has studied ILs [EMIM] [EtSO₄] used in the aromatics + cyclic hydrocarbons systems (e.g. toluene + cyclohexane and methylcyclohexane mixtures) at 298.15 K (Martínez-Reina, 2012). In addition, Orchillés *et al.* (2010) also studied about benzene and cyclohexane. Table 2.6 lists the common ILs as entrainers used in the extractive distillation (Pereiro *et al.*, 2012).

Table 2.6 ILs used in (Aromatics + Cyclic hydrocarbons) system (Pereiro *et al.*, 2012)

Azeotrope	ILs
Benzene + cyclohexane	[BMIM][PF ₆], [HMIM][BTI], [HMIM][PF ₆], [OMIM][BTI]
Toluene + cyclohexane	[EMIM] [EtSO ₄]
Toluene + methylcyclohexane (MCH)	[EMIM] [EtSO ₄]

2.5 Property and Thermodynamic Parameters

2.5.1 Solubility Parameter

2.5.1.1 Definition of Solubility Parameter

Hildebrand and Scott (Barton, 1991) originally defined the relation between the Hildebrand solubility parameter (δ_i) with the cohesive energy

density (c_{ii}), the enthalpy of vaporization (Δh_{vap}) and the molar volume (v_i) as shown in Equation 2.4.

$$\delta_i [\text{MPa}^{1/2}] = c_{ii}^{1/2} = \left(\frac{\Delta h_{vap} - RT}{V_i} \right)^{1/2} \quad (2.4)$$

The Hildebrand solubility parameter can be expressed as the miscibility of compounds (Roughton *et al.*, 2012). If solubility parameter values of two constituents are close to each other, the mixture of these constituents is easily formed into the homogeneous system. Therefore, this parameter can be used as a screening tool to indicate the suitable entrainers of an azeotropic mixture (Roughton *et al.*, 2012).

2.5.1.2 Hildebrand Solubility Parameter Model for ILs

According to the previous work, (Roughton *et al.*, 2012) proposed the group contribution (GC) model of the Hildebrand solubility parameter for ILs (δ_{IL}) at 298.15 K as shown in Equation 2.5, which can be used to predict their properties. A good fit between the Hildebrand solubility parameter GC model and the experimental data is obtained with a value of 0.34% AARD (average absolute relative deviation) and 0.305 maximum relative deviation (Roughton *et al.*, 2012).

$$\delta_{IL} [\text{MPa}^{1/2}] = \delta_{Alkyl\ chain}^C + \delta_{Cation}^C + \delta_{Anion}^C = \sum_{Alkyl\ chain} n_i C_i + \sum_{Cation} n_j C_j + \sum_{Anion} n_k C_k + b \quad (2.5)$$

Where,

- i is the subscript of alkyl chain group (on cation).
- j is the subscript of cation group.
- k is the subscript of anion group.
- n is the number of each type of group.
- C is the contribution of each type of group.
- b is a constant = 4.547 MPa^{1/2} (intercept).

In Kulajanpeng (2014), the Hildebrand solubility parameter of ILs have been extended from Roughton *et al.* (2012). 39 experimental data of ILs at 298.15 K were developed in the group contribution (GC) of the Hildebrand solubility parameter model for ILs as summarized in Table 2.7 (Kulajanpeng, 2014). When comparing with experimental data as shown in Figure 2.11, the model could give a good fit of 0.319% AARD and 3.29 maximum relative deviation (Kulajanpeng, 2014).

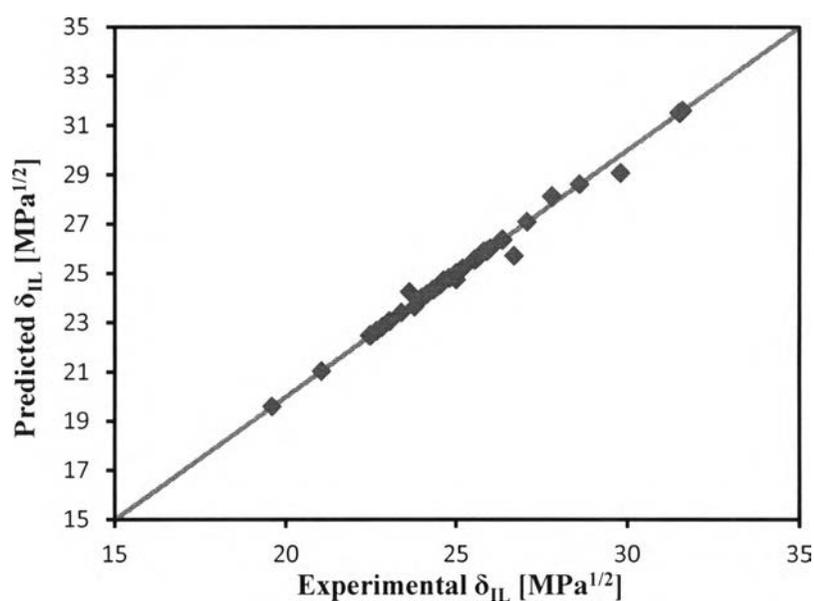


Figure 2.11 Fitting plot between experimental data and the extended Hildebrand solubility parameter model for ILs (Kulajanpeng, 2014).

Table 2.7 Extended GC of Hildebrand solubility parameter model for ILs (Kulajanpeng, 2014)

	Ionic Liquid Group	C_i (MPa^{1/2})
Alkyl chain group (i)	CH ₃	1.28
	CH ₂	-0.24
	CH	-0.04

Table 2.7 Extended GC of Hildebrand solubility parameter model for ILs
(Continued) (Kulajanpeng, 2014)

	Ionic Liquid Group	Ci (MPa^{1/2})
	CH ₂ O	-2.22
	OH [HY]	3.04
Cation groups (j)	Imidazolium [IM]	5.14
	Pyridinium [PY]	4.95
	Pyrrolidonium [PYR]	5.31
	Phosphonium [P]	-0.05
	Sulfonium [S]	-0.79
	Piperidinium [PIP]	2.84
	Ammonium [A]	3.32
Anion groups (k)	Trifluoroacetate [TFA]	0.62
	Thiocyanide [SCN]	0.25
	Trifluormethane sulfonate [CF ₃ SO ₃]	-1.81
	2-(2-Methoxyethoxy)ethyl sulfate [MDEGSO ₄]	0.33
	Trifluoroacetate [CF ₃ COO]	0.62
	Octyl sulfat [OcSO ₄]	0.33
	Tosylate [TOS]	-1.22
	Bis(trifluoromethylsulfonyl)imide [BTI]	1.24
	Dimethyl phosphate [DMP]	1.9
	Thiocyanide [SCN]	0.25
	Diethyl phosphate [DEP]	1.01
	Tetrafluoroborate [BF ₄]	7.13
	Hexafluorophosphate [PF ₆]	4.61
	Chloride [Cl]	-0.33
	Acetate [Ac]	0.22
	Dicyanamide [DCA]	0.9

Table 2.7 Extended GC of Hildebrand solubility parameter model for ILs (Continued) (Kulajanpeng, 2014)

	Ionic Liquid Group	C_i (MPa^{1/2})
	Nitrate [NO ₃]	3.32
	Tetracyanoborate [TCB]	1.18
	Ethylsulfate [EtSO ₄]	-0.49
	Methylsulfate [MeSO ₄]	0.96
	Trifluorotris(perfluoroethyl)phosphate [FAP]	0.24
	Hexafluoroantimonate [SbF ₆]	7.03
Constant value	b	17.48

2.5.2 Critical Property Parameter

2.5.2.1 Critical Property model for ILs

The critical properties of several ILs (e.g. critical pressure (P_c), critical temperature (T_c), critical volume (V_c), normal boiling temperature (T_b), and acentric factor (ω)) were predicted by the extended group contribution (GC) of critical property model for ILs from the concepts of Lydersen (2009) and Joback (1987) as summarized in Table 2.8 (Valderrama *et al.*, 2009). These properties can be calculated by using Equations 2.6 to 2.12 in Table 2.9 and the accuracy of these equations can be confirmed by comparing the liquid densities (ρ_L) of the ILs in Equation 2.10 with the experimental data (Valderrama *et al.*, 2009).

Table 2.8 Extended GC of critical property model for ILs (Valderrama *et al.*, 2009)

Group	M_i (g/mol)	ΔT_b (K)	ΔT_c (K)	ΔP_c (bar)	ΔV_c (cm³/mol)
Without Rings					
-CH ₃	15.035	23.58	0.0275	0.3031	66.81
-CH ₂ -	14.027	22.88	0.0159	0.2165	57.11

Table 2.8 Extended GC of critical property model for ILs (Continued) (Valderrama *et al.*, 2009)

Group	M_i (g/mol)	ΔT_b (K)	ΔT_c (K)	ΔP_c (bar)	ΔV_c (cm ³ /mol)
Without Rings					
>CH-	13.019	21.74	0.0002	0.114	45.7
>C<	[>C-] ⁻ 12.011	18.18	-0.0206	0.0539	21.78
=CH ₂	14.027	24.96	0.017	0.2493	60.37
=CH-	13.019	18.25	0.0182	0.1866	49.92
=C<	12.011	24.14	-0.0003	0.0832	34.9
=C=	12.011	26.15	-0.0029	0.0934	33.85
≡CH	13.019		0.0078	0.1429	43.97
≡C-	-COO- 12.011		0.0078	0.1429	43.97
-OH (alcohol)	17.008	92.88	0.0723	0.1343	30.4
-O-	-[O] ⁻ 16.000	22.42	0.0051	0.13	15.61
>C=O	28.011	94.97	0.0247	0.2341	69.76
-CHO	29.019	72.24	0.0294	0.3128	77.46
-COOH	45.018	169.06	0.0853	0.4537	88.6
-COO-	44.010	81.1	0.0377	0.4139	84.76
-HCOO-	45.018		0.036	0.4752	97.77
=O (others)	16.000	-10.50	0.0273	0.2042	44.03
-NH ₂	16.023	73.23	0.0364	0.1692	49.1
-NH ₃	17.031	73.23	0.0364	0.1692	49.1
-NH-	15.015	50.17	0.0119	0.0322	78.96
>N-	14.007	11.74	-0.0028	0.0304	26.7
=N-	14.007	74.6	0.0172	0.1541	45.54
-CN	26.018	125.66	0.0506	0.3697	89.32
-NO ₂	42.006	152.54	0.0448	0.4529	123.62
-F	18.999	-0.03	0.0228	0.2912	31.47
-Cl	35.453	38.13	0.0188	0.3738	62.08

Table 2.8 Extended GC of critical property model for ILs (Continued) (Valderrama *et al.*, 2009)

Group	M_i (g/mol)	ΔT_b (K)	ΔT_c (K)	ΔP_c (bar)	ΔV_c (cm³/mol)	
Without Rings						
-Br	79.904	66.86	0.0124	0.5799	76.6	
-I	126.905	93.84	0.0148	0.9174	100.79	
-B	10.811	-24.56	0.0352	0.0348	22.45	
-P	30.974	34.86	-0.0084	0.1776	67.01	
-S-	32.066	117.52	0.0006	0.6901	184.67	
-SO2	64.065	147.24	-0.0563	-0.0606	112.19	
With Rings						
-CH2-	14.027	27.15	0.0116	0.1982	51.64	
>CH-	13.019	21.78	0.0081	0.1773	30.56	
=CH-	13.019	26.73	0.0114	0.1693	42.55	
>C<	12.011	21.32	-0.0180	0.0139	17.62	
=C<	12.011	31.01	0.0051	0.0955	31.28	
-O-	16.000	31.22	0.0138	0.1371	17.41	
-OH (phenol)	17.008	76.34	0.0291	0.0493	-17.44	
>CO	28.011	94.97	0.0343	0.2751	59.32	
>NH	15.015	52.82	0.0244	0.0724	27.61	
>N-	[>N<] ⁺	14.007	68.16	0.0063	0.0538	25.17
-N=	[>N=] ⁺	14.007	57.55	-0.0011	0.0559	42.15

Table 2.9 Critical property model for ILs (Valderrama *et al.*, 2009)

	Model equation	Constant
The method	$T_b(K) = 198.2 + \sum n \Delta T_b \quad (2.6)$ $T_c(K) = \frac{T_b}{A + B \sum n \Delta T_c - (\sum n \Delta T_c)^2} \quad (2.7)$ $P_c(\text{bar}) = \frac{M}{(C_M + \sum n \Delta P_M)^2} \quad (2.8)$ $V_c\left(\frac{\text{cm}^3}{\text{mol}}\right) = E_M + \sum n \Delta V_M \quad (2.9)$	A=0.5073 B=1.0121 C=0.2573 D=6.75
Density model for testing	$\rho = \frac{A}{B} + \frac{2}{7} \left\{ \frac{A \ln B}{B} \right\} \frac{(T - T_b)}{(T_c - T_b)} \quad (2.10)$	A=a+(bM/V _c) B=(c/V _c +d/M)V _c ^δ a=0.3411 b=2.0443 c=0.5386 d=0.0393 δ=1.0476
Critical compressibility factor	$Z_c = \frac{P_c V_c}{(RT_c)} \quad (2.11)$	R=84.31 (bar•cm ³ /mol•K)
Acentric factor	$\omega = \frac{(T_b - 43)(T_c - 43)}{(T_c - T_b)(0.7T_c - 43)} \log \left[\frac{P_c}{P_b} \right] - \frac{(T_c - 43)}{(T_c - T_b)} \log \left[\frac{P_c}{P_b} \right] + \log \left[\frac{P_c}{P_b} \right] - 1 \quad (2.12)$	P _b =1.01325 bar

2.5.3 Capacity and Selectivity Parameters

The average experimental activity coefficient at infinite dilution for each solute in ILs is able to directly estimate the capacity of ILs in equation 2.13 and selectivity of ILs in equation 2.14 for the selection of conventional solvents or entrainers for extractive distillation (Toppoff *et al.*, 1999).

2.5.3.1 Capacity of ILs

The capacity describes the solubility of target solute to be extracted by IL that if there is a small value for the activity coefficient, it indicate a high solubility in ILs and can be defined as; Capacity = 1 / (Activity coefficient at infinite dilution for target solute in ILs) or

$$C_2^\infty = 1/\gamma_2^\infty \quad (2.13)$$

2.5.3.2 Selectivity of ILs

Apart from the capacity, the selectivity should be considered along with capacity and far from 1 for to minimize the number of theoretical stage required. Selectivity = (Activity coefficient at infinite dilution for product in ILs) / (Activity coefficient at infinite dilution for target solute in ILs) or

$$S_{12}^\infty = \gamma_1^\infty/\gamma_2^\infty \quad (2.14)$$

One way to increase the relative volatility of mixtures when the ratio of saturated vapor pressures is constant for isothermal systems in Equation 2.15 is by changing the ratio of the activity coefficients called selectivity in Equation 2.16.

$$\alpha_{12} = \frac{y_1/x_1}{y_2/x_2} = \frac{\gamma_1 P_1^o}{\gamma_2 P_2^o} \quad (2.15)$$

$$S_{12} = (\gamma_1/\gamma_2)_s \quad (2.16)$$

At infinite dilution, the activity coefficient for each component is determined to be the highest value in ILs. Nevertheless, the trend of capacity and selectivity is directly counteracted following to their equations. In fact, the effective entrainers should be high selectivity along with high capacity to improve the separation capability and reduce the formation of a second liquid phase in the ED column. Therefore, it is desirable to have ILs with high selectivity (high degree of separation) and high capacity (avoid formation of a second liquid phase)

2.5.4 Binary Parameters

2.5.4.1 COSMO-RS Model

The COSMO-RS is one of the efficient models to predict the thermodynamic properties by using the chemical quantum data and atom-specific parameters (Diedenhofen *et al.*, 2010). According to some related researches, the results show the mean relative deviations between the experimental data and the predictive value around 79.4% for vapor-liquid equilibrium and more than 100% for the activity coefficients at infinite dilution (γ_i^∞) of hydrocarbons (Diedenhofen *et al.*, 2010).

2.5.4.2 UNIFAC Model

The UNIFAC model concept was based on the functional group concepts and proposed by Fredenslund *et al.* (1975). It can be applied to predict the activity coefficients at both finite concentration and infinite dilution (γ_i^∞) from a combinatorial component ($\ln \gamma_i^C$), referred to a contribution from size and shape of the molecules and a residual component ($\ln \gamma_i^R$), referred to a contribution related to interaction energy), as expressed in Equation 2.17 (Fredenslund *et al.*, 1975).

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \quad (2.17)$$

Lei *et al.* (2009) extended the group contribution of the UNIFAC model for ionic liquid (UNIFAC-IL) and used to predict the vapor-liquid equilibrium and efficiently screened the suitable ionic liquids as entrainers in separation processes (Lei *et al.*, 2009). UNIFAC-IL showed a good performance of screening the candidates and optimizing based on minimum concentration needed to break the azeotrope (Lei *et al.*, 2009). The authors claimed that the UNIFAC-IL model is one of the accurately predictive model to design the suitable ionic liquids (Lei *et al.*, 2009).

2.5.4.3 NRTL Model

The Non-Random Two-Liquid (NRTL) model is based on the Wilson hypothesis that the local concentration around a molecule is different from the bulk concentration and correlated to the activity coefficient model from the

activity coefficients (γ_i^∞) of each compound in the mixture. It is generally applied in the calculation of phase equilibrium (Renon *et al.*, 1968). Furthermore, the model is satisfied for all completely miscible systems. For Equations (2.18-2.20) below, the activity coefficients are calculated as following by Renon *et al.* (1968):

$$\ln \gamma_i = \frac{\sum_{j=1}^n \tau_{ij} x_j G_{ji}}{\sum_{k=1}^n x_k G_{ki}} + \sum_{j=1}^n \frac{x_j G_{ij}}{\sum_{k=1}^n x_k G_{kj}} \left(\tau_{ij} - \frac{\sum_{m=1}^n \tau_{mj} x_m G_{mj}}{\sum_{k=1}^n x_k G_{kj}} \right) \quad (2.18)$$

where,

$$G_{ji} = \exp(-\alpha_{ji} \tau_{ji}) \quad (2.19)$$

$$\tau_{ji} = a_{ij} + \frac{b_{ij}}{T} \quad (2.20)$$

where,

R is the gas constant, 8.314 J•mol/K.

T is the absolute temperature, K.

a_{ij} , b_{ij} are the energy parameter of i-j interaction.

If parameter $\alpha_{ij} = \alpha_{ji}$ corresponds to the complete randomness or an ideal solution. Mostly, the value sets $\alpha_{ij} = 0.3$ and the binary interaction parameters (Δg_{ij}) are estimated from experimental data (Renon *et al.*, 1968).

2.6 Previous Methodology of Kulajapeng (2014) for Screening of ILs as Entrainers and Design of IL-Based Separation Processes

A previous methodology for the screening of ionic liquids as entrainers and for the design of ionic liquids-based separation processes in various homogeneous systems has been developed and it can be divided into 4 steps as shown in Figure 2.14. Step-1 the selected azeotrope was proposed and the stability of the ionic liquids is considered by using data collected from literatures such as thermal stability (thermal decomposition) and chemical stability (hydrolysis). Step-2 involves the screening of ionic liquids by using the miscibility of the ionic liquids in the target component. The best candidates (no more 5 ionic liquids) for aqueous systems and

non-aqueous systems are next determined. Step-3 was employed to design and simulate the feasible process by Pro/II 9.1 program. Optimization of some key parameters were performed, for instance, reflux ratio (RR), number of stages (N_s), feed stage location (N_f), and ionic liquid flowrate, to investigate the minimum energy requirement and quantity of materials used. All candidates were used as entrainers in the extractive distillation and ionic liquid recovery column. Step-4 was the design flexibility to employ the design of one azeotropic system for other azeotropic system in the same series, for instance, ethanol + water and isopropanol + water.

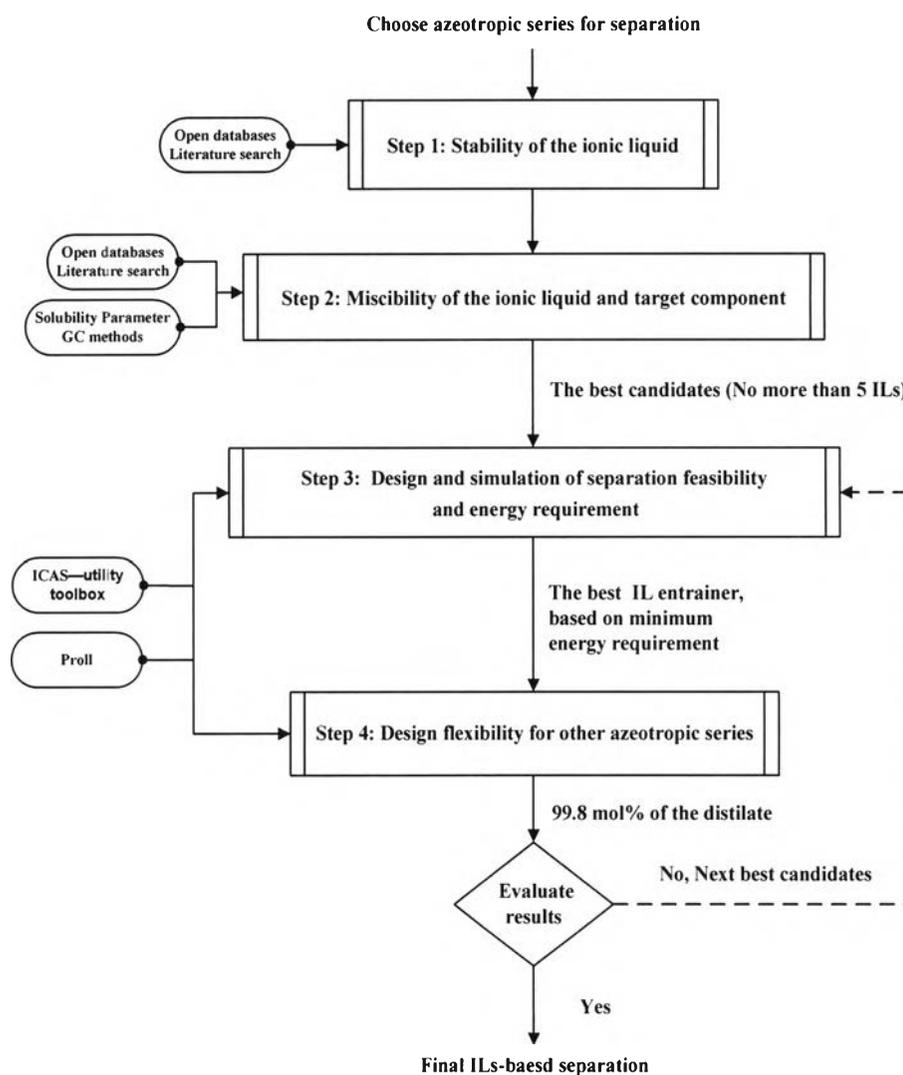


Figure 2.12 Previous methodology for screening of ILs as entrainers and design of IL-based separation processes (Kulajanpeng, 2014).

2.7 Economic Evaluation

To evaluate the viability of the use of ionic liquid in extractive distillation of azeotropic systems, a techno-economic analysis will be performed by using a software tool namely Economic Analysis Tools or ECON software (Saengwirun, 2012).

The screenshot displays the 'Project name page' of the ECON software. At the top, there is a title bar with the text 'ECONOMIC ANALYSIS TOOLS' and a logo on the left. To the right of the title bar are two buttons: 'HELP' and 'USED-MODEL'. Below the title bar, the interface is divided into four main sections:

- Project Name:** Contains two input fields, 'Project Name' and 'Case No.', and a 'Next' button.
- Money Currency:** Contains five radio button options: 'US United State Dollar', 'GBP United Kingdom Pounds', 'DKK Denmark Kroner', 'THB Thailand baht', and 'EUR Euro'. A 'Currency data' button is located to the right.
- Import Data:** Contains a text input field with the path 'C:\ECON\HDADataFile\HDADataFile_1' and a 'Load File' button.
- Utility List:** Contains a radio button option 'Use Utility Price from ECON' and a 'Put Utility Price' button.

Figure 2.13 Project name page of ECON software (Saengwirun, 2012).

2.7.1 ECON Software

The ECON software was developed in visual basic for applications related to economic analysis. ECON contains seven sections (Saengwirun, 2012):

- Equipment cost calculation
- Capital cost calculation
- Operating cost calculation
- Economic analysis

- PIE chart analysis
- Sensitivity analysis
- Alternative comparison

The cost calculations in ECON are based on the cost model given in *“Plant Design and Economics for Chemical Engineers”*. An overview of ECON software architecture is presented in Figure 2.13 and the activity diagram that highlights the work flow and data flow is presented in Figure 2.14 (Saengwirun, 2012).

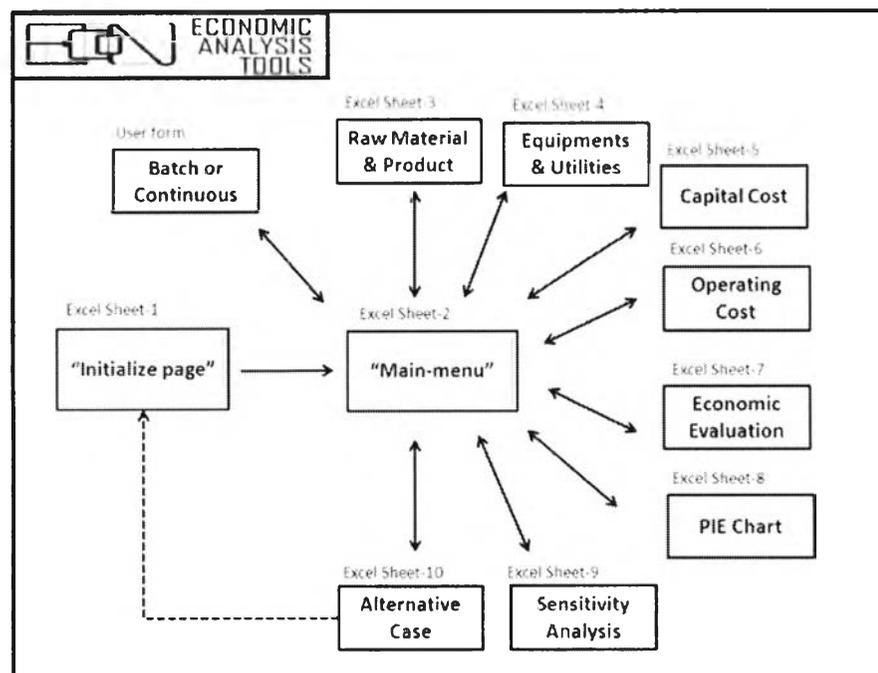


Figure 2.14 ECON software architecture (Saengwirun, 2012).

As shown in Figure 2.15, ECON consists of ten EXCEL work-sheets, where the initialize, the main-menu and process and chemical data to be given by the user. The ECON EXCEL worksheet consists of the following components (Saengwirun, 2012):

- Initial Page
- Main-Menu
- Raw materials & Products

- Equipments & Utilities
- Capital Cost
- Total Product Cost
- Economic Evaluation
- PIE Chart
- Sensitivity Analysis
- Alternative Comparison

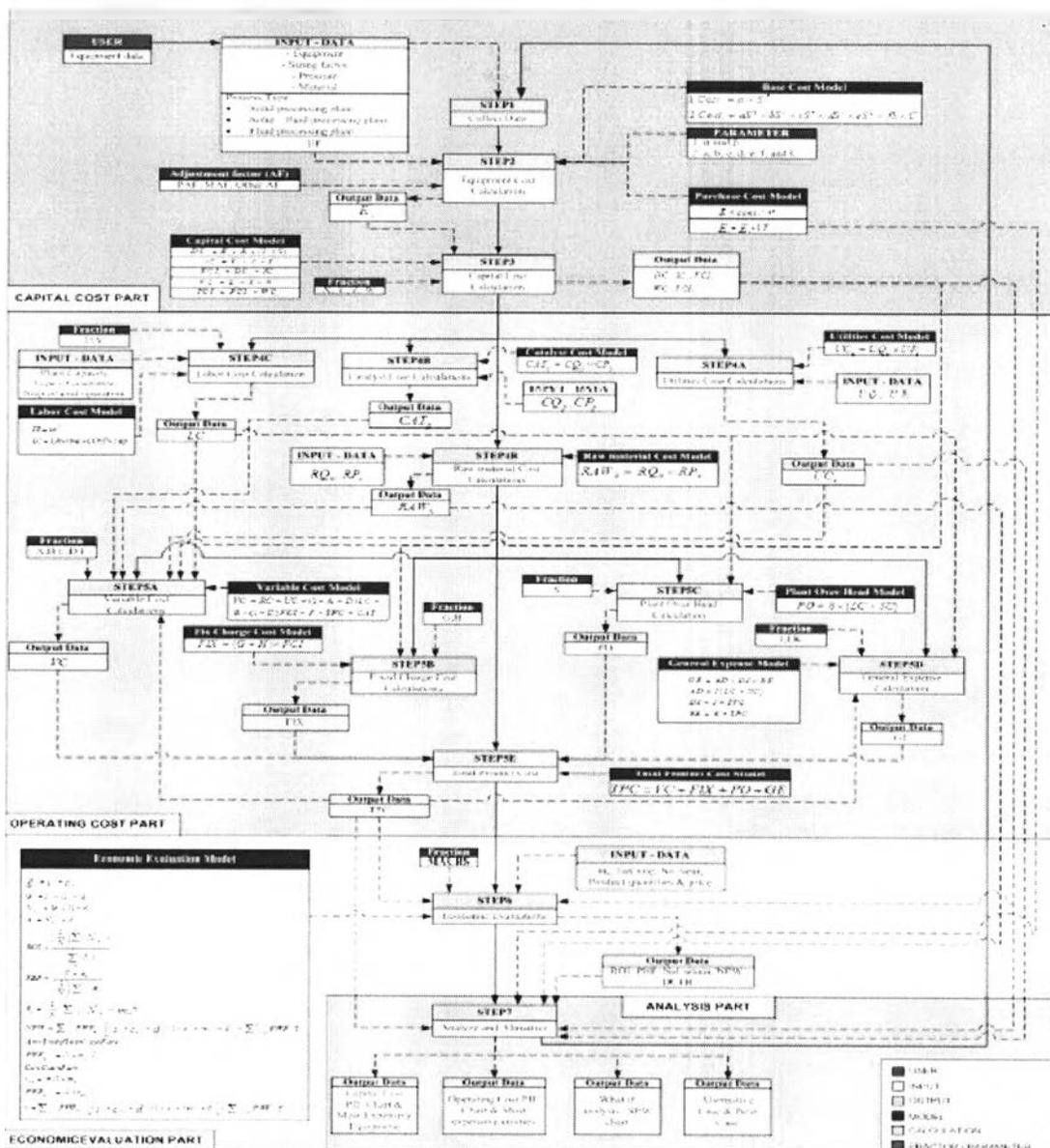


Figure 2.15 Activities diagram of ECON software (Saengwirun, 2012).