CHAPTER II
LITERATURE REVIEW

2.1 Azeotropes

In the petrochemical and chemical industries, the separation of components with close boiling points or azeotropic mixtures is often concerned. These mixtures cannot be separated efficiently by using a simple distillation. A well-known example of an azeotrope is 95.63% ethanol and 4.37% water (by weight). Separation of the ethanol-water azeotrope is a problematic process in bioethanol production due to its high energy cost of separation.

2.1.1 Definition of Azeotropes

An azeotrope is a mixture of two or more pure components in such a ratio that its composition cannot be changed by original distillation. This is because when an azeotrope is boiled, the resulting vapor has the same ratio of constituents as the original mixtures of liquids. As the composition is unchanged by boiling, azeotropes are also called constant boiling mixtures. The word azeotrope is derived from the Greek word meaning, "boiling without changing." (Halder, 2009).

2.1.2 Conditions for the Occurrence of Azeotropic Behavior

The reliable knowledge of the occurrence of azeotropic points in binary and higher systems is of special importance for the design of distillation processes. The number of theoretical stages of a distillation column required for the separation depends on the separation factor (α_{12}), e.g. the ratio of the Ki-factors (Ki) of the components i (i = 1, 2).

For a binary system, the following relation is valid for homogenous systems at the azeotropic point using the simplified equation (2.1):

$$\alpha_{12} = \frac{K_1}{K_2} = \frac{y_1/x_1}{y_2/x_2} = \frac{\gamma_1 P_1^s}{\gamma_2 P_2^s} \qquad (2.1)$$

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^s is the pure component vapor pressure. In distillation processes, only the difference between the separation factor and unity can be performed for the separation. If the separation factor is close to unity, a large number of theoretical stages are required for the separation. If the binary system to be separated shows an azeotropic point ($\alpha_{12} = 1$), the separation is impossible by simple distillation, even with an infinitely large number of stages. Following. Equation (2.1) azeotropic behavior will always occur in homogeneous binary systems when the vapor pressure ratio P_1^s/P_2^s is equal to the ratio of the activity coefficients γ_2/γ_1 (Lide, D.R. 2005).

There are two types of azeotropic systems: 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).

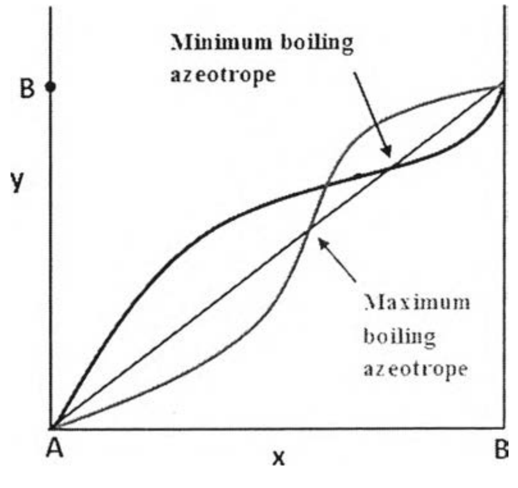

Figure 2.1 Liquid-vapor equilibrium for azeotropic mixtures (Balzhiser *et al.*, 1972).

2.1.3.1 Minimum Boiling or Positive Azeotrope

The system exhibits a minimum in its boiling point at precisely the same composition that produces a maximum in the vapor pressure curve. Such a system is classified as a minimum-boiling azeotrope or positive azeotropes (shown in Figure 2.2) and will be shown to exhibit positive deviations from ideal solution behavior (Balzhiser *et al.*, 1972).

A famous example of minimum-boiling or positive azeotrope is 95.63% ethanol and 4.37% water (by weight). Ethanol boils at 78.4 °C, water boils at 100 °C, but the azeotrope boils at 78.2 °C, which is lower than either of its constituents. Indeed 78.2 °C is the minimum temperature at which any ethanol/water solution can boil at atmospheric pressure) Halder, (2009).

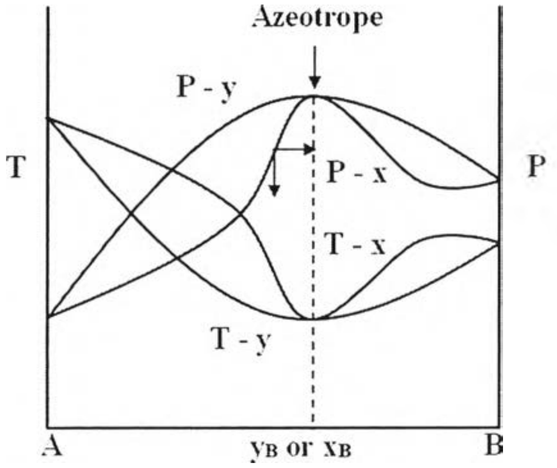

Figure 2.2 Binary system exhibiting a minimum boiling temperature azeotrope or positive azeotrope (a maximum in the vapor pressure curve) (Balzhiser *et al.*, 1972).

2.1.3.2 Maximum Boiling Azeotropes or Negative Azeotrope

The behavior of the maximum-boiling azeotrope or nagative azeotropes illustrated in Figure 2.3 shows the vapor pressure of solution at constant temperature passing through a minimum at precisely the same composition that the T-x (or boiling-point) curve exhibits a maximum. This type of system is referred to as a maximum-boiling azeotrope. Such a system always produces negative deviations from ideal solution behavior (Balzhiser *et al.*, 1972).

An example of maximum-boiling or negative azeotrope is Hydrochloric acid at a concentration of 20.2% Hydrochloric acid and 79.8% water (by weight). Hydrogen chloride boils at −84 °C and water at 100°C, but the azeotrope boils at 110 °C, which is higher than either of its constituents. Indeed, 110 °C is the maximum temperature at which anyhydrochloric acid solution can boil (Halder, 2009).

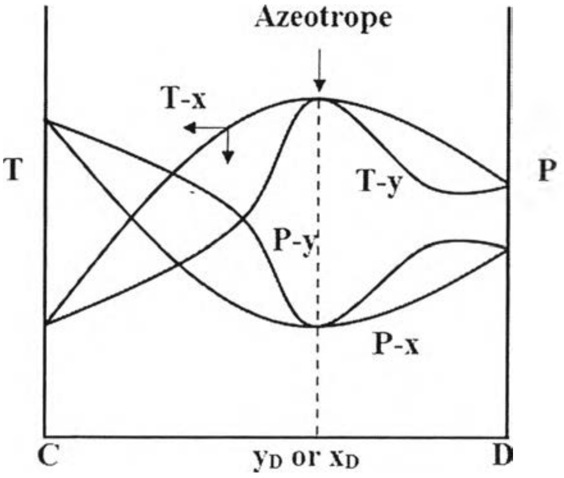

Figure 2.3 Binary system exhibiting a maximum boiling temperature azeotrope or negative azeotrope (a minimum in the vapor pressure curve) (Balzhiser *et al.*, 1972).

2.1.4 Homogeneous and Heterogeneous Azeotropes

An azeotrope can be either a homogeneous or heterogeneous azeotrope. Approximately 90% of the azeotropic mixtures are homogeneous (Lide, 2001) which contains a single liquid phase (completely miscible mixtures). Meanwhile, the multiple liquid-phase behavior (partially miscible mixtures) is called heterogeneous azeotrope (Perry *et al.*, 2008). The common examples of homogeneous and heterogeneous azeotrope are shown in Table 2.1 (Lide, 2001, Pereiro *et al.*, 2012).

Table 2.1 Azeotropic data for binary mixtures (Lide, 2001, Pereiro *et al.*, 2012)

Component 1	Component 2	T_{az}/K	$y_{1,az}$	P_{az}/kPa	Type
(Water + alcohols)					
Water	Ethanol	351.3	0.103	101.33	OX
Water	2-Propanol	353.7	0.326	101.33	OX
Water	1-Propanol	360.8	0.568	101.33	OX
Water	1-Butanol	365.5	0.754	101.33	EX
(Water + tetrahydrofuran)					
Water	Tetrahydrofuran	336.7	0.183	101.33	OX
(Alcohols + esters)					
Methanol	Methyl acetate	328.2	0.348	107.19	OX
Ethanol	Ethyl acetate	344.9	0.459	101.33	OX
(Alcohols + ketones)					
Methanol	Acetone	328.3	0.24	101.33	OX
Ethanol	2-Butanone	347.2	0.508	101.33	OX
(Alcohols + aliphatics hydrocarbons)					
Methanol	Heptane	332	0.728	101.33	OX
Ethanol	Hexane	331.7	0.341	101.33	OX
Ethanol	Heptane	345.2	0.668	101.33	EX
(Alcohols + halogenated)					
Methanol	Chloroform	328.2	0.352	107.99	OX
Ethanol	Chloroform	332.5	0.159	101.33	OX
(Aromatic + aliphatic hydrocarbons)					
Benzene	Hexane	341.5	0.05	101.33	OX
Benzene	Cyclohexane	353.2	0.546	109.18	OX

O: homogeneous azeotrope in a completely miscible system.

E: heterogeneous azeotrope.

X: pressure maximum (minimum-boiling azeotrope).

2.1.5 Separation of Azeotropic Mixtures

Azeotropes can be separated using several methods such as extractive distillation, azeotropic distillation, pressure swing distillation, liquid–liquid extraction, adsorption, and membranes. the most common separation process in the azeotropic system is extractive distillation by adding a new heavy chemical compound , namely entrainer which interacts with the components by enhancing their relative volatilities (Pereiro *et al.*, 2012).

2.2 Ionic Liquid

2.2.1 Definition of Ionic Liquids

Ionic liquids are liquids that consist exclusively of ions. This definition includes liquids that are traditionally known as molten salts with a melting point below 100°C. They are typically organic salts or eutectic mixtures of an organic salt and an inorganic salt (Freemantle, 2009). Several synonyms and abbreviations have been used in the scientific literature for organic salts with low melting points namely, ionic liquid (ILs), room-temperature ionic liquid (RTIL), ambient-temperature ionic liquid, non-aqueous ionic liquid (NAIL), molten organic salt, fused organic salt, low molting salt, neoteric solvent, and designer solvent (Freemantle, 2009).

2.2.2 Structure of Ionic Liquid

Most common ionic liquids are formed through the combination of the cation (e.g., imidazolium, pyridinium, pyrrolidinium, quaternary ammonium, tetra alkylphosphonium, etc.), the anion (e.g., hexafluorophosphate $[PF_6]^-$, tetrafluoroborate $[BF_4]^-$, trifluoromethanesulfonate $[OTf]^-$, halide $[Cl^-, Br^-, I^-]$, nitrate $[NO_3]^-$, acetate $[OAc]^-$, etc.), and the substituents. The substituents on the cations (the “R” groups) are mainly alkyl chains, but can contain any of a variety of other functional groups as well (e.g., fluoroalkyl, alkenyl, methoxy, etc.) (Brennecke and Maginn, 2001). Some combinations of ionic liquids have even been found that differ so much in their physicochemical nature (Werner *et al.*, 2010). Some well-known classes of ionic liquid systems are showed in Figure 2.4 (Brennecke and Maginn, 2001).

The guidelines on the effect of anion option on the miscibility of ILs and water were highlighted by Seddon et al. (2000). They mentioned that imidazolium salts with halide, acetate $[OAc]^-$, nitrate $[CF_3SO_3]^-$ and trifluoroacetate $[CF_3CO_2]^-$ anions are totally miscible with water, whereas the $[PF_6]^-$ and $[BTI]^-$ imidazolium salts are immiscible, and $[BF_4]^-$ and $[CF_3SO_3]^-$ imidazolium salts can be totally miscible or immiscible depending on the substituents on the cation (Brennecke, J.F. and Maginn, E.J. 2001).

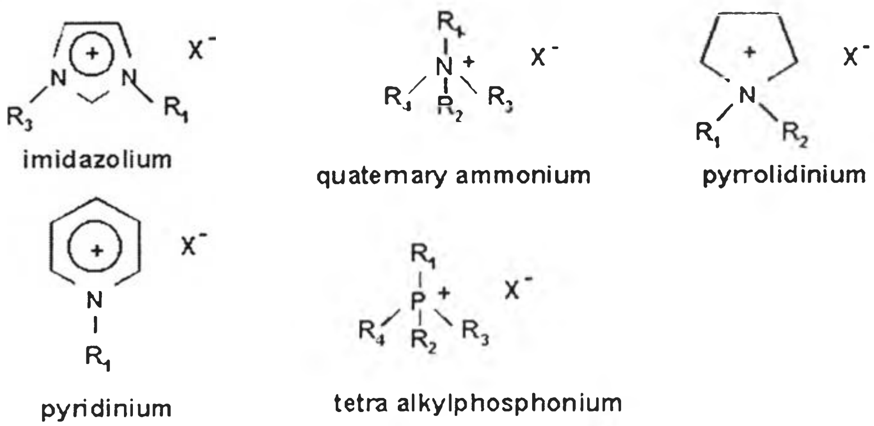

Figure 2.4 Some well-known classes of ionic liquid systems. The anion (X^-) can be any of a variety of species: imidazolium, pyridinium, quaternary ammonium, tetra alkylphosphonium, and pyrrolidinium salts, including nitrate $[NO_3]^-$, acetate $[OAc]^-$, trifluoroacetate $[CF_3CO_2]^-$, tetrafluoroborate $[BF_4]^-$, triflate $[OTf]^-$, hexafluorophosphate $[PF_6]^-$, and bis(trifluoromethylsulfonyl)imide $[BTI]^-$ (Brennecke and Maginn, 2001).

2.2.3 Attraction of Ionic Liquid

In the last two decades, ionic liquids have recently attracted the attention of chemists around the world for various reasons following (Freemantle, 2009):

- Ionic liquids have wider liquid ranges than molecular organic solvents.

- Unlike traditional volatile organic compounds (VOCs), ionic liquids have negligible vapor pressures, and do not evaporate under normal conditions. Therefore, they do not loss to atmosphere and do not pollute the product at the top of the column.
- Ionic liquids are generally non-flammable and many remain thermally stable at temperature higher than conventional volatile organic compounds.
- Ionic liquids have wide electrochemical windows.
- Ionic liquids can be used as reaction media and/or catalysts for a wide variety of chemical reactions.
- Ionic liquids could contribute significantly to the development of green chemistry and green technology by, for example:
    - Replacing toxic, flammable volatile organic solvents;
    - Reducing or preventing chemical waste and pollution;
    - Improving the safety of chemical processes and products.
- Ionic liquids have a wide range of solubilities and miscibilities because they have dual functionality (bulky cations and anions). For example, some ionic liquids are hydrophilic while others are hydrophobic.
- Ionic liquids can be used for separations and extractions of chemicals from aqueous and molecular organic solvents.
- The physical, chemical and biological properties of ionic liquids can be “tuned” or “tailored” by:
    - Switching anions or cations or alkyl chain length;
    - Designing specific functionalities into the cations and/or anions;
    - Mixing two or more simple ionic liquids.

A wide range of applications of ionic liquids are shown in Figure 2.5. ILs can be mainly applied for seven applications, namely solvents, separation, heat strorage, electroelastic materials, analytics, lubricant & additives, liquid crystal, and electrolytes. ILs is a suitable solvent for synthesis, catalysis and purification, and is also used in electrochemical devices and processes, such as rechargeable lithium batteries and electrochemical capacitors, etc. In areas of separations, ILs is commonly used as entrainer in extractive distillation and extraction (Shukla and Saha, 2013).

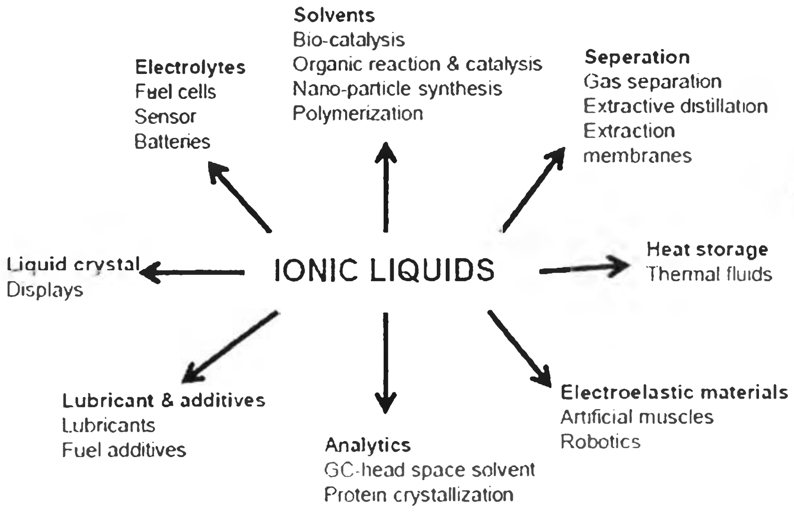

Figure 2.5 Applications of Ionic Liquids (Shukla and Saha, 2013).

2.2.4 Ionic Liquid as Entrainers

Recently, as concern about the environmental issues and the new principles of green chemistry, ionic liquids (ILs) have become a popular "green" media for engineers (Pereiro *et al.*, 2012). As "green solvents", ILs have become increasingly attractive options for the replacement organic solvents in extractive distillation due to their many unique structures and properties, such as non-volatility, no flammability, thermal stability, high dissolving ability, and good performance in altering the relative volatility of the mixtures (Li *et al.*, 2009, Pereiro *et al.*, 2012). Furthermore, ILs can be tuned or tailored for use in specific applications by accurately selecting or designing the chemical nature of the cation, the anion and the cation alkly length (Jork *et al.*, 2005, Pereiro *et al.*, 2012, Roughton *et al.*, 2012). Since the entrainer properties can be fine-tuned, the extractive distillation processes with ionic liquids as entrainers can reduce the energy consumption and environmental impact when compared to conventional organic solvent (Seiler *et al.*, 2004, Pereiro *et al.*, 2012, Roughton *et al.*, 2012).

The large number of publications of different azeotropes has been studied with ILs using different anions and cations as entrainer. Most of the studies (75%) were using 1-alkyl-3-methylimidazolium cations (Pereiro *et al.*, 2012). The variety of anions is generally much greater, with emphasizing on $[Cl]^-$, $[PF_6]^-$, $[BF_4]^-$, $[OTf]^-$, $[NTf_2]^-$ and $[EtSO_4]^-$ as displayed in Figure 6 (Pereiro *et al.*, 2012).

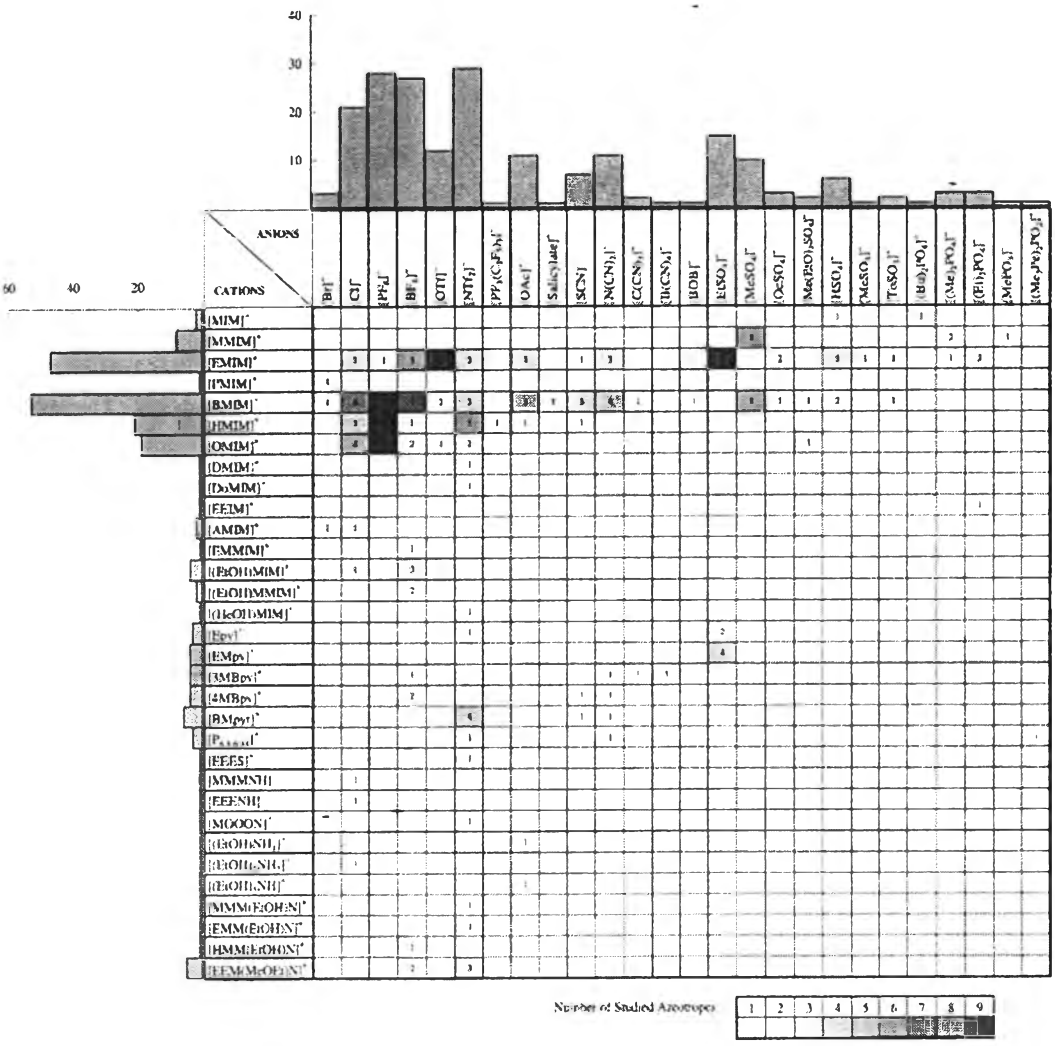

Figure 2.6 Mapping of azeotropes in the matrix of ILs anions and cations used as separating agents or entrainer. The colors refer to the number of different studied azeotropes from literature per ion combination; the length of the bars gives the count per ion (Pereiro *et al.*, 2012).

2.3. Group Contribution Methods

2.3.1 Solubility Parameter

2.3.1.1 Definition of Solubility Parameter

Hildebrand and Scott (Barton, 1991) originally defined the Hildebrand solubility parameter (δ_i) as the square root of the cohesive energy density (c_{ii}), which is the ratio of the enthalpy of vaporization (Δh_{vap}) to the molar volume (v_i) as shown in Equation (2.2).

$$\delta_i = c_{ii}^{1/2} = \left(\frac{\Delta h_{vap} - RT}{v_i}\right)^{\frac{1}{2}} \tag{2.2}$$

The Hildebrand solubility parameter is used to indicate whether compounds will be miscible. Compounds with similar solubility parameter values are more likely to form a miscible solution. Solubility parameter is one of the key parameters for selecting an entrainer, therefore the solubility parameters can be suitably used as complementary prescreening tool for selecting possible candidates (Roughton *et al.*, 2012).

It should be noted that the phase splitting of liquid mixtures plays an important role in simulation and process design, for example, in extractive distillation; the formation of two liquid phases due to the addition of the solvent is undesirable. Immiscibility in the distillation column leads to lower efficiency, control challenges, and creates foaming, which can drastically lower the capacity and lead to premature flooding, liquid carryover, and solvent losses (Gutiérrez *et al.*, 2012).

2.3.1.2 Solubility Parameter for Ionic Liquids

Roughton *et al.* (2012) proposed group contribution solubility parameter model for ILs (δ_{IL}) as shown in Equation (2.3) which was used to predict the solubility parameter for 24 different ionic liquids at 298.15 K. The developed model provided a good fit of experimental data with a value of 0.34 % AARD (percent average absolute relative deviation) between experimental and predicted solubility parameters values with the maximum relative deviation of 0.305.

$$\delta_{IL} = \delta^{C}_{\text{Alkyl chain}} + \delta^{C}_{\text{Cation}} + \delta^{C}_{\text{Anion}}$$
$$= \sum_{\text{Alkyl chain}} n_i C_i + \sum_{\text{Cation}} n_j C_j + \sum_{\text{Anion}} n_k C_k + b \qquad (2.3)$$

Where, subscript i, j, and k represent alkyl chain groups, cation groups, and anion groups respectively. n_i describes the number of groups of type i, C_i is the contribution of group i to the overall solubility parameter value (shown on Table 2.2), and b is a constant (intercept = 4.547).

Table 2.2 Group contribution values for ionic liquid Hildebrand solubility parameter model (Roughton *et al.*, 2012)

	Ionic liquid group	**Contribution ($MPa^{1/2}$)**
Cation groups	Imidazolium $[Im]^+$	1.427
	Pyridinium $[Py]^+$	1.355
	Pyrrolidonium $[Pyr]^+$	1.765
	Phosphonium $[P]^+$	−13.633
	Sulfonium $[S]^+$	−16.101
Anion groups	Trifluoroacetate $[CF_3CO_2]^-$	1.720
	Thiocyanate $[SCN]^-$	1.342
	Trifluormethanesulfonate $[OTf]^-$	−0.629
	2-(2-Methoxyethoxy)ethylsulfate $[Me(EtO)_2SO_4]^-$	1.603
	Octyl sulfate $[OcSO_4]^-$	−0.367
	Tosylate $[TOS]^-$	−0.065
	Bis(trifluoromethylsulfonyl)imide $[BTI]^-$	−2.485
	Dimethylphosphate $[DMP]^-$	2.918
	Diethylphosphate $[(Et)_2PO_4]^-$	2.120
	Tetrafluoroborate $[BF_4]^-$	8.403
	Hexafluorophosphate $[PF_6]^-$	6.319

Table 2.2 Group contribution values for ionic liquid Hildebrand solubility parameter model (Roughton *et al.*, 2012) (Continued).

	Ionic liquid group	**Contribution ($MPa^{1/2}$)**
	Chloride $[Cl]^-$	−4.000
Alkyl chain groups	CH_3	9.094
	CH_2	−0.322
	CH_2O	0.496
Intercept	b	4.547

2.3.2 Liquid Density of Ionic Liquids

Valderrama and Robles (2007) predicted critical temperature (T_C), critical pressure (P_C), critical volume (V_C), normal boiling temperature (T_b), and acentric factor (ω) of ionic liquids using an extended group contribution method based on the well-known concepts of Lydersen (Lydersen, 1995) and of Joback and Reid (Joback and Reid, 1987). The accuracy of the method was determined by calculating the liquid densities of the ionic liquids. The liquid densities of the ionic liquids (ρ_L) have been estimated as shown in Equation (2.4). The generalized correlation was based on the equation of Spencer and Danner (Spencer and Danner, 1972) and only the normal boiling temperature, the molecular weight, and the critical properties were needed in the calculation:

$$\rho_L = \frac{MP_C}{RT_C}\left[\frac{0.3445P_CV_C^{1.0135}}{RT_c}\right]^{\Omega} \tag{2.4}$$

$$\Omega = -\left[\frac{1+(1-T_R)^{\frac{2}{7}}}{1+(1-T_{bR})^{\frac{2}{7}}}\right]$$

In these equations, R is the ideal gas constant, T_R is the reduced temperature ($T_R = T/T_c$), and T_{bR} is the reduced temperature at the normal boiling point ($T_{bR} = T_b/T_c$). The normal boiling temperature and the critical temperature were taken from the equations of Joback-Reid (Equations 2.5 and 2.6), whereas the critical pressure and critical volume were considered from the equations of Lydersen (Equations 2.7 and 2.8). The authors modified the parameters involved in different equations for the critical properties. The equation for the normal boiling point was kept as in the original method. The modified Lydersen–Joback–Reid equestions were summarized in the following four equations:

$$T_b = 198.2 + \sum n\,\Delta T_{bM} \tag{2.5}$$

$$T_C = \frac{T_b}{A_M + B_M \sum n\,\Delta T_M - (\sum n\,\Delta T_M)^2} \tag{2.6}$$

$$P_C = \frac{M}{(C_M + \sum n\Delta P_M)^2} \tag{2.7}$$

$$V_C = E_M + \sum n\Delta V_M \tag{2.8}$$

$$\omega = \frac{(T_b - 43)(T_C - 43)}{(T_C - T_b)(0.7T_C - 43)}\log\left[\frac{P_C}{P_b}\right] - \frac{(T_C - 43)}{(T_C - T_b)}\log\left[\frac{P_C}{P_b}\right] + \log\left[\frac{P_C}{P_b}\right] - 1 \tag{2.9}$$

Where T_b and T_c are given in Kelvin, P_c is given in bars, and V_c is given in cm^3/mol. n_i is the number of times that a group appears in the molecule, T_b is the normal boiling temperature (K), M is the molecular mass (g/mol), and $A_M = 0.5703$, $B_M = 1.0121$, $C_M = 0.2573$, and $E_M = 6.75$. The group contributions are given in Table 2.3, where ΔT_M is the modified contribution to the critical temperature, ΔP_M is the modified contribution to the critical pressure, and ΔV_M is the modified contribution to the critical volume.

Table 2.3 Groups considered for the modified Lydersen–Joback–Reid method (Valderrama and Robles, 2007)

groups	ΔT_{bM}	ΔT_M	ΔP_M	ΔV_M
		Without Rings		
–CH3	23.58	0.0275	0.3031	66.81

Table 2.3 Groups considered for the modified Lydersen–Joback–Reid method (Valderrama and Robles, 2007) (Continued)

groups	ΔT_{bM}	ΔT_M	ΔP_M	ΔV_M
–CH2–	22.88	0.0159	0.2165	57.11
>CH–	21.74	0.0002	0.114	45.7
>C<	18.18	–0.0206	0.0539	21.78
=CH2	24.96	0.017	0.2493	60.37
=CH–	18.25	0.0182	0.1866	49.92
=C<	24.14	–0.0003	0.0832	34.9
=C=	26.15	–0.0029	0.0934	33.85
≡CH		0.0078	0.1429	43.97
≡C–		0.0078	0.1429	43.97
–OH (alcohol)	92.88	0.0723	0.1343	30.4
–O–	22.42	0.0051	0.13	15.61
>CO	94.97	0.0247	0.2341	69.76
–CHO	72.24	0.0294	0.3128	77.46
–COOH	169.06	0.0853	0.4537	88.6
–COO–	81.1	0.0377	0.4139	84.76
HCOO–		0.036	0.4752	97.77
=O (others)	–10.50	0.0273	0.2042	44.03
–NH2	73.23	0.0364	0.1692	49.1
>NH	50.17	0.0119	0.0322	78.96
>N–	11.74	–0.0028	0.0304	26.7
–N=	74.6	0.0172	0.1541	45.54
–CN	125.66	0.0506	0.3697	89.32
–NO2	152.54	0.0448	0.4529	123.62
–F	–0.03	0.0228	0.2912	31.47
–Cl	38.13	0.0188	0.3738	62.08
–Br	66.86	0.0124	0.5799	76.6
–I	93.84	0.0148	0.9174	100.79
		With Rings		
–CH2–	27.15	0.0116	0.1982	51.64

Table 2.3 Groups considered for the modified Lydersen–Joback–Reid method (Valderrama and Robles, 2007) (Continued)

groups	ΔT_{bM}	ΔT_M	ΔP_M	ΔV_M
		With Rings		
>CH–	21.78	0.0081	0.1773	30.56
=CH–	26.73	0.0114	0.1693	42.55
>C<	21.32	–0.0180	0.0139	17.62
=C<	31.01	0.0051	0.0955	31.28
–O–	31.22	0.0138	0.1371	17.41
–OH (phenol)	76.34	0.0291	0.0493	–17.44
>CO	94.97	0.0343	0.2751	59.32
>NH	52.82	0.0244	0.0724	27.61
>N–		0.0063	0.0538	25.17
–N=	57.55	–0.0011	0.0559	42.15
		New Groups		
–B	–24.56	0.0352	0.0348	22.45
–P	34.86	–0.0084	0.1776	67.01
–SO2	147.24	–0.0563	–0.0606	112.19

2.3.3 Heat Capacity Estimation of Ionic Liquids

Gardas and Coutinho (2008) predicted the liquid heat capacity (C_{pL}) of imidazolium-, pyridinium-, and pyrrolidinium-based cations containing hexafluorophosphate $[PF_6]^-$, tetrafluoroborate $[BF_4]^-$, bis(trifluoromethanesulfonyl) amide $[Tf_2N]^-$, bromide $[Br]^-$, ethyl sulfate $[EtSO_4]^-$, or trifluoromethane sulfonate $[OTf]^-$ as anions, covering a wide range of temperatures (196.36-663.10 K) and liquid heat capacity (264.8-825.0 J mol^{-1} K^{-1}) by using the second-order group additivity method as shown in equation 2.10.

$$C_{pL} = R\left[A + B\left(\frac{T}{100}\right) + D\left(\frac{T}{100}\right)^2\right] \tag{2.10}$$

$$A = \sum_{i=1}^{k} n_i a_i$$

$$B = \sum_{i=1}^{k} n_i b_i$$

$$D = \sum_{i=1}^{k} n_i d_i$$

Where R is the gas constant (R = 8.314472 J mol^{-1} K^{-1}) and T is the absolute temperature (in Kelvin), n_i is the number of groups of type i, k is the total number of different types of groups, and the parameters a_i, b_i, and d_i (estimated for ILs) are given in Table 2.4.

Table 2.4 Group Contributions for parameters A, B, and D (Gardas and Coutinho, 2008)

Species	a_i	b_i (K)	d_i (K^2)
Cations			
1,3-dimethylimidazolium (+)	11.93	8.794	−1.584
1-methylpyridinium (+)	54.063	−13.390	1.28
1,1-dimethylpyrrolidinium (+)	42.446	−9.419	1
Anions			
$[PF6]^-$	4.674	−0.379	1.11
$[BF4]^-$	3.017	−1.061	0.968
$[Tf2N]^-$	14.161	5.316	0.357
$[Br]^-$	28.638	−20.704	3.928
$[EtSO4]^-$	22.335	−6.164	1.522
$[CF3SO3]^-$	29.551	−11.280	2.453
Groups			
CH_2	−1.133	2.443	−0.259
CH_3	6.218	−9.318	1.328
dimethyl ammonium	28.98	−10.669	1.555

2.4 Computer Aided Molecular Design (CAMD) Method

Computer aided molecular design (CAMD) problems was defined by Gani (2004) as

"Given a set of building blocks and a specified set of target properties; Determine the molecule or molecular structure that matches these properties".

The group contribution based property prediction methods have been employed in most of the CAMD problems to evaluate the generated compound regarding the specified set of target properties (Gani *et al.*, 1991, Harper *et al.*, 1999). In principle, CAMD-based techniques can be employed for a very large range of problems as diverse as solvent design/selection, CFC substitutes, alternative process fluids, polymer design, and drug design (Harper *et al.*, 1999).

The main steps of any CAMD method are to generate chemically feasible molecular structures, to estimate the target properties of the generated structures and to screen/select those that satisfy the specified property constraints. Typical pure component (macroscopic) target properties are boiling points, melting points, heat of vaporization, partition coefficients, viscosity, surface tension, thermal conductivity, solubility parameter and many more. In case of mixture properties, solubilities of solids, liquids and gases in solvents is a very common target property, mixture viscosities and diffusivity are also quite common for CAMD problems dealing with solvents (Gani, 2004).

Figure 2.7 illustrates a typical group contribution based CAMD method, where the pre-design phase defines the basic needs, the design phase determines the feasible candidates (generates molecules and tests for desired properties) and the post-design phase performs higher level analysis of the molecular structure and the final selection of the product (Harper *et al.*, 1999, Gani, 2004).

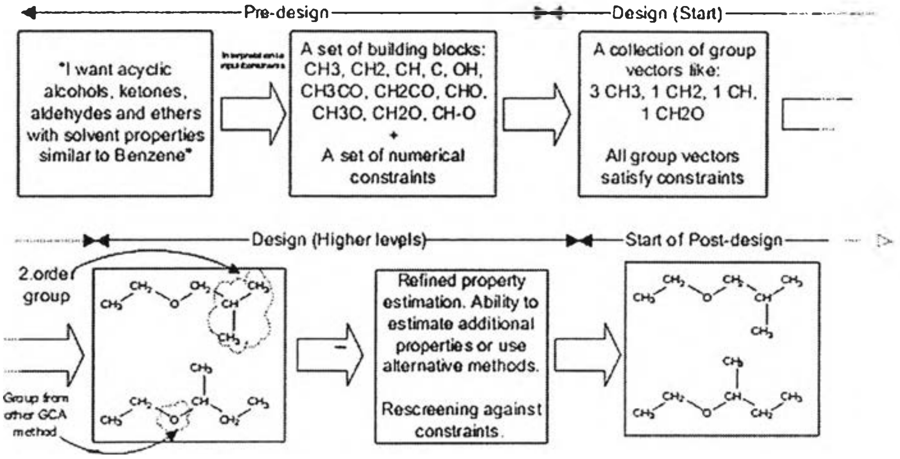

Figure 2.7 Basic steps of CAMD (Harper *et al.*, 1999, Gani, 2004).

2.4.1 CAMD Method in the Design of Ionic Liquid

CAMD has been used in the design of ionic liquid (McLeese *et al.*, 2010, Roughton *et al.*, 2012). In Figure 2.8, The forward problem was concerned with the development of predictive physicochemical or thermophysical property models based on chemical structure, which could then be used in the reverse problem to optimize chemical molecular structure for a given set of the target properties (Roughton *et al.*, 2012).

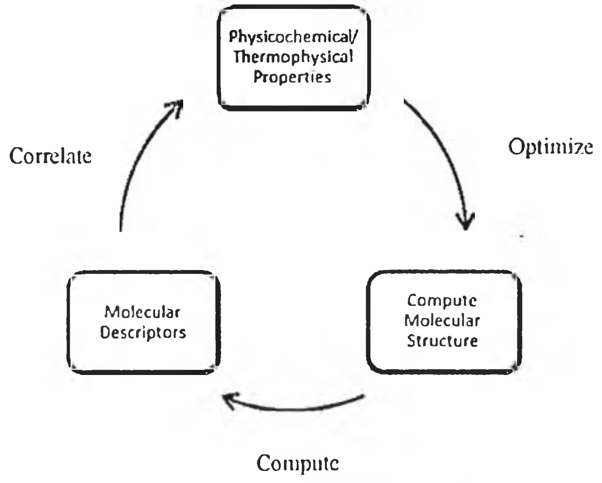

Figure 2.8 Computer-aided molecular design approach utilizing optimization of molecular structure (McLeese *et al.*, 2010, Roughton *et al.*, 2012).

2.5 Predictive Thermodynamic Models

The predictive thermodynamic models are very crucial in separation processes. For extractive distillation, the predictive thermodynamic models are used as screening tools to design the optimal ionic liquid, and it clearly shows a reduction in experimental work (Lei *et al.*, 2012). The most important of all the obvious properties is the activity coefficient, which can be used to calculate relative volatility or selectivity, and thus evaluate the possible ionic liquids. For this purpose, a priori prediction method like the COSMO-RS (conductor-like screening model for real solvents) and the classical thermodynamic models, namely NRTL (Non-Random Two-Liquid) and UNIFAC (UNIversal quasichemical Functional-group Activity Coefficients) models can be used for predicting vapor–liquid equilibrium (VLE) for the systems containing ionic liquid (Lei *et al.*, 2008).

2.5.1 COSMO-RS Model

The COSMO-RS model is a novel and efficient method for the priori prediction of thermophysical data. It is based on quantum chemistry and uses only atom-specific parameters, which can be used to predict the thermodynamic properties of solvent-ionic liquid systems. The COSMO-RS model is used to the best advantage only by its developers, their colleagues, and subscribers. Although it requires only molecular structure and is independent of experimental data, some researchers reported the mean relative deviations between experimental data and predicted results up to 79.4% for VLE and more than 100% for γ_i^{∞} of alkanes, alkenes, cycloalkenes, and alcohols when they used the COSMO-RS model to predict the activity coefficients at infinite dilution γ_i^{∞} of solutes in methylimidazolium-based ILs. Thus, it seems that significant deviations occur when using the COSMO-RS model. Moreover, unlike the UNIFAC model, the COSMO-RS model cannot be existed in such famous simulation programs as ASPEN PLUS, PROII and ChemCAD (Lei *et al.*, 2009).

2.5.2 UNIFAC Models

The UNIFAC model is based on the functional group concept was proposed by Fredenslund et al (Fredenslund *et al.*, 1975). It can be applied at infinite dilution and finite concentrations. This model has a combinatorial contribution to the activity coefficient ($\ln\gamma_i^C$ essentially due to differences in size and shape of the molecules) and a residual contribution ($\ln\gamma_i^R$, essentially due to energetic) as shown by Equation 2.11.

$$\ln\gamma_i = \ln\gamma_i^C + \ln\gamma_i^R \tag{2.11}$$

- Combinatorial Part.

The combinatorial part $\ln\gamma_i^C$ can be calculated using the following equation;

$$\ln\gamma_i^C = 1 - V_i + \ln V_i - 5q_i\left(1 - \frac{V_i}{F_i} + \ln\left(\frac{V_i}{F_i}\right)\right) \tag{2.12}$$

$$F_i = \frac{q_i}{\sum_j q_j x_j}; \qquad V_i = \frac{r_i}{\sum_j r_j x_j} \tag{2.13}$$

Where V_i (volume/mole fraction ratio) and F_i (surface area/mole fraction ratio) can be calculated from the relative van der Waals volumes (r_i) and van der Waals volumes molecular surface areas (q_i) of the molecules as the sum of the group volume and group area parameters, R_k and Q_k:

$$r_i = \sum_k v_k^{(i)} R_k; \qquad q_i = \sum_k v_k^{(i)} Q_k \tag{2.14}$$

Where, $v_k^{(i)}$ is the number of functional groups of type k in molecule i. The group parameters R_k and Q_k are normally obtained from van der Waals group volumes (V_k) and surface areas (A_k) given by Bondi (Bondi, 1964):

$$R_k = \frac{V_k}{15.17}; \quad Q_k = \frac{A_k}{2.5 \times 10^9} \tag{2.15}$$

- Residual Part.

$$\ln\gamma_i^R = \sum_k v_k^{(i)}\left[\ln\Gamma_k - \ln\Gamma_k^{(i)}\right] \tag{2.16}$$

Γ_k and $\Gamma_k^{(i)}$ are the group residual activity coefficient of group k in a reference solution containing only molecules of type i.

$$\ln\Gamma_k = Q_k\left[1 - \ln\left(\sum_m \theta_m \psi_{mk}\right) - \sum_m\left(\frac{\theta_m \psi_{km}}{\sum_n \theta_n \psi_{nm}}\right)\right] \tag{2.17}$$

$$\theta_m = \frac{Q_m X_m}{\sum_n Q_n X_n}; \quad X_m = \frac{\sum_i v_m^{(i)} x_i}{\sum_i \sum_k v_k^i x_i} \tag{2.18}$$

Where, θ_m is the surface area fractions and X_m is the fraction of group m in the mixture. The group interaction parameter ψ_{nm} is defined by

$$\psi_{nm} = \exp\left[-\left(\frac{a_{nm}}{T}\right)\right] \tag{2.19}$$

The group interaction parameter (a_{nm}) characterizes the interaction between groups n and m. For each group-group interaction, there are two parameters: $a_{nm} \neq a_{mn}$. Equations (9) and (10) also hold for $\ln\Gamma_k^{(i)}$, except that the group composition variable, θ_k, is now the group fraction of group k in pure fluid i. In pure fluid, $\ln\Gamma_k = \ln\Gamma_k^{(i)}$, which means that, as $x_i \rightarrow 1$, $\gamma_i^R \rightarrow 1$. γ_i^R must be close to unity because as $x_i \rightarrow 1$, $\gamma_i^C \rightarrow 1$ and $\gamma_i \rightarrow 1$. Therefore, the group parameters (R_k, Q_k, a_{nm}, and a_{mn}) should be given beforehand to solve the above equations (Lei *et al.*, 2009).

Lei *et al.* (2012) attempted to extend the group parameters of the UNIFAC model for ILs. They added the new ILs groups for 33 main groups and 53 subgroups into the current UNIFAC parameter matrix. In this work, the ILs was divided into several groups, but the design of cation and anion was kept as a whole since the ionic pair has a strong electrostatic interaction. Then, they discussed the predicting vapor-liquid equilibrium of the systems with ionic liquids at finite concentration, and screened the suitable ionic liquids in separation processes using the UNIFAC model. The authors found that, for nonpolar (hexane/benzene, heptane/benzene, and cyclo-hexane/benzene) systems, the calculated results may be not so satisfactory because in this case a majority of ILs have better selectivity and capacity for the separation of nonpolar system than the conventional NMP (N-methyl-pyrrolidone) and sulfolane. Among the ILs studied, the [CPMIM][N(CN)$_2$] was the most potential IL with the highest selectivity and enough capacity comparable to sulfolane. And for polar (ethanol/water) system, a majority of ILs have better selectivity and capacity for the separation of polar system than the conventional EG (Ethylene Glycol). Among others, the [EMIM][SCN] was the most potential IL with the highest selectivity and enough capacity comparable to EG. The authors concluded that the predicted results by the UNIFAC model were quantitatively based on experimental data, and were more accurate than the a priori COSMO-RS model. This statement also confirmed by Xue *et al.* (2012).

Roughton *et al.* (2012) developed the UNIFAC model for ionic liquids (UNIFAC-IL) for predicting the VLE of ternary systems containing ionic liquids and screening the candidates based on minimum concentration needed to break the azeotrope. The authors estimated the UNIFAC-IL group interaction parameters for several common azeotropes such as acetone–methanol, 1-propanol–water, 2-propanol–water, ethyl acetate–ethanol, and ethanol–water. In overall, the results showed a good prediction of the experimentally observed VLE. The authors also claimed that the UNIFAC-IL predictions for the designed ionic liquids would be reasonably accurate.

2.5.3 NRTL Model

The Non-Random Two-Liquid model (NRTL model) is an activity coefficient model that correlates the activity coefficients (γ_i) of a compound i with its mole fractions x_i in the liquid phase. It is frequently applied in the field of chemical engineering to calculate phase equilibrium. The NRTL is applicable to partially miscible as well as completely miscible systems. For general equations, the activity coefficients are calculated as follows (Renon and Prausnitz, 1968):

$$\ln\gamma_i = \frac{\sum_{j=1}^{n} \tau_{ji} x_j G_{ji}}{\sum_{k=1}^{n} x_k G_{ki}} + \sum_{j=1}^{n} \frac{x_j G_{ij}}{\sum_{k=1}^{n} x_k G_{kj}} \left(\tau_{ij} - \frac{\sum_{m=1}^{n} \tau_{mj} x_m G_{mj}}{\sum_{k=1}^{n} x_k G_{kj}} \right) \tag{2.20}$$

Where,

$$G_{ji} = \exp(-\alpha_{ji}\tau_{ji}) \tag{2.21}$$

$$\tau_{ji} = a_{ij} + \frac{b_{ij}}{T} \tag{2.22}$$

Where R is the gas constant and T is the absolute temperature, a_{ij} and b_{ij} are an energy parameter characteristic of the i-j interaction. The parameter $\alpha_{ij} = \alpha_{ji}$ is related to the non-randomness in the mixture ($\alpha_{ij} = 0$ corresponds to complete randomness or an ideal solution). The value of α_{ij} can often be set as 0.20, 0.3 or 0.47, with a typical choice of α_{ij}= 0.3. The binary interaction parameters Δg_{ij} are estimated from experimental data.

2.6 Extractive Distillation with Ionic Liquids

Extractive distillation with ionic liquids as the separating agent (entrainer) is a novel process for producing high-purity products containing azeotropic mixtures. This process integrates the advantages of liquid solvent (easy operation) and solid salt (high separation ability), and no entrainment problem of the solvent into the top product of the column as compared to extractive distillation with the mixture of liquid solvent and solid salt (Lei *et al.*, 2003). Unfortunately, the extractive distillation with ionic liquids reveals some disadvantages, for instance, the prices of ionic liquids are probably expensive and ionic liquids contain halogen anions which can form hydrogen fluoride (corrosive and toxic substance) during the hydrolysis (Huang *et al.*, 2008). Nevertheless, a wide range of IL applications regularly provide either better yields or lower toxicities than conventional volatile organic solvents (Pereiro *et al.*, 2012).

The process diagram of extractive distillation with ionic liquids is shown in Figure 2.9. The regeneration column can be evaporation, film evaporation, stripping with hot gas, and precipitation. However, the best option for the regeneration column will probably be a flash column, which requires low energy consumption, and then remove the last impurity products by using a strip column (Meindersma *et al.*, 2012).

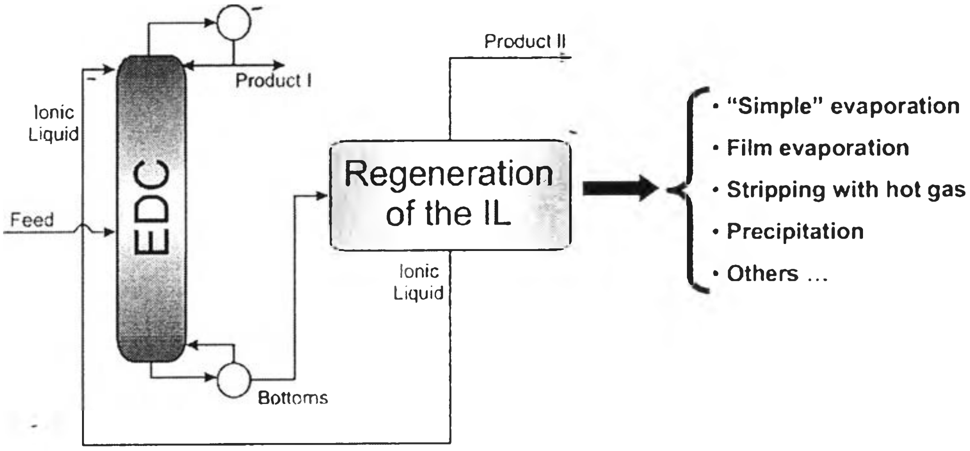

Figure 2.9 The process diagram of extractive distillation with ionic liquids (EDC= extractive distillation column) (Meindersma *et al.*, 2012).

2.6.1 Aqueous Systems

2.6.1.1 (Water + Ethanol) System

The uses of ILs as entrainers have been studied extensively for the ethanol + water system. As shown in Table 2.5, ILs indicates a salting out effect, which enhances the relative volatility of the ethanol and may even eliminate the azeotropic phenomena at a specific IL content (Pereiro *et al.*, 2012).

Table 2.5 Ionic liquids used as azeotrope breakers on literature for the separating of water + ethanol, ethanol/water relative volatility from VLE data (α^{VLE}) at azeotropic composition (Pereiro *et al.*, 2012)

Azeotrope	Ionic liquids	α^{VLEa}	Remarks	Reference
Water + ethanol	[EMIM][OTf]	1.27	VLE data at 100 kPa	Orchillés *et al.* (2009)
	[EMpy][EtSO$_4$]	2.40^b	VLE data at 101.3 kPa	Calvar *et al.* (2010)
	[BMIM][Cl]	1.38	VLE data at 30, 40 100 kPa	Geng *et al.* (2009)
	[BMIM][OTf]	1.71^c	VLE data at 314.2 and 331.7 K	Mokhtarani and Gmehling (2010)
	[OMIM][OTf]	0.95^d		
	[HMIM][Cl]	1.31	VLE data at 100 kPa	Zhang *et al.* (2009)
	[BMIM][MeSO$_4$]	2.38^b	VLE data at 101.3 kPa	(Calvar *et al.*, 2009)
	[EMIM][EtSO$_4$]	2.02^b	VLE data at 101.3 kPa	(Calvar *et al.*, 2008)
	[EMIM][BF$_4$]	1.37	VLE data at 100 kPa	Ge *et al.* (2008)
	[EMIM][N(CN)$_2$]	1.36		
	[BMIM][N(CN)$_2$]	1.53		
	[EMIM][OAc]	1.63		
	[BMIM][OAc]	1.46		
	[HMIM][Cl]	0.39	VLE data at 101.3 kPa	Calvar *et al.* (2007)
	[BMIM][Cl]	1.87^b	VLE data at 101.3 kPa	Calvar et al., 2006

Table 2.5 Ionic liquids used as azeotrope breakers on literature for the separating of water + ethanol, ethanol/water relative volatility from VLE data (α^{VLE}) at azeotropic composition (Pereiro *et al.*, 2012) (Continued)

Azeotrope	**Ionic liquids**	α^{VLEa}	**Remarks**	**Reference**
	[MMIM][DMP]	1.17^e	VLE data at 101.3 kPa	Zhao *et al.* (2006)
	[EMIM][$(Et)_2PO_4$]	1.41^e		
	[BMIM][Br]	1.06^e		
	[BMIM][Cl]	1.25^e		
	[BMIM][PF_6]	1.19^e		
	[EMIM][BF_4]	1.44	VLE data at 363.15 K	Jork *et al.* (2004)
	[BMIM][BF_4]	1.34		
	[BMIM][Cl]	1.55		

a Ethanol molar fraction ≈ 0.95 and IL molar fraction ≈ 0.10.
b Ethanol molar fraction ≈ 0.55 and IL molar fraction ≈ 0.10.
c Ethanol molar fraction ≈ 0.90 and IL molar fraction ≈ 0.50.
d Ethanol molar fraction ≈ 0.95 and IL molar fraction ≈ 0.80.
e Ethanol molar fraction ≈ 0.95 and IL molar fraction ≈ 0.05.

Ge *et al.* (2008) measured the ternary systems of (water + ethanol + an IL) using an ebulliometer at 100 kPa and obtained the activity coefficients and relative volatilities from experimental data without the thermodynamic model of the liquid phase. The authors pointed out that the suitable entrainer for the separation of the ethanol + water mixtures was [EMIM][OAc] as compared to among the eight ILs studied ([BMIM][BF_4], [EMIM][BF_4], [BMIM][$N(CN)_2$], [EMIM][$N(CN)_2$], [BMIM][Cl], [EMIM][Cl], [BMIM][OAc], and [EMIM][OAc]), due to its better enhancement of the relative volatility, as well as its relatively low viscosity and melting point. The authors also concluded that the anion contributes a stronger role in interaction on the activity coefficients than the cation. The analysis of the activity coefficients of several ILs with water and with ethanol showed that the interaction of the anions with water and with ethanol follow the same order: $[OAc]^- \approx [Cl]^- > [N(CN)_2]^- > [BF_4]^-$, canceling out most of the effect, explaining no dramatic increase in the relative volatility.

Verma and Banerjee (2010) studied the use of ILs as entrainer for the aqueous azeotropic systems: water + ethanol, water + 2-propanol, and water + tetrahydrofuran (THF). They applied the "COnductor-like Screening MOdel for Real Solvents" (COSMO-RS) as a tool to predict the ternary vapor + liquid equilibria for the azeotropic mixture with a combination of 10 cations (imidazolium, pyridinium, quinolium) and 24 anions. The relative volatility was used to screen the potential ionic liquids for each system. They concluded that the imidazolium based cation were the best entrainer for the separation of the three systems at their azeotropic point. ILs with [MMIM] cation in combination with acetate [OAc], chloride [Cl], and bromide [Br] anion gave the highest relative volatility. The entrainer properties of ILs were also found to be proportional to the weight fraction of ILs.

Orchillés *et al.* (2011) measured the vapor–liquid equilibrium (VLE) data for the ternary system of ethanol (1), water (2) and 1-Ethyl-3-methylimidazolium dicyanamide ($[EMIM][N(CN)_2]$) (3) at 100 kPa using a recirculating still. The authors mentioned that the $[EMIM][N(CN)_2]$ IL was one of the best entrainers for the extractive distillation of the ethanol + water mixtures, due to the breaking of azeotrope at 100 kPa for ionic liquid mole fractions as low as 0.019. Although, the effect produced by the $[EMIM][N(CN)_2]$ on the VLE of the ethanol + water system was slightly smaller than that produced by [EMIM][Cl], [EMIM][OAc], or [BMIM][OAc], and its price was noticeably higher. In spite of that, $[EMIM][\ N(CN)_2]$ has the advantage of its smaller viscosity and melting point, as well as its larger decomposition temperature. The Mock's electrolyte nonrandom two-liquid (NRTL) model was used to correlate the experimental data showing good agreement.

Roughton *et al.* (2012) purposed the methodology and tool set for the simultaneous design of ionic liquid entrainers and azeotropic separation processes applied for acetone–methanol and ethanol–water azeotropic system. The overall methodology for simultaneous design of ionic liquid entrainers and IL-based separation processes is shown in Figure 2.10. The details for each step are follows:

- Selection of azeotropic systems.
- The solubility parameter was set as a key target property to screen the designed candidates through CAMD.
- The UNIFAC-IL was used to predict the VLE of ternary systems containing ionic liquids, which is used to confirm the breaking of azeotrope.
- The designed candidates were screened again based on the minimum concentration of ionic liquid needed to break the specific azeotrope.
- The UNIFAC-IL model was then used to generate driving force diagrams for near-optimal design of the extractive distillation column.
- The entire separation process consisting of the distillation unit and ionic liquid recovery stage was simulated using ChemCAD to determine energy requirements.

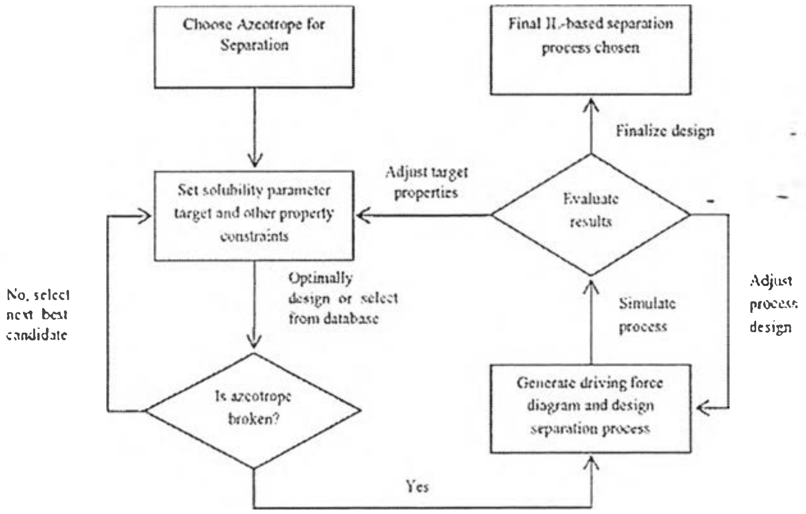

Figure 2.10 Overall methodology for simultaneous design of ionic liquid entrainers and IL-based separation processes proposed by Roughton *et al.* (2012).

The authors found that the final design candidates for the acetone-methanol was 1-Octyl-4-methylpyridinium trifluoromethane sulfonate, [OMpy][OTf] which provided the lowest energy consumptions and reduced the energy consumption by 24.9% compared to the experimentally selected ILs 1-Ethyl-3-methyl trifluoromethane sulfonate, [EMIM][OTf]. Whereas for ethanol-water system, 1,3-Dimethylimidazolium dimethylphosphate, [MMIM][DMP] was the final design candidates which consumed the lowest energy requirements and reduced heat duty by 26.5% when compared to the experimentally selected ILs [EMIM][OTf]. In case of ethanol–water separation, [MMIM]][DMP] was compared in term of the energy saving to the previously published simulation results (Seiler *et al.*, 2004) using a conventional entrainer, 1,2-ethanediol, and an experimentally selected ionic liquid, 1-Ethyl-3-methylimidazolium tetrafluoroborate or [EMIM] [BF_4] (Seiler *et al.*, 2004). [MMIM]][DMP] showed an energy savings of 28.8% as compared to the conventional entrainer (1,2-ethanediol) and an energy savings of 5.8% as compared to the experimentally selected ionic liquid [EMIM][BF_4] (Seiler *et al.*, 2004).

In conclusion, by comparing ionic liquids containing the imidazolium-based cation, $[EMIM]^+$, in term of their relative volatility of the system at $x_{Ethanol} = 0.95$, the interaction of the anions with water and with ethanol follows the same order: $[OAc]^- \approx [Cl]^- > [N(CN)_2]^- > [BF_4]^-$ (Ge *et al.*, 2008, Pereiro *et al.*, 2012). At low ethanol concentrations, the imidazolium-based cation showed a higher enhancement of the relative volatility than that of the $[EMpy]^+$ cation (Pereiro *et al.*, 2012). In term of the effect of the alkyl chain length of both the anion and the cation, the increase in the cation's chain length leads to a less effective entrainer since the relative volatility decreases at all concentrations. This indicates that small cations possess stronger IL + water interactions than the larger ones, forcing the ethanol into the vapor phase, thus increasing relative volatility (Pereiro *et al.*, 2012). The selection of ILs as entrainer for the ethanol/water system through several methods showed that the imidazolium based cations were the best entrainer for the separation of the ethanol + water system. According to energy savings, the [MMIM][DMP] (Roughton *et al.*, 2012) was favorable as a new alternative entrainer for the ethanol + water system in extractive distillation.

2.6.1.2 (Water + other Alcohols) Systems

There are several azeotropic mixtures of other alcohols + water homogeneous binary system studied in the literature including, 1-propanol, 2-propanol, and 2-methyl-2-propanol as shown in Table 2.6 (Pereiro *et al.*, 2012).

Table 2.6 Lists the ILs used as azeotrope breakers for the (water + other alcohols) longer than ethanol binary systems (Pereiro *et al.*, 2012)

Azeotrope	**Ionic liquids**	α^{VLE}	**Remarks**	**Reference**
Water + 1-propanol	[EMIM][OTf]	1.36[a]	VLE data at 100 kPa	(Orchillés *et al.*, 2008)
	[EMIM][BF_4]	1.52[b]	VLE data at 100 kPa	Zhang *et al.* (2007)
	[BMIM][BF_4]	1.37[b]		
Water + 2-propanol	[EMIM][$EtSO_4$]	1.41[c]	VLE data at 333.15 K: headspace gas chromatography	Kim *et al.* (2010)
	[BMIM][BF_4]	1.51[c]		
	[HMIM][NTf_2]	1.41[d]	VLE data at 332 K: headspace gas chromatography	Westerholt *et al.* (2009)
	[BMpyr][NTf_2]	1.51[d]		
	[BMIM][BF_4]	1.32[c]	VLE data at 101.3 kPa	Li *et al.* (2009)
	[EMIM][BF_4]	1.95[c]	VLE data at 101.3 kPa	Li *et al.* (2007)

Table 2.6 Lists the ILs used as azeotrope breakers for the (water + other alcohols) longer than ethanol binary systems (Pereiro *et al.*, 2012) (Continued)

Azeotrope	Ionic liquids	α^{VLE}	Remarks	Reference
Water + 2-propanol	[BMIM][BF$_4$]	1.32^c	VLE data at 100 kPa	Zhang *et al.* (2007)
	[EMIM][BF$_4$]	2.19^c	VLE data at 100 kPa	Zhang *et al.* (2007)
	[BMIM][OAc]	2.12^a	VLE data at 100 kPa	Zhang *et al.* (2007)
	[EMIM][OAc]	2.18^a		
	[BMIM][Cl]	2.20^a	VLE data at 101.3 kPa	
	[EMIM][N(CN)$_2$]	1.74^a	VLE data at 101.3 kPa	
	[EMIM][BF$_4$]	1.58^a	VLE data at 100 kPa	
	[BMIM][N(CN)$_2$]	1.50^a	VLE data at 100 kPa	
	[EMIM][NTf$_2$]	n.a.	VLE data at 100 kPa	Döker and Gmehling (2005)
	[BMIM][NTf$_2$]	n.a.		
Water + 2-methyl-2-propanol	[EMIM][OAc]	3.28^a	VLE data at 100 kPa	Zhang *et al.* (2009)
	[BMIM][OAc]	2.58^a		
	[HMIM][OAc]	2.43^a		
	[EMIM][Cl]	3.58^a		
	[BMIM][Cl]	2.29^a		
	[HMIM][Cl]	2.05^a		

a 2-Propanol molar fraction ≈ 0.95 and IL molar fraction ≈ 0.25.
b 1-Propanol molar fraction ≈ 0.43 and IL molar fraction ≈ 0.24.
c 2-Propanol molar fraction ≈ 0.67 and IL molar fraction ≈ 0.20.
d Water/2-propanol relative volatility; 2-propanol molar fraction ≈ 0.38 and IL molar fraction ≈ 0.95.

The study of water + 1-propanol azeotropic system was only carried out with two distinct anions ($[BF_4]^-$ and $[OTf]^-$). The minimum molar fraction of IL needed to break the water + 1-propanol azeotrope at $x_{1\text{-Propanol}}$ 0.43 is smaller for $[EMIM][BF_4]$, 0.30 (Zhang *et al.*, 2007), than for [EMIM][OTf], 0.34 (Orchillés *et al.*, 2008). $[OTf]^-$ anion ILs has small relative volatility (see Table 6) compared to the $[BF_4]$ demonstrating its inferior entrainer capacity. Zhang et al. (Zhang *et al.*, 2007) studied the effect of increasing the alkyl chain length of the cation ($[EMIM]^+$ and $[BMIM]^+$) in the azeotrope water + 1-propanol. They found that at the same weight fraction of ILs w_{IL}= 0.7, the azeotrope was broken only in the case of the ILs with $[EMIM]^+$ cation. Therefore, for water + 1-propanol system, smaller alkyl chain length of the cation was more adequate for azeotrope breaking (Pereiro *et al.*, 2012).

Zhang *et al.* (2007) proposed a procedure for experimental evaluation of ionic liquids (ILs) as entrainers, and measured the vapor–liquid equilibria (VLE) for ternary systems of water + 2-propanol + IL at 100 kPa ($x_{2\text{-Propanol}}$ = 0.95, IL-free basis) and correlated the experimental VLE data using the NRTL model. Seven ILs were investigated, namely $[EMIM][BF_4]$, $[BMIM][BF_4]$, $[EMIM][N(CN)_2]$, $[BMIM][N(CN)_2]$, [EMIM][OAc], [BMIM][OAc], and [BMIM][Cl]. They mentioned that the effect on the relative volatility of 2-propanol to water was mainly dependent on the anion in the order: $[Cl]^-$ > $[OAc]^-$ > $[N(CN)2]^-$ > $[BF_4]^-$. This order was in agreement with that found for water + ethanol azeotrope. Among the seven ILs studied, the ILs with $[OAc]^-$ or $[Cl]^-$ as the anion, and $[EMIM]^+$ as the cation, have the most significant ability to enhance the relative volatility of the mixture of water and 2-propanol.

Kim *et al.* (2010) measured the isothermal vapor-liquid equilibrium (VLE) data at T=333.15 K for the 2-propanol + water + ILs ($[EMIM][EtSO_4]$ and $[BMIM][BF_4]$) system with different concentrations using the headspace gas chromatography (HSGC) technique. The experimental VLE data (ILs-free base) were correlated with the Wilson, NRTL, and UNIQUAC models. Of all concentrations used in their study, the authors were not able to break the azeotrope, rather deviating it to higher concentrations of alcohol, from $x_{Alcohol} = 0.68$ to 0.88 and 0.84 using a mole fraction of 0.2 of [EMIM][EtSO$_4$] and [BMIM][BF$_4$]. Direct comparison of the relative volatility (Table 6) for [BMIM][BF$_4$] and [EMIM][EtSO$_4$] showed that the [EtSO$_4$]$^-$ anion was not a good option as an azeotrope breaker for this system (Pereiro *et al.*, 2012).

Only Zhang et al. (2009) studied on the effect of ILs on the phase behavior of water + 2-methyl-2-propanol (tert-butyl alcohol, TBA). They also measured the VLE data of water (1) + TBA (2) + IL (3) system at 100 kPa and correlated data using the NRTL models. The six distinct ILs based on the anions [Cl]$^-$ and [OAc]$^-$ and the cations [EMIM]$^+$, [BMIM]$^+$, [HMIM]$^+$, namely [EMIM][OAc], [BMIM][OAc], [HMIM][OAc], [EMIM][Cl], [BMIM][Cl], and [HMIM][Cl] were investigated. They found that the [EMIM][Cl] ILs had the largest effect on enhancement of the relative volatility. In addition, [EMIM][OAc], had also significant enhancing effect. Considering the relatively low viscosity and melting point of [EMIM][OAc], this IL might be a favorable candidate as entrainer for the separation of water and TBA by extractive distillation. This result was similar to the system of water + 2-propanol (Zhang *et al.*, 2007) and water + ethanol (Ge *et al.*, 2008).

2.6.2.3 *Water + Tetrahydrofuran System*

Generally, the tetrahydrofuran production requires 99.9% purity for commercial use; however, the THF + water mixture shows a minimum boiling azeotrope at $x_{THF} = 0.817$. The VLE behavior of the (THF + water + IL) ternary systems has been studied to evaluate the feasibility of extractive distillation techniques as shown in Table 2.7.

Table 2.7 Lists the ionic liquids used as azeotrope breakers for the (THF + water) system in the literature for extractive distillation (Pereiro *et al.*, 2012)

Azeotrope	**Ionic Liquids**	$\alpha^{\mathrm{VLE}a}$	**Remarks**	**Reference**
Water + THF	[EMIM][BF_4]	4.4	VLE data at 337.15 K: headspace gas chromatography	Jork *et al.* (2004)
	[BMIM][BF_4]	3.24		
	[OMIM][BF_4]	2.5		
	[BMIM][Cl]	37.26		
	[EMIM][Cl]	31.14	VLE data at 337.15 K: headspace gas chromatography	Jork *et al.* (2005)
	[EMIM][$EtSO_4$]	13.59		
	[EMIM][$ToSO_3$]	11.41		
	[EMIM][$OcSO_4$]	12.87		
	[EMIM][OTf]	3.92		
	[EMIM][BF_4]	4.35		
	[EMIM][PF_6]	2.21		
	[EMIM][NTf_2]	1.5		
	[BMIM][OAc]	36.86		
	[BMIM][Cl]	31.35		
	[BMIM][HSO_4]	8.5		
	[BMIM][Salicylate]	8.33		
	[BMIM][SCN]	8.68		
	[BMIM][$N(CN)_2$]	8.33		
	[BMIM][$MeSO_4$]	8.62		
	[BMIM][$Me(EtO)_2SO_4$]	9.32		
	[BMIM][$OcSO_4$]	22.03		
	[BMIM][BF_4]	3.52		
	[BMIM][BOB]	15.67		
	[BMIM][NTf_2]	1.26		

a azeotropic composition and IL molar fraction ≈ 0.30

Jork *et al.* (2004) studied the influence of the ILs structure on the relative volatility of THF + water azeotropic mixture in extractive distillation, and also measured the VLE for THF + water + imidazolium-based ILs, namely [EMIM][BF_4], [BMIM][BF_4], [OMIM][BF_4] and [BMIM][Cl]. They concluded that the IL [EMIM][BF_4] was a suitable entrainer for long-term application in thermal separation processes. In spite of its transition from slightly yellow to black, the ternary THF + water + [EMIM][BF_4] VLE phase diagram was not found to change at all. This was not proof of the chemical stability of the IL investigated in long-term application within aqueous media. Therefore the authors suggested that chemical reactions appearing in this mixture might have very minor impacts on the observed thermodynamic behavior. The authors also mentioned that ILs with shortening the length of the alkyl chain of the cation increases the impact of the ILs on the VLE slightly.

Jork, et. al. (2005) used the COSMO-RS as a tool to predict the activity coefficients at infinite dilution of both an azeotropic aqueous (tetrahydrofuran + water) and a close-boiling aromatic test system (methylcyclohexane + toluene) containing ionic liquids (8 different cations and 24 different anions), and then screened ionic liquids as entrainers in extractive distillation. The authors pointed out that a higher degree of branching or longer alkyl substituents on the cation, as well as a low nucleophilicity of the anion decreases both selectivity and capacity at infinite dilution in the tetrahydrofuran + water system. The small, unbranched, and polar ions without sterical shielding effects around their charge centers such as $[OAc]^-$, $[Cl]^-$, $[DMP]^-$, and $[MAcA]^-$ seem to be efficient ionic liquid entrainers for tetrahydrofuran + water system. The anions containing fluorine promote a more uniform distribution of the electrons (e.g., $[OTf]^-$ and $[BMA]^-$), and reduce the polarity. Thus, the entrainer suitability of the preselected ionic liquids in aqueous systems was decreased. The authors also mentioned that the anions containing cyclic or aromatic groups were not being capable of acting as entrainers for the tetrahydrofuran + water system.

In overall, the relative volatility of the low-boiling compound (THF) increases as the alkyl group was shortened: octyl > butyl > ethyl. The effect of anions on the relative volatility of the (THF + water) system at the azeotropic point (x_{THF} = 0.817) showed that [BMIM][OAc], [BMIM][Cl], and [EMIM][OAc] exhibited the highest entrainer efficiencies (Pereiro *et al.*, 2012). The relative volatilities of the THF + water + [BMIM][OAc], [BMIM][Cl], and [EMIM][Cl] as compared to those of THF + water + [BMIM][BF_4], [EMIM][BF_4], and [OMIM][BF_4] obviously explained that the exchange of the anion results in a much larger change in the relative volatility of the low-boiling component than the modification of the cation's alkyl chain length. [BMIM][OAc] was shown to be the most suitable for the THF + water separation. With respect to the selective interactions and the increasing relative volatility of the THF, the imidazolium salts composing the acetate ($[OAc]^-$) and chloride ($[Cl]^-$) anions were the best among all the anions studied (Pereiro *et al.*, 2012).

2.6.2 Non-Aqueous Systems

2.6.2.1 Alcoholic Systems

Orchillés *et al.* (2007) studied the separation of ethyl acetate and ethanol by extractive distillation using [EMIM][OTf] as entrainer. They found that [EMIM][OTf] breaking the azeotrope at a specific IL mole fraction of 0.20, and showed a significant salting-out effect. It also showed an enhancement of the relative volatility of the ethyl acetate near the azeotropic point; however, this effect was unnoticeable at low ethyl acetate concentrations.

Li *et al.* (2009) studied the use of ILs as separating agent for the separation of ethyl acetate and ethanol. They investigated three ILs, namely [BMIM][BF_4], [OMIM][BF_4], and [EMIM][BF_4] by measuring the vapor-liquid equilibrium (VLE) data of the ethyl acetate (1) + ethanol (2) containing ILs at 101.32 kPa. They found that all ILs studied showed a significant enhancement of salting-out effect. The authors argue that EMIM][OTf] should be selected as entrainer when compared with the tetrafluoroboratebased ILs.

In conclusion, the separation of ethyl acetate and ethanol by extractive distillation using ILs as entrainer has been widely studied. As illustrated in Figure 2.11, the influence of ILs on the relative volatility of ethyl acetate to ethanol of the four ILs at x_{IL} = 0.30 was in the following order: [OMIM][BF_4] >

$[EMIM][BF_4]$ > [EMIM][OTf] > $[BMIM][BF_4]$ and was mostly due to the difference in polarity of the ILs and the demixing effect (Li *et al.*, 2009). These results clearly showed that the tetrafluoroborates-based anion ($[BF_4]^-$) should be used as new alternative entrainers for the separation of ethylacetate + ethanol by extractive distillation (Pereiro *et al.*, 2012).

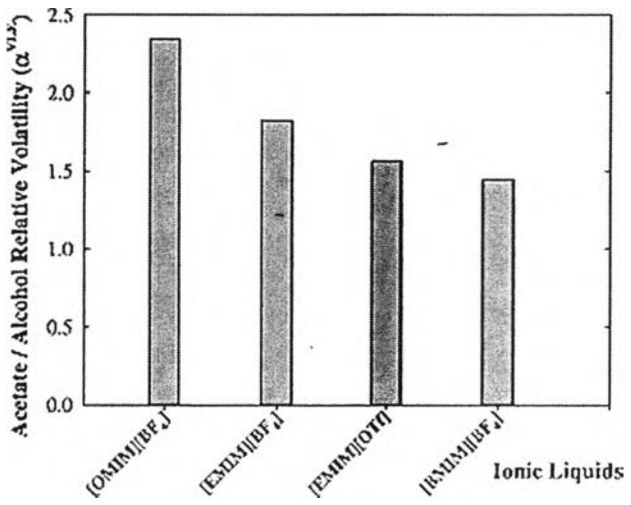

Figure 2.11 Acetate/alcohol relative volatility versus IL (Orchillés *et al.*, 2007, Vercher *et al.*, 2007, Li *et al.*, 2009) used for (ethanol+ ethyl acetate) system at azeotropic composition ($x_{\text{Ethyl acetate}} \approx 0.54$) and $x_{IL} \approx 0.30$ (Pereiro *et al.*, 2012).

2.6.2.2 Olefin + Paraffinic Hydrocarbons Systems

Lei *et al.* (2006) studied the separation of olefins (1-hexene) and paraffins (n-hexane) with ionic liquids in extractive distillation. The authors employed the COSMO-RS as a tool for screening ILs and verified the calculated results at infinite dilution by experimenting. The authors found that the anion played an important role in improving the separation ability, and the suitable ionic liquids should have small molecular volume (the shorter the alkyl chain length), unbranched group and sterical shielding effect around anion charge center ($[PF_6]^-$, $[BOB]^-$,$[B(CN)_4]^-$, $[BTA]^-$, $[CF_3SO_3]^-$, $[BMB]^-$, etc.). Although N-methyl-2-pyrrolidone (NMP) solvent screened by CAMD exhibited the highest selectivity among all the entrainers at 313.15 and 333.15 K, NMP is not thermally and chemically stable which is easy to be decomposed. Therefore, the authors concluded that [EMIM][BTA] and [C_8Chin][BTA] were the best entrainers at 313.15K and 333.15 K, respectively. The extractive distillation process is often operated under normal pressure and the temperature close to 333.15K and thus [C_8Chin][BTA] was the best among all the entrainers investigated from the viewpoint of selectivity.

Gutiérrez *et al.* (2012) applied the COSMO-RS-Based ionic liquid selection for methylcyclohexane/toluene, 1-hexene/n-hexane, and ethanol/water separation in an extractive distillation. The authors used COSMO therm activity coefficients at infinite dilution to design suitable ILs. They found that the longer the alkyl chain, the lower the selectivities and activity coefficients (higher solubility), and the higher the degree of branching, the lower the selectivity; meanwhile, the solubility increases because of the decrease of the activity coefficients. The authors then concluded that the influence of the anion on the activity coefficients and selectivities followed the same trend with aromatics/nonaromatics (toluene/methylcyclohexane). Therefore, the ILs selected for the separation of aromatics/nonaromatics was also considered suitable for the separation of olefin/paraffin (1-hexene/n-hexane). By the experimental verification, as illustrated in Figure 2.12, none of the studied ILs was able to significantly increase the relative volatility at finite dilution (real solution) as compared to the conventional solvent NMP. It was found that only the IL [C6-MIM][TCB] reached a slightly higher relative volatility. However, the increase was not big enough to consider this solvent as a suitable replacement. Moreover, the ILs have solubility constraints that force the use of large a solvent-to-feed (S/F) ratios to avoid the formation of two liquid phases.

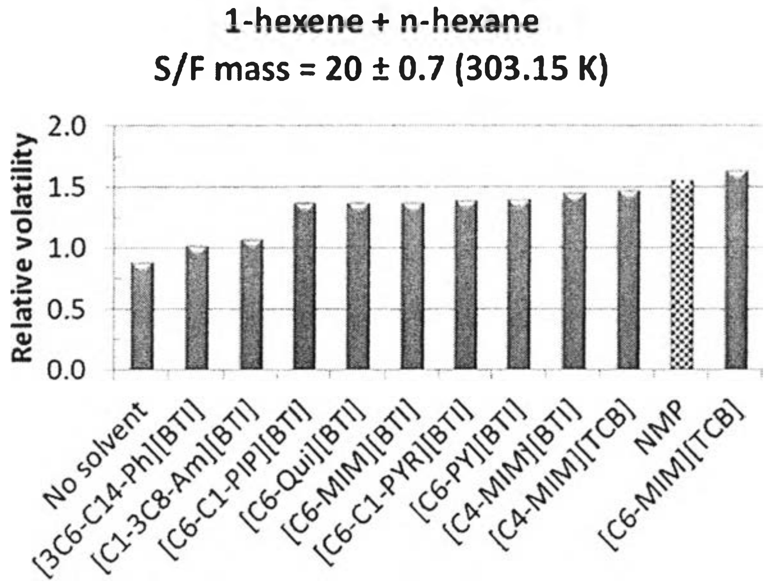

Figure 2.12 Relative volatilities for the system 1-hexene (80 wt %)/n-hexane (20 wt %) using ILs at 303.15 K (Gutiérrez *et al.*, 2012).

2.6.2.3 Aromatic + Aliphatic Hydrocarbons Systems

Mokhtarani and Gmehling (2010) studied the use of ionic liquid as entrainer for hexane + benzene and benzene + cyclohexane separation using extractive distillation. The authors measured the VLE data for the ternary systems hexane + benzene and benzene + cyclohexane with an ionic liquid as entrainer for four ionic liquids, namely [HMIM][BTI], [OMIM][BTI], [OMIM][OTF], and [BMIM][OTF]. The results showed that the [HMIM][BTI] and [OMIM][BTI] as entrainer enhanced the separation factor for hexane + benzene and benzene + cyclohexane systems. The authors concluded that this two ILs may replace the conventional solvents as entrainer for extractive distillation processes.

Gonfa *et al.* (2012) studied on the screening of potential ionic liquid entrainers for benzene and cyclohexane separation using COSMO-RS model. They predicted the activity coefficients at infinite dilution for 2640 ionic liquids (44 anions and 60 cations) and compared them with experimental results to check the reliability of the prediction. They found that structural variations of the ionic liquid entrainer caused converse changes in selectivity and capacity, and ILs with a shorter and unbranched alkyl substituent of the cation and with anions with sterical shielding (e.g., $[PF_6]^-$, $[BOB]^-$, $[B(CN)_4]^-$, $[BTA]^-$, $[CF_3SO_3]^-$, $[BMB]^-$) were favorable for higher selectivity. The imidazolium and the thiazolium had higher selectivity but lower solvent capacity, whereas the phosphonium and the guanidinium cations had higher capacities.