ACTIVITY COEFFICIENTS AT INFINITE DILUTION FOR ILS: METHYLTRIOCTYLAMMONIUM CATION AND BIS (TRIFLUOROMETHYLSULFONYL)IMIDE OR THIOSALICYLATE ANIONS USING GLC

By

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PREFACE

The work described in this thesis was carried out by the author under the supervision of Professor N. Deenadayalu, from year 2008 to 2009. These studies represent original work by the author and have not been submitted in any form to another tertiary institution. Where use is made of the work of others, it has been clearly stated in the text.

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Abstract

The activity coefficients at infinite dilution (γ_{13}^{∞}) were calculated for alkanes, alkenes, cycloalkanes, alkynes, ketones, alcohols and aromatic compounds from gas liquid chromatography (glc) measurements at three temperatures (303.15 and 313.15 and 323.15) K. The γ_{13}^{∞} values were calculated from the retention data for two ionic liquids (ILs) with the same cation but different anions. The ionic liquids: [methyltrioctylammonium bis(trifluoromethylsulfonyl)imide and methyltrioctylammonium thiosalicylate] were used as the stationary phase. The γ_{13}^{∞} data for methyltrioctylammonium thiosalicylate were higher than for methyltrioctylammonium bis(trifluoromethylsulfonyl)imide.

For each temperature and each ionic liquid, γ_{13}^{∞} values were determined for two columns and the average γ_{13}^{∞} values were used for the calculation of the partial molar excess enthalpies at infinite dilution, $\Delta H_1^{E\infty}$, using the Gibbs-Helmholtz equation. Graphs of In γ_{13}^{∞} vs $1/T$ were plotted to determine $\Delta H_1^{E\infty}$ at T = 303.15 K. The selectivity, S_{12}^{∞}, value for the hexane/benzene separation was calculated from the ratio of the avarage γ_{13}^{∞} values to determine the suitability of the ILs as an entrainer for extractive distillation in the separation of aromatic and aliphatic compounds.The S_{12}^{∞} values were also compared to the literature values for other ionic liquids. It was found that the longer chain alkyl group attached to the cation or anion gave lower S_{12}^{∞} values. Both ILs have S_{12}^{∞} values greater than one and in theory can be used as an entrainer for the hexane/ benzene separation. The capacities at infinite dilutions, k_1^{∞}, were also calculated from the inverse of the avarage γ_{13}^{∞} values for each IL at each temperature.

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List of symbols

γ_{13}^{∞}	Activity coefficients at infinite dilution
P_o	Column outlet pressure (equal to the atmospheric pressure)
$P_o J_2^3$	Mean column pressure
n_3	Number of moles of solvent in the stationary phase
T_{col}	Column temperature
T_f	Flow meter temperature
P_o	Saturated vapour pressure of the solute at temperature T
B_{11}	Second virial coefficient of pure solute
V_1^*	Molar volume of the solute
V_1^{∞}	Saturated liquid molar volume of the solute at infinite dilution in the solvent
B_{12}	Mixed second virial coefficient of the solute and the carrier gas
V_N	Net retention volume of the solute
P_{ow}	Saturation pressure of water
U_o	Flow rate at the outlet
t_r	Retention time of solute
t_G	Retention time of air
$\Delta H_1^{E\infty}$	Partial molar excess enthalpy at infinite dilutions

S_{12}^{∞}	Selectivity at infinite dilution
k	Capacity
V_R	Retention volume of the solute
V_3	Solvent volume
K	Equilibrium partition coefficient
R	Gas constant
V_G	Gas hold-up volume
P_c	Critical pressure
T_c	Critical temperature
V_c	Critical volume
$\bar{x}$	Mean of a set of data
σ or S	Standard deviation

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CHAPTER 1

1. INTRODUCTION

The word “separation,” refers to obtaining a product in pure form by the removal of unwanted reactants/ chemicals. Separation processes are essential and major activity in refineries, in material processing, pharmaceutical and chemical industries. On average, in all industries separation technology takes up to 60-80 % of the total production cost (Holbrey *et al.* 2002; Wasserscheid *et al*. 2003; Eckert and Sherman, 1996). It is important to use the most cost effective separation technology to minimize waste, improve energy efficiency, and increase the efficiency of raw material use, ie. separation technologies have the potential to minimize waste and maximize productivity by separating valuable materials that can still be re-used or sold as by-products from waste streams. Common separation methods are: distillation, crystallization, adsorption, membrane processes, absorption and stripping, and liquid-liquid extraction (Wasserscheid *et al.* 2003).

Some of the separation processes are avoided because of common problems such as azeotrope formation. The distillation process offers some advantages, 90 % of all separations involve distillation (Gmehling and Brehm, 1996). In the petrochemical industry one of the main separation problems is that of the separation of aliphatic and aromatic compounds. In distillation processes the activity coefficient at infinite dilution is used to determine the entrainer to be used for the separation. Other separation processes such as liquid-liquid extraction can be advantageous, when separation problems such as unfavorable separation factors ($0.95 < S_{12}^{\infty} < 1.05$) or azeotropic points occur (Letcher, 2004). The extraction process does not depend on a difference of vapour pressure between the compounds to be separated but on relative magnitudes of the activity coefficients at infinite dilution of the compounds to be separated (Letcher, 2004). As a result, extraction processes are mostly used in separating different aromatic compounds (C_6-C_{12}) from different aliphatic compounds (C_6-C_{12}). Extractive distillation, extraction and absorption processes require a highly selective solvent (entrainers) (Holbrey *et al.* 2002; Wasserscheid *et al*. 2003).

The Fischer Tropsch synthesis is a catalyzed chemical reaction in which synthesis gas, (mixture of carbon monoxide and hydrogen) is converted to water , and converted into liquid hydrocarbons of various forms (Van Nierop *et al.* 2000).

$(2n+2)H_2 + nCO \rightarrow C_nH_{(2n+2)} + nH_2O$

Sasol is one of the petroleum industries using this kind of synthesis, to produce a synthetic petroleum substitute, typically from coal, natural gas or biomass, for a use as synthetic lubrication oil or as synthetic fuel for motor vehicles and some air craft engines. The Fischer Tropsch process is operated in the temperature range of 150-300 ^{o}C. Higher temperatures lead to faster reactions and higher conversion rates, but also tend to favour methane production. The design of a biomass gasifier integrated with a Fischer–Tropsch synthesis reactor is aimed at achieving a high yield of liquid hydrocarbons (Prins *et al*. 2004). The hydrocarbons that are produced have a large range of carbon number consisting of alkanes, alkenes, aromatic compounds, ketones and these compounds need to be separated.

In this work the separation of binary mixtures was investigated for the ILs: methyltrioctylammonium bis(trifluoromethylsulfonyl)imide and methyltrioctylammonium thiosalicylate. The activity coefficients at infinite dilution (γ_{13}^{∞}) were calculated for alkanes, alkenes, cycloalkanes, alkynes, ketones, alcohols and aromatic compounds from gas liquid chromatography (glc) measurements at three temperatures (303.15 and 313.15 and 323.15) K.

CHAPTER 2

2.1 Ionic liquids and Separation

Excellent reviews by Welton, (1999); and Wasserheid and Keim, (2000), detailed the use of ionic liquids in synthetic and catalytic applications. One of the main successes of ionic liquids as reaction solvents has been in transition metal catalyzed reactions. Ionic liquids are able to dissolve organometalic compounds and therefore provide a medium for transition metal catalyst. Different products (C_1-C_{15} hydrocarbons) are also produced in Fischer Tropsch synthesis (Van Nierop *et al.* 2000), by changing the conventional catalysts to ionic liquid based catalyst.

Sasol's syngas conversion plants in South Africa utilize both the high and the low temperature Fischer–Tropsch processes (Espinoza *et al.* 1999 and Steynberg *et al.* 1999). The high temperature process is mainly used for the production of gasoline and chemicals like alpha olefins. The low-temperature Sasol Slurry Phase Fischer Tropsch technology, which was developed by Sasol Technology (PTY) LTD, produces linear-chained hydrocarbon waxes and paraffins. Apart from hard wax, candle wax and speciality Fischer Tropsch waxes, high-quality diesel is also produced in this process (Van Dyk *et al.* 2006). In order to avoid an over sizing of the column (e. g. distillation column) which would lead to an increase of the investment and operating costs, reliable information about the separation factor at infinite dilution is required.

2.1.1 Typical separation processes

2.1.1.1 Extractive Distillation

Large scale industrial distillation applications include both batch and continuous fractional, vacuum, azeotropic, extractive, and steam distillation. The most widely used industrial applications of continuous, steady-state fractional distillation are in petroleum refineries, petrochemical and chemical plants, and natural gas processing plants (Letcher, 2004).

Extractive distillation is a distillation process for the separation of azeotropic systems or systems with separation factors S_{12}^{∞} close to unity. Figure 1.1 is an illustration of a typical extractive distillation process, which is normally used for the separation of aliphatic and aromatic compounds. In this separation process, the high boiling entrainers are introduced near the top of the extractive distillation column, to alter the volatilities in such a way that the separation factor S_{12}^{∞} attains a value very different from unity (Letcher, 2004; Wasserscheid *et al*. 2003).

The presence of entrainers in the column during the separation process causes the aliphatic compounds to become more volatile. The "lightest" products (those with the lowest boiling point) exit from the top of the column and the "heaviest" products (those with the highest boiling point or both the aromatic hydrocarbons and the entrainer remain at the bottom of the column) exit from the bottom of the column and are often called the “bottoms”, making it easier for the aliphatic hydrocarbons to be separated. In the second distillation column, a high boiling entrainer can easily be separated from the aromatic hydrocarbon and be recycled to the first column. Better purity of the product, is influenced by the number of theoretical stages realized and the selectivity of the entrainer used (Letcher, 2004; Wasserscheid *et al*. 2003).

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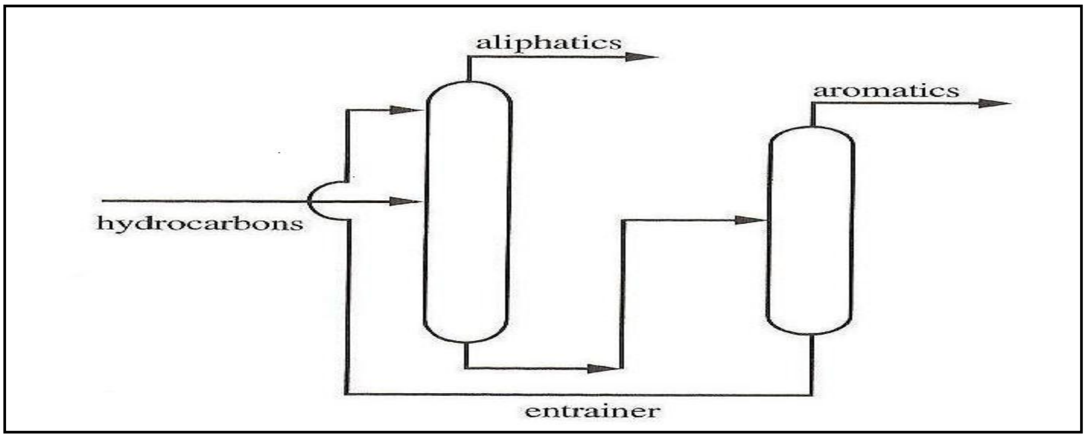

Figure 1.1 Schematic diagram of an extractive distillation process (Letcher, 2004)

2.1.1.2 Liquid-Liquid Extraction

In liquid-liquid extraction, selective solvents are also required, which are partially miscible with the liquid stream to be separated. A typical multistage counter-current liquid-liquid extraction process for the separation of aliphatic and aromatic hydrocarbons is shown in Figure 1.2, below. In this process, with the help of a selective solvent (extractant) the aliphatic compounds are separated from the aromatic compounds in the feed stream. Distillation is used for the removal of the selective solvent from the extract and raffinate stream leaving the extraction column (Letcher, 2004; Wasserscheid *et al*. 2003).

. This separation process is used in industry for the following separation processes:

- Separation of systems with similar boiling points (eg, separation of aromatic compounds from aliphatic hydrocarbons);
- Separation of azeotropic mixtures (extraction of acetic or formic acid from aqueous media);

- Separation of temperature sensitive compounds;
- Separation of mixtures with high boiling points;
- Extraction of organic compounds from salt solutions.

The selectivity, which strongly influences the number of separation stages, together with the capacity of the solvent, strongly influences the investment cost of a separation process. Entrainers with high selectivity and capacity are required, but unfortunately, in most cases, high selectivity values are linked to low capacity values. The low capacity of water for example, is the reason that in spite of its high selectivity, it is not used for the separation of aliphatic and aromatic compounds (Letcher, 2004; Wasserscheid *et al*. 2003).

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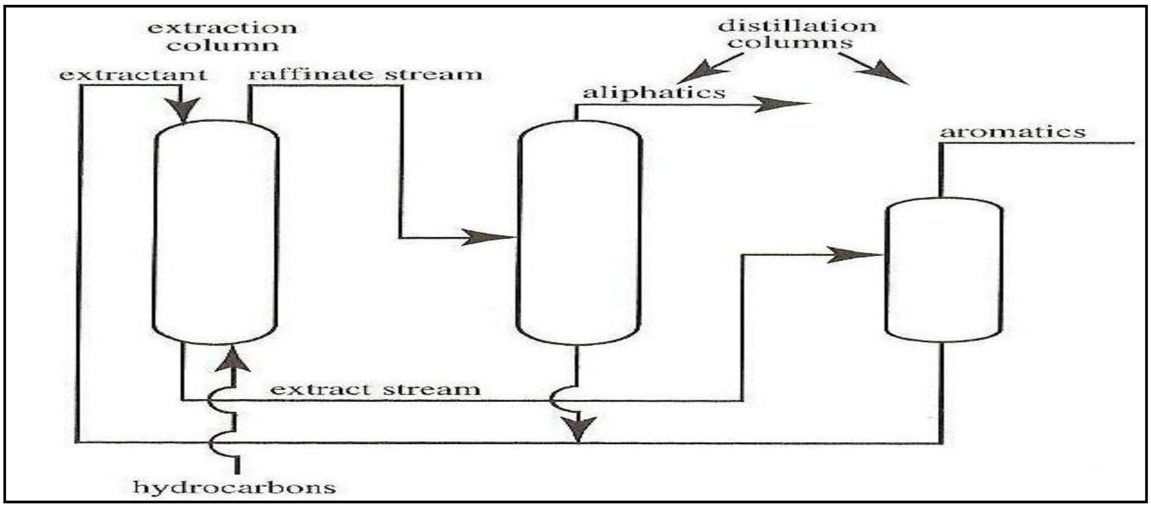

Figure 1.2 Schematic diagram of a typical liquid-liquid extraction process (Letcher, 2004)

2.1.2 Choice of solvent for separations

The choice of the solvent system is a critical step in the method development of a separation. The correct choice of the solvent mixture will ensure the successful separation of the compounds in the mixture. Therefore, several articles have been published on different ways to efficiently obtain the most suitable solvent system for a specific separation (Domanska *et al*. 2007; Gruber *et al.* 1998; Gruber *et al.* 1997). Factors affecting solvent selection include flammability, toxicity, cost, reactivity, and stability. Understanding the potential hazards (e.g., flammability, toxicity, and stability) during storage is critical because it requires more caution in its use and handling (Letcher, 2004).

2.1.3 Suitable properties for selective solvents

Organic compounds are typically used as selective solvents. All selective solvents for the separation process are required to have the following common properties:

1. High capacity
2. High selectivity
3. Negligible corrosivity
4. Simple purification
5. Non toxic
6. Low viscosity
7. Low melting points
8. Chemical stability
9. Availability and low cost of the solvent

10. A sufficiently large density differences between the two liquid phases
11. Large miscibility gap with the feed and the raffinate stream
12. The extractant is almost insoluble in the raffinate phase
13. The compound to be removed should have a reasonable solubility
14. Large boiling points differences between the solvent and solute to (minimize impurities in the distillate of extractive distillation column.

Selective solvents (ionic liquids) for extractive distillation should have a boiling point that is at least 40 ^{0}C higher than the solute or compound to be separated. The boiling point difference determines the reflux ratio in ILs. ILs seem to satisfy some of the criteria above and was investigated in this way. ILs has different chemical and physical properties in terms of it melting points, density, viscosity, surface tension, thermal stability and miscibility and vapour pressure, which makes it easy to characterize and identify it limitations in application (Zhang *et al*. 2006). The relationship between the structures of an ionic liquid and its melting point is of great value, if predictive methods are to be developed. Usually, ionic liquids have high melting points whereas the organic salts have far lower melting points. This effect is due to low symmetry, weak intermolecular interaction and a good distribution of charge in the cation of ILs (Welton, 1999 and Fitzwater *et al.* 2005).

The melting points of the ILs decrease significantly as the number of carbon atoms in the side chain increase (from methyl to butyl). The more unsymmetrical it is, the more difficult it become for the ions to pack together. This effect continues up to a chain length of 10 carbon atoms. Longer chain length begins to interact with one another and increase the melting point. The longer chain on the aromatic ring allows for greater distribution of charge on the cation (Wasserscheid and Keim, 2000).

The extremely low vapor pressure of most ILs is the main reason ILs are useful in green chemistry. In chemical processes, they are easily recyclable and produce minimum pollution by vaporization of ions of the IL (Fitzwater *et al.* 2005; Rogers and Seddon 2002; Rogers and Seddon 2003b; Rogers and Seddon 2005). IL vapor pressure is most often non-measurable at room temperature. This property has been reported by Wasserscheid and Keim (2000); Welton (1999) and Seddon (1997)

For an ionic liquid to exist in the vapour phase, it would have to exist in its principal ions and not change form. A large amount of energy would be needed for these large ions to exist at high temperatures, and be thermally stable. The thermal stability of an ionic liquid is limited by the strength of its hetero-atom carbon and hetero-atom hydrogen bonds. It is easier to break hetero-atom bonds rather than vaporize the ions, this leads to an upper limit of a liquid range of an ionic liquid (Wasserscheid and Keim 2000). Ionic liquids comprising of alkylated amines or phosphanes do not have high thermal stability (Wasserscheid and Keim 2000). Ionic liquids comprising of imidazolium cation have high thermal stability (Huddleston *et al*. 2001). Over 30 ionic liquids were investigated for thermal stability using differential scanning calorimetry and thermo-gravimetric analysis. For most of the ionic liquids the thermal decomposition temperature was greater than 400 ^{0}C. It was also discovered that the thermal decomposition is endothermic with inorganic anions and exothermic with organic anions and the halide anions reduces the thermal stability of an ionic liquid (Ngo *et al*. 2000).

The density of ionic liquids is dependent on both the anion and the cation. The effect of cation can be seen by comparing some of the chlorinated melts. Density decreases with an increase in carbon chain length on the cation (Fannin *et al*. 1984). The effect of the anion on the density is more pronounced. The halide salts have significantly lower densities than the more complex anions. The viscosity of ionic liquid is mainly determined by their tendency to form hydrogen bonds by Van der Waals interaction (Bonhote *et al.* 1996). When the resultant hydrogen bonding is weak the lower will be the viscosity.

Ionic liquids are highly soluble, non coordinating medium capable of mixing with a variety of organic and inorganic solutes. The general rule of ‘like dissolves like’ applies to ionic liquids as well. Not all ionic liquids are polar or non polar, most of them are somewhere in-between and there are various ways to determine the polarity scale (David *et al.* 2003).

Ionic liquids are also used as extracting agents, entrainers for distillation or membranes separation. Since ionic liquids may exhibit a very high selectivity, their application as entrainers offers an opportunity to improve selected separation processes (Krumen and Gmehling, 2004). The widespread potential application of ionic liquids in the field of transition metal and enzymatic catalysis are: solvent extraction, organic synthesis, thermal energy storage, electrochemical devices and biochemical engineering.

Application of ionic liquids is due to their distinctive properties and has been well documented by many researchers (Letcher and Reddy, 2005a; David *et al.* 2003; Letcher *et al*. 2008; Domanska and Marciniak, 2008; Letcher *et al*. 2005; Berthed et al. 2008; Letcher and Reddy, 2005b; Kato and Gmehling, 2004). Ionic liquids can be used as an acid, base, ligand and also as a precursor salt in preparation of carbenes. Due to their non-volatility, a major pathway for environmental release and contamination has been eliminated. Ionic liquids have been considered as having a low impact on the environment and human health, and have been recognized as a solvent for “green chemistry” (Alonso *et al*, 2007). Ionic liquids are used in a number of industrial applications, example, The Biphasic Acid Scavenging Utilizing Ionic Liquid (BASIL) Process, Cellulose processing, Dimerization, Nuclear industry, Linde’s ionic liquid piston, air products, and in paint additives (Endres and El Abedin, 2006).

The selection of the most suitable solvent is one of the most difficult problems in the extraction processes, since the decision has the greatest influence on the economy of the process. The concept of polarity is used for characterizing suitable parameters. The greater the polarity difference between two liquids, the greater will be the probability that they have a miscibility gap.

Selectivities at infinite dilutions are normally used for the selection of selective solvents (Gmehling and Mollamann, 1998) which is obtained from the ratio of the activity coefficients at infinite dilution. For liquid liquid equilibria selectivities are calculated from the relative ratio of each component to be separated in the raffinate and extractant phase from their mole fractions. The procedure for selecting entrainers for extractive distillation processes is given by Gmehling and Mollamann 1998 and Kolbe *et al*. 1979. The capacity is calculated from the inverse of the activity coefficients at infinite dilution.

In the petrochemical industry for example, separation of olefins and paraffins is a specific problem in the field of hydrocarbons processing. Since the boiling points of olefins and paraffins lies within narrow temperature ranges, it is difficult and expensive to separate them by conventional distillation. Lei *et al*. (2006) used 1-hexene and n-hexane to represent olefins and paraffins , respectively. Ionic liquids were used as the entrainers for this system. The entrainers do not need to be vaporised in extractive distillation process. Four possible entrainers were used for extractive distillation, solid salts, liquid solvents, the mixture of liquid solvents and solid salts, and ionic liquids (Blanco *et al*. 2000; Chen *et al*. 2003 and Hilan *et al*. 2002). Organic high boiling liquids and dissolved salts are suitable entrainers, but extractive distillation with a single liquid entrainer is more widely used in petroleum industry. However, ionic liquids as entrainers in extractive distillation comprise both advantages of liquid solvents and solid salts (Lei *et al*. 2006; Krummen and Gmehling, 2001; Holbrey 2004; and Seiler *et al.* 2004). A futher reason that ILs was chosen for this study.

2.1.4 Ionic liquids in clean separations

ILs has potential applications in the following separation processes: metal extractions, refining and recovery of materials in the nuclear industry, and in the preparation of selective liquid membranes and sensors. Development of new ionic liquids and the study of their physical properties are of great importance in order to obtain enough information to predict solvent characteristics and properties (Carmichael *et al.* 1999, Huddleston *et al.* 2001, and Visser *et al*. 2001). In particular, structural properties of ILs can also be used to develop selective dissolution and extraction/ partitioning schemes. It is important that high quality, reproducible physical data, and thermodynamic properties for ionic liquids are generated to produce a data bank of IL structure and thermodynamic properties which can be used for correlation of structure and properties (Visser *et al*. 2000).

ILs can be used for a number of separation processes to replace volatile organic compounds (Holbrey and Rogers, 2002). Ionic liquids show some interesting properties that allow them to be the preferred substitute of volatile organic solvents with improving performance and less damage to the environment. The separation of aromatic hydrocarbons from aliphatic hydrocarbon mixtures is challenging since these hydrocarbons have close boiling points and several systems of aromatic and aliphatic compounds form azeotropes. Ionic liquid suitability as a selective solvent for the separation of aromatic and aliphatic hydrocarbons have high solubility of aromatic hydrocarbons in the ionic liquid and low solubility of aliphatic hydrocarbons in the ionic liquid. Normally, the solubility of alkanes in ionic liquids is very low, and the mutual solubility of benzene in ionic liquids increase when the alkyl chain of the cation increase (Domanska *et al*. 2007).

ILs research is increasing exponentially because of their use as a replacement solvent for volatile organic compounds (VOCs) (Kozlova et al. 2009). ILs have an ionic character; with thermophysical properties that are different from those of molecular liquids. Ionic liquids are defined as salts with a melting point below the normal boiling point of water (100 ^{0}C), if the salt’s melting point is below room temperature (≤25 °C), the IL is known as a room-temperature ionic liquid (RTIL) (Berthod *et al*. 2008 and Welton 1999). IL is a liquid at room temperature containing only organic cations and inorganic or organic anions. Ionic liquids have been described using different synonyms such as room temperature molten salts, liquid organic salt, low temperature molten salt, ionic fluid and ambient temperature molten salts (Zhang *et al* 2006). Ionic liquids exhibit different bonding interactions, from H-bond to the Van der Waals interaction, and are characterized by the presence of Coloumb interactions among the constituent ions. ILs have extremely low vapour pressure which make them suitable for green chemistry applications (Rogers *et al*. 2002).

The most common ILs in use are those with alkylammonium, alkylphosphonium, N-alkylpyridinium, N,N-dialkylimidazolium, and alkylpyrrolidinium cations, and a variety of organic anions: triflate, dicyanamide, acetate, trifluoroacetate,trifluoromethylsulphonate or inorganic anions, bromide, chloride, nitrite, perchlorate, chloroaluminate, tetrafluoroborate, or hexafluorophosphates (Zhang *et al* 2006).

Organic compounds with a boiling point of ≤100 ^{0}C and a vapor pressure > 1mmHg at 25^{0}C are generally known as volatile organic compounds (VOCs). These compounds are among the most common contaminants in the atmosphere. VOCs are used extensively in chemical industries and occur in numerous products including fuels, solvents, paints, adhesives, deodorants, refrigerants, in combustion exhausts (Spyros *et al*. 2001). VOCs in the atmosphere are of great concern because once such compounds are in a vapour state they are much more mobile and therefore more likely to be released to the environment, they pose a public health risk, and they contribute to a general increase in reactive hydrocarbons in the atmosphere, which can lead to the formation of photochemical oxidants (Spyros *et al*. 2001). When VOCs are oxidized in the presence of oxides nitrogen, they lead to the formation of photochemical smog, harmful to humans, animals and vegetation. Even at very low concentrations, many of these materials are toxic, carcinogenic or mutagens and thus represent a direct health risk to workers (Spyros *et al*. 2001; and Maria *et al*. 2000).The use of these compounds in industrial processes (separation processes) has become a subject of much public concern and had led to active research into their replacement as solvents for inorganic synthesis and electrochemical applications (Verevkin *et al* 2005; and Rogers *et al*. 2002).

VOCs in the atmosphere have increased global warming resulting in the signing of the Kyoto Protocol (1997) by most of the industrialized countries i.e France, Germany, United Kingdom and Japan. The United Nations Framework Convention Climate Change (UNFCCC) and its Kyoto Protocol provide the only international framework for combating climate change. Under the Kyoto Protocol, industrialized countries are required to reduce the emission of carbon dioxide (which is the major contributor to global warming), methane, nitrous oxide, hydrofluorocarbons, perfluorocarbons and sulphur hexafluoride, by an average of 5.2 % during the first commitment period from 2008 to 2012. In order to use ILs for chemical processes for the replacement of VOCs, chemical engineers need IL thermophysical or thermodynamic data to design separation processes.

2.1.5 Thermodynamic properties used in separations

A number of papers have been published on the thermodynamic properties of ionic liquids. Thermodynamic activity coefficients at infinite dilution are a measure of the deviation from ideal behavior in liquid mixtures. Activity coefficient at infinite dilution can be directly used for the selection of solvents for extractive distillation, liquid extraction, solvent aided crystallization, and even chemical reactions (Letcher *et al.* 2005). Activity coefficients at infinite dilution give a direct measure of interactions between unlike molecules in the absence of solute-solute interactions.

Activity coefficients at infinite dilution, γ_{13}^{∞}, are perhaps the most important and fundamental property in the thermodynamic study of liquid mixtures. They are used to obtain other thermodynamic solution properties such as selectivity and excess molar enthalpy at infinite dilution. In order to find a suitable ionic liquid for a specific task, one needs to know the physical, chemical and thermodynamic properties of that particular solvent. Infinite dilution activity coefficients mostly represent the most accurate characterization of system behavior in the dilute regions (Raal and Muhlbauer, 1998). Activity coefficient at infinite dilution γ_{13}^{∞} , are important for the characterization of the behavior of liquid mixtures, fitting G^E (excess Gibbs free energy) model parameters, screening solvents for extraction and extractive distillation, calculation of limiting separation factors necessary for the reliable design of distillation processes, calculation of Henry constants and partition coefficients and the development of predictive methods (Krummen and Gmehling, 2004).

Activity coefficients at infinite dilution, γ_{13}^{∞}, are useful properties to chemical engineers, solution chemists and theoreticians (Sandler, 1996). Various solution theories have been developed due to large number of systems at the infinitely-dilute condition. The γ_{13}^{∞} data is importance in separation process plants that involve liquid-vapour pressure. The γ_{13}^{∞} data are also of great importance in synthesis design and optimization of separation processes, since the largest separation effort is required to remove the last traces of impurities. Furthermore, activity coefficients at infinite dilution values are required for the selection of suitable solvents (entrainers) for separation processes such as extractive distillation and extraction or to check for separation problems (azeotropic points, miscibility gaps) (Gmehling *et al*. 2000, Krummen and Gmehling 2004). To the solution chemists γ_{13}^{∞} data is important in understanding the mixing process. There are many methods for the determination of γ_{13}^{∞} namely: gas-liquid chromatography, non-steady-state gas liquid chromatography, differential ebulliometry, static method and the dilutor method (Eckert and Sherman, 1996). The most common methods are: static method, differential ebulliometry, vapor liquid equilibrium, dilutor method, gas-liquid or dynamic chromatography.

The use of the static cell method and differential ebulliometry are two direct methods of measuring activity coefficients at infinite dilution. In the first of these methods one measures the change in equilibrium phase *d*P due to a very small addition of a second component resulting in a differential composition change *dx.*

The dew point method for measuring activity coefficients at infinite dilution complements the ebulliometric method (Trampe and Eckert, 1993, Suleiman and Eckert, 1994). A solvent or solute of known composition is vaporized and thermostated, then allowed to impinge on a thermostatically-controlled optical dew point sensor.

In this study gas liquid chromatography has been used to determine activity coefficients at infinite dilution, since it is an established method, in different ILs for different solutes, (Letcher and Moollan, 1995, Letcher and Whitehead 1996, Letcher and Whitehead 2000, Letcher and Naicker 2000, Letcher *et al.* 2001, Letcher and Deenadayalu 2001, Heintz *et al*. 2002, Letcher *et al*. 2003, Kato and Gmehling 2004, Letcher *et al*. 2005, Letcher and Reddy 2005, Foco *et al*. 2006, Deenadayalu *et al*. 2006, Heintz *et al*. 2007, Domanska and Marminiak 2008, *Letcher et al.* 2008, Revelli *et al*. 2009, Kozlova *et al*. 2009, Letcher *et al*. 2009).

The partial molar enthalpy is also one of the most important thermodynamic properties due to its relation to other functions of interest. For instance, knowing the excess partial molar enthalpy function at infinite dilution $\Delta H_1^{\mathrm{E}\infty}$, it is possible to calculate the temperature dependence of activity coefficient at infinite dilution γ_{13}^{∞} from the Gibbs-Helmholtz equation (Checoni and Francesconi, 2006). In this way γ_{13}^{∞} is used to determine $\Delta H_1^{\mathrm{E}\infty}$.

Thermodynamic properties of mixtures containing ionic liquids have been investigated from experimental (Inoue *et al.* 2007) and theoretical (Jodry and Mikami, 2004) data to better understand and explain molecular interaction between molecules, as well as to test and develop new models and theories that were able to describe the thermodynamic behavior of ionic liquids. Using these models and theories, the appropriate ionic liquids could be synthesised for organic reactions and other requirements (Li *et al.* 2007).

In this work two ionic liquids with same ammonium cation (methyltrioctylammonium) but different anions (bis(trifluoromethylsulfonyl)imide and thiosalicylate) were studied. These ionic liquids were investigated in order to outline the correlation of each structure with its activity coefficients at infinite dilution data and also to determine the effect of anions on the γ_{13}^{∞} values.

2.2 Literature Review

Heintz *et al.* (2001) investigated the thermodynamic properties of mixtures containing ionic liquids. Activity coefficients at infinite dilution of alkanes, alkenes, and alkylbenzene in 4-methyl-n-butylpyridinium tetrafluoroborate ($[C_{10}H_6BF_4N]$) was determined using gas liquid chromatography. A series of 19 hydrocarbons had been studied at different temperatures ranging from 313.1 K to 363.1) K.

Heintz *et al*. (2002) determined the thermodynamic properties of mixtures containing ionic liquids. Activity coefficients at infinite dilution of polar solutes (linear and branched C_1 to C_6 alcohols, acetone, acetonitrile, ethylacetate, alkylethers and chloromethanes) in 4-methyl n-butyl-pyridinium tetrafluoroborate were determined using gas-liquid chromatography at temperature T = (313.1 to 363.1) K.

Heintz *et al*. (2002) investigated the thermodynamic properties of mixtures containing ionic liquids. Activity coefficients at infinite dilution of hydrocarbons (alkanes alkenes and alkylbenzene) and polar solutes (linear and branched C_1 - C_6 alcohols, acetone, acetonitrile, alkyl ethers, althyl acetate, and chloromethane) in 1-methyl-3-ethyl-imidazolium bis(trifluoromethyl-sulfonyl)amide and 1,2-dimethyl-3-ethyl-imidazolium bis(trifluoromethyl-sulfonyl)amide using gas liquid chromatography was measured. The measurements were done at temperature T = (313 to 363) K. From the temperature dependence of the limiting activity coefficients, partial molar excess enthalpies at infinite dilution of the solutes in the ionic liquid had been derived.

David *et al*. (2003) reported activity coefficients at infinite dilution of hydrocarbons solutes at infinite dilution in the ionic liquid, 1-methyl-3-octyl-imidazolium chloride from gas liquid chromatography. 1-Methyl-3-octyl-imidazolium chloride was used for measurement of γ_{13}^{∞} of alkanes, alkenes, alkynes, cycloalkanes, aromatic hydrocarbons at T = (298.15, 308.15 and 318.15) K. Selectivities for benzene/hydrocarbons are presented and the results indicate that 1-methyl-3-octyl-imidazolium chloride is a reasonable solvent for the separation of alkanes or alkenes from benzene.

Letcher *et al*. (2003) determined the activity coefficients at infinite dilution of organic solutes in 1-hexyl-3-methylimidazolium hexafluorophosphate using gas-liquid chromatography. Activity coefficients at infinite dilution for both polar and nonpolar solutes (alkanes, alkenes, alkynes, cycloalkanes, benzene and methanol) were determined at T = (298.15, 313.15 and 323.15) K. Both partial molar excess enthalpies at infinite dilutions and some selectivities were calculated from the γ_{13}^{∞} values obtained.

Letcher *et al*. (2003) continued with the determination of activity coefficients at infinite dilution of solutes in ionic liquid 1-hexyl-3-methylimidazolium tetrafluoroborate using gas liquid chromatography at temperatures T = (298.15 and 323.15) K. The activity coefficients at infinite dilution, γ_{13}^{∞} data for polar and nonpolar solutes (alkanes, alkenes, alkynes, cycloalkanes, benzene, and methanol) were further used for the calculation of selectivities. Selectivity values at infinite dilution indicated that the ionic liquid $[HMIM^{+}][BF_4^{-}]$, should be a good solvent for the separation of benzene and alkanes. Partial molar excess enthalpy values at infinite dilution were also determined at T = 298.15 K and discussed in terms of intermolecular interaction.

Kato and Gmehling (2004) measured activity coefficient at infinite dilution of various solutes (alkanes, alkenes, alkynes, cycloalkanes, cycloalkenes, aromatics, alcohols, ketones, esters, ethers and water) in five ionic liquids, 1-methyl-3-methyl-imidazolium methylsulfate, 1-methyl-3-methyl-imidazolium methoxysulfate, 1-methyl-3-methyl-imidazolium dimethylphosphate, n-ethylpyradinium bis(trifluoromethylsulfonyl)imide and pyridiniumethoxyethylsulfate, in the temperature range from T = (303.15 to 373.15) K. Additionally, densities of the investigated ionic liquids were measured in the temperature range from T = (293.15 to 353.15) K. Using all the γ_{13}^{∞} data, selectivities and capacities at infinite dilution were determined for different separation problems not only for ionic liquids under study, but also n-methyl-2-pyrrolidone (NMP) and ethylene glycol.

Letcher *et al*. (2005) measured activity coefficients at infinite dilution for organic solutes (alkanes, alkenes, alkynes, cycloalkanes, benzene, carbon tetrachloride and methanol) in ionic liquid 1-hexyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)-imide using gas liquid chromatography at temperatures T = (298.15, 313.15 and 333.15) K. The interaction at the gas-liquid interface between the solutes and the solvent was examined by varying solvent liquid loading on the column.

Heintz *et al.* (2005) determined the thermodynamic properties of mixtures containing ionic liquids. Activity coefficients at infinite dilution of hydrocarbons (alkanes, alkenes, and alkyl benzene), alcohols (linear and branched C_1-C_7), esters, and aldehydes in 1-methyl-3-butyl-imidazolium bis(trifluoromethyl-sulfonyl)amide ($C_{10}H_{15}S_2O_4F_6N_3$) using gas liquid chromatography was measured. Measurements were carried at different temperatures between T = (302 and 385) K.

Heintz and Verevkin (2005) extended the measurements of the thermodynamic properties of mixtures containing ionic liquids. Activity coefficients at infinite dilution of hydrocarbons, alcohols, esters, and aldehydes were determined in 1-methyl-3-octyl-imidazolium tetrafluoroborate using gas liquid chromatography. Activity coefficients at infinite dilution measurements of alkanes, alkenes, alkylbenzene, linear and branched C_1-C_6 alcohols, esters, aldehydes and common solvents (acetone, acetonitrile and 1,4-dioxane) were carried out at different temperatures T = (302 and 396) K.

Deenadayalu *et al.* (2005) determined activity coefficients at infinite dilution of polar and nonpolar solutes in ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imidate using gas chromatography at temperature T = (303.15 or 318.15) K. The results were used to predict solvent potential for the hexane benzene separation using the calculated selectivity values. The activity coefficient at infinite dilution, γ_{13}^{∞} values were compared with those with a similar system from the literature in an attempt to understand the effect that the nature of the cation had on the solute-solvent interactions.

Letcher *et al.* (2005) further determined activity coefficients at infinite dilution of solutes in ionic liquid 1-butyl-3-methylimidazolium octylsulfate [BMIM][$OcOSO_3$] using gas liquid chromatography at a temperature of T = (298.15, 313.15, or 328.15) K. This work is the part of research on activity coefficient at infinite dilution in ionic liquids. The selectivities were calculated at T = 298.15 K, and the results indicated that this ionic liquid should not be considered to be a solvent for the separation of alkanes and aromatic compounds.

Letcher *et al*. (2005) measured activity coefficients at infinite dilution for organic solutes (alkanes, alkenes, alkynes, cycloalkanes, aromatic hydrocarbons, carbon tetrachloride and methanol) in the ionic liquid 1-butyl-3-methyl-imidazolium 2-(2-methoxyethoxy) ethyl sulphate using gas liquid chromatography at T = (298.15, 303.15 and 308.15) K. The results were used to predict the solvent potential for the hexane/benzene separation from calculated selectivity values and the partial molar excess enthalpies at infinite dilution values were calculated from the experimental γ_{13}^{∞} values obtained over the temperature range.

Deenadayalu *et al.* (2006) measured activity coefficients at infinite dilution using polar and non polar solutes in the ionic liquid 1-methyl-3-octyl-imidazolium diethyleneglycol-monomethylethersulfate at T = (288.15, 298.15 and 313.15) K. Activity coefficient at infinite dilution for 14 solutes were measured using gas liquid chromatography. A mass percentage packing greater than 20% was used, and two columns were prepared with different percent loadings.

Inoue *et al.* (2006) measured activity coefficients at infinite dilution of n-alkanes in 4-methyl-n-butylpyridinium tetrafluoroborate using gas liquid chromatography. The ionic liquid used was 4-methyl-n-butylpyridinium tetrafluoroborate for the analysis of octane, nonane and decane at T = (297 to 344) K. The partial molar excess enthalpies at infinite dilution values and the heat of solution for the solutes in the ionic liquid were calculated from the infinite dilution activity coefficients.

Mutelet and Jaubert (2006) accurately determined the activity coefficients at infinite dilution of solutes in ionic liquids using inverse gas chromatography. Two different ionic liquids were used; 1-butyl-3-methylimidazolium octyl sulphate and 1-ethyl-3-methylimidazolium tosylate for the measurement of activity coefficients at infinite dilution for 29 organic compounds at T = (321.15 to 343.15) K.

Sumartschenkowa *et al.* (2006) experimentally studied the thermodynamic properties of mixtures containing ionic liquids 1-ethyl-3-methylimidazolium ethyl sulfate [EMIM][EtSO$_4$] using gas liquid chromatography and transpiration method. Activity coefficients at infinite dilution γ_{13}^{∞} of 46 solutes such as alkanes, alkenes, alkyl benzenes, alcohols (linear and branched C$_1$-C$_6$), esters, aldehydes, cyclohexanone oxime, and e-caprolactam were measured at different temperatures between T = (302.9 and 322.9) K. From the temperature dependence of the limiting activity coefficients, partial molar excess enthalpies at infinite dilution of the solutes in the ionic liquid had been derived. Activity coefficients at infinite dilution of water in the ionic liquid [EMIM][EtSO$_4$] were derived by extrapolation from the VLE data to the infinite dilution of water.

Zhou and Wang, (2006) measured activity coefficients at infinite dilution γ_{13}^{∞} of alkanes, alkenes, alkyl benzenes in 1-butyl-3-methylimidazolium tetrafluoroborate using gas liquid chromatography. Both Foco *et al.* 2006 and Zhou and Wang (2006) determined γ_{13}^{∞} for hexane at temperature T = 323.15 K, and the results had a significant difference when compared (76.5 by Foco *et al.*2006 and 54.2 by Zhou and Wang) The activity coefficients at infinite dilution γ_{13}^{∞} of all 17 hydrocarbons were measured using the ionic liquid as the column stationary phase at temperatures between T = (303.15 and 343.15) K. From the temperature dependence of the limiting activity coefficients, partial molar excess enthalpies at infinite dilution of the solutes in the ionic liquid had been derived.

Heintz *et al.* (2006) investigated the thermodynamic properties of mixtures containing ionic liquids. Activity coefficients at infinite dilution of hydrocarbons, alcohols, esters and aldehydes in 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide were determined using gas-liquid chromatography. The measurements were conducted at temperature T = (301 and 396) K. From the temperature dependence of the limiting activity coefficients, partial molar excess enthalpies at infinite dilution of the solutes in the ionic liquid had been derived.

Heintz *et al.* (2006) studied the thermodynamic properties of mixtures containing ionic liquids. Activity coefficients at infinite dilution of hydrocarbons (alkanes, alkenes and alkylbenzene), alcohols (linear and branched C_1-C_6), esters and aldehydes in trimethyl-butylammonium bis(trifluoromethylsulfonyl)amide using gas liquid chromatography were determined. The measurements were conducted at different temperatures between T = (302 and 393) K. Vapour liquid equilibria (VLE) of binary mixtures containing methanol, ethanol and propan-1-ol in trimethyl-butylammonium bis(trifluoromethylsulfonyl)amide were studied by using a static method. Activity coefficients of solutes in the ionic liquid and their osmotic coefficients in trimethyl-butylammonium bis(trifluoromethylsulfonyl)amide were determined from the VLE data and described formally by using the NRTL equation. γ_{13}^{∞} and $\Delta H_1^{E\infty}$ for methanol ethanol and propan-1-ol in trimethyl-butylammonium bis(trifluoromethylsulfonyl)amide were derived from both gas chromatography and the static method.

Foco *et al.* (2006) accurately measured activity coefficients at infinite dilution in 1-alkyl-3-methylimidazolium tetrafluoroborate ionic liquids, where the alkyl groups were: 1-ethyl-, 1-butyl-, 1-hexyl-, and 1-octyl. The data was measured using gas-liquid chromatography at T =

(303, 323 and 343) K, for all polar and nonpolar solutes (alkanes, alcohols, ketones, ethers, aromatic hydrocarbons, halogenated compounds) in 1-alkyl-3-methylimidazolium tetrafluoroborate ionic liquids.

Heintz *et al*. (2007) measured activity coefficients at infinite dilution and enthalpies of solution of methanol, 1-butanol and 1-hexanol in 1-hexyl-3-methyl-imidazolium bis(trifluoromethyl-sulfonyl)imide. The measurements were carried out at temperature T = (298 and 396) K using gas chromatography. Additionally, enthalpies of solution of the same alcohols in the 1-hexyl-3-methyl-imidazolium bis(trifluoromethyl-sulfonyl)imide] were measured at T = 298.15 K in the same range of low concentration using titration calorimetry. The results at infinite dilution were compared with those indirectly obtained from the activity coefficients at infinite dilution.

Letcher and Reddy (2007) determined the activity coefficients at infinite dilution of organic solutes in the ionic liquid, tributylmethylphosphonium methylsulphate by gas-liquid chromatography. Activity coefficients at infinite dilution of organic solutes (alkanes, alkenes, alkynes, cycloalkanes and benzene) were determined in the phosphonium based ionic liquid at T = (308.15, 318.15 and 328.15) K. The γ_{13}^{∞} values obtained for tributylmethylphosphonium methylsulphate in this investigation were compared to those obtained for other ionic liquids available in literature. This comparison allowed for assessment of the potential for the use of different ionic liquids as solvents in industrial solvent-enhanced separation processes such as extractive distillation.

Wang *et al*. (2007) determined the activity coefficients at infinite dilution of alkanes, alkenes, alkyl benzenes in 1-propyl-2,3-dimethylimidazolium tetrafluoroborate using gas liquid chromatography. The activity coefficients at infinite dilution γ_{13}^{∞} of all 17 organic solutes were measured using the ionic liquid as the column stationary phase at temperatures between T = (303.15 and 363.15) K.

Mutelet *et al.* (2007) investigated the thermodynamic properties of mixtures containing ionic liquids: activity coefficients at infinite dilution of organic compounds in 1-propyl boronic acid-3-alkylimidazolium bromide and 1-propenyl-3-alkylimidazolium bromide using inverse gas chromatography were measured. Activity coefficients at infinite dilution of organic compounds in eight room temperature ionic liquids of the family of 1-propyl boronic acid-3-lkylimidazolium bromide and 1-propenyl-3-lkylimidazolium bromide (with alkyl = methyl, octyl, decyl, or dodecyl) were determined at T = 323.15K. With the use of all available γ_{13}^{∞} data, the selectivities at infinite dilution were determined.

Zhou *et al.* (2007) studied the activity coefficients at infinite dilution of polar solutes in 1-butyl-3-methylimidazolium tetrafluoroborate using gas liquid chromatography. Foco *et al.* (2006) also determined activity coefficients at infinite dilution on 1-butyl-3-methylimidazolium tetrafluoroborate, they both did acetone at T = 323 K, both γ_{13}^{∞} values were found to be similar (1.2). Activity coefficients at infinite dilution of 17 solutes included linear and branched C_1-C_5 alcohols, chlorinated methane, acetone, acetonitrile, ethyl acetate, 1,4 dioxane and cyclohexanone in the hydrophilic ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate, over a temperature range of T = (301.15 to 343.15) K were determined. From the temperature dependence of the limiting activity coefficients; partial molar excess enthalpies at infinite dilution of the solutes in the ionic liquid had been derived.

Mutelet and Jaubert (2007) measured activity coefficients at infinite dilution in 1-hexadecyl-3-methylimidazolium tertrafluoroborate ionic liquid. In their work, activity coefficients at infinite dilution data for 31 organic compounds (alkanes, alkenes, alkynes, cycloalkanes,cycloalkenes, aromatic hydrocarbons and alcohols) were measured using inverse gas chromatography at temperature T = (323.15, 333.15 and 343.15) K. The Flory-Huggins interaction parameter and solubility parameter were calculated from experimental retention data.

Domanska and Marciniak (2008) accurately measured activity coefficients at infinite dilution of aromatic and aliphatic hydrocarbons, alcohols and water in the new ionic liquid 1-ethyl-3-methylimidazolium thiocyanate using gas liquid chromatography. The γ_{13}^{∞} for 29 solutes (alkanes, alkenes, alkynes, cycloalkanes, aromatic hydrocarbons, alcohols and water) were determined at temperatures from 298.15 K to 368.15 K. The selectivities for the hexane/benzene and cyclohexane/benzene separation problems were calculated from the γ_{13}^{∞} and compared to other ionic liquids taken from literature, ie. NMP and sulfolane.

Ge and Wang (2008) determined the activity coefficients at infinite dilution of polar solutes in 1-butyl-3-methylimidazolium trifluoromethanesulfonate using gas liquid chromatography. Activity coefficients at infinite dilution γ_{13}^{∞} of 17 polar solutes (linear and branched C_1-C_5 alcohols, chlorinated methane, acetone, acetonitrile, ethyl acetate, 1,4 dioxane and cyclohexanone) were measured at different temperatures between T = (303.15 and 363.15) K. The partial molar excess enthalpies at infinite dilution of the solute in the ionic liquid were also derived from the temperature dependence of the γ_{13}^{∞} values.

Ge *et al.* (2008) determined the activity coefficients at infinite dilution of organic solutes in 1-ethyl-3-methylimidazolium tetrafluoroborate using gas liquid chromatography. The same ionic liquid was used by Foco *et al.* (2006) to determined the activity coefficients at infinite dilution for benzene at temperature T = 303 K and the γ_{13}^{∞} results were different (

γ_{13}^{∞} = 2.4 by Foco *et al*. and γ_{13}^{∞} = 2.1 by Ge *et al*) The activity coefficients at infinite dilution γ_{13}^{∞} of 25 organic solutes (with mass fraction purity of more than 99%), alkanes, alkenes, alkyl benzenes, acetonitrile, acetone, 1,4dioxane, tetrahydrofuran, ethyl acetate, and chloromethane were measured using the ionic liquid as the column stationary phase at temperatures between T = (303.15 and 363.15) K.

Letcher *et al.* (2008) measured the activity coefficients at infinite dilution for organic solutes in the ionic liquid trihexyltetradecylphosphonium bis(2,4,4-trimethylpentyl) phosphinate using gas liquid chromatography at T = (303.15, 308.15, 313.15 and 318.15) K. Both the partial molar excess enthalpies and selectivity at infinite dilution were calculated from the γ_{13}^{∞} values obtained over the temperature under study.

Letcher *et al.* (2008) further determined activity coefficients at infinite dilution of solutes in ionic liquid, trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl)amide [BMIM][OcOSO$_3$] using gas liquid chromatography at a temperature T = (303.15 ,308.15, 313.15, or 318.15) K. The selectivities were calculated at T = 308.15 K, and the results indicated that this ionic liquid should not be considered to be a solvent for the separation alkanes and aromatic compounds.

Kozlova *et al.* (2008) determined the activity coefficients at infinite dilution of hydrocarbons, alkylbenzene, and alcohols in the paramagnetic ionic liquid 1-butyl-3-methyl-imidazolium tetrachloridoferrate(III) using gas-liquid chromatography. The measurements of the γ_{13}^{∞} values were carried out at different temperatures, T = (305 to 403) K for all solutes (alkanes, alkenes, alkylbenzene and C_1-C_6 alcohols). The γ_{13}^{∞} values of ionic liquids containing 1-butyl-3-methyl-imidazolium cation and different non magnetic anions were compared at T = 298 K with results for 1-butyl-3-methyl-imidazolium tetrachloridoferrate (III). No significant effects caused by the paramagnetic anion observed.

Revelli *et al.* (2009) determined the activity coefficients at infinite dilution of organic compounds in trihexyl(tetradecyl)phoshonium bis(trifluoromethylsulphonyl)imide using inverse gas chromatography for 39 Polar and nonpolar compounds (alkanes, alkenes, alkynes, cycloalkanes, aromatic hydrocarbons and alcohols) at T = (302.45, 322.35 and 342.45) K. The modified linear free energy relationship (LFER) model proposed by Sprunger and co-workers was also used to characterize the nature of the solute interactions with this ionic liquid.

A summary of the literature review containing the pertinent results are given in Table 2.1.

Table 2.1 Summary of literature review for activity coefficients at infinite dilution of ILs and solutes.

Author/s	**Technique/s**	**IL/Solvent**	**Solutes**	**Data Measured**	**T (K) Range**	**Observation/s**
Heintz *et al.* (2001)	G.L.C	4-methyl-n-butylpyridinium tetrafluoroborate	alkanes, alkenes, and alkylbenzene	γ_{13}^{∞} and $\Delta H_1^{E\infty}$	313.1 K to 363.1 K	The γ_{13}^{∞} values increase with an increase in carbon number and decrease with temperature increase, and that applies for all other solutes except for aromatic hydrocarbons. Benzene has the lowest γ_{13}^{∞} values.
Heintz *et al*. (2002)	G.L.C	4-methyl n-butyl-pyridinium tetrafluoroborate	alcohols, acetone, acetonitrile, ethylacetate, alkylethers and chloromethanes	γ_{13}^{∞} and $\Delta H_1^{E\infty}$ om	313.1 K to 363.1 K	The Alcohols and other solvent's γ_{13}^{∞} values decrease with an increase in temperature and increase with the number of carbon atoms while for chloromethanes and acetone the γ_{13}^{∞} values increase with temperature. Branching in the alkyl chain of alkanols decreases slightly the positive values of $\Delta H_1^{E\infty}$, when compared with the linear isomers.
Heintz *et al*. (2002)	G.L.C	1-methyl-3-ethyl-imidazolium bis(trifluoromethyl-sulfonyl)amide and 1,2-dimethyl-3-ethyl-imidazolium bis(trifluoromethyl-sulfonyl)amide	Alkanes, alkenes, alkylbenzene, alcohols, acetone, acetonitrile, alkyl ethers, althyl acetate, and chloromethane	γ_{13}^{∞} and $\Delta H_1^{E\infty}$	313 K to 363 K	The γ_{13}^{∞} values of acetronitrile and acetone are distinctively lower in comparison to those of the ester and other solutes. The introduction of double bond on linear alkanes and branching of the alkyl chain in alkanols slightly decrease the positive $\Delta H_1^{E\infty}$ values.

David *et al*. (2003)	G.L.C	1-methyl-3-octyl-imidazolium chloride	alkanes, alkenes, alkynes, cycloalkanes, and aromatic hydrocarbons	γ_{13}^{∞}, $\Delta H_1^{E\infty}$, and S_{12}^{∞}	298.15 K to 318.15 K	Hexyne and toluene has the lowest γ_{13}^{∞} values. The $\Delta H_1^{E\infty}$ of all solutes are positive, indicating that dissociation effects outweigh association effects in mixtures involving very low hydrocarbon concentration. Alkanes are more selective as compare to other solvents, this is due to higher S_{12}^{∞} values.
Letcher *et al*. (2003)	G.L.C	1-hexyl-3-methylimidazolium hexafluorophosphate	alkanes, alkenes, alkynes, cycloalkanes, benzene and methanol	γ_{13}^{∞}, $\Delta H_1^{E\infty}$ and S_{12}^{∞}	298.15 K to 323.15 K	The γ_{13}^{∞} values increase with an increase in carbon number and decrease with temperature increase, and that applies for all other solutes except for benzene and alkynes. Benzene has a weak induced dipole-dipole interaction between its molecules; this is due to its negative $\Delta H_1^{E\infty}$ value. This ionic liquid would make a good solvent in separation; this is due to high S_{12}^{∞} values obtained.
Letcher *et al*. (2003)	G.L.C	1-hexyl-3-methylimidazolium tetrafluoroborate	alkanes, alkenes, alkynes, cycloalkanes, benzene, and methanol	γ_{13}^{∞}, $\Delta H_1^{E\infty}$ and S_{12}^{∞}	298.15 and 323.15	The γ_{13}^{∞} data for polar and nonpolar solutes were further used for the calculation of selectivities. Selectivity values indicated that the ionic liquid would be a good solvent for the separation of benzene and alkanes. Partial molar excess enthalpy values at infinite dilution were also determined at *T* = 298.15 K and discussed in terms of intermolecular interaction.

Kato and Gmehling (2004)	Dilutor technique	1-methyl-3-methyl-imidazolium methylsulfate, 1-methyl-3-methyl-imidazolium methoxyethylsulfate, 1-methyl-3-methyl-imidazolium dimethylphosphate, n-ethylpyradinium bis(trifluoromethylsulfonyl)imide and pyridiniumethoxyethylsulfate,	alkanes, alkenes, alkynes, cycloalkanes, cycloalkenes, aromatics, alcohols, ketones, esters, ethers and water	γ_{13}^{∞}, S_{12}^{∞} and K	303.15 K to 373.15 K	Heptane had a highest γ_{13}^{∞} value of 377. The γ_{13}^{∞} data from all five ionic liquids were further used for the calculation of selectivities and capacity. Out of five ionic liquids studied, 1-methyl-3-methyl-imidazolium methoxyehylsulfate can be considered the best entrainer, this is due to it higher selectivity value values.
Letcher *et al*. (2005)	G.L.C	1-hexyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)-imid	alkanes, alkenes, alkynes, cycloalkanes, benzene, carbon tetrachloride and methanol	γ_{13}^{∞}, $\Delta H_1^{E\infty}$ and S_{12}^{∞}	298.15 K to 333.15 K	All solutes has γ_{13}^{∞} values greater than 1 except for benzene (0.674) at 298.15 K. The $\Delta H_1^{E\infty}$ value of benzene is negative (-900 J/mol) and also the lowest. High selectivity was obtain at 298.15 K , and hence the ionic liquid under study is a good entrainer in separation processes.

Heintz *et al.* (2005)	G.L.C	1-methyl-3-butyl-imidazolium bis(trifluoromethyl-sulfonyl)amide	alkanes, alkenes, alkyl benzene, alcohols, esters, and aldehydes	γ_{13}^{∞}, and $\Delta H_{1}^{E\infty}$	302 K and 385 K	The γ_{13}^{∞} values of all solutes increase with an increase in carbon number as expected. Three cyclic hydrocarbons with same number of carbons (cyclohexane, cyclohexene and 1,3-cycloexadiene) were studied. The introduction of double bond on cyclic hydrocarbons decreases the γ_{13}^{∞} value. The introduction of double bond lowered the positive values of $\Delta H_{1}^{E\infty}$.
Heintz and Verevkin (2005)	G.L.C	1-methyl-3-octyl-imidazolium tetrafluoroborate	hydrocarbons, alcohols, esters, and aldehydes	γ_{13}^{∞}, and $\Delta H_{1}^{E\infty}$	302 K and 396 K	The γ_{13}^{∞} values increase with an increase in carbon number as expected. Acetonitrile have lowest γ_{13}^{∞} value of 0.62. Cyclization of the skeleton (e.g. cyclohexane) reduces the γ_{13}^{∞} value in comparison with linear alkane (e.g., hexane). The introduction of double bond did not lower the positive values of $\Delta H_{1}^{E\infty}$.
Deenadayalu *et al.* (2005)	G.L.C	1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imidate	alkanes, alkenes, alkynes, cycloalkanes, benzene and methanol	γ_{13}^{∞}, $\Delta H_{1}^{E\infty}$ and S_{12}^{∞}	303.15 K and 318.15 K	The γ_{13}^{∞} values of the cyclic alkanes is smaller when compared with linear alkane and become even smaller for alkenes and alkynes. For the separation of hexane/benzene, the selectivity is high enough (37.5) for the ionic liquid under study to be considered as a selective solvent. Benzene has the lowest and negative $\Delta H_{1}^{E\infty}$ value.
Letcher *et al.* (2005)	G.L.C	1-butyl-3-methylimidazolium octyl sulfate	alkanes, alkenes, alkynes, cycloalkanes, benzene, toluene, carbon tetrachloride and methanol	γ_{13}^{∞}, $\Delta H_{1}^{E\infty}$ and S_{12}^{∞}	298.15 K to 328.15 K	The γ_{13}^{∞} values increase with an increase in temperature and in carbon number except for methanol. The $\Delta H_{1}^{E\infty}$ values are all negative except for methanol. The S_{12}^{∞} values are not satisfactory but can be used as a solvent in separation processes.

Letcher *et al*. (2005)	G.L.C	1-butyl-3-methyl-imidazolium 2-(2-methoxyethoxy) ethyl sulphate	alkanes, alkenes, alkynes, cycloalkanes, aromatic hydrocarbons, carbon tetrachloride and methanol	γ_{13}^{∞}, $\Delta H_1^{E\infty}$ and S_{12}^{∞}	298.15 K at 308.15 K	For alkenes in this work, the γ_{13}^{∞} values changes little with temperature. In general, $\Delta H_1^{E\infty}$ values increase with increase in carbon number, opposite effect is observed with ionic liquid under study. For the hexane/benzene separation, the ionic liquid under study gave a very high selectivity value of 39.7, therefore considered the best entrainer.
Deenadayalu *et al.* (2006)	G.L.C	1-methyl-3-octyl-imidazolium diethyleneglycol-monomethylethersulfate	alkanes, alkenes, alkynes, cycloalkanes, benzene, and methanol	γ_{13}^{∞}, $\Delta H_1^{E\infty}$ and S_{12}^{∞}	288.15 K to 313.15 K	The γ_{13}^{∞} values increase with an increase in carbon number and decrease with temperature increase, and that applies for all 13 solutes, benzene showed the opposite effect. All solutes has a positive values except for benzene (-700 J/mol). S_{12}^{∞} value for the hexane/benzene separation is within the accepted range, therefore the IL under study is a good entrainer.
Inoue *et al.* (2006)	G.L.C	4-methyl-n-butylpyridinium tetrafluoroborate	n-alkanes	γ_{13}^{∞} and $\Delta H_1^{E\infty}$	297 K to 344 K	The γ_{13}^{∞} values were determined by the flow rate of the carrier gas. The partial molar excess enthalpies at infinite dilution values and the heat of solution for the solutes in the ionic liquid were calculated from the infinite dilution activity coefficients.
Mutelet and Jaubert (2006)	G.L.C	1-butyl-3-methylimidazolium octyl sulphate and 1-ethyl-3-methylimidazolium tosylate	alkanes, alkynes, alcohol, ether, ketonescyclohexane, benzene, chlorinated hydrocarbon, acetronitrile and 1-nitropropane	γ_{13}^{∞}	321.15 K to 343.15 K	Benzene (1.45) and methanol (0.36) has the lowest γ_{13}^{∞} value when compared to other 27 solutes.

Sumartschenkowa *et al*. (2006)	G.L.C	1-ethyl-3-methylimidazolium ethyl sulfate	alkanes, alkenes, alkyl benzenes, alcohols (linear and branched C_1-C_6), esters, aldehydes, cyclohexanone oxime, and e-caprolactam	γ_{13}^{∞} and $\Delta H_1^{E\infty}$	302.9 K and 322.9 K	Trichloromethane and 1—hexene gave a low γ_{13}^{∞} value. The $\Delta H_1^{E\infty}$ values are positive and decrease slightly with increasing chain length of linear alkanes and alkenes. The $\Delta H_1^{E\infty}$ value of linear alcohol, aldehydes and esters are positive and does not change with increasing chain length. the
Zhou and Wang, (2006)	G.L.C	1-butyl-3-methylimidazolium tetrafluoroborate	alkanes, alkenes, alkyl benzenes	γ_{13}^{∞}, $\Delta H_1^{E\infty}$ and S_{12}^{∞}	303.15 K and 343.15 K	The γ_{13}^{∞} values of linear alkanes increase with an increase in chain length. The skeletal branching of alkanes (e.g., cyclohexane and methylcyclohexane) reduces the values in comparison with the corresponding linear alkanes. The S_{12}^{∞} values for three isomeric xylene at 303.15 K were, 1.25, 1.06 and 1.18, respectively. These results indicate that the ionic liquid understudy is not an ideal solvent for separation processes. The $\Delta H_1^{E\infty}$ value decreased as the double bonds were introduced on linear alkanes.

Heintz *et al*. (2006)	G.L.C	1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide	hydrocarbons, alcohols, esters and aldehydes	γ_{13}^{∞} and $\Delta H_1^{E\infty}$	301 K and 396 K	From the temperature dependence of the limiting activity coefficients, partial molar excess enthalpies at infinite dilution of the solutes in the ionic liquid had been derived.
Heintz *et al*. (2006)	G.L.C and static method.	trimethyl-butylammonium bis(trifluoromethylsulfonyl)amide	alkanes, alkenes, alkylbenzene, alcohols, esters and aldehydes	γ_{13}^{∞} and $\Delta H_1^{E\infty}$	302 K to 393 K	The γ_{13}^{∞} and $\Delta H_1^{E\infty}$ for methanol ethanol and propan-1-ol in trimethyl-butylammonium bis(trifluoromethylsulfonyl)amide were derived from both gas chromatography and the static method. Polar solvents has a very low γ_{13}^{∞} values and hence the $\Delta H_1^{E\infty}$ values.
Heintz *et al*. (2007)	G.L.C	1-hexyl-3-methyl-imidazolium bis(trifluoromethyl-sulfonyl)imide	solution of methanol, 1-butanol and 1-hexanol	γ_{13}^{∞}	298 K and 396 K	Enthalpies of solution of the same alcohols in the 1-hexyl-3-methyl-imidazolium bis(trifluoromethyl-sulfonyl)imide] were measured at T = 298.15 K in the same range of low concentration using titration calorimetry. The results at infinite dilution were compared with those indirectly obtained from the activity coefficients at infinite dilution.

Letcher and Reddy (2007)	G.L.C	tributylmethylphosphonium methylsulphate	alkanes, alkenes, alkynes, cycloalkanes and benzene	γ_{13}^{∞}, $\Delta H_1^{E\infty}$ and S_{12}^{∞}	308.15 K to 328.15 K	The γ_{13}^{∞} values o alcohols at the lo affinity of the sol $\Delta H_1^{E\infty}$ value o linear alkanes. Th solvents in terms o separation of vari cycloalkane/arom
Wang *et al.* (2007)	G.L.C	1-propyl-2,3-dimethylimidazolium tetrafluoroborate	alkanes, alkenes, alkyl benzenes	γ_{13}^{∞}, $\Delta H_1^{E\infty}$ and S_{12}^{∞}	303.15 K to 363.15 K	The γ_{13}^{∞} values o length. The skelet alkanes decrease results shows that an ideal solvent f
Mutelet *et al.* (2007)	inverse gas chromatography	1-propyl boronic acid-3-alkylimidazolium bromide and 1-propenyl-3-alkylimidazolium bromide		γ_{13}^{∞} and S_{12}^{∞}	323.15 K	The γ_{13}^{∞} values o different columns retained by partiti solute adsorption decreasing length
Zhou *et al.* (2007)	G.L.C	1-butyl-3-methylimidazolium tetrafluoroborate	alcohols, chlorinated methane, acetone, acetonitrile, ethyl acetate, 1,4 dioxane and cyclohexanone	γ_{13}^{∞}, $\Delta H_1^{E\infty}$ and S_{12}^{∞}	301.15 K to 343.15 K	The $\Delta H_1^{E\infty}$ v the linear alkanol 1; therefore 1-but vital role in separ
Mutelet and Jaubert (2007)	G.L.C	1-hexadecyl-3-methylimidazolium tertrafluoroborate	alkanes, alkenes, alkynes, cycloalkanes,cycloalkenes, aromatic hydrocarbons and alcohols	γ_{13}^{∞} and S_{12}^{∞}	323.15 K to 343.15 K	The Flory-Huggin calculated from e
Domanska and Marciniak (2008)	G.L.C	1-ethyl-3-methylimidazolium thiocyanate	alkanes, alkenes, alkynes, cycloalkanes, aromatic hydrocarbons, alcohols and water	γ_{13}^{∞}, $\Delta H_1^{E\infty}$ and S_{12}^{∞}	298.15 K to 368.15 K	The γ_{13}^{∞} values o Alkanes has the h interaction betwe is extremely high 3-methylimidazol separation proces

Ge and Wang (2008)	G.L.C	1-butyl-3-methylimidazolium trifluoromethanesulfonate	alcohols, chlorinated methane, acetone, acetonitrile, ethyl acetate, 1,4 dioxane and cyclohexanone	γ_{13}^{∞}, $\Delta H_1^{E\infty}$ and S_{12}^{∞}	303.15 K to 363.15 K	The γ_{13}^{∞} value of alkanes slightly re 10, therefore, 1-b can be used as a excess enthalpies were also derived
Ge *et al.* (2008)	G.L.C	1-ethyl-3-methylimidazolium tetrafluoroborate	alkanes, alkenes, alkyl benzenes, acetonitrile, acetone, 1,4dioxane, tetrahydrofuran, ethyl acetate, and chloromethane	γ_{13}^{∞}, $\Delta H_1^{E\infty}$ and S_{12}^{∞}	303.15 K to 363.15 K	The γ_{13}^{∞} values o this trend is oppos For aromatics, the solutes studied. Th methylimidazoliu processes.
Letcher *et al.* (2008)	G.L.C	trihexyltetradecylphosphonium bis(2,4,4-trimethylpentyl) phosphinate	alkanes, alkenes, alkynes, cycloalkanes	γ_{13}^{∞}, $\Delta H_1^{E\infty}$ and S_{12}^{∞}	303.15 K to 318.15 K	The selectivity va entrainers such as result shows the i

Letcher *et al.* (2008)	G.L.C	trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl)amide	alkanes, alkenes, alkynes, cycloalkanes, and aromatic hydrocarbons	γ_{13}^{∞}, $\Delta H_1^{E\infty}$ and S_{12}^{∞}	303.15 K to 318.15 K	The calculated $\Delta H_1^{E\infty}$ values, independent of temperature are negative for all solutes studied except for alcohols. The small selectivity obtained here indicates that this IL is not the best solvent for use in solvent extraction processes.
Kozlova *et al.* (2008)	G.L.C	1-butyl-3-methyl-imidazolium tetrachloridoferrate(III)	alkanes, alkenes, alkylbenzene and C_1-C_6 alcohols	γ_{13}^{∞}, and $\Delta H_1^{E\infty}$	305 K to 403 K	Values of γ_{13}^{∞} for benzene and alkylbenzenes are distinctively lower in comparison with those of the alkanes and alkenes. The $\Delta H_1^{E\infty}$ values for alkanes, alkene, and alkanols are positive and hardly change with chain length increase.
Revelli *et al.* (2009)	G.L.C	trihexyl(tetradecyl)phoshonium bis(trifluoromethylsulphonyl)imide	alkanes, alkenes, alkynes, cycloalkanes, aromatic hydrocarbons and alcohols	γ_{13}^{∞}, and S_{12}^{∞}	302.45 K to 342.45 K	The γ_{13}^{∞} values are below unity apart from the alkanes and alcohols indicating strong affinity of the solutes for the ionic liquid. Selectivity values for the investigated IL are very low, indicating the limited potential of this phosphonium IL for separation.

CHAPTER 3

3. EXPERIMENTAL

3.1 Introduction

Dynamic chromatography is the oldest method for the direct measurement of activity coefficients at infinite dilution (James and Martin, 1952). In this method, the solvent (IL) was loaded into the column and a very small amount of sample (solute) was injected. The residence time is the measure of the gas liquid partition coefficient. Normally the gas phase is ideal or nearly ideal, so that the results give the Henry's Law constant of the solute in the solvent i.e γ^{∞} (James and Martin 1952). This process is an equilibration of a solute between two immiscible phases i.e. the gas phase and the liquid phase on the packing. The chromatographic technique may be used to measure the:

1. Activity coefficients at infinite dilution
2. Second virial coefficients of gas mixtures
3. Partition coefficients
4. Adsorption and partition isotherms
5. Complex formation constants

Other properties that can be measured with less accuracy from temperature variation studies or secondary measurements, includes surface area, heat of adsorption, excess enthalpy and excess entropies of solution. In this work the γ_{13}^{∞} have been calculated from gas liquid chromatography (g.l.c) technique. The two most common restrictions of this method are:

1. Solvent bleeding
2. Adsorption effect

Solvent bleeding can be overcome by either weighing the column before and after the experiment, or by inserting a pre-column containing the non volatile solvent. Adsorption effects can be eliminated by measuring the retention time using different columns with different solvent loading or with solvent mass loading of greater than 20%. The g.l.c method has a number of advantages, some of which are:

1. Very good separation
2. Analysis are rapid and easily made
3. Small amount of sample or chemicals are needed
4. Good detection system and hence the purity of the solute is not crucial
5. Quantitatively analyzed

Gas liquid chromatography is also a well established and accurate method that has been used to measure activity coefficients at infinite dilution (Welton, 1999; Earle, 2000). γ_{13}^{∞} values are used to understand the interaction of a volatile solute with a non volatile solvent. This method works best for systems in which the solvents are polar and has low volatility while the solute has a high volatility. It has been extended to a level where the solvents with medium volatility can be analyzed (Bayles *et al.* 1993 and Thomas *et al.* 1982). This method is considered to be the most accurate for the measurement of systems with low volatility solvent- high volatility solute combination. This method was developed by Everett and Cruickshank, 1965 and is very cheap to construct. Figure 3.1 below is the schematic diagram of the g.l.c equipment used in this work.

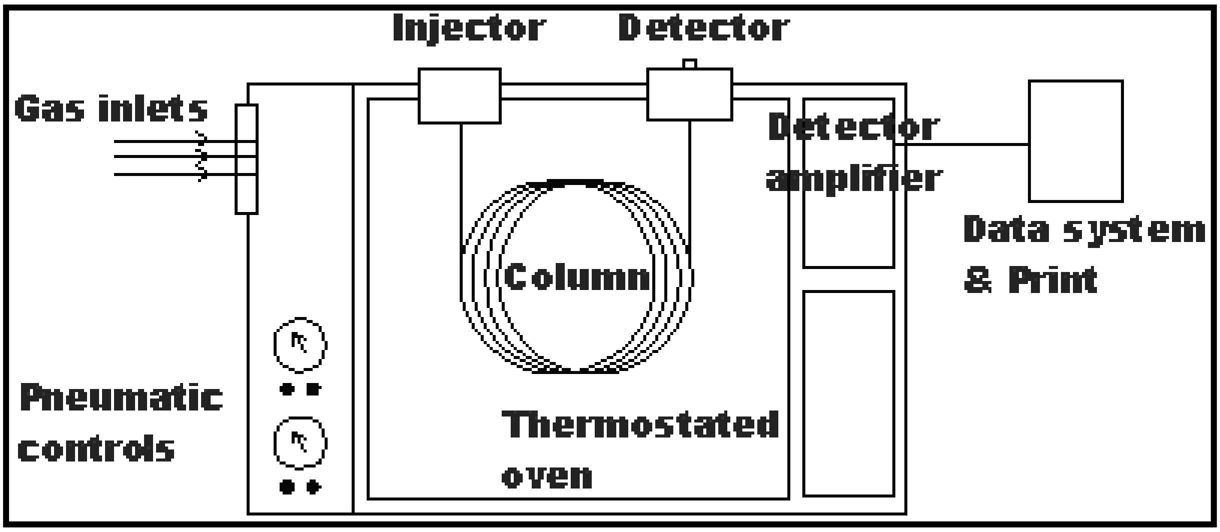

Figure 3.1 Schematic diagram of Shimadzu GC-2014 gas-liquid chromatography equipment

In g.l.c work the non volatile solvent is coated onto a solid support (celite), which is packed into the column. The inert gas flows through the small spaces between the packing particles thus bringing the solute into contact with the large surface area. Carrier gas (helium) is used as a transport medium. A very small amount of solute is injected into the column; this forms a solute zone which equilibrates between the gaseous and liquid phases. The solute zone is carried through the column by the carrier gas and is then recorded as a peak (retention time) by a thermal conductivity detector. The different interactions of different solutes with the gaseous and liquid phases results in peaks of different retention times.

3.2 Thermal conductivity detector (TCD)

In a thermal conductivity detector the power is converted to heat in the sample filament and the temperature increases until the heat lost is equal to the electrical power input. The thermal conductivity detector is a nondestructive, concentration sensing detector. A heated filament is cooled by the flow of a carrier gas, ●, see Figure 3.2 below.

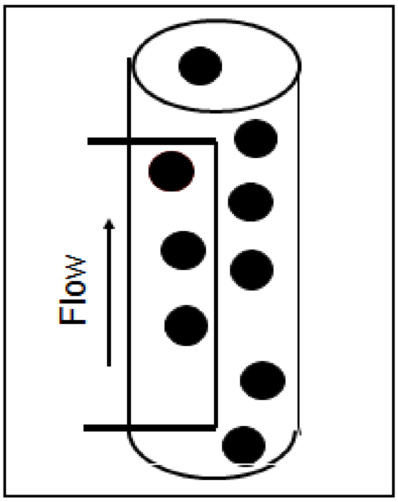

Figure 3.2 Schematic diagram of unheated filament

When the carrier gas is contaminated by the sample, ▲, the cooling effect of the sample changes. The difference in cooling is used to generate a detector signal, see Figure 3.3 below.

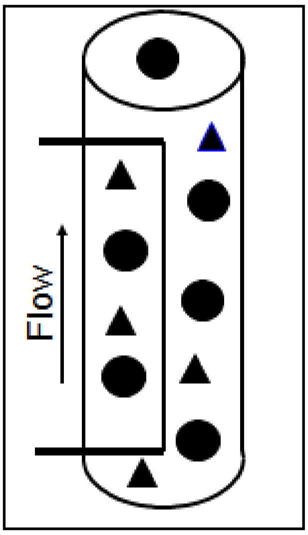

Figure 3.3 Schematic diagram of heated filament with carrier gas

When a separated compound elutes from the column, the thermal conductivity of the mixture of carrier gas and compound gas is lowered. The filament in the sample column becomes hotter than the control column. The imbalance between control and sample filament temperature is measured by a simple gadget and a signal is recorded.

Advantages of TCD

1. Responds to most compounds
2. Adequate sensitivity for many compounds
3. Good linear range of signal
4. Simple construction
5. Nondestructive detection
6. Signal quite stable if carrier gas flow rate, block temperature, and filament power are effectively controlled

3.3 Rotary evaporator

Rotary evaporation is most often and conveniently applied to separate "low boiling" solvents. However, careful application also allows removal of a solvent from a sample containing a liquid compound if there is minimal co-evaporation (azeotropic behavior), and a sufficient difference in boiling points at the chosen temperature and reduced pressure (Craig *et al.* 1950). The key advantages of a rotary evaporator are:

1. That the centrifugal force and the frictional force between the wall of the rotating flask and the liquid sample result in the formation of a thin film of warm solvent being spread over a large surface.

2. The forces created by the rotation suppress violent, unpredicted boiling ("bumping"). The combination of these characteristics and the conveniences built into modern rotary evaporators allow for quick, gentle evaporation of solvents from most samples, even in the

hands of relatively inexperienced users. Refer to the photograph of a rotary evaporator used in Figure 3.4 below.

Figure 3.4 Photograph of a Rotary Evaporator

In this work, the rotary evaporation equipment was used during the preparation of the stationary phase. Dichloromethane was added to the chromosorb and IL to ensure that the IL was coated on the solid support. Dichloromethane was evaporated from a mixture of the measured amount of silanized chromosorb WHP 80/100 mesh and ionic liquid.

3.4 Experimental method for measuring activity coefficient at infinite dilution using g.l.c.

3.4.1 Materials

The solutes were purchased from Aldrich and Fluka, with a purity that ranged from 98.5 – 99.8 %. The solutes were used without further purification in both column loadings for each IL. The solutes used were pentane, hexane, heptane, octane, nonane, cyclopentane, cyclohexane, cycloheptane, cyclooctane, 1-pentene, 1-hexene, 1-octene, pentyne, hexyne, octyne, methanol, ethanol, propanol, acetone, butanone, benzene, and toluene. Further purification was not necessary because the chromatographic column separated all the impurities, leaving the major solute free of impurities. Hence, impurities had a negligible effect on the retention times of the major peaks. The ILs: methyltrioctylammonium bis(trifluoromethylsulfonyl)imide and methyltrioctylammonium thiosalicylate were also supplied by Fluka with a purity that ranged from 95- 98 %. See Figure 3.5 and 3.6 for the chemical structures of the ILs.

3.4.2 Apparatus and Methodology

The mass percent water content in the ionic liquids was tested using a Karl-Fischer Coulometer [Metrohm 831] and was found to be less than 0.04 mass % .

The IL was coated on silanized chromosorb WHP 80/100 mesh (supplied by Supelco) with the help of a rotary evaporator and packed into a stainless steel column (3 mm i.d x 1.1 m length, 304 stainless steel). Before packing the columns, each column was washed with hot soapy water, rinsed with cold water, and flushed with acetone to reduce the drying period. The ionic liquid was carefully weighed, dissolved in dichloromethane and then quantitatively transferred to a pre-weighed amount of the support material (chromosorb) in a roundbottomed flask. The mixture was then gently shaken and evaporated, with moderate rotation of the rotary evaporator. Two different columns with different mass percent (25 % and 30%) of ionic liquid were prepared at DUT Physical Chemistry Laboratories to verify that no adsorption had occurred on the packing. Before the start of each experiment the column was conditioned by passing helium carrier gas through at a very high flow rate (about 42 ml/min) for about 2 hours (Domanska and Marciniak, 2008 ; and Letcher and Reddy, 2005). A graduated soap bubble flow meter was placed at the outlet of the detector, and it was used to determine the flow rate. The flow rate was set for a series of runs and allowed to stabilize for at least 15 min before making any solute retention time measurements. All measurements were undertaken at the UKZN Therno-group Laboratories.

Experiments were performed using a Shimadzu GC-2014 gas chromatograph apparatus, equipped with a thermal conductivity detector, an auto-sampler and auto-injector. Retention times and chromatograms related to each run were made available on a PC monitor by means of GC Solution Workstation software. The instrumental temperature accuracy is ± 0.1 K with temperature stability of ± 0.01 K. The retention data obtained from the chromatography experiments were then used for the calculation of γ_{13}^{∞} values of the solutes in the ILs. All measurements were carried out at three temperatures (303.15, 313.15, and 323.15) K. Air was used to measure the retention time of a gas (t_G). For precision purposes, t_G was measured before and after solute measurements. About 8 uL of air was injected and 0.1 uL to 0.3ul of solutes were injected separately in three replicates using an auto-injector. A test system was first studied using hexadecane as a stationary phase, with *n*-hexane as the solute, to ensure internal consistency. The experimental γ_{13}^{∞} values obtained were compared to the literature γ_{13}^{∞} value and was found to be within the experimental error. The maximum percentage error in γ_{13}^{∞} was < 5.6 %.

In this work γ_{13}^{∞} were calculated from gas liquid chromatography (g.l.c) measurements for different solutes at different temperatures (303.15, 313.15 and 323.15) K using methyltrioctylammonium bis(trifluoromethylsulfonyl)imide [MOA][TF_2N] and methyltrioctylammonium thiosalicylate [MOA][TS] as the stationary phases.

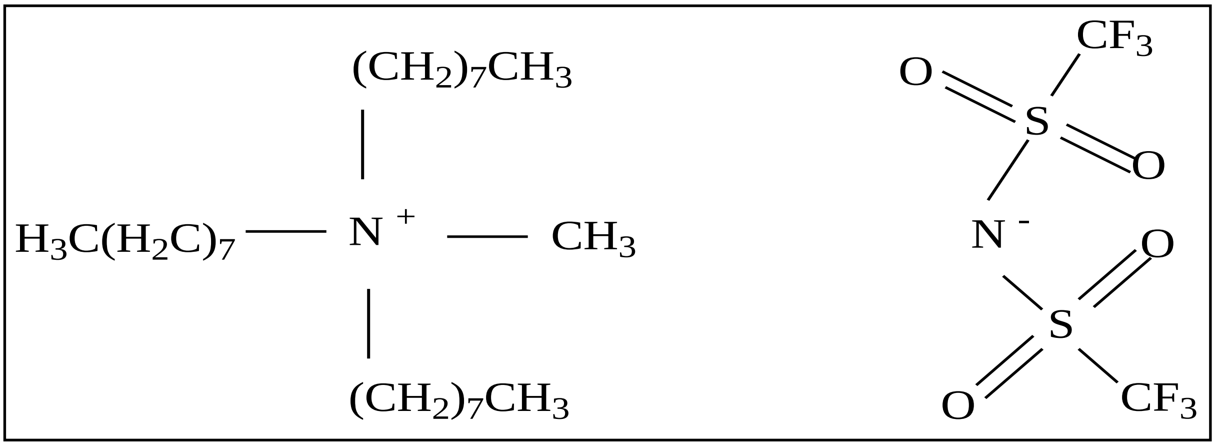

Figure 3.5 Structure of methyltrioctylammonium bis(trifluoromethylsulfonyl)imide [MOA][TF2N]

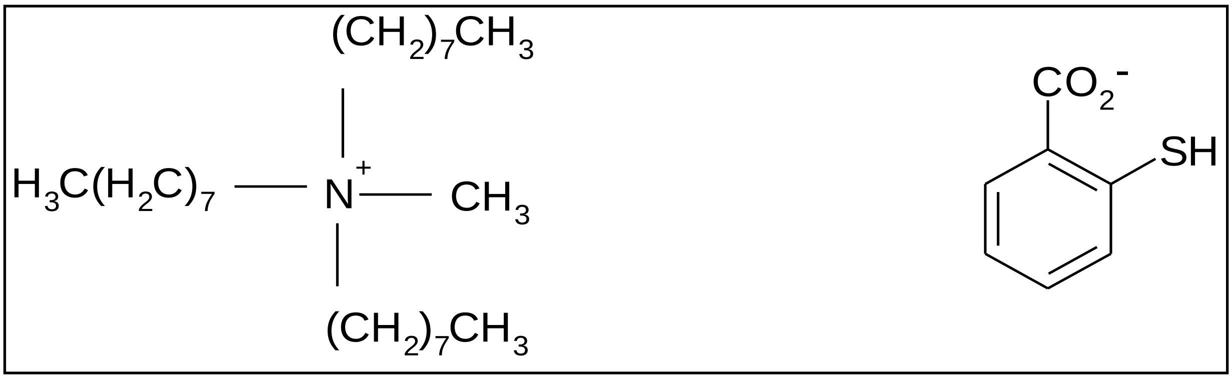

Figure 3.6 Structure of methyltrioctylammonium thiosalicylate [MOA][TS]

The partial molar excess enthalpies at infinite dilution value $\Delta H_1^{E\infty}$ were calculated at 303.15 K using the Gibbs equation from the γ_{13}^{∞} values obtained at different temperatures. The selectivity values were calculated from the γ_{13}^{∞} results to determine the ability of ILs to separate binary mixtures by extractive distillation.

CHAPTER 4

4. Theory

4.1 Theoretical Framework

In 1941 Martin and Synge published a paper on general chromatography, stating that it would be possible to use gas as a mobile phase and liquid as a stationary phase. They related the equilibrium partition coefficient, K, to retention properties using a plate theory. Their general equation, when considered in relation to gas-liquid chromatography (for zero pressure difference across the column) relates the retention volume of the solute, V_R, to the gas hold-up volume, V_G, and net retention volume of solute KV_3 according to:

$$V_R = V_G + KV_3 \tag{1}$$

In this work the solute will be referred to as component 1, the carrier gas as component 2 and the solvent as component 3. Everett and Cruickshank *et al.* 1965 developed an equation that was used to obtain activity coefficients at infinite dilution γ_{13}^{∞} of a volatile solute in an involatile solvent from gas liquid chromatography results (Everett 1965, Cruickshank 1969).

$$\text{In } \gamma_{13}^{\infty} = \ln\left(\frac{n_3 RT}{V_N P_1^*}\right) - \left(\frac{(B_{11} - V_1^*)P_1^*}{RT}\right) + \left(\frac{(B_{12} - V_1^{\infty})P_o J_2^3}{RT}\right) \tag{2}$$

where

V_N (*s*) is the net retention volume of the solute, P_o (*kPa*) column outlet pressure (equal to the atmospheric pressure), $P_o J_2^3$ (*kPa*) mean column pressure, n_3 (*mmol*) number of moles of solvent in the stationary phase, T (*K*) column temperature, P_1^* (*kPa*) saturated vapor pressure of the solute at temperature T, B_{11} (cm^3/mol) the second virial coefficient of pure solute, V_1^* (cm^3/mol) molar volume of the solute-carrier gas interaction, V_1^∞ (cm^3/mol) is the saturated liquid molar volume of the solute at infinite dilution in the solvent and B_{12} (cm^3/mol) mixed second virial coefficient of the solute and the carrier gas.

The factor J_2^3 appearing in equation 2 corrects for the influence of the pressure drop along the column (Letcher and Whitehead, 1996).

$$J_2^3 = \frac{2}{3}\left(\frac{(P_\mathrm{i}/P_\mathrm{o})^3 - 1}{(P_\mathrm{i}/P_\mathrm{o})^2 - 1}\right) \tag{3}$$

The corrected flow rate (U_o) of the carrier gas measured with a bubble flow meter at the column outlet, was expressed at column temperature and was corrected for vapour pressure of water according to the equation below:

$$U_\mathrm{o} = U.\left(1 - \frac{P_\mathrm{w}}{P_\mathrm{o}}\right).\frac{T}{T_\mathrm{f}} \tag{4}$$

where U, is the flow rate of the carrier gas, P_w, saturation pressure of water, P_o, column outlet pressure, T, temperature of column and T_f, temperature of flow meter

Values of V_N were calculated using equation 5 below:

$$V_N = J_2^3.Uo(t_R - t_G) \tag{5}$$

The values of , B_{11}, second virial coefficient of pure solute, B_{12} , mixed second virial coefficient of the solute and the carrier gas, P_1^*, saturated vapour pressure of the solute at temperature T and V_1^*, molar volume of the solute, were calculated using the McGlashan and Potter equations (McGlashan *et al.* 1951, Letcher and Moollan 1995).

$$B_{12}/V_{\mathrm{c},12} = 0.43 - 0.886(T_{\mathrm{c},12}/T)^2 - 0.0375(n_{12} - 1)(T_{\mathrm{c},12}/T)^{4.5} \tag{6}$$

where T_c is the critical temperature, V_c , is the critical volume

$$T_{\mathrm{c},12} = 128(T_{\mathrm{c},11}.T_{c,12})^{1/2}.(I_{c,11}.I_{c,12})^{1/2}.(V_{c,11}V_{c,22}/N_{c,12}^2\,T_{c,12}) \tag{7}$$

where

$$I_{\mathrm{c},12}.(V_{\mathrm{c},12})^2 = (I_{11} + I_{22}).\left[(V_{\mathrm{c},11})^{1/3} + (V_{\mathrm{c},22})^{1/3}\right]^6 \tag{8}$$

and

$$V_{\mathrm{c},12} = \left[(V_{\mathrm{c},11})^{1/3} + (V_{\mathrm{c},22})^{1/3}\right]^3/8 \tag{9}$$

and

$$V_{12} = (n_1 + n_2)/2 \tag{10}$$

where I, is the ionization potential (eV) obtained from the CRC Handbook of Chemistry and Physics, 1984.n, is the number of carbon atoms in helium and is assigned a value of 1 for helium.

The partial molar excess enthalpies at infinite dilution values $\Delta H_1^{\mathrm{E}\infty}$ were calculated using activity coefficients at infinite dilution data, by the Gibbs-Helmholtz equation (Letcher and Whitehead 1996).

$$\left[\frac{\partial \ln \gamma_{\mathrm{i}}^{\infty}}{\partial\left(\frac{1}{T}\right)}\right]=\frac{\Delta H_{1}^{\mathrm{E}\infty}}{R} \tag{11}$$

where R, is the universal gas constant, 1, refers to the solute.

The outlet pressure P_o was atmospheric pressure, the inlet pressure, P_i, varied between 28 and 48 kPa depending on the flow rate of the carrier gas. The inlet pressure was measured by the instrument.

The selectivity provide a useful index for the selection of suitable entrainers and at infinite dilution, it is given by:

$$S_{12}^{\infty}=\frac{\gamma_{1}^{\infty}}{\gamma_{2}^{\infty}} \tag{12}$$

where 1 refers to a solute and 2 refers to benzene. S_{12}^{∞} values > 1 implies that a solvent is suitable for use as entrainer. Solvent capacity , k , is used with S_{12}^{∞} to determine the suitability of a solvent as an entrainer. Solvent capacity at infinite dilution is defined as:

$$k=\frac{1}{\gamma_{1}^{\infty}} \tag{13}$$

Therefore, a suitable entrainer should possess both a high selectivity and a high solvent capacity for the components to be separated.

The chemical nature of the groups that makes up an ionic liquid plays a vital role in determining the magnitude of the activity coefficient at infinite dilution, S_{12}^{∞} and k_{1}^{∞} of the solute dissolved in the ionic liquid (Deenadayalu *et al*. 2006). In this work the relationship between the structure of the IL and γ_{13}^{∞} and S_{12}^{∞} are explored

4.2 Error Calculation of γ_{13}^{∞}

In every analysis conducted, the error associated with the results is important. This either random error (is caused by any factors that randomly affect measurement of the variable across the sample) or systematic error (is caused by any factors that systematically affect measurement of the variable across the sample) error. An exact error must be diagnosed in this kind of analysis (Skoog *et al*.1996) and the equation bellow was used

$$\frac{S_{\gamma}}{\gamma} = \sqrt{\left(\frac{S_{n_3}}{n_3}\right)^2 + \left(\frac{S_T}{T}\right)^2 + \left(\frac{S_{V_\mathrm{N}}}{V_\mathrm{N}}\right)^2} \qquad (14)$$

Reporting a measured standard deviation alone does not indicate the significance of the probable errors. A more informative way to indicate probable error is to report relative standard deviation (RSD)**.** The RSD is the ratio of the measurement standard deviation to the mean of the quantity being measured. In this work, solutes were measured in triplicate (three retention times and hence three γ_{13}^{∞} values for each solute at each temperature).

4.2.1 Mean of activity coefficient at infinite dilution

These quantities provide a measure of the uncertainty in a mean determined from repetitive measurements, using equation 15 below.

$$\bar{x}_{\gamma_{13}^{\infty}} = \frac{\sum \gamma_{13}^{\infty}}{n} \tag{15}$$

4.2.2 Standard deviation of activity coefficient at infinite dilution

The standard deviation, *s*, is a statistical measure of the precision for a series of repetitive measurements. The advantage of using *s* to quote uncertainty in a result is that it has the same units as the experimental data. Under a normal distribution, ± one standard deviation encompasses 68% of the measurements and ± two standard deviations encompasses 96% of the measurements.

$$S = \frac{\sqrt{\sum (x_1 - \bar{x})^2}}{n-1} \tag{16}$$

4.2.3 Relative standard deviation of activity coefficient at infinite dilution

The relative standard deviation (RSD) is useful for comparing the uncertainty between different measurements of varying absolute magnitude. The RSD is calculated from the standard deviation, *s*, and is commonly expressed as parts per thousand (ppt) or percentage (%):

$$RSD = \frac{s}{\bar{x}} .100 \tag{17}$$

CHAPTER 5

5. RESULTS

The results for γ_{13}^{∞} for each column for the temperatures (303.15 and 313.15 and 323.15) K for the Ils, methyltrioctylammonium bis(trifluoromethylsulfonyl)imide and methyltrioctylammonium thiosalicylate are given in Tables 5.1 to 5.2. The moles of the IL in each column are also given in Tables 5.1 and 5.2. The average γ_{13}^{∞} values for the ILs: methyltrioctylammonium bis(trifluoromethylsulfonyl)imide and methyltrioctylammonium thiosalicylate, is given in Tables 5.3 and 5.4, respectively. The activity coeffficient at infinite dilution, were calculated using eqn. 2, Everett and Cruickshank equation.

The partial molar excess enthalpies at infinite dilutions were calculated from the average γ_{13}^{∞} values using the eqn. 11, Gibbs –Helmholts equation and are also given in Table 5.5 for IL: methyltrioctylammonium bis(trifluoromethylsulfonyl)imide and Table 5.6 for IL: methyltrioctylammonium thiosalicylate. The error in $\Delta H_1^{E\infty}$ was estimated to be 10 % of the $\Delta H_1^{E\infty}$ value. The linear correlation values (R^2) obtained from the graph of $\ln \gamma_{13}^{\infty}$ versus 1/T, are also given in Tables 5.5 and 5.6.

The selectivity at infinite dilution, was calculated using equation 12 from the average γ_{13}^{∞} values of the solute/benzene separation for methyltrioctylammonium bis(trifluoromethylsulfonyl)imide and methyltrioctylammonium thiosalicylate IL at T = (303.15 and 313.15 and 323.15) K and is given in Tables 5.7 and 5.8, respectively.

The capacity values at infinite dilution were calculated using equation 13 for methyltrioctylammonium bis(trifluoromethylsulfonyl)imide and methyltrioctylammonium thiosalicylate IL at T = (303.15 and 313.15 and 323.15) K, and are given in Tables 5.9 and 5.10, respectively.

Table 5.1 n_3 and γ_{13}^{∞} values of the IL: methyltrioctylammonium bis(trifluoromethylsulfonyl)imide for each column at T = (303.15 and 313.15 and 323.15) K

Solutes	n_3 / 10^{-3} mol					
	1.8	2.0	1.8	2.0	1.8	2.0
			γ_{13}^{∞}			
	T = 303.15 K		T = 313.15 K		T = 323.15 K	
Pentane	1.01	1.00	0.99	0.99	1.00	0.98
Hexane	1.13	1.13	1.11	1.12	1.11	1.10
Heptane	1.30	1.31	1.26	1.28	1.25	1.25
Octane	1.52	1.54	1.46	1.49	1.44	1.43
1-Pentene	0.78	0.78	0.76	0.74	0.76	0.78
1-Hexene	0.89	0.88	0.85	0.85	0.88	0.87
Pentyne	0.53	0.52	0.52	0.53	0.54	0.55
Hexyne	0.59	0.59	0.59	0.59	0.60	0.62
Cyclopentane	0.71	0.71	0.69	0.70	0.70	0.69
Cyclohexane	0.84	0.84	0.80	0.81	0.80	0.79
Cycloheptane	0.95	0.94	0.90	0.91	0.89	0.88
Cyclooctane	1.08	1.07	1.01	1.03	0.99	1.03
Methanol	0.88	0.89	0.81	0.82	0.79	0.81
Ethanol	0.94	0.95	0.85	0.87	0.80	0.83
Benzene	0.32	0.31	0.31	0.31	0.31	0.32

Table 5.2 n_3 and γ_{13}^{∞} values of the IL: methyltrioctylammonium thiosalicylate for each column at T = (303.15 and 313.15 and 323.15) K

Solutes	n_3 / 10^{-3} mol					
	2.3	2.8	2.3	2.8	2.3	2.8
			γ_{13}^{∞}			
	T = 303.15 K		T = 313.15 K		T = 323.15 K	
Pentane	1.81	1.81	1.75	1.75	1.70	1.65
Hexane	2.07	2.07	1.98	1.96	1.92	1.87
Heptane	2.37	2.28	2.29	2.22	2.21	2.15
Octane	2.77	2.72	2.68	2.61	2.55	2.47
Nonane	3.21	3.11	3.07	3.03	2.98	2.88
1-Pentene	1.39	1.40	1.36	1.36	1.33	1.28
1-Hexene	1.57	1.55	1.53	1.51	1.51	1.46
1-Octene	2.09	2.06	2.06	2.02	2.00	1.93
Pentyne	0.63	0.63	0.65	0.65	0.67	0.67
Hexyne	0.70	0.69	0.72	0.72	0.75	0.75
Octyne	0.88	0.84	0.92	0.90	0.94	0.94
Cyclopentane	1.10	1.08	1.07	1.05	1.04	1.00
Cyclohexane	1.34	1.32	1.28	1.26	1.23	1.19
Cycloheptane	1.42	1.40	1.36	1.32	1.31	1.25
Cyclooctane	1.57	1.57	1.50	1.45	1.44	1.37
Benzene	0.51	0.48	0.50	0.48	0.50	0.47
Toluene	0.62	0.59	0.62	0.59	0.62	0.58
Acetone	0.69	0.65	0.66	0.63	0.64	0.61
Butanone	0.66	0.62	0.64	0.61	0.62	0.59

Table 5.3 Average γ_{13}^{∞} together with $\alpha\gamma_{13}^{\infty}$ for the IL: methyltrioctylammonium bis(trifluoromethylsulfonyl)imide at T = (303.15 and 313.15 and 323.15) K

Solutes	γ_{13}^{∞}	$\alpha\ \gamma_{13}^{\infty}$	γ_{13}^{∞}	$\alpha\ \gamma_{13}^{\infty}$	γ_{13}^{∞}	$\alpha\ \gamma_{13}^{\infty}$
	T = 303.15 K		T = 313.15 K		T = 323.15 K	
Pentane	1.02	0.57	0.99	0.02	0.99	0.00
Hexane	1.13	0.00	1.11	0.08	1.11	0.00
Heptane	1.31	0.00	1.27	0.00	1.25	0.00
Octane	1.54	0.00	1.47	0.04	1.44	0.14
1-Pentene	0.78	0.00	0.73	0.00	0.77	0.07
1-Hexene	0.89	0.00	0.85	0.00	0.88	0.00
Pentyne	0.53	0.00	0.52	0.00	0.55	0.00
Hexyne	0.59	0.00	0.59	0.00	0.61	0.00
Cyclopentane	0.78	0.00	0.70	0.00	0.70	0.00
Cyclohexane	0.84	0.00	0.81	0.00	0.80	0.26
Cycloheptane	0.94	0.00	0.90	0.24	0.88	0.15
Cyclooctane	1.07	0.00	1.02	0.03	1.01	018
Methanol	0.89	0.66	0.82	0.00	0.80	0.00
Ethanol	0.94	0.61	0.86	0.13	0.81	0.34
Benzene	0.31	0.00	0.31	1.03	0.31	0.29

Table 5.4 Average γ_{13}^{∞} together with $\alpha\gamma_{13}^{\infty}$ for the IL: methyltrioctylammonium thiosalicylate at T = (303.15 and 313.15 and 323.15) K

Solutes	γ_{13}^{∞}	$\alpha\gamma_{13}^{\infty}$	γ_{13}^{∞}	$\alpha\ \gamma_{13}^{\infty}$	γ_{13}^{∞}	$\alpha\gamma_{13}^{\infty}$
	T = 303.15 K		T = 313.15 K		T = 323.15 K	.
Pentane	1.81	0.68	1.75	1.60	1.68	1.24
Hexane	2.07	0.87	1.97	0.92	1.90	0.49
Heptane	2.32	0.44	2.25	4.40	2.18	0.35
Octane	2.74	1.25	2.64	1.44	2.51	0.42
Nonane	3.16	0.83	3.05	1.81	2.93	0.04
1-Pentene	1.39	0.64	1.36	4.37	1.31	1.17
1-Hexene	1.56	0.59	1.52	3.42	1.48	0.46
1-Octene	2.07	2.21	2.04	2.25	1.96	0.00
Pentyne	0.63	0.35	0.65	0.00	0.67	0.44
Hexyne	0.69	5.03	0.72	3.30	0.75	0.17
Octyne	0.86	0.95	0.91	4.14	0.94	0.20
Cyclopentane	1.09	0.46	1.06	0.37	1.02	0.51
Cyclohexane	1.33	4.56	1.27	0.45	1.21	0.21
Cycloheptane	1.41	1.33	1.34	0.85	1.28	1.13
Cyclooctane	1.57	0.66	1.47	2.63	1.40	0.00
Benzene	0.49	2.20	0.49	1.26	0.49	0.09
Toluene	0.61	1.42	0.60	0.02	0.60	0.00
Acetone	0.67	0.57	0.65	0.47	0.62	0.25
Butanone	0.64	2.28	0.63	0.90	0.60	0.11

Table 5.5 Partial molar excess enthalpies at infinite dilution, $\Delta H_1^{E\infty}$, and R^2 values for the IL: methyltrioctylammonium bis(trifluoromethylsulfonyl)imide

Solutes	$\Delta H_1^{E\infty}$ / J mol^{-1}	R^2
Pentane	1785	0.95
Hexane	1172	0.95
Heptane	1715	0.94
Octane	2699	0.98
1-Pentene	4387	0.97
1-Hexene	3960	0.99
Pentyne	-2403	0.95
Hexyne	-4550	0.97
Cyclopentane	1913	1.00
Cyclohexane	2047	0.96
Cycloheptane	2824	0.97
Cyclooctane	2459	0.87
Methanol	4096	0.93
Ethanol	5949	0.98
Benzene	-863	0.88

Table 5.6 Partial molar excess enthalpies at infinite dilution, $\Delta H_1^{E\infty}$, and R^2 values for the IL: methyltrioctylammonium thiosalicylate

Solutes	$\Delta H_1^{E\infty}$ / J mol^{-1}	R^2
Pentane	5384	0.99
Hexane	6897	0.99
Heptane	5899	0.99
Octane	9396	0.99
Nonane	9396	0.99
1-Pentene	3551	0.98
1-Hexene	3099	0.99
1-Octene	4478	0.93
Pentyne	-1660	0.99
Hexyne	-2157	0.99
Octyne	-3267	0.99
Cyclopentane	2942	0.99
Cyclohexane	4597	0.99
Cycloheptane	5314	0.99
Cyclooctane	6622	0.99
Benzene	355	0.98
Toluene	160	0.99
Acetone	2142	0.99
Butanone	1370	0.96

Table 5.7 Selectivity values for the solute/benzene separation for IL: methyltrioctylammonium bis(trifluoromethylsulfonyl)imide at T =(303.15 and 313.15 and 323.15) K

Solutes	S_{12}^{∞}		
	T = 303.15 K	T = 313.15 K	T = 323.15 K
Pentane	3.3	3.2	3.1
Hexane	3.7	3.6	3.5
Heptane	4.2	4.1	4.0
Octane	5.0	4.7	4.5
1-Pentene	2.5	2.3	2.2
1-Hexene	2.9	2.7	2.5
Pentyne	1.7	1.7	1.7
Hexyne	1.8	1.9	1.9
Cyclopentane	2.3	2.2	2.1
Cyclohexane	2.7	2.6	2.5
Cycloheptane	3.1	2.9	2.8
Cyclooctane	3.5	3.3	3.2
Methanol	2.9	2.6	2.5
Ethanol	3.0	2.8	2.6
Benzene	1.0	1.0	1.0

Table 5.8 Selectivity values for the solute/benzene separation for IL: methyltrioctylammonium thiosalicylate at *T* = (303.15 and 313.15 and 323.15) K

Solutes	S_{12}^{∞}		
	T = 303.15 K	*T* = 313.15 K	*T* = 323.15 K
Pentane	3.7	3.6	3.5
Hexane	4.2	4.0	3.9
Heptane	4.7	4.6	4.5
Octane	5.5	5.4	5.2
Nonane	6.4	6.2	6.0
1-Pentene	2.8	2.8	2.7
1-Hexene	3.2	3.1	3.1
1-Octene	4.2	4.2	4.0
Pentyne	1.3	1.3	1.4
Hexyne	1.4	1.5	1.5
Octyne	1.7	1.9	1.9
Cyclopentane	2.2	2.2	2.1
Cyclohexane	2.7	2.6	2.5
Cycloheptane	2.9	2.7	2.6
Cyclooctane	3.2	3.0	2.9
Benzene	1.0	1.0	1.0
Toluene	1.2	1.2	1.2
Acetone	1.4	1.3	1.3
Butanone	1.3	1.3	1.2

Table 5.9 Capacity values for the IL: methyltrioctylammonium bis(trifluoromethylsulfonyl)imide at *T* = (303.15 and 313.15 and 323.15) K

Solutes	k_2^∞		
	303.15 K	313.15 K	323.15 K
Pentane	0.98	1.01	1.02
Hexane	0.88	0.90	0.91
Heptane	0.77	0.79	0.80
Octane	0.65	0.68	0.70
1-Pentene	1.28	1.38	1.43
1-Hexene	1.13	1.18	1.24
Pentyne	1.94	1.91	1.83
Hexyne	1.83	1.70	1.64
Cyclopentane	1.41	1.44	1.48
Cyclohexane	1.20	1.24	1.26
Cycloheptane	1.06	1.11	1.14
Cyclooctane	0.93	0.98	0.99
Methanol	1.13	1.22	1.25
Ethanol	1.06	1.17	1.23
Benzene	3.23	3.21	3.16

Table 5.10 Capacity values for the IL: methyltrioctylammonium thiosalicylate at T = (303.15 and 313.15 and 323.15) K

Solutes	k_2^∞		
	303.15 K	313.15 K	323.15 K
Pentane	0.55	0.57	0.60
Hexane	0.48	0.51	0.53
Heptane	0.43	0.44	0.46
Octane	0.36	0.38	0.40
Nonane	0.32	0.33	0.34
1-Pentene	0.72	0.74	0.77
1-Hexene	0.64	0.66	0.67
1-Octene	0.48	0.49	0.51
Pentyne	1.59	1.55	1.50
Hexyne	1.44	1.38	1.34
Octyne	1.16	1.10	1.06
Cyclopentane	0.91	0.94	0.98
Cyclohexane	0.75	0.79	0.82
Cycloheptane	0.71	0.75	0.78
Cyclooctane	0.64	0.68	0.71
Benzene	2.02	2.04	2.06
Toluene	1.65	1.65	1.66
Acetone	1.48	1.54	1.61
Butanone	1.57	1.60	1.66

Figures 5.1 to 5.11 are the graphs of In γ_{13}^{∞} versus 1/T for ILs: methyltrioctylammonium bis(trifluoromethylsulfonyl)imide and methyltrioctylammonium thiosalicylate, which were used for the calculation of the partial molar enthalpy at infinite dilution using the Helmholtz equation (eqn. 11, given on page 44).

Figures 5.12 to 5.17 are the graphs of activity coefficients at infinite dilution versus carbon number for the homologous series, for both methyltrioctylammonium bis(trifluoromethylsulfonyl)imide IL and methyltrioctylammonium thiosalicylate IL at T = (303.15 and 313.15 and 323.15) K.

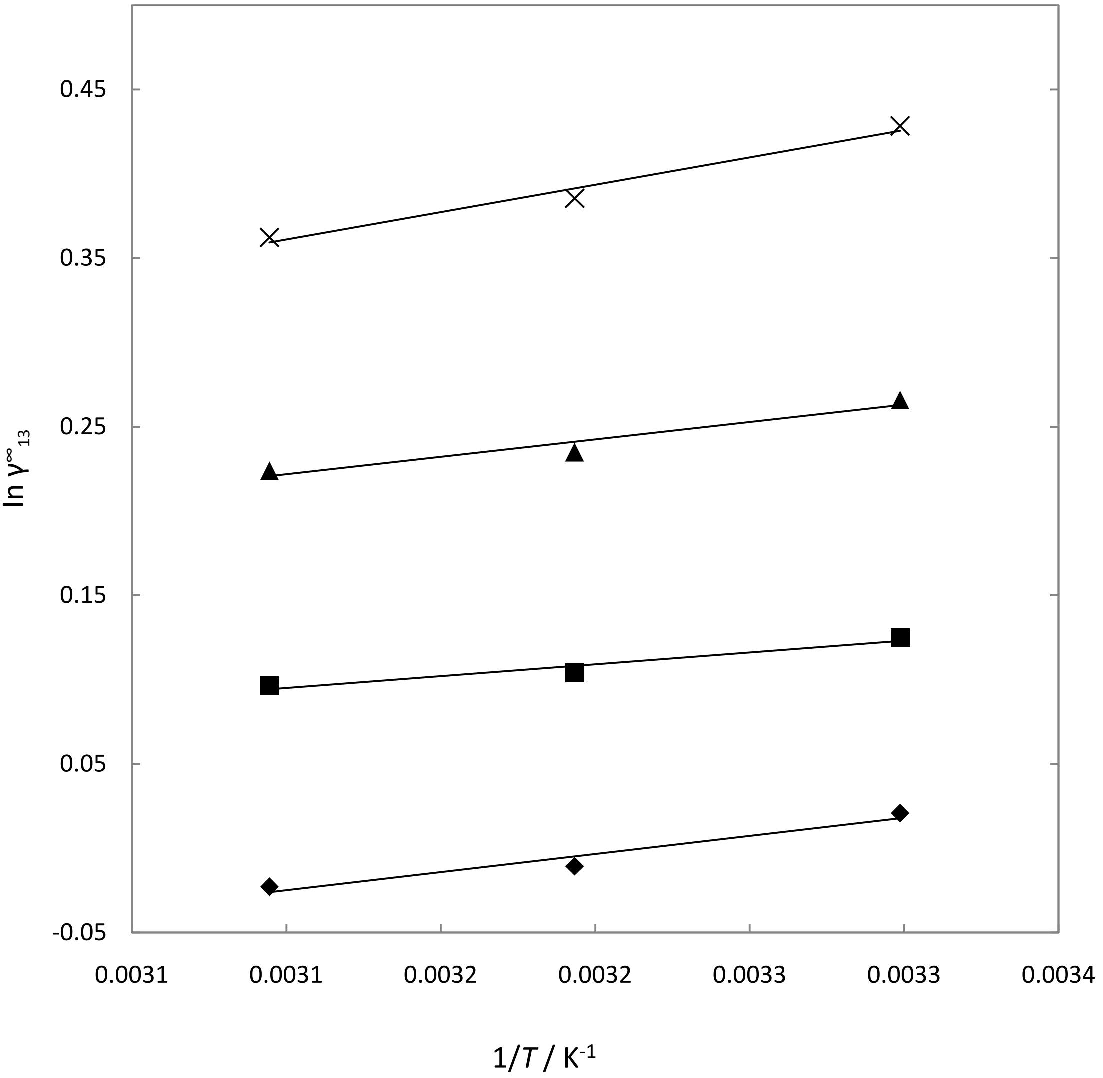

Figure 5.1 Graph of ln γ_{13}^{∞} versus 1/*T* for the solutes: ♦, pentane; ■, hexane; ▲, heptane; ×, octane, for IL: methyltrioctylammonium bis(trifluoromethylsulfonyl)imide

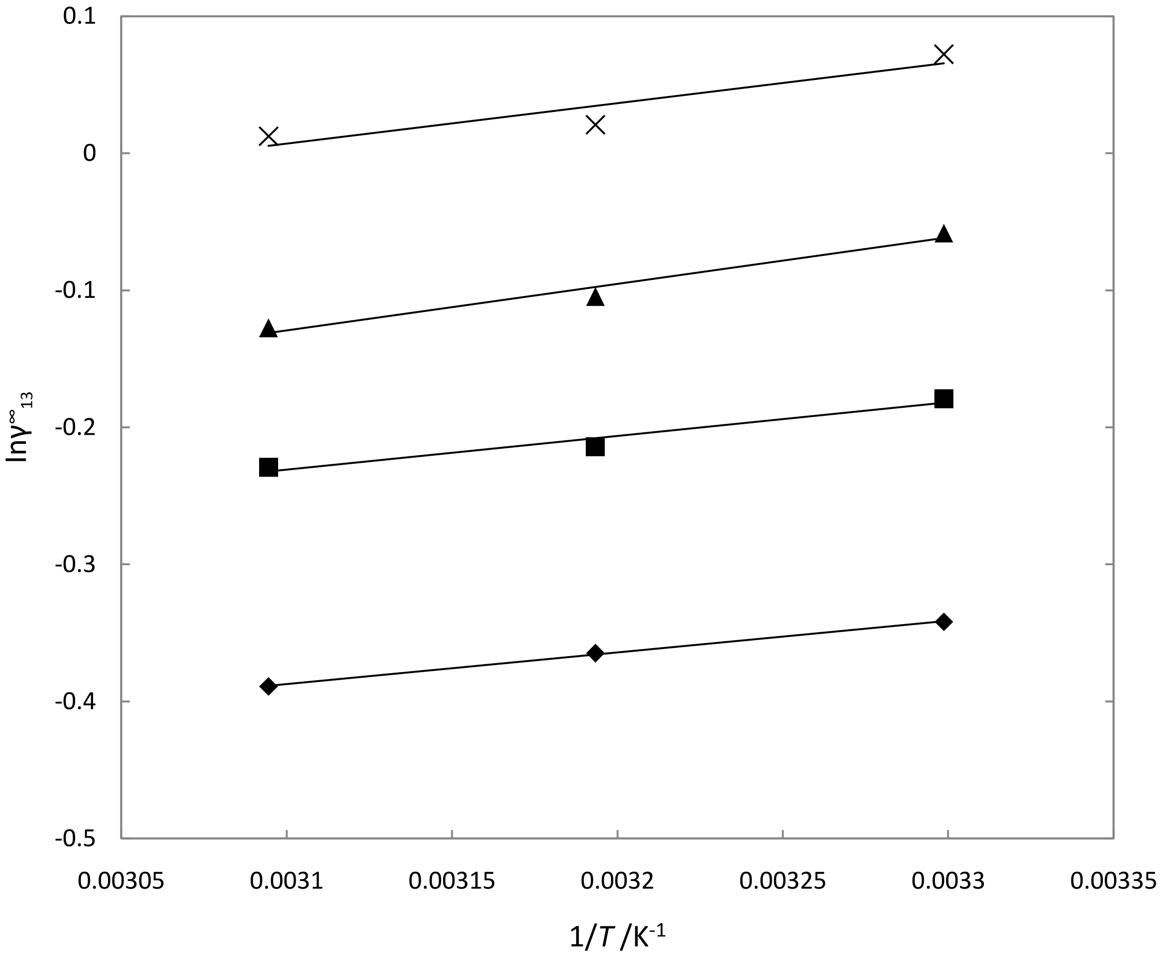

Figure 5.2 Graph of ln γ_{13}^{∞} versus 1/*T* for the solutes: ♦, cyclopentane; ■, cyclohexane; ▲, cycloheptane; ×, cyclooctane, for IL: methyltrioctylammonium bis(trifluoromethylsulfonyl)imide

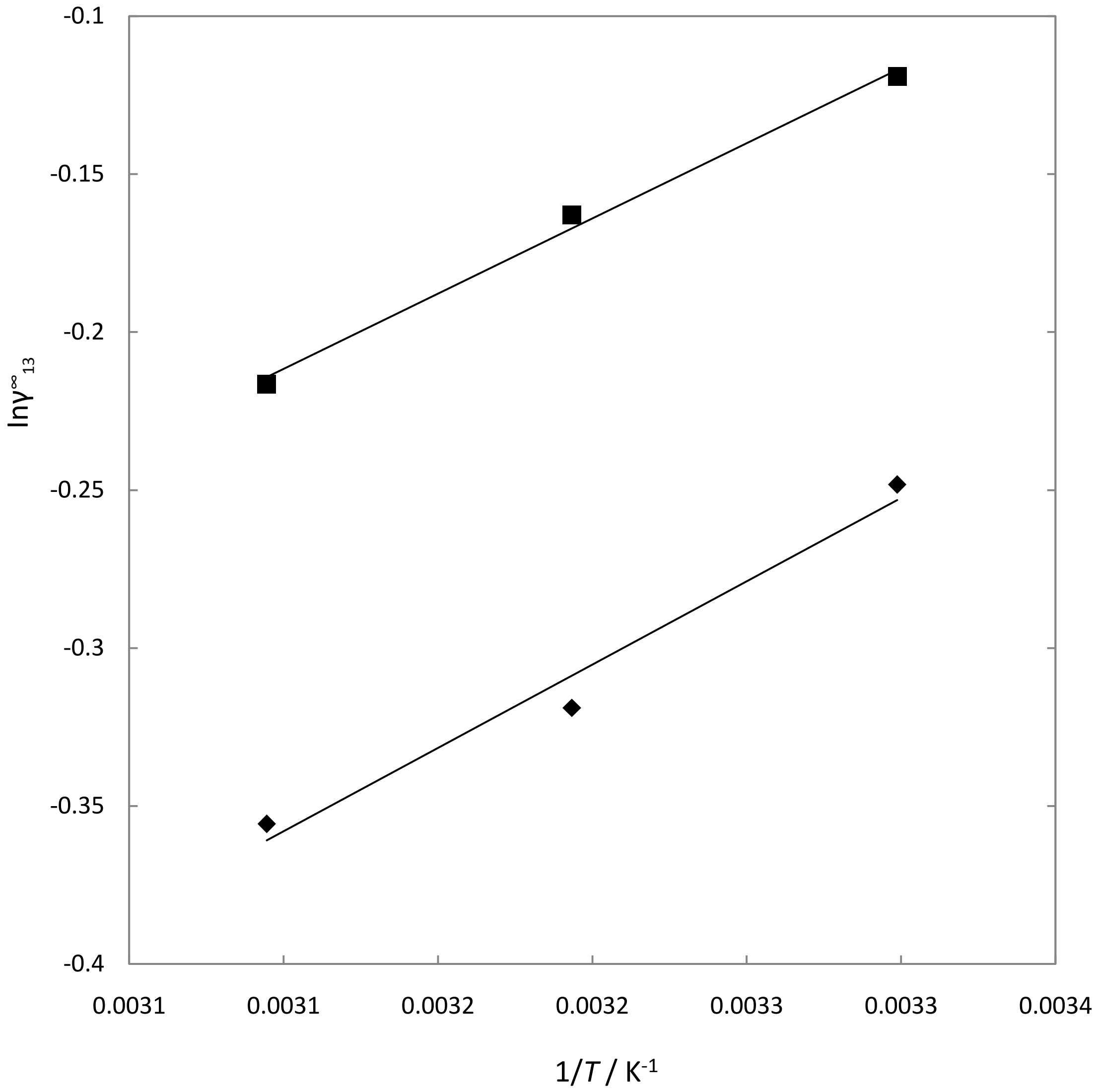

Figure 5.3 Graph of ln γ_{13}^{∞} versus 1/*T* for the solutes: ♦, 1-pentene; ■, 1-hexene, for IL: methyltrioctylammonium bis(trifluoromethylsulfonyl)imide

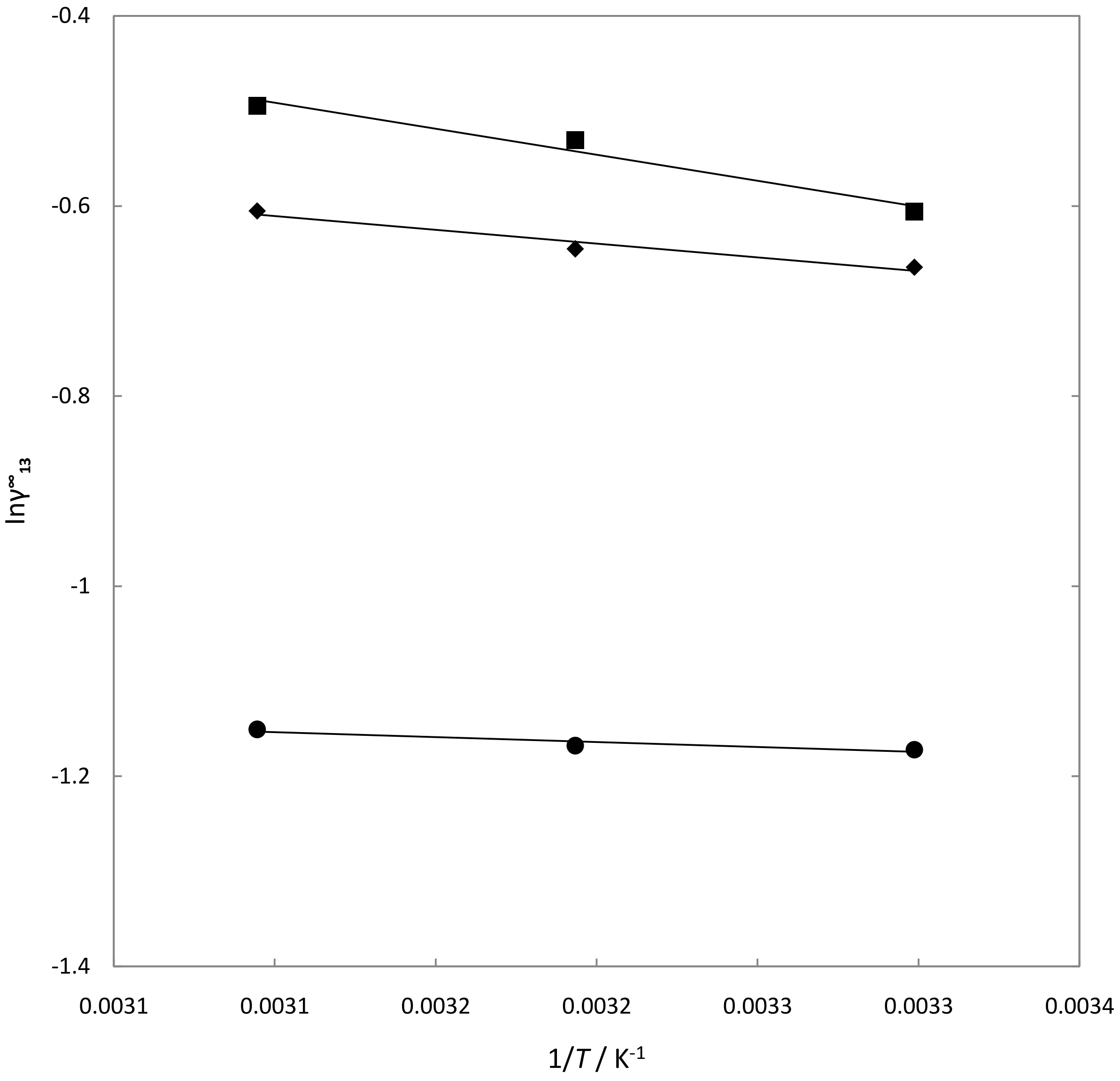

Figure 5.4 Graph of ln γ_{13}^{∞} versus 1/*T* for the solutes: ♦, pentyne; ■, hexyne; ●, benzene, for IL: methyltrioctylammonium bis(trifluoromethylsulfonyl)imide

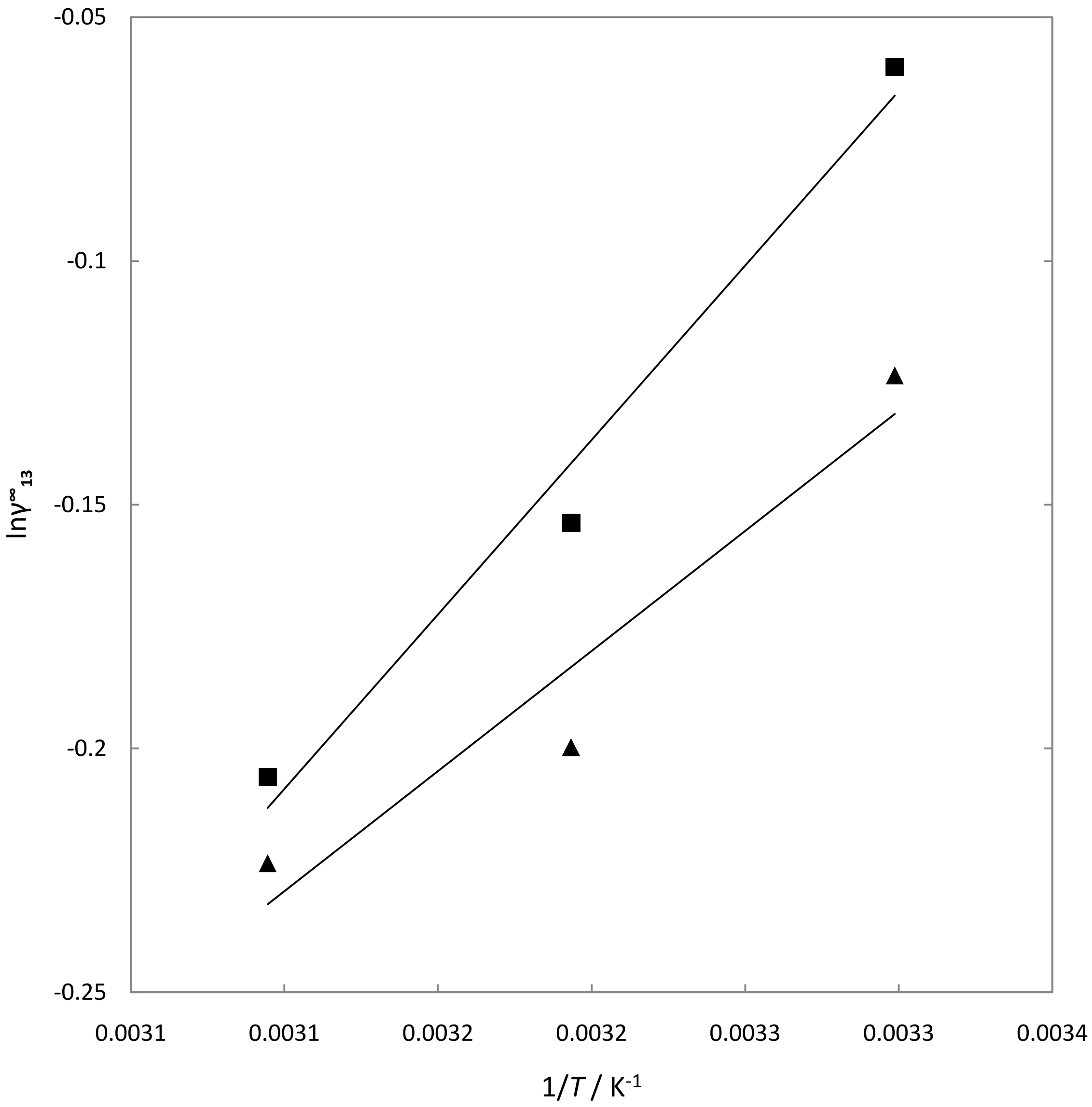

Figure 5.5 Graphs of ln γ_{13}^{∞} versus 1/*T* for the solutes: ▲, methanol; ■, ethanol, for IL: methyltrioctylammonium bis(trifluoromethylsulfonyl)imide

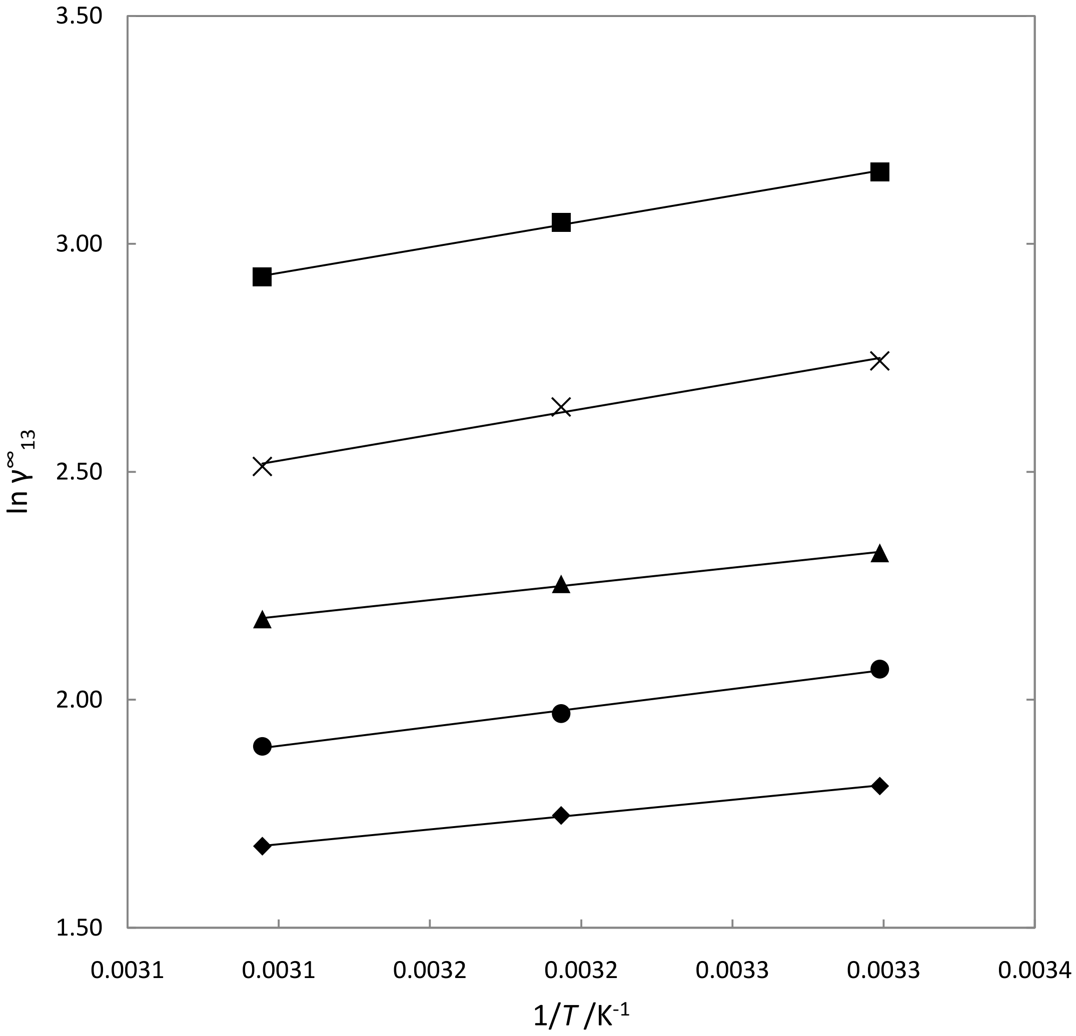

Figure 5.6 Graphs of ln γ_{13}^{∞} versus 1/*T* for the solutes: ♦, pentane; ●, hexane; ▲, heptane; ×, octane; ■, nonane, for IL: methyltrioctylammonium thiosalicylate

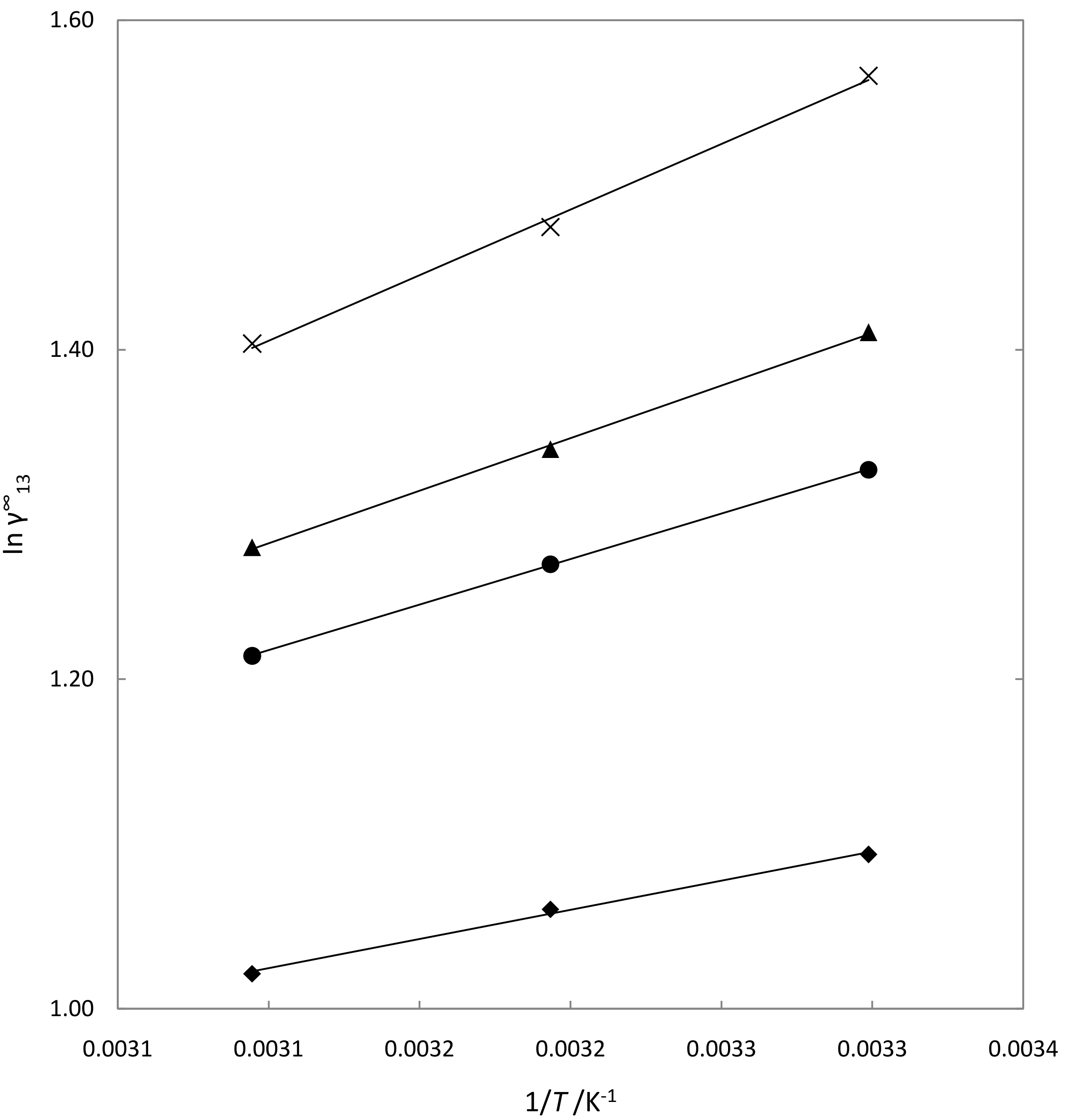

Figure 5.7 Graphs of ln γ_{13}^{∞} versus 1/*T* for the solutes: ♦, cyclopentane; ●, cyclohexane; ▲, cycloheptane; ×, cyclooctane, for IL: methyltrioctylammonium thiosalicylate

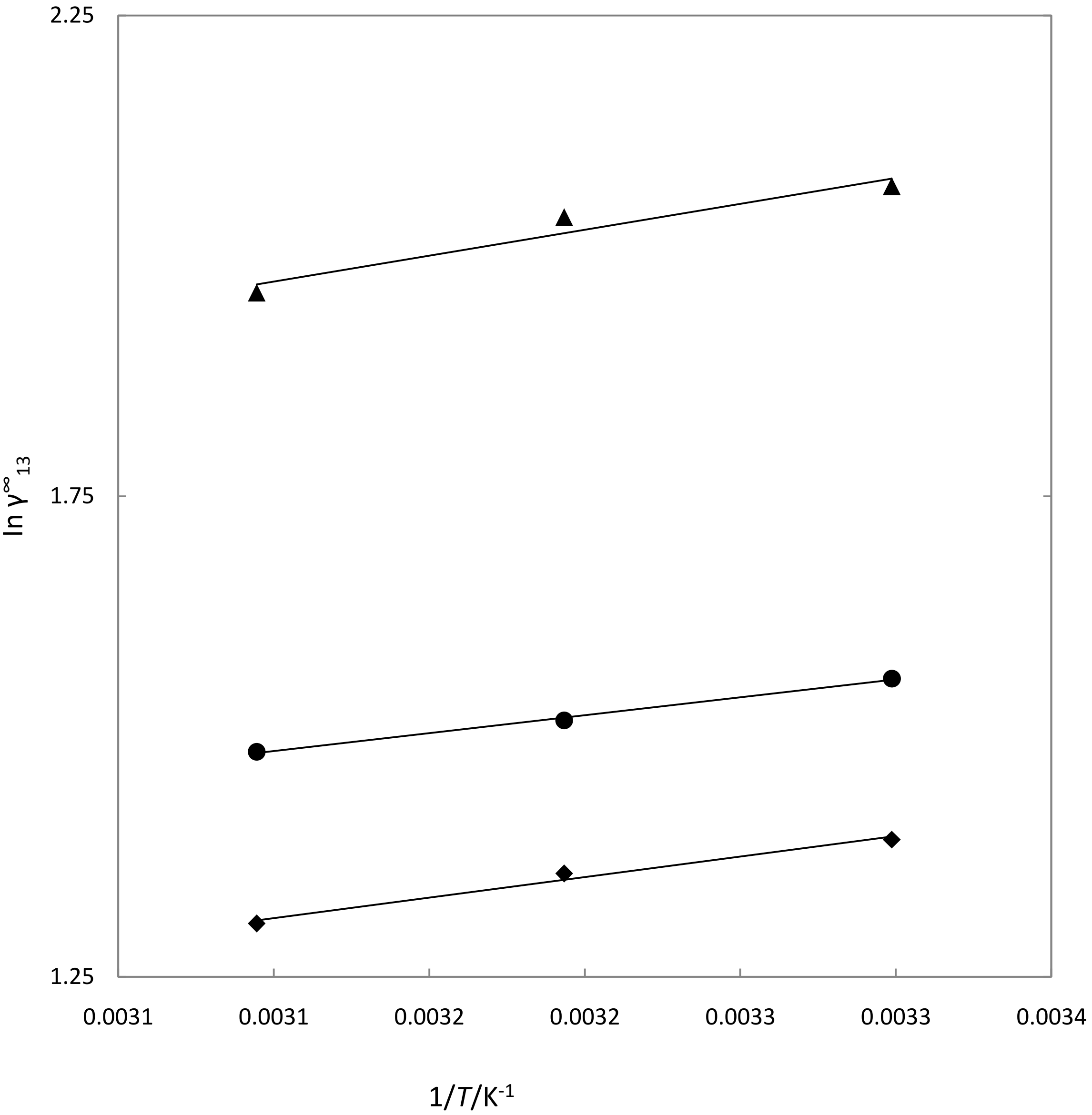

Figure 5.8 Graphs of ln γ_{13}^{∞} versus 1/T for the solutes: ♦, 1-pentene; ●, 1-hexene; ▲, 1-octene, for IL: methyltrioctylammonium thiosalicylate

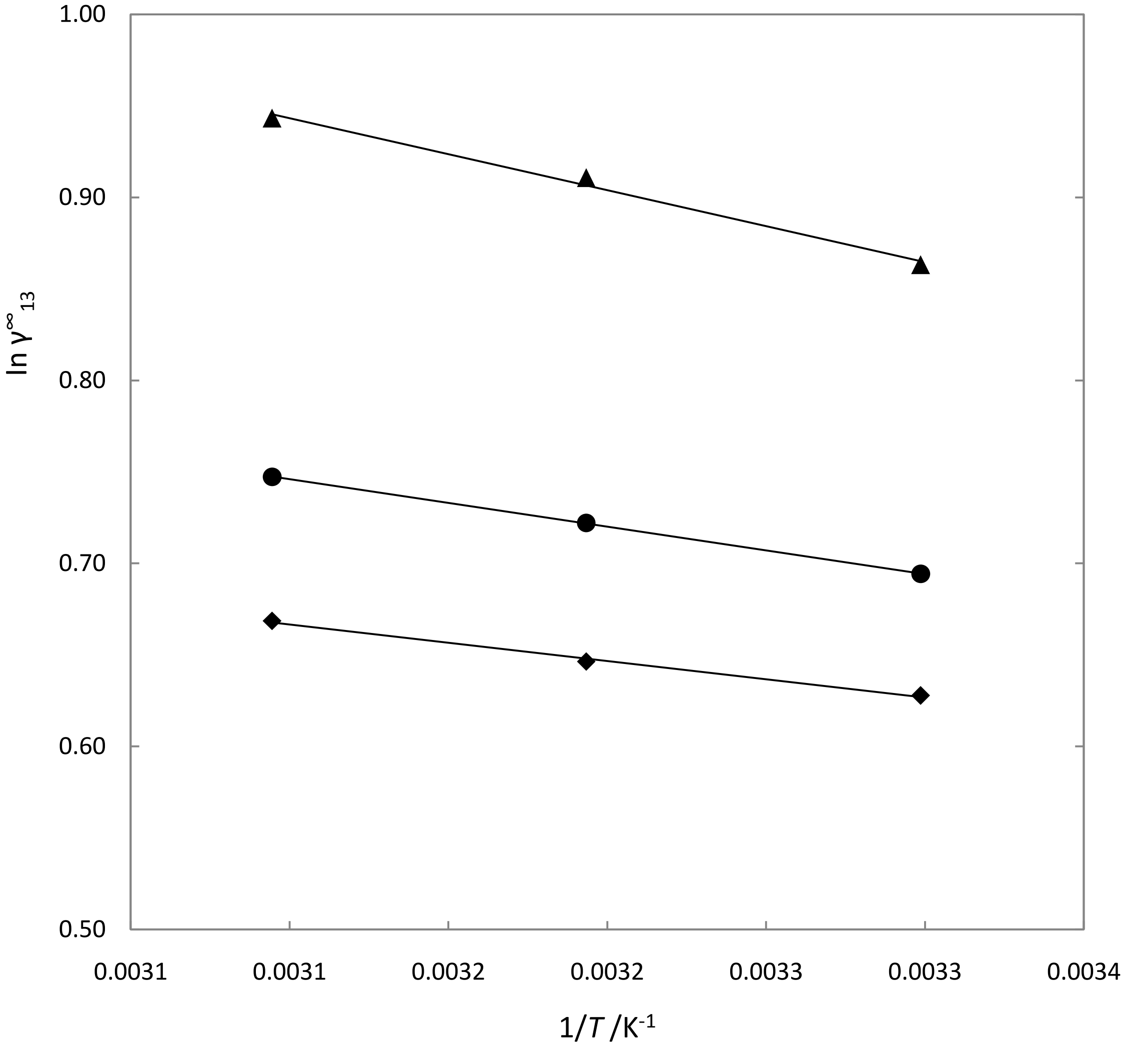

Figure 5.9 Graphs of ln γ_{13}^{∞} versus 1/*T* for the solutes: ♦, pentyne; ●, hexyne; ▲, octyne, for IL: methyltrioctylammonium thiosalicylate

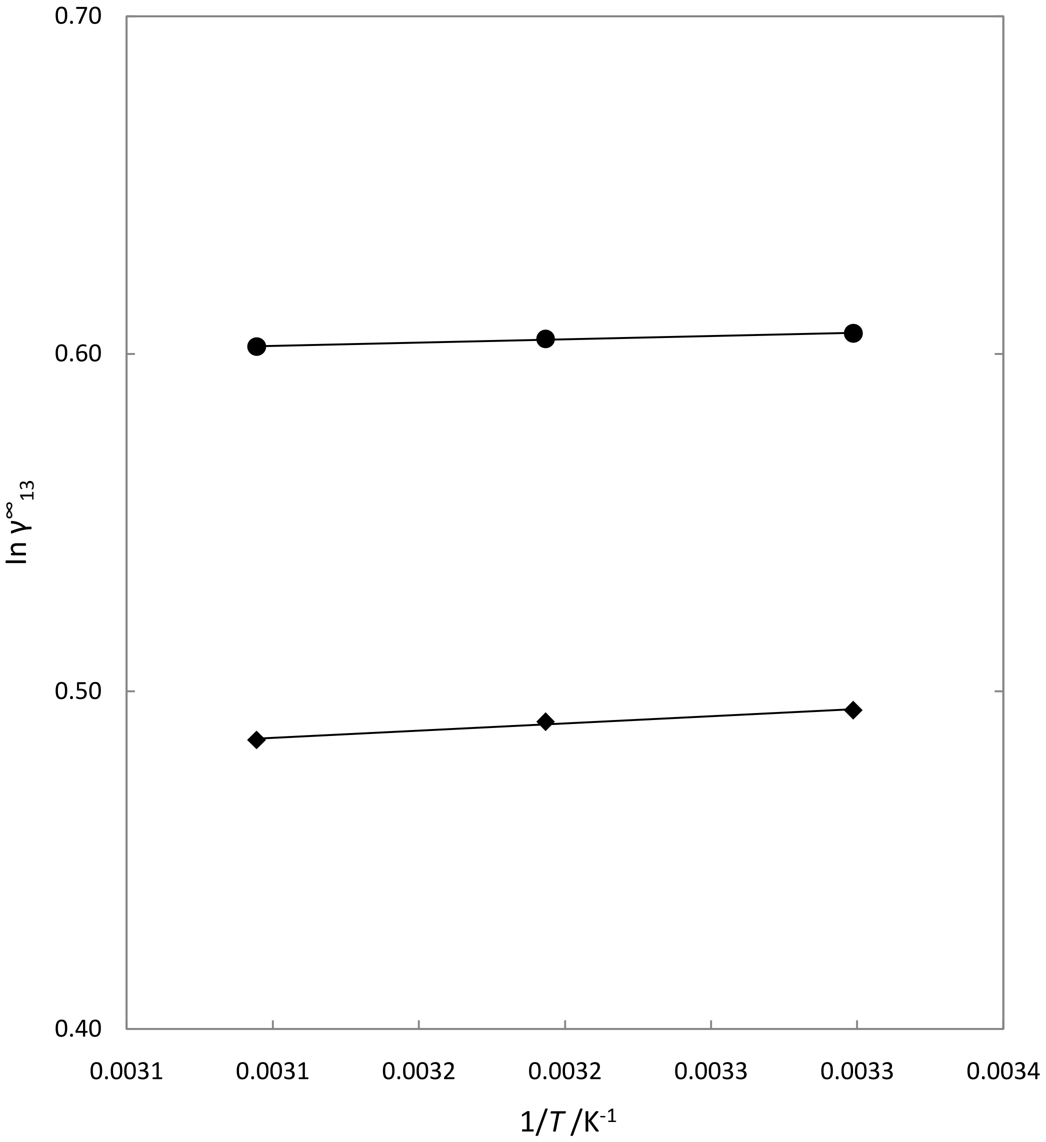

Figure 5.10 Graphs of ln γ_{13}^{∞} versus 1/*T* for the solutes: ♦, benzene; ●, toluene, for IL: methyltrioctylammonium thiosalicylate

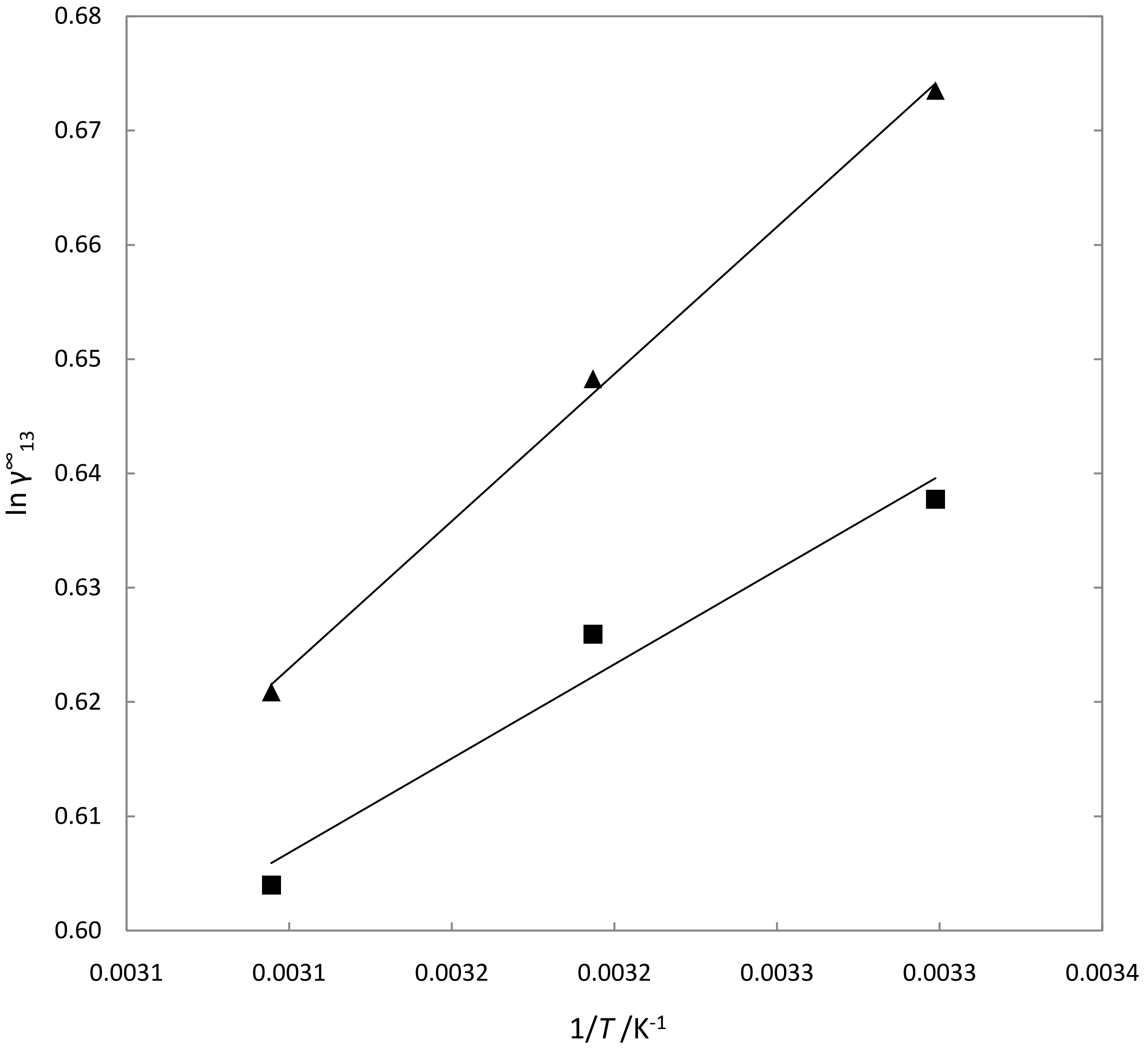

Figure 5.11 Graphs of ln γ_{13}^{∞} versus 1/*T* for the solutes: ▲, acetone; ■, butanone, for IL: methyltrioctylammonium thiosalicylate

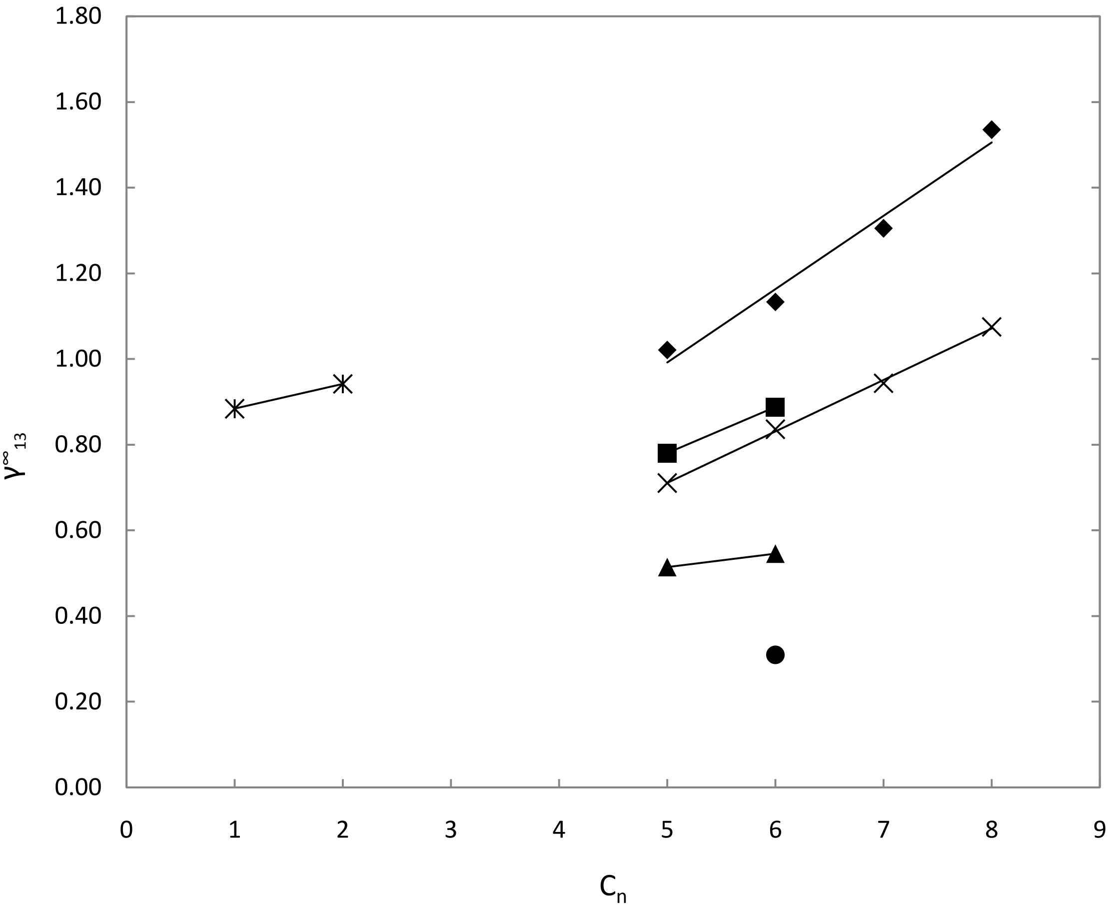

Figure 5.12 Activity coefficients at infinite dilution, γ_{13}^{∞}, versus the carbon number (C_n) at T = 303.15 K: ♦, alkanes; ■, 1-alkenes; ▲, alkynes; ●, benzene; ×, cycloalkanes; *, alcohols, for IL: methyltrioctylammonium bis(trifluoromethylsulfonyl)imide

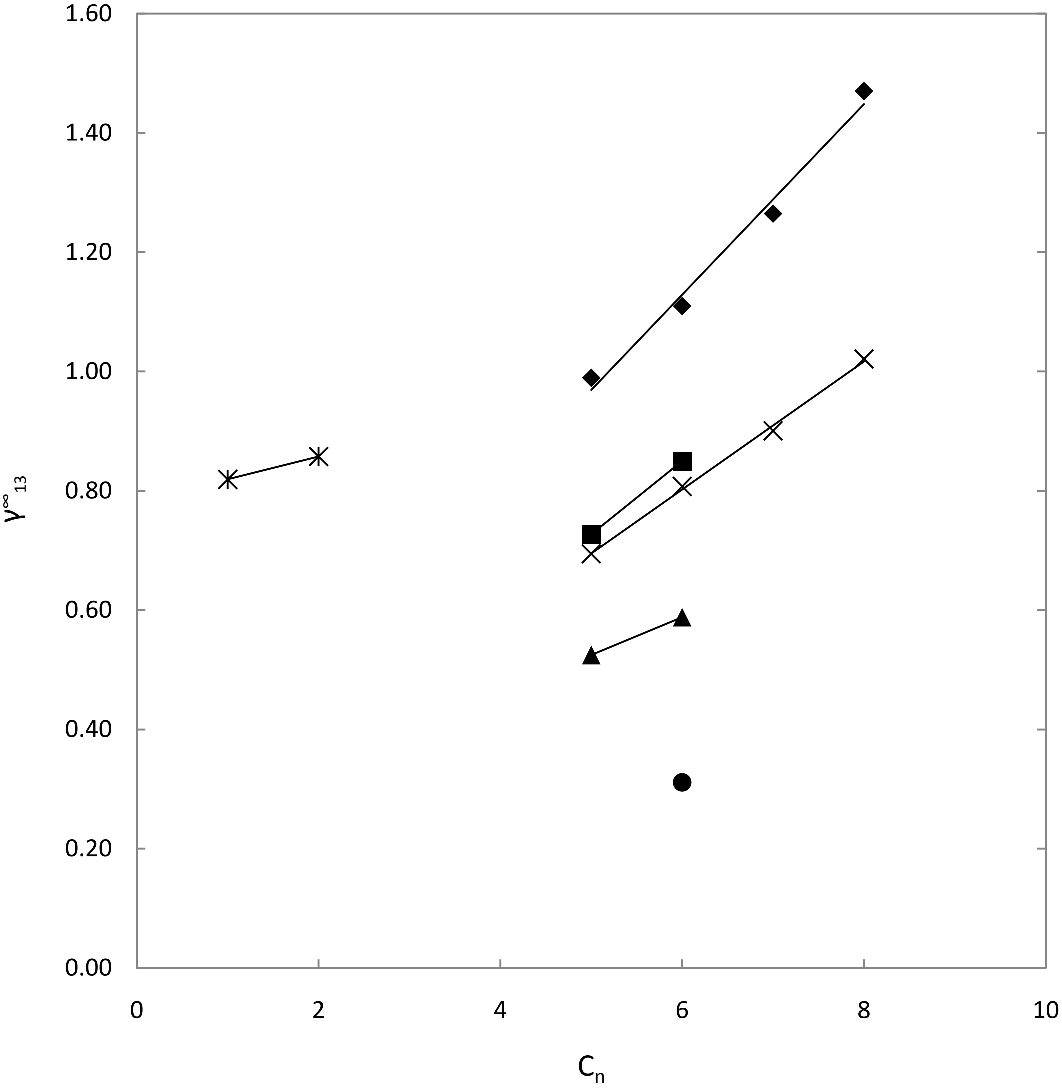

Figure 5.13 Activity coefficients at infinite dilution, γ_{13}^{∞}, versus the carbon number (C_n) at *T* = 313.15 K: ♦, alkanes; ■, 1-alkenes; ▲, alkynes; ●, benzene; ×, cycloalkanes; *, alcohols, for IL: methyltrioctylammonium bis(trifluoromethylsulfonyl)imide

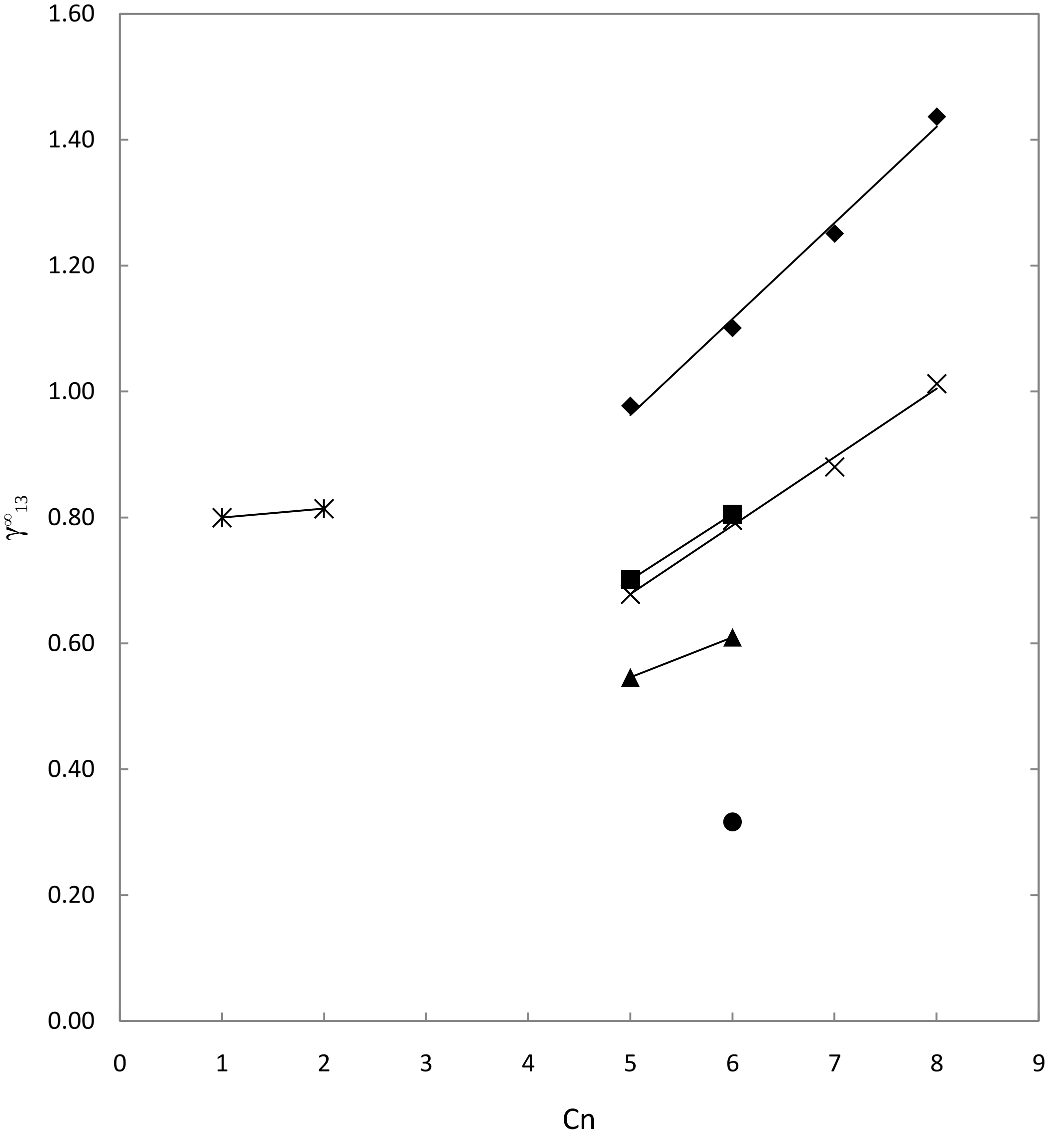

Figure 5.14 Activity coefficients at infinite dilution, γ^{∞}_{13}, versus the carbon number (C_n) at T = 323.15 K: ♦, alkanes; ■, 1-alkenes; ▲, alkynes; ●, benzene; ×, cycloalkanes; *, alcohols, for IL: methyltrioctylammonium bis(trifluoromethylsulfonyl)imide

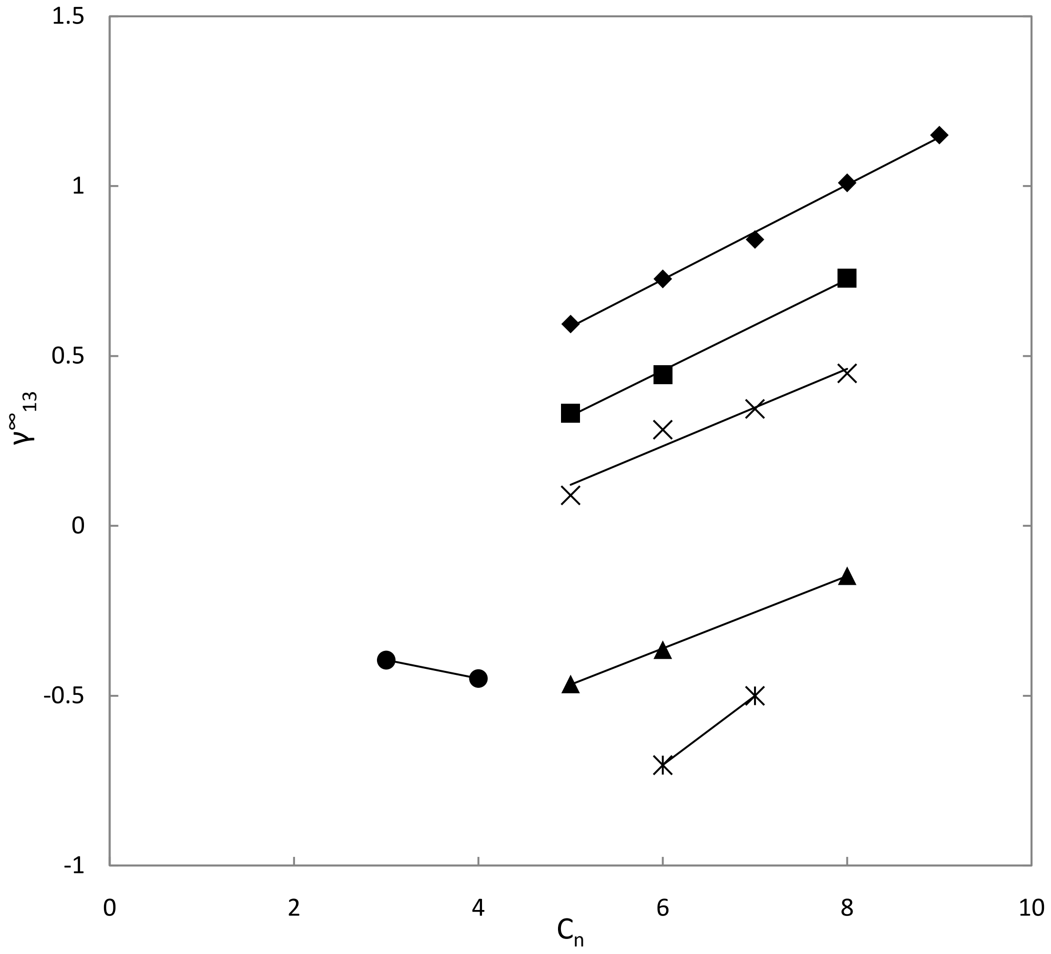

Figure 5.15 Activity coefficients at infinite dilution, γ_{13}^{∞}, versus the carbon number (C_n) at T = 303.15 K: ♦, alkanes; ■, 1-alkenes; ▲, alkynes; ●, ketones; ×, cycloalkanes; *, aromatic hydrocarbons, for IL: methyltrioctylammonium thiosalicylate

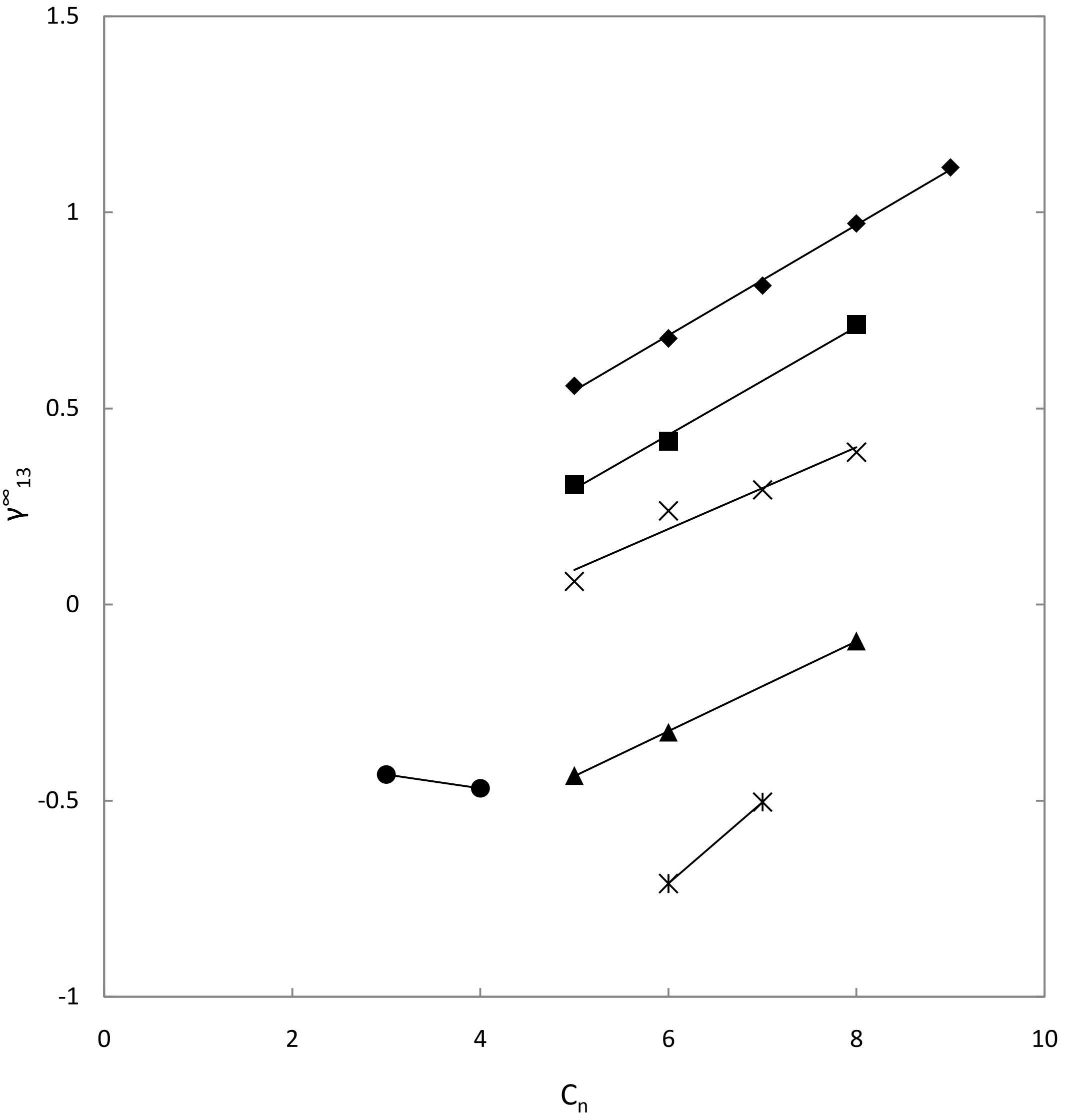

Figure 5.16 Activity coefficients at infinite dilution, γ_{13}^{∞}, versus the carbon number (C_n) at T = 303.15 K: ♦, alkanes; ■, 1-alkenes; ▲, alkynes; ●, ketones; ×, cycloalkanes; *, aromatic hydrocarbons, for IL: methyltrioctylammonium thiosalicylate

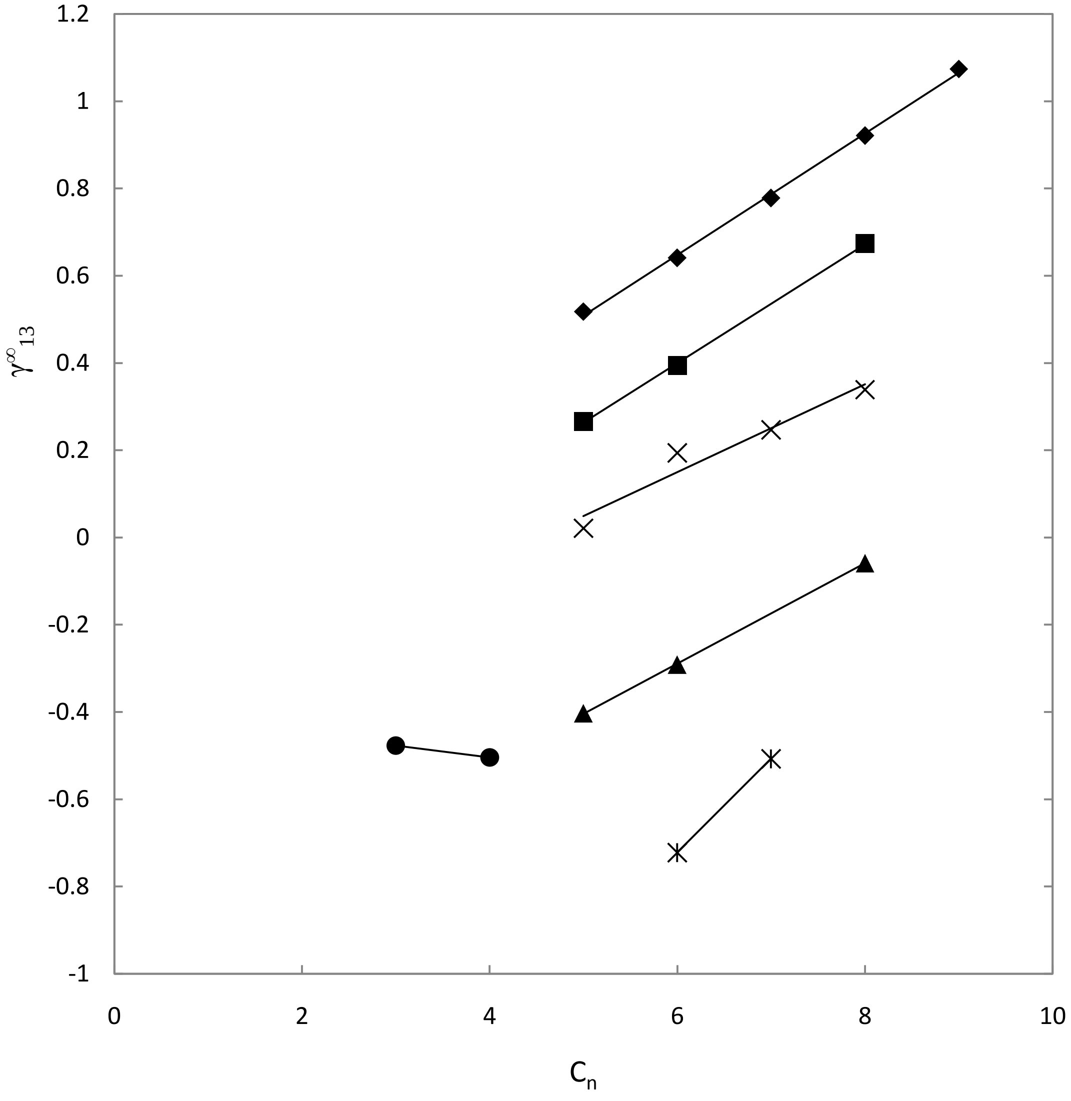

Figure 5.17 Activity coefficients at infinite dilution, γ_{13}^{∞}, versus the carbon number (C_n) at T = 303.15 K: ♦, alkanes; ■, 1-alkenes; ▲, alkynes; ●, ketones; ×, cycloalkanes; *, aromatic hydrocarbons, for IL: methyltrioctylammonium thiosalicylate

CHAPTER 6

6. Discussion

The activity coefficients at infinite dilution were used for the selection of suitable solvents for extractive distillation for the reliable design of thermal separation processes. To access the usefulness of an IL the selectivity and capacity have been determined for the IL: methyltrioctylammonium bis(trifluoromethylsulfonyl)imide and methyltrioctylammonium thiosalicylate.

6.1 Methyltrioctylammonium bis(trifluoromethylsulfonyl)imide [MOA][TF^{2}N]

The error in γ_{13}^{∞} were determined using the "error propagation" method, where the uncertainty in the moles of solvent, net retention volume and temperature are used (see eqn. 14, page 45). From Table 5.1 the γ_{13}^{∞} values obtained from both columns at different temperatures shows a very little or no deviation. This indicates that there was no adsorption of the solute onto the packing. This was also verified by observing that there was no peak tailing. From Table 5.3 the average γ_{13}^{∞} values for alkanes, alkenes, cycloalkanes, and alcohols, decrease with an increase in temperature but also increases with an increase in carbon number at a fixed temperature. For the alkynes the average γ_{13}^{∞} increase with temperature and with an increase in carbon number.

Benzene and the alkynes have the lowest γ_{13}^{∞} values compared to the linear non polar alkanes. This indicates a strong intermolecular interaction between the benzene or alkynes molecules with cation [MOA] of the solvent due to the delocalized π electrons in benzene and the two lone pairs of electrons in alkynes. The alkenes have one lone pair of electrons which can interact with the cation of the IL but to a lesser extent than the benzene and alkynes molecules. The cyclic alkanes are non polar and can interact with the octyl group (non polar) attached to the ammonium cation. The alcohols possible interact through the hydrogen of the OH group with the anion of the IL through hydrogen bonding with the lone pair of electrons on the oxygen atoms. The linear alkanes with less number of carbons have the least interaction with the IL. For a homologous series, the γ_{13}^{∞} values of all solutes (alkanes, alkenes, cycloalkanes alkynes, alcohols, and benzene) increases with an increase in the carbon number see Figure 5.12 to 5.14. The cyclic hydrocarbons have lower γ_{13}^{∞} values than the aliphatic hydrocarbons and for all solutes γ_{13}^{∞} decrease with temperature.

The graphs of ln γ_{13}^{∞} vs $1/T$ was plotted to determine using Gibbs-Helmholtz equation (eqn. 11, given on page 44). All solutes except benzene and alkynes had a positive slope. The graph of ln γ_{13}^{∞} vs $1/T$ for benzene and alkynes had a negetive slope indicating a very strong interaction between the IL and benzene molecules or alkynes molecules.

The $\Delta H_1^{\mathrm{E}\infty}$ values are positive for all the alkanes, alkenes, cycloalkanes and alcohols. The positive $\Delta H_1^{\mathrm{E}\infty}$ values indicate that the addition of a small amount of these solutes results in a decrease in IL-IL or solute-solute interactions. For the alkynes and benzene, the $\Delta H_1^{\mathrm{E}\infty}$ values are negative. This implies that there is an attraction force between solute molecules and the IL. This further indicated a weak induceddipole-dipole interaction between the alkynes or benzene molecules and the cation of the IL.The values of $\Delta H_1^{\mathrm{E}\infty}$ are given in Table 5.5, together with the linear correlation (R^2) values. The error in $\Delta H_1^{\mathrm{E}\infty}$ values is estimated to be < 10 %. For the alkanes, alkenes, cycloalkanes, alkynes, and alcohols, $\Delta H_1^{\mathrm{E}\infty}$ values increase as the carbon number of the akyl chain increases.

The selectivity values for separation of mixtures containing benzene were calculated from the ratio of the γ_{13}^{∞} results at T = (303.15 and 313.15 and 323.15) K, as defined by (Tiegs *et al.* 1986) and are given in Table 5.7.

6.2 Methyltrioctylammonium thiosalicylate [MOA] [TS]

In Table 5.2 the γ_{13}^{∞} values for the two columns are given for the IL, methyltrioctylammonium thiosalicylate. Table 5.4 lists the average γ_{13}^{∞} values of the solutes at different temperatures T = (303.15 and 313.15 and 323.15) K. The γ_{13}^{∞} values within a homologous series (alkanes, alkenes, alkynes, cycloalkanes, and aromatic hydrocarbons) increases with the length of the alkyl chain indicating a decrease in solubility of the IL: methyltrioctylammonium thiosalicylate with increasing carbon number of the carbon solute, for example pentane < hexane <heptanes <octane <nonane. The trend is reversed for ketones where γ_{13}^{∞} values of acetone > butanone. As can be observed from Table 5.4, the γ_{13}^{∞}values of benzene, alkynes and ketones are the lowest when compared to the other three hydrocarbons groups (alkanes, alkenes, and cycloalkanes), this indicated a higher molecular affinity of the aromatic ring, the triple bond such as C≡C, and the polar group such as C=O groups to methyltrioctylammonium thiosalicylate cation. The non polar and less polarised hydrocarbons (alkanes, alkenes, and cycloalkanes) have γ_{13}^{∞} values > 1 because of the low interaction with the IL: methyltrioctylammonium thiosalicylate. The order of the γ_{13}^{∞} results in Table 5.4 is evidence that alkanes are almost immiscible in ionic liquids (Domanska and Laskowska, 2009). Figure 5.15 to 5.17 represents the graphs of γ_{13}^{∞}versus carbon number of the solute.

From Table 5.6 all the $\Delta H_1^{E\infty}$ values increase with the carbon number for all the solutes except for alkynes, aromatic hydrocarbons and ketones (where decrease with an increase in carbon number), similar to the findings of (Domanska and Marciniak, 2008). The alkynes $\Delta H_1^{E\infty}$ values in this work are negative, for aromatic compounds are positive but very small; this indicates higher intermolecular interactions than the rest of the solutes. The minimum regression coefficient (R^2) is 0.93.

From Table 5.8 the selectivities at infinite dilutions for the IL: methyltrioctylammonium thiosalicylate increases for a homologous series except for ketones where it decrease at all temperature. The selectivity values are highest for the alkanes group and > 1 for all solutes. In general the S_{12}^{∞} values are slightly larger for the [MOA] [TS] IL than for [MOA] [TF_2N]. At T = 303.15 K, selectivities were compared for both ionic liquids under this study. Both the selectivity values are almost the same with a highest difference of 0.55. At all temperatures, the selectivity values are greater than 1, which indicated the possibility of methyltrioctylammonium thiosalicylate as an entrainer in extractive distillation. The capacity value for benzene is 2.04 at T = 313.15 K the highest for all the solutes in the IL.

To place this research in context with the available data in literature, the ILs; methyltrioctylammonium thiosalicylate and methyltrioctylammonium bis(trifluoromethylsulfonyl)imide, with similar cations or anions and are compared with literature and summarized in Table 6.1.

Table 6.1 Selectivity values at infinite dilution for hexane/benzene separation for ILs: methyltrioctyl ammonium bis(trifluoromethylsulfonyl)imide and methyltrioctylammonium thiosalicylate and literature ILs

IL	T/ K	S_{12}^{∞}
methyltrioctylammonium bis(trifluoromethylsulfonyl)imide	303.15	3.5
methyltrioctylammonium thiosalicylate	303.15	4.2
1-hexyl-3-methyl-imidazolium bis (trifluoromethylsulfonyl)imide	298.15	12.4
trihexyltetradecylphosphonium bis (2,4,4-trimethylpentyl) phosphinate	308.15	1.5
trihexyl(tetradecyl)- phosphonium tris(pentafluoroethyl) trifluorophosphate	308.15	3.3
trihexyl(tetradecyl)phosphonium bis(trifluoromethylsulfonyl)imide	298.15	2.8
1-hexyl-3-methylimidazolium hexafluorophosphate	298.15	21.6
3-hexyl-1-methylimidazolium tetrafluoroborate	298.15	23
n-ethylpyridinium bis(trifluoromethylsulfonyl)imide	303.15	26.6
1-hexadecyl-3-methylimmidazolium tetrafluoroborate	298.15	2.8
tributylmethylphosphonium methylsulphate	308.15	10.2
1-methyl-3-ethylimidazolium bis(trifluoromethylsulfonyl)imide	313.15	21.5
1,2-dimethyl-3-ethylimidazolium bis(trifluoromethylsulfonyl)imide	313.15	23.4
1-methyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	303.15	29.8
1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	293.15	25.5
1-butyl-3- methylimidazolium bis(trifluoromethylsulfonyl)imide	293.15	17.3
triethylsulphonium bis(trifluoromethylsulfonyl)imide		26.4

The ILs with [TF2N] anions has either a large alkyl (no of carbon atoms) group or a small alkyl group attached to the cation. The S_{12}^{∞} values seem to depend on the carbon atoms of the attached group. The $[Tf_2N]^-$ ILs with shorter alkyl chain have higher S_{12}^{∞} values while those with longer alkyl chain have smaller S_{12}^{∞} values for example, trihexyl(tetradecyl)phosphonium bis(trifluoromethylsulfonyl)imide (20 carbon atoms and S_{12}^{∞} value of 2.8) and 1-methyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (2 carbon atoms, and S_{12}^{∞} value of 2.8). To determine the effect of the type of cation on S_{12}^{∞} , both n-ethylpyridinium bis(trifluoromethylsulfonyl)imide (26.6) and 1-methyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (29.8) have two carbon atoms, but due to C-C group of the alkyl group it seems that this leads to a small S_{12}^{∞} . For other ILs with different anions S_{12}^{∞} values of an IL is influenced by the alkyl group attached i.e. 1-methyl-3-hexylimidazolium tetrafluoroborate and 1-hexyl-3-methyl-imidazolium bis (trifluoromethylsulfonyl)imide both have 7 carbon atoms but different anions and hence different S_{12}^{∞} values of 23 and 12.4. Again it seems that an anion with less or no alkyl groups results in a high S_{12}^{∞} values. Similar for 1-butyl-3- methylimidazolium bis(trifluoromethylsulfonyl)imide (5 carbon atoms and S_{12}^{∞} value of 17.3) and 1-hexyl-3-methylimidazolium hexafluorophosphate (7 carbon atoms and S_{12}^{∞} value of 21.6). All these trends have indicated that not only the size of alkyl chain, type of cation and anion plays a major role in the size of selectivity value. Due to the long alkyl chain contained by the ionic liquid under study, the S_{12}^{∞} values are smaller when compared to S_{12}^{∞} values from the literature. This study serves to benchmark the potential of ILs for extractive distillation purposes.

CONCLUSION

In this work the γ_{13}^{∞} was calculated for Ils; methyltrioctylammonium bis(trifluoromethylsulfonyl)imide and methyltrioctylammonium thiosalicylate. For the IL; methyltrioctylammonium bis (trifluoromethylsulfonyl) imide the γ_{13}^{∞} values ranged between 1.01 to 1.54 for alkanes, 0.78 to 0.89 for alkenes, 0.53 to 0.59 for alkynes, 0.78 to 1.07 for cycloalkanes and 0. 89 to 0.94 for alcohols at T = 303.15 K and for the IL; methyltrioctylammonium thiosalicylate the γ_{13}^{∞} values ranged between 1.81 to 3.16 for alkanes, 1.39 to 2.07 for alkenes, 0.63 to 0.86 for alkynes, 1.09 to 1.57 for cycloalkanes, 0.49 to 0.61 for aromatic hydrocarbons and 0.67 to 0.64 for ketones T = 303.15 K. The γ_{13}^{∞} value for IL; methyltrioctylammonium thiosalicylate is greater than for IL: methyltrioctylammonium bis (trifluoromethylsulfonyl) imide.

From the linear graph of ln γ_{13}^{∞}versuss 1/T, the $\Delta H_{1}^{E\infty}$ was determined using the Gibbs Helmoltz equation. The selectivity values were calculated for both ILs and have been found to be greater than one. For the IL; methyltrioctylammonium thiosalicylate had a greater S_{12}^{∞} value than IL; methyltrioctylammonium bis(trifluoromethylsulfonyl)imide. A comparison of S_{12}^{∞} of the ILs showed that the larger the alkyl group on the anion or cation the smaller the S_{12}^{∞}. Since S_{12}^{∞} is greater than one for both ILs, it can be concluded that both ILs can be used for extractive distilation.

For both Ils the capacity K for benzene was the highest indicating that benzene had the greatest solubility in the Ils.

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APPENDICES

APPENDIX A

A.1 Critical Constant

The critical properties for the solutes used in the calculation of γ_{13}^{∞} are given in Table A.1.

The saturated vapour presure, molar volume and the virial coefficients used in the calculation of γ_{13}^{∞} are given in Table A.2.

Table A.1 Critical constants and ionization energy of the solutes and the carrier gas used in the calculation of the virial coefficients

Solute	T_c/K	P_c/kPa	V_c /cm^{3}mol^{-1}	I/eV
Pentane	469.70	3369.06	304.00	10.35
Hexane	507.40	3014.42	370.00	10.13
Heptane	540.30	2733.75	432.00	9.92
Octane	568.80	2494.62	492.00	9.82
Nonane	594.70	2279.81	555.20	9.72
1-Pentene	464.70	3526.11	300.00	9.51
1-Hexene	504.00	3206.00	350.00	9.44
1-Octene	566.60	2624.32	464.00	9.43
Pentyne	493.40	4053.00	278.00	10.05
Hexyne	539.29	3762.20	331.00	9.95
Octyne	598.46	3100.55	441.00	9.95
Cyclopentane	511.70	4509.98	259.00	10.51
Cyclohexane	553.80	4080.36	308.00	9.86
Cycloheptane	604.20	3819.95	353.00	9.97
Cyclooctane	647.20	3559.55	410.00	9.76
Methanol	512.60	8095.87	118.00	10.85
Ethanol	516.20	6383.48	167.00	10.47
Benzene	562.10	4894.00	259.00	9.25
Toluene	591.70	4113.80	316.00	8.82
Acetone	508.10	4701.48	209.00	9.70
Butan-2-one	535.60	4154.33	267.00	9.52
Helium	5.20	227.46	57.50	24.59

Table A.2 Saturated vapor pressure P_1^*, molar volume V_1^*, virial coefficients B_{11} and B_{12} used in the calculation of γ_{13}^{∞} at T = (303.15 and 313.15 and 323.15) K

Solutes	T /K	P_1^* / kPa	V_1^* / $cm^{3\cdot} mol^{-1}$	B_{11} / $cm^{3\cdot} mol^{-1}$	B_{12} / $cm^{3\cdot} mol^{-1}$
Pentane	303.15	81.54	114.36	-1120	47
	313.15	115.14	116.34	-1031	47
	323.15	158.78	118.44	-952	48
Hexane	303.15	24.91	132.68	-1813	53
	313.15	37.15	134.63	-1655	54
	323.15	53.86	136.69	-1517	55
Heptane	303.15	7.79	149.07	-2758	60
	313.15	12.33	151.03	-2499	60
	323.15	18.85	153.07	-2275	61
Octane	303.15	2.46	164.39	-4001	66
	313.15	4.15	166.37	-3601	66
	323.15	6.72	168.42	-3258	67
Nonane	303.15	0.78	180.13	-5664	72
	313.15	1.41	182.15	-5071	72
	323.15	2.41	184.25	-4563	73
1-Pentene	303.15	100.58	113.64	-1075	47
	313.15	140.60	115.66	-990	47
	323.15	192.25	117.8	-915	48
1-Hexene	303.15	30.46	126.31	-1683	52
	313.15	44.90	128.19	-1536	52
	323.15	64.59	130.17	-1409	53
1-Octene	303.15	3.04	155.59	-3726	63
	313.15	5.05	157.47	-3354	64
	323.15	8.07	159.43	-3036	64
Pentyne	303.15	69.85	104.33	-1166	43
	313.15	100.73	105.91	-1070	44
	323.15	141.48	107.58	-9863	45

Table A.2 Continued

Solutes	T /K	P_1^* / kPa	V_1^* / $cm^{3} \cdot mol^{-1}$	B_{11} / $cm^{3} \cdot mol^{-1}$	B_{12} / $cm^{3} \cdot mol^{-1}$
Hexyne	303.15	21.40	120.34	-1935	49
	313.15	32.54	121.85	-1760	49
	323.15	48.06	123.42	-1609	50
Octyne	303.15	2.27	150.15	-4245	59
	313.15	3.87	151.74	-3810	60
	323.15	6.32	153.39	-3437	61
Cyclopentane	303.15	51.33	95.03	-1198	41
	313.15	73.95	96.37	-1098	41
	323.15	103.81	97.78	-1010	42
Cyclohexane	303.15	16.23	109.03	-1949	46
	313.15	24.63	110.35	-1770	46
	323.15	36.25	111.72	-1615	47
Cycloheptane	303.15	3.75	120.58	-3214	50
	313.15	6.09	121.84	-2893	51
	323.15	9.54	123.13	-2617	51
Cyclooctane	303.15	0.99	136.71	-5163	55
	313.15	1.72	137.97	-4613	56
	323.15	2.87	139.28	-4143	57
Methanol	303.15	21.83	39.27	-360	24
	313.15	35.39	39.87	-340	24
	323.15	55.48	40.51	-321	25
Ethanol	303.15	10.41	54.21	-585	30
	313.15	17.83	55.05	-546	30
Benzene	323.15	15.91	91.23	-1714	40
	303.15	24.38	92.30	-1555	41
	313.15	36.18	93.42	-1418	42
Toluene	323.15	4.89	108.12	-2688	47
	303.15	7.89	109.29	-2422	47
	313.15	12.28	110.50	-2193	48

Table A.2 Continued

Solutes	T /K	P_1^* / kPa	V_1^* / $cm^{3} \cdot mol^{-1}$	B_{11} / $cm^{3} \cdot mol^{-1}$	B_{12} / $cm^{3} \cdot mol^{-1}$
Acetone	303.15	37.77	74.68	-788	35
	313.15	56.25	75.78	-7308	36
	323.15	81.42	76.93	-680	36
Butan-2-one	303.15	15.21	92.86	-1271	42
	313.15	23.64	94.09	-1168	42
	323.15	35.57	95.38	-1078	43

APPENDIX B

B.1 Sample Calculations

1.1 Activity coefficient at infinite dilution for pentane using IL: methyltrioctylammonium bis(trifluoromethylsulfonyl)imide at T = 303.15 K.

$$J_2^3 = \frac{2}{3}\left(\frac{(P_\mathrm{i}/P_\mathrm{o})^3 - 1}{(P_\mathrm{i}/P_\mathrm{o})^2 - 1}\right)$$

$$= \frac{2}{3}\left(\frac{(135810\,\mathrm{Pa}/100310\,\mathrm{Pa})^3 - 1}{(135810\,\mathrm{Pa}/100310\,\mathrm{Pa})^2 - 1}\right)$$

= 0.667 (1.4823/0.8331)

= 1.1868

$$U_\mathrm{o} = U.\left(1 - \frac{P_\mathrm{w}}{P_\mathrm{o}}\right).\frac{T}{T_\mathrm{f}}$$

$$\mathrm{U_o} = 7.283\mathrm{E}\ \text{-}07\ \mathrm{m^3/s}.\left(1 - \frac{2555.40\ \ \mathrm{Pa}}{100310\ \ \mathrm{Pa}}\right).\frac{303.15\ \ \mathrm{K}}{294.65\ \ \mathrm{K}}$$

= 7.283E-07 $\mathrm{m^3/s}$. (-0.975) . 1.0289

= 7.31E-07 $\mathrm{m^3/s}$

$$V_\mathrm{N} = J_2^3.U_\mathrm{O}(t_\mathrm{R} - t_\mathrm{G})$$

$$= 1.1868 * 7.31\text{E} - 07\ \text{m}^3/\text{s} * (93.76\ \text{s} - 20.04\ \text{s})$$

$$= 1.1868 * 7.31\text{E-}07\ \text{m}^3/\text{s} * 73.72\ \text{s}$$

$$= 6.396\text{E-}05\ \text{m}^3$$

The γ_{13}^{∞} equation is subdivided into three terms

Term 1

$$\ln\left(\frac{n_3 RT}{V_{\text{N}} P_1^*}\right)$$

$$\ln\left(\frac{0.002044\text{mol} * 8.315\text{Pa.m}^3\ /\text{K.mol} * 303.15\text{K}}{6.396\text{E-}05\,\text{m}^3 * 81527.67\text{Pa}}\right)$$

In (5.1523/ 5.2145)

= -0.01199

Term 2

$$\left(\frac{(B_{11} - V_1^*)P_1^*}{RT}\right)$$

$$\left(\frac{\left(-0.00112019\text{m}^3/\text{mol} - 0.000114358\,\text{m}^3/\text{mol}\right)81527.67\text{Pa}}{8.315\text{Pa.m}^3\ /\text{K. mol} * 303.15\text{K}}\right)$$

$$= \left(\frac{-100.65}{2520.692}\right)$$

= -0.0399

Term 3

$$\left(\frac{(2B_{12}-V_1^{\infty})P_{\mathrm{o}}J_2^3}{RT}\right)$$

$$\left(\frac{(2*4.67184\text{E-}05\,\mathrm{m^3/mol}-0.000114358\,\mathrm{m^3/mol})100310\,\mathrm{Pa}*1.1868}{8.315\,\mathrm{Pa.m^3/K.mol}*303.15\,\mathrm{K}}\right)$$

(-2.491/2520.692)

= -0.000988

But

$$\text{In }\gamma_{13}^{\infty}=\ln\left(\frac{n_3RT}{V_{\mathrm{N}}P_1^*}\right)-\left(\frac{(B_{11}-V_1^*)P_1^*}{RT}\right)+\left(\frac{(2B_{12}-V_1^{\infty})P_{\mathrm{o}}J_2^3}{RT}\right)$$

Therefore ,

$$\text{In }\gamma_{13}^{\infty}=Term1-Term2+Term3$$

= -0.01199 – (-0.0399) + (-0.000988)

= 0.026922

γ_{13}^{∞} = 1.02

The excess molar enthalpy, selectivity and capacity at infinite dilution were all calculated using the activity coefficient at infinite dilution value above.

1.2 Excess molar enthalpy at infinite dilution for pentane using IL: methyltrioctylammonium bis(trifluoromethylsulfonyl)imide at *T* = 303.15 K.

$$\left[\frac{\partial \ln \gamma_{\mathrm{i}}^{\infty}}{\partial\left(\frac{1}{T}\right)}\right] = \frac{\Delta H_1^{\mathrm{E}\infty}}{R}$$

Where,

$\left[\frac{\partial \ln \gamma_{\mathrm{i}}^{\infty}}{\partial\left(\frac{1}{T}\right)}\right]$ is equal to slope from the graph of In γ_{13}^{∞} versus 1/T .

From the graph, the slope pentane = 214.7

$$214.7 = \frac{\Delta H_1^{\mathrm{E}\infty}}{8.315}$$

$$\Delta H_1^{\mathrm{E}\infty} = 8.315 \times 214.7$$

$$= 1785 \text{ J/mol}$$

1.3 Selectivity at infinite dilution

$$S_{12}^{\infty} = \frac{\gamma_1^{\infty}}{\gamma_2^{\infty}}$$

Where 1 refers to a solute (pentane) and 2 refers to benzene.

Therefore, $S_{12}^{\infty} = \frac{1.027}{0.31}$

$$= 3.3$$

1.4 Capacity at infinite dilution

$$k_1^{\infty} = \frac{1}{\gamma_1^{\infty}}$$

Where 1 referes to the solute (pentane)

Therefore, $K_1^{\infty} = \frac{1}{1.027}$

$$= 0.98$$

B.2 Sample Error Calculations

$$\bar{x}\gamma_{13}^{\infty} = \frac{\sum(x_1 + x_2 + \ldots)}{n}$$

$$= \frac{\sum(1.002+1.002+1.003)}{3}$$

= 1.002

$$\sigma = \frac{\sqrt{\sum(x_1 - \bar{x})^2}}{n-1}$$

$$\sigma = \frac{\sqrt{(1.002-1.0023333)^2} + (1.002-1.0023333)^2 + (1.003-1.0023333)^2}{3-1}$$

σ = 5.773E-04

$$RSD = \frac{s}{\bar{x}}.100$$

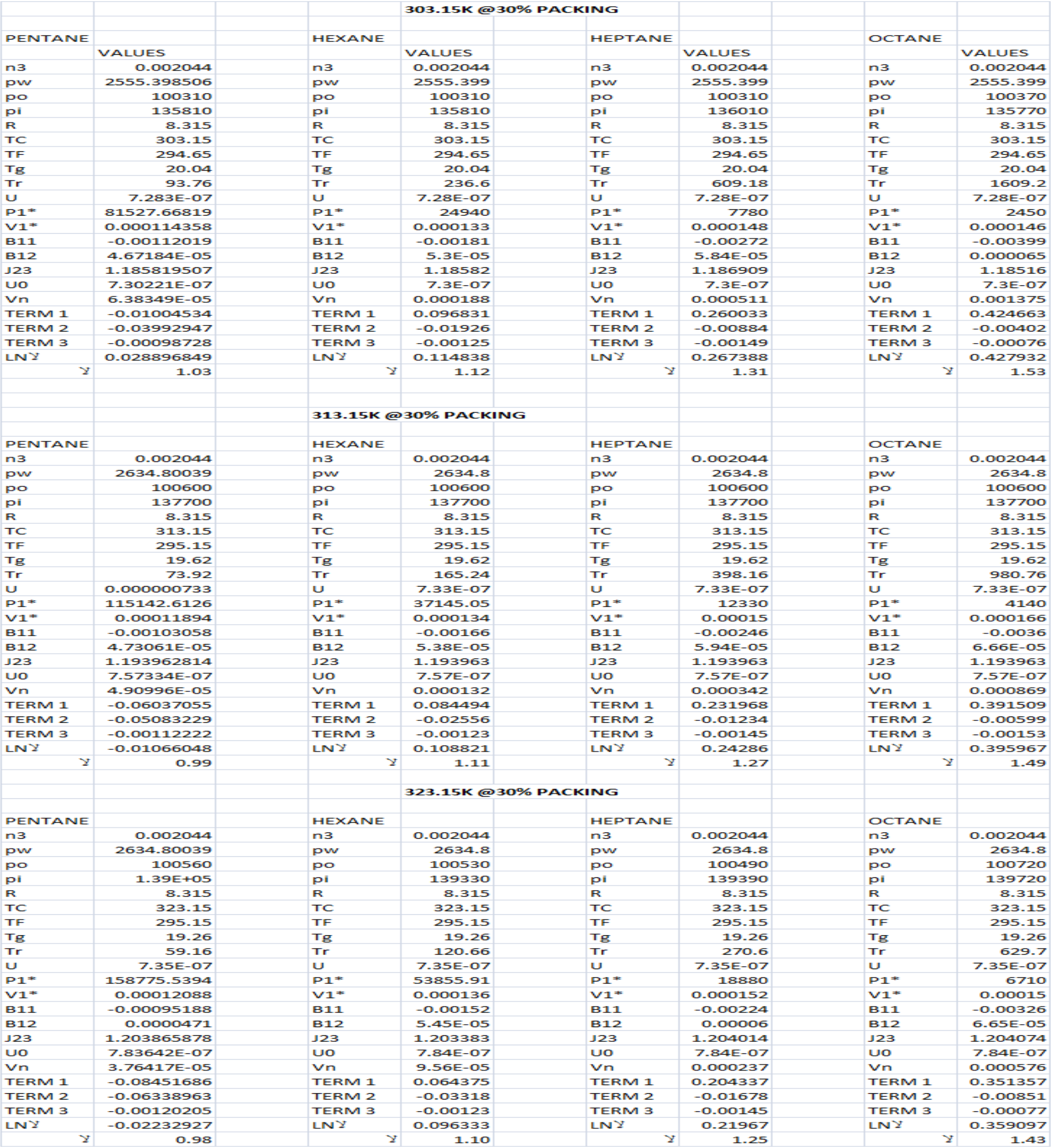
$$RSD = \frac{5.773\text{E-}04}{1.0023333}.100$$

$$= 0.058\ \%$$

APPENDIX C

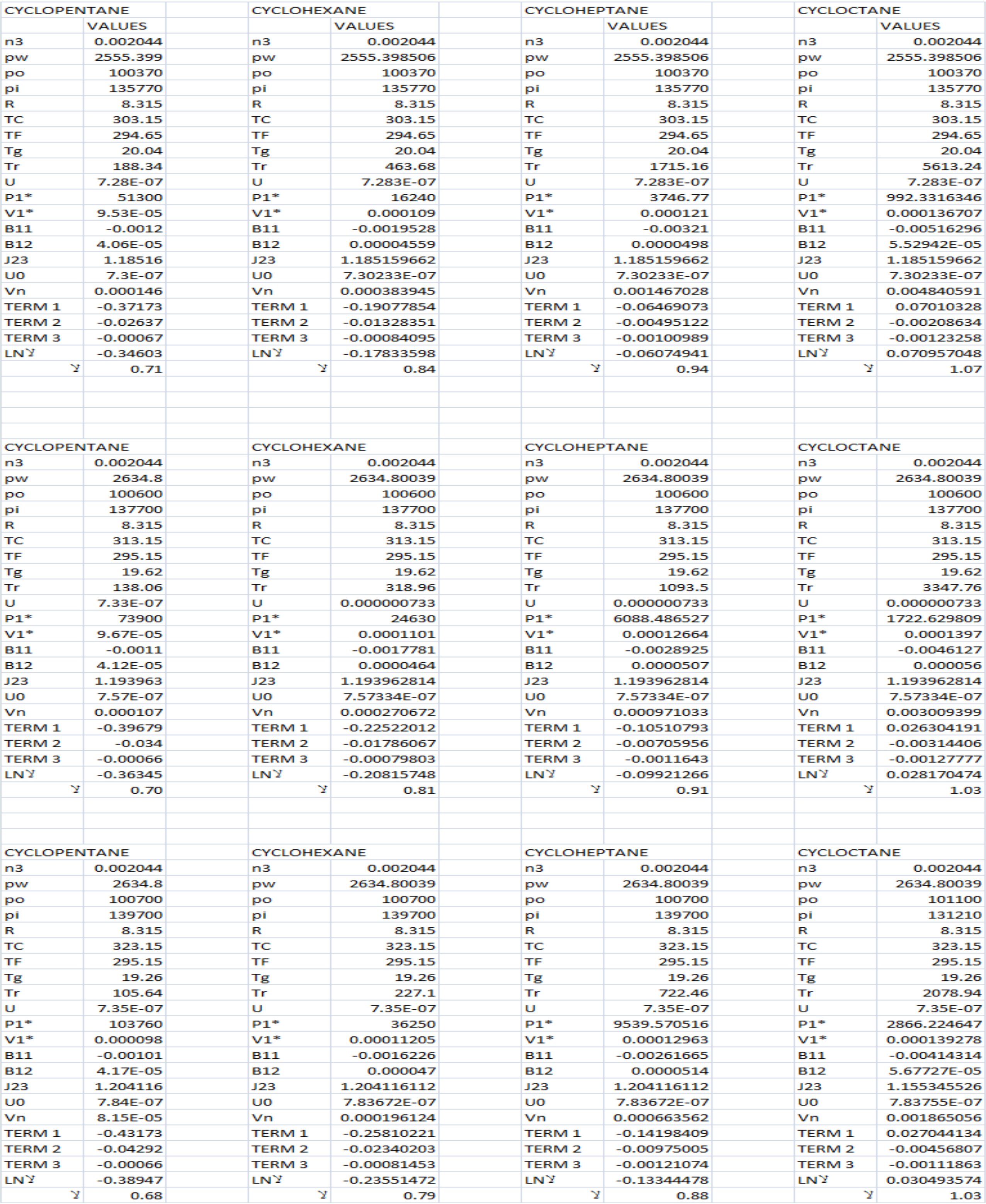
C. Spread sheet calculations for each IL for each column at each temperature

Table C.1 γ_{13}^{∞} calculations for IL: methyltrioctylammonium bis(trifluoromethylsulfonyl)imide for alkanes at T = (303.15 and 313.15 and 323.15) K for a 29.63% column loading



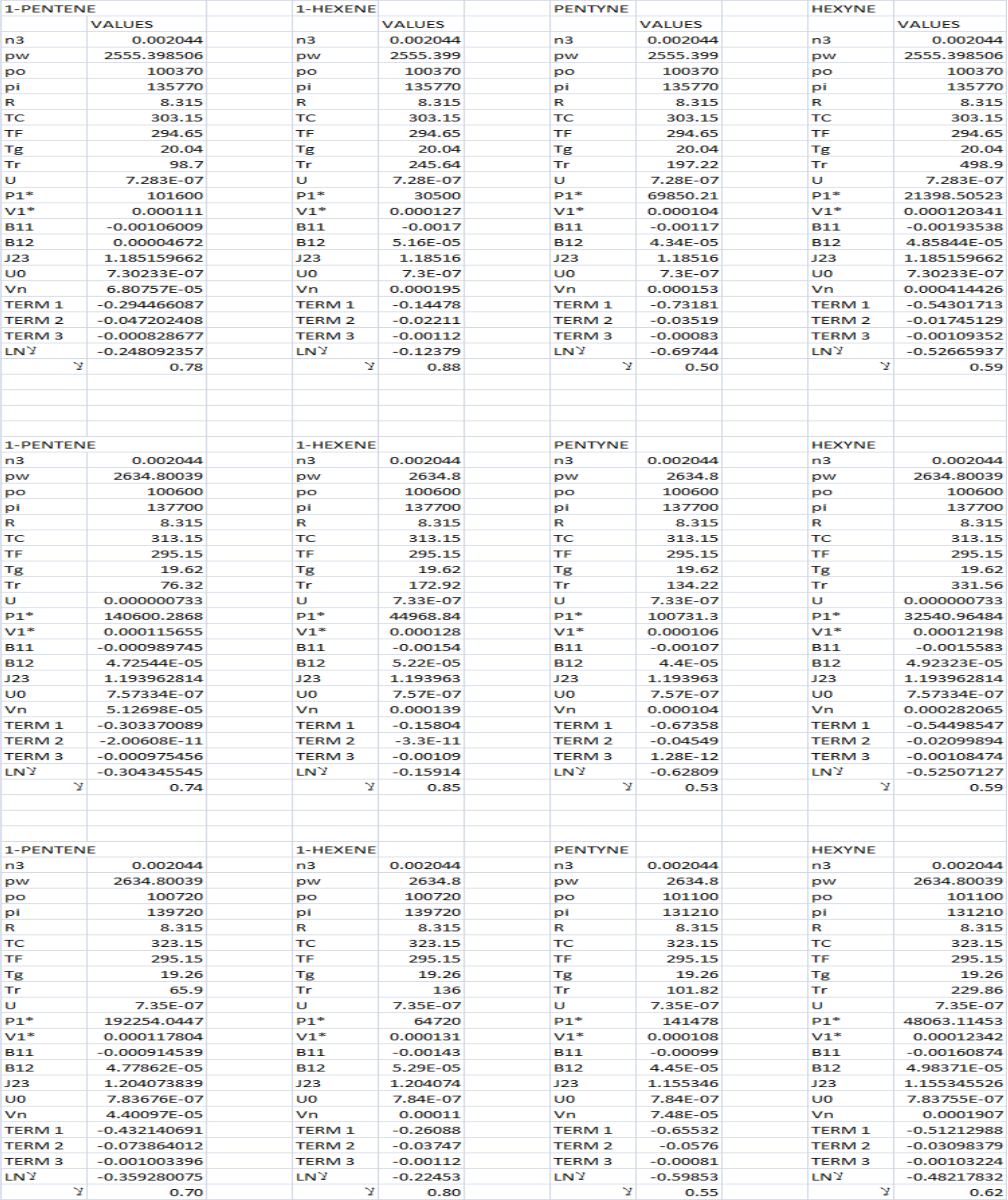
				303.15K @30% PACKING						
PENTANE			HEXANE			HEPTANE			OCTANE	
	VALUES			VALUES			VALUES			VALUES
n3	0.002044		n3	0.002044		n3	0.002044		n3	0.002044
pw	2555.398506		pw	2555.399		pw	2555.399		pw	2555.399
po	100310		po	100310		po	100310		po	100370
pi	135810		pi	135810		pi	136010		pi	135770
R	8.315		R	8.315		R	8.315		R	8.315
TC	303.15		TC	303.15		TC	303.15		TC	303.15
TF	294.65		TF	294.65		TF	294.65		TF	294.65
Tg	20.04		Tg	20.04		Tg	20.04		Tg	20.04
Tr	93.76		Tr	236.6		Tr	609.18		Tr	1609.2
U	7.283E-07		U	7.28E-07		U	7.28E-07		U	7.28E-07
P1*	81527.66819		P1*	24940		P1*	7780		P1*	2450
V1*	0.000114358		V1*	0.000133		V1*	0.000148		V1*	0.000146
B11	-0.00112019		B11	-0.00181		B11	-0.00272		B11	-0.00399
B12	4.67184E-05		B12	5.3E-05		B12	5.84E-05		B12	0.000065
J23	1.185819507		J23	1.18582		J23	1.186909		J23	1.18516
U0	7.30221E-07		U0	7.3E-07		U0	7.3E-07		U0	7.3E-07
Vn	6.38349E-05		Vn	0.000188		Vn	0.000511		Vn	0.001375
TERM 1	-0.01004534		TERM 1	0.096831		TERM 1	0.260033		TERM 1	0.424663
TERM 2	-0.03992947		TERM 2	-0.01926		TERM 2	-0.00884		TERM 2	-0.00402
TERM 3	-0.00098728		TERM 3	-0.00125		TERM 3	-0.00149		TERM 3	-0.00076
LNγ	0.028896849		LNγ	0.114838		LNγ	0.267388		LNγ	0.427932
γ	1.03		γ	1.12		γ	1.31		γ	1.53
			313.15K @30% PACKING							
PENTANE			HEXANE			HEPTANE			OCTANE	
n3	0.002044		n3	0.002044		n3	0.002044		n3	0.002044
pw	2634.80039		pw	2634.8		pw	2634.8		pw	2634.8
po	100600		po	100600		po	100600		po	100600
pi	137700		pi	137700		pi	137700		pi	137700
R	8.315		R	8.315		R	8.315		R	8.315
TC	313.15		TC	313.15		TC	313.15		TC	313.15
TF	295.15		TF	295.15		TF	295.15		TF	295.15
Tg	19.62		Tg	19.62		Tg	19.62		Tg	19.62
Tr	73.92		Tr	165.24		Tr	398.16		Tr	980.76
U	0.000000733		U	7.33E-07		U	7.33E-07		U	7.33E-07
P1*	115142.6126		P1*	37145.05		P1*	12330		P1*	4140
V1*	0.00011894		V1*	0.000134		V1*	0.00015		V1*	0.000166
B11	-0.00103058		B11	-0.00166		B11	-0.00246		B11	-0.0036
B12	4.73061E-05		B12	5.38E-05		B12	5.94E-05		B12	6.66E-05
J23	1.193962814		J23	1.193963		J23	1.193963		J23	1.193963
U0	7.57334E-07		U0	7.57E-07		U0	7.57E-07		U0	7.57E-07
Vn	4.90996E-05		Vn	0.000132		Vn	0.000342		Vn	0.000869
TERM 1	-0.06037055		TERM 1	0.084494		TERM 1	0.231968		TERM 1	0.391509
TERM 2	-0.05083229		TERM 2	-0.02556		TERM 2	-0.01234		TERM 2	-0.00599
TERM 3	-0.00112222		TERM 3	-0.00123		TERM 3	-0.00145		TERM 3	-0.00153
LNγ	-0.01066048		LNγ	0.108821		LNγ	0.24286		LNγ	0.395967
γ	0.99		γ	1.11		γ	1.27		γ	1.49
				323.15K @30% PACKING						
PENTANE			HEXANE			HEPTANE			OCTANE	
n3	0.002044		n3	0.002044		n3	0.002044		n3	0.002044
pw	2634.80039		pw	2634.8		pw	2634.8		pw	2634.8
po	100560		po	100530		po	100490		po	100720
pi	1.39E+05		pi	139330		pi	139390		pi	139720
R	8.315		R	8.315		R	8.315		R	8.315
TC	323.15		TC	323.15		TC	323.15		TC	323.15
TF	295.15		TF	295.15		TF	295.15		TF	295.15
Tg	19.26		Tg	19.26		Tg	19.26		Tg	19.26
Tr	59.16		Tr	120.66		Tr	270.6		Tr	629.7
U	7.35E-07		U	7.35E-07		U	7.35E-07		U	7.35E-07
P1*	158775.5394		P1*	53855.91		P1*	18880		P1*	6710
V1*	0.00012088		V1*	0.000136		V1*	0.000152		V1*	0.00015
B11	-0.00095188		B11	-0.00152		B11	-0.00224		B11	-0.00326
B12	0.0000471		B12	5.45E-05		B12	0.00006		B12	6.65E-05
J23	1.203865878		J23	1.203383		J23	1.204014		J23	1.204074
U0	7.83642E-07		U0	7.84E-07		U0	7.84E-07		U0	7.84E-07
Vn	3.76417E-05		Vn	9.56E-05		Vn	0.000237		Vn	0.000576
TERM 1	-0.08451686		TERM 1	0.064375		TERM 1	0.204337		TERM 1	0.351357
TERM 2	-0.06338963		TERM 2	-0.03318		TERM 2	-0.01678		TERM 2	-0.00851
TERM 3	-0.00120205		TERM 3	-0.00123		TERM 3	-0.00145		TERM 3	-0.00077
LNγ	-0.02232927		LNγ	0.096333		LNγ	0.21967		LNγ	0.359097
γ	0.98		γ	1.10		γ	1.25		γ	1.43

Table C.2 γ_{13}^{∞} calculations for IL: methyltrioctylammonium bis(trifluoromethylsulfonyl)imide for cycloalkanes at T = (303.15 and 313.15 and 323.15) K for a 29.63% column loading



CYCLOPENTANE		CYCLOHEXANE		CYCLOHEPTANE		CYCLOCTANE	
	VALUES		VALUES		VALUES		VALUES
n3	0.002044	n3	0.002044	n3	0.002044	n3	0.002044
pw	2555.399	pw	2555.398506	pw	2555.398506	pw	2555.398506
po	100370	po	100370	po	100370	po	100370
pi	135770	pi	135770	pi	135770	pi	135770
R	8.315	R	8.315	R	8.315	R	8.315
TC	303.15	TC	303.15	TC	303.15	TC	303.15
TF	294.65	TF	294.65	TF	294.65	TF	294.65
Tg	20.04	Tg	20.04	Tg	20.04	Tg	20.04
Tr	188.34	Tr	463.68	Tr	1715.16	Tr	5613.24
U	7.28E-07	U	7.283E-07	U	7.283E-07	U	7.283E-07
P1*	51300	P1*	16240	P1*	3746.77	P1*	992.3316346
V1*	9.53E-05	V1*	0.000109	V1*	0.000121	V1*	0.000136707
B11	-0.0012	B11	-0.0019528	B11	-0.00321	B11	-0.00516296
B12	4.06E-05	B12	0.00004559	B12	0.0000498	B12	5.52942E-05
J23	1.18516	J23	1.185159662	J23	1.185159662	J23	1.185159662
U0	7.3E-07	U0	7.30233E-07	U0	7.30233E-07	U0	7.30233E-07
Vn	0.000146	Vn	0.000383945	Vn	0.001467028	Vn	0.004840591
TERM 1	-0.37173	TERM 1	-0.19077854	TERM 1	-0.06469073	TERM 1	0.07010328
TERM 2	-0.02637	TERM 2	-0.01328351	TERM 2	-0.00495122	TERM 2	-0.00208634
TERM 3	-0.00067	TERM 3	-0.00084095	TERM 3	-0.00100989	TERM 3	-0.00123258
LNγ	-0.34603	LNγ	-0.17833598	LNγ	-0.06074941	LNγ	0.070957048
γ	0.71	γ	0.84	γ	0.94	γ	1.07
CYCLOPENTANE		CYCLOHEXANE		CYCLOHEPTANE		CYCLOCTANE	
n3	0.002044	n3	0.002044	n3	0.002044	n3	0.002044
pw	2634.8	pw	2634.80039	pw	2634.80039	pw	2634.80039
po	100600	po	100600	po	100600	po	100600
pi	137700	pi	137700	pi	137700	pi	137700
R	8.315	R	8.315	R	8.315	R	8.315
TC	313.15	TC	313.15	TC	313.15	TC	313.15
TF	295.15	TF	295.15	TF	295.15	TF	295.15
Tg	19.62	Tg	19.62	Tg	19.62	Tg	19.62
Tr	138.06	Tr	318.96	Tr	1093.5	Tr	3347.76
U	7.33E-07	U	0.000000733	U	0.000000733	U	0.000000733
P1*	73900	P1*	24630	P1*	6088.486527	P1*	1722.629809
V1*	9.67E-05	V1*	0.0001101	V1*	0.00012664	V1*	0.0001397
B11	-0.0011	B11	-0.0017781	B11	-0.0028925	B11	-0.0046127
B12	4.12E-05	B12	0.0000464	B12	0.0000507	B12	0.000056
J23	1.193963	J23	1.193962814	J23	1.193962814	J23	1.193962814
U0	7.57E-07	U0	7.57334E-07	U0	7.57334E-07	U0	7.57334E-07
Vn	0.000107	Vn	0.000270672	Vn	0.000971033	Vn	0.003009399
TERM 1	-0.39679	TERM 1	-0.22522012	TERM 1	-0.10510793	TERM 1	0.026304191
TERM 2	-0.034	TERM 2	-0.01786067	TERM 2	-0.00705956	TERM 2	-0.00314406
TERM 3	-0.00066	TERM 3	-0.00079803	TERM 3	-0.0011643	TERM 3	-0.00127777
LNγ	-0.36345	LNγ	-0.20815748	LNγ	-0.09921266	LNγ	0.028170474
γ	0.70	γ	0.81	γ	0.91	γ	1.03
CYCLOPENTANE		CYCLOHEXANE		CYCLOHEPTANE		CYCLOCTANE	
n3	0.002044	n3	0.002044	n3	0.002044	n3	0.002044
pw	2634.8	pw	2634.80039	pw	2634.80039	pw	2634.80039
po	100700	po	100700	po	100700	po	101100
pi	139700	pi	139700	pi	139700	pi	131210
R	8.315	R	8.315	R	8.315	R	8.315
TC	323.15	TC	323.15	TC	323.15	TC	323.15
TF	295.15	TF	295.15	TF	295.15	TF	295.15
Tg	19.26	Tg	19.26	Tg	19.26	Tg	19.26
Tr	105.64	Tr	227.1	Tr	722.46	Tr	2078.94
U	7.35E-07	U	7.35E-07	U	7.35E-07	U	7.35E-07
P1*	103760	P1*	36250	P1*	9539.570516	P1*	2866.224647
V1*	0.000098	V1*	0.00011205	V1*	0.00012963	V1*	0.000139278
B11	-0.00101	B11	-0.0016226	B11	-0.00261665	B11	-0.00414314
B12	4.17E-05	B12	0.000047	B12	0.0000514	B12	5.67727E-05
J23	1.204116	J23	1.204116112	J23	1.204116112	J23	1.155345526
U0	7.84E-07	U0	7.83672E-07	U0	7.83672E-07	U0	7.83755E-07
Vn	8.15E-05	Vn	0.000196124	Vn	0.000663562	Vn	0.001865056
TERM 1	-0.43173	TERM 1	-0.25810221	TERM 1	-0.14198409	TERM 1	0.027044134
TERM 2	-0.04292	TERM 2	-0.02340203	TERM 2	-0.00975005	TERM 2	-0.00456807
TERM 3	-0.00066	TERM 3	-0.00081453	TERM 3	-0.00121074	TERM 3	-0.00111863
LNγ	-0.38947	LNγ	-0.23551472	LNγ	-0.13344478	LNγ	0.030493574
γ	0.68	γ	0.79	γ	0.88	γ	1.03

Table C.3 γ_{13}^{∞} calculations for IL: methyltrioctylammonium bis(trifluoromethylsulfonyl)imide for alkenes and alkynes at T = (303.15 and 313.15 and 323.15) K for a 29.63% column loading

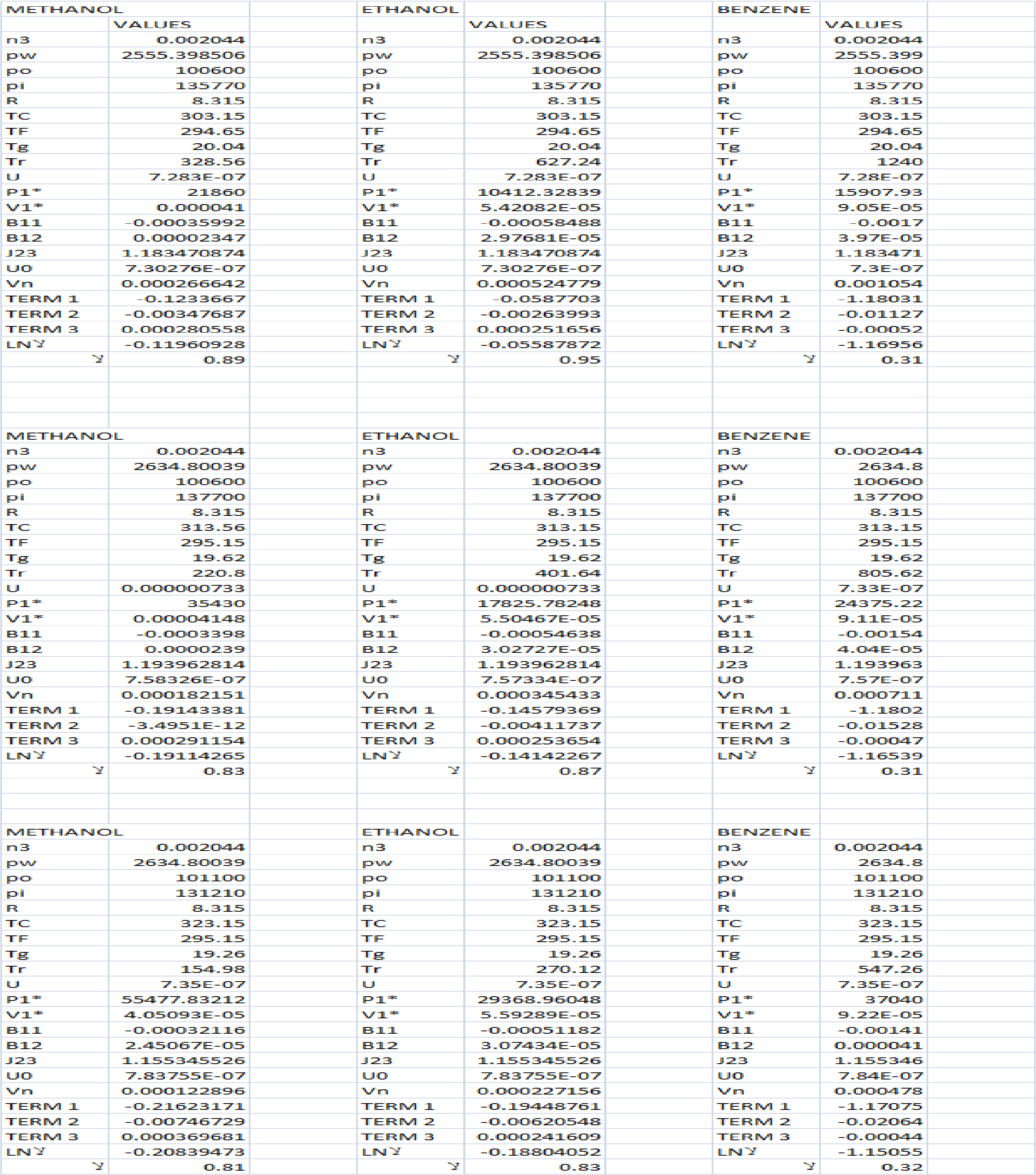


1-PENTENE		1-HEXENE		PENTYNE		HEXYNE	
	VALUES		VALUES		VALUES		VALUES
n3	0.002044	n3	0.002044	n3	0.002044	n3	0.002044
pw	2555.398506	pw	2555.399	pw	2555.399	pw	2555.398506
po	100370	po	100370	po	100370	po	100370
pi	135770	pi	135770	pi	135770	pi	135770
R	8.315	R	8.315	R	8.315	R	8.315
TC	303.15	TC	303.15	TC	303.15	TC	303.15
TF	294.65	TF	294.65	TF	294.65	TF	294.65
Tg	20.04	Tg	20.04	Tg	20.04	Tg	20.04
Tr	98.7	Tr	245.64	Tr	197.22	Tr	498.9
U	7.283E-07	U	7.28E-07	U	7.28E-07	U	7.283E-07
P1*	101600	P1*	30500	P1*	69850.21	P1*	21398.50523
V1*	0.000111	V1*	0.000127	V1*	0.000104	V1*	0.000120341
B11	-0.00106009	B11	-0.0017	B11	-0.00117	B11	-0.00193538
B12	0.00004672	B12	5.16E-05	B12	4.34E-05	B12	4.85844E-05
J23	1.185159662	J23	1.18516	J23	1.18516	J23	1.185159662
U0	7.30233E-07	U0	7.3E-07	U0	7.3E-07	U0	7.30233E-07
Vn	6.80757E-05	Vn	0.000195	Vn	0.000153	Vn	0.000414426
TERM 1	-0.294466087	TERM 1	-0.14478	TERM 1	-0.73181	TERM 1	-0.54301713
TERM 2	-0.047202408	TERM 2	-0.02211	TERM 2	-0.03519	TERM 2	-0.01745129
TERM 3	-0.000828677	TERM 3	-0.00112	TERM 3	-0.00083	TERM 3	-0.00109352
LNƔ	-0.248092357	LNƔ	-0.12379	LNƔ	-0.69744	LNƔ	-0.52665937
Ɣ	0.78	Ɣ	0.88	Ɣ	0.50	Ɣ	0.59

1-PENTENE		1-HEXENE		PENTYNE		HEXYNE	
n3	0.002044	n3	0.002044	n3	0.002044	n3	0.002044
pw	2634.80039	pw	2634.8	pw	2634.8	pw	2634.80039
po	100600	po	100600	po	100600	po	100600
pi	137700	pi	137700	pi	137700	pi	137700
R	8.315	R	8.315	R	8.315	R	8.315
TC	313.15	TC	313.15	TC	313.15	TC	313.15
TF	295.15	TF	295.15	TF	295.15	TF	295.15
Tg	19.62	Tg	19.62	Tg	19.62	Tg	19.62
Tr	76.32	Tr	172.92	Tr	134.22	Tr	331.56
U	0.000000733	U	7.33E-07	U	7.33E-07	U	0.000000733
P1*	140600.2868	P1*	44968.84	P1*	100731.3	P1*	32540.96484
V1*	0.000115655	V1*	0.000128	V1*	0.000106	V1*	0.00012198
B11	-0.000989745	B11	-0.00154	B11	-0.00107	B11	-0.0015583
B12	4.72544E-05	B12	5.22E-05	B12	4.4E-05	B12	4.92323E-05
J23	1.193962814	J23	1.193963	J23	1.193963	J23	1.193962814
U0	7.57334E-07	U0	7.57E-07	U0	7.57E-07	U0	7.57334E-07
Vn	5.12698E-05	Vn	0.000139	Vn	0.000104	Vn	0.000282065
TERM 1	-0.303370089	TERM 1	-0.15804	TERM 1	-0.67358	TERM 1	-0.54498547
TERM 2	-2.00608E-11	TERM 2	-3.3E-11	TERM 2	-0.04549	TERM 2	-0.02099894
TERM 3	-0.000975456	TERM 3	-0.00109	TERM 3	1.28E-12	TERM 3	-0.00108474
LNƔ	-0.304345545	LNƔ	-0.15914	LNƔ	-0.62809	LNƔ	-0.52507127
Ɣ	0.74	Ɣ	0.85	Ɣ	0.53	Ɣ	0.59

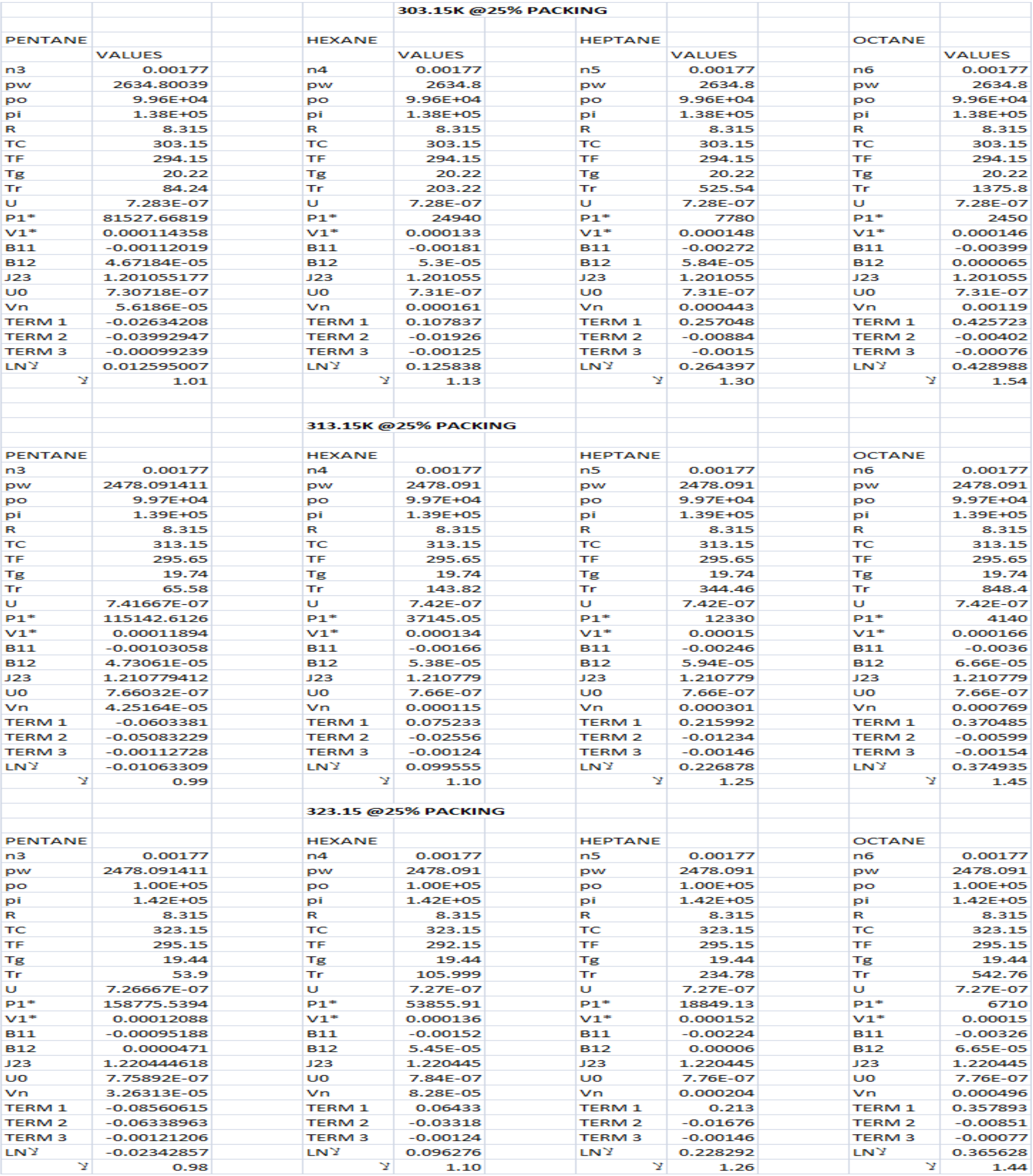
1-PENTENE		1-HEXENE		PENTYNE		HEXYNE	
n3	0.002044	n3	0.002044	n3	0.002044	n3	0.002044
pw	2634.80039	pw	2634.8	pw	2634.8	pw	2634.80039
po	100720	po	100720	po	101100	po	101100
pi	139720	pi	139720	pi	131210	pi	131210
R	8.315	R	8.315	R	8.315	R	8.315
TC	323.15	TC	323.15	TC	323.15	TC	323.15
TF	295.15	TF	295.15	TF	295.15	TF	295.15
Tg	19.26	Tg	19.26	Tg	19.26	Tg	19.26
Tr	65.9	Tr	136	Tr	101.82	Tr	229.86
U	7.35E-07	U	7.35E-07	U	7.35E-07	U	7.35E-07
P1*	192254.0447	P1*	64720	P1*	141478	P1*	48063.11453
V1*	0.000117804	V1*	0.000131	V1*	0.000108	V1*	0.00012342
B11	-0.000914539	B11	-0.00143	B11	-0.00099	B11	-0.00160874
B12	4.77862E-05	B12	5.29E-05	B12	4.45E-05	B12	4.98371E-05
J23	1.204073839	J23	1.204074	J23	1.155346	J23	1.155345526
U0	7.83676E-07	U0	7.84E-07	U0	7.84E-07	U0	7.83755E-07
Vn	4.40097E-05	Vn	0.00011	Vn	7.48E-05	Vn	0.0001907
TERM 1	-0.432140691	TERM 1	-0.26088	TERM 1	-0.65532	TERM 1	-0.51212988
TERM 2	-0.073864012	TERM 2	-0.03747	TERM 2	-0.0576	TERM 2	-0.03098379
TERM 3	-0.001003396	TERM 3	-0.00112	TERM 3	-0.00081	TERM 3	-0.00103224
LNƔ	-0.359280075	LNƔ	-0.22453	LNƔ	-0.59853	LNƔ	-0.48217832
Ɣ	0.70	Ɣ	0.80	Ɣ	0.55	Ɣ	0.62

Table C.4 γ_{13}^{∞} calculations for IL: methyltrioctylammonium bis(trifluoromethylsulfonyl)imide for alcohols and benzene at T = (303.15 and 313.15 and 323.15) K for a 29.63% column loading



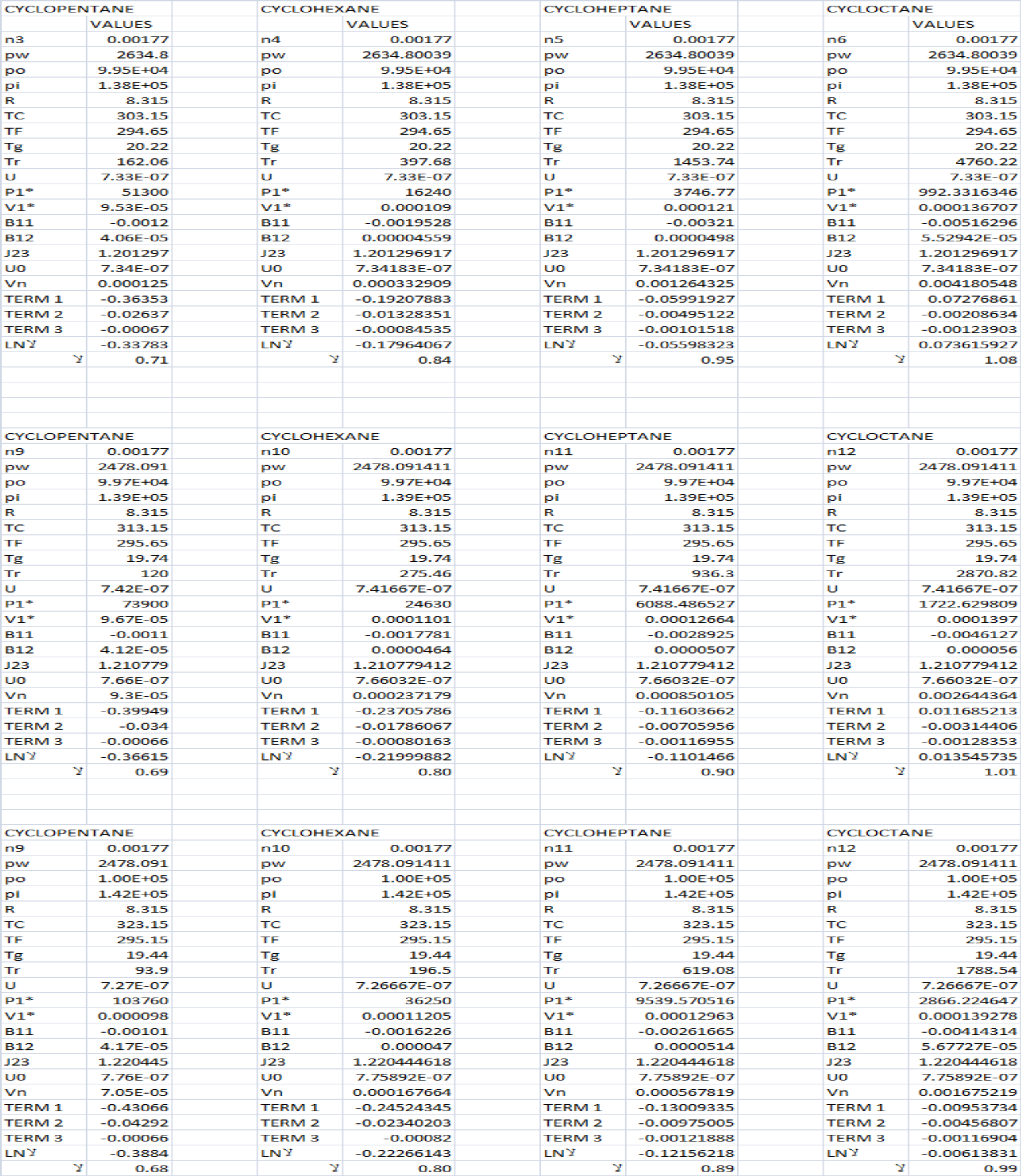
METHANOL			ETHANOL			BENZENE		
	VALUES			VALUES			VALUES	
n3	0.002044		n3	0.002044		n3	0.002044	
pw	2555.398506		pw	2555.398506		pw	2555.399	
po	100600		po	100600		po	100600	
pi	135770		pi	135770		pi	135770	
R	8.315		R	8.315		R	8.315	
TC	303.15		TC	303.15		TC	303.15	
TF	294.65		TF	294.65		TF	294.65	
Tg	20.04		Tg	20.04		Tg	20.04	
Tr	328.56		Tr	627.24		Tr	1240	
U	7.283E-07		U	7.283E-07		U	7.28E-07	
P1*	21860		P1*	10412.32839		P1*	15907.93	
V1*	0.000041		V1*	5.42082E-05		V1*	9.05E-05	
B11	-0.00035992		B11	-0.00058488		B11	-0.0017	
B12	0.00002347		B12	2.97681E-05		B12	3.97E-05	
J23	1.183470874		J23	1.183470874		J23	1.183471	
U0	7.30276E-07		U0	7.30276E-07		U0	7.3E-07	
Vn	0.000266642		Vn	0.000524779		Vn	0.001054	
TERM 1	-0.1233667		TERM 1	-0.0587703		TERM 1	-1.18031	
TERM 2	-0.00347687		TERM 2	-0.00263993		TERM 2	-0.01127	
TERM 3	0.000280558		TERM 3	0.000251656		TERM 3	-0.00052	
LNγ	-0.11960928		LNγ	-0.05587872		LNγ	-1.16956	
γ	0.89		γ	0.95		γ	0.31	
METHANOL			ETHANOL			BENZENE		
n3	0.002044		n3	0.002044		n3	0.002044	
pw	2634.80039		pw	2634.80039		pw	2634.8	
po	100600		po	100600		po	100600	
pi	137700		pi	137700		pi	137700	
R	8.315		R	8.315		R	8.315	
TC	313.56		TC	313.15		TC	313.15	
TF	295.15		TF	295.15		TF	295.15	
Tg	19.62		Tg	19.62		Tg	19.62	
Tr	220.8		Tr	401.64		Tr	805.62	
U	0.000000733		U	0.000000733		U	7.33E-07	
P1*	35430		P1*	17825.78248		P1*	24375.22	
V1*	0.00004148		V1*	5.50467E-05		V1*	9.11E-05	
B11	-0.0003398		B11	-0.00054638		B11	-0.00154	
B12	0.0000239		B12	3.02727E-05		B12	4.04E-05	
J23	1.193962814		J23	1.193962814		J23	1.193963	
U0	7.58326E-07		U0	7.57334E-07		U0	7.57E-07	
Vn	0.000182151		Vn	0.000345433		Vn	0.000711	
TERM 1	-0.19143381		TERM 1	-0.14579369		TERM 1	-1.1802	
TERM 2	-3.4951E-12		TERM 2	-0.00411737		TERM 2	-0.01528	
TERM 3	0.000291154		TERM 3	0.000253654		TERM 3	-0.00047	
LNγ	-0.19114265		LNγ	-0.14142267		LNγ	-1.16539	
γ	0.83		γ	0.87		γ	0.31	
METHANOL			ETHANOL			BENZENE		
n3	0.002044		n3	0.002044		n3	0.002044	
pw	2634.80039		pw	2634.80039		pw	2634.8	
po	101100		po	101100		po	101100	
pi	131210		pi	131210		pi	131210	
R	8.315		R	8.315		R	8.315	
TC	323.15		TC	323.15		TC	323.15	
TF	295.15		TF	295.15		TF	295.15	
Tg	19.26		Tg	19.26		Tg	19.26	
Tr	154.98		Tr	270.12		Tr	547.26	
U	7.35E-07		U	7.35E-07		U	7.35E-07	
P1*	55477.83212		P1*	29368.96048		P1*	37040	
V1*	4.05093E-05		V1*	5.59289E-05		V1*	9.22E-05	
B11	-0.00032116		B11	-0.00051182		B11	-0.00141	
B12	2.45067E-05		B12	3.07434E-05		B12	0.000041	
J23	1.155345526		J23	1.155345526		J23	1.155346	
U0	7.83755E-07		U0	7.83755E-07		U0	7.84E-07	
Vn	0.000122896		Vn	0.000227156		Vn	0.000478	
TERM 1	-0.21623171		TERM 1	-0.19448761		TERM 1	-1.17075	
TERM 2	-0.00746729		TERM 2	-0.00620548		TERM 2	-0.02064	
TERM 3	0.000369681		TERM 3	0.000241609		TERM 3	-0.00044	
LNγ	-0.20839473		LNγ	-0.18804052		LNγ	-1.15055	
γ	0.81		γ	0.83		γ	0.32	

Table C.5 γ_{13}^{∞} calculations for IL: methyltrioctylammonium bis(trifluoromethylsulfonyl)imide for alkanes at T = (303.15 and 313.15 and 323.15) K for a 25.33% column loading



				303.15K @25% PACKING						
PENTANE			HEXANE			HEPTANE			OCTANE	
	VALUES			VALUES			VALUES			VALUES
n3	0.00177		n4	0.00177		n5	0.00177		n6	0.00177
pw	2634.80039		pw	2634.8		pw	2634.8		pw	2634.8
po	9.96E+04		po	9.96E+04		po	9.96E+04		po	9.96E+04
pi	1.38E+05		pi	1.38E+05		pi	1.38E+05		pi	1.38E+05
R	8.315		R	8.315		R	8.315		R	8.315
TC	303.15		TC	303.15		TC	303.15		TC	303.15
TF	294.15		TF	294.15		TF	294.15		TF	294.15
Tg	20.22		Tg	20.22		Tg	20.22		Tg	20.22
Tr	84.24		Tr	203.22		Tr	525.54		Tr	1375.8
U	7.283E-07		U	7.28E-07		U	7.28E-07		U	7.28E-07
P1*	81527.66819		P1*	24940		P1*	7780		P1*	2450
V1*	0.000114358		V1*	0.000133		V1*	0.000148		V1*	0.000146
B11	-0.00112019		B11	-0.00181		B11	-0.00272		B11	-0.00399
B12	4.67184E-05		B12	5.3E-05		B12	5.84E-05		B12	0.000065
J23	1.201055177		J23	1.201055		J23	1.201055		J23	1.201055
U0	7.30718E-07		U0	7.31E-07		U0	7.31E-07		U0	7.31E-07
Vn	5.6186E-05		Vn	0.000161		Vn	0.000443		Vn	0.00119
TERM 1	-0.02634208		TERM 1	0.107837		TERM 1	0.257048		TERM 1	0.425723
TERM 2	-0.03992947		TERM 2	-0.01926		TERM 2	-0.00884		TERM 2	-0.00402
TERM 3	-0.00099239		TERM 3	-0.00125		TERM 3	-0.0015		TERM 3	-0.00076
LNƔ	0.012595007		LNƔ	0.125838		LNƔ	0.264397		LNƔ	0.428988
Ɣ	1.01		Ɣ	1.13		Ɣ	1.30		Ɣ	1.54
			313.15K @25% PACKING							
PENTANE			HEXANE			HEPTANE			OCTANE	
n3	0.00177		n4	0.00177		n5	0.00177		n6	0.00177
pw	2478.091411		pw	2478.091		pw	2478.091		pw	2478.091
po	9.97E+04		po	9.97E+04		po	9.97E+04		po	9.97E+04
pi	1.39E+05		pi	1.39E+05		pi	1.39E+05		pi	1.39E+05
R	8.315		R	8.315		R	8.315		R	8.315
TC	313.15		TC	313.15		TC	313.15		TC	313.15
TF	295.65		TF	295.65		TF	295.65		TF	295.65
Tg	19.74		Tg	19.74		Tg	19.74		Tg	19.74
Tr	65.58		Tr	143.82		Tr	344.46		Tr	848.4
U	7.41667E-07		U	7.42E-07		U	7.42E-07		U	7.42E-07
P1*	115142.6126		P1*	37145.05		P1*	12330		P1*	4140
V1*	0.00011894		V1*	0.000134		V1*	0.00015		V1*	0.000166
B11	-0.00103058		B11	-0.00166		B11	-0.00246		B11	-0.0036
B12	4.73061E-05		B12	5.38E-05		B12	5.94E-05		B12	6.66E-05
J23	1.210779412		J23	1.210779		J23	1.210779		J23	1.210779
U0	7.66032E-07		U0	7.66E-07		U0	7.66E-07		U0	7.66E-07
Vn	4.25164E-05		Vn	0.000115		Vn	0.000301		Vn	0.000769
TERM 1	-0.0603381		TERM 1	0.075233		TERM 1	0.215992		TERM 1	0.370485
TERM 2	-0.05083229		TERM 2	-0.02556		TERM 2	-0.01234		TERM 2	-0.00599
TERM 3	-0.00112728		TERM 3	-0.00124		TERM 3	-0.00146		TERM 3	-0.00154
LNƔ	-0.01063309		LNƔ	0.099555		LNƔ	0.226878		LNƔ	0.374935
Ɣ	0.99		Ɣ	1.10		Ɣ	1.25		Ɣ	1.45
			323.15 @25% PACKING							
PENTANE			HEXANE			HEPTANE			OCTANE	
n3	0.00177		n4	0.00177		n5	0.00177		n6	0.00177
pw	2478.091411		pw	2478.091		pw	2478.091		pw	2478.091
po	1.00E+05		po	1.00E+05		po	1.00E+05		po	1.00E+05
pi	1.42E+05		pi	1.42E+05		pi	1.42E+05		pi	1.42E+05
R	8.315		R	8.315		R	8.315		R	8.315
TC	323.15		TC	323.15		TC	323.15		TC	323.15
TF	295.15		TF	292.15		TF	295.15		TF	295.15
Tg	19.44		Tg	19.44		Tg	19.44		Tg	19.44
Tr	53.9		Tr	105.999		Tr	234.78		Tr	542.76
U	7.26667E-07		U	7.27E-07		U	7.27E-07		U	7.27E-07
P1*	158775.5394		P1*	53855.91		P1*	18849.13		P1*	6710
V1*	0.00012088		V1*	0.000136		V1*	0.000152		V1*	0.00015
B11	-0.00095188		B11	-0.00152		B11	-0.00224		B11	-0.00326
B12	0.0000471		B12	5.45E-05		B12	0.00006		B12	6.65E-05
J23	1.220444618		J23	1.220445		J23	1.220445		J23	1.220445
U0	7.75892E-07		U0	7.84E-07		U0	7.76E-07		U0	7.76E-07
Vn	3.26313E-05		Vn	8.28E-05		Vn	0.000204		Vn	0.000496
TERM 1	-0.08560615		TERM 1	0.06433		TERM 1	0.213		TERM 1	0.357893
TERM 2	-0.06338963		TERM 2	-0.03318		TERM 2	-0.01676		TERM 2	-0.00851
TERM 3	-0.00121206		TERM 3	-0.00124		TERM 3	-0.00146		TERM 3	-0.00077
LNƔ	-0.02342857		LNƔ	0.096276		LNƔ	0.228292		LNƔ	0.365628
Ɣ	0.98		Ɣ	1.10		Ɣ	1.26		Ɣ	1.44

Table C.6 γ_{13}^{∞} calculations for IL: methyltrioctylammonium bis(trifluoromethylsulfonyl)imide for cycloalkanes at T = (303.15 and 313.15 and 323.15) K for a 25.33% column loading

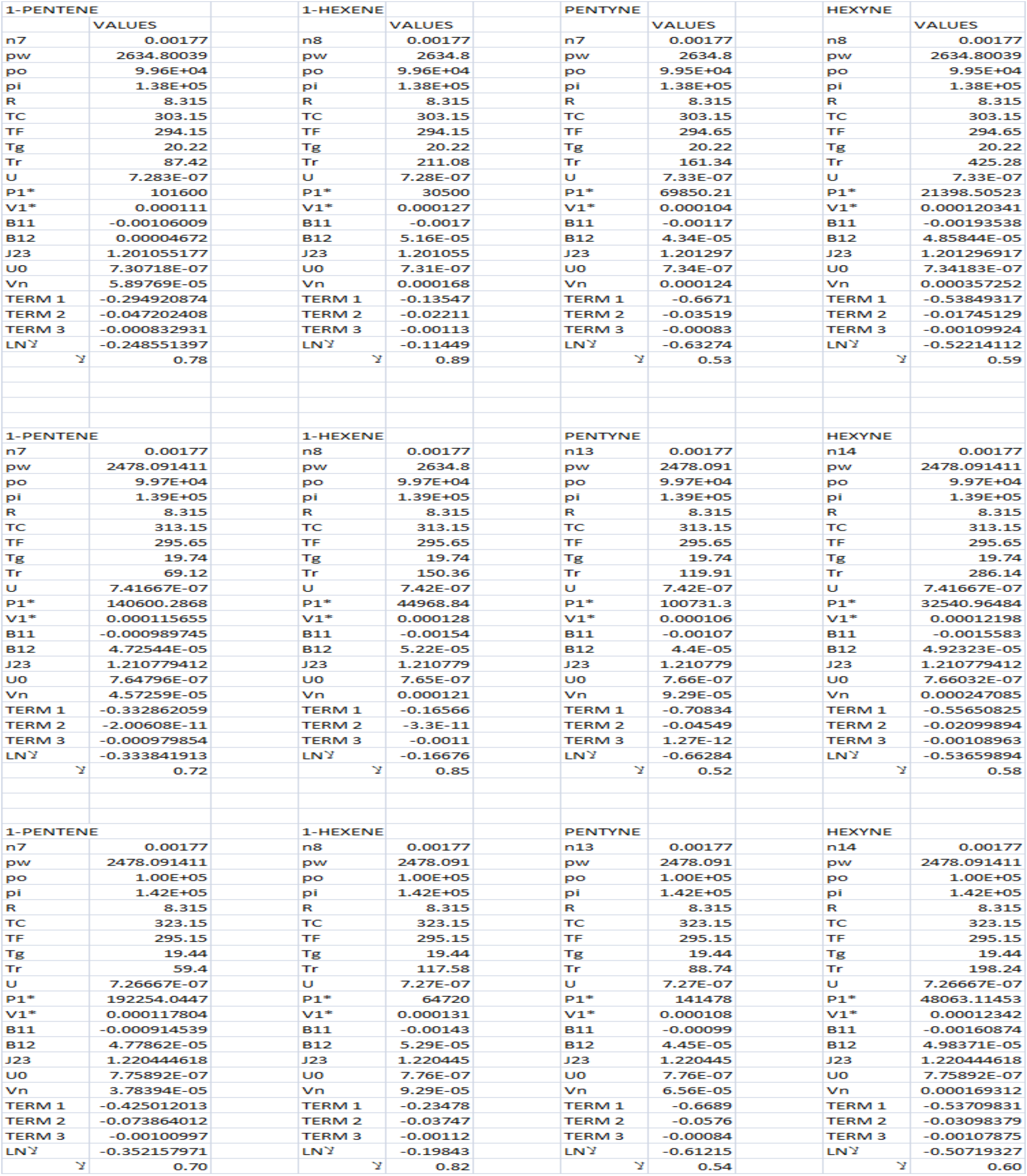


CYCLOPENTANE		CYCLOHEXANE		CYCLOHEPTANE		CYCLOCTANE	
	VALUES		VALUES		VALUES		VALUES
n3	0.00177	n4	0.00177	n5	0.00177	n6	0.00177
pw	2634.8	pw	2634.80039	pw	2634.80039	pw	2634.80039
po	9.95E+04	po	9.95E+04	po	9.95E+04	po	9.95E+04
pi	1.38E+05	pi	1.38E+05	pi	1.38E+05	pi	1.38E+05
R	8.315	R	8.315	R	8.315	R	8.315
TC	303.15	TC	303.15	TC	303.15	TC	303.15
TF	294.65	TF	294.65	TF	294.65	TF	294.65
Tg	20.22	Tg	20.22	Tg	20.22	Tg	20.22
Tr	162.06	Tr	397.68	Tr	1453.74	Tr	4760.22
U	7.33E-07	U	7.33E-07	U	7.33E-07	U	7.33E-07
P1*	51300	P1*	16240	P1*	3746.77	P1*	992.3316346
V1*	9.53E-05	V1*	0.000109	V1*	0.000121	V1*	0.000136707
B11	-0.0012	B11	-0.0019528	B11	-0.00321	B11	-0.00516296
B12	4.06E-05	B12	0.00004559	B12	0.0000498	B12	5.52942E-05
J23	1.201297	J23	1.201296917	J23	1.201296917	J23	1.201296917
U0	7.34E-07	U0	7.34183E-07	U0	7.34183E-07	U0	7.34183E-07
Vn	0.000125	Vn	0.000332909	Vn	0.001264325	Vn	0.004180548
TERM 1	-0.36353	TERM 1	-0.19207883	TERM 1	-0.05991927	TERM 1	0.07276861
TERM 2	-0.02637	TERM 2	-0.01328351	TERM 2	-0.00495122	TERM 2	-0.00208634
TERM 3	-0.00067	TERM 3	-0.00084535	TERM 3	-0.00101518	TERM 3	-0.00123903
LNɣ	-0.33783	LNɣ	-0.17964067	LNɣ	-0.05598323	LNɣ	0.073615927
ɣ	0.71	ɣ	0.84	ɣ	0.95	ɣ	1.08

CYCLOPENTANE		CYCLOHEXANE		CYCLOHEPTANE		CYCLOCTANE	
n9	0.00177	n10	0.00177	n11	0.00177	n12	0.00177
pw	2478.091	pw	2478.091411	pw	2478.091411	pw	2478.091411
po	9.97E+04	po	9.97E+04	po	9.97E+04	po	9.97E+04
pi	1.39E+05	pi	1.39E+05	pi	1.39E+05	pi	1.39E+05
R	8.315	R	8.315	R	8.315	R	8.315
TC	313.15	TC	313.15	TC	313.15	TC	313.15
TF	295.65	TF	295.65	TF	295.65	TF	295.65
Tg	19.74	Tg	19.74	Tg	19.74	Tg	19.74
Tr	120	Tr	275.46	Tr	936.3	Tr	2870.82
U	7.42E-07	U	7.41667E-07	U	7.41667E-07	U	7.41667E-07
P1*	73900	P1*	24630	P1*	6088.486527	P1*	1722.629809
V1*	9.67E-05	V1*	0.0001101	V1*	0.00012664	V1*	0.0001397
B11	-0.0011	B11	-0.0017781	B11	-0.0028925	B11	-0.0046127
B12	4.12E-05	B12	0.0000464	B12	0.0000507	B12	0.000056
J23	1.210779	J23	1.210779412	J23	1.210779412	J23	1.210779412
U0	7.66E-07	U0	7.66032E-07	U0	7.66032E-07	U0	7.66032E-07
Vn	9.3E-05	Vn	0.000237179	Vn	0.000850105	Vn	0.002644364
TERM 1	-0.39949	TERM 1	-0.23705786	TERM 1	-0.11603662	TERM 1	0.011685213
TERM 2	-0.034	TERM 2	-0.01786067	TERM 2	-0.00705956	TERM 2	-0.00314406
TERM 3	-0.00066	TERM 3	-0.00080163	TERM 3	-0.00116955	TERM 3	-0.00128353
LNɣ	-0.36615	LNɣ	-0.21999882	LNɣ	-0.1101466	LNɣ	0.013545735
ɣ	0.69	ɣ	0.80	ɣ	0.90	ɣ	1.01

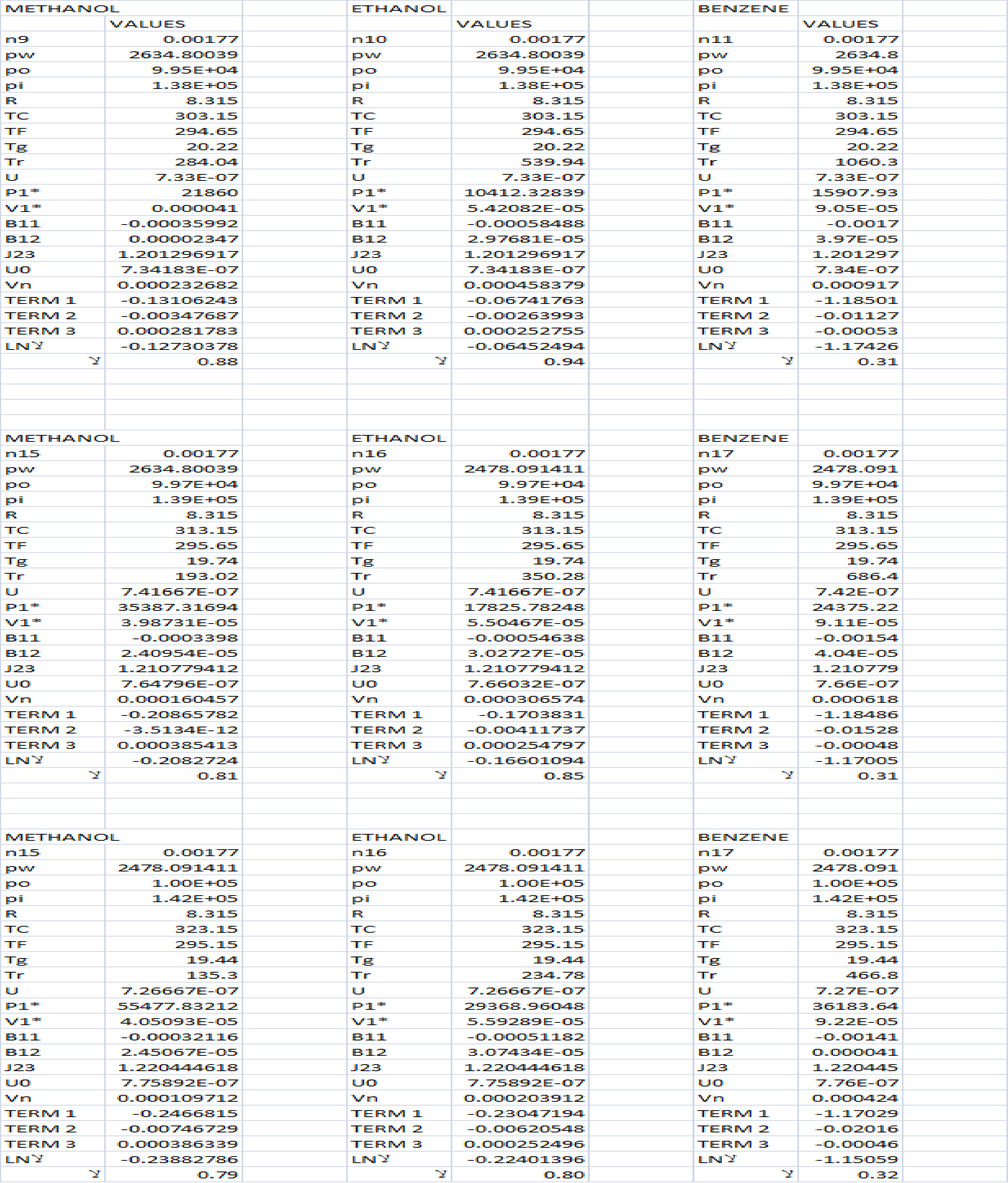
CYCLOPENTANE		CYCLOHEXANE		CYCLOHEPTANE		CYCLOCTANE	
n9	0.00177	n10	0.00177	n11	0.00177	n12	0.00177
pw	2478.091	pw	2478.091411	pw	2478.091411	pw	2478.091411
po	1.00E+05	po	1.00E+05	po	1.00E+05	po	1.00E+05
pi	1.42E+05	pi	1.42E+05	pi	1.42E+05	pi	1.42E+05
R	8.315	R	8.315	R	8.315	R	8.315
TC	323.15	TC	323.15	TC	323.15	TC	323.15
TF	295.15	TF	295.15	TF	295.15	TF	295.15
Tg	19.44	Tg	19.44	Tg	19.44	Tg	19.44
Tr	93.9	Tr	196.5	Tr	619.08	Tr	1788.54
U	7.27E-07	U	7.26667E-07	U	7.26667E-07	U	7.26667E-07
P1*	103760	P1*	36250	P1*	9539.570516	P1*	2866.224647
V1*	0.000098	V1*	0.00011205	V1*	0.00012963	V1*	0.000139278
B11	-0.00101	B11	-0.0016226	B11	-0.00261665	B11	-0.00414314
B12	4.17E-05	B12	0.000047	B12	0.0000514	B12	5.67727E-05
J23	1.220445	J23	1.220444618	J23	1.220444618	J23	1.220444618
U0	7.76E-07	U0	7.75892E-07	U0	7.75892E-07	U0	7.75892E-07
Vn	7.05E-05	Vn	0.000167664	Vn	0.000567819	Vn	0.001675219
TERM 1	-0.43066	TERM 1	-0.24524345	TERM 1	-0.13009335	TERM 1	-0.00953734
TERM 2	-0.04292	TERM 2	-0.02340203	TERM 2	-0.00975005	TERM 2	-0.00456807
TERM 3	-0.00066	TERM 3	-0.00082	TERM 3	-0.00121888	TERM 3	-0.00116904
LNɣ	-0.3884	LNɣ	-0.22266143	LNɣ	-0.12156218	LNɣ	-0.00613831
ɣ	0.68	ɣ	0.80	ɣ	0.89	ɣ	0.99

Table C.7 γ_{13}^{∞} calculations for IL: methyltrioctylammonium bis(trifluoromethylsulfonyl)imide for alkenes and alkynes at T = (303.15 and 313.15 and 323.15) K for a 25.33% column loading



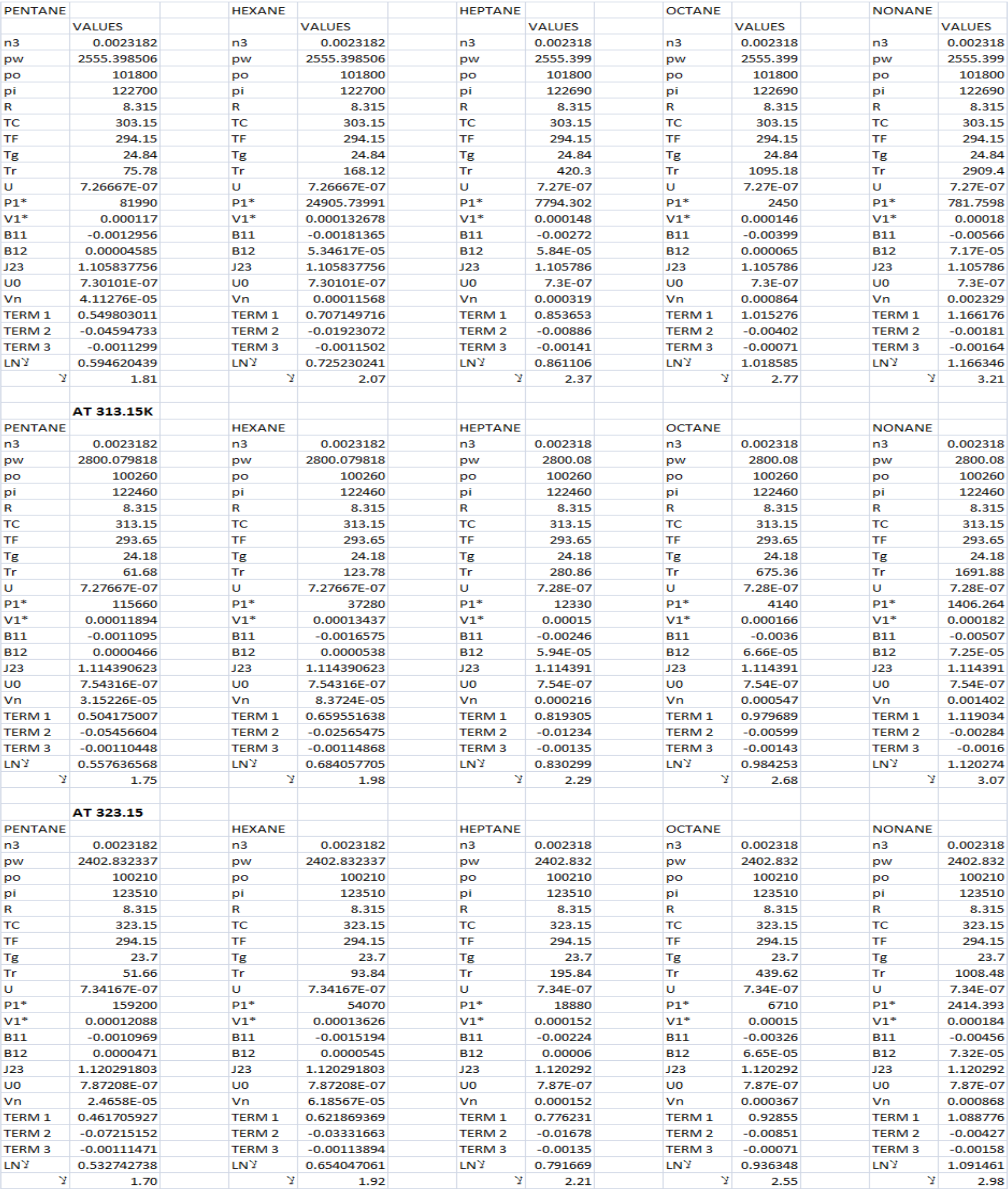
1-PENTENE		1-HEXENE		PENTYNE		HEXYNE	
	VALUES		VALUES		VALUES		VALUES
n7	0.00177	n8	0.00177	n7	0.00177	n8	0.00177
pw	2634.80039	pw	2634.8	pw	2634.8	pw	2634.80039
po	9.96E+04	po	9.96E+04	po	9.95E+04	po	9.95E+04
pi	1.38E+05	pi	1.38E+05	pi	1.38E+05	pi	1.38E+05
R	8.315	R	8.315	R	8.315	R	8.315
TC	303.15	TC	303.15	TC	303.15	TC	303.15
TF	294.15	TF	294.15	TF	294.65	TF	294.65
Tg	20.22	Tg	20.22	Tg	20.22	Tg	20.22
Tr	87.42	Tr	211.08	Tr	161.34	Tr	425.28
U	7.283E-07	U	7.28E-07	U	7.33E-07	U	7.33E-07
P1*	101600	P1*	30500	P1*	69850.21	P1*	21398.50523
V1*	0.000111	V1*	0.000127	V1*	0.000104	V1*	0.000120341
B11	-0.00106009	B11	-0.0017	B11	-0.00117	B11	-0.00193538
B12	0.00004672	B12	5.16E-05	B12	4.34E-05	B12	4.85844E-05
J23	1.201055177	J23	1.201055	J23	1.201297	J23	1.201296917
U0	7.30718E-07	U0	7.31E-07	U0	7.34E-07	U0	7.34183E-07
Vn	5.89769E-05	Vn	0.000168	Vn	0.000124	Vn	0.000357252
TERM 1	-0.294920874	TERM 1	-0.13547	TERM 1	-0.6671	TERM 1	-0.53849317
TERM 2	-0.047202408	TERM 2	-0.02211	TERM 2	-0.03519	TERM 2	-0.01745129
TERM 3	-0.000832931	TERM 3	-0.00113	TERM 3	-0.00083	TERM 3	-0.00109924
LNγ	-0.248551397	LNγ	-0.11449	LNγ	-0.63274	LNγ	-0.52214112
γ	0.78	γ	0.89	γ	0.53	γ	0.59
1-PENTENE		1-HEXENE		PENTYNE		HEXYNE	
n7	0.00177	n8	0.00177	n13	0.00177	n14	0.00177
pw	2478.091411	pw	2634.8	pw	2478.091	pw	2478.091411
po	9.97E+04	po	9.97E+04	po	9.97E+04	po	9.97E+04
pi	1.39E+05	pi	1.39E+05	pi	1.39E+05	pi	1.39E+05
R	8.315	R	8.315	R	8.315	R	8.315
TC	313.15	TC	313.15	TC	313.15	TC	313.15
TF	295.65	TF	295.65	TF	295.65	TF	295.65
Tg	19.74	Tg	19.74	Tg	19.74	Tg	19.74
Tr	69.12	Tr	150.36	Tr	119.91	Tr	286.14
U	7.41667E-07	U	7.42E-07	U	7.42E-07	U	7.41667E-07
P1*	140600.2868	P1*	44968.84	P1*	100731.3	P1*	32540.96484
V1*	0.000115655	V1*	0.000128	V1*	0.000106	V1*	0.00012198
B11	-0.000989745	B11	-0.00154	B11	-0.00107	B11	-0.0015583
B12	4.72544E-05	B12	5.22E-05	B12	4.4E-05	B12	4.92323E-05
J23	1.210779412	J23	1.210779	J23	1.210779	J23	1.210779412
U0	7.64796E-07	U0	7.65E-07	U0	7.66E-07	U0	7.66032E-07
Vn	4.57259E-05	Vn	0.000121	Vn	9.29E-05	Vn	0.000247085
TERM 1	-0.332862059	TERM 1	-0.16566	TERM 1	-0.70834	TERM 1	-0.55650825
TERM 2	-2.00608E-11	TERM 2	-3.3E-11	TERM 2	-0.04549	TERM 2	-0.02099894
TERM 3	-0.000979854	TERM 3	-0.0011	TERM 3	1.27E-12	TERM 3	-0.00108963
LNγ	-0.333841913	LNγ	-0.16676	LNγ	-0.66284	LNγ	-0.53659894
γ	0.72	γ	0.85	γ	0.52	γ	0.58
1-PENTENE		1-HEXENE		PENTYNE		HEXYNE	
n7	0.00177	n8	0.00177	n13	0.00177	n14	0.00177
pw	2478.091411	pw	2478.091	pw	2478.091	pw	2478.091411
po	1.00E+05	po	1.00E+05	po	1.00E+05	po	1.00E+05
pi	1.42E+05	pi	1.42E+05	pi	1.42E+05	pi	1.42E+05
R	8.315	R	8.315	R	8.315	R	8.315
TC	323.15	TC	323.15	TC	323.15	TC	323.15
TF	295.15	TF	295.15	TF	295.15	TF	295.15
Tg	19.44	Tg	19.44	Tg	19.44	Tg	19.44
Tr	59.4	Tr	117.58	Tr	88.74	Tr	198.24
U	7.26667E-07	U	7.27E-07	U	7.27E-07	U	7.26667E-07
P1*	192254.0447	P1*	64720	P1*	141478	P1*	48063.11453
V1*	0.000117804	V1*	0.000131	V1*	0.000108	V1*	0.00012342
B11	-0.000914539	B11	-0.00143	B11	-0.00099	B11	-0.00160874
B12	4.77862E-05	B12	5.29E-05	B12	4.45E-05	B12	4.98371E-05
J23	1.220444618	J23	1.220445	J23	1.220445	J23	1.220444618
U0	7.75892E-07	U0	7.76E-07	U0	7.76E-07	U0	7.75892E-07
Vn	3.78394E-05	Vn	9.29E-05	Vn	6.56E-05	Vn	0.000169312
TERM 1	-0.425012013	TERM 1	-0.23478	TERM 1	-0.6689	TERM 1	-0.53709831
TERM 2	-0.073864012	TERM 2	-0.03747	TERM 2	-0.0576	TERM 2	-0.03098379
TERM 3	-0.00100997	TERM 3	-0.00112	TERM 3	-0.00084	TERM 3	-0.00107875
LNγ	-0.352157971	LNγ	-0.19843	LNγ	-0.61215	LNγ	-0.50719327
γ	0.70	γ	0.82	γ	0.54	γ	0.60

Table C.8 γ_{13}^{∞} calculations for IL: methyltrioctylammonium bis(trifluoromethylsulfonyl)imide for alcohols and benzene at T = (303.15 and 313.15 and 323.15) K for a 25.33% column loading



METHANOL			ETHANOL			BENZENE		
	VALUES			VALUES			VALUES	
n9	0.00177		n10	0.00177		n11	0.00177	
pw	2634.80039		pw	2634.80039		pw	2634.8	
po	9.95E+04		po	9.95E+04		po	9.95E+04	
pi	1.38E+05		pi	1.38E+05		pi	1.38E+05	
R	8.315		R	8.315		R	8.315	
TC	303.15		TC	303.15		TC	303.15	
TF	294.65		TF	294.65		TF	294.65	
Tg	20.22		Tg	20.22		Tg	20.22	
Tr	284.04		Tr	539.94		Tr	1060.3	
U	7.33E-07		U	7.33E-07		U	7.33E-07	
P1*	21860		P1*	10412.32839		P1*	15907.93	
V1*	0.000041		V1*	5.42082E-05		V1*	9.05E-05	
B11	-0.00035992		B11	-0.00058488		B11	-0.0017	
B12	0.00002347		B12	2.97681E-05		B12	3.97E-05	
J23	1.201296917		J23	1.201296917		J23	1.201297	
U0	7.34183E-07		U0	7.34183E-07		U0	7.34E-07	
Vn	0.000232682		Vn	0.000458379		Vn	0.000917	
TERM 1	-0.13106243		TERM 1	-0.06741763		TERM 1	-1.18501	
TERM 2	-0.00347687		TERM 2	-0.00263993		TERM 2	-0.01127	
TERM 3	0.000281783		TERM 3	0.000252755		TERM 3	-0.00053	
LNϒ	-0.12730378		LNϒ	-0.06452494		LNϒ	-1.17426	
ϒ	0.88		ϒ	0.94		ϒ	0.31	
METHANOL			ETHANOL			BENZENE		
n15	0.00177		n16	0.00177		n17	0.00177	
pw	2634.80039		pw	2478.091411		pw	2478.091	
po	9.97E+04		po	9.97E+04		po	9.97E+04	
pi	1.39E+05		pi	1.39E+05		pi	1.39E+05	
R	8.315		R	8.315		R	8.315	
TC	313.15		TC	313.15		TC	313.15	
TF	295.65		TF	295.65		TF	295.65	
Tg	19.74		Tg	19.74		Tg	19.74	
Tr	193.02		Tr	350.28		Tr	686.4	
U	7.41667E-07		U	7.41667E-07		U	7.42E-07	
P1*	35387.31694		P1*	17825.78248		P1*	24375.22	
V1*	3.98731E-05		V1*	5.50467E-05		V1*	9.11E-05	
B11	-0.0003398		B11	-0.00054638		B11	-0.00154	
B12	2.40954E-05		B12	3.02727E-05		B12	4.04E-05	
J23	1.210779412		J23	1.210779412		J23	1.210779	
U0	7.64796E-07		U0	7.66032E-07		U0	7.66E-07	
Vn	0.000160457		Vn	0.000306574		Vn	0.000618	
TERM 1	-0.20865782		TERM 1	-0.1703831		TERM 1	-1.18486	
TERM 2	-3.5134E-12		TERM 2	-0.00411737		TERM 2	-0.01528	
TERM 3	0.000385413		TERM 3	0.000254797		TERM 3	-0.00048	
LNϒ	-0.2082724		LNϒ	-0.16601094		LNϒ	-1.17005	
ϒ	0.81		ϒ	0.85		ϒ	0.31	
METHANOL			ETHANOL			BENZENE		
n15	0.00177		n16	0.00177		n17	0.00177	
pw	2478.091411		pw	2478.091411		pw	2478.091	
po	1.00E+05		po	1.00E+05		po	1.00E+05	
pi	1.42E+05		pi	1.42E+05		pi	1.42E+05	
R	8.315		R	8.315		R	8.315	
TC	323.15		TC	323.15		TC	323.15	
TF	295.15		TF	295.15		TF	295.15	
Tg	19.44		Tg	19.44		Tg	19.44	
Tr	135.3		Tr	234.78		Tr	466.8	
U	7.26667E-07		U	7.26667E-07		U	7.27E-07	
P1*	55477.83212		P1*	29368.96048		P1*	36183.64	
V1*	4.05093E-05		V1*	5.59289E-05		V1*	9.22E-05	
B11	-0.00032116		B11	-0.00051182		B11	-0.00141	
B12	2.45067E-05		B12	3.07434E-05		B12	0.000041	
J23	1.220444618		J23	1.220444618		J23	1.220445	
U0	7.75892E-07		U0	7.75892E-07		U0	7.76E-07	
Vn	0.000109712		Vn	0.000203912		Vn	0.000424	
TERM 1	-0.2466815		TERM 1	-0.23047194		TERM 1	-1.17029	
TERM 2	-0.00746729		TERM 2	-0.00620548		TERM 2	-0.02016	
TERM 3	0.000386339		TERM 3	0.000252496		TERM 3	-0.00046	
LNϒ	-0.23882786		LNϒ	-0.22401396		LNϒ	-1.15059	
ϒ	0.79		ϒ	0.80		ϒ	0.32	

Table C.9 γ_{13}^{∞} calculations for IL: methyltrioctylammonium thiosalicylate for alkanes at *T* = (303.15 and 313.15 and 323.15) K for a 20.74% column loading



PENTANE			HEXANE			HEPTANE			OCTANE			NONANE	
	VALUES			VALUES			VALUES			VALUES			VALUES
n3	0.0023182		n3	0.0023182		n3	0.002318		n3	0.002318		n3	0.002318
pw	2555.398506		pw	2555.398506		pw	2555.399		pw	2555.399		pw	2555.399
po	101800		po	101800		po	101800		po	101800		po	101800
pi	122700		pi	122700		pi	122690		pi	122690		pi	122690
R	8.315		R	8.315		R	8.315		R	8.315		R	8.315
TC	303.15		TC	303.15		TC	303.15		TC	303.15		TC	303.15
TF	294.15		TF	294.15		TF	294.15		TF	294.15		TF	294.15
Tg	24.84		Tg	24.84		Tg	24.84		Tg	24.84		Tg	24.84
Tr	75.78		Tr	168.12		Tr	420.3		Tr	1095.18		Tr	2909.4
U	7.26667E-07		U	7.26667E-07		U	7.27E-07		U	7.27E-07		U	7.27E-07
P1*	81990		P1*	24905.73991		P1*	7794.302		P1*	2450		P1*	781.7598
V1*	0.000117		V1*	0.000132678		V1*	0.000148		V1*	0.000146		V1*	0.00018
B11	-0.0012956		B11	-0.00181365		B11	-0.00272		B11	-0.00399		B11	-0.00566
B12	0.00004585		B12	5.34617E-05		B12	5.84E-05		B12	0.000065		B12	7.17E-05
J23	1.105837756		J23	1.105837756		J23	1.105786		J23	1.105786		J23	1.105786
U0	7.30101E-07		U0	7.30101E-07		U0	7.3E-07		U0	7.3E-07		U0	7.3E-07
Vn	4.11276E-05		Vn	0.00011568		Vn	0.000319		Vn	0.000864		Vn	0.002329
TERM 1	0.549803011		TERM 1	0.707149716		TERM 1	0.853653		TERM 1	1.015276		TERM 1	1.166176
TERM 2	-0.04594733		TERM 2	-0.01923072		TERM 2	-0.00886		TERM 2	-0.00402		TERM 2	-0.00181
TERM 3	-0.0011299		TERM 3	-0.0011502		TERM 3	-0.00141		TERM 3	-0.00071		TERM 3	-0.00164
LNγ	0.594620439		LNγ	0.725230241		LNγ	0.861106		LNγ	1.018585		LNγ	1.166346
γ	1.81		γ	2.07		γ	2.37		γ	2.77		γ	3.21
	AT 313.15K												
PENTANE			HEXANE			HEPTANE			OCTANE			NONANE	
n3	0.0023182		n3	0.0023182		n3	0.002318		n3	0.002318		n3	0.002318
pw	2800.079818		pw	2800.079818		pw	2800.08		pw	2800.08		pw	2800.08
po	100260		po	100260		po	100260		po	100260		po	100260
pi	122460		pi	122460		pi	122460		pi	122460		pi	122460
R	8.315		R	8.315		R	8.315		R	8.315		R	8.315
TC	313.15		TC	313.15		TC	313.15		TC	313.15		TC	313.15
TF	293.65		TF	293.65		TF	293.65		TF	293.65		TF	293.65
Tg	24.18		Tg	24.18		Tg	24.18		Tg	24.18		Tg	24.18
Tr	61.68		Tr	123.78		Tr	280.86		Tr	675.36		Tr	1691.88
U	7.27667E-07		U	7.27667E-07		U	7.28E-07		U	7.28E-07		U	7.28E-07
P1*	115660		P1*	37280		P1*	12330		P1*	4140		P1*	1406.264
V1*	0.00011894		V1*	0.00013437		V1*	0.00015		V1*	0.000166		V1*	0.000182
B11	-0.0011095		B11	-0.0016575		B11	-0.00246		B11	-0.0036		B11	-0.00507
B12	0.0000466		B12	0.0000538		B12	5.94E-05		B12	6.66E-05		B12	7.25E-05
J23	1.114390623		J23	1.114390623		J23	1.114391		J23	1.114391		J23	1.114391
U0	7.54316E-07		U0	7.54316E-07		U0	7.54E-07		U0	7.54E-07		U0	7.54E-07
Vn	3.15226E-05		Vn	8.3724E-05		Vn	0.000216		Vn	0.000547		Vn	0.001402
TERM 1	0.504175007		TERM 1	0.659551638		TERM 1	0.819305		TERM 1	0.979689		TERM 1	1.119034
TERM 2	-0.05456604		TERM 2	-0.02565475		TERM 2	-0.01234		TERM 2	-0.00599		TERM 2	-0.00284
TERM 3	-0.00110448		TERM 3	-0.00114868		TERM 3	-0.00135		TERM 3	-0.00143		TERM 3	-0.0016
LNγ	0.557636568		LNγ	0.684057705		LNγ	0.830299		LNγ	0.984253		LNγ	1.120274
γ	1.75		γ	1.98		γ	2.29		γ	2.68		γ	3.07
	AT 323.15												
PENTANE			HEXANE			HEPTANE			OCTANE			NONANE	
n3	0.0023182		n3	0.0023182		n3	0.002318		n3	0.002318		n3	0.002318
pw	2402.832337		pw	2402.832337		pw	2402.832		pw	2402.832		pw	2402.832
po	100210		po	100210		po	100210		po	100210		po	100210
pi	123510		pi	123510		pi	123510		pi	123510		pi	123510
R	8.315		R	8.315		R	8.315		R	8.315		R	8.315
TC	323.15		TC	323.15		TC	323.15		TC	323.15		TC	323.15
TF	294.15		TF	294.15		TF	294.15		TF	294.15		TF	294.15
Tg	23.7		Tg	23.7		Tg	23.7		Tg	23.7		Tg	23.7
Tr	51.66		Tr	93.84		Tr	195.84		Tr	439.62		Tr	1008.48
U	7.34167E-07		U	7.34167E-07		U	7.34E-07		U	7.34E-07		U	7.34E-07
P1*	159200		P1*	54070		P1*	18880		P1*	6710		P1*	2414.393
V1*	0.00012088		V1*	0.00013626		V1*	0.000152		V1*	0.00015		V1*	0.000184
B11	-0.0010969		B11	-0.0015194		B11	-0.00224		B11	-0.00326		B11	-0.00456
B12	0.0000471		B12	0.0000545		B12	0.00006		B12	6.65E-05		B12	7.32E-05
J23	1.120291803		J23	1.120291803		J23	1.120292		J23	1.120292		J23	1.120292
U0	7.87208E-07		U0	7.87208E-07		U0	7.87E-07		U0	7.87E-07		U0	7.87E-07
Vn	2.4658E-05		Vn	6.18567E-05		Vn	0.000152		Vn	0.000367		Vn	0.000868
TERM 1	0.461705927		TERM 1	0.621869369		TERM 1	0.776231		TERM 1	0.92855		TERM 1	1.088776
TERM 2	-0.07215152		TERM 2	-0.03331663		TERM 2	-0.01678		TERM 2	-0.00851		TERM 2	-0.00427
TERM 3	-0.00111471		TERM 3	-0.00113894		TERM 3	-0.00135		TERM 3	-0.00071		TERM 3	-0.00158
LNγ	0.532742738		LNγ	0.654047061		LNγ	0.791669		LNγ	0.936348		LNγ	1.091461
γ	1.70		γ	1.92		γ	2.21		γ	2.55		γ	2.98

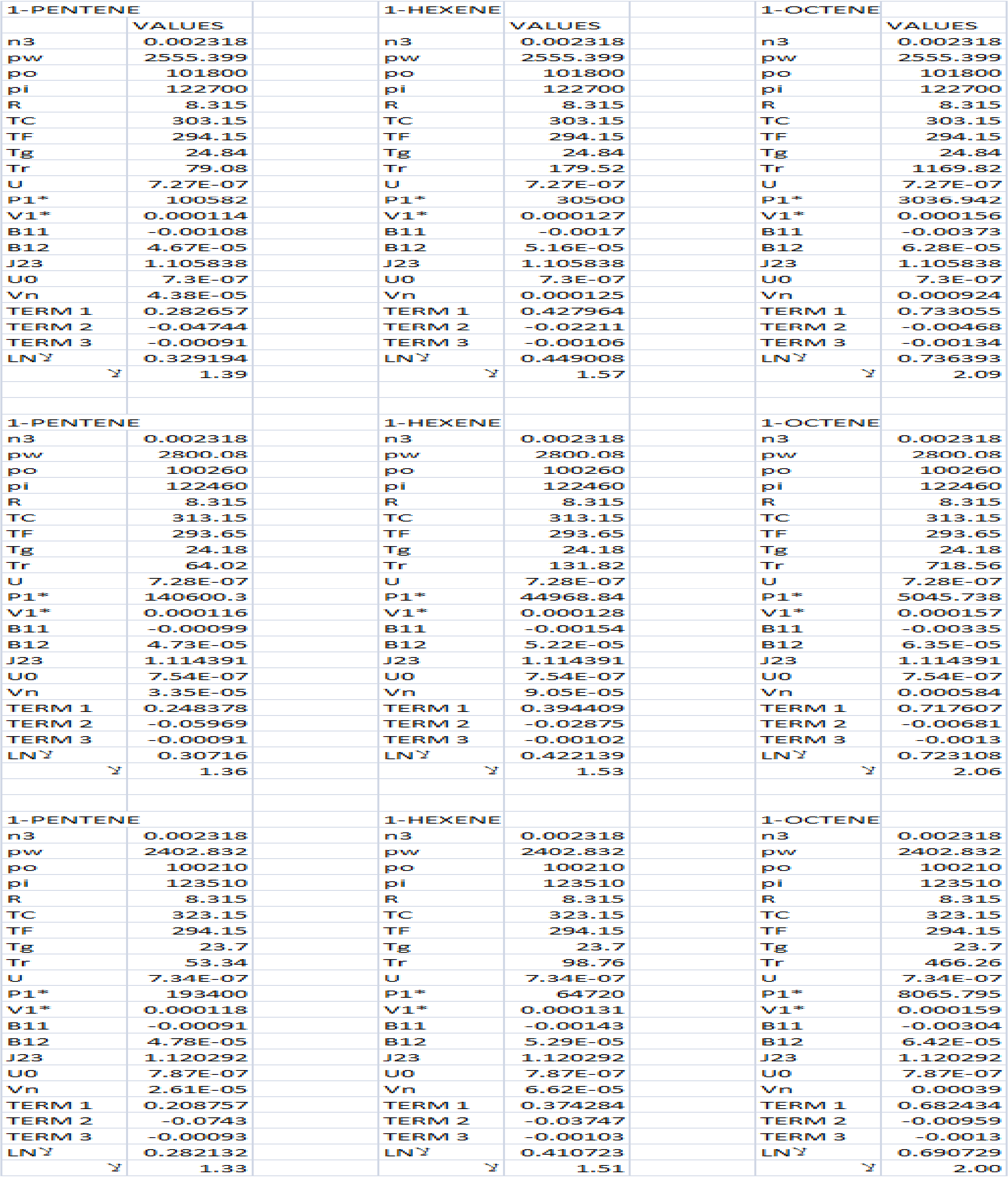
Table C.10 γ_{13}^{∞} calculations for IL: methyltrioctylammonium thiosalicylate for cycloalkanes at T = (303.15 and 313.15 and 323.15) K for a 20.74% column loading

CYCLOPENTANE		CYCLOHEXANE		CYCLOHEPTANE		CYCLOOCTANE	
	VALUES		VALUES		VALUES		VALUES
n3	0.002318	n3	0.002318	n3	0.002318	n3	0.002318
pw	2555.399	pw	2555.399	pw	2555.399	pw	2555.399
po	101800	po	101800	po	101800	po	101800
pi	122700	pi	122700	pi	122700	pi	122700
R	8.315	R	8.315	R	8.315	R	8.315
TC	303.15	TC	303.15	TC	303.15	TC	303.15
TF	294.15	TF	294.15	TF	294.15	TF	294.15
Tg	24.84	Tg	24.84	Tg	24.84	Tg	24.84
Tr	156.06	Tr	361.8	Tr	1391.58	Tr	4685.94
U	7.27E-07	U	7.27E-07	U	7.27E-07	U	7.27E-07
P1*	51300	P1*	16240	P1*	3746.771	P1*	992.3316
V1*	9.53E-05	V1*	0.000109	V1*	0.000121	V1*	0.000137
B11	-0.0012	B11	-0.00195	B11	-0.00321	B11	-0.00516
B12	4.06E-05	B12	4.56E-05	B12	4.98E-05	B12	5.53E-05
J23	1.105838	J23	1.105838	J23	1.105838	J23	1.105838
U0	7.3E-07	U0	7.3E-07	U0	7.3E-07	U0	7.3E-07
Vn	0.000106	Vn	0.000272	Vn	0.001103	Vn	0.003763
TERM 1	0.072483	TERM 1	0.279607	TERM 1	0.345971	TERM 1	0.44774
TERM 2	-0.02637	TERM 2	-0.01328	TERM 2	-0.00495	TERM 2	-0.00209
TERM 3	-0.00063	TERM 3	-0.0008	TERM 3	-0.00096	TERM 3	-0.00117
LNƔ	0.098217	LNƔ	0.292095	LNƔ	0.349966	LNƔ	0.44866
Ɣ	1.10	Ɣ	1.34	Ɣ	1.42	Ɣ	1.57

CYCLOPENTANE		CYCLOHEXANE		CYCLOHEPTANE		CYCLOCTANE	
n3	0.002318	n3	0.002318	n3	0.002318	n3	0.002318
pw	2800.08	pw	2800.08	pw	2800.08	pw	2800.08
po	100260	po	100260	po	100260	po	100260
pi	122460	pi	122460	pi	122460	pi	122460
R	8.315	R	8.315	R	8.315	R	8.315
TC	313.15	TC	313.15	TC	313.15	TC	313.15
TF	293.65	TF	293.65	TF	293.65	TF	293.65
Tg	24.18	Tg	24.18	Tg	24.18	Tg	24.18
Tr	117.96	Tr	255.6	Tr	897.48	Tr	2820.48
U	7.28E-07	U	7.28E-07	U	7.28E-07	U	7.28E-07
P1*	73900	P1*	24630	P1*	6088.487	P1*	1720
V1*	9.67E-05	V1*	0.00011	V1*	0.000127	V1*	0.00014
B11	-0.0011	B11	-0.00178	B11	-0.00289	B11	-0.00461
B12	4.12E-05	B12	4.64E-05	B12	5.07E-05	B12	0.000056
J23	1.114391	J23	1.114391	J23	1.114391	J23	1.114391
U0	7.54E-07	U0	7.54E-07	U0	7.54E-07	U0	7.54E-07
Vn	7.88E-05	Vn	0.000195	Vn	0.000734	Vn	0.002351
TERM 1	0.035506	TERM 1	0.230971	TERM 1	0.300492	TERM 1	0.400794
TERM 2	-0.034	TERM 2	-0.01786	TERM 2	-0.00706	TERM 2	-0.00314
TERM 3	-0.00061	TERM 3	-0.00074	TERM 3	-0.00108	TERM 3	-0.00119
LNƔ	0.068894	LNƔ	0.24809	LNƔ	0.306469	LNƔ	0.402745
Ɣ	1.07	Ɣ	1.28	Ɣ	1.36	Ɣ	1.50

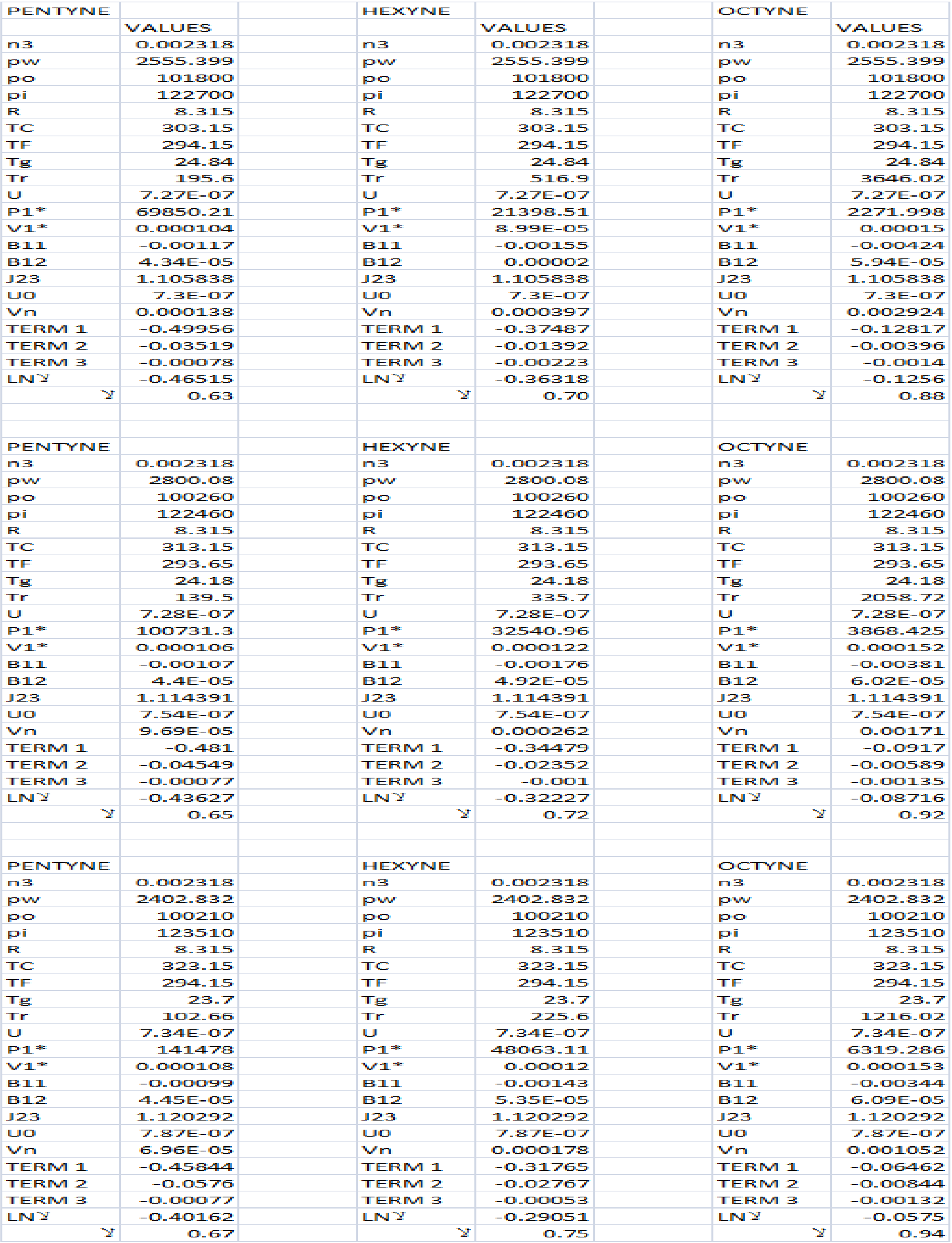
CYCLOPENTANE		CYCLOHEXANE		CYCLOHEPTANE		CYCLOCTANE	
n3	0.002318	n3	0.002318	n3	0.002318	n3	0.002318
pw	2402.832	pw	2402.832	pw	2402.832	pw	2402.832
po	100210	po	100210	po	100210	po	100210
pi	123510	pi	123510	pi	123510	pi	123510
R	8.315	R	8.315	R	8.315	R	8.315
TC	323.15	TC	323.15	TC	323.15	TC	323.15
TF	294.15	TF	294.15	TF	294.15	TF	294.15
Tg	23.7	Tg	23.7	Tg	23.7	Tg	23.7
Tr	92.04	Tr	185.1	Tr	593.94	Tr	1745.88
U	7.34E-07	U	7.34E-07	U	7.34E-07	U	7.34E-07
P1*	103760	P1*	36250	P1*	9539.571	P1*	2866.225
V1*	0.000098	V1*	0.000112	V1*	0.000123	V1*	0.000139
B11	-0.00101	B11	-0.00162	B11	-0.00262	B11	-0.00414
B12	4.17E-05	B12	0.000047	B12	5.12E-05	B12	5.68E-05
J23	1.120292	J23	1.120292	J23	1.120292	J23	1.120292
U0	7.87E-07	U0	7.87E-07	U0	7.87E-07	U0	7.87E-07
Vn	6.03E-05	Vn	0.000142	Vn	0.000503	Vn	0.001519
TERM 1	-0.00393	TERM 1	0.188317	TERM 1	0.261136	TERM 1	0.3583
TERM 2	-0.04292	TERM 2	-0.0234	TERM 2	-0.00973	TERM 2	-0.00457
TERM 3	-0.00061	TERM 3	-0.00075	TERM 3	-0.00087	TERM 3	-0.00108
LNƔ	0.038373	LNƔ	0.210965	LNƔ	0.269994	LNƔ	0.361793
Ɣ	1.04	Ɣ	1.23	Ɣ	1.31	Ɣ	1.44

Table C.11 γ_{13}^{∞} calculations for IL: methyltrioctylammonium thiosalicylate for alkenes at T = (303.15 and 313.15 and 323.15) K for a 20.74% column loading



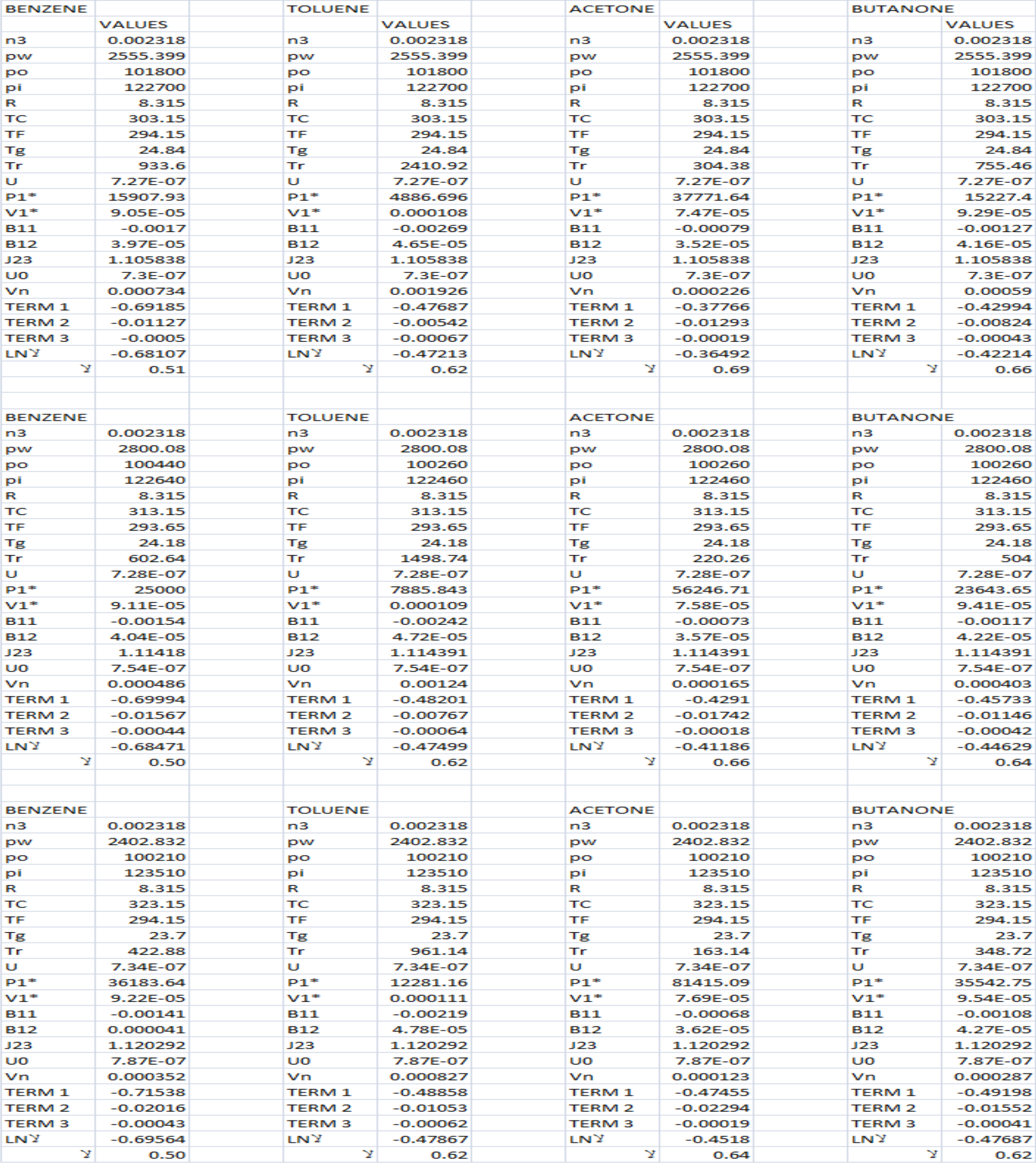
1-PENTENE			1-HEXENE			1-OCTENE	
	VALUES			VALUES			VALUES
n3	0.002318		n3	0.002318		n3	0.002318
pw	2555.399		pw	2555.399		pw	2555.399
po	101800		po	101800		po	101800
pi	122700		pi	122700		pi	122700
R	8.315		R	8.315		R	8.315
TC	303.15		TC	303.15		TC	303.15
TF	294.15		TF	294.15		TF	294.15
Tg	24.84		Tg	24.84		Tg	24.84
Tr	79.08		Tr	179.52		Tr	1169.82
U	7.27E-07		U	7.27E-07		U	7.27E-07
P1*	100582		P1*	30500		P1*	3036.942
V1*	0.000114		V1*	0.000127		V1*	0.000156
B11	-0.00108		B11	-0.0017		B11	-0.00373
B12	4.67E-05		B12	5.16E-05		B12	6.28E-05
J23	1.105838		J23	1.105838		J23	1.105838
U0	7.3E-07		U0	7.3E-07		U0	7.3E-07
Vn	4.38E-05		Vn	0.000125		Vn	0.000924
TERM 1	0.282657		TERM 1	0.427964		TERM 1	0.733055
TERM 2	-0.04744		TERM 2	-0.02211		TERM 2	-0.00468
TERM 3	-0.00091		TERM 3	-0.00106		TERM 3	-0.00134
LNγ	0.329194		LNγ	0.449008		LNγ	0.736393
γ	1.39		γ	1.57		γ	2.09
1-PENTENE			1-HEXENE			1-OCTENE	
n3	0.002318		n3	0.002318		n3	0.002318
pw	2800.08		pw	2800.08		pw	2800.08
po	100260		po	100260		po	100260
pi	122460		pi	122460		pi	122460
R	8.315		R	8.315		R	8.315
TC	313.15		TC	313.15		TC	313.15
TF	293.65		TF	293.65		TF	293.65
Tg	24.18		Tg	24.18		Tg	24.18
Tr	64.02		Tr	131.82		Tr	718.56
U	7.28E-07		U	7.28E-07		U	7.28E-07
P1*	140600.3		P1*	44968.84		P1*	5045.738
V1*	0.000116		V1*	0.000128		V1*	0.000157
B11	-0.00099		B11	-0.00154		B11	-0.00335
B12	4.73E-05		B12	5.22E-05		B12	6.35E-05
J23	1.114391		J23	1.114391		J23	1.114391
U0	7.54E-07		U0	7.54E-07		U0	7.54E-07
Vn	3.35E-05		Vn	9.05E-05		Vn	0.000584
TERM 1	0.248378		TERM 1	0.394409		TERM 1	0.717607
TERM 2	-0.05969		TERM 2	-0.02875		TERM 2	-0.00681
TERM 3	-0.00091		TERM 3	-0.00102		TERM 3	-0.0013
LNγ	0.30716		LNγ	0.422139		LNγ	0.723108
γ	1.36		γ	1.53		γ	2.06
1-PENTENE			1-HEXENE			1-OCTENE	
n3	0.002318		n3	0.002318		n3	0.002318
pw	2402.832		pw	2402.832		pw	2402.832
po	100210		po	100210		po	100210
pi	123510		pi	123510		pi	123510
R	8.315		R	8.315		R	8.315
TC	323.15		TC	323.15		TC	323.15
TF	294.15		TF	294.15		TF	294.15
Tg	23.7		Tg	23.7		Tg	23.7
Tr	53.34		Tr	98.76		Tr	466.26
U	7.34E-07		U	7.34E-07		U	7.34E-07
P1*	193400		P1*	64720		P1*	8065.795
V1*	0.000118		V1*	0.000131		V1*	0.000159
B11	-0.00091		B11	-0.00143		B11	-0.00304
B12	4.78E-05		B12	5.29E-05		B12	6.42E-05
J23	1.120292		J23	1.120292		J23	1.120292
U0	7.87E-07		U0	7.87E-07		U0	7.87E-07
Vn	2.61E-05		Vn	6.62E-05		Vn	0.00039
TERM 1	0.208757		TERM 1	0.374284		TERM 1	0.682434
TERM 2	-0.0743		TERM 2	-0.03747		TERM 2	-0.00959
TERM 3	-0.00093		TERM 3	-0.00103		TERM 3	-0.0013
LNγ	0.282132		LNγ	0.410723		LNγ	0.690729
γ	1.33		γ	1.51		γ	2.00

Table C.12 γ_{13}^{∞} calculations for IL: methyltrioctylammonium thiosalicylate for alkynes at T = (303.15 and 313.15 and 323.15) K for a 20.74% column loading



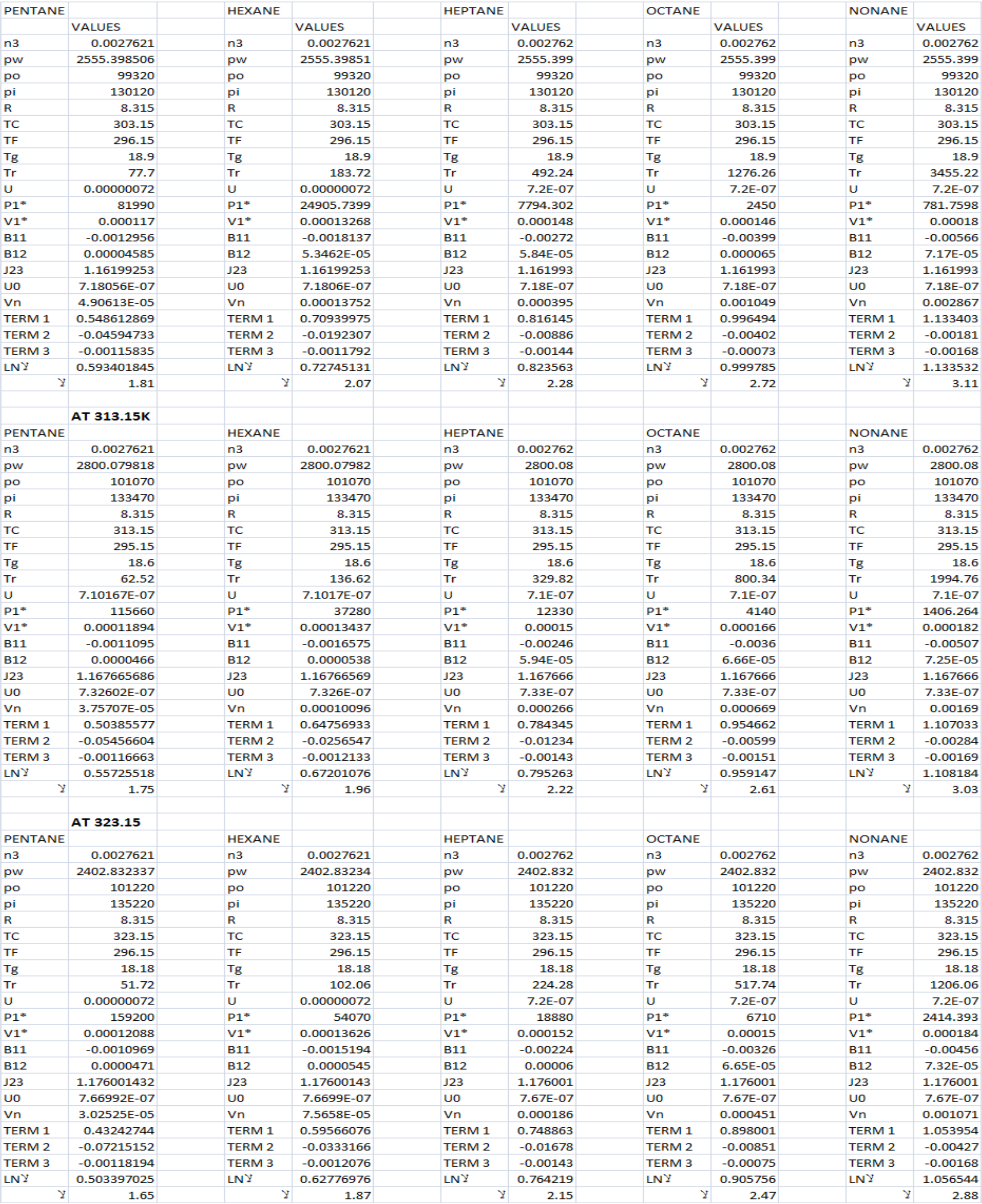
PENTYNE			HEXYNE			OCTYNE	
	VALUES			VALUES			VALUES
n3	0.002318		n3	0.002318		n3	0.002318
pw	2555.399		pw	2555.399		pw	2555.399
po	101800		po	101800		po	101800
pi	122700		pi	122700		pi	122700
R	8.315		R	8.315		R	8.315
TC	303.15		TC	303.15		TC	303.15
TF	294.15		TF	294.15		TF	294.15
Tg	24.84		Tg	24.84		Tg	24.84
Tr	195.6		Tr	516.9		Tr	3646.02
U	7.27E-07		U	7.27E-07		U	7.27E-07
P1*	69850.21		P1*	21398.51		P1*	2271.998
V1*	0.000104		V1*	8.99E-05		V1*	0.00015
B11	-0.00117		B11	-0.00155		B11	-0.00424
B12	4.34E-05		B12	0.00002		B12	5.94E-05
J23	1.105838		J23	1.105838		J23	1.105838
U0	7.3E-07		U0	7.3E-07		U0	7.3E-07
Vn	0.000138		Vn	0.000397		Vn	0.002924
TERM 1	-0.49956		TERM 1	-0.37487		TERM 1	-0.12817
TERM 2	-0.03519		TERM 2	-0.01392		TERM 2	-0.00396
TERM 3	-0.00078		TERM 3	-0.00223		TERM 3	-0.0014
LN γ	-0.46515		LN γ	-0.36318		LN γ	-0.1256
γ	0.63		γ	0.70		γ	0.88
PENTYNE			HEXYNE			OCTYNE	
n3	0.002318		n3	0.002318		n3	0.002318
pw	2800.08		pw	2800.08		pw	2800.08
po	100260		po	100260		po	100260
pi	122460		pi	122460		pi	122460
R	8.315		R	8.315		R	8.315
TC	313.15		TC	313.15		TC	313.15
TF	293.65		TF	293.65		TF	293.65
Tg	24.18		Tg	24.18		Tg	24.18
Tr	139.5		Tr	335.7		Tr	2058.72
U	7.28E-07		U	7.28E-07		U	7.28E-07
P1*	100731.3		P1*	32540.96		P1*	3868.425
V1*	0.000106		V1*	0.000122		V1*	0.000152
B11	-0.00107		B11	-0.00176		B11	-0.00381
B12	4.4E-05		B12	4.92E-05		B12	6.02E-05
J23	1.114391		J23	1.114391		J23	1.114391
U0	7.54E-07		U0	7.54E-07		U0	7.54E-07
Vn	9.69E-05		Vn	0.000262		Vn	0.00171
TERM 1	-0.481		TERM 1	-0.34479		TERM 1	-0.0917
TERM 2	-0.04549		TERM 2	-0.02352		TERM 2	-0.00589
TERM 3	-0.00077		TERM 3	-0.001		TERM 3	-0.00135
LN γ	-0.43627		LN γ	-0.32227		LN γ	-0.08716
γ	0.65		γ	0.72		γ	0.92
PENTYNE			HEXYNE			OCTYNE	
n3	0.002318		n3	0.002318		n3	0.002318
pw	2402.832		pw	2402.832		pw	2402.832
po	100210		po	100210		po	100210
pi	123510		pi	123510		pi	123510
R	8.315		R	8.315		R	8.315
TC	323.15		TC	323.15		TC	323.15
TF	294.15		TF	294.15		TF	294.15
Tg	23.7		Tg	23.7		Tg	23.7
Tr	102.66		Tr	225.6		Tr	1216.02
U	7.34E-07		U	7.34E-07		U	7.34E-07
P1*	141478		P1*	48063.11		P1*	6319.286
V1*	0.000108		V1*	0.00012		V1*	0.000153
B11	-0.00099		B11	-0.00143		B11	-0.00344
B12	4.45E-05		B12	5.35E-05		B12	6.09E-05
J23	1.120292		J23	1.120292		J23	1.120292
U0	7.87E-07		U0	7.87E-07		U0	7.87E-07
Vn	6.96E-05		Vn	0.000178		Vn	0.001052
TERM 1	-0.45844		TERM 1	-0.31765		TERM 1	-0.06462
TERM 2	-0.0576		TERM 2	-0.02767		TERM 2	-0.00844
TERM 3	-0.00077		TERM 3	-0.00053		TERM 3	-0.00132
LN γ	-0.40162		LN γ	-0.29051		LN γ	-0.0575
γ	0.67		γ	0.75		γ	0.94

Table C.13 γ_{13}^{∞} calculations for IL: methyltrioctylammonium thiosalicylate for aromatic hydrocarbons and ketones at T = (303.15 and 313.15 and 323.15) K for a 20.74% column loading



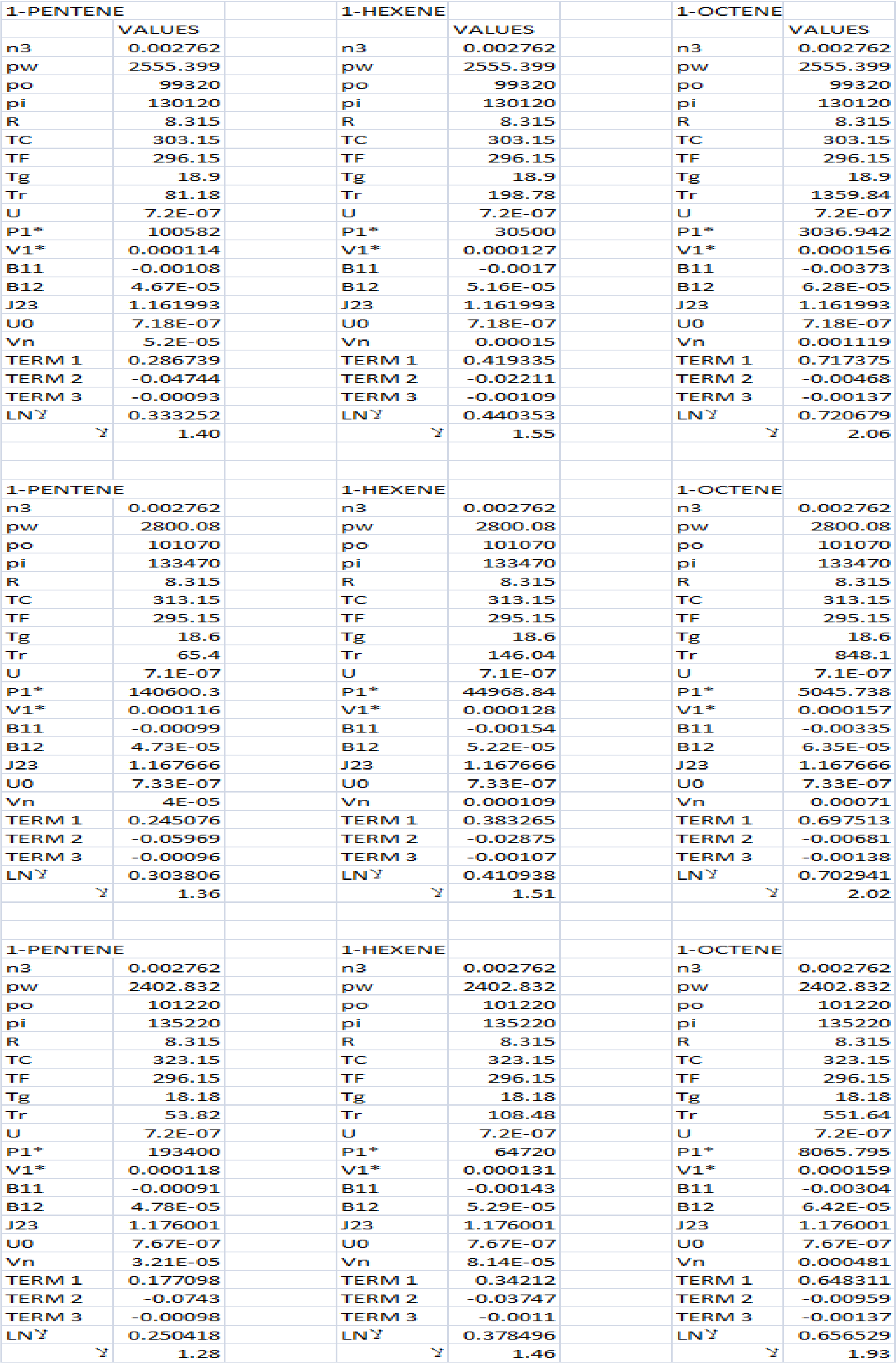
BENZENE		TOLUENE		ACETONE		BUTANONE	
	VALUES		VALUES		VALUES		VALUES
n3	0.002318	n3	0.002318	n3	0.002318	n3	0.002318
pw	2555.399	pw	2555.399	pw	2555.399	pw	2555.399
po	101800	po	101800	po	101800	po	101800
pi	122700	pi	122700	pi	122700	pi	122700
R	8.315	R	8.315	R	8.315	R	8.315
TC	303.15	TC	303.15	TC	303.15	TC	303.15
TF	294.15	TF	294.15	TF	294.15	TF	294.15
Tg	24.84	Tg	24.84	Tg	24.84	Tg	24.84
Tr	933.6	Tr	2410.92	Tr	304.38	Tr	755.46
U	7.27E-07	U	7.27E-07	U	7.27E-07	U	7.27E-07
P1*	15907.93	P1*	4886.696	P1*	37771.64	P1*	15227.4
V1*	9.05E-05	V1*	0.000108	V1*	7.47E-05	V1*	9.29E-05
B11	-0.0017	B11	-0.00269	B11	-0.00079	B11	-0.00127
B12	3.97E-05	B12	4.65E-05	B12	3.52E-05	B12	4.16E-05
J23	1.105838	J23	1.105838	J23	1.105838	J23	1.105838
U0	7.3E-07	U0	7.3E-07	U0	7.3E-07	U0	7.3E-07
Vn	0.000734	Vn	0.001926	Vn	0.000226	Vn	0.00059
TERM 1	-0.69185	TERM 1	-0.47687	TERM 1	-0.37766	TERM 1	-0.42994
TERM 2	-0.01127	TERM 2	-0.00542	TERM 2	-0.01293	TERM 2	-0.00824
TERM 3	-0.0005	TERM 3	-0.00067	TERM 3	-0.00019	TERM 3	-0.00043
LNɣ	-0.68107	LNɣ	-0.47213	LNɣ	-0.36492	LNɣ	-0.42214
ɣ	0.51	ɣ	0.62	ɣ	0.69	ɣ	0.66
BENZENE		TOLUENE		ACETONE		BUTANONE	
n3	0.002318	n3	0.002318	n3	0.002318	n3	0.002318
pw	2800.08	pw	2800.08	pw	2800.08	pw	2800.08
po	100440	po	100260	po	100260	po	100260
pi	122640	pi	122460	pi	122460	pi	122460
R	8.315	R	8.315	R	8.315	R	8.315
TC	313.15	TC	313.15	TC	313.15	TC	313.15
TF	293.65	TF	293.65	TF	293.65	TF	293.65
Tg	24.18	Tg	24.18	Tg	24.18	Tg	24.18
Tr	602.64	Tr	1498.74	Tr	220.26	Tr	504
U	7.28E-07	U	7.28E-07	U	7.28E-07	U	7.28E-07
P1*	25000	P1*	7885.843	P1*	56246.71	P1*	23643.65
V1*	9.11E-05	V1*	0.000109	V1*	7.58E-05	V1*	9.41E-05
B11	-0.00154	B11	-0.00242	B11	-0.00073	B11	-0.00117
B12	4.04E-05	B12	4.72E-05	B12	3.57E-05	B12	4.22E-05
J23	1.11418	J23	1.114391	J23	1.114391	J23	1.114391
U0	7.54E-07	U0	7.54E-07	U0	7.54E-07	U0	7.54E-07
Vn	0.000486	Vn	0.00124	Vn	0.000165	Vn	0.000403
TERM 1	-0.69994	TERM 1	-0.48201	TERM 1	-0.4291	TERM 1	-0.45733
TERM 2	-0.01567	TERM 2	-0.00767	TERM 2	-0.01742	TERM 2	-0.01146
TERM 3	-0.00044	TERM 3	-0.00064	TERM 3	-0.00018	TERM 3	-0.00042
LNɣ	-0.68471	LNɣ	-0.47499	LNɣ	-0.41186	LNɣ	-0.44629
ɣ	0.50	ɣ	0.62	ɣ	0.66	ɣ	0.64
BENZENE		TOLUENE		ACETONE		BUTANONE	
n3	0.002318	n3	0.002318	n3	0.002318	n3	0.002318
pw	2402.832	pw	2402.832	pw	2402.832	pw	2402.832
po	100210	po	100210	po	100210	po	100210
pi	123510	pi	123510	pi	123510	pi	123510
R	8.315	R	8.315	R	8.315	R	8.315
TC	323.15	TC	323.15	TC	323.15	TC	323.15
TF	294.15	TF	294.15	TF	294.15	TF	294.15
Tg	23.7	Tg	23.7	Tg	23.7	Tg	23.7
Tr	422.88	Tr	961.14	Tr	163.14	Tr	348.72
U	7.34E-07	U	7.34E-07	U	7.34E-07	U	7.34E-07
P1*	36183.64	P1*	12281.16	P1*	81415.09	P1*	35542.75
V1*	9.22E-05	V1*	0.000111	V1*	7.69E-05	V1*	9.54E-05
B11	-0.00141	B11	-0.00219	B11	-0.00068	B11	-0.00108
B12	0.000041	B12	4.78E-05	B12	3.62E-05	B12	4.27E-05
J23	1.120292	J23	1.120292	J23	1.120292	J23	1.120292
U0	7.87E-07	U0	7.87E-07	U0	7.87E-07	U0	7.87E-07
Vn	0.000352	Vn	0.000827	Vn	0.000123	Vn	0.000287
TERM 1	-0.71538	TERM 1	-0.48858	TERM 1	-0.47455	TERM 1	-0.49198
TERM 2	-0.02016	TERM 2	-0.01053	TERM 2	-0.02294	TERM 2	-0.01552
TERM 3	-0.00043	TERM 3	-0.00062	TERM 3	-0.00019	TERM 3	-0.00041
LNɣ	-0.69564	LNɣ	-0.47867	LNɣ	-0.4518	LNɣ	-0.47687
ɣ	0.50	ɣ	0.62	ɣ	0.64	ɣ	0.62

Table C.14 γ_{13}^{∞} calculations for IL: methyltrioctylammonium thiosalicylate for alkanes at T = (303.15 and 313.15 and 323.15) K for a 29.62% column loading



PENTANE			HEXANE			HEPTANE			OCTANE			NONANE	
	VALUES			VALUES			VALUES			VALUES			VALUES
n3	0.0027621		n3	0.0027621		n3	0.002762		n3	0.002762		n3	0.002762
pw	2555.398506		pw	2555.39851		pw	2555.399		pw	2555.399		pw	2555.399
po	99320		po	99320		po	99320		po	99320		po	99320
pi	130120		pi	130120		pi	130120		pi	130120		pi	130120
R	8.315		R	8.315		R	8.315		R	8.315		R	8.315
TC	303.15		TC	303.15		TC	303.15		TC	303.15		TC	303.15
TF	296.15		TF	296.15		TF	296.15		TF	296.15		TF	296.15
Tg	18.9		Tg	18.9		Tg	18.9		Tg	18.9		Tg	18.9
Tr	77.7		Tr	183.72		Tr	492.24		Tr	1276.26		Tr	3455.22
U	0.00000072		U	0.00000072		U	7.2E-07		U	7.2E-07		U	7.2E-07
P1*	81990		P1*	24905.7399		P1*	7794.302		P1*	2450		P1*	781.7598
V1*	0.000117		V1*	0.00013268		V1*	0.000148		V1*	0.000146		V1*	0.00018
B11	-0.0012956		B11	-0.0018137		B11	-0.00272		B11	-0.00399		B11	-0.00566
B12	0.00004585		B12	5.3462E-05		B12	5.84E-05		B12	0.000065		B12	7.17E-05
J23	1.16199253		J23	1.16199253		J23	1.161993		J23	1.161993		J23	1.161993
U0	7.18056E-07		U0	7.1806E-07		U0	7.18E-07		U0	7.18E-07		U0	7.18E-07
Vn	4.90613E-05		Vn	0.00013752		Vn	0.000395		Vn	0.001049		Vn	0.002867
TERM 1	0.548612869		TERM 1	0.70939975		TERM 1	0.816145		TERM 1	0.996494		TERM 1	1.133403
TERM 2	-0.04594733		TERM 2	-0.0192307		TERM 2	-0.00886		TERM 2	-0.00402		TERM 2	-0.00181
TERM 3	-0.00115835		TERM 3	-0.0011792		TERM 3	-0.00144		TERM 3	-0.00073		TERM 3	-0.00168
LNɣ	0.593401845		LNɣ	0.72745131		LNɣ	0.823563		LNɣ	0.999785		LNɣ	1.133532
ɣ	1.81		ɣ	2.07		ɣ	2.28		ɣ	2.72		ɣ	3.11
	AT 313.15K												
PENTANE			HEXANE			HEPTANE			OCTANE			NONANE	
n3	0.0027621		n3	0.0027621		n3	0.002762		n3	0.002762		n3	0.002762
pw	2800.079818		pw	2800.07982		pw	2800.08		pw	2800.08		pw	2800.08
po	101070		po	101070		po	101070		po	101070		po	101070
pi	133470		pi	133470		pi	133470		pi	133470		pi	133470
R	8.315		R	8.315		R	8.315		R	8.315		R	8.315
TC	313.15		TC	313.15		TC	313.15		TC	313.15		TC	313.15
TF	295.15		TF	295.15		TF	295.15		TF	295.15		TF	295.15
Tg	18.6		Tg	18.6		Tg	18.6		Tg	18.6		Tg	18.6
Tr	62.52		Tr	136.62		Tr	329.82		Tr	800.34		Tr	1994.76
U	7.10167E-07		U	7.1017E-07		U	7.1E-07		U	7.1E-07		U	7.1E-07
P1*	115660		P1*	37280		P1*	12330		P1*	4140		P1*	1406.264
V1*	0.00011894		V1*	0.00013437		V1*	0.00015		V1*	0.000166		V1*	0.000182
B11	-0.0011095		B11	-0.0016575		B11	-0.00246		B11	-0.0036		B11	-0.00507
B12	0.0000466		B12	0.0000538		B12	5.94E-05		B12	6.66E-05		B12	7.25E-05
J23	1.167665686		J23	1.16766569		J23	1.167666		J23	1.167666		J23	1.167666
U0	7.32602E-07		U0	7.326E-07		U0	7.33E-07		U0	7.33E-07		U0	7.33E-07
Vn	3.75707E-05		Vn	0.00010096		Vn	0.000266		Vn	0.000669		Vn	0.00169
TERM 1	0.50385577		TERM 1	0.64756933		TERM 1	0.784345		TERM 1	0.954662		TERM 1	1.107033
TERM 2	-0.05456604		TERM 2	-0.0256547		TERM 2	-0.01234		TERM 2	-0.00599		TERM 2	-0.00284
TERM 3	-0.00116663		TERM 3	-0.0012133		TERM 3	-0.00143		TERM 3	-0.00151		TERM 3	-0.00169
LNɣ	0.55725518		LNɣ	0.67201076		LNɣ	0.795263		LNɣ	0.959147		LNɣ	1.108184
ɣ	1.75		ɣ	1.96		ɣ	2.22		ɣ	2.61		ɣ	3.03
	AT 323.15												
PENTANE			HEXANE			HEPTANE			OCTANE			NONANE	
n3	0.0027621		n3	0.0027621		n3	0.002762		n3	0.002762		n3	0.002762
pw	2402.832337		pw	2402.83234		pw	2402.832		pw	2402.832		pw	2402.832
po	101220		po	101220		po	101220		po	101220		po	101220
pi	135220		pi	135220		pi	135220		pi	135220		pi	135220
R	8.315		R	8.315		R	8.315		R	8.315		R	8.315
TC	323.15		TC	323.15		TC	323.15		TC	323.15		TC	323.15
TF	296.15		TF	296.15		TF	296.15		TF	296.15		TF	296.15
Tg	18.18		Tg	18.18		Tg	18.18		Tg	18.18		Tg	18.18
Tr	51.72		Tr	102.06		Tr	224.28		Tr	517.74		Tr	1206.06
U	0.00000072		U	0.00000072		U	7.2E-07		U	7.2E-07		U	7.2E-07
P1*	159200		P1*	54070		P1*	18880		P1*	6710		P1*	2414.393
V1*	0.00012088		V1*	0.00013626		V1*	0.000152		V1*	0.00015		V1*	0.000184
B11	-0.0010969		B11	-0.0015194		B11	-0.00224		B11	-0.00326		B11	-0.00456
B12	0.0000471		B12	0.0000545		B12	0.00006		B12	6.65E-05		B12	7.32E-05
J23	1.176001432		J23	1.17600143		J23	1.176001		J23	1.176001		J23	1.176001
U0	7.66992E-07		U0	7.6699E-07		U0	7.67E-07		U0	7.67E-07		U0	7.67E-07
Vn	3.02525E-05		Vn	7.5658E-05		Vn	0.000186		Vn	0.000451		Vn	0.001071
TERM 1	0.43242744		TERM 1	0.59566076		TERM 1	0.748863		TERM 1	0.898001		TERM 1	1.053954
TERM 2	-0.07215152		TERM 2	-0.0333166		TERM 2	-0.01678		TERM 2	-0.00851		TERM 2	-0.00427
TERM 3	-0.00118194		TERM 3	-0.0012076		TERM 3	-0.00143		TERM 3	-0.00075		TERM 3	-0.00168
LNɣ	0.503397025		LNɣ	0.62776976		LNɣ	0.764219		LNɣ	0.905756		LNɣ	1.056544
ɣ	1.65		ɣ	1.87		ɣ	2.15		ɣ	2.47		ɣ	2.88

Table C.15 γ_{13}^{∞} calculations for IL: methyltrioctylammonium thiosalicylate for alkenes at T = (303.15 and 313.15 and 323.15) K for a 29.62% column loading

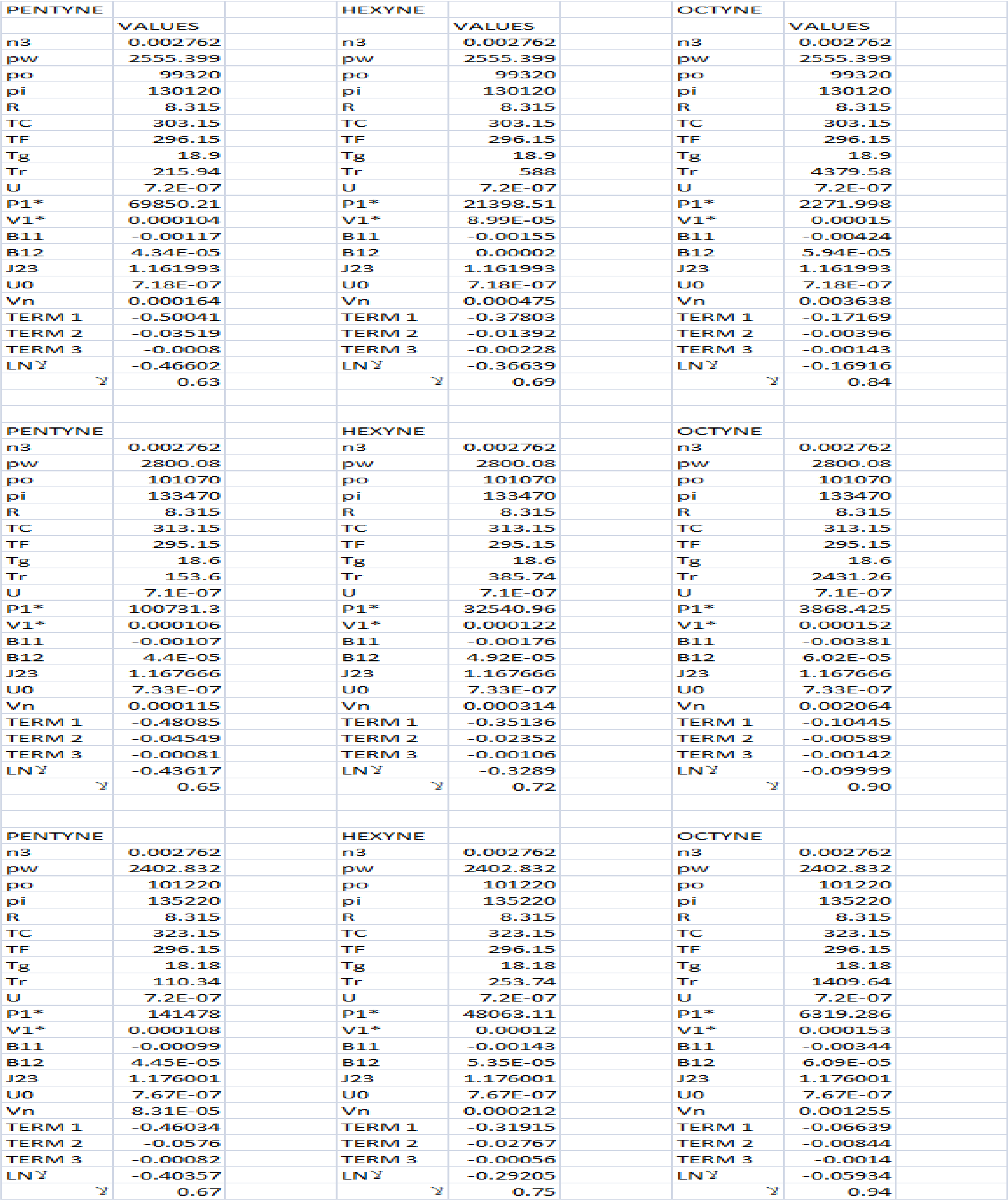


1-PENTENE			1-HEXENE			1-OCTENE		
	VALUES			VALUES			VALUES	
n3	0.002762		n3	0.002762		n3	0.002762	
pw	2555.399		pw	2555.399		pw	2555.399	
po	99320		po	99320		po	99320	
pi	130120		pi	130120		pi	130120	
R	8.315		R	8.315		R	8.315	
TC	303.15		TC	303.15		TC	303.15	
TF	296.15		TF	296.15		TF	296.15	
Tg	18.9		Tg	18.9		Tg	18.9	
Tr	81.18		Tr	198.78		Tr	1359.84	
U	7.2E-07		U	7.2E-07		U	7.2E-07	
P1*	100582		P1*	30500		P1*	3036.942	
V1*	0.000114		V1*	0.000127		V1*	0.000156	
B11	-0.00108		B11	-0.0017		B11	-0.00373	
B12	4.67E-05		B12	5.16E-05		B12	6.28E-05	
J23	1.161993		J23	1.161993		J23	1.161993	
U0	7.18E-07		U0	7.18E-07		U0	7.18E-07	
Vn	5.2E-05		Vn	0.00015		Vn	0.001119	
TERM 1	0.286739		TERM 1	0.419335		TERM 1	0.717375	
TERM 2	-0.04744		TERM 2	-0.02211		TERM 2	-0.00468	
TERM 3	-0.00093		TERM 3	-0.00109		TERM 3	-0.00137	
LNϒ	0.333252		LNϒ	0.440353		LNϒ	0.720679	
ϒ	1.40		ϒ	1.55		ϒ	2.06	
1-PENTENE			1-HEXENE			1-OCTENE		
n3	0.002762		n3	0.002762		n3	0.002762	
pw	2800.08		pw	2800.08		pw	2800.08	
po	101070		po	101070		po	101070	
pi	133470		pi	133470		pi	133470	
R	8.315		R	8.315		R	8.315	
TC	313.15		TC	313.15		TC	313.15	
TF	295.15		TF	295.15		TF	295.15	
Tg	18.6		Tg	18.6		Tg	18.6	
Tr	65.4		Tr	146.04		Tr	848.1	
U	7.1E-07		U	7.1E-07		U	7.1E-07	
P1*	140600.3		P1*	44968.84		P1*	5045.738	
V1*	0.000116		V1*	0.000128		V1*	0.000157	
B11	-0.00099		B11	-0.00154		B11	-0.00335	
B12	4.73E-05		B12	5.22E-05		B12	6.35E-05	
J23	1.167666		J23	1.167666		J23	1.167666	
U0	7.33E-07		U0	7.33E-07		U0	7.33E-07	
Vn	4E-05		Vn	0.000109		Vn	0.00071	
TERM 1	0.245076		TERM 1	0.383265		TERM 1	0.697513	
TERM 2	-0.05969		TERM 2	-0.02875		TERM 2	-0.00681	
TERM 3	-0.00096		TERM 3	-0.00107		TERM 3	-0.00138	
LNϒ	0.303806		LNϒ	0.410938		LNϒ	0.702941	
ϒ	1.36		ϒ	1.51		ϒ	2.02	
1-PENTENE			1-HEXENE			1-OCTENE		
n3	0.002762		n3	0.002762		n3	0.002762	
pw	2402.832		pw	2402.832		pw	2402.832	
po	101220		po	101220		po	101220	
pi	135220		pi	135220		pi	135220	
R	8.315		R	8.315		R	8.315	
TC	323.15		TC	323.15		TC	323.15	
TF	296.15		TF	296.15		TF	296.15	
Tg	18.18		Tg	18.18		Tg	18.18	
Tr	53.82		Tr	108.48		Tr	551.64	
U	7.2E-07		U	7.2E-07		U	7.2E-07	
P1*	193400		P1*	64720		P1*	8065.795	
V1*	0.000118		V1*	0.000131		V1*	0.000159	
B11	-0.00091		B11	-0.00143		B11	-0.00304	
B12	4.78E-05		B12	5.29E-05		B12	6.42E-05	
J23	1.176001		J23	1.176001		J23	1.176001	
U0	7.67E-07		U0	7.67E-07		U0	7.67E-07	
Vn	3.21E-05		Vn	8.14E-05		Vn	0.000481	
TERM 1	0.177098		TERM 1	0.34212		TERM 1	0.648311	
TERM 2	-0.0743		TERM 2	-0.03747		TERM 2	-0.00959	
TERM 3	-0.00098		TERM 3	-0.0011		TERM 3	-0.00137	
LNϒ	0.250418		LNϒ	0.378496		LNϒ	0.656529	
ϒ	1.28		ϒ	1.46		ϒ	1.93	

Table C.16 γ_{13}^{∞} calculations for IL: methyltrioctylammonium thiosalicylate for cycloalkanes at T = (303.15 and 313.15 and 323.15) K for a 29.62% column loading

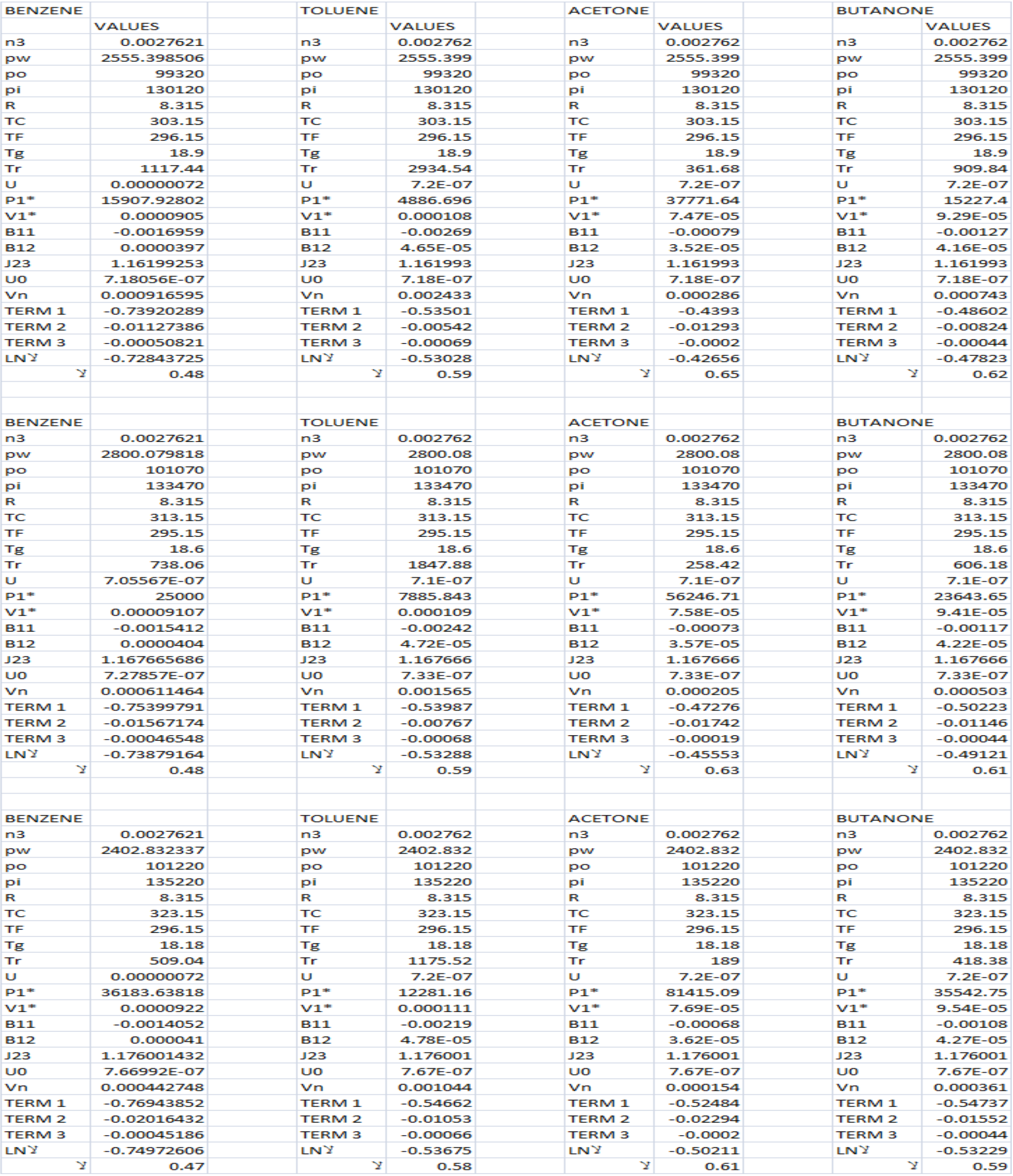
CYCLOPENTANE			CYCLOHEXANE			CYCLOHEPTANE			CYCLOOCTANE		
	VALUES			VALUES			VALUES			VALUES	
n3	0.002762		n3	0.002762		n3	0.002762		n3	0.002762	
pw	2555.399		pw	2555.399		pw	2555.399		pw	2555.399	
po	99320		po	99320		po	99320		po	99320	
pi	130120		pi	130120		pi	130120		pi	130120	
R	8.315		R	8.315		R	8.315		R	8.315	
TC	303.15		TC	303.15		TC	303.15		TC	303.15	
TF	296.15		TF	296.15		TF	296.15		TF	296.15	
Tg	18.9		Tg	18.9		Tg	18.9		Tg	18.9	
Tr	172.86		Tr	414.54		Tr	1613.76		Tr	5393.1	
U	7.2E-07		U	7.2E-07		U	7.2E-07		U	7.2E-07	
P1*	51300		P1*	16240		P1*	3746.771		P1*	992.3316	
V1*	9.53E-05		V1*	0.000109		V1*	0.000121		V1*	0.000137	
B11	-0.0012		B11	-0.00195		B11	-0.00321		B11	-0.00516	
B12	4.06E-05		B12	4.56E-05		B12	4.98E-05		B12	5.53E-05	
J23	1.161993		J23	1.161993		J23	1.161993		J23	1.161993	
U0	7.18E-07		U0	7.18E-07		U0	7.18E-07		U0	7.18E-07	
Vn	0.000128		Vn	0.00033		Vn	0.001331		Vn	0.004484	
TERM 1	0.054968		TERM 1	0.26137		TERM 1	0.333916		TERM 1	0.447685	
TERM 2	-0.02637		TERM 2	-0.01328		TERM 2	-0.00495		TERM 2	-0.00209	
TERM 3	-0.00065		TERM 3	-0.00082		TERM 3	-0.00098		TERM 3	-0.0012	
LNϒ	0.080687		LNϒ	0.273838		LNϒ	0.337888		LNϒ	0.448575	
ϒ	1.08		ϒ	1.32		ϒ	1.40		ϒ	1.57	
CYCLOPENTANE			CYCLOHEXANE			CYCLOHEPTANE			CYCLOCTANE		
n3	0.002762		n3	0.002762		n3	0.002762		n3	0.002762	
pw	2800.08		pw	2800.08		pw	2800.08		pw	2800.08	
po	101070		po	101070		po	101070		po	101070	
pi	133470		pi	133470		pi	133470		pi	133470	
R	8.315		R	8.315		R	8.315		R	8.315	
TC	313.15		TC	313.15		TC	313.15		TC	313.15	
TF	295.15		TF	295.15		TF	295.15		TF	295.15	
Tg	18.6		Tg	18.6		Tg	18.6		Tg	18.6	
Tr	130.68		Tr	294.6		Tr	1070.34		Tr	3389.28	
U	7.1E-07		U	7.1E-07		U	7.1E-07		U	7.1E-07	
P1*	73900		P1*	24630		P1*	6088.487		P1*	1720	
V1*	9.67E-05		V1*	0.00011		V1*	0.000127		V1*	0.00014	
B11	-0.0011		B11	-0.00178		B11	-0.00289		B11	-0.00461	
B12	4.12E-05		B12	4.64E-05		B12	5.07E-05		B12	0.000056	
J23	1.167666		J23	1.167666		J23	1.167666		J23	1.167666	
U0	7.33E-07		U0	7.33E-07		U0	7.33E-07		U0	7.33E-07	
Vn	9.59E-05		Vn	0.000236		Vn	0.0009		Vn	0.002883	
TERM 1	0.014955		TERM 1	0.212514		TERM 1	0.27228		TERM 1	0.371686	
TERM 2	-0.034		TERM 2	-0.01786		TERM 2	-0.00706		TERM 2	-0.00314	
TERM 3	-0.00065		TERM 3	-0.00078		TERM 3	-0.00114		TERM 3	-0.00126	
LNϒ	0.048308		LNϒ	0.229591		LNϒ	0.278195		LNϒ	0.37357	
ϒ	1.05		ϒ	1.26		ϒ	1.32		ϒ	1.45	
CYCLOPENTANE			CYCLOHEXANE			CYCLOHEPTANE			CYCLOCTANE		
n3	0.002762		n3	0.002762		n3	0.002762		n3	0.002762	
pw	2402.832		pw	2402.832		pw	2402.832		pw	2402.832	
po	101220		po	101220		po	101220		po	101220	
pi	135220		pi	135220		pi	135220		pi	135220	
R	8.315		R	8.315		R	8.315		R	8.315	
TC	323.15		TC	323.15		TC	323.15		TC	323.15	
TF	296.15		TF	296.15		TF	296.15		TF	296.15	
Tg	18.18		Tg	18.18		Tg	18.18		Tg	18.18	
Tr	100.62		Tr	212.7		Tr	714.18		Tr	2118.48	
U	7.2E-07		U	7.2E-07		U	7.2E-07		U	7.2E-07	
P1*	103760		P1*	36250		P1*	9539.571		P1*	2866.225	
V1*	0.000098		V1*	0.000112		V1*	0.000123		V1*	0.000139	
B11	-0.00101		B11	-0.00162		B11	-0.00262		B11	-0.00414	
B12	4.17E-05		B12	0.000047		B12	5.12E-05		B12	5.68E-05	
J23	1.176001		J23	1.176001		J23	1.176001		J23	1.176001	
U0	7.67E-07		U0	7.67E-07		U0	7.67E-07		U0	7.67E-07	
Vn	7.44E-05		Vn	0.000175		Vn	0.000628		Vn	0.001894	
TERM 1	-0.03882		TERM 1	0.154353		TERM 1	0.214529		TERM 1	0.312496	
TERM 2	-0.04292		TERM 2	-0.0234		TERM 2	-0.00973		TERM 2	-0.00457	
TERM 3	-0.00065		TERM 3	-0.0008		TERM 3	-0.00092		TERM 3	-0.00114	
LNϒ	0.003446		LNϒ	0.176956		LNϒ	0.223335		LNϒ	0.315924	
ϒ	1.00		ϒ	1.19		ϒ	1.25		ϒ	1.37	

Table C.17 γ_{13}^{∞} calculations for IL: methyltrioctylammonium thiosalicylate for alkynes at T = (303.15 and 313.15 and 323.15) K for a 29.62% column loading



PENTYNE			HEXYNE			OCTYNE		
	VALUES			VALUES			VALUES	
n3	0.002762		n3	0.002762		n3	0.002762	
pw	2555.399		pw	2555.399		pw	2555.399	
po	99320		po	99320		po	99320	
pi	130120		pi	130120		pi	130120	
R	8.315		R	8.315		R	8.315	
TC	303.15		TC	303.15		TC	303.15	
TF	296.15		TF	296.15		TF	296.15	
Tg	18.9		Tg	18.9		Tg	18.9	
Tr	215.94		Tr	588		Tr	4379.58	
U	7.2E-07		U	7.2E-07		U	7.2E-07	
P1*	69850.21		P1*	21398.51		P1*	2271.998	
V1*	0.000104		V1*	8.99E-05		V1*	0.00015	
B11	-0.00117		B11	-0.00155		B11	-0.00424	
B12	4.34E-05		B12	0.00002		B12	5.94E-05	
J23	1.161993		J23	1.161993		J23	1.161993	
U0	7.18E-07		U0	7.18E-07		U0	7.18E-07	
Vn	0.000164		Vn	0.000475		Vn	0.003638	
TERM 1	-0.50041		TERM 1	-0.37803		TERM 1	-0.17169	
TERM 2	-0.03519		TERM 2	-0.01392		TERM 2	-0.00396	
TERM 3	-0.0008		TERM 3	-0.00228		TERM 3	-0.00143	
LNγ	-0.46602		LNγ	-0.36639		LNγ	-0.16916	
γ	0.63		γ	0.69		γ	0.84	
PENTYNE			HEXYNE			OCTYNE		
n3	0.002762		n3	0.002762		n3	0.002762	
pw	2800.08		pw	2800.08		pw	2800.08	
po	101070		po	101070		po	101070	
pi	133470		pi	133470		pi	133470	
R	8.315		R	8.315		R	8.315	
TC	313.15		TC	313.15		TC	313.15	
TF	295.15		TF	295.15		TF	295.15	
Tg	18.6		Tg	18.6		Tg	18.6	
Tr	153.6		Tr	385.74		Tr	2431.26	
U	7.1E-07		U	7.1E-07		U	7.1E-07	
P1*	100731.3		P1*	32540.96		P1*	3868.425	
V1*	0.000106		V1*	0.000122		V1*	0.000152	
B11	-0.00107		B11	-0.00176		B11	-0.00381	
B12	4.4E-05		B12	4.92E-05		B12	6.02E-05	
J23	1.167666		J23	1.167666		J23	1.167666	
U0	7.33E-07		U0	7.33E-07		U0	7.33E-07	
Vn	0.000115		Vn	0.000314		Vn	0.002064	
TERM 1	-0.48085		TERM 1	-0.35136		TERM 1	-0.10445	
TERM 2	-0.04549		TERM 2	-0.02352		TERM 2	-0.00589	
TERM 3	-0.00081		TERM 3	-0.00106		TERM 3	-0.00142	
LNγ	-0.43617		LNγ	-0.3289		LNγ	-0.09999	
γ	0.65		γ	0.72		γ	0.90	
PENTYNE			HEXYNE			OCTYNE		
n3	0.002762		n3	0.002762		n3	0.002762	
pw	2402.832		pw	2402.832		pw	2402.832	
po	101220		po	101220		po	101220	
pi	135220		pi	135220		pi	135220	
R	8.315		R	8.315		R	8.315	
TC	323.15		TC	323.15		TC	323.15	
TF	296.15		TF	296.15		TF	296.15	
Tg	18.18		Tg	18.18		Tg	18.18	
Tr	110.34		Tr	253.74		Tr	1409.64	
U	7.2E-07		U	7.2E-07		U	7.2E-07	
P1*	141478		P1*	48063.11		P1*	6319.286	
V1*	0.000108		V1*	0.00012		V1*	0.000153	
B11	-0.00099		B11	-0.00143		B11	-0.00344	
B12	4.45E-05		B12	5.35E-05		B12	6.09E-05	
J23	1.176001		J23	1.176001		J23	1.176001	
U0	7.67E-07		U0	7.67E-07		U0	7.67E-07	
Vn	8.31E-05		Vn	0.000212		Vn	0.001255	
TERM 1	-0.46034		TERM 1	-0.31915		TERM 1	-0.06639	
TERM 2	-0.0576		TERM 2	-0.02767		TERM 2	-0.00844	
TERM 3	-0.00082		TERM 3	-0.00056		TERM 3	-0.0014	
LNγ	-0.40357		LNγ	-0.29205		LNγ	-0.05934	
γ	0.67		γ	0.75		γ	0.94	

C.18 γ_{13}^{∞} calculations for IL: methyltrioctylammonium thiosalicylate for aromatic hydrocarbons and ketones at T = (303.15 and 313.15 and 323.15) K for a 29.62% column loading



BENZENE			TOLUENE			ACETONE			BUTANONE	
	VALUES			VALUES			VALUES			VALUES
n3	0.0027621		n3	0.002762		n3	0.002762		n3	0.002762
pw	2555.398506		pw	2555.399		pw	2555.399		pw	2555.399
po	99320		po	99320		po	99320		po	99320
pi	130120		pi	130120		pi	130120		pi	130120
R	8.315		R	8.315		R	8.315		R	8.315
TC	303.15		TC	303.15		TC	303.15		TC	303.15
TF	296.15		TF	296.15		TF	296.15		TF	296.15
Tg	18.9		Tg	18.9		Tg	18.9		Tg	18.9
Tr	1117.44		Tr	2934.54		Tr	361.68		Tr	909.84
U	0.00000072		U	7.2E-07		U	7.2E-07		U	7.2E-07
P1*	15907.92802		P1*	4886.696		P1*	37771.64		P1*	15227.4
V1*	0.0000905		V1*	0.000108		V1*	7.47E-05		V1*	9.29E-05
B11	-0.0016959		B11	-0.00269		B11	-0.00079		B11	-0.00127
B12	0.0000397		B12	4.65E-05		B12	3.52E-05		B12	4.16E-05
J23	1.16199253		J23	1.161993		J23	1.161993		J23	1.161993
U0	7.18056E-07		U0	7.18E-07		U0	7.18E-07		U0	7.18E-07
Vn	0.000916595		Vn	0.002433		Vn	0.000286		Vn	0.000743
TERM 1	-0.73920289		TERM 1	-0.53501		TERM 1	-0.4393		TERM 1	-0.48602
TERM 2	-0.01127386		TERM 2	-0.00542		TERM 2	-0.01293		TERM 2	-0.00824
TERM 3	-0.00050821		TERM 3	-0.00069		TERM 3	-0.0002		TERM 3	-0.00044
LNɣ	-0.72843725		LNɣ	-0.53028		LNɣ	-0.42656		LNɣ	-0.47823
ɣ	0.48		ɣ	0.59		ɣ	0.65		ɣ	0.62
BENZENE			TOLUENE			ACETONE			BUTANONE	
n3	0.0027621		n3	0.002762		n3	0.002762		n3	0.002762
pw	2800.079818		pw	2800.08		pw	2800.08		pw	2800.08
po	101070		po	101070		po	101070		po	101070
pi	133470		pi	133470		pi	133470		pi	133470
R	8.315		R	8.315		R	8.315		R	8.315
TC	313.15		TC	313.15		TC	313.15		TC	313.15
TF	295.15		TF	295.15		TF	295.15		TF	295.15
Tg	18.6		Tg	18.6		Tg	18.6		Tg	18.6
Tr	738.06		Tr	1847.88		Tr	258.42		Tr	606.18
U	7.05567E-07		U	7.1E-07		U	7.1E-07		U	7.1E-07
P1*	25000		P1*	7885.843		P1*	56246.71		P1*	23643.65
V1*	0.00009107		V1*	0.000109		V1*	7.58E-05		V1*	9.41E-05
B11	-0.0015412		B11	-0.00242		B11	-0.00073		B11	-0.00117
B12	0.0000404		B12	4.72E-05		B12	3.57E-05		B12	4.22E-05
J23	1.167665686		J23	1.167666		J23	1.167666		J23	1.167666
U0	7.27857E-07		U0	7.33E-07		U0	7.33E-07		U0	7.33E-07
Vn	0.000611464		Vn	0.001565		Vn	0.000205		Vn	0.000503
TERM 1	-0.75399791		TERM 1	-0.53987		TERM 1	-0.47276		TERM 1	-0.50223
TERM 2	-0.01567174		TERM 2	-0.00767		TERM 2	-0.01742		TERM 2	-0.01146
TERM 3	-0.00046548		TERM 3	-0.00068		TERM 3	-0.00019		TERM 3	-0.00044
LNɣ	-0.73879164		LNɣ	-0.53288		LNɣ	-0.45553		LNɣ	-0.49121
ɣ	0.48		ɣ	0.59		ɣ	0.63		ɣ	0.61
BENZENE			TOLUENE			ACETONE			BUTANONE	
n3	0.0027621		n3	0.002762		n3	0.002762		n3	0.002762
pw	2402.832337		pw	2402.832		pw	2402.832		pw	2402.832
po	101220		po	101220		po	101220		po	101220
pi	135220		pi	135220		pi	135220		pi	135220
R	8.315		R	8.315		R	8.315		R	8.315
TC	323.15		TC	323.15		TC	323.15		TC	323.15
TF	296.15		TF	296.15		TF	296.15		TF	296.15
Tg	18.18		Tg	18.18		Tg	18.18		Tg	18.18
Tr	509.04		Tr	1175.52		Tr	189		Tr	418.38
U	0.00000072		U	7.2E-07		U	7.2E-07		U	7.2E-07
P1*	36183.63818		P1*	12281.16		P1*	81415.09		P1*	35542.75
V1*	0.0000922		V1*	0.000111		V1*	7.69E-05		V1*	9.54E-05
B11	-0.0014052		B11	-0.00219		B11	-0.00068		B11	-0.00108
B12	0.000041		B12	4.78E-05		B12	3.62E-05		B12	4.27E-05
J23	1.176001432		J23	1.176001		J23	1.176001		J23	1.176001
U0	7.66992E-07		U0	7.67E-07		U0	7.67E-07		U0	7.67E-07
Vn	0.000442748		Vn	0.001044		Vn	0.000154		Vn	0.000361
TERM 1	-0.76943852		TERM 1	-0.54662		TERM 1	-0.52484		TERM 1	-0.54737
TERM 2	-0.02016432		TERM 2	-0.01053		TERM 2	-0.02294		TERM 2	-0.01552
TERM 3	-0.00045186		TERM 3	-0.00066		TERM 3	-0.0002		TERM 3	-0.00044
LNɣ	-0.74972606		LNɣ	-0.53675		LNɣ	-0.50211		LNɣ	-0.53229
ɣ	0.47		ɣ	0.58		ɣ	0.61		ɣ	0.59

APPENDIX D

D.1 Published paper:

Activity Coefficients at Infinite Dilution for Different Solutes in an Ammonium Ionic Liquid

Using Gas Liquid Chromatography at *T* = (303.15 and 313.15 and 323.15) K