Ionic Liquids in Micro Extractions and Gas Chromatographic Stationary Phases

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Ionic liquids in Micro Extractions and Gas Chromatographic Stationary Phases

Submitted by

Ramkumar Dhandapani

DISSEPTION

Submitted to the Department of Chemistry and Biochemistry at Seton Hall University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

May, 2014
We certify that we have read this dissertation and that in our opinion it is adequate to scientific scope and quality as a dissertation for the degree of Doctor of Philosophy.

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Acknowledgement

First and foremost, I thank God for guiding my life and giving me the strength needed to persevere. My sincere thanks to my father Late. Dhandapani who always wished that I should go abroad to do my research. I am happy that I was able to fulfill his dreams.

One google search in February 2010 “Snow + New Jersey” brought me all the way from my home town in India to the United States of America to pursue my research. My true and heart felt thank to my mentor Dr. Nicholas Snow for all his guidance, suggestions, and continuous support. The knowledge that he shares with his students is inexpressible by words. I thank Dr. Yuri Kazakevich for all his input on my dissertation as well as his suggestions with my research. I would also like to thank Dr. Sergiu Gorun for the knowledge I gained while working in his group. A special thanks for the time my dissertation committee members have spent for me. My thanks to Dr. Wyatt Murphy and Dr. David Sabatino for giving valuable suggestions during my matriculate exam and for being the committee members for my exam.

I would also like to thank Dr. Cosimo Antonacci for his advice on my future career paths. I would like to extend a special thanks to Dr. Alexander Fadeev and Dr. Rosario LoBrutto for inspiring lectures in their areas of specialization.

I thank Supelco- Sigma Aldrich for providing ionic liquid columns free of cost for my research work. I thank Shimadzu Scientific for all their assistance and support with the GC- MS/MS. My thanks is due to Johnson & Johnson for providing the GC-MS used during this research. I thank Sanofi-Aventis for providing funding necessary to perform this research. My thanks to the
Center for Functional Materials and Center for Academic Industry Partnership for the financial support provided for the research.

I want to thank the Separation Science Group at Seton Hall University especially Shilpi Chopra, Michelle Schmidt, and Atsu Apedo for their friendship and general help in the lab. I would like to extend a special thanks to Hemanthbai Patel for his coordination and knowledge sharing while working for Dr. Sergiu Gorun.

I am truly grateful to my family. A special thanks to my mother Mrs. Revathi Dhandapani, as this would not have been possible without her. My heartfelt thanks to my wife Lakshmi Ramkumar and my daughter Tejashwini Ramkumar for their unconditional love. Thanks to my sister Mrs Agilandeshwari Dhandapani Mate and my brother in law Abhijeet Mate for their affection and valuable suggestions during the course of my research.
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Abstract

The interest of using ionic liquids as gas chromatographic stationary phase has increased in recent years. The low volatility, tailorable physico-chemical property and high thermal stability of ionic liquids make them an ideal choice for gas chromatographic stationary phase. For the present research, commercially available ionic liquid capillary columns were investigate for thermodynamics and kinetics of the retention of alkanes and aromatic hydrocarbons. Van’t Hoff plot was made and the thermodynamic parameters $\Delta G$, $\Delta H$, $\Delta S$ were determined. The thermodynamic parameters of SLB-IL 59 and SLB-IL 61 were compared with a conventional polyethylene glycol based stationary phase Stabile Wax -10 having similar Rohrschneider-McReynolds constants. A plot of $\Delta H$, $\Delta S$ were made against claimed polarity of the ionic liquid columns. Though the polarity numbers were similar for all the three, the trend in $\Delta S$ was different. This shows that Rohrschneider-McReynolds constants by themselves do not predict the actual polarity of these columns and the five probe molecules used for ascertaining the McReynolds constant does not account for all the possible interactions.

The thermodynamics of retention of aromatic hydrocarbons on ionic liquid stationary phase SLB IL-100 using air as carrier gas was studied. This was compared with the thermodynamic parameters using helium as the carrier gas. A Van Deemter plot was made for SLB-IL 100 using aromatic hydrocarbons as probe analyte and air as career gas. Air when used as carrier gas showed lower optimum value in the Van’ Deemter curve and showed a steeper rise in the slope to the right of the optimum value. The kinetic study revealed the possibility of using ionic liquid stationary phase with air as career gas. The stability of ionic liquid stationary phases in the presence of oxygen in air escalates its commercial usage to new horizon of applications.
Ionic liquid–static headspace single drop micro extraction (IL-SHS SDME) involving three phase equilibrium was performed to extract aromatic hydrocarbons from water. A quick extraction was performed by taking the analyte in a 2 ml vial with 0.5 ml headspace volume. Two ionic liquids, 1-Butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide and 1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, both having same anion were individually used for the extraction. A direct, no interface introduction of ionic liquid into the gas chromatographic inlet was performed. Ionic liquid stationary phase was used for the chromatographic separation and GC MS for instrumental analysis. The partition coefficient of the aromatic hydrocarbons between the ionic liquid and water were determined by depletion study. The partition coefficient was higher for the aromatic hydrocarbons when 1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide was used as the extracting micro droplet. The extraction method was then extended for quantitative analysis. The method presented a precision lower than 6.5%, recovery of 88.9% to 98.1% and the limit of quantitation were 60 pg L$^{-1}$ for aromatic hydrocarbons. Real samples of drinking water were collected from different source and aromatic hydrocarbons were not detected in any of them.

Ionic liquid–submerged single drop micro extraction (IL-SSDME) involving two phase equilibrium and ionic liquid–static headspace single drop micro extraction (IL-SHS SDME) involving three phase equilibrium were compared in terms of their partition coefficient. Ideally both the extractions were expected to give close values for the partition coefficient. But in actual IL-SHS SDME showed superior extraction when compared to IL-SSDME.
Ionic liquid based microextractions not only served as ‘green’ alternative to traditional extraction but also proved to be selective, efficient and time saving sample preparation and pre-concentration technique.
Chapter 1: Introduction
Gas Chromatography

The beginning of chromatography was with Ramsey\(^1\) as he separated mixture of gases on charcoal and Michael Tswett\(^2\) separated pigments by liquid chromatography. Tswett coined the word chromatography which meant color writing and is considered as the founder of chromatography. In the present world most separations are done on complex mixtures that are not colored and the term chromatography is not related to the literal meaning. Gas chromatography is a form of chromatography where the mobile phase is a gas. Modern gas chromatography employs stationary phases which are liquid films supported on the walls of thin capillary tubes. Gas chromatography has been used for the analysis of gases, liquids and solids. The volatile analyte once injected in the hot inlet, enters along with the carrier gas into the gas chromatographic column, where it gets partitioned between the liquid stationary phase and the gaseous mobilephase. Volatile samples are preferred for gas chromatographic analysis. If a compound is not volatile, it can be derivated, converting it to a volatile form. Gas chromatography can be a fast analytical technique, requires small sample volume (µL) and is relatively inexpensive and reliable for quantitative analysis. To understand the basic concepts behind chromatographic separation, the basic thermodynamics and kinetics of gas chromatography are discussed in the following section.

Process type in chromatography

Ideal chromatography infers that the exchange between the two phase is thermodynamically reversible. The mass transfer is very high and the longitudinal and other diffusion process are small enough to be ignored. In nonideal chromatography, these assumptions cannot be made. The distribution isotherms may be either linear or non linear in and the chromatographic system may be either ideal or non ideal.
Based on the two sets of condition, there can be four kind of systems: (1) Linear ideal chromatography: which is the most desired theoretically. The transport of the solute will depend on the distribution constant (partition coefficient) and the ratio of the amount of the two phases in the column. (2) Linear non ideal chromatography: In this system the band or zone broadens because of diffusion effect and non equilibrium. This broadening mechanism is symmetrical and the resulting elution band approaches the shape of the Gaussian curve. This best explains liquid or gas chromatography and can be viewed in two ways (a) Plate theory which visualizes the chromatographic system as a discontinuous process functioning the same as an extraction system that consist of large number of equivalent plates and (b) Rate theory which considers the chromatographic system as continuous medium where mass transfer and distribution phenomena are accounted for. (3) Nonlinear – ideal chromatography involves fast mass transfer and longitudinal diffusion is not significant and may be ignored in the description of the system. The composition of lateral diffusion and laminar flow is important in this system. The end result is self shaping front and diffuse rare boundaries in the band. Liquid- solid chromatography is a representative of this system type. (4) Non linear- Nonideal chromatography, where diffuse front and rear boundaries occur and definite tailing of the rear boundary happens. Gas- solid chromatography is best described by this theory.

**Thermodynamics of gas chromatographic retention**

The thermodynamic equilibrium constant, termed as the distribution constant, $K_c$ is given by the ratio of molar concentration of the solute in stationary phase and in the mobile phase. It determines how fast the analyte moves down the column. So if two analyte are mixed together and analyzed in an isothermal run, the analyte that is retained more in the stationary phase has
higher Kc and the other analyte, that elutes faster, would have a lower Kc value. In gas chromatographic analysis, Kc can be determined using the following expression

\[ Kc = \beta \times k \]  \hspace{1cm} \text{Equation (1)}

Where \( \beta \) is the phase volume ratio and \( k \) is the retention factor

\[ \beta = \frac{r_c}{2d_f} \]  \hspace{1cm} \text{Equation (2)}

Where \( r_c \) is the radius of the capillary column and \( d_f \) is the film thickness of the capillary column.

The retention factor is given by

\[ k = \frac{(t_r - t_0)}{t_0} \]  \hspace{1cm} \text{Equation (3)}

Where \( t_r \) is the retention time of the analyte and \( t_0 \) is the holdup time.

Thus from the retention time of the analyte at particular isothermal run and the holdup time of the column, one can calculate the distribution constant.\(^3\)

The distribution constant is related to the free energy change for the chromatographic process by the following expression

\[ \Delta G = -RT \ln(Kc) \]  \hspace{1cm} \text{Equation (4)}
Where $\Delta G$ is the free energy change associated with the chromatographic process, $R$ is the gas constant and $T$ is the temperature in kelvin.

The free energy change $\Delta G$ is related to the enthalpy change $\Delta H$ and entropy change $\Delta S$ by the equation:

$$\Delta G = \Delta H - T\Delta S$$  \hspace{1cm} \text{Equation (5)}$$

Equating equation (4) and (5), we get

$$-RT \ln (K_c) = \Delta H - T\Delta S$$  \hspace{1cm} \text{Equation (6)}$$

$$\ln (K_c) = -\Delta H/RT + \Delta S/R$$  \hspace{1cm} \text{Equation (7)}$$

Thus a plot of $\ln K_c$ against $1/T$ should be linear as shown in Figure 1 if the chromatographic retention follows only partition process and the plot is called as Van’t Hoff plot.\textsuperscript{4} Since Equation (7) is in the form of the general equation for straight line, the thermodynamic parameters $\Delta H$ can be found from (-slope*R) and $\Delta S$ can be determined from the (intercept*R) of the linear plot.
Figure 1: Van’t Hoff plot for the exothermic process, adopted from reference 4

Kinetics of gas chromatographic retention

The most popular research of the kinetics of chromatography was first published by van Deemter, Zuiderweg and Klinkenberg in 1956\(^5\). Band broadening can be represented in terms of height equivalent to a theoretical plate HETP, as a function of average linear velocity \(u\).

The simple form of the equation is represented as follows:

\[
\text{HETP} = A + \frac{B}{u} + C \cdot u \tag{8}
\]

Where A term represents the eddy diffusion, the B term represents longitudinal molecular diffusion and the C term represents mass transfer. From Equation (8), the HETP is inversely
related to the plate number N or the number of theoretical plates. N represents the efficiency of the column. N is represented by Equation (9)

\[ N = 16 \left( \frac{t_r}{W_b} \right)^2 \]  

Equation (9)

Where \( t_r \) is the retention time of the analyte peak and \( W_b \) is the width of the analyte peak at the base. For a chromatographic separation, smaller the value of HETP, narrower the peaks are. Thus each of the three terms should be minimized to lower the HETP and to increase the efficiency (number of theoretical plates, N) of the column.

Since capillary gas chromatography uses open tubular capillary columns and does not have any packing, one would expect that the rate equation would not have the A term. The B can be represented in terms of diffusion coefficient \( D_G \) as follows:

\[ B = 2D_G \]  

Equation (10)

A smaller value of diffusion coefficient \( D_G \) in the gas phase leads to a smaller B term. In general, a low diffusion coefficient can be obtained by using carrier gas with large molecular weight. If we consider Equation (8), the B term is divided by the linear velocity. This implies that higher linear velocity would also minimize the contribution of B term to the overall peak broadening.

The C term in Equation (8) relates to the mass transfer of the solute either in the stationary phase \( C_s \) or in the mobile phase \( C_M \). Fast solute sorption and desorption will keep the solute molecules
close together and keep the band broadening to a minimum. is the aditive of the mass transfer of the solute in the mobile phase $C_M$ and mass transfer of the solute in the stationary phase $C_S$. So the Equation (8) can be re written for gas chromatography as follows:

$$HETP = \frac{B}{u} + (C_S + C_M) u$$  \hspace{1cm} \text{Equation (11)}$$

The Equation (11) is the simplified form of Golay equation.

The $C_s$ term in Equation (11) is given by:

$$C_s = \frac{2kd_f^2}{3(1+k)^2 D_s}$$  \hspace{1cm} \text{Equation (12)}$$

Where $d_f$ is the average film thickness of the liquid stationary phase. And $D_s$ is the diffusion coefficient of the solute in the stationary phase. To minimize the contribution of this term, the film thickness of the stationary phase should be small and the diffusion coefficient should be large. Rapid diffusion through thin films allows the solute molecules to stay close together. Thin film coated stationary phases are made by coating small amount of liquid on the capillary walls. However, the diffusion coefficient is controlled by selecting low viscous stationary phase. The $C_s$ minimizes when the mass transfer into and out of the stationary phase is very fast. The other part of the Equation (12) is $k/(1+k)$. Larger the $k$ value, greater the solubility of the analyte in the stationary phase. The ratio $k/(1+k)$ is minimized by large value of $k$ but to a small extent beyond a $k$ value of 20.

The mass transfer in the mobile phase is given by Equation (13)
\[ C_M = \frac{(1+6k+11k^2)r_c^2}{(24D_G(1+k)^2)} \]  

Equation (13)

Where \( r_c \) is the radius of the column.

The mass transfer in mobile phase can be visualized as the profile of a solute zone as a consequence of nonturbulent flow through the capillary tube. Inadequate mixing in the gas phase results in band broadening because the solute molecule in the center of the column moves ahead of those at the wall. Small diameter column minimizes the broadening because the mass transfer distance is made relatively small.

Thus the relative importance of the two C terms in the rate equation depends mainly on the film thickness and column radius. In general, for thin film column (<0.2 µm), the C term is controlled by mass transfer in the mobile phase, for thick film column (2-5 µm), it is controlled by mass transfer in the stationary phase and for intermediate film thickness (0.2 to 2 µm) both \( C_M \) and \( C_S \) need to be considered.

Van Deemter’s plot is the plot of HETP against the average linear velocity. It is an asymmetrical hyperbola as shown in Figure 2. As evident from the equation (11) the B term is multiplied and the C term is divided by the linear velocity. There is a minimum representing the optimum linear velocity in the curve to get maximum efficiency. In order to optimize the speed of analysis, lighter carrier gas like hydrogen or helium are preferred. The slope of the curve to the right of the optimum value in Figure 2 is important to consider. If the slope is smaller then the
compromise in the efficiency with speed of analysis is minimum. The commonly used carrier
gases for GC analysis are Helium, Nitrogen, Hydrogen. However the choice is also subjective to

![Van Deemter Plot](image)

**Figure 2: Typical example of Van Deemter plot**, adopted from reference 3.

the type of detector used, speed of analysis, thick or thin film column used for analysis. Since air
is composed of 70% Nitrogen, it is a worthwhile trial to use air as carrier gas to reduce the cost
of analysis. However the need for stable stationary phases that can withstand air oxidation is
desired. The other drawback is the narrow range of analytes that are stable to air oxidation.
Gas chromatographic inlet systems for capillary columns

Capillary columns have stringent requisite for sample injection systems. A very fast injection involving very narrow profile, very small quantity usually less than 1 µg. The capillary peaks are very narrow with a peak width of few seconds. Thus very fast injections are required to reduce band broadening due to slow injection.

Split Injection

This is one of the simplest and easiest injection mode to use. A schematic diagram of a typical split inlet is shown in Figure 3. First, the carrier-gas flows in to the top of the inlet, just below the septum. Here, the carrier-gas flow splits between a septum purge vent and the glass liner. The septum purge is at slow flow, typically a few milliliters per minute, that passes underneath the septum and is vented, to prevent any carry over from the septum from entering
the inlet and the capillary column. The other flow path goes into the glass liner, where the syringe needle deposits the sample. In a split injection, there is usually a large (typically 50–100 mL/min) flow of carrier gas through the glass liner. Ideally, the injected sample will be vaporized and mixed with the carrier gas. At the end of the inlet liner, there are two possible exits: the capillary column and the purge vent. A capillary column typically has a relatively low volumetric flow rate (about 1 mL/min), which is determined by the column head pressure setting and the column dimensions, and the purge vent has a higher flow (typically 50–100 mL/min), which is controlled by a needle valve. The ratio of the volumetric flow rate out of the purge vent to the volumetric flow rate in the capillary column is termed the split ratio and provides a control over the actual volume of sample entering the column. Care should be taken when using the split ratio to estimate actual injected sample volume, or when using it in comparisons between methods on different instruments. There are differences between instruments and
measurement techniques that may affect the measured flows. For example, the column volumetric flow rate measured by injecting a nonretained substance is the average column flow rate, not the flow rate at the inlet, while a flow meter connected to the split purge vent measures the volumetric flow rate at the vent, not in the inlet. With newer, electronically controlled systems, the flows are measured directly at the inlet, or are calculated from the entered inlet conditions and column dimensions.

The problems faced by analysts using the split inlet relate to sample discrimination and nonlinear splitting, both of which cause split injection to produce confusing results. Discrimination results from sample heating that occurs in several locations and results from the inlet temperature and liner geometry and may occur in the high or low end of sample volatility. Nonlinear splitting is the loss of some components, relative to others that may have similar volatility, and is an indication of sample chemistry or reactivity problems. To an extent, discrimination occurs in all heated inlets, due to heating of the syringe needle. Making the injection as rapid as possible, by using a fast autosampler, mitigates this problem. Further, as part of method development, the choice of glass sleeve geometry and the inlet temperature should be optimized. Nonlinear splitting occurs as a result of adsorption of sample components on inlet surfaces or contaminants. Ensuring the cleanliness of the liner including column and septum pieces prevents this. If adsorption is suspected, then inlet components such as the glass sleeve and metal components should be deactivated.

A typical example where split injection is used is when finding the chromatographic purity of a volatile solvent. If 1µL of the solvent is injected into the injector, the vapor volume would be
1000 times the original volume. So if the entire quantity entering the inlet passes into the column, it would over load the column as well as saturate the detector. For example, a split ratio of 1:50 is set during the split injection. This mode of injection is a fast injection resulting in high resolution separation and does not need dilution of samples. The disadvantage includes discrimination of high molecular weight sample in the solute such that the sample entering the column is not the representative of the sample injected as mentioned in the previous paragraph. This mode of injection is not suitable for trace level analysis of analytes.

**Splitless injection**

Almost all capillary gas chromatographs, the split/splitless inlet combines the capabilities of both and can operate in either “split mode,” to perform a split injection, or “splitless mode,” to perform a splitless injection. A schematic diagram of a splitless inlet, in both the “purge on” and “purge off” configurations is shown in Figure 4 and Figure 5 respectively. In the “purge on” configuration (Figure 4), the inlet operates as a split inlet. To perform a splitless injection, the purge valve is switched to the OFF position, as shown in the top figure. Since the inlet is backpressure-regulated, the flow is redirected so that the inlet pressure is maintained, which maintains flow through the column, but the volumetric flow through the glass sleeve is greatly reduced. While the purge valve remains off, an injected sample has no place to go from the glass sleeve, but into the column. As in the split inlet, the splitless inlet is heated to ensure sample vaporization and mixing with the carrier gas.
Figure 4: Diagrams of splitless inlet with purge off, adopted from reference 104.
After a period of time, typically 30–45 sec, the purge valve is turned to the ON state. In order to maintain the pressure in the inlet, a large flow of carrier gas is passed through the glass sleeve and through the purge vent. There are several factors that contribute to the surprising result that splitless injection, which requires a long time to complete, results in sharp peaks. These require that instrumental conditions, such as the glass sleeve, the inlet temperature, the column temperature and dimensions, injection solvent, and volume and flow rates, be carefully optimized.

Usually, for splitless injection, the sample to be analyzed is diluted in a volatile solvent. The sample when injected vaporizes and slowly enters the cold column where both sample and
solvent condenses. The split valve is opened and the residual vapors left in the inlet are sent out of the system. The preferred mode of oven operation in this case would be a temperature program. Initially only the volatile solvent is vaporized and carried through the column. While this process is going on, the samples are refocused into a narrow band. After some times, the analytes are vaporized at the hot column and chromatographed. Thus high resolution of the high boiling analytes are observed. This injection mode is ideal for trace analysis. The Splitless mode is 20 to 50 folds more sensitive than split mode because more sample enters the column. The splitless injection suffers from few disadvantages like, slow injection, starting with cold column. Temperature programmed GC analysis is required. The optimization of temperature programme, vent opening time or the injection time is very much required while operating in splitless mode. It is not suitable for very volatile samples and a minimum of $30^0$C difference in the boiling point of the diluting solvent and the analyte is requires.

Unlike split injection, which is very rapid, a splitless injection may require up to 1 min for the injection process to complete. It is obvious that splitless injection would be useless if the injected bands were one minute wide when eluted. Therefore, there must be several mechanisms involved in band broadening and band focusing in splitless injection. There are four major processes that contribute to the eventual sharp bands seen in splitless injection:

1. Band broadening in time which arises simply from the time required for the injected material to eject from the inlet and to enter the column.
2. Band broadening in space which occurs from the spreading of dissolved analyte in the solvent, as it condenses inside the initial length of the capillary column. To mitigate these
two causes of band broadening, two band-focusing processes occur. 

3. Cold trapping which occurs for low-volatility analytes. If the initial column temperature is low enough, lower volatility analytes will be frozen in a narrow band at the column head.

4. Solvent effect focusing which occurs for higher-volatility analytes. The solvent effects, depicted schematically in Figure 6, occur in two ways: (a) the solvent vapor re-condenses rapidly when it reached a column cooled below its boiling point, resulting in a rapid, several-hundredfold reduction in volume, trapping analyte molecules in this flooded zone; and (b) as the carrier gas flows over the flooded zone, it evaporates from the inlet end, becoming progressively smaller, concentrating the analytes as it evaporates. So, cold trapping can be used to focus low volatility analytes, while solvent effects are used to focus more volatile analytes.

Figure 6: Solvent focusing occurs in two stages: as the vaporized solvent recondenses from a gas to a liquid and as the solvent slowly evaporates when the oven temperature is increased, adopted from reference 104.
Other type of capillary inlets

Other type of capillary inlets are direct injection, on column, cold on column, programmed temperature vaporization (PTV) inlet. In a direct injection the vaporized sample directly enters the column. On column as the name signifies, employs the injection of sample directly on to the column. This requires precise alignment of the needle into the capillary column. Both these techniques require thin film and wide diameter capillary column. This results is better trace analysis and good quantitation though there is a compromise in resolution. While both high resolution and good quantitation are possible with cold on-column injection. Here the liquid sample is injected either to the cold liner or the cold column. The cold injector is rapidly heated and the vaporized sample is carried through the column. This mode produces minimal decomposition of thermally labile samples. The PTV on the other hand is heated rapidly at a programmed rate. Usually the liner employed is smaller in diameter than those of other injection modes. The sample is injected into the PTV inlet port while it is relatively cold followed by a rapid temperature programme. In this injection, thermal discrimination is eliminated. This mode of injection is suitable for large volume injection which is desirable for trace level analysis.

Inlet requirement for the present research

Having understood the advantages and disadvantages of various injection modes for capillary gas chromatography, the type of injection mode to be adopted for the analysis purely depends on the purpose of the analysis. The experiments conducted in the research which are explained in Chapter 2 and 3 involved liquid samples containing analytes at higher concentration. So Split mode of injections was used. The experiments in Chapter 4 and 5 involved introduction of ionic liquid containing the extracted analyte into the inlet. The intention of the analysis was trace level
analysis of aromatic hydrocarbons. These experiments also needed the desorption of analytes from the ionic liquid into the inlet. So splitless injection mode was used for these experiments. The precautions taken while performing the sample introduction in ionic liquid microextraction will be explained in Chapter 4.

**Detectors in gas chromatography**

There are over 60 different detectors that can be used in Gas chromatographic analysis. Flame ionization detector, thermal conductivity detector, electron capture detector, flame photometric detector, mass spectrometer are few examples. In this research we have used flame ionization detector and mass spectrometer.

**Flame Ionization Detector**

The flame ionization detector is a non selective detector. It can also be classified under the mass flow type detector. Several factors contribute to the popularity of the FID. First, the FID responds to virtually all organic compounds that burn in the oxygen-hydrogen flame and gives favorable sensitivity. The detector response is not affected by modest changes in flow, pressure, or temperature. It does not respond to common carrier gas impurities such as CO\textsubscript{2} and water under normal operation, although trace hydrocarbon levels in the detector gases will affect baseline stability. The linear range extends to about 10\textsuperscript{7} orders of magnitude.

The schematic of flame ionization detector is shown in Figure 7. The column effluent is mixed with hydrogen and led to a small burner tip which is surrounded by high flow of air to support
combustion. An igniter is provided for lighting the flame. The collector electrode is biased about +300 V relative to the flame tip and the collector current is amplified as high impedance circuit.

Figure 7: Schematic of flame ionization detector, adopted from reference 104.
Mass spectrometry

The schematic diagram showing the major components of a typical capillary GCMS system is presented in Figure 8. The gaseous effluent from the chromatographic system is directed through the transfer line into the ion source. The vaporized analytes are then ionized, producing molecular and/or fragment ions, which are then mass resolved utilizing a mass filter and detected. The resulting mass spectrum is a plot of the relative intensity of these ions versus their mass-to-charge ratio ($m/z$). Since most ions produced are singly charged, their $m/z$ values are indicative of their masses. The source, mass analyzer and mass detector are maintained under vacuum.

Figure 8: Schematic of GCMS, adopted from reference 104
The analyte should be ionized in the source in order to be propelled further by electric and magnetic field. There are various ionization techniques. Electron ionization is the most common ionization for GC MS. Here the effluent from the column passes through a heated ionization source at low vacuum. The electrons are drawn out from the tungsten filament by the collector voltage of 70 eV. The voltage applied to the filament defines the energy of the electron. These high energy electron excites the neutral molecule, causing ionization. This ionization technique mostly produces positive ions with single charge as shown below

\[
\text{M}^+ + e^- \quad \longrightarrow \quad \text{M}^+ + 2e^-
\]  

Equation (14)

Since 70 eV is strong enough to cause the \( \text{M}^+ \) ion to fragment further, EI produces the most stable ions instead of the parent ion. Another convenience of using the EI source is that the library spectrum are always using EI source and can be used to match the mass spectrum of the compound of interest during the analysis. For the present work EI source is used as the ion source. There are other alternate means of ionization which includes chemical ionization (CI), negative chemical ionization (NCI) and fast atomic bombardment (FAB).

After the ionization, the charged ions are repelled and attracted by charged lenses into the mass analyzer. Here the ionic species are separated by their mass to charge ratio (m/z) by either magnetic or electric field. Quadrupole, ion trap and time of flight are few typical mass analyzers suitable for GCMS. The schematic of quadrupole mass analyzer is shown in Figure 9. It consists of four hyperbolic rods at right angle to each other. A DC voltage is applied to all rods, adjacent rods having opposite charge, the signs of the voltage are rapidly reversed. Thus the ions of the
analyte molecules are rapidly attracted and then repelled. Radio frequency is also applied to the four rods. Based on the radio frequency and the DC potential applied, ions of only one mass to charge ratio will pass through the rod and reach the detector. The RF/DC ratio is ramped up rapidly to allow a sequential range of m/z to pass through the mass filter.

After the separation of ions in the mass analyzer, the detector which is a continuous dynode version of an electron multiplier, is used to count the ions and generate the mass spectra.

**Figure 9: Schematic of quadrupole mass analyzer**, adopted from reference 104.

During the analysis the mass analyzer can be run in scan mode where in a range of masses 50 m/z to 500 m/z can be scanned or in selected ion monitoring (SIM) the mass analyzer is asked to selectively see only small number of ions with particular m/z. For the present research we have
used scan mode for experiments which are explained in Chapter 2 and SIM mode for experiments that are explained in Chapter 4 and Chapter 5.

**Ionic Liquids**

Room temperature Ionic liquids (RTILs) are salts that are liquid at room temperature and exist entirely as ionic species. Metallic salts like sodium chloride are ionic solids with high melting point. Ionic liquids on the other hand, are liquid at concurrent temperature. Due to the stearic nature of the anion and/or cation, the ionic liquid has the inability to sit in order in a crystal lattice, causing them to remain as liquid. They are also termed as non molecular ionic solvents. The low vapor pressure of ionic liquids makes them green substitutes to conventional organic solvents. They are very versatile as a solvent. The structure of a typical ionic liquid is shown in Figure 10. There are three distinct parts of the ionic liquid, namely cation (represented in green color), anion (represented in red color) and the side chain (represented in blue color) or the linkage group.

![Figure 10: Structure of ionic liquid 1-Butyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide](image)

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The cation is usually organic (e.g., imidazolium, pyridinium, pyrrolidinium, phosphonium, ammonium), the anions can be either organic (e.g., trifluoromethyl sulfonate $[\text{CF}_3\text{SO}_3]^-$, bis[(trifluoromethyl)sulfonyl]imide $[(\text{CF}_3\text{SO}_2)_2\text{N}]^-$) or inorganic (e.g., $\text{Cl}^-$, $\text{PF}_6^-$, $\text{BF}_4^-$) and the linkage group can be either a nonpolar chain (alkane chain), polar chain (polyethylene glycol back bone) or a nonpolar chain with pendant groups. Based on the different combination of the cation, anion and the side chain there exists $10^{18}$ ionic liquids. 

Due to the possibility of different combination of cation anion and the side chain, the physico-chemical properties of the ionic liquid can be tailored based on the analytical needs. Therefore they are called as designer solvents. The ease of synthesis and commercial availability of ionic liquids, facilitates it application in various fields. The characteristic features of ionic liquids are the low volatility, negligible vapor pressure, thermal stability, high viscosity, polarizablity, unique selectivity, surface tension and wetting properties. These features of ILs, combined with their ease of preparation, have resulted in a remarkable increase in their use.

**History of ionic liquids**

Ionic liquids (ILs) have a very long history. Gabriel and Weiner found ethanolammonium nitrate (m.p. 52–55°C) in 1888. The “first” RTIL ethylammonium nitrate $[\text{EtNH}_3][\text{NO}_3]$ with melting point 120°C was reported in 1914. A new class of RTILs that consist of dialkylimidazolium chloroaluminate, were reported by Wilkes et al. in 1982. These chloroaluminate ILs did not receive considerable interest due to their reactivity to moisture and many chemicals. The true emergence of ILs as broadly useful solvents occurred with the first development of air and
moisture-stable imidazolium salts in 1992. Wilkes and Zaworotko synthesized stable RTILs containing weakly complexing anions, such as BF$_4^-$ 16. In addition to their extensive use as solvents in organic synthesis, ILs have been used more recently in analytical chemistry. Since the late 1990s, a plethora of papers have been published, which have demonstrated the enormous potential of ILs for chemical analysis17, 18, 19.

**Physical properties of ionic liquid**

A fundamental understanding of the physical properties of ionic liquid should be known before applying it to the intended purpose. Physical properties including liquid range, thermal stability, heat capacity and heat transfer, vapor pressure, surface tension are to be considered while selecting the ionic liquid for specific application.

**Liquid range and thermal stability**

The liquid range is defined as the temperature range between the melting point or glass transition temperature and the boiling point or the thermal decomposition temperature. Ionic liquids have fairly wide liquid range than molecular solvents. For example 1-alkyl-3-methyl imidazolium salts usually have a glass transition temperature of -70$^0$ C to -90$^0$ C and thermal decomposition temperature ranges from 320$^0$ C to 540$^0$ C. To give an analogy of how big the liquid range is, one can compare it with water which exists as liquid between 0$^0$ C and 100$^0$ C. The high thermal decomposition temperature means high thermal stability which extends the use of ionic liquids at higher temperature. It has been observed that the poly cationic and poly anionic ionic liquids show higher thermal stability and find application in preparing gas chromatographic stationary phases. 20
Heat capacity and heat transfer

The specific heat capacity is defined as the energy required to rise the temperature of unit mass of the substance by one kelvin. In 2003 Holbrey and coworkers reported the heat capacity of five ionic liquids with imidazolium cation\textsuperscript{21}. They ranged from 1.17 to 1.80 J g\textsuperscript{-1}K\textsuperscript{-1} at 100\textdegree{}C and increased linearly with temperature. Wilkes and coworkers suggested that ionic liquids might be used as heat transfer fluids. They also concluded the superiority of ionic liquids to the existing heat transfer fluids.

Vapor pressure

Ionic liquids have strong coulombic interactions which results in lack of measurable vapor pressure at temperature up to their decomposition temperature\textsuperscript{22}. In general the vapor pressure of the ionic liquids especially the imidazolium based ionic liquids with short alkyl chain, is negligible at room temperature (22\textdegree{}C) and show no evidence of distillation below their thermal decomposition temperature.

Surface tension

There are very few reported data about the surface tension of ionic liquids. The surface tension of ILs is related to the structure of the cations and anions that comprise them. It has been reported that the surface tension of imidazolium-based monocationic ionic liquids decreases significantly with an increasing length of the alkyl chain\textsuperscript{23}. For example, the surface tension for 1-butyl-3-methylimidazolium hexafluorophosphate (BMIM-PF\textsubscript{6}), 1-hexyl-3 methylimidazolium
hexafluorophosphate and 1-octyl-3-methylimidazolium hexafluorophosphate varies from 44.81, 39.02, and 35.16 dyne/cm, respectively. Similar trends have been observed for ammonium and phosphonium-based ILs. However, the trend for dicationic imidazolium-based ILs is not as obvious. Their surface tension decreases by 1.6 dyne/cm when the linkage chain is varied from 3 to 9 carbon chains for dicationic Ionic liquids with the 1- methylimidazolium cation and paired with the NTf$_2^-$ anion. The increasing length of the alkyl chain in the three position of the imidazolium ring has more effect on the resulting surface tension than the linkage chain separating the two cations. Ionic liquids containing halide anions exhibit higher values of surface tension compared to lower surface tension values for larger anions. In addition, the surface tension tends to decrease with increasing size of the anion following the sequence: tetrafluoroborate (BF$_4^-$) > hexafluorophosphate (PF$_6^-$) > trifluoromethanesulfonate (TfO$^-$) > bis(trifluoromethylsulfonyl)imide (NTf$_2^-$). Ionic liquids possessing surface tension values ranging from 30 to 50 dyne/cm typically exhibit superior wetting ability on the wall of untreated capillary columns thus making them the ideal candidate for gas chromatographic stationary phases. If poor wetting of the walls of the capillary column occurs, the stationary phase appears as droplets and exhibits poor separation efficiency.

**Ionic liquids as gas chromatographic stationary phase**

Gas chromatographic stationary phases in general are polymeric and can be broadly classified into one containing polysiloxane back bone and the other containing a polyethylene glycol backbone. The former is used to make nonpolar to mid polar columns while the later to make polar columns. The column manufacturers produce variation in polarity of these columns by providing structural modifications such as introducing pendent groups to the polymeric chain.
For example, DB-5 is the brand name for the GC stationary phase containing 5% phenyl, 95% methyl polysiloxane and DB-FFAP is the brand name for the stationary phase polyethylene glycol modified with nitroterephthalic acid. In a way the number of possible combination of pendent group to produce desired physic chemical property is restricted. In both the cases there are active hydroxyl groups which are susceptible to degradation. Especially for polyethyleneglycol based stationary phases, the active hydroxyl groups at the polymer terminal limits its use at high temperature operation and causes phase degradation and results in column bleeding.

Table 1: Comparison of polymeric and Ionic liquid GC stationary phases

<table>
<thead>
<tr>
<th>Properties</th>
<th>Stationary phases</th>
<th>Ionic liquid Stationary phases</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl polysiloxane back bone</td>
<td>Polyethyleneglycol backbone</td>
<td>Polymeric backbone</td>
</tr>
<tr>
<td>Nature</td>
<td>Polymeric</td>
<td>Polymeric</td>
</tr>
<tr>
<td>Polarity</td>
<td>Non polar to mid polar</td>
<td>Polar</td>
</tr>
<tr>
<td>Active hydroxyl groups</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Structural modifications</td>
<td>Limited</td>
<td>Limited</td>
</tr>
<tr>
<td>Thermal stability</td>
<td>Stable(&gt;260 °C)</td>
<td>Stable(&lt; 260 °C)</td>
</tr>
<tr>
<td>Stability to air and moisture</td>
<td>Not stable</td>
<td>Not Stable</td>
</tr>
<tr>
<td>Type of analysis</td>
<td>Non polar analytes</td>
<td>Polar analytes</td>
</tr>
</tbody>
</table>

From the analyst’s perspective, the general rule of thumb is to select nonpolar columns for non polar analytes and polar columns for polar analytes. So if there is a mixture of compound( both
polar and nonpolar) given for the analysis, the analyst is forced to compromise good chromatographic figures of merit for one set of compound. In such cases a gas chromatographic stationary phase with versatility in selectivity is desirable.

Ionic liquids have unique and tailorable physico-chemical properties such as high viscosity, low vapor pressure, wide liquid range, thermal stability, surface tension and wetting ability, dual selectivity for polar and nonpolar analytes, no active hydroxyl group and so they are the ideal candidate for making gas chromatographic stationary phase. A comparison of polymeric GC stationary phase with ionic liquid stationary phase is shown in Table 1. A typical dicationic, dianionic ionic liquid commercially available as gas chromatographic stationary phase (SLB-IL 100) is shown in Figure 11.

Figure 11: Structure of ionic liquid used in commercially available gas chromatographic stationary phase SLB-IL 100, Structure adopted and redrawn from reference 73.
The dual polar and non polar nature\textsuperscript{27} of the ionic liquid results in unique selectivity and separation of mixture of polar and nonpolar analytes simultaneously. Also the poly cationic and anionic ionic liquids exhibit high thermal stability and improved liquid range. Figure 12 shows the comparison of commercially available ionic liquid stationary phases with polymeric stationary phases based on Mc Reynold's number.

![GC Column Polarity Scale](image)

**Figure 12:** Comparison of commercially available ionic liquid stationary phases with polymeric stationary phases based on Mc Reynold's number, adopted from reference 73 and 105.

The commercially available ionic liquids are arranged on the right side and ranked in ascending order of the Mc Reynold’s number while on the left side, conventional polymeric stationary phases are arranged. There are commercially available ionic liquid stationary phases in market.
that promises polarity similar to and higher than the conventional polymeric polyethyleneglycol column and yet can withstand higher temperature.

**Characterization of Ionic liquids stationary phase**

The general retention mechanisms related with packed or capillary GC columns as well as common solvation models used to illustrate the retention behavior and to characterize various solvation interactions are summarized below.

**Adsorption-Partition mechanism**

While packed gas chromatographic columns were popular for gas chromatographic analysis in 1980’s, Poole and coworkers attempted to find whether the retention in these columns followed a partition or adsorption mechanism. A plot of net retention volume ($V_N$) over volume of liquid phase per gram of packing ($V_L$) was plotted against inverse of the volume of liquid phase per gram of packing $1/V_L$ as shown in Figure 12. The plot was linear with zero slope when partition predominated and showed positive slope when adsorption mechanism predominates. It was observed from the plot that the retention of alkanes is almost controlled completely by partitioning on the tetrapentylammonium 4-toluenesulfonate stationary phase while by interfacial adsorption on the tetraethylammonium 4-toluenesulfonate stationary phase. A simpler way to demonstrate would be to plot $V_N$ against $V_L$ and if the line passes through the origin, the mechanism is partition and if it has a positive intercept, the mechanism will be adsorption. In other words, if the retention depends on the volume of the liquid phase, it goes through the origin signifying that there is no other interaction except with the liquid stationary phase. Another approach shown by authors were to plot net retention volume per gram of stationary phase against percentage loading of the stationary phase. The plot gave a positive intercept with
negligible change in retention volume when extrapolated to zero, when adsorption mechanism was followed. However if there was a linear increase in net retention with increase of the phase

Figure 13: Plot of $V_N/V_L$ with $1/V_L$ for $n$-alkanes with 9–15 carbon numbers on
(a) tetrapentylammonium 4-toluenesulfonate and (b) tetraethylammonium 4-
Toluenesulfonate, adopted from reference 28.

loading, partition would predominate$^{28,29}$. Thus they were able to conclude if a particular column separated the analyte of interest by partition or adsorption.
**Kovats retention index**

In order to estimate the polarity of the stationary phase, one needs to depend on the retention behavior of the solute on the particular stationary phase. Retention volume and retention factor gives a good estimate of the retention behavior of analytes. However they are subjected to too many variables. A simpler approach was adopted by Kovats\textsuperscript{30}. The adjusted retention volume $V_N$ of homologous series of n-alkanes were determined. The kovalt’s retention index, I, was assigned 100 times the number of carbons in the aliphatic chain. For example propane was given I value of 300 and butane was given I value of 400. A plot of natural log of retention volume was made against the I value which followed a linear pattern as shown in Figure 14. For the unknown solute, this plot was used as the calibration plot, the experimental value of adjusted retention time or adjusted retention volume were determined by injecting the unknown solute.

![Figure 14: Kovats retention index plot, adopted from reference 30.](image-url)
and the retention index $I$ was calculated using the following Equation (14):

$$I = 100 \times \left[ \frac{(\log(V_N^u) - \log(V_N^x))}{\log(V_N^x) + 1 - \log(V_N^u)} \right] + 100x$$  \hspace{1cm} \text{Equation (14)}$$

Where the subscript $u$ stands for the solute with unknown $I$ value and $x$, $(x+1)$ stands for the number of carbons present in the alkanes present in the alkane just before and just after the solute with unknown $I$ value. Alkanes were a set of universal standards for establishing $I$ values, other homologous series were also used by industries based on the analyte or solute of particular interest. Thus Kovalts retention index became popular method, replacing absolute retention parameters which were adopted before.

**Rohrschnider- McReynolds constants**

This method adopted the determination of Kovalts retention index of analyte on non polar stationary phase squalane and then on the stationary phase whose polarity has to be determined. Then $\Delta I$, the difference in the $I$ value between the nonpolar squalane column and the column of interest was determined. Rohrschnider used 5 probe analytes to compare the retention index on squalane and any other liquid phase. They were benzene, Ethanol, 2-butanone and pyridine. Then the $\Delta I$ value was determined for all the five probe analytes. Each of the probe analyte measured characteristic intermolecular interaction as shown in Table 2. The $\sum \Delta I$ or the sum of the $\Delta I$ values were determined and normalized with respect to the non polar column to predict
the polarity number of the stationary phase for which polarity has to be determined. In 1970 McReynolds went ahead and proposed ten probe analytes including, benzene, n-butanol, 2-pentanone, nitropropane, pyridine, 2-methyl-2-pentanone, iodobutane, 2-octyne, 1,4-dioxane, cis-hydrindane to replace the five probe analytes used before.

Table 2: Probe analytes used for calculating retention index

<table>
<thead>
<tr>
<th>Rohrschnider</th>
<th>Mc Reynolds</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>Benzene</td>
</tr>
<tr>
<td>Ethanol</td>
<td>n-Butanol</td>
</tr>
<tr>
<td>2-Butanone</td>
<td>2-Pentanone</td>
</tr>
<tr>
<td>Nitromethane</td>
<td>Nitropropane</td>
</tr>
<tr>
<td>Pyridine</td>
<td>Pyridine</td>
</tr>
<tr>
<td></td>
<td>2-Methyl-2-pentanol</td>
</tr>
<tr>
<td></td>
<td>Iodobutane</td>
</tr>
<tr>
<td></td>
<td>2-Octyne</td>
</tr>
<tr>
<td></td>
<td>1,4-Dioxane</td>
</tr>
<tr>
<td></td>
<td>Cis- Hydrindane</td>
</tr>
</tbody>
</table>

Even today the polarity of commercially available ionic liquids are predicted using McReynold’s number as shown in Figure 15. The commercially available ionic liquids assigned polarity number based on McReynolds number by Supelco-Sigma Aldrich. It is seen that the
A contribution from each probe analyte is summed up and represented as P in the Figure 15. Following this column is polarity number denoted by P.N. Here an assumption is made that SPB octyl has a polarity number 1. The P value of other columns are normalized with respect to SPB Octyl column. The discrepancy in the calculation of polarity number will be further discussed in Chapter 2.

### GC Column Polarity Scale

<table>
<thead>
<tr>
<th>Column</th>
<th>Benzene</th>
<th>n-Butanol</th>
<th>2-Pentanone</th>
<th>Nitropropane</th>
<th>Pyridine</th>
<th>P</th>
<th>P.N.</th>
</tr>
</thead>
<tbody>
<tr>
<td>SPB-Octyl</td>
<td>17</td>
<td>-20</td>
<td>8</td>
<td>19</td>
<td>8</td>
<td>28</td>
<td>1</td>
</tr>
<tr>
<td>Equity-1</td>
<td>11</td>
<td>10</td>
<td>33</td>
<td>60</td>
<td>16</td>
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P (Polarity) = sum of the first 5 McReynolds Constants.
P.N. (Polarity Number) = Polarity (P) normalized to SLB-IL100 (set at P=100).

**Figure 15:** Polarity index calculation for commercial ionic liquid columns by Supelco-Sigma Aldrich, adopted from reference 70.
Abraham’s solvation model

Abraham and co-workers by utilized large number of test probes that are capable of undergoing multiple interactions with stationary phase\textsuperscript{34, 35}. This model can be applied to characterize liquid or gas phase interactions between solutes and liquid phases. The solvation model is a linear free energy relationship based on the assumption that the total free energy change for the transfer of solute X from the gas phase to the liquid phase is the linear sum of the contributions from different individual free energies. The solvation of solute X includes three steps: (1) a cavity of suitable size is created in the solvent; (2) the solvent molecules reorganize around the cavity; and (3) the solute is introduced into the cavity followed by the occurrence of the various interaction between the solute and solvent. The test probes interact with the solvent through different types of interactions depending on their structural properties. Five parameters, referred to as solute descriptors ($E, S, A, B, L$) are utilized to describe the properties of the solute which have been determined for hundreds of probe molecules. Each solute descriptor is described as follows: $E$ is the excess molar refraction calculated from the solute’s refractive index; $S$ is the solute dipolarity/polarizability; $A, B$ are the solute hydrogen bond acidity and hydrogen bond basicity, respectively; and $L$ is the solute gas–liquid partition coefficient on hexadecane at 298K. The model is described in Equation (15).

$$\log k = c + eE + sS + aA + bB + lL$$ \hspace{1cm} \text{Equation (15)}

According to Equation (12), $k$ is the retention factor of a given solute on a stationary phase at a specific temperature. The system constants $e, s, a, b, l$ are used to describe the solvation properties of stationary phase and are defined as follows: $e$ is the ability of the solvent to interact
with solute via $\pi$-$\pi$ or n-$\pi$ interactions; $s$ is a measure of the dipolarity/polarizability of the solvent; $a$ and $b$ are measure of the solvent hydrogen bond acidity and hydrogen bond basicity, respectively; $l$ describes the overall dispersive-type interactions. The system constants are obtained by multiple linear regression analysis of the solute descriptors and retention factors. The value of each system constant describes the contribution of the particular interaction to the overall solute–solvent retention mechanism. It is important to stress the fact that the value of the system constants is temperature dependent.

**Other studies**

In modern gas chromatography, wall coated open tubular capillary columns have replaced packed columns for gas chromatographic separation. Various groups have attempted to refine the above mentioned models\(^{36, 37}\). Most of them considered that simplicity of just selecting five to ten probe analytes to find Mc Reynold’s number to account for all kind of interactions leads to ambiguity in the ascertained polarity. The classification of the RTILs based upon dipolarity and basicity provides a model that can be used to pick RTILs for specific organic reactions, liquid extractions, or GLC stationary phases. It was established by Anderson that as compared to conventional organic solvents, RTILs are much more complex solvent systems capable of undergoing many types of interactions. Characterizing them with a single “polarity” term fails to describe the type and magnitude of individual interactions that make each RTIL unique. The solvation model uses many solute probe molecules in conjunction with inverse GC to quantitatively determine the importance of different RTIL interactions as a function of temperature. These results are especially useful in explaining solvent behavior between broad classes of RTILs. Even today, there are questions about choosing the right scale or method that
can depict the characteristic retention aspects of ionic liquids as stationary phase. Especially for the commercially available ionic liquid stationary phases, whose structure and type of bonded phase are proprietary and may not be disclosed to the user, easily available parameters that assist in selecting the column is desirable.

**Ionic liquid in microextraction**

Sample preparation plays a vital role in analytical chemistry. It includes extraction and preconcentration of target analytes. Conventional liquid-liquid extraction generally employs large amount of extracting solvents and is time consuming. Ionic liquids have been used for liquid-liquid extraction of metal ions, small organic molecules and large biological compound. Since liquid-liquid extraction employs large volume of the extracting medium, the end result leads to generation of hazardous waste. To solve this issue, liquid phase micro extraction or ionic liquid micro extraction started to evolve. Ionic liquids have an ideal role to play when used as the extracting solvent in microextraction due to their physico-chemical properties and unique selectivity. Ionic liquid submerged single drop microextraction (IL-SSDME) involves liquid phase microextraction in direct immersion mode. Here a single drop of ionic liquid is dispersed in the medium from which the analyte has to be extracted. After the extraction, the layers are allowed to separate. Ionic liquid static headspace single drop microextraction (IL-SHSSDME) involves suspending the single drop of the ionic liquid in the headspace. In both cases, after the extraction is completed, the ionic liquid is retracted into a syringe and introduced into analytical instruments like GC or HPLC for the qualitative and/or quantitative screening of analytes. Experiments involving exhaustive dynamic headspace microextraction (IL-DHME) have also been reported. In this case, the extracting solvent ionic
liquid is used as a trap by purging with the vapors of the analyte. Since this extraction method involves the motion of the phases, it is termed as dynamic headspace microextraction. There are also several modified forms of ionic liquid based microextractions reported recently\textsuperscript{50, 51, 52}.

**Other Analytical Applications:**

Ionic liquids are finding diverse application in various fields of analytical chemistry. The following section discusses their applications in detail.

**Solid phase microextraction**

Solid-phase microextraction (SPME) is a fast, solventless alternative to conventional liquid phase extraction. It integrates sampling, extraction, concentration and introduction to chromatography into a single solvent-free step. A SPME method using a disposable IL coating was developed to quantitatively analyze benzene, toluene, ethylbenzene, xylene in paints\textsuperscript{53}. This coating material has some obvious advantages: lower cost, minimum carryover, and comparable reproducibility to commercial fibers. The partitioning behavior of different types of compounds in IL-aggregates coated on SPME was studied, and monocationic ILs generally provided higher extraction power than dicationic analogues. Polymeric imidazolium-based IL coatings were synthesized and applied to extract esters\textsuperscript{54}. This type of coating showed high thermal stability, long lifetimes, and provided good analyte recoveries, comparable to those using polydimethylsiloxane fibers. Recently, two new ILs, which contained styrene units, were used to prepare silica-bonded polymeric SPME adsorbents\textsuperscript{55}. These SPME fibers can work successfully in both the headspace mode and immersion mode.
**Solvent for headspace GC**

Headspace GC avoids direct liquid or solid probing and greatly decreases matrix interference. One acidic, one basic, and one neutral compound were dissolved in different ILs with appropriate acidity and basicity. They were detected by headspace GC and their detection limits were in the low ppm level. Residual solvents (acetonitrile, dichloromethane, N-methyl-2-pyrrolidone, toluene, DMF, and n-butyl ether) in pharmaceuticals were determined by headspace GC using 1-butyl-3-methylimidazolium BF₄ (\([\text{BMIM}][\text{BF}_4]\)) as the solvent. These analytes have relatively low volatility (boiling point > 150 °C), so higher temperature headspace procedure is necessary. Due to its good thermal stability, \([\text{BMIM}][\text{BF}_4]\) worked exceedingly well and gave better sensitivity than DMSO as the solvent.

**Thin layer chromatography**

Most recent TLC stationary phases use silica gel as the solid support. The silica surface has residual acidic silanol groups, which have deleterious effects on separations. For example, unsymmetric (tailing), broad peaks are observed, especially for basic analytes. Therefore, amine additives are often added to block the acidic surface and ameliorate these effects. ILs, with proton acceptor properties, provide the potential for this application. Kaliszanz et al. first reported that IL additives in the mobile phase suppressed free silanol effects on the retention of basic drug compounds in TLC. Eight basic compounds were not moved from the application spot either on the bare silica or on the octadecylsilica plates using acetonitrile eluent. Traditional amine additives (triethylamine, dimethyloctylamine, and ammonia) could not completely suppress the effect of free silanols. The tested ILs were imidazolium BF₄ types (1-ethyl-3-methylimidazolium [EMIM], 1-methyl-3-hexylimidazolium, and 1-hexyl-3-
heptyloxyethylimidazolium tetrafluoroborate). ILs decreased the retention of basic analytes more effectively than other alkylamines.

Addition of ILs to the mobile phase in column-based LC separations could be traced to a publication in 1986, which reported ILs used as organic modifiers. Alkylammonium nitrate or thiocyanate salt was mixed with another solvent of low viscosity and used as the mobile phase. Later, the same group conducted detailed studies on the solvent properties of six ILs used in microcolumn RPLC. They found that the solvent selectivities were controlled by proton acceptor-donor and weak dispersive interactions, influenced by the cation size and the nature of the IL anions.

**LC stationary phases**

More recently, development of new LC stationary phases based on ILs received greater attention. Liu et al. are among the first to examine this application. They synthesized anion exchange stationary phases with immobilized imidazolium-based ILs. The new columns successfully separated anions, amines, and nucleotides, and they exhibited both a strong anion exchange character and a reversed phase interaction.

**Capillary electrophoresis**

CE has become a powerful separation technique in recent years due to low sample and reagent consumption, high efficiency and simplicity. Generally fused-silica capillaries are used for CE, and silanol groups on the inner surface are normally negatively charged. This results in the formation of an electroosmotic flow (EOF). Also, the inner capillary surface could participate in
interacting with analytes, further affecting separations. The capillary surface could be chemically modified to reverse EOF when cationic ions absorb or bond to the inner surface. Several groups reported that ILs were covalently bonded to the capillary wall to modify the surface. A 1-methylimidazolium-based IL was covalently bonded to a fused-silica capillary surface to reverse the EOF.

**MALDI matrices**

MALDI (matrix-assisted laser desorption ionization) is a soft ionization technique for mass spectrometry, which allows detection of intact, large biomolecules, and synthetic polymers. The analyte is dissolved in a volatile solvent containing the matrix and then spotted on the MALDI plate. The matrix plays a key role in this technique in preventing analyte molecules from being destroyed by direct laser energy absorption and facilitating their volatilization and ionization. Matrix selection is crucial in MALDI-MS analysis. An ideal matrix should possess the following properties: absorption at the laser wavelength, capabilities of dissolving or cocrystallizing with the sample, low volatility, suppressing analyte decompositions, and promoting the ionization of analytes. The unique properties of ILs (low volatility and wide solubility with various types of compounds), make them suitable for working as MALDI matrixes. Armstrong et al. first developed effective ILs as MALDI matrixes. Typical imidazolium, pyridinium and phosphonium ILs were ineffective matrixes as they did not adequately promote the ionization of the sample. When ILs were formulated using anions of popular solid matrixes and specific prononated cations, then peptides, proteins and polyethylene glycol could be detected with high sensitivity and good reproducibility.
Chapter 2: Retention of alkanes and aromatic hydrocarbons on ionic liquid stationary phases
Introduction

Ionic liquid is a salt similar to sodium chloride. The former is a liquid ionic species due to the bulky anion while the latter is a crystalline solid. Due to the combination of anions, cations and the linkage groups, ionic liquids have unique selectivity for analytes. Molten salts were used as gas chromatographic stationary phase in 1959 by Barber et al. However useful chromatographic performance and selectivity of ionic liquid as gas chromatographic stationary phase was first demonstrated by Poole et al in 1982. Using packed gas chromatographic columns, attempts were made to find if the retention in ionic liquid columns followed a partition or adsorption mechanism for particular analyte by Poole’s group. Referring to Figure 13 in Chapter 1, a plot of net retention volume versus inverse of the volume of liquid phase per gram of packing generates a linear plot with zero slope when partition predominated and showed positive slope when adsorption mechanism predominates. Another approach shown by Poole was to plot net retention volume per gram of stationary phase against percentage loading of the stationary phase. The plot gave a positive intercept with negligible change in retention volume when extrapolated to zero, when adsorption mechanism was followed. However if there was a linear increase in net retention with increase of the phase loading, partition would predominate. This observation is consistent with the view that adsorption at support-liquid interface is dominant for phases of low polarity and at the gas liquid interface for polar phases. Usually non polar compounds are retained on polar stationary phases by interfacial adsorption indicating that gas liquid partition is of minor importance for retention.

The physico-chemical properties of ionic liquids are favorable for coating them as a liquid film in capillary gas chromatographic. The analogy of liquid-liquid extraction, where the partition
coefficient remains the same at a particular temperature irrespective of the phase volumes of the acceptor and donor phase, can be applied to the gas chromatographic separation. In the present work, a simpler approach was adopted to predict the predominant mechanism of retention of probe analytes on commercially available ionic liquid stationary phases. Thus considering chromatographic separation as an equilibrium process, the thermodynamic parameter Kc was compared for ionic liquid stationary phase with different column length, internal diameter and phase ratio. If partitioning of the analytes between liquid and vapor phase is the dominant mechanism then the Kc would not vary with column length, internal diameter and phase ratio. If the Kc varies with column length, internal diameter and phase ratio, then adsorption mechanism dominates the retention process.

The biggest advantage of ionic liquid stationary phases are the high selectivity, thermal stability and longer liquid temperature range. While a conventional polar polymeric polyethylene glycol stationary phase has the upper temperature limit of 280°C, the ionic liquid stationary phase claimed to have similar polarity can go up to 300°C. Commercially available 1,2,3-tris(2-cyanoethoxy)propane based stationary phase (TCEP) also called as Mc Nair’s Stationary phase has its upper temperature limit is 140°C. However the extremely polar ionic liquid column SLB-IL 111 can go up to 270°C. This feature is extremely useful, allowing chromatographers to analyze high boiling components at higher temperature without decomposing the stationary phase. Ionic liquids are gaining more applications in multi dimensional chromatography. Experiments using Ionic liquid stationary phase as secondary column or primary column are gaining popularity. Separation of fatty acid methyl esters, polar and nonpolar mixtures,
polycyclic aromatic hydrocarbons\textsuperscript{77}, in the analysis of flavors and fragrance compounds\textsuperscript{78} and chiral separation.\textsuperscript{79}

The ionic liquid stationary phases that are commercially available, exclusively from Supelco-Sigma Aldrich, are assigned a polarity number based on the Mc Reynolds constant\textsuperscript{73}. The detailed description of polarity index calculation is explained in Chapter 1. To calculate the polarity index, the $\Delta I$ value for Benzene, n-Butanol, 2-Pentanone, Nitropropane and Pyridine were used as the probe analytes. The sum of $\Delta I$ values for the probe analytes were calculated. Then the sum of $\Delta I$ was normalized against the sum of $\Delta I$ of SPB-Octyl column to get the polarity number. Based on the calculated polarity number, the commercially available ionic liquid stationary phases are ranked from polar to extremely polar (polarity number 59 to 111).

The principle used for calculation of polarity number for conventional polymeric column is applied by Supelco to the ionic liquid columns. More rigorously, it would be worthy to account for the retention features of these columns in terms of the thermodynamic parameters including $K_c$, $\Delta H$, $\Delta S$.

**Objective of the experiment**

The key objectives of the study are shown in Figure 16, which included the determination of thermodynamic parameters of retention of alkanes and aromatic hydrocarbons on commercially available ionic liquid stationary phases. The Vant’ Hoff plots were constructed for alkanes and aromatic hydrocarbons (refer Chapter 1, page 24). From the slope and intercept of the Vant’ Hoff plot, $\Delta H$ and $\Delta S$ were determined. From these thermodynamic parameters, the predominant mechanism of retention was explored.
Figure 16: The schematic representation of the objective of the experiment.

The thermodynamic parameters of retention for same ionic liquid stationary phase with different column length were compared to predict if the retention followed partition or adsorption of analytes. The Thermodynamic parameters of retention of conventional polyethylene glycol based stationary phase was compared with the ionic liquid stationary phase claimed to have similar polarity. The $-\Delta G$ value of analytes on different ionic liquid stationary phases were correlated to their structure to see their relationship to the alkyl groups in the linkage group. The same study was made based on the depicted polarity. This gave an insight of the ambiguity in the claimed polarity number of these columns.
Experimental

Materials and Chemicals

Nonane, decane, undecane, dodecane, tridecane, tetradecane, benzene, toluene, ethylbenzene, butylbenzene, hexylbenzene, heptylbenzene, hexane, Supelcowax-10 with dimensions 30 m, 0.25 mm, 0.25 µm were purchased from Supelco Sigma-Aldrich. The ionic liquid stationary phase SLB-IL 59, SLB-IL 60, SLB-IL 61 and SLB-IL 100 having dimensions 30 m, 0.25 mm, 0.20 µm and SLB-IL 100 with dimensions 15 m, 0.10 mm, 0.08 µm were provided by Sigma-Aldrich. The aromatic hydrocarbons analysis was performed on Agilent GC 6890 coupled to 5973 MS detector system (Agilent Technologies, Palo Alto, CA, USA) equipped with CTC Analytics CombiPal autosampler (Zwingen, Switzerland) while the analysis of alkanes were performed in HP-5890 GC with flame ionization detector (GC-FID).

GC-FID and GC-MS parameters

The retention of alkanes were studied using GC-FID. Since the literature showed evidence of change in selectivity for aromatic hydrocarbons, the retention of aromatic hydrocarbons were studied using GC-MS to be certain about the elution order. Based on the experiment performed, a particular column was installed in the chromatographic system. The inlet temperature was maintained at 250 °C. The inlet was maintained at constant pressure with linear velocity of 14 cm sec⁻¹. The split ratio was set as 50:1. The injection volume was 1 µL. The isothermal runs were performed at 40 °C (313 K), 45 °C (318 K), 50 °C up to 80 °C (353 K). For the flame ionization detector, the detector temperature was set as 250 °C. The hydrogen and air flow were set as 30 mL min⁻¹ and 300 mL min⁻¹, respectively. For the MS, transfer line temperature, source and
quard temperature was set at 250 °C, 150 °C and 250 °C respectively. The MS was operated at 70 eV in scan mode from mass range 50 m/z to 500 m/z.

**Standard preparation**

The diluting solvent for working standard solution was hexane. 0.01% of nonane, decane, undecane, dodecane, tridecane and tetradecane were prepared in hexane and was named as alkanes working standard. The aromatic hydrocarbon working standard was prepared by mixing 0.01% of benzene, toluene, ethyl benzene, butylbenzene, hexylbenzene and heptylbenzene in hexane. 1±0.1 µL of the working standards were injected into the chromatographic system. After each run the syringe was cleaned with hexane five times.

**Experimental**

**Retention of alkanes and aromatic hydrocarbons on ionic liquid stationary phase**

A summary of the column chosen for particular experiment is summarized in Table 3. To study the retention of alkanes and aromatic hydrocarbons on ionic liquid stationary phase, the respective working standards were injected at isothermal oven temperature using a SLB-IL 100 stationary phases having dimension 30 m, 0.25 mm, 0.20 µm and SLB-IL 100, SLB-IL 111 and SLB-IL 82 having dimensions 15 m, 0.10 mm, 0.08 µm respectively. To compare the retention of alkanes on polyethylene glycol stationary phase, SLB-IL 59 and SLB-IL 60, Supelco wax10 column having dimensions 30 m, 0.25 mm, 0.25 µm was installed in the GC oven and the alkanes working standard was injected at each isothermal temperature. The same experiment was repeated using SLB-IL 59, SLB-IL 60 having dimensions 30 m, 0.25 mm, 0.20 µm.
the case the hold up ($t_0$) time was considered as the time at which the diluting solvent started to eluted.

Table 3: Columns choosen for the study and experiments performed

<table>
<thead>
<tr>
<th>Column, Dimension</th>
<th>Dimensions</th>
<th>Objectives of the experiment</th>
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<td>SLB-IL 100</td>
<td>30 m, 0.25 mm, 0.20 µm</td>
<td>Retention of alkanes and aromatic hydrocarbons</td>
</tr>
<tr>
<td></td>
<td>15 m, 0.10 mm, 0.08 µm.</td>
<td></td>
</tr>
<tr>
<td>SLB-IL 111, SLB-IL 100, SLB-IL 82</td>
<td>15 m, 0.10 mm, 0.08 µm.</td>
<td>Correlation of structure of ionic liquid to the retention of alkanes</td>
</tr>
<tr>
<td>SLB-IL 59, SLB-IL 60</td>
<td>30 m, 0.25 mm, 0.20 µm</td>
<td>Comparison of polyethylene glycol column and IL having similar polarity</td>
</tr>
<tr>
<td>Stabile Wax- 10</td>
<td>30 m, 0.25 mm, 0.25 µm</td>
<td></td>
</tr>
</tbody>
</table>

Van’t Hoff plot and statistical validation of the data

The retention time of the peaks at each temperature was determined from the chromatogram of isothermal runs. From the retention time, and the holdup time $t_0$, $k$ was calculated using Equation 2, plugging the $k$ value into Equation 1 (Chapter 1) gave the $K_c$. A plot of $\ln K_c$ vs $1/T$ (kelvin$^{-1}$) was plotted for all the above experiments. The plot was examined for linear behavior. The residue of the least square regression was examined for a linear trend. From the slope and y-intercept $\Delta H$, $\Delta S$ were calculated. The error in slope and intercept at 95% confidence interval
were calculated. Further propagation of error in slope and intercept were calculated and reported as uncertainty in the calculation of $\Delta H$, $\Delta S$.

**Results and Discussion**

**Retention of alkanes on ionic liquid stationary phase**

The thermodynamics of retention of alkanes on ionic liquid column was explored by examining the Van’t Hoff plot. The plots presented $R^2$ value greater than 0.999. As shown in Figure 17, the Van’t Hoff plots for alkanes using the SLB-IL 100 showed a linear pattern. If Van’t Hoff plot considers partition as the only mechanism involved in the process. It was proved in literature that multiple interaction in HPLC stationary phase were not inferred just from the classical thermodynamic approach using the Van’t Hoff plot.  

![Figure 17: Van’t Hoff’s plot for alkanes on SLB-IL100, 30m x 0.25 mm x 0.20 µm.](image)
The $\Delta G$ associated with the chromatographic process should be the same irrespective of the column length, phase ratio and internal diameter. Figure 7 shows a plot of $\Delta G$ against $T$ for alkanes on 30 m and 15 m column of SLB-IL 100. The phase volume ratio of both the columns were the same. The free energy change calculated in each case resulted in a negative value indicating a spontaneous chromatographic process. The analytes when injected in the hot inlet are in vapor form. They condense on the column head and the process is exothermic and spontaneous. With increase in temperature the $\Delta G$ value becomes less negative. However, since both the 30 m and 15 m columns had the same phase volume ratio $\beta$, one would expect a fairly close $\Delta G$ value if only partition of analyte from the vapor phase to the ionic liquid stationary phase occurred. In other words, identical color lines should overlap or lie close to each other in Figure 18., if the mechanism strictly followed partition. Thus change in free energy with temperature tells that the original assumption of only partition mechanism exists in the chromatographic process is not correct. In order to account for the contribution of adsorption and partition mechanism towards the retention of analytes, a new model has to be proposed with the help of equilibrium constants or a superposition of different constants.
Figure 18: Comparison of ΔG vs T for alkanes on SLB-IL100 : 30 m and 15 m column.

The linear free energy relationship was also observed for alkanes with increase in carbon chain. The vertical lines in Figure 18 signifies that the ΔG had a linear relationship with the number of carbons in the alkyl chain (from Nonane to Tetradecane).

In Table 4, the difference in ΔG value between a 30 m and a 15 m SLB-IL 100 stationary phase for retention of alkanes are reported. The ΔG value increased with increase in the carbon chain and increased with decrease in temperature. This is clear from the table that the ΔΔG value are increasing towards the bottom right corner. This means that the thermodynamic property ΔG is different for higher alkanes in the homologous series.
Table 4: Comparison of ΔΔG value for alkanes at different temperature.

<table>
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<tr>
<th>Temperature</th>
<th>ΔΔG (KJ/mol)</th>
<th>Nonane</th>
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<th>Undecane</th>
<th>Dodecane</th>
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<td>17</td>
<td>19</td>
</tr>
<tr>
<td>328</td>
<td></td>
<td>0</td>
<td>-2</td>
<td>14</td>
<td>16</td>
<td>17</td>
<td>19</td>
</tr>
<tr>
<td>323</td>
<td></td>
<td>-1</td>
<td>-3</td>
<td>15</td>
<td>16</td>
<td>18</td>
<td>20</td>
</tr>
<tr>
<td>318</td>
<td></td>
<td>-1</td>
<td>-3</td>
<td>15</td>
<td>17</td>
<td>18</td>
<td>20</td>
</tr>
<tr>
<td>313</td>
<td></td>
<td>-2</td>
<td>-3</td>
<td>15</td>
<td>17</td>
<td>19</td>
<td>21</td>
</tr>
</tbody>
</table>

The Kc for same ionic liquid stationary phase with different column length, film thickness and internal diameter were compared. The Kc is a thermodynamic quantity which should be the same at a given temperature irrespective of the column length. Table 5 shows the difference in distribution constant (ΔKc) for alkanes between a 15 m and 30 m length ionic liquid stationary phase SLB-IL 100. The Kc values for 15 m, 0.10 mm, 0.08 µm. was higher than 30 m, 0.25 mm, 0.2 µm. The thinner film column has larger surface area and hence adsorption is more important in the thinner film column. A Kc of 200 is is equal to a k value of 0.6. Examining the data for SLB-IL 100 showed ΔKc < 200 for Dodecane at 323 K, 318 K and 313 K; Tridecane at 333 K, 328 K, 323 K, 318 K, 313 K and for tetradecane at 348 K, 343 K, 338 K, 333 K, 328 K, 323 K, 318 K. The larger the difference in Kc between a 15 m and a 30 m column, the greater is the adsorption. The Van’t Hoff plot assumes partitioning of alkanes between the ionic liquid stationary phase and the carrier gas (helium) is the only mechanism, was linear for alkanes with R² < 0.999. However, due to larger ΔKc, residual adsorption mechanism is noticed for higher alkanes at lower temperature. This was also supported by the asymmetric peaks for higher
alkanes at lower temperature. With higher carbon chains, the mechanism tends towards adsorption and partition.

Table 5: Difference in $K_c$ for alkanes between 15m and 30 m SLB-IL 100 stationary phase

<table>
<thead>
<tr>
<th>$T$ (K) *</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>353</td>
<td>17±1</td>
<td>26±1</td>
<td>43±1</td>
<td>68±2</td>
<td>111±2</td>
<td>180±4</td>
</tr>
<tr>
<td>348</td>
<td>20±1</td>
<td>31±1</td>
<td>51±1</td>
<td>83±2</td>
<td>137±3</td>
<td>228±5</td>
</tr>
<tr>
<td>343</td>
<td>22±1</td>
<td>37±1</td>
<td>62±2</td>
<td>104±2</td>
<td>176±4</td>
<td>298±7</td>
</tr>
<tr>
<td>338</td>
<td>25±1</td>
<td>44±2</td>
<td>75±2</td>
<td>130±3</td>
<td>224±5</td>
<td>389±9</td>
</tr>
<tr>
<td>333</td>
<td>30±1</td>
<td>53±2</td>
<td>93±3</td>
<td>164±4</td>
<td>289±6</td>
<td>513±11</td>
</tr>
<tr>
<td>328</td>
<td>35±2</td>
<td>64±2</td>
<td>116±3</td>
<td>210±5</td>
<td>379±8</td>
<td>687±15</td>
</tr>
<tr>
<td>323</td>
<td>43±2</td>
<td>79±3</td>
<td>147±4</td>
<td>273±7</td>
<td>503±11</td>
<td>933±21</td>
</tr>
<tr>
<td>318</td>
<td>52±3</td>
<td>100±3</td>
<td>190±5</td>
<td>359±9</td>
<td>677±15</td>
<td>1286±29</td>
</tr>
<tr>
<td>313</td>
<td>66±3</td>
<td>128±4</td>
<td>248±7</td>
<td>480±11</td>
<td>925±20</td>
<td>1800±40</td>
</tr>
</tbody>
</table>

* GC oven temperature in Kelvin

** Difference in $K_c$ for aromatic hydrocarbons between 15m and 30 m column

Retention of aromatic hydrocarbons on ionic liquid stationary phase

The Van’t Hoff’s plot for aromatic hydrocarbons on SLB-IL 100 showed $R^2 > 0.995$. Table 6 shows the comparison of the $\Delta K_c$ of aromatic hydrocarbons on SLB-IL 100 15 m, 0.10 mm, 0.08 µm and 30 m, 0.25 mm, 0.20 µm.
Table 6: Difference in Kc for aromatic hydrocarbons between 15m and 30 m SLB-IL 100 stationary phase

<table>
<thead>
<tr>
<th>T *(K)</th>
<th>Benzene</th>
<th>Toluene</th>
<th>Ethylbenzene</th>
<th>Butylbenzene</th>
<th>Hexylbenzene</th>
<th>Heptylbenzene</th>
</tr>
</thead>
<tbody>
<tr>
<td>353</td>
<td>19±3</td>
<td>41±17</td>
<td>66±2</td>
<td>179±4</td>
<td>492±11</td>
<td>831±13</td>
</tr>
<tr>
<td>348</td>
<td>28±3</td>
<td>53±20</td>
<td>80±2</td>
<td>221±5</td>
<td>646±14</td>
<td>1124±17</td>
</tr>
<tr>
<td>343</td>
<td>31±4</td>
<td>59±24</td>
<td>98±2</td>
<td>274±6</td>
<td>839±18</td>
<td>1471±22</td>
</tr>
<tr>
<td>338</td>
<td>33±4</td>
<td>67±29</td>
<td>113±3</td>
<td>344±8</td>
<td>1090±24</td>
<td>1961±30</td>
</tr>
<tr>
<td>333</td>
<td>36±5</td>
<td>75±35</td>
<td>131±3</td>
<td>422±10</td>
<td>1407±32</td>
<td>2594±40</td>
</tr>
<tr>
<td>328</td>
<td>40±6</td>
<td>172±29</td>
<td>159±4</td>
<td>527±13</td>
<td>1835±42</td>
<td>3479±55</td>
</tr>
<tr>
<td>323</td>
<td>49±7</td>
<td>204±37</td>
<td>200±5</td>
<td>690±16</td>
<td>2506±57</td>
<td>4857±75</td>
</tr>
<tr>
<td>318</td>
<td>59±8</td>
<td>135±64</td>
<td>240±6</td>
<td>876±22</td>
<td>3366±78</td>
<td>NA ***</td>
</tr>
<tr>
<td>313</td>
<td>70±10</td>
<td>172±79</td>
<td>301±8</td>
<td>1144±29</td>
<td>4486±108</td>
<td>NA ***</td>
</tr>
</tbody>
</table>

* GC oven temperature in Kelvin

** Difference in Kc for aromatic hydrocarbons between 30m and 15 m column

*** Not analyzed

The ΔKc is much higher for aromatic hydrocarbons when compared to alkanes using the same column. The ΔKc was greater than 200 for toluene at 323 K, ethylbenzene at 323 K, 318K , 313 K; butyl benzene at 348 K, 343 K, 338 K, 333 K, 323 K, 318K , 313 K; hexyl and heptylbenzene at 353 K, 348 K, 343 K, 338 K, 333 K, 323 K, 318K , 313 K. Thus the adsorption is more pronounced for the retention of aromatic hydrocarbons on SLB-IL 100. column. Table 7 shows the comparison of difference in ΔG between a 30 m and 15 m stationary phase for aromatic
hydrocarbons. Here too the right hand side of the table shows larger ΔΔG signifying a significant amount adsorption along with the dominant partition mechanism.

Table 7: Comparison of ΔΔG of aromatic hydrocarbons at different temperature.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Benzene</th>
<th>Toluene</th>
<th>Ethyl Benzene</th>
<th>Butyl Benzene</th>
<th>Hexyl Benzene</th>
<th>Heptyl Benzene</th>
</tr>
</thead>
<tbody>
<tr>
<td>353</td>
<td>1</td>
<td>3</td>
<td>4</td>
<td>7</td>
<td>9</td>
<td>11</td>
</tr>
<tr>
<td>348</td>
<td>1</td>
<td>3</td>
<td>4</td>
<td>7</td>
<td>10</td>
<td>11</td>
</tr>
<tr>
<td>343</td>
<td>2</td>
<td>3</td>
<td>5</td>
<td>7</td>
<td>10</td>
<td>12</td>
</tr>
<tr>
<td>338</td>
<td>2</td>
<td>4</td>
<td>5</td>
<td>8</td>
<td>11</td>
<td>12</td>
</tr>
<tr>
<td>333</td>
<td>2</td>
<td>4</td>
<td>5</td>
<td>8</td>
<td>11</td>
<td>13</td>
</tr>
<tr>
<td>328</td>
<td>2</td>
<td>4</td>
<td>5</td>
<td>8</td>
<td>12</td>
<td>13</td>
</tr>
<tr>
<td>323</td>
<td>2</td>
<td>4</td>
<td>6</td>
<td>9</td>
<td>12</td>
<td>14</td>
</tr>
<tr>
<td>318</td>
<td>3</td>
<td>5</td>
<td>6</td>
<td>9</td>
<td>13</td>
<td>NA*</td>
</tr>
<tr>
<td>313</td>
<td>3</td>
<td>5</td>
<td>6</td>
<td>10</td>
<td>13</td>
<td>NA*</td>
</tr>
</tbody>
</table>

* Not analyzed as these peaks were expected to elute with run time more than 60 min.

With reference to the structure of the ionic liquid used in SLB-IL-100, there are multiple interactions between the analyte and the ionic liquid. The π-electron cloud of the probe aromatic hydrocarbons can interact with the two cations and the alkane chain with the linkage group of the ionic liquid (Figure 11, Chapter 1). Thus multiple interaction of analytes is very well demonstrated. This is supported by a change in the selectivity for alkanes and aromatic hydrocarbons with increase in temperature as reported earlier by the column manufacturer. However all our experiments were performed at isothermal temperature, separately for alkanes and aromatic hydrocarbons at optimum linear velocity to avoid misinterpretation of peak elution order. No cross-over in Van’t Hoff plot was observed at the chosen temperature within the homologous series. This signified that the cross over and the mechanism of the multiple
interaction was influenced by the temperature and linear velocity of carrier gas. In other words, the ionic liquid used in SLB-IL 100 interacts differently with analytes at different temperature.

**Correlation of structure to retention**

Recently the structure of few of the ionic liquid stationary phase were revealed by Supelco. The structure of ionic liquid SLB-IL 82, SLB-IL 100 and SLB-IL 111 are shown in Figure 19 which were very similar in structure. SLB-IL82 and SLB-IL 100 differed only with respect to the number of carbons in the linkage chain. While SLB-IL 100 differed in the number of carbons in the linkage group and the vinyl group attached to the cation, instead of the methyl groups at 1,3 position in SLB-IL 82 and SLB-IL 111. The free energy changes associated with the chromatographic process for the retention of alkanes on these three ionic liquid stationary phase were determined.

The linkage group had 5 carbons for SLB-IL 111, 9 carbon chain for SLB-IL 100 and 12 carbons for SLB-IL 82. In general, a plot of $\Delta G$ against number of carbons in the analyte is linear. The $\Delta G$ of alkanes should be related to the number of carbon chain in the ionic liquid linearly if the retention of alkanes are controlled only by the linkage group in the ionic liquid. So the thermodynamic parameter $\Delta G$ for alkanes were compared with the number of carbons in the linkage group. Referring Table 8, the $R^2$ values were greater than 0.999 for the correlation of $\Delta G$ and number of carbons in the linkage group of the ionic liquid. There was linear relationship between the number of carbons in the linkage group and the $\Delta G$ and the retention of alkanes in all the three columns were controlled by the length of the carbon chain only. With reference to
Figure 19: Structure of ionic liquid stationary phase SLB-IL 100, SLB-L 111, SLB-IL 82, adopted from reference 105.
Table 8: Correlation between ΔG of alkanes and the number of carbons in the IL

<table>
<thead>
<tr>
<th>Number of carbons in the linkage group</th>
<th>Polarity number</th>
<th>ΔG (J/mole) at different temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>353 K</td>
</tr>
<tr>
<td>Dodecane</td>
<td>5</td>
<td>111</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>82</td>
</tr>
<tr>
<td></td>
<td>R² for Polarity number and ΔG</td>
<td>0.98587</td>
</tr>
<tr>
<td></td>
<td>R² for number of carbons and ΔG</td>
<td>0.99863</td>
</tr>
<tr>
<td>Decane</td>
<td>5</td>
<td>111</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>82</td>
</tr>
<tr>
<td></td>
<td>R² for Polarity number and ΔG</td>
<td>0.97443</td>
</tr>
<tr>
<td></td>
<td>R² for number of carbons and ΔG</td>
<td>0.99998</td>
</tr>
<tr>
<td>Undecane</td>
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<td>111</td>
</tr>
<tr>
<td></td>
<td>9</td>
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</tr>
<tr>
<td></td>
<td>12</td>
<td>82</td>
</tr>
<tr>
<td></td>
<td>R² for Polarity number and ΔG</td>
<td>0.98249</td>
</tr>
<tr>
<td></td>
<td>R² for number of carbons and ΔG</td>
<td>0.99944</td>
</tr>
<tr>
<td>Dodecane</td>
<td>5</td>
<td>111</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>82</td>
</tr>
<tr>
<td></td>
<td>R² for Polarity number and ΔG</td>
<td>0.97790</td>
</tr>
<tr>
<td></td>
<td>R² for number of carbons and ΔG</td>
<td>0.99995</td>
</tr>
<tr>
<td>Tetradecane</td>
<td>5</td>
<td>111</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>82</td>
</tr>
<tr>
<td></td>
<td>R² for Polarity number and ΔG</td>
<td>0.981402</td>
</tr>
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<td></td>
<td>R² for number of carbons and ΔG</td>
<td>0.99962</td>
</tr>
<tr>
<td>Hexadecane</td>
<td>5</td>
<td>111</td>
</tr>
<tr>
<td></td>
<td>9</td>
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<td></td>
<td>12</td>
<td>82</td>
</tr>
<tr>
<td></td>
<td>R² for Polarity number and ΔG</td>
<td>0.981841</td>
</tr>
<tr>
<td></td>
<td>R² for number of carbons and ΔG</td>
<td>0.99955</td>
</tr>
</tbody>
</table>
Figure 19, the ionic liquid in SLB-IL 82, 100 and 111 has few difference in structure. The main difference was the length of the linkage group. SLB-IL82 and SLB-IL 100 differed only with respect to the number of carbons in the linkage chain. While SLB-IL 100 differed in the number of carbons in the linkage group and the vinyl group attached to the cation, instead of the methyl groups at 1,3 position in SLB-IL 82 and SLB-IL 111. The major difference in structure was the length of the linkage group that controlled the retention of alkanes on these ionic liquid stationary phases. In other words the hydrophobic non bonded interaction of the linkage group in the ionic liquid with that of the probe analytes (alkanes) chain was the contributing factor to the retention. The R^2 values were calculated for ΔG and the polarity number of the column and they did not show a linear relationship. Since only three ionic liquids were commercially available having similar structure, the type of non linear relationship between polarity number and ΔG was not studied. The linear relationship between ΔG and carbons in linkage group and non linear relationship between ΔG and polarity number signifies that the structure of the ionic liquid is directly related to the retention and not the polarity number. The polarity number were not a representation of the retention because they were calculated by Supelco Sigma Aldrich (refer Figure 12 in Chapter 1) (1) by summing up the difference in Kovats retention index ΔI of all the five probe analytes and normalizing against SPB-octyl column’s polarity number. (2) SPB-octyl had negative ΔI value for n-Butanol which when summed up with other probe analyte’s polarity value, causes an error. (3) For the SPB-octyl column polarity of 28 was considered as polarity number 1. Due to these ambiguity in calculation, the polarity number or the McReynold’s number is not a representative of the retention. Due to the summation of the retention index of probe analytes and normalization against a non polar column the actual interaction of each probe analyte used, is not related to the polarity number.
Comparison of Ionic liquid stationary phase with polyethyleneglycol stationary phase

Supelcowax-10 is a commercially available stationary phase bearing polyethyleneglycol backbone. It is always compared with the SLB-IL 59 and SLB-IL 60 in terms of the polarity number. It has been iterated by the manufacturer that SLB-IL 59 and SLB-IL 60 columns are similar to Supelcowax-10. The polarity index number for Supelcowax-10 is predicted as 52 and that for the SLB-IL 59 and SLB-IL 60 are 59 and 60 respectively. The detailed calculation of the polarity number is provided by the column manufacture in reference 70. To understand the real meaning of the claimed polarity number, a plot of $-\Delta H^0$ against polarity number and $-\Delta S^0$ against polarity number (Figure 20, 21) were drawn. It was seen from Figure 20 that the $-\Delta H^0$ was highest for SLB-IL 59 and lowest for SLB-IL 60 for all the alkane probe analytes. Thus no trend

![Comparison of $-\Delta H^0$ for alkanes on SUPELCOWAX, SLB-IL-59 and SLB-IL-60](image)

Figure 20 : Comparison of $-\Delta H^0$ for alkanes on SUPELCOWAX, SLB-IL-59 and SLB-IL-60
in – ΔH was observed with polarity number. Interestingly, ΔS in Figure 21 showed: a continuous increase with polarity number for dodecane, tridecane and tetradecane; linear for undecane; increase followed by decrease for nonane and decane while going from Supelcowax-

<table>
<thead>
<tr>
<th>Name Of the Compound</th>
<th>ΔH (KJ mol⁻¹)</th>
<th>ΔS (J mol⁻¹ K⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>WAX</td>
<td>SLB-IL60</td>
</tr>
<tr>
<td>Toluene</td>
<td>-34</td>
<td>-33</td>
</tr>
<tr>
<td>Ethyl benzene</td>
<td>-38</td>
<td>-36</td>
</tr>
<tr>
<td>Propyl benzene</td>
<td>-43</td>
<td>NA*</td>
</tr>
<tr>
<td>Butyl benzene</td>
<td>-47</td>
<td>-44</td>
</tr>
<tr>
<td>Hexyl benzene</td>
<td>-40</td>
<td>-52</td>
</tr>
</tbody>
</table>

10 to SLB-IL 59 and SLB-IL 60. This means that the disorderliness is different for the alkanes from one column to another and also the trend changes from lower to higher members based on the length of the carbon chain.
The reason for observed trend Figure 21. is attributed to discrepancy (refer page 82) in the model used for the calculation of polarity number. The five molecules used for the calculation of Mc Reynold’s number were not representative of all possible interactions (24).

**Table 9: Comparison of Ionic liquid stationary phase with polyethyleneglycol stationary phase in terms of thermodynamic parameters.**

* Not analyzed

A direct comparison of the retention of the thermodynamic parameters of ionic liquid stationary phase with polyethyleneglycol based polymeric stationary phase was made for the retention of aromatic hydrocarbons as shown in Table 6. The ΔH values for Stabilewax-10, SLB-IL 60, SLB-IL 61 were pretty close to each other while the ΔS for the homologous series differed very much from that of Stabile wax-10. This exhibited the basic difference in the type of interactions in an ionic liquid stationary phase to that in the polymeric polyethyleneglycol phase. In the former case, there existed phenyl π-π interaction between the probe analyte and the ionic liquid stationary phase, nonbonded interaction between the hydrocarbon chain of the aromatic hydrocarbon and the linkage group of the ionic liquid. How ever the ΔH and ΔS of the stabile wax 10, SLB-IL 60, SLB-IL 61 and SLB-IL 100 are similar. Considering that SLB-IL 100 is very highly polar, it wouldn’t retain the higher members like butyl benzene and hexyl benzene to the same extent like how the SLB-IL 60 does. In other words , deviation would be bigger for compounds with longer hydrocarbon chain.

The consideration that the interaction of five probe analytes are additive, while calculating the polarity number is an over simplification. Normalization of the additive value with respect to
another additive value creates more error in the predicted polarity number. As shown in our experiment, members of even the same homologous series behave differently on the ionic liquid stationary phases than polyethyleneglycol phase. So, just considering one member as a representative for the entire homologous series for calculating polarity number is not accurate. It would be realistic to correlate two stationary phases based on the structural entity and depict the type of interactions possible.

**Figure 22: Structure of a polyethyleneglycol phase**

The structure of polyethyleneglycol stationary phase is shown in Figure 22. Since the structure of SLB-IL 59 and SLB-IL 61 are proprietary and not known it is harder to predict the type of interactions present in the IL columns. With the knowledge of the structure, one could definitely tell that the ionic liquids are salts (two heterocyclic cations connected to each other by hydrocarbon linkage chain and in association with two anions) with while Stabilewax 10 is a polyethylene glycol based stationary phase and the type of interactions present are very much different in each of them.
Conclusions

Ionic liquid stationary phases are attractive alternatives to conventional polyethylene glycol stationary phases. The distribution constant at different temperature were determined for alkanes and aromatic hydrocarbons on commercially available ionic liquid stationary phases. Thermodynamic parameters for the chromatographic process using ionic liquid stationary phase were evaluated. The retention mechanism was predominantly partitioning for the alkanes. At lower temperature, for higher member of alkanes in the homologous series, there was considerable amount of adsorption along with the partition. The polarity number was not linearly related to the ΔG for alkanes while it was linearly related to the length of the alkyl chain present in the linkage group of the ionic liquid. For aromatic hydrocarbons, huge difference in Kc was observed between 15 m and 30 m SLB-IL 100 stationary phase indicating mixed mechanism of adsorption and partition. To exactly predict the contribution of each mechanism towards retention of analytes, a new model has to be proposed. The retention of alkanes and aromatic hydrocarbons on ionic liquid stationary phase were compared with polyethyleneglycol stationary phase in terms of their polarity number. The ambiguity in the calculated polarity number was established from the plot of thermodynamic parameters against the polarity number.
Chapter 3: Air as carrier gas using ionic liquid stationary phase
Introduction

The carrier gas plays an important role in the gas chromatographic retention process. In a gas chromatographic system, the analytes get partitioned between the liquid film in the stationary phase and the carrier gas which is the mobile phase. The carrier gas needs to be inert so that it does not leach the stationary phase. The diffusion coefficient, purity of carrier gas, availability are other parameters to be considered. The carrier gases that are used for GC analysis includes helium, hydrogen and nitrogen. The choice of the carrier gas is also dependent on the type of detector used. For example, ultra high pure nitrogen is used for electron capture detector and helium/ hydrogen are used for mass detector. Nitrogen and helium are commonly used for flame ionization detector. The decision to choose the right carrier gas is based on the Van Deemter curve. Hydrogen and helium are lighter gases and suitable for fast GC analysis while nitrogen is very cheap source. About 77% of the atmospheric air composition is nitrogen. The other major gas is 20% oxygen. So if one considers air, it is predominantly composed of nitrogen. There are not many attempts to use air as carrier gas in the literature. The main reason is oxygen and moisture that can leach the stationary phase and cause bleeding of column. The active hydroxyl groups in the polyethyleneglycol based and polydimethylsiloxane based stationary phases are susceptible to oxidation. Air, composed of 77% nitrogen, would be beneficial for analyzing highly volatile gases under narrow temperature ranges where increasing stationary phase interaction is desirable. Air when used as carrier gas would be very useful for field samples. However, its application would be limited based on the type of detector used, analyte stability to air.
Ionic liquid stationary phases are superior to conventional polymeric gas chromatographic stationary phases for the following reasons: unique selectivity, thermal stability, no active hydroxyl group in their structure. Commercially available ionic liquids have promises about their stability to air and moisture. So they would be ideal candidate to study the effect of air as carrier gas on retention. Attempts were made by Supelco- Sigma Aldrich to use air as carrier gas using SLB-IL-59 as stationary phase. Their application note shows the stability of SLB-IL 59 using air as carrier gas\textsuperscript{88}. They have also compared its stability with polyethyleneglycol stationary phase using air as carrier gas. Figure 23 shows the stability of SLB-IL 59 using air as carrier gas. It was seen that the peak shapes remained Gaussian even after 200 injections and no degradation of the phase was noticed. They also compared it with polyethyleneglycol stationary phase which started phase degradation during 100\textsuperscript{th} injection and the stationary phase completely degraded by 200 injections.

\textbf{Figure 23: Stability of SLB IL 59 while using air as carrier gas adopted from Supelco-Sigma Aldrich’s application note\textsuperscript{88}}
The thermodynamic and kinetic behavior of retention of analytes using air as carrier gas are not explored to any depth in literature. In the present research, attempts were made to explore the thermodynamics and kinetics of retention of aromatic hydrocarbons on ionic liquid stationary phase.

**Objective**

The objective of the study was to use air as carrier gas and ionic liquid column SLB-IL 100 as gas chromatographic stationary phase. The key objectives of the study are listed in Figure 1 which includes: the determination of thermodynamic parameters like ΔH, ΔS for the retention of aromatic hydrocarbons on ionic liquid stationary phase SLB-IL-100 using air as carrier gas and to compare the retention behavior in terms of thermodynamic parameters when helium is used as carrier gas, studying the kinetics using air as carrier gas and explore its merits and demerits in terms of Van Deemter’s plot and extending the application of air as carrier gas for separation of o, m, p-xylene.

![Objective of the analysis: Air as carrier gas using ionic liquid stationary phase](image)

*Figure 24: Objective of the analysis: Air as carrier gas using ionic liquid stationary phase*
Experimental

Materials and Chemicals

Benzene, toluene, ethylbenzene, butylbenzene, hexylbenzene, heptylbenzene, ortho, meta, para-xylene, hexane were purchased from Supelco Sigma-Aldrich. The ionic liquid stationary phase SLB-IL 100 was donated by Sigma-Aldrich.

GC-FID parameters

The aromatic hydrocarbons analysis using air, helium as were performed on GC-Flame ionization detector (GC-FID), HP-5890 model. The ionic liquid stationary phase, SLB-IL 100 with dimensions 15 m, 0.10 mm, 0.08 μm was installed in the chromatographic system. For the thermodynamic study, the inlet temperature was maintained at 250 °C. The split ratio was set as 1:50. The injection volume was 1 μL. The isothermal runs were performed at 40 °C (313 K), 45 °C (318 K), 50 °C up to 80 °C (353K) respectively. For the flame ionization detector, the detector temperature was set as 250 °C. The hydrogen and air flow were set as 30 mL min⁻¹ and 300 mL min⁻¹, the inlet was maintained at constant pressure with linear velocity of 14 cm sec⁻¹. The carrier gas was changed to helium and the same conditions were used for thermodynamic studies using helium as carrier gas.

A kinetic study was performed using air as carrier gas. The inlet temperature was maintained at 250 °C. The split ratio was set as 1:50. The injection volume was 1 μL. The isothermal runs were performed at 70 °C (343 K). For the flame ionization detector, the detector temperature was set as 250 °C. The hydrogen and air flow were set as 30 mL min⁻¹ and 300 mL min⁻¹. The carrier gas
pressure mode was constant pressure mode and the experiments were run individually at 5, 8, 10, 15 and 20 cm/sec.

For the separation of xylene isomers, the inlet temperature was maintained at 250°C. The split ratio was set as 1:50. The oven was set at 50°C for 1 minute, 20°C/min until 240°C with a final hold time of 5 minutes. Air was used as the carrier gas at a constant inlet pressure. The injection volume was 1 µL. For the flame ionization detector, the detector temperature was set as 250°C. The hydrogen and air flow were set as 30 mL min⁻¹ and 300 mL min⁻¹, the inlet was maintained at 205°C.

**Standard preparation**

The thermodynamic and kinetic studies were performed using hexane as diluting solvent. The aromatic hydrocarbon working standard was prepared by mixing 0.01% of benzene, toluene, ethyl benzene, butylbenzene, hexylbenzene and heptylbenzene in hexane. Exactly 1±0.1 µL of the working standards were injected in to the chromatographic system. After each run the syringe was cleaned with hexane five times.

This working standard was used for the separation of xylene isomers consisted of 0.01% benzene, benzene, toluene, ethyl benzene, butylbenzene, hexylbenzene and heptylbenzene, and o, m, p-xylene in methanol.
**Experiments performed**

The thermodynamic parameters of retention were calculated by finding the Kc values at various temperature using helium and air as carrier gas respectively. A Van’t Hoff’s plot was drawn for each aromatic hydrocarbon using helium and air as carrier gases and the thermodynamic parameters ΔH and ΔS were determined from the slope and the intercept of the linear regression. To account for the kinetic behavior, the standards were injected at 70°C at different linear velocities. The efficiency of the peaks were determined from the number of theoretical plates(N). From this the height equivalent theoretical plates (HETP) were calculated. A Van Deemter plot of HETP against the carrier gas linear velocity was made for the ionic liquid stationary phase SLB-IL 100 with air as carrier gas. For the separation of xylenes isomers, a temperature program of 50°C for 1 minute, 20°C/min until 240°C with a final hold time of 5 minutes was used because the working standard mixture had both high and low boiling aromatic hydrocarbons.

**Results and Discussion**

**Air vs Helium comparison based on thermodynamic parameters for the retention of aromatic hydrocarbons**

Theoretically, the carrier gas impacts the speed of the analysis and the efficiency. The Kp which is equal to the partial pressure of analyte in vapor phase to that in the stationary phase. So, the Kp of analytes using two different carrier gas, both at same pressure profile should be same. The Kc values were calculated at different temperature using helium, air as carrier gas respectively. At lower temperature there was a big difference in the Kc value between helium and air as shown in Table 10. The effect got more pronounced for higher members of the homologous
series. This was because at lower temperature, the analytes had more time to spend with the stationary phase than the mobile phase. So the true effect of change in partition coefficient with change in the mobile phase was revealed for the higher members of the homologous series. At lower temperature, the Kc values were higher for air when compared to helium while at higher temperature, helium showed higher partition coefficient. In recent literature it is reported that the Kc values changes with change in the carrier gas. The velocity, viscosity, thermal expansion of gases with temperature can cause a change in the Kc values.

Table 10: Comparison of Kc of aromatic hydrocarbons using helium and air as carrier gas on SLB-IL 100 stationary phase

<table>
<thead>
<tr>
<th>Oven Temperature (K)</th>
<th>353</th>
<th>348</th>
<th>343</th>
<th>338</th>
<th>333</th>
<th>323</th>
<th>318</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Helium</td>
<td>76</td>
<td>97</td>
<td>111</td>
<td>126</td>
<td>148</td>
<td>170</td>
<td>200</td>
</tr>
<tr>
<td>Air</td>
<td>74</td>
<td>84</td>
<td>97</td>
<td>100</td>
<td>133</td>
<td>187</td>
<td>223</td>
</tr>
<tr>
<td>ΔKc</td>
<td>2</td>
<td>14</td>
<td>14</td>
<td>26</td>
<td>14</td>
<td>-17</td>
<td>-23</td>
</tr>
<tr>
<td>Toluene</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Helium</td>
<td>142</td>
<td>173</td>
<td>203</td>
<td>239</td>
<td>285</td>
<td>345</td>
<td>421</td>
</tr>
<tr>
<td>Air</td>
<td>132</td>
<td>152</td>
<td>180</td>
<td>203</td>
<td>260</td>
<td>387</td>
<td>481</td>
</tr>
<tr>
<td>ΔKc</td>
<td>10</td>
<td>22</td>
<td>23</td>
<td>36</td>
<td>25</td>
<td>-42</td>
<td>-60</td>
</tr>
<tr>
<td>Ethyl Benzene</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Helium</td>
<td>216</td>
<td>260</td>
<td>315</td>
<td>379</td>
<td>461</td>
<td>564</td>
<td>698</td>
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<tr>
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<td>194</td>
<td>230</td>
<td>278</td>
<td>324</td>
<td>413</td>
<td>636</td>
<td>809</td>
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<tr>
<td>ΔKc</td>
<td>22</td>
<td>30</td>
<td>37</td>
<td>55</td>
<td>48</td>
<td>-71</td>
<td>-111</td>
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<tr>
<td>Butyl benzene</td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Helium</td>
<td>546</td>
<td>674</td>
<td>850</td>
<td>1067</td>
<td>1351</td>
<td>1716</td>
<td>2219</td>
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<tr>
<td>Air</td>
<td>486</td>
<td>594</td>
<td>750</td>
<td>931</td>
<td>1194</td>
<td>1988</td>
<td>2653</td>
</tr>
<tr>
<td>ΔKc</td>
<td>60</td>
<td>80</td>
<td>99</td>
<td>136</td>
<td>158</td>
<td>-272</td>
<td>-434</td>
</tr>
<tr>
<td>Hexyl benzene</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Helium</td>
<td>1436</td>
<td>1850</td>
<td>2419</td>
<td>3162</td>
<td>4170</td>
<td>5531</td>
<td>7457</td>
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<td>2112</td>
<td>2752</td>
<td>3633</td>
<td>6563</td>
<td>9161</td>
</tr>
<tr>
<td>ΔKc</td>
<td>163</td>
<td>239</td>
<td>307</td>
<td>410</td>
<td>537</td>
<td>-1032</td>
<td>-1703</td>
</tr>
<tr>
<td>Heptyl benzene</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Helium</td>
<td>2355</td>
<td>3101</td>
<td>4120</td>
<td>5501</td>
<td>7407</td>
<td>10046</td>
<td>13837</td>
</tr>
<tr>
<td>Air</td>
<td>2082</td>
<td>2680</td>
<td>3584</td>
<td>4765</td>
<td>6404</td>
<td>12049</td>
<td>17229</td>
</tr>
<tr>
<td>ΔKc</td>
<td>274</td>
<td>421</td>
<td>536</td>
<td>736</td>
<td>1003</td>
<td>-2003</td>
<td>-3392</td>
</tr>
</tbody>
</table>
The Van’t Hoff plot of aromatic hydrocarbons using SLB-IL 100 with air, helium as carrier gas is shown in Figure 25. The plot was linear for both the carrier gas. The intercepts were very close for benzene, toluene and ethyl benzene using helium and air as carrier gases. The intercept started to vary with the higher members like hexyl benzene and heptyl benzene. The difference in intercept means a difference in ΔS value for helium and air as carrier gas.

**Figure 25:** Van't Hoff plot for aromatic hydrocarbons using air, helium as carrier gas
The thermodynamic parameters -ΔH and -ΔS that were determined from the Van’t Hoff plot for aromatic hydrocarbons on SLB-IL 100 stationary phase using helium and air as carrier gas are listed in Table 11. The -ΔH for aromatic hydrocarbons using helium as carrier were different from that of air. The higher members of the homologous series showed pronounced difference than the lower members. There was a difference in change in entropy between the two helium and air as well. The ΔS value signified the disorderliness of the system. Helium is much lighter than air and air predominantly contains nitrogen. Thus helium travelling faster than air causing lesser disorderliness. Since air is mainly composed of nitrogen and oxygen, it would be worth while to study the thermodynamics individually with air, nitrogen and compare the data with that of air.

Table 11: Comparison of ΔH₀ and ΔS₀ for aromatic hydrocarbons using helium and air as carrier gas on SLB-IL 100 stationary phase

<table>
<thead>
<tr>
<th>Compound</th>
<th>ΔH₀ (KJ mole⁻¹)</th>
<th>ΔS₀ (J mole⁻¹ K⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Helium</td>
<td>Air</td>
</tr>
<tr>
<td>Benzene</td>
<td>-24</td>
<td>-30</td>
</tr>
<tr>
<td>Toluene</td>
<td>-28</td>
<td>-35</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>-30</td>
<td>-38</td>
</tr>
<tr>
<td>Butylbenzene</td>
<td>-36</td>
<td>-45</td>
</tr>
<tr>
<td>Hexylbenzene</td>
<td>-43</td>
<td>-53</td>
</tr>
<tr>
<td>Heptylbenzene</td>
<td>-46</td>
<td>-56</td>
</tr>
</tbody>
</table>
Kinetics of retention of Aromatic hydrocarbons using ionic liquid stationary phase:
The plot of HETP against average linear velocity for benzene toluene and propyl benzene using air as carrier gas is shown in Figure 12. It was seen that all the three curves were u shaped with a very narrow plateau. This observation was very similar to that of Van Deemter’s plot of nitrogen reported in literature. This was typical because the major composition of air was nitrogen. Thus the curves showed low optimum B term. The lowest HETP was observed at 15 cm/sec linear velocity. Since the curve was very sharp, the range of linear velocity over which the low HETP prevailed were very small. So if one needs to use air as carrier gas, they would have to run their experiments within the small range to get highest efficiency. In other words there was a very narrow range at which air could be used as a carrier gas to get maximum efficiency. The curve started to rise with very steep slope after the optimum linear velocity, demonstrating a dominant C term. So if one would increase the flow of the carrier gas beyond the optimum, there would be
Figure 26: HETP vs linear velocity for analytes using air as carrier gas and ionic liquid stationary phase SLB IL-100

a compromise of efficiency due to the mass transfer coefficient C term. Thus air would not be suitable for fast GC analysis. However it is less expensive and could be used as carrier gas based on the goal of the analysis.
Separation of xylene isomers using air as carrier gas and ionic liquid stationary phase

There was a threat of using air as carrier gas because of the oxygen present in air can oxidize the stationary phase causing column bleeding. This would result in appearance of ghost peaks, inconsistent retention time and poor repeatability of resolution for closer eluting peaks.

Figure 27: Chromatogram of aromatic hydrocarbons on SLB IL 100 using air as career gas.

The chromatogram of aromatic hydrocarbons including xylene isomers were injected into GC installed with SLB-IL 100 column and air as carrier gas. The chromatogram is presented in Figure 27. The chromatogram shows well defined sharp peaks. No base line disturbance or ghost peaks were observed. Clear base to base separation of xylene isomers were achieved using air as carrier gas. The resolution between p and m-xylene was 2.51. This separation was possible due to the unique selectivity of ionic liquids to the positional isomers. Referring to the structure
of the ionic liquid SLB IL-100 (Figure 11, Chapter 1), the heteroaromatic dication offers π-π interaction while the hydrocarbon linkage group offers non bonded interaction. Due to these interactions, the SLB-IL 100 was able to distinguish even very similar structures like xylene isomers. In other words, the partition coefficient of the three isomers of xylene were entirely different on the ionic liquid stationary phase. SLB-IL 100. There existed the π interaction of the dicationic ionic liquid stationary phase with the π electron clouds of the xylene isomer and also the non bonded interaction of the methyl groups at different position in the xylene isomers were to a different extent with that of the nine carbon linkage group in the ionic liquid.

Unlike conventional gas chromatographic stationary phases, ionic liquid stationary phase does not contain active hydroxyl group that are prone to oxidation. The structure of the ionic liquid is resonance stabilized due to the delocalized electron clouds of the cations and the linkage hydrocarbon chain group connecting the two cations stays intact. The ionic liquid stationary phase SLB-IL 100 was installed in the GC oven with air as carrier gas for six months. There were no discrepancy in the peak shape and retention time as well as no ghost peaks were observed during the course of time. Thus ionic liquid stationary phase proved to resist the torcher from the oxygen present in air. This opens a new gateway of application of ionic liquid stationary phase, especially for quantitative analysis of field samples using air as carrier gas. However, this application is restricted to analytes that are stable in air even in the hot inlet like alkanes and aromatic hydrocarbons.
Conclusion

Air was successfully employed as the carrier gas for gas chromatographic analysis using ionic liquid as the stationary phase. The thermodynamic properties of retention of aromatic hydrocarbons on ionic liquid stationary phase SLB-IL 100 using air as carrier gas was determined. This was compared with the thermodynamic properties of aromatic hydrocarbons, obtained using helium as carrier gas. The Kc values were different from air and Helium. In literature it was reported before that there would be change in the partition coefficient with change in the carrier gas. The kinetics of the chromatographic process using air as carrier gas was also studied. The study showed that air when used as carrier gas had a lower optimum B term over a very narrow range and a dominant C term. So air could not be used for fast GC applications. However air served as the cheap alternate to helium or hydrogen. Further air was used as the carrier gas to separate xylene isomers and a clear base to base separation of o, m, p-xylene was achieved using SLB-IL 100 stationary phase. The ionic liquid column with air as carrier gas was installed in the gas chromatographic instrument for six months continuously and showed consistent retention, peak shape and no ghost peaks, thus demonstrated the stability of ionic liquid stationary phase SLB-IL 100 even under extreme conditions. This feature would open new doors to the analysis of sample using air as carrier gas for field samples.
Chapter 4: Partition coefficient by depletion study for ionic liquid single drop microextraction of aromatic hydrocarbons from water and quantitative estimation by no Interface gas chromatography mass spectrometry
Introduction

Sample preparation plays a very important role in analytical chemistry. It involves extraction, preconcentration and separation of the analytes from the matrix components. As seen in Figure 14, the time spent in sample preparation is 61% and is the major sector of the pie chart. Hence there is a need for quick and easy ways to perform sample preparation. This data was published in 1991\textsuperscript{83} and in recent years much research has focused on ways to reduce the sample preparation time.

![Pie chart showing time spent during various activities while performing analysis](image)

**Figure 28:** Time spent during various activities while performing analysis, adopted from reference 83.
The other concern with conventional sample preparation methods is generation of hazardous waste. So in addition to quick and easy way of sample preparation, one should look for responsible volumes of organic solvents for extractions. Thus micro extractions are effective substitutes for conventional extraction.

Ionic liquids are salts that are liquid at room temperature. They exhibit unique selectivity and are versatile as solvents for microextraction. Since they are ionic species that are liquid at room temperature, and not a solvent, the extraction performed using ionic liquids are green. Ionic liquid static headspace single drop microextraction (IL-SHS SDME) and ionic liquid submerged single drop microextraction (IL-SSDME) are two modes to perform micro extraction using ionic liquids. In the present research, attempts are made to understand the chemistry behind the ionic liquid based extractions by determining the thermodynamic property Kc of the extraction.

The conventional IL-SHS SDME, reported in literature is performed as follows. The extraction solvent is just one drop of liquid, suspended on the syringe needle, which is put in the headspace. Typically 5 to 8mL of the sample or standard solution containing sodium chloride and 50µL of concentrated HNO₃ were placed in a 10 mL or 20 mL glass vial which was tightly sealed with a silicone septum. Later on the GC syringe, previously filled with 2µL of ionic liquid, was inserted in the vial through the septum until its needle tip was located about 1 cm above the surface of the stirred solution. The plunger was depressed and a microdrop of the acceptor phase was exposed on the headspace above the aqueous solution. After the extraction, the drop was retracted into the syringe. This procedure employed a 10.0 ml vial and even for the volatile analyte like benzene, toluene it took 30 min for headspace equilibration at 80 ºC.
Typically it takes 30-60 minutes to equilibrate based on the nature of the analyte, the ionic liquid used and the temperature at which the extraction is performed\textsuperscript{84}.

The biggest challenge in using ionic liquid based SDME for analysis is introduction into the gas chromatographic inlet. As ionic liquids are nonvolatile, the direct introduction of ionic liquid into the gas chromatographic inlet is not desirable, leads to clogging of the capillary column and destroys the stationary phase.\textsuperscript{85} Due to this reason samples for ionic liquid based extraction are either analyzed by high performance liquid chromatography \textsuperscript{86} or a special interface is designed to introduce the ionic liquid into the gas chromatographic inlet\textsuperscript{87}.

The schematic representation of the interface used for SDME is shown in Figure 29. The interface consisted of three main integrated components: an injection zone, a removable unit and a transfer line. The injection zone was fitted with a polydimethylsiloxane septum and connected to a carrier gas line. This zone was connected downstream to a removable unit that consists of a 3-mm i.d. perfluoroalkoxy (PFA) tubing packed with cotton. This tube can be easily removed for clean up purposes. A transfer line, provided with a 5-cm needle, was used to connect the removable unit to the GC inlet. The interface was connected to the carrier gas line, whose flow rate could be controlled by means of a millimetre valve. The total flow through the capillary column was the sum of the carrier gas from the interface plus the helium supply line of the GC, which allowed the use of the electronic control pressure system of the GC in order to have constant flow rates through the column.
Figure 29: Interface used for sample introduction in IL-SDME, adopted from reference 87.
The interface, however creates increased complexity in design and usage. Rapid transfer of the analyte from the interface into the inlet is a challenge, cleaning and replacing the dirty interface can be complex and the interfaces are not commercially available. Chromatograms presented in the literature using such interface do not show symmetric peak shape due to the slow transfer of the analyte into the column head.\textsuperscript{85, 87} The interface described in literature is similar to the traditional inlet but not an integral part of the automated GC. So it did not help with the complete transfer and/or fast transfer of the analyte to the column. For this work, understanding the fundamentals of the splitless injection enabled a no-interface introduction of the analyte into the inlet. Further, an ionic liquid stationary phase was installed in the oven instead of a conventional polymeric stationary phase (5\% phenyl, 95\% methyl polysiloxane). Additionally, earlier reported methods employing interface suggested changing glass wool in the interface after every 5 injections.\textsuperscript{87} However with the present methodology of sample introduction, there was no need to change the liner for more than 100 injections.

Headspace solid phase microextraction is an equilibrium technique introduced by Pawliszyn et al\textsuperscript{88} and the fiber-sample partition coefficient of the analytes have been determined by depletion studies\textsuperscript{89}. Consecutive extractions of the analytes from a single vial resulted in decrease or depletion in the concentration of the analyte in the extracting phase. Since IL-SHS SDME is an equilibrium technique similar to HS-SPME, the depletion study can be applied to determine the ionic liquid/water extraction ratio and partition coefficient. The ionic liquid – water partition coefficient of the analyte is a thermodynamic parameter that provides an insight into how efficiently the analytes can be extracted. To the best of our knowledge, this is the first time a depletion study is used for the determination of partition coefficient of IL-SHS SDME.
The ionic liquid/water partition coefficient and its trend in the homologous series of aromatic hydrocarbons were explored using the ionic liquid 1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide as extracting medium. While there has been extensive studies on partition coefficient in SPME, there is little literature on partition coefficient in IL-SHS SDME.

**Objective of the analysis**

The Key objectives of the experiment are shown in Figure 15, which were (i) to perform IL-SHS SDME that is time efficient (ii) to introduce ionic liquid directly into the gas chromatograph without an interface (iii) to have a selective extraction as well as a selective separation (iv) to determine the partition coefficient of the extraction by depletion study (v) to compare the partition coefficient of of analyte belonging to the homologous series of aromatic hydrocarbons (vi) to compare the extraction efficiency of 1-Butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide to that of 1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide in IL-SHS SDME (vii) to validate the extraction method and apply it to real sample analysis.
Figure 30: IL SHS SDME, the objective of the analysis

Theory

IL-SHS SDME is a three phase equilibrium process. Figure 31 shows the equilibrium involved in the IL-SHS SDME. The first equilibrium exists between the liquid phase (aqueous sample) and the vapor phase. The second equilibrium exists between the vapor phase and the ionic liquid. Thus there are three phases and two equilibrium processes involved in IL-SHS SDME. The partition coefficient $K_{IL/S}$ would be the product of the partition coefficient of individual equilibrium process.
The extraction ratio \( E \) is defined as the ratio of the amount of analyte in the ionic liquid after extraction \( n_{IL,x} \), to the amount of analyte in the sample before extraction \( n_{s,x-1} \):

\[
E = \frac{n_{IL,x}}{n_{s,x-1}}
\]

Equation (16)

where \( x \) denotes the number of the consecutive extraction steps. \( E \) is a very useful parameter to characterize the efficiency of IL-SHS SDME as it indicates the fraction of analyte that is actually used in analysis. Starting with an initial amount in the sample of \( n_{s,0} \), after the first extraction the amount remaining in the sample \( n_{s,1} \) is reduced by the fraction sorbed by the ionic liquid \( n_{IL,1} \) (Equation (17)). The latter is proportional to the initial amount \( n_{s,0} \) with the extraction ratio as factor (Equation (16)).
\[ n_{s,1} = n_{s,0} - n_{IL,1} = n_{s,0} - En_{s,0} = n_{s,0} (1 - E) \]  \hspace{1cm} \text{Equation (17)}

After desorption, the same sample is extracted again and the remaining amount \( n_{s,2} \) can be calculated using the considerations described above.

\[ n_{s,2} = n_{s,1} - n_{IL,2} = n_{s,0} (1 - E) - En_{s,1} = n_{s,0} (1 - E)^2 \]  \hspace{1cm} \text{Equation (18)}

On the basis of the Equation. (17) and (18) the general geometric sequence can be developed for \( x \) extractions:

\[ n_{s,x} = n_{s,0} (1 - E)^x \]  \hspace{1cm} \text{Equation (19)}

Using Equation. (19) the amount of analyte in the sample can be described as a function of the number of extractions. As the extracted amount \( n_{IL} \) is defined as difference between two consecutive extractions, the following relationship is obtained by application of Equation. (19) where \( n_{IL,x} \) is proportional to \( n_{s,x-1} \).

\[ n_{IL,x} = n_{s,x-1} - n_{s,x} = n_{s,0} (1 - E)^{x-1} - n_{s,0} (1 - E)^x = n_{s,0} E (1 - E)^{x-1} \]  \hspace{1cm} \text{Equation (20)}

If the peak areas of the depletion experiment that are proportional to the extracted amount \( n_{IL} \) are plotted against the number of extractions \( x \) the resulting curve can be fitted with \( f(x) = ab^x \)
according to Equation (20) with \( a = n_{s,0} E \) and \( b=1−E \). The extraction ratio \( E \) can be easily determined from the slope \( b \). The data analysis can be simplified by plotting the logarithmical peak areas against the number of extraction which results in a linear relationship. After linear regression, the extraction ratio can be easily determined from the slope of the equation which would be \( \log(1−E) \).

\[
\log n_{il,x} = \log(n_{s,0} E) + (x - 1) \log(1 - E)
\]

Equation (21)

The ionic liquid and sample volumes are incorporated in the calculation of the partition coefficients \( K_{IL/s} \),

\[
K_{IL/S} = \frac{C_{IL}}{C_s} = \frac{V_s}{V_{IL}} \cdot \frac{n_{IL}}{n_s} = \frac{n_{il}V_s}{V_{il}(C_0V_s - n_{il})}
\]

Equation (22)

where \( K_{IL/s} \) is the partition coefficient between the acceptor ionic liquid phase IL and the aqueous sample s, \( n_{il} \) the amount of analyte extracted by the ionic liquid, \( c_0 \) the initial concentration of the analytes in the sample and \( V_s, V_{il} \) is the volumes of the sample and the ionic liquid, respectively. The partition coefficient may be expressed as ratio of the analyte concentrations in the ionic liquid \( C_{IL} \) and in the sample \( C_s \). Partition coefficients are typically used in the literature as they are independent from initial concentrations and sample volumes. While \( V_s, V_{il} \) and \( C_0 \) are known, the extracted amount, \( n_{il} \) has to be determined. Under equilibrium conditions, the extraction ratios \( E \) can be used to determine the Ionic liquid sample
partition coefficients. Otherwise, an apparent partition coefficient is obtained as a practical alternative that characterizes real conditions met in routine analysis.

Following Equation (16) substitution of $n_{il} = En_{s,0}$ in Equation (22) results in the following term:

$$K_{IL/S} = \frac{V_s}{V_{IL}} \ast \frac{E}{(1 - E)} \quad \text{Equation (23)}$$

In contrast to Equation (22), Equation (23) is independent from the absolute analyte amounts $n_{il}$ and $n_{s,0}$. Therefore, the initial concentration of an analyte in a sample is not required for the determination of partition coefficients. Thus the partition coefficient can be found out even for unknown samples if one does not know the initial concentration of the analytes in it. The same model discussed above was employed by Zimmerman to determine the fiber/sample partition coefficient of pesticide compounds in headspace SPME. Since HS–SPME is an equilibrium technique like IL-SHS SDME with negligible volume change, the depletion study was adopted for in the later procedure to find the ionic liquid/sample partition coefficient. Thus Equation. (23) has 2 components in it; the volume component and the extraction ratio. The volume of the ionic liquid $V_{IL}$ and the volume of the sample $V_s$ can be directly measured and the $1-E$ and $E$ values can be calculated from the linear regression.

**Experimental**

**Materials used**

Ultrapure water was produced in the lab using MilliQ Plus Ultra (Billerica, MA). Ionic liquids: 1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, 1-Butyl-1-methylpyrroolidinium bis(trifluoromethylsulfonyl)imide, aromatic hydrocarbons and all other chemicals used for the
extraction were purchased from Sigma-Aldrich (St. Louis, MO). The ionic liquid column SLB-IL 76 was donated by Supelco Sigma-Aldrich (St. Louis, MO). The ultra inert low pressure drop liner with wool was supplied by Restek (Bellefonte, PA). A 10 µL syringe with teflon tip plunger and a bevel tip needle of 22 gauge were purchased from Hamilton (Switzerland). An ultra sound bath from Cole Palmer (Vernon Hills, IL) was used.

**Standard and sample preparation**

A stock solution of 100 µg mL\(^{-1}\) of each naphthalene, biphenyl, benzene, toluene, ethyl benzene, propyl benzene, butyl benzene, pentyl benzene, hexyl benzene, heptyl benzene, octyl benzene and nonyl benzene were prepared in methanol. Further dilutions were made as per the concentration required. The final dilution in every case was made by spiking appropriate quantity of standard in a 2 mL vial for IL-SHS SDME containing 1.5 ml of 200 mg mL\(^{-1}\) aqueous sodium chloride solution made in Millipore water.

The public water from different places were collected in amber colored bottles and kept closed until analysis. 1.5 ml of the water was transferred into a 2 mL vial for IL-SHS SDME and 200 mg sodium chloride was added. The vial was closed with the screw cap and subjected to IL-SHS SDME.

**IL-SHS SDME procedure**

IL-SHS SDME as performed in this was quite different from what is described in the literature. Considering the main objective of fast and sensitive extraction, fundamental principles of static headspace extraction was applied to the initial two phase extraction\(^{90}\). The peak area in a
static headspace extraction can be given by the Equation (24). Where $C_g$ represents the concentration of the analyte in the gaseous phase and $C_s$ represents the concentration of the analyte in the sample (aqueous phase in the present experiment) or the initial concentration of the analyte, $K_{SV}$ represents the partition coefficient of the analyte, $\beta$ represents the phase volume ratio which is given by the volume of the vapor phase to the volume of the sample and $A$ represents the peak area

$$A \propto C_g = C_s /(K_{SV} + \beta)$$

Equation (24)

Thus the peak area is static headspace extraction is proportional to the concentration of analyte in the headspace of the vial which is equal to the concentration of analyte in the initial sample over the sum of partition coefficient and phase ratio. If $K_{SV}$ is much higher when compared to $\beta$ then the phase volume ratio has no or very little influence on the sensitivity as per Equation (24). If $\beta$ is higher than $K_{SV}$ then the phase volume ratio has a higher influence on the sensitivity. The probe analytes chosen for the present study are volatile aromatic hydrocarbons and they prefer to stay in the headspace than in the sample matrix. Here, since the analytes have preference to the vapor phase, $K_{SV}$ would be smaller than the phase ratio. Hence the phase volume ratio would have greater influence on the sensitivity. Irrespective of the dimension of the partition coefficient, reducing the size of the vial and reducing the headspace volume would reduce would help in fastere equilibration. Taking this into consideration, the headspace volume of 0.5 ml in a 2.0 ml vial was chosen for the analysis which resulted in the $\beta$ value of 0.33. Thus the initial step in the optimization process was to optimize the two phase equilibrium between the aqueous phase and the vapor phase. An ultrasound bath was used to equilibrate the headspace. This was
followed by the exposure of the ionic liquid to the headspace. Thus the complex three phase equilibrium process was optimized at every step to produce maximum sensitivity.

A schematic diagram of IL-SHS SDME performed in our lab is shown in Figure 32. This represents the practical sequence of tasks performed in the laboratory. The first step represented by Step A in the figure was to take the ionic liquid 1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (IL1) in a 10.0 mL microsyringe and to exactly adjusted the plunger to 2.0 µL. Thus the syringe had 2 µL of ionic liquid in it and needle volume of approximately 0.5 µL. Due to the viscosity and surface tension of the ionic liquid, a syringe with a Teflon plunger was used. The next step as shown in Step B was to measure exactly 1.5 ml of the sample or working standard containing the analyte in a 2.0 ml screw cap vial and add a small magnetic stir bar to it. The vial was closed with a screw cap and placed in an ultrasound bath for 7.0 min. Step C was the final step where the vial containing the analyte was kept in a magnetic stirring plate at a speed of approximately 1200 rpm. The septum was pierced with the needle of the syringe and the needle stayed in the headspace of the vial 0.2 cm above the liquid phase. The 2.0 µL of the ionic liquid was dispensed slowly to form a droplet that suspends as a pendant from the tip of the needle. The drop was exposed to the headspace for 8 minute after which the drop was retracted into the syringe. The same procedure was repeated using the ionic liquid 1-Butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide (IL2).
The extraction was followed by the introduction of the extracted analyte into the gas chromatographic inlet. As the ionic liquids are non volatile salts, they could clog the capillary column, remain forever in the glass liner and cause undesirable carryover of the analyte co-solvent from injection to injection. To avoid this, an interface is commonly used as evident from the literature. However the interface was an additional element and was not an integrated part of the GC system. In order to avoid the use of the interface and to perform a no interface sample introduction, the following schematic design was proposed which is shown in Figure 33. The Step A of the figure involved suspending the ionic liquid as a drop in the hot inlet. This was
Figure 33: No interface introduction of ionic liquid containing the extracted analyte by Step A) Suspending the ionic liquid containing the extracted analyte at syringe tip inside the hot splitless inlet and retracting the ionic liquid in to the syringe after injection Step B) Purging the inlet with carrier gas to clean the inlet.

followed by retracting the ionic liquid back in the syringe after the injection was completed while the needle of the syringe was still in the inlet. Thus instead of injecting the ionic liquid into the gas chromatographic inlet, only the analyte of interest was allowed to go to the column while the ionic liquid was retained back. Since the inlet was operated in splitless mode, continuous purging of carrier gas in the inlet and rapid opening of vent valve after the injection helped maintain a clean inlet as shown in Figure 17, Step B. As an additional layer of safety, the ultra inert glass liner with glass wool in the center was used. Since the inlet was run in splitless mode, the carrier gas flushed the inlet after every injection and any residual analyte was taken to the
split vent and provided a clean inlet for the next injection. Instead of a conventional polymeric stationary phase, ionic liquid stationary phase SLB IL 76 was installed in the gas chromatographic oven.

**GC/MS Parameters**

The GC/MS analysis was performed using a 6890A GC coupled to 5973 MS detector system (Agilent Technologies, Palo Alto, CA, USA). The analysis was carried out in constant flow mode with a flow rate of 1 mL min$^{-1}$. The ionic liquid column SLB-IL 76, 30 m x 0.25 mm x 0.20 µm was installed in the GC oven. All injections were performed in splitless mode. The inlet temperature was set at 300 ºC. The oven temperature program was 35 ºC (hold for 1 min) increased at the ramp of 20 ºC min$^{-1}$ up to 225 ºC (hold for 4.5 min) with a total run time of 15 min. Transfer line, ion source and quard temperatures were set at 270, 250 and 150 ºC respectively. A quadrupole MSD was operated in single ion monitoring (SIM) during runs. In the SIM, 78, 91, 128 and 154 m/z were chosen as the quantitative ions.

**Depletion study**

In order to determine the ionic liquid/water extraction ratio and the apparent partition coefficient of the analyte, depletion study was performed for IL-SHS SDME. This was performed by doing consecutive extraction of the analytes from the same vial, according to the method of Zimmerman.\(^{89}\)
Results and Discussion

Sample introduction

No interface sample introduction was achieved by suspending the ionic liquid in the splitless inlet and retracting it back. The liner used in the experiment worked in the same way as the interface described in the literature. However, as the liner was an integrated part of the inlet system, complete and fast transfer of the analyte into the GC column head was achieved. Further, Ionic liquid stationary phase was installed in the GC inlet. The ionic liquid stationary phase not only supported the sample introduction but also provided good selectivity for closer eluting analytes like nonyl benzene and naphthalene as shown in Figure 34.

Figure 34: A typical chromatogram of 60 ng mL⁻¹ aromatic hydrocarbons extracted by IL-SHS SDME.
Prior to the IL-SHS SDME method development, a liquid injection of 12 aromatic hydrocarbons were injected using Stabile Wax-10 column and only 11 peaks were observed signifying the coelution of Nonyl benzene and biphenyl as shown in Figure 33. Another notable difference was that biphenyl eluted before naphthalene.

![Chromatogram of liquid injection of 12 aromatic hydrocarbons using Stabile Wax-10 column.](image)

Thus Ionic liquid stationary phase SLB-IL 76 used for the chromatographic separation offered unique selectivity. Due to the presence of cations, anions and linkage group in it, the ionic liquid stationary phase was able to separate all the 12 peaks. Prior to the sample introduction method optimization, conventional GC stationary phase with 5% biphenyl and 95% dimethylpolysiloxane was used for the analysis and the column damaged, especially upon accidental introduction of the ionic liquid from the inlet. In a nutshell, sample introduction mode, inlet mode, design of the liner and the ionic liquid stationary phase allowed a no interface sample introduction. A typical chromatogram of 60 ng mL\(^{-1}\) of aromatic hydrocarbons extracted by using IL-SHS SDME is shown in Figure 34. The sharper peaks were observed due to a rapid
transfer of the analyte from the inlet to the column head. Previously reported literature also suggested the change of the glass wool in the interface after every 5 consecutive injections. Since the ionic liquid was not injected into the inlet, this method of sample introduction did not need change or cleaning of the liner. However as a safety measure, the liner was inspected and cleaned after every 100 injections.

**Challenges faced during method optimization**

At the start of the project, several trials were made for sample introduction before considering no interface sample introduction. A splitless liner with a glass wool and a guard column were used for the initial optimization trials, as reported in the literature\(^9\). However the ionic liquid for our study were different and the probe analytes were different too. The initial chromatogram is presented in Figure 36.

**Figure 36: Chromatogram obtained by the first injection of IL-SHS SDME**
The chromatogram showed very sharp peaks. However upon third consecutive injections, the chromatogram showed irregular peak shapes and also carry over from the previous injection as shown in Figure 37. Further injections produced clouted hump instead of individual peaks as shown in Figure 38. Also the point at which the pressfit connected the analytical column to the guard column, residue of charred ionic liquid was noticed. After the injection about one meter of the column was cut near the inlet side, conditioned over night at 250°C in the presence of helium. The column was tested with liquid injection of aromatic hydrocarbons and it was found that the column was irreversibly damaged. It was clear that the ionic liquid when injected directly into the inlet clogged the column. Due to the nonvolatile nature of the ionic liquid, they were found as residue deposited in the head of the column and produced a very dirty inlet.

Figure 37: Chromatogram obtained by the third injection of IL-SHS SDME
After the optimization of the no interface sample introduction, described in the following section, the inlet was maintained at 150°C and precision was performed using IL1. The intention was to allow only the analyte into the inlet and to retract the ionic liquid back. The precision data is shown in Table 17. It was noticed that the % RSD for 5 injections were very high.

Further trials were made using an inlet temperature of 300°C and good reproducibility of results were observed as shown in Table 18. We were able to retract the ionic liquid back into the syringe even while suspending in a 300°C hot inlet. Thus it was necessary to understand the extraction and sample introduction procedure to optimize the process and it involved a learning curve.
Table 12: Precision of IL-SSDME at 150 °C inlet temperature before complete method optimization using IL1

<table>
<thead>
<tr>
<th>Name</th>
<th>Injection1</th>
<th>Injection2</th>
<th>Injection3</th>
<th>Injection4</th>
<th>Injection5</th>
<th>%RSD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>95698872</td>
<td>45374301</td>
<td>67489949</td>
<td>52815299</td>
<td>32037184</td>
<td><strong>34.0</strong></td>
</tr>
<tr>
<td>Toluene</td>
<td>106285443</td>
<td>67470612</td>
<td>77732749</td>
<td>67184437</td>
<td>41659770</td>
<td><strong>23.1</strong></td>
</tr>
<tr>
<td>Ethyl Benzene</td>
<td>176337624</td>
<td>99930586</td>
<td>137485106</td>
<td>117134408</td>
<td>78525811</td>
<td><strong>24.8</strong></td>
</tr>
<tr>
<td>Propyl Benzene</td>
<td>207220447</td>
<td>129301935</td>
<td>167942854</td>
<td>147965476</td>
<td>106203016</td>
<td><strong>20.5</strong></td>
</tr>
<tr>
<td>Butyl Benzene</td>
<td>141326415</td>
<td>87393674</td>
<td>114261782</td>
<td>102658211</td>
<td>75968226</td>
<td><strong>20.4</strong></td>
</tr>
<tr>
<td>Naphthalene</td>
<td>50354770</td>
<td>31518115</td>
<td>40203468</td>
<td>36445915</td>
<td>31713375</td>
<td><strong>20.1</strong></td>
</tr>
<tr>
<td>Anthracene</td>
<td>13327445</td>
<td>8847466</td>
<td>10478045</td>
<td>9520570</td>
<td>8544071</td>
<td><strong>18.7</strong></td>
</tr>
</tbody>
</table>
Table 13: Precision of IL-SSDME at 150 °C inlet temperature before complete method optimization using IL1

<table>
<thead>
<tr>
<th>Name</th>
<th>Injection1</th>
<th>Injection2</th>
<th>Injection3</th>
<th>Injection4</th>
<th>Injection5</th>
<th>% RSD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>66059647</td>
<td>71128309</td>
<td>77560549</td>
<td>67489949</td>
<td>76533322</td>
<td>7.2</td>
</tr>
<tr>
<td>Toluene</td>
<td>84949392</td>
<td>91854181</td>
<td>93264708</td>
<td>77732749</td>
<td>88737085</td>
<td>7.1</td>
</tr>
<tr>
<td>Ethyl Benzene</td>
<td>118374335</td>
<td>127723999</td>
<td>148962576</td>
<td>137485106</td>
<td>147728523</td>
<td>9.6</td>
</tr>
<tr>
<td>Propyl Benzene</td>
<td>147579265</td>
<td>153537265</td>
<td>180219165</td>
<td>167942854</td>
<td>179499592</td>
<td>9.0</td>
</tr>
<tr>
<td>Butyl Benzene</td>
<td>101572584</td>
<td>108732988</td>
<td>123820246</td>
<td>114261782</td>
<td>119518861</td>
<td>7.7</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>41959646</td>
<td>48276711</td>
<td>43574711</td>
<td>40203468</td>
<td>42732279</td>
<td>7.0</td>
</tr>
<tr>
<td>Anthracene</td>
<td>10611188</td>
<td>12458573</td>
<td>11695943</td>
<td>10478045</td>
<td>11442655</td>
<td>7.2</td>
</tr>
</tbody>
</table>
While doing the extraction, most of the time the ionic liquid was successfully suspended as droplet. But 1 out of 20 showed a failure of the ionic liquid falling down into the aqueous solution. During our trials we noticed that the failure was less if the droplet size was little lesser than the maximum volume the syringe could suspend. Initially 2.5 µL of the ionic liquid was suspended and it fell down 3 out of 6 times after few minutes of suspending it as a droplet, while the failure reduced to 1 out of 20.

The need for automation of the process is really in demand and that’s when the IL-SHS SDME could be used by different section of analysts excluding human errors. The automation of the IL-SHS SDME has been reported with the interface and it would be much easier especially with the no interface sample introduction.

**Method optimization**

The method optimization was performed for IL-SHS SDME using IL2 in flame ionization detector and presented in Figure 39. Seven 2 mL vials, each containing 1.5 mL of the sample in, the vial were taken. They were sonicated for 4, 5, 6…11 minutes respectively, followed by singledrop microextraction. The extraction was performed at different sonication time. Figure 39 represents a plot of peak area against sonication time. It was found that 8.0 min gave the maximum area response for all the analytes.

After optimizing the sonication time, the extraction time was optimized. The extraction time was the time for which the ionic liquid was exposed to the headspace of the vial. After the sonication of analytes in the vial, the ionic liquid was exposed to the headspace of the vial for 5, 7, 8 and 9
min respectively. A plot of peak area against the extraction time was made as shown in Figure 40. The peak area of for 7.0 min extraction was maximum and was considered as the optimized extraction time.

To optimize the salt concentration, 100, 150, 200…400 mg of sodium chloride per 1mL was added to individual vial and IL-SHS SDME was performed on each of them. A histogram of peak area against mg/mL of Sodium chloride was made as shown in Figure 41. A salt concentration of 200 mg/mL gave the highest peak area for all the analytes.

Once the analytes were extracted by IL-SHS SDME, they were desorbed in the inlet. The time for which the ionic liquid has to be exposed to the hot inlet was optimized. The IL-SHS SDME was performed and ran at injection time(splitless time/ desorption time) of 2, 5, 10, 15 and 20 sec. A histogram of peak area against the injection time is shown in Figure 42. The optimized injection time was found to be 15 sec. It was found if the ionic liquid was exposed to the hot inlet for more than 20 sec, it was difficult to retract it back into the syringe.
Figure 39: Optimization of sonication time

![Optimization of Sonication Time](image)

Figure 40: Optimization of extraction time

![Optimization of Extraction Time](image)
Figure 41: Optimization of NaCl concentration

Figure 42: Optimization of injection time
Apparent partition coefficient by depletion study in IL-SHS SDME:

To visualize the extraction ratio of the two ionic liquids under consideration, IL-SHS SDME of the two ionic liquids were performed and the peak areas were compared. As seen in Figure 43, the ionic liquid 1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (IL2) exhibited 60% higher peak area than 1-Butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide (IL1). Since the peak areas are based on the extracted ion chromatogram in a GC-MS, it only gave a rough estimate of how better the extraction was with IL2 when compared to IL1.

Figure 43: Comparison of IL-SHS SDME of 1-Butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl) imide and 1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide in terms of peak area.
Further to determine the extraction ratio and the apparent partition coefficient, IL-SHS SDME was performed six times consecutively on a 1.5 mL aliquot of 60 ng L\(^{-1}\) aromatic hydrocarbon standard solution using IL1 and injected into the gas chromatographic inlet immediately after every extraction. The same procedure was repeated using IL2. During the extractions, the peak area started to reduce from extraction to extraction. This was because of the depletion of analytes from the sample. Since the amount of analytes extracted was proportional to the peak area, the peak area started to reduce exponentially with each extraction. A plot of logarithm peak area against extraction number was made and were linear with a correlation coefficient greater than 0.98 for the aromatic hydrocarbons. The depletion plots for aromatic hydrocarbons using IL1 are shown in Figure 44. and that of bicyclic aromatic hydrocarbons using IL1 are shown in Figure 45. Biphenyl showed R\(^2\) value of 0.97 while all other analytes showed R\(^2\) greater than 0.98. Pentyl benzene was not available while performing IL-SHS SDME using IL1 as the extracting medium and was not included in the standard preparation.
Figure 44: Depletion of analytes during consecutive extraction in IL-SHS SDME using 1-Butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide as extracting ionic liquid.
Figure 45: Depletion of analytes during consecutive extraction of bicyclic aromatic hydrocarbons in IL-SHS SDME using 1-Butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide as extracting ionic liquid.

Referring to table 9, the highest partition coefficient was observed for Ethyl benzene and the lowest was for Hexyl benzene. Considering the structure of IL1, the butyl chain is the main source of interaction with the alkyl chain of the aromatic hydrocarbon. The $K_{IL/S}$ were in the range of 200 to 300. The only possible source of interaction in IL1 is the alkyl chain with the alkyl chain of the aromatic hydrocarbon and the π electron cloud in the anion with the π electron cloud of the aromatic hydrocarbon. There was not a considerable difference in the $K_{IL/S}$ in the homologous series. This was because the length of the linkage group alkyl chain in the IL1 had only 4 carbons in it. In other words the 4 carbon alkyl chain in the ionic liquid was not able to distinguish much between the alkyl chains of the aromatic hydrocarbon. If we compare Benzene, Naphthalene and biphenyl, there was not big difference in the $K_{IL/S}$. Again the anion in the ionic
liquid interacted with the π electron cloud of the mono and bicyclic aromatic ring to the same extent.

Table 14: Calculation of apparent coefficient in IL-SHS SDME using 1-Butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide at 22 °C

<table>
<thead>
<tr>
<th>Compound Name</th>
<th>R²</th>
<th>Residual Error</th>
<th>Slope</th>
<th>1-E</th>
<th>E</th>
<th>K&lt;sub&gt;IL/S&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>0.988</td>
<td>0.05</td>
<td>-0.16</td>
<td>0.70</td>
<td>0.30</td>
<td>200</td>
</tr>
<tr>
<td>Toluene</td>
<td>0.989</td>
<td>0.07</td>
<td>-0.21</td>
<td>0.62</td>
<td>0.38</td>
<td>300</td>
</tr>
<tr>
<td>Ethyl Benzene</td>
<td>0.990</td>
<td>0.06</td>
<td>-0.21</td>
<td>0.61</td>
<td>0.39</td>
<td>300</td>
</tr>
<tr>
<td>Propyl Benzene</td>
<td>0.989</td>
<td>0.06</td>
<td>-0.19</td>
<td>0.64</td>
<td>0.36</td>
<td>300</td>
</tr>
<tr>
<td>Butyl Benzene</td>
<td>0.981</td>
<td>0.06</td>
<td>-0.15</td>
<td>0.70</td>
<td>0.30</td>
<td>200</td>
</tr>
<tr>
<td>Hexyl Benzene</td>
<td>0.971</td>
<td>0.07</td>
<td>-0.14</td>
<td>0.73</td>
<td>0.27</td>
<td>200</td>
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<tr>
<td>Heptyl Benzene</td>
<td>0.980</td>
<td>0.07</td>
<td>-0.17</td>
<td>0.68</td>
<td>0.32</td>
<td>200</td>
</tr>
<tr>
<td>Octyl Benzene</td>
<td>0.984</td>
<td>0.07</td>
<td>-0.18</td>
<td>0.66</td>
<td>0.34</td>
<td>300</td>
</tr>
<tr>
<td>Nonyl Benzene</td>
<td>0.988</td>
<td>0.06</td>
<td>-0.19</td>
<td>0.65</td>
<td>0.35</td>
<td>300</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>0.986</td>
<td>0.06</td>
<td>-0.19</td>
<td>0.65</td>
<td>0.35</td>
<td>300</td>
</tr>
<tr>
<td>Biphenyl</td>
<td>0.970</td>
<td>0.08</td>
<td>-0.16</td>
<td>0.69</td>
<td>0.31</td>
<td>200</td>
</tr>
</tbody>
</table>

The depletion of analytes with consecutive extraction in IL-SHS SDME using IL2 is represented in Figure 46. The IL2 has an aromatic ring (imidazolium ring) in addition to the four carbon side chain. The R² values were greater than 0.98 for the aromatic hydrocarbons while biphenyl showed R² value of 0.90. The slope and the intercept of each line was quite different from each other which signified a difference in K<sub>IL/S</sub> for the aromatic hydrocarbons. The experiment was
repeated twice and the standard deviation were considered as the uncertainty. The extraction ratio and the $K_{\text{IL/S}}$ for IL-SHS SDME using IL2 are summarized in Table 13. Heptyl benzene showed the highest $K_{\text{IL/S}}$ of 673 while Nonyl benzene showed the lowest $K_{\text{IL/S}}$ of 288. Hypothetically, the $K_{\text{IL/S}}$ were expected to increase from benzene to 3 or four membered alkyl chain of the homologous series and then plateau. However the observed trend was a zig zag pattern among the

![Depletion of Aromatic Hydrocarbons](image)

**Figure 46:** shows the depletion of aromatic hydrocarbons upon consecutive extraction in IL-SHS SDME using IL2.
Table 15: Apparent coefficient in IL-SHS SDME using 1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide at 22 °C

<table>
<thead>
<tr>
<th>Name</th>
<th>IL-SHS SDME 22°C</th>
<th></th>
<th>K_{IL/S} ± STDEV</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>E ± STDEV</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BENZENE</td>
<td>0.28±0.01</td>
<td>318±20</td>
<td></td>
</tr>
<tr>
<td>TOLUENE</td>
<td>0.40±0.01</td>
<td>494±31</td>
<td></td>
</tr>
<tr>
<td>ETHYL BENZENE</td>
<td>0.44±0.01</td>
<td>594±25</td>
<td></td>
</tr>
<tr>
<td>PROPYL BENZENE</td>
<td>0.38±0.03</td>
<td>453±51</td>
<td></td>
</tr>
<tr>
<td>BUTYL BENZENE</td>
<td>0.34±0.03</td>
<td>394±47</td>
<td></td>
</tr>
<tr>
<td>PENTYL BENZENE</td>
<td>0.40±0.04</td>
<td>497±92</td>
<td></td>
</tr>
<tr>
<td>HEXYL BENZENE</td>
<td>0.44±0.01</td>
<td>590±33</td>
<td></td>
</tr>
<tr>
<td>HEPTYL BENZENE</td>
<td>0.47±0.04</td>
<td>659±107</td>
<td></td>
</tr>
<tr>
<td>OCTYL BENZENE</td>
<td>0.47±0.01</td>
<td>673±9</td>
<td></td>
</tr>
<tr>
<td>NONYL BENZENE</td>
<td>0.29±0.09</td>
<td>288±158</td>
<td></td>
</tr>
<tr>
<td>NAPHTHALENE</td>
<td>0.30±0.01</td>
<td>315±5</td>
<td></td>
</tr>
<tr>
<td>BIPHENYL</td>
<td>0.10±0.01</td>
<td>81±11</td>
<td></td>
</tr>
</tbody>
</table>

homologous series. This was because of the inherent character of the ionic liquid to interact both with the carbon chain as well as the aromatic moiety of the analyte. In other words, the π-π
interaction between the ionic liquid and the aromatic hydrocarbons and the non-bonded interaction between the aliphatic chain in the ionic liquid with that of the aromatic hydrocarbon’s aliphatic chain occurs to a different extent. Benzene and naphthalene exhibited very close $K_{IL/S}$ while biphenyl reported $K_{IL/S}$ of 81.

To do a comparison of the effect of carbon chain on the partition coefficient of both LI1 and IL2, a plot of apparent partition coefficient against the number of carbons in the aliphatic chain was drawn as shown in Figure 47. The IL2 clearly exhibited superior partition coefficient when compared to IL1 due to the presence of heterocyclic aromatic ring that interacted with the $\pi$ electron cloud of the aromatic hydrocarbon homologous series. If one wishes to selectively extract higher members of aromatic hydrocarbons from biphenyl, IL2 would serve as a target selective extracting solvent under the specified experimental conditions. The $K_{IL/S}$ for Naphthalene should be much higher than benzene for the IL2 as it has two fused rings. However there was not much difference noticed between the two. The reason is that the extraction was performed at 22°C by salting out and the vapor pressure of naphthalene at this temperature is low, causing less analyte concentration in vapor phase when compared to volatile benzene, during the first equilibrium process of the IL-SHS SDME.
Figure 47: Comparison of IL2 and IL1 in terms of partition coefficient and the study of the effect of alkyl chain of the analyte on $K_{IL/S}$.

Validation of IL-SHS SDME method

The IL-SHS SDME extraction method using IL2 showed high extraction ratio and partition coefficient. So the extraction method using IL2 was validated as per standard method validation guidelines and extended to real sample analysis. The validation results are presented in Table 14. The following parameters were performed to establish the analytical figures of merit of the extraction procedure IL-SHS SDME.
<table>
<thead>
<tr>
<th>Name</th>
<th>Precision %RSD</th>
<th>Accuracy %Recovery±SD</th>
<th>Linearity (60 pg L⁻¹ - 60 ng mL⁻¹)</th>
<th>Precision at QL 60 pg L⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>4.3</td>
<td>89.0 ± 2</td>
<td>0.99527</td>
<td>12.7</td>
</tr>
<tr>
<td>Toluene</td>
<td>3.9</td>
<td>91 ± 1</td>
<td>0.99386</td>
<td>9.3</td>
</tr>
<tr>
<td>Ethyl benzene</td>
<td>3.6</td>
<td>91 ± 2</td>
<td>0.99152</td>
<td>7.3</td>
</tr>
<tr>
<td>Propyl benzene</td>
<td>3.2</td>
<td>91 ± 1</td>
<td>0.98210</td>
<td>13.0</td>
</tr>
<tr>
<td>Butyl benzene</td>
<td>3.2</td>
<td>91 ± 1</td>
<td>0.98224</td>
<td>7.5</td>
</tr>
<tr>
<td>Pentyl benzene</td>
<td>6.2</td>
<td>89 ± 1</td>
<td>0.99324</td>
<td>11.4</td>
</tr>
<tr>
<td>Hexyl benzene</td>
<td>3.4</td>
<td>94 ± 2</td>
<td>0.99650</td>
<td>11.7</td>
</tr>
<tr>
<td>Heptyl benzene</td>
<td>4.0</td>
<td>96± 2</td>
<td>0.98926</td>
<td>13.6</td>
</tr>
<tr>
<td>Octyl benzene</td>
<td>4.5</td>
<td>97 ± 2</td>
<td>0.98241</td>
<td>14.6</td>
</tr>
<tr>
<td>Nonyl benzene</td>
<td>5.5</td>
<td>98 ± 3</td>
<td>0.94856</td>
<td>18.0</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>4.3</td>
<td>96 ± 1</td>
<td>0.98420</td>
<td>15.7</td>
</tr>
<tr>
<td>Biphenyl</td>
<td>2.9</td>
<td>96 ± 2</td>
<td>0.98001</td>
<td>8.1</td>
</tr>
</tbody>
</table>
**Precision**

The precision of an analytical procedure expresses the closeness of agreement (degree of scatter) between a series of measurements obtained from multiple sampling of the same homogeneous sample under the prescribed conditions. The precision of an analytical procedure is usually expressed as the variance, standard deviation, %relative standard deviation or coefficient of variation of a series of measurement. Repeatability is one form of precision measurement. This was checked by performing extraction five times on five different vials, each containing 60 ng mL\(^{-1}\) of the analyte in aqueous solution. The % relative standard deviation were less than 6.5% for all the analytes showing the repeatability of the IL-SHS SDME method.

**Accuracy**

The accuracy of an analytical procedure expresses the closeness of agreement between the value which is accepted either as a conventional true value or an accepted reference value and the value found. To study the accuracy of the extraction method, the river water sample was spiked with 60 ng mL\(^{-1}\) of the aromatic hydrocarbon standard in aqueous solution and the IL-SHS SDME was performed. The (actual concentration/ theoretical concentration *100) gave the % recovery which represented the accuracy of the method. The procedure was repeated by taking 10 ng mL\(^{-1}\) aromatic hydrocarbons in river water and spiking it with 50 ng mL\(^{-1}\) aromatic hydrocarbon to it. This was repeated twice and the accuracy results reported in table 11 were the average of the three % Recovery. The standard deviation of the three %recovery were calculated and mentioned as the uncertainty.
**Linearity and range**

The specified range is normally derived from linearity studies and depends on the intended application of the procedure. It is established by confirming that the analytical procedure provides an acceptable degree of linearity, accuracy and precision when applied to samples containing amounts of analyte within or at the extremes of the specified range of the analytical procedure. The IL SHS SDME procedure was performed at five different concentrations. The method was linear from 60 pg mL\(^{-1}\) to 60 ng mL\(^{-1}\) for most of the aromatic hydrocarbons. The R\(^2\) values are presented in table 14.

**Limit of Quantitation (LOQ)**

The quantitation limit of an individual analytical procedure is the lowest amount of analyte in a sample which can be quantitatively determined with suitable precision and accuracy. Several approaches for determining the quantitation limit are possible, depending on whether the procedure is a non-instrumental or instrumental. Visual evaluation may be used for non-instrumental methods but may also be used with instrumental methods. The quantitation limit is generally determined by the analysis of samples with known concentrations of analyte and by establishing the minimum level at which the analyte can be quantified with acceptable accuracy and precision.

Based on the visual method, the limit of quantitation of The limit of quantitation 60 pg L\(^{-1}\) was obtained. The chromatogram is shown in Figure 48. Even at such low level, clean and sharp peaks were noticed. This is mainly because of the fast and complete mass transfer that happened in the inlet due to the no interface sample introduction. Further, precision was performed at the
The limit of quantitation and the % relative standard deviation was found to be less than 15.0% at 60 pg L\(^{-1}\) for all the analytes except naphthalene which showed a % relative standard deviation of 15.7 and nonyl benzene which showed a % relative standard deviation of 18.0%. The blanks injected before and after the injection did not show any carry over. This is the lowest reported limit of quantitation using ionic liquid based extraction for aromatic hydrocarbons to the best of our knowledge.\(^{86,87,91}\) Such low limit of quantitation was possible due to (1) the no interface complete analyte transfer from inlet to the column (2) Efficient extraction using appropriate ionic liquid containing \(\pi-\pi\) interaction. Faster equilibration of the headspace was possible by using small vial and least possible headspace volume and use of ultrasonic bath prior to the introduction of the extracting solvent.

![Chromatogram](image.png)

Figure 48: Chromatogram of 60 pg L\(^{-1}\) of aromatic hydrocarbons in aqueous solution extracted by IL-SHS SDME by using IL2.
Real sample analysis:

The real water samples were collected from different sources and examined for aromatic hydrocarbon contamination. Public water collected from two different cities in New Jersey and one from New York city was examined. A river water from New Jersey was also examined. The sample showed negative results to the aromatic hydrocarbon contamination. The river water sample collected was spiked with 60 ng mL$^{-1}$ of the aromatic hydrocarbons to determine the % recovery. This was performed thrice and the standard deviation was represented as the error in the recovery. The % recovery was between 88.9± 2.1 to 97.2 ± 2.4. In between each sample a blank injection was performed to make sure that there was no carry over. The chromatogram is presented in Figure 49.

![Figure 49: Chromatogram of blank injection performed using milliQ water by IL-SHS SDME by using IL2.](image)

Usually, in solid phase microextraction, carry over is observed and there arises the need to bake the fiber after each injection. However with IL-SHS SDME, the ionic liquid was taken freshly for every extraction, extracted, suspended in the inlet, retracted back into the syringe after
injection, and finally discarded into waste. Another notable point is that the inlet was run in splitless mode and there was a continuous flushing of the inlet with carrier gas.

Conclusion

A time efficient IL-SHS SDME was performed using the ionic liquid: 1-Butyl-1-methylpyrrrolidinium bis(trifluoromethylsulfonyl)imide (IL1) and 1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (IL2) (50% less time than the previous reported value\textsuperscript{87}). A true no interface sample introduction was performed to introduce the ionic liquid into the gas chromatographic inlet. The ionic liquid/water apparent partition coefficient ($K_{IL/S}$) of aromatic hydrocarbons were determined by depletion study. The $K_{IL/S}$ ranged from 187 (for Hexyl benzene) to 318 (for ethyl benzene) using IL1, whereas IL2 showed $K_{IL/S}$ in the range 81±11 (for biphenyl) to 670±9 (for Octyl benzene) IL2 showed superior extraction ratio and $K_{IL/S}$. So, the IL-SHS SDME method using IL2 was extended to quantitative analysis and was found to be precise with % relative standard deviation (RSD) less than 6.0% for all analytes, recovery of 89±2% to 96±2%. The method was linear from 60 pg L\textsuperscript{-1} to 60 ng mL\textsuperscript{-1}. The limit of quantitation were 60 pg L\textsuperscript{-1}. The extraction method was applied to real samples like drinking water and river water and aromatic hydrocarbons were not detected in any of these samples.
Chapter 5: Ionic Liquid Static Headspace Single Drop Micro Extraction (IL-SHS SDME) and Submerged Single Drop Microextraction (IL-SSDME) of Aromatic Hydrocarbons from Water
Introduction

Having known the versatility of ionic liquids, their applications in microextraction branched enormously. Direct immersion (DI) of solvent drop into the aqueous sample is a generally applicable mode of performing SDME. Here, the needle of a 10 µL syringe containing 1–3 µL of water immiscible organic solvent is penetrated through the septum of the vial until the tip protrudes below the meniscus of sample solution. The plunger is depressed to cause the solvent to form a drop suspended from the needle tip. After equilibration for a pre-determined period of time, whilst the solution is being continuously stirred, the drop is retracted back into the syringe and immediately subjected to analysis by instrumental methods. For solvent drop stability during extraction, it was important to remove any insoluble or particulate matter from the sample, choose an organic solvent that is least soluble in water and has low vapour pressure but has optimum extraction efficiency for analyte, and work at a stirring rate so that the drop is not dislodged. Since a water immiscible solvent is used, DI-SDME was subjected to analysis by GC method\textsuperscript{92}. n-Octane\textsuperscript{93} and toluene\textsuperscript{94} gave best extraction efficiency for non-polar compounds, whereas chloroform was used to extract polar alkaloids\textsuperscript{95}, and analysis by GC. One application analyzed 3 µL of toluene extract by reversed-phase HPLC, selected among other non-polar solvents such as xylene, tetrachloroethane, and iso-octane\textsuperscript{96}. However, only one compound, decabromodiphenyl ether, was analyzed that simplified the chromatography. Dibutyl phthalate was used in DI-SDME and found to have good compatibility with the mobile phase in reversed-phase HPLC\textsuperscript{97}. The main shortcoming of the DI-SDME process is the instability of the drop when an organic solvent is used as extractant. This fact limits the usable volume of the extracting medium, affecting directly the precision and also the sensitivity of the analysis.
Ionic liquids have been proposed as alternative to organic solvents due to their low vapor pressure and high viscosity that allow formation of larger and reproducible extraction drop. A contemporary approach to overcome the stability of the liquid drop in two phase extraction is to do IL-SSDME. Aromatic amines were extracted by IL-SSDME where ionic liquid was used as extracting media for the extraction of aromatic amines from aqueous sample solutions by using an ultrasound assisted liquid–liquid phase microextraction method. For the instrumental analysis, HPLC was used. Higher enrichment factors were achieved for the method compared to the conventional SDME in a much lower extraction time.

A comparison of IL-SHS SDME and IL-SSDME is shown in the Figure 50. In this research, one mode of ionic liquid microextraction namely: IL-SHS SDME was discussed in Chapter 4. As

Figure 50: Comparison of three phase and two phase ionic liquid microextraction
represented in the left side of the figure, IL-SHS SDME involved a three phase extraction involving two equilibrium processes. The first equilibrium exists between the sample and the vapor phase.

\[ K_{Vap/S} = \frac{[Vap]}{[S]} \quad \text{Equation (25)} \]

Where \( K_{Vap/S} \) is the partition coefficient of the analyte between the sample aqueous phase and the vapor phase, \([Vap]\) and \([S]\) are the concentration of the analyte in the vapor phase and sample aqueous phase.

The second equilibrium exists between the vapor phase and the ionic liquid.

\[ K_{IL/Vap} = \frac{[IL]}{[Vap]} \quad \text{Equation (26)} \]

Where \( K_{IL/Vap} \) is the partition coefficient of the analyte between vapor phase and the ionic liquid, \([IL]\) is the concentration of the analyte in the ionic liquid phase.

Over all, the ionic liquid-sample partition coefficient \( K_{IL/S} \) is the product of Equation (25) and Equation (26)

\[ K_{IL/S} = K_{Vap/S} \times K_{IL/Vap} = \frac{[Vap]}{[S]} \times \frac{[IL]}{[Vap]} = \frac{[IL]}{[S]} \quad \text{Equation (27)} \]

IL-SSDME is shown in the right side of Figure 50 and is a liquid-liquid extraction which uses a microliter volume of the acceptor phase (ionic liquid) and is a two phase extraction. The partition coefficient \( K_{IL/S} \) is given by
Comparing Equation (27) Equation(28) it is inferred that, if both the extractions are optimized to equilibrium condition, the end result $K_{IL/S}$ for the two phase and the three phase extraction should be the same irrespective of the number of equilibrium processes involved in the extraction at a given temperature. This work is intended to compare the two extractions IL-SHS SDME and IL SSDME in terms of their partition coefficient.

**Objective**

Figure 51 outlines the key objectives of the experiment. In Chapter 4, the IL-SHS SDME.

![Figure 51: Objectives of the experiment](image-url)
method was optimized to equilibrium conditions and the partition coefficient data was discussed. It was seen that the IL2 exhibited superior extraction ratio and partition coefficient compared to IL1. Taking this into consideration, IL2 was chosen for the IL-SSDME. The objective of the present study was to compare IL-SHS SDME and IL SSDME in terms of their partition coefficient using IL2 as the extracting solvent. The practical difference between the two extraction procedure in terms of the extraction time, ease to perform the experiment were also compared.

Experimental

Materials used

Ultrapure water was generated in the laboratory by a MilliQ Plus Ultra (Billerica, MA). Ionic liquids: 1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, aromatic hydrocarbons and all other chemicals used for the extraction were purchased from Sigma-Aldrich (St. Louis, MO). The ionic liquid column SLB-IL 76 was donated by Supelco Sigma-Aldrich (St. Louis, MO). The ultra inert low pressure drop liner with deactivated glass wool was supplied by Restek (Bellefonte, PA). A 25 µL syringe with blunt needle tip and teflon tip plunger, a 10 µL syringe with teflon tip plunger and bevel tip needle of 22gauge were purchased from Hamilton (Switzerland). An ultra sound bath from Cole Palmer (Vernon Hills, IL) was used.

Standard and sample preparation

A stock solution of 100 µg mL⁻¹ of each naphthalene, biphenyl, benzene, toluene, ethyl benzene, propyl benzene, butyl benzene, pentyl benzene, hexyl benzene, heptyl benzene, octyl benzene and nonyl benzene were prepared in methanol. Further dilutions were made as per the
concentration required. The final dilution in every case was made by spiking appropriate quantity of standard in a 2 mL microcentrifuge tubes containing 1.5 ml of 200 mg mL\(^{-1}\) aqueous sodium chloride solution made in Millipore water.

**IL- SSDME procedure**

The ILSHS SDME was performed as shown in the schematic in Figure 51. Step A involved taking 10.0 µL of 1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide in a 25.0 µL syringe having teflon tip plunger and blunt tip needle. Further in Step B the 10.0 µL ionic liquid was dispensed into a microcentrifuge tube containing 1.5 mL of the aqueous analyte.

![IL-SSDME schematic](image)

*Figure 52: Schematic representation of IL-SHS SDME*
containing 200 mg mL\(^{-1}\) of sodium chloride in it. This was sonicated in an ultrasound bath for 3.0 minutes. After the extraction, the tube was centrifuged at 12000 rpms for 2.0 min to separate layers which is shown in step C. Since the ionic liquid considered for the present study was denser than water, it formed the lower layer and hence the name IL-SSDME (ionic liquid-submerged single drop microextraction) was given to the extraction procedure. Finally, in step D, the ionic liquid was retracted using the blunt tip microsyringe and dispensed into a small volume sample holder. For sample introduction, 2.0 µL of the ionic liquid containing the extracted analyte was taken from the small volume sample holder using a 10.0 µL syringe with beveled tip. For the sample introduction into the gas chromatographic inlet, no interface sample introduction procedure described in Figure 33 of Chapter 4 was adopted.

**GC/MS Parameters**

The GC/MS analysis was performed using a 6890A GC coupled to 5973 MS detector system (Agilent Technologies, Palo Alto, CA, USA). The analysis was carried out in constant flow mode with a flow rate of 1 mL min\(^{-1}\). The ionic liquid column SLB-IL 76, 30 m x 0.25 mm x 0.20 µm was installed in the GC oven. All injections were performed in splitless mode. The inlet temperature was set at 300 °C. The oven temperature program was 35 °C (hold for 1 min) increased at the ramp of 20 °C min\(^{-1}\) up to 225 °C (hold for 4.5 min) with a total run time of 15 min. Transfer line, ion source and quard temperatures were set at 270, 250 and 150 °C respectively. A quadrupole MSD was operated in single ion monitoring (SIM) during runs. In the SIM, 78, 91, 128 and 154 m/z were chosen as the quantitative ions.
Depletion study

In order to determine the ionic liquid/water extraction ratio and the apparent partition coefficient of the analyte, depletion study was performed in IL-SSDME. A 1 µg/mL of aromatic hydrocarbons and bicyclic aromatic hydrocarbons were subjected to consecutive extraction of the analytes from the same microcentrifuge tube. After every extraction the IL2 containing the extracted analyte was removed as stated in Step D of Figure 52 followed by repetition of Step A to step D by adding 10.0 µL of IL2 to the same microcentrifuge tube. The formula described in Equation (23), Chapter 4, was used for calculating the apparent partition coefficient in the IL-SSDME. The depletion study was repeated using 3 µg/mL solution. The depletion was independent of the initial concentration of the analyte as per the proposed modes and could even be performed on unknown sample concentration. The standard deviation of the two trials were reported as the uncertainty in the calculated $K_{IL/S}$.

Results and Discussion

Method Optimization

The IL-SSDME method was optimized to equilibrium condition as shown in Figure 53 to 55. The first parameter under consideration was the volume of the ionic liquid. Since the IL-SSDME was different from IL-SHS SDME in terms of retracting the ionic liquid after extraction and it was difficult to completely remove 2 µL of ionic liquid from the aqueous phase, the optimization trial for the volume of the ionic liquid was started from 5 µL. The IL-SSDME was performed using 5 µL, 10 µL, 12.5 µL, 15 µL, 20 µL, 22.5 µL of ionic liquid respectively. A
histogram of peak area against the volume of ionic liquid was plotted as shown in Figure 53. It was found that the peak area started reducing after 10 µL and 10 µL gave the maximum peak.

![Optimization of the volume of Ionic liquid](image)

**Figure 53: Optimization of method parameters of IL-SSDME using IL2 as extracting solvent.**

The sonication time or the extraction time was optimized by performing the extraction for 2, 3, 4 and 5 min respectively. The histogram of peak area against sonication time is represented in Figure 54. It was observed that 3 and 4 min extraction showed almost similar peak area. So 3 min was chosen as the optimum extraction time.
Figure 55. shows the effect of salt concentration on the extraction. It was noticed that the extraction without salt showed better response than that with salt. The peak area reduced with the addition of salt. However the intended purpose of the analysis was to compare the partition coefficient in IL-SSDME with the IL- SHS SDME which employed a salt concentration of 200 mg mL\(^{-1}\). So the salt concentration was still maintained as 200 mg mL\(^{-1}\) for IL-SSDME.

The optimized volume of IL2 for IL-SSDME was 10 µL, the extraction time or the sonication time was optimized was 3.0 min and the salt concentration was 200 mg/mL sodium chloride. Thus the IL-SSDME was a very quick extraction compared to IL-SHS SDME.
Figure 55: Effect of salt concentration on IL-SSDME

Apparent partition coefficient by depletion study in IL-SSDME:
To understand IL-SSDME and to explore the differences from IL-SHS SDME, depletion study was performed using ionic liquid 1-Butyl-3-methylimidazolium. The Equation (23) presented in Chapter 4 was used for calculating the apparent partition coefficient. Since the amount of analytes extracted was proportional to the peak area, the peak area started to reduce exponentially with number of extraction. A plot of logarithm peak area against extraction number was made and were linear with a correlation coefficient greater than 0.98 for the aromatic hydrocarbons. The depletion plots for aromatic hydrocarbons using IL1 are shown in Figure 29. and that of bicyclic aromatic hydrocarbons using IL1 are shown in Figure 30. Biphenyl showed $R^2$ value of 0.95 while all other analytes showed $R^2$ greater than 0.98. It was
also observed that biphenyl showed better correlation coefficient in IL-SSDME than IL SSDME while performing depletion studies. This is because biphenyl is less volatile and its vapor pressure is less and gave poor response in IL-SSDME, while in SSDME it is in direct contact with the extracting ionic liquid and depleted better. The slope of the linear regression gave log(1-E), from which the extraction ratio (E) was calculated. By applying the volume of the extracting ionic liquid (10 µL), volume of the aqueous phase (1.5 mL) and the extraction ratio to Equation (23), the ionic liquid/ water apparent partition coefficient of aromatic hydrocarbons in the two phase extraction were calculated. Based on the Figure 56 and 57, it was clear that the slope of some of the hydrocarbons were different from the other. The slope for naphthalene, biphenyl and benzene were very different from each other.
Depletion Study in IL-SSDME for Aromatic Hydrocarbons

Log (peak area) vs. Extraction number

Nonyl benzene  Benzene  Toluene  Ethyl benzene  Propyl benzene
Butyl benzene  Pentyl benzene  Hexyl benzene  Heptyl benzene  Octyl benzene

Figure 56: Depletion of analytes during consecutive extraction of aromatic hydrocarbons in IL-SSDME using 1-Butyl-1-methylpyrroolidinium bis(trifluoromethylsulfonyl)imide as extracting ionic liquid.
Depletion Study in IL-SSDME for Bicyclic Aromatic Hydrocarbons

Figure 57: Depletion of analytes during consecutive extraction of bicyclic aromatic hydrocarbons in IL-SSDME using 1-Butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide as extracting ionic liquid.

Referring to Table 15, the highest $K_{IL/S}$ was observed for heptyl benzene and the lowest was for benzene. Biphenyl showed the lowest $K_{IL/S}$ among the bicyclic aromatics, and Naphthalene showed the highest $K_{IL/S}$. Compared to benzene, biphenyl showed half the $K_{IL/S}$, while Naphthalene showed more than double the $K_{IL/S}$ of benzene. Considering the structure of IL2, the butyl chain and the imidazolium hetero aromatic ring are the main source of interaction. The $K_{IL/S}$ started to increase from benzene to butyl benzene, then plateaus out as expected. Hydrocarbon. There was not a considerable difference in the $K_{IL/S}$ in the homologous series. This was because the length of the linkage group alkyl chain in the IL2 had only 4 carbons in it. The
π-π was the primary and the stronger interaction and dispersive interaction was the less strong secondary interaction. Since all the aromatic hydrocarbons had the same aromatic moiety and the

Table 17: Apparent coefficient in IL-SSDME using 1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide at 22 °C

<table>
<thead>
<tr>
<th>Name</th>
<th>IL-SSDME (Two phase extraction) 22°C</th>
<th>E± STDEV</th>
<th>K ± STDEV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>0.27±0.01</td>
<td>57±1</td>
<td></td>
</tr>
<tr>
<td>Toluene</td>
<td>0.44±0.01</td>
<td>121±3</td>
<td></td>
</tr>
<tr>
<td>Ethyl benzene</td>
<td>0.59±0.02</td>
<td>215±19</td>
<td></td>
</tr>
<tr>
<td>Propyl benzene</td>
<td>0.67±0.04</td>
<td>309±54</td>
<td></td>
</tr>
<tr>
<td>Butyl benzene</td>
<td>0.68±0.04</td>
<td>325±59</td>
<td></td>
</tr>
<tr>
<td>Pentyl benzene</td>
<td>0.67±0.03</td>
<td>311±49</td>
<td></td>
</tr>
<tr>
<td>Hexyl benzene</td>
<td>0.64±0.02</td>
<td>270±21</td>
<td></td>
</tr>
<tr>
<td>Heptyl benzene</td>
<td>0.61±0.01</td>
<td>237±5</td>
<td></td>
</tr>
<tr>
<td>Octyl benzene</td>
<td>0.60±0.01</td>
<td>223±10</td>
<td></td>
</tr>
<tr>
<td>Nonyl benzene</td>
<td>0.59±0.01</td>
<td>220±1</td>
<td></td>
</tr>
<tr>
<td>Naphthalene</td>
<td>0.48±0.02</td>
<td>137±10</td>
<td></td>
</tr>
<tr>
<td>Biphenyl</td>
<td>0.16±0.03</td>
<td>28±6</td>
<td></td>
</tr>
</tbody>
</table>
only differentiation was the alkyl chain in them, the ionic liquid tried to interact alike in terms of \( \pi-\pi \) interaction and at the same time distinguished them based on its four membered alkyl chain’s interaction with the analyte. After butyl benzene there was not much difference in \( K_{IL/S} \) taking the error bars into consideration. This was well illustrated when plot of \( K_{IL/S} \) against the number of carbons in the alkyl chain was made as shown in Figure 58. In other words the 4 carbon alkyl chain in the ionic liquid was able to differentiate 0 to 4 alkyl chains whereas saw 5 to 9 carbon alkyl chain in the same manner as the 4 carbon alkyl chain during IL-SSDME.

![Figure 58: Study of the effect of the alkyl chain on the partition coefficient in IL-SSDME using IL2 as the extracting medium.](image-url)
The side by side comparison of IL-SHS SDME and IL-SSDME was done on the basis of $K_{IL/S}$ for aromatic hydrocarbons using the IL2 as illustrated in Figure 59. The primary observation was that IL-SSDME exhibited superior $K_{IL/S}$ compared to IL-SSDME, contradicting the expected outcome of the experiment. Theoretically, both the three phase and the two phase extractions should give the same $K_{IL/S}$ at the given temperature using the same ionic liquid. The trend was also explained clearly in terms of the free energy change associated with the phase transfer of the analyte. The $-\Delta G_{IL/S}$ in KJ/mole were calculated using Equation (4) in Chapter 1.

**IL-SHS SDME Vs IL -SSDME**

![Graph comparing partition coefficients of IL-SHS SDME and IL-SSDME](image)

*Figure 59: Comparison of IL-SHS SDME and IL-SSDME in terms of the partition coefficient of aromatic hydrocarbons using IL2 as the extracting medium.*
A plot of $-\Delta G_{IL/S}$ was plotted against the number of carbons in the alkyl chain in the aromatic hydrocarbons for IL-SHS SDME and ILSSDME as shown in Figure 60. It was clearly seen that the $-\Delta G_{IL/S}$ increased initially and plateaued after 3 carbon alkyl chain for SSDME. While for SSDME, peak valley and again a peak was observed. The three phase equilibrium was more spontaneous as indicated by higher $-\Delta G_{IL/S}$ value. The gap between the blue and red line indicated the difference in the spontaneity of the three phase and two phase equilibrium. For 3, 4 and 5 carbon alkyl chains, the $-\Delta G_{IL/S}$ are very close for IL-SHS SDME and IL-SSDME.

![Comparison of IL-SHS SDME and IL-SSDME](image)

**Figure 60:** Comparison of IL-SHS SDME and IL-SSDME in terms of $-\Delta G_{IL/S}$ of aromatic hydrocarbons using IL2 as the extracting medium.

The anticipated reasons for lower $K_{IL/S}$ in IL-SSDME are summarized as follows. (i) The ionic liquid could have degraded and/or slightly soluble in the liquid phase. This reason was supported by the sonication time optimization and effect of salt concentration represented in Figure 53 and Figure 55, that showed decrease in peak area upon extraction for 5.0 min and
decrease in peak area with salt concentration respectively. (ii) The added sodium chloride directly interacted with the cation and the anion of the ionic liquid suppressing the partition coefficient of the aromatic hydrocarbon. (iii) the analytes tend to escape to the vapor phase during the sonication process while dispersing the ionic liquid while it favored in IL-SHS SDME by increasing the concentration of the analytes in the vapor phase. (iv) in IL-SHS SDME, the headspace vapor/ionic liquid equilibrium kinetics might be faster than the ionic liquid/sample or vapor/ionic liquid kinetics. (v) The polar groups of ionic liquid is surrounded by the polar water molecule and the ionic liquid becomes wet. Aromatic hydrocarbons being hydrophobic are less soluble in wet ionic liquid thereby reducing $K_{IL/S}$ in IL-SSDME.
Figure 61: Comparison of IL-SHS SDME against IL-SSDME in terms of the partition coefficient of benzene, naphthalene and biphenyl using IL2 as the extracting medium.
The Comparison of IL-SHS SDME against IL-SSDME in terms of the partition coefficient of benzene, naphthalene and biphenyl using IL2 is shown in Figure 61. The trend was better explained in terms of \(-\Delta G_{\text{IL/S}}\) as shown in Figure 62.

![Comparison of IL-SHS SDME and IL-SSDME](image.png)

<table>
<thead>
<tr>
<th></th>
<th>Benzene</th>
<th>Naphthalene</th>
<th>Biphenyl</th>
</tr>
</thead>
<tbody>
<tr>
<td>IL-SHDME</td>
<td>14</td>
<td>12</td>
<td>10</td>
</tr>
<tr>
<td>IL-SSDME</td>
<td>12</td>
<td>10</td>
<td>8</td>
</tr>
</tbody>
</table>

**Figure 62: Comparison of IL-SHS SDME against IL-SSDME in terms of \(-\Delta G_{\text{IL/S}}\) coefficient of benzene, naphthalene and biphenyl using IL2 as the extracting medium.**

It was seen that there was gap in between the red and the blue line. The gap between the two extractions indicated the difference in the spontaneity of the three phase and two phase equilibrium. Considering the blue line, the \(-\Delta G_{\text{IL/S}}\) was higher for naphthalene (2 fused benzene rings) compared to benzene in IL-SSDME while biphenyl (two attached benzene rings attached) showed least value. The reason could be that the ionic liquid in liquid phase could interact with
only one of the two phenyl groups which ever is in the same plane as that of the ionic liquid’s hetero aromatic moiety. Considering the red line, the ionic liquid was not able to distinguish between benzene and naphthalene, while biphenyl was the least spontaneous.

Table 18: Comparison of IL-SHS SDME and IL-SSDME in terms of its practical usage

<table>
<thead>
<tr>
<th>Practical attributes</th>
<th>IL-SHS SDME</th>
<th>IL-SSDME</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equilibration time</td>
<td>Headspace: 7 min</td>
<td>Total time: 3 min</td>
</tr>
<tr>
<td></td>
<td>Extraction using IL: 8 min</td>
<td>15 min</td>
</tr>
<tr>
<td>Sample introduction</td>
<td>No interface sample introduction</td>
<td></td>
</tr>
<tr>
<td>Automation</td>
<td>Semi automation and automation are possible</td>
<td></td>
</tr>
<tr>
<td>Challenging part of the extraction</td>
<td>Suspending the drop in the headspace without falling down</td>
<td>Retracting the extracted layer</td>
</tr>
<tr>
<td>Precision</td>
<td>%RSD &lt;3.5%</td>
<td>%RSD &lt;6.5%</td>
</tr>
<tr>
<td>High extraction ratio</td>
<td>For volatile analytes</td>
<td>For semivolatile analytes</td>
</tr>
</tbody>
</table>

The Table 16 summarizes the comparison of IL-SHS SDME and IL-SSDME in terms of their practical usage. IL-SSDME is a very quick extraction and involved just 3.0 min to equilibrate while IL-SHS SDME took 15 minutes for the extraction. Both these techniques can be used as a sample prep and pre concentration technique followed by no interface sample introduction into gas chromatographic inlet. Both these extraction techniques can be automated. The most challenging part of the IL-SSDME was to suspend the single drop of ionic liquid without letting it drop. In order to do that, the surface tension, viscosity of the ionic liquid, internal diameter of the syringe’s needle, volume of the ionic liquid should be considered. The challenging part in IL-
SSDME was retracting the ionic liquid into the syringe after the extraction, especially if the volume of the IL droplet is less than 3µL. Since IL-SSDME involves less labor intensive work than IL-SHS SDME, it showed better repeatability than the later.

**Conclusion**

A time efficient IL-SSDME method was developed which took 3.0 min for extraction. The IL-SSDME method was precise with %RSD less than 3.5% for all analytes. The apparent partition coefficient was determined by depletion studies. The highest $K_{IL/S}$ was observed for Butyl benzene ($325 \pm 59$) and the lowest $K_{IL/S}$ was observed for benzene ($57 \pm 1$) among the aromatic hydrocarbons. While biphenyl showed the lowest $K_{IL/S}$ ($28\pm6$), benzene ($57\pm1$) and naphthalene showed the highest $K_{IL/S}$ ($137\pm10$) among mono and bicyclic aromatic hydrocarbons. As expected the $K_{IL/S}$ started to plateau after 4 carbon alkyl chain. A comparison of IL-SHS SDME and IL-SSDME was made in terms of their partition coefficient. Theoretically, both were expected to show same $K_{IL/S}$. In actual IL-SHS SDME showed superior extraction ratio and $K_{IL/S}$. The trend was well explained in terms of $-\Delta G_{IL/S}$. The plot of $-\Delta G_{IL/S}$ against number of carbons in the alkyl chain for ILSSDME showed a clear plateau after 3 carbon alkyl chain while the IL-SHS SDME showed a peak and valley followed by another peak. This trend in IL SHS SDME could be because of the preference of the aromatic hydrocarbon’s alkyl chain and aromatic ring in vapor phase to interact with either the alkyl chain or the hetero aromatic moiety. The observed decrease in $K_{IL/S}$ in IL-SSDME could be because of the solubility/degradation of ionic liquid in aqueous medium, effect of sodium chloride, analytes escaping to vapor phase.
Chapter 6: Merits, demerits and future of the applications of ionic liquids in analytical separation science
Special features of the IL-SDME

The key features of the ionic liquid single drop micro extraction are described in Figure 63. The IL-SHS SDME was a fast extraction method which took just 15 min to equilibrate. No interface sample introduction was performed by using a splitless inlet. This greatly simplifies automation and use of the method. Also the lack of a separate interface helped in fast and direct mass transfer of the analyte to the column, improving sensitivity and peak width. The use of ionic liquids for the extraction and stationary phase for the chromatographic separation, was demonstrated. The partition coefficient determined by depletion study served as a tool to choose the ionic liquid for an intended purpose. The LOQ reported are in ppq and it extends the use of ionic liquids to ultra trace level analysis even with simple instrumentation.
Figure 63: Special features of the developed single drop micro extraction method
Draw backs of ionic liquid based extractions

Ionic liquids are definitely a green alternates to conventional sample preparation and pre-concentration procedures. There is additional research needed in several areas. Purification by sparging with high purity nitrogen as discussed by von Wald et al. is effective but inconvenient\textsuperscript{100}. The commercially available ionic liquids with better purity or simpler methods of purifying them in the lab need to be developed. There are numerous ionic liquids that are commercially available but there is not an effective way to classify them based on their solvation properties. Solution–vapor partition coefficients vary considerably for analytes dissolved in ionic liquids. Much further study of liquid–vapor partitioning is therefore needed to aid in the selection and method development process. Compared to other solvents, ILs have relatively high cost to purchase and purify. This could be addressed only if more vendors are ready to manufacture ionic liquids in bulk in order to use them as green alternatives to conventional solvents.

Conclusion

Room temperature ionic liquids are ionic species that are liquid at room temperature. Their physic-chemical properties can be tailored by changing the combination of cation, anion and the side chain. They have negligible vapor pressure, wide liquid range, thermal stability and exhibit unique selectivity. They find many applications in the field of analytical chemistry. In this research, the applications of ionic liquid as gas chromatographic stationary phase and as medium for microextractions were explored.
Ionic liquid stationary phases are attractive alternatives to conventional polyethylene glycol stationary phases. Due to the dual nature of ionic liquid, they are suitable for the separation of polar and non-polar analytes. To explore the retention of alkanes and aromatic hydrocarbons, the distribution constant at different temperature were determined for alkanes and aromatic hydrocarbons on commercially available ionic liquid stationary phases. Thermodynamic parameters for the chromatographic process using ionic liquid stationary phase were evaluated. The retention mechanism was predominantly partitioning for the alkanes. At lower temperature, for higher member of alkanes in the homologous series, there was considerable amount of adsorption along with the partition. The polarity number was not linearly related to the $\Delta G$ for alkanes while it was linearly related to the length of the alkyl chain present in the linkage group of the ionic liquid. For aromatic hydrocarbons, huge difference in $K_c$ was observed between 15 m and 30 m. SLB-IL 100 stationary phase indicating mixed mechanism of adsorption and partition. The retention of alkanes and aromatic hydrocarbons on ionic liquid stationary phase were compared with polyethylene glycol stationary phase in terms of their polarity number. The ambiguity in the calculated polarity number was established from the plot of thermodynamic parameters against the polarity number.

Air was successfully employed as the carrier gas for gas chromatographic analysis using ionic liquid as the stationary phase. Ionic liquid stationary phase SLB-IL 100 did not have any active hydroxyl group in its structure and was stable to oxidation. The thermodynamic properties of retention of aromatic hydrocarbons on ionic liquid stationary phase SLB-IL 100 using air as carrier gas were determined. This was compared with the thermodynamic properties of aromatic hydrocarbons, obtained using helium as carrier gas. The $K_c$ values were different from air and
Helium. In literature it was reported before that there would be change in the partition coefficient with change in the carrier gas. The kinetics of the chromatographic process using air as carrier gas was also studied. The study showed that air when used as carrier gas had a lower optimum B term over a very narrow range and a dominant C term. So air could not be used for fast GC applications. However air served as the cheap alternate to helium or hydrogen. Further air was used as the carrier gas to separate xylene isomers and a clear base to base separation of o, m, p-xylene was achieved using SLB-IL 100 stationary phase. The ionic liquid column with air as carrier gas was installed in the gas chromatographic instrument for six months continuously and showed consistent retention, peak shape and no ghost peaks, thus demonstrated the stability of ionic liquid stationary phase SLB-IL 100 even under extreme conditions. This feature would open new doors to the analysis of sample using air as carrier gas for field samples.

A time efficient IL-SHS SDME was performed using the ionic liquid: 1-Butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide (IL1) and 1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (IL2) (50% less time than the previous reported value \(^{87}\)). A true no interface sample introduction was performed to introduce the ionic liquid into the gas chromatographic inlet. The ionic liquid /water apparent partition coefficient (\(K_{\text{IL/S}}\)) of aromatic hydrocarbons were determined by depletion study. The \(K_{\text{IL/S}}\) ranged from 187 (for Hexyl benzene) to 318 (for ethyl benzene) using IL1, whereas IL2 showed \(K_{\text{IL/S}}\) in the range 81±11 (for biphenyl) to 670±9 (for Octyl benzene) IL2 showed superior extraction ratio and \(K_{\text{IL/S}}\). So, the IL-SHS SDME method using IL2 was extended to quantitative analysis and was found to be precise with % relative standard deviation (RSD) less than 6.0% for all analytes, recovery of 89±2% to 96±2%. The method was linear from 60 pg L\(^{-1}\) to 60 ng mL\(^{-1}\). The limit of quantitation
were 60 pg L\(^{-1}\). The extraction method was applied to real samples like drinking water and river water and aromatic hydrocarbons were not detected in any of these samples.

A time efficient IL-SSDME method was developed which took 3.0 min for extraction. The IL-SSDME method was precise with %RSD less than 3.5% for all analytes. The apparent partition coefficient was determined by depletion studies. The highest \(K_{\text{IL/S}}\) was observed for Butyl benzene (325 ± 59) and the lowest \(K_{\text{IL/S}}\) was observed for benzene (57 ± 1) among the aromatic hydrocarbons. While biphenyl showed the lowest \(K_{\text{IL/S}}\) (28±6), benzene (57±1) and naphthalene showed the highest \(K_{\text{IL/S}}\) (137±10) among mono and bicyclic aromatic hydrocarbons. As expected the \(K_{\text{IL/S}}\) started to plateau after 4 carbon alkyl chain. A comparison of IL-SHS SDME and IL-SSDME was made in terms of their partition coefficient. Theoretically, both were expected to show same \(K_{\text{IL/S}}\). In actual IL-SHS SDME showed superior extraction ratio and \(K_{\text{IL/S}}\). The trend was well explained in terms of \(-\Delta G_{\text{IL/S}}\). The plot of \(-\Delta G_{\text{IL/S}}\) against number of carbons in the alkyl chain for ILSSDME showed a clear plateau after 3 carbon alkyl chain while the IL-SHS SDME showed a peak and valley followed by another peak. This trend in IL SHS SDME could be because of the preference of the aromatic hydrocarbon’s alkyl chain and aromatic ring in vapor phase to interact with either the alkyl chain or the hetero aromatic moiety. The observed decrease in \(K_{\text{IL/S}}\) in IL-SSDME could be because of the solubility/degradation of ionic liquid in aqueous medium, effect of sodium chloride, analytes escaping to vapor phase.
List of Publications


In preparation

1. Partition coefficient by depletion study for ionic liquid single drop microextraction of aromatic hydrocarbons from water and quantititative estimation by no interface gas chromatography mass spectrometry.

2. Retention of alkanes and aromatic hydrocarbons on ionic liquid stationary phases.

3. Separation of metal phthalocyanines by normal phase: method development and scaleup to semi-prep HPLC.
Future work

The present research focused on determining the partition coefficient of aromatic hydrocarbons homologous series. The trial could be performed at different temperature to study the $K_{IL/S}$ changes with temperature. Also it would be interesting to explore the $K_{IL/S}$ of different functional groups using probe analytes benzene, chlorobenzene, nitrobenzene, phenol and study the effect of the functional groups on $K_{IL/S}$.

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