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# IONIC LIQUIDS: RECENT JOURNEY THROUGH CHROMATOGRAPHIC SEPARATION

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## ABSTRACT

Ionic liquids (ILs), despite some of their crucial disadvantages, have been established to be the apt and relevant replacement of the volatile organic compounds (VOCs) in the industrial and academic sectors as solvents. Recent investigations on thriving multifaceted applications of ionic liquids have unleashed that they are really among beneficial "environmentally-benign" solvents as far as their impact on the ecosystem is concerned. This caused them to be an exciting and lucrative domain to explore in a wider fashion and many of the leading research groups are involved in the manifestation of their inherent undisclosed legacy. While exploring the efficacy of ILs, it was found that ILs or IL-based mixed solvent systems were very good alternative of conventional solvents and could act as mobile/stationary phases or additives in gas chromatography (GC), multidimensional gas chromatography (MDGC), inverse gas chromatography (IGC), high performance liquid chromatography (HPLC) and capillary electrophoresis (CE) very efficiently. Their (IL's) efficacy in improvising and synchronizing the mode and nature of the chromatographic separation is well-established, undoubtedly commendable and unique in many ways. In this review we have put our concentration on the recent, beneficial and some less-explored aspects of the implementation of ILs in the above said chromatographic separation domain.

**Keywords:** Ionic Liquids, Chromatography, Benign alternative stationary/mobile phase/capillary coatings.

## 1. INTRODUCTION

There is a huge and dramatic development in science and technology during last few decades which made our life more and more convenient and invulnerable. With manifold evolvement of beneficial and prolific scientific inventions and discoveries, it is now widely perceived that next few decades are going to be extremely technology-dependent. Unfortunately, there are some detrimental effects of this enormous development, too. There are some long-standing problems, especially environment-related and if they are not solved in a proper and philosophical way, the safeguard of our human civilization may see an impending jeopardy [1]. One of the striking and long-lasting global problems is excessive usage of huge amount of toxic, hazardous, flammable, and highly volatile organic solvents in several fields of industries and academia. These volatile organic compounds (as known as VOCs) are difficult to separate or remove from the products, recycle or reuse, and dispose of which made them acutely environmentally-damaging [2]. In fact, according to Montreal Protocol, some of the common organic solvents have been proposed to be of limited usage and in some cases absolutely banned for their hazardous role on earth's ozone layer [1a,3].

Ionic Liquids (sometimes called Room Temperature Ionic Liquids), with some of its unique properties like least amount of vapour pressure, wide range of thermal stability, very large liquid range, ability to dissolve wide varieties of solutes; yet non-coordinating, high ionic conductivity etc. have emerged as a suitable and apt alternative of VOCs with right potential to act as an environmentally-benign solvent in different chemical industries and academia [4]. The ionic Liquids (ILs) are normally comprised of an organic cation and an inorganic anion; by changing one of them, one may alter some of its important properties like viscosity, density, hydrophobicity, dipolarity/polarizability, melting points and water miscibility to a significant extent [5]. This type of interesting molecular architecture of ILs is essentially drawing the attention of scientist community altogether. Again, due to its low temperature liquid range ILs hold back dissociation, disproportion and degradation reactions which further extends the lifetime of species which are normally unstable in conventional solvents. Till now this class of solvents (i.e., ILs) have been explored in a vivid way which has been registered by the exponential growth in number of publications regarding their analytical applications during last two decades [6-9]. In this review their applications in chromatographic separation would be enunciated briefly with majorly focussing upon the recent efforts.

After the discovery by Russian botanist M. S. Tswett in 1900, through years, chromatography has been a very useful as well as a dependable method of separating the mixture of inorganic and organic compounds and a reliable means for analysis of several types of samples with sheer ease [10]. Here it is noteworthy that the real-world samples viz., medicines, gasolines, foods, bloods, cosmetics, to name a few, are generally comprised of dozens, hundreds and thousands of chemical components. Chromatography is a technique which by means of several fundamental intermolecular interactions such as dispersion, H-bonding, dipole-dipole interaction etc., separates and later quantifies the individual components of mixtures or in other words, real-world samples [11]. The incorporation of ILs in 1990s as the part of the chromatographic separations was later compared to their usage as solvents in organic synthesis. Specific application of ILs in separation science were reviewed by many groups [12-17]. Sometimes they are used as additives in capillary electrophoresis running buffers, LC mobile phases etc. Obviously, their role in these types of separations is multifaceted [18]. There are many scopes to discuss about the recent implementations of ILs in chromatography and the theme of our review would be centralized within the role of ILs in chromatographic separations such as gas chromatography (GC), multidimensional gas chromatography (MDGC), inverse gas chromatography (IGC), high performance liquid chromatography (HPLC) and capillary electrophoresis (CE).

## 2. CHROMATOGRAPHIC APPLICATIONS OF ILS

ILs, a novel solvent, have been used in several types of chromatographic procedures. In order to have proper understanding about their role in chromatographic separation, scientists explored ILs in wider way and after its exploration, it was perceived that they have huge potential to alter/modify the mode of chromatographic separation technique. The first attempt of using ILs in chromatography was by Barber *et al.* in 1950s [19] and later it was carried forward by Poole and co-workers in the beginning of 1980s [20]. The cutting-edge capacity of ILs to act as stationary phase in chromatography is due to IL's inherent properties said earlier and moreover, it was also noticeable that it has ability to act as coating on the inner-wall of the fused-silica capillaries owing to its wetting attributes. Among several types of chromatographic separations, Gas Chromatography (GC) has been used or employed and discussed here most vividly.

### 2.1. Gas Chromatography

Armstrong group was one of the earlier groups to use RTILs as stationary phase GC and their works mainly centralized about exploration of ILs to show dual-nature selectivity (i.e., for both polar and non-polar type of mobile phases) behaviour. It was found that when ILs [bmim][Cl] and [bmim][$PF_6$](bmim = 1-butyl-3-methylimidazolium) were used as a solvent to dissolve *permethylated-13-cyclodextrin* (BPM) and *dimethylated-β-cyclodextrin* (BDM) to prepare stationary phases for capillary columns in gas chromatography for chiral separation (due to their ability to dissolve large quantity of chiral selectors and viscosity), they served the purpose well but were not superior to the commercially available chiral selectors, probably due to formation of an inclusion complex with the cyclodextrin cavity [21]. In an earlier study they had shown the ability of these ILs to perform better as a stationary phase in GC when coated onto silica capillary [22]. Later, Anderson and Armstrong prepared 1-benzyl-3-methylimidazolium trifluoromethanesulfonate ([bemim][TfO]) and 1-(4-methoxyphenyl)-3-methylimidazolium trifluoromethanesulfonate ([mpmim][TfO]) IL-based stationary phases in GC which are rather highly stable and having 'bulky' imidazolium groups. Their columns could be operated up to even 250°C and could separate efficiently a wide variety of analyte mixtures including alkanes, alcohols, polycyclic aromatic hydrocarbons, and isomeric sulfoxides etc. [23]. From all the examples it could unequivocally be said that imidazolium-based ionic liquids are the most acceptable compounds to be used for the generation of GC stationary phases owing to some of their unique properties. The retention of solute molecules on GC stationary phases was a very intricate process and to trace out the various factors involved, initially Rohrschneider-McReynolds approach was used. It was later replaced by a superior Abraham solvation parameter model which is still being considered as the best model as far as these types of complicated simulations are concerned.

In order to exemplify the successful implementation of Abraham Model, we have chosen to show an outstanding work by Alvarez *et al.* [24]. They employed two ionic liquids (ILs), namely (S,S)-1-butyl-3-(2′-hydroxycyclohexyl)-3H-imidazol-1-ium tetrafluoroborate (IL-1) and (S,S)-1-butyl-3-(2′-acetyl-cyclohexyl)-3H-imidazol-1-iumtetrafluoroborate (IL-2) as the stationary phase in the gas chromatography and obtained a very good column efficiency along with a wide operating temperature range and good thermal stability. The comparatively higher thermal stability of the former IL is supposed to be due to the presence of C-OH moiety rather than the C-OAc as present in the latter IL, which, in turn, made the latter one unable to participate in quite a number of chromatographic separations. After a thorough comparative study of the system constants (viz., e, s, a, b, l) obtained by Abraham solvation parameter model, it could be concluded that IL-1 is superior than IL-2 with respect to HBD (hydrogen bond donating) acidity (b-term), and inferior with respect to HBA (hydrogen bond accepting) basicity (a-term) and tendency to interact with the dipolar/polarizable solutes (s-term). The next term i.e., e-term (which is negative here) described the domination of anions over cations as far as the tendency to interact with the solutes through n- and π-electron pairs are concerned. Finally, the positive l-term values indicated exoergic dispersion interaction would exceed the endoergic cavity interaction. All these term values evoked largely on the fact of the successful employment of the above-mentioned ILs as high stability selective stationary phase in the gas chromatographic process.

Recently, Luis *et al.* prepared a series of silica-supported polymeric IL (PIL)-based stationary phases where they used a vinylic L-valine ionic liquid derivative (amino acid-based IL, AAIL) as a monomer and a divinyl benzene (DVB) as a cross-linking agent to provide the silica surface a homogeneous coating onto it to improve the thermal stability as well as column efficiency [25]. They utilized Abraham model to evaluate the solvation parameters of the stationary phases based on AAIL-DVB system they explored. Again, in order to have additional insight into the system, they used Grob test for the optimization of the effect of the amount of the AAIL and the crosslinker on the overall chromatographic separation process to improve the retention, selectivity and resolution of the columns. Here it is mention-worthy that the enhanced nucleophilicity of the anion of the IL may decrease the thermal stability, while its co-ordinating ability can outline the quality of the chromatographic separation. Conversely, ILs with non-coordinating anions produce stationary phases which often yield poor separations and overlapping peaks. These two facts could be exemplified with bis [(trifluoromethyl)sulfonyl]imide ($NTf_2^-$) and hexafluorophosphate ($PF_6^-$) anions, respectively. To curb this problem they had used an amino acid-based IL which had extra functional groups in its structure which were able to provide subordinate interactions such as hydrogen bonding, hydrophobic or aromatic interactions which made them quite viable to be used as a stationary phase in GC leading to the recent preparation and characterization of some new AAILs-based gas chromatography stationary phase. Problems regarding the stationary phases such as flaws in preparing highly homogeneous coatings and thermal instability were cured by the PILs which combined the main features ILs with typical properties of polymers such as improved mechanical stability and processibility [26-29]. Moreover, Anderson *et al.* produced a cross-linked PIL which provided an enhanced thermal stability to a remarkable extent than its mono-cationic or di-cationic analogue which brought about a huge jump in research in this field [30]. Luis *et al.* used divinylbenzene (DVB) for the first time as a crosslinker for PIL-based stationary phases for GC due to its simplicity, cheapness and commercial availability. Nonetheless, it could be used as a simple design element in tuning the morphological properties of the resulting polymeric matrices. In order to have a better conceptualization about the effect of the DVB on the efficiency of PIL-based stationary phases, PILs with varying amounts of DVB as the crosslinking agents (e.g., 0, 10, 20, 30, 40, and 60 % w/w) were prepared and their efficiency was compared. Interestingly, it was seen that optimum degree of crosslinking must have to be within 20%, above which the interaction sites from AAIL confined at the highly crosslinked sections became less accessible to the analytes [31,32]. The thermal stability was evaluated by two methods- (i) temperature-programmed GC method and (ii) isothermal method; which again displayed the higher efficiency of 20% DVB over other compositions. While going to compare the solvation parameters, it was observed in all the cases that, the HBA basicity (a-term) and the dipole interactions (s-term) were the dominant system constants, followed by the HBD acidity (b-term) and the dispersion forces (l-term). The remaining e-term being slightly negative, indicated about no interaction between solutes and the stationary phases through π- or n-electrons. Subsequent Grob test [33,34] also supported the above result of solvation parameter coefficients through its best peak symmetries and less mass transfer losses for 20% DVB-PIL system.

Nakamoto *et al.* while working with electronic noses (devices to identify or quantify volatile compounds or odors) [35], faced some challenges or in other words, found some fields of improvement of the sensors such as selectivity, sensitivity, stability, cost, response time, reproducibility, and portability etc. [36-40]. Solution to these was merely to develop new sensor materials with newer configurations and array [41]. In this line of works they tried studying electronic noses using an array of quartz crystal microbalance (QCM) sensors coated with gas chromatographic stationary phases [42]. They are having advantages like low cost, commercial availability, easy manipulation, stability, and simplicity in the electronic circuits compared to other complex gas sensing devices like surface acoustic waves (SAW), thin film bulk acoustic resonators (FBAR), or cantilevers having higher sensitivities. Room Temperature Ionic Liquids (RTILs) with their enormous number of cation-anion combinations show excellent efficacy in sensing gases, application of which is already documented as sensor material coatings for QCM sensors, although in a minor scale [43-46]. Resistance changes and resonance frequency shifts are the two features which were exfoliated while trying to improve their classification of different gases by means of sensing. Comparative studies with and without the presence of RTIL in the sensing array were performed vigorously with 23 QCM sensors coated with RTIL and 5 QCM with conventional coating material (all of them conventionally used as stationary phases in gas chromatography) to have an insight into RTIL's efficiency in sensing gases.

Recently, Cagliero *et al.* with the aim of introducing complementary stationary phases for GC with unique selectivity as a support to the traditional stationary phases in the flavor, fragrance and natural product fields, explored a phosphonium-based IL $[P_{66614}^{+}][Cl^{-}]$ (trihexyl(tetradecyl)phosphonium chloride) due to their sheer success as a stationary phase (having unique selectivity property) in routine analysis of moderate-to-high volatile samples with different polarity, functional groups and structure [47]. Their probe mainly concerned with long term IL column stability, optimization of maximum allowable operating temperature (MAOT) (reportedly as low as 210°C), column efficiency, geometry and performance. The focus was obviously on the analysis of compounds mostly belonging to flavor and fragrance field (FFMix), fatty acid methyl esters (FAMEs) and some essential oils.

Armstrong group tried to explore the varied selectivity of the geminal dicationic ILs, which often show higher thermal stabilities compared to the conventional monocationic ILs, by varying its structures in different GC processes. The geminal dicationic ILs have three main structural moieties (viz. cationic head groups, a linkage chain and the counter ions) that may be modified to achieve certain structural features which may redefine the mode of chromatographic separation properties of IL stationary phases. For this, they synthesized a series of thermally stable geminal dicationic ILs among which nine ILs were proved to be high thermogravimetric analysis stable which were further tested with inverse GC-flame ionization detector (GC-FID) to display short-term stability [48-56]. These selected ILs were composed of several combination of five different cations, two different alkane linker chains, and two different anions and their varied type of test mixtures were subjected to GC chromatography as different stationary phases and following the corresponding separation patterns the effect of structural modifications on the polarity and selectivity were evaluated. Here it is to be mentioned that the three general types of dications of ILs used by them were: i) Imidazolium, e.g., benzylmethylimidazolium; ii) Pyrrolidinium, e.g., methyl- and butyl-pyrrolidinium; iii) Phosphonium, e.g., tripropylphosphonium. These dicationic moieties were linked by two alkane chains e.g., 9 carbon ($C_9$) and 12 carbon ($C_{12}$) and the consequential dications got paired with anions viz., $NTf_2^-$ and $PFOS^-$. They generalised the conclusion obtained from the observations of elution pattern of high-temperature chromatographic experiments with test mixes viz., FAME, Grob, Polar Plus, PAM-HC etc. injected within IL-coated capillary column along with commercially available most polar column SLB IL 111 that, polarity of stationary phase was inversely proportional to the length of the alkane chain length. Eventually, phosphonium ILs are less polar than both the imidazolium and pyrrolidinium ILs, and $NTf_2^-$ anions are more polar than analogous ILs with $PFOS^-$ anions. From Grob and Polar Plus test mixes it was concluded that all the ILs showed reasonable retention which was the reflection of their 'dual nature' behavior.

## 2.2. Multidimensional Gas Chromatography

Multidimensional Gas Chromatography (MDGC) has been emerged as a very reliable method to analyse volatile or semi-volatile complex samples like petrochemicals, food additives, forensic samples, cosmetics, and pharmaceutical compounds etc. which require very sophisticated tools to analyse. MDGC with IL-based column was first reported in 2006 and is a combination of two or more independent separation processes which generically improves the quality, wideness and accuracy of the chromatographic process [57]. As for example, heart-cutting MDGC (H/C MDGC) instrumentation consisted of two connected columns which uses a flow-switching device to direct a particular portion of primary column effluent into the secondary column to improve the separation of the heart-cut region. Again, in 2D GC (GC×GC) two columns containing stationary phases with different selectivity (i.e., nonpolar × polar or polar × nonpolar column configuration) are connected to pass the eluted compounds from first column to the second so as to maximize the peak capacity and related elution efficiencies [58-61]. Recent development in the powerful instrumentation and data analysis of the tool for MDGC have been reviewed by Synovec *et al.* ILs with triflate anions, glucaminium-based ILs, and metal-containing ILs has been explored to fine tune the separation selectivity via MDGC recently [62]. To overcome the bottlenecks of performing direct GC analysis of aqueous samples, such as, poor peak asymmetry, poor sensitivity and efficiency, strong adsorption, and stationary phase degradation etc. Cagliero *et al.* proposed the use of water-miscible IL-based stationary phases. Compared to the conventional stationary phases based on polydimethyl (siloxane) (PDMS) and polyethylene glycol (PEG), IL-based stationary phases were considered as more polar which was proved via calculation and derivation as their McReynolds constants. Mondello *et al.* introduced the way of naming commercial Supelco IL GC columns as SLB IL59, SLB IL 100 etc. following the polarity scale system referred to as polarity number (PN) [63]. An excellent review by Mondello *et al.* in this regard is really referrable for having a deeper insight into the topic starting from its early developments [64].

Till date, most of the IL-based MDGC columns have been applied for the analysis of FAMEs [56]. Several groups explored this MDGC study on FAMEs and expanded the efficacy of its application to a greater and wider dimension. Delmonte *et al.* contributed hugely in this field donating his endeavour in searching the excellence of MDGC compared to commercially available single 200 m SLB IL 111 column and it was found that most portion of the FAMEs were resolved when a second dimension of separation is incorporated in the chromatographic column [65-67]. Zeng *et al.* combined 2D GC and MDGC to achieve an integrated system for the analysis of FAME utilizing SLB IL-76,100 and -111 columns and for the betterment of peak capacity and retention behavior [68]. Nosheen and co-workers used GC × GC taking commercially available SLB IL -59, -61, -76, -82, -100, -111) for analysing safflower oil which contained a complex mixture of C18 saturated and unsaturated FAs [69]. Kulsing *et al.* employed correlation between molecular simulation and linear solvation energy relationships to make a reliable prediction about the equivalent chain length of FAMEs on each IL-based column for GC × GC. [70]. Nolvachai *et al.* developed a theoretical concept and subsequently a model for the simplification of the process of selecting proper IL-based column and tried to obtain an acceptable and significant difference between the 1D and 2D processes for the separation of FAMEs using IL-based stationary phases in terms of switchable results by varying the column diameters and surface thickness of the IL-coated layers [71,72]. Webster *et al.* described a method of H/C MDGC with electron and chemical ionization mass spectrometry for identifying as well as quantifying very tracer amount of contamination within FAMEs in diesel fuel [73]. They took the help of MDGC in measuring the contamination of marine and naval diesel fuels generated from product mixing or adulteration with biodiesel or FAMEs to a very trace number of individual FAMEs with resolution and quantification. Wong *et al.* used GC × GC with a polar × apolar column set to study Copaifera oleoresin in which they had chosen diterpenic acid methyl esters (DAME) instead of FAME as analyte [74]. Pojjanapornpun and co-workers explored neoteric inert IL-based stationary phases viz., SLB-IL60i, SLB-IL76i and SLB-IL111i along with conventional IL-based columns for the separation of FAMEs and obtained similar retention time and distribution patterns but reduced peak widths, peak tailing and lower column bleed. They also observed that the SLB-IL111i × SLB IL59 column set may be a good choice for GC × GC analysis of FAMEs [75].

Other mixture of chemicals was also experimented for separation via MDGC and quite an appreciable success was achieved through the journey. Ros *et al.* explored

GC × GC employing a polar × IL-based column sets to bring about the solution for the problem arose due to the co-elution of polychlorinated biphenyl (PCB) congeners [76]. Zapadlo and co-workers used the GC × GC with highly polar IL-based columns (e.g., SLB-IL59) for the analysis of PCBs and achieved the goal of separating 196 out of 209 PCB congeners which were identified by utilizing GC × GC coupled with a time-of-flight MS (TOFMS) detector [77,78]. Similar studies were performed by Mahe *et al.* and Antle *et al.* for the separation of polycyclic aromatic sulfur heterocycles (PASHs) and polyaromatic hydrocarbons (PAHs). [79,80] In petrochemicals and fuel sector similar efficacy of MDGC were observed by Mogollan *et al.*, Cappelli Fontanive *et al.*, and Manzaro *et al.* [81-83].

## 2.3. Inverse Gas Chromatography

Inverse GC is another technique which has been explored with alkyl-, benzyl-, cyclohexyl-, ether-, alcohol-, and cyano-functionalized ILs to examine some of their physical and thermodynamic properties like gas to liquid partition coefficients, infinite dilution activity coefficients ($\gamma^{\infty}$), retention behaviour, surface energy of the materials, absorption/adsorption properties, diffusion coefficients, phase transitions and solubility parameters mostly within the approximate temperature range 310 K to 350 K which further predicted about their phase behaviour [84]. This method can also provide necessary information about interionic distances and possible dielectric constants. Initially, enthalpies and entropies of transfer were determined for six different ILs by dissolving in eight n-alkanes [85]. Activity co-efficients ($\gamma^{\infty}$) values were collected for 52 compounds within ILs (1,3-dimethoxyimidazoliumbis ((trifluoromethyl)sulfonyl)imide, 1-(methylethylether)-3-methylimidazolium bis((trifluoromethyl)sulfonyl) imide, 1-ethanol-3-methylimidazolium bis((trifluoro-methyl)-sulfonyl)imide, and 1-(3-cyanopropyl)-3-methylimidazolium dicyanamide, trimethyl-butylammonium $NTf_2$ and 1-hexadecyl-3-methylimidazolium $BF_4$ [86-88]. From all activity co-efficient ($\gamma^{\infty}$)values, selectivity at infinite dilution ($S_{12}^{\infty}$) were determined which was verified by LSER (Linear Solvation Energy Relationship) method following Abraham model which came out to be very helpful in optimizing and designing the separation process specially of aromatics, alcohols, and chloroalkanes from alkanes [89,90].

Acree Jr. *et al.* studied the measurement of infinite dilution activity coefficients ($\gamma_i^{\infty}$) and gas-to-ionic liquid partition coefficient for a set of organic solutes dissolving in four ionic liquids with the help of inverse gas chromatography [91]. This group till now performed measurement of $\gamma_i^{\infty}$ in more than 40 different ionic liquids with varying polarity and hydrogen bonding character based on inverse gas liquid chromatography methods and usually ionic liquids acted as a stationary phase in this type of chromatographic pathway. In this recent study, they calculated detailed parametrization studies for organic solids dissolved in both benzyl and cyclohexylmethyl-functionalized ILs based on the bis(trifluoromethylsulfonyl)imide anion. Measurement of $\gamma_i^{\infty}$ and gas-to-liquid partition coefficient were executed for 48 organic solutes dissolved in four different ILs viz., 1-benzyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([BzmIm][$Tf_2N$]), 1-benzyl-1-methylpyrrolidiniumbis(trifluoromethyl sulfonyl)imide([BzmPyrr][$Tf_2N$]), 1-cyclohexylmethyl-3-methylimidazolium bis(trifluoromethyl sulfonyl)imide ([ChxmIm][$Tf_2N$]), and N-cyclohexylmethylpyridinium bis(trifluoromethylsulfonyl) imide ([ChxPy][$Tf_2N$])using inverse gas chromatography within the temperature range of 323.15 K to 373.15 K. The data obtained were extrapolated to 298.15 K and results obtained therein were correlated with the renowned Abraham solvation parameter model mathematically. It was observed that the order of solubility of N-alkanes followed the order [ChxmIm]>[ChxPy]>[BzmPyrr]>[BzmIm] among cations and apolar compounds interacted with these ILs very weakly. It is to be noted that a benzyl group containing IL is less susceptible to interact with an organic compound compared to a cyclohexylmethyl analogue and irrespective of the structures of ILs, $\gamma_i^{\infty}$ values are inversely proportional to the temperature, apparently with some exceptions which agreed well with the experimental values obtained by Acree *et al.* Interestingly, they also observed that in separating hexane/pyridine or hexane/thiophene, all of them, mainly, [BzmIm][$Tf_2N$] performed better than sulfolanes as far as their selectivity and capacity values were concerned. The Abraham model was successfully used to derive the correlations to describe experimental gas-to-organic solvent and water-to-organic solvent partition coefficient values which further was utilized to predict the $\gamma_i^{\infty}$. Here it is to be mentioned that similar work was performed by Karpinska *et al.* in which they used nearly 64 solutes dissolve in both ILs 1-benzyl-3-methylimidazolium dicyanamide ([BzmIm][DCA]) and [BzmIm][$Tf_2N$] [92].

Recently, Abliz *et al.* made use of inverse gas chromatography for the investigation of the physio-chemical properties of four 1-alkyl-3-methylimidazolium bromide ($[C_nC_1Im]Br$, n= 5, 6, 7, 8) within the temperature range 303.15K to 343.15 K in which 28 organic solvents were used as a probe [93]. Extrapolation of the obtained data to room temperature (i.e., 298.15 K) gave satisfactory and conceivable results. The investigation was conducted in a comparative fashion with IGC method including the specific retention volume and the calculation of Flory-Huggins interaction parameter along with Hilderbrand solubility parameters ($\delta_2$) and Hansen solubility parameters (HSPs) (by HSPiP method) to obtain the miscibility/solubility and $\delta_2$ of ILs in various organic solvents [94,95]. Combination and comparison of all these methods yielded brilliant result with good agreement and accuracy between simulative and experimental values.

Silver ion has been applied in various separation techniques such as a carrier in facilitated transport membranes (FTMs) [96], as an absorbent for ethylene ether and FAME separation, and as a stationary phase additive for the separation of alkene isomers etc. to name a few [97]. To improve separation performance, number of ionic liquids (ILs) have been used as a solvent to dissolve silver salts and it was found that the structural features of IL solvents along with anions of the silver salts strongly affect the olefin capacity and selectivity giving rise to excellent separation performance caused by fast molecular diffusion as well as efficient transport of the olefin ligands via shifting between silver ion centers [98]. Being a versatile and useful technique in characterizing advanced materials, IGC has been proved to be ideal for the study of silver(I) ion temporal stability and effect of important conditions like temperature and gas exposure on it in various mixtures of silver salts and ILs with different anion and cation compositions. Very recently, Anderson *et al.* performed this type of study where chromatography columns containing a thin layer of silver salt and IL mixtures were taken as a stationary phase which was exposed to pure gas streams and variable temperature conditions [99]. It was observed by them that silver ion-olefine complexation was more favorable in cases where silver ions were dissolved in ILs with longer chain lengths (e.g., $[dmim^+]$) compared to the ILs with shorter chain lengths (e.g., $[bmim^+]$). Again, among other compositions, the mixture $[Ag^+][NTf_2^-]/[bmim^+][NTf_2^-]$ was shown to be most ideal composition for Ag(I) ion-olefin complexation due to its higher stability at varied conditions.

## 2.4. High Performance Liquid Chromatography

Utilization of ionic liquids in high performance liquid chromatography (HPLC) has a long way of history [100]. Use of ILs mainly as additives with aqueous- or organic- based mobile phases as recorded by different groups like Shetty *et al*. (used ethylammonium nitrate and propylammonium nitrate ILs)[101] and Waichigo *et al.* (used ethylammonium methanoate) [102] are mention-worthy. Some other groups also reported about the efficacy of ILs as mobile phase modifier [103]. For all the cases where IL additive used, an improvement in the signals was observed compared to the more common ammonium ethanoate and in some cases, they gave lower retention volume. It was opined that ILs with longer alkyl chain are more effective that the shorter one in shielding the residual silanol groups. Holbrey *et al*. showed that imidazolium based ILs form liquid clathrates with aromatic hydrocarbons creating an extended structure effectively that could modify the separation when used as mobile phase additives [104]. It was conceived after vigorous experimentation that, most of the ILs used as mobile phase additives exhibited improved peak shape along with good resolution compared to the commonly used ammonium ethanoate mobile phase additives especially when $(bmim)^+$and $(bmim)^+$ paired with methyl sulphate anion $(C_1SO_4)^-$ were used [103a]. In one of the recent works, Wuilloud *et al*. studied the IL-assisted determination and separation method of selenite [Se(IV)], selenate [Se(VI)], selenomethionine (SeMet) and Se-methylselenocysteine (SeMeSe-Cys) by reversed-phase high-performance liquid chromatography coupled to hydride generation atomic fluorescence spectrometry (RP-HPLC-HG-AFS) which proved to be superior method than very sensitive ICP-MS coupled RP-HPLC method [105,106]. It should be mentioned that the multivariate optimization improved the HG-AFS sensitivity for every type of Se species in presence of ILs, length of whose alkyl chain determined the hydride generation conditions, retention time and resolution. It was observed that longer the alkyl chain length, stronger is the retention of the Se (VI). ILs used in these studies were mainly imidazolium and phosphonium-based ILs viz., 1-butyl-3-methylimidazoliumchloride ([bmim]Cl), 1-hexyl-3-methylimidazolium chloride ([hmim]Cl), 1-octyl-3-methylimidazolium chloride ([omim]Cl),1-dodecyl-3-methylimidazolium bromide ([dmim]Br), 1-hexadecyl-

3-methylimidazolium bromide ([hdmim]Br) and tributyl(methyl)phosphonium methylsulphate ($[P_{4,4,4,1}]$ $CH_3SO_4$). Interestingly, by running same chromatographic column inorganic as well as organic Se-species could be separated and even very complexmatrix of food samples with Se could be speciated by following their methodologies incorporating ILs. Similar study on As-compounds were also done by this group separately [107]. In this study, As(III), Arsenate(VI), dimethylarsonic acid (DMA) and monomethylarsonic acid (MMA) were separated and identified with the help of RP-HPLC-HG-AFS in which the ILs played the role of a modifier. The experimental result showed that with the increase in the chain length of the ILs, the retention time got reduced as a consequence of the decreased interaction between the IL cationic and the anionic As species.

In a recent study, Hong Yu *et al.* Demonstrated how the determination and separation of o-, m-, p-amino benzoic acids were achieved by HPLC using IL with common anion $BF_4^-$ as mobile phase additive and reverse-phase C18 which inhibits significantly the signal tailing usually generated from mobile phase used without ILs [108]. In another novel approach, they reported the determination of morpholinium cations by HPLC-IUV (IUV stands for indirect ultra violet) method which involved imidazolium ILs as background UV absorbents which also brought about improvement to the separation of the analyte [109]. Anderson *et al.* reported application of HPLC compatible neat PIL-based (polymeric IL) SPME (solid phase micro-extraction) sorbent coatings for the analysis of phenolics, insecticides and pharmaceutical drugs for the first time [110]. They immobilized six structurally diverse PIL-based sorbent coatings on nitinol supports and applied as stationary phase sorbent materials for SPME. This type of analysis is supposed to widen the variety of analytes and matrices, particularly polar, non-volatile and ionisable compounds. In another study, Hyvarinen *et al.* showed that ILs could take a primary role in separating sugar and/or its derivatives from lignocellulosic biomass via hydrolysis and depolymerisation at elevated temperature and in harsh conditions, the sugars tend to degrade which could be avoided by maintaining very low temperature and short treatment times [111]. In this method, galactose, glucose, mannose and xylose were the main monosaccharides obtained upon IL-treatment (ILs used are: 1-ethyl-3-methylimidazolium chloride or 1-ethyl-3-methylimidazolium acetate) of wood samples. Row *et al.* utilized IL-assisted ligand exchange HPLC for chiral separation and determination of ofloxacin enuntiomers in which it was observed that, with increase in the chain length of the ILs, the extent of retention and separation got decreased caused by steric hindrance and prevention of coordination between amino acid anions and ofloxacin by longer chains [112]. Albertsson *et al.* first proposed and utilized aqueous two-phase liquid system (ATPS) in separating components of biological materials and proteins with the help of countercurrent chromatography (CCC) which was further used by others very frequently [113]. Berthod *et al.* demonstrated a newer aqueous two-phase liquid system (ATPS) containing ILs (e.g, 1-butyl-3-methyl imidazolium chloride ([bmim]Cl)) which was proved to be more effective in separating components like proteins by CCC with higher discriminating factor and lower intrinsic hydrophobicity compared to conventional ATPS constituent polyethylene glycol 1000 (PEG1000) [114].

## 2.5. Capillary Electrophoresis

Capillary Electrophoresis (CE) is a reliable and time-saving analytical technique with low sample consumption and high separation efficiency which runs on the principle of differences in electrophoretic mobility of the analytes through a running buffer. ILs being composed of cations and anions, have the ability to act as an efficient background electrolytes, additives and capillary wall modifier in electrophoretic separations [115,116]. The efficacy of ILs in achieving the improvement in different CE-based separations is due to its inherent unique properties like wide liquid range, good solvating power for cations and anions, low vapor pressure etc. to name a few, which resembles mostly with the criteria for a good CE running buffer and additives. Readers may go through good review articles by López-Pastor *et al.* and Aboul-Enein *et al.* in which several important aspects about the role of ILs in CE were described [117,118]. Hyϋarinen *et al.* showed that ILs might have important role as a background electrolyte (BGE) in the processing and analysis of sugar or any other carbohydrate in woody lignocellulosic biomass via hydrolysis and depolymerisation at elevated temperature [111]. Here ILs act both as a chromophore for indirect detection of the analyte by UV-vis spectroscopy and as a reactant to interact selectively with the analyte for the facilitation of the separation process. Superiority of phosphonium-based ILs over imidazolium one as pseudo-stationary phase in electrokinetic capillary chromatography (EKC) for suppression and reversal of the electroosmotic flow (EOF) to separate several charged ions which are susceptible to direct UV detection rather than indirect one is well established [119-122]. Wiedmer *et al.* demonstrated the similar application of these phosphonium-based ILs as pseudo-stationary phase in the separation of neutral aromatics (mainly benzene and benzene derivatives) via direct UV detection [123]. They utilized a 50 mM IL dispersion of [P14444]Cl (tributyltetradecylphosphonium chloride) in sodium phosphate buffer at pH 8.9 (ionic strength of 10 mM) and showed that the reagent to be adsorbed dynamically by the fused silica capillary and served well as a semi-permanent coatings in CE to modulate the EOF significantly. Several other ILs like tributyl (hexadecyl) phosphonium bromide ([P16444]Br), tetrabutyl-phoshonium chloride ([P4444]Cl), and triisobutyl-methylphosphonium tosylate ([P1444][OTs]) etc. were also used in these assay. [P16444]Br came out to be most effective EOF suppressor. Here it is to be mentioned that other factors like concentration of ILs, influence of BGE, pH etc. has significant effect on this type of separation. This work suggests the probable implementation of CE in characterizing different types of ILs and their interactions with some selected analytes.

## 3. CONCLUSION

The manifold types of the chromatographic separation processes made them multifaced utility method to achieve several goals of separation analysis for different types of samples. The ILs are gaining progressively more popularity and finding its niche in the field of separation science as alternative environmentally-benign solvent to act as mobile phase additive or stationary phase recently. Despite IL's toxic feature in some instances, after their better-tuning according to our need, they have become convincingly prolific from every aspect and meet our expectation as solvents in separation science. They have been proved to be highly prosperous as well as prospective and cherishing as far as their pertinent role in chromatography as modifier of conventional solvents in different proportions is concerned. As the method of chromatography is incorporated with so many difficulties in separating multi-component mixtures, finding easier and intuitive pathways was a great challenge for scientific community and along this trying path ILs as if became a friendly pathfinder.

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### *Conflict Of Interest*

The author doesn't have any Conflict of Interest.

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