Advance Analytical Course

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Lecture No. # 38

Today, we will study applications of ionic liquids in analytical chemistry. This is a completely new area for the students of graduation and under graduation level, and therefore, it needs a bit of introduction, but it is one of the most latest analytical tool that has been used in analytical chemistry and in analysis, and therefore, I felt that an introduction to use of ionic liquids is a must.

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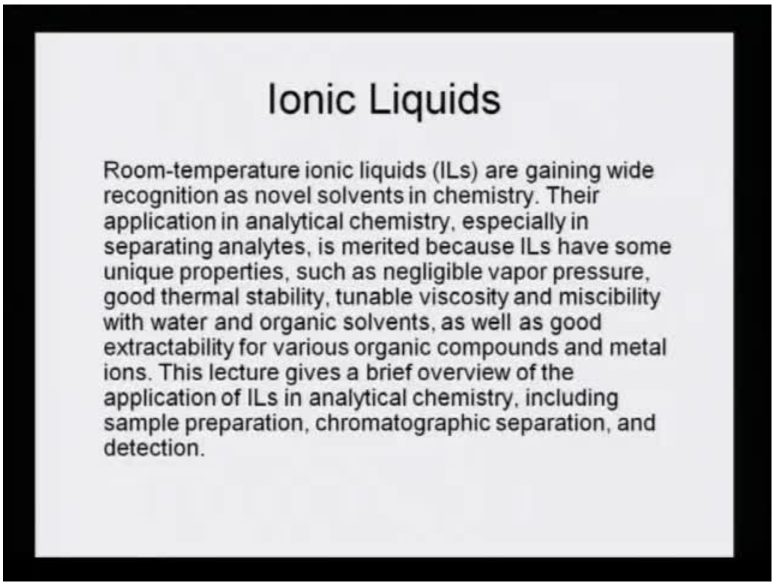

Ionic Liquids

Room-temperature ionic liquids (ILs) are gaining wide recognition as novel solvents in chemistry. Their application in analytical chemistry, especially in separating analytes, is merited because ILs have some unique properties, such as negligible vapor pressure, good thermal stability, tunable viscosity and miscibility with water and organic solvents, as well as good extractability for various organic compounds and metal ions. This lecture gives a brief overview of the application of ILs in analytical chemistry, including sample preparation, chromatographic separation, and detection.

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Ionic liquids - room temperature ionic liquids or ILs are gaining wide recognition as novel solvents in chemistry. Their application in analytical chemistry, especially in separating analytes, is merited because the ionic liquids have some unique properties such as negligible vapour pressure, good thermal stability, tunable viscosity and miscibility with water and organic solvents as well as good extractability from various organic compounds and metal ions.

This lecture gives a brief overview of the application of ionic liquids in analytical chemistry including sample preparation, chromatographic separation and detection. So, you understand that you know when we were talking about sample preparation, our main criteria was that the sample or the analyte should completely dissolve and come out of the matrix and if there is a substance like for example, ionic liquids which has very good properties, very adaptable for good extraction would not it be the ideal situation to use it. Yes, the answer is that this is just the ideal medium to extract the analyte. Why? Because it has very important properties, particularly it has negligible vapour pressure, it has good thermal stability; that means it does not dissociate or associate or get any kind of decomposition. It has a viscosity, which can be, you know manipulated or tunable viscosity and it is immiscible in water and most of the organic solvents.

Thus it has a good extractability property for extracting both the organic compounds as well as metal ions. You know we were looking at the separation processes and we looked at so many types of extraction processes and from one method to another method, we were changing because the maximum amount of compound should come in the analyte. I mean the analyte should come in the solvent so that the extraction is most efficient and here are ionic liquids which can do the needful.

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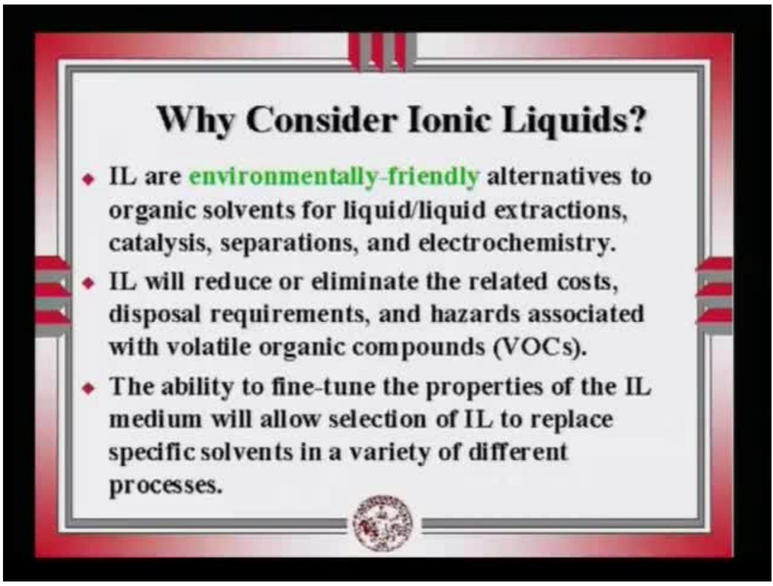

Why Consider Ionic Liquids?

- IL are environmentally-friendly alternatives to organic solvents for liquid/liquid extractions, catalysis, separations, and electrochemistry.
- IL will reduce or eliminate the related costs, disposal requirements, and hazards associated with volatile organic compounds (VOCs).
- The ability to fine-tune the properties of the IL medium will allow selection of IL to replace specific solvents in a variety of different processes.

Why consider ionic liquids? Ionic liquids are environmentally friendly alternatives to organic solvents for liquid/liquid extractions, catalysis, separation and electrochemistry.

So, they are expected to be environmentally friendly and therefore, they can be a good alternative for the use of these very not so liked the organic solvents, which have volatile organic compounds or VOCs..

The organic the ionic liquids will reduce or eliminate the related cost disposal requirement and hazards associated with volatile organic compounds. Now, if we try to look at the various solvents that are normally used, for example, diethyl ether or dichloromethane, which are the usual solvents for extraction, they are very volatile and therefore, they there are hazards associated with these volatile solvents and in place of that if ionic liquids can be used, there is an edge over because VOCs are very dangerous to handle and they are hazardous as well.

The ability to fine-tune the properties of the ionic liquid medium will allow selection of ionic medium to replace specific solvent in a variety of different processes. So, now ionic liquids actually can be chosen in such a manner that maximum, you know analyte can be extracted from the medium and this selection can also replace some of the solvents, which were traditionally used therefore making the process, a safe process.

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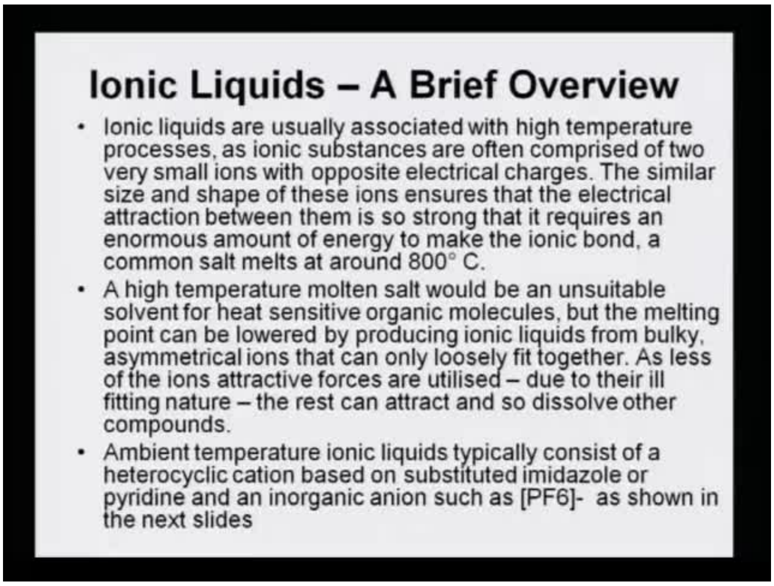

Ionic Liquids – A Brief Overview

- Ionic liquids are usually associated with high temperature processes, as ionic substances are often comprised of two very small ions with opposite electrical charges. The similar size and shape of these ions ensures that the electrical attraction between them is so strong that it requires an enormous amount of energy to make the ionic bond, a common salt melts at around 800° C.
- A high temperature molten salt would be an unsuitable solvent for heat sensitive organic molecules, but the melting point can be lowered by producing ionic liquids from bulky, asymmetrical ions that can only loosely fit together. As less of the ions attractive forces are utilised – due to their ill fitting nature – the rest can attract and so dissolve other compounds.
- Ambient temperature ionic liquids typically consist of a heterocyclic cation based on substituted imidazole or pyridine and an inorganic anion such as [PF6]- as shown in the next slides

Now, ionic liquids, if we try to take a brief overview, we will be able to understand it even better. Ionic liquids are usually associated with high temperature processes as ionic substances are often comprised of two very small ions with opposite electrical charges as the name suggests. Ionic liquid - that means there will be ions and ions will always appear in pairs.

But these pairs of positive and negative ions will be very small in These ions are very small in size and with opposite electrical charges. The similar size and shape of these ions ensure that the electrical attraction between them is too is so strong that it requires an enormous amount of energy to make the ionic bond; a common salt melts at about 800 degrees centigrade.

So, you see that if we try to look at the ionic liquid, these ionic liquids will be comprising of cation and anion, which are of opposite charge and they are very small, but they form the ionic bond because of the electro static attraction and if you take a simple example of sodium chloride (common salt), it melts at 800 degree centigrade.

A high temperature molten salt would be an unsuitable solvent for heat sensitive organic molecules, but the melting point can be lowered by producing ionic liquids from bulky, asymmetrical ions that can only loosely fit together. As less of the ions' attract forces are utilized, due to their ill-fitting nature, the rest can attract and so, dissolve other compounds. So, if we have similar sized ions, the problem is that it melts at a very high temperature and at that high temperature, it is possible that heat sensitive organic compounds may not survive and they may it may not be a suitable solvent for such compounds. However, if the there are bulky groups fitted, then these ions are disproportionate and some of the attractive forces can be used to dissolve the organic compounds.

Ambient temperature or room temperature ionic liquids typically consist of a heterocyclic cation based on substituted imidazole or pyridine or an inorganic anion such as PF4 PF6 as shown in the next slide. So, the most common ionic liquids which exist in room at room temperature are either imidazole or pyridine and they have an anion which could be PF6.

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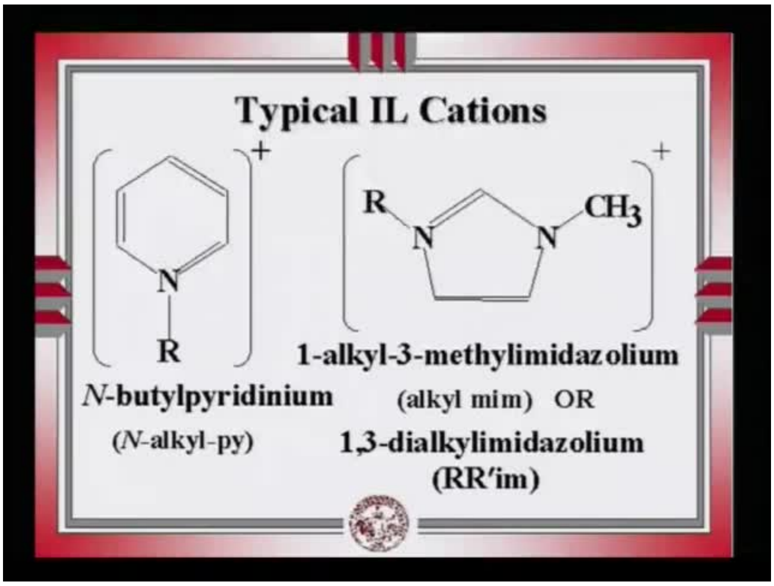

Typical IL Cations

***N*-butylpyridinium**

(*N*-alkyl-py)

1-alkyl-3-methylimidazolium

(alkyl mim) OR

1,3-dialkylimidazolium

(RR′im)

Now, typically, N-butylpyridinium ion can be the typical cation of ionic liquids or 1-alkyl-3-methylimidazolium or 1, 3-dialkylimidazolium cations are the common cations that are very typical of ionic liquids.

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Anions for RTIL

- $[PF_6]^-$ for moisture stable, water immiscible IL
- $[BF_4]^-$ for moisture stable, but water miscible IL depending on the ratio of ionic liquid:water, system temperature, and alkyl chain length in the cation.
- Less common anions include:

Triflate [TfO] Nonaflate [NfO] Bis(triflyl)amide $[Tf_2N]$

$CF_3SO_2^-$ $CF_3(CF_2)_3SO_2^-$ $(CF_3SO_2)_2N^-$

Trifluoroacetate [TA] Heptafluorobutanoate [HB]

$CF_3CO_2^-$ $CF_3(CF_2)_3CO_2^-$

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Anions for the room temperature liquid ionic liquids - PF6 minus for moisture stable, water immiscible ionic liquids, BF 4 minus for moisture stable, but water miscible ionic liquids depending on the ratio of ionic liquid to water, system temperature and alkyl chain length in the cation, one can modify these anions. Less common anions are the triflate, the nonaflate, bistrifylamide and so on, trifluoroacetate and heptafluorobutanoate. So, these are some of the other anions. Since ionic liquids will have cation and anion, cation and anion must be so chosen that they are not interfering with the analyte and therefore, wherever moisture stable ionic liquids have to be prepared, PF6 minus is the choice, but it is water immiscible. So, if water immiscible compounds have to be extracted, then PF6 is the ideal anionic choice, but wherever water miscibility is possible, BF4 minus can be used, but however, there are other anions also, which can be chosen.

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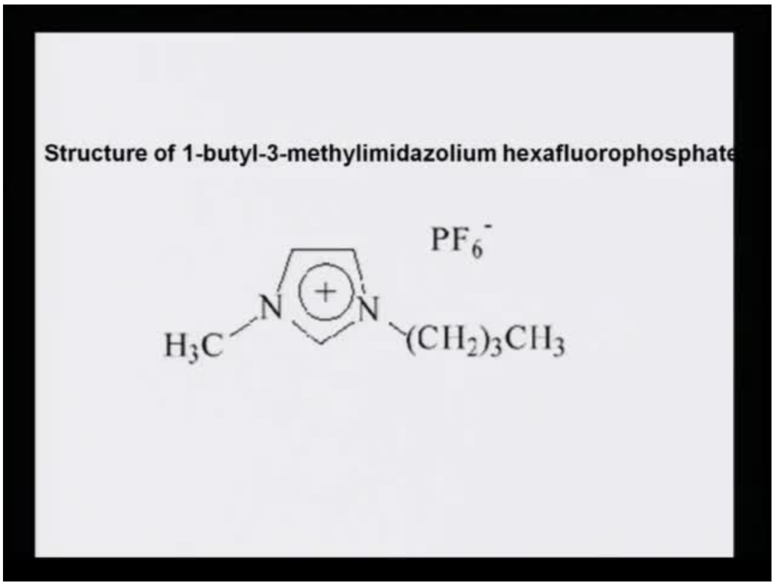

Structure of 1-butyl-3-methylimidazolium hexafluorophosphate

The structure of 1-butyl-3-methylimidazolium hexaflourophosphate – now, this is a particular ionic liquid, where there is a cation and there is an anion. which is Hexafluorophosphate is the anion and 1- butyl-3-methylimidazolium is the cation with the positive charge.

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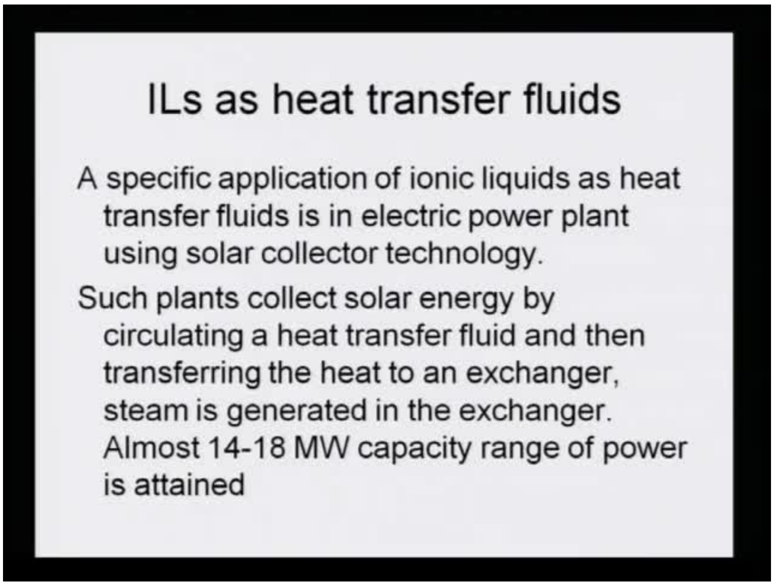

ILs as heat transfer fluids

A specific application of ionic liquids as heat transfer fluids is in electric power plant using solar collector technology.

Such plants collect solar energy by circulating a heat transfer fluid and then transferring the heat to an exchanger, steam is generated in the exchanger. Almost 14-18 MW capacity range of power is attained

Now, ionic liquids are like heat transfer fluids. A specific application of ionic liquids as heat transfer fluid is in electric plant, power plant using solar collector technology. So, you see, they have great use, not only in the extraction of organic compounds or inorganic metals, but they also have a role and a specific application as heat transfer fluids, particularly in electrical power plant, where solar collector technology is being used.

Such plants collect solar energy by circulating a heat transfer fluid and then transferring the heat to an exchanger, steam is generated in the exchanger. Almost 14 to 18 megawatt capacity range of power is attained. So, just by the use of the ionic liquid, appropriate ionic liquid, heat can be transferred from the solar energy, it can be transferred to an exchanger and then the exchanger then generates steam and almost, you know heat energy or power of the order of 14 to 18 megawatt capacity can be attained.

Now, let us try to look at some more properties of room temperature ionic liquids. Why I am emphasizing on ionic liquids is that it is one of the most recent advancement in analytical chemistry and as a part of this course, I thought that introducing you all to this particular topic of ionic liquids will give you an insight of the advancement that has really taken place and how for a variety of purpose, not only analytical chemistry, the ionic liquids play a very important role in extraction, separation and so on.

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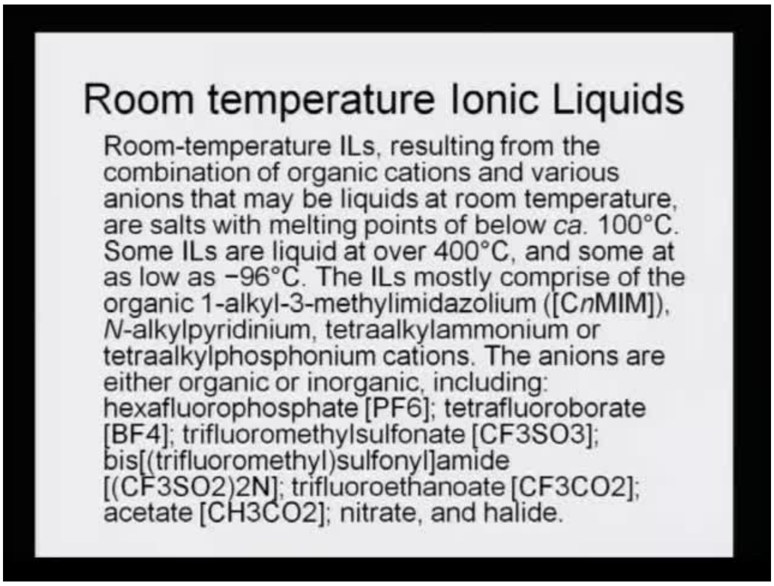

Room temperature Ionic Liquids

Room-temperature ILs, resulting from the combination of organic cations and various anions that may be liquids at room temperature, are salts with melting points of below *ca.* 100°C. Some ILs are liquid at over 400°C, and some at as low as −96°C. The ILs mostly comprise of the organic 1-alkyl-3-methylimidazolium ([C*n*MIM]), *N*-alkylpyridinium, tetraalkylammonium or tetraalkylphosphonium cations. The anions are either organic or inorganic, including: hexafluorophosphate [PF6]; tetrafluoroborate [BF4]; trifluoromethylsulfonate [CF3SO3]; bis[(trifluoromethyl)sulfonyl]amide [(CF3SO2)2N]; trifluoroethanoate [CF3CO2]; acetate [CH3CO2]; nitrate, and halide.

Room temperature ionic liquids resulting from the combination of organic cations and various anions that may be liquids at room temperature are salts with melting point of below 100 degrees. Some ionic liquids are liquids at over 400 degrees and some as low as minus 96 degree centigrade. So, you see that the range of their existence as ionic liquids can be ranging from temperature minus 96 to 400 degree centigrade.

But ideally the ones which are more popularly are used are in the range of 100 degrees. The ionic liquids mostly comprise of organic 1-alkyl-3-methylimidazolium, N-alkylpyridinium, tetraalkylammonium and tetraalkylphosphonium cations. So, these are the 4 varieties of cations that one would come across most popularly, when one is looking at the room temperature ionic liquids.

What are these different ionic liquids, we will take a look at it once again. 1-alkyl-3-methylimidazolium, 1-alkylpyridinium, tetraalkylammonium and tetraalkylphosphonium cations are the most common cations. The anions are either organic or inorganic, including hexafluorophosphate, tetrafluoroborate, trifluoromethylsulphonate, bistrifluormethylsulfonylamide, trifluoroethanoate and acetate, nitrate, halide. These are various types of anions that are used to make the liquid ionic liquids.

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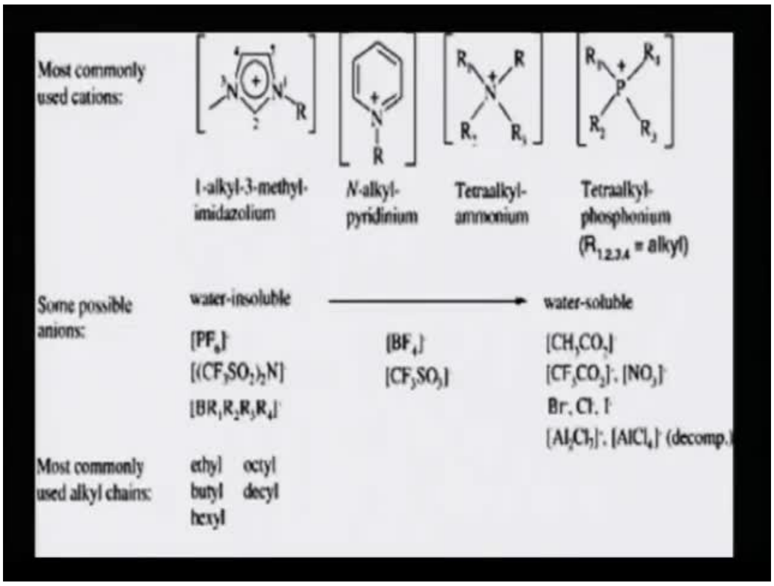

Most commonly used cations:

1-alkyl-3-methyl-imidazolium

N-alkyl-pyridinium

Tetraalkyl-ammonium

Tetraalkyl-phosphonium ($R_{1,2,3,4}$ = alkyl)

Some possible anions:

water-insoluble → water-soluble

$[PF_6]^-$
$[(CF_3SO_2)_2N]^-$
$[BR_1R_2R_3R_4]^-$

$[BF_4]^-$
$[CF_3SO_3]^-$

$[CH_3CO_2]^-$
$[CF_3CO_2]^-$, $[NO_3]^-$
Br^-, Cl^-, I^-
$[Al_2Cl_7]^-$, $[AlCl_4]^-$ (decomp.)

Most commonly used alkyl chains:

ethyl octyl
butyl decyl
hexyl

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Now, here are some of the examples shown pictorially. The same thing which I have just told you, most commonly used cations are 1-alkyl-3-methylimidazolium, N-alkyl-pyridinium, tetraalkyl ammonium and tetraalkyl phosphonium. This, we just look at it. Some of the possible anions, which are water insoluble and they slowly they move towards the soluble and depending on the solubility factor, the choice of anion can be made. It can be PF 6 minus or it can be BF 4 minus or it can be CS 3 CO 2 minus - that is the acetate. Similarly, we have different other types of sulphonates and nitrates and we can have also halides like bromide, chloride, iodide. Most commonly used alkyl chains are ethyl, butyl, hexyl, octyl and decyl.

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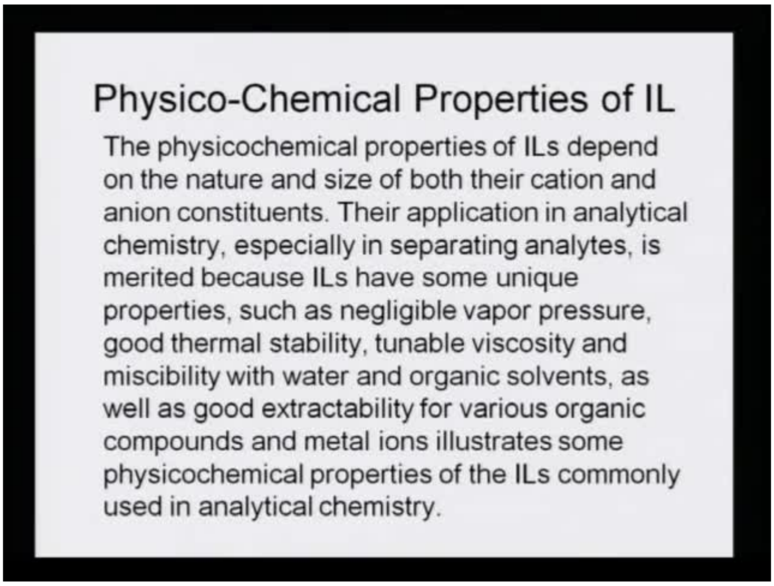

Physico-Chemical Properties of IL

The physicochemical properties of ILs depend on the nature and size of both their cation and anion constituents. Their application in analytical chemistry, especially in separating analytes, is merited because ILs have some unique properties, such as negligible vapor pressure, good thermal stability, tunable viscosity and miscibility with water and organic solvents, as well as good extractability for various organic compounds and metal ions illustrates some physicochemical properties of the ILs commonly used in analytical chemistry.

Physicochemical properties of ionic liquids - because the entire functionality would depend on the physicochemical properties of the ionic liquids and this depends on the nature and size of both their cation and anion constituent. Obviously, whatever is the cation and whatever is the anion which is making a combination to make the ionic liquid will generate its own physicochemical properties. Their application in analytical chemistry, especially in separating analytes is merited because the ionic liquids have some very unique properties such as negligible vapour pressure, good thermal stability, tunable viscosity and miscibility with water and organic solvents as well as good extractability for various organic compounds and ion metal ions illustrates some of the physicochemical properties of the ionic liquids commonly used in the analytical chemistry.

Now, why the choice of specifically using the this particular cation 1-alkyl-3-methylimidazolium or N-alkylpyridinium is because there it must have a property which will enhance the miscibility or the extractability of the analyte; otherwise, why should one use liquid ionic liquids at all in analytical chemistry? So, the fact that these liquids, ionic liquids came into use or were introduced into analytical chemistry itself is a significance that it must have an added advantage and when such a cation and a chosen anion is taken, it is to see what kind of compound has to be extracted. If it is an organic compound, then water miscibility is not desirable.

(Refer Slide Time: 20:03) So, such a combination of cation and anion will be taken up as shown in this previous slide, where I had shown that wherever the water miscibility has to be enhanced the borate has to be taken - tetrafluoroborate. If the organic compound has to be extracted, then it is the hexaphosphate, fluorophosphate that needs to be taken into account. So, therefore, these properties, these physico properties are already like well-designed. One can make a tailor made ionic liquid for a specific extraction and that is the beauty of its use in analytical chemistry.

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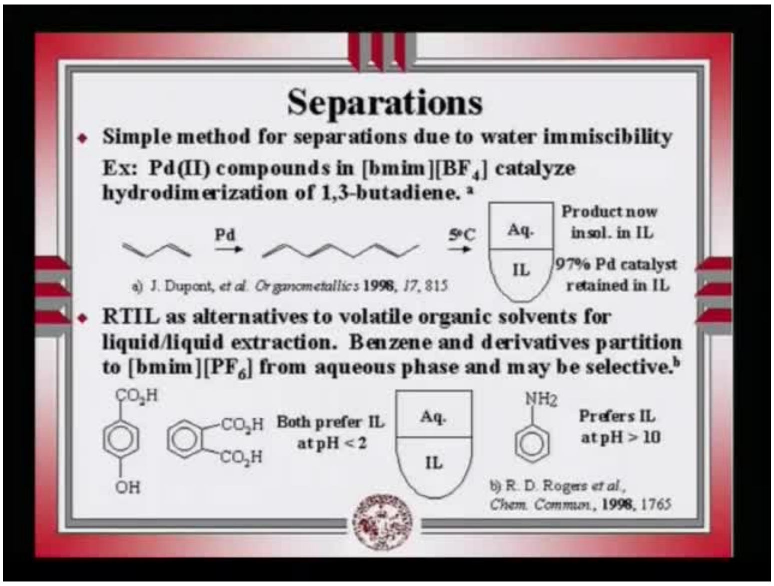

Separations

- **Simple method for separations due to water immiscibility**
  Ex: Pd(II) compounds in [bmim][BF_4] catalyze hydrodimerization of 1,3-butadiene. [a]

a) J. Dupont, *et al.* *Organometallics* 1998, *17*, 815

- **RTIL as alternatives to volatile organic solvents for liquid/liquid extraction. Benzene and derivatives partition to [bmim][PF_6] from aqueous phase and may be selective.** [b]

b) R. D. Rogers *et al.*, *Chem. Commun.*, 1998, 1765

Now, how does the separation process actually take place? Let us try to look and understand. Simple method for separation due to water immiscibility - for example, palladium 2 compound in bmim borate, tetrafluoroborate catalyze the hydrodimerization of 1, 3-butadiene. Now, this reaction has been conducted and at 5 degree centigrade in the aqueous and in presence of ionic liquid, product now is insoluble in ionic liquid and 97 percent of the palladium catalyst is retained in the ionic liquid.

So, what happens, that the catalyst remains 97 percent in the ionic liquid, whereas the product goes into the aqueous. So, that is how they are separated. While the reaction is taking place because of water immiscibility of the new compound or of the catalyst, the product goes into the aqueous layer, whereas the catalyst remains with the ionic liquid.

Room temperature ionic liquid as alternative to volatile organic solvents for liquid/liquid extraction - one example of that has been taken. Benzene and derivatives partition to this bmim PF6 from aqueous phase and may be selective. So, if such a situation is taken where hydroxybenzoic acid and dibenzoic acid, both prefer to be in ionic liquids at pH below 2 and therefore, the ammonium compound that will be present or will if that is present and that has to be separated, the ammonium or the aniline prefers to be in the ionic liquid at pH, which is above 10. Therefore, by preference we can see where the acids will come, what should be the pH of the aqua solution so that they can be separated? If the acids have to be separated, aromatic acids and similarly, the amino compounds or the anilines can be separated by simply monitoring the pH.

Use of ionic liquid in extraction - we just try to understand and look how they are once they can be separated, you understood that the choice of ionic liquid or the pH of the ionic liquid can be a good measure or parameter to control the type of compound that has to be separated.

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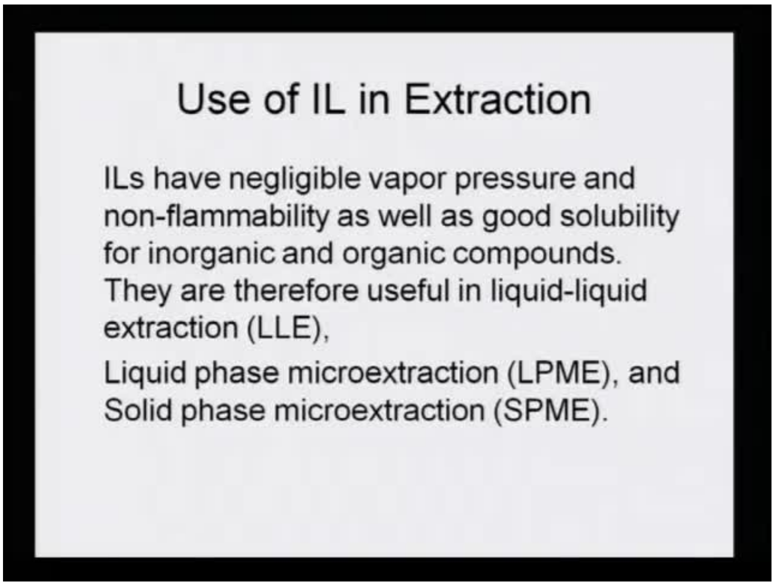

Use of IL in Extraction

ILs have negligible vapor pressure and non-flammability as well as good solubility for inorganic and organic compounds. They are therefore useful in liquid-liquid extraction (LLE),

Liquid phase microextraction (LPME), and Solid phase microextraction (SPME).

Similarly, the ionic liquids also have a role to play in extraction. Ionic liquids have negligible vapour pressure and non-inflammability as well as good solubility for inorganic and organic compounds.

They are therefore useful in liquid-liquid extraction, liquid phase micro extraction and liquid phase and solid phase micro extraction, that is, SPME. So, you will see that what we had learnt in the previous extraction lecture is still applicable for ionic liquids and for if the such ionic liquid separation processes can be applied to liquid/liquid extraction, they can be also applied in micro extraction, where liquid phase micro extraction can be utilized or they can be even used in the examples of solid phase micro extraction.

So, they have great versatility, whether it is a simple, you know aqueous and ionic liquid or organic solvent and ionic liquid, that liquid-liquid extraction also can take place in the case of liquid phase micro extraction, that is, LPME, it is applicable and so, it is applicable for solid phase micro extraction or SPME.

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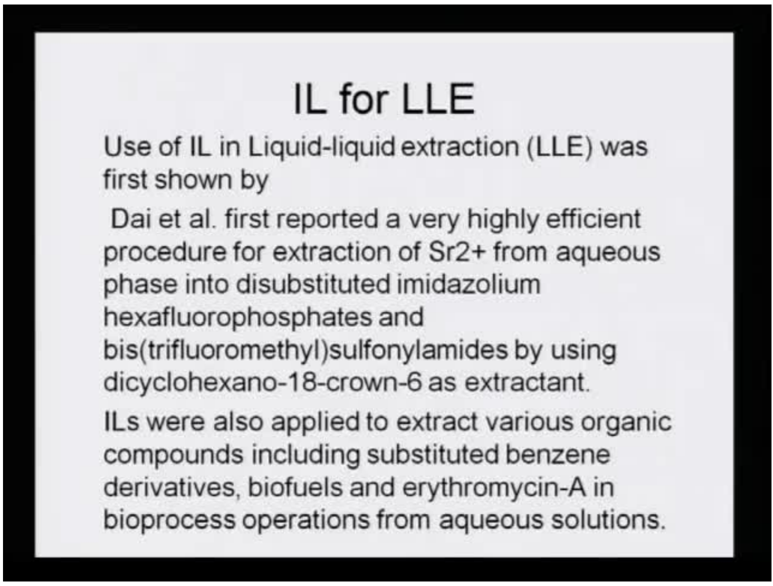

IL for LLE

Use of IL in Liquid-liquid extraction (LLE) was first shown by

Dai et al. first reported a very highly efficient procedure for extraction of Sr2+ from aqueous phase into disubstituted imidazolium hexafluorophosphates and bis(trifluoromethyl)sulfonylamides by using dicyclohexano-18-crown-6 as extractant.

ILs were also applied to extract various organic compounds including substituted benzene derivatives, biofuels and erythromycin-A in bioprocess operations from aqueous solutions.

When we try to see more in detail as to how this ionic liquid actually works in liquid-liquid extraction, use of ionic liquid in liquid-liquid extraction that is LLE was first shown by Dai et al., who first reported a very highly efficient process, a procedure for extraction of strontium from aqueous phase into disubstituted imidazolium hexafluorophosphates and bistrifluoromethylsulfonylamides by using dicyclohexanol-18-crown-6 as extractant. So, you see crown ether was used as an extractant and 2 different types of cations, that is, imidazolium, disubstituted imidazolium hexafluorophosphate or bistrifluoromethylsulfonylamide was used along with the crown ether, dicyclohexanol-18-crown-6.

Ionic liquids were also applied to extract various organic compounds including substituted benzene derivatives, bio-fuels, erythromycin-A in bioprocesses, process operation from aqueous solution. So, it is not that ionic liquids are only meant for inorganic compounds like the strontium example that we discussed, they are also very good and applicable for the extraction of various aromatic compounds, that is, benzene derivatives which are substituted, they can be extracted with the help of ionic liquids, bio-fuels can be extracted, erythromycin-A can also be extracted from the bioprocesses and therefore, it is more versatile. It is not just specific to organic compounds or inorganic compounds, but it also can be applied to the biological system for extraction of very specific compounds.

How is ionic liquid, then applied in liquid phase micro extraction? Liquid phase micro extraction, we have learnt quite in detail about this extraction process because it is it has an edge over liquid-liquid extraction and it is like miniaturization, where very small quantities have to be extracted.

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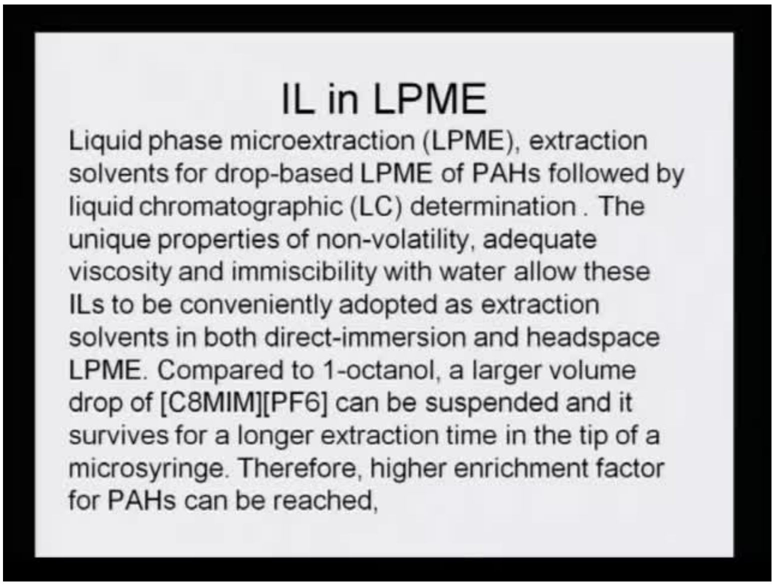

IL in LPME

Liquid phase microextraction (LPME), extraction solvents for drop-based LPME of PAHs followed by liquid chromatographic (LC) determination . The unique properties of non-volatility, adequate viscosity and immiscibility with water allow these ILs to be conveniently adopted as extraction solvents in both direct-immersion and headspace LPME. Compared to 1-octanol, a larger volume drop of [C8MIM][PF6] can be suspended and it survives for a longer extraction time in the tip of a microsyringe. Therefore, higher enrichment factor for PAHs can be reached,

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Extraction solvents for drop-based liquid phase micro extraction of poly aromatic hydro carbons, that is, PAH followed by liquid chromatography, that is, LC determination can be brought about with the help of ionic liquids. The unique properties of non-volatility, adequate viscosity and immiscibility with water allow these ionic liquids to be conveniently brought as extraction solvents in both direct immersion and headspace LPME.

So, you see that the advantage of using ionic liquids in the LPME extraction, liquid phase micro extraction is for compounds like PAH, which are in micro quantities or trace quantities; so, very small quantities are required and it is because the ionic liquids have very unique properties, they are non-volatile and have adequate viscosity and they can be they are immiscible to water, and therefore, they just adapt, according to the process required; it can both be direct immersion or with the head headspace attachment of the headspace.

So, the adaptability with ionic liquids is that it can be used in many ways and as per the requirement of the analyte, it can be adapted. Compared to 1-octanol, a larger volume drop of C8MIM PF6 can be suspended and it survives for a longer extraction time in the tip of a microsyringe. Therefore, higher enrichment factor for poly aromatic hydro carbons can be reached.

So what it is done, it is like a probe and the probe has at the end, large volume drop of this particular ionic liquid, which is hexafluorophosphate and because of that ionic liquid's presence, the higher and higher amount of PAH goes and attaches there. So, it is separated and it is just hold held at the tip of the microsyringe. So even the, you know adaptability on the liquid phase micro extraction is very fissile, when ionic liquids are used.

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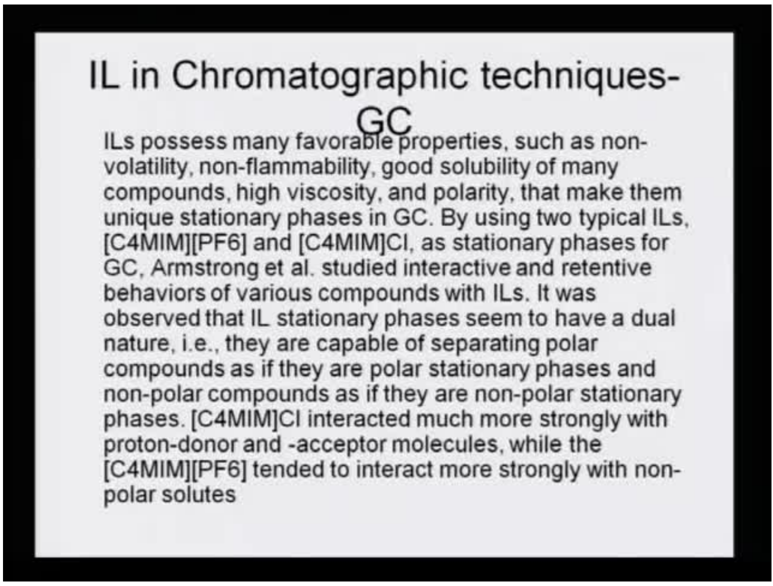

IL in Chromatographic techniques-GC

ILs possess many favorable properties, such as non-volatility, non-flammability, good solubility of many compounds, high viscosity, and polarity, that make them unique stationary phases in GC. By using two typical ILs, [C4MIM][PF6] and [C4MIM]Cl, as stationary phases for GC, Armstrong et al. studied interactive and retentive behaviors of various compounds with ILs. It was observed that IL stationary phases seem to have a dual nature, i.e., they are capable of separating polar compounds as if they are polar stationary phases and non-polar compounds as if they are non-polar stationary phases. [C4MIM]Cl interacted much more strongly with proton-donor and -acceptor molecules, while the [C4MIM][PF6] tended to interact more strongly with non-polar solutes

How are now ionic liquids also applicable in chromatographic techniques such as GC? Ionic liquids possess many favourable properties such as non-volatility, non-flammability, good solubility of many compounds high viscosity and polarity; that makes them unique stationary phase in GC.

By using two typical ionic liquids such as the C4MIM PF6 and C4MIM chloride as stationary phases for GC, Armstrong et al. studied interactive and retentive behaviour of various compounds with ionic liquids. It was observed that ionic liquids stationary phases seem to have a dual nature; they are capable of separating polar compounds, as if they are polar stationary phases and non-polar compounds, as if they are non-polar stationary phases. So, C4MIM chloride interacted much more strongly with the proton donor and acceptor molecules, while the C4MIM PF6 tended to interact more strongly with the non-polar solutes.

So, you see that even in GC and in the chromatographic separation techniques, the ionic liquid as stationary phase can act beautifully in the separation process. Why, because they have this unique property that they are non-volatile, non-flammable, they have good solubility, very high viscosity and they have a certain polarity, which matches the polarity with the analyte.

So, if the stationary phase or the column is filled with such ionic liquids such as C4MIM chloride and C4MIM hexafluorophosphate, they have the tendency for choosing the most polar and the most non-polar analyte and therefore, they are most ideally suited for separation of both the types of compounds on the same GC.

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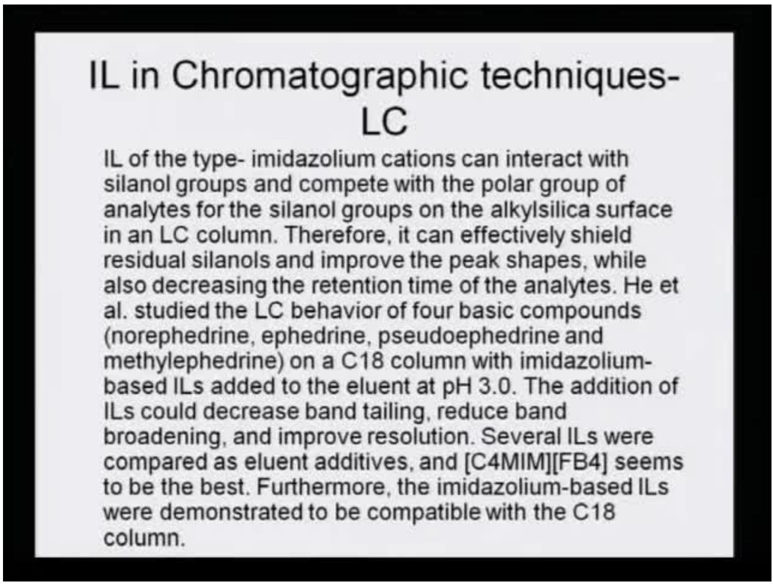

IL in Chromatographic techniques- LC

IL of the type- imidazolium cations can interact with silanol groups and compete with the polar group of analytes for the silanol groups on the alkylsilica surface in an LC column. Therefore, it can effectively shield residual silanols and improve the peak shapes, while also decreasing the retention time of the analytes. He et al. studied the LC behavior of four basic compounds (norephedrine, ephedrine, pseudoephedrine and methylephedrine) on a C18 column with imidazolium-based ILs added to the eluent at pH 3.0. The addition of ILs could decrease band tailing, reduce band broadening, and improve resolution. Several ILs were compared as eluent additives, and [C4MIM][FB4] seems to be the best. Furthermore, the imidazolium-based ILs were demonstrated to be compatible with the C18 column.

How is ionic liquid then again useful in liquid chromatography? We saw that it is useful in gas chromatography. The ionic liquids of the type imidazolium cations can interact with the silanol group and compete with the polar group of the analytes for the silanol group on the alkylsilica surface in an LC, liquid chromatographic column.

Therefore, it can effectively shield residual silanols and improve the peak shape, while also decreasing the retention time of the analyte. He et al. studied the liquid chromatographic behaviour of 4 basic compounds norrephedrine, ephedrine, pseudoephedrine and methylephedrine on C 18 column with imidazolium based liquid ionic liquids added to the eluent at pH 3. The addition of the ionic liquids could decrease band tailing, reduce band broadening and improve resolution.

Several ionic liquids were compared as eluent additives such as C4MIM BF4 seems to be the best. Furthermore, the imidazolium based ionic liquids were demonstrated to be compatible with C 18 column. So, what was done, the column was C 18, but the eluent had the ionic liquids; so, that had the property to separate the norephedrine, ephedrine, pseudoephedrine and methylephedrine very effectively because they all differ in their polarities and it was possible to separate all of them with the help of these ionic liquids and ionic liquids chosen from the four, five categories that I had mentioned were found to be quite good in making these separations very effective and the pH also was maintained very well at 3 pH so that the addition of ionic liquid added one more advantage.

The peaks became narrower because the separation was very effective, there was no band tailing and there was no band residue, band broadening, which are usually the problem, when such interrelated or very similar structured compounds are separated. They tend to come together, but by the addition of these ionic liquids, the resolution improved and the separation also improved and that was because these ionic liquids have a tendency to participate in the, you know separation process and that participation was possible because the polar group of the analyte, you know competes with the imidazolium cation versus silanol group of the C 18 column. Therefore, this competition, the imidazolium picks up the compound more effectively than the silanol of the C 18 silanol group of the C 18 column and that is why the preferential separation takes makes it more effective and more appropriate.

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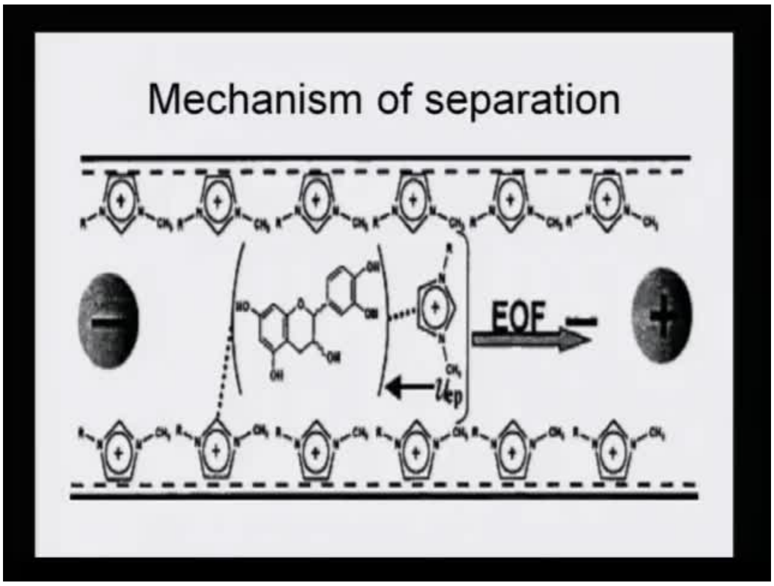
Mechanism of separation

So, this is the kind of mechanism of separation that actually takes place. The role of the immidazole, how it, you know effectively pulls out the compound.

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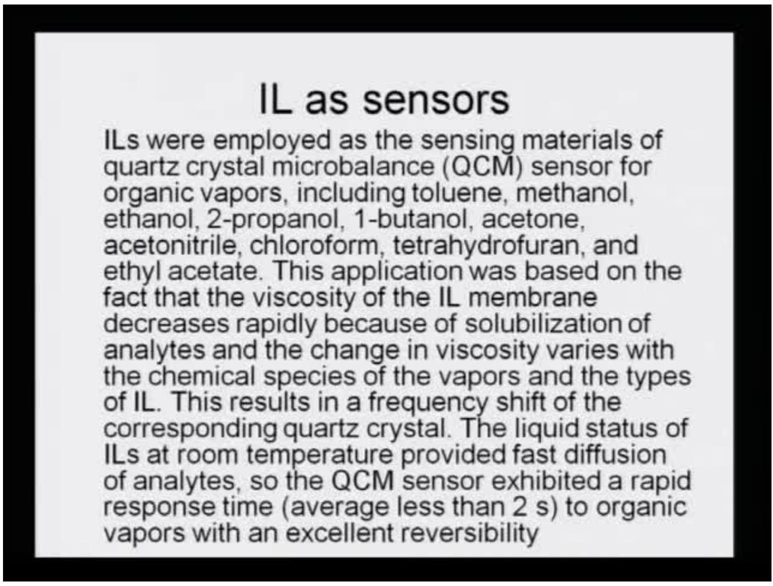
IL as sensors

ILs were employed as the sensing materials of quartz crystal microbalance (QCM) sensor for organic vapors, including toluene, methanol, ethanol, 2-propanol, 1-butanol, acetone, acetonitrile, chloroform, tetrahydrofuran, and ethyl acetate. This application was based on the fact that the viscosity of the IL membrane decreases rapidly because of solubilization of analytes and the change in viscosity varies with the chemical species of the vapors and the types of IL. This results in a frequency shift of the corresponding quartz crystal. The liquid status of ILs at room temperature provided fast diffusion of analytes, so the QCM sensor exhibited a rapid response time (average less than 2 s) to organic vapors with an excellent reversibility

Then ionic liquids are also used as sensors, but we will not go into too much of detailing of the sensor. It is just for your information that ionic liquids were employed as sensing material of quartz crystal micro balance sensor for organic vapours including toluene, methanol, ethanol, 2-propanol, 1-butanol, acetone, acetonitrile, chloroform, tetrahydrofuran and ethyl acetate. This application was based on the fact that the viscosity of the ionic liquid membrane decreases rapidly because of the solubilization of the analyte and the change in viscosity varies and therefore, it is analyzed by the quartz crystal.

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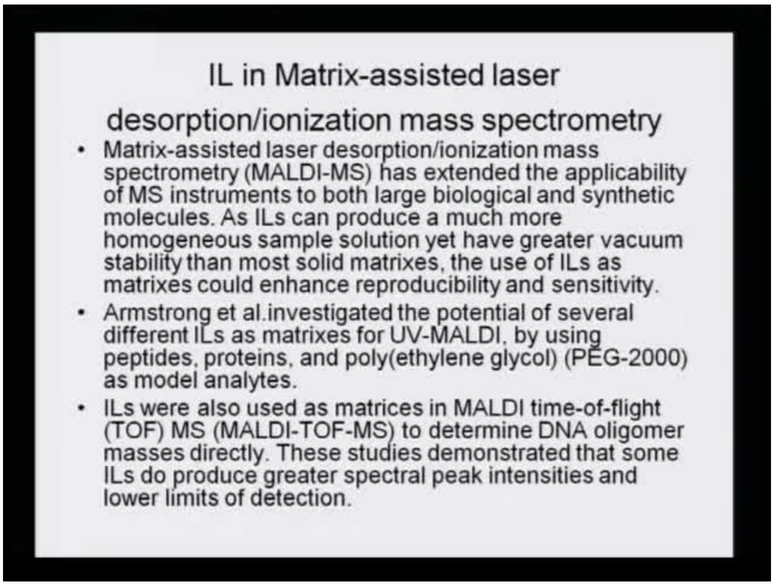

IL in Matrix-assisted laser desorption/ionization mass spectrometry

- Matrix-assisted laser desorption/ionization mass spectrometry (MALDI-MS) has extended the applicability of MS instruments to both large biological and synthetic molecules. As ILs can produce a much more homogeneous sample solution yet have greater vacuum stability than most solid matrixes, the use of ILs as matrixes could enhance reproducibility and sensitivity.
- Armstrong et al.investigated the potential of several different ILs as matrixes for UV-MALDI, by using peptides, proteins, and poly(ethylene glycol) (PEG-2000) as model analytes.
- ILs were also used as matrices in MALDI time-of-flight (TOF) MS (MALDI-TOF-MS) to determine DNA oligomer masses directly. These studies demonstrated that some ILs do produce greater spectral peak intensities and lower limits of detection.

It is also used in Ionic liquids are used in MALDI. We just discussed MALDI yesterday. I will not go into the details of that; it is just for your information that ionic liquids have great opportunities and great usability, whether it is, you know separating compounds or it is doing chromatographic separation or doing extraction; in various fields, it can be utilized most effectively.