Possibilities and Limitations of Ionic Liquids in Electrochemical and Electroanalytical Measurements (A Review)

Tomáš Weidlich [1*], Matěj Stočes [2], and Ivan Švancara [2]

[1] Institute of Environmental Protection, Faculty of Chemical Technology, University of Pardubice, Doubravice, CZ-532 10 Pardubice, Czech Republic;

[2] Department of Analytical Chemistry, Faculty of Chemical Technology, University of Pardubice, Studentská 573, HB/C, CZ-532 10 Pardubice, Czech Republic.

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Abstract: A review (with 155 refs.) concerning the current achievements and typical trends in the chemistry of (room temperature) ionic liquids, (RT)ILs, with particular emphasis on their applicability in electrochemical and electroanalytical measurements. The latter is documented on a rapid progress of ionic liquid-modified carbon paste electrodes (IL-CPEs), the so-called carbon ionic liquid electrodes (CILEs), and related configurations in the last half-decade, within the period of 2005-2010.

Keywords: (Room temperature) ionic liquids; Basic physicochemical properties; Electrochemical characterisation; Ionic liquid-modified carbon paste electrodes (IL-CPEs); Carbon ionic-liquid electrodes (CILEs); Review.

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* Author to whom correspondence should be addressed. E-mail: tomas.waidlich@upce.cz

Introduction

The terms of room-temperature ionic liquid, RTIL, non-aqueous ionic liquid, NIL, molten salt, liquid organic salt, and fused salt came on the verge of two millennia; all variants having been described as the specific system, representing the **salt in the liquid state** [**1**].

As known, conventional molten salts exhibit a high melting point (e.g., 801 ^{o}C for NaCl and 614 ^{o}C for LiBr), which greatly limits their use as solvents in most applications [2]. In contrast to high temperature melts that are commonly referred to as molten salts, ionic liquids are — as their name implies — salts being liquid at low temperatures; many of them at a room temperature or even below, when the molten form is to be composed wholly of the respective ions [3]. Generally adopted upper temperature limit for the classification of an "ionic liquid" is 100 °C (though some solidify to glasses after cooling) and higher melting-point ionic systems are typically referred to as molten salts [4].

In some cases, the ionic liquids are free-flowing liquids at room temperatures and, in this case, they can be called the room temperature ionic liquids, RTILs, or — more often — (**room-temperature**) **ionic liquids**, (**RT**)**ILs**, with a formal nuance in denotation and the abbreviation used. There is no reliable way to predict the precise melting point of organic salts and the identification of new room-temperature ionic liquids is quite a hit and miss affair. (By paraphrasing the formulation from one of the first review reports on (RT)ILs [1]: "... *There is no exact specification on what is the room temperature, it just happens to be a temperature at which rooms are being kept or eventually conditioned, and the salts with melting points in an interval of 20°-30°C are unlikely to have great differences in their structures and interionic interactions*"). The low melting points are a result of the chemical composition of (RT)ILs, which contain larger asymmetric organic cations compared to their counterparts of molten salts: the asymmetry lowers the lattice energy, and hence the melting point, of the resulting ionic medium. In some cases, even the anions are relatively large and may contribute to a lowering of the melting point [2]. Of course, these latter liquids have real advantages over higher melting salts in terms of practical handling.

Typical Properties and Applicability of Ionic Liquids

Basic Physicochemical Characterisation. Typical properties of ionic liquids, including their melting points, are dependent on both the nature of the cation and the anion [4-6]. Regarding the chemical structure, typical cations of ionic liquids are generally bulky, asymmetric

ammonium or phosphonium salts, or heteroaromatics, with low symmetry, weak inter-molecular interactions, and of low-charge densities. The choice of cation has a strong impact on the properties of a liquid. An unsymmetrical 1,3-dialkyl-imidazolium cation still appears to be the best candidate to start the preparation of a low-melting salt of any anion chosen.

Typically, the anions are inorganic in nature, being represented by Br^-, Cl^-, PF_6^-, BF_4^-, NO_3^-, SO_4^{2-}, $R\text{-}O\text{-}SO_2^-$, $CF_3SO_3^-$, and $[(CF_3SO_2)_2N]^-$ although, more recently, some typically organic anions (e.g., $R\text{-}CO_2^-$) have also been proposed. A more representative survey of the cations and the anions forming a majority of so-far reported (RT)ILs is shown in Fig. 1.
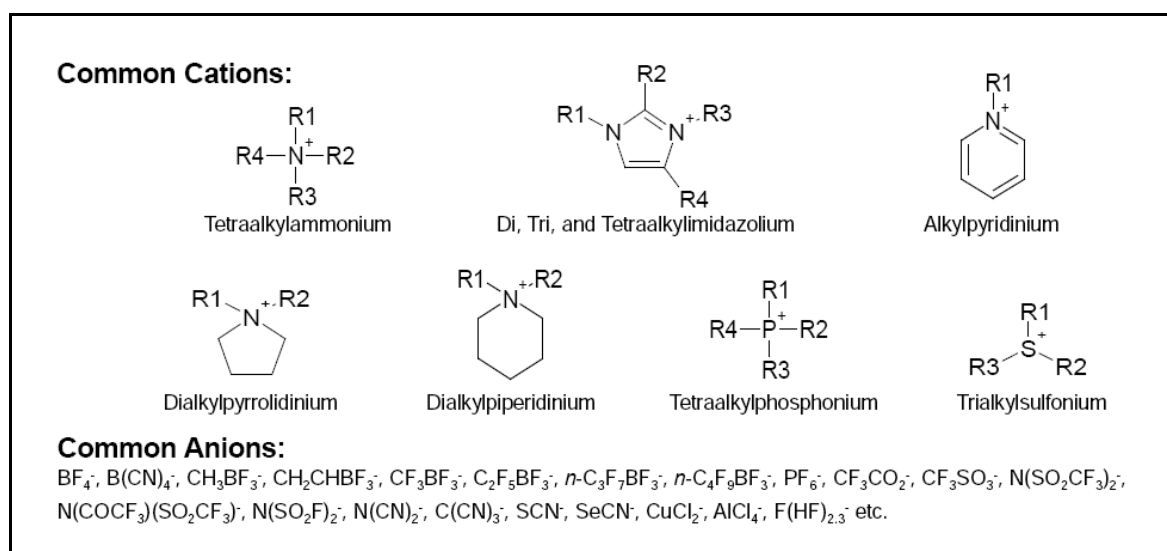

Common Cations:

Tetraalkylammonium

Di, Tri, and Tetraalkylimidazolium

Alkylpyridinium

Dialkylpyrrolidinium

Dialkylpiperidinium

Tetraalkylphosphonium

Trialkylsulfonium

Common Anions:
BF_4^-, $B(CN)_4^-$, $CH_3BF_3^-$, $CH_2CHBF_3^-$, $CF_3BF_3^-$, $C_2F_5BF_3^-$, $n\text{-}C_3F_7BF_3^-$, $n\text{-}C_4F_9BF_3^-$, PF_6^-, $CF_3CO_2^-$, $CF_3SO_3^-$, $N(SO_2CF_3)_2^-$, $N(COCF_3)(SO_2CF_3)^-$, $N(SO_2F)_2^-$, $N(CN)_2^-$, $C(CN)_3^-$, SCN^-, $SeCN^-$, $CuCl_2^-$, $AlCl_4^-$, $F(HF)_{2.3}^-$ etc.

Figure 1. *Cations and anions used for the preparation of ionic liquids* (reproduced from [4])

The individual ionic liquids fall into the two main groups, (i) protic and (ii) aprotic (RT)ILs. The **protic ionic liquids** (**PILs**) are a subclass of ILs, which are easily produced through the combination of a Brønsted acid and a Brønsted base. The key properties that distinguish PILs from the **aprotic ionic liquids** (**AILs**) is the proton transfer from the acid to the base, leading to the presence of proton-donor and proton-acceptor sites, which can be utilised to build up a hydrogen-bonded network. Both PILs and AILs have a number of unique properties, with the exception of some Brønsted acidic ILs [7]. On the other hand, a very beneficial property of many PILs is their easy-to-perform distillation, as long as they do not undergo decomposition before boiling [7].

Two Principal Employments of (RT)ILs. Ionic liquids are attractive substances due to the two main reasons as (i) potential solvents and/or (ii) effective catalysts for a number of reasons. Regarding the role of a **solvent**, one can specify a quintet of characteristic features:

(i-a) Ionic liquids can be found that are good solvents for a broad spectrum of inorganic, organic and polymeric materials and are immiscible with numerous organic solvents.

(i-b) AILs exhibit very low vapor pressures under ambient conditions and thus are effectively non-volatile [8]; hence, there are possible applications in the process intensification and as non-aqueous polar alternatives in biphasic systems;

(i-c) Being composed of two parts, there is a synthetic flexibility that is not available for the single component molecular solvents;

(i-d) Non-flammability [8];

(i-e) High thermal stability [9].

When considering the ILs as **catalyst**(**s**), one should emphasise three typical aspects:

(ii-1) (RT)ILs form ideal "immobilization" media for polar and charged reagents, including catalysts, thus offering the advantage of easy product separation [10];

(ii-2) (RT)ILs are also emerging as competent solvents for oxidation reactions;

(ii-3) In fact, ionic liquids have a rate acceleration effect on some catalytic reactions, and they are often considered as green alternatives to volatile organic solvents although their toxicity and biodegradability are yet to be fully determined [11-14].

Note: With respect to the principal importance of catalysis-assisted effects attainable with various (RT)ILs, these phenomena are discussed again in a separate section (see below).

Availability of (RT)ILs and a Survey of the Most Typical Applications. At present, most of ionic liquids are the commonly marketed stuff and can be purchased as the fine chemicals from special manufacturers or, more frequently, from renowned dealers / suppliers in a range of rather diverse quality. (Recently, the syntheses of the so-called "task-specific" ionic liquids with special or even unique use — according to client's requirement — have become quite an attractive business.) Numerous (RT)ILs are also being obtainable in ordinary laboratories; often, on one's own, when using commercially available reagents.

Based on renowned review articles or further significant reports from the field [1-16], the summarisation of typical applications can be made in a very brief way:

• Polymerization reactions; • Diels-Alder cyclo-addition reactions; • Friedel-Crafts alkylation and acylation reactions • Regio-selective alkylation reactions • Arene exchange reactions on ferrocene • Transition-metal catalyzed hydrogenation of the olefins • Heck's coupling reaction • Wittig's reaction • Electrophilic nitration of aromatic compounds • Organoboron-mediated reduction of the aldehydes • Separations and membrane technologies • Electrochemistry and electroanalytical measurements.

Catalytic Phenomena at (RT)ILs

In catalytic processes and not only with (RT)ILs, two factors are of particular importance [6]: (i) the **solubility of the reaction components** (starting materials, products, catalyst, co-solvents) and the **specific interactions** that may take place between the solvent and the solute(s) to enhance or reduce the reactivity of any of the solute species. Certainly, the **miscibility** of any given substance **with ionic liquids** is dependent on the particular ions of which the (RT)IL of interest is composed, as well as upon the properties of the solute.

This idea of the need for the solvent and solute to have complimentary properties for mixing, forms the basis of the so-called Abraham solvation model [17], which has been used by Anderson et al. [18] to measure the solvent properties of ionic liquids. Had they used the gas chromatography (GC) and the respective retention times of a range of probe solutes upon a variety of columns with ionic liquids immobilised as the stationary phases, they were able to make some general statements as to how the ionic liquids were behaving. The ionic liquids were interacting with solute via high dipolar and dispersion forces and also acting as strong hydrogen bond bases. The dipolar forces and hydrogen bond basicity varied with the different ionic liquids, whereas the dispersion forces were nearly constant for all of the ionic liquids studied. The hydrogen bond basicity was dominated by the choice of anion. When hydrogen bond acidity was observed it arose from the cation of the ionic liquid, although the anion also greatly influenced this property. Not surprisingly that the ionic liquids with aromatic ions were more capable of π–π and n–π type interactions with solutes [18].

A number of more specific studies of miscibilities has also been reported, such as those of various gases in $[C_4C_1im][PF6]$ [19], of a variety of $[C_nC_1im][PF6]$ (n = 4–8) ionic liquids in butanol [20], or $[C_nC_1im][PF6]$ (n = 2 or 4) in both aromatic and cyclo-aliphatic hydrocarbons have also been conducted [21].

In general, ionic liquids form biphasic mixtures with supercritical carbon dioxide (scCO$_2$), with the ionic liquid showing very low solubility in the CO_2 layer, but the carbon dioxide having significant solubility in the ionic liquid [22-23]. This has excited a great deal of attention as a way of producing a 'green' biphasic reaction system, in which the catalyst is trapped in the ionic liquid layer and the reagent and products can be added and removed in the CO_2 layer [24-28].

The **miscibility of (RT)ILs with water** is particularly interesting. All ionic liquids described to date are hygroscopic. Some will mix with water in all compositions, whereas the others eventually saturate and then form two separated layers [29].

This behaviour is principally controlled by the anion of the ionic liquid, with the cation having a secondary effect. The reason for this is that strong hydrogen bonds can form between the water and the anion of the ionic liquid [30]. The solubility of water in ionic liquids can be manipulated by adding short chain alcohols to biphasic systems to increase mixing [31-32], or adding salts to separate otherwise water miscible ionic liquids [33]. For instance, the [CnC1im][BF$_4$] ionic liquids provide borderline cases in the way that their miscibility with water can be controlled thermally [34]. Such behaviour has been used to generate a thermally controlled reaction system, where the reaction mixture is monophasic at the temperature of reaction, allowing maximum mixing of the starting materials, but biphasic at room temperature, allowing facile separation of the products and catalyst [35].

The ways in which solvent(s) may interact with solutes can also be studied by analyzing the effect of changing the solvent on the spectra of probe dyes. This forms the basis of the Kamlet-Taft system [36-40], which is seen as a measure of interactions between solute species and their immediate solvent environment. It gives complimentary scales of hydrogen bond acidity (α), hydrogen bond basicity (β) and dipolarity / polarizability effects (π*) and has been used recently to describe a variety of ionic liquids [41], where "π*" is the value that most resembles our qualitative notions of "polarity" in the absence of hydrogen bonding effects. All of the π* values for the ionic liquids are high in comparison with most non-aqueous molecular solvents. However, there is no way in which the ionic liquids could be thought of as "super polar". The α-values are largely determined by the nature of the cation, with a smaller anion effect. It is worthy of noting that some of ionic liquids that showed moderately high values here, showed no hydrogen bond donor characteristics in the GC experiment [18] described above. As the conjugate bases of strong acids, the anions of the ionic liquids might be expected to have low β-values in comparison to other solvents. However, although those found in this study are not as high as for acetone, they are comparable to acetonitrile, which is thought of as an electron pair donor solvent.

The strong interest in ILs for catalyzed reactions is due to the expected immobilization of the catalyst in the IL that would allow the recycling of the tandem catalyst / solvent. In catalysis, there is the particular concern of how the solvent can interact with the metal centre itself and interfere with the reactivity of the active site. The value of λ_{max} for the d→d band of an exemplary square-planar cation of [Cu(acac)(tmen)][BPh$_4$] (see also Fig. 2 overleaf), which correlates well with the solvent donor numbers [42], could then be used to measure this parameter for ionic liquids [41,43].
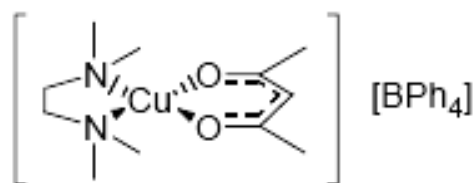
Figure 2. *The structure of an ionic liquid with the square-planar cation* (taken from [42])

This value is dominated by the nature of the anion of the ionic liquid and correlates well with the β-values described above. It might seem surprising, since the anions that are used to make ionic liquids are usually described as non-coordinating, that any great difference between the ionic liquids is seen. The fact that these so-called non-coordinating ions very clearly do coordinate into the metal centre may reveal something about the nature of coordination as such – in contrast to a molecular solvent, this feature in an ionic liquid can then have a very profound effect in the catalytic processes.

If one considers a cationic metal centre that is coordinatively unsaturated with vacant orbitals dissolved in a molecular solvent; the individual possibilities are:

 (i) an anion can directly coordinate to the metal centre;
 (ii) the anion and the cation may be well separated in the solvent, with the cation coordinated to molecules of the solvent, or the cation and anion can exist as either;
 (iii) an intimate; or
 (iv) a solvent separated ion-pair.

In a pure ionic liquid there are no molecules available to separate the ions and the cations of the ionic liquid will be repelled by the charge on the metal complex. Hence, in an ionic liquid, the above-listed options (i) and (iii) are the only ones available. The cationic centre will always be closely associated with the anions. Since the anions are in the neighbourhood and there is no other source of potential electron pairs (until deliberately added as a reagent) and being the solvent and therefore in vast excess, they will interact with the metal centre to some extent.

Therefore, it can be concluded herein that the anions of ionic liquids are more likely to coordinate to a transition metal centre than the same anions in a molecular solvent. Among others, it has a direct reflection in the electrochemistry with (RT)ILs as documented in the following sections.

Electrochemistry and Electroanalysis with (RT)ILs

Over the past decade, (RT)ILs have also attracted considerable interest of numerous electro-chemists and electroanalysts for their use as non-aqueous electrolytes or modifying agents in special electrode configurations. All the fundamental aspects on the use of (RT)ILs, their physicochemical and electrochemical properties have been surveyed already in the first pioneering papers or review articles [44-47], emphasising that the conductivity and electrochemical stability are the most important features. Together with other specific properties, such as the negligible vapour pressure and non-flammability, (RT)ILs appear to be almost ideal electrolytes for many interesting applications as documented in still-growing number of publications [48-50].

Principal Physicochemical Properties of (RT)ILs with Respect to Their Use in Electro-chemical and Electroanalytical Measurements

Conductivity. A mentioned above, basic properties of (RT)ILs principally rely on their conductivity. Typical values are in the range of 1.0-10.0 mS·cm^{-1}. Recently, interesting materials with conductivities above 20 mS·cm^{-1} based on the imidazolium cation were described: 1-Et-3-MIM thiocyanate and 1-Et-3-MIM dicyanamide [51]. Of course, an aqueous solution of a typical inorganic salt (e.g. NaCl) shows a higher conductivity. But if one compares other properties of this solution with an (RT)IL, two significant disadvantages become obvious – (i) aqueous electrolytes are liquid over a more narrow temperature range and a limitation due to the fact that (ii) water is volatile.

Electrochemical Stability (Inertness). Another important property of (RT)ILs is their wide potential range (the so-called "electrochemical window"), which is a measure for their electrochemical stability against undesirable oxidation and reduction processes:

$$\text{Cation}^+ + e^- \longrightarrow \text{Neutral species} \qquad (1a)$$

$$\text{Anion}^- \longrightarrow \text{Neutral species} + e^- \qquad (1b)$$

Obviously, the electrochemical window is sensitive to impurities: halides are oxidized much easier than molecular anions (e.g., stable fluorine-containing anions such as bis(trifluoro-methylsulfonyl)imide, where the negative charge is delocalized over larger volume.

As a consequence, contamination with halides leads to significantly lower elechochemical stabilities, which can be illustrated by the following relations: **Cation stability** ... R-Py$^+$ < di-R-Imi$^+$ < tri-R-sulfonium+ < tetra-R-ammonium$^+$, and **Anion stability** ... Hal$^-$ < AlCl$_4^-$ < PF$_6^-$ < bis(trifluoromethylsolfonyl)imide.

Viscosity / Density. This characteristic of a capability to flow and of the surface deformability is yet another property to be considered for an ionic liquid; especially, in electrochemistry, where this is probably the main drawback. As known, (RT)ILs are viscous liquids with viscosities of 1-3 orders of magnitude higher than those of conventional solvents, including water or aqueous solutions [52]. In electrochemical studies, this property is important because of exerting a strong effect on the rate of mass transport within solution, as well as upon the conductivity of some salts. For a cation given, the viscosity of (RT)ILs is strongly determined by the nature of the anion [52]. The viscosity is the lowest for ionic liquids containing the large anion and higher for those containing non-planar symmetric anions; see Table I.

Table I: *Specification of viscosity* for selected (RT)ILs* (after [53,54])

RTIL	viscosity (mPa s)^a
[BMIm][PF$_6$]	308
[BMIm][NTf$_2$]	52
[BMIm][OTf]	90
[BMIm][BF$_4$]	154
[EMIm][BF$_4$]	37−66.5
[EMIm][NTf$_2$]	32−34
[HexMIm][PF$_6$]	690
[HexMIm][NTf$_2$]	87
[HexMIm][BF$_4$]	314
[OctMIm][PF$_6$]^b	866−857
[OctMIm][NTf$_2$]^b	119
[OctMIm][BF$_4$]^b	135
[DecMIm][NTf$_2$]^c	152
[Et$_3$Hex][NTf$_2$]	220
[HexP][NTf$_2$]	54
[OctP][NTf$_2$]^b	134
[Pyr$_4$][NTf$_2$]	85
[Pyr$_3$][NTf$_2$]	63
[BMMIm][NTf$_2$]	105^d
[BMMIm][BF$_4$]	269^d

Legend and abbreviations used: *) data for t = 20 ^{o}C; a) taken from [53] and refs. therein, b) variable data, c) unsure value, d) taken from [54]. M ... methyl, E(t) ... ethyl, B ... butyl, Hex ... hexyl, Oct ... octyl,   Dec ... decyl, Im ... imidazolinium, Pyr ... pyridinium; OTf ... trifluoromethanesulfonate, NTf$_2$ ... bis[tri(fluoromethyl)sulphonyl]imide.

The most viscous ionic liquids are then ion-associates with hexafluorophoshate, $[PF_6]^-$. In general, even other fluorinated anions, such as $[BF_4]^-$, $[SbF_6]^-$, $[OTf]^-$, or $[NTf_2]^-$ (see legend in Table 2) form viscous ionic liquids due to the formation of stable hydrogen bonds or thanks to the increased van-der-Waals forces [31,32,34,46,55].

Cations also influence the viscosity of (RT)ILs. In general, for any type of cation, the longer the alkyl substituents, the higher the viscosity because of the increasing van-der- Waals interactions between the voluminous cations [55]. The increase in viscosity for a series of [3-R-1-MIm][NTf2] salts was found to be linear with the increase of the number of $-CH_2$-homologous groups, whereas a more complex behaviour was associated with the corresponding [3-R-1-MIm][PF_6] derivatives [56]. Thus, the correlation of the physico-chemical properties of (RT)ILs with their structures implements a subtle balance between the electrostatic and inductive forces, when the branching of the alkyl chains in [3-R-1-MIm]-based compounds reduces the viscosity [52]. In contrast, the introduction of a methyl group into the 2-position of a cation gives rise to a [1-R-2,3-MMIm] analogue, thus inducing the increase in viscosity (see again Table 2). This result appears counter-intuitive since the additional M-group eliminates the possibility of forming a strong H-bonded interaction between the cation and the anion. From such a H-bond suppression, a weaker cation / anion interaction is expected, resulting in a significant decrease of viscosity. Indeed, calculations performed on "simple" ionic-liquid-like salts of the [BMIm][Cl] and [BMMIm][Cl] type have demonstrated that the strength of the cation / anion interaction became weaker in the [BMMIm][Cl] associate compared to [BMIm][Cl]; however, the [BMMIm][Cl] exhibits a higher viscosity than that measured for [BMIm][Cl] [57].

Two different main factors were demonstrated to contribute to the increase of the overall viscosity. First, a significant decrease of entropy in the methylated salt has been evidenced due to a restricted number of ion-pair conformers that could be formed [57]. Such reduced ion-pair configurational variations have resulted in a better consolidation (the so-called "molecular order") inside the ionic liquid. Secondly, the butyl chain rotation is inhibited because of steric repulsion from the methyl group and this could also be demonstrated in form of a participating in an increase of the molecular arrangement. When the molecular order inside the ionic liquid is high, the viscosity naturally increases [57].

In conclusion, it can be stated that the electrostatic interactions dominate among the characteristic physicochemical properties of (RT)ILs, distinguishing them from common organic solvents. But, when considering the ionic liquids of similar structure, the differences in viscosity are mainly affected by the -H- bonds and van-der-Waals interactions [52,55].

A Few Examples on Electrochemical Applications of (RT)ILs

In brief, a number of applications of (RT)ILs requires their high conductivity. However, some particular ionic liquids fulfilling this criterion and exhibiting extremely high conductivities (e.g., [1-E-3-M-Im][SCN] or [1-E-3-M-Im][N(CN$_2$)]) offer rather poor electrochemical stability. Nevertheless, such materials are still good candidates in applications, where the stability can be improved by means of special procedures and where so enhanced thermal stability can be combined with high conductivity and non-volatility. This is the case of [1-dodecyl-3-methylimidazolium] [iodide] and its functioning in dye-sensitised solar cells [58].

The electrochemically most stable materials with comparable low conductivities, for instance: N-butyl-N-methylpyrrolidinium bis(trifluoromethylsulphonyl)imide (i.e., [BMPyr] [NTf$_2$], triethylsulphonium bis(trifluoromethylsulphonyl)imide (i.e., [Et$_3$SO] [NTf$_2$]), and N-methyl-N-trioctylammonium bis(trifluoromethylsulphonyl)imide (i.e., [MOct$_3$N] [NTf$_2$] are popular electrolytes to be used in the batteries [59] and fuel cells [60], for metallic layer depositions [61,62], or electrochemical synthesis of some nanoparticles [63]. Furthermore, one can also exploit of (RT)ILs in situations, where conductivity and electrochemical stability are needed both together. For example, imidazolium-based (RT)ILs with particularly stable anions, such as tetrafluoroborate, BF_4^-, or trifluoromethanesulphonate, OTf, are the materials of choice for manufacturing electronic components; e.g., super-capacitors [64].

Finally, ionic liquids have occasionally been employed in attractive electrochemical studies; one of which being illustrated in Fig. 3. A very interesting cyclic voltammogram (reproduced from [65]) depicts a consecutive redox transformation of 5×10^{-3} M [(n-C$_4$H$_9$)$_4$N]$_4$[S$_2$W$_{18}$O$_{62}$] in a solution of (room-temperature) ionic liquid of the [Bu$_3$MIm][PF$_6$] type, when using the glassy carbon electrode (GCE) and a sweep rate of 100 mV s^{-1}.

As seen, both oxidation and reduction scans comprise unusual sequences with six well-developed and almost ideally reversible peaks (!)
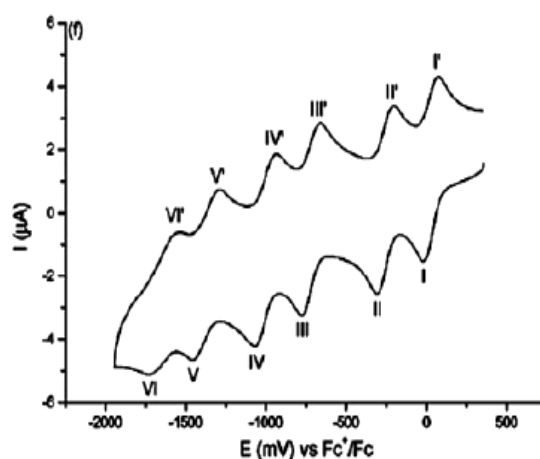

Figure 3. *The overall electrode transformation of the ion-associate of the tetraalkyl ammonium / heteropolyanion type.* (reproduced from [65])

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Carbon Paste Electrodes versus Ionic Liquids

The compositional and functional basis of a **carbon paste electrode** (**CPE**), representing for decades apparently the most popular electrode obtainable on one's own via simple laboratory preparation (see e.g. [66]) is almost ideal platform for using (RT)ILs. In the heterogeneous matrix, CPEs contain a liquid binder as one of the main major constituents; the second being carbon powder. Within this configuration, a (RT)IL can be used as (i) <u>additional component</u> (usually, in the form of a <u>modifier)</u> or (ii) <u>replacement of the original pasting liquid</u>, overtaking its role in all aspects. These unique features of carbon pastes being another evidence of their extraordinary adaptability to modern technologies and materials [66] has also been noticed in some recent reviews devoted to (RT)ILs and their applications in special electrochemical studies [67] or practically oriented electroanalytical measurements [68].

Similarly as with the electrochemistry as such, also electrochemical measurements with CPEs may advantageously utilise a number of specific properties of (RT)ILs; namely, their excellent solvating properties, high conductivity, non-volatility, low toxicity, wide polarisation range, and good electrochemical stability. To date, more or less innovative configurations of various electrodes, (bio)sensors, or detection units for flowing streams have been the subject of interest in approx. 80 reports [71-150], resulting in the establishment of a special sub-area within the electrochemistry and electroanalysis with CPEs.

The first pioneering attempts with ionic liquid based carbon pastes were initiated by Liu et al. [71], followed by Maleki & Safavi with co-workers [72,76,78,80,81], Yan et al. [73], Opallo's [74,75], and Compton's [77] groups, and particularly by several research groups working independently in the vast Chinese region [79,82-91]. All these research activities fall into the mid-2000s; therefore, the rise of these novel carbon paste-based configurations could not be captured in the hitherto most extensive review on CPEs (published within an encyclopedia [66]), whereas the two subsequent articles [69,70] would do so; the latter having surveyed both IL-CPEs and CILEs in a separate section — being prepared additionally upon the referees' and Editor-in-chief request — and representing, in fact, the first attempt to review this new family of carbon paste electrodes in its full variabity and entirety at once.

When considering the continuing investigations of the most active groups ([93], [94,95], and [96,99,102]), as well as some contributions by other scientific teams [98,100, 103], the newly constituted field cover an extensive and very diverse experimental work — from the basic characterisations [71-75], including comparative studies with "traditional"

CPEs ([74,76,77,78,93]; see also Fig. 4) *via* studies on the specific ion / charge transfer in ionic liquids [74,75], conductivity changes [77,93] or electrocatalytic effect [71-75,79,80], up to the first analytical applications to determine selected inorganic species, organic compounds and pollutants, pharmaceuticals, or numerous biologically active compounds (see below).
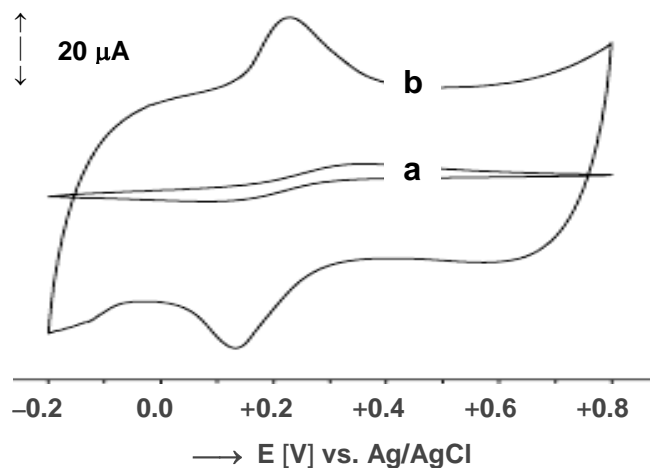

Figure 4. *Cyclic voltammograms of the $[Fe(CN)_6]^{3/4-}$ redox pair* at two different carbon paste electrodes. Legend: (**a**) traditional CPE and (**b**) carbon and ionic liquid-based paste electrode (CILE). Exp. conditions: 0.1 M KCl (pH 6.5), 0.005 M $K_3[Fe(CN)_6]$, scan rate: 10 mV·s^{-1}. (redrawn from [71])

In fact, the combination of CPEs and (RT)ILs offers quite diverse configurations that deserves to be presented in more detail. At first, one has (i) **ionic-liquid**-modified **carbon paste electrodes (IL-CPEs**; see e.g. [71,80]), followed by the so-called (ii) **carbon** (composite) **ionic liquid electrodes** (**CILEs**; under this name first introduced by Maleki & Safavi [72]). Slightly "younger" is yet another group of (iii) **carbon nanotubes ionic liquid electrodes** (**CNT-ILEs** [77,93,107,150]), where the ordinary graphite powder was replaced by its nano-carbon alternative. Furthermore, there are special configurations having been proposed very recently and introducing (iv) **mixtures of ionic liquids** with new forms of carbon; namely, **carbon nanofibers** ([146]; prepared by electrospinning [151]) and **graphene** ([147,149]; i.e., a structure with mono-atomic layer of the *sp*-bonded carbons). Finally, the survey of ionic liquid-based carbon pastes can be completed by a unique arrangement of (v) **carbon nanotube-paste electrode** (**CNTPE**) immersed **in an ionic liquid** serving as the proper supporting electrode [103] or (vi) hybrid configurations of the **glassy carbon substrate** covered with a thin layer of **ionic liquid**-based **carbon pastes** and related coatings ([73, 98,149] and [92]) that has not been quoted in the above-mentioned "mini-review" [70]. Variants (**iii**)-(**v**) represent the combinations of ionic liquid(s) with other trendy materials — novel forms of carbon —, giving rise to the paste mixtures of "new generation", in which both traditional components are replaced by alternate moieties.

Considering the CNTPE configuration, it represents in itself a special phenomenon, when the respective database of more than 80 reports has also spawned a separate sub-family of carbon paste-based electrodes (see [70] and section *2.2.2* therein, as well as [152]). Finally, rather curious example (**v**) can also be considered as a certain transient element between the CILEs and CNTPEs, possessing some extraordinary features, such as a long-term stability at a temperature of about 60 $^\circ$C, enabled by special ultra-long ("aligned") nanotubes [103].
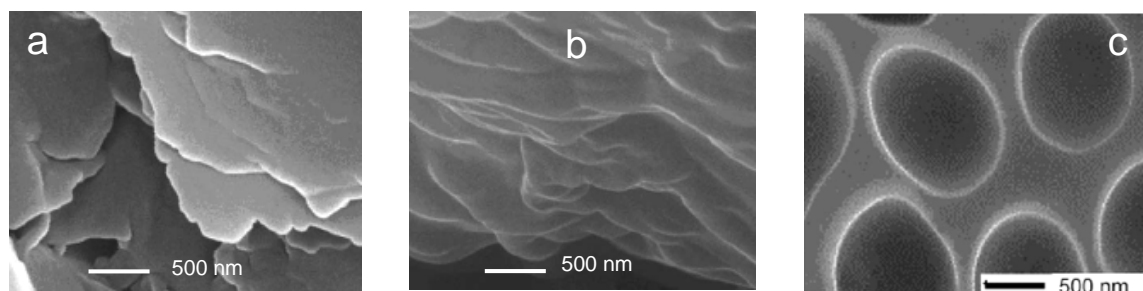

Figure 5. Typical microstructures and the surface morphology of (**a**) traditional CPE, (**b**) CILE, and (**c**) ionic liquid-based film attached to the GCE substrate (reproduced from [71] and [92]).

Regarding the individual types of ionic liquids used, their choice was often routine and conservative, preferring almost exclusively the quaternary cations of alkyl / heterocyclic structure (namely: [n-alkyl-pyridium]$^+$A$^-$, [N-butyl-N-methyl-pyrrolidinium]$^+$A$^-$ or even [R,R'-imidazolium]$^+$A$^-$, where the actual anion was PF$_6^-$, Br$^-$, or bis(trifluoromethyl-sulfonyl)imide, NTf$_2$.) Perhaps the only atypical (RT)IL was poly(Na-4-styrene-sulphonato-1-butyl-3-methyl-imidazolium hexafluorophosphate (PSS-BMIMPF$_6$ [92]) whose extraordinary large polymeric cation gives rise to a very attractive microstructure as shown in Fig. 5 C.

Among instrumental techniques coupled with CILEs or IL-CPEs, the most frequent were voltammetric measurements (e.g. [71-76,80,90,100]), including the effective detection with the rotated disc electrode (RDE, [77]), together with amperometric detections (e.g. [84,95,102,123]), feasible also in the FIA mode [83,94]. Occasionally, there also were combinations with potentiometric indication [78,107,116,121,150] and electrochemi-luminescence detection [83,111,118], or additional studies with the aid of scanning electron microscopy (SEM [108]) or electrochemical impedance spectroscopy (EIS [93]) to reveal and characterise all the alterations and nuances at the ionic-liquid modified electrode surfaces. And, finally, to identify the form of special surface-modifying agent(s), some spectral techniques were also employed (UV/Vis spectrometry and FT-IR [120,128,143]).

The applicability of all the configurations of ionic liquid-based carbon pastes described above can be illustrated on a survey in Table II, gathering the data from all the original papers listed as the references [71-150]. (The dead-line for literature search was the early autumn of 2010 and hence, some newest publications might not be included.)

Table II: *CILEs, IL-CPEs, and CNT-ILEs: Survey of Analytical Applications*

- INORGANIC SPECIES (with specification of the real samples analysed *) // single cations: **Cd^{2+}** and **Pb^{2+}** [126], **Cd^{2+}, Pb^{2+}** and **Cu^{2+}** (soil [142]), **Hg^{2+}** [150]; **Ce^{3+}** [121], **Yb^{3+}** [148], **Pr^{3+}** [107], **Er^{3+}** (soil [116,140]), **Tb^{3+}** [145]; anions: **NO$_2^-$** [71,85,88,105], **SO$_3^{2-}$** (mineral water, grape-juice, non-alcoholic beer [93]), **BrO$_3^-$** [144], **IO$_3^-$** (table salt [106]), **ClO$_4^-$** and **PF$_6^-$** [74]; molecules: **H$_2$O$_2$** (rain water [84]), [85,88,91,102, 112,114, 117,123,131,141,143]), **O$_2$** [102], and **N$_2$H$_4$** [94].

- ORGANIC SUBSTANCES (with specification of samples) // basic derivatives: **phenol** and *2,4-dichlorphenol* [81], **hydroquinone** (skin cosmetics [86], waste water [104]), **anthraquinone** [138], **dihydroxybenzene isomers** (wastewater [136]), **metol** (photographic baths [124,125]), **catechol** [81,99], **dihydroxybenzoic acid** [133], **tri-chloracetic acid** [88,91,102,105,114,117,128,131,135,137]; organic pollutants: *p*-**aminophenol** (waste water [89], **tripropylamine** [83], *Methylparathion* herbicide (water [98]), **nitromethane** [149]; *p*-**nitrophenol** [132], **TNT** (explosives [147]).

- PHARMACEUTICALS (clinical samples or biological fluids**) // commercial products / tablets: *Dobesilate* (calcium [82]), *Fentanyl* (citrate [111]), *Paracetamol* [100]; abuse drugs: *Heroin* [134] and *Methamphetamine* [127].

- BIOLOGICALLY IMPORTANT COMPOUNDS (clinical samples or biological fluids) // aminoacids: **cysteine** [112], purines: **guanosine** [109,113], **uric acid** [73,76]; vitamins: **ascorbic acid** [72,76,79]; saccharides: **glucose** [97,101,115,129]; neuro-transmitters: **dopamine** [72,76,87], **adenosine** [108]; enzymes & coenzymes: **NADH** [72,146]; proteins & metaloproteins: α-**fetoprotein** [110]; **hemoglobin** [85,88,102,114, 120,128,131,135,141,143], **myoglobin** [105,117]; antioxidants: **rutin** [130]; macro-molecules: **DNA** (and the **respective forms** [96,122,139]).

*Legend: *) unspecified references mean determinations in model, **) if not stated otherwise*

With respect to the overall abundance of the above-discussed variants of ionic liquid-containing carbon paste electrode — i.e., the three-component configuration of IL-CPEs and qualitatively new types of binary carbon pastes represented by CILEs and CNT-ILEs — their occurrence in the so-far performed studies is largely in favour of the latter, appearing in more than 90% of the respective reports.

Among various CILEs, one can also find quite atypical constructions, such as two micro-variants [94,119], electrically heated assemblies [95,118], or sophisticated composite layers containing a graphite material, an ionic liquid, and some additional constituent(s) / stabiliser(s) in one integrated system [102,135,141,149]. Surprisingly, quite rare are also the detections in flowing streams [83,94], although the resultant effectiveness can be really remarkable as illustrated by the corresponding amperograms in Fig. 6.
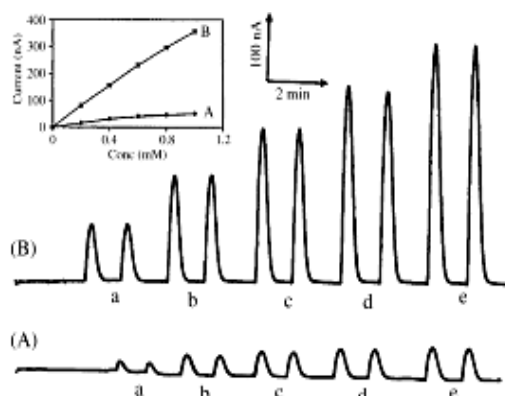

Figure 6. *Flow injection analysis of model samples* using (**A**) traditional CP-based detector and (**B**) carbon ionic liquid paste electrode (CILE). Legend: **a-e**) responses (as replicates) to increasing concentrations of 0.2-1.0 mM N_2H_4. Exp. conditions: 0.05 M phosphate buffer (pH 7.4), working potential of the detector: +0.4 V vs. Ag/AgCl, flow rate: 1.5 mL·min^{-1}. (reproduced from [94])

Besides applications surveyed in the table, there are further promising employments of some particular ionic-liquids when combined with the carbon paste matrix. One of such eventualities was reported very recently by our research group [153]. The respective study has concerned the development and characterisation of an ammonium tetrafluorobismuthate(III)-modified carbon paste electrode (NH_4BiF_4-CPE), where the compound of interest — although being a solid — is a primary member of ionic liquids of the $[Q^+][BiF_4^-]$ type (where "Q" is a voluminous inorganic / organic structure). As proved experimentally with NH_4BiF_4, such a substance would serve as the internal source of metallic film generated *in situ* – identically as in Bi_2O_3-CPE or Sb_2O_3-CPE [154], respectively, belonging to the family of currently popular environmentally friendly non-mercury electrodes for trace analysis of heavy metals. And, in prospect, any truly liquid substance of the $[Q^+][Bi^{III}(L)_4^-]$, $[Q^+][Sb^{III}(L)_4^-]$, or even $[Q^+][Sb^V(L)_6^-]$ structure (where "L" is an anionic ligand) would totally replace the pasting liquid in carbon paste mixtures in the same way like any other ionic liquid may do in the CILEs and CNT-ILEs. At present, suitable candidates for such liquid compounds are considered; some of them with respect to laboratory synthesis (similarly as NH_4BiF_4 [153]), while one — namely: tetra-*n*-butylammonium hexafluoroantimonate, $[(C_4H_9)_4N^+][SbF_6^-]$ — being obtainable as fine chemical.

A remarkable collection of fifteen papers [136-150], appearing within this calendar year, is the best indication that the recently established area of CILEs and related electrodes would continue in rapid development, reflecting also the newest achievements in synthesis of ionic liquids and similar fluids. All these trends are now carefully watched to be captured in a debut monograph on CPEs, announced to be issued in the middle of next year [155].

Abbreviations & Symbols // Further Specification

ac	.....	acetyl
Ag/AgCl	.....	silver/silver chloride (reference electrode)
AIL	.....	aprotic ionic liquid
B(u)	.....	butyl
Bi_2O_3-CPE	.....	bismuth (tri)oxide (bulk-modified) carbon paste electrode
^oC	.....	degree Celsius
CILE(s)	.....	carbon ionic liquid (paste) electrode(s)
CNT(s)	.....	carbon nanotube(s)
CNT-ILE(s)	.....	carbon nanotubes ionic liquid electrode(s)
CNTPE(s)	.....	carbon nanotubes paste electrode(s)
CPE(s)	.....	carbon paste electrode(s)
Et	.....	ethyl
FIA	.....	flow injection analysis
FT-IR	.....	Fourier transform-infrared (spectroscopy)
GC	.....	gas chromatography
GCE	.....	glassy carbon electrode
IL	.....	ionic liquid
IL-CPE(s)	.....	ionic liquid (modified) carbon paste electrode(s)
im	.....	imidazolinium
OTf	.....	trifluoromethanesulfonate
M(e)	.....	methyl
MIm	.....	methyl-imidazolinium
MIM	.....	dimethyl-imidazolinium
n	.....	number (of)
NIL	.....	non-aqueous ionic liquid
NTf_2	.....	bis[tri(fluoromethyl)sulphonyl]imide.
Ph	.....	phenyl

PIL	.....	protic ionic liquid
Py	.....	pyridinium
R	.....	alkyl
RDE	.....	rotated disc electrode
(RT)IL	.....	(room temperature) ionic liquid
S	.....	Siemens // conductivity unit
Sb_2O_3-CPE	.....	antimony(tri)oxide (bulk-modified) carbon paste electrode
SEM	.....	scanning electron microscopy
UV/Vis	.....	ultraviolet/visible (spectroscopy)
$\lambda_{(max)}$	......	wave length (maximum)
π (-π)	.....	type of bond // electron configuration

Acknowledgements

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