



ELECTROCHEMICAL PROCESS FOR PRODUCING IONIC LIQUIDS

FIELD OF THE INVENTION

[0001] The present invention pertains to an electrochemical process for producing ionic liquids which are useful, for example, to replace organic solvents in chemical reactions. The present invention is particularly useful for making hydrophilic ionic liquids of high purity.

BACKGROUND AND SUMMARY OF THE INVENTION

[0002] Ionic liquids are salts that are liquid at ambient or near ambient temperatures. Ionic liquids have a number of uses which include replacing organic solvents in chemical processes and reactions, extracting organic compounds from aqueous waste streams, and as electrolytes in devices such as capacitors and batteries. This is because, unlike conventional organic solvents, ionic liquids are non-volatile and non-flammable. These properties are advantageous to help reduce losses to evaporation, eliminate volatile organic emissions, and improve safety.

[0003] Other properties of ionic liquids have also proved advantageous. For example, many ionic liquids have a broad temperature range at which they remain liquid and also are stable over a broad pH range. This is beneficial for high temperature processes with a demanding pH. Further, some ionic liquid systems can be used as both a solvent and catalyst. For example, [bmim]-Al₂Cl₇ and [emim]-Al₂Cl₇ can be employed as a solvent and catalyst in Friedel-Crafts reactions wherein bmim is 1-butyl-3-methylimidazolium and emim is 1-ethyl-3-methylimidazolium.

[0004] Ionic liquids are conventionally prepared by metathesis, i.e., double decomposition reaction, whereby the reaction of two compounds forms two new compounds – one of which is the ionic liquid. For example, reacting [emim]Cl with AgNO₃ will yield [emim]NO₃ and AgCl.



[0005] Unfortunately, such metathesis reactions produce a mole of waste, e.g., one mole of AgCl per mole of product. In addition, the ionic liquids often contain impurities from incomplete reactions and solvent contamination. A further problem with metathesis is that it requires the separation of the two compounds which are produced. While this can be accomplished readily when the ionic liquid is hydrophobic, it is more difficult when the ionic liquid is hydrophilic. In addition, the required reagents (e.g., AgNO₃) are expensive and difficult to recycle.

[0006] For the aforementioned reasons, it would be desirable to discover a new process for preparing ionic liquids. It would further be desirable if such a process was capable of making both hydrophobic and hydrophilic ionic liquids with low amounts of waste and impurities and without the use of an organic solvent.

[0007] Advantageously, new processes have been discovered to make ionic liquids. The processes comprise using an electrochemical cell which comprises an anode and a cathode. The cell is charged with solutions and subjected to electrolysis to produce the desired ionic liquid. The ionic liquid is then recovered. Alternatively, a precursor to the ionic liquid is made in an electrochemical cell. The precursor is then converted, chemically or otherwise, to the desired ionic liquid. The instant inventive processes can produce ionic liquids having a purity of 99% or higher.

DETAILED DESCRIPTION OF THE INVENTION

[0008] As used herein "ionic liquid" means a salt comprising a cation and an anion. The salt is a liquid at ambient or near ambient temperatures.

[0009] As used herein "hydrophilic ionic liquid" means an ionic liquid which is partially or wholly miscible with water.

[0010] As used herein "hydrophobic ionic liquid" means an ionic liquid which is relatively immiscible with water, i.e., forms two phases at ambient conditions.

[0011] As used herein "composition" includes a mixture of the materials that comprise the composition, as well as, products formed by the reaction or the decomposition of the materials that comprise the composition.

[0012] As used herein a "mixture" of metals includes both an intimate mixture of two or
5 more metals such as an alloy, as well as, one or metals coated upon one or more metals.

[0013] As used herein "derived from" means made or mixed from the specified materials, but not necessarily composed of a simple mixture of those materials. Substances "derived from" specified materials may be simple mixtures of the original materials, and may also include the reaction products of those materials, or may even be wholly composed of reaction
10 or decomposition products of the original materials.

[0014] Any numerical values recited herein include all values from the lower value to the upper value in increments of one unit provided that there is a separation of at least 2 units between any lower value and any higher value. As an example, if it is stated that the amount of a component or a value of a process variable such as, for example, temperature, pressure,
15 time and the like is, for example, from 1 to 90, preferably from 20 to 80, more preferably from 30 to 70, it is intended that values such as 15 to 85, 22 to 68, 43 to 51, 30 to 32 and the like, are expressly enumerated in this specification. For values which are less than one, one unit is considered to be 0.0001, 0.001, 0.01 or 0.1 as appropriate. These are only examples of what is specifically intended and all possible combinations of numerical values between the
20 lowest value and the highest value enumerated are to be considered to be expressly stated in this application in a similar manner.

Electrochemical Cell

[0015] The processes of the instant invention all involve subjecting an electrochemical cell to electrolysis. The type of electrochemical cell will vary depending upon, for example,
25 the starting materials, the ionic liquid to be made, the purity desired, the cathode and anode

employed, and the specific method to be employed. Suitable anodes, cathodes, cell configurations, and means for dividing the cells are described in U.S. Patent Nos. 4,714,530; 5,853,555; 5,968,338; and 5,951,845 which are incorporated by reference in their entirety. The term "electrochemical cell" includes, for example, both electrolytic cells and
5 electro dialysis cells.

[0016] Generally, the electrochemical cell comprises one or more cathodes and one or more anodes and can be made of one electrolyzer or two or more electrolyzers in parallel or series. The cathode can be any of any size, shape, or material so long as it provides sufficient free electrons to produce the desired product. Suitable cathodes include, for example, nickel,
10 iron, stainless steel, nickel plated titanium, graphite, carbon steel (iron) or mixtures thereof. Suitable anodes include, for example, titanium, tantalum, zirconium, hafnium, or mixtures thereof. Often the anode will have a non-passivable and catalytic film which may comprise metallic noble metals such as platinum, iridium, ruthenium, rhodium, or mixtures or oxides thereof.

15 [0017] The cell may also comprise a means for dividing the cell into two or more compartments. These compartments generally include a catholyte compartment which houses a cathode and a catholyte solution and an anolyte compartment which houses an anode and an anolyte solution. The means for dividing includes, for example, membranes, nanoporous materials, diaphragms, asbestos, etc. Types of dividing membranes may include
20 cation-exchange membranes, anion exchange membranes, and bipolar membranes. The use of such means for dividing is discussed in U.S. Patent Nos. 4,714,530; 5,853,555; 5,968,338; and 5,951,845 which are incorporated by reference in their entirety.

Solutions of the Electrochemical Cell

[0018] The processes of the present invention usually comprise charging the
25 electrochemical cell with solutions that will form the ionic liquid or an ionic liquid precursor

when the cell is subjected to electrolysis. The solutions can be introduced into the electrochemical cell in any order or even created *in situ* within the cell so long as the desired ionic liquid or ionic liquid precursor is formed when subjected to electrolysis.

[0019] Generally, the electrochemical cell is charged with at least two solutions. One solution, hereinafter the “first solution”, is either a solution which comprises the desired cation of the ionic liquid to be produced or a solution that when subjected to electrolysis produces the desired cation. Another solution, hereinafter the “second solution”, is either a solution which comprises the desired anion of the ionic liquid to be produced or a solution that when subjected to electrolysis produces the desired anion. For some applications, the desired cation may be a mixture of different cations and/or the desired anion may be a mixture of different anions. Generally, the solutions are aqueous, however, any solvent which does not react significantly under electrolysis conditions may be employed.

[0020] The concentrations of the solutions are not particularly critical so long as the solutions are sufficiently concentrated for the electrolysis reaction to occur and produce the desired ionic liquid at the desired purity. Generally, the concentration of the solutions should be at least about 0.5, preferably at least about 1, most preferably at least about 1.5 in molarity (M). On the other hand, the concentration of the solutions should generally be less than about 3, preferably less than about 2.5, most preferably less than about 2 M.

Cation of Ionic Liquid to be Produced

[0021] The desired cation of the ionic liquid to be produced includes, for example, “onium” cations. Onium cations include cations such as substituted or unsubstituted ammonium, phosphonium, and sulfonium cations. Preferred onium cations include, for example, substituted or unsubstituted N-alkyl or N-aryl pyridinium, pyridazinium, pyrimidinium, pyrazinium, imidazolium, pyrazolium, thiazolium, oxazolium, triazolium, imidazolinium, methylpyrrolidinium, isothiazolium, isoxazolium, oxazolium, pyrrolium, and

thiophenium. The substituents include one or more of the following groups: halo, alkyl, and aryl groups such as phenyl. In addition, two adjacent substituents may be joined together to form an alkylene radical thereby forming a ring structure converging on N. The alkyl, phenyl, and alkylene radicals may be further substituted. Another particularly preferred cation is an ammonium cation substituted by one or more groups such as alkyl and aryl groups such as phenyl. Many Such cations and substituted cations are described in U.S. Patent Nos. 5,827,602 and 5,965,054 which are incorporated by reference in their entirety.

[0022] As described above, the desired cation of the ionic liquid may be part of a solution which comprises the desired cation of the ionic liquid to be produced or the desired cation may be produced from a solution that when subjected to electrolysis produces the desired cation. In either case, there is typically an associated anion which is preferably different from the desired anion of the ionic liquid to be produced. The type of anion is not critical so long as it does not interfere with the formation of the desired ionic liquid. Suitable anions include, for example, halide anions such as chloro, fluoro, bromo, and iodo, hydroxide, ethylsulfate, triflate, formate, alkylsulfate, triflate, trifluoroacetate, perfluoroalkylcarboxylate, perfluoroalkylsulfonate, and methylcarbonate, etc.

[0023] It is also often advantageous to employ a process wherein the solution which comprises the desired cation of the ionic liquid to be produced also comprises as the undesired anion, an anion which is converted electrochemically or otherwise to a gaseous by-product such as hydrogen, ammonia, carbon dioxide, or nitrogen. In this manner, the undesired gas bubbles from the solution and there are less undesirable ions in solution to be separated from the desired ions of the ionic liquid.

Anion of Ionic Liquid to be Produced

[0024] The desired anion of the ionic liquid to be produced can be charged to the cell as part of a solution or may be produced from a solution that when subjected to electrolysis

produces the desired anion. For example, if acetate is the desired anion of the ionic liquid then an acetate solution could be employed or an aldehyde or ester solution could be employed and electrochemically converted to an acetate solution.

[0025] If the desired anion is part of a solution that is charged to the cell then there is
5 generally an associated cation that is preferably different from the desired cation of the ionic liquid to be produced. The type of associated cation is not critical so long as it does not interfere with the formation of the desired ionic liquid. Suitable associated cations include, for example, hydrogen, ammonium, sodium, phosphonium, sulfonium, potassium, etc. Examples of solutions that produce the desired anion include organic salts, inorganic salts,
10 organic acid, and inorganic acids. Preferable solutions include aqueous solutions of acetic acid, nitric acid, and salts thereof.

[0026] It is also often advantageous to employ a process wherein the solution which comprises the desired anion of the ionic liquid to be produced also comprises as the undesired cation, a cation which is converted electrochemically or otherwise to a gaseous by-product
15 such as hydrogen, ammonia, carbon dioxide, or nitrogen. In this manner, the undesired gas bubbles from the solution and there are less undesirable ions in solution to be separated from the desired.

Electrolysis

[0027] The amount and duration of current to be employed depends generally on the size,
20 shape, and composition of the cell and electrodes, as well as, the concentration and nature of the solutions in the electrochemical cell. Generally, the larger the amount of current the shorter the reaction time and vice versa. However, if the amount of current is too large then undesirable side reactions may occur or power consumption may be excessive. Correspondingly, if the amount of current is too small then no reaction may occur or the

reaction may be too slow. Generally, one of skill in the art may readily use electrochemical principles such as Faraday's law to determine the proper amount of current for a given cell.

[0028] The electrolysis can be conducted to produce the ionic liquid batch-wise or continuously. If electrolysis is conducted batch-wise then current is generally applied until
5 the ionic liquid has been formed in its desired amount and purity. This can often be determined by using a means for indicating the extent of reaction. One such means is a pH meter. If the electrolysis is to be conducted on a continuous basis then the starting solutions are replenished as the reaction proceeds and the desired product may be recovered continuously. An additional step in the ionic liquid recovery process might be to remove
10 residual acid (e.g. acetic acid) prior to evaporating the water. Acid can be removed by an anion exchange resin, among other methods.

Ionic Liquid Recovery

[0029] The ionic liquid may be recovered by any suitable means the most efficient of which may vary depending upon the type and desired purity of the ionic liquid and the type
15 of cell. Preferable means of recovery include rotary evaporation or distillation, azeotropic distillation, crystallization, pervaporization, drying agents, and reverse osmosis.

Precursor Method

[0030] A variation of the aforementioned methods of producing ionic liquids using electrolysis involves producing a precursor solution to the ionic liquid in an electrochemical
20 cell, converting the precursor solution to the desired ionic liquid and recovering it. Suitable precursor solutions that can be produced by electrolysis include, for example, solutions comprising anions such as hydroxide, carbonate, bicarbonate, acetate, and formate. A particularly preferable solution comprises onium hydroxides. Such processes are described, for example, in U.S. Patent Nos. 4,714,530; 5,853,555; 5,968,338; and 5,951,845 which are
25 incorporated by reference in their entirety. Once the precursor solution has been made via