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(54) Title: MIXTURES OF AMMONIA AND IONIC LIQUIDS

(57) Abstract: Mixtures of ammonia and ionic liquids are provided that are suitable for use as absorption cooling fluids in absorption cycles, and ammonia storage.

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TITLE

MIXTURES OF AMMONIA AND IONIC LIQUIDS

TECHNICAL FIELD

The present invention relates to mixtures of ammonia and ionic liquids for use as absorption cooling fluids and ammonia storage.

BACKGROUND

The absorption refrigeration cycle is more than a 100 year old technique. Although the vapor compression cycle took over most of air-conditioning and refrigerating applications, the well-known refrigerant-absorber systems (H_2O/LiBr and NH_3/H_2O) are still being used for certain applications, particularly in the field of industrial applications or large-scale water chiller systems. Recently, more attention has been directed toward recovery of waste heat using the NH_3/H_2O system (Erickson DC, *et al.*, "Heat-activated dual-function absorption cycle", ASHRAE Trans. 2004, 110). Inherent drawbacks to using LiBr and NH_3 as refrigerants include the corrosiveness of LiBr and the toxicity and flammability of NH_3. In the late 1950s, some pioneering works proposed new refrigerant-absorbent pairs for the absorption cycle, using fluoroalkane refrigerants with organic absorbents (Eiseman BJ, "A comparison fluoroalkane absorption refrigerants", ASHRAE J. 1959, 1, 45; Mastrangelo SVR. "Solubility of some chlorofluorohydrocarbons in tetraethylene glycol ether", ASHRAE J. 1959, 1, 64). Such studies continue actively even at the present time, especially among academic institutions. One drawback to using fluorinated hydrocarbons as refrigerants is the potentially adverse environmental impacts that may result from their use. Needed are new refrigerant-absorber systems.

Room-temperature ionic liquids (RTILs) are a new class of solvents and molten salts with a melting point of less than about 100 °C. Because of the negligible vapor pressure, they are often called (environmentally-friendly) "green solvents", compared with ordinary volatile organic compounds (VOCs). For the past several years, worldwide research on thermodynamic and transport properties of pure RTILs and their mixtures with various chemicals have been conducted. As a new type of solvent with immeasurable vapor pressure, room-temperature ionic liquids are being considered as absorbers with various refrigerants. For instance, Shiflett et al, US 2006/0197053 A1 disclose the use of ionic liquids as absorbents with fluorinated hydrocarbons as the refrigerant in absorption cycles. Although several other refrigerants are mentioned, including the possibility of ammonia, no example or data enabling the possibility were disclosed. Knowledge of solvent phase behaviors is highly important to determine the attractiveness of using ionic liquids in these applications as well as in new applications such as absorption cooling or heating.

Another need is a medium to store and transport volatile materials. Ammonia, for instance, is typically stored in high-pressure cylinders; or in water, as ammonium hydroxide. However, in applications where water, a medium with a significant vapor pressure at room temperature, can not be tolerated, ammonium hydroxide is not a suitable medium for storing ammonia. Conventional adsorbents, such as surface-modified active carbons and ion-exchanged zeolites, have been used for storage of ammonia. However, the ammonia storage capacities are not very high, for instance, for Cu form of Y-zeolite the storage capacity is about 5 millimol of ammonia per gram (Ind. Eng. Chem. Res. 2004, 43, 7484-7491).

Alkaline earth halides and their hydrated forms MgClOH, $CaCl_2$, $CaBr_2$, and $SrBr_2$ have been found to have higher capacities on the order of 25 to 40 millimol per gram (i.e. MgClOH is 26 millmol per gram). One issue with the alkaline earth halides is the adsorption requires heat to completely remove the ammonia from the surface in order to regenerate the solid. For instance, $MgCl_2$-$CaCl_2$ at 298 K adsorbs about 46 millimol of ammonia per gram of solid at 80 kPa; and further increase in pressure results in no further increase in ammonia adsorbed. Release of the pressure and evacuation of the adsorbant, followed by a second adsorption measurement shows far less ammonia can be adsorbed. For example a second adsorption measurement resulted in 14 millimol of ammonia per gram of solid at the same temperature (298 K) and pressure (80 kPa). This indicates that the absorption process is irreversible even after 1 hour of evacuation to remove all the ammonia from the first adsorption experiment. Needed are mediums that can reversibly store significant quantities of ammonia and also have very low or no vapor pressure themselves.

SUMMARY

One aspect of the invention is a composition comprising ammonia and at least one ionic liquid wherein the composition comprises about 1 to about 99 mole % of ammonia over a temperature range from about -40 to about 130 °C at a pressure from about 1 to about 110 bar.

Another aspect of the invention is an absorption cycle comprising a composition of the invention useful for heating or cooling.

Another aspect of the invention is a process for storing ammonia comprising absorbing ammonia in an ionic liquid to provide a composition comprising about 1 to about 99 mole % of ammonia over a temperature range from about -40 to about 130 °C at a pressure from about 1 to about 110 bar.

BRIEF DESCRIPTION OF DRAWINGS

Figure 1 illustrates a schematic diagram of a simple absorption refrigeration cycle.

Figure 2 illustrates a schematic diagram of a sample holder used in preparing compositions of the invention.

Figure 3 illustrates *PTx* phase equilibria of NH_3 / [emim][Tf_2N] mixtures.

DETAILED DESCRIPTION

All patents and patent applications cited herein are hereby incorporated by reference. Herein all trademarks are designated with capital letters.

In this disclosure, a number of terms are used for which the following definitions are provided.

An “alkane” is a saturated hydrocarbon having the general formula C_nH_{2n+2}, and may be a straight-chain, branched or cyclic.

An “alkene” is an unsaturated hydrocarbon that contains one or more carbon-carbon double bonds, and may be a straight-chain, branched or cyclic. An alkene requires a minimum of two carbons. A cyclic compound requires a minimum of three carbons.

An “aromatic” is benzene and compounds that resemble benzene in chemical behavior.

A “fluorinated ionic liquid” is an ionic liquid having at least one fluorine on either the cation or the anion. A ”fluorinated cation” or “fluorinated anion” is a cation or anion, respectively, comprising at least one fluorine.

A “halogen” is bromine, iodine, chlorine or fluorine.

A “heteroaryl” group is an alkyl group having a heteroatom.

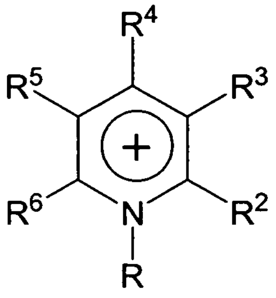
A “heteroatom” is an atom other than carbon or hydrogen in the structure of an alkanyl, alkenyl, cyclic or aromatic compound.

An “ionic liquid” is an organic salt that is fluid at about 100 °C or below, as more particularly described in *Science* (2003) 302:792-793.

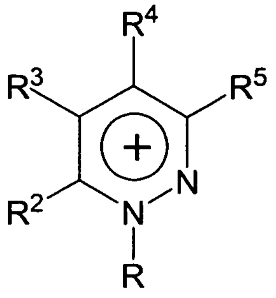
“Optionally substituted with at least one member selected from the group consisting of”, when referring to an alkane, alkene, alkoxy, fluoroalkoxy, perfluoroalkoxy, fluoroalkyl, perfluoroalkyl, aryl or heteroaryl, means that one or more hydrogens on the carbon chain may be independently substituted with one or more of one or more members of the group. For example, substituted C_2H_5 may, without limitation, be CF_2CF_3, CH_2CH_2OH or CF_2CF_2I.

Ionic liquids can be synthesized, or obtained commercially from several companies such as Merck KGaA (Darmstadt, Germany) or BASF (Mount Olive, NJ). The synthesis of several ionic liquids useful in the compositions of the invention is disclosed in the Shiflett, et al, US 2006/0197053 A1.

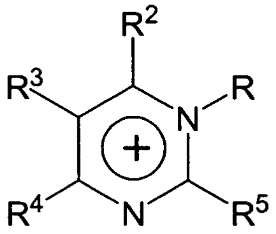
In one embodiment of the invention, the ionic liquid has a cation, herein defined as *Group A Cations,* selected from the group consisting of:



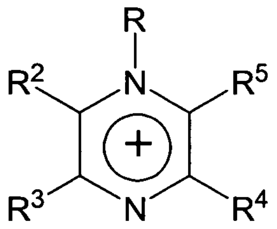
pyridinium



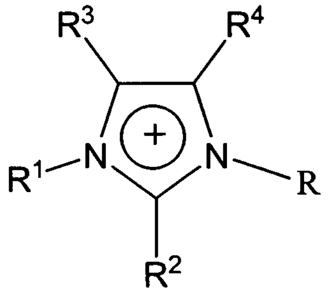
pyridazinium



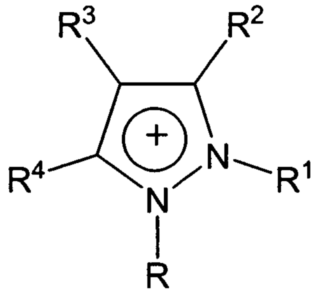
pyrimidinium



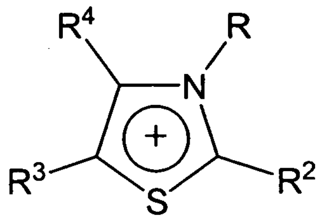
pyrazinium



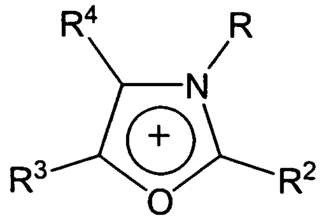
imidazolium



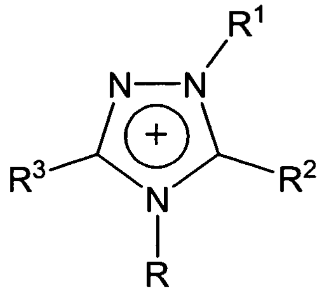
pyrazolium



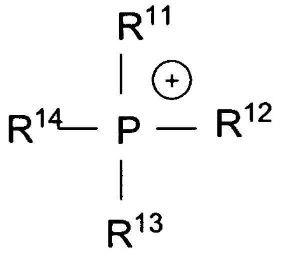
thiazolium



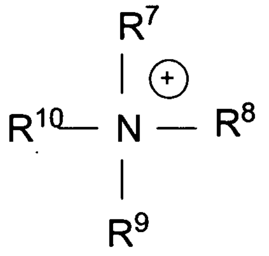
oxazolium



triazolium



and



phosphonium

ammonium

wherein R, R^1, R^7, R^8, R^9, and R^{10} are independently selected from the group consisting of:

(i) hydrogen

(ii) $-CH_3$, $-C_2H_5$, or C_3 to C_{25} straight-chain, branched or cyclic alkane or alkene, optionally substituted with at least one member selected from the group consisting of Cl, Br, F, I, OH, NH_2 and SH;

(iii) $-CH_3$, $-C_2H_5$, or C_3 to C_{25} straight-chain, branched or cyclic alkane or alkene comprising one to three heteroatoms selected from the group consisting of O, N and S, and optionally substituted with at least one member selected from the group consisting of Cl, Br, F, I, OH, NH_2 and SH;

(iv) C_6 to C_{20} unsubstituted aryl, or C_3 to C_{25} unsubstituted heteroaryl having one to three heteroatoms independently selected from the group consisting of O, N and S; and

(v) C_6 to C_{25} substituted aryl, or C_3 to C_{25} substituted heteroaryl having one to three heteroatoms independently selected from the group consisting of O, N and S; and wherein said substituted aryl or substituted heteroaryl has one to three substituents independently selected from the group consisting of:

(1) $-CH_3$, $-C_2H_5$, or C_3 to C_{25} straight-chain, branched or cyclic alkane or alkene, optionally substituted with at least one member selected from the group consisting of Cl, Br, F I, OH, NH_2 and SH,

(2) OH,

(3) NH_2, and

(4) SH;

R^2, R^3, R^4, R^5, and R^6 are independently selected from R and a halogen; R^{11}, R^{12}, R^{13}, and R^{14} are independently selected from R with the proviso that R^{11}, R^{12}, R^{13}, and R^{14} are not hydrogen; and

wherein, optionally, at least two of R, R^1, R^2, R^3, R^4, R^5, $R^{6,}$ R^7, R^8, R^9, $R^{10,}$ R^{11}, R^{12}, R^{13},and R^{14} can together form a cyclic or bicyclic alkanyl or alkenyl group;

and an anion, herein defined as *Group A Anions*, selected from the group consisting of $[CH_3CO_2]^-$, $[HSO_4]^-$, $[CH_3OSO_3]^-$, $[C_2H_5OSO_3]^-$, $[AlCl_4]^-$, $[CO_3]^{2-}$, $[HCO_3]^-$, $[NO_2]^-$, $[NO_3]^-$, $[SO_4]^{2-}$, $[PO_4]^{3-}$, $[HPO_4]^{2-}$, $[H_2PO_4]^-$, $[HSO_3]^-$, $[CuCl_2]^-$, Cl^-, Br^-, I^-, SCN^-, and a fluorinated anion.

In another embodiment, ionic liquids useful for the invention comprise fluorinated cations wherein at least one member selected from R, R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8, R^9, R^{10}, R^{11}, R^{12}, R^{13} and R^{14} comprises one or more fluorines. Included in these materials are fluorinated cations wherein one or more R^2, R^3, R^4, R^5, and R^6, may be fluorine; and wherein one or more R, R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8, R^9, R^{10}, R^{11}, R^{12}, R^{13} and R^{14} may be an alkyl, alkenyl or an aromatic group containing one or more fluorinated carbon atoms; including perfluorinated alkyl, alkenyl and aromatic groups.

Preferred fluorinated anions for the compositions of the invention, defined here as *Group B Anions*, are selected from the group consisting of: $[BF_4]^-$, $[BF_3CF_3]^-$, $[BF_3C_2F_5]^-$, $[PF_6]^-$, $[PF_3(C_2F_5)_3]^-$, $[SbF_6]^-$, $[CF_3SO_3]^-$, $[HCF_2CF_2SO_3]^-$, $[CF_3HFCCF_2SO_3]^-$, $[HCClFCF_2SO_3]^-$, $[(CF_3SO_2)_2N]^-$, $[(CF_3CF_2SO_2)_2N]^-$, $[(CF_3SO_2)_3C]^-$, $[CF_3CO_2]^-$, $[CF_3OCFHCF_2SO_3]^-$, $[CF_3CF_2OCFHCF_2SO_3]^-$, $[CF_3CFHOCF_2CF_2SO_3]^-$, $[CF_2HCF_2OCF_2CF_2SO_3]^-$, $[CF_2ICF_2OCF_2CF_2SO_3]^-$, $[CF_3CF_2OCF_2CF_2SO_3]^-$, $[(CF_2HCF_2SO_2)_2N]^-$, $[(CF_3CFHCF_2SO_2)_2N]^-$; and F^-.

In another embodiment, ionic liquids useful in the invention comprise a *Group A Cation* as defined above; and a *Group B Anion* as defined above.

In another embodiment, ionic liquids useful in the invention comprise *Group A Cation* as defined above, wherein at least one member selected from R, R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8, R^9, R^{10}, R^{11}, R^{12}, R^{13} and R^{14} comprises one or more fluorines; and an anion selected from *Group A Anions*, as defined above. In a preferred embodiment the ionic liquids useful in the invention consists essentially of *Group A Cation* as defined above, wherein at least one member selected from R, R^1, R^2, R^3, R^4, R^5,

R^6, R^7, R^8, R^9, R^{10}, R^{11}, R^{12}, R^{13} and R^{14} comprises one or more fluorines; and an anion selected from *Group A Anions*, as defined above.

In another embodiment, ionic liquids useful in the invention comprise *Group A Cation* as defined above, wherein at least one member selected from R, R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8, R^9, R^{10}, R^{11}, R^{12}, R^{13} and R^{14} comprises one or more fluorines; and an anion comprises a *Group B Anion*, as defined above.

In another embodiment, preferred ionic liquids useful for the invention comprise an imidazolium as the cation, and an anion selected from the group consisting of *Group B Anions*, as defined above, and $[CH_3OSO_3]^-$. In a preferred embodiment, the ionic liquids useful for the invention consist essentially of an imidazolium as the cation, and an anion selected from the group consisting of *Group B Anions*, as defined above, and $[CH_3OSO_3]^-$.

In another embodiment, preferred ionic liquids useful for the invention comprise1-butyl-3-methylimidazolium as the cation, and an anion selected from the group consisting of *Group B Anions*, as defined above, and $[CH_3OSO_3]^-$.

In another embodiment, preferred ionic liquids useful for the invention comprise 1-ethyl-3-methylimidazolium as the cation, and an anion selected from the group consisting of *Group B Anions*, as defined above, and $[CH_3OSO_3]^-$.

In another embodiment, preferred ionic liquids useful for the invention comprise 1-ethyl-3-methylimidazolium as the cation, and $[(CF_3CF_2SO_2)_2N]^-$, $[PF_6]^-$, or $[HCF_2CF_2SO_3]^-$ as the anion.

In another embodiment, preferred ionic liquids useful for the invention comprise 1,3-dimethylimidazolium as the cation, and an anion selected from the group consisting of *Group B Anions*, as defined above, and $[CH_3OSO_3]^-$.

In another embodiment, preferred ionic liquids useful in the invention comprise a *Group A Cation* as defined above; and the anion is

$[CH_3CO_2]^-$. More preferred ionic liquids within this group are those wherein the cation is an ammonium cation. In a preferred embodiment, ionic liquids useful in the invention consist essentially of an ammonium cation; and the anion is $[CH_3CO_2]^-$. An especially preferred ionic liquid is wherein the cation is N,N-dimethylammonium ethanol.

Mixtures of ionic liquids may also be useful for mixing with ammonia for use in absorption cooling cycles, for storage of ammonia.

A useful method for characterization of the ionic liquids useful in the invention is the determination of viscosity using a capillary viscometer (Cannon-Manning semi-micro viscometer) over a temperature range (283.15 to 373.15 K) as disclosed in "Standard Test Method for Kinematic Viscosity of Transparent and Opaque Liquids and the Calculation of Dynamic Viscosity", ASTM method D445-88. Preferably the ionic liquid useful in the invention has a viscosity, as measured by ASTM method D445-88 method, at 25 °C, of less than 100 centipoise (cp). The lower the viscosity of the ionic liquid, the lower the pumping power required to move a composition through an absorption cycle. Lower pumping power increases the overall efficiency of an absorption cycle. The calculated coefficient of performance (COP), as described in the examples, does not factor-in pumping power requirements. Table A lists the viscosity of several ionic fluids useful in the invention.

TABLE A

Viscosity of ionic fluids at 25 °C (cp)

Name	cp
1-butyl-3-methylimidazolium hexfluorophosphate	351
1-ethyl-3-methylimidazolium bis(pentafluoroethylsulfonyl)imide	85
3-methyl-1-propylimidazolium bis(trifluoromethylsulfonyl)imide	60
1-hexyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate	92
1,2-dimethyl-3-propylimidazolium tris(trifluoromethylsulfonyl)methide	636
1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	31
1-ethyl-3-methylimidazolium acetate	93
1-butyl-3-methylimidazolium 1,1,2,3,3,3-hexafluoropropanesulfonate	267
1-butyl-3-methylimidazolium 1,1,2-trifluoro-2-(perfluoroethoxy)ethanesulfonate	311
1-butyl-3-methylimidazolium 1,1,2-trifluoro-2-(trifluoromethoxy)ethanesulfonate	217
tetradecyl(trihexyl)phosphonium 1,1,2,-trifluoro-2-(perfluoroethoxy)ethanesulfonate	448
tributyl(tetradecyl)phosphonium 1,1,2,3,3,3-hexafluoropropanesulfonate	774
1-butyl-3-methylimidazolium tetrafluoroborate	122
1-butyl-3-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide	80
1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	47
1-butyl-3-methyljimidazolium 1,1,2,2-tetrafluoroethanesulfonate	146
1-butyl-3-methyljimidazolium dicyanamide	< 100
1-ethyl-3-methylimidazolium tetrafluoroborate	< 100
1-butyl-1-methylpyrrolidinium dicyanamide	< 100
1-ethyl-3-methylimidazolium thiocyanate	< 100
1-butyl-3-methylimidazolium tricyanomethide	< 100
N-butyl-3-methylpyridinium dicyanamide	< 100

The compositions comprising ammonia and ionic liquid can be prepared adding a weighed amount of ionic fluid to a sealable vessel, followed by applying a vacuum, with heating if so desired, to remove any residual water. The vessel can be tared and then ammonia gas added. The vessel is sealed and the mixture equilibrated with occasional agitation to provide a solution of ammonia in the ionic liquid.

The ammonia solutions can be used as a storage medium for anhydrous ammonia. Heating the ammonia- ionic liquid mixture is sufficient to drive the ammonia into the vapor phase, leaving behind the ionic liquid that has substantially no measurable vapor pressure. The ammonia- ionic liquid composition can be heated to about 200 °C, or about 150 °C, or preferably about 100 °C, or less, to liberate the ammonia from solution.

The compositions are also useful in absorption cycles for heating or cooling. An embodiment of the invention is an absorption cycle comprising a composition comprising ammonia and at least one ionic liquid wherein the composition comprises about 1 to about 99 mole % of ammonia over a temperature range from about -40 to about 130 °C at a pressure from about 1 to about 110 bar. A schematic diagram for a simple absorption cycle is shown in Figure 1. The system is composed of condenser and evaporator units with an expansion valve similar to an ordinary vapor compression cycle, but an absorber-generator solution circuit replaces the compressor. The circuit maybe composed of an absorber, a generator, a heat exchanger, a pressure control device and a pump for circulating the solution.

One embodiment is an absorption cycle wherein the ionic liquid comprises a *Group A Cation* as defined above; and a *Group A Anions* as defined above.

In another embodiment the absorption cycle comprises an absorber side having an exit, and a generator side having an exit, wherein the absorber side has a concentration of ionic liquid at the exit of greater than about 70 % by weight of said composition; and the generator side has a concentration of ionic liquid at the exit of greater than about 80 % by weight of said composition. In this embodiment a preferred ionic liquid comprises a N,N-dimethylammonium ethanol cation.

In another embodiment, in the absorption cycle, the absorber side has a concentration of ionic liquid at the exit of greater than about 80 % by weight of said composition; and the generator side has a concentration of ionic liquid at the exit of greater than about 90 % by weight of said composition. In this embodiment a preferred ionic liquid comprises an imidazolium cation.

The starting volumes of the ionic and liquid and ammonia will depend on the specific system components being used in the absorption cycle.

In order to understand the absorption cycle and to evaluate the cycle performance, thermodynamic property charts such as temperature-pressure-concentration (*TPX*) and enthalpy-temperature (*HT*) diagrams are required. These charts correspond to the familiar *PH* (pressure-enthalpy) or *TS* (temperature-entropy) diagram in the vapor compression cycle analysis. However, the use of these charts may not be as straightforward as vapor compression with a compressor, where the compression process is theoretically a single isentropic path, while the absorption cycle employs the so-called generator-absorber solution circuit, and several thermodynamic processes are involved.

The *PH* or *TS* diagram in the vapor compression cycle is constructed using equations of state (EOS), and the cycle performance and all thermodynamic properties can be calculated according to the discussion and equations described in Shiflett et al, US 2006/0197053 A1. The results of these calculations for several compositions of the invention are listed in Table 9 (Example 9). The well-known refrigerant-absorbent pair, NH_3/H_2O also has been calculated and is for comparison. In the case of NH_3/H_2O, the absorbent H_2O has a non-negligible vapor pressure at the generator exit, and in practical applications a rectifier (distillation) unit is required in order to separate the refrigerant from absorbent water. The effect of vapor pressure and extra power requirement due to the rectifier have been ignored; thus, the calculated *COP* is over-estimated for the present performance comparison. As the COP values indicate, several compositions have properties similar to the convention ammonia-water absorption cycle.

Preferred compositions for absorption cycles and storage processes have about 5 mol % to about 95 mol % ammonia; about 10 mol % to about 95 mol % ammonia; and about 25 mol % to about 85 mol % ammonia.

EXAMPLES

General Methods and Materials

High purity, anhydrous ammonia (purity ≥99.999 %, semiconductor grade, CAS no. 2664-41-7) was obtained from MG Industries (Philadelphia, PA). The following ionic liquids were used in the examples: 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6], assay ≥ 96 %, CAS no. 174501-64-5), 1-hexyl-3-methylimidazolium chloride ([hmim][Cl], assay ≥97 %, CAS no. 171058-17-6), 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([emim][Tf_2N], assay ≥ 97 %, CAS no. 174899-82-2), 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF_4], assay ≥97 %, CAS no. 174501-65-6), 1-ethyl-3-methylimidazolium acetate ([emim][CH_3COO], assay ≥90 %, CAS no. 143314-17-4), 1-ethyl-3-methylimidazolium ethylsulfate ([emim][$EtOSO_3$], assay ≥95 %, CAS no. 343573-75-5), and 1-ethyl-3-methylimidazolium thiocyanate ([emim][SCN], assay ≥95 %, CAS no. 331717-63-6). They were obtained from Fluka (Buchs, Switzerland) also distributed by Sigma-Aldrich in the United States. The N,N-dimethylethanolammonium ethanoate (also called acetate, assay ≥99 %) was obtained from Bioniqs (York, England).

All of the ionic liquid samples were dried and degassed, with the exception of N,N-dimethylethanolammonium ethanoate, by placing the samples in borosilicate glass tubes and applying a course vacuum with a diaphragm pump (Pfeiffer, model MVP055-3) for about 3 h. The samples were then dried at a pressure of about 4 x 10^{-7} kPa while simultaneously heating and stirring the ionic liquids at a temperature of about 348 K for 48 h.

The syntheses of non-commercially available anions (potassium 1,1,2,2-tetrafluoroethanesulfonate, potassium-1,1,2-trifluoro-2-(perfluoroethoxy)ethanesulfonate, potassium-1,1,2-trifluoro-2-(trifluoromethoxy)ethanesulfonate, and sodium 1,1,2,3,3,3-hexafluoropropanesulfonate) and ionic liquids (1-butyl-2,3-dimethylimidazolium 1,1,2,2-tetrafluoroethanesulfonate, 1-butyl-methylimidazolium 1,1,2,2-tetrafluoroethanesulfonate, 1-ethyl-3-methylimidazolium 1,1,2,2-tetrafluoroethane sulfonate, 1-ethyl-3-methylimidazolium 1,1,2,3,3,3-hexafluoropropanesulfonate, 1-hexyl-3-methylimidazolium 1,1,2,2-tetrafluoroethanesulfonate, 1-dodecyl-3-methylimidazolium 1,1,2,2-tetrafluoroethanesulfonate, -hexadecyl-3-methylimidazolium 1,1,2,2-tetrafluoroethanesulfonate, 1-octadecyl-3-methylimidazolium 1,1,2,2-tetrafluoroethaneulfonate, 1-propyl-3-(1,1,2,2-TFES) imidazolium 1,1,2,2-tetrafluoroethanesulfonate, 1-butyl-3-methylimidazolium 1,1,2,3,3,3-hexafluoropropanesulfonate, 1-butyl-3-methylimidazolium 1,1,2-trifluoro-2-(trifluoromethoxy)ethanesulfonate, 1-butyl-3-methylimidazolium 1,1,2-trifluoro-2-(perfluoroethoxy)ethanesulfonate, tetradecyl(tri-n-butyl)phosphonium 1,1,2,3,3,3-hexafluoropropanesulfonate, tetradecyl(tri-n-hexyl)phosphonium 1,1,2-trifluoro-2-(perfluoroethoxy)ethanesulfonate, tetradecyl(tri-n-hexyl)phosphonium 1,1,2-trifluoro-2-(trifluoromethoxy)ethanesulfonate, 1-ethyl-3-methylimidazolium 1,1,2,2-tetrafluoro-2-(pentafluoroethoxy)sulfonate, and tetrabutylphosphonium 1,1,2-trifluoro-2-(perfluoroethoxy)ethanesulfonate) are described Shiflett, et al. US 2006/0197053 A1.

The following method was employed to determine if mixtures of ammonia and ionic liquids were soluble. Six static phase equilibrium cells were constructed as shown in Figure 2. Each cell was made using SWAGELOK fittings, two SWAGELOK ball valves (SS-426S4), stainless steel tubing, and a pressure transducer (Dwyer Instruments, model 682-5). The internal volume of each cell was calculated by measuring the mass of methanol required to completely fill the cell. Knowing the density of methanol at the fill temperature, the volume was calculated. The internal volume of each cell (V_T) was in the range of about 13.4 to 15.3 ± 0.1 cm^3. The lower half (part A) of the cell as shown in Figure 2 was used to prepare the NH_3 / ionic liquid mixtures. Ionic liquid was loaded by mass (0.5 to 2 g) and weighed on an analytical balance, with a resolution of 0.1 mg, inside a nitrogen purged dry box. A syringe fitted with a stainless steel needle (Popper & Son, Inc. model 7937, 18 x 152.4 mm pipetting needle) which fit through the open ball valve (valve 1) was used to fill the cell with ionic liquid. The ball valve was closed and the cell was removed from the dry box. The cell was connected to a diaphragm pump to remove residual nitrogen and weighed again to obtain the initial ionic liquid mass.

The NH_3 gas was loaded by mass (0.02 to 0.8 g) from a high pressure gas cylinder. The NH_3 gas pressure was regulated to about 500 kPa with a two-stage gas regulator (Matheson Gas Products). The sample tubing between the gas regulator and cell was evacuated prior to filling with NH_3 gas. The cell was placed on an analytical balance and gas was slowly added until the desired mass of NH_3 was obtained. For samples that required more than 0.1 g of NH_3, the cell was cooled in dry ice to condense NH_3 gas inside the cell. To obtain the final mass of NH_3 added to the cell, the sample valve (valve 1) was closed and the cell was disconnected from the gas cylinder, and weighed on the analytical balance. The upper half of the cell (part B) which included the pressure transducer was connected with a Swagelok fitting to the lower half (part A). The interior volume of part B was evacuated through valve 2 using the diaphragm pump. Valve 2 was closed and capped and valve 1 was opened. The six sample cells were placed inside a tank and the temperature was controlled with an external temperature bath, either a water bath (VWR International, Model 1160S), or an oil bath (Tamson Instruments TV4000LT hot oil bath), circulating through a copper coil submerged in the tank. The temperature was initially set at about 283 K. The sample cells were vigorously shaken to assist with mixing prior to being immersed in the tank. The water or oil level in the tank was adjusted such that the entire cell was under fluid including the bottom 2 cm of the pressure transducer. The cells were rocked back and forth in the tank to enhance mixing. The pressure was recorded every hour until no change in pressure was measured. To ensure the samples were at equilibrium and properly mixed, the cells were momentarily removed from the tank and again vigorously shaken. The cells were placed back in the tank and the process was repeated until no change in pressure was measured. In all cases the cells reached equilibrium in 4 to 8 hours. The process was repeated at higher temperatures of about 298 K, 323 K and 348 K. Additional measurements at 355 K were made for [bmim][PF_6] and [bmim][BF_4] examples, and 373 K measurements were made for ([emim][$EtOSO_3$], [emim][SCN], and N,N-dimethylethanolammonium ethanoate.

The Dwyer pressure transducers were calibrated against a Paroscientific Model 760-6K pressure transducer (range 0 to 41.5 MPa, serial no. 62724). This instrument is a NIST certified secondary pressure standard with a traceable accuracy of 0.008 % of full scale (FS). Also, due to the fact that the pressure transducers were submerged in the water or oil bath, the pressure calibration was also corrected for temperature effects. The Fluke thermometer was calibrated using a standard platinum resistance thermometer (SPRT model 5699, Hart Scientific, range 73 to 933 K) and readout (Blackstack model 1560 with SPRT module 2560). The Blackstack instrument and SPRT are also a certified secondary temperature standard with a NIST traceable accuracy to ± 0.005 K. The temperature and pressure uncertainties were ± 0.1 K and ± 0.13 % full scale (0 – 7 MPa). Liquid phase NH_3 mole fractions are calculated based on the prepared feed composition and the volume of the sample container, and the detailed method is described in the following subsection.

Given that a mixture of NH_3 + RTIL was prepared in a container (volume V_T) with a mole of NH_3 (M_1) and a mole of RTIL (M_2), the following principles were used in order to find out a mole fraction (x_1) of NH_3 in the liquid phase at a given system temperature and pressure (i.e., equilibrium T and P).

The present method is based on the following liquid molar volume formula for an *N*-component system:

$$\overline{V_L} = \frac{1}{2}\sum_{i,j=1}^{N}\left(V_1^0 + V_2^0\right)\left(1 - m_{ij}\right)x_i x_j\,,\quad m_{ii} = 0 \text{ and } m_{ij} = m_{ji}\,.$$

(1)

This is the same form as the mixing rule for the volume parameter (*b*) in the common cubic EOS with the binary interaction parameter. In the case of a binary system (*N* = 2),

$$\overline{V_L} = V_1^0 x_1 + V_2^0 x_2 - m_{12}\left(V_1^0 + V_2^0\right)x_1 x_2\,,$$

(2)

where $x_1 = \dfrac{M_{L1}}{M_{L1} + M_2}$, and $x_2 = 1 - x_1$,

(3)

(M_{L1} is a NH_3 mole in the liquid phase).

It should be mentioned here that eqs 1 and 2 are *exact* when m_{12} = 0 (or m_{ij} = 0); that is when the excess volume is zero.

A physical liquid volume, V_L, is given by:

$$V_L = \left(M_{L1} + M_2\right)\overline{V_L}\,.$$

(4)

Then, a mass balance equation provides, when the gas phase is pure NH_3:

$$M_1 = D_g\left(V_T - V_L\right) + M_{L1}\,.$$

(5)

Inserting eq 4 into eq 5 using eqs 2 and 3, and then rearranging the equation, we can obtain the following quadratic equation for M_{L1}:

$$AM_{L1}^2 + BM_{L1} + C = 0\,,$$

(6)

and the solution is:

$$M_{L1} = \frac{-B + \sqrt{B^2 - 4AC}}{2A}$$

(7)

where *A*, *B*, and *C* are given by:

$$A \equiv 1 - D_g V_1^0$$

(8)

$$B \equiv D_g \{V_T - M_2(V_1^0 + V_2^0)(1 - m_{12})\} + M_2 - M_1$$

(9)

$$C \equiv D_g M_2 (V_T - M_2 V_2^0) - M_1 M_2,$$

(10)

with the following notations,

D_g = NH3 gaseous molar density (mol/cc) at the system *T* and *P*,

V_1^0 = NH3 saturated liquid molar volume (cc/mol) at the system *T*,

V_2^0 = RTIL saturated liquid molar volume (cc/mol) at the system *T*,

m_{12} = a binary interaction parameter for the mixture volume.

D_g and V_1^0 are calculated with an accurate equation of state such as that in REFPROP (NIST reference), while V_2^0 is obtained from the liquid density and molecular weight of RTIL. The liquid density (ρ_2) has been fitted to experimental data with a linear *T* function.

$$\rho_2 = a_0 + a_1 T$$

(11)

Then, by setting a proper value in m_{12}, the solution of eq 7 gives x_1, from eq 3. Although this information about x_1 is sufficient for the present purpose, it is instructive to show the following relations. The liquid volume, eq 4 as well as liquid (molar) quality factor α can also be calculated:

$$\alpha = \frac{M_{L1} + M_2}{M_1 + M_2}.$$

(12)

Also, the excess molar volume, $\overline{V}^E$, is given by $\overline{V}^E = -m_{12}\left(V_1^0 + V_2^0\right)x_1 x_2$ based on eq 2. When an excess molar volume is 10 % of the total molar volume at a 50/50 mole % mixture, m_{12} will be ± 0.2. Then, if we use m_{12} = 0, instead of $m_{12} = \pm 0.2$, the maximum error in x_1 is about 0.3 mole % at the highest T and the highest x_1, and typical errors are equal to or less than 0.1 mole %. In the present study, we estimated m_{12} to be 0.2, based on the excess molar volume measurement for NH_3 (about 47-50 mole %) and [emim][Tf_2N] mixtures at 298 K; $\overline{V}^E$ = -15 ± 5 cm^3 mol^{-1}.

EXAMPLE 1

Experimental solubility (*TPx*) data for ammonia in [bmim][PF_6] are summarized in Table 1.

TABLE 1

NH_3 (1) + [bmim][PF_6] (2)		
T / K	*P* / MPa	100x_1 / mol %
283.4	0.138	37.1 ± 1.4
283.4	0.194	47.1 ± 1.0
283.4	0.259	58.4 ± 0.5
283.4	0.517	86.2 ± 0.4
298.0	0.174	35.1 ± 3.0
298.0	0.272	43.5 ± 1.7
298.0	0.362	55.7 ± 1.1
298.0	0.609	74.0 ± 0.6
298.0	0.796	85.4 ± 0.4
324.6	0.274	29.2 ± 2.5
324.6	0.423	38.9 ± 1.5
324.6	0.583	49.2 ± 1.0
324.6	1.083	68.1 ± 0.6
324.6	1.567	82.8 ± 0.4
347.2	0.345	25.3 ± 2.1
347.2	0.546	33.4 ± 1.3
347.2	0.772	43.1 ± 0.9
347.2	1.492	61.7 ± 0.5
347.2	2.385	79.1 ± 0.4
355.8	0.371	23.9 ± 2.0
355.8	0.585	31.8 ± 1.3
355.8	0.835	41.1 ± 0.9
355.8	1.623	59.6 ± 0.5
355.8	2.700	77.3 ± 0.4
298.6	0.184	34.4 ± 2.9
298.6	0.275	43.4 ± 1.7
298.6	0.372	55.4 ± 1.1
298.6	0.635	73.7 ± 0.6
298.6	0.822	85.3 ± 0.4

EXAMPLE 2

Experimental solubility (*TPx*) data for ammonia in [bmim][BF_4] are summarized in Table 2.

TABLE 2

NH_3 (1) + [bmim][BF_4] (2)		
T / K	P / MPa	100x_1 / mol %
282.2	0.091	20.1 ± 16.5
282.2	0.134	30.3 ± 6.8
282.2	0.187	40.4 ± 3.4
282.2	0.290	58.2 ± 1.4
282.2	0.396	70.9 ± 0.8
282.2	0.497	84.4 ± 0.4
298.4	0.128	17.3 ± 14.2
298.4	0.196	26.6 ± 6.0
298.4	0.272	36.7 ± 3.1
298.4	0.437	54.8 ± 1.3
298.4	0.613	68.3 ± 0.8
298.4	0.818	83.3 ± 0.4
323.6	0.196	12.2 ± 10.1
323.6	0.308	19.9 ± 4.5
323.6	0.432	29.2 ± 2.5
323.6	0.713	47.3 ± 1.2
323.6	1.049	62.2 ± 0.7
323.6	1.535	80.5 ± 0.4
347.5	0.257	8.0 ± 6.6
347.5	0.409	14.0 ± 3.2
347.5	0.582	21.9 ± 1.9
347.5	0.977	39.1 ± 1.0
347.5	1.493	54.2 ± 0.7
347.5	2.375	75.9 ± 0.4
355.1	0.275	6.8 ± 5.6
355.1	0.445	11.7 ± 2.7
355.1	0.629	19.5 ± 1.7
355.1	1.058	36.4 ± 1.0
355.1	1.626	51.6 ± 0.6
355.1	2.570	74.9 ± 0.4
298.6	0.127	17.4 ± 14.3
298.6	0.196	26.7 ± 6.0
298.6	0.271	36.7 ± 3.1
298.6	0.437	54.8 ± 1.3
298.6	0.616	68.3 ± 0.8
298.6	0.807	83.4 ± 0.4

EXAMPLE 3

Experimental solubility (*TPx*) data for ammonia in [emim][Tf_2N] are summarized in Table 3.

TABLE 3

NH_3 (1) + [emim][Tf_2N] (2)		
T / K	P / MPa	$100x_1$ / mol %
283.3	0.114	22.0 ± 18.1
283.3	0.222	50.4 ± 4.3
283.3	0.330	63.4 ± 2.3
283.3	0.479	81.1 ± 1.0
283.3	0.606	93.1 ± 0.5
283.3	0.618	94.8 ± 0.4
299.4	0.136	17.1 ± 14.2
299.4	0.287	43.0 ± 3.6
299.4	0.434	56.8 ± 2.1
299.4	0.698	76.8 ± 1.0
299.4	0.969	92.1 ± 0.5
299.4	0.994	94.3 ± 0.4
323.4	0.171	8.9 ± 7.5
323.4	0.379	30.5 ± 2.6
323.4	0.582	44.4 ± 1.6
323.4	1.019	67.3 ± 0.9
323.4	1.711	88.8 ± 0.5
323.4	1.840	92.6 ± 0.4
347.6	0.196	4.5 ± 4.1
347.6	0.457	19.8 ± 1.7
347.6	0.709	32.3 ± 1.2
347.6	1.285	55.8 ± 0.8
347.6	2.488	81.8 ± 0.5
347.6	2.860	88.6 ± 0.4
298.4	0.145	13.7 ± 11.4
298.4	0.288	42.7 ± 3.6
298.4	0.427	57.3 ± 2.1
298.4	0.683	77.2 ± 1.0
298.4	0.940	92.2 ± 0.5
298.4	0.958	94.4 ± 0.4

EXAMPLE 4

Experimental solubility (*TPx*) data for ammonia in [hmim][Cl] are summarized in Table 4.

TABLE 4

NH_3 (1) + [hmim][Cl] (2)		
T / K	*P* / MPa	100x_1 / mol %
283.1	0.044	9.5 ± 8.2
283.1	0.094	25.4 ± 3.5
283.1	0.151	36.3 ± 1.9
283.1	0.252	56.2 ± 1.0
283.1	0.415	74.5 ± 0.5
283.1	0.511	83.7 ± 0.4
297.8	0.059	8.6 ± 7.3
297.8	0.133	23.1 ± 3.2
297.8	0.216	33.7 ± 1.8
297.8	0.377	53.7 ± 1.0
297.8	0.647	72.8 ± 0.5
297.8	0.816	82.8 ± 0.4
324.3	0.103	6.0 ± 5.1
324.3	0.198	19.4 ± 2.7
324.3	0.327	29.4 ± 1.6
324.3	0.633	47.9 ± 0.9
324.3	1.186	68.1 ± 0.5
324.3	1.600	79.9 ± 0.4
347.9	0.102	6.5 ± 5.5
347.9	0.246	17.2 ± 2.4
347.9	0.436	25.3 ± 1.3
347.9	0.883	41.9 ± 0.8
347.9	1.727	62.4 ± 0.5
347.9	2.490	75.6 ± 0.4
298.1	0.053	9.0 ± 7.7
298.1	0.111	24.6 ± 3.4
298.1	0.190	34.9 ± 1.8
298.1	0.373	53.6 ± 1.0
298.1	0.649	72.8 ± 0.5
298.1	0.819	82.8 ± 0.4

EXAMPLE 5

Experimental solubility (*TPx*) data for ammonia in [emim][CH_3COO] are summarized in Table 5.

TABLE 5

NH_3 (1) + [emim][CH_3COO] (2)		
T / K	P / MPa	$100x_1$ / mol %
282.5	0.321	62.4 ± 1.2
282.5	0.435	74.9 ± 0.8
282.5	0.488	80.2 ± 0.4
282.5	0.525	83.4 ± 0.4
282.5	0.535	84.7 ± 0.4
282.5	0.550	87.7 ± 0.4
298.3	0.470	59.9 ± 2.0
298.3	0.667	73.0 ± 1.2
298.3	0.765	78.8 ± 0.8
298.3	0.820	82.5 ± 0.8
298.3	0.850	83.9 ± 0.8
298.3	0.898	87.1 ± 0.4
324.5	0.792	53.8 ± 4.0
324.5	1.178	68.3 ± 3.2
324.5	1.420	75.0 ± 2.4
324.5	1.568	79.5 ± 1.6
324.5	1.633	81.4 ± 1.6
324.5	1.774	85.2 ± 1.2
348.5	1.098	47.3 ± 6.8
348.5	1.710	62.0 ± 6.0
348.5	2.134	69.4 ± 5.2
348.5	2.423	75.1 ± 4.0
348.5	2.569	77.3 ± 3.6
348.5	2.891	81.9 ± 2.8
298.2	0.463	60.1 ± 2.0
298.2	0.662	73.1 ± 1.2
298.2	0.759	78.9 ± 0.8
298.2	0.818	82.5 ± 0.8
298.2	0.845	83.9 ± 0.8
298.2	0.896	87.1 ± 0.4

EXAMPLE 6

Experimental solubility (*TPx*) data for ammonia in [emim][EtOSO$_3$] are summarized in Table 6.

TABLE 6

NH_3 (1) + [emim][EtOSO$_3$] (2)		
T / K	P / MPa	$100x_1$ / mol %
282.7	0.287	53.6 ± 0.9
282.7	0.427	70.7 ± 0.6
282.7	0.517	80.5 ± 0.3
282.7	0.544	83.9 ± 0.2
282.7	0.586	87.5 ± 0.1
297.6	0.418	51.8 ± 1.4
297.6	0.651	69.4 ± 0.9
297.6	0.802	79.8 ± 0.5
297.6	0.855	83.3 ± 0.4
297.6	0.916	87.1 ± 0.2
322.3	0.706	47.7 ± 2.6
322.3	1.166	66.1 ± 1.9
322.3	1.510	77.8 ± 1.2
322.3	1.641	81.8 ± 0.9
322.3	1.771	86.2 ± 0.5
347.5	1.051	42.4 ± 4.4
347.5	1.819	61.3 ± 3.8
347.5	2.500	74.4 ± 2.6
347.5	2.790	79.0 ± 2.1
347.5	3.091	84.4 ± 1.3
372.3	2.461	56.2 ± 6.2
372.3	3.593	69.7 ± 5.1
372.3	4.118	74.7 ± 4.5
372.3	4.777	81.2 ± 3.2
298.1	0.421	51.8 ± 1.4
298.1	0.653	69.4 ± 0.9
298.1	0.812	79.8 ± 0.5
298.1	0.869	83.3 ± 0.4
298.1	0.933	87.1 ± 0.2

EXAMPLE 7

Experimental solubility (*TPx*) data for ammonia in [emim][SCN] are summarized in Table 7.

TABLE 7

NH_3 (1) + [emim][SCN] (2)		
T / K	*P* / MPa	100x_1 / mol %
283.2	0.244	45.1 ± 0.7
283.2	0.364	65.2 ± 0.5
283.2	0.447	73.1 ± 0.4
283.2	0.502	78.6 ± 0.2
283.2	0.547	81.9 ± 0.2
283.2	0.590	87.6 ± 0.1
298.1	0.307	44.4 ± 0.9
298.1	0.536	64.2 ± 0.7
298.1	0.672	72.3 ± 0.5
298.1	0.747	78.1 ± 0.4
298.1	0.815	81.5 ± 0.3
298.1	0.911	87.4 ± 0.1
322.6	0.535	41.6 ± 1.6
322.6	0.961	61.8 ± 1.4
322.6	1.241	70.4 ± 1.1
322.6	1.420	76.6 ± 0.8
322.6	1.562	80.4 ± 0.6
322.6	1.777	86.9 ± 0.3
348.0	0.840	37.8 ± 2.7
348.0	1.553	58.1 ± 2.6
348.0	2.045	67.3 ± 2.2
348.0	2.419	74.1 ± 1.7
348.0	2.711	78.4 ± 1.4
348.0	3.174	85.8 ± 0.8
372.8	1.149	34.0 ± 4.4
372.8	2.144	54.2 ± 4.1
372.8	2.958	63.3 ± 3.5
372.8	3.576	70.8 ± 3.2
372.8	4.120	75.4 ± 2.8
372.8	5.007	83.9 ± 1.7
298.1	0.314	44.3 ± 0.9
298.1	0.540	64.2 ± 0.7
298.1	0.666	72.4 ± 0.5
298.1	0.772	78.0 ± 0.4
298.1	0.831	81.5 ± 0.3
298.1	0.930	87.4 ± 0.1

EXAMPLE 8

Experimental solubility (*TPx*) data for ammonia in N,N-dimethylethanolammonium ethanoate $[(CH_3)_2NHCH_2CH_2OH][CH_3COO]$ are summarized in Table 8.

TABLE 8

NH_3 (1) + $[(CH_3)_2NHCH_2CH_2OH][CH_3COO]$ (2)		
T / K	P / MPa	$100x_1$ / mol %
283.2	0.136	47.7 ± 3.7
283.2	0.198	62.0 ± 2.4
283.2	0.288	71.6 ± 1.8
283.2	0.316	76.8 ± 1.2
283.2	0.415	81.9 ± 0.8
283.2	0.491	86.5 ± 0.5
298.1	0.163	47.5 ± 3.8
298.1	0.278	61.6 ± 2.4
298.1	0.431	71.3 ± 1.8
298.1	0.500	76.5 ± 1.2
298.1	0.641	81.6 ± 0.8
298.1	0.769	86.4 ± 0.5
322.7	0.277	46.6 ± 4.2
322.7	0.463	60.9 ± 2.3
322.7	0.786	70.4 ± 1.7
322.7	0.980	75.7 ± 1.1
322.7	1.250	80.9 ± 0.7
322.7	1.521	86.0 ± 0.5
348.0	0.433	45.4 ± 4.7
348.0	0.693	60.0 ± 3.1
348.0	1.335	69.1 ± 2.0
348.0	1.680	74.5 ± 1.3
348.0	2.164	79.9 ± 1.0
348.0	2.689	85.3 ± 0.6
372.8	1.994	67.5 ± 2.2
372.8	2.529	73.1 ± 1.3
372.8	3.305	78.5 ± 0.7
372.8	4.249	84.4 ± 0.5
298.1	0.401	71.4 ± 2.0
298.1	0.496	76.5 ± 1.2
298.1	0.637	81.6 ± 0.8
298.1	0.791	86.4 ± 0.5

EXAMPLE 9

Absorption cycle calculations were developed for compositions of invention using the computer code developed by Yokozeki in "Theoretical performances of various refrigerant-absorbent pairs in a vapor-absorption refrigeration cycle by the use of equations of state", 2005, Applied Energy, 80, 383-399. The detailed assumptions made in the cycle calculation are described in that reference, and in US 2006/0197053 A1, Shiflett, et al, specifically paragraphs 0063 through 0094. Proper binary interaction parameters for the equation of state have been determined using the present *PTx* data. Results of the present invention for the cycle performance are compared in Table 9, together with the well-known ammonia-water system. The energy efficient performance, also called coefficient of performance (COP), is explained in detail in the above references. The ammonia-RTIL COPs are somewhat lower than that of the ammonia-water system. However, in this calculation, the extra energy cost required for a rectifier unit required to condense water, which has a significant vapor pressure, was not considered in the ammonia-water case. Because the ionic liquids have no measurable vapor pressure, a rectifier is not required in the cycle. In actual applications, ammonia + ionic liquid pairs may compete with the cycle performance of the traditional absorption cycle using ammonia and water. An additional benefit is the reduced cost of cycle equipment because no rectifier for the absorbent is required.

Table 9 - Comparisons of Thermodynamic Absorption Cycle*).

Example No. - System (1)/(2)	f	x_{gen} (mass %)	x_{abs} (mass %)	COP
1 - NH_3/[bmim][PF_6]	17.27	94.5	89.0	0.575
2 - NH_3/[hmim][Cl]	14.26	93.9	87.3	0.525
3 - NH_3/[emim][Tf_2N]	24.57	96.3	92.4	0.589
4 - NH_3/[bmim][BF_4]	12.98	95.7	88.3	0.557
5 - NH_3/[emim][CH3COO]	12.55	92.3	85.0	0.573
6 - NH_3/[emim][EtOSO3]	17.55	95.2	89.8	0.485
7 - NH_3/[emim][SCN]	12.42	92.7	85.3	0.557
8 -NH_3/[$(CH_3)_2NHCH_2CH_2OH$][CH3COO]	7.60	84.1	73.1	0.612
Comparative Control - NH_3/Water	2.54	59.5	36.1	0.646

*)Cycle condition: T(generator)/T(condenser)/T(absorber)/T(evaporator) = 100/40/30/10 °C ; f: mass-flow-rate ratio (= solution / refrigerant); x_{gen}: absorbant mass % (ionic liquid mass %) at the generator exit; x_{abs}: absorbant mass % (ionic liquid mass %) at the absorber exit.

EXAMPLE 10

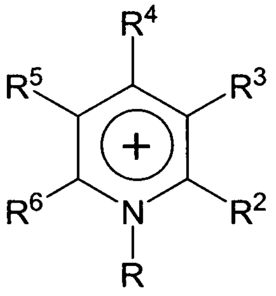
This example illustrates that ionic liquids can absorb large amounts of ammonia reversibly as a function of pressure. Figure 3 is a plot of the mole percent of ammonia absorbed into the ionic liquid [emim][Tf_2N]. At 298 K, the ionic liquid absorbs almost 10 mole percent at 80 kPa (0.08 MPa). This converts into a storage capacity of about 0.3 millimol per gram of ionic liquid, which is much less than the 25 to 40 millimol per gram of solid mentioned previously. However, if the temperature is lowered to 283 K the storage capacity increases to almost 20 mole percent at 80 kPa (0.08 bar) which is 0.6 millimol per gram of ionic liquid. Most importantly if the pressure is increased, then large amounts of ammonia can be stored in the ionic liquid. For example, at pressures of about 1 MPa over 90 mole percent ammonia can be stored in the ionic liquid which is about 25 millimol of ammonia per gram of ionic liquid. This compares well with the best solid adsorbents and most importantly the absorption/desorption process is completely reversible with no loss of capacity in the ionic liquid to store additional ammonia. Also, other ionic liquids with a lower molecular weight such as [emim][acetate] can reach even greater concentrations closer to 50 millimol of ammonia per gram of ionic liquid. Also, if the temperature is lowered to 283 K, pressures closer to 0.5 MPa (or 5 atm) can achieve the same ammonia storage capacities of 25 to 50 millimol ammonia per gram of ionic liquid. Finally, this example is merely illustrative. Other combinations of temperature and pressure (i.e. temperatures lower than 283 K) maybe possible to reach 25 to 50 millimol ammonia per gram of ionic liquid at even lower pressures such as 80 kPa.

CLAIMS

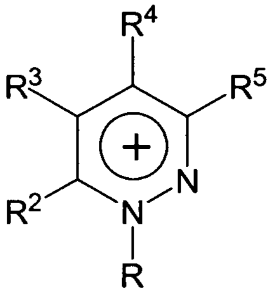
What is claimed is:

1. A composition comprising ammonia and at least one ionic liquid wherein the composition comprises about 1 to about 99 mole % of ammonia over a temperature range from about -40 to about 130 °C at a pressure from about 1 to about 110 bar.

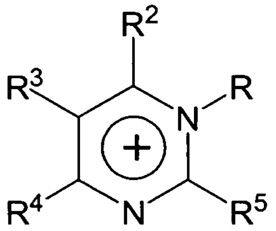
2. The composition of Claim 1 wherein said at least one ionic liquid has a cation selected from the group consisting of:



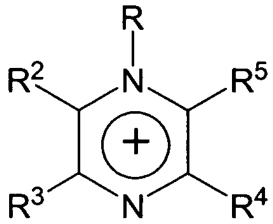
Pyridinium



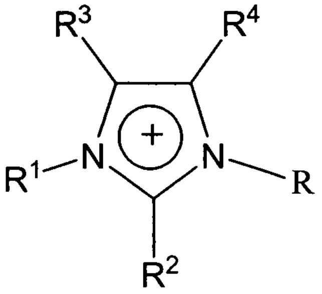
Pyridazinium



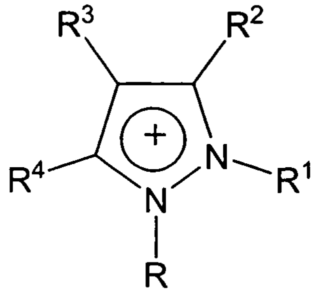
Pyrimidinium



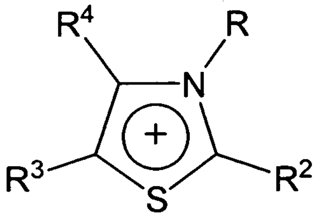
Pyrazinium



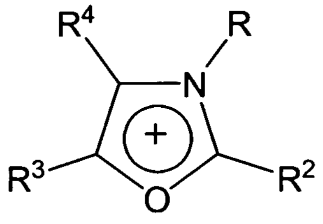
Imidazolium



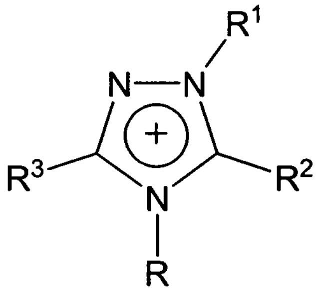
Pyrazolium



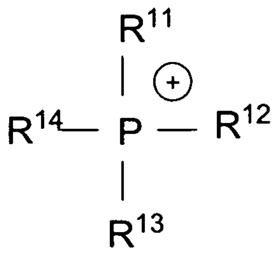
Thiazolium



Oxazolium



Triazolium



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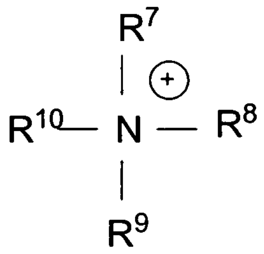


Phosphonium

Ammonium

wherein R, R^1, R^7, R^8, R^9, and R^{10} are independently selected from the group consisting of:

(i) hydrogen

(ii) -CH_3, -C_2H_5, or C_3 to C_{25} straight-chain, branched or cyclic alkane or alkene, optionally substituted with at least one member selected from the group consisting of Cl, Br, F, I, OH, NH_2 and SH;

(iii) $-CH_3$, $-C_2H_5$, or C_3 to C_{25} straight-chain, branched or cyclic alkane or alkene comprising one to three heteroatoms selected from the group consisting of O, N and S, and optionally substituted with at least one member selected from the group consisting of Cl, Br, F, I, OH, NH_2 and SH;

(iv) C_6 to C_{20} unsubstituted aryl, or C_3 to C_{25} unsubstituted heteroaryl having one to three heteroatoms independently selected from the group consisting of O, N and S; and

(v) C_6 to C_{25} substituted aryl, or C_3 to C_{25} substituted heteroaryl having one to three heteroatoms independently selected from the group consisting of O, N and S; and wherein said substituted aryl or substituted heteroaryl has one to three substituents independently selected from the group consisting of:

(1) $-CH_3$, $-C_2H_5$, or C_3 to C_{25} straight-chain, branched or cyclic alkane or alkene, optionally substituted with at least one member selected from the group consisting of Cl, Br, F I, OH, NH_2 and SH,

(2) OH,

(3) NH_2, and

(4) SH;

R^2, R^3, R^4, R^5, and R^6 are independently selected from R and a halogen; R^{11}, R^{12}, R^{13}, and R^{14} are independently selected from R with the proviso that R^{11}, R^{12}, R^{13}, and R^{14} are not hydrogen; and

wherein, optionally, at least two of R, R^1, R^2, R^3, R^4, R^5, $R^{6,}$ R^7, R^8, R^9, $R^{10,}$ R^{11}, R^{12}, R^{13},and R^{14} can together form a cyclic or bicyclic alkanyl or alkenyl group;

and,

an anion selected from the group consisting of $[CH_3CO_2]^-$, $[HSO_4]^-$, $[CH_3OSO_3]^-$, $[C_2H_5OSO_3]^-$, $[AlCl_4]^-$, $[CO_3]^{2-}$, $[HCO_3]^-$, $[NO_2]^-$, $[NO_3]^-$, $[SO_4]^{2-}$, $[PO_4]^{3-}$, $[HPO_4]^{2-}$, $[H_2PO_4]^-$, $[HSO_3]^-$, $[CuCl_2]^-$, Cl^-, Br^-, I^-, SCN^-, and a fluorinated anion.

3. The composition of claim 2 wherein at least one of R, R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8, R^9, R^{10}, R^{11}, R^{12}, R^{13}, and R^{14} comprises one or more fluorine(s).

4. The composition of claim 2 wherein said at least one ionic liquid comprises a fluorinated anion and the fluorinated anion is selected from the group consisting of $[BF_4]^-$, $[BF_3CF_3]^-$, $[BF_3C_2F_5]^-$, $[PF_6]^-$, $[PF_3(C_2F_5)_3]^-$, $[SbF_6]^-$, $[CF_3SO_3]^-$, $[HCF_2CF_2SO_3]^-$, $[CF_3HFCCF_2SO_3]^-$, $[HCClFCF_2SO_3]^-$, $[(CF_3SO_2)_2N]^-$, $[(CF_3CF_2SO_2)_2N]^-$, $[(CF_3SO_2)_3C]^-$, $[CF_3CO_2]^-$, $[CF_3OCFHCF_2SO_3]^-$, $[CF_3CF_2OCFHCF_2SO_3]^-$, $[CF_3CFHOCF_2CF_2SO_3]^-$, $[CF_2HCF_2OCF_2CF_2SO_3]^-$, $[CF_2ICF_2OCF_2CF_2SO_3]^-$, $[CF_3CF_2OCF_2CF_2SO_3]^-$, $[(CF_2HCF_2SO_2)_2N]^-$, $[(CF_3CFHCF_2SO_2)_2N]^-$, and F^-.

5. The composition of Claim 2 wherein the cation comprises imidazolium and the anion is selected from the group consisting of $[BF_4]^-$, $[BF_3CF_3]^-$, $[BF_3C_2F_5]^-$, $[PF_6]^-$, $[PF_3(C_2F_5)_3]^-$, $[SbF_6]^-$, $[CF_3SO_3]^-$, $[HCF_2CF_2SO_3]^-$, $[CF_3HFCCF_2SO_3]^-$, $[HCClFCF_2SO_3]^-$, $[(CF_3SO_2)_2N]^-$, $[(CF_3CF_2SO_2)_2N]^-$, $[(CF_3SO_2)_3C]^-$, $[CF_3CO_2]^-$, $[CF_3OCFHCF_2SO_3]^-$, $[CF_3CF_2OCFHCF_2SO_3]^-$, $[CF_3CFHOCF_2CF_2SO_3]^-$, $[CF_2HCF_2OCF_2CF_2SO_3]^-$, $[CF_2ICF_2OCF_2CF_2SO_3]^-$, $[CF_3CF_2OCF_2CF_2SO_3]^-$, $[(CF_2HCF_2SO_2)_2N]^-$, $[(CF_3CFHCF_2SO_2)_2N]^-$, and $[CH_3OSO_3]^-$.

6. The composition of Claim 5 wherein cation is 1-butyl-3-methylimidazolium.

7. The composition of Claim 5 wherein cation is 1-ethyl-3-methylimidazolium.

8. The composition of Claim 7 wherein the anion is selected from the group consisting of $[(CF_3CF_2SO_2)_2N]^-$, $[PF_6]^-$, and $[HCF_2CF_2SO_3]^-$.

9. The composition of Claim 5 wherein the cation comprises 1,3-dimethylimidazolium.

10. The composition of claim 2 wherein the anion is $[CH_3CO_2]^-$.

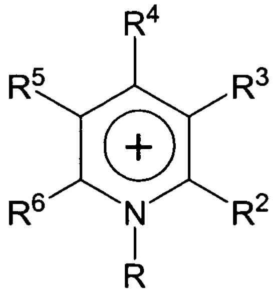
11. The composition of claim 10 wherein the cation is N,N-dimethylammonium ethanol.

12. The composition of claim 1 wherein the composition comprises about 5 to 95 mol % of ammonia.

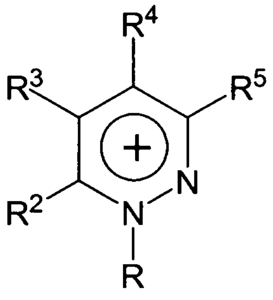
13. The composition of claim 1 wherein the ionic liquid has a viscosity at 25 °C of less than 100 cp.

14. An absorption cycle comprising a composition comprising ammonia and at least one ionic liquid wherein the composition comprises about 1 to about 99 mole % of ammonia over a temperature range from about -40 to about 130 °C at a pressure from about 1 to about 110 bar.

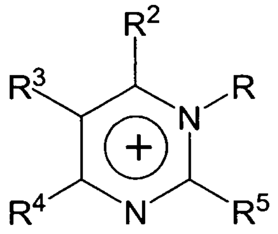
15. An absorption cycle of claim 14 wherein said at least one ionic liquid has a cation selected from the group consisting of:



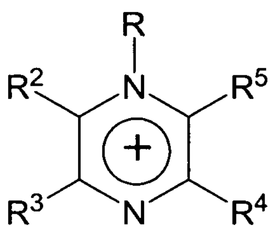
Pyridinium



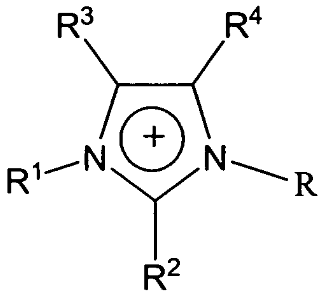
Pyridazinium



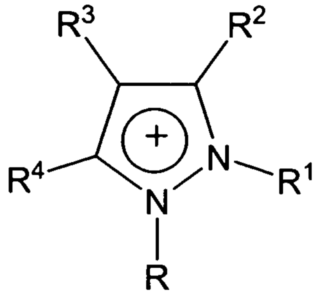
Pyrimidinium



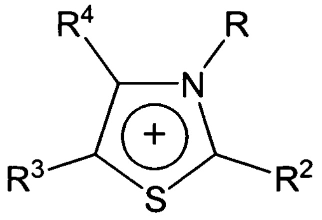
Pyrazinium



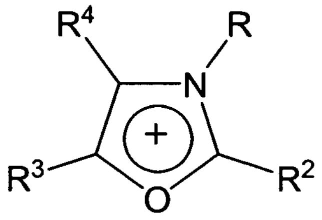
Imidazolium



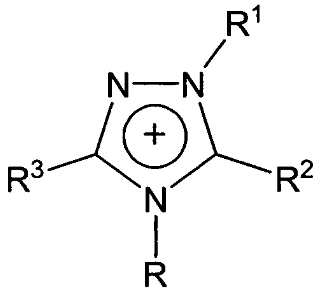
Pyrazolium



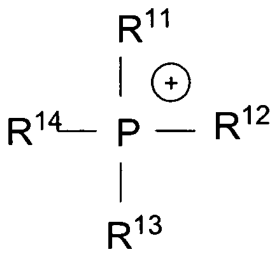
Thiazolium



Oxazolium

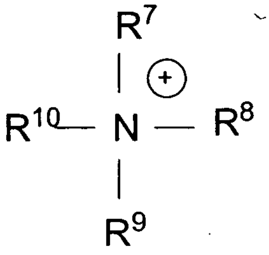


Triazolium



Phosphonium

and



Ammonium

wherein R, R^1, R^7, R^8, R^9, and R^{10} are independently selected from the group consisting of:

(i) Hydrogen

(ii) $-CH_3$, $-C_2H_5$, or C_3 to C_{25} straight-chain, branched or cyclic alkane or alkene, optionally substituted with at least one member selected from the group consisting of Cl, Br, F, I, OH, NH_2 and SH;

(iii) $-CH_3$, $-C_2H_5$, or C_3 to C_{25} straight-chain, branched or cyclic alkane or alkene comprising one to three heteroatoms selected from the group consisting of O, N and S, and optionally substituted with at least one member selected from the group consisting of Cl, Br, F, I, OH, NH_2 and SH;

(iv) C_6 to C_{20} unsubstituted aryl, or C_3 to C_{25} unsubstituted heteroaryl having one to three heteroatoms independently selected from the group consisting of O, N and S; and

(v) C_6 to C_{25} substituted aryl, or C_3 to C_{25} substituted heteroaryl having one to three heteroatoms independently selected from the group consisting of O, N and S; and wherein said substituted aryl or substituted heteroaryl has one to three substituents independently selected from the group consisting of:

(1) $-CH_3$, $-C_2H_5$, or C_3 to C_{25} straight-chain, branched or cyclic alkane or alkene, optionally substituted with at least one member selected from the group consisting of Cl, Br, F I, OH, NH_2 and SH,

(2) OH,

(3) NH_2, and

(4) SH;

R^2, R^3, R^4, R^5, and R^6 are independently selected from R and a halogen;

R^{11}, R^{12}, R^{13}, and R^{14} are independently selected from R with the proviso that R^{11}, R^{12}, R^{13}, and R^{14} are not hydrogen; and

wherein, optionally, at least two of R, R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8, R^9, R^{10}, R^{11}, R^{12}, R^{13},and R^{14} can together form a cyclic or bicyclic alkanyl or alkenyl group;

and,

an anion selected from the group consisting of $[CH_3CO_2]^-$, $[HSO_4]^-$, $[CH_3OSO_3]^-$, $[C_2H_5OSO_3]^-$, $[AlCl_4]^-$, $[CO_3]^{2-}$, $[HCO_3]^-$, $[NO_2]^-$, $[NO_3]^-$, $[SO_4]^{2-}$, $[PO_4]^{3-}$, $[HPO_4]^{2-}$, $[H_2PO_4]^-$, $[HSO_3]^-$, $[CuCl_2]^-$, Cl^-, Br^-, I^-, SCN^-, and a fluorinated anion.

16. The absorption cycle of Claim 15 comprising an absorber side having an exit, and a generator side having an exit, wherein the absorber side has a concentration of ionic liquid at the exit of greater than about 70 % by weight of said composition; and the generator side has a concentration of ionic liquid at the exit of greater than about 80 % by weight of said composition.

17. The absorption cycle of Claim 16 wherein the absorber side has a concentration of ionic liquid at the exit of greater than about 80 % by weight of said composition; and the generator side has a concentration of ionic liquid at the exit of greater than about 90 % by weight of said composition.

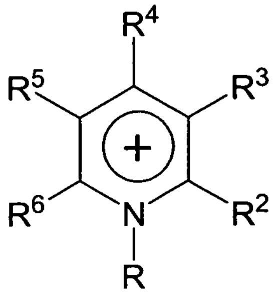
18. The absorption cycle of claim 17 wherein the ionic liquid comprises an imidazolium cation.

19. The absorption cycle of claim 16 wherein the ionic liquid comprises a N,N-dimethylammonium ethanol cation.

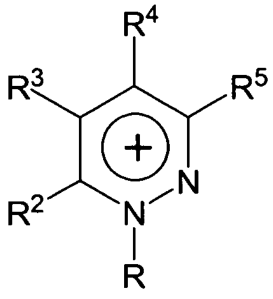
20. A process for storing ammonia comprising absorbing ammonia in an ionic liquid to provide a composition comprising about 1 to about 99 mole % of ammonia over a temperature range from about -40 to about 130 °C at a pressure from about 1 to about 110 bar.

21. The process of claim 20 wherein the composition comprises about 10 to 95 mole % ammonia.

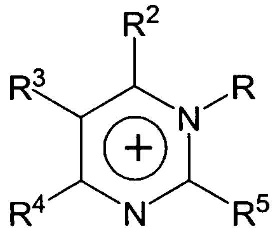
22. The process of claim 20 wherein the ionic liquid has a cation selected from the group consisting of:



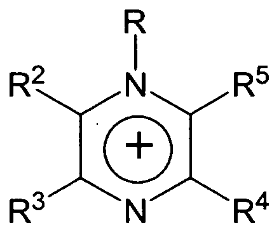
Pyridinium



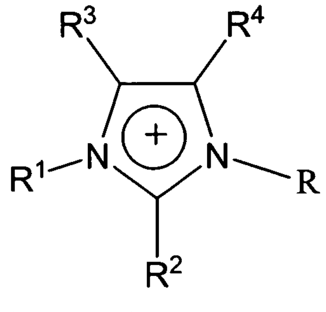
Pyridazinium



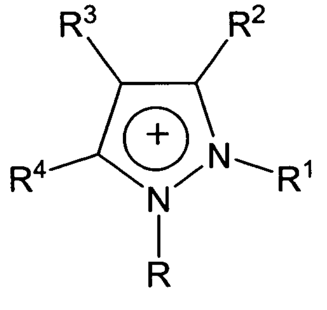
Pyrimidinium



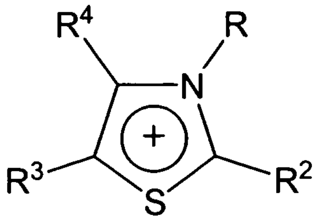
Pyrazinium



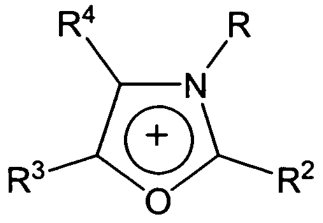
Imidazolium



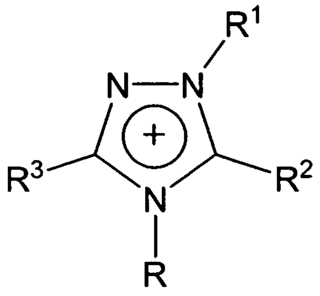
Pyrazolium



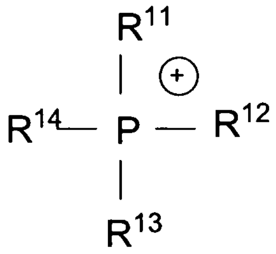
Thiazolium



Oxazolium

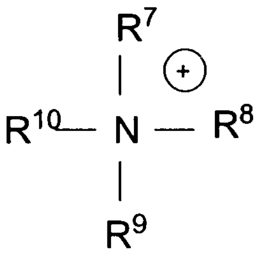


Triazolium



Phosphonium

and



Ammonium

wherein R, R^1, R^7, R^8, R^9, and R^{10} are independently selected from the group consisting of:

(i) hydrogen

(ii) $-CH_3$, $-C_2H_5$, or C_3 to C_{25} straight-chain, branched or cyclic alkane or alkene, optionally substituted with at least one member selected from the group consisting of Cl, Br, F, I, OH, NH_2 and SH;

(iii) $-CH_3$, $-C_2H_5$, or C_3 to C_{25} straight-chain, branched or cyclic alkane or alkene comprising one to three heteroatoms selected from the group consisting of O, N and S, and optionally substituted with at least one member selected from the group consisting of Cl, Br, F, I, OH, NH_2 and SH;

(iv) C_6 to C_{20} unsubstituted aryl, or C_3 to C_{25} unsubstituted heteroaryl having one to three heteroatoms independently selected from the group consisting of O, N and S; and

(v) C_6 to C_{25} substituted aryl, or C_3 to C_{25} substituted heteroaryl having one to three heteroatoms independently selected from the group consisting of O, N and S; and wherein said substituted aryl or substituted heteroaryl has one to three substituents independently selected from the group consisting of:

(4) $-CH_3$, $-C_2H_5$, or C_3 to C_{25} straight-chain, branched or cyclic alkane or alkene, optionally substituted with at least one member selected from the group consisting of Cl, Br, F I, OH, NH_2 and SH,

(5) OH,

(6) NH_2, and

(4) SH;

R^2, R^3, R^4, R^5, and R^6 are independently selected from R and a halogen; R^{11}, R^{12}, R^{13}, and R^{14} are independently selected from R with the proviso that R^{11}, R^{12}, R^{13}, and R^{14} are not hydrogen; and

wherein optionally at least two of R, R^1, R^2, R^3, R^4, R^5, $R^{6,}$ R^7, R^8, R^9, $R^{10,}$ R^{11}, R^{12}, R^{13},and R^{14} can together form a cyclic or bicyclic alkanyl or alkenyl group; and,

an anion selected from the group consisting of $[CH_3CO_2]^-$, $[HSO_4]^-$, $[CH_3OSO_3]^-$, $[C_2H_5OSO_3]^-$, $[AlCl_4]^-$, $[CO_3]^{2-}$, $[HCO_3]^-$, $[NO_2]^-$, $[NO_3]^-$, $[SO_4]^{2-}$, $[PO_4]^{3-}$, $[HPO_4]^{2-}$, $[H_2PO_4]^-$, $[HSO_3]^-$, $[CuCl_2]^-$, Cl^-, Br^-, I^-, SCN^-, and a fluorinated anion.