

A SOLVENT DRYING COMPOSITION AND PROCESSES THEREFOR**FIELD OF THE INVENTION**

[0001] The present disclosure relates to a solvent drying composition and processes therefor.

- 5 The present disclosure more specifically relates to a solvent drying composition that in use releases water from a solvent mixture. The present disclosure also relates to a process for recovering a solvent drying composition, more specifically to a process for recovering a solvent drying composition used in an osmotic process.

BACKGROUND OF THE INVENTION

- 10 [0002] The extraction of water or drying of water from solvent mixtures is typically a high energy and time-consuming task.

- [0003] Jessop et. al. in US 2014/0076810 describe a reversible water or aqueous solution and its use. The reversible water or aqueous solution is formed by adding an ionisable additive comprising an ionisable functional group having at least one nitrogen atom. The additive is further
15 described as a monoamine, a diamine, a triamine, a tetramine or a polyamine, such as a polymer or a biopolymer. The reversible water or aqueous solution is capable of reversibly switching between an initial ionic strength and an increased ionic strength by using a trigger, such as bubbling with CO₂, CS₂ or COS or treatment with a Bronsted acid such as formic acid, hydrochloric acid, sulphuric acid or carbonic acid. To enable this reversibility the ionic form of the additive should be capable of
20 deprotonation through the action of the ionising trigger. This necessarily requires a reversible interaction between the ionic form of the trigger and the additive as shown in Figure 1 of Jessop. The reversibility of the water or aqueous solution allows for the control of solubility or insolubility of various hydrophobic liquids or solvents in the water or aqueous solution. This provides a means of separating moderately hydrophobic solvents from the switchable water. However, one of the
25 difficulties with the Jessop work is that it is difficult to disassociate the CO₂ from the amine to achieve the reversible water. Trace amounts of CO₂ and amine can remain solubilised in the draw solution and heating, stripping and the kinetics of recovery are slow, energy intensive in the order of hours to minutes.

- [0004] It is an object of the present invention to provide a solvent drying composition that
30 overcomes these difficulties or to at least provide a useful alternative.

SUMMARY OF THE INVENTION

[0005] In a first aspect, the present invention provides a solvent drying composition for use in recovering water from a solvent, the composition comprising a complex of:

- 5 a) at least one amine or ammonium salt containing compound and
b) at least one carboxylic acid containing compound or an alkylsulfonic acid; or a combination thereof,

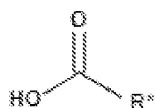
wherein in use the water is released from the solvent upon migration of the composition through the solvent, the released water forming an immiscible aqueous layer with the solvent.

10 [0006] In a second aspect, the present invention provides a solvent drying composition, the composition comprising of:

- a) a complex of at least one amine or ammonium salt containing compound and at least one carboxylic acid containing compound or an alkylsulfonic acid; or a combination thereof, in a solvent comprising
15 b) at least one amine containing compound at least one enolisable carbonyl and water,
wherein in use water in the solvent is released to form an immiscible aqueous layer with the solvent drying composition.

[0007] In one embodiment the carboxylic acid containing compound is selected from one or more of the following:

- a) a compound of Formula I,



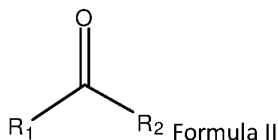
Formula I

- wherein R* is selected from, -C₁-C₇ alkyl-OH, -C₁-C₇ alkyl, -C₁-C₇ alkyl-NH₂, -C₁-C₇ alkyl-NHR₃ and -C₁-C₇ alkyl NR₃R₄, wherein each R₃ and R₄ are selected from -H, -OH, -halo, -
25 C₁-C₇ alkyl, -C₁-C₇ alkyl-OH, -C(O)OH, -C(O)-H, or -C(O)-(C₁-C₇ alkyl); and
b) a polymer containing one or more carboxylic acid groups.

[0008] In one embodiment the alkylsulfonic acid is isoethionic acid.

[0009] In another embodiment the solvent comprises at least a secondary or tertiary amine or a combination thereof.

[0010] In one embodiment the solvent comprises at least one enolisable carbonyl of Formula II,



wherein

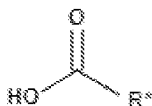
- a) R₁ and R₂ are independently selected from a -C₁-C₇ alkyl or a -C₃-C₇ monocyclic; or
- b) one of R₁ or R₂ is selected from a -O-(C₁-C₇ alkyl) and the other is selected from a -C₁-C₇ alkyl, or
- 10 c) R₁ and R₂ together, with the carbonyl of Formula II, form a 3-15 membered monocyclic ketone or a 3-15 membered monocyclic heterocyclic ketone.

[0011] In one embodiment the carboxylic containing compound of Formula I is selected from acetic acid, citric acid and glycolic acid or a combination thereof.

- 15 [0012] In one embodiment the molar ratio of the at least amine or ammonium salt containing compound to the at least one carboxylic acid containing compound or an alkylsulfonic acid or a combination thereof; is selected from about 1:99 or 99:1; or about 1:50 or 50:1; or about 1:10 or 10:1; or about 1:5 or 5:1; or about 1:3 or 3:1; or about 1:2 or 2:1; or about 1:1.

- 20 [0013] In a third aspect, the present invention provides a solvent drying composition, the composition comprising:

- a) a complex of at least one amine or ammonium salt containing compound and
- b) at least one carboxylic acid containing a compound of Formula I,



Formula I

- 25 wherein R* is selected from, -C₁-C₇ alkyl-OH, -C₁-C₇ alkyl, -C₁-C₇ alkyl-NH₂, -C₁-C₇ alkyl-NHR₃ and -C₁-C₇ alkyl NR₃R₄, wherein each R₃ and R₄ are selected from -H,

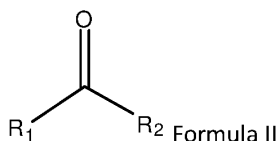
-OH, -halo, -C₁-C₇ alkyl, -C₁-C₇ alkyl-OH, -C(O)OH, -C(O)-H, or -C(O)-(C₁-C₇ alkyl);
 or an alkylsulfonic acid; or a combination thereof; in a solvent comprising
 c) at least one amine containing compound, at least one enolisable carbonyl
 and water,

5 wherein in use the water in the solvent is released to form an immiscible aqueous layer with
 the solvent drying composition.

[0014] In one embodiment the complex of the at least one amine or ammonium salt
 containing compound and the at least one carboxylic acid containing compound of Formula 1 is
 10 irreversibly protonated.

[0015] In another embodiment the solvent comprises at least a secondary or tertiary amine
 or a combination thereof.

[0016] In one embodiment the solvent comprises at least one enolisable carbonyl of
 15 Formula II,



wherein

- d) R₁ and R₂ are independently selected from a -C₁-C₇ alkyl or a -C₃-C₇ monocyclic; or
- e) one of R₁ or R₂ is selected from a -O-(C₁-C₇ alkyl) and the other is selected from a -C₁-C₇
 20 alkyl, or
- f) R₁ and R₂ together, with the carbonyl of Formula II, form a 3-15 membered monocyclic
 ketone or a 3-15 membered monocyclic heterocyclic ketone.

[0017] In one embodiment the -carboxylic acid containing compound of Formula I is selected
 25 from acetic acid, citric acid and glycolic acid or a combination thereof.

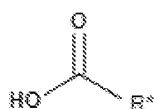
[0018] In one embodiment the alkylsulfonic acid is isoethionic acid.

[0019] In one embodiment the complex of the at least one amine or ammonium salt
 containing compound and the at least one carboxylic acid containing compound of Formula I is
 30 irreversibly protonated.

[0020] In one embodiment the molar ratio of the at least amine or ammonium salt containing compound to the at least one carboxylic acid containing compound or an alkylsulfonic acid or a combination thereof; is selected from about 1:99 or 99:1; or about 1:50 or 50:1; or about 1:10 or 10:1; or about 1:5 or 5:1; or about 1:3 or 3:1; or about 1:2 or 2:1; or about 1:1.

[0021] In a fourth aspect, the present invention provides a complex composition wherein the complex comprises at least one amine or ammonium salt containing compound and at least one carboxylic acid containing compound selected from one or more of the following:

a) compound of Formula I,



Formula I

wherein R* is selected from, -C₁-C₇ alkyl-OH, -C₁-C₇ alkyl, -C₁-C₇ alkyl-NH₂, -C₁-C₇ alkyl-NHR₃ and -C₁-C₇ alkyl NR₃R₄, wherein each R₃ and R₄ are selected from -H, -OH, -halo, -C₁-C₇ alkyl, -C₁-C₇ alkyl-OH, -C(O)OH, -C(O)-H, or -C(O)-(C₁-C₇ alkyl);

b) a polymer containing one or more carboxylic acid groups; or an alkylsulfonic acid; or a combination thereof

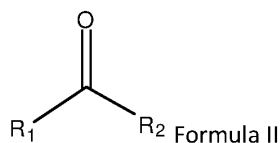
the complex being suitable for use in recovering water from a solvent, wherein water is released from the solvent upon migration of the composition through the solvent, the released water forming an immiscible aqueous layer with the solvent

and wherein the solvent comprises:

- a) at least one amine containing compound,
- b) at least one enolisable carbonyl, and
- c) water.

[0022] In another embodiment the solvent comprises at least a secondary or tertiary amine or a combination thereof.

[0023] In one embodiment the solvent comprises at least one enolisable carbonyl of Formula II,



wherein

- a) R_1 and R_2 are independently selected from a $-C_1-C_7$ alkyl or a $-C_3-C_7$ monocyclic; or
- b) one of R_1 or R_2 is selected from a $-O-(C_1-C_7$ alkyl) and the other is selected from a $-C_1-C_7$ alkyl, or
- c) R_1 and R_2 together, with the carbonyl of Formula II, form a 3-15 membered monocyclic ketone or a 3-15 membered monocyclic heterocyclic ketone.

[0024] In one embodiment the at least one amine containing compound of the complex is a secondary or tertiary amine or combination thereof.

[0025] In one embodiment the carboxylic acid containing compound of Formula I is selected from acetic acid, citric acid and glycolic acid or a combination thereof.

[0026] In one embodiment the alkylsulfonic acid is isoethionic acid.

[0027] In one embodiment the molar ratio of the at least amine or ammonium salt containing compound to the at least one carboxylic acid containing compound or an alkylsulfonic acid or a combination thereof; is selected from about 1:99 or 99:1; or about 1:50 or 50:1; or about 1:10 or 10:1; or about 1:5 or 5:1; or about 1:3 or 3:1; or about 1:2 or 2:1; or about 1:1.

[0028] In one embodiment the complex of the at least one amine or ammonium salt containing compound and the at least one carboxylic acid containing compound of Formula I is irreversibly protonated.

[0029] In a fifth aspect, the present invention provides a method of recovering water from a solvent, the method including the steps of contacting the solvent drying composition for use in recovering water from a solvent, the composition comprising a complex of:

- a) at least one amine or ammonium salt containing compound and
- b) at least one carboxylic acid containing compound, or an alkylsulfonic acid; or a combination thereof;

and allowing the migration of the complex composition through the solvent, whereupon the water is released from the solvent forming an immiscible aqueous layer with the solvent.

[0030] In one embodiment method includes the step of separating the recovered water from the immiscible solvent layer.

[0031] In one embodiment the solvent comprises:

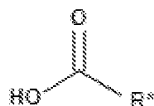
- 5 a) at least one amine containing compound,
b) at least one enolisable carbonyl.

[0032] In a sixth aspect, the present invention provides a method of recovering water from a solvent, the method including the steps of contacting the solvent drying composition for use in recovering water from a solvent, the composition comprising

- 10 a) at least one amine containing compound,
b) at least one enolisable carbonyl.

contacting the solvent with a complex composition wherein the complex comprises at least one amine or ammonium salt containing compound and at least:

- (a) an alkylsulfonic acid; or
15 (b) at least one carboxylic acid containing compound of Formula I,



Formula I

wherein R* is selected from, -C₁-C₇ alkyl-OH, -C₁-C₇ alkyl, -C₁-C₇ alkyl-NH₂, -C₁-C₇ alkyl-NHR₃ and -C₁-C₇ alkyl NR₃R₄, wherein each R₃ and R₄ are selected from -H, -OH, -halo, -C₁-C₇ alkyl, -C₁-C₇ alkyl-OH, -C(O)OH, -C(O)-H, or -C(O)-(C₁-C₇ alkyl); or

- 20 (c) a combination thereof; and

allowing the migration of the complex composition through the solvent, whereupon the water is released from the solvent forming an immiscible aqueous layer with the solvent.

[0033] In one embodiment method includes the step of separating the recovered water from the immiscible solvent layer.

[0034] In one embodiment the solvent comprises:

- a) at least one amine containing compound,
- b) at least one enolisable carbonyl.

[0035] In another aspect, the present invention provides a process for using a solvent drying composition as defined above to recover water from a solvent, the composition comprising a complex
5 of:

- a) at least one amine or ammonium salt containing compound and
- b) at least one carboxylic acid containing compound or an alkylsulfonic acid; or a combination thereof,

wherein in use the water is released from the solvent upon migration of the composition through
10 the solvent, the released water forming an immiscible aqueous layer with the solvent;
the process comprising the steps of:

- 1) bringing the solvent drying composition into contact with the solvent to release the water from the solvent upon migration of the composition through the solvent, the released water and solvent drying composition forming an immiscible aqueous layer with the solvent, and
15 2) recovering the solvent drying composition from the immiscible aqueous layer.

[0036] In one embodiment the process includes the step of recovering the solvent.

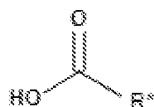
[0037] In one embodiment the recovered solvent drying composition is recycled for use in a further solvent drying process. In a preferred embodiment the process of recovering the solvent drying composition is a continuous recovery process.

20 **[0038]** In one embodiment the step of recovering the solvent drying solution is achieved by one or more of the following techniques, membrane distillation, pervaporation, osmosis, pressure driven membrane processes, osmotically driven membrane processes, osmotically assisted pressure driven membrane processes, pressure assisted osmotically driven membrane processes, filtration, mechanical vapor recompression, evaporation based processes, water specific reactant, or
25 crystallisation techniques or the like.

[0039] In one embodiment the step of recovering the solvent drying solution is achieved by a pressure assisted osmosis technique.

[0040] In one embodiment the at least one carboxylic acid containing compound is selected from one or more of the following:

- a) a compound of Formula I,



Formula I

wherein R* is selected from, -C₁-C₇ alkyl-OH, -C₁-C₇ alkyl, -C₁-C₇ alkyl-NH₂, -C₁-C₇ alkyl-NHR³ and -C₁-C₇ alkyl NR³R⁴, wherein each R³ and R⁴ are selected from -H, -OH, -halo, -C₁-C₇ alkyl, -C₁-C₇ alkyl-OH, -C(O)OH, -C(O)-H, or -C(O)-(C₁-C₇ alkyl); and

- b) a polymer containing one or more carboxylic acid groups.

[0041] In one embodiment the alkylsulfonic acid is isoethionic acid.

[0042] In one embodiment the -carboxylic containing compound of Formula I is selected from acetic acid, citric acid and glycolic acid or a combination thereof.

[0043] In one embodiment the molar ratio of the at least amine or ammonium salt containing compound to the at least one carboxylic acid containing compound or an alkylsulfonic acid or a combination thereof; is selected from about 1:99 or 99:1; or about 1:50 or 50:1; or about 1:10 or 10:1; or about 1:5 or 5:1; or about 1:3 or 3:1; or about 1:2 or 2:1; or about 1:1.

[0044] In another embodiment the at least one amine containing compound is a secondary or tertiary amine or a combination thereof.

[0045] In one embodiment the carboxylic acid containing compound is a metal salt -carboxylic acid complex.

[0046] In one embodiment the metal salt-carboxylic acid complex is selected from one or more of the following: metal salts having a valency of less than 6, 4 such as Na salts, Fe (II) salts, Fe (III) salts, Cu (II) salts, Al(II) salts, Al(III) salts, Sr (II) salts, Li salts and Ag salts. In one embodiment the metal salts have a valency of less than 4.

[0047] In one embodiment the -carboxylic acid containing compound of Formula I is selected from acetic acid, citric acid and glycolic acid or a combination thereof.

[0048] In one embodiment the complex comprising:

- a) at least one amine or ammonium salt containing compound and
- b) at least one carboxylic acid containing compound or an alkylsulfonic acid; or a combination thereof,

is irreversibly protonated.

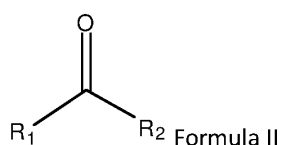
[0049] In one embodiment the solvent is the solvent from which the water is recovered comprises at least one amine containing compound and at least one enolisable carbonyl.

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[0050] In another embodiment the solvent comprises at least a secondary or tertiary amine or a combination thereof.

[0051] In one embodiment the solvent comprises at least one enolisable carbonyl of Formula II,

10



wherein

- a) R₁ and R₂ are independently selected from a -C₁-C₇ alkyl or a -C₃-C₇ monocyclic; or
- b) one of R₁ or R₂ is selected from a -O-(C₁-C₇ alkyl) and the other is selected from a -C₁-C₇ alkyl, or
- c) R₁ and R₂ together, with the carbonyl of Formula II, form a 3-15 membered monocyclic ketone or a 3-15 membered monocyclic heterocyclic ketone or acetophenone.

[0052] The foregoing brief summary broadly describes the features and technical advantages of certain embodiments of the present invention. Further technical advantages will be described in the detailed description of the invention and examples that follows.

[0053] Novel features that are believed to be characteristic of the invention will be better understood from the detailed description of the invention when considered in connection with any accompanying figures and examples. However, the figures and examples provided herein are intended to help illustrate the invention or assist with developing an understanding of the invention, and are not intended to limit the invention's scope.

BRIEF DESCRIPTION OF THE DRAWINGS

[0054] Figure 1: shows a calibration curve of ethylpiperidine concentration at lower concentrations.

[0055] Figure 2 shows the drying capacity of various amine/acid complexes compared to that of the prior art.

[0056] Figure 3 shows the drying capacity of various amine/amino acid complexes.

5 [0057] Figure 4 schematically shows a quintuple counter current regeneration process using a commercial brine.

[0058] Figure 5 shows a plot of the various water contents in each stage of the counter current regeneration process outlined in Figure 4

[0059] Figure 6: shows schematically a process diagram for a pressure assisted osmotic process to recover a solvent drying composition.

10 [0060] Figure 7 shows a process diagram for a continuous process system for recovering a solvent drying composition.

[0061] Figure 8: shows a graph of the reverse osmosis flux (LMH) data and the rejection % data of 20% (by vol.) diluted drying solvent solution at 60 bar.

15 [0062] Figure 9: shows the flux data results obtained from 5 different membranes at different pressures.

[0063] Figure 10: shows the rejection % results obtained from 5 different membranes at different pressures.

[0064] Figure 11: shows a process diagram for recovering a solvent drying composition using an electrostatic coalescer.

20 DETAILED DESCRIPTION OF THE INVENTION

[0065] The following description sets forth numerous exemplary configurations, parameters, and the like. It should be recognised, however, that such description is not intended as a limitation on the scope of the present invention but is instead provided as a description of exemplary embodiments.

25 DEFINITIONS

[0066] In each instance herein, in descriptions, embodiments, and examples of the present invention, the terms "comprising", "including", etc., are to be read expansively, without limitation. Thus, unless the context clearly requires otherwise, throughout the description and the claims, the

words “comprise”, “comprising”, and the like are to be construed in an inclusive sense as to opposed to an exclusive sense, that is to say in the sense of “including but not limited to”.

[0067] The term “about” or “approximately” usually means within 20%, more preferably within 10%, and most preferably still within 5% of a given value or range. Alternatively, the term “about” means within a log (i.e., an order of magnitude) preferably within a factor of two of a given value.

[0068] As used herein, the term “at least one amine or ammonium salt containing compound” means any compound that includes an -NH₃, -NHR³ or -NR³R⁴ group or an ammonium salt of -NH₄⁺ with the proviso that ammonium bicarbonate is excluded, wherein each R³ and R⁴ are selected from -H, -OH, -halo, -C₁-C₇ alkyl, -C₁-C₇ alkyl-OH, -C(O)OH, -C(O)-H, or -C(O)-(C₁-C₇ alkyl);

[0069] As used herein, the term “carboxylic acid containing compound” is any compound having an -COOH group or a salt thereof, including polymeric compounds, such as polyacrylic acid, copolymers such as poly(acrylic acid-co-maleic acid) solution and the like.

[0070] As used herein, the term “alkylsulfonic acid” includes any compound having a S(O)₂OH functional group or a salt thereof, where R is a C₁-C₇ alkyl, wherein C₁-C₇ alkyl is as defined below.

[0071] As used herein, the term “C₁-C₇ alkyl” refers to a fully saturated branched or unbranched hydrocarbon moiety, which may be a straight or a branched chain of a particular range of 1-7 carbons. Preferably the alkyl comprises 1 to 7 carbon atoms, or 1 to 4 carbon atoms. Representative examples of C₁-C₇alkyl include, but are not limited to, methyl, ethyl, *n*-propyl, *iso*-propyl, *n*-butyl, *sec*-butyl, *iso*-butyl, *tert*-butyl, *n*-pentyl, isopentyl, neopentyl, *n*-hexyl, 3-methylhexyl, 2,2- dimethylpentyl, 2,3-dimethylpentyl, *n*-heptyl, and the like. For example, the expression C₁-C₄-alkyl includes, but is not limited to, methyl, ethyl, propyl, butyl, isopropyl, *tert*-butyl and isobutyl. In one embodiment the C₁-C₇ alkyl group may be substituted with one or more of the following groups: -halo, -OH, -CN, -NO₂, -C≡CH, -SH, -C₁-C₇ alkyl, -(C₁-C₇ alkyl)-OH, -NH₂, -NH(C₁-C₇ alkyl), -N(C₁-C₇ alkyl)₂, -O (C₁-C₇ alkyl), -C(O)-O-(C₁-C₇ alkyl), -C(O)OH; -C(O)-H, or -C(O)-(C₁-C₇ alkyl).

[0072] The term “C₃-C₇ monocyclic” as used herein is a 3-, 4-, 5-, 6-, or 7-membered saturated or unsaturated monocyclic ring. Representative C₃-C₇ monocyclic groups include, but are not limited to, cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, phenyl, and cycloheptyl. In one embodiment, the C₃-C₇ monocyclic cycloalkyl group may be substituted with one or more of the following groups: -halo, -OH, -CN, -NO₂, -C≡CH, -SH, -C₁-C₇ alkyl, -(C₁-C₇ alkyl)-OH, -NH₂, -NH(C₁-C₇ alkyl), -N(C₁-C₇ alkyl)₂, -O (C₁-C₇ alkyl), -C(O)-O-(C₁-C₇ alkyl), -C(O)OH; -C(O)-H, or -C(O)-(C₁-C₇ alkyl).

[0073] The term “3- to 15-membered monocyclic ketone” refers to a 3- to 15- membered non-aromatic monocyclic ring system containing a ketone functional group. Representative examples of a 3- to 15-membered monocyclic ketone include, but are not limited to cyclopropanone, cyclobutanone, cyclopentanone, cyclohexanone, cycloheptanone, cyclooctanone, cyclononanone, cyclodecanone, cycloundecanone, cyclododecanone, cyclotridecanone; cyclotetradecanone and cyclopentadecanone.

[0074] In one embodiment, the 3- to 15-membered monocyclic ketone may be substituted with one or more of the following groups-halo, -OH, -CN, -NO₂, -C≡CH, -SH, -C₁-C₇ alkyl, -(C₁-C₇ alkyl)-OH, -NH₂, -NH(C₁-C₇ alkyl), -N(C₁-C₇ alkyl)₂, -O (C₁-C₇ alkyl), -C(O)-O-(C₁-C₇ alkyl), -C(O)OH; -C(O)-H, or -C(O)-(C₁-C₇ alkyl).

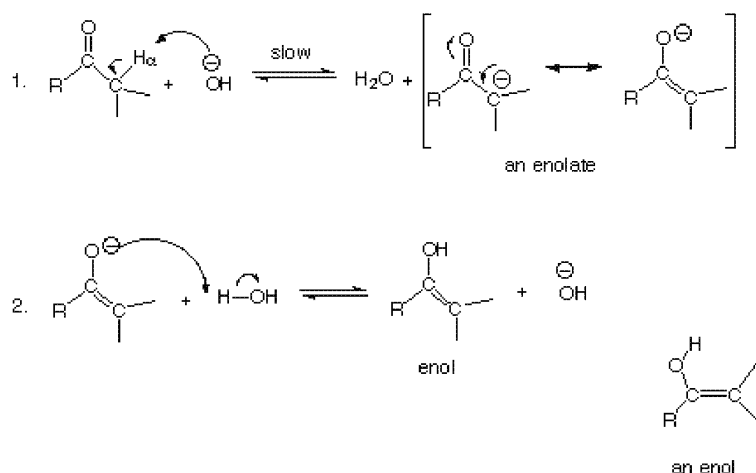
[0075] The term “3- to 15-membered monocyclic heterocyclic ketone” refers to: (i) a 3- or 4-membered non-aromatic monocyclic cycloalkyl in which 1 of the ring carbon atoms has been replaced with an N, O or S atom; or (ii) a 5- to 15-membered non-aromatic monocyclic cycloalkyl in which 1-4 of the ring carbon atoms have been independently replaced with a N, O or S atom. Representative examples of a 3- to 15-membered monocyclic heterocyclic ketone having one N, O or S atom include, but are not limited to oxiran-2-one, thiiran-2-one, oxetan-2-one, oxetan-3-one, azetidin-3-one, thietan-2-one, thietan-3-one, dihydrofuran-2(3H)-one, dihydrofuran-3(2H)-one, pyrrolidin-3-one, dihydrothiophen-3(2H)-one, dihydrothiophen-2(3H)-one, tetrahydro-2H-pyran-2-one, dihydro-2H-pyran-3(4H)-one, dihydro-2H-pyran-4(3H)-one, piperidin-3-one, piperidin-4-one, tetrahydro-2H-thiopyran-2-one, dihydro-2H-thiopyran-3(4H)-one, dihydro-2H-thiopyran-4(3H)-one, oxepan-2-one, oxepan-3-one, oxepan-4-one, thiepan-2-one, thiepan-3-one, thiepan-4-one, azepan-3-one, azepan-4-one, oxocan-2-one, oxocan-3-one, oxocan-4-one, oxocan-5-one, thiocan-2-one, thiocan-3-one, thiocan-4-one, thiocan-5-one, azocan-3-one, azocan-3-one, azocan-4-one, azocan-5-one, azonan-3-one, azonan-4-one, azonan-5-one, oxonan-2-one, oxonan-3-one, oxonan-4-one, oxonan-5-one, thionan-2-one, thionan-3-one, thionan-4-one, thionan-5-one, oxacycloundecan-2-one, oxacycloundecan-3-one, oxacycloundecan-4-one, oxacycloundecan-5-one, oxacycloundecan-6-one, azacycloundecan-3-one, azacycloundecan-4-one, azacycloundecan-5-one, azacycloundecan-6-one, thiacycloundecan-2-one, thiacycloundecan-3-one, thiacycloundecan-4-one, thiacycloundecan-5-one, thiacycloundecan-6-one, oxacyclododecan-2-one, oxacyclododecan-3-one, oxacyclododecan-4-one, oxacyclododecan-5-one, oxacyclododecan-6-one, oxacyclododecan-7-one, azacyclododecan-3-one, azacyclododecan-4-one, azacyclododecan-5-one, azacyclododecan-6-one, azacyclododecan-7-one, thiacyclododecan-2-one, thiacyclododecan-3-one, thiacyclododecan-4-one, thiacyclododecan-5-one, thiacyclododecan-6-one, thiacyclododecan-7-one, oxacyclotridecan-2-one, oxacyclotridecan-3-one,

oxacyclotridecan-4-one, oxacyclotridecan-5-one, oxacyclotridecan-6-one, oxacyclotridecan-7-one, azacyclotridecan-3-one, azacyclotridecan-4-one, azacyclotridecan-5-one, azacyclotridecan-6-one, azacyclotridecan-7-one, thiacyclotridecan-2-one, thiacyclotridecan-3-one, thiacyclotridecan-4-one, thiacyclotridecan-5-one, thiacyclotridecan-6-one, thiacyclotridecan-7-one, oxacyclotetradecan-2-one, oxacyclotetradecan-3-one, oxacyclotetradecan-4-one, oxacyclotetradecan-5-one, oxacyclotetradecan-6-one, oxacyclotetradecan-7-one, oxacyclotetradecan-8-one, azacyclotetradecan-3-one, azacyclotetradecan-4-one, azacyclotetradecan-5-one, azacyclotetradecan-6-one, azacyclotetradecan-7-one, azacyclotetradecan-8-one, thiacyclotetradecan-2-one, thiacyclotetradecan-3-one, thiacyclotetradecan-4-one, thiacyclotetradecan-5-one, thiacyclotetradecan-6-one, thiacyclotetradecan-7-one, thiacyclotetradecan-8-one, oxacyclopentadecan-2-one, oxacyclopentadecan-3-one, oxacyclopentadecan-4-one, oxacyclopentadecan-5-one, oxacyclopentadecan-6-one, oxacyclopentadecan-7-one, oxacyclopentadecan-8-one, azacyclopentadecan-3-one, azacyclopentadecan-4-one, azacyclopentadecan-5-one, azacyclopentadecan-6-one, azacyclopentadecan-7-one, azacyclopentadecan-8-one, thiacyclopentadecan-2-one, thiacyclopentadecan-3-one, thiacyclopentadecan-4-one, thiacyclopentadecan-5-one, thiacyclopentadecan-6-one, thiacyclopentadecan-7-one, thiacyclopentadecan-8-one. In one embodiment, the 3- to 15-membered monocyclic heterocyclic ketone group may be substituted with one or more of the following groups-halo, -OH, -CN, -NO₂, -C≡CH, -SH, -C₁-C₆ lower alkyl, -(C₁-C₇ alkyl)-OH, -NH₂, -NH(C₁-C₇ alkyl), -N(C₁-C₇ alkyl)₂, -O (C₁-C₇ alkyl), -C(O)-O-(C₁-C₇ alkyl), -C(O)OH; -C(O)-H, or -C(O)-(C₁-C₇ alkyl). For the avoidance of doubt, the 3-5 membered monocyclic heterocyclic ketone does not include any amide groups where the ketone enolisable carbonyl group is adjacent a N atom in the cyclic structure.

[0076]

The term "halo" as used herein refers to -F, -Cl, -Br or -I.

25 [0077] The term "an enolisable carbonyl" means a compound that has one or more carbonyl functional groups and wherein at least one of the carbonyl functional groups has alpha hydrogens (H_α) that may be removed by a base to form an enolate and then an enol as shown in the reaction scheme below.



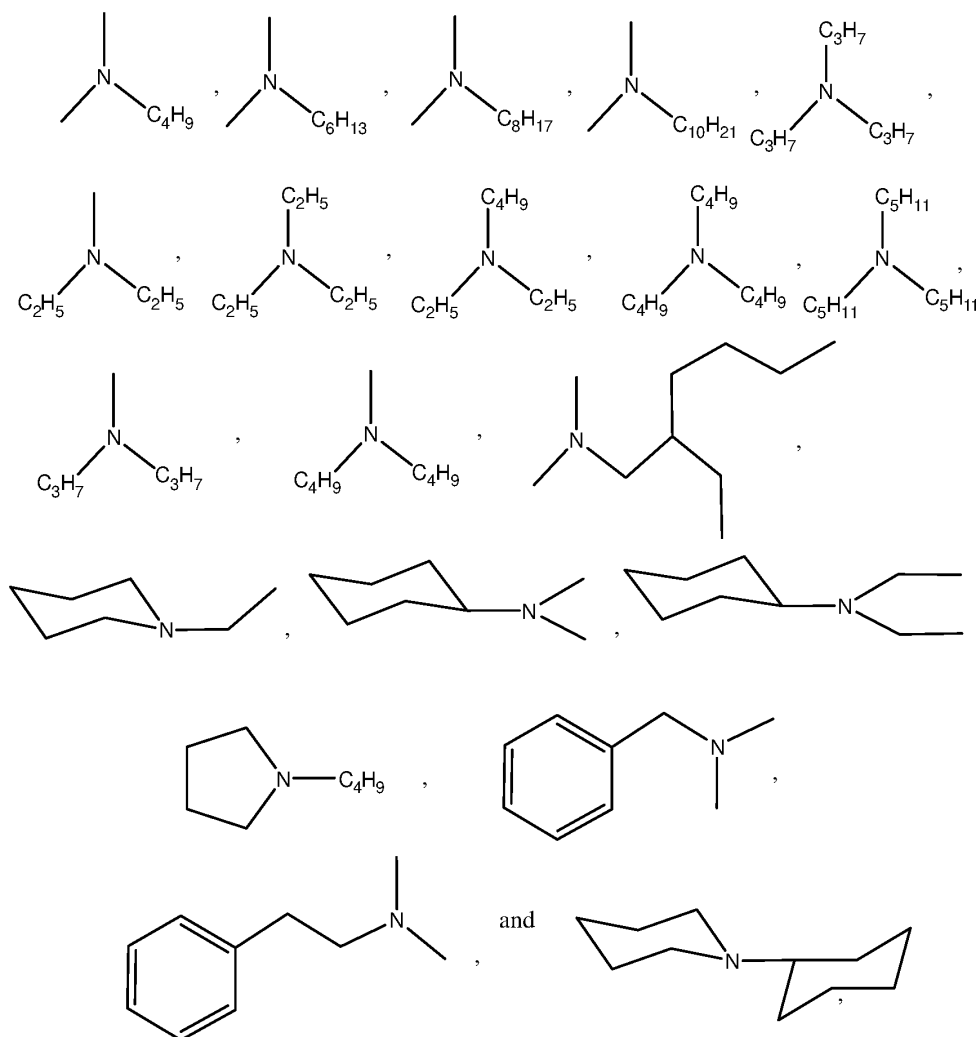
- It is to be understood that the term enolisable carbonyl as used in the specification does not include a compound having solely an aldehyde functional group, a compound having solely a carboxylic acid functional group, a compound having solely an amide functional group, a compound having solely an acyl halide functional group or acetylacetone. The enolisable carbonyls of the invention include those exemplified in the specification and without limitation also include the following enolisable carbonyls:
- 1-acetonaphthone, 2-acetonaphthone, 4-methyl-1-acetonaphthone, 1'-hydroxy-2'-acetonaphthone, 2'-hydroxy-1'-acetonaphthone, 2-methoxy-1-acetonaphthone, 4-fluoro-1-acetonaphthone; 2-acetylphenanthrene, 3-acetylphenanthrene, 4-acetylphenanthrene, 9-acetylphenanthrene, 6-bromo-9-acetylphenanthrene, 9-fluoro-10-acetylphenanthrene, 9-fluorenone, 9-fluorenone oxime, 2-nitro-9-fluorenone, 3-nitro-9-fluorenone, 4-nitro-9-fluorenone, 2,6-dinitro-9-fluorenone, 2,7-dinitro-9-fluorenone, 2,3,7-trinitro-9-fluorenone, 2-fluoro-9-fluorenone, 1-bromo-9-fluorenone, 2-bromo-9-fluorenone, 2,7-dichloro-9-fluorenone, 2,7-dibromo-9-fluorenone, 2-hydroxy-9-fluorenone, 4-hydroxy-9-fluorenone; 1-methylfluoren-9-one; 4-methylfluoren-9-one; 3,4-dihydro-2(1H)-quinolinone, 7-hydroxy-3,4-dihydro-2(1H)-quinolinone, 6-hydroxy-3,4-dihydro-2(1H)-quinolinone, 8-bromo-2,3-dihydro-4(1H)-quinolinone, 3-butyl-4-hydroxy-1-methyl-2(1H)-quinolinone, 6-fluoro-4,4-dimethyl-3,4-dihydro-2(1H)-quinolinone, 8-fluoro-4,4-dimethyl-3,4-dihydro-2(1H)-quinolinone, 2,6-dimethyl-4(1H)-quinolinone, 3-butyl-4-hydroxy-1-methyl-2(1H)-quinolinone, 1-indanone, 5,6-dimethoxy-1-indanone, 6-bromo-1-indanone, 6-methoxy-1-indanone, 2-bromo-1-indanone, 4-bromo-1-indanone, 5-bromo-1-indanone, 5-chloro-1-indanone, 6-chloro-1-indanone, 4,7-dimethyl-1-indanone, 2-methyl-1-indanone, 4-methyl-1-indanone, 5-fluoro-1-indanone, 6-fluoro-1-indanone, 6-(trifluoromethyl)-1-indanone, 4-methoxy-1-indanone, 3,5-dimethoxy-1-indanone, 4,7-dimethoxy-1-indanone, 5-hydroxy-1-indanone, 4-hydroxy-1-indanone, 7-hydroxy-1-indanone, 2-indanone oxime, 2,2-di(methylthio)-1-indanone, (2,4-

dimethoxyphenyl)acetone, 3,5-dimethoxyacetophenone, 4-(4-methoxyphenyl)-2-butanone, 3-methoxyphenylacetone, 4-methoxy acetophenone, 4-methoxy-2-phenylacetophenone, 2,5-dimethylphenylacetone, 3,4,5-trimethoxyphenylacetone, 4-hydroxy-3-phenylbutan-2-one, 3-hydroxy-4-phenylbutan-2-one, 3-hydroxy-3-phenylbutan-2-one, 4-hydroxy-4-phenylbutan-2-one, 1-hydroxy-3-phenylbutan-2-one, 3-hydroxy-1-phenylbutan-2-one, 3-hydroxy-1,3-diphenylbutan-2-one, 4-hydroxyphenylacetone, 3,4-dihydroxyphenylacetone, 4-nitrophenylacetone, acetophenone, 4-methyl acetophenone, benzylacetone, 3-methylphenylacetone, 4-methylphenylacetone, 4-ethylphenylacetone, 1-phenylbutan-2-one, 3-phenylbutan-2-one, 4-phenylbutan-2-one, 1-bromo-4-phenylbutan-2-one, 3-methyl-1-phenylbutan-2-one, 3-methyl-4-phenylbutan-2-one, ethyl phenyl ketone, butyl phenyl ketone, cyclopropyl phenyl ketone, cyclopentyl phenyl ketone, cyclobutyl phenyl ketone, cyclohexyl phenyl ketone, 2-phenylcyclopentanone, 3-phenylcyclopentanone, 2-phenylcyclohexanone, 3-phenylcyclohexanone, 2-phenylcycloheptanone, 3-phenylcycloheptanone, 4-chlorophenyl acetone, 4-chloro-2-phenylacetophenone, 2,6-dichlorophenylacetone, 3-chlorophenylacetone, 2,6-difluorophenylacetone, 1-bromo-1-phenylbutan-2-one, 3-bromo-4-phenylbutan-2-one, 1-bromo-4-phenylbutan-2-one, 3-chloro-4-phenylbutan-2-one, 2-acetylthiophene, cyclopropyl-2-thienyl ketone, 2-acetylfuran, 2-furyl methyl ketone, 1-acetylpyrrole, 2-acetylpyrrole, 4-methyl-2-phenylacetophenone, 1,3-diphenylacetone, 4,4-diphenylbutan-2-one, benzophenone, 4-naphthyl phenyl ketone, 2-benzoylpyridine, 3-benzoylpyridine, 4-benzoylpyridine, 2-(4-chlorobenzoyl) pyridine, 2-benzoylthiophene, 2-benzoylpyrrole, di(3-thiophenyl) methanone, 3-phenyl-1-(2-thienyl)-2-propen-1-one, and piperonyl acetone.

[0078] The term “amine containing compound, includes any compound that includes one or more amine functionalities, but does not include a heterocyclic amine where the heterocyclic ring includes an oxygen or sulphur atom as well as at least one amine group; such as for example 4-ethylmorpholine.

[0079] The term “tertiary amine containing compound” preferably means a compound having at least one tertiary amine group, but it is to be appreciated that the compound may have more than one tertiary amine group or further may be a mixture of tertiary amine containing compounds. Preferably the tertiary amine containing compound is a base, such as a Lewis base. If the base is a Lewis base, it is envisaged that a Lewis adduct may be formed with the enolisable carbonyl. In one embodiment it is preferred that the tertiary amine containing compound is immiscible with water at or above 20 degrees Celsius under one standard atmosphere of pressure. The solution may include a combination of more than one tertiary amine containing compound. The tertiary amine containing compound may be aliphatic, conjugated, asymmetric or cyclic or a combination thereof.

[0080] Examples of suitable tertiary amine containing compounds include the following:



[0081] In one embodiment the tertiary amine containing compound is selected from 1-ethylpyrrolidine, ethylpiperidine, 2-methylpyridine and N-methylpiperidine.

- 5 **[0082]** In one embodiment the tertiary amine containing compound is selected from a -N(C₁-C₇ alkyl)₃. In another embodiment the tertiary amine containing compound is selected from a -N(C₁-C₄ alkyl)₃. In yet a further embodiment the tertiary amine containing compound is -N(C₂ alkyl)₃ (triethylamine).

10 **[0083]** It will be appreciated that the above listed tertiary amine containing compounds are simple enough for production on an industrial scale.

[0084] It is to be appreciated that the molar ratio of the at least one tertiary amine containing compound to the one or more enolisable carbonyls of Formula II may be present in a

number of molar ratios including of about 1:99 or 99:1; of about 1:50 or 50:1; of about 1:10 or 10:1; of about 1:5 or 5:1; of about 1:3 or 3:1; of about 1:2 or 2:1 or of about 1:1.

[0085] It is to be appreciated that the molar ratio of the at least amine or ammonium salt containing compound to the at least one carboxylic acid containing compound or an alkylsulfonic acid or a combination thereof; is selected from about 1:99 or 99:1; or about 1:50 or 50:1; or about 1:10 or 10:1; or about 1:5 or 5:1; or about 1:3 or 3:1; or about 1:2 or 2:1; or about 1:1.

EXAMPLES

[0086] The examples described herein are provided for the purpose of illustrating specific embodiments of the invention and are not intended to limit the invention in any way. Persons of ordinary skill can utilise the disclosures and teachings herein to produce other embodiments and variations without undue experimentation. All such embodiments and variations are considered to be part of this invention.

Preparative Examples.

Preparation Example 1. – Water absorbing solvent mixture solution

[0087] Preparation of a water absorbing solvent mixture for testing purposes. The following method was employed to generate a standard water absorbing solvent mixture solution.

1. Commercially available, analytical grade 2-butanone (also known as methylethyl ketone MEK) and triethylamine (TEA) was mixed in a 2:1 molar ratio as follows in Table 1 to create the water absorbing solvent mixture in its “dry” state (without water):

Table 1:

Total quantity of solvent mixture made (L)	2-Butanone (L)	Triethylamine (L)
1	0.563	0.437
2	1.125	0.875
5	2.813	2.187
10	5.626	4.374
20	11.253	8.747

2. 10% deionised water was added to the solvent mixture in the amounts shown below in Table 2 and well shaken. The addition of water to the solvent mixture created a “wet solvent mixture”.

Table 2:

Volume of solvent mixture (L)	Volume of water to add (mL)
1	100
2	200
5	500
10	1000
20	2000

3. Once the wet solvent mixture had been prepared, various complexes of [amine* + carboxylic acid containing compound] -could be studied as drying agents, ie agents for removing water from the solvent mixture. This would involve adding the selected drying agent to the wet solvent mixture with vigorous shaking. The drying agent was added at a water:drying agent ratio of 2:1 as shown in Table 3.

Table 3:

Volume of solvent mixture (L)	Volume of DI water added to solvent mixture (mL)	Volume of Drying Agent to add (mL) to wet solvent mixture
1	100	50
2	200	100
5	500	250
10	1000	500
20	2000	1000

4. The two liquids were allowed to fully separate.
5. The drying agent (bottom layer) was decanted and disposed of.
6. A Standard Addition test (in triplicate) was carried out to calculate the concentration of water in the sample, using a gas chromatogram.

[0088] All GC data was collected on a SHIMADZU Nexis 2030 gas chromatograph

- 15 fitted with a SUPELCO WATERCOL 1910 column. The GC parameters were set up as shown below:

Parameter	Setting
Injection Volume	1.0 μ L
Injection temperature	250 °C

	Injection mode	Split
	Split ratio	100.0
	Carrier gas	He
	Carrier gas pressure	53.1 kPa
5	Column flow	0.93 mL/min
	Liner velocity	22.0 cm/s
	Column length	30.0 m
	Column inner diameter	0.32
	Column method	Isocratic
10	Column temperature	163.0 °C
	Total time	9 min
	Detector	TCD
	TCD sample rate	40 ms
	TCD current	70 mA
15	Makeup gas	He
	Makeup flow	8.0 mL/min
	TCD temperature	200 °C

Column Method:

Rate (°C / min)	Temperature (°C)	Hold Time (min)
	100.00	2.55
25.0	168.0	5.0

20 Total program time 10:27 min

Preparative Example 2. – Drying Agent complex

[0089] The drying agent complex was made up to a molar ratio of 1:1 of citric acid : ethylpiperidine 10% excess citric acid was then added to ensure that all the ethylpiperidine had complexed to form the complex [amine* + carboxylic acid containing compound] to
 25 remove any chance of “free” ethylpiperidine.

Example 1 – The water absorbency of various complexes [amine* + carboxylic acid containing compound]

[0090] Several complexes of amine with citric acid or amine with glycolic acid were evaluated for regenerant capabilities. The complexes of citric acid and glycolic acid were prepared at the same molality of 6.9 mol/kg. Various combinations of solvent mixtures were prepared as outlined in Table 4 below for reaction with either 6.9 mol/kg of citric acid or glycolic acid to form the various complexes [amine* + carboxylic acid containing compound] which were then be tested for water absorbing capabilities:

Table 4: The composition of the various solvent mixtures

Various solvent mixtures	Molar ratio
Triethylamine:MEK	0.5:1
Ethylpiperidine:MEK	0.5:1
(Triethylamine:Ethylpiperidine):MEK	(0.3:0.2):1

10

[0091] The complexes [amine* + carboxylic acid containing compound] obtained were tested for their water recovery capabilities by the following procedures:

0.2ml of the various complexes were each added to 20ml of the wet solvent mixture (prepared in accordance with Preparative Example 1 above).

- The resulting mixture was mixed by a Vortex mixer for 30 seconds and then separated by the centrifuge fitted with a 130mm diameter 4 arm swing rotor at 4000 rpm for 60 seconds.
- The remaining water in the solvent mixture was measured using gas chromatography through the method of standard addition.

20 [0092] The results obtained are tabulated in table 5.

Table 5: Composition of new amine/acid complex combination (by contacting acid + amine complex with wet solvent mixture) and their water absorbing capabilities.

Acid	Acid weight (g)	Moles (mol)	Distilled water (g)	The molality mol/kg	Amine	Ratio of Amine to MEK (X:1)	Wet solvent mixture used (mL)	H ₂ O in Wet solvent mixture %	Complex used (mL)	H ₂ O in Dry solvent mixture %
Glycolic	5.24	0.069	10.0	6.90	TEA	0.5	20.0	7.10	0.2	6.00
Glycolic	5.24	0.069	10.0	6.90	EP	0.5	20.0	7.10	0.2	6.00

Glycolic	5.24	0.069	10.0	6.90	TEA and EP	0.3:0.2	20.0	7.10	0.2	5.90
Citric acid	13.2	0.069	10.0	6.90	TEA	0.5	20.0	7.10	0.2	5.20
Citric	13.2	0.069 0	10.0	6.90	EP	0.5	20.0	7.10	0.2	5.30
Citric	13.2	0.069 0	10.0	6.90	TEA and EP	0.3:0.2	20.0	7.10	0.2	5.30
Citric	13.2	0.069 0	10.0	6.90	IBA	0.5	20	7.10	0.2	6
Citric	13.2	0.069 0	10.0	6.90	PYR	0.5	20	7.10	0.2	5.8

TEA = triethylamine; EP = ethylpiperidine; IBA = isobutylamine; PYR = pyrrolidine

[0093] The results shown in Table 5 demonstrate that amine/acid salts also exhibit regen water-absorbing abilities, hence can function as a regenerant as well. With the same concentration, the water-absorbing ability of citric salts was better than glycolic salts.

Example 1 continued – The water absorbency of various complexes [ammonium salt + carboxylic acid containing compound]

[0094] Complexes of ammonium salts with citric acid were evaluated for water recovery capabilities. Dry and wet solvent mixtures were prepared as per preparative example 1 above.

Ammonium citrate was prepared as follows:

- Citric acid (13.96 g, 0.073 mol) was added to 10ml of wt 28% ammonia in water (NH₄OH: 2.55g, 0.073 mol).
- The mixture was stirred at room temperature for 30 mins.

15 The preparation of saturated solution is below as follows:

- A quantity of acids was added to 10mL of distilled water.
- The solution was stirred at the room temperature.
- Once no more acid dissolves, the stirring was stopped and the saturated solution was used.

[0095] In Table 6, some potential ammonium salt regenerants were made as saturated solutions. The regenerant composition and source are listed in the table. The procedure to measure water absorption capability is as follows:

- 0.2ml of the various Regenerants are each added to 20ml of the wet solvent mixture.
- It was mixed by a Vortex mixer for 30 seconds and then separated by the centrifuge fitted with a 130mm diameter 4 arm swing rotor at 4000 rpm for 60 seconds.
- Remaining water in the solvent mixture was checked by the GC through the method of standard addition.

Table 6: Potential ammonium salt regenerants

Ammonium salt	Source of Salts	Percentage Concentration of water in wet solvent mixture (%)	Percentage Concentration of water in the solvent mixture after drying with the ammonium salt acid complex (%)
Ammonium citrate	Prepared according to the method above	7.10	4.40
Isethionic acid ammonium salt	Sigma-Aldrich	7.10	5.4

*Ammonium citrate was prepared as the method above.

[0096] A range of carboxylic group containing compounds were tested to determine their water absorbing capacities. As above, wet solvent mixture samples were prepared according to preparative example 1 above. Various carboxylic containing compounds were purchased from Sigma-Aldrich, such as poly(acrylic acid-co-maleic acid) solution, Poly(acrylic acid), glycolic acid and tartaric. The carboxylic acid containing compounds were prepared as shown in Table 6 and Table 7. The samples in Table 6 were diluted in half concentration and used for the tests, which were evaluated in Table 7.

Table 7: The table showing the potential acids at the molality of -COOH of 9.80 mol/kg

Potential carboxylic acid	Weight used (g)	MW of the Regenerant (g/mol)	Number of -COOH Groups in Regenerant	Moles of Potential Regen (mol)	Moles of -COOH group (mol)	Distilled water (kg)	The molality of -COOH (mol/kg)
Poly(acrylic acid-co-maleic acid) solution	10.0	3000	48.0	0.0033	0.16	0.016	9.8
Poly(acrylic acid) solution	7.20	1800	25.0	0.0040	0.098	0.010	9.8
Glycolic acid	7.45	76.1	1.00	0.098	0.098	0.010	9.8
Tartaric Acid	7.35	150	2.00	0.049	0.098	0.010	9.8
Citric acid	6.34	192	3.00	0.033	0.098	0.010	9.8

[0097] The molality (mol/kg) of -COOH was calculated using the formula:

$$\frac{\text{Moles of } -\text{COOH}}{\text{The weight of distilled water}}$$

5

Table 8: The table showing the potential carboxylic acids at the molality of 0.200 mol/kg

Potential carboxylic acid	weight (g)	MW of the carboxylic acid (g/mol)	The moles of acids (mol)	Distilled water (kg)	The molality (mol/kg)
poly(acrylic acid-co-maleic acid) solution	10.0	3000	0.0033	0.017	0.2
Poly(acrylic acid) solution	3.60	1800	0.0020	0.010	0.20
glycolic acid	0.152	76.05	0.0020	0.010	0.2
tartaric Acid	0.300	150	0.0020	0.010	0.2
citric acid	0.384	192	0.0020	0.010	0.2

[0098] The molality (mol/kg) was calculated using the formula:

$$\frac{\text{Moles of acids}}{\text{The weight of distilled water}}$$

[0099] The following steps were taken to measure the water releasing capabilities for these carboxylic acid group containing candidates:

- 5
 - 0.2ml of each carboxylic acid containing compound was added to 20ml of the wet solvent mixture.
 - The resulting combination was mixed by the instrument of mixer for 30 seconds and then separated by the centrifuge fitted with a 130mm diameter 4 arm swing rotor at 4000 rpm for 60 seconds.
- 10
 - Remaining water in the solvent mixture was checked by the GC through the method of standard addition.

Observation and analysis:

Table 9: The Water Absorbing Capabilities of the Various Acids of half concentration in Table 7

The molality of -COOH (4.90 mol/kg)		
New Acid Regenerants	Concentration of water in wet solvent mixture(%)	Percentage Concentration of water in solvent mixture after drying with Regenerant (%)
Poly(acrylic acid) solution	7.10	6.40
glycolic acid	7.10	5.00
poly(acrylic acid-co-maleic acid) solution	7.10	6.50
Tartaric Acid	7.10	5.90
Citric acid	7.10	5.30

Table 10: The Water Absorbing Capabilities of the Various Acids in Table 7

The molality of -COOH (9.80 mol/kg)		
New Regenerants	Concentration of water in wet solvent mixture (%)	Percentage Concentration of water in solvent mixture after

		drying with Regenerant (%)
Poly(acrylic acid) solution	7.10	5.40
glycolic acid	7.10	4.40
poly(acrylic acid-co-maleic acid) solution	7.10	5.80
Tartaric Acid	7.10	4.90
Citric acid	7.10	4.40

Table 11: The Water Absorbing Capabilities of the Various Acids in Table 8

The molality of 0.20 mol/kg		
New Regenerants	Concentration of water in wet solvent mixture (%)	Percentage Concentration of water in solvent mixture after drying with Regenerant (%)
Poly(acrylic acid) solution	7.10	6.40
glycolic acid	7.10	8.50
poly(acrylic acid-co-maleic acid) solution	7.10	5.80
Tartaric Acid	7.10	8.80
Citric acid	7.10	8.10

[00100] The results showed that increasing the -COOH concentration also increased the water absorbing capacities Poly(acrylic acid-co-maleic acid) showed the best potential as a regenerant at a low concentration.

Example 2 – Amine Complex Cross over Experiment

[00101] This experiment was conducted to determine how much amine cross-over could be detected between the amine in the drying agent complex and the solvent mixture. The drying agent complex was tested against solvent mixtures at a wetness of 7.1%. The solvent mixture comprised a molar ratio of 1:2 TEA:MEK prepared in accordance to Preparative Example 1. Equal volumes of wet solvent mixture and drying agent were mixed and the resulting combination was vortexed for 30 seconds and then separated by the centrifuge fitted with a 130mm diameter 4 arm swing rotor at 4000 rpm for 60 seconds. The samples were allowed to equilibrate overnight prior to testing. The

results are shown in Table 12 and a gas chromatography calibration curve for ethylpiperidine is shown in Figure 1.

Table 12:

Wet solvent mixture (MEK:TEA) Sample	Ethylpiperidine measured in the solvent mixture(ppm)
7.1 %	2289

- 5 **[00102]** It can be seen that very little ethylpiperidine in ppm is crossing over into the solvent mixture meaning that the complex of [ethylpiperidine + citric acid] largely maintained its integrity as a complex throughout the passage of the complex through the (MEK:TEA) solvent mixture. Very little ethylpiperidine was measured in the solvent mixture. Had the ethylpiperidine crossed over and equilibrated with the triethylamine measurements of up to around 168,000 ppm would have been
10 expected.

Example 3:

- [00103]** The drying capacity of various complexes [amine* + carboxylic acid containing compound] was tested and compared with the water recovery agents disclosed in *Jessop et al.* US 2014/0076810.
- 15 **[00104]** Wet solvent (TEA:MEK 1:2) prepared according to Preparative Example 1 was used and its water content was measured using gas chromatography. To 20ml of the wet solvent mixture, 0.2ml of the following drying agents were prepared and added to the solvent mixture and then the water content of the wet solvent mixture was remeasured using gas chromatography. TEA : CO₂ was prepared by adding TEA.H₂CO₃ (0.0098mol, 1.60g) was added to distilled water (0.0556, 1g). A mixture
20 of 9.8mol/kg of TEA : CO₂ was formed and used. TEA : Formic acid, TEA : Citric acid and TEA : Glycolic was at the same molality of 9.8 mol/ kg and used to yield the results shown in Table 13 and Figure 2.

Table 13:

Drying Agent	Water remaining %	Water removed %
Wet solvent mixture control (no drying agent)	8.4	0
TEA CO ₂ (prior art)	8.0	0.4
TEA Formic acid (prior art)	7.5	0.9
TEA Citric acid	7.1	1.3
TEA Glycolic	7.5	0.9

[00105] The results in Table 13 and Figure 2 show that the triethylamine : citric acid complex and the triethylamine : glycolic acid complex provided greater or comparative water removal when compared to the system described in *Jessop et al.* US 2014/0076810.

5 **Example 4: Measurement of the pH of the carboxylic acid : triethylamine complex to demonstrate the irreversibility of protonation of the carboxylic acid/triethylamine complex.**

[00106] The irreversibility of the protonation of the carboxylic acid in the complex can be shown by comparing the changes in the pH showing that substantially all the free protons have been removed when triethylamine has been added – see Table 14. The pH data also supports the fact that
10 the amine is in mostly salt form.

Table 14:

Citric Acid in presence of copper or iron chloride	Triethylamine	pH	Solution colour
CuCl ₂ + Citric Acid	None added	0.63	Light blue
FeCl ₃ + Citric Acid	None added	0.82	Red/brown
CuCl ₂ + Citric Acid	TEA	7.82	Blue
FeCl ₃ + Citric Acid	TEA	7.58	Yellow

Example 5: Amino Acids + Amine combination

[00107] A range of amino acids were tested as the carboxylic group containing compounds to
15 determine their water absorbing capacities. As above, wet solvent mixture samples were prepared according to preparative example 1 above. The amino acids were purchased from Sigma-Aldrich. The drying capacity of an amine* + various amino acid combinations were tested.

[00108] Wet solvent (TEA:MEK 1:2) prepared according to Preparative Example 1 was used and its water content was measured using gas chromatography. To 20ml of the wet solvent mixture,
20 0.2ml of the following drying agents were prepared and added to the solvent mixture and then the water content of the wet solvent mixture was remeasured using gas chromatography. Saturated amino acid solutions were mixed with TEA to form the TEA : lysine, TEA : glycine, TEA : sarcosine and TEA : N, N- dimethylglycine complexes respectively and used to yield the results shown in Table 15 and Figure 3.

25

Table 15:

Drying Agent	Percentage Concentration of water in wet solvent mixture (%)	Percentage Concentration of water in solvent mixture after drying with Regenerant (%)
TEA : Glycine	7.10	6.8
TEA : Lysine	7.10	5.7
TEA : N,N-Dimethylglycine	7.10	5.6
TEA : Sarcosine	7.10	5.3

[00109] The results in Table 15 and Figure 3 show that a triethylamine : amino acid complex can act as a drying agent. This complex is able to dry the wet solvent by effective removal of water.

5

Example 6: Combinations of varying drying agents

[00110] A water absorbing solvent mixture was prepared according to Example 1 described above. A synthetic brine was added to the water absorbing solvent mixture in ratio of 20:1. (20 parts water absorbent solvent mixture to 1 part brine). The synthetic brine had the composition detailed in Table 16.

10

Table 16: Synthetic Brine Composition

Salts	g/l
NaCl	22.8
MgCl ₂	0.2348
KCl	0.1206
CaCl ₂	2.4459
SrCl ₂	0.289
BaCl ₂	0.3044

[00111] After the addition of the brine to the water absorbing solvent mixture, the wetness of the solvent mixture was determined by gas chromatography to be 8.136%. A series of drying agents were prepared according to Table 17.

15

Table 17: Composition of drying agents

No.	Drying Agents	Combination	Acid 1 (g)	Moles of Acid 1	Acid 2 (g)	Moles of Acid 2	Weight of Water (g)	Molality of -COOH (mol/kg)	Mole ratio of -COOH
1	Acid 1: Tartartic acid; Acid 2: Methoxyacetic acid	1	3.6771	0.0245	4.4139	0.0490	10	9.8	1:1
		2	2.4514	0.0163	5.8852	0.0653	10	9.8	1:2
2	Acid 1: Glycolic acid; Acid 2: Methoxyacetic acid	1	3.7265	0.0490	4.4139	0.0490	10	9.8	1:1
		2	2.4843	0.0327	5.8852	0.0653	10	9.8	1:2
3	Acid 1: Tartartic acid; Acid 2: citric acid	1	3.6771	0.0245	3.1380	0.0163	10	9.8	1:1
		2	1.8395	0.0123	4.7094	0.0245	10	9.8	1:2
4	Acid 1: Methoxyacetic acid; Acid 2: citric acid	1	4.4139	0.0490	3.1380	0.0163	10	9.8	1:1
		2	2.9426	0.0327	4.1840	0.0218	10	9.8	1:2
5	Acid1: glycolic acid; Acid2: Tartartic acid	1	3.7265	0.0490	3.6771	0.0245	10	9.8	1:1
		2	1.0650	0.0140	6.3055	0.0420	10	9.8	1:2
6	Acid1: Isethionic Acid Ammonium salt; Acid2: Citric acid	1	7.0148	0.0490	3.1380	0.0163	10	9.8	1:1
		2	4.6766	0.0327	4.1840	0.0218	10	9.8	1:2
7	Acid1: Lysine; Acid2: citric acid	1	7.1633	0.0490	3.1380	0.0163	10	9.8	1:1
		2	3.5835	0.0245	4.7094	0.0245	10	9.8	1:2

- [00112] 0.2 ml of the drying agent prepared according to compositions 1 to 7 was added to 20 mls of the wet solvent mixture prepared above. The combination of the drying agent and the wet solvent mixture was mixed by vortex and then centrifuged to separate the respective layers. The wetness of the solvent mixture was then measured again by gas chromatography to determine how much water had been removed from the wet solvent mixture by the drying agent. The results are shown in Table 18.

Table 18: Viscosity, PH and conductivity of the Drying Agent

Drying Agent, all at 9.8 Mol/Kg of COOH and all measurements taken at 18 °C. Original solvent wetness was 8.136 %								
Acid 1	Acid 2	Mole ratio of -COOH	pH before adding TEA	pH after adding TEA	Viscosity (m.Pas)	Temp (°C)	Conductivity (ms/cm)	Wetness After Drying agent (%)
Tartaric acid	MA acid	1:1	0.81	8.81	24.83	18	5.88	7.251
		1:2	0.819	8.99	18.81		5.53	7.331
Glycolic acid	MA acid	1:1	0.94	9.03	15.74	18	7.09	7.316
		1:2	0.94	8.92	15		6.66	7.285
Tartaric acid	Citric acid	1:1	0.69	7.86	154	18	4.4	7.346
		1:2	0.7	9.14	63.44		3.31	7.379
MA acid	Citric acid	1:1	0.97	8.81	29.73	18	4.78	7.447
		1:2	0.86	8.74	39.94		4	7.327
Glycolic acid	Tartaric acid	1:1	0.84	8.7	26.63	18	6.82	7.269
		1:2	0.46	8.64	34.55		5.09	7.317
Lysine	Citric acid	1:1	5.71	9.58	50.83	18	3.75	7.566
		1:2	3.36	8.95	73.15		3.23	7.479
Citric acid			-0.31	8.14	161	18.3	1.112	7.298

MA = methoxyacetic acid

- [00113] The results from Table 18 show that methoxyacetic acid provides a higher osmotic pressure in combination with tartaric acid and glycolic acid. In contrast, the osmotic pressure of the drying agents was low when the drying agent combination included lysine. It can also be seen that the viscosity of the drying agent combinations varies too. The combination of tartaric acid and citric acid has the highest viscosity.

15 Example 7: Combinations of varying drying agents with different solvent drying mixtures

- [00114] A range of solvent drying mixtures were prepared as shown in Table 19. The molar ratio of amine to ketone was 1:2.

Table 19.

Ketone Amine	Mass	Density	Volume (mL)	Mole	Mole ratio (Amine: Ketone)
MEK	74.122	0.806	171.73	1.87	0.5:1
Ethylpiperidine	113.2	0.824	128.27	0.93	
Cyclohexanone	98.15	0.948	180.35	1.74	0.5:1
Ethylpiperidine	113.2	0.824	119.65	0.87	
MEK	74.122	0.806	177.71	1.93	0.5:1
4-Ethylmorpholine	115.1735	0.91	122.29	0.97	
Cyclohexanone	98.15	0.948	186.19	1.80	0.5:1
4-Ethylmorpholine	115.1735	0.91	113.81	0.90	
MEK	74.122	0.806	180.92	1.97	0.5:1
N,N-Diethylmethanamine	87.16	0.72	119.08	0.98	
Cyclohexanone	98.15	0.948	189.32	1.83	0.5:1
N,N-Diethylmethanamine	87.16	0.72	110.68	0.91	

- [00115] Gas chromatography calibrations for the solvent mixtures were prepared. These were made using 0.5, 0.49, 0.48, 0.47, 0.46 and 0.45 ml of absorbent with 0, 0.01, 0.02, 0.03, 0.04 and 0.05 ml of water respectively. The drying agents were prepared according to Table 20.

Table 20: Drying agents

Sample	Concentration of COOH (mol/Kg)	Weight of Compound (g)	Mole of acid	Water (ml)	Number of - COOH
Citric acid	9.8	3.138	0.016	5	3
Glycolic acid	9.8	3.726	0.049	5	1
Tartaric acid	9.8	3.677	0.025	5	2
Lysine	9.8	7.163	0.049	5	1

- [00116] The ability of the ketone/amine solvent mixture to absorb water was tested in accordance with the following procedure:

10 mls of distilled water was added to 10 ml of the ketone/amine mix in a volumetric ratio of 1:1.

- 1 The resulting mixture was vortexed for 30 seconds and then heated to 50 degrees Celsius.
- 2 After 1-2 hours, the top layer of the vortexed mixture was analysed by gas chromatography.
- 3 The wetness of the methylethylketone and ethylpiperidine mixture was measured to be 12.6%.
- 4 The wetness of the cyclohexanone and ethylpiperidine mixture was measured to be 8.3%.
- 5 The wetness of the methylethylketone and 4-ethylmorpholine mixture was not measurable because the mixture did not separate into two phases even when heated to 70 degrees Celsius.
- 6 The wetness of the cyclohexanone and 4-ethylmorpholine mixture was not measurable because the mixture did not separate into two phases even when heated to 70 degrees Celsius.

[00117] The ability of a drying agent being able to release the water within the ketone/amine solvent mixture was also tested. The following drying agents were prepared by adding an excess of an amine, triethylamine (10 mls for citric acid, glycolic acid, tartaric acid and 5 ml for lysine), to the drying agent detailed in Table 20. The resulting drying agent, amine combination was then analysed for pH, viscosity and conductivity at around 19.3 degrees Celsius. The results obtained are tabulated in Table 21.

Table 21:

Drying Agent and Amine	Concentration of COOH (mol/Kg)	pH before adding TEA	pH after adding TEA	Viscosity (m.Pas)	Temperature (°C)	Conductivity (ms/cm)
Citric acid.TEA	9.8	0.69	8.25	68.2	19.3	3.35
Glycolic acid.TEA	9.8	0.84	9.09	18.7	19.2	8.27
Tartaric acid.TEA	9.8	0.46	7.76	34.6	19.3	5.68
Lysine TEA	9.8	10.61	10.68	74.77	19.3	1.403

[00118] It can be observed that viscosity and conductivity were obtained from the various combinations. For example, the combination of lysine and TEA gave the highest viscosity, while the

combination of glycolic acid and TEA gave the lowest viscosity. The wetness of the various solvent mixtures (ketone plus amine) with different drying agent combinations (acid plus amine) was analysed by GC and the results are shown in Table 22 below.

Table 22:

Ketone Amine combination	Mole ratio (Amine: Ketone)	Water content of Wet ketone amine combination (%)	Water content of dry ketone amine combination (Glycolic) (%)	Water content of dry ketone amine combination (Citric) (%)	Water content of dry ketone amine combination (Tartaric) (%)	Water content of dry ketone amine combination (Lysine) (%)
MEK	0.5:1	11.931	10.625	10.526	10.491	10.81
EP						
CH	0.5:1	7.722	6.842	6.728	6.744	7.155
EP						
MEK	0.5:1	10.071	10.838	9.813	9.868	10.085
4-EM						
CH	0.5:1	9.563	9.814	9.102	9.224	9.497
4-EM						
MEK	0.5:1	10.905	10.726	10.267	10.285	10.42
N,N-DMA						
Cyclohexano ne	0.5:1	12.505	11.418	11.034	11.155	11.569
N,N-DMA						

5 EP = ethylpiperidine; CH = cyclohexanone; 4-EM = 4- ethylmorpholine NN-DMA – N,N-diethylmethylanine

[00119] It can be seen from the results in Table 22 that the drying agents do not dry every amine: ketone solution, and notably the solutions that include 4-ethylmorpholine (EM) became wetter after mixing with a drying agent.

10

Example 8 – Use of counter current regeneration to optimise recovery and reduce reverse osmosis requirements using a commercial brine sample

[00120] A range of methylethylketone to triethylamine (Absorbent) mixes were prepared by adding 1 mL of a commercial brine to 20 mL of methylethylketone to triethylamine (2% wet in a MEK

to TEA 1:2 ratio). The resulting sample was vortexed for 30 seconds and centrifuged for 1 min (4000 RPM). The commercial brine sample had the following composition as outlined in Table 23.

Table 23: Brine Sample 1 composition

Analyte	Concentration (mg/L)
Alkalinity, Bicarbonate as CaCO ₃	293.000
Chloride	1950.000
Sulfate	5950.000
Barium	0.012
Calcium	501.000
Magnesium	359.000
Manganese	0.011
Potassium	3.620
Sodium	3100.000
Strontium	6.930
Boron	30.700
Iron	ND
Total Dissolved Solids	12300.000

- 5 [00121] For the initial experiment A (standard Regeneration) – see Figure 4, the Absorbent was regenerated five times with pure Regenerant (1 mL). The pure regenerant was made in a stepwise fashion using 1 litre of water, 1322 grams of citric acid, 112 grams of CuCl₂ (dihydrate), 2.22 L triethylamine and 0.25 litres of methylethylketone (2 butanone).

- [00122] Figure 4 shows the steps in this experiment::
- 10 - The dilute Regenerant from the 2nd Regeneration is re-used for the 1st Regeneration of the following stage.
- The dilute Regenerant from the 3rd Regeneration is re-used for the 2nd Regeneration of the following stage.
- 15 - The dilute Regenerant from the 4th Regeneration is re-used for the 3rd Regeneration of the following stage.
- The 5th Regeneration always used Pure Regenerant (1 mL) – denoted as PP Regen in Figure 4.
- The dilute Regenerant from the 5th Regeneration is re-used for the 4th Regeneration of the next stage.

[00123] Gas chromatography analysis throughout each step for the counter current regeneration process was conducting using the parameters noted below: All GC data was collected on a SHIMADZU Nexis 2030 gas chromatograph fitted with a SH-Rxi-624Sil MS column. The GC parameters were set up as shown below:

5	Parameter	Setting
	Injection Volume	0.5 µL
	Injection temperature	250 °C
	Injection mode	Split
	Split ratio	50.0
10	Carrier gas	He
	Carrier gas pressure	53.1 kPa
	Column flow	1.16 mL/min
	Liner velocity	24.0 cm/s
	Column length	30.0 m
15	Column inner diameter	0.32
	Column method	Gradient
	Column temperature	250.0 °C
	Total time	9 min
	Detector	TCD
20	TCD sample rate	40 ms
	TCD current	60 mA
	Makeup gas	He
	Makeup flow	8.0 mL/min
	TCD temperature	200 °C

25 GC Column Method:

Rate (°C / min)	Temperature (°C)	Hold Time (min)
	100.0	2.00
10.00	125.0	0.00
50.00	200.0	3.00

Total program time 9.00 min

[00124] The GC analysis was conducted to determine the presence of water in the Absorbent and to track the reduction of the water levels in the Absorbent at each stage of regenerating or drying the absorbent. The GC results are shown below in Table 24 and plotted in Figure 5.

5 **Table 24:**

Stages	Wet %	1 (1 st Reg) %	2 (2 nd Reg) %	3 (3 rd Reg) %	4 (4 th Reg) %	5 (5 th Reg) %
A	5.2	3.0	2.0	1.5	1.3	1.2
B	5.2	3.4	2.3	1.7	1.4	1.2
C	5.2	3.7	2.6	1.9	1.5	1.3
D	5.2	3.9	2.8	2.0	1.5	1.3
E	5.2	4.0	2.9	2.2	1.6	1.3
F	5.2	4.1	3.0	2.2	1.6	1.3

[00125] From the above results it can be seen that that after the 5th Regeneration even after re-using the Regenerant throughout all other stages the results are fairly stable and ultimately give a very low water percentage (1.3%).

10

[00126] The inventors have established that the water recovery performance of the Complex [amine* + carboxylic acid containing compound] is superior to the water recovery agents described in Jessop *et al.* US 2014/0076810 as shown in Example 3. Without wanting to be bound to any mechanistic theory, it is notable that the [amine* + carboxylic acid containing compound] of the present invention is irreversibly protonated, whereas Jessop *et al.* US 2014/0076810 clearly teaches that the amine should not be irreversibly protonated. Unlike Jessop, which requires the switchability function of the drying agent, the present examples show that switchability is not a necessary function of the drying agent/regenerant. The inventors have also been able to establish that when a Complex [amine* + carboxylic acid containing compound] is mixed with a solvent mixture [amine + enolisable carbonyl + water], the amine* of the complex may be the same or different from the amine in the solvent mixture. This is because the integrity of the complex is substantially maintained as the complex passes through the solvent mixture, which is unlike what is described in Jessop. It also means that the complex or salt form of the amine is not reversible by temperature or air stripping.

25 **Example 9**

[00127] A diluted solvent drying solution was processed using a reverse osmosis membrane. The diluted solvent drying solution (20 litres) comprised 20% by volume of the solvent drying composition and 80% by volume of distilled water. The diluted solvent drying composition was prepared by dissolving together (FeCl₃) and citric acid in the molar ratio of 1: 10 and then diluting the

dissolved composition with 80% of distilled water. The total dissolved solids (TDS) of the 20 % (by vol.) of the solvent drying composition was approximately 287 grams. With reference to Figure 6, the reverse osmosis system comprising the following components are illustrated:

- 1 Feed tank consisting of dilute solvent drying solution
- 5 • 2 Flow meter at the Feed outlet
- 3 High pressure pump with closed loop control of pressure in front of the membrane (Dow FILMTEC™ seawater reverse osmosis element SW30 – 2540 with active area of 2.8 m2) by manipulation of pump speed
- 4 Membrane vessel
- 10 • 5 Concentrate stream with restriction valve
- 6 Permeate outflow
- 7 Permeate collection tank
- 8 control valves

[00128] Prior to use of the osmosis system shown in Figure 6, the membrane in the membrane vessel 4 was conditioned by running deionised water through the membrane for 2 hours before dosing the feed with the diluted solvent drying solution. The diluted solvent drying solution from the feed tank 1 was pushed to the high-pressure level using a high-pressure pump 3. The semi-permeable membrane inside of each membrane vessel 4 restrains most of the solvent drying composition. Only the permeate consisting of low dissolved salt and water gets through the membrane, while the concentrate stream 5 is fed back into the feed tank 1. The permeate outflow 6 is fed into the permeate collection tank 7. The electrical conductivity of the permeate was measured as an indicator of permeate quality and rejection %.

Measurement conditions:

- Max. operating temperature: 40°C
- 25 • Max. membrane operating temperature: 45°C
- Pressure (bar): 60
- The permeate flow rate and conductivity measurements of both concentrate and permeate were collected at the below mentioned time intervals.

Table 25: Feed: 20 % (by vol.) diluted solvent drying solution

	Time	Flux (LMH)	Rejection %
60 bar	2	3.51	97.33
	4	3.58	98.22
	6	3.74	98.32
	8	3.56	98.25
	10	3.45	98.13

	12	3.25	97.93
	14	2.98	97.71
	16	2.88	97.38
	18	2.74	97.04
	20	2.68	97.01
	30	1.80	94.30
	40	1.75	93.77
	50	1.63	93.68
	60	0.65	93.00
	70	0.09	93.03

[00129] The results shown in Table 25 are also shown plotted in Figure 8.

[00130] **Osmotic pressure and concentration measurements:** 100uL of sample was taken
 5 from both feed and permeate and run through the Osmometer. The units were converted from mOsmol/kg to atm and the concentration of salt in both the streams was calculated and tabulated.

[00131] The following formulae were used to calculate flux, salt rejection and water recovery.

Flux measurement:

$$J_w = \frac{\text{Flow rate of Permeate } \left(\frac{\text{mL}}{\text{min}}\right) \times 60}{1000 \times \text{Membrane active area}}$$

10 **Salt rejection % by conductivity method:**

$$\frac{\text{Conductivity of feed solution } \left(\frac{\text{mS}}{\text{cm}}\right) - \text{Conductivity of Permeate water } \left(\frac{\text{mS}}{\text{cm}}\right)}{\text{Conductivity of feed solution } \left(\frac{\text{mS}}{\text{cm}}\right)} \times 100$$

Salt rejection % by osmotic pressure method:

$$\frac{\text{Osmotic pressure of feed (atm)} - \text{Osmotic pressure of permeate (atm)}}{\text{Osmotic pressure of feed (atm)}} \times 100$$

Water recovery % - Method 1:

15
$$\frac{\text{Volume of (Feed - Concentrate) (L)}}{\text{Volume of feed (L)}} \times 100$$

Water recovery % - Method 2:

$$\frac{\text{Volume of permeate collected at end of test (L)}}{\text{Volume of feed (L)}} \times 100$$

[00132] A second embodiment of the process of the present invention is shown in Figure 7. This embodiment illustrates a process where more than one solvent drying composition regeneration

step may be employed to recover the solvent drying composition complex. As shown in Figure 7, the diluted regenerant (the dilute solvent drying composition) is recovered from the coalescer column COL-102 after an industrial process involving the removal of water from a brine feed stock. The diluted solvent drying composition is then subjected to a multi-stage reverse osmosis recovery phase to concentrate (ie remove water) the solvent drying composition (regenerant) in a continuous loop operation, whereby the regenerant is recovered and then fed back into the earlier stages of the industrial process to facilitate the removal of water from a brine solution. It is to be appreciated that the coalescer column may be an electrostatic coalescer column, because the solvent drying composition is a good insulator and electrostatic coalescing may improve the overall performance of the process. Figure 11 shows a process diagram that includes an electrostatic coalscer (COL-202).

Example 10 – Other Membranes

[00133] Various other membranes were also tested under the following conditions and compared to the membrane used above:

[00134] Solvent Drying Composition – The diluted solvent drying composition was prepared by dissolving together (FeCl₃) and citric acid in the molar ratio of 1: 10 and then diluting the dissolved composition with 80% of distilled water. The total dissolved solids (TDS) of the 20 % (by vol.) of the solvent drying composition was approximately 287 grams.

Example 10.1 Membrane 1 TriSep™ TS-80

20 Membrane specifications:

- Flux (GFD/psi): 220/110
- Max. operating pressure (bar): 41
- Max. operating temperature (°C): 45
- Chlorine tolerance: 0.1 ppm
- 25 • Membrane active area: 0.0142 m²
- Feed solution: 5% Solvent Drying solution (by vol.)

Membrane 1 Results:

[00135] The results at various pressures and times for flux and salt rejection data are shown below in Tables 26 - 28.

Table 26: Flux (LMH) and salt rejection % data for TriSep™ TS-80

Pressure (bar)	Permeate Flux (LMH)	Rejection %
20	11.15	59.09
25	11.59	59.97
30	14.46	60.47

35	17.71	60.31
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Table 27: Flux (LMH) at different pressures at regular time interval for TriSep™ TS-80

Pressure (bar)	20	25	30	35
Time (min)	Flux (LMH)	Flux (LMH)	Flux (LMH)	Flux (LMH)
5	10.72	11.04	15.41	18.10
10	11.74	12.51	13.53	16.56
15	10.50	11.55	14.82	18.02
20	11.38	11.74	14.44	18.54
25	11.10	11.18	14.59	17.32
30	11.48	11.55	13.96	17.74

Osmotic pressure data

- 5 **Table 28:** Calculating rejection % using Osmotic pressure measurements of feed and permeate streams

Pressure (bar)	Osmotic pressure of feed (bar)	Osmotic pressure of permeate (bar)	Reduction %
20.00	2.71	1.22	54.79
25.00	2.68	1.16	56.80
30.00	2.74	1.20	56.21
35.00	2.67	1.24	53.64

Example 10.2 Membrane 2 Dow filmtec Flat sheet Membrane, SW30XLE, PA-TFC, RO**Membrane specifications:**

- 10
- Flux (GFD/psi): 23-29/880
 - Max. operating pressure (bar): 68.9
 - Max. operating temperature (°C): 45
 - Chlorine tolerance: 0.1 ppm
 - Membrane active area: 0.0142 m²
- 15
- Feed solution: 5% Solvent Drying solution (by vol.)

Membrane 2 Results:

[00136] The results at various pressures and times for flux and salt rejection data are shown below in Tables 28-30.

- 20 **Table 29:** Flux (LMH) and salt rejection % data

Pressure (bar)	Permeate Flux (LMH)	Rejection %
20	7.08	62.48

25	8.82	69.39
30	11.09	80.25
35	14.98	86.79
40	18.49	88.57

Table 30: Flux (LMH) at different pressures at regular time intervals

Pressure (bar)	20	25	30	35	40
Time (min)	Flux (LMH)	Flux (LMH)	Flux (LMH)	Flux (LMH)	Flux (LMH)
5	7.10	9.30	11.26	13.98	17.59
10	7.18	8.45	11.21	16.74	18.34
15	6.87	8.41	11.26	14.90	18.11
20	7.24	8.54	11.04	14.56	18.97
25	6.84	9.35	11.21	14.73	18.68
30	7.28	8.86	10.59	14.97	19.27

Osmotic pressure data

- 5 **Table 31:** Calculating rejection % using Osmotic pressure measurements of feed and permeate streams

Pressure (bar)	Measured osmotic pressure of feed (bar)	Measured osmotic pressure of permeate (bar)	Reduction %
20.00	2.49	0.67	72.96
25.00	2.82	0.47	83.33
30.00	2.67	0.37	86.02
35.00	2.71	0.21	92.24
40.00	2.68	0.19	93.05

Example 10.3 Membrane 3 Toray Flat Sheet Membrane - UTC-82V, PA, RO**Membrane specifications:**

- 10
- Flux (GFD/psi): 27/798
 - Max. operating pressure (bar): 55
 - Max. operating temperature (°C): 25
 - Membrane active area: 0.0142 m²
 - Feed solution: 5% Solvent Drying solution (by vol.)
- 15

Membrane 3 Results:

[00137] The results at various pressures and times for flux and salt rejection data are shown below in Tables 32-34.

Table 32: Flux (LMH) and salt rejection % data

Pressure (bar)	Permeate Flux (LMH)	Rejection %
20	23.84	67.11
25	27.73	76.30
30	29.67	75.17
35	34.30	78.22
40	38.96	81.86
45	48.59	85.65

5

Table 33: Flux (LMH) at different pressures at regular time intervals

Pressure (bar)	20	25	30	35	40
Time (min)	Flux (LMH)	Flux (LMH)	Flux (LMH)	Flux (LMH)	Flux (LMH)
5	25.18	27.65	30.36	35.88	38.70
10	23.41	28.21	29.80	35.95	38.28
15	23.88	27.34	29.87	33.18	38.79
20	23.73	27.37	30.22	33.33	38.45
25	23.49	27.30	29.54	34.90	38.70
30	23.32	28.53	28.25	32.54	40.82

Osmotic pressure calculations:

Table 34: Calculating rejection % using Osmotic pressure measurements of feed and permeate streams

Pressure (bar)	Measured osmotic pressure of feed (bar)	Measured osmotic pressure of permeate (bar)	Reduction %
20.00	3.78	0.96	74.73
25.00	3.35	0.78	76.76
30.00	3.48	0.71	79.72
35.00	3.41	0.61	82.19

10

40.00	3.55	0.52	85.39
45.00	3.68	0.45	87.67

Example 10.4 Membrane 4 Synder Flat sheet Membrane, NFX, PA-TFC, NF

Membrane specifications:

Flux (GFD/psi): 20-25/110

5 Max. operating pressure (bar): 30

Max. operating temperature (°C): 35

Chlorine tolerance (ppm hours): 500

Membrane active area: 0.0142 m²

Feed solution: 5% Solvent Drying solution (by vol.)

10

Membrane 4 Results:

[00138] The results at various pressures and times for flux and salt rejection data are shown below in Tables 35-37.

Table 35: Flux (LMH) and salt rejection % data

Pressure (bar)	Permeate Flux (LMH)	Rejection %
20	40.49	56.55
25	47.45	54.67
30	59.05	52.42
35	65.62	53.39

15

Table 36: Flux (LMH) at different pressures at regular time intervals

Pressure (bar)	20	25	30	35
Time (min)	Flux (LMH)	Flux (LMH)	Flux (LMH)	Flux (LMH)
5	42.81	44.20	55.79	63.78
10	45.63	45.21	54.29	67.38
15	42.69	49.94	59.36	67.25
20	35.56	49.94	63.56	60.23
25	38.45	48.21	60.41	68.34
30	37.77	47.17	60.87	66.76

Osmotic pressure calculations:**Table 37:** Calculating rejection % using Osmotic pressure measurements of feed and permeate streams

Pressure (bar)	Measured osmotic pressure of feed (bar)	Measured osmotic pressure of permeate (bar)	Reduction %
20	3.48	0.95	72.73
25	3.20	0.80	74.90
30	3.10	0.69	77.65
35	3.26	0.97	70.15

5 **Example 10.5 Dow filmtec Flat sheet Membrane, SW30HR, PA-TFC, RO Membrane****Membrane specifications:**

- Flux (GFD/psi): 18-24/800
- Max. operating pressure (bar): 68.9
- Max. operating temperature (°C): 45
- Chlorine tolerance (ppm hours): 0.1
- Membrane active area: 0.0142 m²
- Feed solution: 5% Solvent Drying solution (by vol.)

Results:

- 15 **[00139]** The results at various pressures and times for flux and salt rejection data are shown below in Tables 38-40.

Table 38: Flux (LMH) and salt rejection % data

Pressure (bar)	Permeate Flux (LMH)	Rejection %
35	7.74	84.78
40	13.18	93.32

Table 39: Flux (LMH) at different pressures at regular time intervals

Pressure (bar)	35	40
Time (min)	Flux (LMH)	Flux (LMH)
5	7.43	12.08
10	7.65	20.79
15	7.75	11.58
20	7.47	11.47

25	7.93	11.65
30	8.23	11.51

Osmotic pressure calculations:**Table 40:** Calculating rejection % using Osmotic pressure measurements of feed and permeate streams

Pressure (bar)	Measured osmotic pressure of feed (bar)	Measured osmotic pressure of permeate (bar)	Reduction %
35	3.52	0.24312	93.09
40	3.43	0.08104	97.64
45	3.64	0.072936	98.00

5

[00140] The results of the various membranes are shown in Figures 9 and 10. It can be seen from Figures 9 and 10 that the results of the membranes are able to recover water from the dilute solvent drying solution using a range of commercially available membranes.

10 **Example 11: Determination of whether different metal salts affect the water capacity of the solvent drying composition.**

[00141] A range of solvent drying compositions were prepared with different metal salts and their respective water capacities were determined by gas chromatography. The solvent drying compositions were prepared as follows:

- 15
1. A quantity of a specific metal salt (detailed in Table 41 below) was added to a solution of citric acid (6.6gm or 0.340 mol) in distilled water (5 ml).
 2. The resulting mixture was stirred at 80 degrees Celsius for 20 minutes.
 3. Excess triethylamine was added to the stirred mixture from step 2 to generate the solvent drying composition.

20 **Table 41:**

Metal salt used	Metal salt weight (g)	Moles of Metal Salt (mol)	Weight of citric acid (g)	Moles of citric acid (mol)	distilled water (g)	Mole ratio (X:10 citric acid)
NaCl	0.2008	0.0034	6.6	0.0344	5	1

Na₂CO₃	0.3641	0.0034	6.6	0.0344	5	1
SrCl₂	0.5445	0.0034	6.6	0.0344	5	1
AlCl₃	0.8295	0.0034	6.6	0.0344	5	1
FeCl₃	0.5572	0.0034	6.6	0.0344	5	1
CuCl₂	0.5857	0.0034	6.6	0.0344	5	1
Fe(NO₃)₃	1.3879	0.0034	6.6	0.0344	5	1
Fe₂(SO₄)₃	1.3737	0.0034	6.6	0.0344	5	1
CuSO₄	0.5483	0.0034	6.6	0.0344	5	1
Cu(OH)₂	0.3400	0.0034	6.6	0.0344	5	1

[00142] The properties of the solvent drying compositions prepared are detailed in Table 42 below:

Table 42:

Solvent Drying Composition	pH before adding TEA	pH after adding TEA	Viscosity (m.Pas)	Temp (°C)	Osmotic Pressure (atm)	Conductivity (ms/cm)
NaCl.citrate	0.04	8.05	288	18	194	1.119
Na₂CO₃.citrate	1.58	8.09	375	18	186	1.182
SrCl₂.citrate	1.27	8.18	381.32	18	194	0.949
AlCl₃.citrate	-0.43	8.29	209.22	18	-	1.569
FeCl₃.citrate	-0.28	8.06	219.68	18	186	1.96
CuCl₂.citrate	0.17	8.13	238.36	18	158	1.559
Fe(NO₃)₃.citrate	-0.24	8.22	166.18	18	-	2.2
Fe₂(SO₄)₃.citrate	-0.14	8.25	274.14	18	182	1.111
CuSO₄.citrate	0.04	8.16	278	18	-	1.258
Cu(OH)₂.citrate	0.98	8.016	537.23	18	108	1.005

5

[00143] It can be seen that the viscosity of each solvent drying composition varies as the metal salt changes. The above solvent drying compositions were then reacted with wet absorbent as follows:

1. 0.2 ml of each solvent drying composition outlined in Table X was added to 20 ml of wet absorbent.
2. The resulting mixture was mixed by vortex mixer for 30 seconds and then separated by centrifuge.
3. A GC analysis of the water remaining in the absorbent after mixing with the solvent drying compositions was analysed and the results shown in Table 43 below.

15

Table 43 The water absorption capacities of Regenerants

Solvent Drying Composition	Wet Absorbent used (mL)	Water content in wet Absorbent (%)	Volume of Solvent Drying Composition (mL)	Water content in Absorbent after drying with Solvent Drying Composition (%)	Valence state
NaCl.citrate	20	7.793	0.2	6.635	1
Na ₂ CO ₃ .citrate	20	7.793	0.2	6.522	1
SrCl ₂ .citrate	20	7.793	0.2	6.581	2
AlCl ₃ .citrate	20	7.793	0.2	6.778	3
FeCl ₃ .citrate	20	7.793	0.2	6.76	3
CuCl ₂ .citrate	20	7.793	0.2	6.802	2
Fe(NO ₃) ₃ .citrate	20	7.793	0.2	6.834	3
Fe ₂ (SO ₄) ₃ .citrate	20	7.793	0.2	6.634	3
CuSO ₄ .citrate	20	7.793	0.2	6.723	2
Cu(OH) ₂ .citrate	20	7.793	0.2	6.699	2

[00144] It can be seen from the results shown in Table 43 that the water absorption capacity of each solvent drying composition is not substantially altered as the metal salt changes.

5

[00145] The present invention and its embodiments have been described in detail. However, the scope of the present invention is not intended to be limited to the particular embodiments of any process, manufacture, composition of matter, compounds, means, methods, and/or steps described in the specification. Various modifications, substitutions, and variations can be made to the disclosed material without departing from the spirit and/or essential characteristics of the present invention. Accordingly, one of ordinary skill in the art will readily appreciate from the disclosure that later modifications, substitutions, and/or variations performing substantially the same function or achieving substantially the same result as embodiments described herein may be utilized according to such related embodiments of the present invention. Thus, the following claims are intended to encompass within their scope modifications, substitutions, and variations to combinations, kits, compounds, means, methods, and/or steps disclosed herein.

10

15

Claims:

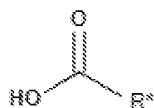
1 A solvent drying composition, the composition comprising of:

- 5 a) a complex of at least one amine or ammonium salt containing compound and at least one carboxylic acid containing compound or an alkylsulfonic acid; or a combination thereof, in a solvent comprising
- b) at least one amine containing compound at least one enolisable carbonyl and water,
- wherein in use water in the solvent is released to form an immiscible aqueous layer with the solvent drying composition.

10

2 The composition as claimed in claim 1 wherein the carboxylic acid containing compound is selected from one or more of the following:

- a) compound of Formula I,



Formula I

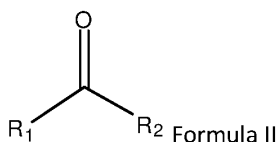
- 15 wherein R* is selected from, -C₁-C₇ alkyl-OH, -C₁-C₇ alkyl, -C₁-C₇ alkyl-NH₂, -C₁-C₇ alkyl-NHR³ and -C₁-C₇ alkyl NR³R⁴, wherein each R³ and R⁴ are selected from -H, -OH, -halo, -C₁-C₇ alkyl, -C₁-C₇ alkyl-OH, -C(O)OH, -C(O)-H, or -C(O)-(C₁-C₇ alkyl);
- b) a polymer containing one or more carboxylic acid groups.

20 3 The composition as claimed in claim 1 or claim 2, wherein the solvent from which the water is recovered comprises at least one amine containing compound and at least one enolisable carbonyl.

4 The composition as claimed in any one of claims 1 to 3, wherein the solvent comprises at least a secondary or tertiary amine or a combination thereof.

5 The composition as claimed in any one of claims 1 to 4, wherein the solvent comprises at least

25 one enolisable carbonyl of Formula II,



Formula II

wherein

- a) R_1 and R_2 are independently selected from a $-C_1-C_7$ alkyl or a $-C_3-C_7$ monocyclic or a phenyl; or
- b) one of R_1 or R_2 is selected from a $-O-(C_1-C_7 \text{ alkyl})$ and the other is selected from a $-C_1-C_7$ alkyl, or
- 5 c) R_1 and R_2 together, with the carbonyl of Formula II, form a 3-15 membered monocyclic ketone or a 3-15 membered monocyclic heterocyclic ketone or acetophenone.

6 The composition as claimed in any one of claims 1 to 5, wherein the carboxylic acid containing compound of Formula I is selected from acetic acid, citric acid and glycolic acid or a combination thereof.

10

7 The composition as claimed in any one of claims 1 to 5, wherein the alkylsulfonic acid is isoethionic acid.

8 The composition as claimed in any one of claims 1 to 7, wherein the molar ratio of the at least one amine or ammonium salt containing compound to the at least one carboxylic acid containing compound or an alkylsulfonic acid; or a combination thereof, is about 1:99 or 99:1.

15

9 The composition as claimed in any one of claims 1 to 8, wherein the molar ratio of the at least one amine or ammonium salt containing compound to the at least one carboxylic acid containing compound or an alkylsulfonic acid; or a combination thereof, is about 1:50 or 50:1.

20

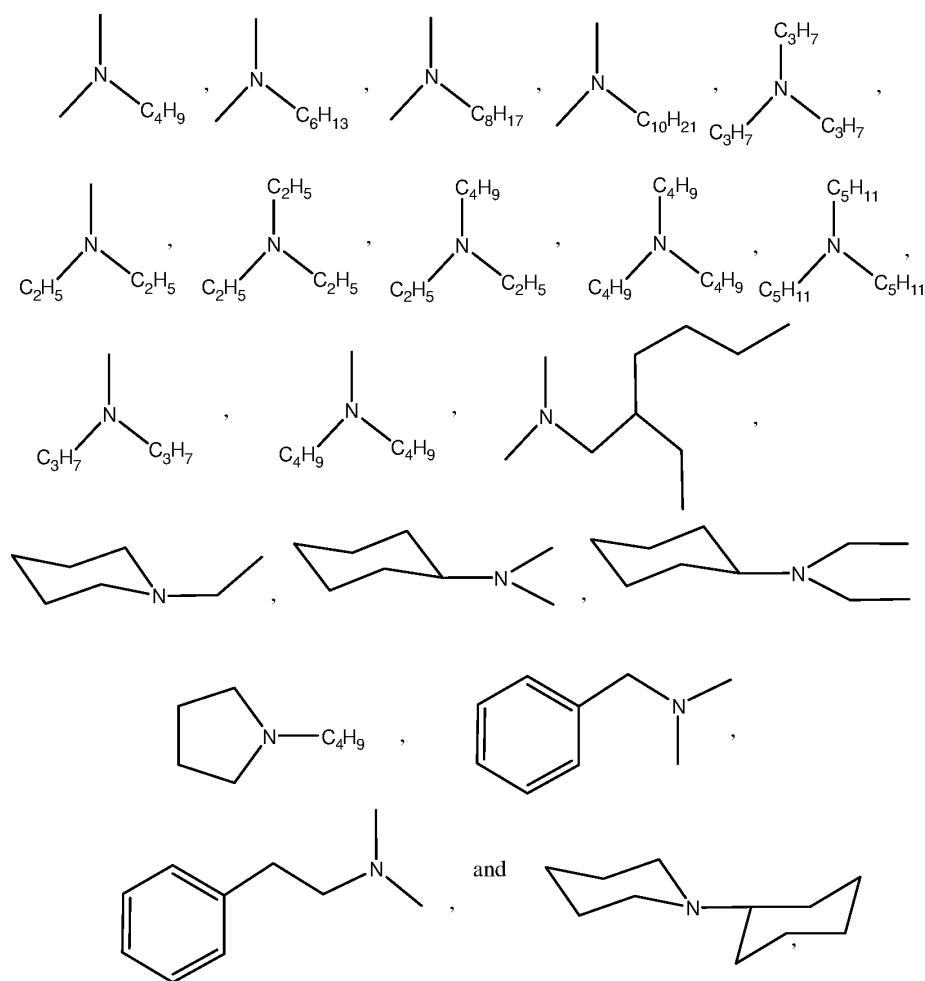
10 The composition as claimed in any one of claims 1 to 9, wherein the molar ratio of the at least one amine or ammonium salt containing compound to the at least one carboxylic acid containing compound or an alkylsulfonic acid; or a combination thereof, about 1:10 or 10:1.

25 11 The composition as claimed in any one of claims 1 to 10, wherein the molar ratio of the at least one amine or ammonium salt containing compound to the at least one carboxylic acid containing compound or an alkylsulfonic acid; or a combination thereof, about 1:5 or 5:1.

12 The composition as claimed in any one of claims 1 to 11, wherein the molar ratio of the at least one amine or ammonium salt containing compound to the at least one carboxylic acid containing compound or an alkylsulfonic acid; or a combination thereof, about 1:3 or 3:1.

30

- 13 The composition as claimed in any one of claims 1 to 12, wherein the molar ratio of the at least one amine or ammonium salt containing compound to the at least one carboxylic acid containing compound or an alkylsulfonic acid; or a combination thereof, of about 1:2 or 2:1.
- 5 14 The composition as claimed in any one of claims 1 to 12, wherein the molar ratio of the at least one amine or ammonium salt containing compound to the at least one carboxylic acid containing compound or an alkylsulfonic acid; or a combination thereof, a ratio of about 1:1.
- 15 The composition as claimed in any of claims 1 to 14 wherein the solvent includes at least one amine containing compound, which amine may be the same or different from the amine containing compound in the complex.
- 10 16 The composition as claimed in any one of the claims 1 to 15, wherein the at least one amine containing compound of the complex or solvent is selected from a conjugated, aliphatic, asymmetric or cyclic tertiary amine.
- 15 17 The composition as claimed in claim 16, wherein the tertiary amine containing compound is selected from the following:



18 The composition as claimed in claim 16 or claim 17, wherein the at least one tertiary amine containing compound is selected from a -N(C₁-C₇ alkyl)₃.

5

19 The composition as claimed in any one of claims 16 to 18, wherein the at least one tertiary amine containing compound is selected from a -N(C₁-C₄ alkyl)₃.

20 The composition as claimed in any one of claims 16 to 19, wherein the at least one tertiary
10 amine containing compound is -N(C₂ alkyl)₃ (triethylamine).

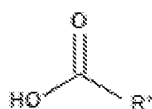
21 The composition as claimed in claim 16 or claim 17, wherein the at least one tertiary amine
containing compound is ethylpiperidine.

- 22 The composition as claimed in any one of claims 5 to 21, wherein R₁ of Formula II is a -C₁-C₇ alkyl.
- 23 The composition as claimed in any one of claims 5 to 22, wherein R₁ of Formula II is further
5 substituted with one or more substituents selected from -OH, -C₁-C₇ alkyl, -(C₁-C₇ alkyl)-OH, -NH₂, -NH(C₁-C₇ alkyl), -N(C₁-C₇ alkyl)₂, -C(O)OH; -C(O)-H, or -C(O)-(C₁-C₇ alkyl).
- 24 The composition as claimed in any one of claims 5 to 15 wherein Formula II, is 2-butanone.
- 10 25 The composition as claimed in any one of claims 5 to 24, wherein the molar ratio of the at least one tertiary amine containing compound to the one or more enolisable carbonyls of Formula II are present in a ratio of about 1:99 or 99:1.
- 26 The composition as claimed in any one of claims 5 to 25, wherein the molar ratio of the at
15 least one tertiary amine containing compound to the one or more enolisable carbonyls of Formula II are present in a ratio of about 1:50 or 50:1.
- 27 The composition as claimed in any one of claims 5 to 26, wherein the molar ratio of the at least one tertiary amine containing compound to the enolisable carbonyl of Formula II are present in
20 a ratio of about 1:10 or 10:1.
- 28 The composition as claimed in any one of claims 5 to 27, wherein the molar ratio of the at least one tertiary amine containing compound to the one or more enolisable carbonyls of Formula II are present in a ratio of about 1:5 or 5:1.
25
- 29 The composition as claimed in any one of claims 5 to 28, wherein the molar ratio of the at least one tertiary amine containing compound to the one or more enolisable carbonyls of Formula II are present in a ratio of about 1:3 or 3:1.
- 30 30 The composition as claimed in any one of claims 5 to 29, wherein the molar ratio of the at least one tertiary amine containing compound to the one or more enolisable carbonyls of Formula II are present in a ratio of about 1:2 or 2:1.

31 The composition as claimed in any one of claims 5 to 30, wherein the molar ratio of the at least one tertiary amine containing compound to the one or more enolisable carbonyls of Formula II are present in a ratio of about 1:1.

5 32 The composition as claimed in any one of claims 1 to 31, wherein the at least one amine or ammonium salt containing compound and at least one carboxylic acid containing compound or an alkylsulfonic acid; or a combination thereof, is irreversibly protonated.

33 A complex composition comprising at least one amine or ammonium salt containing compound and at least an alkylsulfonic acid; or at least one carboxylic acid containing compound of
10 Formula I; or a combination thereof;



Formula I

wherein R* is selected from, -C₁-C₇ alkyl-OH, -C₁-C₇ alkyl, -C₁-C₇ alkyl-NH₂, -C₁-C₇ alkyl-NHR³ and -C₁-C₇ alkyl NR³R⁴, wherein each R³ and R⁴ are selected from -H, -OH, -
15 halo, -C₁-C₇ alkyl, -C₁-C₇ alkyl-OH, -C(O)OH, -C(O)-H, or -C(O)-(C₁-C₇ alkyl);

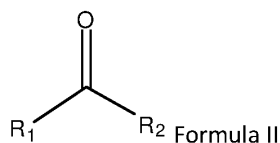
the complex being suitable for use in recovering water from a solvent, wherein water is released from the solvent upon migration of the composition through the solvent, the released water forming an immiscible aqueous layer with the solvent

and wherein the solvent comprises:

- 20 a) at least one amine containing compound,
- b) at least one enolisable carbonyl, and
- c) water.

34 The complex as claimed in claim 33 wherein the solvent comprises at least a secondary or tertiary amine or a combination thereof.

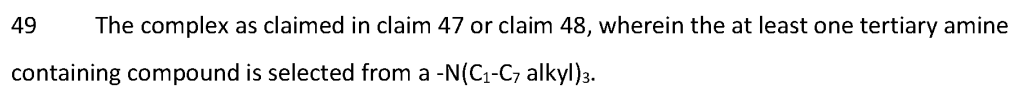
25 35 The complex as claimed in claim 33 or claim 34, wherein the solvent comprises at least one enolisable carbonyl of Formula II



wherein

- a) R_1 and R_2 are independently selected from a $-\text{C}_1\text{-C}_7$ alkyl or a $-\text{C}_3\text{-C}_7$ monocyclic or a phenyl; or
 - 5 b) one of R_1 or R_2 is selected from a $-\text{O}-(\text{C}_1\text{-C}_7 \text{ alkyl})$ and the other is selected from a $-\text{C}_1\text{-C}_7$ alkyl, or
 - c) R_1 and R_2 together, with the carbonyl of Formula I, form a 3-15 membered monocyclic ketone or a 3-15 membered monocyclic heterocyclic ketone or acetophenone.
- 10 36 The complex as claimed in any one of claims 33 to 35 wherein the at least one amine containing compound of the complex is a secondary or tertiary amine or combination thereof.
- 15 37 The complex as claimed in any one of claims 33 to 36 wherein the carboxylic acid containing compound of Formula I is selected from acetic acid, citric acid and glycolic acid or a combination thereof.
- 18 38 The complex as claimed in any one of claims 33 to 37 wherein the alkylsulfonic acid is isoethionic acid.
- 20 39 The complex as claimed in any one of claims 33 to 38, wherein the molar ratio of the at least one amine or ammonium salt containing compound to the at least one carboxylic acid containing compound or an alkylsulfonic acid; or a combination thereof, is about 1:99 or 99:1.
- 25 40 The complex as claimed in any one of claims 33 to 39, wherein the molar ratio of the at least one amine or ammonium salt containing compound to the at least one carboxylic acid containing compound or an alkylsulfonic acid; or a combination thereof, is about 1:50 or 50:1.
- 30 41 The complex as claimed in any one of claims 33 to 40, wherein the molar ratio of the at least one amine or ammonium salt containing compound to the at least one carboxylic acid containing compound or an alkylsulfonic acid; or a combination thereof, about 1:10 or 10:1.

- 42 The complex as claimed in any one of claims 33 to 41, wherein the molar ratio of the at least one amine or ammonium salt containing compound to the at least one carboxylic acid containing compound or an alkylsulfonic acid; or a combination thereof, about 1:5 or 5:1.
- 5 43 The complex as claimed in any one of claims 33 to 42, wherein the molar ratio of the at least one amine or ammonium salt containing compound to the at least one carboxylic acid containing compound or an alkylsulfonic acid; or a combination thereof, about 1:3 or 3:1.
- 44 The complex as claimed in any one of claims 33 to 43, wherein the molar ratio of the at least one amine or ammonium salt containing compound to the at least one carboxylic acid containing compound or an alkylsulfonic acid; or a combination thereof, of about 1:2 or 2:1.
- 10 45 The complex as claimed in any one of claims 33 to 44, wherein the molar ratio of the at least one amine or ammonium salt containing compound to the at least one carboxylic acid containing compound or an alkylsulfonic acid; or a combination thereof, a ratio of about 1:1.
- 15 46 The complex as claimed in any of claims 33 to 45 wherein the solvent includes at least one amine containing compound, which amine may be the same or different from the amine containing compound in the complex.
- 20 47 The complex as claimed in any of claims 33 to 46 wherein the at least one amine containing compound of the complex or solvent is selected from a conjugated, aliphatic, asymmetric or cyclic tertiary amine.
- 48 The complex as claimed in claim 47, wherein the tertiary amine containing compound is selected from the following:



50 The complex as claimed in any one of claims 47 to 49, wherein the at least one tertiary amine containing compound is selected from a $-N(C_1-C_4 \text{ alkyl})_3$.

53 The complex as claimed in claim 47 or claim 48, wherein the at least one tertiary amine
containing compound is ethylpiperidine.

- 54 The complex as claimed in any one of claims 35 to 53, wherein R₁ of Formula II is a -C₁-C₇ alkyl.
- 55 The complex as claimed in any one of claims 35 to 54, wherein R₁ of Formula II is further
5 substituted with one or more substituents selected from -OH, -C₁-C₇ alkyl, -(C₁-C₇ alkyl)-OH, -NH₂, -NH(C₁-C₇ alkyl), -N(C₁-C₇ alkyl)₂, -C(O)OH; -C(O)-H, or -C(O)-(C₁-C₇ alkyl).
- 56 The complex as claimed in any one of claims 35 to 55, wherein Formula II, is 2-butanone.
- 10 57 The complex as claimed in any one of claims 33 to 56, wherein the molar ratio of the at least one tertiary amine containing compound to the one or more enolisable carbonyls of Formula II are present in a ratio of about 1:99 or 99:1.
- 58 The complex as claimed in any one of claims 33 to 57, wherein the molar ratio of the at least
15 one tertiary amine containing compound to the one or more enolisable carbonyls of Formula II are present in a ratio of about 1:50 or 50:1.
- 59 The complex as claimed in any one of claims 33 to 58, wherein the molar ratio of the at least one tertiary amine containing compound to the enolisable carbonyl of Formula II are present in a
20 ratio of about 1:10 or 10:1.
- 60 The complex as claimed in any one of claims 33 to 59, wherein the molar ratio of the at least one tertiary amine containing compound to the one or more enolisable carbonyls of Formula II are present in a ratio of about 1:5 or 5:1.
- 25 61 The complex as claimed in any one of claims 33 to 60, wherein the molar ratio of the at least one tertiary amine containing compound to the one or more enolisable carbonyls of Formula II are present in a ratio of about 1:3 or 3:1.
- 30 62 The complex as claimed in any one of claims 33 to 61, wherein the molar ratio of the at least one tertiary amine containing compound to the one or more enolisable carbonyls of Formula II are present in a ratio of about 1:2 or 2:1.

63 The complex as claimed in any one of claims 33 to 62, wherein the molar ratio of the at least one tertiary amine containing compound to the one or more enolisable carbonyls of Formula II are present in a ratio of about 1:1.

5 64 The complex as claimed in any one of claims 33 to 63, wherein the at least one amine or ammonium salt containing compound and at least one carboxylic acid containing compound or an alkylsulfonic acid; or a combination thereof, is irreversibly protonated.

65 A method of recovering water from a solvent, the method including the steps of contacting
10 the solvent drying composition for use in recovering water from a solvent, the composition comprising a composition as claimed in any one of claims 1 to 32 and allowing the migration of the complex composition through the solvent, whereupon the water is released from the solvent forming an immiscible aqueous layer with the solvent.

66 The method as claimed in claim 65 wherein the method includes the step of separating the
15 recovered water from the immiscible solvent layer.

67 A method of recovering water from a solvent, the method including the steps of contacting the solvent with a complex composition as claimed in any one of claims 33 to 64 and allowing the migration of the complex through the solvent, whereupon the water is released from the solvent forming an immiscible aqueous layer with the solvent.

20 68 The method as claimed in claim 67 wherein the method includes the step of separating the recovered water from the immiscible solvent layer.

69 The method as claimed in claim 65 or claim 66, wherein the method includes the step of contacting the solvent with one or more solvent drying compositions.

70 The method as claimed in claim 69, wherein the solvent is contacted with one or more solvent
25 drying compositions iteratively to iteratively release water therefrom.

71 The method as claimed in claim 70, wherein one or more solvents are contacted with one or more solvent drying compositions iteratively in a counter-current process.

72 A method of recovering water from a solvent, the method including the steps of contacting the solvent with a complex composition as claimed in any one of claims 33 to 64; and allowing the
30 migration of the complex through the solvent, whereupon the water is released from the solvent forming an immiscible aqueous layer with the solvent.

73 The method as claimed in claim 72 wherein the method includes the step of separating the recovered water from the immiscible solvent layer.

74 The method as claimed in claim 72 or claim 73, wherein the method includes the step of contacting the solvent with one or more complex compositions.

5 75 The method as claimed in claim 74, wherein the solvent is contacted with one or more complex compositions iteratively to iteratively release water therefrom.

76 The method as claimed in claim 75, wherein one or more solvents are contacted with one or more complex composition iteratively in a counter-current process.

77 A process for using a solvent drying composition to recover water from a solvent, the
10 composition comprising a complex of:

- a. at least one amine or ammonium salt containing compound and
- b. at least one carboxylic acid containing compound or an alkylsulfonic acid; or a combination thereof,

wherein in use the water is released from the solvent upon migration of the composition through
15 the solvent, the released water forming an immiscible aqueous layer with the solvent,
the process comprising the steps of:

1) bringing the solvent drying composition into contact with the solvent to release the water from the solvent upon migration of the composition through the solvent, the released water and solvent drying composition forming an immiscible aqueous layer with the solvent, and

20 2) recovering the solvent drying composition from the immiscible aqueous layer.

78 The process as claimed in claim 77 further including the step of recovering the solvent.

79 The process as claimed in claim 78 wherein the recovered solvent drying composition is recycled for use in a further solvent drying process.

80 The process as claimed in claim 79, wherein the process of recovering the solvent drying
25 composition is a continuous recovery process.

81 The process as claimed in any one of claims 77, 79 or claim 80 wherein the step of recovering the solvent drying solution is achieved by one or more of the following techniques, membrane distillation, pervaporation, osmosis, pressure driven membrane processes, osmotically driven membrane processes, osmotically assisted pressure driven membrane processes, pressure assisted

osmotically driven membrane processes, filtration, mechanical vapor recompression, evaporation based processes, water specific reactant, or crystallisation techniques or the like.

82 The process as claimed in claim 81, wherein the step of recovering the solvent drying solution is achieved by a pressure assisted osmosis technique.

5 83 The process as claimed in any one of claims 77 to 82 wherein the process includes a coalescence step to recover the solvent drying composition from the immiscible aqueous layer with the solvent.

84 The process as claimed in claim 82, wherein an electrostatic coalescer is used for the coalescence step.

10 85 The process as claimed in any one of claims 77 to 84 wherein the at least one amine containing compound is a secondary or tertiary amine or a combination thereof.

86 The process as claimed in any one of claims 77 to 85 wherein the -carboxylic acid containing compound of Formula I is selected from acetic acid, citric acid and glycolic acid or a combination thereof.

15 87 The process as claimed in any one of claims 77 to 86 wherein the carboxylic acid containing compound is a metal salt -carboxylic acid complex.

88 The process as claimed in claim 87 wherein the metal salt-carboxylic acid complex is selected from one or more of the following: metal salts having a valency of less than or the same as 6, Na salts, Fe (II) salts, Fe (III) salts, Cu (II) salts, Al(II) salts, Al(III) salts, Sr (II) salts, Li salts and Ag salts.

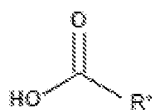
20 89 The process as claimed in claim 88, wherein the metal salt is selected from one or more of the following: NaCl, NaCO₃, SrCl₂, AlCl₃, FeCl₃, Fe(NO₃)₃, Fe₂(SO₄)₃, CuCl₂, CuSO₄, Cu(OH)₂, AgF, AgCl and AgBr.

90 The process as claimed in any one of claims 87 to 89, wherein the carboxylic acid is selected from one or more of the following, glycolic acid, citric acid, tartaric acid, poly(acrylic acid-co-maleic acid, poly acrylic acid, sarcosine, acetic acid, carbonic acid and formic acid.

25

91 The process as claimed in any one of claims 77 to 90, the at least one carboxylic acid containing compound is selected from one or more of the following:

a) a compound of Formula I,



Formula I

wherein R* is selected from, -C₁-C₇ alkyl-OH, -C₁-C₇ alkyl, -C₁-C₇ alkyl-NH₂, -C₁-C₇ alkyl-NHR³ and -C₁-C₇ alkyl NR³R⁴, wherein each R³ and R⁴ are selected from -H, -OH, -halo, -C₁-C₇ alkyl, -C₁-C₇ alkyl-OH, -C(O)OH, -C(O)-H, or -C(O)-(C₁-C₇ alkyl); and

- 5 b) a polymer containing one or more carboxylic acid groups.

92 The process as claimed in any one of claims 77 to 91, wherein the carboxylic containing compound of Formula I is selected from acetic acid, citric acid and glycolic acid or a combination thereof.

- 10 93 The process as claimed in any one of claims 77 to 92, wherein the alkylsulfonic acid is isoethionic acid.

94 The process as claimed in any one of claims 77 to 93, wherein the molar ratio of the at least amine or ammonium salt containing compound to the at least one carboxylic acid containing compound or an alkylsulfonic acid or a combination thereof; is about 1:99 or 99:1.

- 15 95 The process as claimed in any one of claims 77 to 94, wherein the molar ratio of the at least amine or ammonium salt containing compound to the at least one carboxylic acid containing compound or an alkylsulfonic acid or a combination thereof; is about 1:50 or 50:1.

- 96 The process as claimed in any one of claims 77 to 95, wherein the molar ratio of the at least amine or ammonium salt containing compound to the at least one carboxylic acid containing compound or an alkylsulfonic acid or a combination thereof; is about 1:10 or 10:1.
- 20

97 The process as claimed in any one of claims 77 to 96, wherein the molar ratio of the at least amine or ammonium salt containing compound to the at least one carboxylic acid containing compound or an alkylsulfonic acid or a combination thereof; is about 1:5 or 5:1.

- 98 The process as claimed in any one of claims 77 to 97, wherein the molar ratio of the at least amine or ammonium salt containing compound to the at least one carboxylic acid containing compound or an alkylsulfonic acid or a combination thereof; is about 1:3 or 3:1.
- 25

99 The process as claimed in any one of claims 77 to 98, wherein the molar ratio of the at least amine or ammonium salt containing compound to the at least one carboxylic acid containing compound or an alkylsulfonic acid or a combination thereof; is about 1:2 or 2:1.

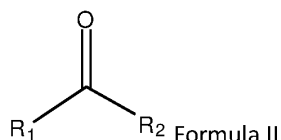
5 100 The process as claimed in any one of claims 77 to 99, wherein the molar ratio of the at least amine or ammonium salt containing compound to the at least one carboxylic acid containing compound or an alkylsulfonic acid or a combination thereof; is about 1:1.

101 The process as claimed in any one of claims 77 to 100 wherein the complex comprising:

- a) at least one amine or ammonium salt containing compound and
10 b) at least one carboxylic acid containing compound or an alkylsulfonic acid; or a combination thereof,
is irreversibly protonated.

102 The process as claimed in any one of claims 77 to 101 wherein the solvent from which the
15 water is recovered comprises at least one amine containing compound and at least one enolisable carbonyl.

103 The process as claimed in claim 100 wherein the solvent comprises at least one enolisable carbonyl of Formula II,

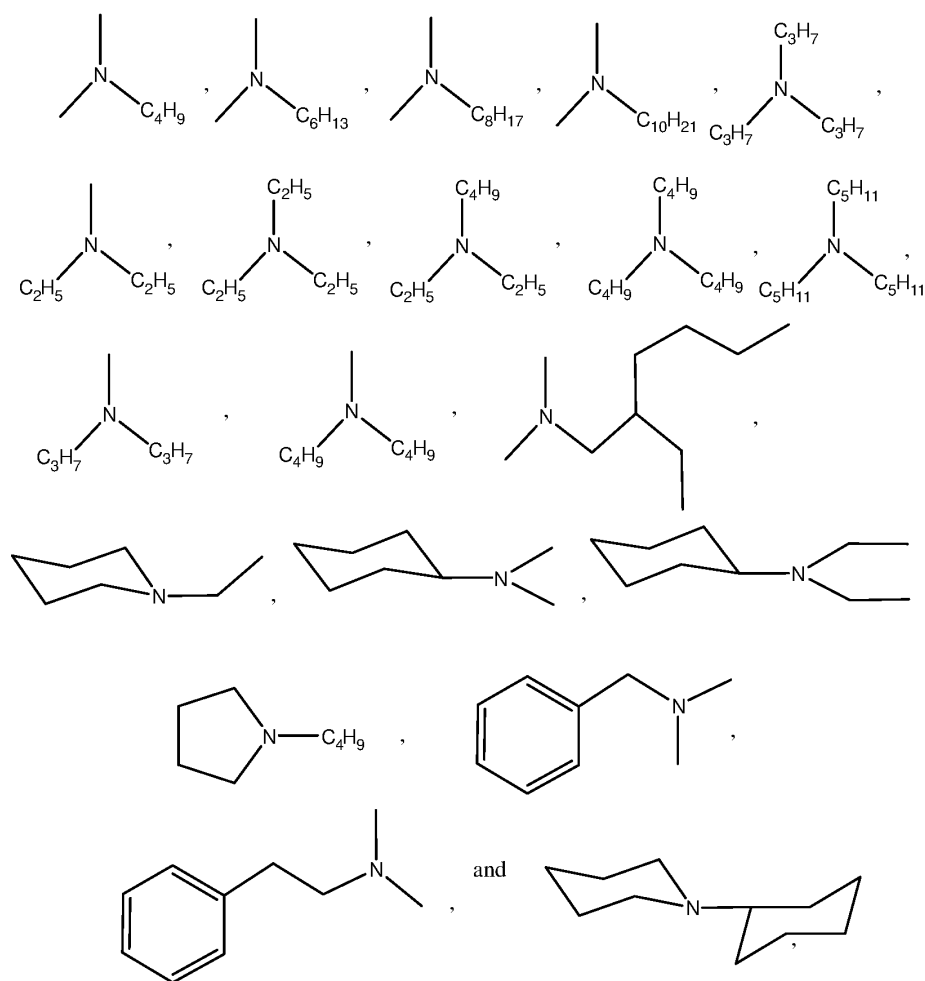


20 wherein R₁ and R₂ are independently selected from a -C₁-C₇ alkyl or a -C₃-C₇ monocyclic; or one of R₁ or R₂ is selected from a -O-(C₁-C₇ alkyl) and the other is selected from a -C₁-C₇ alkyl, or R₁ and R₂ together, with the carbonyl of Formula II, form a 3-15 membered monocyclic ketone or a 3-15 membered monocyclic heterocyclic ketone or acetophenone.

104 The process as claimed in any of claims 77 to 102 wherein the solvent includes at least one
25 amine containing compound, which amine may be the same or different from the amine containing compound in the complex.

105 The process as claimed in any one of the claims 77 to 104, wherein the at least one amine containing compound of the complex or solvent is selected from a conjugated, aliphatic, asymmetric or cyclic tertiary amine.

106 The process as claimed in claim 105, wherein the tertiary amine containing compound is
5 selected from the following:



107 The process as claimed in claim 106, wherein the at least one tertiary amine containing
compound is selected from a -N(C₁-C₇ alkyl)₃.

108 The process as claimed in claim 107, wherein the at least one tertiary amine containing
10 compound is selected from a -N(C₁-C₄ alkyl)₃.

109 The process as claimed in claim 108, wherein the at least one tertiary amine containing
compound is -N(C₂ alkyl)₃(triethylamine).

- 110 The process as claimed in claim 109, wherein the at least one tertiary amine containing compound is ethylpiperidine.
- 111 The process as claimed in claim 110, wherein R₁ of Formula II is a -C₁-C₇ alkyl.
- 112 The process as claimed in claim 103 or claim 111, wherein R₁ of Formula II is further substituted with one or more substituents selected from -OH, -C₁-C₇ alkyl, -(C₁-C₇ alkyl)-OH, -NH₂, -NH(C₁-C₇ alkyl), -N(C₁-C₇ alkyl)₂, -C(O)OH; -C(O)-H, or -C(O)-(C₁-C₇ alkyl).
- 113 The process as claimed in any one of claims 103, 111 or 112 wherein Formula II, is 2-butanone.
- 114 The process as claimed in any one of claims 102 to 113, wherein the molar ratio of the at least one tertiary amine containing compound to the one or more enolisable carbonyls of Formula II are present in a ratio of about 1:99 or 99:1.
- 115 The process as claimed in any one of claims 102 to 114, wherein the molar ratio of the at least one tertiary amine containing compound to the one or more enolisable carbonyls of Formula II are present in a ratio of about 1:50 or 50:1.
- 116 The process as claimed in any one of claims 102 to 115, wherein the molar ratio of the at least one tertiary amine containing compound to the enolisable carbonyl of Formula II are present in a ratio of about 1:10 or 10:1.
- 117 The process as claimed in any one of claims 102 to 116, wherein the molar ratio of the at least one tertiary amine containing compound to the one or more enolisable carbonyls of Formula II are present in a ratio of about 1:5 or 5:1.
- 118 The process as claimed in any one of claims 102 to 117, wherein the molar ratio of the at least one tertiary amine containing compound to the one or more enolisable carbonyls of Formula II are present in a ratio of about 1:3 or 3:1.
- 119 The process as claimed in any one of claims 102 to 118, wherein the molar ratio of the at least one tertiary amine containing compound to the one or more enolisable carbonyls of Formula II are present in a ratio of about 1:2 or 2:1.
- 120 The process as claimed in any one of claims 102 to 119, wherein the molar ratio of the at least one tertiary amine containing compound to the one or more enolisable carbonyls of Formula II are present in a ratio of about 1:1.