A THERMO-RESPONSIVE SOLUTION, AND METHOD OF USE THEREFOR

FIELD OF THE INVENTION

[0001] The present disclosure relates to a thermo-responsive solution and in particular, a solution suitable for use in an osmosis process that is suitable for separating or purifying solutes and or water from an aqueous solution on a large scale and under energy efficient conditions.

BACKGROUND OF THE INVENTION

[0002] US patent 3,130,156 to Neff is directed to a forward osmosis desalination process, which describes the use of a 2 molar solution of ammonium bicarbonate being used to draw water from seawater across a semi-permeable membrane. According to Neff, the dilute solution obtained that contains the water and ammonium bicarbonate mixture is then heated to convert the ammonium bicarbonate solute into its constituent gases of ammonia and carbon dioxide. The gases are then released from the solution to leave behind purified water. It is to be appreciated that considerable amounts of energy are required to vaporise the gases. Additionally, only relatively small quantities of water are purified from a large volume of seawater meaning that the ratio of energy input required in the process to the yield of purified water obtained is low. This means that this process is not suitable for large scale applications.

[0003] The Neff concept was further developed and refined by McGinnis, as described in US patent 7,560,029, into a more energy efficient desalination process that is scalable. The principle of adding a mixture of ammonia and carbon dioxide with resultant aqueous species of ammonium carbonate, ammonium bicarbonate and ammonium carbamate to adjust the osmotic equilibrium in a forward osmosis process is used in McGinnis. Furthermore, the resultant separated water was purified by heating to drive off ammonia and carbon dioxide. The water separated in this process will still be tainted slightly by ammonia and its presence means that an odour will be detectable.

[0004] Jessop *et. al.* in US 2014/0076810 describes a switchable water or aqueous solution and its use. The switchable 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 described as a monoamine, a diamine, a triamine, a tetramine or a polyamine, such as a polymer or a biopolymer. The switchable 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 CO_2, CS_2 or COS or treatment with Bronsted acids. The switchability 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. One of the difficulties with the Jessop work is that is difficult to disassociate the CO_2 from the amine to achieve the switchable water. Trace amounts of CO_2 and amine can remain solubilised in the draw solution and heating and stripping and the kinetics of recovery are slow – of the order of hours to minutes.

[0005] US 2013/0240444 to Jung *et. al.* describes the use of a temperature sensitive oligomer, wherein the oligomer has a repeating unit of $–C(=O)N(R)_2$ (ie an amide functional group) where each R may be linear or branched or together they form a nitrogen containing heterocycle for use as a draw solution. The oligomer may be used in an osmotic draw solution for separating out a solute in an aqueous medium. The draw solute is recoverable by a phase separation at a temperature greater than or equal to a lower critical solution temperature. The lower critical solution temperature (LCST) is the critical temperature below which the components of a mixture are miscible. The word lower indicates that the LCST is a lower bound to a temperature interval of partial miscibility, or miscibility for certain compositions only. In other words, the thermosensitive nature of the oligomer exhibits sharply decreased water solubility in response to a small increase in temperature leading to precipitation. At a temperature lower than the LCST the oligomer or polymers therefrom may be easily dissolved in water, but at temperatures higher than or equal to the LCST the hydrophilicity of the oligomer or polymers therefrom may decrease and the hydrophobic interactions predominate. One of the problems with oligomers and polymers is that they are relatively large molecules and large molecules create a diffusion concentration polarisation which lowers effective osmotic potential of the forward osmosis system by making the draw solution less drawable. Relatively large molecules and polymers also rely on precipitation mechanisms rather than emulsification to recover the draw solute, necessitating a secondary filtration mechanism that increases system cost and complexity.

[0006] US 2014/0158621 to Lee at al. also describes a thermo-responsive draw solute based on a compound or material including at least one amide functional group, or a carboxylic acid functional group, that can be applied to water desalination and purification based on forward osmosis. Similar to Jung above, Lee also describes the use and applicability of an amide type functional group in a thermo-responsive draw solution and the reliance on the LCST to effect phase separation of a solute from the draw solution in a forward osmosis application. One of the problems with oligomers and polymers is that they are relatively large molecules and large molecules create a diffusion concentration polarisation which lowers effective osmotic potential of the forward osmosis system by making the draw solution less drawable. Relatively large molecules and polymers also rely on precipitation mechanisms rather than emulsification to recover the draw solute, necessitating a secondary filtration mechanism that increases system cost and complexity.

[0007] US patent 6,858,694 to Onishi *et. al* describes a stimuli responsive polymer derivative which exhibits both a lower critical solution temperature and an upper critical solution temperature (UCST), causing its reversible dissolution and precipitation depending on the hydrogen ion concentration. The polymers described in '694 also rely on an amide type functional group that are described as exhibiting keto-enol tautomerisation. One of the problems with polymers is that they are relatively large molecules and large molecules create a diffusion concentration polarisation which lowers effective osmotic potential of the forward osmosis system by making the draw solution less drawable.

[0008] US 2016/0175777 to Ikeda *et al*. describes an improved forward osmosis apparatus employing a draw solution that utilises an anion and cation source. In particular the anions are derived from CO_2, ie a substance that generates anions when dissolved in water, such as carbonic acid anions and or hydrogen carbonate anions. The cation source is an amine compound, which generates cations when dissolved in water. The draw solution is broadly described as a solution having a cation source and an anion source. The physical separation of the CO_2 relies on gaseous separation, which is a relatively complex and energy inefficient process. Their preferred amines are fully miscible and have a molecular weight of less than 74.

[0009] Despite the efforts described above the draw solutions described remain largely unsatisfactory, they either rely on expensive components, require considerable energy levels to recover the draw solution or rely on large molecules that are inefficient from a draw solution perspective. It is an object of the present invention to provide a solution that overcomes these difficulties or to at least provide a useful alternative.

SUMMARY OF THE INVENTION

[0010] The present invention is directed to a thermo-responsive solution and its use in osmotic processes.

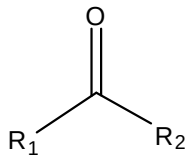
[0011] In one aspect the present invention provides a thermo-responsive osmotic solution having a lower critical solution temperature in a solvent suitable for use in osmosis comprising:

a) at least one tertiary amine containing compound; and
b) at least one enolisable carbonyl;

wherein in use at least one of the base or the at least one enolisable carbonyl is immiscible with water at or above 20 degrees Celsius and at 1 atmosphere.

[0012] In a further aspect the present invention provides a thermo-responsive osmotic solution having a lower critical solution temperature in a solvent suitable for use in osmosis comprising:

a) at least one tertiary amine containing compound; and
b) at least one enolisable carbonyl of Formula I,



Formula I

wherein

c) R_1 and R_2 are independently selected from a -C_1-C_7 alkyl or a -C_3-C_7 monocyclic; or
d) 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
e) R_1 and R_2 together, with the carbonyl of Formula I, form
    1) a 3-15 membered monocyclic ketone or
    2) a 3-15 membered monocyclic heterocyclic ketone;

and

wherein in use at least one of the base or the at least one enolisable carbonyl is immiscible with water at or above 20 degrees Celsius and at 1 atmosphere.

[0013] In another aspect the present invention provides a method for separating a first solution including one or more solvents, using a thermo-responsive solution as defined above, the method comprising:

1) bringing the first solution into contact with a semi-permeable membrane;
2) allowing one or more solvents in the first solution to flow through the semi-permeable membrane from the first solution into the thermo-responsive solution by osmosis to form a second solution, wherein the thermo-responsive solution is at a higher osmotic concentration than the first solution;
3) raising the temperature of the second solution to or above the lower critical solution temperature of the thermo-responsive solution to cause the thermo-responsive solution to become immiscible with the one or more solvents from the first solution that have passed through the semi-permeable membrane; and
4) separating the one or more solvents that have passed through the semipermeable membrane from the immiscible thermo-responsive solution.

[0014] In another aspect the present invention provides a method for separating a first solution including one or more solvents, using a thermo-responsive solution as defined above, the method comprising:

1) bringing the first solution into contact with a semi-permeable membrane;
2) allowing one or more solvents in the first solution to flow through the semi-permeable membrane from the first solution into the thermo-responsive solution by osmosis to form a second solution, wherein the thermo-responsive solution is at a higher osmotic concentration than the first solution;
3) adjusting the lower critical solution temperature of the thermo-responsive solution to cause the thermo-responsive solution to become immiscible with the one or more solvents from the first solution that have passed through the semi-permeable membrane; and
4) separating the one or more solvents that have passed through the semipermeable membrane from the immiscible thermo-responsive solution.

[0015] In one embodiment the the lower critical solution temperature of the thermo-responsive solution is adjusted by adding one or more tertiary amine containing compounds as defined, or by by adding or more enolisable carbonyls as defined above or by adding combinations of the one or more tertiary amine containing compounds with the one or more enolisable compounds.

[0016] 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.

[0017] 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

[0018] Figure 1: shows schematically an osmotic separation process.

[0019] Figure 2 shows the differential scanning calorimetry (DSC) analysis for a triethylamine plus acetone in water solution demonstrating a change of enthalpy at 32.25°C, which coincides with the observed solubility/polarity shift.

[0020] Figure 3 shows the differential scanning calorimetry (DSC) analysis for a triethylamine plus 2-butanone in water solution demonstrating a change of enthalpy at 24.42°C, which coincides with the observed solubility/polarity shift.

[0021] Figure 4 shows a series of photos 4(a), 4(b) and 4(c) showing the observable differences of a triethylamine plus 2-butanone in water solution demonstrating a change in physical properties of the solution over a temperature range. It can be seen in Figure 4(a) at 26.65°C the base, ketone and water mixture is miscible. At 26.89°C the base, ketone and water mixture has become turbid in appearance (see Figure 4(b)) as a result of the base and ketone mixture becoming an emulsion with water and at 27.05°C the base and ketone mixture are immiscible with water.

[0022] Figure 5 shows a series of photos showing the observable differences of a triethylamine plus cyclohexanone in water solution demonstrating a change in physical properties of the solution over a temperature range. It can be seen in Figure 5(a) at 15.21°C the base, ketone and water mixture is miscible. At 15.38°C the base, ketone and water mixture has become turbid in appearance (see Figure 5(b)) as a result of the base and ketone mixture becoming an emulsion with water and at 18.33°C the base and ketone mixture are immiscible with water.

[0023] Figure 6 shows the transmittance versus temperature plots of various draw solutions showing a clear change in transmission at the LCST of the respective draw solution. .

[0024] Figure 7(a) shows a plot of the transmittance % versus the termperature curve of a draw solution of TEA: MEK: water (0.5:1.0:5.0 respectively). Figures 7(a) and 7(b) show the first and second derivative plots of the transmittance curve showin in Figures 7(a). .

[0025] Figure 8 shows a plot of the visual LCST of a draw solution with varying molar ratios of TEA in the draw solution versus the molar ratio of TEA.

[0026] Figure 9 shows a plot of the visual LCST of a draw solution with varying molar ratios of MEK in the draw solution versus the molar ration of MEK.

[0027] Figure 10 shows schematically the flux experiment setup described below in the examples.

[0028] Figure 11 shows a plot of the average water flux through a membrane involving a TEA – MEK draw solution.

[0029] Figure 12 shows a plot of the average water flux trhough a membrane involving a TEA – cycloppentanone draw solution.

[0030] Figure 13 shows the FTIR spectra of TEA.

[0031] Figure 14 shows the FTIR spectra of MEK.

[0032] Figure 15 shows the FTIR spectra of TEA/MEK in a 1:1 molar ratio.

[0033] Figure 16 shows the FTIR spectra of TEA/MEK/water in a 1:1:5 molar ratio.

DETAILED DESCRIPTION OF THE INVENTION

[0034] 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.

Definitions

[0035] 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".

[0036] The term "osmosis" is to be understood as a membrane based separation process that relies on the semipermeable character of a semi-permeable membrane to remove dissolved solutes or to effect separation of a solvent from dissolved solutes, and wherein the driving force for separation is osmotic pressure. The term "osmotic solution" means a solution that creates osmotic pressure across the semi-permeable membrane.

[0037] 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.

[0038] As used herein, the term "C_1-C_7 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 C_1-C_7 alkyl 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 C_1-C_4-alkyl includes, but is not limited to, methyl, ethyl, propyl, butyl, isopropyl, tert-butyl and isobutyl. In one

embodiment the C_1-C_7 alkyl group may be substituted with one or more of the following groups: -halo, -OH, -CN, -NO_2, -CΞCH, -SH, -C1-C7 alkyl, -(C_1-C_7 alkyl)-OH, -NH_2, -NH(C_1-C_7 alkyl),-N(C_1-C_7 alkyl)$_2$, -O (C_1-C_7 alkyl), -C(O)-O(-C_1-C_7 alkyl), -C(O)OH; -C(O)-H, or -C(O)-(C_1-C_7 alkyl).

[0039] The term "C_3-C_7 monocyclic" as used herein is a 3-, 4-, 5-, 6-, or 7-membered saturated or unsaturated monocyclic ring. Representative C_3-C_7 monocyclic groups include, but are not limited to, cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, phenyl and cycloheptyl. In one embodiment, the C_3-C_7 monocyclic cycloalkyl group may be substituted with one or more of the following groups: -halo, -OH, -CN, -NO_2, -CΞCH, -SH, -C_1-C_7 alkyl, -(C_1-C_7 alkyl)-OH, -NH_2, -NH(C_1-C_7 alkyl),-N(C_1-C_7 alkyl)$_2$, -O (C_1-C_7 alkyl), -C(O)-O(-C_1-C_7 alkyl), -C(O)OH; -C(O)-H, or -C(O)-(C_1-C_7 alkyl).

[0040] 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.

[0041] In one embodiment, the 3- to 15-membered monocyclic ketone may be substituted with one or more of the following groups-halo, -OH, -CN, -NO_2, -CΞCH, -SH, -C_1-C_7 alkyl, -(C_1-C_7 alkyl)-OH, -NH_2, -NH(C_1-C_7 alkyl),-N(C_1-C_7 alkyl)$_2$, -O (C_1-C_7 alkyl), -C(O)-O(-C_1-C_7 alkyl), -C(O)OH; -C(O)-H, or -C(O)-(C_1-C_7 alkyl).

[0042] 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(3*H*)-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)-

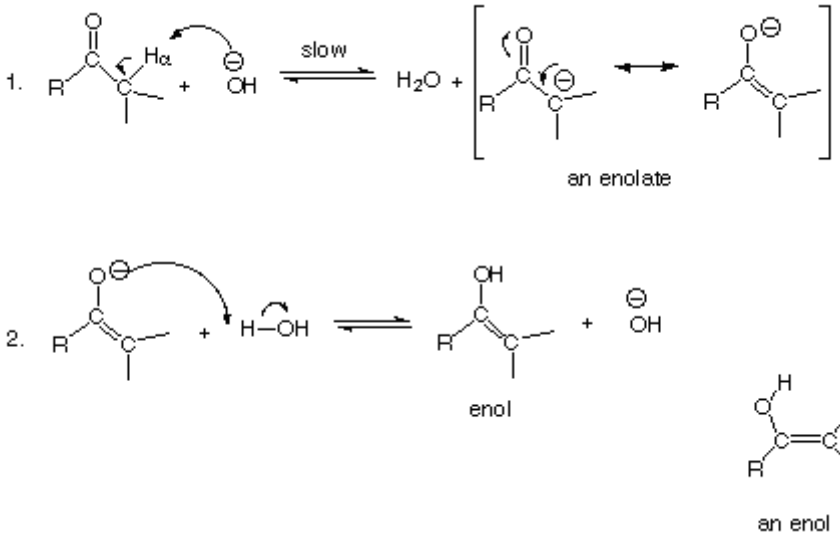
one, dihydro-2H-thiopyran-4(3H)-one, oxepan-2-one, oxepan-3-one, oxepan-4-one, thiepan-2-one, thiepan-3-one, thiepan-4-one, azepan-3-one, azepan-4-one, oxocan-2-one, oxocan-3-one, oxocan-4-one, oxocan-5-one, thiocan-2-one, thiocan-3-one, thiocan-4-one, thiocan-5-one, azocan-3-one, azocan-3-one, azocan-4-one, 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, -NO_2, -CΞCH, -SH, -C_1-C_6 lower alkyl, -(C_1-C_7 alkyl)-OH, -NH_2, -NH(C_1-C_7 alkyl),-N(C_1-C_7 alkyl)$_2$, -O (C_1-C_7 alkyl), -C(O)-O(-C_1-C_7 alkyl), -C(O)OH; -C(O)-H, or -C(O)-(C_1-C_7 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.

[0043] The term "halo" as used herein refers to -F, -Cl, -Br or -I.

[0044] The term immiscible as used herein, means not fully miscible or capable of forming a single continuous phase with the solvent phase.

[0045] 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.

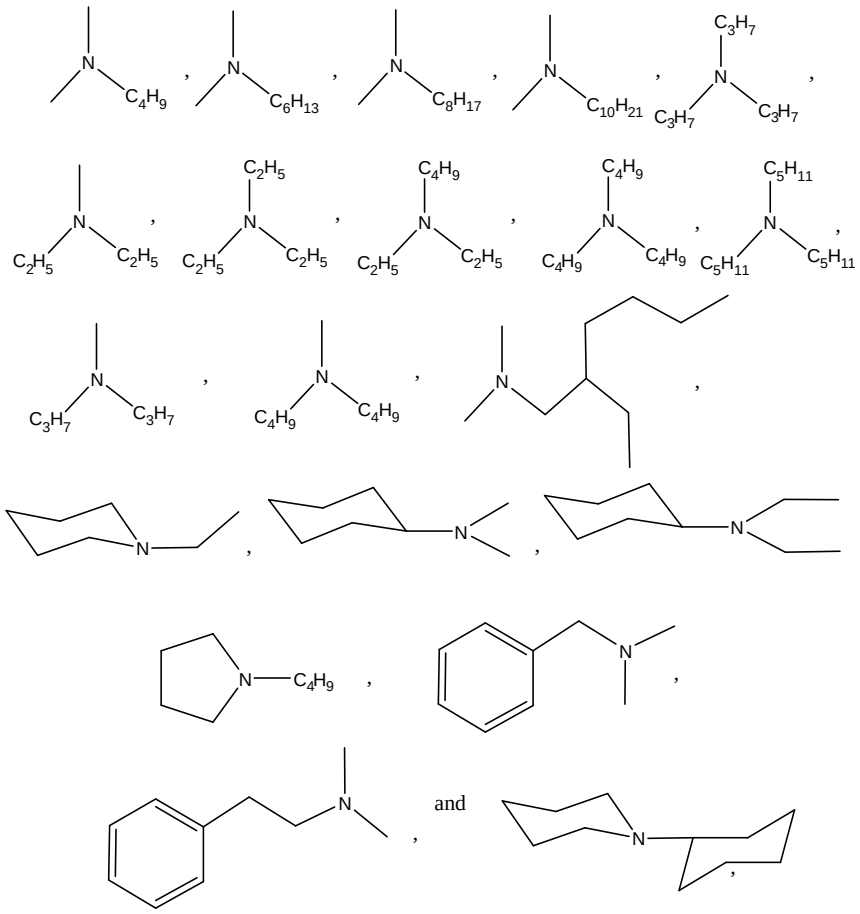


[0046] It is to be understood that the term enolisable carbonyl as used in the specification does not include a compound having solely an aldehyde functional group, a compound having solely a carboxylic acid functional group, a compound having solely an amide functional group, a compound having solely an acyl halide functional group or acetylacetone.

[0047] The term enolisable carbonyl, without limitation includes one or more of the following: acetone, acetophenone, methylethylketone (2-butanone), cyclohexanone, cyclopentanone, 2-propanone, 2-pentanone, 3-pentanone, 4-methyl-2-pentanone, 2-octanone and 3-methyl-2-butanone. In a preferred embodiment the term enolisable carbonyl includes one or more of the following acetone, acetophenone, cyclohexanone, cyclopentanone, 2-propanone, 2-pentanone, 3-pentanone, 4-methyl-2-pentanone, 2-octanone and 3-methyl-2-butanone.

[0048] The term "tertiary amine containing compound" is preferably one that is 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 can be aliphatic, conjugated, asymmetric or cyclic.

[0049] Examples of suitable tertiary amines include the following:



[0050] In one embodiment the base is selected from a -N(C_1-C_7 alkyl)$_3$. In another embodiment the base is selected from a -N(C_1-C_4 alkyl)$_3$. In yet a further embodiment the base is -N(C_2 alkyl)$_3$ (triethylamine).

[0051] It will be appreciated that the above listed amines are simple enough for production on an industrial scale.

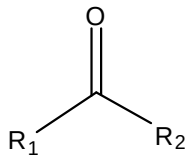
[0052] The term "thermo-responsive solution" means a solution that exhibits a drastic and discontinuous change of its solubility with temperature.

[0053] The term "lower critical solution temperature" (LCST) means the critical temperature below which the properties (optical, conductivity and/or pH) of the solution begin to change on the continuum to the components of the solution becoming miscible.

[0054] The present invention is directed to a thermo-responsive osmotic solution and its use in osmosis processes. The inventor has conducted research into looking for alternative thermo-responsive solutions that are likely to be readily scalable on an industrial scale, whilst also providing very efficient diffusion and osmotic potential properties both cost and energy efficiently. The inventor has determined that a suitable thermo-responsive osmotic solution having a lower critical solution temperature in a solvent for use in osmosis comprises:

b) at least one tertiary amine containing compound ; and

c) at least one enolisable carbonyl of Formula I,



Formula I

wherein

d) 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

e) 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

f) R_1 and R_2 together, with the carbonyl of Formula I, form

1) a 3-15 membered monocyclic ketone or

2) a 3-15 membered monocyclic heterocyclic ketone;

and

wherein in use at least one of the base or the at least one enolisable carbonyl is immiscible with water at 20 degrees Celsius and at 1 atmosphere.

[0055] In one embodiment, R_1 and R_2 of Formula I are independently selected from a -C_1-C_7 alkyl. In another embodiment R_1 and R_2 are independently selected from methyl and ethyl. In one embodiment the enolisable carbonyl is selected from 2-butanone, acetone, isobutylketone. In one embodiment the solution includes a combination of more than one enolisable carbonyl of Formula I. In one embodiment the combination of enolisable carbonyls of Formula I includes the following combinations;

A. 2 butanone and 2-propanone;

B. 2-propanone and cyclohexanone;

C. 2 butanone and cyclohexanone;

D. 2 propanone, 2 butanone and cyclohexanone;

E. 2-propanone and 2-pentanone;

F. Cyclopentanone and acetophenone;

G. Cyclopentanone and 2-octanone;

H. Cyclopentanone and 4methyl-2-pentanone;

I. 2-butanone, cyclopentanone and 2-propanone; and

J. 2-propanone, 3-pentanone and 3-methyl-2-butanone.

[0056] In one embodiment the solution includes a combination of more than one tertiary amine containing compound of Formula I. In one embodiment the combination of tertiary amine containing compounds includes the following combinations;

A. Triethylamine and 1-ethylpiperidine;

B. Triethylamine and diethylmethylamine;

C. Triethylamine, diethylmethylamine and 1-ethylpiperidine; and

D. Triethylamine, diethylmethylamine and dimethylbenzylamine;

[0057] In one embodiment R_1 of Formula I is selected from a -C_1-C_7 alkyl and

R_2 is selected from a -O-(C_1-C_7 alkyl). In a further embodiment the enolisable carbonyl is selected from ethyl formate or methyl formate.

[0058] In a further embodiment wherein R_1 and R_2 of Formula I together form a cyclic system selected from a 3-15 membered monocyclic ketone or a monocyclic ester. In one embodiment the enolisable carbonyl is selected from cyclohexanone or tetrahydro-2H-pyran-2-one.

[0059] It is to be appreciated that when R_1 and R_2 together form a cyclic system, the cyclic system may be further substituted with one or more substituents selected from -halo, -OH, -CN, -NO_2, -C≡CH, -SH, -C_1-C_7 alkyl, -(C_1-C_7 alkyl)-OH, -NH_2, -NH(C_1-C_7 alkyl),-N(C_1-C_7 alkyl)$_2$, -O (C_1-C_7 alkyl), -C(O)-O(-C_1-C_7 alkyl), -C(O)OH; -C(O)-H, or -C(O)-(C_1-C_7 alkyl) or the like.

[0060] It is to be appreciated that the molar ratio of the base to the enolisable carbonyl of Formula I may vary widely and may be from about 1:99 or 99:1; or from about 1:50 or 50:1 or from about 1:10 or 10:1 or from about 1:5 or 5:1 or from about 1:3 or from about 3:1 or from about 1:2 or from about 2:1. In a preferred embodiment the molar ratio is about 1:1. A chemistry technician would be able to routinely determine the most suitable molar ratio depending on the purpose for which the thermo-responsive solution is to be employed. A range of molar ratios for various thermo-responsive solutions are shown in Figures 7 to 9.

[0061] In one embodiment the solvent is water.

[0062] In a further aspect there is provided an osmotic process or method for separating a first solution including one or more solvents, using a thermo-responsive solution as defined above. The method comprises:

1) bringing a first solution into contact with a semi-permeable membrane;
2) allowing one or more solvents in the first solution to flow through the semi-permeable membrane from the first solution into the thermo-responsive solution by osmosis to form a second solution, wherein the thermo-responsive solution is at a higher osmotic concentration than the first solution;
3) raising the temperature of the second solution to or above the lower critical solution temperature of the thermo-responsive solution to cause the thermo-

responsive solution to become immiscible with the one or more solvents from the first solution that have passed through the semi-permeable membrane; and

4) separating the one or more solvents that have passed through the semipermeable membrane from the immiscible thermo-responsive solution.

[0063] In another aspect the present invention provides a method for separating a first solution including one or more solvents, using a thermo-responsive solution as defined above, the method comprising:

1) bringing the first solution into contact with a semi-permeable membrane;
2) allowing one or more solvents in the first solution to flow through the semi-permeable membrane from the first solution into the thermo-responsive solution by osmosis to form a second solution, wherein the thermo-responsive solution is at a higher osmotic concentration than the first solution;
3) adjusting the lower critical solution temperature of the thermo-responsive solution to cause the thermo-responsive solution to become immiscible with the one or more solvents from the first solution that have passed through the semi-permeable membrane; and
4) separating the one or more solvents that have passed through the semipermeable membrane from the immiscible thermo-responsive solution.

[0064] In one embodiment the lower critical solution temperature of the thermo-responsive solution is adjusted by adding one or more tertiary amine containing compounds as defined, or by by adding or more enolisable carbonyls as defined above or by adding combinations of the one or more tertiary amine containing compounds with the one or more enolisable compounds.

[0065] It is to be appreciated that the first solution in the above aspects may include one or more dissolved solutes. In a further embodiment the first solution is selected from seawater, brackish water, industrial water waste streams, compromised water sources, sewage, wastewater liquors, digestates, food & beverage processing effluents, grey water, fruit juices, vegetable juices, milk, produced waters, leachates, flue gas scrubber discharge or the like.

EXAMPLES

[0066] 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.

Example 1:

[0067] In a first example, the inventor took equal molar ratios of acetone as the enolisable carbonyl plus triethylamine as the base in a volume of water in a test tube. A DSC scan of that solution showed that there was a thermo-responsive point at 32.25 °C at which the lower critical solution temperature was reached – see Figure 2. It was observed that close to that point the solution went from a miscible mixture of acetone/tertiary amine in water through an emulsion to an immiscible mixture of acetone/tertiary amine in water.

Example 2:

[0068] In a second example, the inventor took equal molar ratios of 2-butanone as the enolisable carbonyl plus triethylamine as the base in a volume of water in a test tube. A DSC scan of that solution showed that there was a thermo-responsive point at 24.42°C at which the lower critical solution temperature was reached – see Figure 3. It was observed that close to that point the solution went from a miscible mixture of 2-butanone /tertiary amine in water to an immiscible mixture of 2-butanone /tertiary amine in water. A series of photographs shown as Figures 4(a) to 4(c) show the observable changes to the solution mixture. It can be seen in Figure 4(a) at 26.65°C the base and 2-butanone mixture is miscible. At 26.89°C the base and ketone mixture has become turbid in appearance (see Figure 4(b)) as a result of the base and ketone becoming an emulsion with the water. With a further temperature increase it can be seen in Figure 4(c) that at 27.05°C the base and 2-butanone are immiscible with the water.

[0069] The inventor has determined that the effect observed in the solutions is reproducible. The DSC analysis further determined that the solubility/polarity shift is an

endothermic phenomenon, suggesting that some form of enthalpy of fusion is occurring and that the mixing of the components in their soluble state with water is exothermic.

It is to be recognised that the different temperature at which the solubility/polarity switch is seen varies depending on the nature of the composition of the thermo-responsive solution. It is to be appreciated that over the temperature at which the solubility or polarity switch is seen the ketone base mixture passes from a miscible mixture through an emulsion to a ketone and base mixture that is immiscible with water.

Example 3:

[0070] In a third example, the inventor took equal molar ratios of cyclohexanone as the enolisable carbonyl plus triethylamine as the base in a volume of water in a test vials and slowly increased the temperature of the mixture. A series of photographs shown as Figures 5(a) to 5(c) show the observable changes to the solution mixture. The series of photographs show the observable differences of a triethylamine plus cyclohexanone in water solution demonstrating a change in physical properties of the solution over a temperature range. It can be seen in Figure 5(a) at 15.21°C the base and ketone mixture is miscible with water. At 15.38°C the base and ketone mixture has become turbid in appearance (see Figure 5(b)) as a result of the base and ketone becoming an emulsion with water and at 18.33°C the base and ketone are immiscible with water.

Example 4:

[0071] It is to be understood that the LCST measured above in Examples 1 to 3 was supported by visual changes in terms of visibility or otherwise of the immiscible vs miscible layers. The exact point of the optical change can be difficult to judge visually. It has been found that it is easier to measure the optical properties of various test solutions to determine the transition of the LCST using a UV-Vis-NIR spectrometer. Transmittance of the test solutions at different temperatures was recorded using Stellar Net's SILVER-Nova fiber optic spectrometer which has a wide wavelength range of 190-1110nm. The light source was SL1 tungsten-halogen lamps effective for reflectance, transmittance and absorbance measurements. A dip probe connected the light source and a spectrometer was used to measure the characteristics of the draw solution.

Materials and methodology

[0072] Various test draw solutions were prepared using triethylamine (TEA), methyl ethyl ketone (MEK), N-ethylpiperidine, diethylymethylamine, cyclohexanone and diethylmethylamine and water various molar ratios and combinations in a 25mL glass vial. The transmittance was recorded for every 2 seconds at a wavelength of 850nm over varying temperatures. Resistance temperature detector (RTD) probe was inserted along with the dip probe to record the temperatures simultaneous to the episodes captured every 2 seconds. The main objective was to record a transition in the transmittance at the LCST where the solution transforms from a clear solution (100% transmittance) below LCST to cloudy above it. The controller used to ramp the temperature at the rate of 2°C/min was a Qpod-2e which has Peltier based cuvette holder with magnetic stirring. For one test solution using TEA, MEK and water in the molar ratios of 0.5:1:5 (respectively) first and second derivative curves were also obtained.

Results

[0073] Data from the experiment was used to obtain the transmittance % vs temperature curves at 850nm as shown in Figure 6. Figure 6 shows the transmittance curve of the draw solutions recorded at varying temperatures at 850nm. A sharp drop in transmission % was observed for all draw solutions at the LCST. For one test solution using TEA, MEK and water in the molar ratios of 0.5:1:5 (respectively) a transmission curve was obtained as shown in Figure 7(a) and then first and second derivative curves as shown in Figures 7(b) and 7(c) respectively were also obtained. The inventors are of the view that the point at which the curve intersects the x-axis at just under 28 degrees C of the second derivative curve is to be taken as the LCST for that particular test solution.

Example 5: Molar Ratio

[0074] In a fourth example, the molar ratios of various thermo-responsive solutions comprising triethylamine and a ketone in water at different temperatures were measured and the miscibility of the solution in water was recorded. The results are tabulated below in Table 1-4.

Table 1

Components	water	water; triethylamine; propanone	water; triethylamine; 2-butanone	water; triethylamine; cyclohexanone
Mol Ratio	144 : 0	144 : 6 : 6	144 : 6 : 6	144 : 6 : 6
5 °C	miscible	miscible	miscible	miscible
20 °C	miscible	miscible	miscible	immiscible
50 °C	miscible	immiscible	immiscible	immiscible

[0075] Table 2 shows a table of a range of molar ratios of trimethylamine to 2-butanone in 500 µL of water and the observed effect on the aqueous phase at 5°C and 50°C.

Table 2:

Mol Ratio		triethylamine ($mol.L^{-1}$)	2-butanone ($mol.L^{-1}$)	Water (uL)	triethylamine(uL)	2-butanone (uL)	Aqueous Phase (observed)	
triethylamine : 2-butanone							5 °C **	50 °C **
1	99	0.059	5.797	500.0	8.17	491.83	clear	turbid
2	98	0.116	5.702	500.0	16.23	483.77	clear	turbid
3	97	0.173	5.609	500.0	24.19	475.81	clear	turbid
4	96	0.230	5.516	500.0	32.06	467.94	clear	turbid
5	95	0.285	5.424	500.0	39.82	460.18	clear	turbid
10	90	0.554	4.983	500.0	77.23	422.77	clear	turbid
20	80	1.044	4.177	500.0	145.65	354.35	clear	turbid
30	70	1.482	3.458	500.0	206.68	293.32	clear	turbid
40	60	1.875	2.812	500.0	261.46	238.54	clear	turbid
50	50	2.229	2.229	500.0	310.90	189.10	clear	turbid
60	40	2.551	1.700	500.0	355.75	144.25	clear	turbid
70	30	2.844	1.219	500.0	396.61	103.39	clear	turbid
80	20	3.112	0.778	500.0	434.00	66.00	clear	turbid
90	10	3.358	0.373	500.0	468.35	31.65	clear	turbid
95	5	3.474	0.183	500.0	484.49	15.51	clear	turbid
96	4	3.496	0.146	500.0	487.64	12.36	clear	turbid
97	3	3.519	0.109	500.0	490.77	9.23	clear	turbid
98	2	3.541	0.072	500.0	493.87	6.13	clear	turbid
99	1	3.563	0.036	500.0	496.95	3.05	clear	turbid

**stablisation at 5 °C for 30 mins, immersion in 50 °C for 10 seconds, observe

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[0076] Table 3 shows a table of a range of molar ratios of trimethylamine to propanone in 500 µL of water and the observed effect on the aqueous phase at 5°C and 50°C.

Table 3:

Mol Ratio triethylamine : propanone		triethylamine ($mol.L^{-1}$)	propanone ($mol.L^{-1}$)	Water (uL)	triethylamine (uL)	propanone (uL)	Aqueous Phase (observed)	
							5 °C **	50 °C **
1	99	0.061	6.084	500.0	8.57	491.43	clear	turbid
2	98	0.122	5.979	500.0	17.02	482.98	clear	turbid
3	97	0.182	5.876	500.0	25.35	474.65	clear	turbid
4	96	0.241	5.774	500.0	33.56	466.44	clear	turbid
5	95	0.299	5.674	500.0	41.65	458.35	clear	turbid
10	90	0.577	5.193	500.0	80.48	419.52	clear	turbid
20	80	1.081	4.323	500.0	150.76	349.24	clear	turbid
30	70	1.525	3.557	500.0	212.64	287.36	clear	turbid
40	60	1.918	2.877	500.0	267.56	232.44	clear	turbid
50	50	2.270	2.270	500.0	316.62	183.38	clear	turbid
60	40	2.586	1.724	500.0	360.72	139.28	clear	turbid
70	30	2.872	1.231	500.0	400.57	99.43	clear	turbid
80	20	3.131	0.783	500.0	436.76	63.24	clear	turbid
90	10	3.368	0.374	500.0	469.77	30.23	clear	turbid
95	5	3.479	0.183	500.0	485.21	14.79	clear	turbid
96	4	3.500	0.146	500.0	488.22	11.78	clear	turbid
97	3	3.522	0.109	500.0	491.20	8.80	clear	turbid
98	2	3.543	0.072	500.0	494.16	5.84	clear	turbid
99	1	3.564	0.036	500.0	497.09	2.91	clear	turbid

**stablisation at 5 °C for 30 mins, immersion in 50 °C for 10 seconds, observe

[0077] Table 4 shows a table of a range of molar ratios of trimethylamine to cyclohexanone in 500 µL of water and the observed effect on the aqueous phase at 5°C and 50°C.

Table 4:

Mol Ratio triethylamine : cyclohexanone		Triethylamine ($mol.L^{-1}$)	cyclohexanone ($mol.L^{-1}$)	Water (uL)	triethylamine (uL)	cyclohexanone (uL)	Aqueous Phase (observed)	
							5 °C **	50 °C **
1	99	0.048	4.764	500.0	6.71	493.29	clear	turbid
2	98	0.096	4.699	500.0	13.38	486.62	clear	turbid
3	97	0.143	4.635	500.0	20.00	480.00	clear	turbid

4	96	0.190	4.572	500.0	26.57	473.43	clear	turbid
5	95	0.237	4.509	500.0	33.10	466.90	clear	turbid
10	90	0.467	4.200	500.0	65.09	434.91	clear	turbid
20	80	0.903	3.612	500.0	125.95	374.05	clear	turbid
30	70	1.312	3.061	500.0	182.99	317.01	clear	turbid
40	60	1.696	2.544	500.0	236.55	263.45	clear	turbid
50	50	2.057	2.057	500.0	286.95	213.05	clear	turbid
60	40	2.398	1.599	500.0	334.45	165.55	clear	turbid
70	30	2.720	1.166	500.0	379.31	120.69	clear	turbid
80	20	3.024	0.756	500.0	421.72	78.28	clear	turbid
90	10	3.312	0.368	500.0	461.90	38.10	clear	turbid
95	5	3.450	0.182	500.0	481.20	18.80	clear	turbid
96	4	3.477	0.145	500.0	485.00	15.00	clear	turbid
97	3	3.504	0.108	500.0	488.78	11.22	clear	turbid
98	2	3.531	0.072	500.0	492.54	7.46	clear	turbid
99	1	3.558	0.036	500.0	496.28	3.72	clear	turbid

**stablisation at 5 °C for 30 mins, immersion in 50 °C for 10 seconds, observe

Example 6 – Ketone and Amine Combinations:

[0078] In a fifth example, the molar ratios of various thermo-responsive solutions comprising triethylamine and a mixture of ketones in water at different temperatures were measured and the miscibility of the solution in water was recorded. The results are tabulated below in Table 5.

Table 5

Components	water; triethylamine; propanone; 2-butanone	water; triethylamine; propanone; cyclohexanone	water; triethylamine; 2-butanone; cyclohexanone	water; triethylamine; propanone; 2-butanone; cyclohexanone
Mol Ratio	144 : 6 : 3 : 3	144 : 6 : 3 : 3	144 : 6 : 3 : 3	144 : 6 : 2 : 2 : 2
5 °C	miscible	miscible	miscible	miscible
20 °C	miscible	miscible	immiscible	miscible
50 °C	immiscible	immiscible	immiscible	immiscible

It can be seen from the tabulated results that combinations of ketone mixtures are equally as effective as a single ketone. It can also be noted that the temperatures at which immiscibility occurs can be controlled by selection of the components of the ketone mixture.

MINIMUM RATIOS OF AMINE, KETONES AND WATER

[0079] The following experiments were carried out to determine the minimum ratio of amine, ketone and water respectively in the draw solution to behave as a switchable polar draw solution. The major objective of this experiment was to learn how to manage the solution components in the most economical manner. The model draw solution used for this test was a combination of triethylamine (TEA), methyl ethyl ketone (MEK) and water.

Minimum molar ratio of amine

[0080] The draw solution was prepared using TEA, MEK and water with the molar ratio of TEA varying from 0.1 to 1 in 25 mL glass vials. The quantity and number of moles of TEA with respect to the molar ratio was tabulated (as shown in Table 6). A constant molar ratio of 1: 10 for MEK (4.0061 g) and water (10 g) was maintained throughout. For all the test samples, the visual LCST was recorded using a resistance temperature detector (RTD).

Table 6: Visual LCST data of the draw solution containing TEA, MEK and water with varying ratios of TEA

Triethylamine (TEA)			**LCST**
Quantity	**Number of moles**	**Molar ratio**	**(in °C)**
0.5621	0.0050	0.1	23.7-24.3
1.1243	0.0100	0.2	24.2-24.5
1.68655	0.0150	0.3	26.6-26.8
2.2487	0.0200	0.4	27.3-27.5
2.8109	0.0250	0.5	27.6-27.7
3.3731	0.0300	0.6	27.6-27.8
3.93528	0.0350	0.7	27.6-27.8
4.497467	0.0400	0.8	27.2-27.4
5.05965	0.0450	0.9	27.2-27.5
5.6218	0.0500	1	27.5-27.8

[0081] From Figure 8, it can be seen that the LCST increased with an increase in the molar ratio of TEA from 0.1 to 0.4 in the draw solution. For the molar ratios greater than 0.4, the LCST remained the same. From these results the minimum molar ratio of

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TEA required is 0.5 for the draw solution to behave as a switchable polar solution without altering the LCST.

Minimum molar ratio of ketone

[0082] The draw solution was prepared by using TEA, MEK and water with the molar ratio of MEK varying from 0.1 to 1 in 25 mL glass vials. The quantity and number of moles of MEK with respect to the molar ratio was tabulated (as shown in Table 7). A constant molar ratio of 1: 10 for TEA (5.6218 g) and water (10 g) was maintained throughout. For all the samples, the visual LCST was recorded using a resistance temperature detector (RTD).

Table 7: Visual LCST data of the draw solution containing TEA, MEK and water with varying ratios of MEK

MEK			**LCST**
Ratio	**Quantity(g)**	**Moles**	**(in °C)**
0.1	0.4006	0.0050	19.6-19.8
0.2	0.8012	0.0100	21.2-21.3
0.3	1.2018	0.0150	22.4-22.6
0.4	1.6024	0.0200	23.7-23.8
0.5	2.0031	0.0250	24.5-24.7
0.6	2.4037	0.0300	25.3-25.6
0.7	2.8043	0.0350	25.9-26.02
0.8	3.2049	0.0400	26.4
0.9	3.6055	0.0450	27.1

[0083] From Figure 9, it can be seen that the visual LCST values are increasing with an increase in the molar ratios of MEK and there is no point at which it stabilises or becomes constant. Thus, for all the draw solution formulations, the molar ratio of ketone is maintained as 1.

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Example 7 – Volume ratios:

[0084] In a sixth example, the volumetric ratios of the various components of a thermo-responsive solutions in water at 20 degrees C were studied and their respective miscibilities in water were recorded. The results are tabulated below in Table 8.

Table 8

Components	water	water; propanone	water; 2-butanone	water; cyclohexanone	water; triethylamine
Vol Ratio	50 : 50	50 : 50	50 : 50	50 : 50	50 : 50
20 °C	miscible	miscible	immiscible	immiscible	immiscible

Example 8 – Controls:

[0085] In a seventh example, the various components of a thermo-responsive solutions in water at 20, 30 and 50 degrees C were studied and their respective miscibilities in water were recorded. The results are tabulated below in Tables 9and 10.

Table 9

Components	water	water; triethylamine	water; 2-butanone	water; triethylamine; 2-butanone	triethylamine; 2-butanone
20 °C	miscible	immiscible	immiscible	miscible	miscible
30 °C	miscible	immiscible	immiscible	immiscible	miscible
50 °C	miscible	immiscible	immiscible	immiscible	miscible

Table 10

Components	water	water; triethylamine	water; propanone	water; triethylamine; propanone	triethylamine; propanone
20 °C	miscible	immiscible	miscible	miscible	miscible
30 °C	miscible	immiscible	miscible	miscible	miscible
50 °C	miscible	immiscible	miscible	immiscible	miscible

[0086] It can be seen from Tables 9 and 10 that the miscibility properties of the components can vary significantly depending on the temperature and the components in the mixture. For example, it can be seen in Table 4 that at 20 degrees Celsius (C), both

triethylamine and 2-butanone are immiscible in water. However, at the same temperature, a mixture of both triethylamine and 2-butanone in water is miscible, while at 30 degrees C the mixture becomes immiscible. This exemplifies a thermo-responsive solution.

[0087] Similar results are seen in Table 10, with the exception that in this example, the ketone, propanone, is miscible in water, whereas in contrast in Table 9, 2-butanone was immiscible in water.

Multiple amines and single ketone

[0088] The compounds being used to prepare switchable polar draw solutions for various applications are bases and enolisable carbonyls. Tertiary amines which are basic in nature are combined with ketones which are organic compounds with a carbonyl group and the resulting combinations are checked for a lower critical solution temperature (LCST). The effect of conjugation, substitution and addition of functional groups on the switch point are observed and the data obtained are put to further use depending on the applications in the future. Ketones are selected such that they are in series (for example, 2-propanone, 2-butanone and so on), isomers (for example, 2-pentanone and 3-pentanone), cyclic (for example, cyclopentanone) and conjugated (for example, acetophenone) in nature.

[0089] The draw solutions were formulated to consist of multiple amines and ketones whilst still exhibiting thermo-responsive properties. The ketones were combined with few selected amines in different molar ratios and the LCSTs were recorded on addition of water. Several combinations are described in the following experiment. Additionally, the effect of different ketone/amine combinations on the osmotic pressure was observed.

Instruments

[0090] The temperature was varied to determine the LCST using Qpod-2e which is a Peltier based cuvette holder with constant stirring. The visual LCST temperature was recorded using resistance temperature detector (RTD) probe. The osmolality of the draw solution at 10% by weight in water was determined by freezing point method based osmometer, Osmomat 3000.

Methodology

[0091] The draw solutions were made up with amine(s), ketone(s) and water in the specified molar ratios and the visual LCST of the draw solution was determined. Visual LCST refers to the temperature at which the solution turns cloudy just before it separates out into two phases and the LCST was recorded using the resistance temperature detector (RTD) probe.

[0092] Osmotic pressure of the draw solution was measured for the draw solution with 10% pure draw (by weight) in 90% water (by weight). 50uL of the test sample (chilled draw solution in single phase) was pipetted out into the measuring vessel and attached to the thermistor probe of the osmometer. The test draw solution sample measurement was performed automatically and the osmolality of solute (pure draw) was displayed on the screen. At least 3 trials were performed on each sample and the average was reported.

Types of combinations

[0093] Different types of amines and ketones were combined in different combinations such that they would behave as a switchable polar draw solution. A few draw solution combinations were selected as follows:

- Single amine combined with ketone(s)
- Multiple amines combined with single ketone
- Multiple amines combined with multiple ketones

The following abbreviations are used in Tables 11-14

K1 = Ketone 1, K2 = Ketone 2, K3 = Ketone 3; A1 = Amine 1, A2 = Amine 2, A3 = Amine 3, TEA = triethylamine, 2-P = 2-propanone, 2-PENT = 2-pentanone, 3-P = 3-pentanone, 2-B = 2-Butanone, CH = cyclohexanone, CP = cyclopentanone, 1EP = 1 ethylpiperidine, DEMA = diethylmethylamine, ACET = acetophenone, 2-O = 2-octanone, 4M2P = 4-Methyl-2-pentanone, 3M2B = 3-methyl-2-butanone, DMBA = dimethylbenzylamine

[0094] The following Table 11 summarises the LCST and the osmotic pressure of different combinations of draw solutions containing a single amine with one or more ketone(s): Note: the osmotic pressure is at 10% of pure draw by weight.

Table 11:

A1	K1	K2	K3	Molar ratio of amine: ketone: water	Visual LCST (°C)	Osmotic pressure (mOsmol/kg)
TEA	2-P	-	-	6: 6: 144	45	923.67
TEA	2-B	-	-	6: 6: 144	27	1350
TEA	CH	-	-	6: 6: 144	11.5	905.33
TEA	2-B	2-P	-	6: 3: 3: 144	28.3	1251.000
TEA	2-P	CH	-	6: 3: 3: 144	22.8	710.000
TEA	2-B	CH	-	6: 3: 3: 144	20.5	1020.333
TEA	2-P	2-B	CH	6: 2: 2: 2: 144	25.3	1097.333

Combination of multiple amines and single ketone

[0095] The following table 12 summarises the LCST and the osmotic pressure of combinations of draw solutions containing multiple amines with a single ketone: Note: the osmotic pressure is measured at 10% of pure draw by weight.

Table 12

A1	A2	A3	K1	Molar ratio amines:ketone: water	Visual LCST (°C)	Osmotic pressure (mOsmol/kg)
TEA	1-EP	-	2-B	0.5: 1: 10	22.7	1114
TEA	DEMA	-	2-B	0.5: 1: 10	35.8	1150.3
TEA	1-EP	DEMA	2-B	0.5: 1: 10	31.3	1258.3
TEA	1-EP	-	CP	0.5: 1: 10	22.7	1098.67
TEA	DEMA	-	CP	0.5: 1: 10	32	1054
TEA	1-EP	DEMA	CP	0.5: 1: 10	41.6	1180.3

Combination of amine(s) and two ketones

[0096] The following table 13 summarises the LCST and the osmotic pressure of combinations of draw solutions containing one or more amine(s) with two ketones: Note: the Osmotic pressure is at 10% of pure draw by weight.

Table 13

A1	A2	K1	K2	Molar ratio amine(s):ketone(s):water	Visual LCST (°C)	Osmotic pressure (mOsmol/kg)
TEA	-	2-P	2-PENT	0.5: 1: 10	35.7	1323.3
1-EP	-	2-P	2-PENT	0.5: 1: 10	22.5	1284.3
TEA	1-EP	2-P	2-PENT	0.5: 1: 10	31.9	1181
TEA	-	CP	ACET	0.5: 1: 10	15.6	1017
1-EP	-	CP	ACET	0.5: 1: 10	6.5	995
TEA	1-EP	CP	ACET	0.5: 1: 10	10.5	993.67
TEA	-	CP	2-O	0.5: 1: 10	6.7	1006.6
1-EP	-	CP	2-O	0.5: 1: 10	0	840.6
TEA	1-EP	CP	2-O	0.5: 1: 10	1.5	868
TEA	-	CP	4M2P	0.5: 1: 10	13.1	1141
1-EP	-	CP	4M2P	0.5: 1: 10	9.5	1013.3
TEA	1-EP	CP	4M2P	0.5: 1: 10	12.3	1059.3

Combination of amine(s) and multiple ketones

[0097] The following table 14 summarises the LCST and the osmotic pressure of draw solutions containing combination of one or more amine(s) with multiple ketones:

Table 14:

A1	A2	A3	K1	K2	K3	Molar ratio of A(s):K(s): water	Visual LCST (°C)	Osmotic pressure at 10% of pure draw by weight (mOsmol/kg)
TEA	-	-	2-B	CP	2-P	0.5: 1: 10	30.5	1096.33
1-EP	-	-	2-B	CP	2-P	0.5: 1: 10	29.3	1172.67
TEA	1-EP	DMBA	2-B	CP	2-P	0.5: 1: 10	24	993.67
TEA	-	-	2-P	3-P	3M2B	0.5: 1: 10	15.2	1107
1-EP	-	-	2-P	3-P	3M2B	0.5: 1: 10	5.6	972
TEA	1-EP	DMBA	2-P	3-P	3M2B	0.5: 1: 10	-1	983

[0098] From these results it can be appreciated that effective LCST draw solutions can be prepared from a number of amines and ketones in various combinations and ratios. The results also show that a very wide spread of different temperature LCST draw solutions can be obtained and that a desired temperature of a LCST draw solution could be achieved by using different amines and ketones. It is also to be appreciated that if the LCST of a given draw solution is too high or too low, the LCST could be modified by adding a ketone or an amine. It can also be seen from the results that significant osmotic pressure readings are obtained with a number of these draw solutions.

Example 9 – Flux Experiment

[0099] The flux of water across a semipermeable membrane using draw solutions of the present invention (as detailed in Table 15) have been studied using a test system as illustrated in Figure 10. The test system comprises a gear pump (1) that is used to circulate the feed from the feed tank (3) into the membrane cell (4). A conductivity probe (2) is used to measure the conductivity in the feed tank (3). Three way valve (5) on the feed side of the membrane cell (4) and three way valve (6) on the draw side of the membrane cell (4) are used to isolate the membrane cell when cleaning or replacing the membrane. Another valve (7) is used to isolate the draw side when maintenance is required. This valve (7) can also be used then cleaning or replacing the membrane. A

gear pump (8) on the draw side is used to circulate the draw solution into the membrane cell. A resistance temperature detector (9) is used to control the temperature after the chiller (10), which is a heat exchange used to coll the draw solution before entering the membrane cell (4). A filter (11) is shown that allows the flux experiment to be run at atmospheric pressure without exposing the operator to vapors or fumes. A coalescer cartridge (12) is used to collect the draw solution and water after the membrane cell (4). A draw tank and coaleser (13) are used for separation of the draw solution from water. At the bottom of the draw tank and coalescer (13) is a valve (1) that is used to drain the tank/coalescer. A resistance temperature detector (15) is used ot control the temperature after the heater (16), which is a heat exchanger used to heat the draw solution before being returned to the draw tank and coalesce (13). Two way valve (17) is used to isolate the draw side when cleaning or replacing the membrane. Three way valve (18) on the draw side of the membrane cell (4) and three way valve (19) on the draw side of the membrane cell (4) are used to isolate the membrane cell when cleaning or replacing the membrane. Two way valve (20) is used to isolate the feed side when cleaning or replacing the membrane. The test system was flushed with deionised water (in triplicate) on each side of the semipermeable membrane in the membrance cell (4). The semipermeable membrane was a forward osmosis membrane. The feed side of the membrane cell was filled with deionised water and the draw side of the membrane cell was filled with the selected draw solution being tested. The feed solution pump (1) and draw solution pump (8) were then turned on simultaneously and the test system was left to equilibrate for 2-3 minutes. The water level in the draw tank (13) was recorded and then the system was allowed to operate for 10 minutes. The draw tank (13) was then emptied by removing the water down to the originally noted level in the draw tank and the water was weighed to determine the quantity of water that crossed that membrane in 10 minutes. These last two steps were repeated for the duration of the test. The ratios, draw concentrations and duration of the tests conducted are tabulated below in Table 15.

Table 15:

Draw	Feed	Ratio (amine-ketone)	Draw Conc	Duration	Sampling frequency	Average flux ($l/h/m^2$)
TEA - MEK	Deionised Water	0.5-1.0	10 and 20%	1h 40 min	10 minutes	See Figure 11
	150 mM NaCl aq.					See Figure 11
TEA - CP	Deionised Water	0.5-1.0	10 and 20%	1h 40 min	10 minutes	See Figure 12
	150 mM NaCl aq.					See Figure 12
TEA - CP	Deionised Water	0.5-1.0	5%	1h	10 minutes	1.63
TEA-MEK	Deinonised water	1.0:1.0	100%	1h 40 min	10 minutes	3.733

CP = cyclopentanone

It can be seen from Table 15 and Figures 11 and 12 that the average water flux was affected by temperature and draw solution concentration. The highest water flux rate was seen with a 1.0:1.0 ratio of TEA to MEK. In the case of TEA and MEK, as the temperature increased so did the water flux. As the draw solution concentration doubled the water flux dropped slightly. In contrast with the TEA cyclopentanone draw solution, the water flux increased when the draw solution concentration doubled.

FTIR Experiments

[00100] The draw solutions were analyzed using the FTIR spectrometer. Various ratios of MEK and TEA with water were measured using FTIR. The resulting spectra were then analysed using principal component analysis. The samples investigated were labelled as TEA, MEK, TEA: MEK and TEA: MEK: H_2O.

[00101] Samples were placed into a sample dish on a temperature control stage and analysed. FT-IR spectroscopy was performed using a Bruker Vertex 70 FT-IR spectrometer. Analysis of samples involved obtaining 16 scans to produce each spectrum and a spectral resolution of 0.4 cm^{-1}.

[00102] The resulting spectra are shown as Figures 13-16. it can be seen that the carbonyl peak at around 1712-1719 cm^{-1} is converted to an enol in the presence of water.

The single carbonyl peak at 1712-1719 cm^{-1} (see in Figures 14 and 15) is spilt into a double peak at 1645-1701 cm^{-1} representing the enol form.

[00103] It is to be appreciated that these solutions that exhibit thermo-responsiveness have applicability as draw solutions in osmotic processes. It is to be appreciated that a thermo-responsive solution of the present invention could be used as a draw solution in osmotic processes as illustrated in Figures 1 and 6. The draw solution can be used, for example, to draw water that requires purification through a semi-permeable membrane into the draw solution. Once the draw solution has reached its osmotic potential the draw solution mixture can be heated to its lower critical solution temperature at which point the ketone and amine mixture becomes immiscible in the water solution and the purified/treated water solution can be readily separated (by physical or mechanical separation in a very energy efficient manner) from the draw solution. The draw solution can be recycled and reused in a further osmotic cycle. It is to be appreciated that the lower critical solution temperature can be varied depending on the ketone/amine mix and whether one or more ketones or amines are used. For energy efficient purposes it would be desirable to have a lower critical solution temperature that is not much higher than room temperature.

[00104] 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.

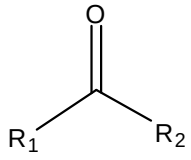
[00105] Accordingly, one of ordinary skill in the art will readily appreciate from the disclosure that later modifications, substitutions, and/or variations performing substantially the same function or achieving substantially the same result as embodiments described herein may be utilised according to such related embodiments of the present invention. Thus, the invention is intended to encompass, within its scope, the modifications, substitutions, and variations to processes, manufactures, compositions of matter, compounds, means, methods, and/or steps disclosed herein.

CLAIMS

1. A thermo-responsive osmotic solution having a lower critical solution temperature in a solvent suitable for use in osmosis comprising:

a) at least one tertiary amine containing compound; and

b) at least one enolisable carbonyl of Formula I,



Formula I

wherein

c) 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

d) 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

e) R_1 and R_2 together, with the carbonyl of Formula I, form

a. a 3-15 membered monocyclic ketone or

b. a 3-15 membered monocyclic heterocyclic ketone;

and

wherein in use at least one of the tertiary amine containing compound or the at least one enolisable carbonyl is immiscible with the solvent at or above 20 degrees Celsius and at 1 atmosphere.

2. The solution as claimed in claim 1, wherein the solution includes a combination of more than one enolisable carbonyl of Formula I.

3. The solution as claimed in claim 1 or claim 2, wherein the solution includes a combination of more than one tertiary amine containing compound.

4. The solution as claimed in any one of claims 1 to 3, wherein the at least one tertiary amine containing compound is a Lewis base.

5. The solution as claimed in any one of claims 1 to 4, wherein the at least one tertiary amine containing compound is immiscible with the solvent at or above 20 degrees Celsius and at 1 atmosphere.

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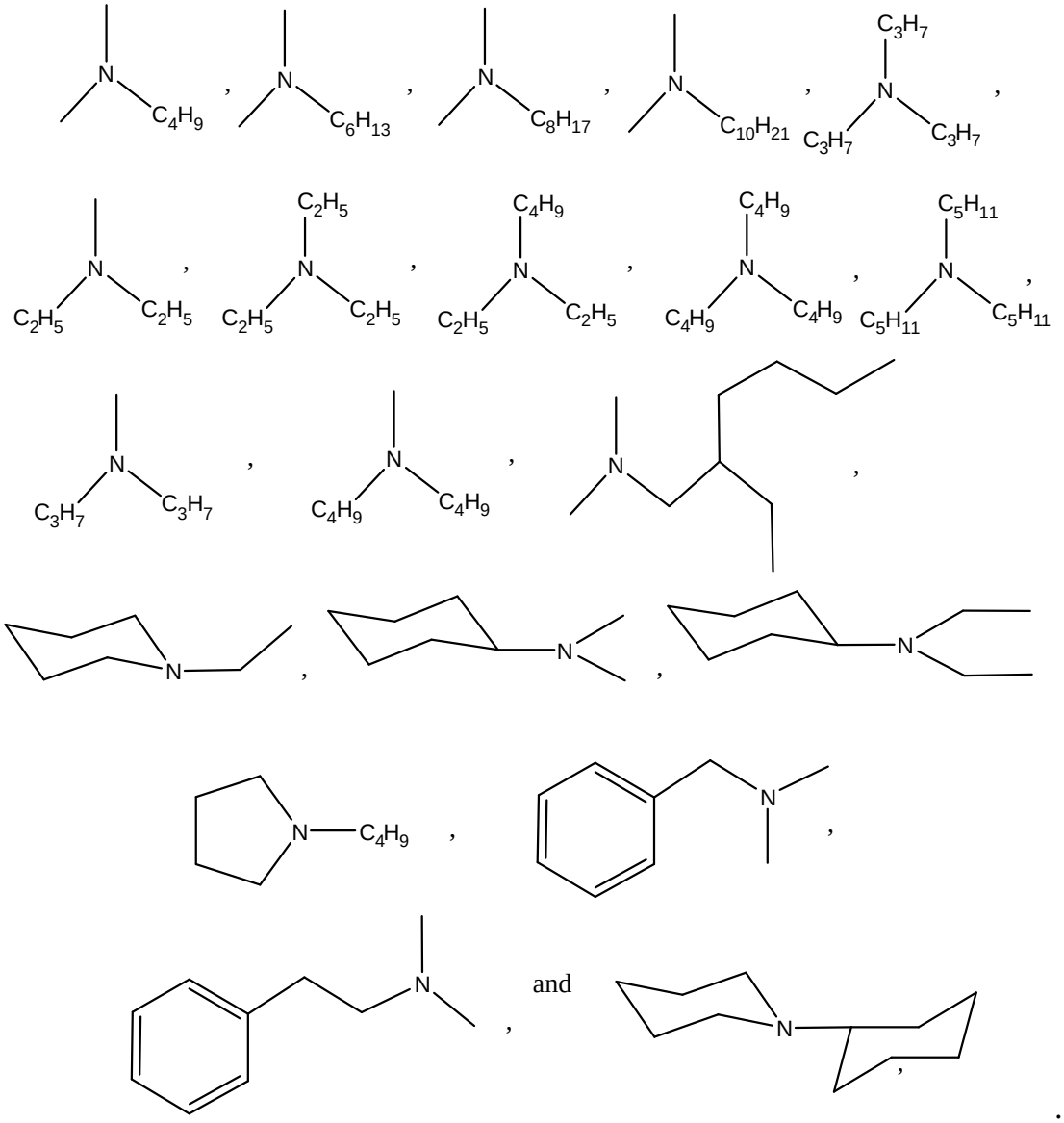
6. The solution as claimed in any one of claims 1 to 5, wherein the at least one tertiary amine containing compound is selected from a conjugated, aliphatic, asymmetric or cyclic tertiary amine.

7. The solution as claimed in claim 6, wherein the tertiary amine is selected from one or more of the following:



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8. The solution as claimed in claim 6, wherein the at least one tertiary amine containing compound is selected from a -N(C_1-C_7 alkyl)$_3$.

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9. The solution as claimed in claim 8, wherein the at least one tertiary amine containing compound is selected from a -N(C_1-C_4 alkyl)$_3$.

10. The solution as claimed in claim 9, wherein the at least one tertiary amine containing compound is -N(C_2 alkyl)$_3$ (triethylamine).

11. The solution as claimed in a claim 4 or any one of claims 5 to 10 when dependent upon claim 4, wherein the lewis base forms a lewis adduct with the enolisable carbonyl.

12. The solution as claimed in any one of claims 1 to 11, wherein R_1 and R_2 of Formula I are independently selected from a -C_1-C_7 alkyl.

13. The solution as claimed in claim 12, wherein R_1 and R_2 are independently selected from methyl and ethyl.

14. The solution as claimed in any one of claims 1 to 10, wherein R_1 and R_2 together with the carbonyl of Formula I, form a cyclic system selected from a 4-8 membered monocyclic ketone or a monocyclic ester.

15. The solution as claimed in claim 1 or claim 2, wherein the one or more enolisable carbonyls of Formula I is selected from acetone, acetophenone, methylethylketone (2-butanone), cyclohexanone, cyclopentanone, 2-propanone, 2-pentanone, 3-pentanone, 4-methyl-2-pentanone, 2-octanone and 3-methyl-2-butanone.

16. The solution as claimed in any one of claims 1 to 12 and 14, wherein each R_1 and R_2 are further substituted with one or more substituents selected from -halo, -OH, -CN, -NO_2, -CΞCH, -SH, -C_1-C_7 alkyl, -(C_1-C_7 alkyl)-OH, -NH_2, -NH(C_1-C_7 alkyl),-N(C_1-C_7 alkyl)$_2$, -O (C_1-C_7 alkyl), -C(O)-O(-C_1-C_7 alkyl), -C(O)OH; -C(O)-H, or -C(O)-(C_1-C_7 alkyl).

17. The solution as claimed in any one of claims 1 to 16, wherein the molar ratio of the at least one base to the one or more enolisable carbonyls of Formula I are present in a ratio of about 1:99 or 99:1.

18. The solution as claimed in claim 17, wherein the molar ratio of the at least one base to the one or more enolisable carbonyls of Formula I are present in a ratio of about 1:50 or 50:1.

19. The solution as claimed in claim 17 or claim 18, wherein the molar ratio of the at least one base to the enolisable carbonyl of Formula I are present in a ratio of about 1:10 or 10:1.

20. The solution as claimed in any one of claims 17 to 19, wherein the molar ratio of the at least one base to the one or more enolisable carbonyls of Formula I are present in a ratio of about 1:5 or 5:1.

21. The solution as claimed in any one of claims 17 to 20, wherein the molar ratio of the at least one base to the one or more enolisable carbonyls of Formula I are present in a ratio of about 1:3 or 3:1.

22. The solution as claimed in any one of claims 17 to 21, wherein the molar ratio of the at least one base to the one or more enolisable carbonyls of Formula I are present in a ratio of about 1:2 or 2:1.

23 The solution as claimed in any one of claims 17 to 22, wherein the molar ratio of the at least one base to the one or more enolisable carbonyls of Formula I are present in a ratio of about 1:1.

24 The solution as claimed in any one of claims 1 to 23, wherein the solvent is water.

25. A method for separating a first solution including one or more solvents, using a thermo-responsive solution as defined in any one of claims 1 to 24, the method comprising:

1) bringing the first solution into contact with a semi-permeable membrane;
2) allowing one or more solvents in the first solution to flow through the semi-permeable membrane from the first solution into the thermo-responsive solution

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by osmosis to form a second solution, wherein the thermo-responsive solution is at a higher osmotic concentration than the first solution;

3) raising the temperature of the second solution to or above the lower critical solution temperature of the thermo-responsive solution to cause the thermo-responsive solution to become immiscible with the one or more solvents from the first solution that have passed through the semi-permeable membrane; and

4) separating the one or more solvents that have passed through the semipermeable membrane from the immiscible thermo-responsive solution.

26. The method as claimed in claim 25, wherein the first solution further includes one or more dissolved solutes.

27. The method as claimed in claim 25 or claim 26, wherein the first solution includes water as a solvent.

28. The method as claimed in any one of claims 25 to 27, wherein the first solution is selected from seawater, brackish water, industrial water waste streams, compromised water sources, sewage, wastewater liquors, digestates, food & beverage processing effluents, grey water, fruit juices, vegetable juices, milk, produced waters, leachates, flue gas scrubber discharge or the like.

29. A method for separating a first solution including one or more solvents, using a thermo-responsive solution as defined in any one of claims 1 to 24, the method comprising:

1) bringing the first solution into contact with a semi-permeable membrane;

2) allowing one or more solvents in the first solution to flow through the semi-permeable membrane from the first solution into the thermo-responsive solution by osmosis to form a second solution, wherein the thermo-responsive solution is at a higher osmotic concentration than the first solution;

3) adjusting the lower critical solution temperature of the thermo-responsive solution to cause the thermo-responsive solution to become immiscible with the one or more solvents from the first solution that have passed through the semi-permeable membrane; and

4) separating the one or more solvents that have passed through the semipermeable membrane from the immiscible thermo-responsive solution.

30. The method as claimed in claim 29, wherein the lower critical solution temperature of the thermo-responsive solution is adjusted by adding one or more tertiary amine containing compounds as defined in any one of claims 1 to 24.

31 The method as claimed in claim 29 or claim 30, wherein the lower critical solution temperature of the thermo-responsive solution is adjusted by adding or more enolisable carbonyls as defined in any one of claims 1 to 24.

32 The method as claimed in any one of claims 29 to 31, wherein the lower critical solution temperature of the thermo-responsive solution is adjusted by adding one or more tertiary amine containing compounds as defined in any one of claims 1 to 24 and by adding or more enolisable carbonyls as defined in any one of claims 1 to 24 or combinations thereof.

33. The method as claimed in any one of claims 29 to 32, wherein the first solution further includes one or more dissolved solutes.

34. The method as claimed in any one of claims 29 to 33, wherein the first solution includes water as a solvent.

35. The method as claimed in any one of claims 29 to 34, wherein the first solution is selected from seawater, brackish water, industrial water waste streams, compromised water sources, sewage, wastewater liquors, digestates, food & beverage processing effluents, grey water, fruit juices, vegetable juices, milk, produced waters, leachates, flue gas scrubber discharge or the like.

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