

Title of Invention: An Ultra-Salt Tolerant Polymer To Form Salt Solutions For Depression Of Freezing Point Of Water

[001] The present application claims priority to Singapore patent application number 10202250990K filed on 13 September 2022 titled "An ultra-salt tolerant polymer, salt solutions and depression of freezing point of water" and which is incorporated by reference herein in its entirety.

Technical Field

[002] The present invention relates to a zwitterionic polymer.

Background

[003] Salts and salt solutions have many industrial applications. For example, salts are used as freezing point depressants for water and salt solutions are useful as heat transfer fluids. These are widely used in deicing of aircraft, airport runways and roadways in countries that encounter a severe winter climate.

[004] One of the widely used applications is for de-icing. In the US, about 10 million tons of road salt are used every year to tackle problems associated with icing during winter. One of the major problems associated with the road salt (which is sodium chloride) is its limited effectiveness in depressing the freezing temperature. It is capable of depressing the freezing temperature up to a temperature of -18 °C and is ineffective in an atmosphere below this temperature. Although the cost of road salt is low, its high corrosiveness is a major problem for the equipment, foliage, and infrastructure. Many alternative salt solutions have been explored to overcome these issues. Acetates of Calcium and Magnesium proposed as substitutes are costlier than road salt. Even though these salts inhibited the degradation of concrete and prevented corrosion, the freezing point depression is less than satisfactory.

[005] Salt solutions are also used in fuel-cell cooling systems, solar energy systems, fire protection systems, hydraulic systems, pharmaceutical reactors, hot water heating systems, air conditioning systems, power station cooling systems, drilling fluids, fishing industry, etc. The concentrated salt solutions used in these applications are also corrosive in nature.

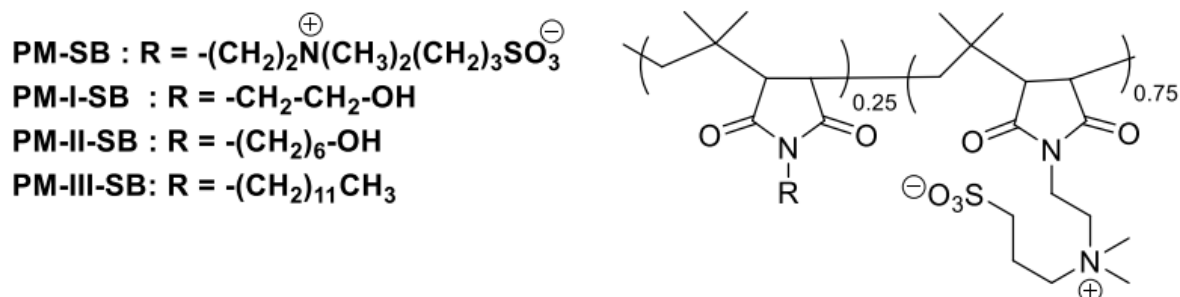
[006] The salt solutions may also be used as secondary cooling fluids. These are potentially suitable for the last mile delivery of vaccines that need to be stored at sub-zero temperatures and distributed to faraway places, particularly in underdeveloped countries.

5 [007] US patent number 6287480 discloses succinate salt based de-icing composition and method of using this salt composition for de-icing applications at airport facilities and for highways, residential and commercial de-icing applications. US patent number 6890451 discloses a de-icing fluid composition and methods for preventing ice formation on surfaces from glycerol containing by products obtained
10 during industrial processing of triglycerides in combination with salt solutions. US patent number 11326084 discloses cold storage material composition for controlling temperature of an article and a technique for using the cold storage material composition. US patent number 9434868 discloses composition for de-icing of surfaces and anti-icing compositions intended to prevent formation of ice on surfaces
15 in freezing conditions. US patent number 6156226 discloses renewable resource and industrial waste derived ice-melting compositions. US patent number 8226846 discloses a combination of low molecular weight carbohydrate with an inorganic freezing point depressant such as a chloride salt. US patent number 6623657 discloses de-icing composition derived from succinic acid or succinic anhydride or both
20 and a neutralizing base such as sodium hydroxide, potassium hydroxide, or ammonium hydroxide mixed with water to produce salt and heat. US patent number 8539821 discloses an aqueous metal ion formate salt and its use for reducing water film on an interior pipeline operating below 0 °C. US patent number 6689289 discloses a combination of carboxylic acids used as aqueous heat transfer fluids, particularly
25 antifreeze coolants and general cooling fluids. WO2017/009652 discloses heat transfer fluid and its use. The heat transfer fluid is useful for ground source heating systems, secondary refrigeration unit systems, heating, ventilating and air conditioning systems, chemical processing, food and beverage production, solar thermal heating, etc. US patent number 7638069 discloses water based heat transfer fluids that provide
30 protection against freezing at low temperatures. US pat. 8679364 discloses de-icers such as acetate, formate and lactate derived from biomass.

[008] Dsouza and Parthiban (*Langmuir* 2019, 35, 13942-13949) describe four copolymaleimide based Zwitterionic polymers as shown below in Scheme 1. The PM-

SB compound (may also be termed ZI-PIBMA) has a isobutylene-maleimide backbone.

Scheme 1: Copolymaleimide based Zwitterionic polymers with a isobutylene-maleimide backbone.

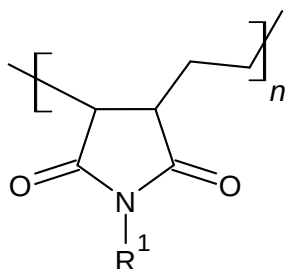


[009] One of the drawbacks of these disclosures is the requirement of high salt concentrations to substantially depress the freezing temperature. Typically, to achieve a freezing point of $-50\text{ }^{\circ}\text{C}$, 50 wt% alkali metal salt solutions such as potassium formate and potassium acetate are needed. In the case of potassium succinate the depression achieved is $-26.8\text{ }^{\circ}\text{C}$. The high concentration of salt makes these solutions corrosive. Potassium acetate poses corrosion problem in certain airport applications because of its corrosive nature to components of aircraft. Salts like calcium chloride and magnesium chloride are non-corrosive. However, the freezing point attainable with these salts are less than satisfactory. For example, US patent number 8226846

[0010] Apart from salt solutions, another method of depressing the freezing temperature of water is to use organic liquids like glycols or a combination of glycols and salt solutions. Commonly used glycols like monoethylene glycol is toxic by ingestion. Additionally, aqueous glycol solutions are corrosive in nature. Importantly, at low temperatures the viscosity of these solutions rises rapidly and such increase in viscosity could induce malfunctioning of equipment. Organic compounds are flammable in general and hence handling of these require extra safety measures. The addition of organic solvents to salt solutions for depressing freezing temperature also reduce the density of fluids that may pose problems for drilling applications where high density fluids are desired. The lowering of density may also cause problems for circulating the heat transfer fluids.

Summary

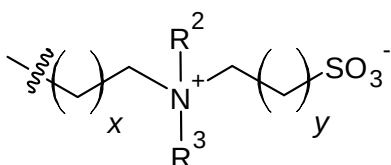
[0011] In a first aspect, there is provided a polymer comprising Formula (I),



(I), wherein R¹ comprises a quaternary ammonium cation and a

- 5 sulfonate anion. Hence, R¹ comprises a sulfobetaine. The polymer may thus be termed as a polysulfobetaine with a positively charged quaternary ammonium cation and a sulfonate anion in the repeating unit.

[0012] Preferably, R¹ has a Formula (II)



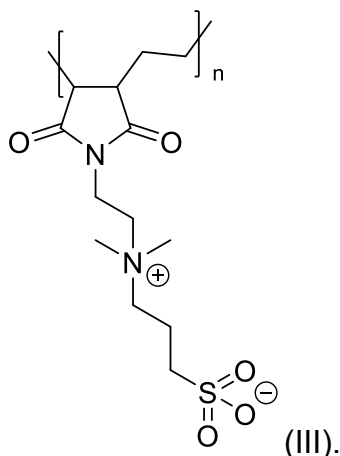
(II), wherein x and y are each independently selected from

- 10 the group consisting of 1, 2, 3, and 4, and R² and R³ are each independently selected from unsubstituted and substituted alkyl groups having 1 to 4 carbon atoms.

[0013] In an embodiment, x and y are each independently selected from 1 or 2, preferably x is 1 and y is 2.

- [0014] In an embodiment, R² and R³ are each independently selected from
15 unsubstituted and substituted alkyl groups having 1 or 2 carbon atoms, preferably R² and R³ are each independently a methyl or an ethyl group, more preferably the methyl group.

[0015] In a second aspect, there is provided a polymer comprising Formula (III),



(III).

[0016] Preferably, in Formula (I) or Formula (III) an average of n is 790 to 4000.

[0017] In an embodiment, the polymer may consists essentially of Formula (I) or Formula (III). In another embodiment, the polymer may consists of Formula (I) or Formula (III).

- 5 [0018] In a third aspect, there is provided a composition comprising the polymer according to the first aspect or the second aspect; and a water soluble salt.

[0019] Preferably, the salt comprises a cation selected from the group consisting of a Group 1 cation, a Group 2 cation, and a Group 13 cation.

- 10 [0020] Preferably, the cation is selected from the group consisting of sodium, potassium, lithium, magnesium, calcium, and aluminium.

[0021] Preferably, the salt comprises a halide anion. Examples of a halide anion include chloride or bromide.

- 15 [0022] In an embodiment, the salt is sodium chloride. In an example, a concentration of sodium chloride is 5 weight percent (wt%) or more, preferably the concentration of sodium chloride is 25 wt% or more, more preferably the concentration of sodium chloride is 25 wt% to 40 wt%, and a concentration of the polymer is 1 wt% or more, preferably the concentration of the polymer is 4 wt% or more, more preferably the concentration of the polymer is 4 wt% to 15 wt%.

- 20 [0023] In an embodiment, the salt is calcium bromide. In an example, a concentration of calcium bromide is 20 weight percent (wt%) or more, preferably the concentration of sodium chloride is 50 wt% or more, more preferably the concentration of sodium chloride is 50 wt% to 91 wt%, and a concentration of the polymer is 1 wt% or more, preferably the concentration of the polymer is 3 wt% or more, more preferably the concentration of the polymer is 3 wt% to 15 wt%.

- 25 [0024] In an embodiment, the salt is calcium chloride. In an example, a concentration of calcium chloride is 20 weight percent (wt%) or more, and a concentration of the polymer is 1 wt% or more, preferably the concentration of the polymer is 3 wt% or more, more preferably the concentration of the polymer is 3 wt% to 15 wt%.

- 30 [0025] In a fourth aspect, there is provided a method of depressing a freezing point of water and increasing a saturation limit of a salt in water, the method comprising adding the polymer according to the first aspect or the second aspect to a salt solution or the composition according to the third aspect to water.

[0026] Use of the polymer according to the first aspect or the second aspect or the composition according to the third aspect to deice a surface.

[0027] Use of the composition according to the third aspect as a heat transfer fluid.

[0028] Advantageously, the polymers having Formula (I) and Formula (III) increases the solubility of salts in water and lowers the freezing temperature of the resultant salt solutions compared to existing similar polymers. Advantageously, only a small amount of the polymer having Formula (I) and Formula (III) is required to improve the solubility of the salt and lower the freezing point of the salt solution. It is believed that the choice of the ethylene copolymer backbone in Formula (I) and Formula (III) provides the improved properties of the polymer compared to existing similar polymers, possibly by providing a stiffer backbone.

[0029] Advantageously, the polymer having Formula (I) and Formula (III) and salt solutions containing the polymer may be used in various industries including deicing surfaces, cold storage like fishing industry, salt brines for refrigeration and fish curing in the fishing industry, large refrigeration installations and as a heat transfer fluid.

[0030] Advantageously, the polymer having Formula (I) and Formula (III) and salt solutions containing the polymer avoids or reduces the corrosive nature of existing salt solutions, and is generally non-toxic and non-flammable making it safer to handle and dispose.

Detailed Description

[0031] In the Figures:

[0032] Figure (FIG.) 1 shows the low temperature differential scanning calorimetric (DSC) analysis of sodium chloride solutions (onset of transitions are indicated).

[0033] It is desirable to lower the salt concentration without adversely affecting the lowering of the freezing point of water and it will be preferable to use non-corrosive salts for depressing the freezing temperature of water.

[0034] FIG. 2 shows the low temperature differential scanning calorimetric analysis of hydrated calcium bromide solutions with and without ZI-PEMA (onset of transitions are indicated).

[0035] FIG. 3 shows the low temperature DSC analysis of aqueous solutions of 20 wt% CaCl_2 without and with 3 wt% ZI-PEMA.

[0036] FIG. 4 shows the low temperature DSC analysis of aqueous salt solutions of 40 wt% $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ without and with 3 wt% ZI-PEMA.

[0037] FIG. 5 shows the comparison of low temperature DSC analysis of hydrated CaBr_2 with polymer and that of mixed salts of CaBr_2 and $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ with 3 wt% ZI-PEMA.

[0038] FIG. 6 shows the low temperature differential scanning calorimetric analysis of 80% $\text{CaBr}_2 \cdot x\text{H}_2\text{O}$ solutions of ZI-PEMA and ZI-PIBMA (rate of cooling: 2 °C/min).

[0039] In the following description, numerous specific details are set forth in order to provide a thorough understanding of various illustrative embodiments of the invention. It will be understood, however, to one skilled in the art, that embodiments of the invention may be practiced without some or all of these specific details. Embodiments described in the context of one of the methods or devices are analogously valid for the other methods or devices. Similarly, embodiments described in the context of a method are analogously valid for a device, and vice versa.

[0040] Features that are described in the context of an embodiment may correspondingly be applicable to the same or similar features in the other embodiments. Features that are described in the context of an embodiment may correspondingly be applicable to the other embodiments, even if not explicitly described in these other embodiments. Furthermore, additions and/or combinations and/or alternatives as described for a feature in the context of an embodiment may correspondingly be applicable to the same or similar feature in the other embodiments.

[0041] Unless defined otherwise or the context clearly dictates otherwise, all technical and Scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this invention belongs. Although any methods and materials similar or equivalent to those described herein can be used in the practice or testing of the invention, the preferred methods and materials are now described.

[0042] Where a combination is disclosed, each subcombination of the elements of that combination is also specifically disclosed and is within the scope of the invention. Conversely, where different elements or groups of elements are disclosed, combinations thereof are also disclosed. Where any element of an invention is disclosed as having a plurality of alternatives, examples of that invention in which each alternative is excluded singly or in any combination with the other alternatives are also hereby disclosed; more than one element of an invention can have such exclusions, and all combinations of elements having such exclusions are hereby disclosed.

[0043] Where a range of values is recited, it is to be understood that each intervening integer value, and each fraction thereof, between the recited upper and lower limits of that range is also specifically disclosed, along with each subrange between such values. The upper and lower limits of any range can independently be included in or
5 excluded from the range, and each range where either, neither or both limits are included is also encompassed within the invention. Where a value being discussed has inherent limits, for example where a component can be present at a concentration of from 0 to 100%, or where the pH of an aqueous solution can range from 1 to 14, those inherent limits are specifically disclosed. Where a value is explicitly recited, it is
10 to be understood that values which are about the same quantity or amount as the recited value are also within the scope of the invention, as are ranges based thereon.

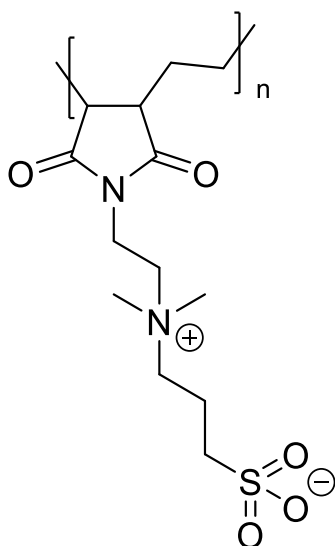
[0044] The term "alkyl" as used herein is a branched or unbranched saturated monovalent hydrocarbon radical of 1 to 24 carbon atoms, such as methyl, ethyl, n-propyl, isopropyl, nbutyl, isobutyl, s-butyl, f-butyl, n-pentyl, isopentyl, s-pentyl,
15 neopentyl, hexyl, heptyl, octyl, nonyl, decyl, dodecyl, tetradecyl, hexadecyl, eicosyl, tetracosyl, and the like. The alkyl group can be cyclic or acyclic. The alkyl group can be branched or unbranched. The alkyl group can also be substituted or unsubstituted. For example, the alkyl group can be substituted with one or more groups including, but not limited to, alkyl, cycloalkyl, alkoxy, amino, ether, halide, hydroxy, nitro, silyl,
20 sulfo-oxo, or thiol, as described herein. A "lower alkyl" group is an alkyl group containing from one to six (e.g., from one to four) carbon atoms. A weight percent (wt. %) of a component, unless specifically stated to the contrary, is based on the total weight of the formulation or composition in which the component is included.

[0045] The term "aryl group" refers to a monovalent aromatic radical which includes
25 carbocyclic aromatic rings and heteroaryl rings (nitrogen, oxygen, and sulphur and the like), and in particular refers to the atom forming the bond being part of the ring structure. The term "aromatic group" may be used interchangeably with the terms "aryl", "aryl ring", "aromatic ring", "aryl group" and "aromatic group". The aryl group may be substituted at any one or more substitutable ring atom. Non-limiting examples of
30 substituents include a halogen, a hydroxyl, an ether, an amine, a carbamate, a carbonate ester, a urea, an aliphatic group (e.g. tolyl, mesityl) an aryl group (e.g. biphenyl), a carbonyl, a carboxylic acid, an ester, an amide, a cyano, a nitro, a thiol, a sulfoxide, and a sulfone. It is understood that the substituent may be further substituted.

[0046] The term “aralkyl” or “arylalkyl” refers to a monovalent alkyl radical substituted with one or more aryl groups. In certain embodiments, the aralkyl has from 7 to 30 (C7-30), from 7 to 20 (C7-20), or from 7 to 16 (C7-16) carbon atoms. Examples of aralkyl groups include, but are not limited to, benzyl, 2-phenylethyl, and 3-phenylpropyl. In certain embodiments, aralkyl are optionally substituted with one or more substituents.

[0047] The term “quaternary ammonium cation” refers to a nitrogen atom bonded to four other groups selected from an alkyl group, an aryl group, an aralkyl group, and in any combinations thereof. The term “sulfonate anion” has a SO_3^- formula.

[0048] A salt tolerant polymer is described herein that depresses the freezing point of water to very low temperatures well below the freezing temperature attainable with the state-of-the-art salt solutions. Depending on the nature of salt, the concentration of salt required to suppress the freezing temperature is lower than conventional alkali salts like potassium formate, potassium acetate, etc. An embodiment of the polymer, a zwitterionic copolymaleimide, with the structural formula (ZI-PEMA) is also capable of enhancing the dissolution limits of salts in water beyond its saturation point. The average number of monomers in the polymer (value of n) is 790 to 4000.



ZI-PEMA

[0049] The salt tolerant polymer described herein enhances the solubility limit of salts in water and substantially lower the freezing temperature of water at low salt concentrations and the depression of freezing temperature is achieved with salt types that minimise issues of corrosion of salt solutions.

[0050] Table 1 shows a comparison of the depressed freezing point of water with a solution of calcium chloride and ZI-PEMA to some existing salt solutions. It may be observed from Table 1 that ZI-PEMA salt polymer significantly lowers the freezing point at a lower salt concentration.

- 5 [0051] **Table 1.** Comparison of salt solutions containing ZI-PEMA and existing solutions described in the prior art.

Salt (wt %)	Additive (wt %)	Freezing point (°C)	Method	Reference (US Patent No.)
Potassium formate (50)	nil	-50.8	D1177-94	6623657
Potassium acetate (50)	nil	-51.8	D1177-94	6623657
Potassium succinate (25)	Propylene glycol (25)	-34.5	D1177-94	6623657
CaCl ₂ (29.6)	Carbohydrate (18.6)	<-43.9	D1177-94	8226846
MgCl ₂ (22.7)	Carbohydrate (18)	<-43.9	D1177-94	8226846
CaCl ₂ (20)	ZI-PEMA (3)	<-60	Low temp DSC	Present work

[0052] The saturation limit of various salts in water and the depression of the freezing temperature of water in the presence of ZI-PEMA was studied and described herein.

- 10 [0053] Monovalent salt - Sodium chloride (NaCl)

[0054] Sodium chloride in water reaches saturation at a concentration of 26 wt%. The limit for salt concentration near saturation for sodium chloride in water is 25.58% (WO 2017/160655). However, it is possible to shift this limit to 35 wt% of sodium chloride with about 4.5 wt% of the ZI-PEMA polymer. This limit increases to 38.5 wt% of sodium chloride with 14.5 wt% of polymer. As shown in FIG. 1, the addition of the ZI-PEMA polymer results in lowering (or depressing) the freezing point of water in the sodium chloride salt solution by more than 7 °C.

- 15 [0055] Table 2 shows the crystallization and melting temperature of different concentrations of aqueous sodium chloride solution with 5 wt% of ZI-PEMA as studied by low temperature differential scanning calorimetry. Deionized water upon cooling at a rate of 2 °C per minute from 20 °C showed a freezing temperature (T_{exo}) of -13 °C and upon subsequent warming at the same rate a melting temperature (T_{endo}) of 3 °C was observed. Due to the ability of ZI-PEMA to increase the solubility of NaCl in water
- 20

these transitions were shifted respectively to -54 °C and -20 °C. Unlike the two transitions noticed for the crystallization in intermediate salt concentrations, the transition noticed in 35 wt% of NaCl solution with ZI-PEMA is similar to polymer free 23 wt% NaCl solution. The presence of two exothermic transitions may be an indication of the presence of water bound to the salt to varying degrees. Even though the depression of freezing point occurred nearly linearly with increasing polymer and salt concentration, not much variation was noticed in the melting transition (T_{endo}) beyond a NaCl concentration of 15 wt% .

[0056] **Table 2.** Crystallization and melting transitions of aqueous sodium chloride solutions

Component	Concentration of salt, wt%	T_{exo} , °C	T_{endo} , °C
DI water	0	-13.27	2.61
NaCl	8	-24.74, -35.47	-5.39, -19.86
NaCl with ZI-PEMA	8	-16.08, -39.56	-4.94, -21.24
NaCl	15	-29.99, -36.49	-18.96
NaCl with ZI-PEMA	15	-32.43, -37.82	-20.41
NaCl	23	-45.82	-18.85
NaCl with ZI-PEMA	23	-36.85, -41.46	-19.65
NaCl with ZI-PEMA	35	-54.07	-19.91

T_{exo} – exothermic transition (midpoint) corresponding to freezing point observed upon cooling from 20 °C to -70 °C in low temperature differential scanning calorimetric analysis at a rate of 2 °C/min.

T_{endo} – endothermic transition (midpoint) corresponding to melting of frozen solid observed upon heating from -70 °C to 20 °C in low temperature differential scanning calorimetric analysis at a rate of 2 °C/min.

[0057] Divalent salt – Calcium bromide (CaBr_2)

[0058] Calcium bromide reaches saturation at 57 wt% and the salt concentration at near saturation for calcium bromide is 55.9 % (WO 2017/160655). Since ZI-PEMA readily dissolves in sodium chloride solution, a 3 wt% ZI-PEMA polymer solution was prepared in 1 wt% sodium chloride solution. In this solution, it was possible to dissolve calcium bromide to make 90.5 wt% of aqueous calcium bromide solution. The freezing point of water continued to lower with an increasing concentration of salt. FIG. 2

compares the role of the polymer in lowering the freezing temperature of water in salt solutions with varying concentration of salt.

[0059] Table 3 shows the crystallization and melting temperature of different concentrations of aqueous calcium bromide solution with 3wt% of ZI-PEMA as studied

5 by low temperature differential scanning calorimetry.

[0060] **Table 3.** Crystallization and melting transitions of aqueous calcium bromide solutions with 3 wt% of ZI-PEMA

Component	Concentration of salt, wt%	T _{exo} , °C	T _{endo} , °C
DI water	0	-13.27	2.61
CaBr ₂ .xH ₂ O	20	-19.73	-4.76
CaBr ₂ .xH ₂ O with ZI-PEMA	20	-24.37	-5.90
CaBr ₂ .xH ₂ O	50	-36.81	-19.41
CaBr ₂ .xH ₂ O with ZI-PEMA	50	-41.18	-21.10
CaBr ₂ .xH ₂ O with ZI-PEMA	60	-52.79	-29.85
CaBr ₂ .xH ₂ O with ZI-PEMA	80	-65.84	-37.17
CaBr ₂ .xH ₂ O with ZI-PEMA	90	Not detected (<-70)	Not detected

T_{exo} – exothermic transition observed upon cooling from 20 °C to -70 °C in low temperature differential scanning calorimetric analysis at a rate of 2 °C/min.

10 T_{endo} – endothermic transition observed upon heating from -70 °C to 20 °C in low temperature differential scanning calorimetric analysis at a rate of 2 °C/min.

[0061] Unlike the sodium chloride solution, in the case of hydrated calcium bromide solution, there was a clear trend that the addition of polymer not only enhanced the solubility limit of salt but also uniformly lowered the crystallization temperature (T_{exo}).

15 The melting transition (T_{endo}) also linearly went down with increasing salt concentration. Thus, there is an apparent difference on the effect of ZI-PEMA between the aqueous solutions of monovalent and divalent cations. The role of different anions involved namely chloride and bromide cannot be ruled out in the observed difference between the salts of mono and divalent cations.

20 [0062] Divalent salt – Calcium chloride (CaCl₂)

[0063] The depression of the freezing temperature of water with other divalent salts like calcium chloride was also studied. In the DSC analysis, 20 wt% calcium chloride showed a freezing point of -35 °C. As shown in FIG. 3, an aqueous solution of 20 wt% calcium chloride containing 3 wt% of ZI-PEMA did not show any transition up to -60 °C and the onset of transition was below -60 °C.

[0064] Trivalent salt – Aluminium chloride (AlCl₃)

[0065] The depression of freezing point of water in the presence of ZI-PEMA was also noticed in the aqueous solution of aluminium chloride as shown in FIG. 4. 40 wt% aqueous aluminium chloride solution showed onset of freezing temperature at -45.98 °C without polymer and at -53.2 °C with 3 wt% of ZI-PEMA. FIG. 4 shows the low temperature DSC studies of aqueous aluminium chloride solutions with and without ZI-PEMA.

[0066] Di and trivalent mixed salts – Calcium bromide and Aluminium chloride

[0067] An aqueous solution of 60 wt% aluminium chloride and 42 wt% calcium bromide containing 3 wt% ZI-PEMA did not show any transition up to -60 °C in the low temperature DSC analysis. In FIG. 2, 50 wt% of aqueous calcium bromide solution showed a freezing temperature of -39.4 °C without ZI-PEMA and -43.4 °C with ZI-PEMA. The low temperature DSC analysis of the aqueous solution of mixed salts is shown in FIG. 5.

[0068] Comparison with ZI-PIBMA (or PM-SB)

[0069] ZI-PIBMA also showed good salt tolerance as indicated by the increasing viscosity with increasing salt concentration and its ability to depress the freezing temperature of salt solutions were studied by low temperature DSC analysis. It was found that ZI-PIBMA did not increase the saturation limit of sodium chloride in water but increased the dissolution of hydrated calcium bromide in water. However, the depression of freezing point caused by ZI-PIBMA was lower than that of ZI-PEMA as shown in FIG. 6.

[0070] The enhanced dissolution of salt achieved with ZI-PEMA and the concomitant depression in freezing temperature of salt solution is far greater for this polymer than any of the previously reported polymer of similar type. The choice of the copolymer for modification such as the sulfobetaine derived from poly(ethylene-alt-maleic anhydride) makes the polymer backbone stiffer. Thus, a polymer with the ethylene-alt-maleic anhydride backbone allows the polymer backbone to be stiffer and may provide the resultant polymer with its improved properties compared to ZI-PIBMA.

[0071] It has been observed that the properties of zwitterionic polymers are highly variable and additional methylene groups between charges may cause changes in the properties of the zwitterionic polymer in an unpredictable manner. Advantageously, ZI-PEMA has been found to increase the concentration of various salts in solution with only a small amount of the zwitterionic polymer while lowering the freezing temperature of the solution significantly thereby increasing the usefulness of these salt solutions in various industries including deicing surfaces, cold storage like fishing industry, and as a heat transfer fluid.

[0072] As shown herein ZI-PEMA may be used to dissolve salts in water for depressing the freezing temperature of water to use as a heat transfer fluid and for increasing the saturation limit of salts in water. The salt solutions with the polymer may be used in deicing applications, as a heat transfer fluid, salt brines for refrigeration and fish curing in the fishing industry, large refrigeration installations and cold storage.

[0073] Experimental

[0074] Preparation of ZI-PEMA

[0075] Poly(ethylene-alt-maleic anhydride) (average Molecular weight 100,000-500,000) purchased from Sigma-Aldrich (11.5439g, 0.09154 mol) was dissolved in N,N-dimethylformamide (120 mL) by heating the mixture at 100 °C in a round bottom flask fitted with a reflux condenser. To this solution, N,N-dimethyl ethylenediamine (DMEDA) (8.07g, 0.09155 mol) was added dropwise. An off-white solid separated upon adding DMEDA. Toluene (50 mL) was added and the reflux condenser was replaced with a Dean-Stark apparatus. The temperature was raised to 160 °C and the water formed in the reaction along with toluene was removed overnight (18h). Then the pale yellow solution was cooled down to 80 °C. About 2 ml of solution was withdrawn and precipitated in diethyl ether, washed with diethyl ether and dried for analysis. Propane sultone (PS) (11.4543g, 0.09381 mol) was added to the remaining solution. An off-white solid separated from the reaction solution after completing the addition of PS. The reaction mixture was heated at 80 °C with stirring for 24 h. After cooling down to room temperature (25 °C), the reaction mixture was transferred to a beaker containing ethyl acetate (500 mL). It was stirred well and the solid was allowed to settle down. The liquid was decanted off and the procedure was repeated two more times. Then the solid was dried in an hot air oven maintained at 60 °C for 48 h. A product yield of 22g was obtained. The ZI-PEMA polymer is insoluble in common organic solvents and hence the molecular weight could not be determined directly.

Based on the known molecular weight of the poly(ethylene-alt-maleic anhydride) used (average molecular weight of 100,000 to 500,000 and the molecular weight of the ZI-PEMA polymer was assumed to convert completely and was calculated as previously described in *Dsouza and Parthiban* Langmuir 2019, 35, 13942-13949. Based on the available information of the polymer by the supplier, it is believed that the average molecular weight referred to by the supplier is measured by light scattering technique. Hence, it is not specified whether the molecular weight of the polymer is the weight average molecular weight or the number average molecular weight which is stated when measured by other techniques like gel permeation chromatography. However, it could still possibly refer to the weight average molecular weight or the number average molecular weight. The average molecular weight range of ZI-PEMA was determined to be from 252,444 to 1,262,220.

[0076] The solid obtained after imidization was insoluble in organic solvents. The following is the FT-IR analysis of the sample:

[0077] KBr pellet (cm^{-1}): 3447.57, 2947.59, 2865.29, 2825.94, 1777.02, 1697.25, 1582.88, 1455.75, 1399.94, 1340.09, 1228.51, 1151.50, 1101.03, 1039.93, 928.11, 861.74, 774.96, 623.22.

[0078] FT-IR analysis of ZI-PEMA (KBr pellet, cm^{-1}): 3447.16, 3041.86, 2958.57, 1771.68, 1700.36, 1489.83, 1400.39, 1358.26, 1190.94, 1042.56, 919.27, 795.83, 733.38, 666.04, 605.07, 527.32.

[0079] ^1H -NMR of ZI-PEMA (D_2O containing traces of NaCl, δ) ppm: 1.45-2.19 (b, 4H), 2.21-2.38 (b, 2H), 2.82-2.91 (b, 2H), 2.96-3.01 (b, 2H), 3.2-3.4 (b, 6H), 3.5-3.7 (b, 4H), 3.85-4.1 (b, 2H).

[0080] ^{13}C -NMR of ZI-PEMA (D_2O containing traces of NaCl, δ) ppm: 180.75, 60.27, 59.56, 51.16, 47.38, 45.21, 37.13, 27.04, 18.37.

[0081] Preparation of salt solutions in deionized water

[0082] Sodium chloride (NaCl) solutions

S/No.	Amount of NaCl, g	Amount of ZI-PEMA, g	Quantity of deionized water, mL	Solution concentration with respect to salt, wt%
1.	0.0098	nil	10	0.1
2.	0.0502	nil	10	0.5
3.	0.1009	nil	10	1
4.	0.1998	nil	10	2

5.	0.5006	nil	10	5
6.	0.8000	nil	10	8
7.	1.0031	nil	10	10
8.	1.4998	nil	10	15
9.	2.0094	nil	10	20
10.	2.3035	nil	10	23
11.	0.010	0.010	10	0.1
12.	0.0523	0.0105	10	0.5
13.	0.2006	0.0103	10	2
14.	0.5005	0.0104	10	5
15.	0.8020	0.0105	10	8
16.	1.0002	0.0101	10	10
17.	1.5004	0.0103	10	15
18.	2.0023	0.0100	10	20
19.	2.2998	0.0098	10	23
20.	3.6027	0.4515	10	36

[0083] Hydrated calcium bromide ($\text{CaBr}_2 \cdot x\text{H}_2\text{O}$) solutions

S/No.	Amount of $\text{CaBr}_2 \cdot x\text{H}_2\text{O}$, g	Amount of ZI-PEMA, g	Amount of NaCl, g	Quantity of deionized water, mL	Solution concentration with respect to $\text{CaBr}_2 \cdot x\text{H}_2\text{O}$, wt%
1.	2.0048	nil	nil	10	20
2.	5.0013	nil	nil	10	50
3.	2.0105	0.3043	0.1022	10	20
4.	5.0856	0.3067	0.1081	10	50
5.	6.1261	0.3024	0.1056	10	61
6.	8.0092	0.3021	0.1003	10	80
7.	9.0485	0.3083	0.1057	10	90

[0084] Calcium chloride (CaCl_2) solutions

S/No.	Amount of CaCl_2 , g	Amount of ZI-PEMA, g	Quantity of deionized water, mL	Solution concentration with respect to salt, wt%
1.	1.0334	nil	5	20
2.	1.0111	0.1508	5	20

[0085] Aluminum chloride hexahydrate ($\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$) solutions

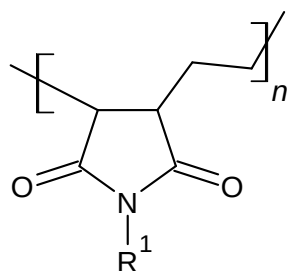
S/No.	Amount of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, g	Amount of ZI-PEMA, g	Quantity of deionized water, mL	Solution concentration with respect to salt, wt%
1.	2.0243	nil	5	40
2.	1.9966	0.1505	5	40

5 Mixed salt solution

S/No.	Amount of $\text{CaBr}_2 \cdot x\text{H}_2\text{O}$, g	Amount of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, g	Amount ZI-PEMA, g	Quantity of deionized water, mL	Solution concentration with respect to $\text{CaBr}_2 \cdot x\text{H}_2\text{O}$ and $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, wt%
1.	2.1158	2.9728	0.1034	5	40 and 60

Claims

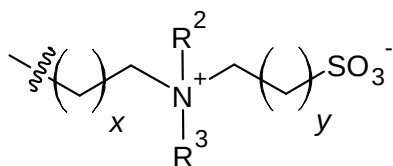
1. A polymer comprising Formula (I),



(I), wherein R¹ comprises a quaternary ammonium cation and a sulfonate anion.

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2. The polymer according to Claim 1, wherein R¹ has a Formula (II)

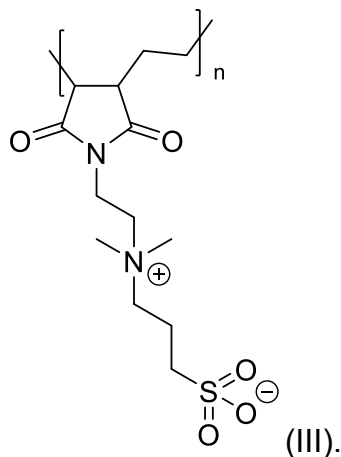


(II), wherein x and y are each independently selected from the group consisting of 1, 2, 3, and 4, and R² and R³ are each independently selected from unsubstituted and substituted alkyl groups having 1 to 4 carbon atoms.

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3. The polymer according to Claim 2, wherein x and y are each independently selected from 1 or 2, preferably x is 1 and y is 2.
4. The polymer according to any one of Claims 2 or 3, wherein R² and R³ are each independently selected from unsubstituted and substituted alkyl groups having 1 or 2 carbon atoms, preferably R² and R³ are each independently a methyl or an ethyl group, more preferably the methyl group.
5. A polymer comprising Formula (III),

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(III).

6. The polymer according to any one of Claims 1 to 5, wherein an average of n is 790 to 4000.
7. A composition comprising the polymer according to any one of Claims 1 to 6; and a water soluble salt.
- 5 8. The composition according to Claim 7, wherein the salt comprises a cation selected from the group consisting of a Group 1 cation, a Group 2 cation, and a Group 13 cation.
9. The composition according to Claim 8, wherein the cation is selected from the group consisting of sodium, potassium, lithium, magnesium, calcium, and
10 aluminium.
10. The composition according to any one of Claims 7 to 9, wherein the salt comprises a halide anion, preferably chloride or bromide.
11. The composition according to any one of Claims 7 to 10, wherein the salt is sodium chloride.
- 15 12. The composition according to Claim 11, wherein a concentration of sodium chloride is 5 weight percent (wt%) or more, preferably the concentration of sodium chloride is 25 wt% or more, more preferably the concentration of sodium chloride is 25 wt% to 40 wt%, and a concentration of the polymer is 1 wt% or more, preferably the concentration of the polymer is 4 wt% or more, more
20 preferably the concentration of the polymer is 4 wt% to 15 wt%.
13. The composition according to any one of Claims 7 to 10, wherein the salt is calcium bromide.
14. The composition according to Claim 13, wherein a concentration of calcium bromide is 20 weight percent (wt%) or more, preferably the concentration of
25 sodium chloride is 50 wt% or more, more preferably the concentration of sodium chloride is 50 wt% to 91 wt%, and a concentration of the polymer is 1 wt% or more, preferably the concentration of the polymer is 3 wt% or more, more preferably the concentration of the polymer is 3 wt% to 15 wt%.
15. The composition according to any one of Claims 7 to 10, wherein the salt is
30 calcium chloride.
16. The composition according to Claim 15, wherein a concentration of calcium chloride is 20 weight percent (wt%) or more, and a concentration of the polymer is 1 wt% or more, preferably the concentration of the polymer is 3 wt% or more, more preferably the concentration of the polymer is 3 wt% to 15 wt%.

17. A method of depressing a freezing point of water and increasing a saturation limit of a salt in water, the method comprising adding the polymer according to any one of Claims 1 to 6 to a salt solution or the composition according to any one of Claims 7 to 16 to water.
- 5 18. Use of the polymer according to any one of Claims 1 to 6 or the composition according to any one of Claims 7 to 16 to deice a surface.
19. Use of the composition according to any one of Claims 7 to 16 as a heat transfer fluid.