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Freezing behaviour and cooling energy storage capabilities of aqua-salt eutectics for milk cold chain

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Abstract
Freezing behaviour, super-cooling degree and cooling energy storage capabilities of aqua-salt eutectics for milk cold chain were studied experimentally for calcium chloride ($CaCl_2$), sodium chloride (NaCl) and sugar at concentrations (5-30%) into distilled water as well as for potable water. The degree of super cooling was more pronounced in case of sugar solution followed by $CaCl_2$ and NaCl solutions. The typical freezing point curve loop of potable water indicated by the presence of dip in the cooling curve between 0 and -5 °C was due to super-cooling that took place till formation of ice crystals. The sloping of freezing curves of distilled water containing different concentrations of salt and sugar could be due to continuous increase in concentration of salt and sugar as pure solvent was frozen out of the solution, resulting continuous freezing point depression. The highest temperature drop (ΔT) for distilled water as well as all solutions in distilled water was observed in the first hour of freezing.

Keywords: freezing, super-cooling, milk, cold-chain, freezing point depression

Introduction

Milk is a complete food created by nature for all the mammalian offspring. From the time immemorial, man learned to domesticate animals for milk which includes cows, buffaloes, sheep, goats and camels, etc. India is the leading milk producer in the world, stood at 146.3 million tonnes [1-2]. The major chunk of milk production in developing counties like India is from millions of small dairy farmers sprawl predominantly in the villages across the country. They maintain an average herd of one or two milch animals, own about 70% of the total milch animal herd of the country. This particular pattern is persistent not only in milk production but also in processing, marketing and distribution as well which is quite opposite to the developed countries of the world, wherein specialized and commercial dairy farming is practiced. At present, the trend in the past two decades indicates that the global milk production grown only by 0.78% as against the growth rate of 4.07% in India [3]. As far as milk cold chain application is concerned, the suitable concentration of aqua-salt could be applied to rapid bring down the temperature within safe limit. Traditionally, Aqueous solutions have been used as single phase (liquid) secondary refrigerants for cooling application in super markets, for ice rinks, heat recovery systems, heat pumps and other applications. They are also increasingly used for freezers in supermarkets and other applications in low temperature refrigeration. These solutions are also used in sorption based air conditioning equipment for dehumidification of air [4-7]. Actually, when one or more substances acting as solutes are mixed with one or more solvents in such proportions as to obtain the lowest possible freezing point for the combination, the resulting solution is called as eutectic solution. The lowest possible freezing temperature is called as eutectic point [8]. Granryd and Melinder [9] reported that the aqueous solutions do not usually freeze to solid ice when ice crystals begin to form and mix with the liquid. Total freezing takes place first when the temperature goes down to the eutectic point for the mixture. This process is called as super-cooling of water as solvent in aqua-salt solution. But, In general, a reduction of about 2.5% in heat transfer value takes place by each 1% increase in $CaCl_2$ concentration. This is due to the reduction in specific heat value of the eutectic solution upon increasing the concentrations of salts [8]. In another study, Hillerns [10] presented review on thermo physical properties and corrosion behaviour of secondary coolants. It was suggested that traditional brines consisting of potassium carbonate or calcium chloride possess favourable thermo physical properties, non-toxic, inexpensive and provide efficient freezing-point depression (29.9% w/w $CaCl_2$ lowers the freezing point to -55 °C) [11-12]. However, uncontrollable corrosivity at temperatures below 0 °C restricts their application to industrial cooling systems with a relatively simple technical design (no mixing installation, any defrosting cycles possible). It was also presented that despite higher costs and inferior thermal transport properties i. e. a very high viscosity; non-toxic food grade propylene glycol is used exclusively for food cooling instead of "injurious-to-health" classified ethylene glycol [13-15].

Thus, ice and salt slurries are being used as sub-zero temperature coolants but there is a need to evaluate the freezing behaviour and to record their cooing storage capabilities at different concentrations as function of temperature in order to establish the appropriate eutectic behaviour of a particular salt-slurry for a specific milk-cold chin application. In this study, the freezing behaviour and cooling energy storage capabilities of aqua-salt eutectics for milk cold chain real time applications were studied from sub-zero to the eutectic temperature ranges.

Materials and Methods

Different eutectic solutions viz. distilled water (DW), aqueous calcium chloride ($CaCl_2$), aqueous sodium chloride (NaCl) and aqueous sugar at different concentrations (5-30%) were studied for freezing behaviour and cooling energy storage capabilities. The analytical grade chemicals and reagents used for investigation were procured from standard and authorized chemical suppliers. The chemicals used for the study were DW (prepared in the laboratory), PG, EG, $CaCl_2$, NaCl, sugar. For all analytical purpose freshly prepared reagents were used adopting standard procedures. Glassware of Borosil and Schott Duran brands procured from the authorized suppliers were used for the study. Different secondary refrigerants or eutectic solutions (base fluids) at different concentrations were used in the experimental trials (Table1).

Table 1: Different eutectic solutions (base fluids) used for the study

Eutectic solution (base fluid)	Concentration in distilled water	Nomenclature of base fluid*
Distilled water	-	DW
Calcium chloride	5,10, 15, 20, 25 and 30%	CaCl
Sodium chloride	5,10, 15, 20 and 25%	NaCl
Sugar	5, 10 and 15%	Sugar
*Nomenclature used throughout		

Different instruments used for experiments during the study are listed in Table 2.

Table 2: Instruments used for experiments during the study

S. No	Instrument	Purpose	Specification
1	Data logger	To record change in temperature with time	Model: CENTER 374. Device equipped with a microprocessor and sensor with an internal memory
2	Thermocouple	To sense and measure change in temperature of the cooling fluids	K-type (chromel + alumel). Temperature range: -200 °C to +1350 °C
3	Deep Freezer	To freeze the eutectic solutions and store cooling energy	Brand: LG, Model: GL-478G5X5. Temperature range: -18 °C to -27 °C
4	Magnetic Stirrer	Mixing and dispersing nanoparticles into base fluids	Model: IKAC-MAG 7

A cooling eutectic fluid (base fluid) was prepared by weighing appropriately and mixing by magnetic stirrer and it was kept for freezing up to around 12 h in deep freezer. The Data logger was used to map the temperature profile of the eutectic aqua-salt solution during freezing and recorded data (change in temperature with time during freezing) were plotted in MS-excel 2013. K-type thermocouples were used to sense and measure change in temperature of cooling fluid during freezing. Basically, it is temperature measuring device works on thermo-electric effect in which two dissimilar metals are joined so as to form a closed circuit. The wires are joined at the ends which form two junctions-a measuring junction and a reference junction. Heating the measuring junction produces a voltage greater than the voltages across the reference junction. The difference between two voltages is measured and voltmeter reading is converted to its corresponding temperatures. The temperature variations of the secondary refrigerants during freezing were measured with K-type thermocouples which is most common, general purpose thermocouple constituted by chromel and alumel. The probes available are compatible in temperature range of -200 °C to + 1350 °C.

Results and Discussion

(DW), calcium chloride ($CaCl_2$), sodium chloride (NaCl) and sugar at different concentrations (5-30%) were tried in the experimental trials to evaluate the freezing, super-cooling, eutectic point and solidification behavior in terms of cooling energy storage and time required. The results of freezing behavior, super-cooling behavior of the cooling fluids as recorded by data logger as temperature map were plotted and presented in Fig. 1-4. The temperature of deep freezer was at -25 °C for entire duration of trials. The quantity of each eutectic solution taken for freezing and related studies was 1.5 L. The temperatures of the eutectic base fluids during freezing were recorded continuously with an interval of 1 min by data logger.

The temperature profile data of distilled water (DW) and potable water (PW) during freezing are presented in Table 3 and Fig 1. It can be seen in the Fig 1 that there was marked difference in the freezing point of DW and PW. This could be due to the presence of minerals and other salts and impurities which influenced freezing point depression in case of PW. As expected, DW started freezing at around 0 °C at around 270 min while typical freezing point curve loop of PW was noticed at around 300 min. The typical freezing point curve loop of PW indicated by the presence of dip in the cooling curve between 0 and -5 °C was due to super-cooling that took place till formation of ice crystals. Then, the sudden rise in temperature was observed which could be due to release of latent heat upon cooling associated with the onset of freezing. After this, temperate remains constant till the freezing of all liquid is completed which is indicated as horizontal line in the Fig 1. The initial temperatures of DW and PW were 25.6 °C and 25.7 °C, respectively. After freezing for 12 h, the final temperatures of DW and PW were -0.6 °C and -0.7 °C. Total temperature drop (ΔT) of DW and PW upon freezing for 12 h was 26.3 °C. The highest temperature drop for DW and PW was 10.9 °C and 11.9 °C, respectively in the first hour of freezing.

Table 3: Temperature (°C) of distilled water and potable water upon freezing

	Freezing time (h)												
	0	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**
DW	25.7	14.8	7.4	3.9	-1.4	-0.5	-0.6	-0.6	-0.6	-0.7	-0.7	-0.6	-0.6
PW	25.6	13.7	7.1	3.3	-1.5	-0.6	-0.6	-0.6	-0.6	-0.7	-0.6	-0.6	-0.7
DW: Distilled water; PW: potable water													

The temperature profile data of DW, calcium chloride ($CaCl_2$), sodium chloride (NaCl) and sugar solutions at different concentrations (5-30%) upon freezing are presented in the Table 4-6 and in the Fig 2-4.

It was observed that (Fig 2-4) the rate of temperature drop of all the eutectics base fluids at different concentrations in the first 2 h cooling time was rapid as indicated by steep slope of curves. Thereafter, the steepness of curves decreased gradually and significant difference in temperature drop was observed with all the base fluids at their respective concentrations as cooling progressed further. Super cooling of all the base fluids at different concentrations was observed before start of freezing which can be seen in the Fig 2-4 as sudden rise in temperature. The degree of super cooling was more pronounced in case of sugar solution followed by $CaCl_2$ and NaCl solutions.

Freezing of DW started at around 0 °C at around 270 min while freezing of other base fluids started at different temperatures below 0 °C at different times after 270 min. Time to start freezing was more with increase in concentrations of salts and sugar in DW. It is because of freezing point depression and thermal properties of salts and sugar. Freezing curve of DW was flat (horizontal line) from its freezing point till end of freezing time (12 h) while temperature of DW containing different concentrations of salts and sugar decreased continuously but slowly as freezing progressed which can be seen as downward sloping freezing curve. The sloping of freezing curves of DW containing different concentrations of salt and sugar could be due to continuous increase in concentration of salt and sugar as pure solvent (DW) was frozen out of the solution, resulting continuous freezing point depression. Freezing data revealed that the freezing of solutions (DW + salt and DW + sugar) involved latent heat exchange as well as sensible heat exchange while freezing of pure solvent (DW) involves only latent heat exchange after the onset of freezing. The highest temperature drop (ΔT) for DW as well as all solutions in DW was observed in the first hour of freezing. The total ΔT of DW, 5, 10, 15, 20, 25 and 30% $CaCl_2$ upon freezing for 12 h were 26.3, 30.2, 33.6, 37.4, 40.4, 44.7 and 45.7 °C, respectively. The total ΔT of DW, 5, 10, 15, 20 and 25% NaCl upon freezing for 12 h were 26.3, 32.8, 36.4, 39.6, 42.6 and 42.8 °C, respectively.

Table 4: Temperature (°C) of distilled water and $CaCl_2$ at different concentrations upon freezing

	Freezing time (h)												
	0	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**
DW	25.7	14.8	7.4	3.9	-1.4	-0.5	-0.6	-0.6	-0.7	-0.7	-0.7	-0.6	-0.6
5%$CaCl_2$	25.8	16.3	7.7	1.4	-2.7	-2.6	-2.7	-2.7	-3.2	-3.3	-3.5	-3.8	-4.4
10%$CaCl_2$	25.5	14.7	6.2	-0.1	-4.8	-4.8	-5.2	-5.5	-6.4	-6	-6.9	-7.4	-8.1
15%$CaCl_2$	25.8	14.8	6.2	-0.2	-5.1	-9.2	-8.2	-8.6	-9.8	-8.7	-10.4	-11.1	-11.6
20%$CaCl_2$	25.4	14.2	5.4	-1.1	-5.9	-9.8	-12.8	-12.4	-13.6	-10.7	-14.2	-14.5	-15
25%$CaCl_2$	25.8	14.8	5.8	-0.9	-5.8	-9.7	-12.8	-15.2	-18.2	-13.4	-17.8	-18.4	-18.9
30%$CaCl_2$	25.7	13.7	4.9	-1.4	-6.2	-10	-12.9	-15.3	-18.6	-17.1	-19.7	-19.9	-20
DW: Distilled water, $CaCl_2$: Calcium Chloride													

Table 5: Temperature (°C) of distilled water and NaCl at different concentrations upon freezing

	Freezing time (h)												
	0	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**
DW	25.7	14.8	7.4	3.9	-1.4	-0.5	-0.6	-0.6	-0.6	-0.7	-0.7	-0.6	-0.6
5%NaCl	25.6	14.6	7.2	1.1	-3.3	-3.7	-4.2	-4.4	-4.8	-5.1	-5.6	-6.1	-7.2
10%NaCl	25.7	14.3	5.9	-0.3	-5	-8.1	-7.7	-8.2	-8.6	-9.1	-9.7	-10.1	-10.7
15%NaCl	25.8	14.8	6.3	0.1	-4.6	-8.3	-11.2	-11.3	-11.8	-12.3	-12.9	-13.4	-13.8
20%NaCl	25.8	18.1	9.2	2.8	-2.1	-6	-9.1	-11.7	-13.7	-15.4	-16.7	-16.5	-16.8
25%NaCl	25.7	18.9	10.1	3.7	-1.1	-4.9	-8	-10.4	-12.4	-14.3	-15.7	-16.6	-17.1
DW: Distilled water, NaCl: Sodium Chloride													

Table 6: Temperature (°C) of distilled water and sugar solution at different concentrations upon freezing

	Freezing time (h)												
	0	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**
DW	25.7	14.8	7.4	3.9	-1.4	-0.5	-0.6	-0.6	-0.6	-0.7	-0.7	-0.6	-0.6
5%sugar	31.8	17.7	9.3	3.2	0.7	-3.4	-1.3	-1.3	-1.3	-1.3	-1.4	-1.5	-1.7
10%sugar	31	15.8	9.3	4.6	0.5	-2.8	-1.7	-1.7	-1.8	-1.9	-2.2	-2.3	-2.8
15%sugar	30.3	17.4	10.7	6	2.3	-0.3	-2.3	-4.1	-2.2	-2.4	-2.9	-3.6	-3.9
DW: Distilled water													

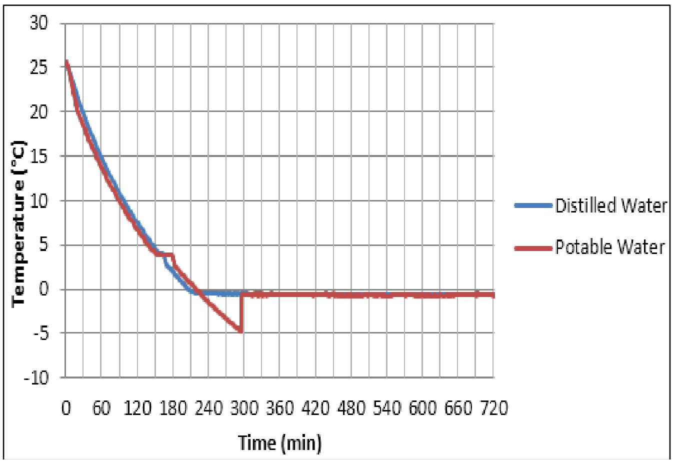

Fig 1: Temperature profile of distilled water and potable water upon freezing

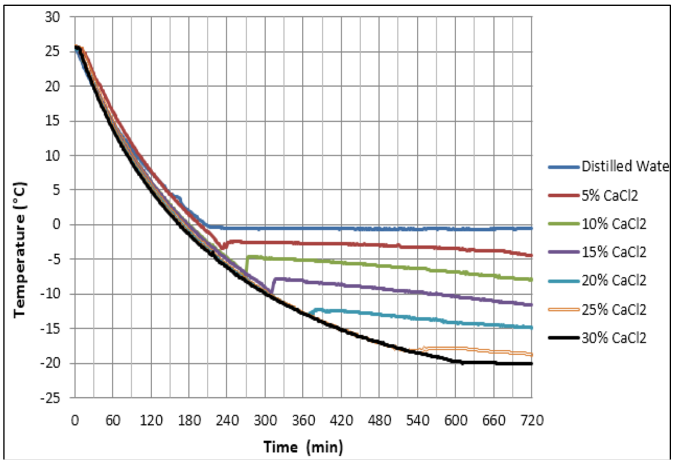

Fig 2: Temperature profile of distilled water and $CaCl_2$ at different concentrations upon freezing

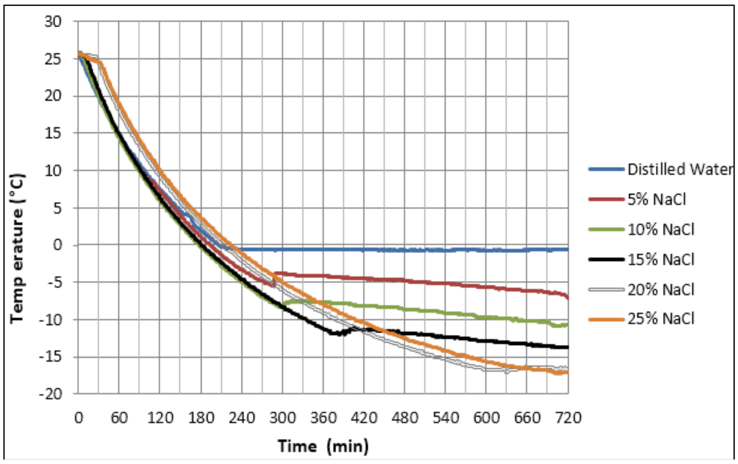

Fig 3: Temperature profile of distilled water and NaCl at different concentrations upon freezing

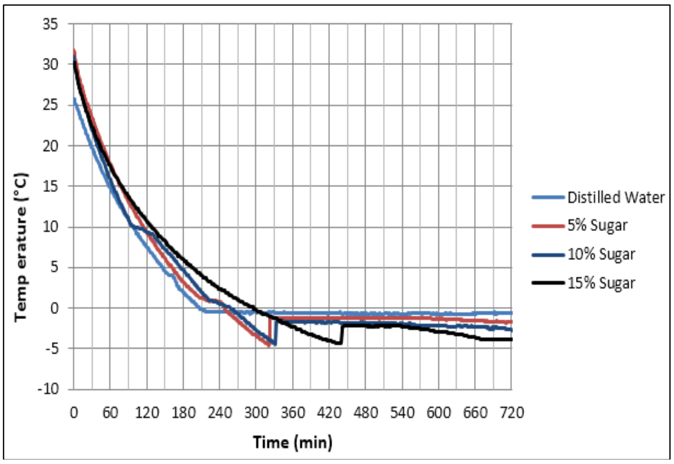

Fig 4: Temperature profile of distilled water and sugar at different concentrations upon freezing

Conclusion

Freezing behaviour, super-cooling degree and cooling energy storage capabilities of aqua-salt eutectics for milk cold chain were evaluated experimentally for calcium chloride ($CaCl_2$), sodium chloride (NaCl) and sugar at concentrations (5-30%) into distilled water as well as for potable water. The degree of super cooling was more pronounced in case of sugar solution followed by $CaCl_2$ and NaCl solutions. The typical freezing point curve loop of potable water indicated by the presence of dip in the cooling curve between 0 and -5 °C was due to super-cooling that took place till formation of ice crystals. The sloping of freezing curves of distilled water containing different concentrations of salt and sugar could be due to continuous increase in concentration of salt and sugar as pure solvent was frozen out of the solution, resulting continuous freezing point depression. The highest temperature drop (ΔT) for distilled water as well as all solutions in distilled water was observed in the first hour of freezing. The freezing data thus generated could be used for design of milk cold chain equipment in real world applications. The developed eutectics can be effectively applied for cooling milk and milk products for rapid and energy efficient cooling and chilling applications.

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