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Ravi Prakash
SRS, ICAR-National Dairy Research Institute, Bengaluru, Karnataka, India

M Manjunatha
SRS, ICAR-National Dairy Research Institute, Bengaluru, Karnataka, India

Mahesh Kumar G
Dairy Science College, Hebbal, Bengaluru, Karnataka, India

Menon Rekha Ravindra
SRS, ICAR-National Dairy Research Institute, Bengaluru, Karnataka, India

Correspondence
Ravi Prakash
SRS, ICAR-National Dairy Research Institute, Bengaluru, Karnataka, India

Sub-zero temperature profile and chilling energy storage behaviour of aqua-glycol eutectics for milk cold chain

Ravi Prakash, M Manjunatha, Mahesh Kumar G and Menon Rekha Ravindra

Abstract
Sub-zero temperature behaviour, super-cooling degree and cooling energy storage capabilities of aqua-glycol eutectics for milk cold chain were studied experimentally for propylene glycol and ethylene glycol at various concentrations (5-30%) into distilled water as well as for potable water. The degree of super cooling was more pronounced in case of ethylene glycol solution followed by propylene glycol solutions. At higher concentrations of glycols, the degree of super-cooling was more while cooling energy storage capabilities were less. The highest temperature drop (ΔT) for distilled water as well as all aqua-glycol solutions was observed in the first hour 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% PG upon freezing for 12 h were 26.3, 29.5, 32.5, 34.9, 37, 39.3 and 40.7°C, respectively. The total ΔT of DW, 5, 10, 15, 20, 25 and 30% EG upon freezing for 12 h were 26.3, 29.4, 33.1, 36.3, 38, 41 and 44.4°C, respectively.

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

Introduction
Milk is a wholesome food fashioned by nature for all the mammalian progeny. From the dawn of the civilization, human being erudite 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 quantity of milk production in developing counties like India and many other Asian countries is from millions of small dairy but scattered dairy farmers sprawl predominantly in the villages across the country. They uphold an average herd of one or tens of milch animals, contribute about 70% of the total milk production of the country. This particular scattered pattern is tenacious not only in milk production, procurement but also in intermediate-processors, 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-glycol could be applied to maintain and speedy bring down the temperature within safe limit. Traditionally, water 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 many other industrial and home applications. They are also increasingly used for refrigerators and 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, according to a traditional definition of eutectic solution says, 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. This is due to the reduction in specific heat value of the eutectic solution upon increasing the concentrations of glycols [8]. After reaching the eutectic temperature, the sudden increase in temperature takes place due to release of heat of formation of ice-crystals. In another study, Hillerns [10] presented review on thermo-physical properties and corrosion behaviour of secondary coolants. In that study, 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, but propylene glycol has been categorised as safe material, could be used in food cooling and freezing appliances [13-15].

Melinder [16] reviewed thermo physical properties of liquid secondary refrigerants and concluded that indirect systems in supermarkets work well for cooling cabinets and have an interesting challenge for low temperature freezers. From the cooling cabinet example, we can see that salt solutions give turbulent flow, while propylene glycol and ethyl alcohol give laminar flow, resulting in lower heat transfer coefficients and larger temperature difference. After considering both thermo physical properties and other general characteristics it was concluded that no secondary refrigerant is ideal for all applications.

Thus, ice and glycols are being used as sub-zero temperature coolants, even in radiators of vehicles in cold countries but there is a need to thoroughly evaluate and study the freezing behaviour and to record their cooing energy storage capabilities at different concentrations as function of temperature in order to establish the appropriate eutectic behaviour of a particular aqua-glycol-slurry for a specific milk-cold chin application. In this study, the sub-zero freezing behaviour and cooling energy storage capabilities of aqua-glycol eutectics for milk cold chain real time applications were studied from sub-zero to the eutectic temperature ranges. The detailed data recorded were plotted, tabulated and discussed in brief.

Materials and Methods

Different eutectic solutions viz, distilled water (DW), aqueous propylene glycol (PG) and aqueous ethylene glycol (EG) 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), potable water (PW), PG and EG. 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
Potable water	-	PW
Propylene glycol	5,10, 15, 20, 25 and 30%	PG
Ethylene glycol	5,10, 15, 20, 25 and 30%	EG
*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

The solutions of glycol as a cooling eutectic fluid (base fluid) were prepared by weighing appropriately on an accurate weighing balance and mixing the solvent and solute by a magnetic stirrer and it was kept for freezing up to around 12 h in a deep freezer maintained at minimum of -28 °C. The Data logger was used for mapping the temperature profile of the eutectic aqua-glycol solution during freezing and the recorded data (change in temperature vs. time during freezing) were plotted in MS-excel. K-type thermocouples were used to sense and measure change in temperature of cooling fluid during freezing and energy storage. 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

Different aqua-glycol as cooling base fluids viz, distilled water (DW), propylene glycol (PG) and ethylene glycol (EG) at different concentrations (5-30%) were tried in the preliminary experimental trials to evaluate the freezing behavior, nature of nucleation, cooling energy storage ability as latent heat. Experiments were conducted to determine the heat transfer behavior of the cooling fluids (or called as base fluids) inside the deep freezer during freezing of cooling fluids and cooling of raw milk. The results of freezing behavior, nucleation characteristics of the base fluids and temperature profile during freezing were mapped by a data logger.

Different base fluids viz, distilled water (DW), potable water (PW), propylene glycol (PG), ethylene glycol (EG) solutions in DW at different concentrations were separately kept for freezing inside deep freezer at -20 °C for a maximum period of 12 h. The temperatures of the cooling fluids being frozen were recorded continuously with an interval of 1 min by data logger.

The temperature profile data of DW and PW during freezing are presented (Table 3 and Fig 1). It can be seen in the Fig 1 that there was marked difference in the freezing points of DW and PW. This might be due to the presence of minerals 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, PG and EG solutions into DW at different concentrations upon freezing are presented in the Table 4-5 and in the Fig 2-3.

It was observed that (Fig 2-3), the rate of temperature drop of all the glycol based 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 cooling base fluids at their respective concentrations as cooling and afterwards freezing 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 2-3 as sudden rise in temperature. This may be due to release of heat of formation after reaching the eutectic temperature of the glycol solution. The degree of super cooling was more pronounced in case of EG followed by PG 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. This delayed onset of freezing was due to increased degree of super-cooling at higher concentrations of glycols primarily because of depression in freezing points. Thus, time to start freezing was more with increase in concentrations of glycols in DW. 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 glycols decreased continuously but slowly as freezing proceeded which can be seen as downward sloping freezing curve. The sloping of freezing curves of DW containing different concentrations of glycols could be due to continuous increase in concentration of glycols as pure solvent (DW) was frozen out of the solution, resulting continuous freezing point depression. Freezing data revealed that the freezing of solutions (DW + glycols) 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% PG upon freezing for 12 h were 26.3, 29.5, 32.5, 34.9, 37, 39.3 and 40.7°C, respectively. The total ΔT of DW, 5, 10, 15, 20, 25 and 30% EG upon freezing for 12 h were 26.3, 29.4, 33.1, 36.3, 38, 41 and 44.4°C, respectively.

Table 4: Temperature (°C) of distilled water and propylene glycol 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%PG	25.3	14	5.7	1.6	-1.8	-2.2	-2.3	-2.3	-2.6	-2.9	-3.2	-3.9	-4.2
10%PG	25.5	13	4.5	-1.8	-3.2	-3.6	-3.8	-4.3	-4.6	-5.2	-5.8	-6.3	-7
15%PG	25.6	13.5	5.1	-1.1	-4.2	-5.9	-5.9	-6.2	-6.7	-7.3	-7.9	-8.5	-9.3
20%PG	25.5	14	5.7	-0.4	-5.2	-8.8	-8.9	-8.9	-8.7	-9.3	-9.9	-10.7	-11.5
25%PG	25.4	14.2	5.4	-1.1	-5.8	-9.7	-10.2	-10.4	-10.9	-11.6	-12.3	-13.2	-13.9
30%PG	25.8	14.6	6.7	0.9	-3.6	-7.3	-10.2	-12.6	-14.2	-13.7	-13.9	-14.3	-14.9
DW: Distilled water, PG: Propylene glycol													

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

	Freezing time (h)												
	0	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**
DW	25.6	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%EG	25.3	16.2	8.6	3	-0.5	-2.6	-2.7	-2.9	-3.1	-3.3	-3.5	-3.8	-4.1
10%EG	25.7	15	7.2	1.3	-2.8	-4.9	-4.9	-5.3	-5.6	-6	-6.5	-6.9	-7.4
15%EG	25.7	13.8	5.7	-0.4	-5.1	-7.2	-7.1	-7.6	-8.1	-8.7	-9.4	-10	-10.6
20%EG	25.8	15.4	6.9	0.6	-4.3	-8.1	-10.2	-9.6	-10.1	-10.7	-11.2	-11.8	-12.2
25%EG	25.9	15.7	6.7	-0.3	-5.7	-9.5	-12.5	-12.9	-12.9	-13.4	-14	-14.5	-15.1
30%EG	27.3	15	6.4	0.2	-4.7	-8.6	-11.6	-14.1	-16.2	-17.1	-16.6	-17.1	-17.1
DW: Distilled water, EG: Ethylene glycol													

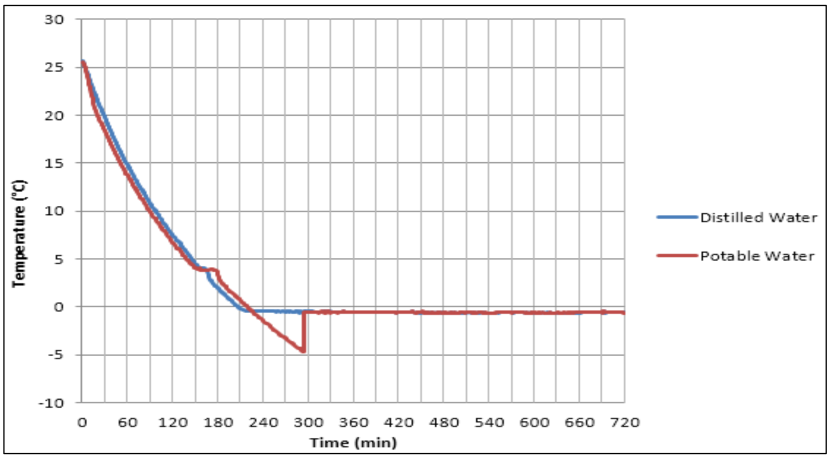

Fig 1: Temperature profile of distilled water and potable water upon freezing

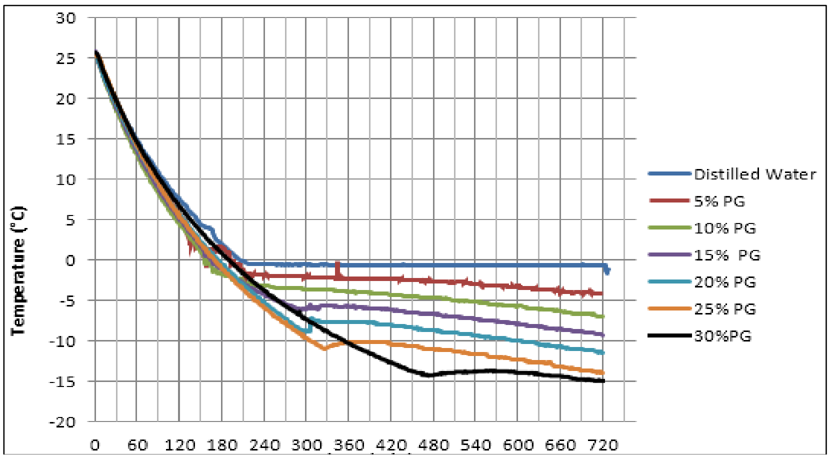

Fig 2: Temperature profile of distilled water and propylene glycol (PG) at different concentrations upon freezing

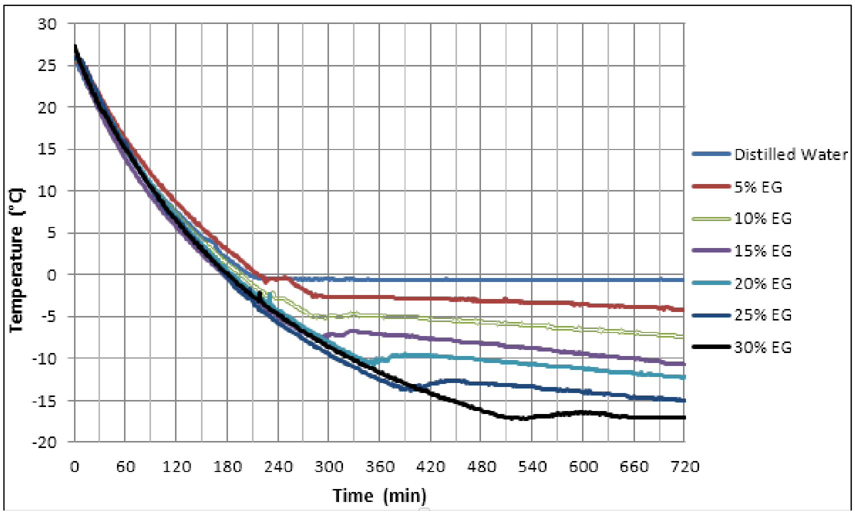

Fig 3: Temperature profile of distilled water and ethylene glycol (EG) at different concentrations upon freezing

Conclusion

Freezing behaviour, rate and super-cooling extent and cooling energy storage capabilities in terms of latent heat of aqua-salt eutectics for milk cold chain were evaluated experimentally for propylene glycol (PG) and ethylene glycol (EG) at various concentrations (5-30%) into distilled water as well as for potable water. The degree of super cooling was more pronounced in case of EG followed by PG solutions. 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% PG upon freezing for 12 h were 26.3, 29.5, 32.5, 34.9, 37, 39.3 and 40.7 °C, respectively. The total ΔT of DW, 5, 10, 15, 20, 25 and 30% EG upon freezing for 12 h were 26.3, 29.4, 33.1, 36.3, 38, 41 and 44.4 °C, respectively. The freezing, super-cooling and cooling energy storage data thus generated could be used for design of milk cold chain equipment in real world applications. The developed aqua-glycol based eutectics can be successfully recommended for cooling milk and milk products for hasty and energy efficient cooling, chilling and refrigeration applications.

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