Journal of AgriSearch, 10 (4): 259-65
An Open Access International Peer Reviewed Quarterly

ISSN : 2348-8808 (Print), 2348-8867 (Online)
https://doi.org/10.21921/jas.v10i04.14383

Characterization of Multi-Component Antifreeze Liquids for Sub-zero Cooling Applications

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ABSTRACT

The aim of this research was to formulate and compare multi component antifreeze liquids (MCAFLs), which can be used as coolant for food cooling applications at sub-zero temperatures. Different antifreeze agents like propylene glycol (PG) and NaCl were used for the preparation of MCAFLs. Trials were carried out to study the effect of PG and NaCl concentration on the cooling behavior of MCAFLs. The typical cooling characteristics of MCAFLs were reflected by the presence of a dip in the temperature profile during the formation of ice crystals and super cooling. At higher concentration of PG and NaCl the degree of super-cooling was less while freezing point depression and cooling energy storage capacity was high. The temperature drop for various PG and NaCl blend concentrations was greatest ($\Delta T = 27$ °C) during the first hour of cooling. The developed formulations can effectively reduce degree of supercooling and lower the freezing point and enhance cooling storage. MCAFLs blends have potential to be used for sub-zero cooling application in food industry.

Keywords: Antifreeze, Cooling application, Concentration, Formulation, Multi component

ARTICLE INFO

Received on	:	15.10.2023
Accepted on	:	24.11.2023
Published online	:	31.12.2023

INTRODUCTION

Water is the most popular cooling medium due to its excellent thermal properties; however, due to its higher freezing point, water is not appropriate for use in cooling application below 0 °C. When water temperature reaches 0°C at atmospheric pressure, its temperature remains constant and a phase transition takes place (Dhingra and Chopra, 2022). However, in other cases, even water's temperature falls below its freezing point, it stays in liquid phase and no phase transition happens. This condition is known as super cooling (Nazir et al. 2019). On water supercooling experiment, it was observed that without any disturbance, liquid water was in supercooling state for more than 5 hours; phase change was not initiated and cannot be used such as phase change material (PCM). In order to freeze water, its molecular structure need to be changed from liquid to ice and without nucleation agent, super cooling state cannot end and initiate phase change (Safari *et al.* 2017). The addition of antifreeze agent to water can reduce the freezing point, minimize the supercooling and also act as nucleating agents (Maeda, 2021). Aqua-glycol and aqua-salt solution are the two base chemicals that are most frequently used to make sub-zero temperature coolants (Prakash *et al.* 2018a). Non-toxic food grade propylene glycol (PG) is used exclusively for cooling of food instead of ethylene glycol. Although PG's latent heat and specific heat are less than pure water, it has the ability to alter the thermal properties of water, such as lowering its freezing point and degree of sub-cooling. The concentration of 60% PG-water solution lowers the freezing point to -60 °C.
Traditional brines composed of potassium carbonate or calcium chloride have advantageous thermo physical properties, are affordable, and effectively lower the freezing point (Vikram *et al.* 2019). However, its application is limited to industrial cooling systems due to unpredictable corrosivity at temperatures below 0 °C. It is reported that aqueous salt-water solutions of NaCl and KCl are good PCM because of their low cost and melting-freezing point below 0 ºC. However, the degree of sub cooling for NaCl solutions is less and freezing point depression is also high in case of NaCl aqueous solution. Compared to other aqueous salt solution, the freezing point of 23.3% NaCl aqueous solution is quite low at -21.1°C. NaCl solution is more efficient in thermal transport properties, stability with metal, cheap and easily available than KCl solution for cooling applications (Zhang *et al.* 2022).
In an experiment on cooling cabinet, PG salt solutions exhibited turbulent flow, while PG solution showed laminar flow resulting in lower heat transfer coefficients and larger temperature difference. Mixtures and eutectics can be also formulated to obtain the required phase change material temperature, making it very attractive in a variety of cooling application. After considering both thermo physical

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properties and other cooling characteristics, it can be said that no secondary coolant is ideal for all cooling applications (Rudonja, 2021).

The purpose of this study was to formulate the different multi component antifreeze liquids (MCAFLs) by using the PG, NaCl and water. PG and NaCl are non-toxic and non-hazardous to the food therefore it can be used as anti-freezing agent for the formulation of secondary coolant in food industry. The effect of PG and NaCl concentration on the cooling behavior of MCAFLs was also studied.

MATERIALS AND METHODS

Formulation

The primary purpose of multi component antifreeze liquids (MCAFL) is to act as a heat transfer fluid in the liquid phase; on the other hand, it could also be used as a matrix for cold thermal energy storage due to its phase change properties. Antifreeze agents were mixed in reverse osmosis (RO) water to formulate a dispersed phase solution. Although both EG and PG are totally soluble in water with no evidence of phase separation, but PG is more preferable than EG in terms of toxicity (Bokov *et al.* 2022). Therefore, PG was selected in the present study. When the solute is added to the solvent in liquid form, as in the case with PG, it is necessary to mix an aqueous solution to the proper proportion by volume rather than by weight. The MCAFL was formulated using a variety of ingredients, including propylene glycol (PG), sodium chloride (NaCl), and multistage filtered reverse osmosis (RO) water. In order to formulate MCAFL, a magnetic stirrer was used to combine PG concentrations in the range of 1:1 to 1:8 (PG: RO water) and 0 to 5% NaCl in RO water (Table 1).

Table 1: Concentration of PG and NaCl in RO water for the formulation of MCAFLs

Blend preparation of MCAFLs Ratio of (PG: RO water) along with NaCl	
1:1	
1:2	0 % NaCl
1:3	1 % NaCl
1:4	2% NaCl
1:5	3% NaCl
1:6	4% NaCl
1:7	5% NaCl
1:8	

Experimental Setup

1. Temperature monitoring module
2. Deep freezer
3. PT-100 Temperature sensors
4. Position of PT-100 sensors
5. Data logger
6. Computer

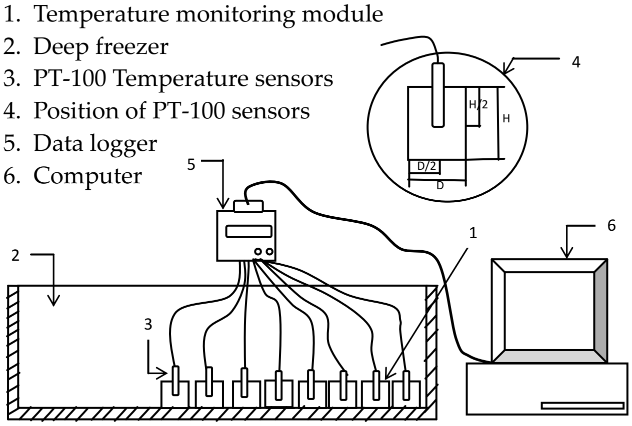

Fig. 1: Experimental set-up for comparison of cooling behavior of MCAFLs

The experimental setup consisted of temperature monitoring module (TMM), temperature data logger and deep freezer (Fig. 1). Trials were conducted to compare the cooling behavior of MCAFLs at the different concentration of PG and NaCl. In TMM (Fig. 2) sample holder cylinder, 100 ml of MCAFL was filled. TMM was designed with provision for inserting the pt-100 temperature sensor (Fig. 3), which connected to a multichannel temperature data logger. Eight TMM were filled with the 1:1, 1:2, 1:3, 1:4, 1:5, 1:6, 1:7, and 1:8 (PG: RO water) solutions respectively and were placed in a deep freezer kept at a temperature of -20 °C. The study performed for 12 hours, and the temperature profile of the MCAFLs during freezing was recorded using a data logger (Fig. 4).

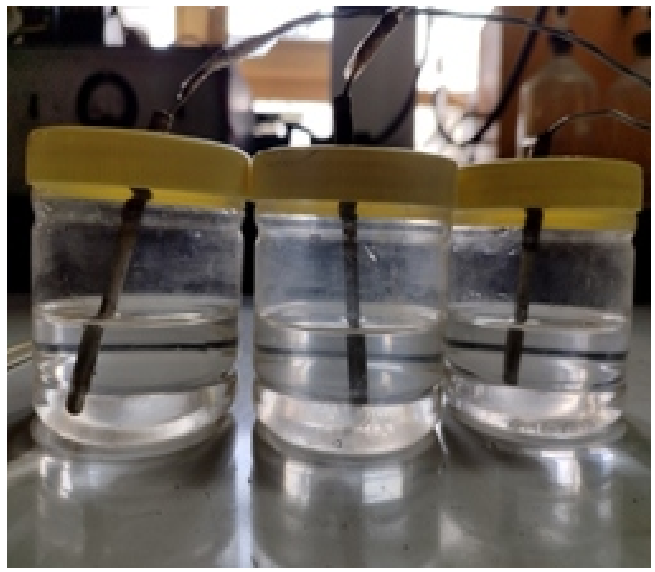

Fig. 2: Temperature monitoring module (TMM)

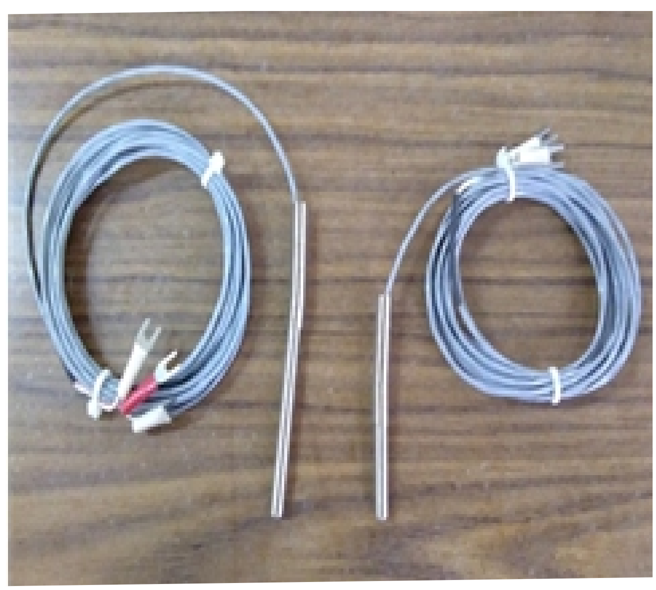

Fig. 3: PT-100 Temperature sensors

Fig. 4: Digital temperature data logger

Plotting of Cooling Curve

Cooling curve enables determination of coolant heat extraction properties using the thermal response obtained for a specific condition. MCAFLs were filled in eight TMMs and subjected to the identical chilling conditions in order to conduct a comparison study. The temperatures of the cooling fluids being frozen were recorded continuously with an interval of 1 min by data logger. To analyze and compare the cooling behavior, temperature versus time plot was generated.

pH of MCAFLs

A water-based solution's pH value indicates how basic or acidic it is. Acidic solutions have a low pH, whereas basic solutions have a higher pH. At room temperature, pure water has a pH of 7, meaning it is neither acidic nor basic (Taheri et al. 2022). The pH scale is logarithmic and shows the concentration of hydrogen ions in the solution inversely. The pH of MCAFLs was determined from the PCSTestr 35 multi-parameter (Fig. 5).

Fig. 5: pH meter

RESULTS AND DISCUSSION

Cooling Characteristics of MCAFLs

The freezing behavior of MCAFLs with respect to the different concentration of PG and NaCl in RO water were almost similar (Fig. 6-8). The growth of ice crystals and the combination of nucleation mixture affect the freezing process. It was observed that the rate of temperature drop of all the MCAFLs was rapid in the first 120 minutes cooling time during freezing as indicated by steep slope of the curves. Thereafter, the steepness of curves decreased gradually and significant difference in temperature drop was observed with increase in the concentration of PG and NaCl.

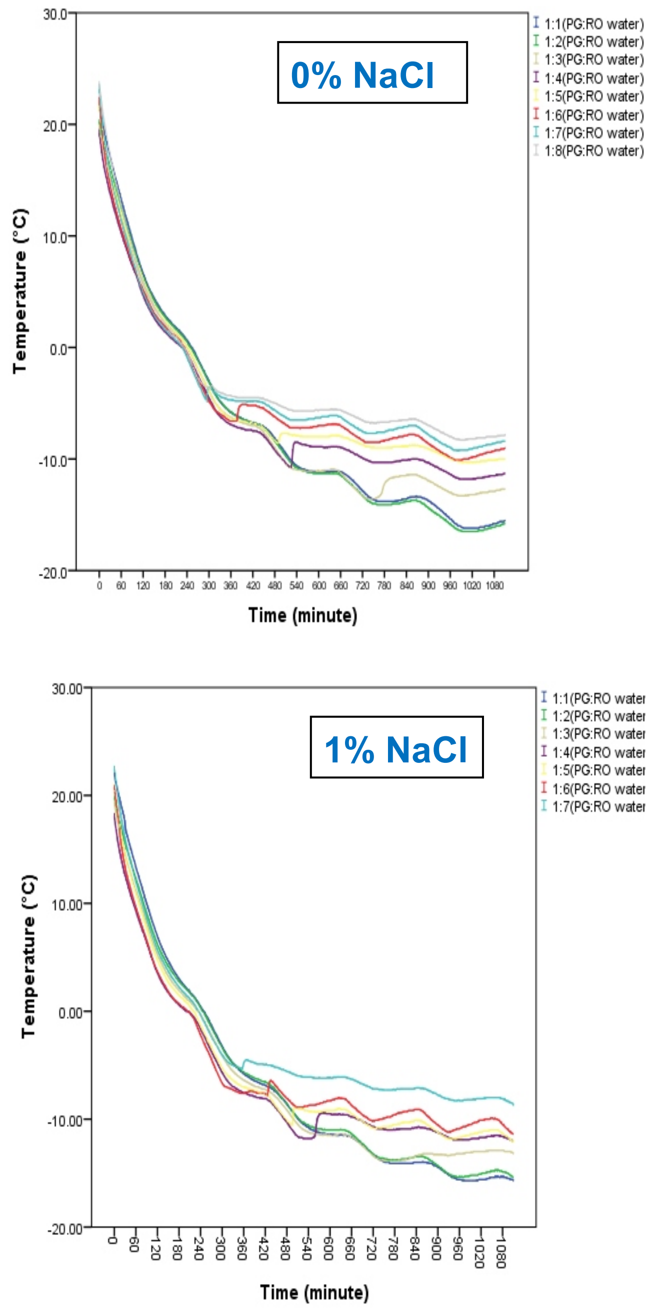

Fig. 6: Cooling behavior of MCAFLs at different concentration of PG for ratio 1:1 to 1:8 (PG: RO water) with 0 and 1 % NaCl

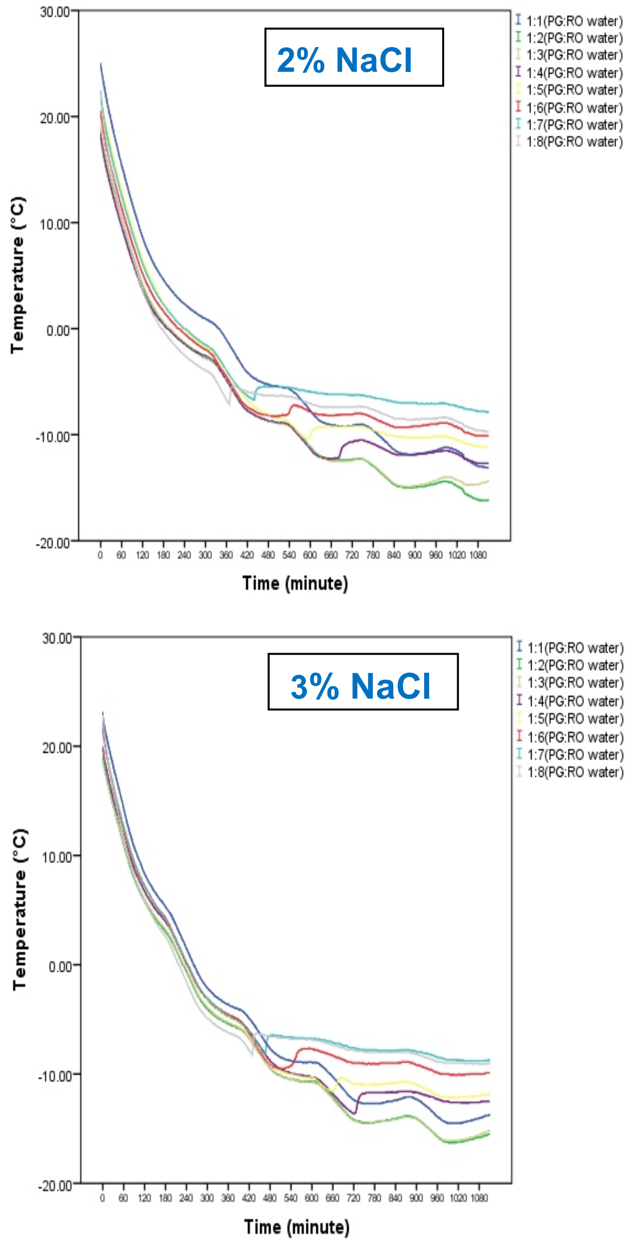

Fig. 7: Cooling behavior of MCAFLs at different concentration of PG for ratio 1:1 to 1:8 (PG: RO water) with 0 and 1 % NaCl

A phenomenon of super cooling was witnessed in all MCAFL solutions and can be easily observed as sudden rise in temperature before initiation of freezing process (Fig 6-8). The cooling curve's lowest temperature signifies the commencement of the growth of ice crystals (nucleation). This is followed by a temperature rises due to relies of latent heat of the phase change. After this temperature rise, the greatest temperature of the cooling curve is known as the freezing point which is associated with the growth of the ice crystals. The difference between the freezing point and the lowest temperature of the cooling curve is called as sub-cooling.

The deviation in the temperature profile plots of MCAFLs were more pronounced in the phase change zone. It can be attributed to freezing point depression (FPD) of different formulation of MCAFLs. Temperature fluctuations in this

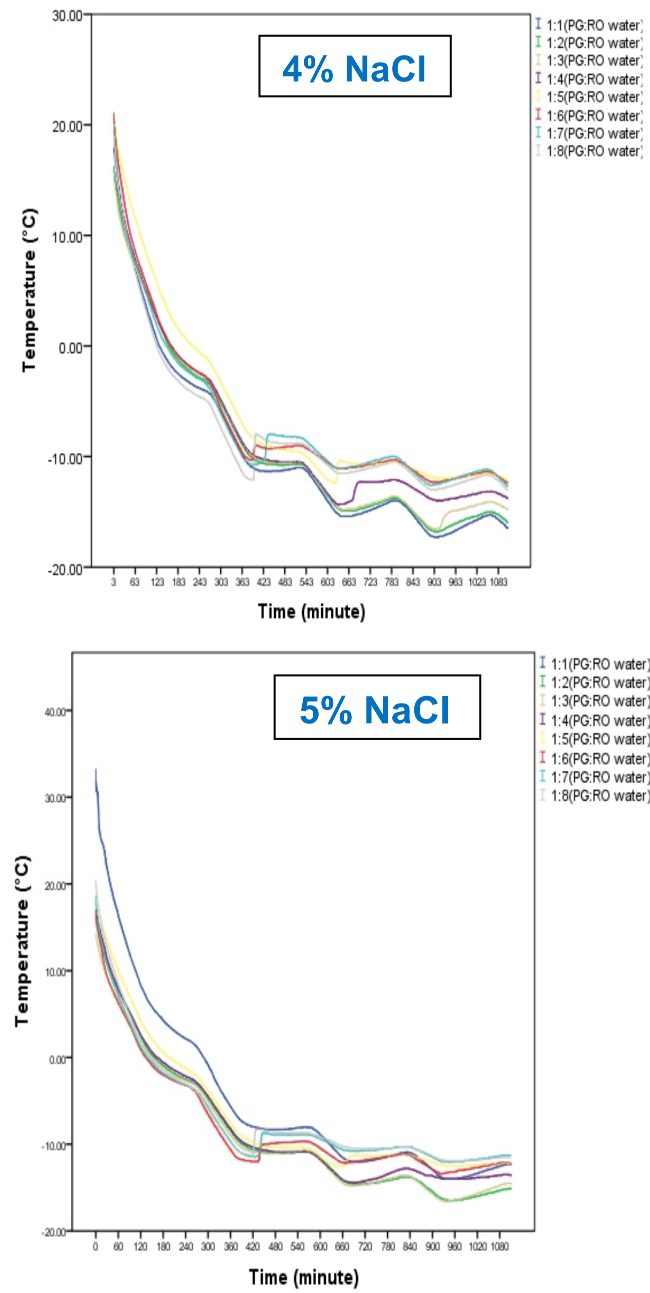

Fig. 8: Cooling behavior of MCAFLs at different concentration of PG for ratio 1:1 to 1:8 (PG: RO water) with 4 to 5% NaCl

region are primarily due to density changes near freezing temperature. The temperature of MCAFLs is dramatically decreased to below 0 °C without being solid because the molecules of antifreeze chemicals (PG and NaCl) in RO water have thermal motion which prevents molecules from crystallizing. As freezing of water proceeds concentration of the PG and NaCl in the remaining water phase gradually increases. Therefore, freezing of MCAFLs was not at a constant temperature rather than a freezing temperature range which is similar to the findings of Prakash *et al.* (2018b).

Effect of PG Concentration

Freezing point depression (FPD) was highest for blend ratio 1:1 (PG: RO water) with 5% NaCl MCAFL at -15.0 °C, while it was lowest (-5 °C) in case of ratio 1:8 (PG: RO water) with 0 % NaCl MCAFL. The difference in freezing point and super cooling temperature and degree of supercooling depends on the amount of solute and its properties (Mulawarman *et al.* 2018). It is observed from the Table 2-7 that at the initial cooling period, the rate of temperature drop of MCAFTs is higher at the higher concentration (1:1 and 1:2 (PG: RO water)) due to the lower specific heat and higher thermal conductivity of PG and NaCl as compared to water but at the time passes in the phase change process, it takes more time for freezing because of the higher amount of latent heat storage (Azmi *et al.* 2017). It was also observed that the MCAFL solutions with ratio 1:1 and 1:2 (PG: RO water) with a different concentration of NaCl did not freeze completely at –20 °C but it was in an ice slurry consistency even after 12 h of freezing. It may be due to the lower eutectic temperature of the mixture (Gupta and Ramachandran, 2018). Total freezing was observed in solutions with ratio 1:3 to 1:8.

Table 2: Temperature (°C) of MCAFLs at different concentration of PG for ratio 1:1 to 1:8 (PG: RO water) with 0% NaCl during freezing

Freezing time (h)	Propylene glycol: RO water							
	1:1	1:2	1:3	1:4	1:5	1:6	1:7	1:8
0	21.8	20.4	19.9	19.5	22.0	22.4	23.6	23.8
2	-12.8	-13.2	-13.2	-9.9	-8.7	-8.3	-7.5	-6.5
4	-16.5	-17.2	-14.4	-13.1	-11.8	-12.2	-11.8	-10.8
6	-16.8	-17.2	-17.3	-17.1	-17.0	-18.2	-18.5	-18.5
8	-17.0	-17.6	-18.3	-18.3	-18.5	-19.3	-19.3	-19.4
10	-17.5	-18.3	-19.1	-19.2	-19.2	-19.9	-19.8	-20.0
12	-17.4	-18.2	-18.7	-18.9	-18.8	-18.9	-18.8	-19.1

Table 3: Temperature (°C) of MCAFLs at different concentration of PG for ratio 1:1 to 1:8 (PG: RO water) with 1% NaCl during freezing

Freezing time (h)	Propylene glycol: RO water							
	1:1	1:2	1:3	1:4	1:5	1:6	1:7	1:8
0	22.3	19.9	19.5	18.3	21.0	20.9	22.7	21.0
2	-13.3	-13.2	-13.4	-10.7	-10.8	-10.1	-7.2	-7.1
4	-17.6	-17.3	-14.4	-13.8	-13.8	-13.2	-10.8	-10.7
6	-17.6	-17.3	-15.9	-15.8	-15.7	-15.5	-15.0	-15.1
8	-18.1	-18.0	-17.4	-17.7	-18.0	-18.0	-18.0	-18.0
10	-17.9	-17.5	-18.0	-18.2	-18.2	-18.0	-18.3	-18.2
12	-17.8	-17.7	-18.3	-18.7	-19.4	-19.5	-18.9	-18.7

Effect of NaCl Concentration

From the cooling curve of MCAFLs different NaCl concentration (0 to 5%) resulted in distinct super cooling and freezing temperature range (Fig. 6-8). Eutectic salt-water solutions frequently experience problem of supercooling due to which it does not quickly solidify when cooled below the freezing point. The nucleation process is accelerated by the

Table 4: Temperature (°C) of MCAFLs at different concentration of PG for ratio 1:1 to 1:8 (PG: RO water) with 2% NaCl during freezing

Freezing time (h)	Propylene glycol: RO water							
	1:1	1:2	1:3	1:4	1:5	1:6	1:7	1:8
0	25.0	19.0	19.1	18.3	22.2	20.5	22.4	22.0
2	-9.2	-12.3	-12.4	-10.7	-9.2	-8.1	-6.2	-7.4
4	-12.8	-15.9	-14.1	-12.9	-11.9	-10.5	-8.9	-10.6
6	-13.8	-16.9	-15.6	-14.9	-14.3	-13.4	-12.8	-14.4
8	-14.7	-18.0	-17.2	-17.2	-17.1	-17.1	-16.7	-18.2
10	-14.1	-17.7	-17.7	-17.6	-18.0	-17.9	-18.0	-18.4
12	-15.3	-18.8	-18.7	-19.0	-19.4	-19.6	-19.3	-20.0

Table 5: Temperature (°C) of MCAFLs at different concentration of PG for ratio 1:1 to 1:8 (PG: RO water) with 3% NaCl during freezing

Freezing time (h)	Propylene glycol: RO water							
	1:1	1:2	1:3	1:4	1:5	1:6	1:7	1:8
0	23.1	19.1	19.4	19.9	22.1	21.7	22.6	22.7
1	-3.6	-5.4	-5.2	-4.6	-4.7	-4.5	-4.6	-6.2
2	-7.5	-9.4	-9.3	-8.7	-9.1	-9.1	-6.5	-6.5
3	-14.1	-15.8	-15.6	-12.6	-12.0	-10.0	-8.8	-9.0
4	-15.5	-17.4	-16.0	-13.8	-13.7	-11.7	-10.5	-11.2
5	-14.7	-16.7	-15.5	-14.3	-14.0	-12.5	-11.7	-12.7
6	-14.8	-16.9	-15.9	-14.9	-14.7	-13.4	-12.8	-14.0
7	-15.6	-17.6	-16.7	-16.0	-16.0	-15.1	-14.8	-16.0
8	-16.0	-18.2	-17.5	-16.9	-17.3	-16.6	-16.4	-17.5
9	-15.0	-17.3	-17.0	-17.0	-17.0	-16.7	-16.8	-17.6

Table 6: Temperature (°C) of MCAFLs at different concentration of PG for ratio 1:1 to 1:8 (PG: RO water) with 3% NaCl during freezing

Freezing time (h)	Propylene glycol: RO water							
	1:1	1:2	1:3	1:4	1:5	1:6	1:7	1:8
0	16.8	16.4	15.9	18.5	21.2	21.4	20.5	19.5
2	-14.9	-14.5	-14.3	-12.3	-10.7	-10.7	-10.5	-11.0
4	-18.5	-17.8	-16.4	-15.4	-13.9	-14.9	-15.0	-15.5
6	-16.4	-16.5	-16.2	-15.8	-15.3	-15.5	-15.5	-15.9
8	-18.3	-18.2	-18.1	-18.0	-17.8	-18.3	-18.5	-18.8
10	-18.3	-18.3	-18.4	-18.5	-18.6	-19.0	-19.4	-19.4
12	-17.1	-17.55	-18.0	-18.1	-18.3	-18.1	-17.9	-18.0

Table 7: Temperature (°C) of MCAFLs at different concentration of PG for ratio 1:1 to 1:8 (PG: RO water) with 5% NaCl during freezing

Freezing time (h)	Propylene glycol: RO water							
	1:1	1:2	1:3	1:4	1:5	1:6	1:7	1:8
0	33.2	16.1	14.3	17.0	19.3	16.8	18.6	20.4
2	-12.0	-14.6	-14.6	-14.2	-11.3	-11.8	-10.7	-10.5
4	-13.1	-15.8	-14.9	-14.3	-13.3	-13.2	-12.5	-12.9
6	-15.1	-17.5	-16.8	-16.4	-16.0	-16.5	-16.0	-16.5
8	-15.7	-18.0	-17.8	-17.6	-17.6	-18.6	-17.8	-18.4
10	-14.0	-16.9	-16.9	-17.6	-17.6	-17.3	-17.1	-17.8
12	-16.0	-18.4	-18.4	-18.7	-18.8	-19.2	-18.7	-19.3

addition of solute, which encourages heterogeneous nucleation. Addition of solute has a significant impact on faster nucleation and lowering of freezing point (Li *et al.* 2023). NaCl acts as a nucleating agent which reduces super cooling time and initiate early freezing. At 5% NaCl concentration, the rate of freezing was slow and consumed more time as compared to lower salt concentration solutions. It could be due to higher latent heat storage and freezing point depression (Rokhim and Fitri, 2023). NaCl is cheap and easily available as compared to other antifreeze chemical which makes it an easy choice for used in coolant formulations.

pH of MCAFLs

The pH data for the MCAFLs is shown in Fig. 9. At 99% confidence level, the pH was significantly altered (p-value<0.01). The MCAFLs' pH was significantly impacted by the concentrations of PG and NaCl. The figure shows that the pH of the MCPCCs increased as the glycol concentration dropped but it declined when the salt concentration increased. At 0% NaCl concentration in MCAFLs, the pH is in the range of 6.7 to 7.3 and at 5% NaCl concentration it is lowest in the range of 5.8 to 7.1. Glycol solution releases acids when there is still residual air present, which lowers pH and promotes corrosion. Rust forms on the surface of ferrous metal and creates corrosion problems when the pH of the ternary mixture drops below 7. In order to reduce the amount of acid that is formed when glycol oxidizes, passivating and buffering corrosion inhibitor solutions are added to glycol solutions. Suitable blends of corrosion inhibitors like buffer system or NaOH mixed with the glycol-water mixture to inhibit corrosion problems. A pH of 9.0 to 9.5 is seen in most concentrated inhibited glycol solutions, whereas a pH of less than 7.0 indicates glycol oxidation.

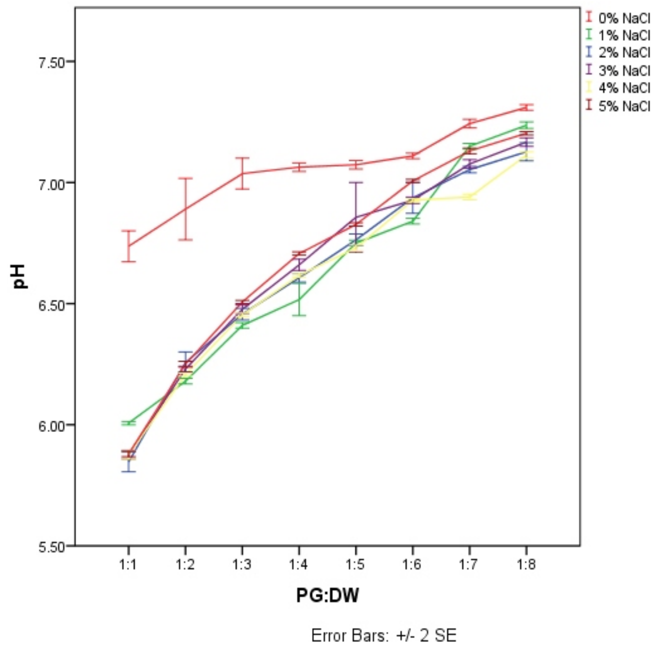

Fig. 9: pH of MCAFLs

CONCLUSION

Cooling behavior of MCAFLs was determined and compared experimentally at different levels of PG and NaCl. Both the components PG and NaCl showed synergetic effect in improving the cooling characteristics. The developed formulation can effectively reduce degree of supercooling, lower the freezing point and enhance cold thermal energy storage. The rate of temperature decrease is higher at the higher PG and NaCl concentration due to lower specific heat and higher thermal conductivity as compared to water. The cooling characteristics data will help to formulate suitable secondary coolant for application in food and dairy processing industry.

CONFLICT OF INTEREST

The authors of this study have no competing interests to declare.

ACKNOWLEDGEMENT

The study was funded by ICAR-National Dairy Research Institute, Karnal under the IRC Project E-44: Development of low-cost farm milk cooling system. All the infrastructural support from ICAR-NDRI, Karnal acknowledged here.

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Citation:

Rohit H K, Chitrnayak, Minz P S, Dabas J k and Ray A. 2023. Characterization of Multi-Component Antifreeze Liquids for Sub-zero Cooling Applications. *Journal of AgriSearch* **10**(4):259-265