

**SIMULATION STUDIES ON THERMAL COOLING
DATA FOR DETERMINATION OF FREEZING
POINT**



**THESIS SUBMITTED TO THE
ICAR - NATIONAL DAIRY RESEARCH INSTITUTE
(DEEMED UNIVERSITY)
KARNAL (HARYANA)
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE AWARD OF THE DEGREE OF
MASTER OF TECHNOLOGY
IN
DAIRY ENGINEERING
BY
BHARATRAJ CHHIMPA
B.TECH. (DAIRY TECHNOLOGY)**

**DAIRY ENGINEERING DIVISION
ICAR - NATIONAL DAIRY RESEARCH INSTITUTE
KARNAL-132001 (HARYANA), INDIA**

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Approved by:

(*R. S. Saial*) 7/9/21
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Dr. P. S. Minz

Sr. Scientist (Dairy Engineering)

CERTIFICATE

This is to certify that the thesis entitled "**SIMULATION STUDIES ON THERMAL COOLING DATA FOR DETERMINATION OF FREEZING POINT**" submitted by **BHARATRAJ CHHIMPA** in partial fulfillment of the requirement for award of the degree of **MASTER OF TECHNOLOGY IN DAIRY ENGINEERING** of the National Dairy Research Institute (Deemed University), Karnal (Haryana) is a bonafide research work carried out by him under my supervision and guidance and no part of the thesis has been submitted for any other degree or diploma.

Date: 9/9/2021

(Dr. P. S. Minz)
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**DEDICATED TO
MY BELOVED
FAMILY,
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MY IDOLIZED GUIDE**

ACKNOWLEDGEMENT

First and foremost, I bow my head to thank the Lord for having bestowed me with all what I needed and showing me the right path at life's cross roads. I express my humble gratitude to my father and my mother for their innumerable sacrifices and support to bring me to this stage of scientific pursuit.

*It was a great pleasure to carry out my research work under the guidance of **Dr. P. S. Minz** (Senior Scale Scientist, Dairy Engineering Division). In his unique way, he provided me with valuable and inspiring guidance, constructive criticism and suggestions throughout the process of this research work. I admire his expertise in planning the projects and immense ability of reasoning and appreciate his perseverance in tackling research problems. He understood me thoroughly and has been very kind to me throughout the period I worked with him and I have greatly benefited from his knowledge and experience.*

*I also express my heartiest gratefulness **Dr. Amita D. Vairat** (Scientist, Dairy Engineering Division) who has contributed all the time to the development of the research work and taught me the essence of the research lies on efforts we put and the process we undergo while conducting research, a thought applicable in research and life. A lifetime lessons were achieved during this period in areas of subject knowledge, technical expertise, to extend the tries up to failures, time management, planning etc. A teacher who treated me like her child and proved as an ideal guru who never ordered but, always students learn from her the way of doing things, a guru who teaches in silence.*

*I am feeling dearth of words to express my best regards and deep sense of gratitude to members of advisory committee members **Dr. Chitranayak** (Senior Scientist, DE Division), **Dr. Amita D. Vairat** (Scientist, DE*

Division), **Dr. Vivek Sharma** (Principal Scientist, Dairy Chemistry Division) and **Dr. P. N. Raju** (Sr. Scientist, Dairy Technology). I am also grateful to other faculty members of the division **Er. Kushboo Kumari** (Scientist, DE Division), **Er. Ankit Deep** (Scientist, DE), **Er. J. K. Dabas** (Technical Officer), **Er. Manju Bala** (Technical Officer), **Er. S. K. Choudhary** (Chief Technical Officer) and **Er. Sunil Kumar** (Assistant Chief Technical Officer) for their guidance. They deserve special thanks and appreciation for their timely help and co-operation.

I am thankful to my senior **Mr. Rohit Hiteshkumar Kalidas** who conducted his research sincerely and generated useful data for me along with his research work. It could be more difficult for me to conduct all such trails within a short period of time due to COVID pandemic but, Rohit sir provided his own raw data for my research work.

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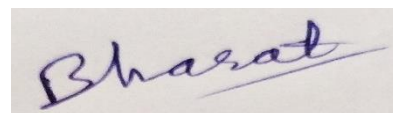
Profound thanks are due to my lab-mate **Sumit Mehta**, classmates **Vinay Kumar**, **Ajith Kumar L.**, **Shubham Kawale** and **Shubham Bhotmange** for their wonderful company throughout my stay at N.D.R.I. I am grateful to my seniors **Mr. Rohit Hiteshkumar Kalidas**, **Mr. Prem Jaishwal**, **Mr. Pawan Mahadik**, **Mr. Vivekanand Sukre**, **Mr. Amit**

Juneja, Mr Bhavesh Chauhan, Ms. Pooja Bhagat, Mr. Sharan Kumar, Mr. Abhinash, Ms. Nagaratna and Ms. Banshree Naskar who have shown the right path to be followed. I would also like to thankfully remember all the teachers, friends, seniors and juniors of NDRI, Karnal.

I also express my sincere thanks specially to **Dr. Tanmay Hazra**, Assistant professor at College of Dairy Science, Amreli who gave moral support and specific guidance during my graduation and post-graduation time. I would like to thank my respected teachers, seniors, classmates and juniors of College of Dairy Science, Amreli who took care of me during graduation degree program and enhance my knowledge and skills. I show love from depth of my heart for my beloved best friend **Mr. Rajeev Pandit** who motivated me during my graduation and post-graduation degree.

Where emotions are involved, words cease to having meaning but only feeling in paying my most heartfelt gratitude to my grandma **Late Asha Devi**, my elder sister **Rakhi** and my younger brother **Shatrughan** who gave me moral support in bringing me up to this stage. Without their affection, love, moral support and blessing, I would not be what I am today.

Financial assistance received in the form of institutional research fellowship by NDRI is gratefully acknowledged. Finally, I thank all those who helped me in my research either directly or indirectly.

A handwritten signature in blue ink, appearing to read 'Bharat', with a horizontal line underneath it.

(BHARATRAJ CHHIMPA)

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सारांश

हिमांक बिंदु के निर्धारण के लिए उष्मीय शीतलन आँकड़ों पर अनुकरण अध्ययन

दुनिया में पिछली कई शताब्दियों से औद्योगिक प्रक्रियाओं और घरेलू कार्यों में खाद्य पदार्थों को ठंडा करना और जमाना एक आम बात है। जैसे-जैसे प्रौद्योगिकियां विकसित हुईं, खाद्य उद्योग के साथ-साथ अन्य उद्योग अधिक से अधिक फले-फूले। कई प्रक्रियाओं में से जमाने की प्रक्रिया का उपयोग, उत्पाद बनाने, भंडारण, खाद्य उत्पादों के आत्म-जीवन को बढ़ाने, गुणवत्ता में सुधार करने के लिए बहुत बार किया जाता है। पदार्थ को ठंडा या जमाने के लिए, एक शीतलन माध्यम की आवश्यकता होती है, जो सामग्री के आवश्यक तापमान से कम तापमान पर बनाए रखा जाता है। एसजेडटीएल (उप-शून्य तापमान द्रव) उन सामग्रियों में से एक है जिसका उपयोग शीतलन माध्यम के रूप में किया जाता है, इसलिए इन तरल पदार्थों के हिमांक बिंदु को पता करना आवश्यक है। किसी भी मिश्रणों के हिमांक बिंदु (एफ. पी.) को पता करने के लिए कई तरीके उपलब्ध हैं लेकिन वे या तो महंगे हैं या समय लेने वाले हैं या तरल के नमूने की आवश्यकता पड़ती है। इस कार्य को करने के लिए अनुकरण विधि सबसे उपयुक्त और नवीन विधि है। इस शोध कार्य में, अनुकरण पद्धति का उपयोग करके ईजी-एसजेडटीएल और पीजी-एसजेडटीएल के मिश्रणों के एफ.पी. पता किए गए थे। उष्मीय शीतलन आँकड़ों को पिछले अध्ययन से एकत्र किया गया और “साइलैब” सॉफ्टवेयर में एक उपयुक्त अनुकरण प्रोग्राम लिखा गया था। ई.जी. और पी.जी. मिश्रणों का उपयोग किया गया था जिनकी सांद्रता 1:1 से 1:8 (ई.जी./पी.जी. : डी.डब्ल्यू.) में भिन्न थी, जिसमें NaCl की अलग-अलग सांद्रता एसजेडटीएल में 0% से 5% तक बदल रही थी। इन सभी मिश्रणों की शीतलन दर (सी.आर.) भी अनुकरण तकनीक द्वारा निर्धारित की गई थी। प्रारंभ में ई.जी. और पी.जी. एसजेडटीएल के सी.आर. बड़े तापमान प्रवणता के कारण उच्च थे और फिर स्थिर मूल्य तक घट गए। लगभग स्थिर सी.आर. बनने के लिए ई.जी. मिश्रणों ने औसतन 80–90 मिनट लिए, जहां पी.जी. के अधिकांश मिश्रणों ने औसतन 100 मिनट लिए। मिश्रणों के लिए निरंतर सी.आर. 0.2 डिग्री सेल्सियस/मिनट से कम थे। अनुकरण परिणामों के आधार पर तैयार किए गए मिश्रणों के तापमान रुपरेखा के अनुसार, ई.जी. मिश्रणों द्वारा उनके एफपी को प्राप्त करने के लिए औसतन 90–110 मिनट लिए गए थे और कुछ मामलों को छोड़कर पी.जी. मिश्रणों के द्वारा अपने हिमांक बिंदु को प्राप्त करने के लिए औसतन 210–230 मिनट लिए गए थे। ई.जी.-एसजेडटीएल (0% से 4% NaCl) के हिमांक बिंदु -14.63°C से -8.27°C के बीच में पाए गए, जो उन मूल्यों के करीब थे जो पिछले अध्ययन में निर्धारित किए गए थे। मिश्रणों में NaCl और ई.जी. की बढ़ती सांद्रता के कारण हिमांक बिंदु अवनमन देखा गया। 5% NaCl ई.जी. मिश्रणों और सभी पी.जी. मिश्रणों (0% से 5% NaCl) के हिमांक बिंदु -3.3°C से 4.23°C के बीच में थे जो उन मूल्यों से बड़े अंतर पर पाए गए जिन्हें हितेश, (2020) द्वारा पिछले अध्ययन में मापा गया था। अनुकरण पद्धति के परिणामों में भिन्नता उष्मीय शीतलन आँकड़ों की अपर्याप्तता के कारण थी। इन मामलों में, पी.जी. एवं NaCl की सांद्रता के बदलने का प्रभाव नहीं देखा गया।

ABSTRACT

SIMULATION STUDIES ON THERMAL COOLING DATA FOR DETERMINATION OF FREEZING POINT

Cooling and freezing of food materials are a common practice in industrial processes and household works for last many centuries in the world. As technologies were developed, industries were flourished more and more along with food industry. Out of many processes, freezing process is used very frequently for making products, storage, increase the self-life of food products, improves quality & preserves nutrient value etc. To cool or freeze the substance, a cooling medium is required which is maintained at lower temperature than the required temperature of material. SZTL is one of the materials which is used as cooling medium, so it is necessary to determine the freezing point of these liquids. Number of methods are available to determine the FP of any solutions but they are either costly or time consuming or require the sample of liquid. Simulation method is the most appropriate and novel method to do this job. In this research work, FPs of the solutions EG-SZTLs & PG-SZTLs were determined by using simulation method. Thermal cooling data were collected from previous study and a suitable simulation program was written in "Scilab" software. EG and PG solutions were used whose concentrations were varying from 1:1 to 1:8 (EG/PG : DW) with different concentration of NaCl changing from 0 % to 5 % in SZTLs. Cooling rate (CR) of these all blends was also determined by simulation technique. Initially the CRs of EG & PG SZTLs were high due to large temperature gradient and then decreased to a constant value. For EG solutions, it took avg. 80-90 min. to become almost constant CR where for PG solutions, it took avg. 100 min. Constant CRs of most of the solutions were below 0.2 °C/min. According to the temperature profiles of solutions which were drawn on the basis of the simulation results, avg. 90-110 min. were taken by the EG solutions to achieve their FPs and avg. 210-230 min. were taken by the PG solutions to achieve their FPs except some cases. FPs of the EG-SZTLs (0 % to 4 % NaCl) were determined between -14.63 °C to -8.27 °C which were close to those values which were determined in the previous study. FPD was observed due to the increasing concentration of NaCl and EG in the solutions. FPs of 5 % NaCl EG solutions and all PG solutions (0 % to 5 % NaCl) were ranging from -3.3 °C to 4.23 °C which were found at large differences from those values which were measured in the previous study by Hitesh, (2020). Variation in the results of simulation method was due to the insufficiency of thermal cooling data. Effect of the changing conc. of PG & NaCl was not observed in these cases.

LIST OF ABBREVIATIONS

ACR	=	Average Cooling Rate
Avg	=	Average
CCM	=	Cooling Curve Method
CSZTLs	=	Composite subzero temperature liquids
CR	=	Cooling Rate
CSV	=	Comma Separated Value
DE	=	Dairy Engineering
DSC	=	Differential Scanning Calorimetry
DMTA	=	Dynamic Mechanical Thermo Analysis
DTA	=	Differential Thermal Analysis
DW	=	Distilled water
EG	=	Ethylene Glycol
FPD	=	Freezing Point Depression
FP	=	Freezing point
Fig	=	Figure
ICAR	=	Indian Council of Agricultural Research
LHTES	=	Latent Heat Thermal Energy Storage
MCR	=	Maximum Cooling Rate
Min.	=	Minute
Max	=	Maximum
Mini	=	Minimum
NFs	=	Nano Fluids
NPT	=	Normal Pressure & Temperature
NVT	=	Normal Volume & Temperature
NDRI	=	National Dairy Research Institute

PEG	=	Poly Ethylene Glycol
PG	=	Propylene Glycol
PCM	=	Phase change material
RO	=	Reverse Osmosis
SM	=	Simulation Method
SPSS	=	Statistical Package for the Social Sciences
SD	=	Standard Deviation
SCP	=	Super Cooling Point
SZTLs	=	Subzero temperature liquids
TP	=	Temperature Profile
UNIQUAC	=	Universal Quasi-Chemical
VPO	=	Vapour Pressure Osmometry

LIST OF NOTATIONS

$^{\circ}\text{C}$	=	Degree Celsius
$^{\circ}\text{K}$	=	Degree Kelvin
R11	=	1 : 1 (EG/PG : water)
R12	=	1 : 2 (EG/PG : water)
R13	=	1 : 3 (EG/PG : water)
R14	=	1 : 4 (EG/PG : water)
R15	=	1 : 5 (EG/PG : water)
R16	=	1 : 6 (EG/PG : water)
R17	=	1 : 7 (EG/PG : water)
R18	=	1 : 8 (EG/PG : water)
g	=	Gram
Cm	=	Centimetre
ml	=	millilitre
mm	=	millimetre
%	=	percent
PT	=	Platinum
kg	=	Kilogram
KJ	=	Kilo joule
nm	=	nanometre
$\beta\text{-SiC}$	=	Beta- Silicon Carbide
θ	=	Theta (angle)
NaCl	=	Sodium Chloride
F(x)	=	Function
T	=	Temperature
t	=	time
$^{\circ}\text{C/min.}$	=	Cooling Rate

Al_2O_3	=	Aluminium Oxide
CuO	=	Cupric Oxide
λ	=	Lambda
$\text{W.m}^{-1}.\text{K}^{-1}$	=	Watt per meter. Kelvin
R	=	Universal gas constant
C_p	=	Specific heat, $\text{kJ/kg } ^\circ\text{K}$
a_w	=	Water Activity
π	=	Osmotic Pressure
$\text{Btu/ hr.ft. } ^\circ\text{F}$	=	British thermal unit/ (hour. Foot. Degree Fahrenheit)
$\text{Kcal/kg}^\circ\text{C}$	=	Kilocalorie per kilogram degree Celsius
$\text{BTU/lb. } ^\circ\text{F}$	=	British thermal unit/ Pound. Degree Fahrenheit
dq/dt	=	Heat difference/ Sec.
H	=	Enthalpy
W	=	Watt

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CHAPTER - 1

INTRODUCTION

1. INTRODUCTION

A well-known process freezing is being used since as early as 1000 B.C. It is widely used in dairy and food industries as well as in some other kind of industries also. It is a process to bring down the temperature of a solution or particular material below its freezing point (FP). Freezing method is used to manufacture products, preservation or safety purpose. In dairy and food industry, the quality of food directly depends on the freezing rate, method of freezing and temperature fluctuation during storage. Crystal size depends on the rate of freezing. Size of crystal becomes smaller and more in numbers when rate of freezing is high but if freezing rate is slow then crystal size becomes larger and less in number. The freezing rate and temperature change are affected by the flow rate of the chilling medium, the physical dimensions and form of the product, and the thermal properties of the food. Freezing is used to safeguard and extend the life of items while causing minimal damage to nutritional contents and physical properties. It slows the growth of microorganisms and retards the chemical reactions like enzyme-catalyzed oxidative browning or oxidation, chemical changes that cause color degradation, moisture loss, postharvest and postslaughter metabolic activities of plant and animal tissues (Augusto et al., 2018).

Freezing point is defined as the temperature where the vapor pressure of the liquid phase and the solid phase becomes identical. It depends on the type of solvent and number of moles of solute. Freezing point of only solvent is always higher than its solution. When solute is added into the solvent, its consequence is lowering the FP of the solvent. It's known as freezing point depression (FPD). The freezing point drops during the freezing process because as water freezes further, it continuously increases the concentration of the residual solution due to solute particle motions in the liquid. The extent of this depression can be obtained from thermodynamic relationships based on equilibrium between the states of the system (Kasiviswanathan et al., 2019). FPD is a colligative property which means the depression in freezing point depends on the number of moles of solute but not the type of solute.

In present scenario, there are so many methods to calculate the freezing point with high accuracy. Methods like Differential scanning calorimetry (DSC),

cryoscope, Osmometer etc. are well known and the most effective instruments which are used for freezing point determination. All these instruments are highly sophisticated and costly. Because of this, it is not commonly used by all kind of users.

Cooling curve is also a method of freezing point determination which is being used for so many years. This curve is plotted between time and temperature of measuring samples. It shows different kind of processes like cooling, supercooling, formation of ice nuclei, crystallization, and solute freezing during freezing of food. Many instruments use this curve directly or indirectly. Its shape changes with the change in cooling rate. This method of FP determination is very cheap and simple.

It is not possible every time to conduct experiments and get suitable result. Sometimes it may be costly, time consuming, impractical or hazardous to attempt all possible combinations of experiment. Simulation is one of the solutions to avoid all these disadvantages. Now-a-days, it is the most effective and novel technique in the field of optimizing, engineering and testing. It gives the best result for a particular type of situation. It is a low-cost, time-saving, and risk-free solution. It is feasible to determine the freezing point using a simulation study. By using proper algorithm in simulation program, thermal properties of sample can be determined, where thermal cooling data are used as primary input variables.

The instrument and equipment required for measuring freezing point are expensive and in few cases higher operational cost is involved. Another method is to manually plot graph of temperature verses time and determine point of intersection. The plot can then be used to determine the freezing point. The procedure is time demanding, has a higher risk of inaccuracy, and necessitates expert curve fitting skills. The simulation tool will aid in the determination of the freezing point quickly. It will save the cost of process due to simulation technique. This research work was undertaken with following objectives:

1. Development of simulation program for determination of freezing point.
2. Determination of freezing point of various subzero cooling liquid complex.

REVIEW OF LITERATURE

2. REVIEW OF LITERATURE

A comprehensive review of literature is explained here for better understanding of various topics like freezing point, freezing point depression, methods for determination of freezing point, factors affecting freezing point and cooling rate of solution, cooling curve, differential scanning calorimeter and simulation studies.

2.1 Freezing point

Freezing is one of the most effective ways to extend the shelf life of food. There are a variety of food preservation procedures available, but freezing is a common and easy-to-use method for preserving food's original quality. Corporeal circumstances can affect the freezing of a material and this effect can be seen under the freezing temperature.

Freezing has three phases, first is the cooling of the item to its FP (precooling or chilling stage). In this phase, just sensible heat is eliminated, and temperature is diminished to progress on ice crystallization of free water. 2nd phase is removing the latent heat of fusion (stage progress). This phase includes the ice formation from water due to the process of crystallization. Along these lines, it is the main point that decides the nature of the frozen item and freezing productivity. The last phase is the tempering phase in which cooling of the solid part take place (Kiani and Sun, 2011). Cooling curve or phase diagram can be used to show the different phenomenon which is happened during freezing process and these are e.g., supercooling, tempering, precooling, ice nucleation, freezing, glass transition points, and eutectic (Cheng et al., 2017).

Because of freezing, numerous physical, synthetic and microbiological variations happen in food items. These progressions can be seen at FP or beneath FP of food substance. The freezing of food basically implies the water solidification in food. These changes are unavoidably convoyed by the amount of dissolved solute materials. Due to the high concentration of solute, some reaction responses are significantly speed up during freezing.

Schwartzberg (1976) presented the idea of thawed water in which emphatically associates with food parts and doesn't freeze during freezing of food.

Freezing comprises of two sequential stages and that are nuclei formation and development of water crystal. Two systems work in these stages, first is homogeneous nucleation and second is heterogeneous nucleation. In homogeneous nucleation, nucleus have to cross the huge energy level to produce another surface for crystallization. In heterogeneous nucleation, a new ice nucleus is not formed but it develops on the pre-formed surface of crystal and it is more easy than homogeneous nucleation. Because various mechanisms occur during the freezing process in which ice nucleation active particles play a critical role, heterogeneous ice nucleation is preferred over homogeneous ice nucleation (Fletcher, 1970).

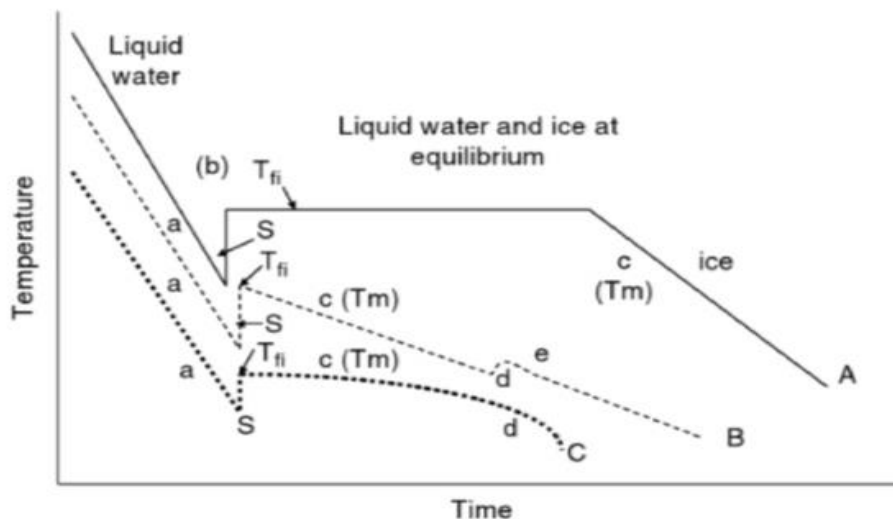


Fig. 2.1: Typical cooling curve. A: water, B: solution, C: foods, S: supercooling, a: ice crystallization temperature, b: initial freezing point, c: end of freezing, d: formation of first solute crystal, e: eutectic point

Due to supercooling or supersaturation, materials precipitate during crystallization which is a significant thermo-physical process in freezing. As referenced previously, this process comprises of two phases, i.e., nucleation and growth of crystal. The nucleation is characterized as the development of either newly formed crystal known as primary nucleation or development of

crystal on a previously formed crystal and that is known as secondary nucleation (Kiani and Sun, 2011).

Many chemical reactions are speed up during freezing of a food material or liquid solutions. The rate of oxidation of nitrile was improved by more than 105 times due to freezing (Takenaka et al., 1992). The rate of oxidation of ascorbic acid was accelerated significantly because of freezing. This oxidation was accomplished by hydrogen peroxide (Hatley et al., 1986). Between the temperature range from +30 to -9 °C, The reaction of alkaline hydrolysis was increased by 20 times for alkyl-4-hydroxybenzoate esters (Shija et al., 1992).

It is well acknowledged that water activity relates to freezing point. Founded on this relation a thermodynamic model was prepared. It was used to find out the freezing point of salty soil by seeing Gibbs energy. The experimental results of UNIQUAC (universal quasi-chemical) model describe that if the critical moisture content is lesser than the initial water content then freezing point is influenced by moisture content very less, but the FP decreases with decreasing the water content if the critical water content is higher than the initial water content (Ming et al., 2020).

2.2 Freezing Point Depression

Thermodynamically, the FPD means the reduction in the potential of a chemical solution contrasted with that of fluid water without salt in it. Decline in chemical potential decreases the freezing tendency of water and solution becomes stable. Balances. It decreases the freezing temperature of water. In the presence of solutes, solvent freeze at lower temperature than that of pure solvent and it gets lower and lower after rising the solute solution (Conde et al., 2018).

Solute concentration and the interaction between solvent & solute affect the depression in freezing point. FPD depends on the water content of substance, as it happens in the models inspected (Góral and Kluza, 2002).

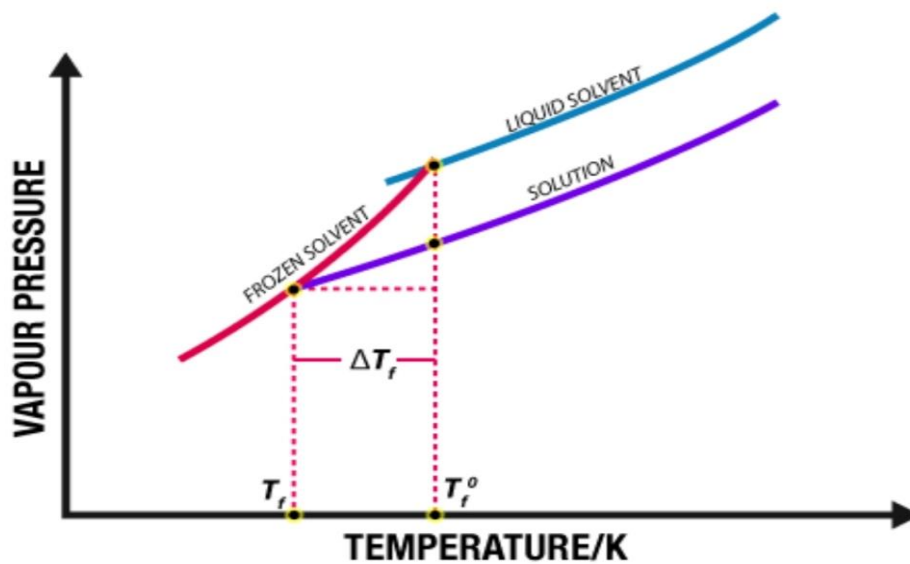


Fig. 2.2: Diagram of Freezing Point Depression

In a homogeneous solution, there are some major and minor elements. The solute part is a minor constituent, while the solvent is the main component. Physical properties of any solution are highly dependent on the major portion due to the big amount of solvent. Colligative properties are affected by the concentration of solute which is determined in moles of solute present in solution per kg of solvent and it is not depends on the nature of solute particles.

Cooling curve is also used for the determination of FPD of solution or food materials (fig. 2.3). In this figure, the FPD of solution is shown between the temperature relating to the C and C' points. Salt or solute particles are rejected from freezing portion to the aqueous or unfrozen portion of the solution during freezing process and remaining unfrozen portion becomes saturated consequently FP is depressed. This phenomenon called as brine rejection (Conde et al., 2018).

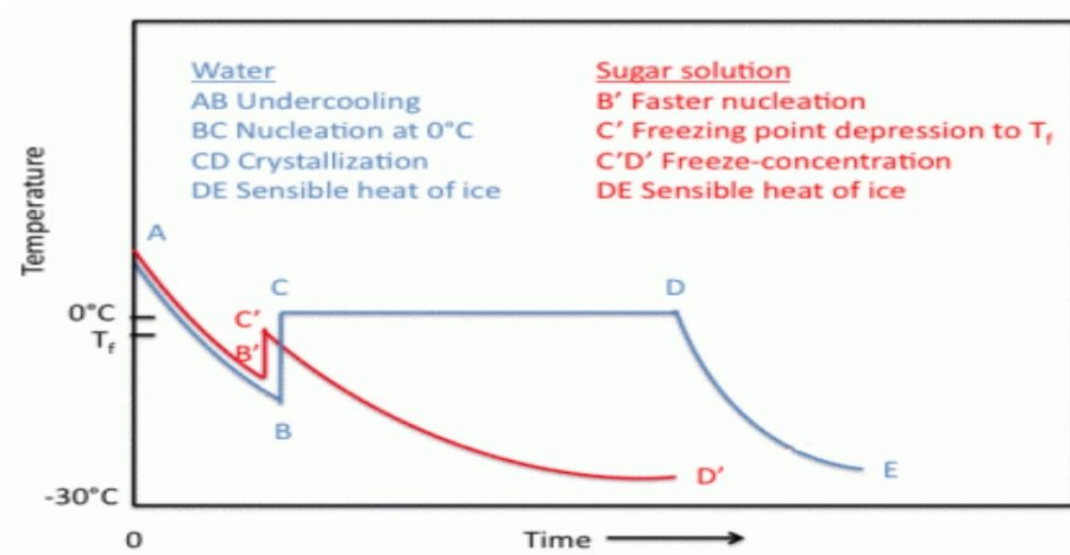


Fig. 2.3: Systematic diagram of cooling curve shows freezing point depression for sugar solution

Several expressions of freezing point laws are available in the literature (Lewis and Randall, 1961; Robinson and Stokes, 1959). On the basis on the Clausius-Clapeyron equation, all expressions have been formed which were based on the second law of thermodynamics with many specific presumptions. The estimated type of the Clausius-Clapeyron formula is given below:

$$\Delta T = \frac{-RTT_0}{\Delta H} \ln a_w$$

where $\Delta T = T_0 - T$, is the FPD, T_0 is the FP of pure solvent, T is the FP of solution, R is the constant of the ideal gas law, ΔH is the average molar heat of fusion between T_0 and T , and a_w is the water activity.

2.3 Methods for determination of freezing point

2.3.1 Cooling curve method

Cooling curve is a temperature-time profile which is used to determine many types of properties of any material like cooling, supercooling, freezing point, crystallization, eutectic point, or subcooling etc. It is very easy to use for measurement of all possible values. Many instruments work by using cooling

curve in its functions and give very accurate results. Now-a-days, many other kinds of sophisticated instruments are available in the market which can provide better result than this, but because of accurate result and convenient in use, it is still in practice of many researchers.

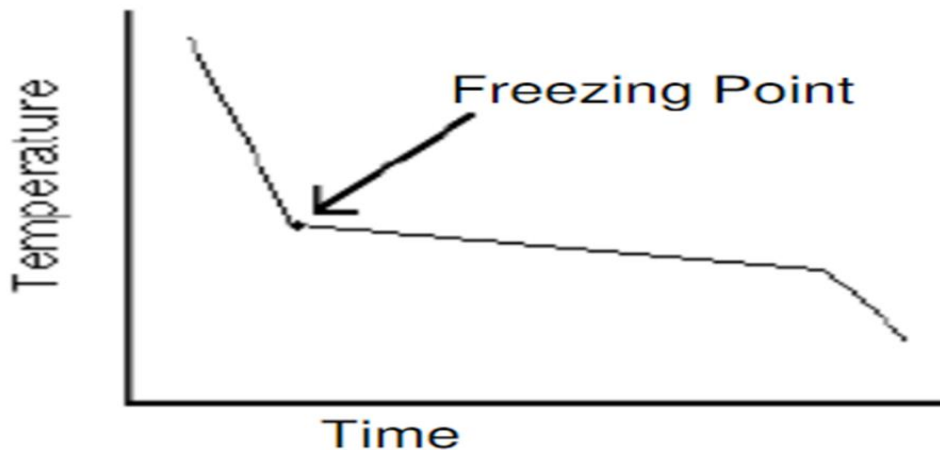


Fig. 2.4: Basic diagram of cooling curve

Cooling curve is a one of the cheapest methods to find out the FP of foods and can be performed by using a simple & conventional refrigerator available at houses. Marini et al. (2014) observed that FP doesn't depends on the freezing methods with different cooling rate because freezing point of the material is a thermal property.

2.3.2 Beckmann apparatus

A large value of supercooling ($>1^{\circ}\text{C}$) can be seen in the Beckmann FP method. It was realized that the supercooling ought not be higher than $0.3\text{--}0.5^{\circ}\text{C}$ otherwise the exact value of FP would be difficult to determine from Beckmann apparatus. It's difficult to keep supercooling within that temperature range by either rapidly mixing the framework or scraping the freezing tube's side wall. Supercooling point can be arrested by a rapid disorder of metastable equilibrium and resulting the shooting up of temperature. However, it can be affected by the additional crystals of the solvent (Karunakaran, 1978).

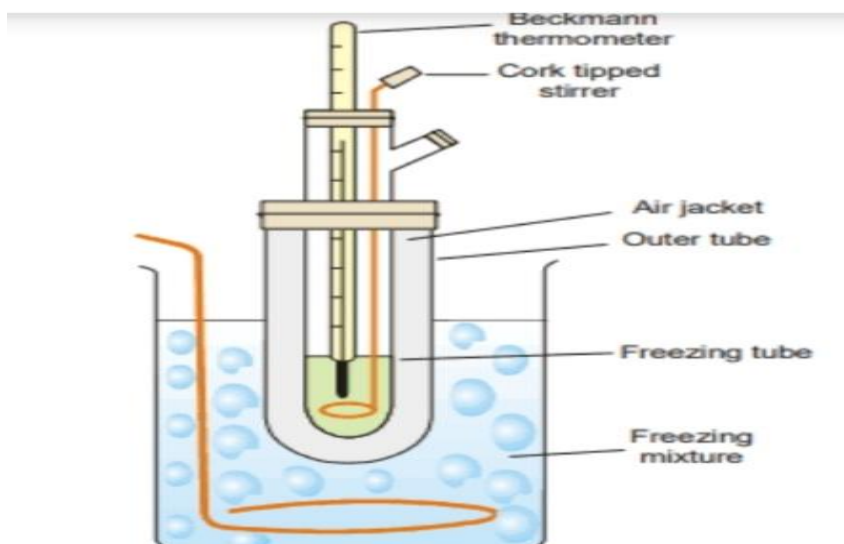


Fig. 2.5: Systematic diagram of Beckmann apparatus

Beckmann freezing set-up has a hole in which stirrer and Beckmann thermometer is inserted. A thin wire of nickel is also inserted in the semimicro tube to mix solvent. Freezing solution have a tube which is placed inside. The thin wire is quickly pulled out from that semimicro tube when supercooling is noticed. Supercooling is prevented expeditiously without changing the solution concentration by addition of small solvent crystals (Karunakaran, 1978).

2.3.3 Freezing Point Depression Osmometer

It is worked on the principle that the freezing point of a solution is related to the osmotic concentration of that solution. Toward the start of an estimation, a microchip-controlled Peltier component is used to cool the sample. During this cycle, the mixture is supercooled underneath 0°C while as yet being fluid. After achieving a specific temperature stirrer wire is rotated to initiate the freezing process. The development of ice crystal results the raising in sample temperature due to the liberation of thermal energy. After a certain time period, thawing & melting of ice crystal is balanced and equilibrium is achieved and temperature of sample becomes constant. The freezing point of sample is then marked on plateau.

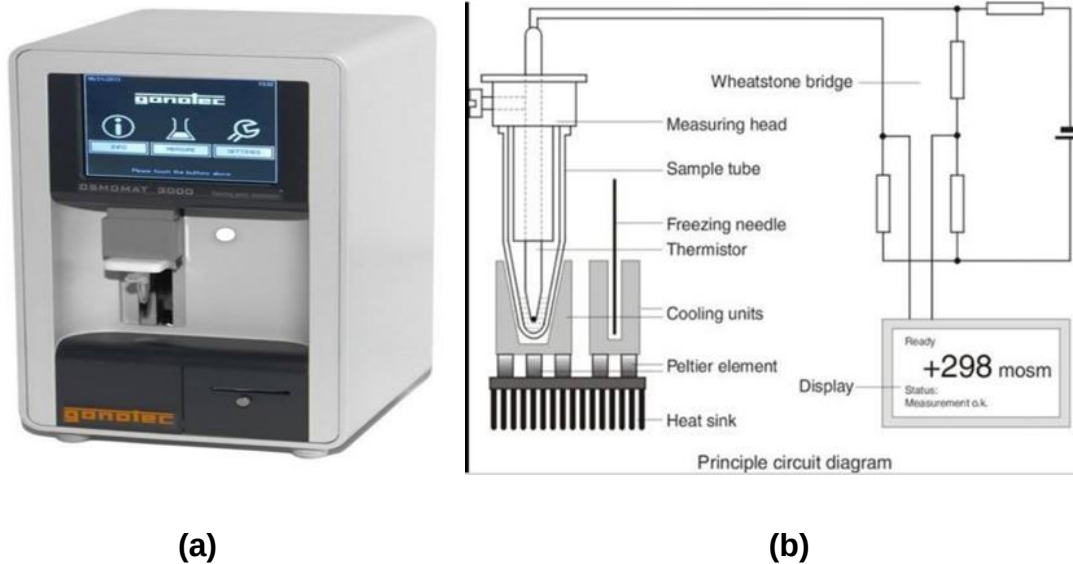


Fig. 2.6: Freezing Point Depression Osmometer with its principle circuit diagram

Most osmometers utilized these days depend on the principle of FP, electrical conductivity, & vapor pressure. For measuring the osmolarity, FPD is generally used. During an experiment, highly diluted standard sample showed a worse result. Acceptable performance was observed very close to the value of tear for the diluted solutions (Verdeal et al., 2015).

2.3.4 Vapor pressure Osmometer

It determines the concentration of osmotically active particles that reduce the vapour pressure of the solution. Its measurement is linked to a drop in the dew point of a pure solvent produced by a drop in the vapour pressure of the solvent caused by the solute. It is not recommended for clinical laboratories since it cannot accurately quantify volatile solutes.

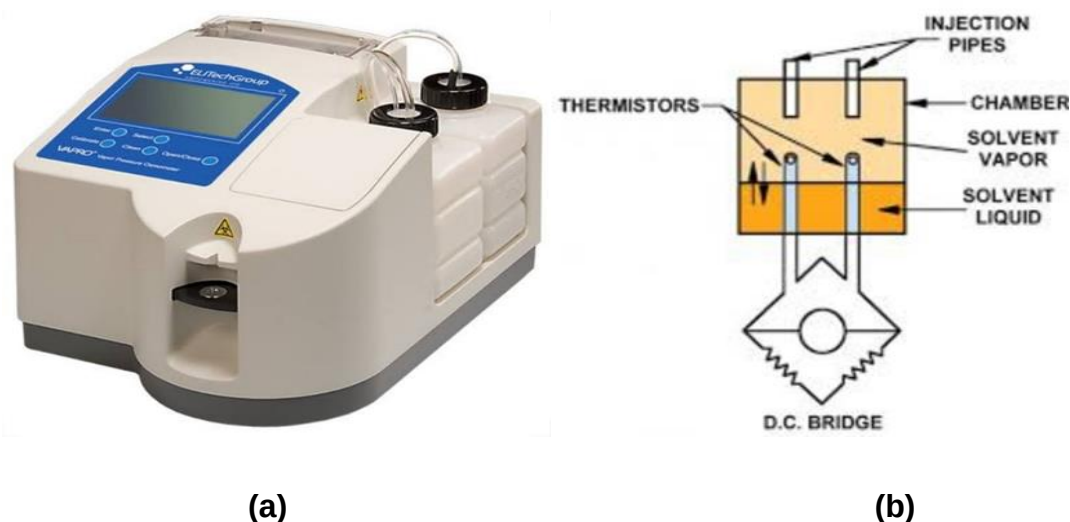


Fig. 2.7: Vapour pressure osmometer with its principle circuit diagram

Vapor Pressing Osmometry is used to determine the molecular weight of organic solvent and aqueous solution. It is also used for the determination of total osmolarity of the biological mixture. It also has the advantage of allowing the measurement of high viscosity and high osmolal concentration solutions (Belaustegi et al., 1991).

2.3.5 Membrane Osmometer

It measures the osmotic pressure of a solution separated by a semi-permeable membrane. This membrane separates two components, one filled with pure solvent and the other with a solution. The activity of the solvent in the two compartments is different. Based on this osmotic pressure, freezing point is calculated.

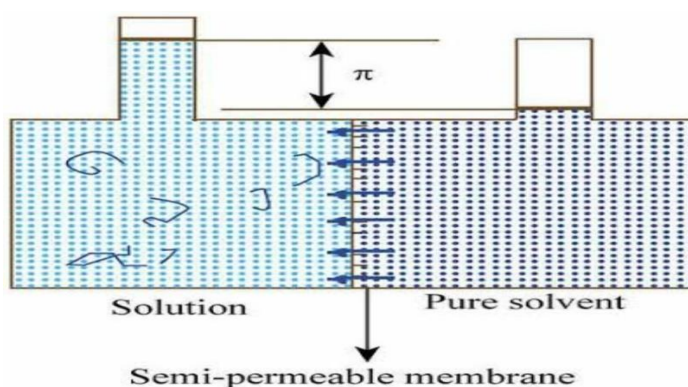


Fig. 2.8: Conceptual diagram of Membrane Osmometer

$$\Pi = -\frac{RT}{V_A} \ln \frac{P_A}{P_A^*} = -\frac{RT}{V_A} \ln a_A$$

(Nabetani et al., 1992)

Here, P_A = Vapour pressure of solvent in a solution (Pa)

P_A^* = Vapour pressure of pure solvent (Pa)

V_A = Partial molar volume of a solvent ($\text{m}^3 \cdot \text{mol}^{-1}$)

a_A = Activity of solvent

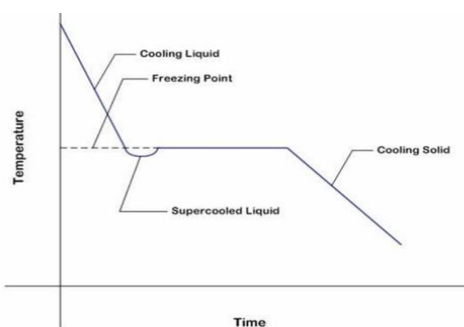
For direct measurement of osmotic pressure, many osmometers are being used but for more concentrated solutions, these are not suitable for pressure determination. Merson & Morgan explained an apparatus based on the reverse osmosis. This method is applicable to high-concentration solutions but requires a large amount of sample solution (Merson and Morgan, 1968).

2.3.6 Cryoscope

It measures F.P. of a liquid or a solution. It uses a principle known as supercooling and the solution remains in its liquid phase because there is no seed crystal. It is a highly advanced and costly instrument to measure the freezing point. It can be used to determine any change in the osmotic pressure of solution.



(a)



(b)

Fig. 2.9: Basic diagram of cryoscope

Thermistor cryoscope technique is another way of FPD estimation and is additionally utilized for estimating of FPD in milk. Accurate FPD data can be obtained for low concentration solutions: for herd milk, for example, a resolution of $\sim 0.001^{\circ}\text{C}$ (Shoemaker et al., 1974; Matthews, 1985). The reproducibility of less than 1 % for solutions at low concentrations can be achieved (Knauer, 1990). The precision of result for high concentrated solutions may be reduced. The precision of the results also becomes worse with the samples of low molecular weight (Matthews, 1985).

2.3.7 Ultrasonic technology

Direct measurement of fat, sugar, protein, etc. are done by using the ultrasound technique and freezing point is calculated on the basis of the composition of milk. The composition and temperature of fish tissue affect the ultrasonic properties. As SNF content increases, ultrasonic velocity increases but it shows the complex relation with fat content of tissue (Reza et al., 1998). Ultrasonic velocity increases with increasing the fat content below a certain temperature and decreases with increasing fat content above that temperature. It can be possible to determine the fat and SNF content of fatty tissues by this technique at minimum two different temperature and SNF of non-fatty tissues can be measured at single temperature (Reza et al., 1998).

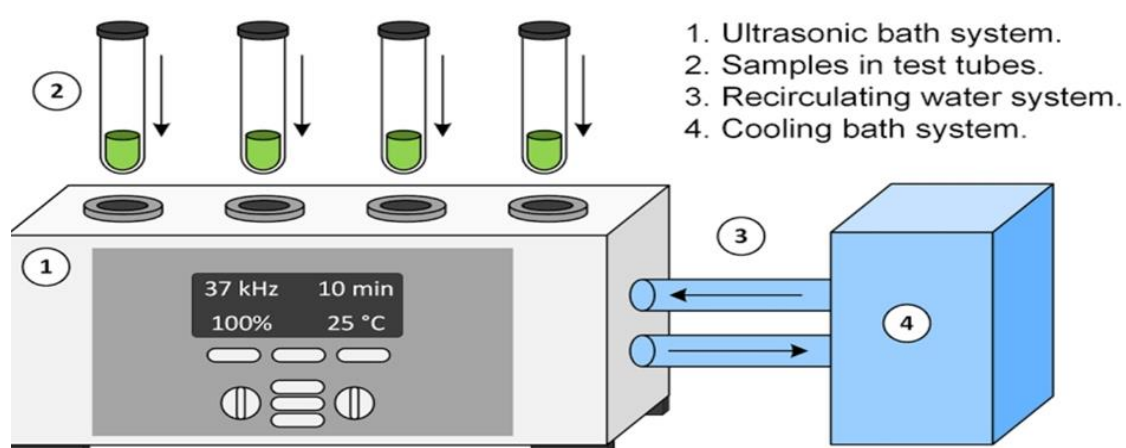


Fig. 2.10: Ultrasonic composition measurement unit

2.4 Factors affecting the Freezing Point and cooling rate of solution

2.4.1 Molar concentration

In chemistry, the amount of a solute or constitution divided by the total volume of the solution known as “molarity”. Number of moles of solute present per litre of the solution is called molarity (Jadhav et al., 2019).

Table 2.1: Freezing Point depression of eutectic salt-water solutions

Solutions	Subcooling (°C)	Freezing point (°C)	FPD (°C)
05 % NaCl	3.87	-3.87/-4.27	-4.8/-3.18
10 % NaCl	6.28	-7.6/-7.7	-7.8/-6.1
15 % NaCl	5.3	-15.19/-15.29	-10.4/-9.2
20 % NaCl	2.79	-18.22/-17.92	-18.92/-14.62
21 % NaCl	2.20	-18.46/-18.26	-18.86/-14.62
22 % NaCl	1.6	-21.95/-21.39	-20.15/-19.65
23 % NaCl	0.2	-20.89/-21.85	-22.15/-19.65
24 % NaCl	0.3	-20.19/-19.9	-3.28/-2.08

(Yilmaz et al., 2010)

It is found that when ice start to make its crystals and mixed up with the fluid then generally solution doesn't become solid. When temperature of whole mixture reaches to the eutectic point total freezing of mixture starts. It is known as the process of supercooling of solvent in the salt & water mixture (Granryd and Melinder, 2005).

Table 2.2: Experimental water freezing point temperatures for aqueous NaCl–EG solutions.

Salt	Salt concentration (mass %)	EG concentration (mass %)	Freezing point (°K)
NaCl	2.6	5.8	269.50
NaCl	5.3	5.1	268.30
NaCl	8.1	8.7	264.80
NaCl	11.1	11.3	261.30
NaCl	15.1	14.9	252.26

(Masoudi et al., 2004)

2.4.2 Vapour Pressure

A solution is created when solute gets dissolved into the solvent. The vapour pressure formed from this solution is lowered by the addition of the solute. Here comes the vapour pressure formula using Raoult's law, which explain how the vapour pressure of a liquid gets changed by the addition of a solute.

$$P_{\text{Solution}} = (X_{\text{Solvent}}) \cdot (P_{\text{Solvent}})$$

P_{Solution} = the vapour pressure of the solution.

X_{Solvent} = the mole fraction of the solvent in the solution.

P_{Solvent} = the vapour pressure of the solvent.

For boiling point elevation, it is necessary for solute particles to have the nature of involatility but it is not a necessary condition for FPD (freezing point depression). The concentration of a solution affects the freezing point of that mixture. As the ice crystals form and water starts to freeze, FPD is observed because the remaining solution becomes more concentrated and consequently the FP of solution decreased until the solution becomes saturated (Pinarbasi et al., 2009).

2.4.3 Thermal properties

Thermal properties explain the response of a material when heat is given or taken from it. It is related to the transfer of heat through material. Cooling rate of any material is highly influenced by these properties. Some of them are explained here.

2.4.3.1 Thermal conductivity

- Thermal conductivity of the pure water and Ethylene glycol:

$$\lambda_w = 0.56276 + 1.874 \times 10^{-3} \times t - 6.8 \times 10^{-6} \times t^2$$

$$\lambda_{eg} = 0.24511 + 1.755 \times 10^{-4} \times t - 8.52 \times 10^{-7} \times t^2$$

- Thermal conductivity of mixtures from the values of the pure liquids:

$$\lambda_M = (1 - X)\lambda_W + X \times \lambda_{eg} - k \times (\lambda_W - \lambda_{eg}) \times (1 - X) \times X$$

(Bohne et al.,1994).

where, t is temperature in °C and,

λ_W and λ_{eg} is thermal conductivity of water and ethylene glycol in W/mK.

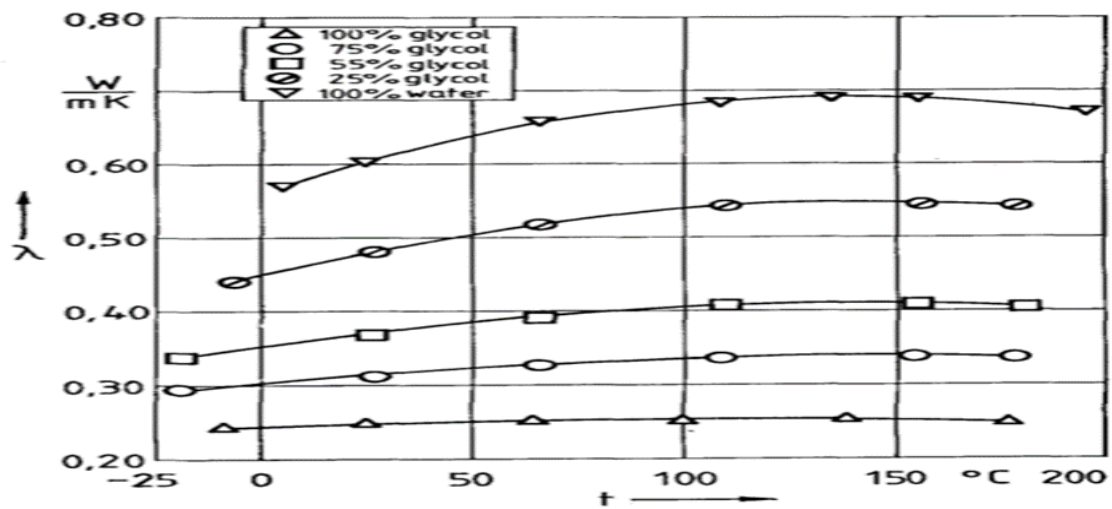


Fig. 2.11: Thermal conductivity of ethylene glycol-water mixtures (Bohne et al., 1984)

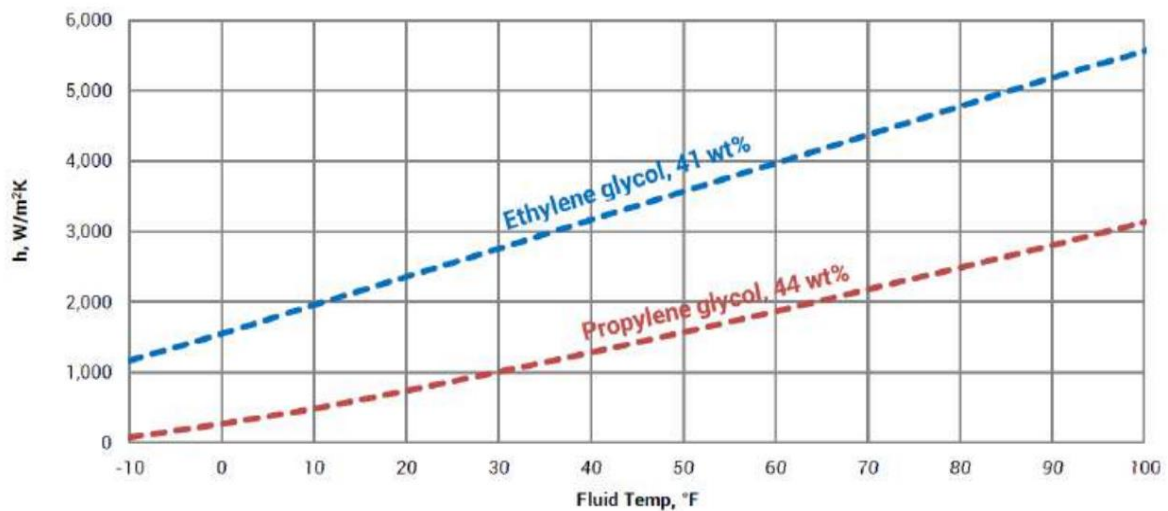


Fig. 2.12: Thermal conductivity of ethylene glycol and propylene glycol solution (Dynalene, 2014)

Table 2.3: Thermal conductivity (Btu/(hr ft²)(F/ft)) at 30 % Volume

Temperature (°F)	EG	PG
10	0.238	0.235
20	0.243	0.239
30	0.247	0.243
40	0.251	0.247
50	0.255	0.251
60	0.259	0.254
70	0.263	0.258
80	0.266	0.261

(Crown solutions, 2018)

2.4.3.2 Specific heat

Specific heat is the heat energy that is needed to raise the temperature of one Kg of the substance by 1°C. It is measured in joules per kilogram degree-Celsius. The specific heat of ethylene glycol-based water solutions is less than the specific heat of clean water. For a heat transfer system with ethylene glycol the circulated volume must be increased compared to a system only with water.

When we operate at temperature below 0 °C then it becomes necessary to add antifreeze into the water. Ethylene glycol (EG) & propanol are antifreeze substance who reduce the thermal transport phenomenon in the water which causes the reduction in thermal-hydraulic work of the heat exchanger considerably (Jayabalan et al., 2017).

Table 2.4: Specific Heat of Ethylene Glycol based Water Solution

Specific Heat - cp - (Btu/lb °F) [kJ/(kg °C)]								
Temperature		Ethylene Glycol Solution (% by volume)						
(°F)	(°C)	25	30	40	50	60	65	100
-40	-40	1)	1)	1)	1)	0.68	0.703	1)
0	-17.8	1)	1)	0.83	0.78	0.723	0.7	0.54
40	4.4	0.913	0.89	0.845	0.795	0.748	0.721	0.562
80	26.7	0.921	0.902	0.86	0.815	0.768	0.743	0.59
120	48.9	0.933	0.915	0.875	0.832	0.788	0.765	0.612
160	71.1	0.94	0.925	0.89	0.85	0.81	0.786	0.64
200	93.3	0.953	0.936	0.905	0.865	0.83	0.807	0.66
240	115.6	2)	2)	2)	2)	2)	0.828	0.689
280	137.8	2)	2)	2)	2)	2)	2)	0.71

1. below freezing point

2. above boiling point

$$1 \text{ Btu}/(\text{lb}_m^\circ\text{F}) = 1 \text{ kcal}/(\text{kg}^\circ\text{C}) = 4,186.8 \text{ J}/(\text{kg K})$$

Table-2.5: Specific Heats of Propylene Glycol Solutions

Specific Heat								
Propylene Glycol Solution (%)	by mass	0	10	20	30	40	50	60
	by vol.	0	10	20	29	40	50	60
Specific Heat cp. (Btu/lboF)[kJ/(kg°C)]		1000	0.980	0.960	0.935	0.895	0.850	0.805

2.5 Cooling curve

Cooling curve is graphic representation of freezing point of a solution, food or solvent. It is plotted between cooling time and cooling temperature. Its main parts are cooling, super cooling, freezing and cooling of liquid.

The freezing process is improved by the quick freeze action, as time is reduced by significant difference due to fast freezing. This experiment explains that FP of high moisture containing food can be calculated by using cooling curve method in a simple apparatus and domestic level refrigerator (Bainy et al., 2015). According to Anderson et al. (2004) who examined five distinct models of household refrigeration system, when it was compared to others then found that the models of quick freeze action dropped the temperature rapidly and had lesser mean temperatures.

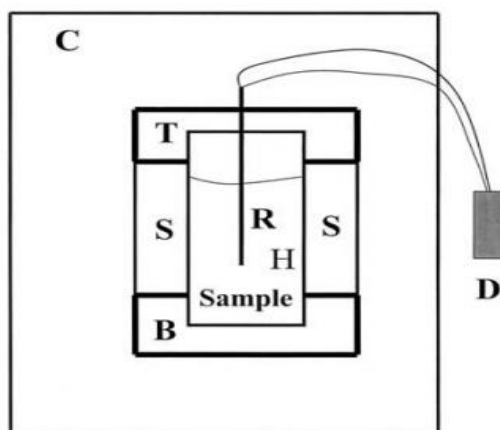


Fig. 2.13: A schematic diagram of the experimental set up. T: top insulated block, B: bottom insulated block, S: side insulated block, R: thermocouple probe, H: stainless steel sample holder, D: temperature recorder, C: chest freezer (-70°C), (Rahman, 1995)

starch gel solution or sugar solution was added into a cylinder made of stainless-steel (height, 4.5cm; internal diameter, 2.2cm; thickness, 1mm) and it was insulated from all directions like at the bottom, top, and side by using polystyrene foam (Fig: 2.13). The volume of cylinder was filled approx. 75 % of its full capacity for all trails. Syrup containing cylinder was placed in the chest freezer maintained between -40°C to -85°C. Thermocouple was used to

measure the temperature and temperature recorder was used to show that temperature. 0.1°C accuracy was found of FP measurement. The cooling rate could be varied by placing the cylinder into polystyrene foam block of different dimensions (Rahman, 1995).

It is usually believed that end of freezing or melting of ice begins near -32°C for the solution of sucrose. This value is very close to the value which was measured by DSC and DMTA methods (Meste & Huang, 1992).

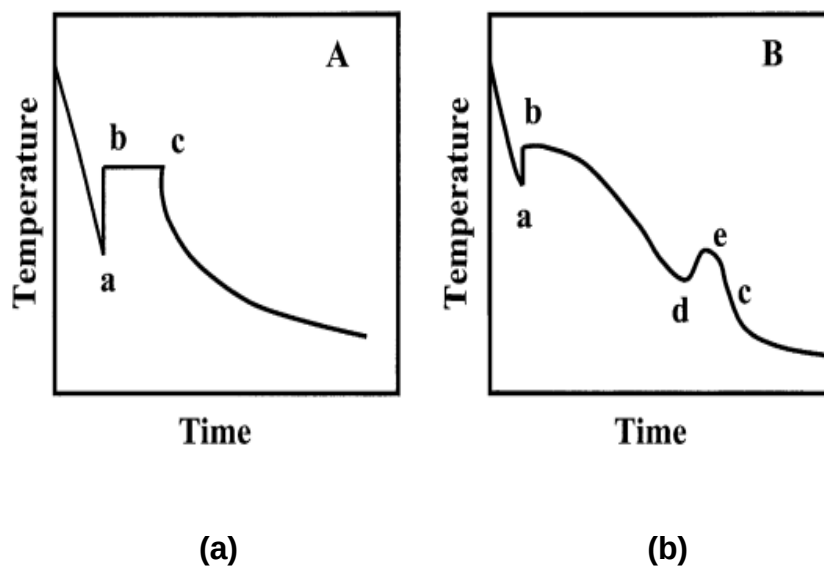


Fig. 2.14: Typical cooling curve. A: water, B: solution, a: ice crystallization temperature, b: equilibrium or initial freezing point (T_c), c: end of freezing, d: formulation of first solute crystal, e: eutectic point (Rahman, 1995)

The abrupt rise in temperature due to the liberation of the heat of fusion after initial supercooling represents the onset of ice crystallization (Rahman et al., 2002). Supercooling is defined as the cooling of liquid beneath the initial temperature of freezing of sample without solidification or ice formulation. Before the initiation of nucleation, water can be supercooled by many degrees. After that crystal nuclei increases its size more than critical radius for its nucleation. Nucleation starts from point 'a' in the fig. 2.14 (a & b) and the rate of liberation of its latent heat is more than the rate of heat removed from the solution (Rahman et al., 2002). Because of this phenomenon, the

temperature increases promptly to the original freezing temperature at the point 'b'. For a solution, point 'a' is found at higher position than pure water because added solutes instantly start the heterogeneous nucleation hence accelerate the nucleation process. Supercooling is greatly decreased by solutes for two reasons. First reason is the fast nucleation than pure solvent and second, lowering the freezing point. After the completion of ice crystallization, the sensible is removed from solid part & water so temperature drops (Rahman et al., 2002).

Determination of FP by plotting graph is utmost commonly used method. Initially the slope of cooling curve decreases to reach its minimum value, which is known as the nucleation of ice and then the slope increases upto the end of the freezing process (Rahman et al., 2002). When the end point of freezing occurs, slope of the curve starts to decrease from its highest value.

$$Y = f(x) = \text{Temp. profile (temp. v/s time)} \dots\dots\dots(1)$$

$$dY/dx = d[f(x)]/dx = dT/dt \dots\dots\dots(2)$$

$$\text{Slope of curve} = \text{Cooling rate} = \tan(\theta) = dY/dx \dots\dots(3)$$

(Here, T = temperature (°C) & t = time (min))

Sometime in supercooling stage, the onset of ice crystallization is marked due to the critical weight of nuclei. Latent heat of fusion is released from crystals which is quicker than the quantity of heat taken out from the solution consequently temperature increases to the point of equilibrium freezing (Rahman et al., 2005). The degree of supercooling depends closely on both the cooling rate and the sample mass (Yamada et al., 1993).

Correct freezing point data can be used to determine features such as water activity, frozen water, bound water, effective molecular weight, state diagram creation, and enthalpy below freezing. (Rahman, 1995). The cooling curve approach, which is both inexpensive and simple, can be used to determine the completion of freezing, which is a common point on a food's state diagram. (Rahman et al., 2002).

Cooling curves were used to determine the freezing time, as well as the time it took for the temperature of the central region of the sample to drop from 0 °C to -5 °C (the essential zone for the formation of maximum ice crystals) and from 0 °C to -18 °C where food freezes practically completely (Chen and Pan, 1997).

The equilibrium or initial freezing point is considered at the temperature where the slowest cooling rate is observed (Rahman and Driscoll, 1994). The cooling curve is analysed to determine other phase and structure changes by calculating the slope (Rahman et al., 2002).

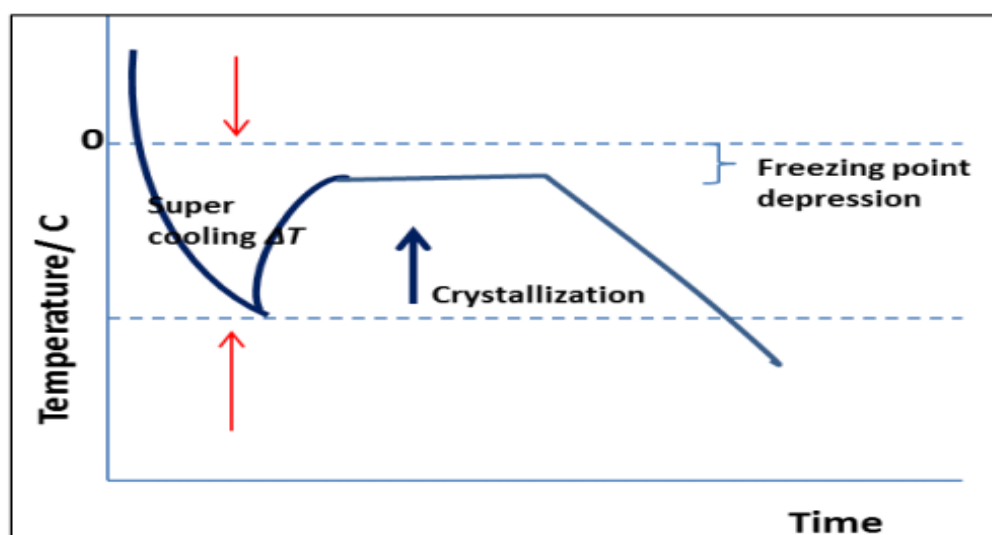


Fig. 2.15: Schematic diagram of freezing curve (Jayawardena et al., 2017)

Jayawardena et al. (2017) used the cooling curve to determine the freezing point of sucrose solution. Purified sugar and distilled water were used at different concentrations to make sucrose solutions. Plastic tube (10 mm in diameter) having a Thermocouple (TECPEL-317 Data logger) with ± 0.1 °C accuracy was filled with approximately 15 ml of all samples. Tubes were frozen entirely at -20 °C in deep freezer and the temperatures were documented with time (Jayawardena et al., 2017).

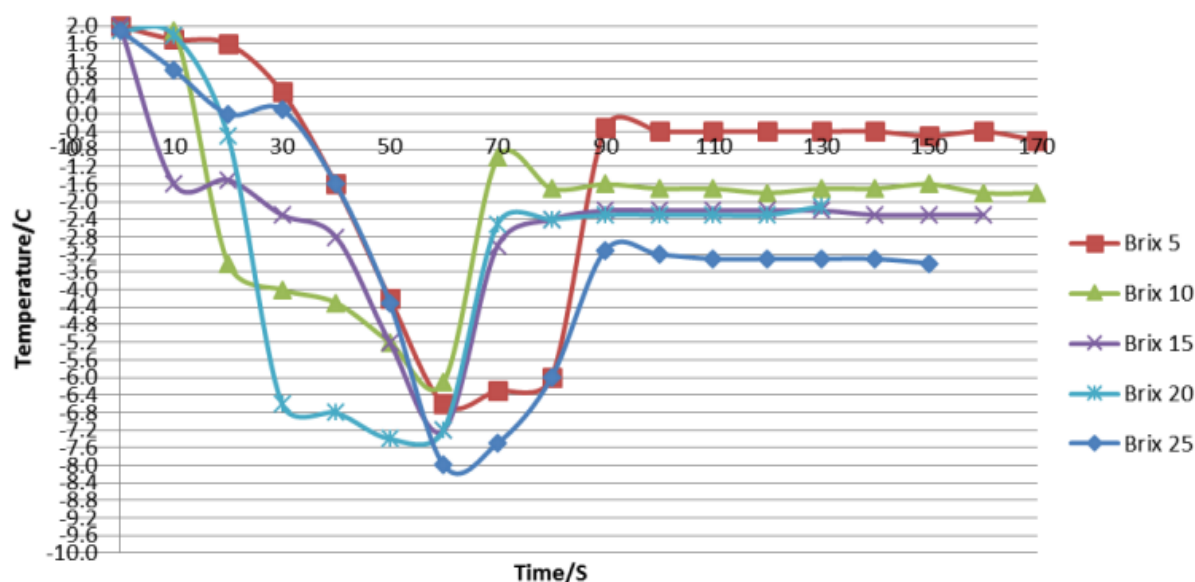


Fig. 2.16: Freezing curve for different Sucrose solutions (Jayawardena et al.,2017)

To get the information about the fraction of the frozen solid in food or material during freezing processes, suitable formulas can be used who give data related to the same. According to Gibbs and Patricio (2008), proper equations were used to calculate the percentage of solidified alloy. A new method was presented to calculate the solid percentage of solidifying alloy by the cooling curve study. It's an equation-based Newtonian technique. It is unique in that the solid section was computed using an equation rather than the older cooling curve method. In this investigation, this strategy produced good agreement when compared to other types of cooling curve methods.

2.6 Differential Scanning Calorimetry (DSC)

The most extensively utilised thermal analysis method is differential scanning calorimetry. The term DSC merely means that a DSC equipment can obtain detectable calorimetric data from a sample during a linear temperature fall or increase. The sample is kept at a specific temperature in this procedure, and the difference between the heat flow rate and a reference is calculated. the means of "DSC" denotes to two identical but slightly dissimilar thermal analysis methods. DSC can measure many characteristic temperatures as

well as many thermal values of the chemical reaction like, the heat of fusion, the crystallization and melting temperatures, and, the heat capacity at a constant rate of cooling and heating (Menczel et al., 2009).

The temperature of sample and reference substances linearly raised at a fixed rate as a function of temperature and time in a precise environment and during transition period, the differential flow of heat is measured by DSC. Qualitative as well as quantitative data are collected which is related to the chemical and physical change that comprise variation in heat capacity, exothermic or endothermic.

In DSC and DTA, both the sample and the reference are cooled and heated at a set temperature at a programmed pace. During heating or cooling of the sample, the system either release or absorb the heat from the sample pan to keep the temperature constant in sample pan and reference pan. The two primary DSCs are power compensation and heat-flux DSCs, which differ in their essential structure in instrumentation.

2.6.1 Power Compensation DSC

In this type of DSC, two separate blocks are made for the sample and reference materials. These blocks are known as furnace. Two sample containers are made of aluminum or platinum metal. Two separate sensors are attached at the bottom point of the cells. That sensors can use the platinum resistance thermocouple. The temperature of the reference and sample is kept at a fixed program value by supplying the differential thermal power to the heating element (as shown in fig. 2.17).

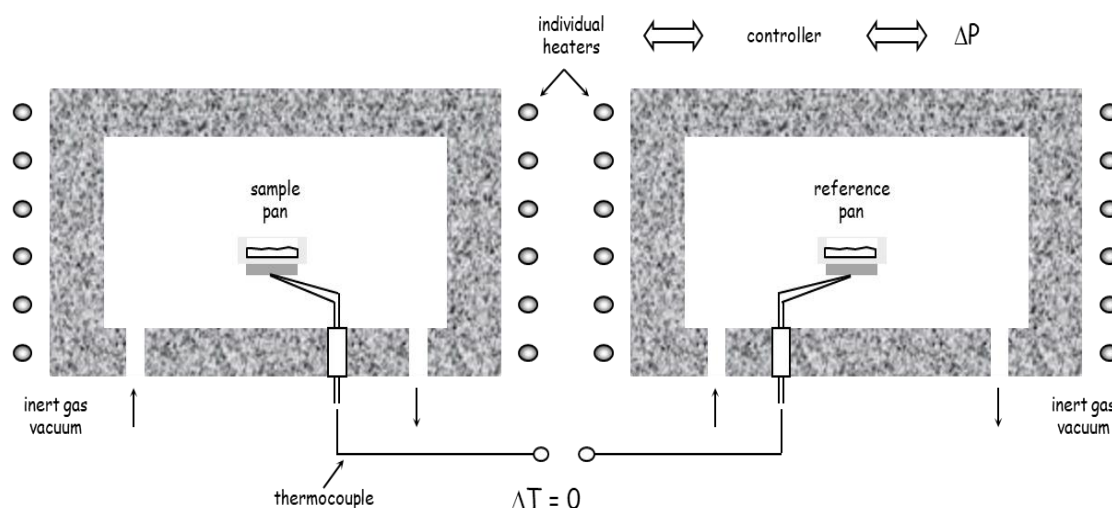


Fig. 2.17: Systematic diagram of Power Compensation DSC

It has two distinct control circuits attached to it, one for controlling the mean temperature and the other for controlling the differential temperature. The required mean temperature of the reference and sample containers is directly proportional to the electrical signal as a function of time in the first type of circuit. In second type of circuit, the differential amplifier gets the feed of sample and reference signals from the resistance sensors made of platinum. The power input into the two different furnaces is regulated by the amplifier output so the temperature of both cells is kept identical.

2.6.2 Heat Flux DSC

In this type of DSC, only single block is made for both reference and sample. A small resistance heat flow track connected to reference and sample. Platinum metal or aluminium are used to make pans which are located on constantan plate. To determine the sample temperature, Chromel-alumel thermocouple sensor is attached while for differential heat flow, chromel-constantan (an alloy of copper-nickel generally made of 45 % nickel and 55 % copper) thermocouple is attached (as shown in fig. 2.18).

The heat supplied to the heating element to maintain the temperature of the reference and sample at the preset value is measured as temperature, and the difference between these temperatures is converted to differential thermal

power(dq/dt).

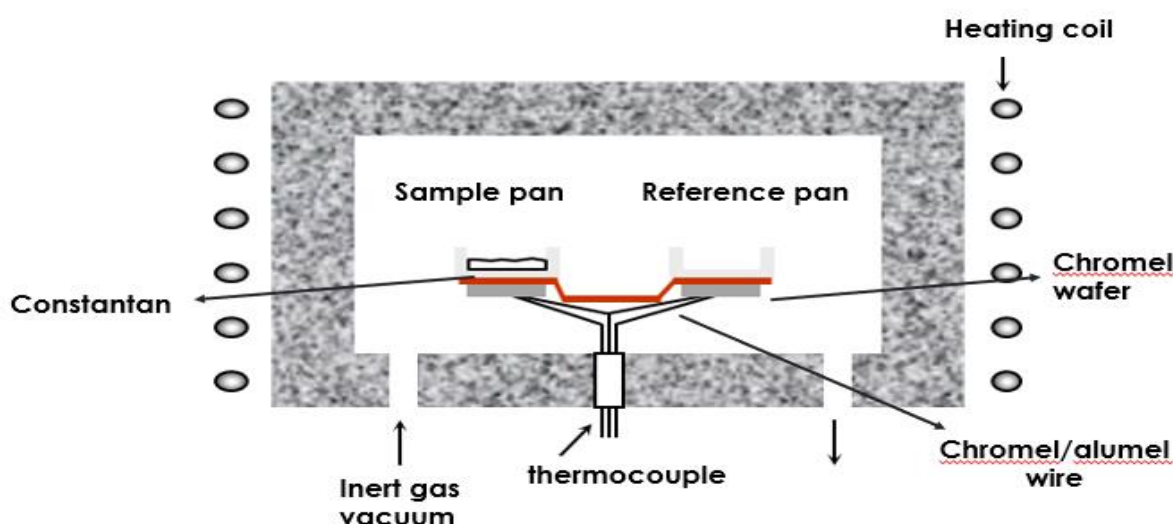


Fig. 2.18: Systematic diagram of heat-flux DSC

via electrically heated constantan thermoelectric disc is heated by supplying the electricity and heat flows into both reference and sample substance. Heat is transferred to both materials via constantan disc. The difference between output of two thermocouple connections is directly proportional to the differential heat flow in the two separate pans. Chromel/alumel junction which is placed below the sample plate is used to determine the sample temperature.

2.6.3 Modulated DSC

Modulated DSC has the heating element and cell arrangements same as in the heat flux type DSC. Fourier Transform program is used to separate the overall signal mathematically into two parts, first is a “reversing heat flow signal” and second is a “non-reversing heat flow signal”. Usually step transitions such as glass transition appears only in the reversing heat flow signal, generally step transition like glass transition is appeared but endothermic and exothermic actions can be appeared in the both signals.

By using quasi-isothermal situations or slow heating rates, direct heat capacity can be measured by new feature of this system. This system has ability to give further insight into a non-equilibrium processes for

macromolecules occur at the time of glass transition (shrinkage, strain release) and at the time of melting and crystallization like recrystallization, crystal perfection, softening of rigid amorphous content etc. (Boller et al., 1994).

If the instrument has reached steady state, the block, sample and reference temperatures T_b , T_a , and T_r , respectively, at time t , are (Boller et al., 1994):

$$T_b(t) = T_o + qt + A_{Tb} \sin(\omega t) \quad (1)$$

$$T_a(t) = T_o + qt - qC_a/K + A_{Ta} \sin(\omega t - \alpha) \quad (2)$$

$$T_r(t) = T_o + qt - qC_r/K + A_{Tr} \sin(\omega t - \beta) \quad (3)$$

where T_o = initial temperature,

q , = linear heating rate

A_T = designate the corresponding oscillation

ω = frequency of oscillation

2.6.4 DSC Thermogram

DSC gives the result of its measurement in the form of a curve in which, heat flow, time of temperature are taken on the axes. This graph is affected by two factors: operational environments like rate of heating, sensor location, equipment environment and constituents of sample vessels and condition of sample like sample size, solubility of gas, size of particle, heat of reaction & thermal conductivity). During process, If the heat is taken by the sample compare to the reference material, an endothermic peak is observed. Similarly, if the exothermic processes take place in the sample, like crystallization, heat will be released from the sample. Because of the difference between the heat flow of sample and reference, quantity of the heat released or absorbed during the transition period is measured by the DSC (Kodre et al., 2014).

By combining the axes of temperature and time, the calorimetric curve accounts for the temperature differential between the sample and the reference. The enthalpy change in a DSC curve is computed by computing the area under the curve. (Chiavarro, 2014).

The DSC method is also used for the checking of fatty and oily foods because it is a rapid, reproducible as well as a sensitive method. The detection of the adulteration of groundnut and caprine body fat mixture at the rate of 5 % in buffalo ghee or bovine ghee is performed by using DSC method (Juliana et al., 2018).

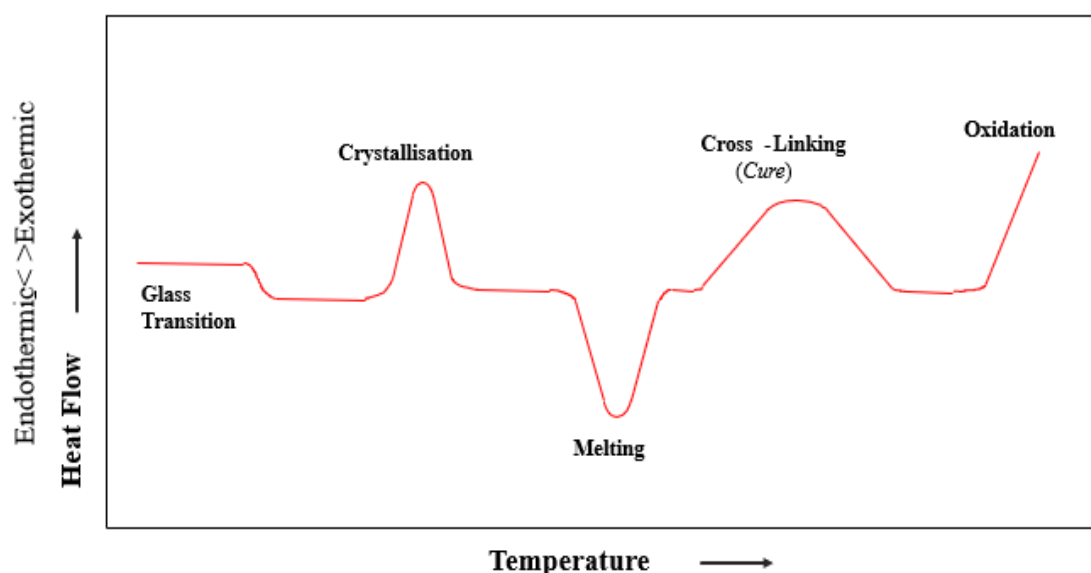


Fig. 2.19: Systematic diagram of DSC thermogram

DSC is used for the more easy and speedy determination of many processes like heat of fusion, glass transition (T_g) temperature, heat of reaction, the heat capacity jump at the glass transition, melting temperature, crystallization temperature, determination of the liquid crystal transitions, fast measurement of purity, thermosets characterization, and rapid heat capacity determination. It is possible to determine the kinetics of chemical reactions, e.g., thermal degradation, degradation by thermo-oxidation or cure. Also, the kinetics determination of polymer crystallization is possible. A list of food industries or biotechnology can be made for the latest operators of DSC (Menczel et al., 2009).

To evaluate cooling, storage time, heating process, or drying, it is desirable to calculate the heat transfer through food material and thermo-physical properties play a significant role in this process. (Pustjens et al., 2016). In the improvement and determination of quality of food, stability and safety of the food material, this analysis can also help to producers (Yildiz, 2009).

Because of its easiness and acceptance, the energy features (heat capacity as well as its integral over enthalpy & temperature), determined by using DSC, have a direct corporal sense but many times explanation may be hard. The benefit of differential scanning calorimetry compared with some different calorimetric methods in the range of broad dynamic about cooling & heating rates, together with temperature modulated operation as well as isothermal operation (Schick, 2009).

The purpose of thermodynamics is to found the fundamental functions for the state of system, the most significant states for DSC are pressure (P), internal energy (U), entropy (S), enthalpy (H), heat capacity (Cp), and volume (V) at isobaric condition. Temperature plays the most significant role in DSC. It is the only quantity to be measured in DSC. Remaining all parameters are determined from the temperature change, from the variation between the temperature of reference and sample material (Menczel et al., 2009).

In a prior study, researchers employed the excess enthalpy of glass, as measured by a DSC equipment, as the optimum parameter for structural material relaxation. The most suitable aging conditions was measured using DSC and highest structural relaxation was observed when annealing was done at 15°C to 25°C which is lower than the glass transition temperature (Suman et al., 2008).

In the 2-D determination system, which is used in almost all heat flow type DSCs as well as in “ultra-fast scanning calorimeter”, the heat flows directly between sample and surrounding oven which is not determined by the sensors placed between heat flow. The heat transfer rate not determined by the sensor can be 50 % of the whole heat transfer rate occurred. We can assume the equal heat loss for both reference and sample side and it also

doesn't change at the time of calibration runs and during measurement, calibration function can theoretically consider those losses (Schick, 2009).

The samples containing freezable water show more complex processes like ice formation and glass transition and the suitable method must be used for it. The endothermic peak was noted as equilibrium or initial FP. By calculating the area of melting endotherm using linear reference line, the latent heat of freezing or melting of ice was determined (Rahman et al., 2005).

2.7 Simulation studies

The mathematical modelling of different systems like chemistry, economics, physics, biology, social science, psychology and in the engineering process of new technology to improve understanding about the operation of these systems use the computer simulation as a useful part. It is a useful junction to decently mathematical model in entertainment, science, & technology. The faith and reliability person put in the computer simulation affected by the legitimacy of this model.

According to previous research, a variety of composite mathematical formulas are employed to create simulation programmes or algorithms. Various sorts of algorithms are developed based on the situation, which varies from problem to problem. It demonstrates that the simulation programmes are based on a problem-solving method.

In general, a simulation model is used to study the actual systems of life which does not presently occur. In certain, one is attentive in calculating the performance of the system beneath study for different values of various input parameters. This calculated measurement of performance is very advantageous in the executive decision procedure (Perros, 2009).

In medicine and life sciences, computer simulations have many forms, like brains and its neurons, computational models of cells, 3-D digital visualization and growth process animation permitting to do experiments not only "in vivo", & "in vitro" as well as "in silico" (Wellmann, 2018).

By using the direct coexistence technique, simulation of molecular dynamics was used for a liquid solution of TIP4P/2005 water with NaCl to find out the

equilibrium line for ice & NaCl solution and the FPD of water at various salt concentrations was calculated below the point of eutectic (Conde et al., 2018). To reduce errors and finite size effects, large samples were being used for determination of the freezing point. Results were found to the experimental FPD proof that the parameters used in this study for the salt solution were a good choice to imitate the properties of thermodynamic of the salt solution with the simulation of molecular dynamics (Conde et al., 2018).

To optimise the logistic chain, simulation is employed for climate change and fresh produce scenarios. It is also used in conjunction with mathematical models to improve packaging technologies in order to retain fresh food safety and quality. These are the tools to offer understandings in the composite dynamic eco-system. They are the basis for elaboration of risk assessment studies to scientifically support management options (Jacxsens et al., 2010).

Now-a-days, in the field of knowledge production, Computer simulations can be used virtually. Perhaps, the “Monte Carlo” as well as “agent based” simulations are one of the best methods. A typical Monte Carlo simulation uses random numbers to provide a stochastic model of a physical phenomenon (Borrelli and Wellmann, 2019).

In the pilot plant, data were collected by experimental study and used to confirm the theoretic model gained by technique of computer simulation. The obtained results show that a satisfied prediction of the most vital data can be taken by the computer simulation. These data are temperature & heating time of the process of meat product heating. It saves time and action in the essays of pilot plant. The computer simulation can also provide data on the temperature grounds in the emulsion of meat and these values are the temperature oof mat product at a particular time. Opposite to this, the experimental data give only the temperature values of that point where thermocouple is placed (Pedro et al., 2010).

Two different simulation methods namely “free-energy method” and “two-phase coexistence solid-liquid method” have been used to Compute the freezing point of the fluid at a certain pressure. The first method determines the freezing point by requiring equivalent free energy of solid and liquid, which

is usually computed using the thermodynamic integration methodology. The second concerns a solid-liquid system coexisting in several statistical ensembles. (Wang et al., 2013).

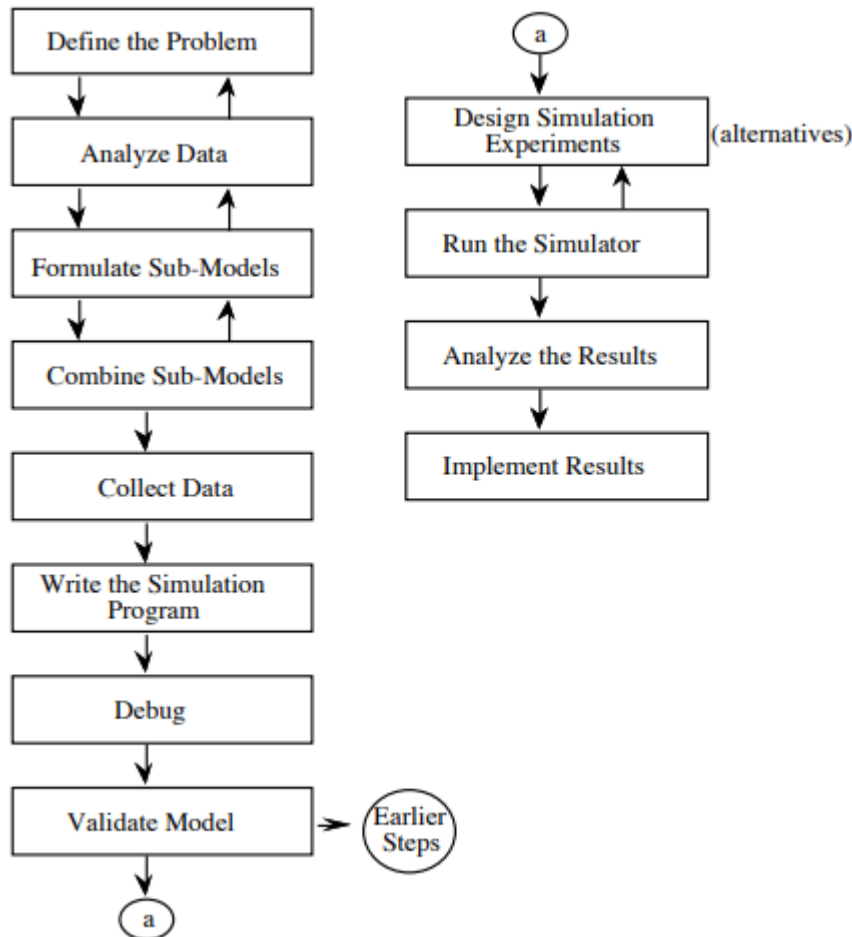


Fig. 2.20: Basic steps involved in carrying out a simulation study (Perros, 2009)

Zhang et al., (2016) worked on the initial profile for the simulation of freezing of a water droplet, but supercooling effect was ignored in this model. Because of this mistake freezing rate decreased thus increased the freezing time. It also gave the smaller water/ice interface height compare to the experimental values because the initial profile was used and density was considered as constant throughout the process of freezing, which results to decrease the time of freezing.

Lennard-Jones particles were used for a study of the structural properties and thermodynamic as a system and by using the isothermal-isobaric (NPT) molecular dynamics computer simulation techniques, Lennard-Jones particles system was cooled down. It can be possible to explain the range of the metastable section enclose supercooled liquid and superheated solid by using NPT with molecular dynamics simulation. The latent heat of fusion and the related coexisting densities were also found in a good agreement along with NVT results (Chokappa and Clancy, 1987).

When creating a simulation model for a real-life system, the full system cannot be reproduced on its own, but it is possible to mimic the system by taking sub-systems based on the difficulties involved. The system's modelling components are involved at various stages of development. It can be graphically represented by using “Beard's managerial pyramid” (Fig. 2.21). The blackened circular areas combinedly form these portions of the system which is going to be simulated separately in the model. All the related variables in the system can be classified into two main groups. First is uncontrollable variable which are taken as assumed and can't be manipulated. Second is controllable variable which can be manipulated and comes into the solutions. The differences between the uncontrollable variables and controllable variables is mainly depended on the scope of the research study (Perros, 2009).

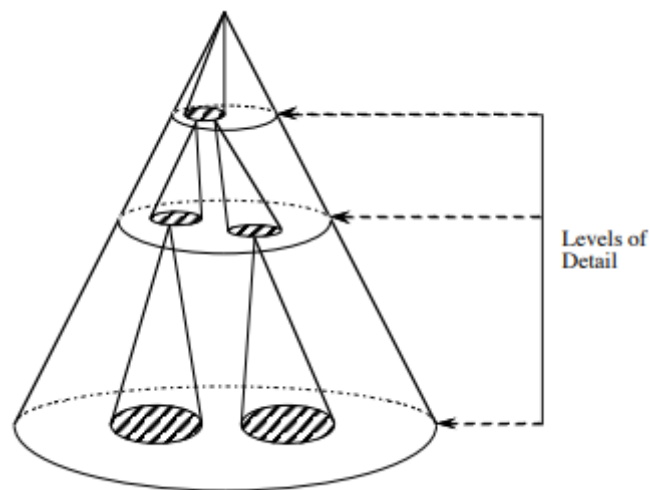


Fig. 2.21: Beard's managerial pyramid (Perros, 2009)

The solubility of the potassium fluoride solution has been determined by using the computer simulation technique. The result of NaCl salt during the ice melting is also investigated by using Molecular Dynamics, in which the variation between the freezing points determined by experiments and its simulation results are around 3°K for the solutions. Computer simulation was also used to explore the NaCl solubility in water by using various fields of force and it was observed that the NaCl solubility in water is affected by the water-ion, ion-ion, & water-water molecule interactions (Fatemi and Foroutan, 2016).

Early on, many engineers and some architects initiated to make use of different computer programs to build, design, test artifacts etc. for various vehicles and airplanes or many instruments. They established a wide range of visualization techniques & modeling which were based on the discretization of the geometrical surface, referred as digital models or computer simulation. In spite of the diversity of disciplines, the wide range of applications as well as questions solved with the aid of the computer simulation. After that, perspective about the simulation changed from a thing of knowledge to a thing of practice.

Refrigerators have also been designed by using computational fluid dynamics simulation. CFD code was applied by using the finite volume technique and a simple algorithm & turbulent stream model were made for 3-D simulations. In this simulation technique, the overall heat transfer coefficients were calculated by converting the thickness of insulated wall, thermal conductivity of wall and the coefficients of heat transfer of outside surfaces. It was observed that the results getting from simulation deviated from the measured values by only 1°C, thus it can be concluded that the accuracy of simulation method is sufficient for research purpose (Fukuyo et al., 2003).

Numerical problems of food are inherent nonlinearity which makes the simulation of freezing of food more difficult. To increase the shelf-life of the food products and reduce the cost, the design of the freezing process is the most vital factor. After many years of studies, researchers have found numerous characteristics of freezing in various food products to precisely

predict many features of the processes. A wide variety of foods were investigated for freezing in which freezing time and temperature were supervised. To simulate the process of freezing, so many studies were focused on the designing of mathematical algorithm or model in which food was assumed as a perfect binary solution. These mathematical algorithm or models were typically resolved numerically but not analytically because of the characteristic temperature dependency of the thermal property which results in depression in freezing point.

Researchers have been discussed many times about the precision of numerical simulation. Experimental data are usually compared with the numerical results. Experimental errors, analytical biasness and less numerical accuracy usually attribute the disagreement between experimental outcomes and numerical simulation results. In addition, density and thermal conductivity of food material are therefore temperature functions due to the conversation of water to solid ice during the process of freezing. The simultaneous changes in the freezing temperature as well as in the thermal properties of the liquid mixture leads the process to an extremely nonlinear mathematical issue (Saad and Scott, 1997).

For the temperature simulation of the food products, it is suggested to use the “two-step finite difference method” with a little time gap and big grid size at the time of one-dimensional way of freezing. This approach of study can also be used to other nonlinear processes such as sublimation, curing, or melting. It is a highly suitable means to compare the various numerical methods and differentiate between various types of error in simulated investigational data (Saad and Scott, 1997).

According to Sanz et al. (1999), in freezing process of food the existence of big ice crystals is a considerable problem when a good quality product is anticipated. A “finite element method” was used to simulate a mathematical model for determination of cooling rate of the product surface. This model was used to find out the rate of freezing that result to a high-quality product, associated to an optimum spreading of small size ice crystals presented outside as well as inside the tissue fiber. The aim of the research work were,

(1) to determine size and position of the ice crystals in the big parts of pork meat frozen with the help of liquid nitrogen, (2) to build the numerical model for freezing processes to simulate the distribution of freezing times along the pork meat (3) to use the model for prediction of finest operating situations (size of sample & rate of freezing) that result the minimum harm related to the development of ice crystal.

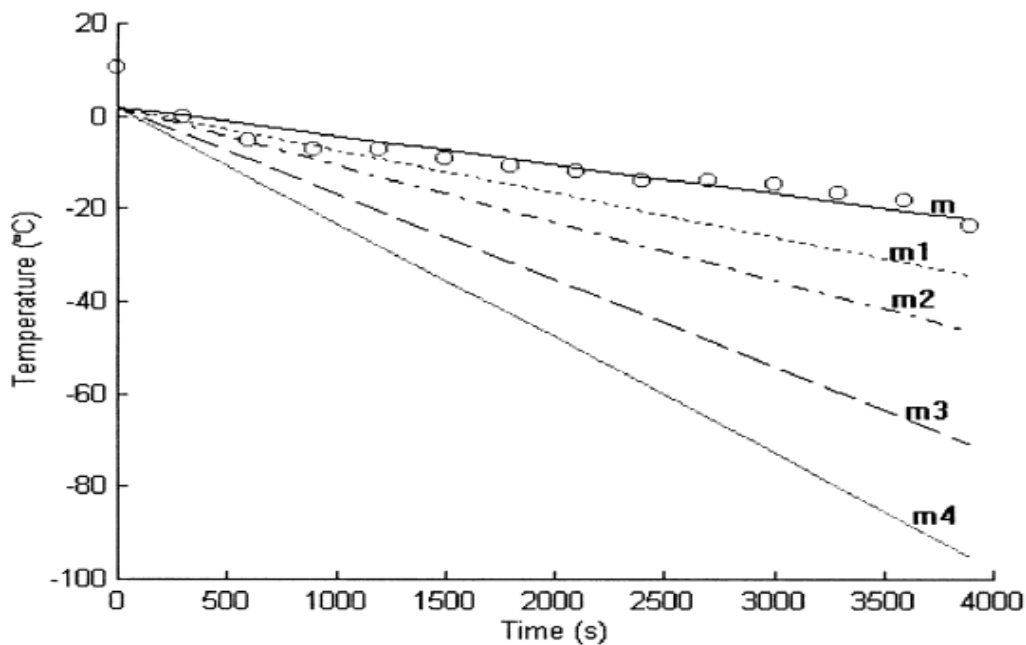


Fig. 2.22: Simulated freezing rates, their slopes being multiples of the original one (m) obtained after fitting the experimental values (circles) to a straight line (Sanz et al., 1999)

The measurement of the success is how fine the results of the numerical simulations match with experimental data in cases where systematic laboratory trials can be conducted, and how fine the simulation model can predict extremely complex phenomenon which is difficult to isolate in the research laboratory (Sethian, 1993).

Following the introduction of the digital computer, CFD has attracted broad attention in the rising period of research. Computational fluid dynamics makes use of extremely powerful and sophisticated computers, as well as mathematics, to create models for various fluid flow scenarios. It is predominantly useful to simulate those conditions, where taking full measurements are impossible like, high temperature and hazardous

environment inside the oven. It provides huge understanding about the particulate separation, heat & mass transfer, weight loss, distribution of flow etc. (Xia and Sun, 2002).

To complete the CFD simulation, three sorts of major steps should be completed. The first is pre-processing, which encompasses all of the procedures that occur prior to the numerical solution process. It entails the conceptualization, meshing, and creation of a computational algorithm or model. Second is processing that involves the solving of mathematical equations of fluid flow using a digital computer. Third one is Post-processing, in which collected data from CFD analysis is evaluated (Shaw, 1992).

Keropok lekor (fish sausage) was frozen and the study was performed experimentally as well as by using numerical simulation under unsteady state heat transfer. Fourier's equations of heat transmission were utilized to develop the numerical model. The primary goal of that study was to use a simulation modelling method to the investigation of food freezing times for diverse goods. It was discovered that the disparity between the predicted and experimental temperature profiles was extremely small. Therefore, the simulation model can be represented as satisfactorily method for the thermal processing of foodstuff (Ibrahim et al., 2007).

Advantages of simulation technique:

1. It consumes less time and cost effective.
2. It can provide good result with minimum error.
3. It requires less technical knowledge.
4. Critical situation can be investigation without any risk.
5. It can avoid danger and loss of life.
6. Condition can be varied and outcomes investigated.
7. It can be formulated according to any particular problem.
8. Simulation study can be speed up or slow down as per requirement.
9. It doesn't upset current processes and system.
10. It can be used when actual system is not available.

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3. MATERIALS AND METHODS

This chapter includes the materials and methodology which were used to conduct experiments to fulfill the objectives of this research work. Some of the materials were used in the previous study which was conducted by Hitesh, (2020) on the topic “Development of Subzero Temperature Based Milk Cooling System” to determine the freezing points of the different blends. Thermal cooling data which were used in this study as primary data was taken from this previous research work.

This research work was completed in two phases. In first phase, simulation program was written on the basis of the thermal & physical properties and the characteristics of cooling curve. Second phase includes the determination of freezing points by using simulation method and comparison of results with previous research work.

3.1 Simulation platform

3.1.1 Simulation software

Scilab software was utilized to determine the cooling rate & freezing point of the solutions and for simulation program. Scilab has high level programming language which is numerically oriented and it is an open source as well as free to use and Scilab is a package of numerical computation with crossed platform. This software has been used for many purposes like simulation in fluid dynamics, signal processing, image enhancement, statistical analysis, modeling, numerical optimization, simulation of implicit & explicit dynamics system and symbolic manipulation. Scilab and GNU Octave are the two main open-source replacements to MATLAB software. Compare to Octave, Scilab gives less stress on the syntactic compatibility with MATLAB, but this has adequate similarities that many authors have been suggested that it is less hard to transmit skills among the many systems.

The language offers an interpreted programming atmosphere with matrices as major data type. With the help of dynamic typing, matrix based computational package, and automated memory managing system, so many numerical difficulties may be presented in reduced number of lines of code, with the comparison to same type of solutions using old-style languages like C, Fortran, and C++. This permits consumers to fast construction of models for a wide range of mathematical complications. While the language provides simple matrix operations such as multiplication, the Scilab package provides a huge library of advanced operations such as composite multiple dimensional arithmetics and correlation.

The user interface and programming language in Scilab are very similar to the interface and programming language Matlab (Shakin et al., 2020). The programs which are formed in Scilab can be transformed to Matlab. Scilab is fully endowed with a powerful programming language whose syntax is easy to use and has all the elements of a high-level programming language (Bunks et al., 2012). Of course, Scilab is less versatile and cobbled than Matlab, but from version to version it is becoming more advanced (Shakin et al., 2020).

To calculate freezing point and cooling rate, a simulation program was written which runs with the help of Scilab software. Proper coding of mathematical expression was done in this simulation method.

3.1.2 System

A Microsoft window 8.0 based computer (Lenevo i7, 64 bit, 3.5 GHz, 4 GB RAM) was used for running the software and programs. The Intel Core i7-4770K is a 3.5 GHz quad-core processor for use with LGA 1150 socket motherboards. When extra power is needed, Intel Turbo Boost Technology can be enabled for a maximum frequency of 3.9 GHz. The Core i7-4770K is compatible with DDR3-

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1333/1600 memory and has 8MB's of cache for retrieving bits of frequently accessed data.

For graphics rendering, the Intel Core i7-4770k utilizes the Intel HD Graphics 4600 chipset. This processor also features Intel Virtualization Technology (VT-x), which helps to improve productivity by isolating computing activities into separate partitions. Intel 64 is also on-board, which works in conjunction with 64-bit operating systems, giving access to 4GB or more of virtual and/or physical memory.

3.2 Experimental data

Composition of different blends of sub-zero temperature liquids are listed in Table 3.1. Thermal cooling data was in form of csv files and were in the form of temperature as a function of time (Table 3.2) and was obtained using thermal data acquisition system (Fig.3.1). Blends were formulation of EG, PG, NaCl, and distilled water in different ratios. Cooling data were for 8 sample (S1-S8) per batch. Each sample cup was of 100 ml capacity.

Table 3.1: Blend formulation of EG & PG solutions

EG blends	
1:1 (EG:DW)	 0% NaCl 1% NaCl 2% NaCl 3% NaCl 4% NaCl 5% NaCl
1:2 (EG:DW)	
1:3 (EG:DW)	
1:4 (EG:DW)	
1:5 (EG:DW)	
1:6 (EG:DW)	
1:7 (EG:DW)	
1:8 (EG:DW)	

PG blends	
1:1 (PG:DW)	 0% NaCl 1% NaCl 2% NaCl 3% NaCl 4% NaCl 5% NaCl
1:2 (PG:DW)	
1:3 (PG:DW)	
1:4 (PG:DW)	
1:5 (PG:DW)	
1:6 (PG:DW)	
1:7 (PG:DW)	
1:8 (PG:DW)	

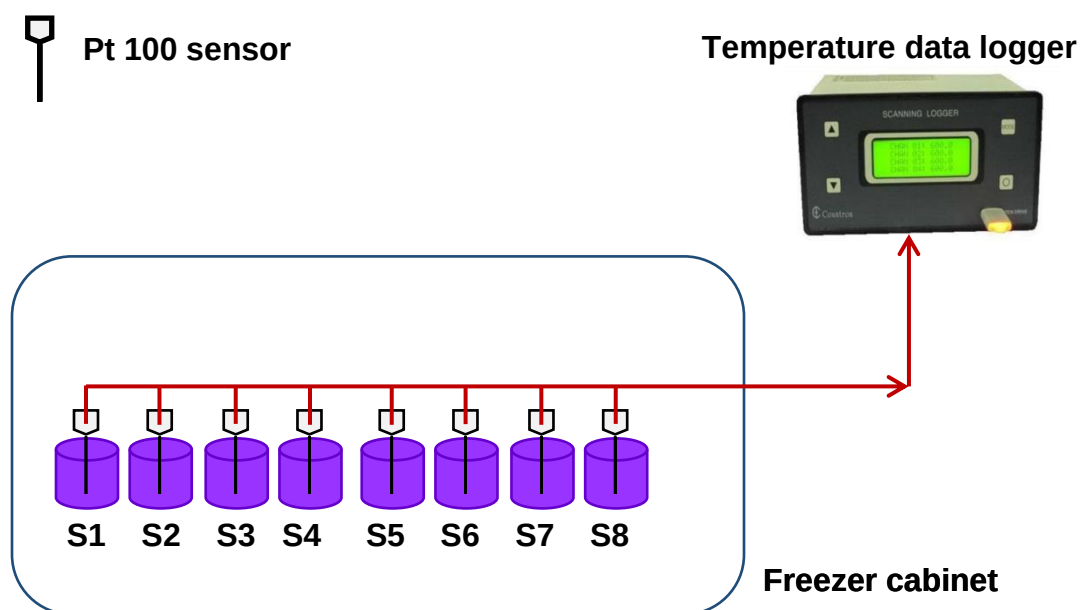


Fig. 3.1: Temperature data acquisition system

Table 3.2: Thermal cooling data sheet

Dt/Mn/Yr	Hr:Min:Se	1	2	3	4	5	6	7
#####	06:11:03	22.3	19.9	19.5	18.3	21	20.9	22.7
#####	06:11:13	22	19.7	19.3	18.1	20.8	20.7	22.4
#####	06:11:23	21.8	19.5	19.1	17.8	20.4	20.5	22.2
#####	06:11:33	21.6	19.4	18.9	17.5	20.2	20.2	22
#####	06:11:43	21.4	19.2	18.7	17.3	19.9	19.9	21.7
#####	06:11:53	21.2	19.1	18.5	17.1	19.7	19.7	21.4
#####	06:12:03	21.2	18.9	18.3	16.8	19.4	19.5	21.2
#####	06:12:13	21	18.8	18.2	16.6	19.1	19.2	21
#####	06:12:23	20.8	18.6	18	16.4	18.9	18.9	20.8

3.3 Simulation procedure

3.3.1 Determination of thermal properties & physical properties of solutions

3.3.1.1 Latent heat

The heat which is absorbed or released during the phase change of the material is known as “latent heat”. It is related to the enthalpy (the total heat of the system). During the release or absorption of the latent heat, temperature of the material remains constant. Substance having high value of latent heat of fusion requires high cooling rate to change the state of matter within a fixed time period.

Latent heat of fusion of ethylene glycol, and water are 181 kJ/kg, & 334 KJ Kg⁻¹ respectively (Ahuja & Ramachandran, 2016; Kumano et al., 2007).

The composite subzero temperature-based fluids also behave like a phase change material (PCMs) which stores cool energy as latent heat of fusion of fluid plus sensible heat below ambient temperature (Hitesh, 2020). Latent heat of EG is high in content that's why it absorbs huge quantity of heat throughout phase transformation.

The PCM is ‘latent heat thermal energy storage’ (LHTES) system which is a new way for the performance improvement of the system of refrigeration by enhancing the heat transfer in the evaporator (Khan et al., 2013).

3.3.1.2 Freezing point depression

When solute is added to the pure solvent then the FP of the solution lower down than the freezing point of sole solvent. This phenomenon called as “freezing point depression (FPD)”. FPD is affected by the solution's concentration as well as its vapour pressure. This is a colligative feature, which indicates that the change is dependent on the quantity of the solute rather than the type of solute.

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To find out the FPD and water content which is unfrozen in frozen soil, the generalized Clapeyron mathematical formula is used. The freezing point of nonsaline soil lowers with water content decreasing and concentration increasing (Zhou et al., 2018). To decrease the FP of water, blend of EG and water is used as anti-freeze solution which is also a conventional coolant. By adding the anti-freeze in water make it possible to use water for wide range of temperature but for that we have to compromise the heat transfer performance because the heat capacity of mixture is less than that of water (Subhedar et al., 2018).

3.3.1.3 Thermal conductivity

The water-based liquids have high thermal conductivity because related to specific heat, water has much more thermal conductivity than other liquid coolants (Mohapatra and Loikits, 2005).

The thermophysical properties of cooling liquids or coolants play an important part in the heat transfer phenomenon of a system. The thermal characteristics of glycols are detrimental to heat transfer and reduce heat transfer efficiency. Efforts have been made to increase the thermal conductivity of glycol. By addition of the solid particles in the fluid in suspension condition, thermal conductivity can be improved. The enhancements in the thermal conductivity of EG-based β -SiC NFs are greater than PG-based NFs (Akilu et al., 2019).

Stable dispersions of solid nano-sized particles (usually <100 nm) in conventional fluids glycol alike are referred as nanofluids (Eastman et al., 1997). During the optimization process, the eminence of the disseminated state of nanofluids is a vital aspect for the thermophysical properties. Improved suspension stability leads to higher electrical and thermal conductivity values as well as better heat transfer capacities (Abdolbaqi et al., 2016).

3.3.2 Method for calculation of freezing point

To determine the freezing point from cooling curve, two basic concepts can be used to formulate an algorithm. These two methods are explained below:

Method-01:

The method which is mentioned here has been used to develop an algorithm which was used in this research work.

The “cooling rate” is the slope of the cooling curve at any point. Cooling rate can be defined as the change in the temperature divided by the change in time. Cooling means removing the thermal energy from a product into a cooling medium and speed at which this process occurs called “cooling rate”. In the fig. 3.7: cooling rate is shown as the slope of the curve at point ‘a’. if the graph having function equation $f(x)$, then differentiation of this function with respect to time gives cooling rate.

$$Y = f(x) \dots\dots\dots(1)$$

$$dY/dx = d[f(x)]/dx \dots\dots\dots(2)$$

$$\text{Slope of curve} = \tan(\Theta) = dY/dx \dots\dots(3)$$

It is assumed, $f(x) = \text{Temp.-time profile}$

So, $T = f(t)$, and

$$\text{Cooling rate} = \tan(\Theta) = dT/dt = (T_2 - T_1)/(t_2 - t_1) \dots\dots\dots(4)$$

Where, $T = \text{temperature } (^{\circ}\text{C})$, & $t = \text{time (min.)}$

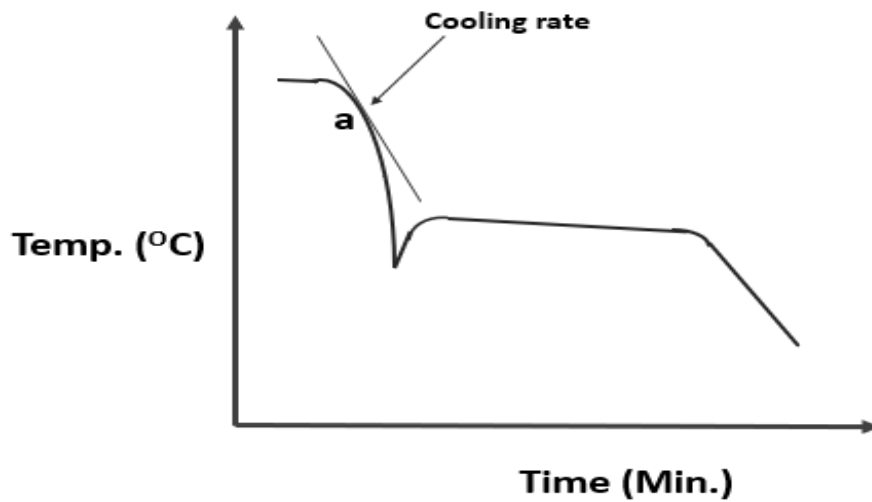


Fig. 3.2: Cooling curve showing cooling rate at point 'a'

Cooling rate is calculated by calculating the 1st derivative of a cooling graph. It increases the precision of the results during the finding of the typical features of the freezing curve. A zero value of the first derivative curve indicates a minimum or maximum on the cooling curve (Barlow & Stefanescu, 1998).

To determine F.P., cooling rate (dT/dt) should be zero because when freezing starts, slope of the curve becomes zero at initial stage and this condition was applied in the algorithm of this simulation program. There are several places on a cooling curve where the slope of the curve becomes zero, allowing us to identify the many processes that occur during the freezing of items using this technique.

Method-02:

This method was used by Kalidas et al. (2020) to determine the FP of the SZTLs. Initially, thermal cooling data were generated by freezing of the SZTLs and then cooling graphs were plotted.

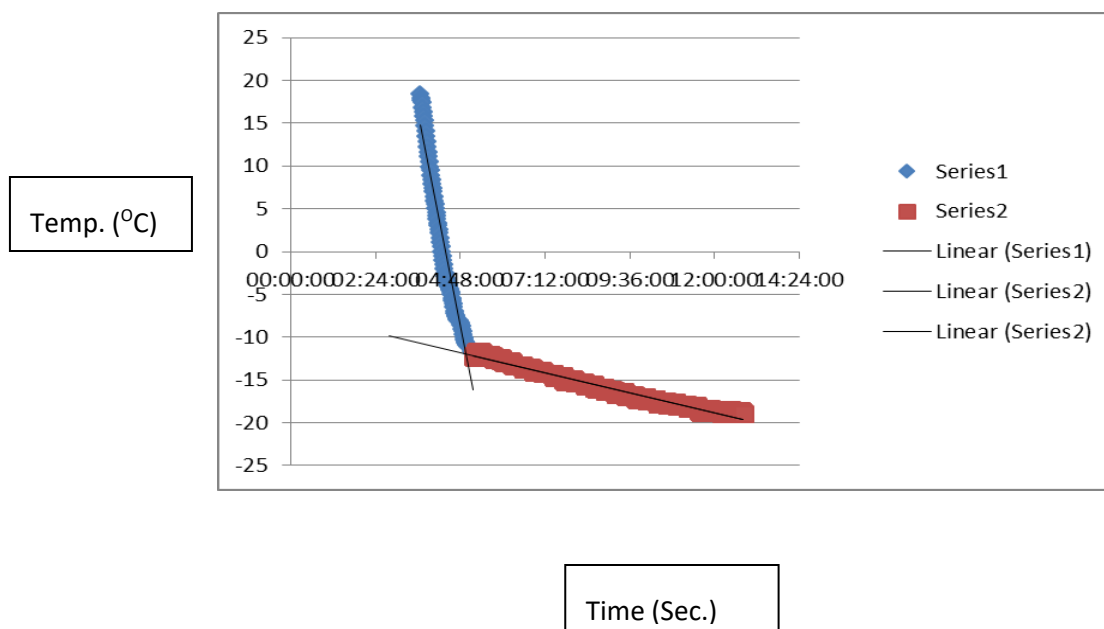


Fig. 3.3: Cooling curve having FP at intersection point

Cooling graphs were divided into two parts. First part was upto the supercooling of solutions and second part was from the initial freezing point to the completion of the crystallization process. Best fitted lines were drawn and intersection point was calculated for these two parts. This intersection point was considered as the freezing point of the solution.

$$Y_1 = a_1x + c_1 \dots \dots \dots (1)$$

$$Y_2 = a_2x + c_2 \dots \dots \dots (2)$$

For some solutions, it is very difficult to separate the solid phase from the liquid phase and supercooling is inevitable (Hoare, 1960).

3.3.3 Develop simulation program for freezing point determination

A suitable algorithm was formulated to develop simulation program for FP determination. The algorithm was based on the properties of the cooling curve. In simulation technique, algorithm plays an important role in selecting what information is considered from input and what kind of output is to be given. Now-a-days, use of algorithms in simulation work is an emerging technology in many fields like research, education, sports, entertainment, security etc. Algorithms need not be software: in the broadest sense, they are encoded procedures for transforming input data into a desired output, based on specified calculations (Gillespie, 2014). For any type of simulation program, a well-designed algorithm is required to perform a certain type of work.

If algorithms are not paired with any databases where they function then it is considered as pointless and inactive machine. Algorithms are not always about exhaustive prediction; sometimes they are about sufficient approximation (Gillespie, 2014). fundamentally as algorithm machines designed to store and read data, apply mathematical procedures to it in a controlled fashion, and offer new information as the output (Light, 1999). These all practices can also be done by human, but it requires more time and work.

Together, data structures and algorithms are two halves of the ontology of the world according to a computer (Manovich 1999). More than anything, algorithms are designed to be and prized for being functionally automatic, to act when triggered without any regular human intervention or oversight (Winner 1978). Algorithms do things, and their syntax embodies a command structure to enable this to happen (Goffey 2008). What we need is an interrogation of algorithms as a key feature of our information ecosystem (Anderson 2011).

As indicated in the previous section, a simulation software was built utilising equations and mathematical expressions. Using suitable coding principles, all of the linked formulas and equations are encoded in the Scilab software. A typical

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simulation program was developed to determine the freezing points and cooling rate of the solutions.

The flow chart which is mentioned below explains the working principle of this simulation program. It shows how the loop runs and identifies the cooling rate equal to zero and based on this function, it determines the freezing point of solutions.

3.3.3.1 Syntax of the simulation program

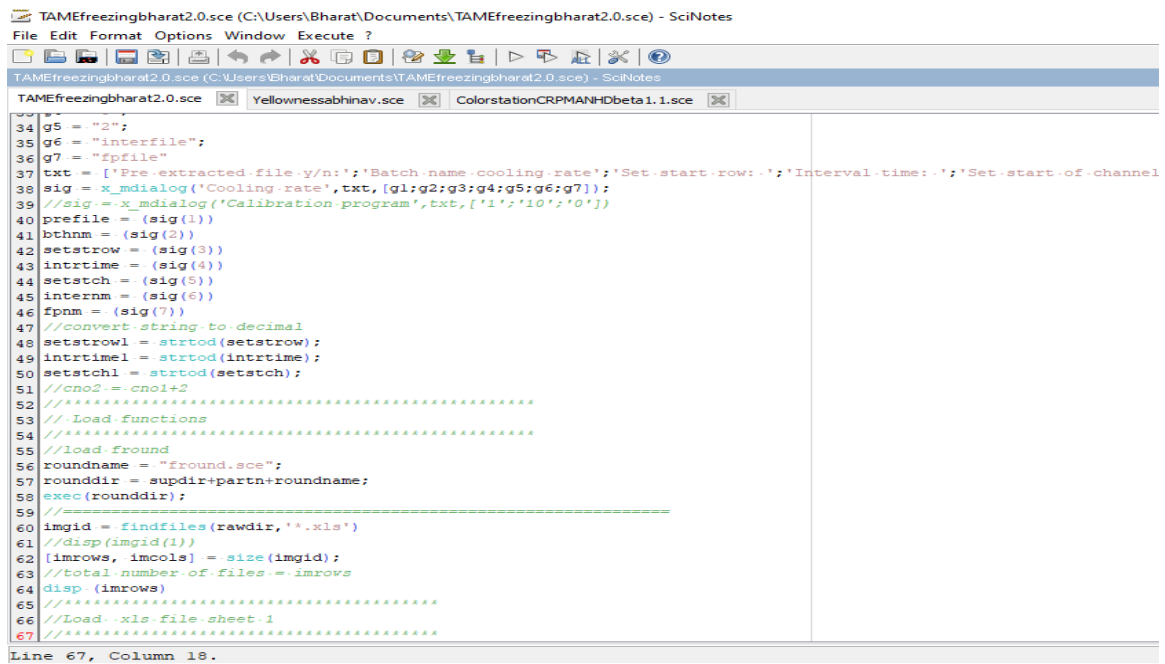
The syntax of this program is shown in the fig. 3.4 ('a' to 'e') below:

```
1 //*****
2 //Installation-check-Tempanaysismodule
3 //*****
4 //make-directories
5 clc
6 clear;
7 tic
8 //presetting-cvs-
9 bRes = csvDefault("eol","linux");
10 curdir=pwd();
11 [partdir, splitter] = strsplit(curdir, ["\"]);
12 partn = "";
13 pic = "Pictures";
14 picbas = partdir(1)+partn+partdir(2)+partn+partdir(3)+partn+pic;
15 mkdir(picbas, 'CST');
16 mkdir(curdir, 'TAM');
17 mvname = "TAM";
18 mvdirl = curdir+partn+mvname;
19 mkdir(mvdirl, 'Rawdata');
20 mkdir(mvdirl, 'Analyzeddata');
21 mkdir(mvdirl, 'Supportdata');
22 picraw = "Rawdata";
23 rawdir = mvdirl+partn+picraw;
24 curname = "Analyzeddata";
25 anadir = mvdirl+partn+curname;
26 supname = "Supportdata";
27 supdir = mvdirl+partn+supname;
28 disp('Installation-check-completed')
29 //copying-of-image-file-from-pictures-CST-to-Curpic
30 g1 = "y";
31 g2 = "coolratel";
32 g3 = "1";
33 g4 = "3";
34 g5 = "2";
```

Line 1, Column 0.

Fig. 3.4 (a)

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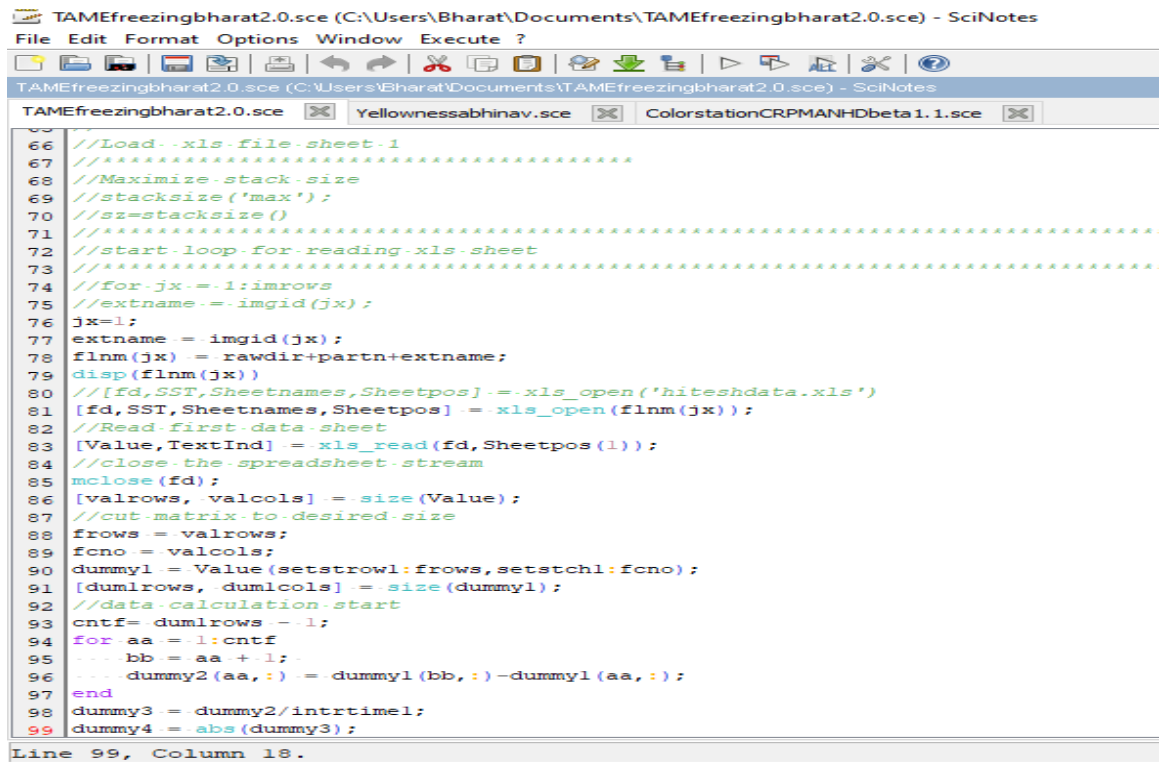
```

TAMEfreezingbharat2.0.sce (C:\Users\Bharat\Documents\TAMEfreezingbharat2.0.sce) - SciNotes
File Edit Format Options Window Execute ?
TAMEfreezingbharat2.0.sce Yellownessabhinav.sce ColorstationCRPMANHDbeta1.1.sce
34 g5 = "2";
35 g6 = "interfile";
36 g7 = "fpfile"
37 txt = ['Pre-extracted file.y/n:','Batch name.cooling.rate','Set.start.row:','Interval.time:','Set.start.of.channel
38 sig = x_mdialog('Cooling.rate',txt,[g1:g2:g3:g4:g5:g6:g7]);
39 //sig = x_mdialog('Calibration.program',txt,['1';'10';'0'])
40 prefile = (sig(1))
41 bthnm = (sig(2))
42 setstrow = (sig(3))
43 intrtime = (sig(4))
44 setstch = (sig(5))
45 internm = (sig(6))
46 fpmn = (sig(7))
47 //convert string to decimal
48 setstrowl = strtod(setstrow);
49 intrtime1 = strtod(intrtime);
50 setstchl = strtod(setstch);
51 //cno2 = cno1+2
52 //*****
53 //Load functions
54 //*****
55 //load fround
56 roundname = "fround.sce";
57 rounddir = supdir+partn+roundname;
58 exec(rounddir);
59 //*****
60 imgid = findfiles(rawdir,'*.xls')
61 //disp(imgid(1))
62 [imrows, imcols] = size(imgid);
63 //total number of files = imrows
64 disp(imrows)
65 //*****
66 //Load .xls file sheet 1
67 //*****

```

Line 67, Column 18.

Fig. 3.4 (b)



```

TAMEfreezingbharat2.0.sce (C:\Users\Bharat\Documents\TAMEfreezingbharat2.0.sce) - SciNotes
File Edit Format Options Window Execute ?
TAMEfreezingbharat2.0.sce Yellownessabhinav.sce ColorstationCRPMANHDbeta1.1.sce
66 //Load .xls file sheet 1
67 //*****
68 //Maximize stack size
69 //stacksize('max');
70 //sz=stacksize()
71 //*****
72 //start loop for reading xls sheet
73 //*****
74 //for jx = 1:imrows
75 //extname = imgid(jx);
76 jx=1;
77 extname = imgid(jx);
78 flnm(jx) = rawdir+partn+extname;
79 disp(flnm(jx))
80 //[[fd,SST,Sheetnames,Sheetpos] = xls_open('hiteshdata.xls')
81 [fd,SST,Sheetnames,Sheetpos] = xls_open(flnm(jx));
82 //Read first data sheet
83 [Value,TextInd] = xls_read(fd,Sheetpos(1));
84 //close the spreadsheet stream
85 mclose(fd);
86 [valrows, valcols] = size(Value);
87 //cut matrix to desired size
88 frows = valrows;
89 fcno = valcols;
90 dummy1 = Value(setstrowl:frows,setstchl:fcno);
91 [dum1rows, dum1cols] = size(dummy1);
92 //data calculation start
93 cntf = dum1rows - 1;
94 for aa = 1:cntf
95     bb = aa + 1;
96     dummy2(aa,:) = dummy1(bb,:) - dummy1(aa,:);
97 end
98 dummy3 = dummy2/intrtime1;
99 dummy4 = abs(dummy3);

```

Line 99, Column 18.

Fig. 3.4 (c)

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```

TAMEfreezingbharat2.0.sce (C:\Users\Bharat\Documents\TAMEfreezingbharat2.0.sce) - SciNotes
File Edit Format Options Window Execute ?
TAMEfreezingbharat2.0.sce (C:\Users\Bharat\Documents\TAMEfreezingbharat2.0.sce) - SciNotes
TAMEfreezingbharat2.0.sce Yellownessabhinav.sce ColorstationCRPMANHDbeta1.1.sce
99 dummy4 = -abs(dummy3);
100 dummy5 = fround(dummy4,2)
101 //generate-time-axis
102 [dum5rows, dum5cols] = size(dummy5);
103 kk = intrtime1
104 for i = 1:dum5rows;
105 jk = kk*i;
106 dummy6(i,1)=jk;
107 end;
108 //join-two-matrix-along-column.
109 dims=2;
110 dummy=cat(dims,dummy6,dummy5)
111 //*****
112 //Write-values-to-xls-file
113 //*****
114 extname = ".csv";
115 bthname = bthnm + extname;
116 filename = fullfile(anadir, bthname);
117 csvWrite(dummy, filename);
118 //write_csv(dummy, filename);
119 //*****
120 //start-calculation-to-create-master-file-mtd-zero
121 //*****
122 //raw-temperature-data
123 tummy1 = dummy1;
124 [tum1rows, tum1cols] = size(tummy1);
125 //raw-cooling-rate-data
126 summy1 = dummy;
127 [sum1rows, sum1cols] = size(summy1);
128 temp = "tempdata";
129 //run-loop-to-find-zero
130 cntrow = sum1rows;
131 cntcol = sum1cols;
132 for bb = 2:cntcol

```

Line 132, Column 17.

Fig. 3.4 (d)

```

TAMEfreezingbharat2.0.sce (C:\Users\Bharat\Documents\TAMEfreezingbharat2.0.sce) - SciNotes
File Edit Format Options Window Execute ?
TAMEfreezingbharat2.0.sce (C:\Users\Bharat\Documents\TAMEfreezingbharat2.0.sce) - SciNotes
TAMEfreezingbharat2.0.sce Yellownessabhinav.sce ColorstationCRPMANHDbeta1.1.sce
125 //raw-cooling-rate-data
126 summy1 = dummy;
127 [sum1rows, sum1cols] = size(summy1);
128 temp = "tempdata";
129 //run-loop-to-find-zero
130 cntrow = sum1rows;
131 cntcol = sum1cols;
132 for bb = 2:cntcol
133     bb2 = bb - 1;
134     for cc = 1:cntrow
135         tmpval = summy1(cc,bb);
136         if tmpval == 0 then
137             stval(cc) = tummy1(cc,bb2);
138             break
139         else
140             stval(cc) = tummy1(cc,bb2);
141         end
142     end
143     fptmp = tummy1(cc,bb2);
144     filename = string(bb2);
145     bth = temp + filename;
146     extname = ".csv";
147     bthname = bth + extname;
148     filename = fullfile(anadir, bthname);
149     csvWrite(stval, filename);
150 end
151 extname = ".csv";
152 bthname = fpthm + extname;
153 filename = fullfile(anadir, bthname);
154 csvWrite(fptmp, filename);
155 tt = toc();
156 disp(tt);
157
158

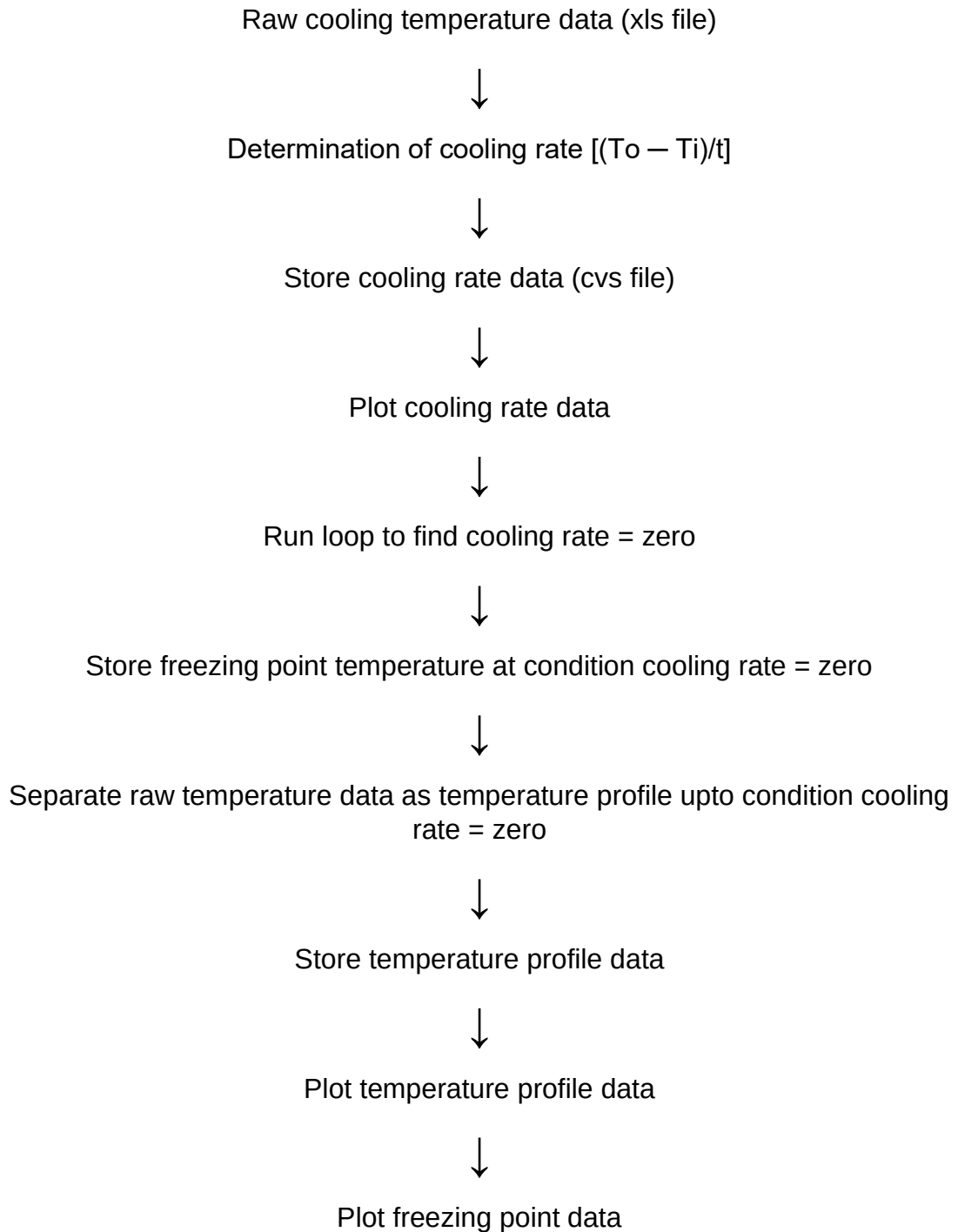
```

Line 158, Column 0.

Fig. 3.4 (e)

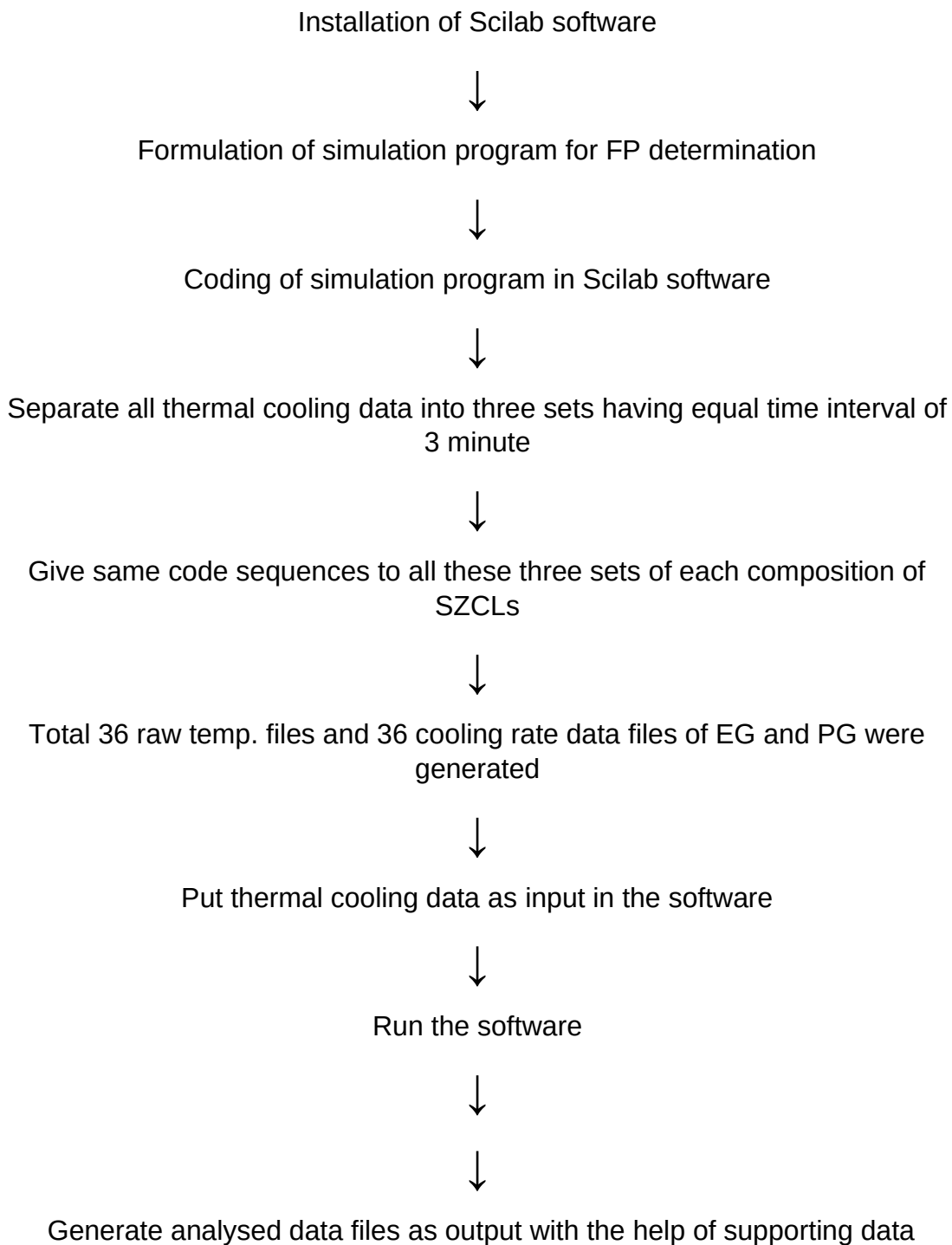
Fig. 3.4: Syntax of the simulation program ('a' to 'e')

3.3.3.2 Flow Chart of simulation program working principle

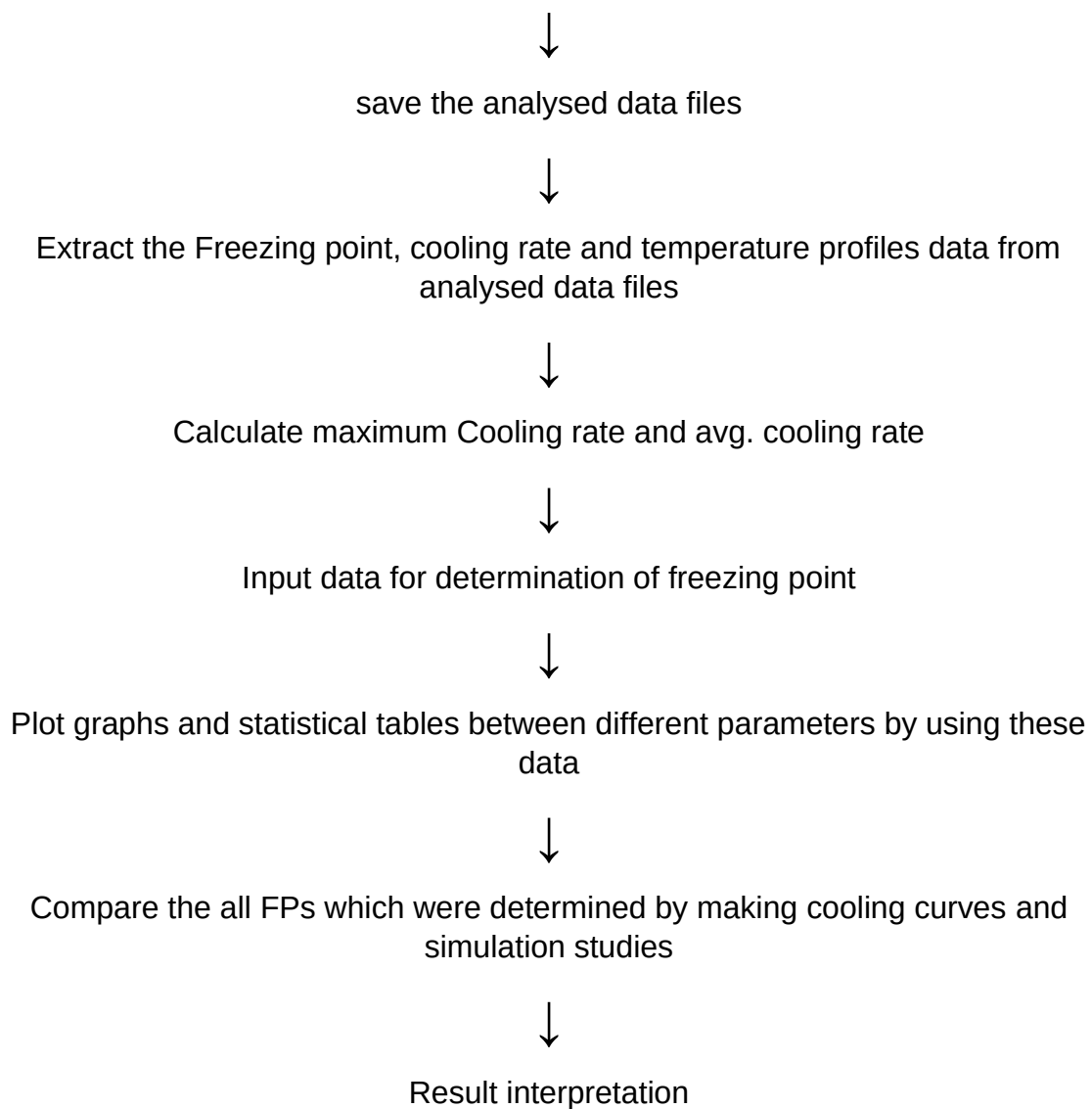


3.3.4 Determination of freezing points by simulation method with the help of thermal cooling data

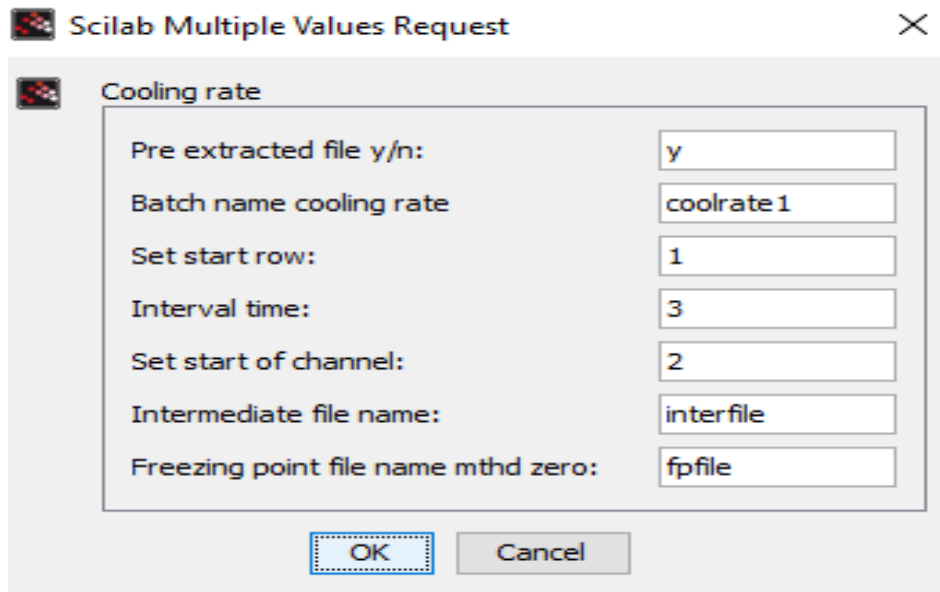
3.3.4.1 Flow Chart of procedure of research work



MATERIALS AND METHODS



MATERIALS AND METHODS



(A)

A1	3,0.429999999999999,0.37,0.2000000000000001,0.3300000000000002,0.4000000000000002,0.7299999999999998,1.0700000000000001																
	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	R
1	3,0.429999999999999,0.37,0.2000000000000001,0.3300000000000002,0.4000000000000002,0.7299999999999998,1.0700000000000001																
2	6,0.37,0.3300000000000002,0.3300000000000002,0.5,0.5,0.469999999999997,0.569999999999995,0.7700000000000002																
3	9,0.37,0.429999999999999,0.469999999999997,0.599999999999998,0.63,0.63,0.6700000000000004,0.7700000000000002																
4	12,0.4000000000000002,0.429999999999999,0.469999999999997,0.63,0.599999999999998,0.599999999999998,0.699999999999996,0.6700000000000004																
5	15,0.4000000000000002,0.469999999999997,0.5,0.569999999999995,0.569999999999995,0.599999999999998,0.599999999999998,0.599999999999998																
6	18,0.4000000000000002,0.429999999999999,0.429999999999999,0.5300000000000003,0.5300000000000003,0.569999999999995,0.569999999999995																
7	21,0.37,0.469999999999997,0.429999999999999,0.5,0.5,0.5300000000000003,0.569999999999995,0.569999999999995																
8	24,0.37,0.4000000000000002,0.4000000000000002,0.469999999999997,0.469999999999997,0.5,0.5,0.569999999999995																
9	27,0.469999999999997,0.429999999999999,0.4000000000000002,0.469999999999997,0.5,0.469999999999997,0.5,0.63																
10	30,0.5300000000000003,0.4000000000000002,0.429999999999999,0.4000000000000002,0.429999999999999,0.429999999999999,0.5300000000000003,0.599999999999998																
11	33,0.599999999999998,0.429999999999999,0.429999999999999,0.4000000000000002,0.469999999999997,0.469999999999997,0.5300000000000003,0.599999999999998																
12	36,0.569999999999995,0.5,0.5,0.5300000000000003,0.5300000000000003,0.5300000000000003,0.599999999999998																
13	39,0.5,0.4000000000000002,0.429999999999999,0.5300000000000003,0.469999999999997,0.5,0.469999999999997,0.5300000000000003																
14	42,0.5,0.469999999999997,0.429999999999999,0.5,0.469999999999997,0.5,0.469999999999997,0.429999999999999																
15	45,0.2300000000000001,0.299999999999999,0.299999999999999,0.2700000000000002,0.299999999999999,0.299999999999999,0.3300000000000002,0.2300000000000001																
16	48,0.13,0.2700000000000002,0.2000000000000001,0.2000000000000001,0.2300000000000001,0.2000000000000001,0.2300000000000001,0.2000000000000001																
17	51,0.13,0.2300000000000001,0.2300000000000001,0.2000000000000001,0.2000000000000001,0.1700000000000001,0.2000000000000001,0.2000000000000001																
18	54,0.2700000000000002,0.2300000000000001,0.2700000000000002,0.299999999999999,0.3300000000000002,0.3300000000000002,0.3300000000000002,0.3300000000000002																
19	57,0.37,0.299999999999999,0.3300000000000002,0.37,0.37,0.3300000000000002,0.3300000000000002,0.13																
20	60,0.299999999999999,0.3000000000000002,0.299999999999999,0.299999999999999,0.299999999999999,0.3300000000000002,0.2300000000000001,0.5699999999999995																
21	63,0.1000000000000001,0.2000000000000001,0.1700000000000001,0.1700000000000001,0.2000000000000001,0.13,0.13,0.1700000000000001,0.13																
22	66,0.029999999999999,0.1700000000000001,0.1000000000000001,0.0700000000000007,0.1000000000000001,0.1000000000000001,0.1000000000000001,0.0700000000000007																
23	69,0.1000000000000001,0.1700000000000001,0.1700000000000001,0.13,0.1700000000000001,0.13,0.13,0.1000000000000001																
	coolrate1																

(B)

Fig. 3.5: Scilab pop-up run window (a) and cooling rate data file (B)

3.3.5 Comparison between the results of simulation method and manual method

Freezing points of the different SZTLs were determined by simulation method and compared with the manual method. Freezing points which were measured by simulation method were explained by tables and bar charts. Thermal cooling data of total ninety-six solutions were taken into consideration for determination of their freezing points in both methods. Forty- eight solutions of Ethylene Glycol with distilled water (conc. From 1:1 to 1:8) having salt concentration from 0 % to 5 % NaCl in each and same for the Propylene Glycol were used.

RESULTS AND DISCUSSION

4. RESULTS AND DISCUSSION

This chapter is about the result and discussion part of the findings of the experiments conducted during this research work. Sub-zero temperature liquids are a group of liquids which are specifically formulated for application under minus temperatures. Such liquids are used as primary or secondary coolants and must possess anti-freeze characteristics when used under the operating temperature range. Glycols such as ethylene glycol and propylene glycol are widely used as base material for coolants. Number of additives like salts, additives, nanoparticle, etc are added for enhancing performance of SZTL. Test solutions comprised of blends of binary solution of glycol/water with different percent of NaCl (1-5 %) had varying freezing points. Manual plotting and determination of freezing point is a time-consuming process. In the present study, thermal cooling data of SZTLs were analyzed. Freezing point of ethylene glycol (EG) and propylene glycol (PG) based SZTLs solutions were determined using simulation technique.

4.1 Determination of cooling rate of SZTLs

Cooling rate of SZTLs were calculated and plotted as a function of time. This cooling rate data was used in the simulation method to identify and segment the cooling curve. As the cooling rate tends to zero, the point can be marked to determine the initial freezing point.

4.1.1 Cooling rate of EG-based SZTLs

Cooling rate (CR) of EG-based SZTLs with 0 % NaCl is shown in the Fig. 4.1 (see table-1 of annexure-I). After 90-100 min from initiation of cooling process, CRs of all blends dropped from 1.1 to 0.20 °C/min. In the later part of cooling, CR became constant (0.2 to 0.0 °C/min). During crystallization phase, CR was found higher when EG concentration was reduced from R11 to R18. In the crystallization phase, mean value of CRs were in the range of 0.058 to 0.093 °C /min. Maximum values were observed for blends R17 and R18 which were 1.1 °C/min and 1.07 °C/min respectively. In general, direct cooling curves do

not clearly give the required parameters and derivative curves are preferred, which can identify smaller peaks corresponding to very small heats of transformation (Gowri and Samuel, 1992).

Cooling rate (CR) of EG-based SZTLs with 1 % NaCl is shown in the Fig. 4.2 (see table-2 of annexure-I). Initially rapid cooling ($1.7\text{ }^{\circ}\text{C/min}$) was observed due to high temperature gradient when initial solution temperature was $20\text{ }^{\circ}\text{C}$ and was exposed to a low temperature environment of $-18\text{ }^{\circ}\text{C}$. CR of all blends exhibited exponential decrease from 1.7 to $0.20\text{ }^{\circ}\text{C/min}$ and then remained almost constant at $0.2\text{ }^{\circ}\text{C/min}$. CR was found higher for diluted EG solutions with higher percentage of water and was of increasing trend from R11 to R18. EG % for various ratios of SZTL R11, R12, R13, R14, R15, R16, R17 and R18 were 50, 33.34, 25, 20, 16.67, 14.28, 12.5, 11.12 %, respectively. Higher concentration of ethylene glycol was not considered as it adversely affects the specific heat and thus the heat transfer capacity. At $0\text{ }^{\circ}\text{C}$, specific heat capacity of 0, 20, 40, 60, 80 and 100 % EG water binary solution is 1.0038, 0.93576, 0.85858, 0.76768, 0.66304 and 0.54467 kcal/(kg $^{\circ}\text{C}$). The specific heat capacity of ethylene glycol and water solution is less than the pure water. It implies that in a heat transfer system using ethylene glycol-based solution, flow rate of the liquid must be increased compared to a system using pure water to compensate the heat transfer. CR was maximum ($1.7\text{ }^{\circ}\text{C/min}$) for R18 while minimum values ($0.83\text{ }^{\circ}\text{C/min}$) were obtained for R12 and R14. Mean value of CR was found higher for diluted solutions. It may be due to the higher thermal conductivity of dilute solution. The thermal conductivity of ethylene glycol is lower than that of water; hence when added to fluid, it can affect the heat transfer performance (Jwo and Teng, 2005).

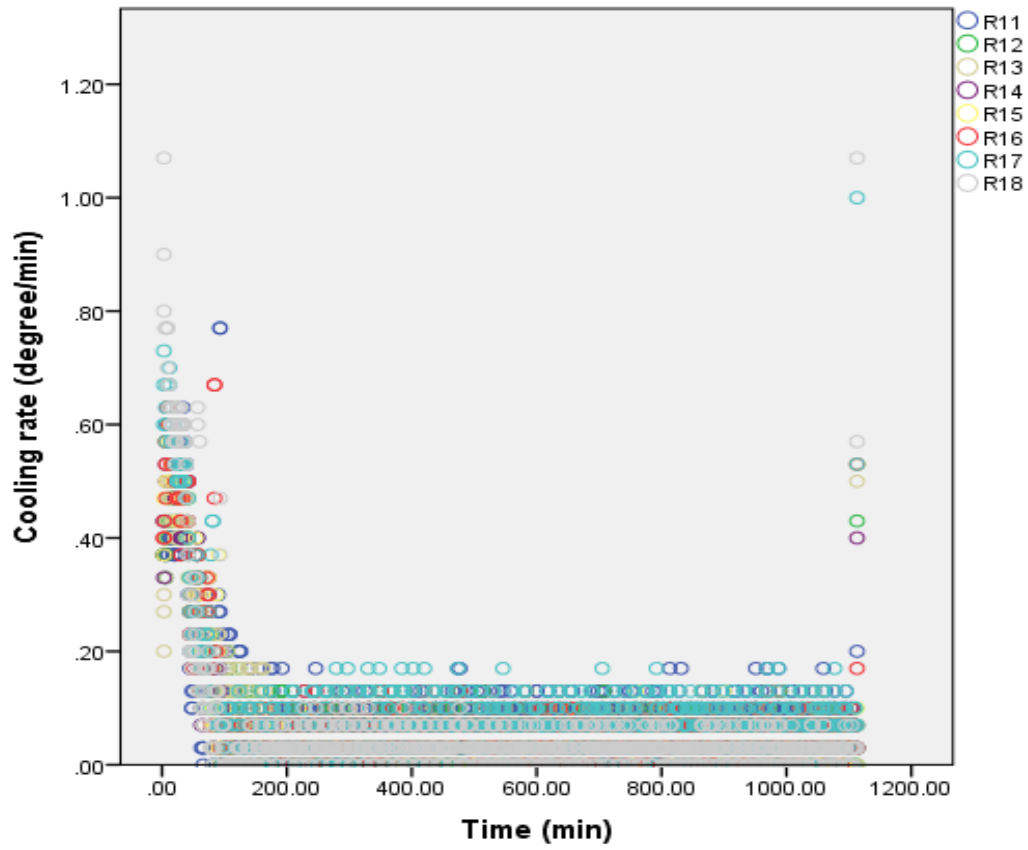


Fig. 4.1: Cooling rate profile of EG-based SZTLs with 0 % NaCl

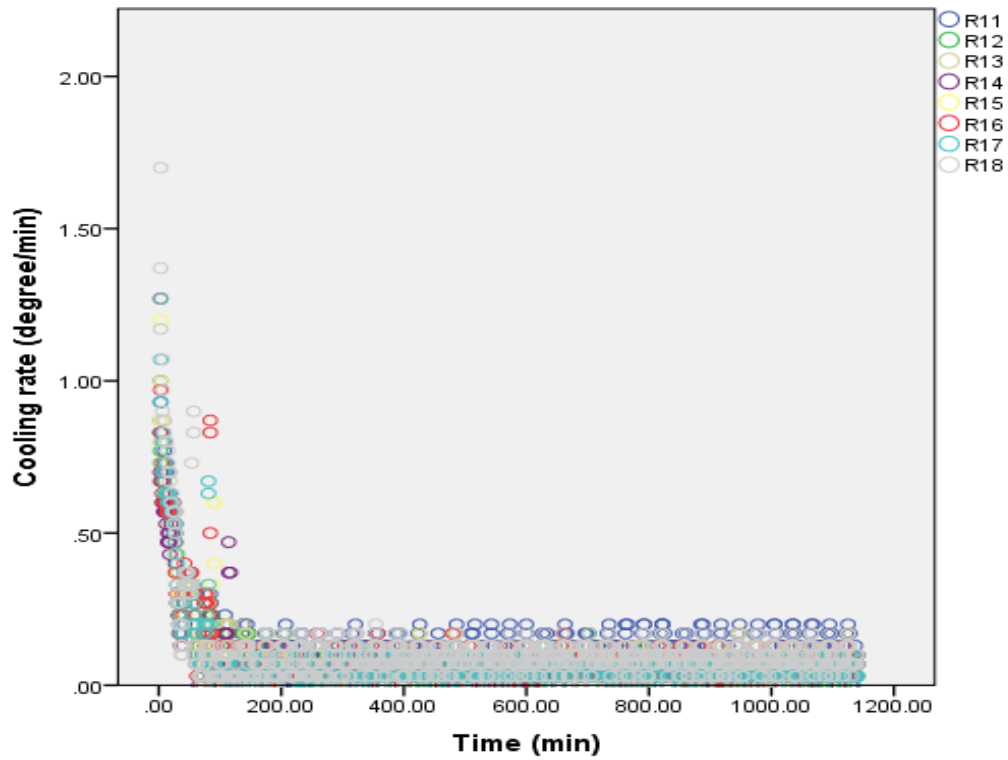


Fig. 4.2: Cooling rate profile of EG-based SZTLs with 1 % NaCl

CR of EG-based SZTLs having 2 % NaCl in their mixture were calculated and results are plotted in the Fig. 4.3 (see table-3 of annexure-I). CR of the blends during the supercooling process was around 1.40 °C/min initially and then reduced to 0.25 °C/min within 90 min. After supercooling process, CR became almost constant between 0.0 to 0.2 °C/min for these blends. Average CR over the entire duration of experiment was found between 0.095 to 0.066 °C/min and it was decreasing as concentration of blends was decreasing. Maximum value (1.37 °C/min) was for R18 which was significantly ($p < 0.05$) higher for R12 and R13 (0.93 °C/min). CR of blend R11 was recorded at higher value and it might be due to high concentration of EG. The tendency of nonpolar groups to adhere to one another in an aqueous environment is known as hydrophobic bonding (Kozak et al., 1968). Solutions of PEG in water provide typical examples of polymer solutions in which strong association and clustering of solvent molecules may occur and in which orientation-dependent interactions are dominant (Saeki et al., 1977).

CR of EG-based SZTLs having 3 % NaCl in their mixture were determined and results are shown in the Fig. 4.4 (see table-4 of annexure-I). CR of the blends during the cooling process was around 1.60 °C/min initially and then reduced to 0.25 °C/min within 80 min. After Newtonian cooling phase, CR became almost constant between 0.0 to 0.2 °C/min for these blends. Undercooling parameters are affected by Increasing the cooling rate for both in the region of liquidus as well as eutectic solidification (Gowri and Samuel, 1992). Average CR was found between 0.068 to 0.1 °C/min. Maximum CR values of R15, R16, R17, and R18 were 1.5 °C/min, 1.67 °C/min, 1.27 °C/min and 1.03 °C/min respectively. After the initiation of the crystallization process, CRs of R15 & R16 were found higher than any other blends. When EG is mixed with water, the properties of the two combines to create a lower freezing point than either could have individually done. This interaction helps to formulate eutectic solutions which provide freeze and burst protection for the closed loop system.

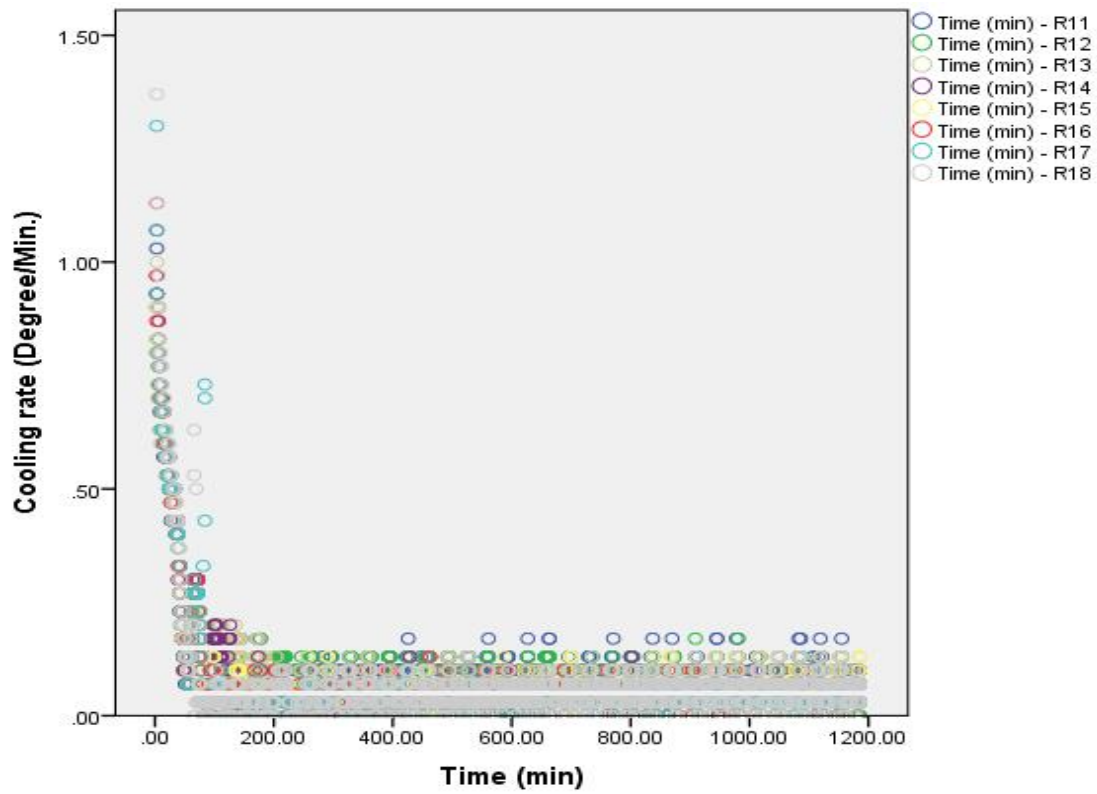


Fig. 4.3: Cooling rate profile of EG-based SZTLs with 2 % NaCl

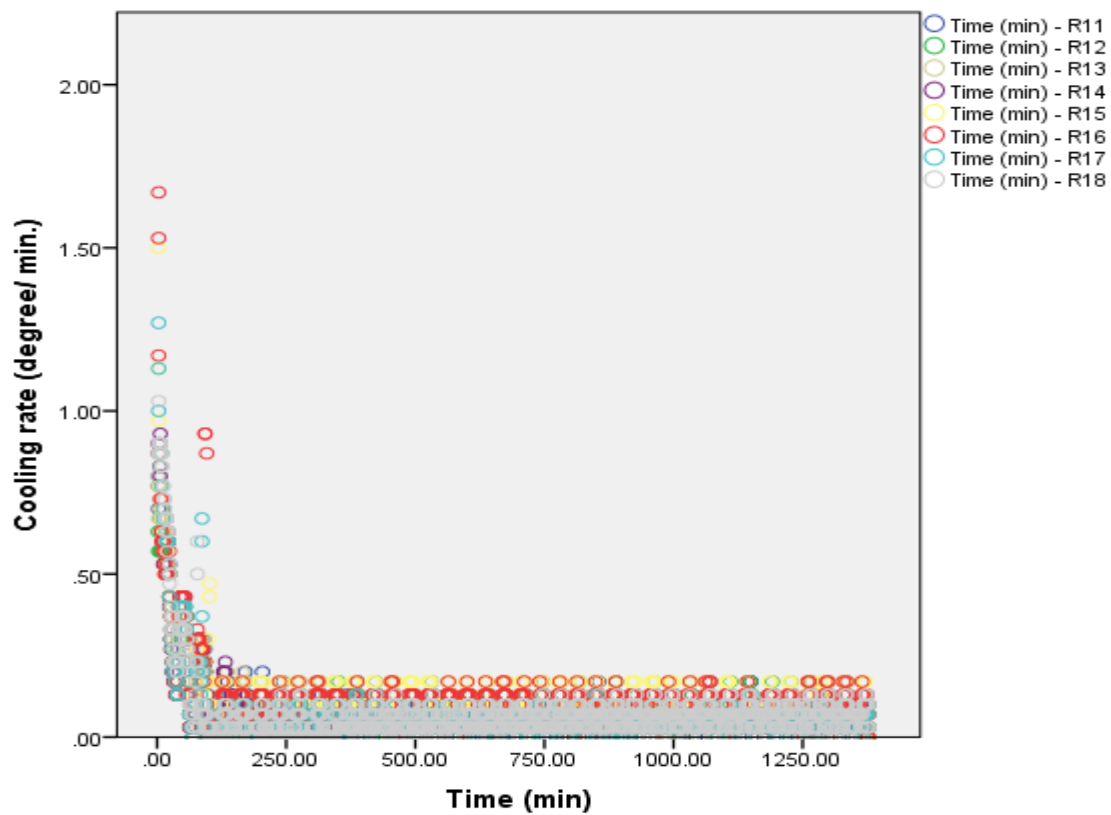


Fig. 4.4: Cooling rate profile of EG-based SZTLs with 3 % NaCl

Cooling rate (CR) of EG-based SZTLs with 4 % NaCl is shown in the Fig. 4.5 (see table-5 of annexure-I). After the initiation of cooling process, CRs of all blends decreased from 1.2 to 0.1 °C/min in next 50 min and then became almost constant (0.12 °C/min) during super cooling phase. The supercooling point (SCP) is defined as the temperature at which spontaneous freezing of body fluids is initiated when cooled below the freezing point (Carrillo et al., 2004). The SCP is indicated by the release of the latent heat of fusion, or exotherm (Denlinger et al., 1991). Maximum CR was in the range of 0.93 to 1.2 °C/min. Mean values during the entire duration of experiments was in range 0.054 to 0.109 °C/min.

CR of EG-based SZTLs having 5 % NaCl in their mixture were determined and results are shown in the Fig. 4.6 (see table-6 of annexure-I). CR of the blends during the Newtonian cooling region was around 1.0 °C/min initially and then reduced to 0.1 °C/min within 80 min. Initial cooling rate observed for R11, R12, R13, R14, R15, R16, R17 and R18 was 0.83, 0.77, 0.97, 0.90, .090, 0.90, and 1.0 °C/min, respectively. After supercooling process, CR dropped in the range of 0.0 to 0.08 °C/min for these blends. Many materials do not immediately solidify at freezing point. Rather, nucleation occurs in them at a lower temperature. This phenomenon is usually termed “supercooling” or “subcooling” in the literature. Understanding, prediction and, if possible, prevention, or at least reduction, of supercooling are very important specifically to latent heat thermal energy storage (LHTES) systems, because the temperature differences in them must be small in order to achieve higher efficiency (Uzan et al., 2017). Average CR for the entire duration of experiment was found between 0.031 to 0.035 °C/min.

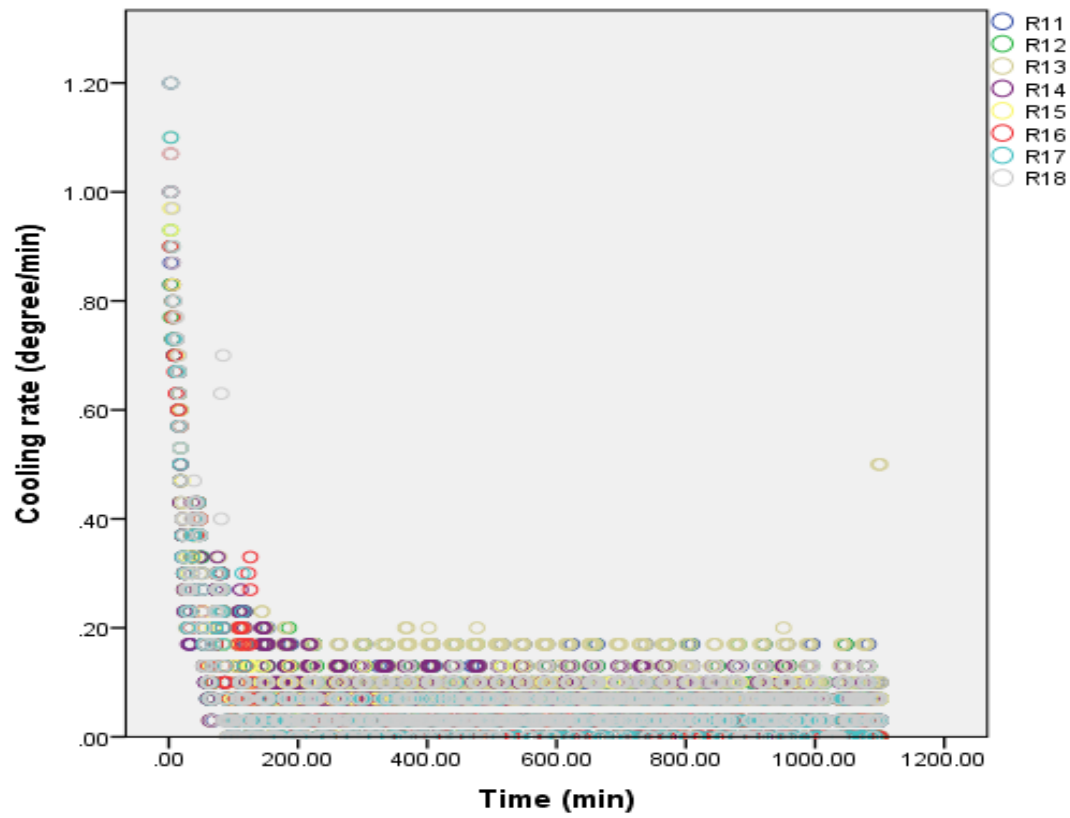


Fig. 4.5: Cooling rate profile of EG-based SZTLs with 4 % NaCl

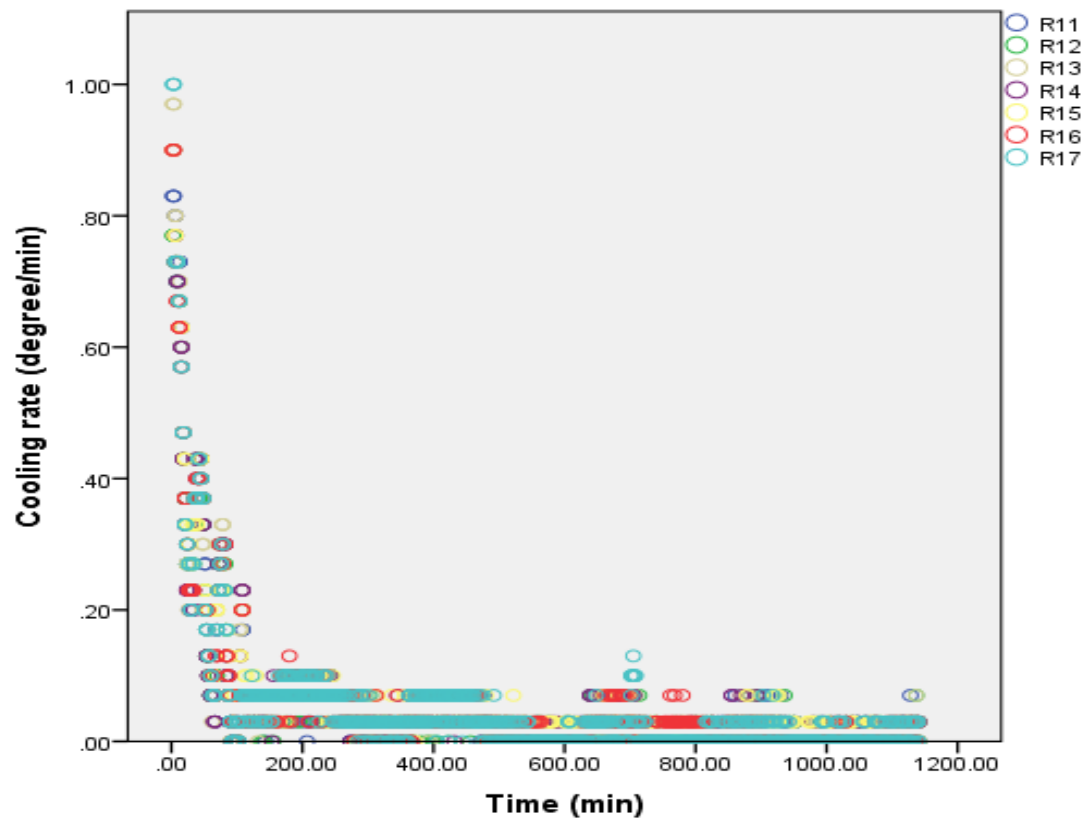


Fig. 4.6: Cooling rate profile of EG-based SZTLs with 5 % NaCl

4.1.2 Cooling rate profile of PG-based SZTLs

CR of PG-based SZTLs solutions with 0 % NaCl was determined and results are shown in the Fig. 4.7 (see table-7 of annexure-I). Initially CRs of some blends (R14, R16 and R17) were in the range of 0.37-0.5 °C/min. CR dropped exponentially to 0.2 °C/min and there were multiple incidences where it was 0 °C/min. The result implies that there was no temperature change during time interval of three minutes. The reason for low rate of cooling may be because the SZTLs were not agitated and the air inside the cooling cabinet was stagnant. Higher rates of cooling could have been possible by use of chilled air blower. There were few isolated cases when high CR was observed as for R11 having CR equal to 1.29 °C/min. It may be due to data acquisition error in the data logger. Mean CRs were found between 0.014 to 0.019 °C/min. Maximum and mean value of CR of PG-based SZTLs (0 % NaCl) was found lower than EG-based SZTLs (0 % NaCl). It was due to rapid freezing method used for EG SZTLs while slow freezing method was employed in case of PG SZTLs. Another possible reason may be higher thermal conductivity of EG solution than PG solution at the same concentration. Thermal conductivity of EG solution is higher than PG solution at the same concentration. Results revealed that the thermal conductivity of nanofluids depends not only on nanoparticle concentrations and temperature, but also in the types of base fluids (Leena and Srinivasan, 2018). Using higher concentration of glycol reduces the amount of heat the system can hold and carry. It causes decrease in efficiency and thus increases energy costs during the cooling or heating process.

CR of PG-based SZTLs solutions with 1 % NaCl was determined and results are shown in the Fig. 4.8 (see table-8 of annexure-I). Initially CRs of blends were ranging from 0.17 to 0.43 °C/min. which decreased to 0.1 °C/min within 100 min of cooling process. Cyclic peaks were observed during the crystallization phase. It may be due to temperature cut off point being set at – 18 °C of cooling cabinet. Baudot and Odagescu (2004) observed the two separated bumps in the crystallization peaks at high cooling rates and the second one decreasing when the cooling rate decreases to the advantage of the first one. Maximum initial CR was 0.43 °C/min for R16 while minimum

value was for R12 (0.17 °C/min). Overall mean value of CR was ranging from 0.044 to 0.049 °C/min. It was observed that CR was decreasing with decreasing in concentration ratio.

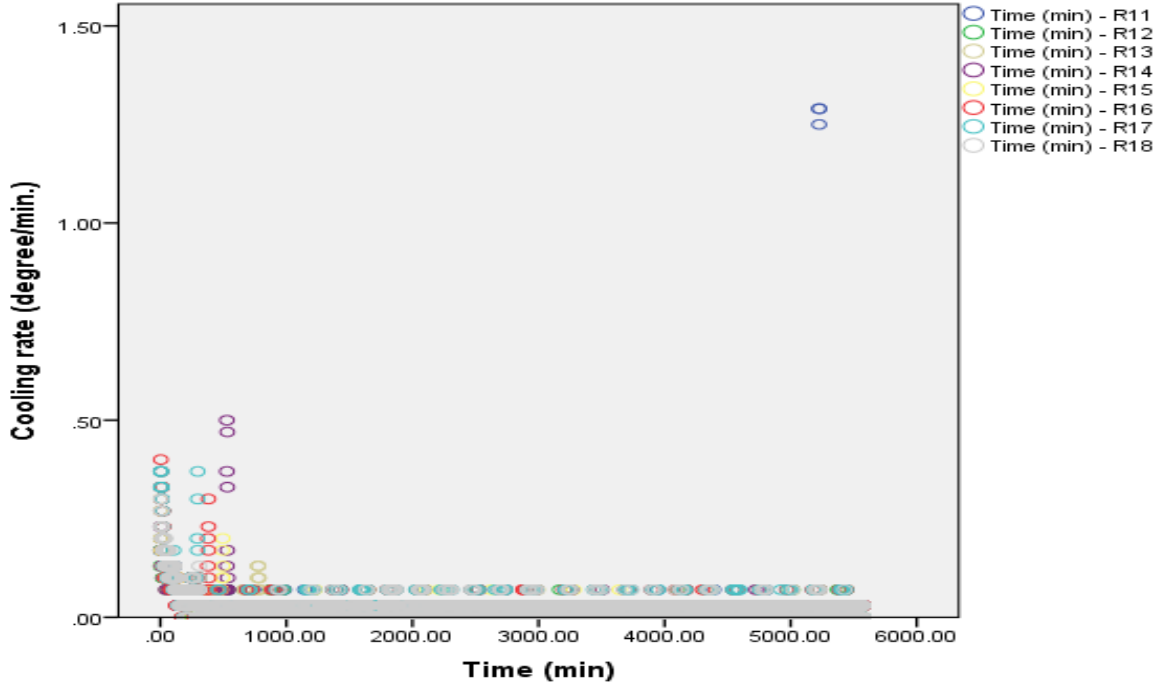


Fig. 4.7: Cooling rate profile of PG-based SZTLs with 0 % NaCl

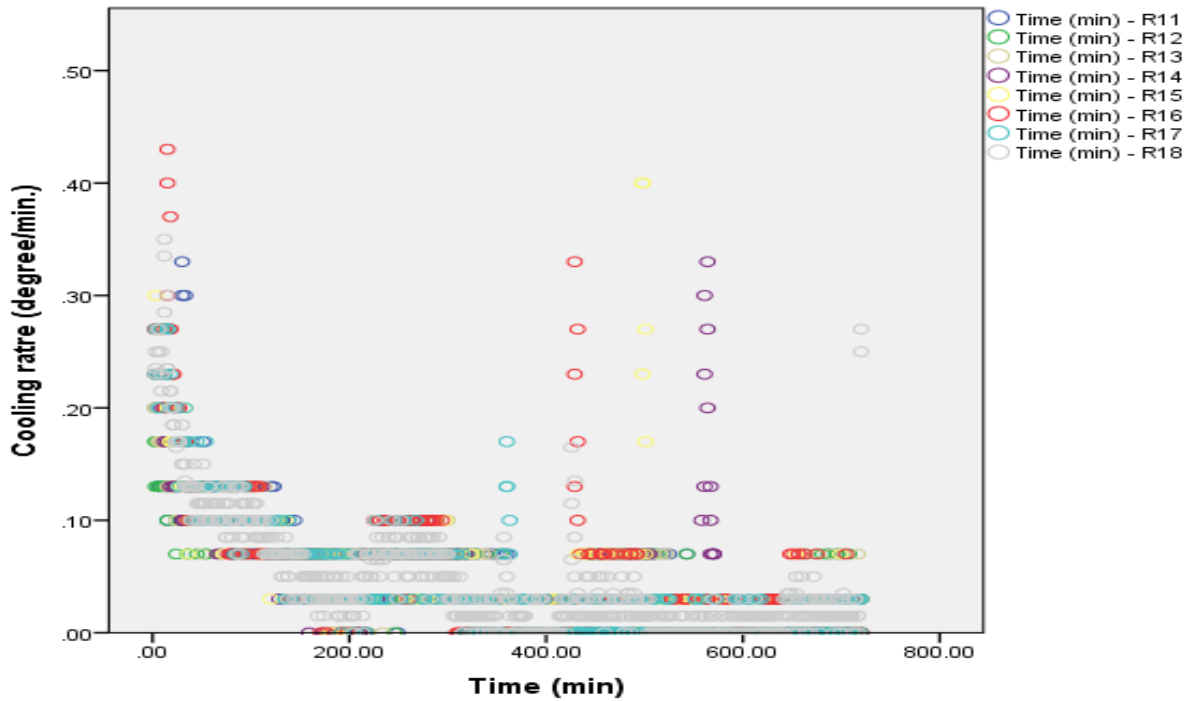


Fig. 4.8: Cooling rate profile of PG-based SZTLs with 1 % NaCl

CR of PG-based SZTLs with 2 % NaCl were determined and obtained results are shown in the Fig. 4.9 (see table-9 of annexure-I). Initial CRs of R18 & R17 were 0.33 °C/min and 0.27 °C/min, respectively. Cooling rate was decreasing for initial 100 min and then became constant below 0.1 °C/min. As concentration ratio was increased from R18 to R11, CR of blend decreased from 0.33 to 0.20 °C/min. It was due to the high content of PG in R11 solution compare with other solutions. Thermal conductivity of PG solution decreases with increase in PG content in solution (ASHRAE handbook, 1985). Average CRs of solution for R11, R12, R13, R14, R15, R16, R17 and R18 were 0.015, 0.014, 0.012, 0.013, 0.016, 0.014, 0.012 and 0.015 °C/min, respectively. Minimum CR value of all these blends was 0.0 °C/min.

CR of PG-based SZTLs with 3 % NaCl were determined results are shown in the Fig. 4.10 (see table-10 of annexure-I). Cooling rate followed an exponential decreasing trend for initial 100 min and then became constant below 0.2 °C/min during the latter part of the study. There were few isolated peaks (6.00 °C/min) and it may be due to the instrumental or logging error. It shows that an algorithm is required to identify and filter out such data points. Average CR decreased from 0.023 to 0.018 °C/min with decrease in concentration ratio. Mean CR value of the solutions having 3 % NaCl was found higher than the solutions having 2 % NaCl. As data have shown by Ramires et al., (1994) that the thermal conductivity was decreasing with increase in concentration of solutions.

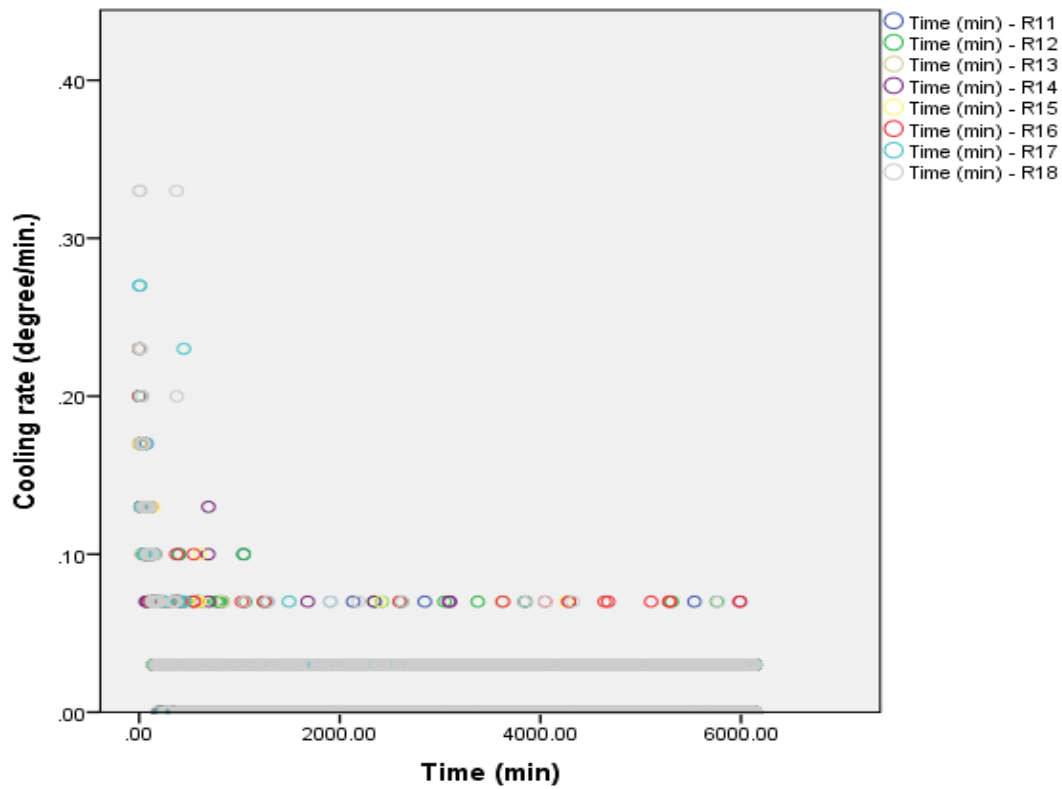


Fig. 4.9: Cooling rate profile of PG-based SZTLs with 2 % NaCl

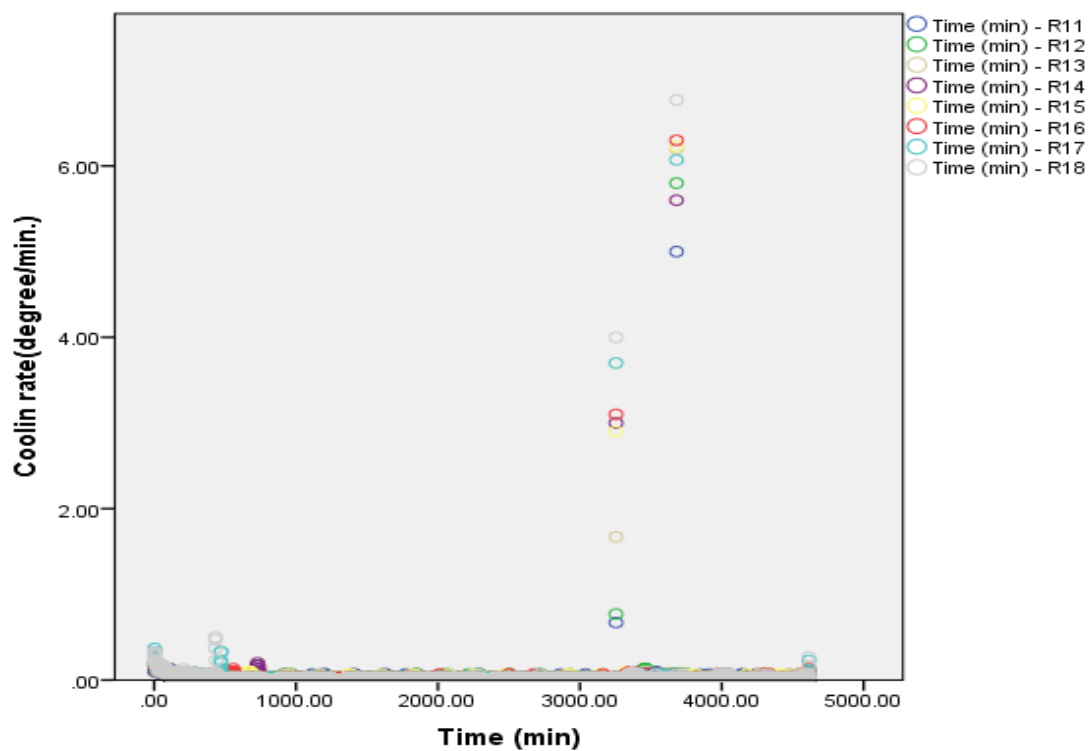


Fig. 4.10: Cooling rate profile of PG-based SZTLs with 3 % NaCl

CR of PG-based SZTLs solutions with 4 % NaCl was determined and results are shown in the Fig. 4.11 (see table-11 of annexure-I). Initially CRs of blends were ranging from 3.5 to 5.23 °C/min. which decreased to 0.1 °C/min. within 100 min. and then became constant between 0.0 to 0.1 °C/min. in this graph. Average CR was decreasing from 0.0215 °C/min. to 0.0153 °C/min. when concentration ratio was increased from R18 to R14 and then average CR increased from 0.0155 °C/min. to 0.0212 °C/min. when concentration ratio was increased from R13 to R11. The CR of PG-SZTLs (4 % NaCl) was lower than the CR of EG-SZTLs (4 % NaCl).

CR of PG-based SZTLs with 5 % NaCl were determined and obtained results are shown in the Fig. 4.12 (see table-12 of annexure-I). Cooling rate was decreasing for initial 200 min. and then became constant below 0.1 °C/min. At this point, initial freezing point was achieved. Maximum CR values were decreasing from 0.77 °C/min. to 0.23 °C/min. when we moved from R18 to R12 except R11 whose CR was found equal to 1.27 °C/min. It is because heat transfer from diluted PG-solution is higher than the concentrated PG-solution. According to Perez-Tavernier et al., (2019), the mixtures of water and glycols are typically employed in order to decrease the FP of water. Average CR of R14 & R15 were 0.01 °C/min. which is minimum avg. CR while highest avg. CR was determined for R11 which was 0.02 °C/min.

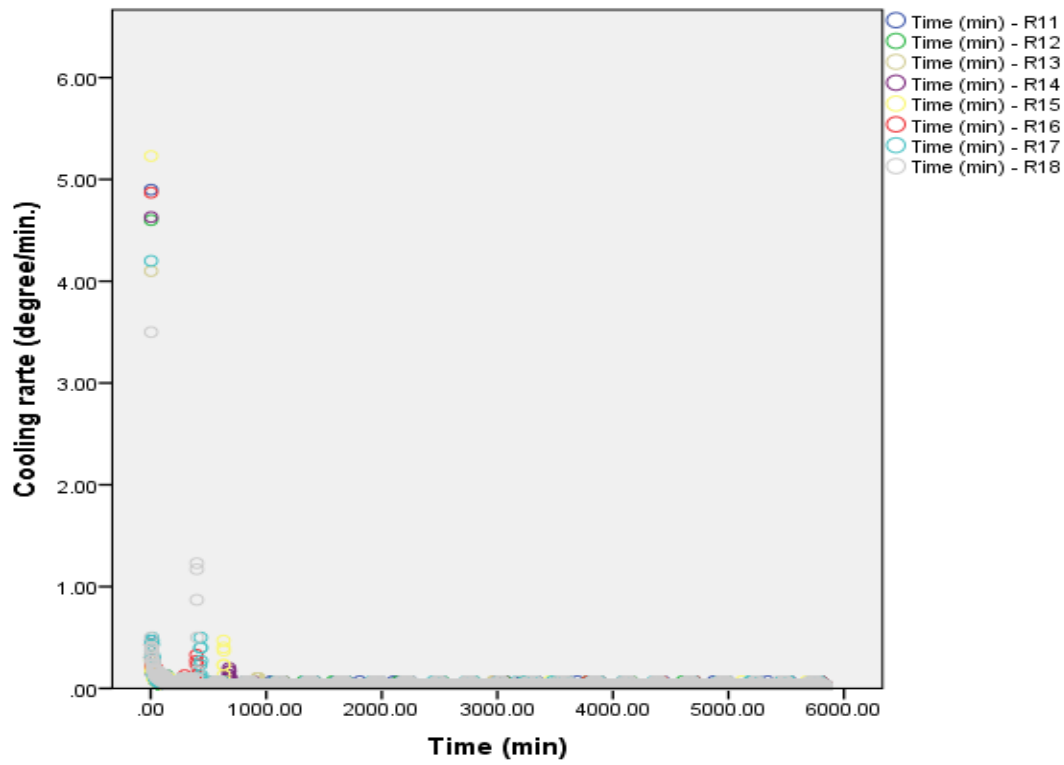


Fig. 4.11: Cooling rate profile of PG-based SZTLs with 4 % NaCl

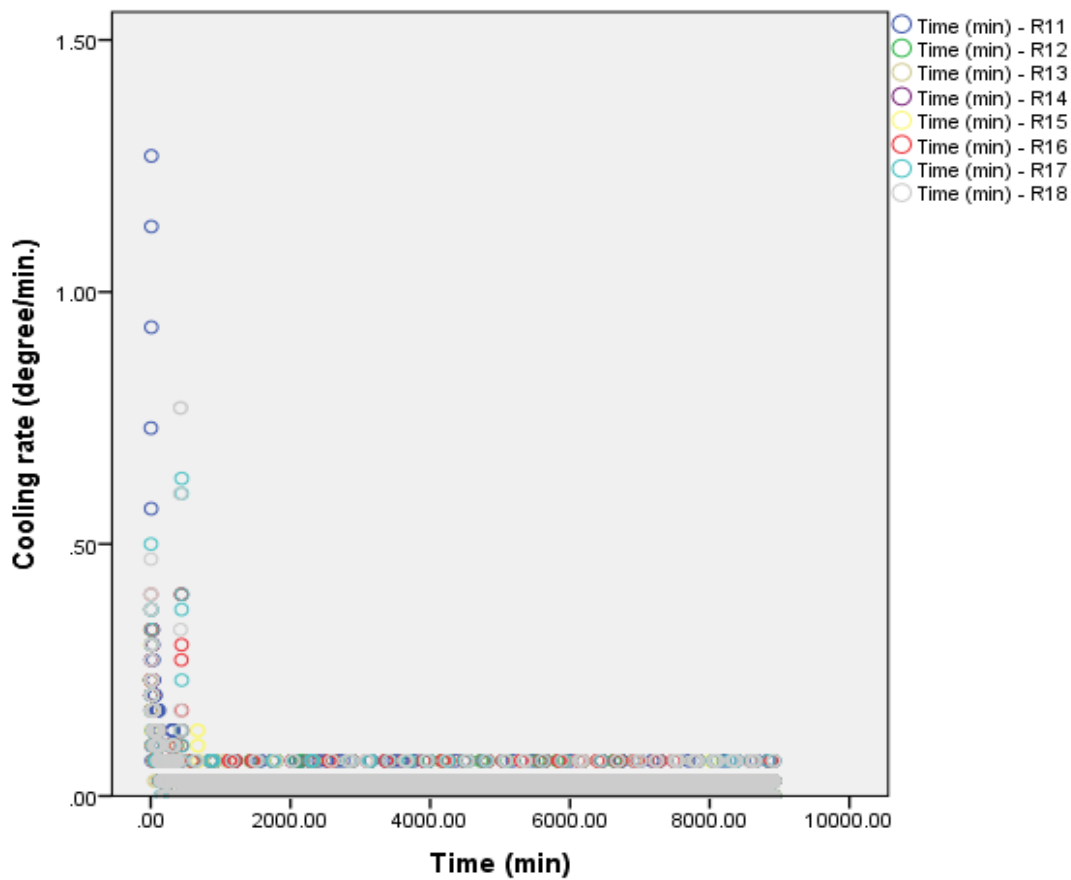


Fig. 4.12: Cooling rate profile of PG-based SZTLs with 5 % NaCl

4.2 Segmented temperature profile during freezing of SZTLs

Simulation program was used to determine the freezing point of the solutions and thermal cooling data were selected upto the initial freezing point. which were based on the condition 'cooling rate = zero'. Selected temperature profiles are drawn below based on the selected thermal cooling data.

4.2.1 Temperature profile of EG-based SZTLs

Segmented temperature profile of EG-SZTLs (0 % NaCl) is shown in the Fig. 4.13. Freezing points of these solutions were found between -8.27°C to -12.9°C . Average time taken by the solutions R11, R12 & R13 to reach at FP were 116 min. where for the solutions from R14 to R18, it was around 100 min. Due to the high concentration of the solutions R11, R12, & R13 heat transfer rate was low subsequently it took more time to freeze. Thermal conductivity and specific heat of the solution was affected by the concentration ratio. When the thermal conductivity of heat transfer fluids increases, their heat transfer property increases too (Wang, 2012).

Temperature profile for EG-SZTLs (1 % NaCl) is shown in the Fig. 4.14. Freezing points of these solutions for R11, R12, R13, R14, R15, R16, R17 and R18 were -11.4 , -12.2 , -10.8 , -10.37 , -11.2 , -9.97 , -9.47 and -9.30°C , respectively. In this figure, it can be clearly observed that FPs of all these solutions are determined at the same time. According to simulation result, total 69 min was taken by the solutions to reach at their freezing point temperature. As concentration decreased from R11 to R18, temperature profile rised in upward direction except R12 which was at higher temperature for the same time. Trend of decreaseing cooling rate of these sloutions were almost similar upto the initiation of freezing of the solutions. Specific heat of the solutions increases as we move from R11 to R18 as the concentration of EG reduces.

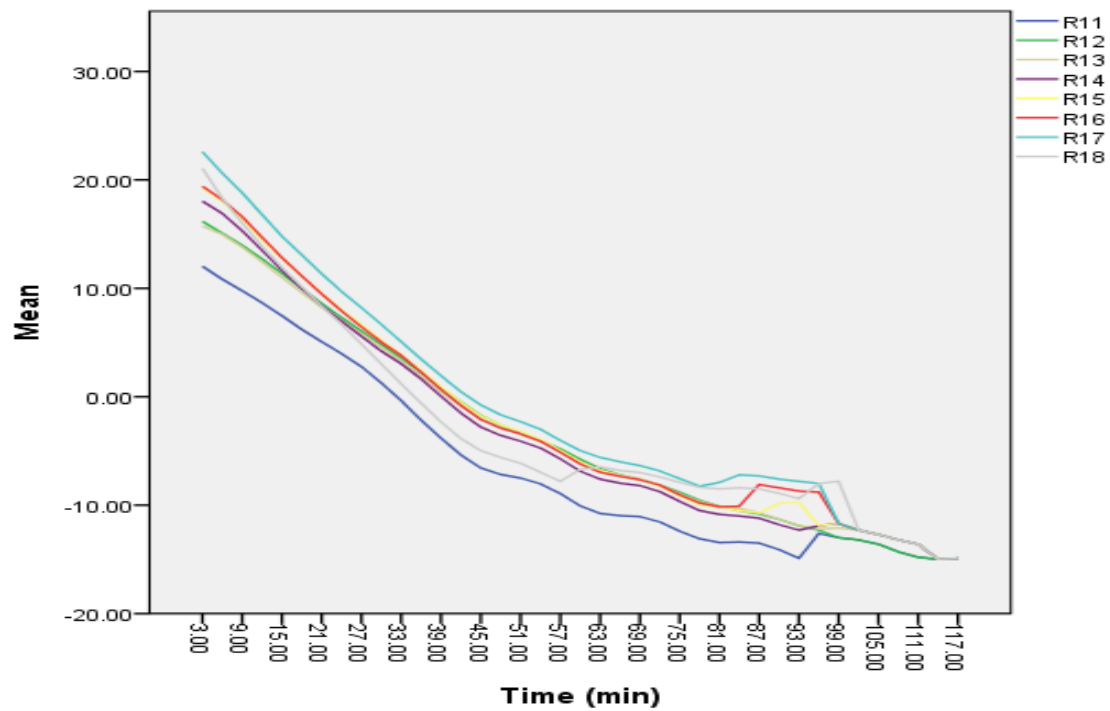


Fig. 4.13: Segmented temperature profile of EG-based SZTLs upto the initial FP with 0 % NaCl

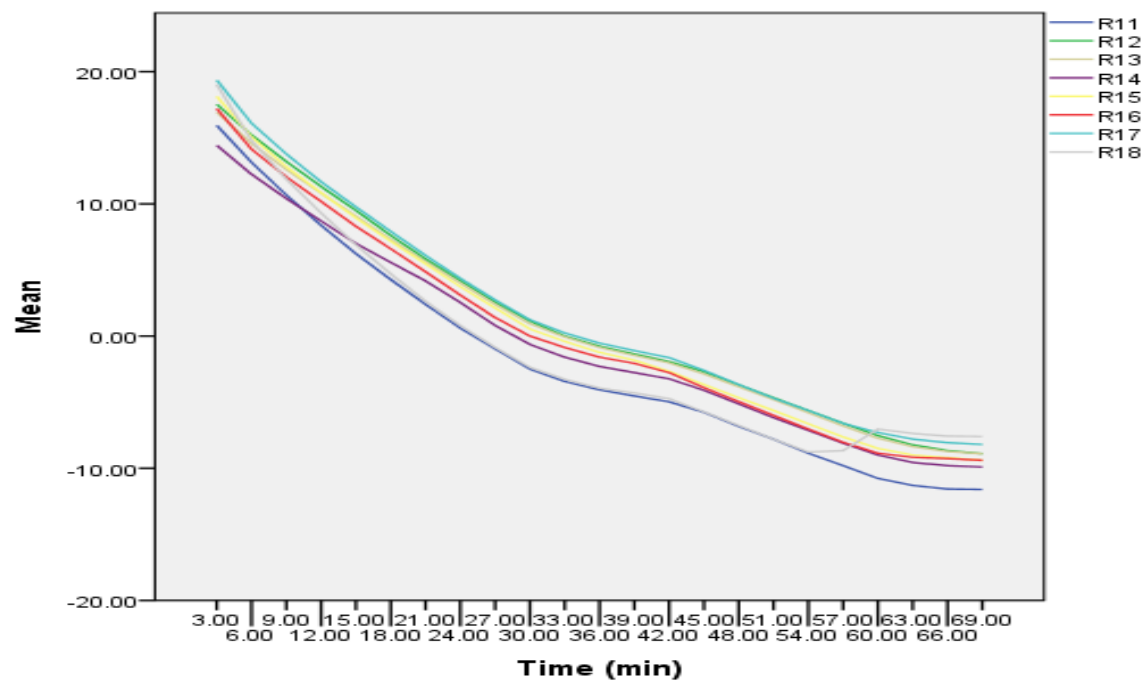


Fig. 4.14: Segmented temperature profile of EG-based SZTLs upto the initial FP with 1 % NaCl

Segmented temperature profile of EG-SZTLs (2 % NaCl) is shown in the Fig. 4.15. Freezing points of these solutions were found between -8.53°C to -14.27°C . For the solutions R14 and R18, it took 117 min. to reach at the freezing points as determined by the simulation program where 93 min. was taken by the solutions R15, R16 and R17 to achieve freezing point temperature. For the solutions R11, R12 and R13, approximately 87 min was required. Comparing with the solutions having 1 % NaCl, freezing point depression of the solutions having 2 % NaCl was observed higher. Selected temperature profile of R16 was found at higher temperature where for R11, R12, and R14, it was found at lower temperature at the same time during cooling process. The thermal conductivity is more sensitive to variations in temperature than the base fluid (Hussein et al., 2017).

Selected TPs are plotted and shown in Fig. 4.16 for the EG-based SZTLs solutions having 3 % NaCl. These TPs were plotted upto initial freezing points of the solutions as determined by the simulation method. Cooling process started from temperature 15 to 20°C . FPs of the blends R11, R12, R13, R14, R15, R16, R17 and R18 were -13.13 , -14.00 , -12.57 , -14.63 , -13.8 , -11.67 , -10.13 and -9.33°C , respectively. Total time taken by the solutions to reach their freezing points was 105 min. Cooling rate of all these solutions were found almost similar upto 80 min immediately after initiation of cooling process and then slight deviations were observed. It experimentally studied the mixture of ethylene glycol and Al_2O_3 nanoparticles at 1.5 % volume concentration in water and mentioned that ethylene glycol has poorer thermal conductivity than water, and the addition of ethylene glycol will only suppress the thermal conductivity of the base fluid (Sundar et al., 2014). Temperature of the blend R12 was recorded higher while R11 and R14 were observed at lower temperature compare with other blends. Cooling rate was high between 3 to 30 minutes and then decrease gradually.

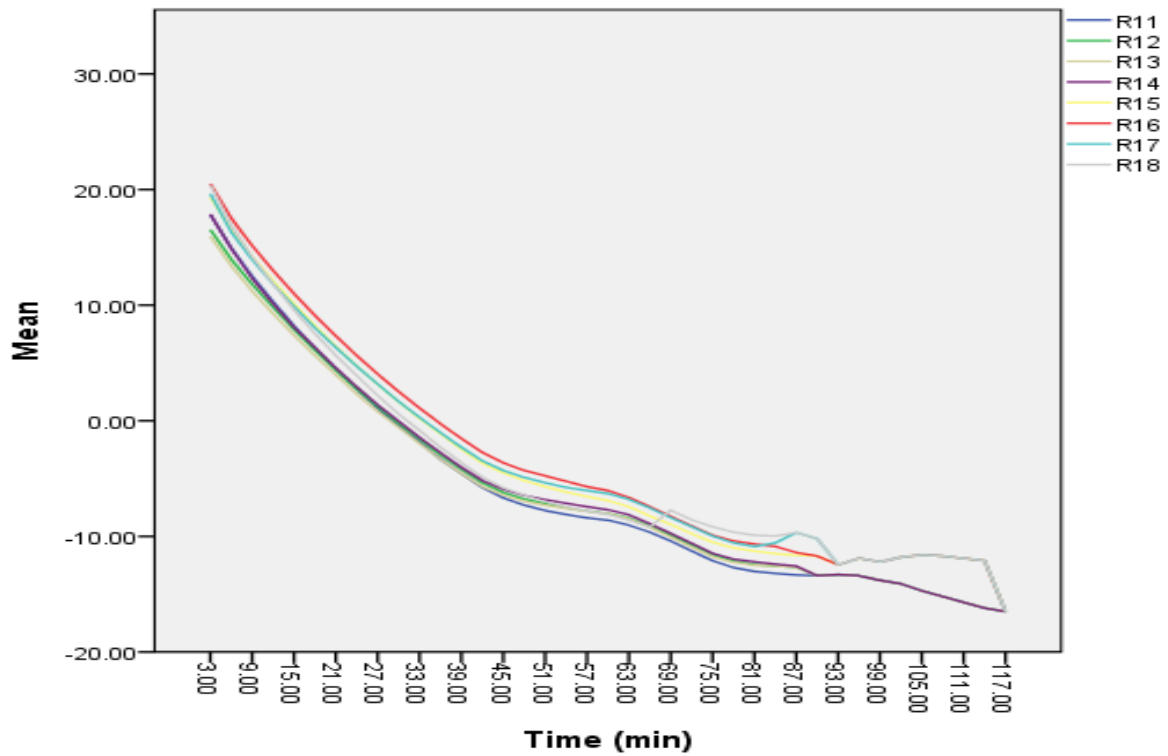


Fig. 4.15: Segmented temperature profile of EG-based SZTLs upto the initial FP with 2 % NaCl

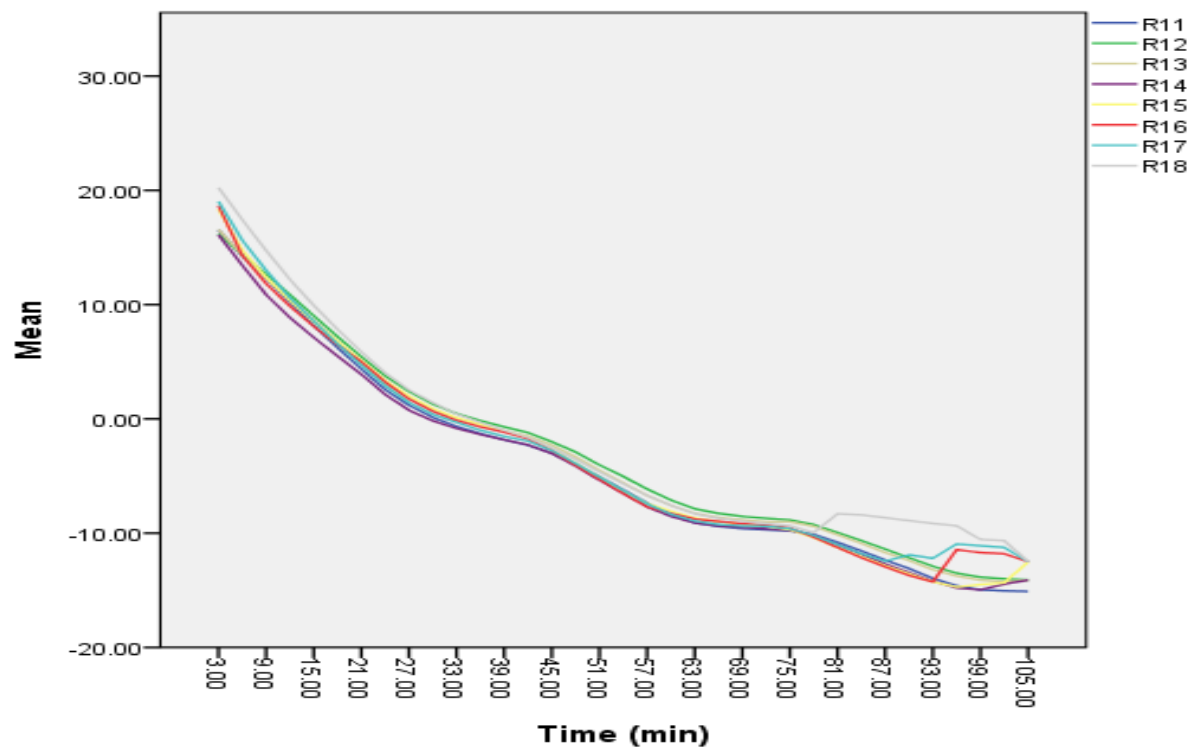


Fig. 4.16: Segmented temperature profile of EG-based SZTLs upto the initial FP with 3 % NaCl

Segmented TPs are plotted in the Fig. 4.17 for the EG-based SZTLs solutions having 4 % NaCl in their composition. These TPs are upto to the Freezing points of the solutions as determined by the simulation method. Cooling process started from temperature 17 °C to 20 °C. FPs of the blends for R11, R12, R13, R14, R15, R16, R17 and R18 were -12.8, -12.03, -12.5, -12.37, -11.97, -11.00, -10.97 and -9.33 °C, respectively. Total 95 min was taken by the solutions to reach their freezing points. It can be observed in the graph as concentration of blends decreased from R15 to R18, the TPs shifted downward but when concentration of blends decreased from R11 to R14, TPs shifted upward. During the initial 25 min, cooling rate was high but after that it was started to decrease slowly upto 95 min. This trend is stronger for the Poly-EGs of larger molar mass, and can explain why solutions of larger Poly-EGs supercool more readily (Zobrist et al., 2003). For the blend R18, temperature raised from -10 to -7 °C in the time interval from 80 to 87 min. FPD in 4 % NaCl solutions were not higher than 3 % NaCl solutions but somewhere FPs of 4 % NaCl solutions were higher than 3 % NaCl solutions.

Segmented TPs were plotted and are depicted in the Fig. 4.18 for the EG-based SZTLs solutions having 5 % NaCl in their composition. These TPs are upto to the Freezing points of the solutions as determined by the simulation method. Cooling process started from temperature 15 °C to 23 °C. Initial FPs obtained by the simulation program for different blends from R11 to R18 were in the range of -0.97 to -3.07 °C. FPs of the solutions should be decrease when we move from R18 to R11, but these results of FPs were in opposite to the expected value. Total time required by the solutions to reach their freezing point was 290 min. Cooling rate during this process was observed almost constant for all these blends. It can be observed in the graph as concentration of blends decreased from R15 to R18, the TPs shifted downward but when concentration of blends decreased from R11 to R14, TPs shifted upward. Freezing point elevation were observed in 5 % NaCl solutions compare to 4 % NaCl solutions. Higher NaCl percentage helped in reducing the freezing point as well as significant improvement in the cooling rate was observed. The results show that the thermal behavior of the CuO nanoparticles has a significant effect on the EG–water mixture (Sahooli and Sabbaghi, 2013).

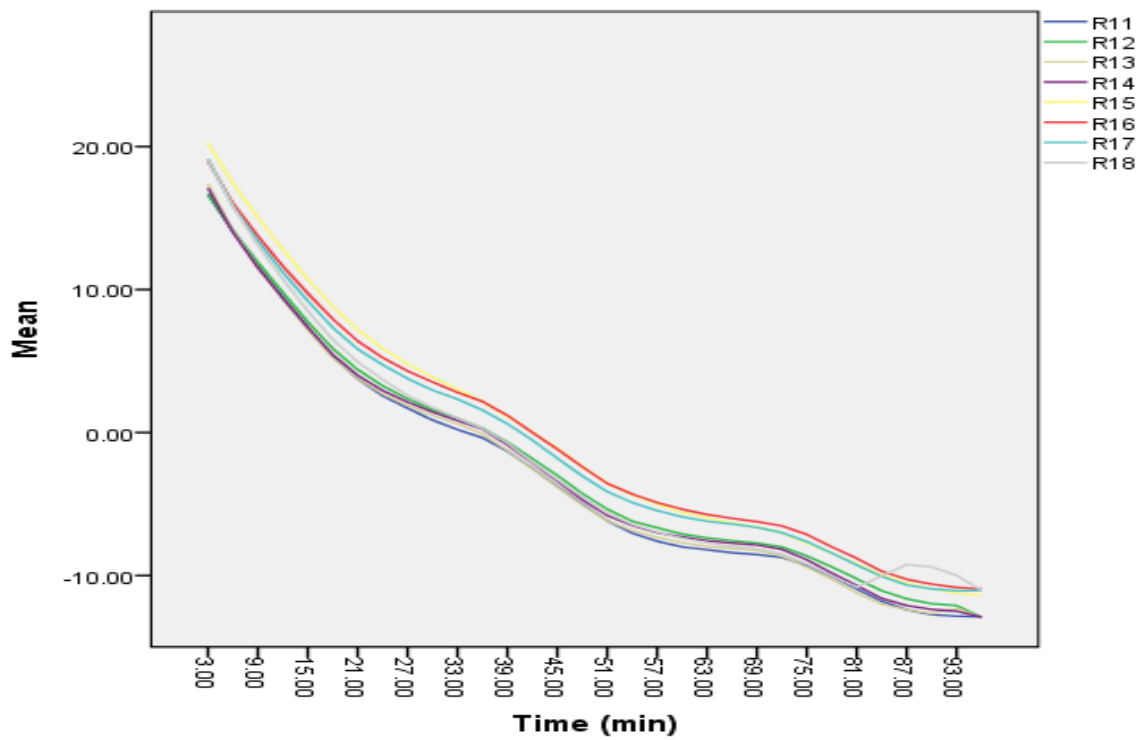


Fig. 4.17: Segmented temperature profile of EG-based SZTLs upto the initial FP with 4 % NaCl

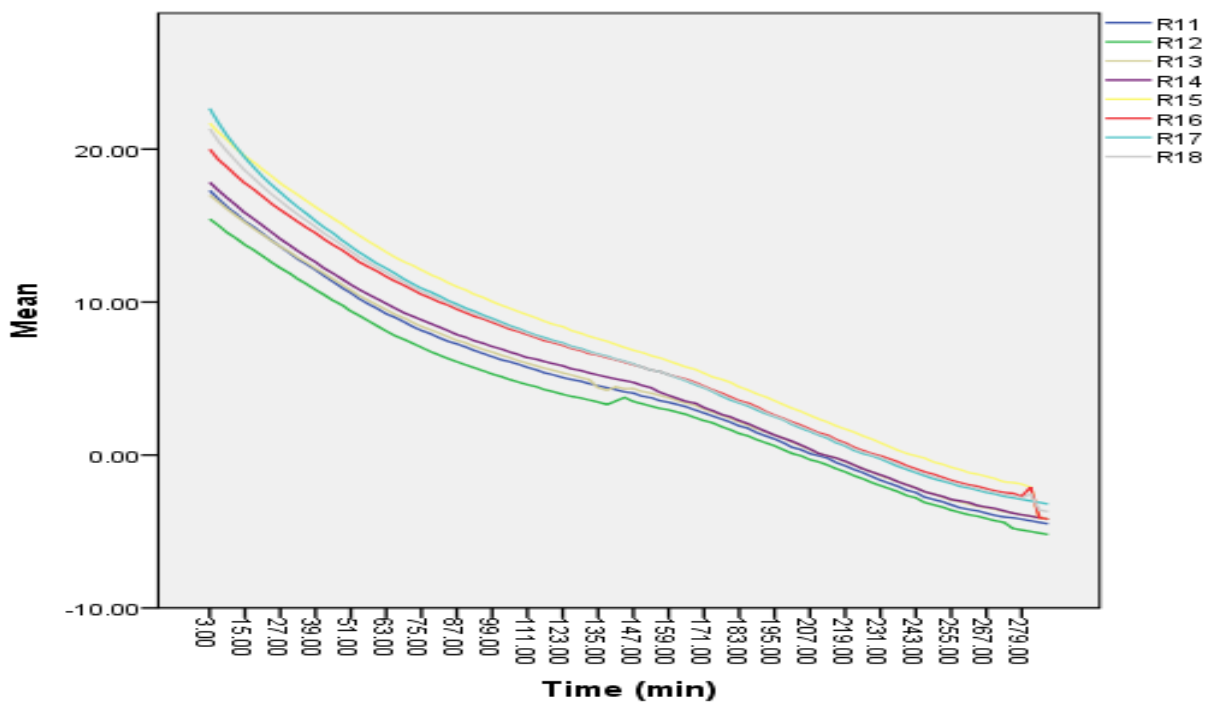


Fig. 4.18: Segmented temperature profile of EG-based SZTLs upto the initial FP with 5 % NaCl

4.2.2 Segmented temperature profile of PG-based SZTLs

TPs of PG-based SZTLs with 0 % NaCl content are shown in the fig. 4.19 which were selected by the simulation method upto the freezing points of the solutions. FPs of these solutions are shown in the table 4.16 which were -0.63 to -0.7 °C for the blends from R11 to R18 respectively. Initial temperatures of blends were from 19 °C to 24 °C. Time taken by the solutions to reach at their freezing point was 210 min. cooling rate for most of the solutions were found almost same and decrease very gradually for next 180 min after initiation of cooling process. In the time interval 180-210 min, fluctuation in the cooling rates were observed for blends R14, R15, R16, R17 & R18. As concentration increased from R18 to R14, TPs were shifted downward but, as concentration increased from R13 to R11, TPs were shifted upward. It may be due to the high concentration ratio of PG blends in R11, R12 & R13.

TPs of PG-based SZTLs with 1 % NaCl content are shown in the Fig. 4.20 which were selected by the simulation method upto the freezing points of the solutions. The simulation program was unable to correctly segment initial FPs of these solutions and the predictions were in the range of 0.87 to 2.1 °C for different blends (R11 to R18). Time taken by the solutions to reach at their segmentation point was between 180-210 min. Cooling rates were found almost equal for all blends and it was lower than the value of cooling rate of EG-based solutions. Previous studies on propylene glycol (PG) water solutions showed that the structure that water adopts in PG-water solutions is different from the rest of aqueous solutions (Minoguchi et al., 2004). After passing of time 160 min. some changes in TPs were observed in blends R16, R14, & R18. Temperature of R14 and R16 were raised by 2-3 °C after 160 min. According to this result, it can be said that segments of these TPs are selected before the achieving of FPs of the solutions. These values of FPs which were determined by simulation method are far away from real FP values of these solutions.

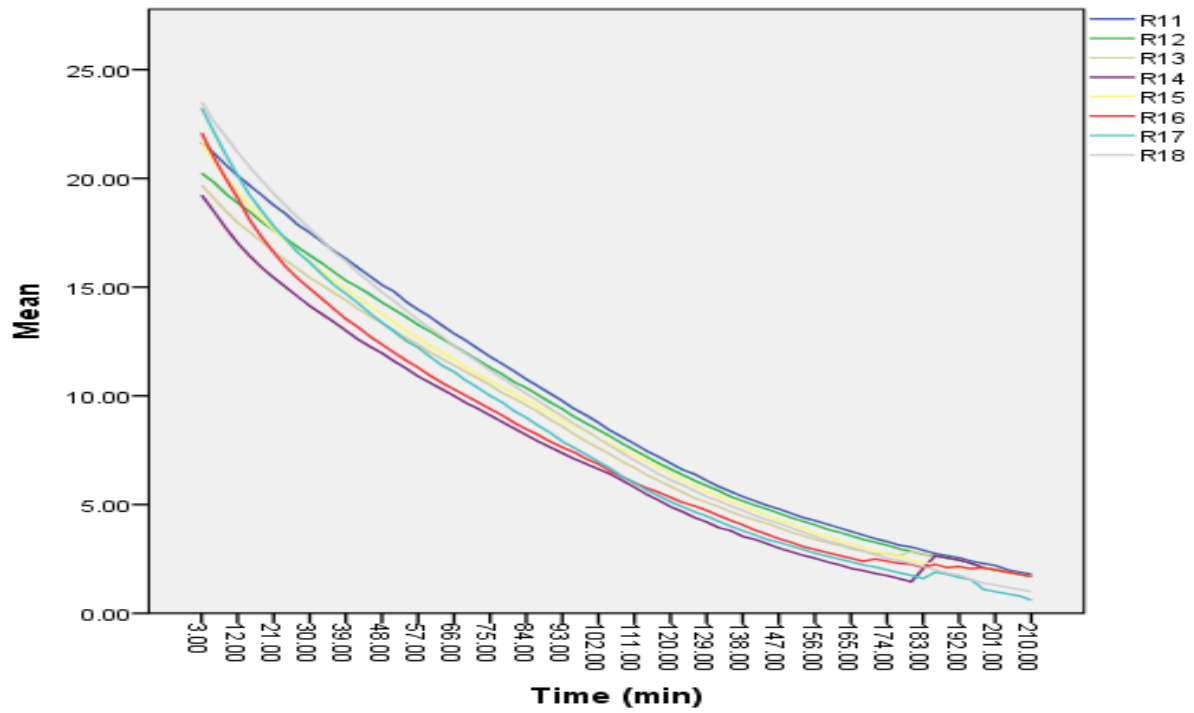


Fig. 4.19: Segmented temperature profile of PG-based SZTLs upto the initial FP with 0 % NaCl

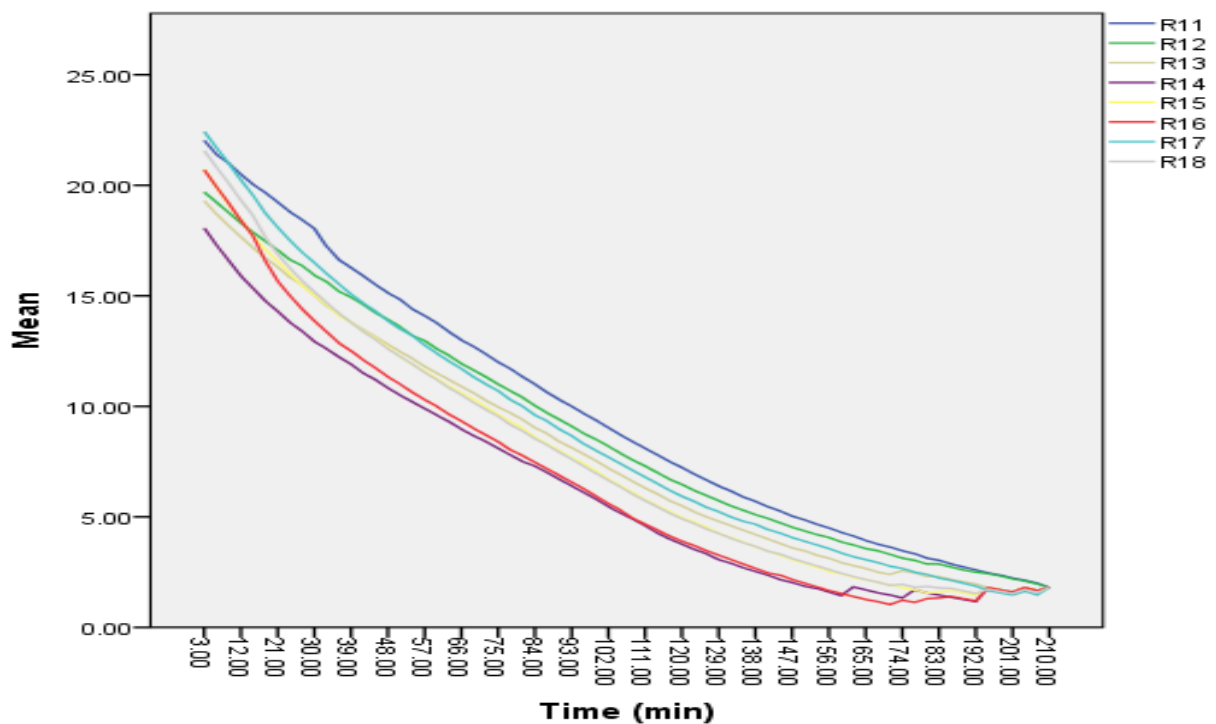


Fig. 4.20: Segmented temperature profile of PG-based SZTLs upto the initial FP with 1 % NaCl

TPs of PG-based SZTLs upto the freezing points of the solutions with 2 % NaCl content are shown in the Fig. 4.21 which were selected by the simulation method. The simulation program was unable to correctly segment initial FPs of these solutions and the predictions were in the range of -0.80 to 2.97 °C for different blends (R11 to R18). Initial temperatures of blends were from 18 °C to 25 °C. Time taken by the solutions to reach at their freezing point was between 200-210 min. For R12 to R15 and R18, temperature raise was approximately 3, 1, 4, 3, and 5 °C, respectively. These changes may be due to the cut-off of electricity. The observation outlines need of a pre-screening algorithm to remove such offsets from temperature data. Cooling rate of all these solutions were almost equal as evident from parallel curves (Fig. 4.21). It has been observed that the viscosity of PG solution is higher than EG & NaCl solution. The liquid phase density decreases and viscosity increases as PG concentration increases in the liquid however, freezing temperature also decreases with it (Rawat & Pratihari, 2018).

Thermal cooling data were taken and segmented TPs of PG-based SZTLs with 3 % NaCl were drawn with the help of simulation method (Fig. 4.22). On the basis of the finding of simulation program, segmentation points of these blends were automatically selected which was in range of 4.23 to -3.07 °C. We define as a recognizable inaccuracy in any phase or activity of modelling and simulation that is not due to lack of knowledge (William et al., 2002). Initial temperatures of blends were recorded between 13 °C to 15 °C and total 174 min was taken to achieve these segmentation points. Temperature of all solutions increased by 5-6 °C during 39 to 48 min and reason behind this temperature increment was electricity cut-off.

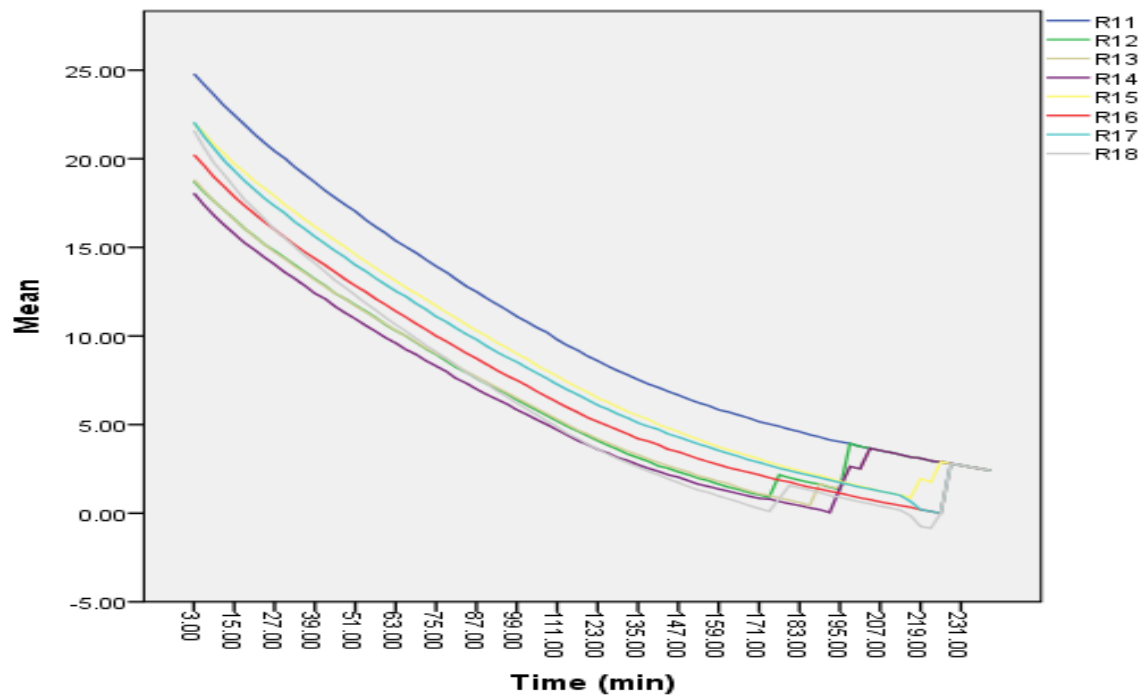


Fig. 4.21: Temperature profile of PG-based SZTLs upto the initial FP with 2 % NaCl

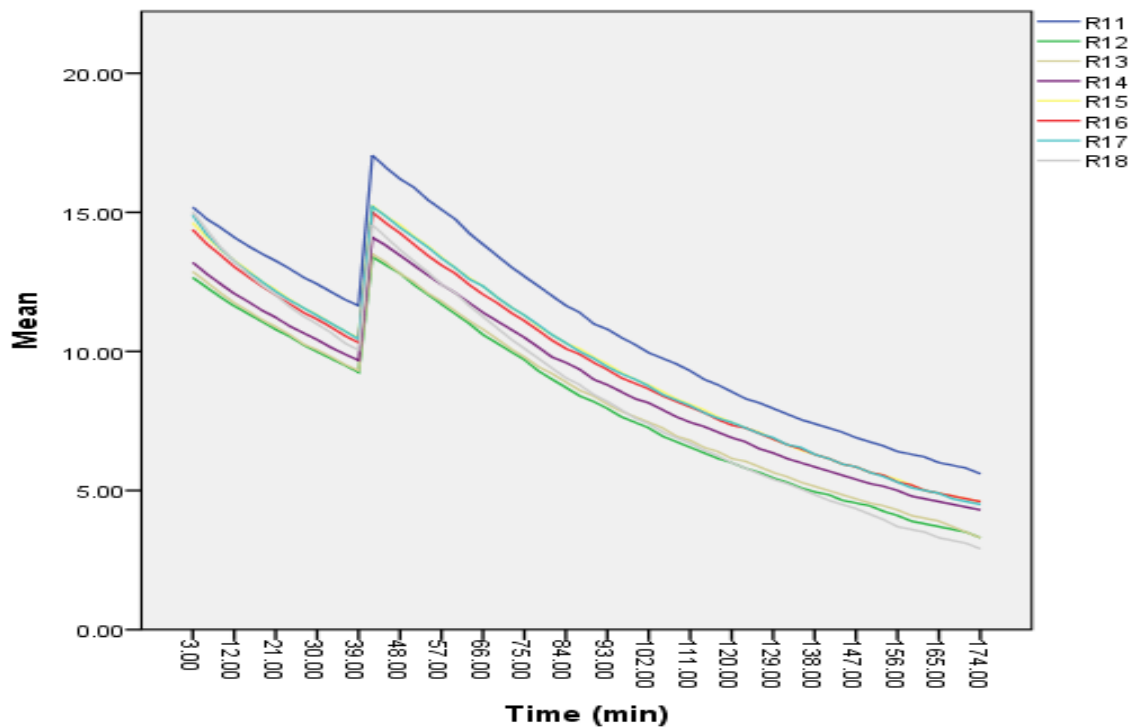


Fig. 4.22: Temperature profile of PG-based SZTLs upto the initial FP with 3 % NaCl

Segmented TPs of PG-based SZTLs with 4 % NaCl were drawn with the help of simulation method. Results are shown in the fig. 4.23. On the basis of the finding of simulation program, FPs of these blends were in the range of -0.57 to -2.93 °C. Initial temperatures of blends were recorded between 16 °C to 21 °C and total 185 min was taken to achieve these FPs. As concentration decreased from R15 to R18, TPs of these solutions showed lower values but when concentration decreased from R11 to R14, TPs of these four blends demonstrated higher values. water becomes crystal as it is cooled and makes study difficult in the state of supercooled. One way to avoid the crystallization is by mixing water with other liquids or salts to reveal the properties of supercooled water (Cerveny et al., 2006).

Segmented TPs of PG-based SZTLs with 5 % NaCl were drawn with the help of simulation method. On the basis of the finding of simulation program, segmentation points of these blends were in the range of 2.97 to -1.23 °C (Fig. 4.24). After completion of 175 min, temperature of blends R14, R16, R17 & R18 started to increase by 3-5 °C and it might be due to cut-off of electricity. This temperature rise did not affect the segmentation of temperature profile curves.

On analysis of data, it was found that rapid freezing is required for accurate selection of the segmentation points. In case of PG based SZTL slow freezing method was employed and the initial maximum cooling rate was < 0.5 °C/min. The reduction in freezing temperature is highest with NaCl among all the four liquids that are EG, PG, NaCl and Ethanol (Rawat & Pratihari, 2018).

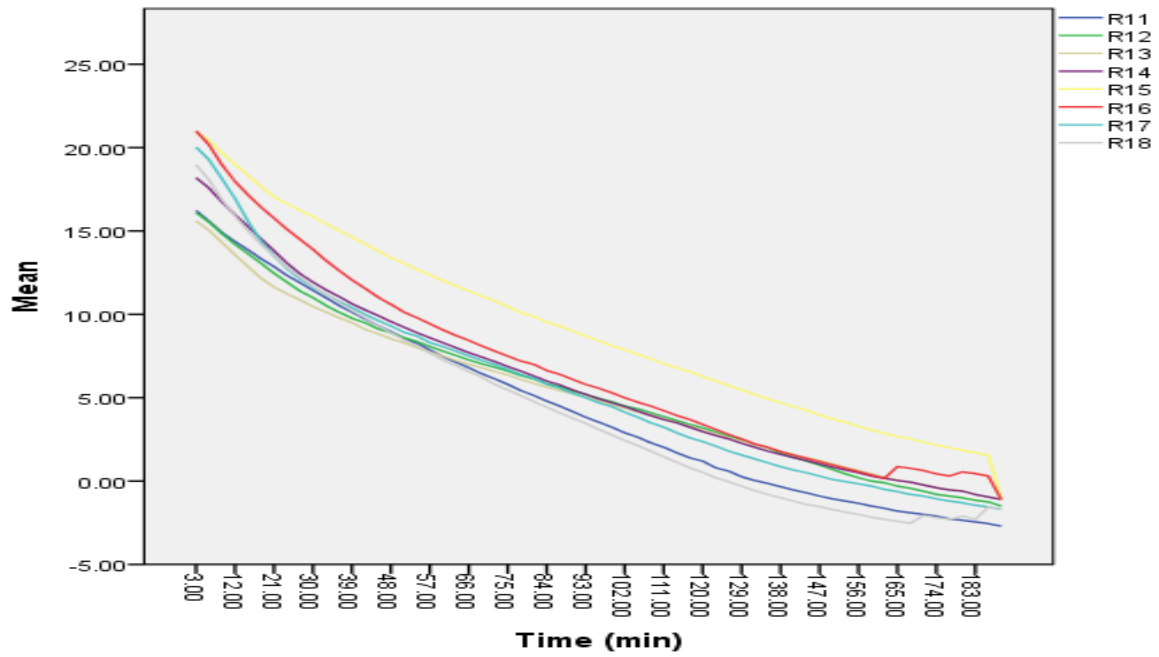


Fig. 4.23: Temperature profile of PG-based SZTLs upto the initial FP with 4 % NaCl

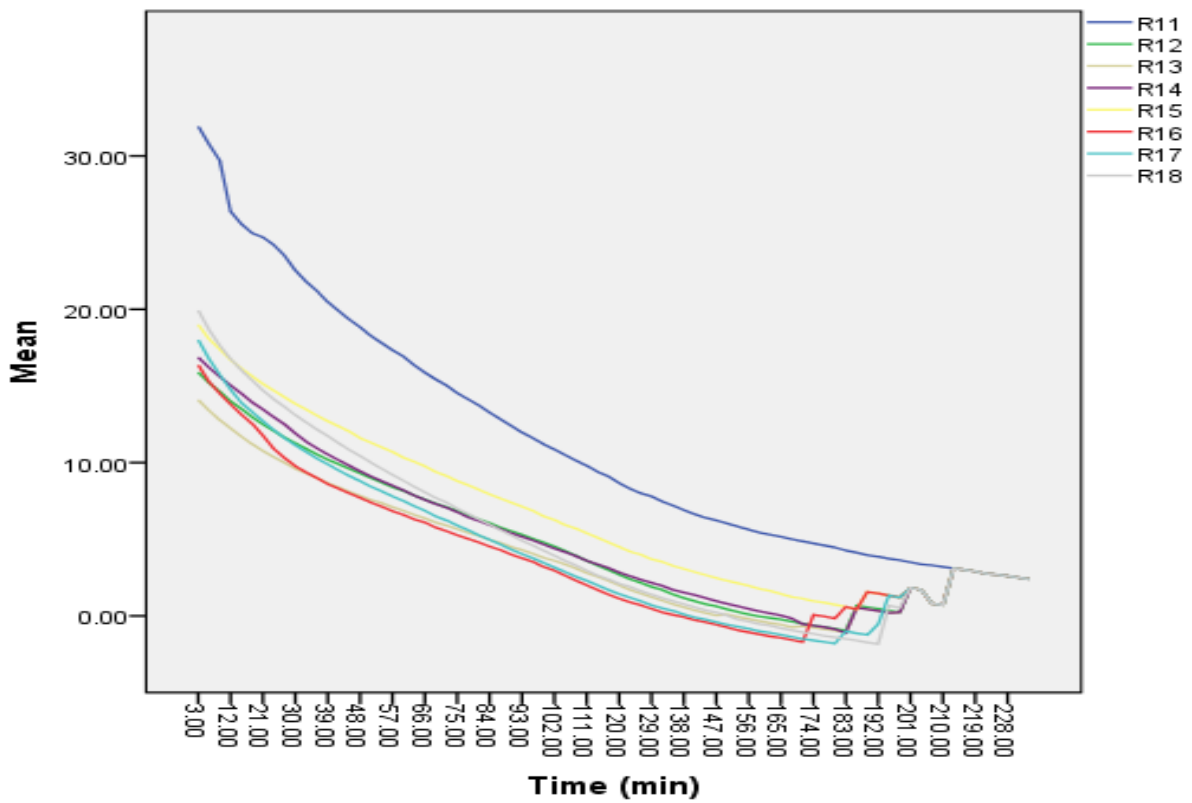


Fig. 4.24: Temperature profile of PG-based SZTLs upto the initial FP with 5 % NaCl

4.3 Comparison of freezing point and cooling rate of SZTLs

Freezing point was determined with the help of simulation technique where average cooling rate & maximum cooling rate were determined by Microsoft office. Mean value of these three parameters are plotted on the graph. These were calculated at different concentration of NaCl from 0 % to 5 % in the solution of EG and PG with distilled water. Total ninety-six solutions were examined for it.

4.3.1 Freezing point and cooling rate of EG-based SZTLs

Freezing point of EG-based SZTLs solution were estimated using the help of simulation program. Predicted freezing point results are shown in the Fig. 4.25. Freezing point depression was observed for solutions having NaCl from concentration 0 % to 4 % when we move from dilute solution ratio R18 to more concentrated ratio R11 (EG: DW). Solution having 5 % NaCl showed the elevation in the freezing point when we move from diluted solution R18 to concentrated solution R11. It is because higher EG concentration has much lower freezing point. In the limit of infinite dilution, the freezing point depression is determined by the number of moles of polymer molecules per unit volume of solution. However, as the polymer concentration is high enough, part of the freezing point depression is contributed by the interaction between two polymers (Wang et al., 2002). FP of solution R18 (0 % NaCl) was -8.30°C which was depressed to -12.90°C for R11 (0 % NaCl). This same phenomenon was observed for 1 % & 2 % NaCl solution where FPD were -9.30°C to -11.40°C and from -8.53°C to -14.27°C respectively when we move from R18 to R11. For solutions having 3 % and 4 % NaCl, FPD were observed from -9.33°C to -13.13°C & from -9.33°C to -12.80°C respectively where decrease in the temperature by 3.8°C for 3 % NaCl solutions and by 3.47°C for 4 % NaCl solutions is less than the expected depression in freezing point. Depression in FPs for the solutions having 4 % NaCl were too much less when solutions were concentrated from R15 to R11. FPs of the solutions having 5 % NaCl in it showed a very high deviation from the expected value of FPs. It may be due to the solutions could not achieve the desired cooling rate. The result outlines the need of temperature profile data at different cooling rates for accurate segmentation of the cooling curve and

prediction of freezing properties. FP of the solution R18 (5 % NaCl) was determined near -3.07°C where FP of the solution R11 (5 % NaCl) was found to -1.37°C . As concentration of the solutions having 5 % NaCl was increased from R18 to R11, FP were raised by 1.7°C which is opposite to the concept of FPD. FP value of solution R12 (5 % NaCl) was 0.5°C which is above than the FP of the pure water. Standard deviations in the value of mean FPs of the 5 % NaCl solutions from R11 to R14 were found very high as shown in the fig. 4.25. It is desirable to minimize this warm-up of a sample in order to obtain the most accurate freezing point value (Cordray et al., 1996). As amount of NaCl was increased from 1 % to 5 % in the different solutions, FP was not affected to the extend when compared to effect of EG:DW ratio.

Cooling rate is the ratio of change in temperature with respect to time (Diez et al., 2017). Mean max. cooling rate & mean average cooling rate are shown in the Fig. 4.26 & Fig. 4.27 respectively. Maximum cooling rate (MCR) was determined of the EG-SZTLs solutions (from R11 to R18) having NaCl from 0 % to 5 % concentration in it. It was observed that MCR was increased when most of the solutions became diluted. Minimum MCR were observed near $2-2.5^{\circ}\text{C}/\text{min}$ for solutions R11 to R16 having 5 % NaCl. For R17 & R18 (5 % NaCl), MCR were found near $0.35^{\circ}\text{C}/\text{min}$. MCR was found lowest for 5 % NaCl solutions among all NaCl concentrations. Among 0 % NaCl solutions, MCR for R18 was around $1.00^{\circ}\text{C}/\text{min}$ and for R11, it was $0.7^{\circ}\text{C}/\text{min}$ where initially it was decreased to $0.5^{\circ}\text{C}/\text{min}$ for R12 but increased further from 0.5 to $0.8^{\circ}\text{C}/\text{min}$. 1 % & 3 % NaCl solutions showed maximum value of MCR which were $1.4^{\circ}\text{C}/\text{min}$ & $1.45^{\circ}\text{C}/\text{min}$ for R18 & R16 respectively. Trend of increasing MCR was found in between the EG solution ratios which follow the statement of but this type of trend was not observed among the clusters of NaCl solutions when we move from 0 % to 4 % NaCl concentration except 5 % NaCl concentration.

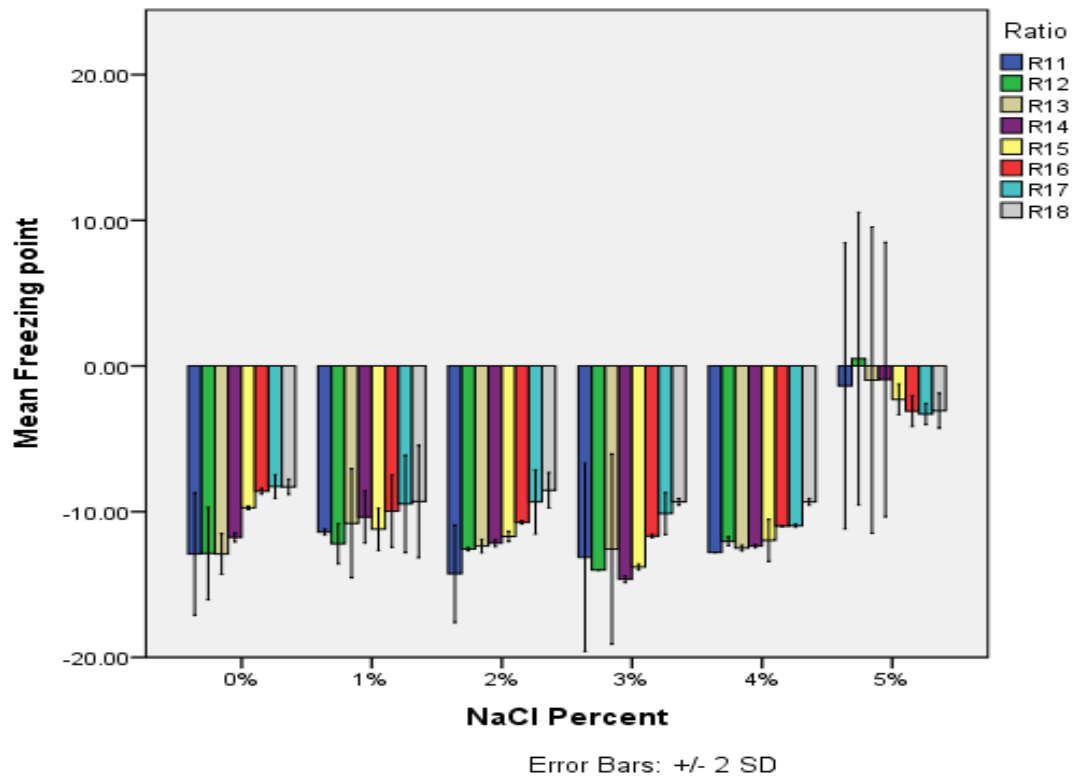


Fig. 4.25: Estimated freezing points of EG-based SZTLs with different concentration of NaCl

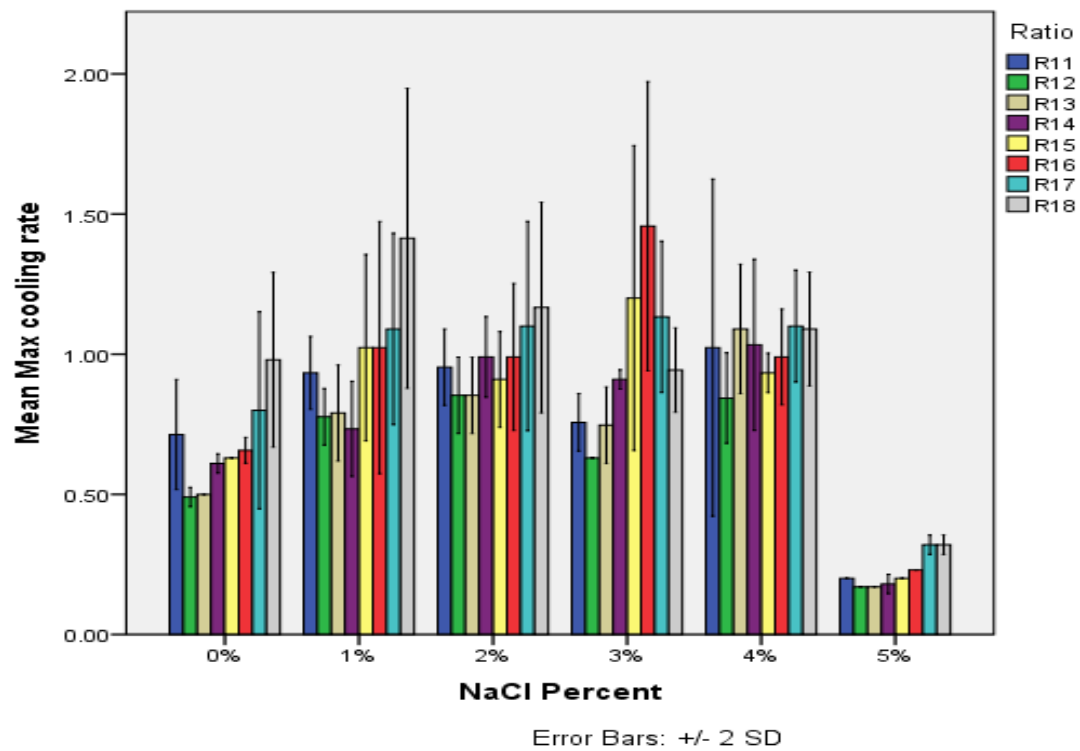


Fig. 4.26: Mean value of max. cooling rate of EG-based SZTLs with different concentration of NaCl

Average cooling rate (ACR) was calculated and results are presented in fig. 4.27. for 0 % NaCl solutions, ACR were found between 0.06 to 0.09 °C/min where ACR was determined at minimum value for 5 % NaCl solutions which were around 0.035 °C/min. For the clusters of 1 %, 2 %, 3 % & 4 % NaCl solutions, ACR were found between 0.07-0.11 °C/min, 0.06-0.08 °C/min, 0.05-0.09 °C/min and 0.04-0.15 °C/min respectively. Cooling rate should be increases as the solution is diluted because water is a good thermal conductor than some other liquid. Water has much higher thermal conductivity than other liquid coolants (Mohapatra and Loikits, 2005). But no such trend was found in between the concentration ratios when we move from R11 to R18 for all type of NaCl concentration. For 0 % NaCl solutions, initially it was decreased from 0.09 to 0.065 °C/min for R11 to R13 and then increased from 0.07 to 0.09 °C/min for R14 to R17 and then again decreased to 0.06 °C/min for R18. For 1 % NaCl solutions, almost same trend was observed as seen in 0 % NaCl solutions. ACR values for 2 % NaCl solutions were found in the same range of 0 % & 1 % NaCl solutions. ACR of the solutions having 3 % NaCl were initially decreased from 0.07 to 0.06 °C/min for R11 to R14 and then increased to 0.09 °C/min for R15 and again decreased to 0.05 °C/min. In SZTLs having 4 % NaCl maximum ACR was found for R13 which was 0.15 °C/min. Standard deviation of R11 & R13 (4 % NaCl) were also recorded as maximum among all type of EG-based solutions.

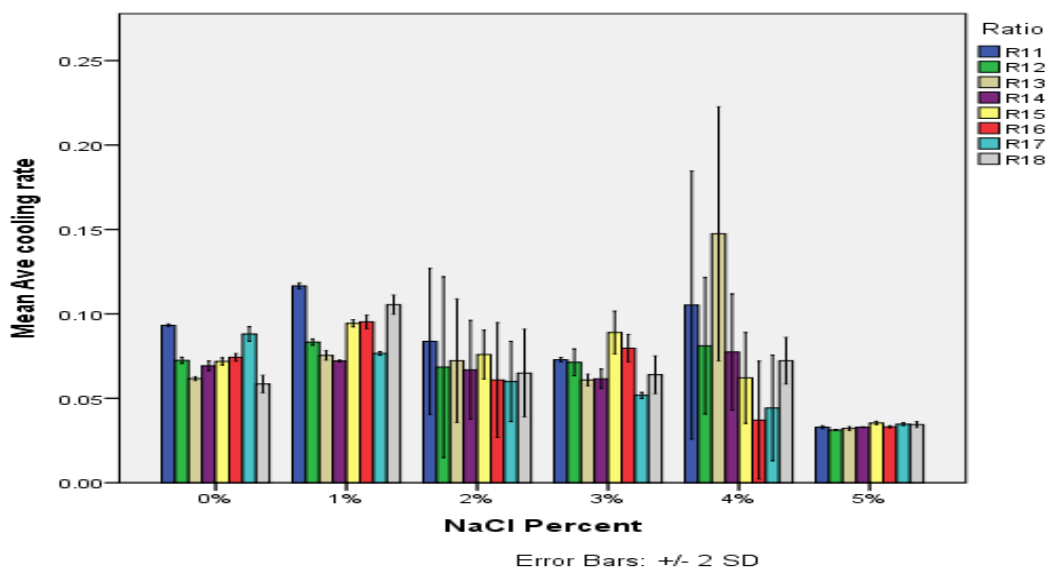


Fig. 4.27: Mean value of average cooling rate of EG-based SZTLs with different concentration of NaCl

4.3.2 Freezing point and cooling rate of PG-based SZTLs

Freezing point of PG-based SZTLs were determined and results are shown in the Fig. 4.28. Most of the FPs of the solutions having 3 %, 4 % & 5 % NaCl concentrations are negative while remaining most of the solutions having 1 %, 2 % & 3 % NaCl were determined as FPs above 0°C. These results of the estimated FPs are far away from the real values of FPs. In 0 % NaCl solutions cluster, FP of R11 & R13 were 2.6 °C while FPs for R12, R14, R16 & R18 were determined as 0.13, 1.33, 1.9 and 0.17 °C, respectively. FP of the solutions R15 and R17 having 0 % NaCl in it were -0.63 °C and -0.7 °C. All solutions (R11 to R18) having 1 % NaCl in their mixture were showed positive FP values. Predicted segmentation points of all these solutions from R11 to R18 were 2.1, 2.4, 1.33, 1.00, 1.53, 0.87, 1.6 & 0.87 °C respectively. The results suggest need for multiple curve segmentation while in the present study only single step segmentation method was used. Decreasing trend in FP values for 1 % NaCl SZTLs when we move from concentrated solution to diluted solution follow the Raoult's law of FPD as all FPs are positive in their values. The segmentation point for the cooling curves of the solutions from R11 to R18 having 2 % NaCl content in their composition were 2.97, 0.43, 0.8, 0.43, 0.8, 0.13, 0.77 and -0.8 °C. Point of segmentation in the cooling curve for FPs of the solutions having 3% NaCl in their composition were 4.23 °C, 2.73 °C & 0.74 °C for R11, R13 and R16 while for R12, R14, R15, R17 & R18 it was -0.1 °C, -2.13 °C, -1.88 °C, -2.01 °C and -3.07 °C respectively. Decreasing trend in the FP values when we move from concentrated solution to diluted solution is opposite to the Raoult's law of FPD here. The addition of ethylene or propylene glycol to water depresses the freezing point of mixture, but also decreases its thermal conductivity (Satti et al., 2017). Estimated initial FPs of the solutions from R11 to R18 having 4 % NaCl in their composition were -2.37 °C, -1.9 °C, -1.17 °C, -0.57 °C, 1.00 °C, -0.87 °C, -1.93 °C and -2.93 °C respectively. Predicted initial FPs of the solutions from R11 to R18 having 5 % NaCl in their composition were 2.97 °C, -1.3 °C, -0.73 °C, -0.03 °C, 0.3 °C, -1.67 °C, -1.23 °C and -1.10 respectively.

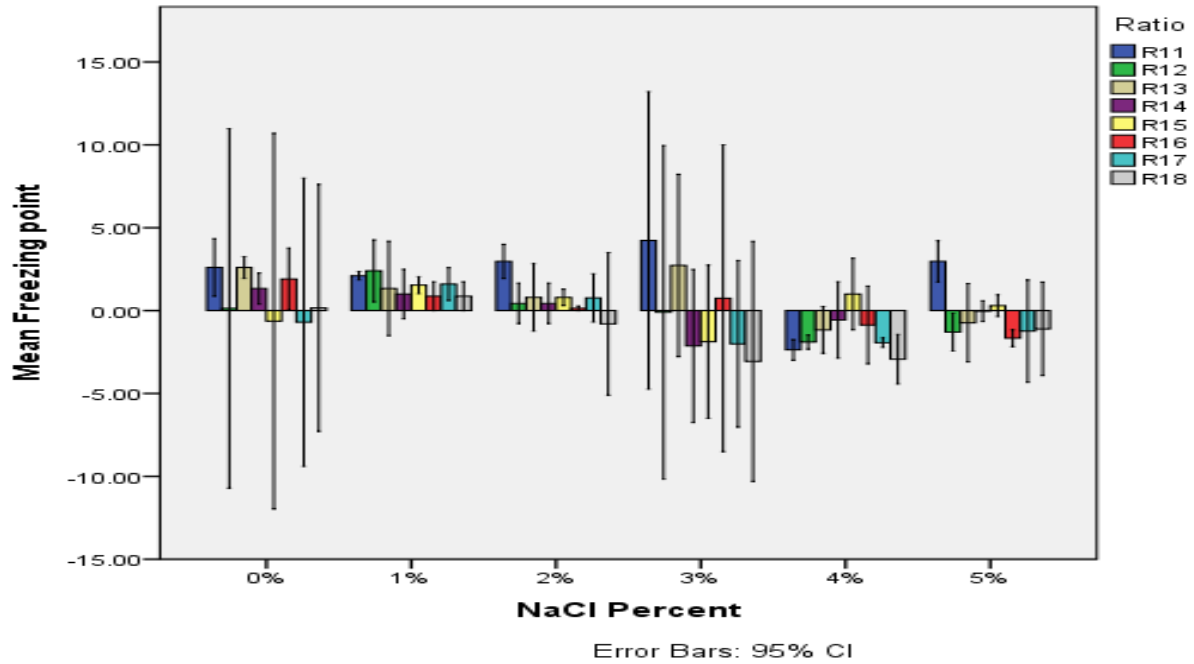


Fig. 4.28: Estimated freezing points of PG-based SZTLs with different concentration of NaCl

Cooling rate PG-based SZTLs was calculated by simulation method and mean value of max. cooling rate (MCR) were determined with the help of Microsoft office. The results are shown in the Fig. 4.29. Cooling rate of PG solutions found less than the cooling rate of the EG solutions except 3 % & 4 % NaCl PG based SZTLs which were much higher than any other values. MCR for 0 % NaCl from R11 to R18 were 1.28 °C/min, 0.18 °C/min, 0.2 °C/min, 0.45 °C/min, 0.29 °C/min, 0.38 °C/min, 0.37 °C/min & 0.29 °C/min respectively. MCR of solutions from R11 to R18 having 1 % NaCl in their composition were 0.31 °C/min, 0.27 °C/min, 0.2 °C/min, 0.3 °C/min, 0.36 °C/min, 0.4 °C/min, 0.27 °C/min and 0.38 °C/min respectively. MCR of solutions from R11 to R18 having 2 % NaCl in their composition were 0.2 °C/min, 0.21 °C/min, 0.21 °C/min, 0.22 °C/min, 0.22 °C/min, 0.22 °C/min, 0.27 °C/min and 0.25 °C/min respectively. As we know that cooling rate increases with decrease in the concentration of solutions because of less hindering of solute in heat transfer process, but here in these solutions having 0 %, 1 % & 2 % NaCl, no such type of increasing trend of CR was observed. Liquids have intrinsically lesser thermal conductivity than that of solid and thermal conductivity of glycols is found lower than water (Satti et al., 2017).

For the solutions from R11 to R18 having 3 % NaCl in their composition MCR were 1.96 °C/min, 2.25 °C/min, 0.27 °C/min, 2.93 °C/min, 3.13 °C/min, 3.21 °C/min, 3.37 °C/min and 3.76 °C/min respectively. Here in 3 % NaCl solutions, as concentration was decreased MCR was increased. MCR of solutions from R11 to R18 having 4 % NaCl in their composition were 1.89 °C/min, 1.72 °C/min, 1.56 °C/min, 1.75 °C/min, 2.02 °C/min, 1.91 °C/min, 1.72 °C/min and 1.87 °C/min respectively. MCR of solutions from R11 to R18 having 5 % NaCl in their composition were 1.11 °C/min, 0.23 °C/min, 0.23 °C/min, 0.22 °C/min, 0.31 °C/min, 0.38 °C/min, 0.54 °C/min and 0.71 °C/min respectively. PG-based SZTLs having 5 % NaCl show the trend of increasing MCR when we move from R11 to R18 concentrations.

Mean value of average cooling rate (ACR) of PG-based SZTLs were determined and results are shown in the fig. 4.30. ACR of the solutions from R11 to R18 with 0 % NaCl were in the range of 0.031-0.035 °C/min where for the solutions having 1% NaCl, it were varying from 0.031 to 0.037 °C/min. ACR of the 2 % and 3 % NaCl solutions clusters as shown in the fig. 4.30 were in the range of 0.030-0.035 °C/min and 0.032-0.035 °C/min respectively. ACR were decreased from R11 to R14 and then increased from R15 to R18 for most of the solutions when we compare in between the different % NaCl SZTLs. Thermal conductivity decreases with increase in concentration and it results in decrease of cooling rate. Thermal conductivity of different solutions of PG & water having PG fraction $x=0.25$, $x=0.5$ & $x=0.75$ are $0.322 \text{ W/m}\cdot\text{K}$, $0.243 \text{ W/m}\cdot\text{K}$, & $0.212 \text{ W/m}\cdot\text{K}$ respectively at 26 °C temperature (Sun & Teja, 2004). ACR of the solutions from R11 to R18 with 4 % NaCl were in the range of 0.038-0.044 °C/min where for the solutions having 5 % NaCl, it were varying from 0.032 to 0.045 °C/min. standard deviation of the solutions having 4 % NaCl were observed as high as shown above where standard deviation of the remaining solutions were not much higher. Effect of the different NaCl concentration was not observed on the average cooling rate of PG-based SZTLs. The thermal conductivity of a liquid can be increased by dispersing solid particles in that liquid (Satti et al., 2017). ACR of the 4 % NaCl solutions was found slightly higher than any other solutions of propylene glycol with NaCl.

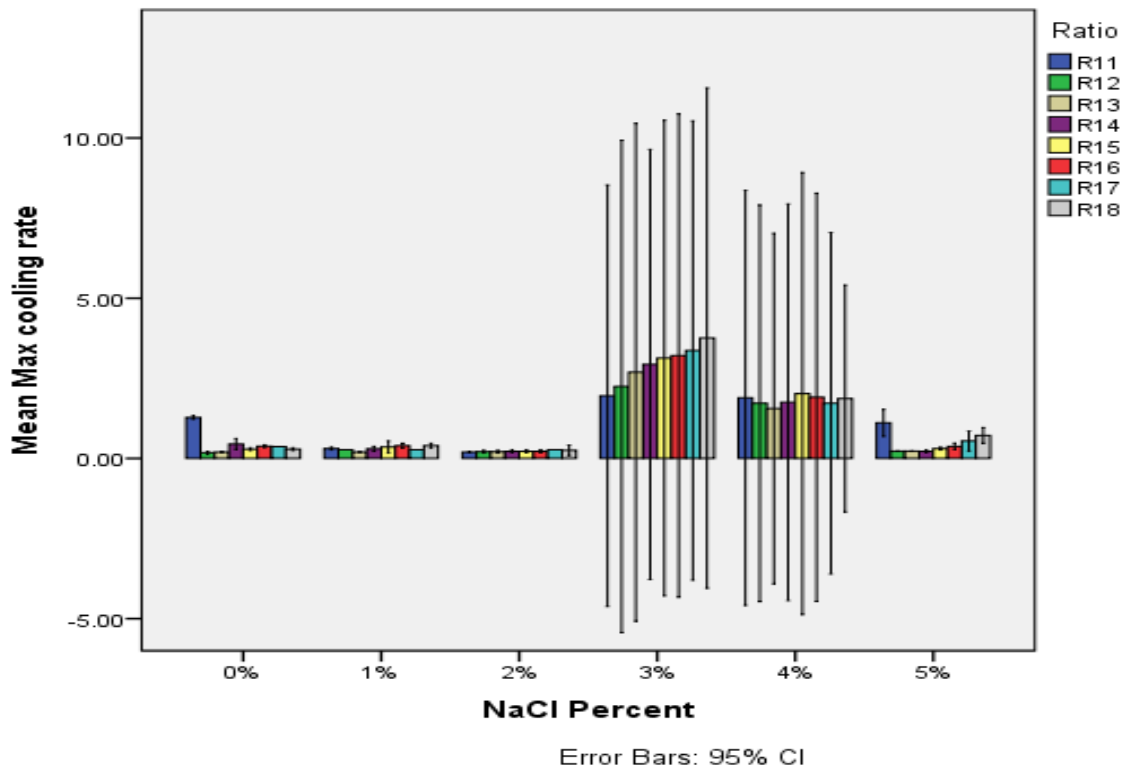


Fig. 4.29: Mean value of max. cooling rate of PG-based SZTLs with different concentration of NaCl

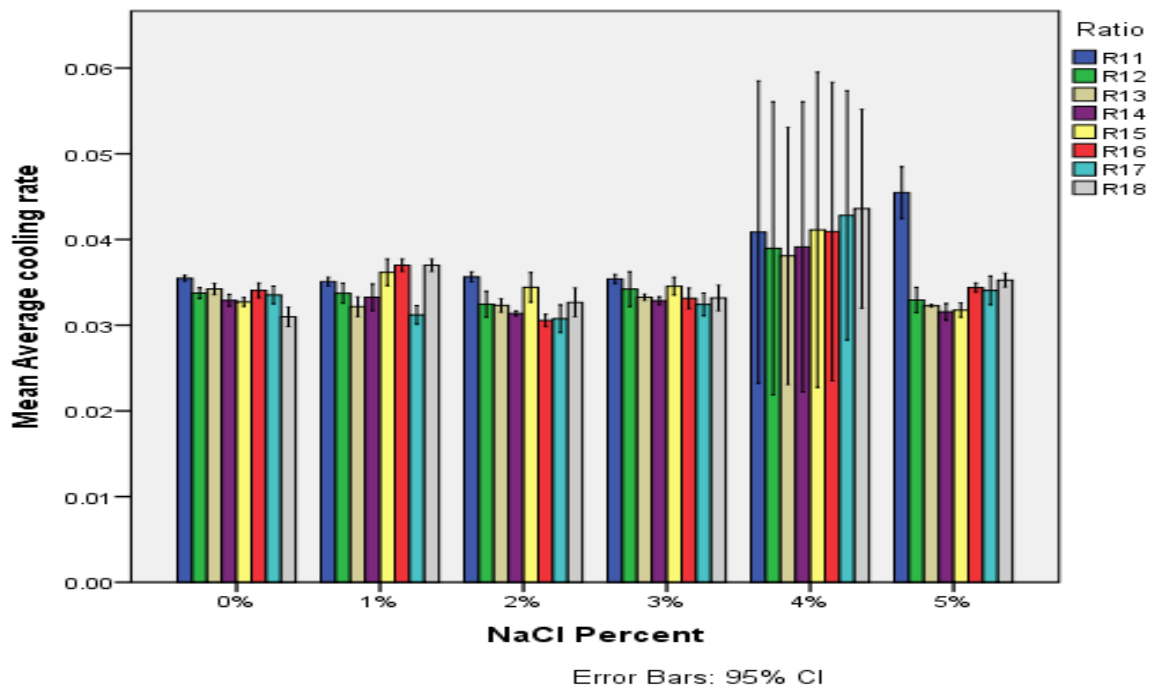


Fig. 4.30: Mean value of average cooling rate of PG-based SZTLs with different concentration of NaCl

4.4 Comparison between the FPs determined by simulation method and manual method

Freezing point of EG and PG-based SZTLs were determined by two methods viz simulation method and manual method. Two different results came out from these two methods. Comparison between these two results is explained here.

4.4.1 Freezing points of EG-based SZTLs

Freezing points of EG-based SZTLs (0 % to 5 % NaCl) which were determined by manual cooling curve method (CCM) as determined by Hitesh et al. (2020) is shown in Table 4.1. The results obtained by simulation method (SM) has been tabulated in Table 4.2.

For 0 % NaCl solutions, FPs varied from -12.9°C to -8.3°C & -14°C to -6.0°C for simulation method (SM) and cooling curve method (CCM) as concentration was decreased from R11 to R18. Min. & max. differences of FP of the same solutions were 0.07°C & 2.3°C respectively. No significant differences were found between the FPs of the same solutions except R18. For 1 % NaCl solutions, FPs varied from -11.4°C to -9.3°C & -16°C to -7.5°C for SM and CCM respectively as concentration was decreased from R11 to R18. Min. & max. differences of FPs of same solutions were 0.03°C & 4.7°C respectively. For the solutions R11, R12, R13 & R14, significant differences ($> 2.0^{\circ}\text{C}$) were found between FPs of same blends.

For 2 % NaCl solutions, FPs varied from -14.27°C to -8.53°C & -17°C to -8.0°C for SM and CCM respectively as concentration was decreased from R11 to R18. Min. & max. variations in FPs of same solutions were 0.17°C & 2.73°C respectively. Difference between FPs for the same solutions was increasing with increasing in concentration ratio except solutions R15 & R17. Differences in FPs for the same solutions e.g., R11, R12 & R13 were found significantly high ($> 2.0^{\circ}\text{C}$). For 3 % NaCl solutions, FPs varied from -14.63°C to -9.33°C & -14.5°C to -8.0°C for SM and CCM respectively as concentration was decreased from R11 to R18 except some solutions. Min. & max. differences of FP of same solutions were 0.13°C & 1.33°C

respectively. Difference between these FPs for same solutions was not significantly high ($< 2.0^{\circ}\text{C}$).

For 4 % NaCl solutions, FPs varied from -12.8°C to -9.33°C & -17°C to -10°C for SM and CCM respectively as concentration was decreased from R11 to R18 except R12. Min. & max. differences of FP of same solutions were 0.67°C & 4.97°C respectively. when compare between both methods, variation in FPs for same solution was increasing with increasing in concentration ratio except R11 and R15. Differences between FPs for same solution e.g., R11, R12, R13, R14 & R16 were significantly high ($> 2.0^{\circ}\text{C}$) but for the rest of the solutions, it was not significantly high ($< 2.0^{\circ}\text{C}$). For 5 % NaCl solutions, FPs varied from -3.3°C to 0.5°C & -17°C to -11°C for SM and CCM respectively. Min. & max. differences of FP of these solutions were 7.93°C & 17.5°C respectively. Variation in FPs for same solution was increasing with increasing in concentration ratio when compare between both methods.

Table 4.1: Freezing point of EG-based SZTLs determined by manual method

EG:DW	NaCl concentration					
	0%	1%	2%	3%	4%	5%
1:1	-14.0	-16.0	-17.0	-14.0	-15.5	-16.5
1:2	-13.5	-16.0	-15.0	-13.0	-17.0	-17.0
1:3	-14.5	-15.5	-15.0	-13.5	-15.0	-16.5
1:4	-11.7	-13.0	-14.0	-14.5	-15.0	-16.5
1:5	-9.2	-11.0	-12.0	-12.5	-13.0	-14.0
1:6	-9.5	-10.0	-10.0	-12.0	-13.0	-12.5
1:7	-7.6	-8.5	-9.5	-10.0	-12.5	-12.0
1:8	-6.0	-7.5	-8.0	-8.0	-10.0	-11.0

Table 4.2: Predicted initial freezing point of EG-based SZTLs determined by simulation method

EG :DW\ %NaCl	0%	1%	2%	3%	4%	5%
R11	-12.90	-11.40	-14.27	-13.13	-12.80	-1.37
R12	-12.86	-12.20	-12.57	-14.00	-12.03	0.50
R13	-12.90	-10.80	-12.37	-12.57	-12.50	-0.97
R14	-11.77	-10.37	-12.17	-14.63	-12.37	-0.93
R15	-9.73	-11.20	-11.70	-13.80	-11.97	-2.30
R16	-8.60	-9.97	-10.73	-11.67	-11.00	-3.10
R17	-8.27	-9.47	-9.33	-10.13	-10.97	-3.30
R18	-8.30	-9.30	-8.53	-9.33	-9.33	-3.07

4.4.2 Freezing points of PG-based SZTLs

Freezing points of PG-based SZTLs (0 % to 5 % NaCl) which were determined by cooling curve method and simulation method, are shown in the table 4.3 & table 4.4 respectively.

For 0 % NaCl PG-based SZTLs, FPs were ranging from -0.7 °C/min. to 2.6 °C/min. and from -12.5 °C/min. to -5.0 °C/min. which were determined by SM and CCM respectively. Max. & min. differences between FPs of the same solutions were 15.1 °C/min. and 4.3 °C/min. respectively. Significant differences (> 2 °C) were found between the FPs of the same solutions. For more concentrated solutions (R11 to R14), FP difference was higher than diluted solutions. For 1 % NaCl PG-based SZTLs, FPs were ranging from 0.87 °C/min. to 2.4 °C/min. and from -16.5 °C/min. to -5.0 °C/min. which were determined by SM and CCM respectively. Max. & min. differences between FPs of the same solutions were 18.9 °C/min. and 5.87 °C/min. respectively. FPs which were measured by using both methods are differ at significant level for the same blends. For 2 % NaCl PG-based SZTLs, FPs were ranging from -0.8 °C/min. to 2.97 °C/min. and from -15.5 °C/min. to -5.5 °C/min. which were determined by SM and CCM respectively. Max. & min. differences between FPs of the same solutions were 16.47 °C/min. and 6.27

$^{\circ}\text{C}/\text{min.}$ respectively. Difference was significant between FPs for same blends and this difference was increasing with increasing concentration of the solutions.

For 3 % NaCl PG-based SZTLs, FPs were ranging from $-3.07\text{ }^{\circ}\text{C}/\text{min.}$ to $4.23\text{ }^{\circ}\text{C}/\text{min.}$ and from $-15.0\text{ }^{\circ}\text{C}/\text{min.}$ to $-6.0\text{ }^{\circ}\text{C}/\text{min.}$ which were determined by SM and CCM respectively. Max. & min. differences between FPs of the same solutions were $17.73\text{ }^{\circ}\text{C}/\text{min.}$ and $2.93\text{ }^{\circ}\text{C}/\text{min.}$ respectively. Difference was significant between FPs for all the same blends and this difference was increasing with increasing concentration of the solutions except R12. For 4 % NaCl PG-based SZTLs, FPs were ranging from $-2.93\text{ }^{\circ}\text{C}/\text{min.}$ to $1.0\text{ }^{\circ}\text{C}/\text{min.}$ and from $-14.5\text{ }^{\circ}\text{C}/\text{min.}$ to $-12.0\text{ }^{\circ}\text{C}/\text{min.}$ which were determined by SM and CCM respectively. Max. & min. differences between FPs of the same solutions were $15.5\text{ }^{\circ}\text{C}/\text{min.}$ and $9.07\text{ }^{\circ}\text{C}/\text{min.}$ respectively. Difference between FPs of the same solutions was increasing when we moved from R18 to R15 and then decreased again from R14 to R11.

For 5 % NaCl PG-based SZTLs, FPs were ranging from $-1.67\text{ }^{\circ}\text{C}/\text{min.}$ to $2.97\text{ }^{\circ}\text{C}/\text{min.}$ and from $-17\text{ }^{\circ}\text{C}/\text{min.}$ to $-12.0\text{ }^{\circ}\text{C}/\text{min.}$ which were determined by SM and CCM respectively. Max. & min. differences between FPs of the same solutions were $17.97\text{ }^{\circ}\text{C}/\text{min.}$ and $10.77\text{ }^{\circ}\text{C}/\text{min.}$ respectively. Difference was significant between FPs for same blends and this difference was increasing with increasing concentration of the solutions except for solution R17.

When we compare the accuracy of this method with some other instrumental methods then we found that the accuracy of simulation method is lower than instrumental methods. The accuracy and reproducibility of DSC are $0.1\text{ }^{\circ}\text{C}$ & $0.05\text{ }^{\circ}\text{C}$ respectively. The accuracy of Backmann method is $0.001\text{ }^{\circ}\text{C}$ and FPD Osmometer has accuracy around 95 %. The simulation method has accuracy around 90 to 95 % ($0.03 - 2.0\text{ }^{\circ}\text{C}$) for EG based SZTLs except the solutions having 5 % NaCl and $2\text{ }^{\circ}\text{C}$ to $15\text{ }^{\circ}\text{C}$ for PG based SZTLs. Cooling curve method has shown its accuracy around 0.05 to $1.0\text{ }^{\circ}\text{C}$ (95 to 98 %).

Table 4.3: Freezing point of PG-based SZTLs determined by cooling curve method

PG:DW	NaCl concentration					
	0%	1%	2%	3%	4%	5%
1:1	-12.5	-13.0	-13.5	-13.5	-14.5	-15.0
1:2	-12.5	-16.5	-15.5	-15.0	-14.0	-17.0
1:3	-12.0	-13.0	-13.5	-14.5	-14.0	-16.0
1:4	-9.5	-10.5	-12.0	-12.0	-16.0	-15.0
1:5	-7.5	-9.5	-9.5	-10.5	-14.5	-13.5
1:6	-5.5	-5.0	-7.5	-6.0	-12.5	-14.0
1:7	-5.0	-5.0	-5.5	-6.0	-12.0	-12.0
1:8	-5.0	-5.0	-7.5	-6.0	-12.0	-12.5

Table 4.4: Predicted initial freezing point of PG-based SZTLs determined by simulation method

PG : DW\ %NaCl	0%	1%	2%	3%	4%	5%
R11	2.60	2.10	2.97	4.23	-2.37	2.97
R12	0.13	2.40	0.43	-0.10	-1.90	-1.30
R13	2.60	1.33	0.80	2.73	-1.17	-0.73
R14	1.33	1.00	0.43	-2.13	-0.57	-0.03
R15	-0.63	1.53	0.80	-1.88	1.00	0.30
R16	1.90	0.87	0.13	0.74	-0.87	-1.67
R17	-0.70	1.60	0.77	-2.01	-1.93	-1.23
R18	0.17	0.87	-0.80	-3.07	-2.93	-1.10

SUMMARY AND CONCLUSIONS

5. SUMMARY AND CONCLUSIONS

The present study on “Simulation studies on thermal cooling data for determination of freezing point” was carried out in which freezing point (FP) of ethylene glycol and propylene glycol based SZTLs with different concentration of NaCl salt were estimated by using of simulation program. To determine the FP of these solutions, first cooling rates were calculated by simulation technique with the help of thermal cooling data. Segmented temperature profiles upto the initial FP of all these EG and PG-based SZTLs were plotted. The FPs determined by simulation method was compared with the FPs of same solutions which were determined by manual cooling curve method. Based on the outcomes of this research work, following inferences are drawn:

- Initially the cooling rate of EG-SZTLs and PG-SZTLs was higher and the temperature profile followed Newtonian cooling behavior. As temperature of solutions decreased, cooling rate also decreased due to the increase in the viscosity of solutions hence heat transfer decreased.
- Heat transfer was found higher in EG-based SZTLs than PG-based SZTLs because of higher thermal conductivity of ethylene glycol compare to propylene glycol.
- At higher concentrations of EG and PG based SZTLs, there was a decrease in subcooling.
- In EG-SZTLs, cooling rate became constant after 80-90 min. of initiation of cooling process where in PG-SZTLs, it took average 100 min. to become constant.
- Average CR of EG-SZTLs were found between 0.05 to 0.1 °C/min. where for PG-SZTLs, it was in the range of 0.03 to 0.04 °C/min.

SUMMARY AND CONCLUSIONS

- Cooling rate of EG-SZTLs solutions was higher than PG-SZTLs solutions. Maximum values of CR of EG solutions were ranging from 0.5 °C/min. to 1.5 °C/min. For PG-SZTLs, max. CRs were found below 0.5 °C/min.
- According to simulation results, average 90- 110 min. were taken by the EG-SZTLs to achieve their initial FPs except 5 % NaCl solution who took 285 min. Average 210- 230 min. were taken by the PG-SZTLs to achieve their initial FPs except 3 % NaCl solution who took 175 min.
- FPD of EG-SZTLs is increased with increasing salt concentration from 0 % NaCl to 4 % NaCl in the solutions. FPD in PG-SZTLs was not observed with increasing salt concentration from 0 % to 5 % NaCl in the solutions.
- Most of the FPs of EG-SZTLs (0 % to 4 % NaCl) solutions which were determined by simulation method were very close to the FPs of these solutions which were determined by cooling curve method.
- Overall, simulation method gave satisfactory results of FPs for EG solutions except 5 % NaCl solutions but for PG solutions, results of predicted FPs were not satisfactory. It was observed that the determination of initial freezing point in case of EZ was successful as the solutions were subjected to higher cooling rates (>1.0 °C/min). While PG based SZTL were subjected to slow cooling (< 0.5 °C/min).
- The data logging interval was of three min which caused difficulty in accurate segmentation of the temperature profile curves.
- The result suggests need for multiple curve segmentation while in the present study only single step segmentation method was used.
- It is concluded that there is potential to use the simulation method for determination of initial freezing point of multi-component solutions. This simulation method gave acceptable results for half of the solution's initial freezing point. Such solutions can be used effectively as heat transfer fluids in dairy and food processing industries. By increasing cooling rate, more precised FPs can be obtained.

Future Study

- ✓ In this study, constant cooling rate of deep freezer was kept. Thermal cooling data can also be generated by varying the cooling rate.
- ✓ Single step segmentation was used in the present study. Multiple step segmentation of the temperature curve can help in accurate prediction of freezing properties.
- ✓ By increasing the temperature data logging rate more precise data can be obtained and all the processes during freezing of substance can be separated by using simulation method and inferences can be drawn.

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ANNEXURE

ANNEXURE

Table 1: Descriptive Statistics of EG-based SZTLs with 0 % NaCl

	N	Range	Minimum	Maximum	Mean	Std. Deviation	Variance
Time (min)	1113	1110.00	3.00	1113.00	558.0000	321.43869	103322.833
R11	1113	.77	.00	.77	.0927	.09266	.009
R12	1113	.50	.00	.50	.0720	.08670	.008
R13	1113	.50	.00	.50	.0612	.08844	.008
R14	1113	.63	.00	.63	.0687	.09896	.010
R15	1113	.63	.00	.63	.0714	.10120	.010
R16	1113	.67	.00	.67	.0737	.10523	.011
R17	1113	1.00	.00	1.00	.0875	.11232	.013
R18	1113	1.07	.00	1.07	.0576	.12935	.017
Valid N (listwise)	1113						

Table 2: Descriptive Statistics of EG-based SZTLs with 1 % NaCl

	N	Range	Minimum	Maximum	Mean	Std. Deviation	Variance
Time (min)	1140	1137.00	3.00	1140.00	571.5000	329.23295	108394.333
R11	1140	1.00	.00	1.00	.1162	.10736	.012
R12	1140	.83	.00	.83	.0827	.09964	.010
R13	1140	.87	.00	.87	.0749	.09873	.010
R14	1140	.83	.00	.83	.0718	.09555	.009
R15	1140	1.20	.00	1.20	.0940	.10816	.012
R16	1140	1.27	.00	1.27	.0950	.10938	.012
R17	1140	1.27	.00	1.27	.0761	.11265	.013
R18	1140	1.70	.00	1.70	.1051	.13153	.017
Valid N (listwise)	1140						

Table 3: Descriptive Statistics of EG-based SZTLs with 2 % NaCl

	N	Range	Minimum	Maximum	Mean	Std. Deviation	Variance
Time (min)	1185	1182.00	3.00	1185.00	594.0000	342.22337	117116.833
R11	1185	1.03	.00	1.03	.0950	.10860	.012
R12	1185	.93	.00	.93	.0822	.10228	.010
R13	1185	.93	.00	.93	.0815	.10079	.010
R14	1185	1.07	.00	1.07	.0739	.10937	.012
R15	1185	1.00	.00	1.00	.0787	.10676	.011
R16	1185	1.13	.00	1.13	.0692	.11040	.012
R17	1185	1.30	.00	1.30	.0658	.11503	.013
R18	1185	1.37	.00	1.37	.0712	.12201	.015
Valid N (listwise)	1185						

Table 4: Descriptive Statistics of EG-based SZTLs with 3 % NaCl

	N	Range	Minimum	Maximum	Mean	Std. Deviation	Variance
Time (min)	1377	1374.00	3.00	1377.00	690.0000	397.64913	158124.833
R11	1377	.80	.00	.80	.0863	.09399	.009
R12	1377	.63	.00	.63	.0835	.08722	.008
R13	1377	.80	.00	.80	.0799	.09130	.008
R14	1377	.93	.00	.93	.0782	.09512	.009
R15	1377	1.50	.00	1.50	.1044	.10313	.011
R16	1377	1.67	.00	1.67	.0967	.11477	.013
R17	1377	1.27	.00	1.27	.0678	.10949	.012
R18	1377	1.03	.00	1.03	.0712	.10744	.012
Valid N (listwise)	1377						

Table 5: Descriptive Statistics of EG-based SZTLs with 4 % NaCl

	N	Range	Minimum	Maximum	Mean	Std. Deviation	Variance
Time (min)	1101	1098.00	3.00	1101.00	552.0000	317.97458	101107.833
R11	1101	6.53	.00	6.53	.1096	.28896	.083
R12	1101	6.77	.00	6.77	.1035	.29581	.088
R13	1101	7.33	.00	7.33	.1243	.32573	.106
R14	1101	7.67	.00	7.67	.1050	.33749	.114
R15	1101	8.13	.00	8.13	.0891	.35532	.126
R16	1101	8.23	.00	8.23	.0695	.36228	.131
R17	1101	8.57	.00	8.57	.0745	.37591	.141
R18	1101	9.03	.00	9.03	.0929	.39419	.155
Valid N (listwise)	1101						

Table 6: Descriptive Statistics of EG-based SZTLs with 5 % NaCl

	N	Range	Minimum	Maximum	Mean	Std. Deviation	Variance
Time (min)	1140	1137.00	3.00	1140.00	571.5000	329.23295	108394.333
R11	1140	.20	.00	.20	.0326	.03705	.001
R12	1140	.17	.00	.17	.0310	.03453	.001
R13	1140	.17	.00	.17	.0319	.03496	.001
R14	1140	.20	.00	.20	.0326	.03685	.001
R15	1140	.20	.00	.20	.0349	.03880	.002
R16	1140	.23	.00	.23	.0327	.03858	.001
R17	1140	.33	.00	.33	.0342	.04704	.002
Valid N (listwise)	1140						

Table 7: Descriptive Statistics of PG-based SZTLs with 0 % NaCl

	N	Range	Minimum	Maximum	Mean	Std. Deviation	Variance
Time (min)	5577	5574.00	3.00	5577.00	2790.0000	1610.08535	2592374.833
R11	5577	1.29	.00	1.29	.0157	.03823	.001
R12	5577	.20	.00	.20	.0145	.02342	.001
R13	5577	.20	.00	.20	.0145	.02401	.001
R14	5577	.50	.00	.50	.0140	.02684	.001
R15	5577	.30	.00	.30	.0148	.02571	.001
R16	5577	.40	.00	.40	.0190	.02928	.001
R17	5577	.37	.00	.37	.0194	.03026	.001
R18	5577	.30	.00	.30	.0164	.02726	.001
Valid N (listwise)	5577						

Table 8: Descriptive Statistics of PG-based SZTLs with 1 % NaCl

	N	Range	Minimum	Maximum	Mean	Std. Deviation	Variance
Time (min)	720	717.00	3.00	720.00	361.5000	207.98878	43259.332
R11	720	.33	.00	.33	.0491	.04516	.002
R12	720	.17	.00	.17	.0454	.03994	.002
R13	720	.20	.00	.20	.0459	.04168	.002
R14	720	.33	.00	.33	.0469	.04984	.002
R15	720	.40	.00	.40	.0495	.05467	.003
R16	720	.43	.00	.43	.0493	.05969	.004
R17	720	.27	.00	.27	.0440	.05418	.003
R18	719	.35	.00	.35	.0464	.05403	.003
Valid N (listwise)	719						

Table 9: Descriptive Statistics of PG-based SZTLs with 2 % NaCl

	N	Range	Minimum	Maximum	Mean	Std. Deviation	Variance
Time (min)	6141	6138.00	3.00	6141.00	3072.0000	1772.89815	3143167.833
R11	6141	.20	.00	.20	.0152	.02460	.001
R12	6141	.23	.00	.23	.0138	.02311	.001
R13	6141	.23	.00	.23	.0118	.02252	.001
R14	6141	.23	.00	.23	.0128	.02294	.001
R15	6141	.23	.00	.23	.0135	.02374	.001
R16	6141	.23	.00	.23	.0142	.02347	.001
R17	6141	.27	.00	.27	.0116	.02431	.001
R18	2047	.33	.00	.33	.0151	.02773	.001
Valid N (listwise)	2047						

Table 10: Descriptive Statistics of PG-based SZTLs with 3 % NaCl

	N	Range	Minimum	Maximum	Mean	Std. Deviation	Variance
Time (min)	4614	4611.00	3.00	4614.00	2308.5000	1332.09115	1774466.833
R11	4614	5.00	.00	5.00	.0228	.07911	.006
R12	4614	5.80	.00	5.80	.0211	.08987	.008
R13	4614	6.20	.00	6.20	.0198	.09763	.010
R14	4614	5.60	.00	5.60	.0158	.09655	.009
R15	4614	6.23	.00	6.23	.0198	.10444	.011
R16	4614	6.30	.00	6.30	.0182	.10654	.011
R17	4614	6.07	.00	6.07	.0169	.10810	.012
R18	4614	6.77	.00	6.77	.0183	.11969	.014
Valid N (listwise)	4614						

Table 11: Descriptive Statistics of PG-based SZTLs with 4 % NaCl

	N	Range	Minimum	Maximum	Mean	Std. Deviation	Variance
Time (min)	5841	5838.00	3.00	5841.00	2922.0000	1686.29559	2843592.833
R11	5841	4.90	.00	4.90	.0212	.06895	.005
R12	5841	4.60	.00	4.60	.0185	.06483	.004
R13	5841	4.10	.00	4.10	.0155	.05867	.003
R14	5841	4.63	.00	4.63	.0153	.06599	.004
R15	5841	5.23	.00	5.23	.0157	.07342	.005
R16	5841	4.87	.00	4.87	.0181	.07036	.005
R17	5841	4.20	.00	4.20	.0213	.06385	.004
R18	5841	3.50	.00	3.50	.0215	.06026	.004
Valid N (listwise)	5841						

Table 12: Descriptive Statistics of PG-based SZTLs with 5 % NaCl

	N	Range	Minimum	Maximum	Mean	Std. Deviation	Variance
Time (min)	8919	8916.00	3.00	8919.00	4461.0000	2574.83773	6629789.333
R11	8919	1.27	.00	1.27	.0200	.03458	.001
R12	8919	.23	.00	.23	.0147	.02123	.000
R13	8919	.23	.00	.23	.0137	.02052	.000
R14	8919	.23	.00	.23	.0105	.02059	.000
R15	8919	.33	.00	.33	.0108	.02120	.000
R16	8919	.40	.00	.40	.0168	.02478	.001
R17	8919	.63	.00	.63	.0139	.02639	.001
R18	8919	.77	.00	.77	.0148	.02805	.001
Valid N (listwise)	8919						