PRODUCTION AND DEVELOPMENT OF DE/ANTI ICING FLUIDS FOR AIRCRAFT

A THESIS SUBMITTED TO
THE GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES
OF
MIDDLE EAST TECHNICAL UNIVERSITY

BY

BARIŞ ERDOĞAN

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR
THE DEGREE OF MASTER SCIENCE
IN
CHEMICAL ENGINEERING

SEPTEMBER 2008

Approval of the thesis:

PRODUCTION AND DEVELOPMENT OF DE/ANTI ICING FLUIDS FOR AIRCRAFT

submitted by **BARIŞ ERDOĞAN** in partial fulfillment of the requirements for the degree of **Master Science in Chemical Engineering Department, Middle East Technical University** by

Prof. Dr. Canan Özgen
Dean, Gradute School of **Natural and Applied Sciences** ____________________

Prof. Dr. Gürkan Karakaş¸
Head of Department, **Chemical Engineering Dept** ____________________

Assoc. Prof. Dr. Yusuf Uludağ
Supervisor, **Chemical Engineering Dept, METU** ____________________

Assoc. Prof. Dr. Göknur Bayram
Co-supervisor, **Chemistry Dept, METU** ____________________

Examining Committee Members:

Prof. Dr. Ülkü Yılmazer
Chemical Engineering Dept, METU ____________________

Assoc. Prof. Dr. Yusuf Uludağ
Chemical Engineering Dept., METU ____________________

Assoc. Prof. Dr. Göknur Bayram
Chemical Engineering Dept., METU ____________________

Assoc. Prof. Dr. Halil Kalıpçılar
Chemical Engineering Dept, METU ____________________

Assoc. Prof. Dr. Serkan Özgen ____________________
Aerospace Engineering Dept, METU

Date: 04/09/2008

I hereby declare that all information in this document has been obtained and presented in accordance with academic rules and ethical conduct. I also declare that, as required by these rules and conduct, I have fully cited and referenced all material and results that are not original to this work.

Name, Last Name: Barış Erdoğan

Signature :

ABSTRACT

PRODUCTION AND DEVELOPMENT OF DE/ANTI ICING FLUIDS FOR AIRCRAFT

Erdoğan, Barış
M.Sc. in Chemical Engineering
Supervisor: Assoc. Prof. Dr. Yusuf Uludağ
Co-supervisor: Assoc. Prof. Dr. Göknur Bayram

September 2008, 109 pages

Aircraft are not allowed to take off prior to cleaning of snow and ice deposits that form on their surfaces under winter conditions to refrain from compromising flight safety. Water based solutions containing mainly ethylene or propylene glycol, or both, are employed either to remove the snow/ice layers or to provide protection against deposition of these layers. The first group of solutions, i.e. de-icing fluids, are Newtonian and have generally low viscosity so that right after their application they fall off the aircraft surfaces, providing little or no further protection against precipitation. Therefore, various anti-icing solutions have then been developed to provide the prolonged protection due to their non-Newtonian and high viscosity characteristics. Although the appropriate ranges of viscosity and surface tension have been determined in a number of studies, actual compositions of these solutions are proprietary. The main objective of this study is to determine the basic interactions between the chemical species in de/anti-icing fluids and their effects on the physical properties of the solutions, especially viscosity, surface tension, freezing point and corrosive effect which enable the design of the de/anti icing fluid composition. A number of polymers and surfactants were dissolved in water-glycol solutions and used in different compositions to get the desired viscosity and surface properties. The dependence of viscosity on polymer concentration, pH of the solutions, glycol content, surfactant concentration, temperature and shear rate were investigated and reported in detail. Among various chemicals, slightly crosslinked and hydrophobically modified polyacrylic acid was utilized as a thickener, sodium oleate and tributyl amine were used as surface agents in the de/anti-icing solutions whose physical properties satisfied the desired requirements.

In addition to the studies about de/anti icing solutions, synthesis of a new polymer namely poly (DADMAC-co-vinyl pyyrolidone) was made and its characterization and performance tests were performed. High swelling ratios (up to 360) were attained with 0.5 % crosslinker in 2-3 minutes. Moreover, swellings of the gels were demonstrated to be independent of pH. It was also thought that such a copolymer having anti-bacterial effect induced by DADMAC (Diallyldimethyl ammonium chloride) segments and biocompatability of NVP (N-vinyl pyyrolidone) component would be of interest in biorelated areas.

Keywords: De-icing fluids, anti-icing fluids, aircraft performance, pseudoplastic rheology, polyacrylic acid, surfactant

ÖZ

UÇAKLARIN BUZLANMALARINI ENGELLEYİCİ VE ÖNLEYİCİ ÇÖZELTİLERİN ÜRETİMİ VE GELİŞTİRİLMESİ

Erdoğan Barış
Yüksek Lisans, Kimya Mühendisliği
Tez Yöneticisi: Doç. Dr. Yusuf Uludağ
Ortak Tez Yöneticisi: Doç Dr. Göknur Bayram

Eylül 2008, 109 sayfa

Uçaklar kış aylarında güvenlik tedbirleri gereğince kanatları üzerinde kar ve buz birikintileri ile birlikte kalkış yapamazlar. Bu yüzden ana bileşeni su ve glikolden oluşan ve uçağın buzlanmasını önleyici ve engelleyici çözeltiler kullanılmaktadır. Birinci tip çözeltiler uçağın yüzeyinde bulunan buz ve kar birikintilerini temizlemek için kullanılırlar. Bu çözeltiler genel olarak Newton yasasına uyarlar ve düşük viskozite değerlerine sahiptirler. Uygulanışlarından sonra kısa sürede kanat üzerinden akıp giderler ve uzun süreli koruma sağlayamazlar. Dolayısıyla uçaklar havalanana kadar ilgili yüzeylere koruma sağlayabilmek için buzlanmayı engelleyici ikinci tip çözeltiler geliştirilmiştir. Bu çözeltiler psödoplastik reolojiye sahiptirler ve yüksek viskozite değerleriyle uzun süreli koruma sağlayabilmektedirler. Bu sıvıların viskozite yüzey gerilimi gibi fiziksel özellikleri bilinse de kompozisyonları gizli kalmıştır. Bu çalışmanın temel amacı buzlanmayı önleyici ve engelleyici çözeltilerin içerisindeki temel kimyasallar arasındaki etkileşimleri araştırmak ve bu etkileşimlerin sıvıların viskozite, yüzey gerilimi, donma noktası ve korozyon etkisi gibi fiziksel özellikleri üzerinde yarattığı değişimleri araştırmaktır. Bu etkileşimlerin aydınlanması ile sıvılar için uygun kompozisyonların bulunması olanaklı olacaktır. Çalışma çerçevesinde birçok polimer ve yüzey aktif madde glikol-su karışımlarında çözülerek değişik konsantrasyonlarda kullanılmıştır. Viskozitenin polimer, glikol, yüzey aktif madde konsantrasyonu, pH, sıcaklık ve kayma hızı ile değişimi gözlenmiş, detaylı olarak rapor edilmiştir. Kullanılan kimyasallar arasında çok az çapraz bağlanmış ve hidrofobik olarak geliştirilmiş poliakrilik asit koyulaştırıcı polimer olarak ve tributilamin ile sodyum oleat yüzey aktif madde olarak istenen fiziksel özelliklere yakın sonuçlar vermişlerdir.

Buzlanmayı önleyici ve engelleyici çözeltilerin üretimi konusunda yapılan çalışmalara ek olarak deneyler sırasında poli(DADMAC-ko-vinil pirolidon) adlı yeni bir polimerin sentezi gerçekleştirilmiştir. Çalışmanın içerisinde bu polimere ait karakterizasyon ve performans testlerine de yer verilmiştir. Elde edilen sonuçlara göre polimerin % 0.5 oranında çapraz bağlanmış formu 2-3 dakikada 360 kat su emebilmektedir. Aynı zamanda jelin emme kapasitesi pH ile değişim göstermemektedir. Bu polimerin DADMAC’tan gelen anti-bakteriyel ve vinilpirolidon’dan gelen biyolojik uyumluluğu ile biyolojik uygulama alanlarında yer bulabileceği düşünülmektedir.

Anahtar sözcükler: Buzlanmayı engelleyici çözeltiler, buzlanmayı önleyici çözeltiler, uçak performansı, psödoplastik reoloji, poliakrilik asit, yüzey aktif madde

To My Family;

ACKNOWLEDGEMENTS

The author wishes to express his deepest gratitude to his supervisor Assoc. Prof. Dr. Yusuf Uludağ and co-supervisor Assoc. Prof Dr. Göknur Bayram for their guidance, advice, criticism, encouragements and insight throughout the research.

The author would also like to thank Assoc. Prof. Dr. Serkan Özgen for his suggestions and comments through out the study.

The author wish to extend his thanks to Prof. Dr. Niyazi Bıçak for his guidance and supervision throughout the polymer synthesis experiments.

The lab mate of Durmuş Sinan Körpe is gratefully acknowledged for his contributions to the laboratory work.

This study was supported by The Scientific and Research Council of Turkey (TÜBİTAK) Project No: 106 M 219.

TABLE OF CONTENTS

CHAPTER

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

SDS : Sodium dodecyl suphate

AOT : 2-ethyl hexyl sulfosuccinate

TBAF : Tetrabutylammonium tetrafluoroborate

DAC : Dimethyldioctadecylammonium chloride

CTAB : Hexadecyltrimethylammonium bromide

Triton X-405 : Polyoxyethylene(40) isooctylphenyl ether

HMPA : Slightly crosslinkled and hydrophobically modified polyacrylic acid

TAP : Tetraally piperazinium dichloride

AIBN : Azobisisobutyronitrile

AMC : Poly (acrylic acid-co-maleic acid)

DA : Poly (DADMAC-co-acrylamide)

DCVP : Poly (DADMAC-co-vinyl pyyrolidone)

PA : Polyacrylamide

PAA : Polyacrylic acid

NaO : Sodium oleate

CMC : Carboxymethylcellulose

BT : Benzotriazole

S : Surfactant

pH C : pH controller

CI : Corrosion inhibitor

cmc: : Critical micelle concentration

DADMAC : Diallyldimethyl ammonium chloride

NVP : N- vinyl pyyrolidone

CHAPTER 1

INTRODUCTION

Aircrafts are not allowed to take off prior to cleaning of snow and ice deposits that form on their surfaces under winter conditions to refrain from compromising flight safety. US Federal Aviation Administration (FAA) proposed the concept of clean airplane and they stated that, according to the rules numbered as 209 and 121629, an airplane can not take off before it is totally cleaned up from all ice and snow deposits on their surfaces [1]. The idea behind these rules is the negative effects of these deposits on aircraft performance. The negative effects of icing can be observed in lifting and friction force on aircraft [1,2]. Due to icing, the total weight of the aircraft increases and so the total lifting force required for take off increases [2]. At the same time, roughness on aircraft surfaces (See Figure 1) due to the ice formation increases and that disturb the airflow on the wings so lift coefficient decreases. These negative effects force the airplane to take-off at higher speeds close to the emergency conditions [2]. Another effect is related to the angle of attack, because of icing, the angle of attack necessary for the maximum lifting force may decrease and this decrease can not be recognized by the sensors of the aircraft [1]. Icing also increases the friction force applied to the aircraft so that the airplanes need higher angle of attack for the same lifting force. The last effect of icing on aircraft performance is observed in decreasing maneuver capability. Because of the frozen control unites of the aircraft, movement ability is significantly reduced. As a result of these all negative effects of ice and snow contamination on aircraft surfaces, aircrafts are not allowed to take off prior to cleaning of these deposits.

De-icing and anti-icing fluids have been utilized in order to remove the snow and frost from the surfaces of the aircraft since 1930s. The major component of these fluids is ethylene or propylene glycol which is a strong freezing point depressant and has high compatibility with aircraft materials. Propylene glycol is more environmentally friendly than ethylene glycol but also it is the one with higher cost [3, 4].

De/anti icing fluids are classified in 4 different types as; type-1, type-2, type-3 and type-4 fluids. Type-1 fluids are generally called de-icing fluids and they are used to clean aircraft surfaces from snow and ice. They contain at least 70 % of glycol and trace amounts of surfactant and corrosion inhibitor. They have a Newtonian rheology in other words; they have constant viscosities over varying shear rates [3]. Type-2 fluids are generally called anti-icing fluids and they are used to protect the aircraft surfaces against further snow and ice contamination. They contain approximately about 50 % of glycol and small amount of thickening agent which makes the solution shear-thinning. Also, there are trace amounts of surfactant and corrosion inhibitor in the mixture [4]. Type-3 fluids are produced for the airplanes which have a low take-off speed in order to take place of type-1 fluids. Type-3 fluids are not produced today [5]. Type-4 fluids are also called anti-icing fluids and they are very similar to type-2 fluids but their viscosities are greater than type-2 fluids so that their hold-over times are greater. Type-4 fluids are generally used in the countries where the winter conditions are tougher [6].

The application of de/anti icing fluids is carried out either with a one-step or two-step procedure. In one step procedure, type-1 fluids are utilized and it is generally applied when it is not snowing. In two-step procedure, first type-1 fluids are used to clean the contamination on the surfaces. Then type-2 fluids are applied and the further contamination is prevented. The important thing here is to apply type-2 fluids right after (in three minutes) the type-1 fluid and to be sure that de-icing fluids are not frozen on the aircraft surfaces [7]. The aircraft surfaces where the de/anti icing fluids are applied can be listed as [2];

- Wing upper surface and leading edge
- Horizontal stabilizer
- Elevator
- Vertical stabilizer
- Rudder

These surfaces are shown in the following Figure 1.1

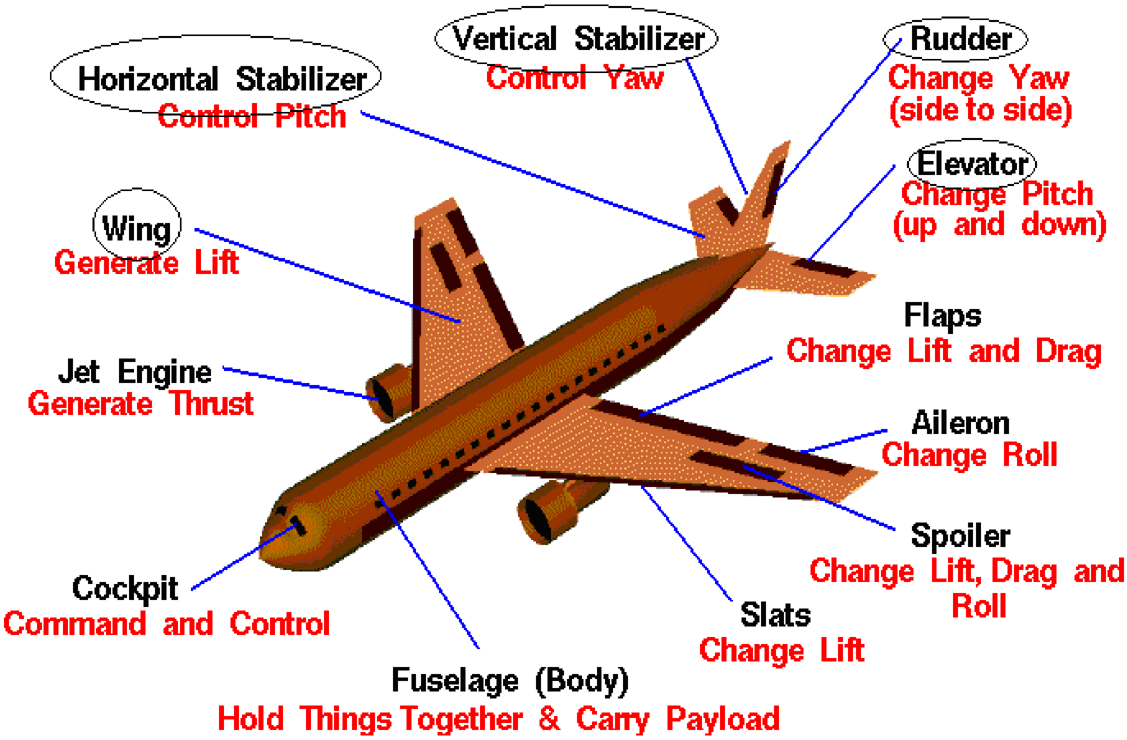


Figure 1.1: The surfaces of the aircraft where the de/anti icing fluids applied

The thickening agent amount in anti-icing fluids increases the holdover time which is an estimated time that the anti-icing fluid will prevent the formation of the ice and the accumulation of snow on the protected surfaces of an aircraft. Holdover time begins when the final application of anti-icing fluid commences and expires when the anti-icing fluid applied to the aircraft loses its effectiveness [4]. Holdover time may vary according to the weather and surface conditions such as; air temperature, humidity, surface temperature, etc. The thickening agent in the anti-icing fluids also adds shear-thinning behavior to the solutions so that fluids can easily flow off from the surfaces of the airplanes during take-off maneuver.

The general physics of the shear-thinning fluids is described by Herschel-Bulkely [4];

$$\tau = \tau_0 + K \cdot \dot{\gamma}^B \qquad (1.1)$$

where; τ : shear stress, τ_0 : yield stress, K: consistency, $\dot{\gamma}$: shear rate, B: power law exponent

In this equation, shear stress over shear rate gives the spontaneous viscosity. The primary term which contributes to holdover time is yield stress; however the flow properties are mainly governed by K and B. Therefore, increasing τ_0 improves holdover, and decreasing K and B improves flow-off behavior.

When the fluids are examined from viscoelastic point of view, the complex modulus is given by,

$$G^* = G' + iG'' \tag{2.2}$$

where, G' is in-phase elastic component or shear storage modulus and G'' is out-phase viscous component or shear loss modulus. The requirements for easier flow is low elasticity where G'' dominates.

Although anti-icing fluids have been in use since 1930, the standards and tests for these fluids are determined and authorized after an aircraft accident occurred in 1982 in Washington DC, USA due to icing problems. In the aftermath of this accident, when public awareness was very high, the International Aviation Industry marshaled its considerable resources toward the goal of eliminating such accidents. Their strategy was threefold **[8]**:

1) To give flight crews, ground crews, flight dispatchers, and traffic controllers, a proper appreciation of the potential lethality of taking-off with wing ice.
2) To develop improved deicing and anti-icing fluids to specify their chemical and physical characteristics and their aerodynamic influence.
3) To define and successfully implement operational procedures that would insure a "clean aircraft" at take-off.

The "clean aircraft" concept is, in large part, assured by the Critical Surface Inspection, which is a pre-flight external inspection of critical surfaces conducted by a qualified person, to determine if the surfaces are contaminated by frost, ice, slush or snow [2].

After FAA declared this threefold strategy, many scientists and engineers tried to produce de/anti icing fluids in better performance qualities. There are two big companies producing the de and anti-icing fluids which are Killfrost and Dow. Their products are quite successful in satisfying the regulations today but the area is wide open to new developments especially in hold-over times and flow-off behavior of fluids. Also there has been no production of de/anti icing fluids in Turkey yet.

Therefore, the main objective of this study is to determine the required chemical species to get the desired physical properties, especially viscosity, surface tension and freezing point which enable the design of the de/anti icing fluid composition. To deal with it, a number of polymers and surfactants were dissolved in water-glycol solutions and used in different compositions to get the desired viscosity and surface properties. The dependence of viscosity on both polymer concentration, pH of the solutions, glycol content, surfactant concentration, and temperature and shear rate were investigated and reported in detail. The relation between polymers and surfactant molecules in glycol-water solutions were further studied and the effect of cationic, anionic and nonionic surfactants on both solution rheology and surface tension were summarized.

CHAPTER 2

BACKGROUND

2.1 The physical properties of the de/anti icing fluids

The basic physical properties of the de/anti icing fluids are determined by Society of Automotive Engineers (SAE) Aerospace Material Specifications (AMS) 1424-1428 standards, and these properties can be measured according to the procedures stated in American Society for Testing and Material (ASTM) standards. The basic physical properties of the fluids are explained in the following sections.

2.1.1 Surface Tension

The de/anti icing fluids are produced in a way that they provide rapid and uniform wetting and spreading on the surface of the aircraft, maximizing the efficiency and effectiveness of its application (ASTM D 971). The value of the surface tension is below 40 Dynes/cm for anti-icing fluids and 45 Dynes/cm for de-icing fluids [9].

2.1.2 Viscosity

Since viscosity varies depending on the force applied on the fluid, when viscosities are measured and compared, it is important to specify precisely the methods of measurement. For instance, viscometer type, viscometer model, temperature, rotation speed, spindle number, and time after beginning of rotation must be reported (ASTM D 445). Therefore, viscosity values are generally given as approximately [9]. For de-icing solutions viscosity values may change between 10 cP to 50 cP at 20 ^{o}C. In the case of anti-icing fluids, low shear rate viscosities strictly determine the hold-over time and it changes around 1000 cP to 1500 cP at 20 °C. The high shear rate viscosity shows the flow-off behavior of these fluids and it is around 100-140 cP at 20 °C. An example of shear rate-viscosity graph of a typical anti-icing fluid is shown in Figure 2.1.

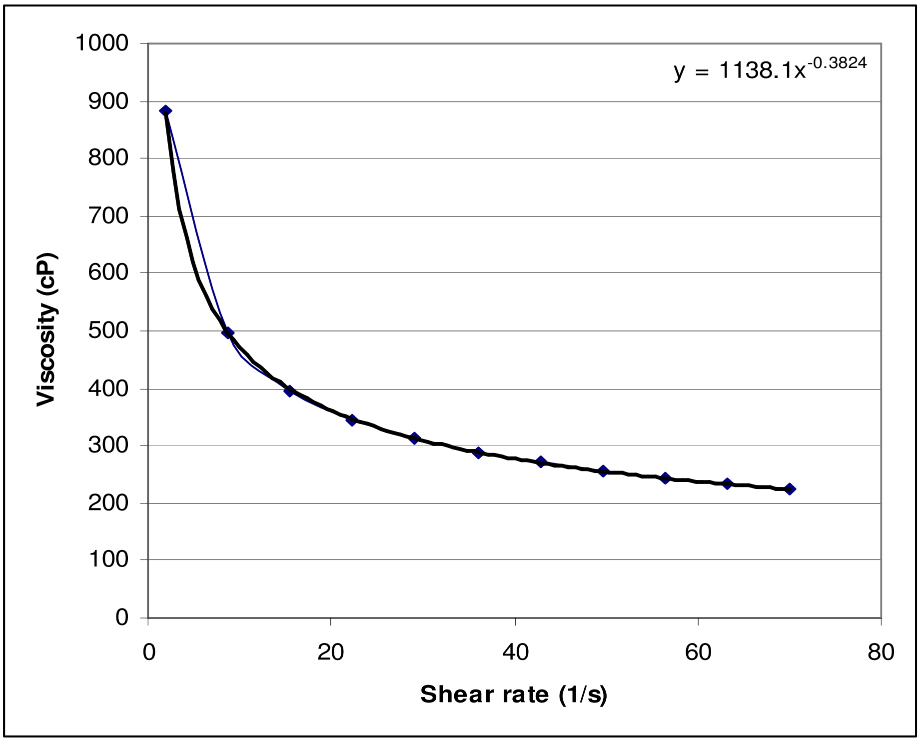


Figure 2.1: The rheological behavior of Killfrost ABC-3 (anti-icing) fluid at 20 °C

The equation shown in the corner of Figure 2.1 is called the power law equation of the fluid and 0.3824 is the power of that equation. Its magnitude shows the shear-thinning behavior of the fluid.

2.1.3 Freezing Point

The freezing point for the solutions is the temperature when the first solid crystals start to occur under a constant pressure. Glycol and the other chemicals present in the fluids decrease the freezing point of the water, which has role of a solvent in the solution. There is no meaning of using de/anti icing fluids if the ambient air temperature is lower than the freezing point temperature of the fluids (ASTM D 1177). The value of the freezing point is typically -20 °C for de-icing fluids and -37 °C for anti-icing fluids [10].

2.1.4 The Lowest Operational Use Temperature

The lowest operational use temperature (LOUT) of an anti-icing fluid is generally recognized as the higher of [10]:

1) The lowest temperature at which it meets the aerodynamics acceptance test for a given type of aircraft, or
2) The freezing point of the fluid plus the freezing point buffer of 7 ^{o}C.

2.1.5 Materials Compatibility

The fluids must not corrode the surfaces of the airplanes, storage tanks and also related equipments. ASTM F 483, F485, F502, F945, F1110, F1111 test methods are used in different places of the aircraft, including the painted areas to measure the corrosive effect of the fluids [2].

2.1.6 pH

The pH value of the de/anti icing fluids is around 7. The value of the pH affects the corrosive effects of the fluids and also changes the viscosity values; therefore it plays a vital role in solution behavior [9, 10].

2.1.7 Flash Point

The flash point of a flammable liquid is the lowest temperature at which it can form an ignitable mixture in air. At this temperature, the vapor may cease to burn when the source of ignition is removed. These fluids have no flash point as measured by the ASTM method D 93. During normal use and under proper storage and handling conditions, de/anti icing fluids are considered to be non-flammable.

The physical properties of currently used de/anti icing fluids are shown in Table 2.1.

Table 2.1: The physical properties of currently used de/anti icing fluids

	UCAR Ultra+ Type 4	*Killfrost ABC-S Type 4*	*UCAR Flight guard AD 480 Type 4*	*Arctica DG Type 1*
Water spray Endurance Test (minutes)	90-120	60-100	90-100	5.5
High Humidity Endurance Test (hours)	10		12	0.5
Freezing Point (^oC)	- 59	-37	-36	-30
The lowest operational use temperature (^oC)	-24	-28	-29	-20
Shelf Life (year)	1	2	1	
Color	Green	Green	Green	Green
*Material compatibility**	Obeys 1,2,3	Obeys 1	Obeys 1	Obeys 1
Surface Tension (Dynes/cm)	35.7	33	33.4	37.9
pH	8.5-9.5	6.5-7.5	6.7-8.7	9.8
Ignition Temperature (^oC)	-	> 100 ^{o}C	> 100 ^{o}C	> 100 ^{o}C
Density (g/cm^3)	1.0875	1.038	1.03	1.1

* SAE AMS 1424D (1), Boeing D6-17487 (2), Douglas CSD #1 Tip II (3)

2.2 De/anti-icing Fluid Patents

Analyzing the de/anti-icing fluid patents gives an idea of what basic chemicals were used so far and what their missions in the solutions are. The chemicals and the mixing procedures in the patents were not clearly identified because of probable commercial concerns. The patents are listed in historical basis and given according to the developments they brought into the area.

Salvador et al. developed a new fluid exhibiting the particular advantage that it has a relatively low viscosity under even at arctic temperatures and low shear rates, which ensures rapid and complete run off of the agent at the take-off of the aircraft even at extreme conditions [11]. In detail the anti-icing fluid is essentially composed of:

(1) 40 to 65 by weight of a glycol belonging to the group of alkylene groups having 2 to 3 carbon atoms and oxylkylene glycols having 4 to 6 carbon atoms.
(2) 35 to 60 % by weight of water.
(3) 0.05 to 1.5 % by weight of a thickener belonging to the group of crosslinked polyacrylates having a viscosity of 1000 to 50.000 mPa.s in a 0.5 % by weight aqueous solution at 20 °C .
(4) 0.05 to 1 % by weight of a water-insoluble component belonging to the group of mineral oils of composite bases.
(5) 0.05 to 1 % by weight of a surfactant belonging to the group of alkali metal alkylarylsulfonates.
(6) 0.01 to 1 % by weight of at least one corrosion inhibitor.

In another study, Tye et al. mentioned a new thickening agent called carrageenan and they claimed that by using this new agent the performance of the anti-icing fluids could be improved. They showed their results in the following graphs which are actually the comparison of the new developed fluids with the earlier ones, in terms of viscosity changes of the fluids with respect to increasing shear rate. In Figure 2.2, the viscosity changes at low shear rates and in Figure 2.3 the viscosity changes at high shear rates are shown [12].

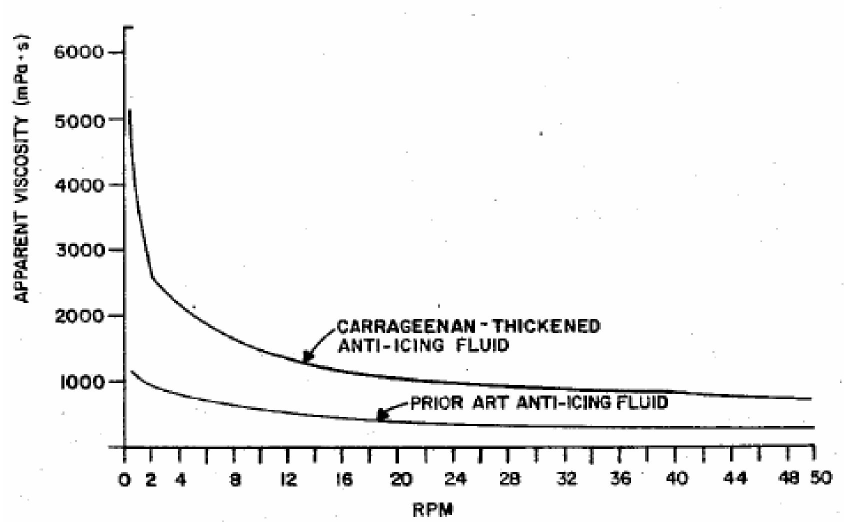


Figure 2.2: The comparison of viscosity changes at low shear rates for carrageenan-thickened fluids with the earlier ones [12]

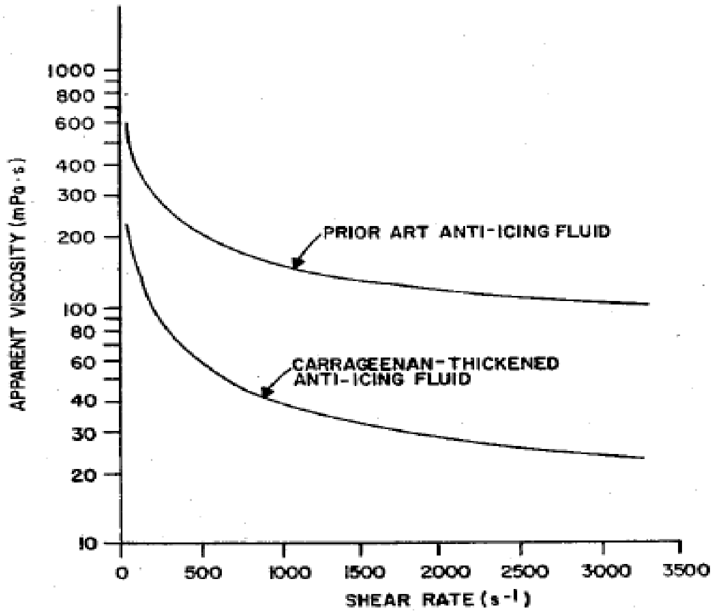


Figure 2.3: The comparison of viscosity changes at high shear rates for carrageenan-thickened fluids with the earlier ones [12]

It was also stated that, the best carrageenan types for the fluid production were iota and kappa carrageenans. The preferred composition of an anti-icing fluid consists of 49.875 % water, 49.875 % glycol and 0.25 % of carrageenan.

In another study, Chan et al. claimed that they found a better fluid in material compatibility and environmental issues [13]. The composition given in the patent is as shown:

(1) 50 to 60 % by weight alkali metal acetate to decrease the freezing point, preferably potassium acetate or sodium acetate.
(2) 0.05 to 0.15 % by weight alkali phosphate ester to decrease the surface tension, for example; octylphenoxy or nonylphenoxy polyethoxy phosphate ethyl ester.
(3) 0.00005 to 0.075 % by weight environmentally friendly dyes.
(4) 0.08 to 0.1 % by weight corrosion inhibitor, phosphoric acid.
(5) 0.015 to 0.025 % by weight second corrosion inhibitor, sodium silicate.

In another patent Jenkins et al. talked about macromolecular polymers that enhance the rheology of the fluids [14]. They claimed that their anti-icing fluid will desirably possess the following attributes:

(i) Formation of essentially continuous film coating, after its application by conventional spraying devices, even on non-horizontal aircraft surfaces critical to the aircraft's aerodynamic performance during take-off/lift-off.
(ii) Extended, long-term protective anti-icing action
(iii) Viscosity and rheology characteristics that promote formation of an effective tenacious protective film coating, yet enabling the fluid coating to flow off the aircraft airfoil surfaces during take-off, prior to aircraft rotation.

They added that this invention was based on the unexpected discovery that certain macromonomer-containing polymers possess particular efficiency as thickeners for glycol-based aircraft anti-icing fluids. The macromonomer-containing polymers useful in this invention comprise:

(1) About 1-99.9, preferably about 10-70, weight percent of one or more unsaturated carboxylic acids

(2) About 0-98.9, preferably about 30-85, weight percent of unsaturated monomers, typically ethyl acrylate

(3) About 0.1- 99, preferably about 5-60, weight percent of one or more unsaturated macromonomers

(4) About 0-20, preferably 0-10, weight percent or polyethylenically unsaturated monomers, typically trimethylol propane triacrylate

In another study, Jenkins et al. stated the effect of hydrophobically modified polymers in the rheology of solutions. The hydrophobic groups in the polymers thicken the solution better and improve its rheological character [15]. The molecular structure of the polymer is shown in the Figure 2.4.

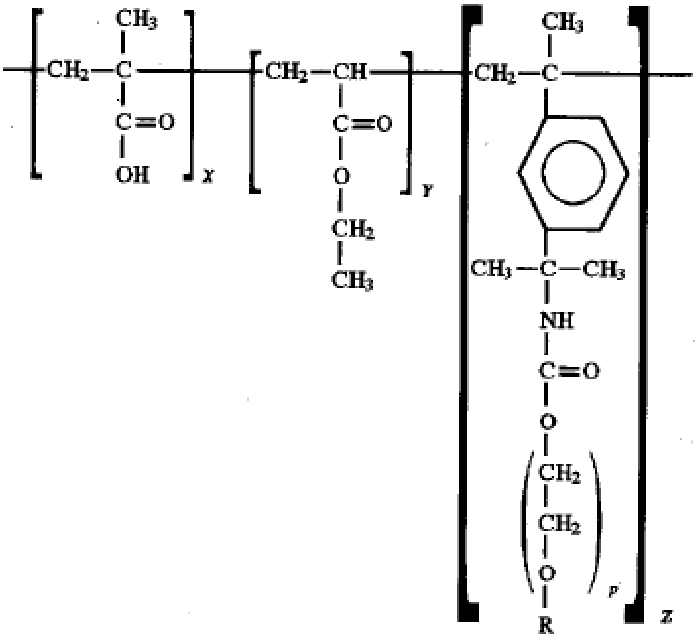


Figure 2.4: The molecular structure of the thickener

In this molecular structure, the monomer with subscript x is methacrylic acid and with subscript y is ethyl acrylate and with subscript z is a hydrophobic monomer with long alkyl groups. Writers gave the composition of an anti-icing fluid that consists of up to 5 wt % thickener and 0.01 to 0.1 wt % surfactants, corrosion inhibitors etc.

In another patent, Carder et al. claimed to produce the anti-icing fluid in a concentrated form and than dilute it prior to usage [16]. They proposed a fluid composition consisting of;

In weight percent;

(1) 40 % glycol, glycerin or the mixture of

(2) Minimum 0.05 % thickener

(3) Trace amounts of hydroxide to keep the pH at 7

(4) Surfactant to increase the thickening effect

(5) Corrosion inhibitor

(6) Dyes

(7) Water

In the last patent examined, Hu et al. claimed that objective of their new fluid is to teach and define an improved de-icing and anti-icing fluid composition having a chemical mechanism to control the diffusion of water and thereby retard the onset of re-freezing of water on the surface of an applied film of an anti-icing fluid. The significance of this invention was not to use a thickening agent in the solutions to have high viscosities, instead Hydrophilic Lipophilic Balance (HLB) agents were used and the desired rheological properties for the de/anti icing fluids could be obtained. It is claimed that, HLB molecules are simply kind of surfactants, and they adjust the HLB values of the solutions so that the rheological behavior of the fluids could be improved [17]. The proposed composition of an anti-icing fluid is as shown;

In weight percent;

- 45-65 % glycol
- 35-65 % water
- 1 ppm-0.5 % surfactant with a HLB value between 4-18
- 1 ppm-0.5 % emulsifying agent
- 1 ppm-1 % pH controller
- 1 ppm-1 % corrosion inhibitor
- 1 ppm-0.5 % foam reducing agent
- 10 ppb-1 % dye

2.3 Hydrophobically modified polymers

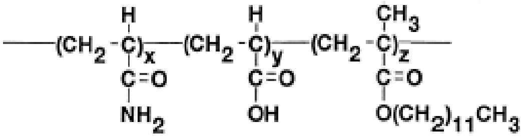
After the analysis of the patents published so far, it can be clearly seen that the thickening agent in an anti-icing fluid plays a vital role in fluid rheology and the polymers are the best candidates to be utilized as thickening agents. Therefore, literature about synthesis and preparation of the polymers that was used in anti-icing fluids were investigated and summarized here.

Among various kind of polymers, acrylamide and acrylic acid based polymers are the most preferred ones to be used as thickening agents, because acrylamide can easily be suited for the manufacture of high-molecular weight polymers and it is the most successful monomer in producing water-soluble copolymers that are effective at polymer concentrations below 1 % by weight [18], and also acrylic acid monomers can be utilized to synthesize polyelectrolytes so that additional rheological improvements can be obtained.

These polymers are generally used in hydrophobically modified forms, because hydrophobic groups placed on a polymer backbone enhance the rheology of the resulting polymer solutions. Hydrophobically modified polymers actually has been the focus of considerable research areas such as; paints, foods, pharmaceutical products and in enhanced oil recovery [19]. A hydrophobically modified polymer usually consists of a major part of hydrophilic backbone and small proportion of hydrophobic groups. When dissolved in aqueous solution, the apolar moieties tend to exclude water and are held together, yielding intra or intermolecular association [20]. Associating polymers have been prepared by two general methods. The first method is the copolymerization of water-soluble and hydrophobic monomers. The second method is the modification of polymers after polymerization to introduce hydrophobic or hydrophilic groups [21].

2.3.1 Hydrophobically modified polyacrylamides

Hydrophobically modified polyacrylamides are commonly prepared using acrylamide by free radical polymerization. Acrylamide is a monomer most suited for the manufacture of high molecular weight water-soluble polymers [22] which are generally polymerized with a hydrophobic monomer and other monomers such as acrylic acid. Figure 2.5 shows the molecular structure of a hydrophobically associating acrylamide/acrylic acid/dodecyl methacrylate copolymer.



$$-(CH_2-\overset{H}{\underset{\underset{NH_2}{C=O}}{C}})_x-(CH_2-\overset{H}{\underset{\underset{OH}{C=O}}{C}})_y-(CH_2-\overset{CH_3}{\underset{\underset{O(CH_2)_{11}CH_3}{C=O}}{C}})_z-$$

Figure 2.5: Molecular structure of hydrophobically associating polyacrylamide *(x: 30-100, y:0-70, z: 0.01-1).*

In the synthesis of hydrophobically modified polyacrylamides, specialized polymerization techniques are always required since acrylamide and hydrophobic comonomers are mutually incompatible [20]. After attempts using heterogeneous [23], inverse emulsion [24], microemulsion [25], and precipitation [26] copolymerization processes, the final commonly accepted method is micellar free radical copolymerization in which an appropriate surfactant is used to solubilize the hydrophobic comonomer [27]. However, the composition of polymer prepared from micellar process always drifts because of the increased reactivity of the hydrophobic monomer when solubilized in micelles [28]. In addition, with this copolymerization technique, it is very difficult to get samples of polyacrylamide and hydrophobically modified polyacrylamide with similar molecular weights under identical experimental conditions. This makes it difficult to distinguish between the modified one and the unmodified polyacrylamide [28]. Furthermore, the reaction mechanism in the micellar method leads to a polymer with a blocky distribution of the hydrophobes along the backbone [27].

2.3.2 Hydrophobically modified polyacrylic acids

Hydrophobically modified polyacrylic acids are different from the polyacrylamide ones in terms of the electrically charged backbone they have. It is well-known that polymer of acrylic acid forms a negatively charged polyelectrolyte. Because of the repulsive forces between the acrylic monomers, the polyacrylic acid chains tend to extend so that the hydrodynamic volume of the chains increase. This increase enhances the viscosity of the aqueous solutions of the polymers. Furthermore, the hydrophobically modified acrylic polymers exhibit the characteristics of hydrophobically modified polyacrylamides and hydrophobic groups in the backbone of the polyacrylic acids interact with each other and transient network through molecular associations are formed. Due to their hybrid nature (i.e. hydrophobes and hydrophilics exist in the same polymer chain), these polymers are used as rheology modifiers in a variety of applications [29]. As in the case of polyacrylamides, to have suitable reaction conditions to synthesize hydrophobically modified polyacrylic acids is a hard task to achieve. Again most preferred method is micellar copolymerization, but it has lots of difficulties as in the case of polyacrylamide synthesis.

In Figure 2.6, there is a typical schematic representation and molecular structure of a hydrophobically modified polyacrylic acid.

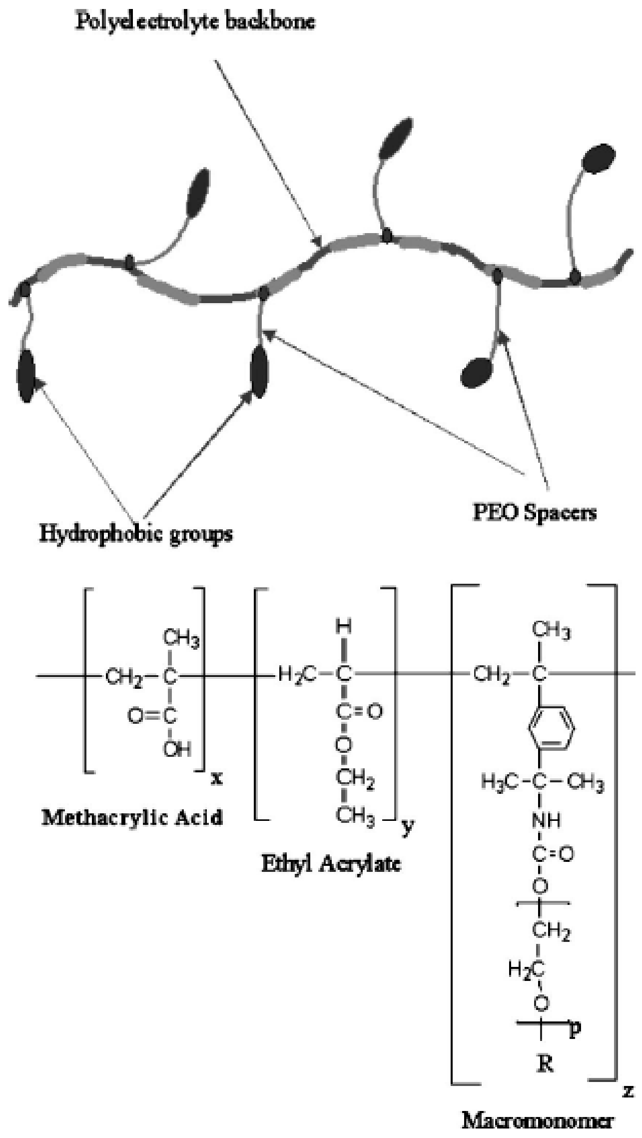


Figure 2.6: Schematic representation of a typical hydrophobically modified polyacrylic acid polymer together with the molecular constitution of the poly(methacrylic-co-ethyl acrylate) as an illustration.

CHAPTER 3

EXPERIMENTAL

The experimental work of this study consists of three main parts which are the preparation of de/anti-icing solutions, the polymer synthesis experiments and lastly the characterization part.

3.1 Preparation of de/anti-icing fluids

Various chemicals were used in the preparation of de/anti-icing fluids as shown in Table 3.1. In every solution preparation, glycol and water were present primarily and the chemicals like thickeners, surfactants or corrosion inhibitors were additionally mixed to get the desired physical properties. The solutions were continuously stirred up to 2 hours to be sure that the mixture was totally homogenized. There was not a strict order of adding different functional chemicals into the solution.

Table 3.1: Chemicals used in the preparation of de/anti-icing fluids

Chemical	*Molecular formula*	*Purity*	*Source*
Water	H_2O	Deionized	Ion exchange resins
Ethylene glycol	$C_2H_4(OH)_2$	99+ % SP. Gr.	Aldrich
Polyacrylic acid	$(CH_2CH\ COOH)n$	Mw: 450000	Aldrich
Poly(acrylic acid-co-maleic acid)	$(CH_2CHCOOH)x(CHCOOHCHCOOH)y$	50 % aq. Solution	Aldrich

Polyacrylic acid partial sodium salt, lightly crosslinked	$(CH_2CH\ COONa)n$		Aldrich
Poly(acrylic acid-co-acrylamide) potassium salt crosslinked	$(CH_2CH\ COOK)x(CH_2CHCONH_2)y$		Aldrich
Poly(acrylic acid) partial sodium salt graft polyethylene oxide crosslinked	$(CH_2CH\ COONa)x\ [CH_2CHCOO(CH_2CH_2O)nH]y$		Aldrich
Benzotriazole	$C_6H_6N_3H$	99 %	Aldrich
Carboxymethylcellulose sodium salt	$C_8H_{16}O_8Na$		Sigma
Oleic acid	$CH_3(CH_2)_7CHCH(CH_2)_7COOH$	~99 % (GC)	Sigma
Sodium dodecyl sulfate (SDS)	$CH_3(CH_2)_{11}OSO_3Na$	99 %	Sigma-Aldrich
Sodium Hydroxide	NaOH	98 %	Sigma-Aldrich
2-ethyl hexyl sulfosuccinate (AOT)	$C_{20}H_{37}O_7NaS$	70 % aqueous solution	GEMS PEC RW
2-Ethoxyphenol	$C_2H_5OC_6H_4OH$	98 %	Aldrich
Hexadecyltrimethylammonium bromide	$CH_3(CH_2)_{15}N(Br)(CH_3)_3$	80 %	Aldrich
Triethylamine	$(C_2H_5)_3N$	99 %	Sigma-Aldrich
Potassium hydrogen phosphate trihydrate	$K_2HPO_4.3H_2O$	99+ %	Aldrich
Tetrabutylammonium tetrafluoroborate (TBAF)	$(CH_3CH_2CH_2CH_2)_4N(BF_4)$	≥99.0%	Fluka
Dimethyldioctadecylammoni-	$[CH_3(CH_2)_{17}]_2N(Cl)(CH_3)_2$	≥97.0%	Fluka

um chloride (DAC)			
Hexadecyltrimethylammonium bromide (CTAB)	$CH_3(CH_2)_{15}N(Br)(CH_3)_3$	≥98%	Sigma
Polyoxyethylene(40) isooctylphenyl ether (Triton X-405)	$(C_9H_{10}O)_nOH$	70 % aqueous solution	Sigma-Aldrich

Slightly crosslinkled and hydrophobically modified polyacrylic acid (HMPA)	$(CH_2CH\ COOH)x(CH_3)y$	99 %	Carbopol Ultrez 10
Tributyl amine	$[CH_3(CH_2)_3]_3N$	>99.5 % (GC)	Fluka

3.2 Polymer synthesis experiments

In order to find the most suitable rheological behavior for the fluids, different polymers were tested and some of them were synthesized directly in the laboratory. The synthesized polymers are namely: poly(acrylic acid-co-maleic acid), poly(DADMAC-co-acrylamide), poly(DADMAC-co-vinylpyyrolidone), polyacrylamide and poly(acrylic acid-co-maleimide). Different reaction procedures were performed for each polymer synthesis as follows:

3.2.1 Poly(acrylic acid-co-maleic acid) synthesis

3.2.1.1 The heat induced reaction

In a 250 mL volume of three-necked flask equipped with a reflux condenser and a nitrogen inlet, 30 ml of 1,4-dioxane was added as solvent. Then, 18 g maleic anhydride, 8.176 g acrylic acid, and 0.164 g AIBN were added into the dropping funnel which was placed onto the three-necked flask under nitrogen. The flask was placed in a constant temperature oil bath and the funnel was opened to have a dropwise flow. The reaction was conducted at 80 ^{o}C under continuous stirring for 3 h. The mixture was then cooled to room temperature and poured into 150 mL of toluene. The solvent was decanted and the residue was dissolved in water and then reprecipitated in toluene and purified. The polymer was isolated by decanting and dried at 70 ^oC under vacuum for 24 h.

3.2.1.2 The redox induced reaction

In an erlenmeyer 36 g DADMAC, 9.8 g maleic anhydride and 30 ml distilled water were mixed and the erlenmeyer was put into ice bath. Then 28 g of NaOH was dissolved in 40 mL water and added to the erlenmeyer slowly. Because the reaction is highly exothermic this procedure was conducted in an ice bath. After the addition of 50 mL of water into the erlenmeyer, 2.28 g ammonium persulphate was added with 2.2 g triethanolamine into the erlenmeyer. Reaction took 5 minutes and then the polymer was dissolved in the erlenmeyer by water and taken out.

The reaction scheme is shown in Figure 3.1.

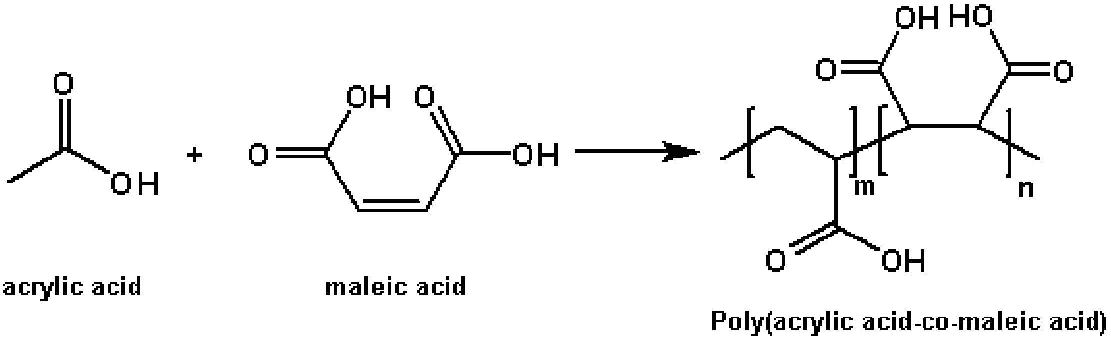


Figure 3.1: The reaction scheme of poly(acrylic acid-co-maleic acid)

3.2.2 Poly(DADMAC-co-acrylamide) synthesis

3.2.2.1 The heat induced reaction

In a 100 mL volume of three-necked flask equipped with a reflux condenser and a nitrogen inlet, 3.054 g acrylamide was dissolved in 7 mL water. Then 12.436 g DADMAC was added with 0.27 g 2, 2'-azo bis-(2-methyl propionamidine) dihydrochloride (initiator). The flask was placed in a constant temperature oil bath. The reaction was conducted at 65 °C under continuous stirring for 2 h. The mixture was dissolved in water and taken out.

3.2.2.2 The redox induced reaction;

6.108 g acrylamide was dissolved in 14 mL of water and added to an erlenmeyer with 24.872 g DADMAC. Then 0.1 g potasyumpersulfate was added as an initiator into the erlenmeyer. The reaction was conducted with the addition of 0.5 mL triethanolamine under room temperature for 5 minutes

The reaction scheme of the copolymer is shown in Figure 3.2.

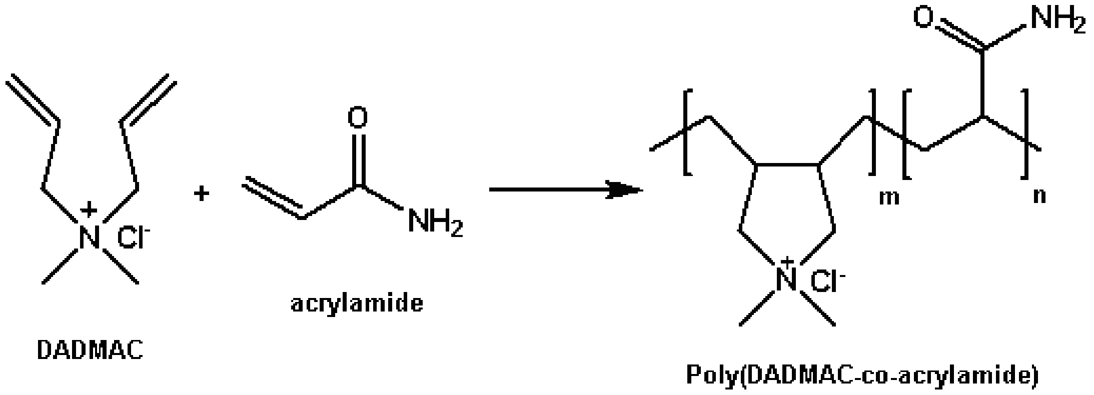


Figure 3.2: The reaction scheme of Poly(DADMAC-co-acrylamide)

3.2.3 Poly(DADMAC-co-vinyl pyyrolidone) synthesis

In a 250 mL volume of three-necked flask equipped with a reflux condenser and a nitrogen inlet, 24.9 g DADMAC solution, 11.2 g vinyl pyrrolidone and 0.562 g 2, 2'-azo bis-(2-methyl propionamidine) dihydrochloride were mixed under nitrogen. Then

32.4 mL distilled water was added so that the final total monomer concentration was to be 40 % by weight. The flask was placed in a constant temperature oil bath. The reaction was conducted at 60 °C under continuous stirring for 1 h. The mixture was cooled to room temperature and poured into 150 mL of isopropanol. The solvent was decanted and the residue was dissolved in 60 mL methanol and reprecipitated in acetone (100 mL). The polymer was isolated by decanting and dried at 70 °C under vacuum for 24 h.

The reaction scheme of the copolymer is shown in Figure 3.3.

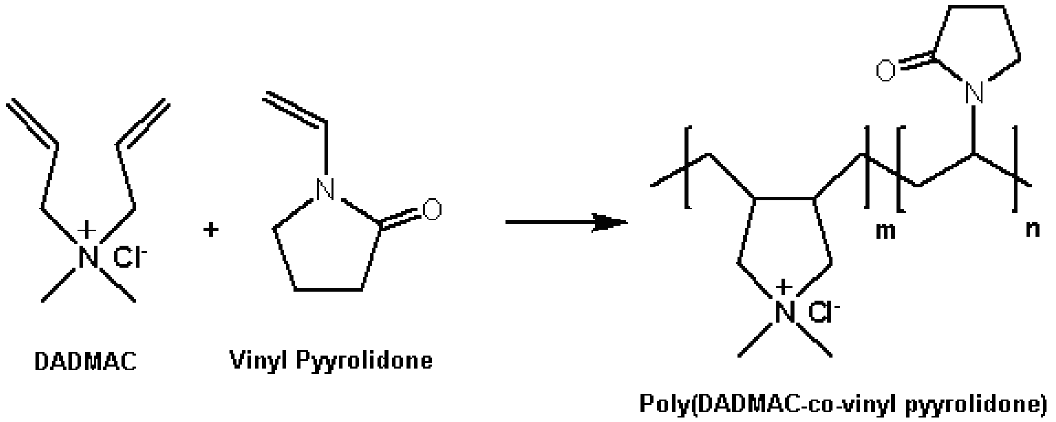


Figure 3.3: The reaction scheme of Poly(DADMAC-co-vinyl pyyrolidone)

3.2.4 Crosslinking Copolymerization of DADMAC with NVP

The crosslinking copolymerization was carried out in highly concentrated aqueous solutions of the monomer mixture (40 %). In a typical procedure, a mixture of 9.94 g (0.04 mol) commercial N,N-diallyl N,N-dimethylammonium chloride solution (65 %), 1.07 g (9.5 $\times 10^{-3}$ mol) 1-vinyl 2-pyrrolidone, 0.16 g (5×10^{-4} mol) TAP and 0.14 g (5×10^{-4} mol) 2, 2'-azo bis-(2-methyl propionamidine) dihydrochloride were placed in a 100 mL volume of three-necked flask equipped with a reflux condenser and a nitrogen inlet. The mixture was purged with nitrogen for 2 minutes.

Then 8.26 mL distilled water was added so that final total monomer concentration was 40 % by weight. The flask was placed in a constant temperature oil bath and the reaction was conducted at 65 °C under continuous stirring.

Generally gelation took place within 15-60 min depending on the crosslinker content. The gel formed was left to stand for 24 h at this temperature, in order to complete the crosslinking polymerization. The resulting transparent gel was broken up and washed with water three times (3×400 mL) in a cotton purse. The gel samples were then transferred onto glass plates and dried at 75 °C under vacuum for 24 h.

3.2.5 Polyacrylamide synthesis

15 g acrylamide was dissolved in an erlenmeyer containing 35 mL water. Then 0.1 g potassium persulphate was added to the solution. After it was dissolved completely, 0.5 mL triethanolamine was added to the erlenmeyer and polymerization reaction was conducted for 5 minutes.

The reaction scheme of polyacrylamide is shown in Figure 3.4.

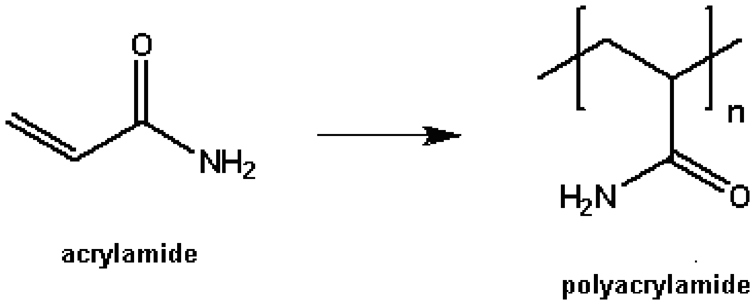


Figure 3.4: The reaction scheme of polyacrylamide

3.2.6 Poly(acrylic acid-co-maleimide) synthesis

Prior to the polymer synthesis, the hydrophobic monomer (maleimide) was synthesized. Equal moles of maleic anhydride and alkyl amine were dissolved in dimethoxane at 80-90 °C. The mixture was stirred until the solution became transparent. Then, in a 250 mL volume of three-necked flask equipped with a reflux condenser, acetic anhydride was added in stoichometric ratio. The mixture was stirred for 3 hours at 120 °C. The mixture was then precipitated in water and the precipitated maleimide was washed with petroleum ether in order to have purification from unreacted monomers. Then, the resulting monomer was left at 50 ^{o}C and dried.

The synthesized maleimide was reacted with acrylic acid in a proper alcohol solution in 1/100 initiator ratio with a crosslinker which was tetraally piperazinium dichloride in a 1/1000 ratio. After waiting for 1 day in order to be sure that the reaction was totally completed, the resulting polymer was precipitated in diethyl ether and then dried at 50 ^{o}C under vacuum.

The chemicals used in the synthesis reactions are given in Table 3.2.

Table 3.2: The chemicals used in polymer synthesis reactions

Chemical	*Molecular formula*	*Purity*	*Source*
Acrylamide	CH_2=CHCONH$_2$	> 98 %	Fluka
Maleic anhydride	$C_4H_2O_3$	> 99 %	Merck
Triethanol amine	$N(CH_2CH_2OH)_3$	99 %	Merck
Acrylic acid	CH_2=CHCOOH	99 %	Aldrich
N-vinyl pyyrolidone	C_6H_9NO	99 %	Aldrich
Acetone	CH_3COCH_3	99.8 %	Merck
Ethanol	CH_3CH_2OH	95 %	Aldrich
Methanol	CH_3OH	99 %	Sigma
Petroleum ether (benzene)	Mixture of hydrocarbons	Analytical grade	Sigma Aldrich
N,N-diallyl N,N-dimethylammonium chloride	$(CH_2{=}CHCH_2)_2N(Cl)(CH_3)_2$	65 wt % aq solution	Aldrich
Acetic anhyride	$(CH_3CO)_2O$	99.5 %	Sigma-Aldrich
Tetraally piperazinium dichloride (TAP)	$(CH_2{=}CHCH_2)_4N(Cl)_2$		Synthesized in laboratory (explained in section 3.2.7)
Azobisisobutyronitrile (AIBN)	$(CH_3)_2C(CN)N{=}NC(CH_3)_2CN$		Synthesized in laboratory
2, 2'- azo bis-(2-	$(C_4N_3H_9)_2$2HCI	97 %	Aldrich

methyl propionamidine) dihydrochloride			
Diethyl ether	$(CH_3CH_2)_2O$	99.7 %	Aldrich

3.2.7 Preparation of tetraallyl piperazinium dichloride (TAP)

TAP was prepared by quaternization of N,N’-diallyl piperazine with allyl chloride. To a 250 mL volume of flat bottom flask, 33.2 g (0.2 mol) N,N’-diallyl piperazine and 36.7 g (0.48 mol) allyl chloride were added and the mixture was left to stand for over two months at room temperature. The white solid was leached in 50 mL of diethyl ether and quickly filtered. The residue was washed with acetone (25 mL) and ether (25 mL). Since the product is very sensitive to humidity, it was stored in closed bottle without further drying. The crude yield was 52.2 g (81.2 %).

3.3 Characterization

3.3.1 Characterization of de/anti icing solutions

The characterization tests of the de/anti-icing fluid mixtures were performed with rheometer, surface tensiometer, pH meter and refrigerator.

3.3.1.1 Rheometer

The rheological behaviour of the polymer solutions was tested by using the Brookfield Rheometer Model LVDV-III U with a spindle no SC4-34 in a small sample adapter. The device has a 0.01-250 rpm speed range. The measurements were conducted at 20 ^oC and the data acquired was processed by using Brookfield Rheocalc computer program.

3.3.1.2 Surface Tensiometer

The surface tension of the solutions was measured by using a Cole Parmer Surface Tensiomat 21 with a platinum-iridium ring (circumference: 5.965 cm). The surface tension values were measured in between 30-70 Dynes/cm.

3.3.1.3 pH meter

pH of the solutions were measured by using Inolab wtw series pH 72e pH meter.

3.3.1.4 Refrigerator

The freezing point of the solutions was tested by using Revco Ult350-5V-32 refrigerator with - 40 ^{o}C minimum stable temperature and 90 L capacity. The freezing point experiments were made by first allowing the solution to freeze with a thermometer inside the beaker, then the frozen solutions were melted at room temperature and the temperature where the solution started to flow was recorded.

3.3.1.5 Corrosion test

The sample of aluminum plates taken from the airplane wings were immersed into solutions at 88 ^{o}C under constant air flow (~2 ml/s). After 15 days, the loss of weight of the plates per area were calculated.

3.3.2 Characterization of the synthesized polymers

The characterization tests of the synthesized polymers were made with Nuclear Magnetic Resonance (NMR) spectra and Gel Permeation Chromatography (GPC). NMR spectra of the polymers were obtained in D_2O by a Bruker Ac (250 MHz) spectrometer. GPC analyses of the polymer samples were performed in water with a flow rate of 0.5 mL / min using Hewlett Packard 1050 A series instrument and aqueous polyethylene glycol solutions were used as standards.

CHAPTER 4

RESULTS AND DISCUSION

4.1 De-icing (Type-1) Fluid Production Results

De-icing fluids are mainly glycol and water mixtures with trace amount of some functional chemicals such as; surfactants, corrosion inhibitor, pH controllers, etc. [17, 30, 31]. The surfactant molecules lower the surface tension of the fluid and allow easier spreading on the surfaces of the airplane. The corrosion inhibitors protect the aircraft surfaces from corrosion and the pH controllers stabilize the solution pH in desired values. To get the desired viscosity, surface tension, freezing point values and also minimum corrosion effect, different compositions of surfactants, pH controllers and corrosion inhibitors are tested with varying glycol-water contents. According to the values cited in the literature, the surface tension of the fluids must be around 40 Dynes/cm at 25 ^{o}C, the viscosity of the fluids must be in between 10-50 cP at 20 ^{o}C, and the freezing point of the 50 % diluted solutions of the fluids must be around -20 ^{o}C [32-35]. All viscosity measurements in this study are made at 20 ^{o}C and surface tension measurements are made at 25 ^{o}C unless a temperature is specified. In choosing the functional chemicals for preparing the fluids, the most frequently used ones are preferred as shown in Table 4.1.

Table 4.1: The functional chemicals used in Type-1 fluid and the composition ranges.

Chemical Type	*Chemical*	*Concentration range (wt %)*
Surfactant (S)	2-Ethoxyphenol	0 – 2
Corrosion inhibitor (CI)	Tributylamine	0 – 4
pH Controller (pH C)	Potassium hydrogen phosphate trihydrate	0 – 0.5

The functional chemicals are tested at their maximum and minimum concentrations and the surface tension, viscosity and the freezing point values are recorded. The results are shown in Table 4.2.

Table 4.2: The effect of the functional chemicals on the physical properties of Type-1 fluids

Sample no	*Glycol (wt %)*	*Water (wt %)*	*S (wt %)*	*CI (wt %)*	*pH C (wt %)*	*Viscosity (cP) **	*Surface Tension (Dynes/cm) ***	*Freezing Point (^oC) ****
1	90	10	0	0	0	13.9	51.6	-30
2	90	9.5	0	0	0.5	13.8	51.8	-31
3	90	8	2	0	0	15.6	50.74	-30
4	90	6	0	4	0	16.5	40.1	-31
5	80	20	0	0	0	9.4	52.1	-25
6	80	19.5	0	0	0.5	10	53.5	-26
7	80	18	2	0	0	10.5	51.1	-25
8	80	16	0	4	0	14.1	40	-25
9	70	30	0	0	0	6.7	55.5	-20
10	70	29.5	0	0	0.5	7.2	54.8	-20
11	70	28	2	0	0	7.4	52	-21
12	70	26	0	4	0	8.75	39.9	-21

(All viscosities were measured at 20 °C and because all the solutions are Newtonian as expected. Only one viscosity value was recorded.)*

*(** All surface tensions were measured at 25 °C)*

*(*** The freezing point tests were made by diluting the solutions with 50 wt % water)*

In Figure 4.1, the effect of functional chemicals on the viscosity of solutions is observed. As it is seen from the graph, the viscosity values of the solutions increase by addition of any of the functional chemicals but they still stay in the desired range. Also it is seen that, solutions exhibit a Newtonian behavior, in other words the viscosity of the solutions does not vary with changing shear rates.

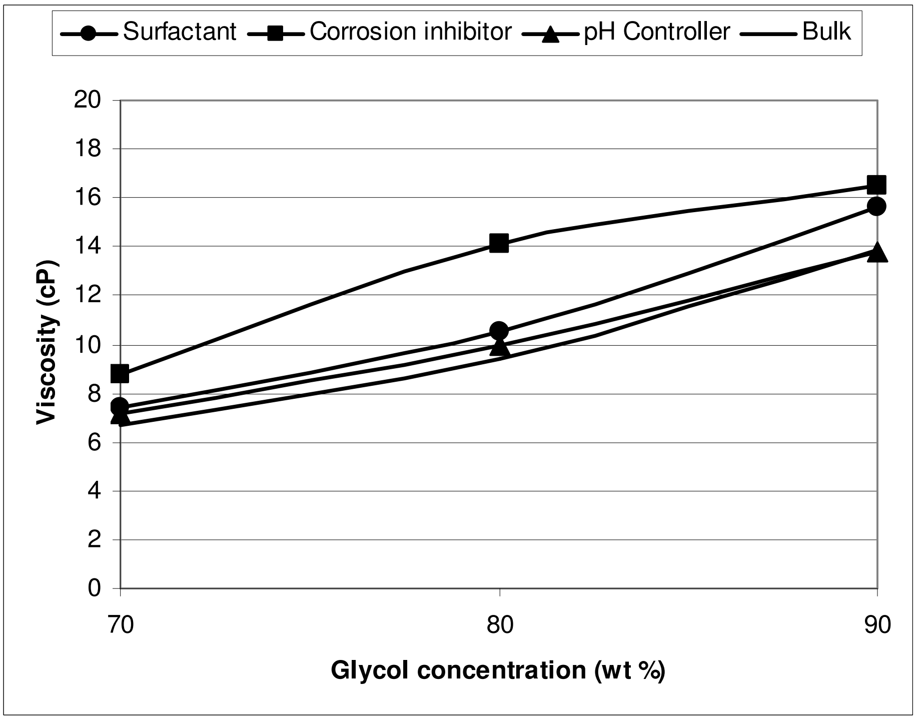


Figure 4.1: The effect of functional chemicals on the viscosity of the solutions at different glycol concentrations

(Bulk solution does not contain any additives)

Figure 4.2 depicts the effect of functional chemicals on the surface tension of the solutions. If each chemical is examined individually it can be said that, pH controller increases the surface tension of the solutions with a small amount. The surfactant alone is insufficient in decreasing the surface tension of the solutions and surprisingly corrosion inhibitor which is tributylamine reduced the surface tension near 40 Dynes/cm. Therefore, it is concluded that, tributylamine is a multifunctional chemical and can be used to reduce the surface tension as well as a corrosion inhibitor.

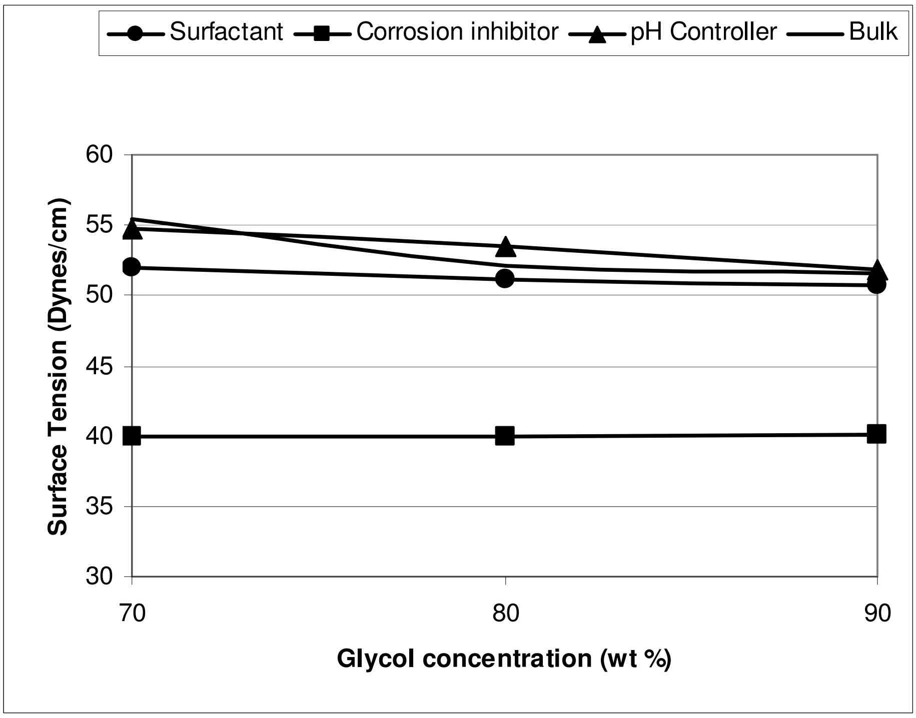


Figure 4.2: The effect of functional chemicals on the surface tension of the solutions at different glycol concentrations.

Figure 4.3 shows the effect of functional chemicals on freezing point. Presence of the chemicals had slight effect on the freezing point of the solutions. Hence glycol content of a solution mainly determines the freezing point.

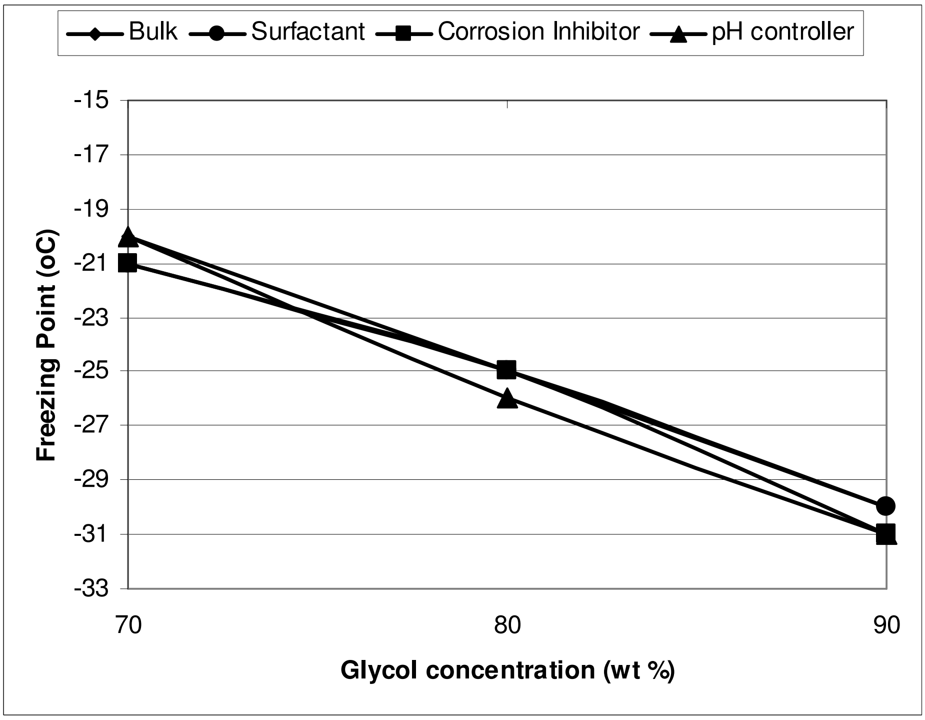


Figure 4.3: The effect of functional chemicals on the freezing point of the solutions at different glycol concentrations.

After the investigation of the effect of each individual chemical on the physical properties of the solutions, the effects of the functional chemicals to the solutions are examined when two or three of them exist together in the solution containing 80 % by weight glycol (See also Table 4.3).

1. Surfactant and pH Controller effect

When these two functional chemicals are used together, it is seen that, the viscosity and freezing point values are in between the desired values (8-15 cP) but surface tension is relatively high (50 Dynes/cm).

2. Surfactant and Corrosion Inhibitor effect

When these two chemicals are used together, the viscosity and the freezing point values again do not change much (8- 15 cP) but the surface tension of the solution decreases more than the case where each chemical used individually (37 Dynes/cm).

3. pH Controller and Corrosion Inhibitor effect

In this case, it is observed that the physical properties of the solution remained constant as in the case where the corrosion inhibitor used alone (8-15 cP, 40 Dynes/cm).

4. Surfactant, Corrosion Inhibitor and pH Controller effect

When three chemicals exist in the solution together, the situation is the same as the one when corrosion inhibitor and surfactant molecules are used together (8-15 cP, 37 Dynes/cm).

Table 4.3: The effect of functional chemicals on the physical properties of the polymer solutions when two or three of them are used together at 80 % glycol concentration.

Chemical Type	*Viscosity (cP) (at 20 ^oC)*	*Surface Tension (Dynes/cm) (at 25 ^oC)*	*Freezing Point (^oC)*
S and pH C	10-15	50	-26
S and CI	10-15	36	-26
pH C and CI	10-15	40	-26
S, pH C and CI	10-15	37	-26

After the observation of the effect of functional chemicals on the solution properties, it is concluded that the viscosity of the solutions always remain in the desired range and it does not vary much with the addition of functional chemicals. The pH controller has no effect on the viscosity, surface tension and freezing point of the solutions. The freezing point of the solutions strongly depends on the glycol content rather than any other functional chemicals. The surfactant which is 2-ethoxyphenol can not reduce the surface tension to desired values, instead the corrosion inhibitor shows double functionality and it can reduce the surface tension and lastly when the surfactant molecules and pH controllers are used together, the surface tension can be reduced to lower values.

If the effect of glycol concentration on the physical properties of the solutions is considered, it is seen that, as the glycol concentration of the solution increases, the freezing point and surface tension of the solution decreases and the viscosity of the solution increases. When we measure the bulk properties of the glycol-water mixtures with no functional chemicals inside (See Table 4.4), we get the expected results.

Table 4.4: The physical properties of the solutions varying in glycol concentration

Glycol (wt %)	*Water (wt %)*	*Viscosity (cP) (@20 ^oC)*	*Surface Tension (Dynes/cm) (@ 25 ^oC)*	*Freezing Point (^oC)*
100	0	16	49	- 12
90	10	13.9	51.6	- 29
80	20	9.4	52.1	- 46
70	30	6.7	55.5	< - 51
0	100	1	72	0

Because reducing the surface tension near 40 Dynes/cm is not an easy task for the surfactants utilized so far, different surfactants are further tested and the effects of these surfactants are discussed in section 4.2.

In conclusion, type-1 fluids are actually basic de-icers and it is possible to adjust the final physical properties of the solutions by changing the concentration of functional chemicals inside the solution. Thus, a final composition for a de-icing fluid can be proposed (See Table 4.5), after testing different functional chemicals and the interactions between them. Actually, the main difficulty in producing this fluid is reducing the surface tension, but that problem is also solved by trying different kinds of surfactants.

Table 4.5: A proposed composition of de-icing fluid and its physical properties

Glycol	% 90
Water	%10
2-Ethoxyphenol	% 0.1
Potassium hydrogen phosphate trihydrate	% 0.2
Tributylamine	% 0.05
Viscosity	15.1 cP
Surface tension	39.1 Dynes/cm
Freezing Point	- 20 ^{o}C

4.2 Anti-icing (Type-2) Fluid Production Results

The major distinction between de-icing and anti-icing fluids stems from their rheology. For de-icing fluids, viscosity does not depend on shear rates, but for anti-icing fluids it must depend on shear rates. This means that when the aircraft is at rest or moving at a low velocity, the viscosity of the type-2 fluids must be high in order not to flow-off from the wings so that type-2 fluids protect the aircraft surfaces from further icing or snowing. However, when the aircraft accelerates to take-off on the runway, due to the increasing shear rate, the viscosity of type-2 fluids must drop rapidly and they must flow-off from the surfaces of the airplane so that they leave a clean surface at the time of lift-off and do not affect the aerodynamics of the airplane [8]. In other words, the anti-icing fluids must be shear-thinning. To have a shear-thinning anti-icing fluid, thickeners are utilized in the solutions. In this study, five different polymers are synthesized as; poly(acrylic acid-co-maleic acid), poly(DADMAC-co-acrylamide), poly(DADMAC-co-vinylpyyrolidone), polyacrylamide, poly(acrylic-co-maleimide). Furthermore, different polymers are purchased namely; polyacrylic acid, poly(acrylic acid-co-maleic acid), lightly crosslinked polyacrylic acid partial sodium salt, crosslinked poly(acrylic acid-co-acrylamide) potassium salt, crosslinked poly(acrylic acid) partial sodium salt graft polyethylene oxide, carboxymethylcellulose sodium salt and slightly crosslinked hydrophobically modified polyacrylic acids. The rheological behavior of these polymers are tested in water-glycol mixtures and recorded by using a rheometer. Also, the effect of other functional chemicals such as corrosion inhibitors, surfactants and pH controllers on the rheology of the solutions are investigated and recorded. Following rheological characterization and obtaining solutions of desired viscosity behavior, surface tension, freezing point or corrosive effect of the polymer solutions are also investigated.

4.2.1 The synthesized polymers and their rheological behaviors

4.2.1.1 Poly (acrylic acid-co-maleic acid) (AMC)

This polymer is initially considered as the best candidate, because most patents refer to copolymers of acrylic based monomers [11, 13-17]. The polymerization reaction has a free-radical polymerization mechanism and the reaction is made by using solution polymerization technique.

4.2.1.2 Poly (DADMAC-co-acrylamide) (DA)

Although, the application area of these copolymers is normally the dewatering processes of mineralized solutions, we first wanted to use this copolymer as a thickening agent. DADMAC monomer in this copolymer is a quaternal molecule with positively charged ions. It is thought that the copolymer chains of this monomer would expand linearly in the aqueous solutions so that the viscosity of the solutions would increase. This copolymerization reaction has a free-radical polymerization mechanism similar to the previous one and the reaction was made by using solution polymerization technique.

4.2.1.3 Poly (DADMAC-co-vinyl pyyrolidone) (DCVP)

This polymer was only synthesized in an earlier study in 1990 [36]. The two monomers have both high solubilities in water so the resulting copolymer has high solubility in water. Vinylpyrrolidone has a biocompatibility and the polyelectrolytes made from this monomer attract attention in various applications such as sludge dewatering and membrane production [37, 38]. This polymer was also never used as a thickener before. The experiments performed so far showed that the characterization results of the previous study are not consistent with our results. Therefore, we decided to study this polymer further and publish a short paper about the copolymerization behavior and characterization of this polymer. These results are shown in Appendix A1.

4.2.1.4 Polyacrylamide (PA)

Polyacrylamide is a famous thickening agent and also acrylamide is a very cheap monomer and it can be used a co-monomer with acrylic acids as cited in the literature [39]. The monomer acrylamide is also known to be carcinogenic but the polymer of acrylamide does not show such effects [40].

The rheological behavior of the synthesized polymers are tested with increasing shear rates in aqueous and glycol solutions in case of the addition of surfactants, corrosion inhibitors and pH controllers and the results are summarized in Table 4.6. According to the results, it can easily be said that none of the polymers achieved to have a strong shear-thinning behavior. The bulk solutions of all the polymers in water totally exhibited Newtonian behavior except that DA and AMC showed small amount of shear-thinning behavior in water-glycol mixtures. Generally additives could not increase the shear-thinning behavior except for Triton X-405 addition into aqueous DA solutions. The addition of potassium hydrogen phosphate trihydrate into the solutions results in lowering the viscosity values in almost all cases. This decrease may be explained by the hindrance effect of the salt which results in the coiling of the polyelectrolyte chains. The only noteworthy result belongs to 5 % of DA polymer in glycol-water mixtures. The viscosity in that case decreases from 198 cP to 161 cP. However, even in that case the polymer amount used in the solution is quite high and the maximum viscosity acquired with respect to that is quite low. Also, by increasing shear rate the viscosity decreases only by 30 cP. Therefore, the trials on new polymers and the explanation of the shear-thinning behavior of solutions are further investigated and shown in the following sections.

Table 4.6: Rheological behavior of the solutions of synthesized polymers with additives

Polymer (percentage)	*Shear rate change (rpm)*	*Viscosity in water (cP)*					*Viscosity in water-glycol mixtures (cP) (50 % - 50 %)*				
		Bulk (No additives)	S_1 (1 mM)	S_2 (1 mM)	CI (1 mM)	pH C (1 mM)	Bulk (No additives)	S_1 (1 mM)	S_2 (1 mM)	CI (1 mM)	pH C (1 mM)
DA (5 % wt)	32-250	125	121-113	125	125	80	198-161	194-164	125	195-162	87-81
AMC (1 % wt)	10-95	11	37	47	15	10	15-11	35	37	15	10
DCVP (5 % wt)	4-37	71	70	71	70	60	72-77	70	70	70	61
PA (5 % wt)	32-250	161	161	160	160	174	160	160	160	160	170

(S_1: Triton X-405, S_2: AOT, CI: Tributylamine, pH C: Potassium hydrogenhosphatetrihydrate)

4.2.2 The Purchased (Commercial) Polymers and Their Rheological Behaviors

4.2.2.1 Polyacrylic acid (PAA) and Poly(acrylic acid-co-maleic acid)

The rheological behavior of polyacrylic acid solutions is varied in terms of PAA concentration, glycol and additive content of the solutions, however no shear-thinning behavior is observed for poly(acrylic acid-co-maleic acid) probably due to its low molecular weight. The viscosity changes are analyzed in terms of different concentrations of PAA, glycol and other additives.

The effect of PAA concentration in the solution can be seen in the Table 4.7

Table 4.7 The effect of polymer concentration on solution (50 % water-50 % glycol) viscosity

PAA concentration (wt %)	*Viscosity at low shear rates (1-10 1/s) (cP)*	*Viscosity at high shear rates (50-70 1/s) (cP)*	*Viscosity loss (difference) (cP)*	*Viscosity loss (percentage %)*
10	11817	11185	632	5.4
8.5	5459	5159	300	5.5
7.5	2998	2894	104	3.5
6.5	1680	1635	45	2.7
6	1065	1033	32	3
5.5	686	686	0	0

It can be observed from Table 4.7 that as the concentration of PAA decreases in the solution, the viscosity at low shear rates, high shear rates and also the difference between them decrease. Moreover, the viscosity loss reaches to zero at 5.5 % PAA concentration. In other words, the entire shear thinning behavior is lost. The reason for that may be the insufficient number of chains to entangle at low polymer concentrations.

The effect of glycol concentration on the solution rheology can be seen in Table 4.8.

Table 4.8: The effect of glycol concentration on solution viscosity at 4 wt % PAA

Glycol concentration (wt %)	*Viscosity at low shear rates (1-10 1/s) (cP)*	*Viscosity at high shear rates (50-70 1/s) (cP)*	*Viscosity loss (difference) (cP)*	*Viscosity loss (Percentage) (%)*
90	1750	1690	60	3.4
80	1600	1532	68	4.3
70	790	742	48	6.1
60	536	500	36	6.7
50	332	304	28	8.4

The dependency of glycol concentration on solution rheology is measured at the concentrations where the effect of polymer concentration disappears, i.e. below 5 wt % PAA. It can be seen from Table 4.8 that, glycol content in the solution decreases the shear-thinning behavior of the solution but not significantly. Since, PAA has relatively low solubility in glycol than water; the solvent-solute interactions may lead to such a shear-thinning behavior.

The effect of additives on the solution rheology can be summarized in Table 4.9.

Table 4.9: The effect of additives on solution (50 % water-50 % glycol) viscosity at 4 wt % PAA

Additive and its percentage	*Viscosity at low shear rates (1-10 1/s) (cP)*	*Viscosity at high shear rates (50-70 1/s) (cP)*	*Viscosity loss (cP)*	*Viscosity loss (Percentage %)*
-	332	304	28	8.4
AOT (1 %)	600	470	130	21.7
Triton X-405 (1 %)	340	310	30	8.8
Potassium hydrogen phosphate trihydrate (0.5 %)	335	312	23	6.9
Tributylamine (1 %)	390	346	44	11.3
Sodium hydroxide (1 %)	1319	1190	129	9.8

When the results presented in Table 4.9 are analyzed, it can be observed that: AOT has a great contribution to the shear-thinning behavior of the solutions. This fact may be explained by the interaction between long polyoxyethylene molecules and polyacrylic acid chains. These interactions are probably interrupted at high shear rates leading to a shear-thinning behavior. In addition, huge viscosity increase due to addition of sodium hydroxide to the solution can also be observed. This happens because of the ionization of the acrylic acid chains at high pHs. The ionized chains hold the solvent molecules and stabilize them which results in solutions with high viscosity. In Figures 4.4 and 4.5, the best rheological behaviors are obtained by using polyacrylic acid for the solutions containing the additives listed in Table 4.9.

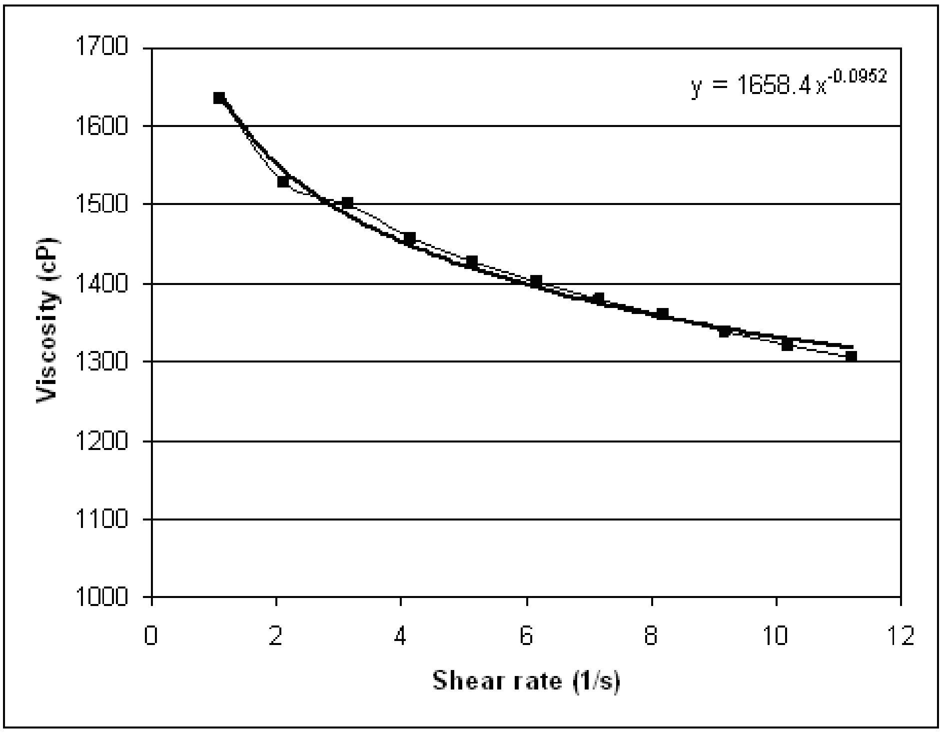


Figure 4.4: Rheological behavior of the solution (50 % water-50 % glycol) containing 4 % PAA, 1 % AOT and 1 % NaOH

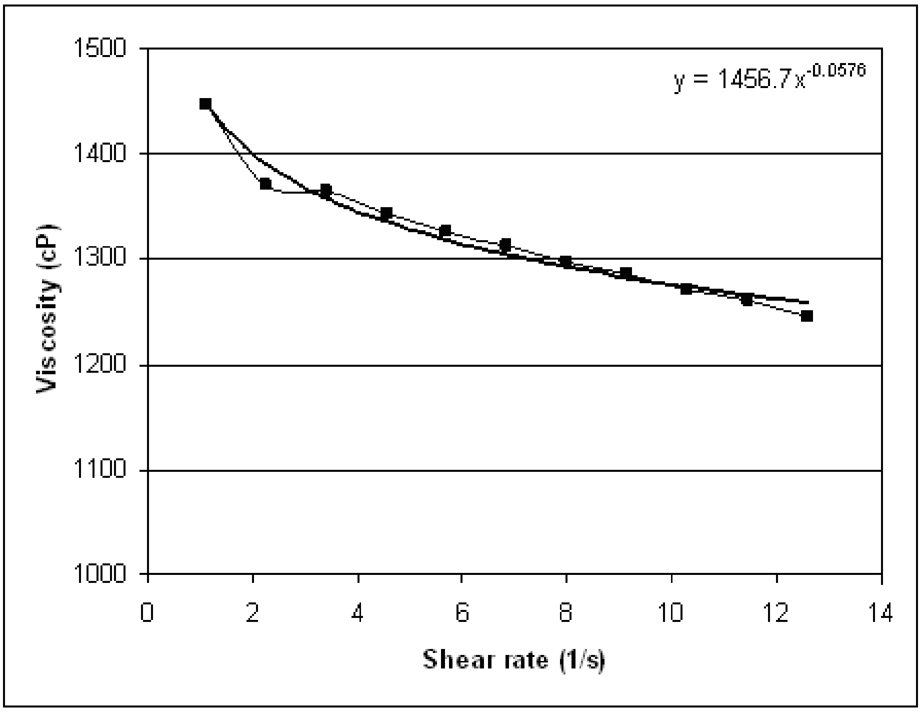


Figure 4.5: Rheological behavior of the solution (50 % water-50 % glycol) containing 4 % PAA, 1 % Triton X-405 and 1 % NaOH

When the performance of the fluids shown in Figure 4.4 and Figure 4.5 are analyzed, the low shear viscosity values seem to be quite enough to have long hold-over times for aircraft. However the high shear viscosity of the fluids is too high to flow-off from the surfaces of the aircraft at desired rates. In other words, the shear-thinning behavior of these solutions is inadequate to be used in aviation. This fact can also be expressed in terms of the power law equations of the fluids. In these equations, the magnitude of the power of "x" (shear rate) shows how fast the fluid will loose its viscosity. In these fluids, this x values are in between 0.05 to 0.1. However in actual type-2 fluids, x values are approximately 0.4 [3], which designates a good shear-thinning behavior.

4.2.2.2 Carboxymethylcellulose

It is known that, carboxymethylcellulose (CMC) is a derivative of cellulose formed by its reaction with alkali and chloroacetic acid. Generally it is used in food industry as a viscosity modifier or thickener, and to stabilize emulsions. The average chain length and degree of substitution are of great importance in the rheology of the CMC solutions; the more-hydrophobic lower substituted CMCs are thixotropic but more-extended higher substituted CMCs are shear-thinning [41].

Although, the rheological behavior of CMC solutions is quite shear-thinning, it is not enough to use in anti-icing fluids. The viscosity change of polymer solutions and the effect of two surfactants on solution rheology are shown in Table 4.10.

Table 4.10: The effect of additives on solution (50 % water-50 % glycol) viscosity at 0.5 wt % CMC

Additive and its weight percentage	*Viscosity at low shear rates (1-10 1/s) (cP)*	*Viscosity at high shear rates (50-70 1/s) (cP)*	*Viscosity loss (cP)*	*Viscosity loss (%)*
-	1160	683	477	41
AOT (0.1 %)	1210	596	614	51
Triton X-405 (0.1 %)	1100	780	320	29

A typical shear rate-viscosity graph of a CMC solution is shown below in Figure 4.6. In the graph, the high shear viscosity is quite low but the low shear viscosity is also too low to protect the aircraft surfaces. The power of x in the equation of the graph is about 0.21 well below 0.4. The relative increase in shear-thinning behavior in the solutions can be explained in terms of hydrophobic interactions occurring between chains. These interactions are discussed in detail in the next part.

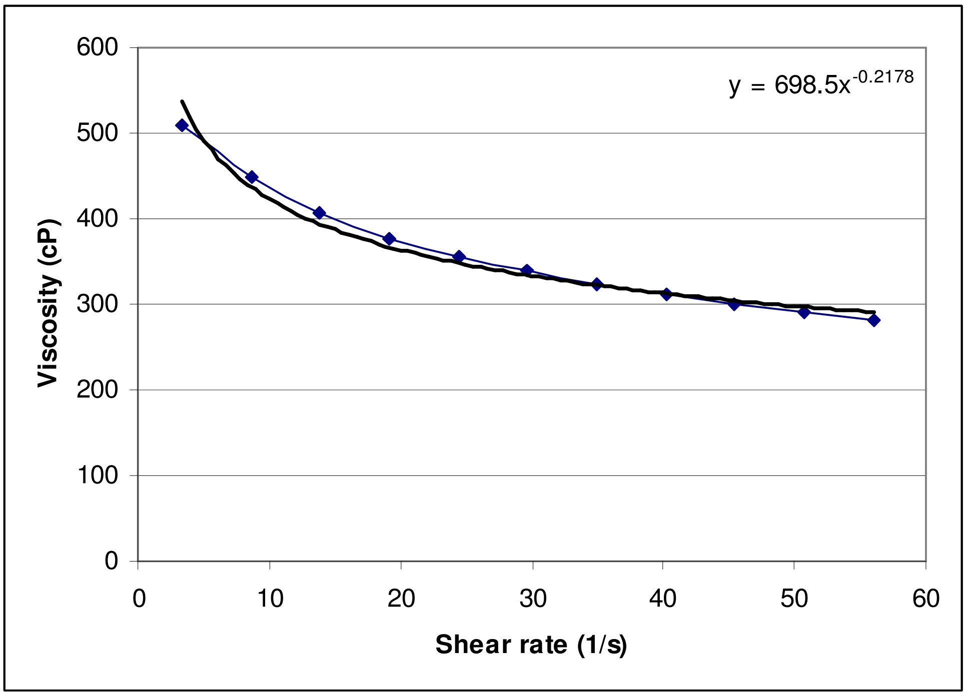


Figure 4.6: The rheological behavior of CMC at 0.5 wt % in aqueous solution.

4.2.2.3 Crosslinked Polyacrylic acids

Rheological behavior of aqueous solutions of four different crosslinked polyacrylic acids are examined; namely, lightly crosslinked polyacrylic acid partial sodium salt, crosslinked poly(acrylic acid-co-acrylamide) potassium salt, crosslinked poly(acrylic acid) partial sodium salt graft polyethylene oxide and slightly crosslinked hydrophobically modified polyacrylic acids (HMPA). The first three of them are actually superabsorbent polymers and they swell when they are faced with water. We could not achieve to dissolve these polymers even at small concentrations and could not get a homogeneous solution; therefore their viscosity values could not be measured. On the other hand, experiments done with HMPA gave very satisfying results and finally the desired rheological behavior for a typical anti-icing solution is acquired.

The rheology of HMPA solutions is affected by various factors such as, polymer concentration, pH of the solution, surfactant concentration, corrosion inhibitor concentration, glycol-water content, and temperature.

4.2.2.3.1 The effect of HMPA concentration on solution rheology

It is widely known that the polymer concentration in the solution increases the viscosity of the solution due to the resistance to flow by dissolved polymer chains. As HMPA is a hydrophobically modified polymer, its behavior in aqueous solutions is interesting. Hydrophobic groups tend to interact with each other, and the rest of the polymer chain which consists of carboxylic acid groups tends to interact with water molecules. The unusual molecular structure of these polymers leads to a non-linear concentration-viscosity relationship. It is known that the viscosity of the solutions mainly changes in the three concentration regimes which is observed in Figure 4.7 and can be explained in terms of different modes of hydrophobic association. In regime 1 ($c<<c_L$), the polymer chains are isolated and, as a result, only intramolecular associations are possible. The solution viscosity in this region is similar to that of unmodified polymer analogs except that HMPA chains do not dissolve in the solution because each chain forms a cluster and is coiled onto itself and they totally behave as a different phase in the aqueous solutions. When the dilute HMPA solutions are left for 1 hour, the phase separation can be observed in terms of coloration in the solution. In regime 2 ($c_L < c < c_U$), the polymer chains become overlapped and the hydrophobes are engaged in intra- and intermolecular associations. Therefore, this region is characterized by a very rapid increase in viscosity due to the transformation from intra- to intermolecular association with an expected strong dependence on concentration. Also, phase separation does not occur in this region and a suspension like mixture of polymer and water forms. In regime 3 ($c > c_U$) the hydrophobes are mainly engaged in intermolecular interactions. Thus, a weaker dependence on concentration is expected [29].

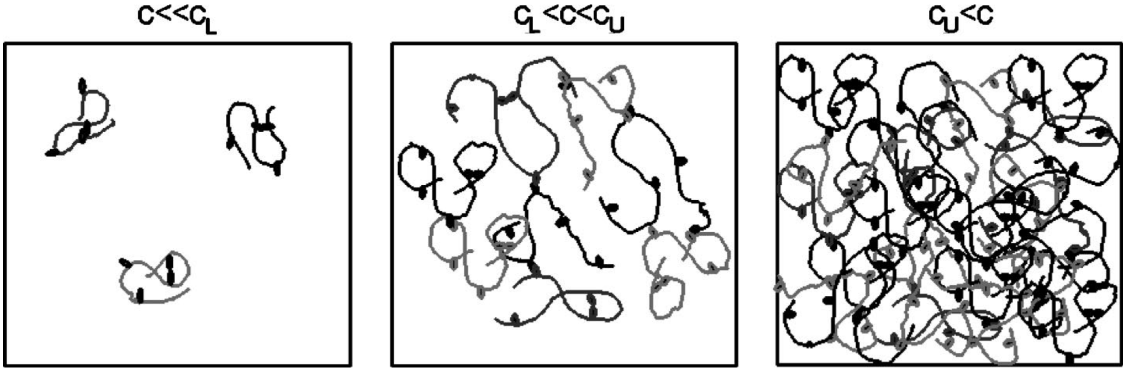


Figure 4.7: Schematic representation of possible hydrophobic interaction modes in different concentration regimes (taken from ref. [29]).

(c_L: lower concentration, c_U: upper concentration)

In Figures 4.8, 4.9 and 4.10, the rheological behavior of the HMPA aqueous solutions in increasing polymer concentration are shown.

The rheological behavior of 1 wt % HMPA solution is seen in Figure 4.8, the low shear viscosity is very low at around 45 cP and the high shear viscosity is around 20 cP. The equation at the corner of the figure is the power law equation of the curve and significance of the equation is explained as mentioned in following chapters.

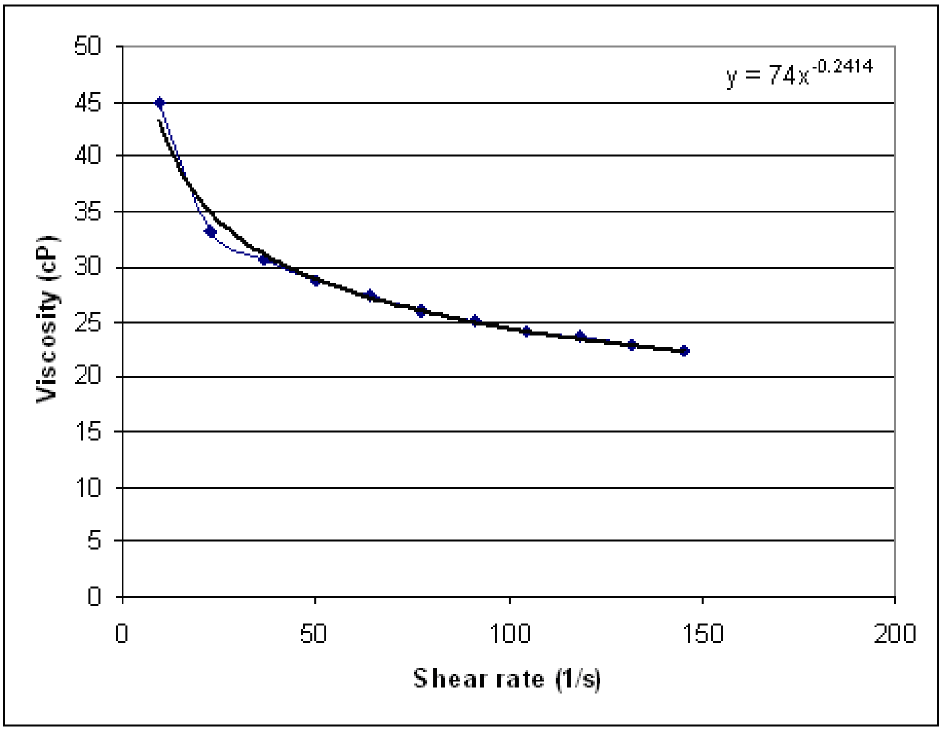


Figure 4.8: Rheological behavior of 1 wt % of HMPA solutions

When the concentration increases to 2 wt %, the viscosity increases drastically (nearly 300 times) as can be seen from Figure 4.9. Here it can be said that the intermolecular hydrophobic interactions become significant. The power of the solution also increased to 0.6895 which can be seen from the equation at the corner of the Figure 4.9.

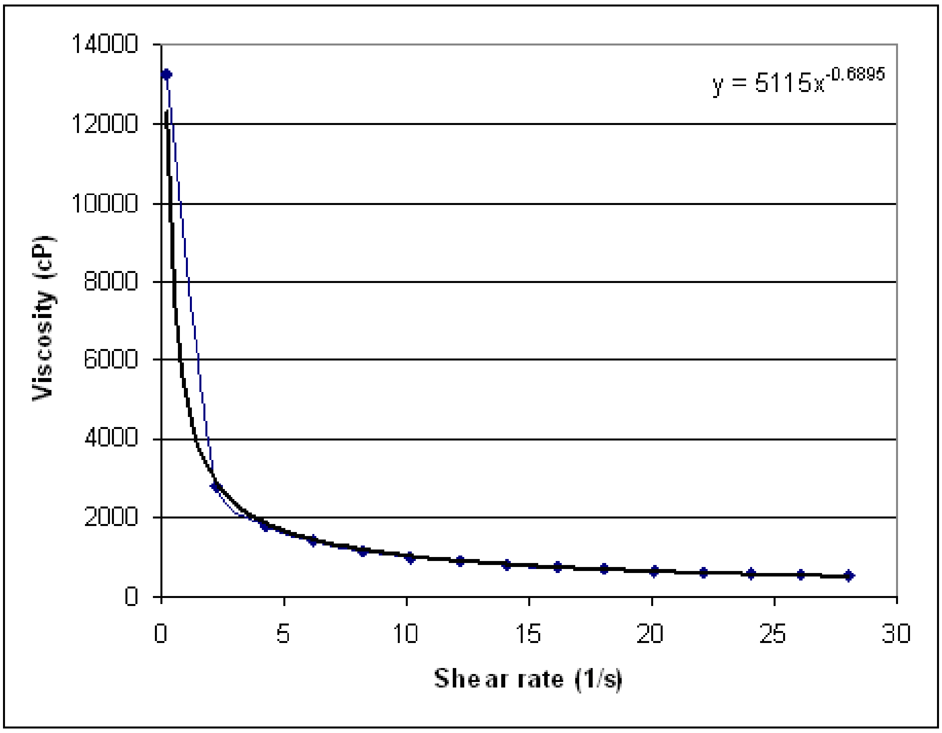


Figure 4.9: Rheological behavior of 2 wt % of HMPA solutions

As can be seen from Figure 4.10, if the polymer concentration is further increased to 4 wt %, the viscosity continues to increase but not as much as in the previous case. Also the power of the fluid increases to 0.8288 which is the twice of the value needed for a typical anti-icing fluid.

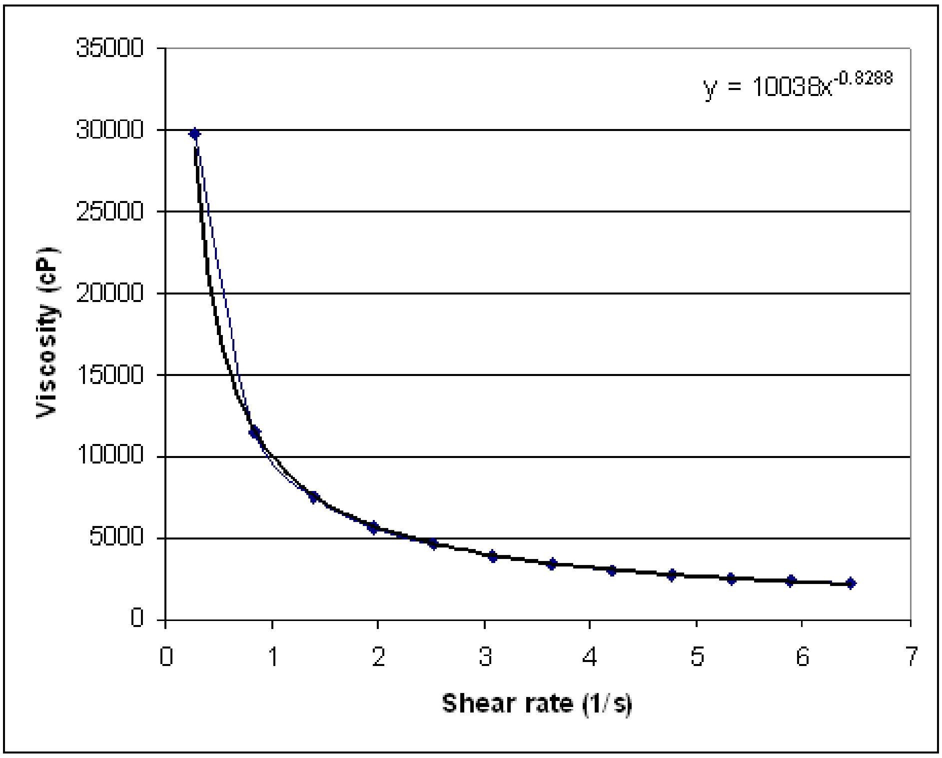


Figure 4.10: Rheological behavior of 4 wt % of HMPA solutions

These observations validate the mechanism behind the interactions of the polymer chains and water molecules. The sharp decrease in viscosity of solutions at high shear rates shows the strong shear-thinning behavior of the solutions. To understand that interesting behavior, first of all the mechanism of pseudoplastic solutions must be analyzed.

Pseudoplastic mechanism

The basics of this mechanism can be explained in terms of entanglements between polymer chains in the solution. At low shear rates these entanglements stay in stable form and stabilize the solvent molecules and increase the solution viscosity. But at higher shear rates these entanglement points start to untangle and chains start to flow in the direction of flow and the viscosity decreases. In other words, polymer chains resist the flow at low shear rates, and at high shear rates this resistance gets lost. In highly hydrophilic homopolymers, these entanglement points occur due to the mechanical reasons. Therefore they can easily untangle at low shear rates. So shear-thinning behavior can not be observed (See Figure 4.11, case I). In order to have a high shear-thinning behavior, these entanglement points must be reinforced by additional secondary forces which cause higher resistance to flow. In general, this modification is done by introducing hydrophobic groups to the hydrophilic polymer backbone. These hydrophobic groups attract each other in the solution and form a network structure in solution. This structure can also be named as a hydrophobically crosslinked polymer chains. These hydrophobic interactions hold the polymer chains in entangled form at low shear rates and resist the flow. However, at high shear rates these interactions start to disappear and the viscosity decreases (See Figure 4.11, case II). When these modified polymers are dissolved in aqueous solution, the hydrophobic groups tend to favor intra- and interpolymer associations to minimize their exposure to the water. Intrapolymer association may dominate at low polymer concentrations, whereas interpolymer association becomes prominent at high polymer concentrations [42, 43].

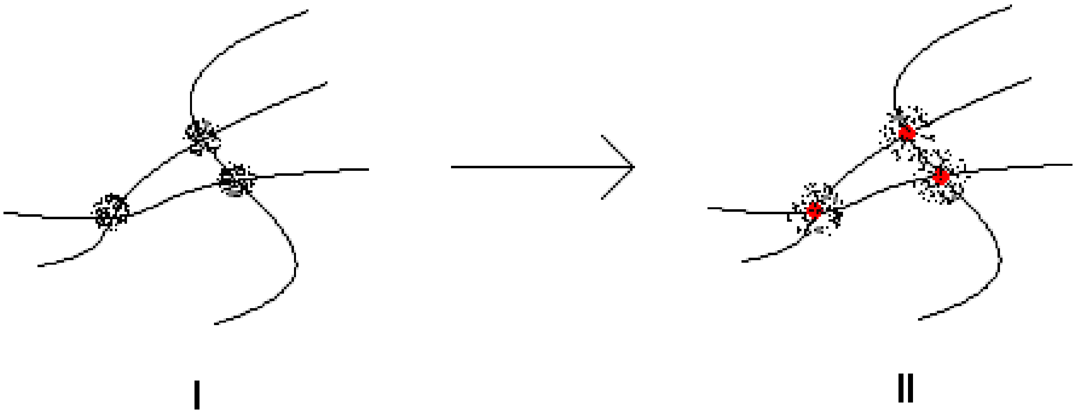


Figure 4.11: The effect of hydrophobic groups on entanglement points and pseudoplastic mechanism *(The red dots represent hydrophobic groups).*

I: In that situation the hydrophilic homopolymers are entangled only by mechanically. Therefore, even at very small shear rates these entanglements start to disappear and polymer chains can not resist the flow. That results in a total Newtonian behavior, same viscosity at all shear rates.

II: In this case, the hydrophilic polymers are modified by binding hydrophobic groups. Hydrophobic groups generally consist of long alkyl molecules and they are like surfactants. This modification introduces new secondary forces to the entanglement points. These new forces do not break down at low shear rates and resist the flow, so that the viscosity of the solution increases. As the shear rate increases these forces can not resist and the viscosity of the solution decreases. In conclusion, the solution gains a strong shear-thinning behavior. Also, when the shear rate is removed, the solution gains its initial viscosity again.

4.2.2.3.2 The effect of ionization degree on solution rheology (pH effect)

The effect of ionization degree of polyacrylic acid chains has a great influence on solution viscosity. As it is mentioned, at low HMPA concentrations the polymer exists as emulsion particles in the form of insoluble carboxylic acid. Each emulsion particle contains polymer molecules in a collapsed configuration. The viscosity of the system prior to neutralization is close to that of water (3 cP). The acid group (COOH) is not hydrolyzed, and there is no intermolecular hydrophobic association (See Figure 4.12 I. case). When NaOH is added to the solutions, it neutralizes the acid group (COOH) on the polymer chain. As a result, the particle is solubilized due to the acid and base reaction and COO^-Na^+ groups are formed along in the polymer chains. As the pH value increases, the repulsion between the negative charges increases hence the coils unfold. This will further result in intramolecular and intermolecular hydrophobic associations. At a pH of approximately 4-6 (See Figure 4.12 II. case) the low shear viscosity reaches a maximum value, then the viscosity starts to decrease and at about pH=9 it reduces to 30 cP which is very close to its first value. This peak in the viscosity value can be explained by optimum ionic repulsion occurred along the polymer backbone. To a certain neutralization degree the repulsion along the chains increase the hydrodynamic volume of the chains. At the same time the secondary forces occurring in intra and inter chain fashion through hydrogen bonding and hydrophobic interactions. These result in high viscosity increment in the solution. However, after certain ionization degree, the ionic repulsion along the chains and between the chains increases too much and the network structure caused by the secondary forces begins to disintegrate. These combined effects cause a sharp fall in solution viscosity. At pH around 9 (See Figure 4.12 III. case) no interchain or intrachain interaction occurs between the polymer chains and the viscosity turns back near to its initial value.

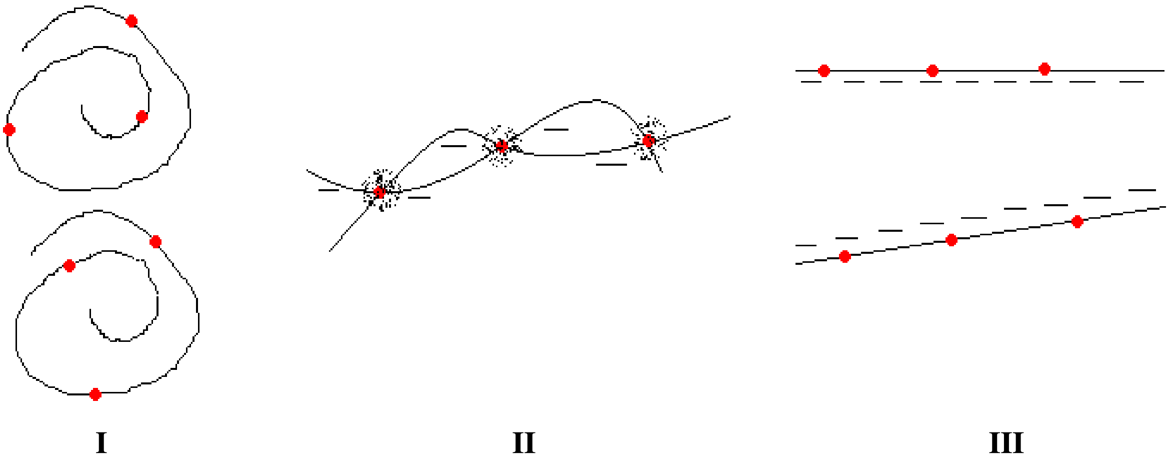


Figure 4.12: The behavior of the chains with respect to their ionization degrees *(The red dots represent the hydrophobic groups)*

The rheological behavior of the HMPA solutions under increasing pH condition is shown in the following figures for different polymer concentrations. They confirm the effect of ionization degree on solution viscosity.

Firstly, in Figure 4.13, the change of low shear viscosity with increasing NaOH concentration is given for a 0.05 wt % HMPA solution. It is seen that the viscosity of the solution starts to increase by the increasing NaOH concentration and after the viscosity reaches maximum it starts to decrease to its initial value.

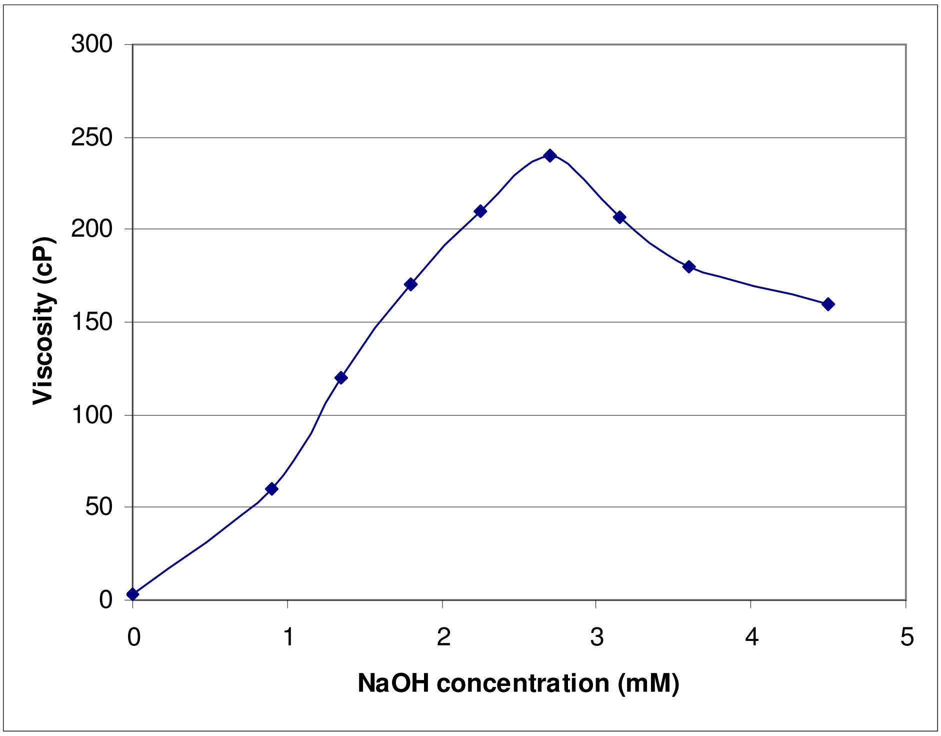


Figure 4.13: The change of low shear viscosity of 0.05 wt % HMPA solutions composed of 50 % water and 50 % glycol with the addition of NaOH

The maximum viscosity obtained for 0.05 wt % HMPA solution is around 250 cP and it is obtained at around 2.8 mM NaOH concentration. This corresponds to the pH value of 6. The molarity of polymer in the solution is calculated as 7 mM by assuming the polymer as a homopolymer of acrylic acid and by taking the molecular weight as 72 g/mole. The maximum viscosity is obtained at NaOH concentration which is around 40 % of the polymer concentration for 50 % water- 50 % glycol mixtures.

When the concentration of the polymer in the solution is increased to 0.075 wt %, it is seen that the viscosity rise in the solution gets larger (See Figure 4.14). This fact can be explained by the increase of the interchain interactions of the hydrophobic groups. These interactions occur in small concentrations relative to the previous unneutralized solutions due to the increase in the hydrodynamic volume of the polymer chains.

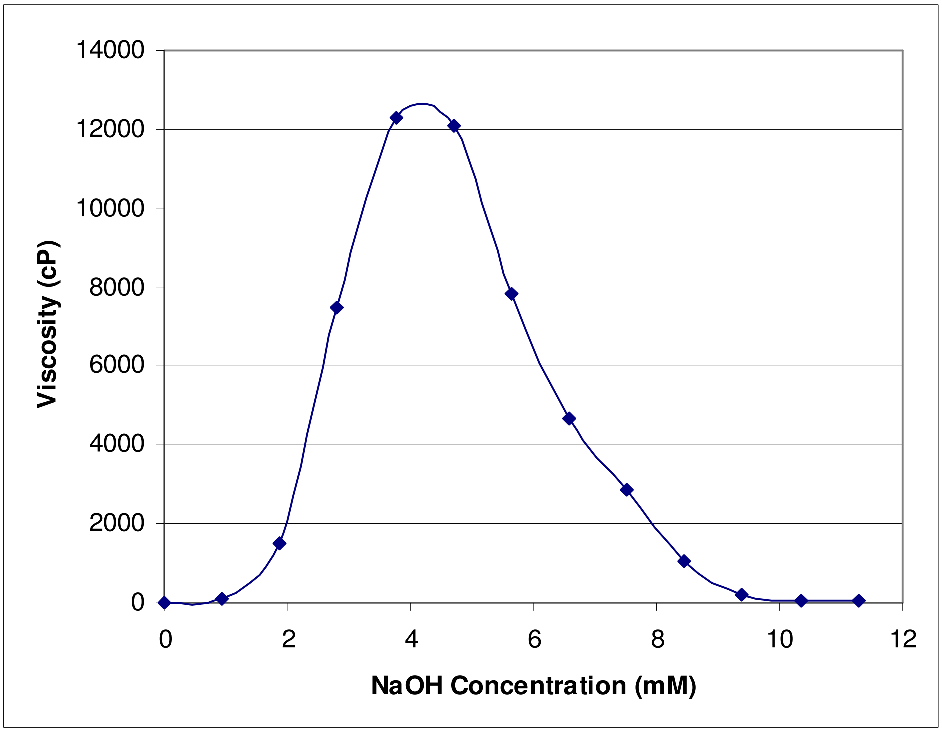


Figure 4.14: The change of low shear viscosity of 0.075 wt % HMPA solutions composed of 50 % water and 50 % glycol with the addition of NaOH

In this case, the maximum viscosity is obtained at around 4.2 mM NaOH concentration and the polymer concentration is 10.42 mM. It can be seen that the required NaOH concentration to achieve the maximum low shear viscosity is again around 40 percent of the polymer concentration in the solution. Therefore it can be concluded that, the ionization degree of the polymer chains reaches its optimum value at 40 % of NaOH concentration with respect to polymer concentration to have a maximum viscosity.

When we look at the pH change in the solution by the addition of NaOH (See Figure 4.15), the viscosity values start to increase at around pH=4 and increases up to pH=6 and reaches it maximum then it starts to decrease.

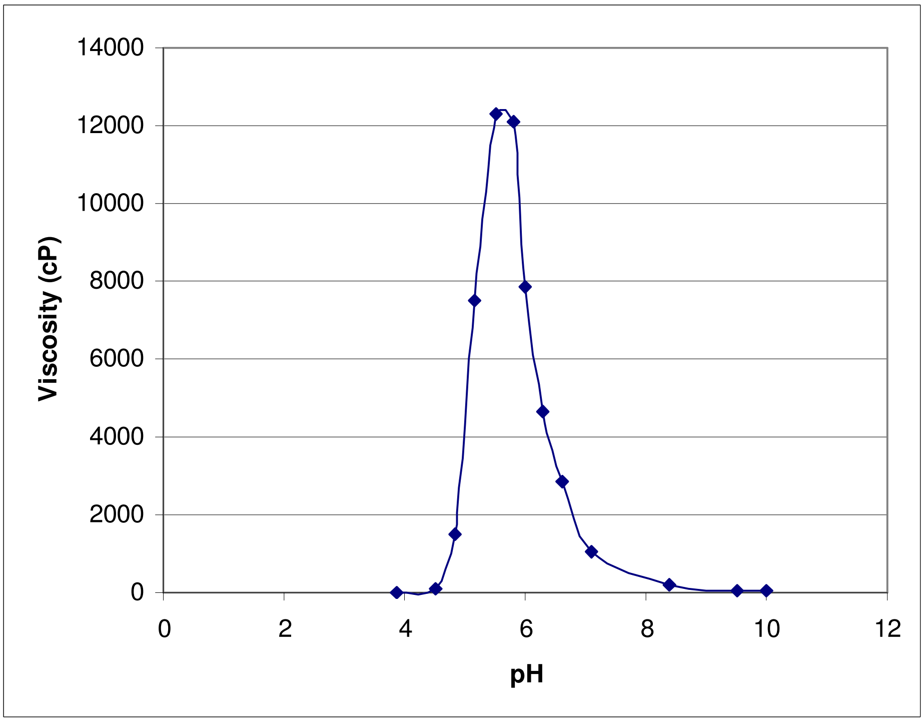


Figure 4.15: The change of low shear viscosity of the 0.075 wt % HMPA solutions composed of 50 % water and 50 % glycol with pH

The viscosity increase with addition of NaOH is tried to be tested on the polymer solutions with a 0.1 wt % polymer concentration but the viscosity of the solution increased to 12000 cP which is over the measurement limits of the LVDV rheometer therefore the viscosity values could not be measured correctly. The reason for that increment can easily be explained by the increase of the interchain interactions of the polymers in the solution.

The small changes in polymer concentrations and pH lead to drastic increases in solution viscosity as can be seen from the Figure 4.14 and Figure 4.15. While the low shear viscosities are affected very much from the pH and polymer concentration, the viscosities at high shear rates do not change that much as shown in Figure 4.16.

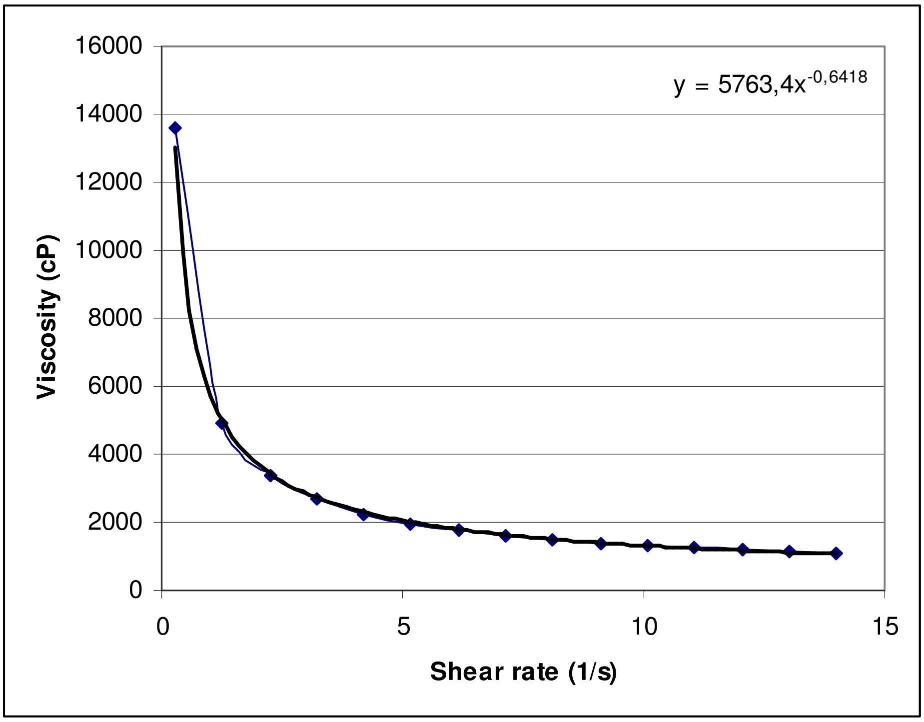


Figure 4.16: The rheological behavior of 0.075 wt % HMPA solution at pH=6 in 50 % water-50 % glycol solution.

The power law equation of the solution prepared by 0.075 wt % HMPA (See Figure 4.16) is:

$$\eta= 5763.4\ \gamma^{-0.6418} \qquad (4.1)$$

In this equation, "γ" represents the shear rate (x) that is exerted on the fluid and "η" represents the viscosity (y) value at that shear rate and 0,6418 is called as the power of the fluid and it determines how much the solution is shear-thinning. As the power of the solution increases, the shear-thinning behavior of the solution increases too.

It is known that the shear rate on the surfaces of the aircraft during take-off is approximately 140 1/s. When 140 is plugged in as "x" value in Equation 4.1, "y" value or viscosity value turns out to be 241.8 cP. It means that, solution has a low shear viscosity at around 13000 and high shear viscosity at around 240 cP. The viscosity loss of this fluid is around 99 %. This high performance of these fluids makes them special and maybe a better candidate as an anti-icing fluid than the commercially available ones. Low shear and high shear viscosity values of these solutions can further be adjusted by changing the concentration of the polymer and pH of the solution.

In Figure 4.17, the change of viscosity at different polymer concentrations can be observed. It is clearly seen that trace amount of changes in polymer concentration in solution leads to drastic changes in viscosity values.

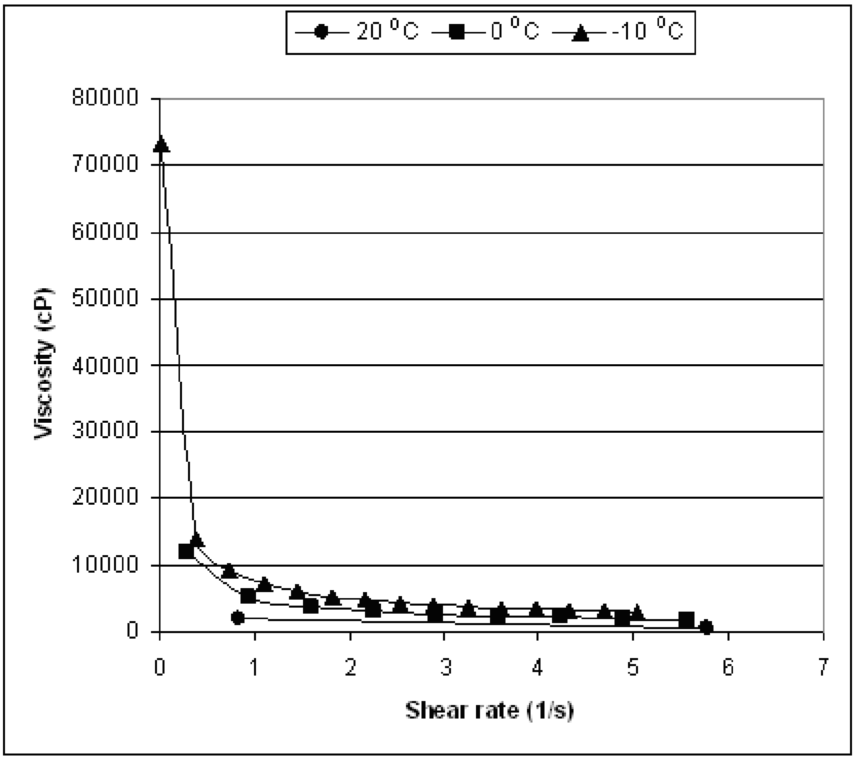


Figure 4.17: The rheological behavior of polymer solutions at different polymer concentrations (at 50 % glycol 50 % water and pH at around 5.2)

4.2.2.3.3 The effect of glycol-water concentration on solution rheology

As it is mentioned before, anti-icing solutions are mainly the mixture of glycol and water, due to the very low freezing point of their mixtures. Generally ethylene glycol is preferred rather than propylene glycol because of economical reasons. The advantage of propylene glycol comes from its environmentally friendly nature. In this study ethylene glycol is preferred. In the currently used anti-icing fluids, 50 % water-50 % glycol by weight is the most preferred composition but there are also solutions containing 60 % and 70 % glycol. Glycol content of the solutions changes the freezing point of the solutions and also their viscosities.

In Figure 4.18, the rheological behavior of HMPA solutions at different glycol concentrations are shown.

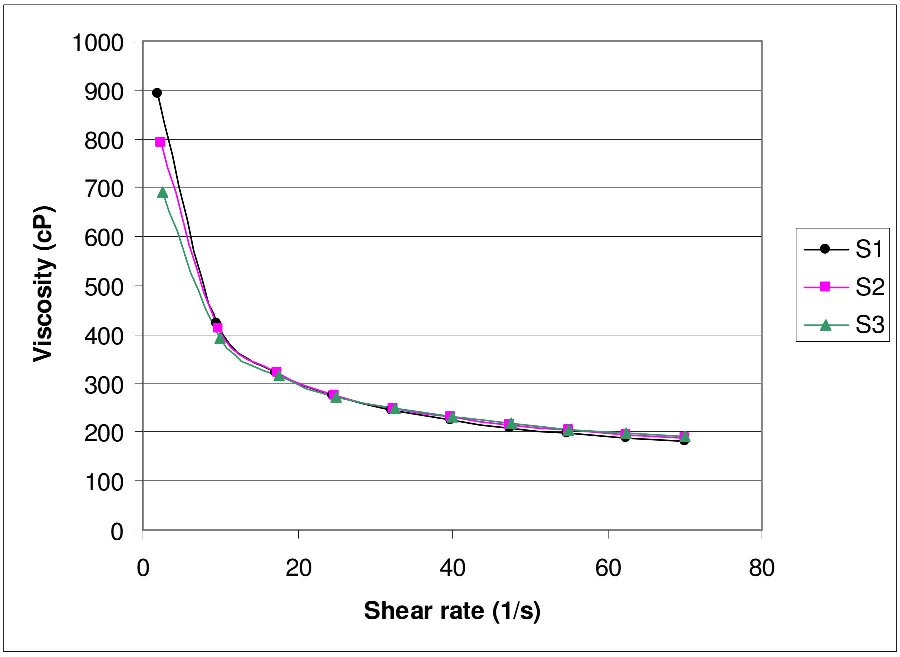
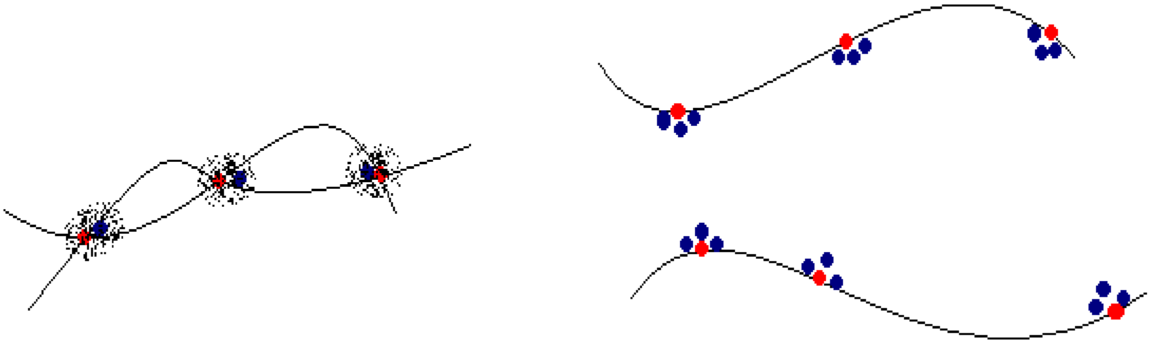


Figure 4.18: The rheological behavior of HMPA solutions at 0.064 wt % concentration with different glycol-water content. *(S1: 50 % water-50 % glycol, S2:40 % water-60% glycol, S3: 30 % water, 70 % glycol)*

It can be seen from the Figure 4.18 that, as the glycol content increases in the solution the low shear viscosity decreases. This fact can be explained by the increase in the hydrogen bonding and the polar-polar interactions between water and carboxylic acid groups. It is also known that the inter- and intramolecular hydrogen bonds formed in ethylene glycol are weaker than those in water [44].

4.2.2.3.4 Dependency of solution rheology on surfactant concentration

Surfactants are used in anti-icing solutions in order to reduce the surface tension and increase the wetting ability of the fluids. The surface tension of the fluids also affects the aerodynamics of the airplane. Surfactant molecules also change the solution rheology interestingly. Up to a certain surfactant concentration, they result in increase in the viscosity and shear thinning behavior of the solutions. But above that concentration they start to decrease the viscosity of the solutions. That's why, with the presence of surfactant molecules in the solution, interpolymer association is enhanced by the interaction between the hydrophobic groups on polymer backbone and surfactant molecules [45-48]. A drastic increase in solution viscosity at concentrations around the surfactant critical micelle concentration (cmc) is attributed to interpolymer cross-linking through the formation of mixed micelles involving the surfactant molecules and the hydrophobes from different polymer chains (See Figure 4.19, C<cmc). A subsequent decrease in viscosity with further increase of the surfactant concentration above the cmc is ascribed to the breakdown of the cross-linking network as sufficient surfactant is available to form micelles with each individual polymer hydrophobe (See Figure 4.19, C>cmc).



C<cmc C>cmc

Figure 4.19: The schematic representation of the polymer chains at above and below cmc *(Red dots represent the hydrophobic groups and blue dots represent the surfactant molecules)*

The interactions of the surfactant molecules with the hydrophobic groups on polymer backbone around cmc and the behavior of the polymer chains can also be observed in Figure 4.20.

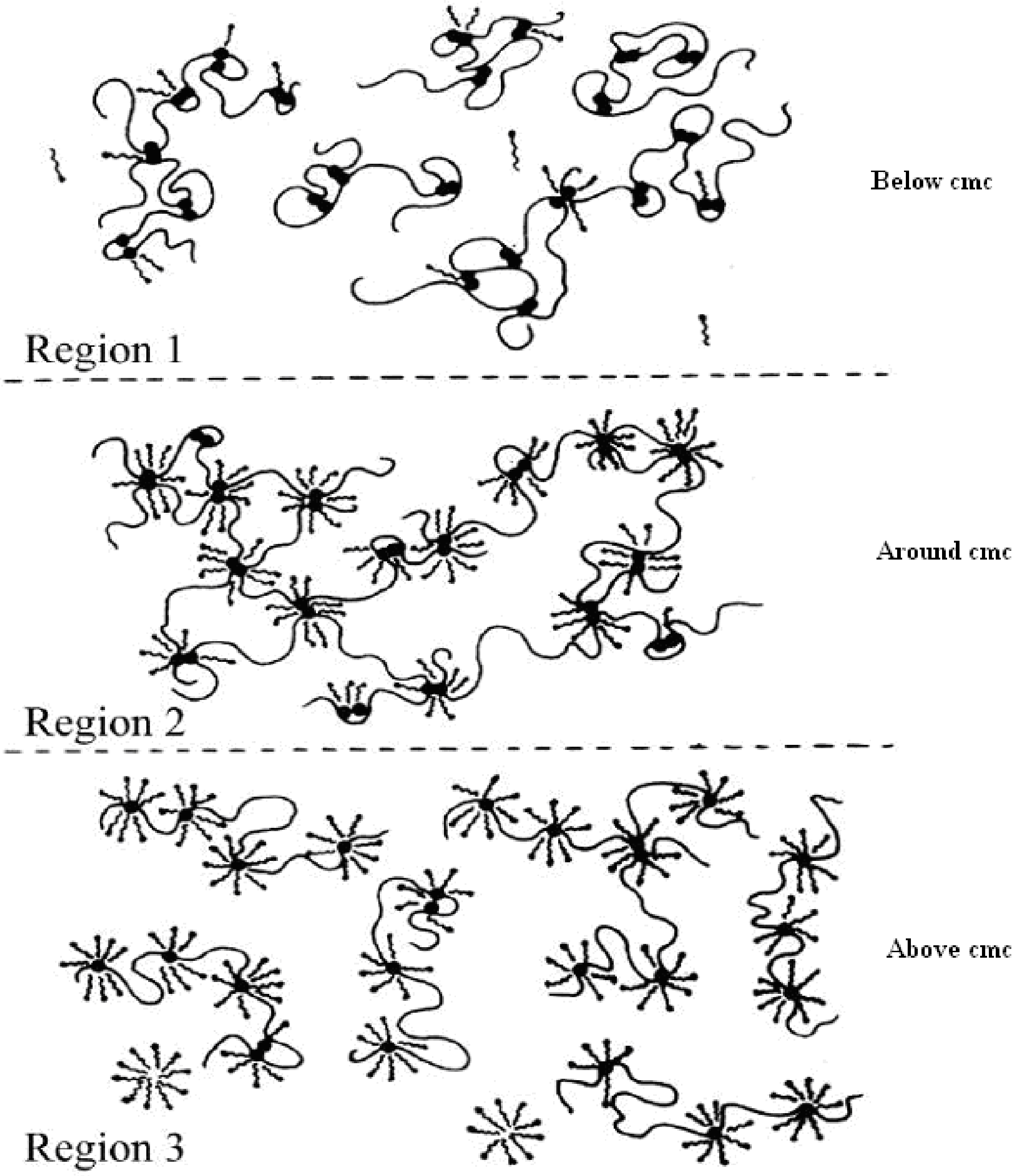


Figure 4.20: Schematic representation of the interactions of hydrophobically modified water soluble polymers with surfactants at three different surfactant concentrations corresponding to Regions 1, 2 and 3. Polymeric hydrophobic microdomains are denoted by the black dots (Taken from reference [45]).

The effect of three anionic, three cationic surfactants and one nonionic surfactant on HMPA solution rheology and surface tension are tested. These surfactants affect the viscosity of the solutions while decreasing the surface tension in general.

4.2.2.3.4.1 The effect of anionic surfactants

- Sodium dodecyl sulphate (SDS)

Sodium dodecyl sulphate is a widely used anionic surfactant. The molecular formula of SDS is $CH_3(CH_2)_{11}SO_4^-Na^+$. When it is dissolved in the solution, sodium metal ionizes and a long alkyl group with SO_4- in the head solubilizes in the water and attract with hydrophobic groups on polymer backbone. The change in surface tension and rheology of the solutions are given in Figures 4.21 and 4.22.

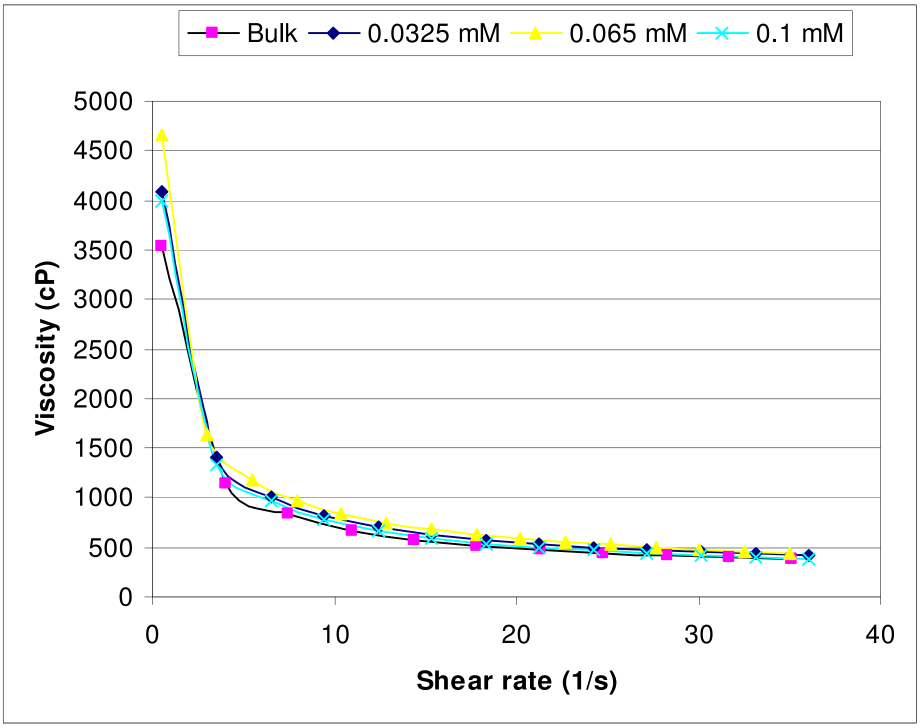


Figure 4.21: The viscosity change of 0.07 wt % HMPA solution (50 % water and 50 % glycol) with addition of SDS

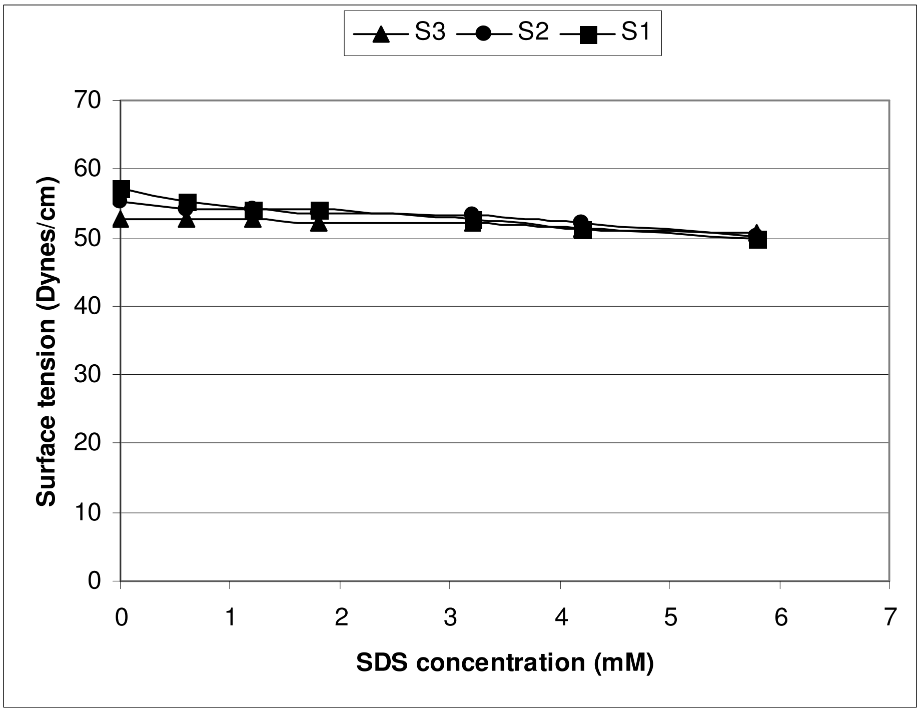


Figure 4.22: The surface tension change of HMPA with addition of SDS at different glycol-water content

(S1: %50 glycol-%50 water, S2: %60 glycol-%40 water, S3: %70 glycol-%30 water)

When SDS concentration increases above 0.065 mM, the viscosity of the polymer solution starts to decrease. In other words, it is experimentally observed that 0.065 mM is critical micelle concentration for SDS in 9.63 mM HMPA solution. The surfactant amount is the 0.675 % of the polymer amount. Unfortunately, the surface tension of the solution does not reduce to 40 Dynes/cm even at 6 mM SDS concentration. Therefore, SDS is not suitable to be used as a surfactant in HMPA solutions.

- Aerosol-T (AOT)

AOT or 2-ethyl hexyl sulfosuccinate is a well-known surfactant too. Its molecular formula is $(CH_2COOC_8H_{17})(CHCOOC_8H_{17})SO_3^-Na^+$. When it is dissolved in water, a long alkyl group is ionized and interacts with hydrophobic groups on the polymer backbone. The change in surface tension and rheology of the solutions are given in Figures 4.23 and 4.24.

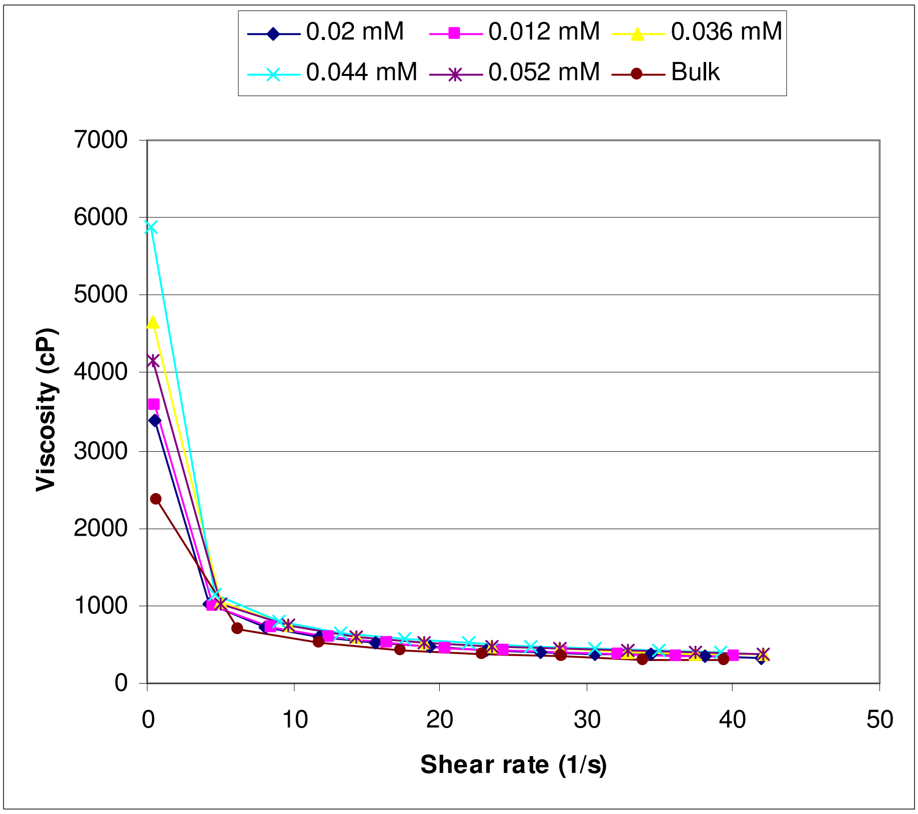


Figure 4.23: The viscosity change of 0.067 wt % HMPA solution (50 % water and 50 % glycol) with addition of AOT

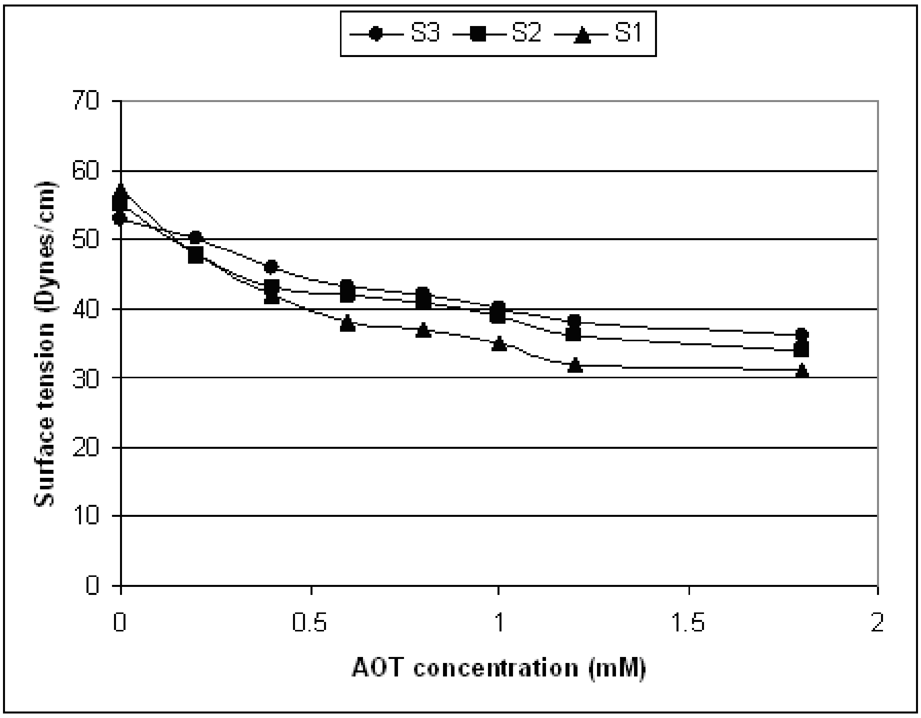


Figure 4.24: The surface tension change of HMPA solution with addition of AOT

(S1: %50 glycol-%50 water, S2: %60 glycol-%40 water, S3: %70 glycol-%30 water)

For AOT, cmc is measured below that is for SDS. Around 0.044 mM AOT, the solution viscosity starts to decrease which shows that all surfactant molecules bind all individual hydrophobes. This concentration is the 0.48 % of the polymer concentration. The surface tension of the AOT-polymer solution decreases to desired values at around 0.5 mM AOT concentration which is 10 times larger than cmc of AOT.

- Sodium oleate (NaO),

Sodium oleate is the chemical that is used in most of the soaps and also it is a well-known anionic surfactant. In this study, NaO is synthesized from oleic acid and sodium hydroxide in methanol as a solvent. The molecular formula of NaO is $CH_3(CH_2)_7(CH)_2(CH_2)_7COO^-Na^+$. It gives a long alkyl group with negatively charged head group when dissolved in water. The change in surface tension and rheology of the solutions are given in Figures 4.25 and 4.26.

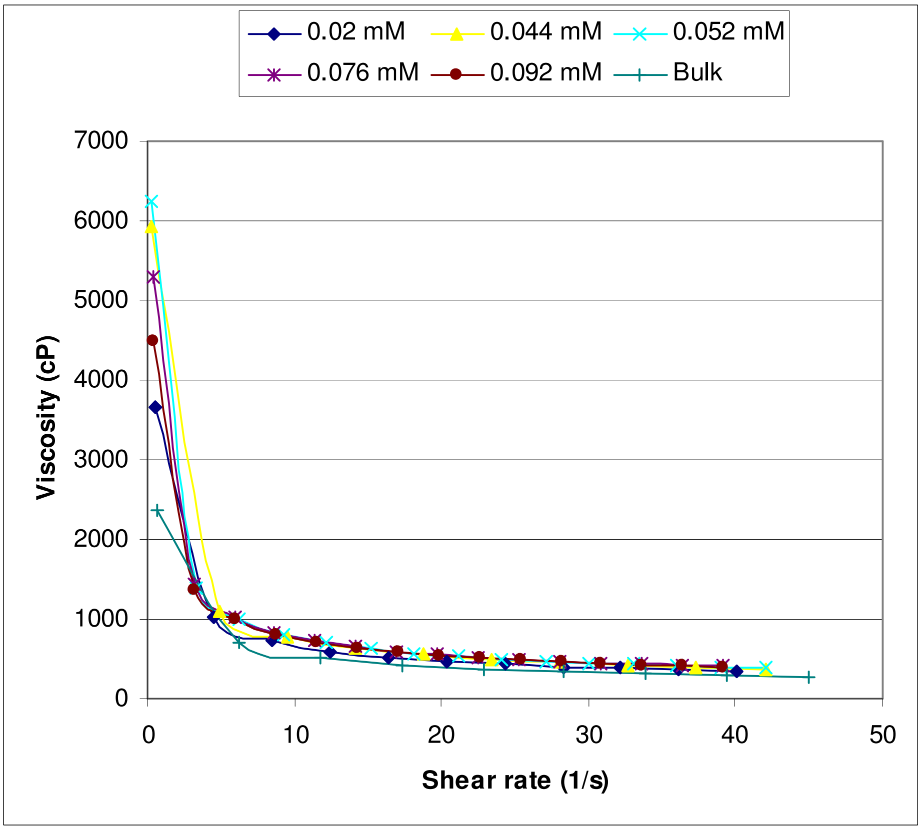


Figure 4.25: The viscosity change of 0.067 wt % HMPA solution (50 % water and 50 % glycol) with addition of NaO

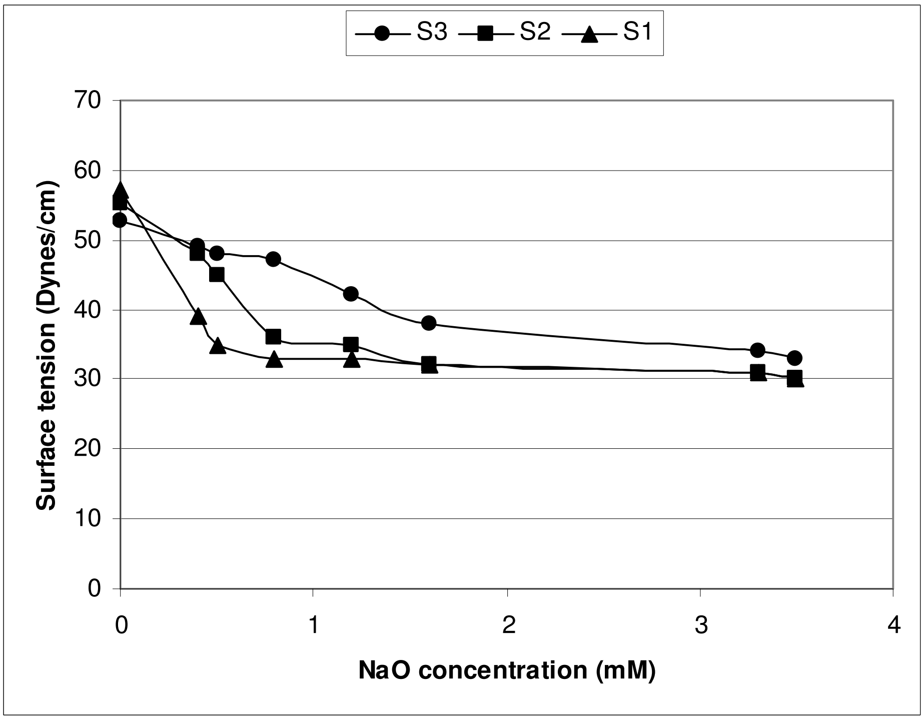


Figure 4.26: The surface tension change of HMPA solution with addition of NaO

(S1: %50 glycol-%50 water, S2: %60 glycol-%40 water, S3: %70 glycol-%30 water)

The best surfactant among these three anionic surfactants is determined as sodium oleate because it is the most successful surface agent in lowering the surface tension. It can reduce the surface tension of the polymer solutions to 40 Dynes/cm at around 0.4 mM concentration and it does not reduce the low shear viscosity of the polymer solutions until 0.052 mM concentration (0.56 % of polymer concentration).

4.2.2.3.4.2 The effect of cationic surfactants

In general, cationic surfactants increased the viscosity of the solutions better than anionic surfactants; even 0.004 mM surfactant in solution can give rise to the viscosity values. Besides, they are very weak in reducing the surface tension of the solutions. This fact can be explained by the enforced polymer network by hydrophobic and electrostatic interactions. Because there are two additional forces that strengthens the network structure, the shear-thinning behavior of polymer solutions get increased more with respect to the case in anionic surfactants. After certain surfactant concentration, on the other hand, the viscosity values start to decrease because surfactant molecules start to interact with each individual hydrophobe molecule in the chain and the network structure is broken similar to anionic surfactant experiments. It is observed that cationic surfactants are very weak in reducing the surface tension of the solutions. The reason for that may be found in the electrostatic interactions between polymer chains and surfactant molecules. These interactions may stiffen the surfactant molecules near thr polymer backbone and exclude them more from the surface interactions relative to the anionic ones. In other words, the alkyl groups with cationic head group may be attracted by the polymer chains and screened there. Therefore they can not contribute to the surface interactions, and surface tension remains at high values. In this study, the effects of three cationic surfactants on solution rheology and surface tension are examined.

- Tetrabutylammonium tetrafluoroborate (TBAF)

Tetrabutylammonium tetrafluoroborate is commonly used as electrolyte in organic solutions. Its chemical formula is $(CH_3CH_2CH_2CH_2)_4N(BF_4)$. When it is dissolved in water, alkyl groups with cationic head group starts to interact with hydrophobic groups on polymer chains. The effects of TBAF concentration on solution rheology are shown in Figures 4.27 and 4.28. 0.008 mM TBAF concentration result is included in a different graph because at that concentration the solution viscosity increases rapidly and reaches to 14000 cP. That obstructs the visualization of the other graphs. TBAF can not reduce the surface tension of the polymer solutions. The effect of all cationic surfactants on surface tension is given in Figure 4.33.

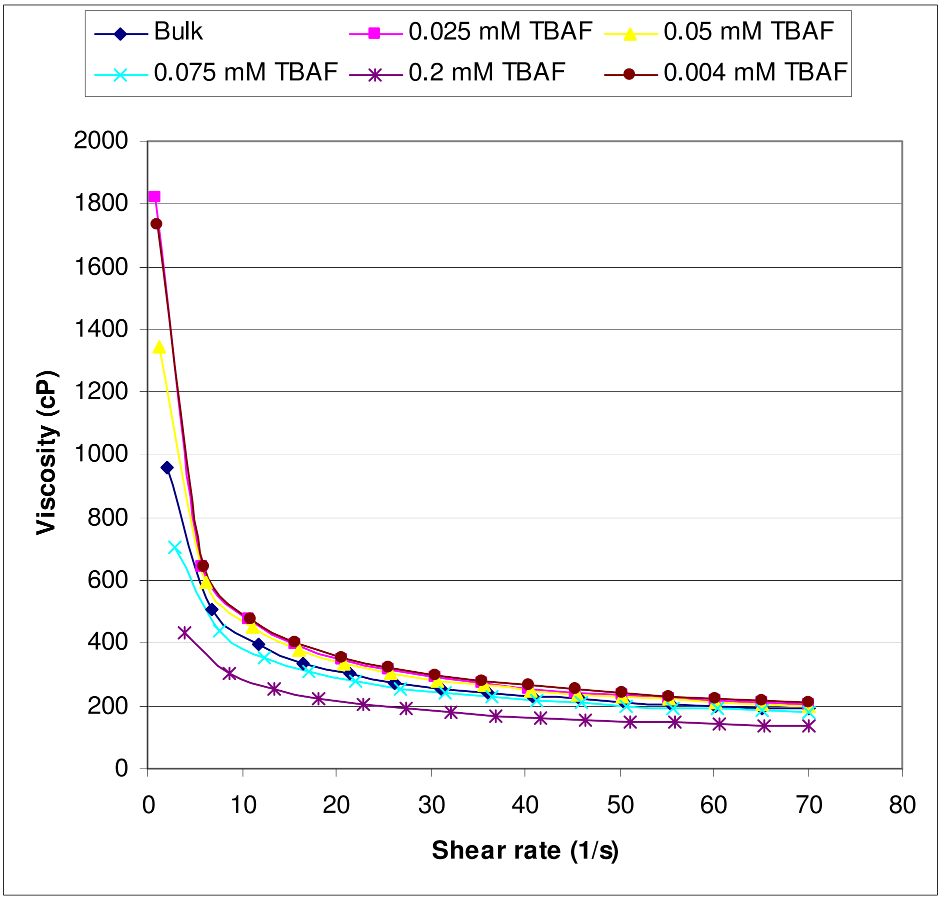


Figure 4.27: The rheological behavior of polymer solutions (0.064 wt % HMPA in 50 % glycol) with the addition of TBAF in low viscosity range

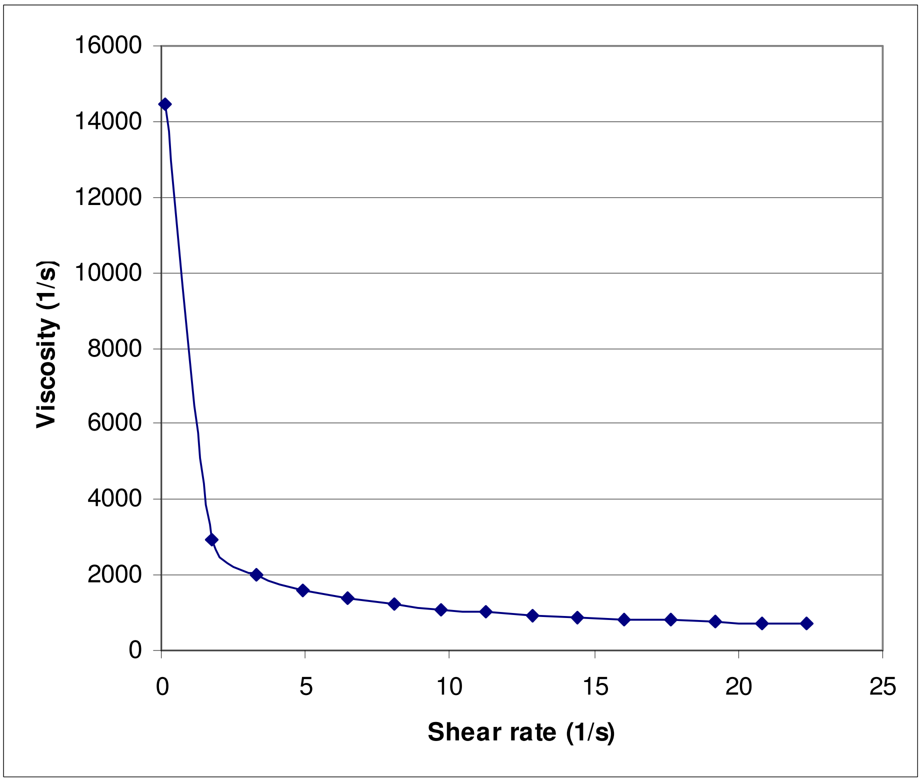


Figure 4.28: The rheological behavior of polymer solution (0.064 wt % HMPA in 50 % glycol) with 0.008 mM TBAF concentration in high viscosity range

The maximum viscosity is acquired with 0.008 mM TBAF concentration. As it is seen from Figure 4.28, the low shear viscosity increases nearly up to 10 times of its bulk value. After 0.008 mM concentration the viscosity of the solution starts to decrease.

- Hexadecyltrimethylammonium bromide (CTAB)

Hexadecyltrimethylammonium bromide (CTAB) is generally used as bactericidal and cationic detergents. Its chemical formula is $CH_3(CH_2)_{15}N(Br)(CH_3)_3$. This surfactant also can not reduce the surface tension of the polymer solutions either. But it changes the rheology of the solutions remarkably. The change of viscosity and surface tension of the solutions are shown in Figures 4.29 and 4.30.

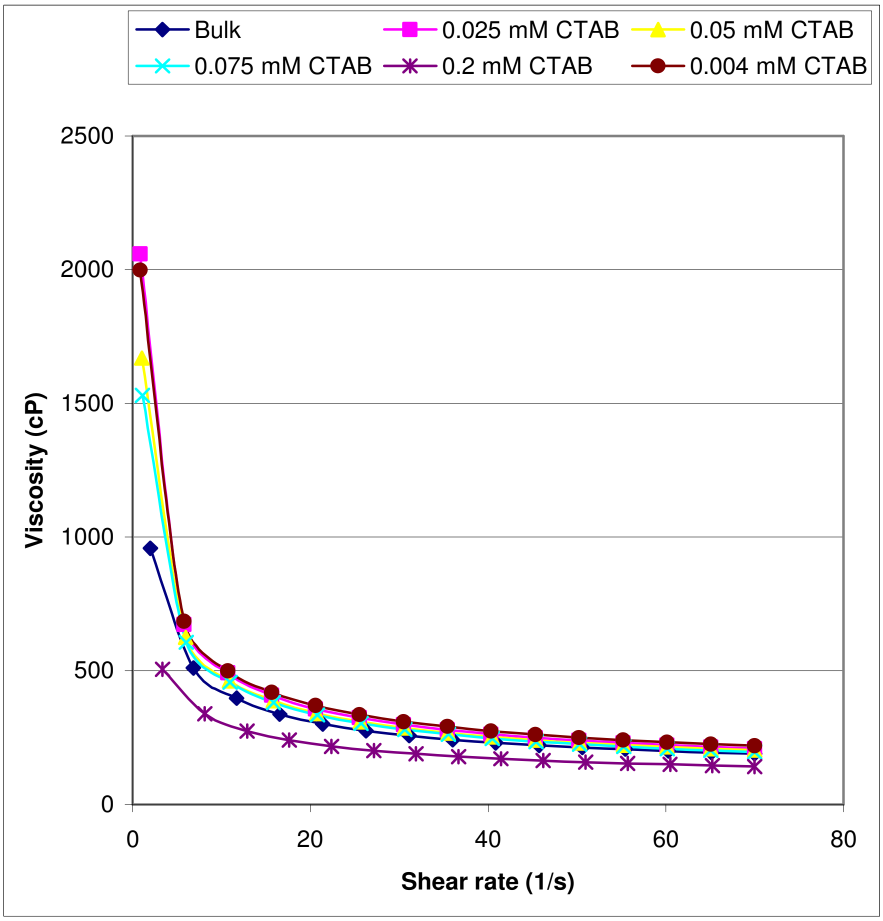


Figure 4.29: The rheological behavior of polymer solutions (0.064 wt % HMPA in 50 % glycol) with the addition of CTAB in low viscosity range

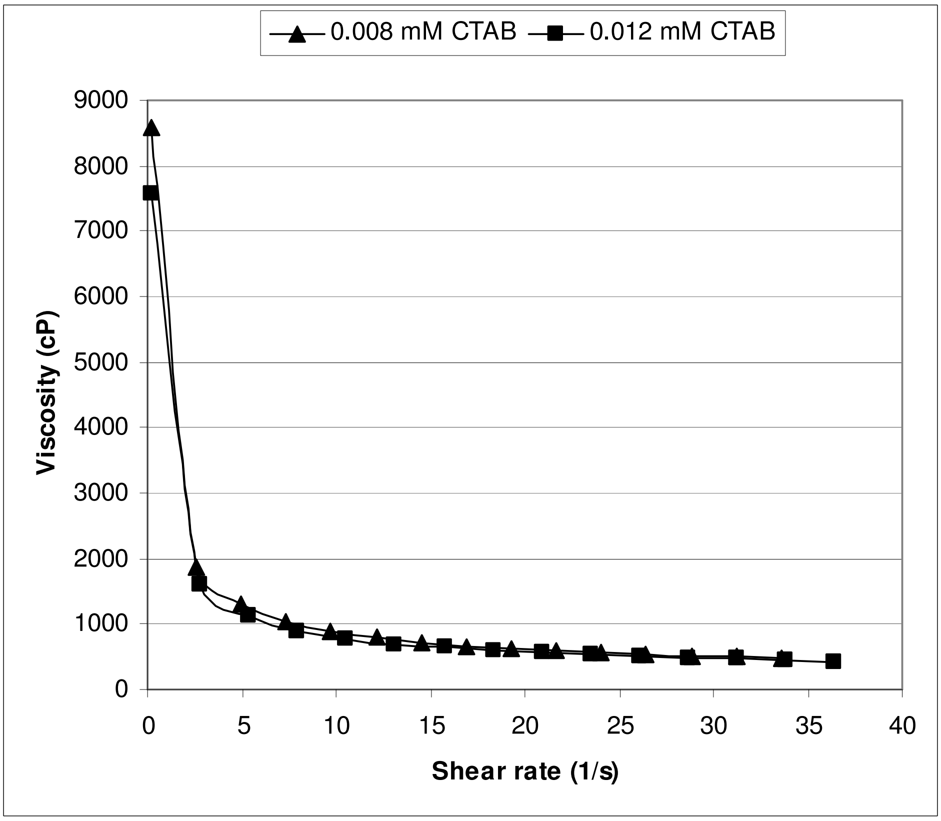


Figure 4.30: The rheological behavior of polymer solution (0.064 wt % HMPA in 50 % glycol) with 0.008 mM and 0.012 mM CTAB concentration in high viscosity range

It can be understood from Figures 4.29 and 4.30 that, the maximum viscosity is obtained at 0.008 mM CTAB concentration. After that concentration, the viscosity starts to decrease.

- Dimethyldioctadecylammonium chloride (DAC)

Dimethyldioctadecylammonium chloride is generally used in fabric softeners, cosmetics, and hair conditioners primarily for its antistatic effects as a well-known surfactant due to its two long-chain hydrocarbon groups. Its chemical formula is $[CH_3(CH_2)_{17}]_2N(Cl)(CH_3)_2$. This surfactant behaves in a similar way as the previous cationic ones and increases the viscosity of the solutions remarkably in certain concentrations, but it is also inefficient in lowering the surface tension of the solutions. The effect of DAC on solution rheology is shown in Figures 4.31 and 4.32.

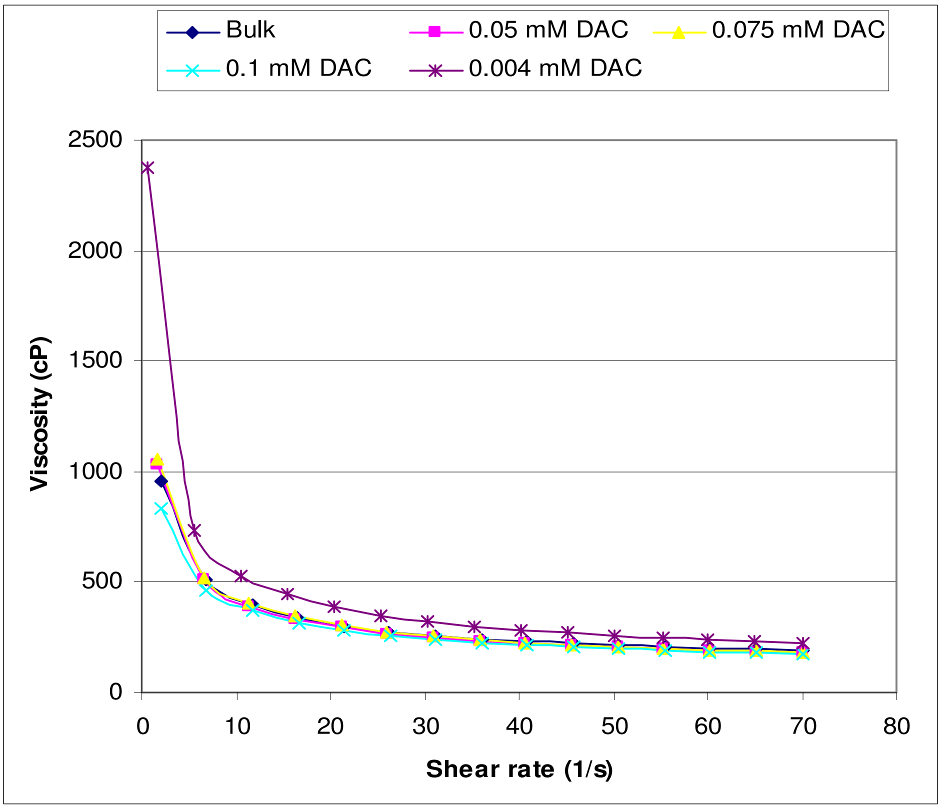


Figure 4.31: The rheological behavior of polymer solutions (0.064 wt % HMPA in 50 % glycol) with the addition of DAC in low viscosity range

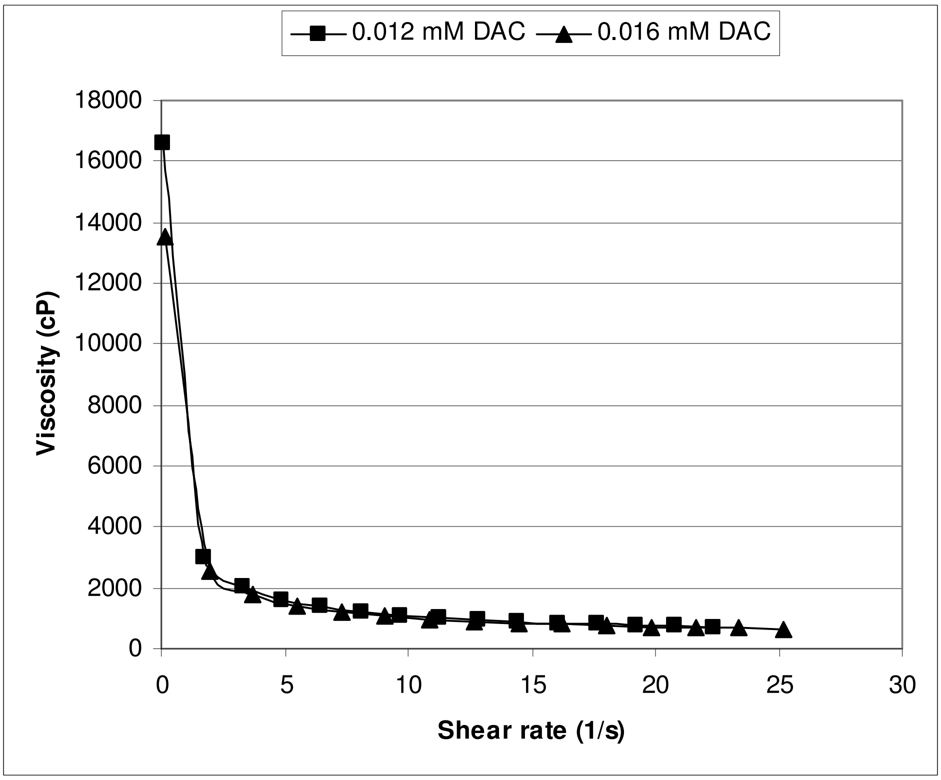


Figure 4.32: The rheological behavior of polymer solutions (0.064 wt % HMPA in 50 % glycol) with the addition of DAC in high viscosity range

It can be clearly seen that the maximum viscosity enhancement is acquired at 0.012 mM DAC concentration. Also this is the best performance in enhancing the viscosity of the solutions among all cationic and anionic surfactants. Like other cationic surfactants, DAC does not reduce the surface tension of the polymer solutions. The behavior of all cationic surfactants in reducing the surface tension is summarized in Figure 4.33.

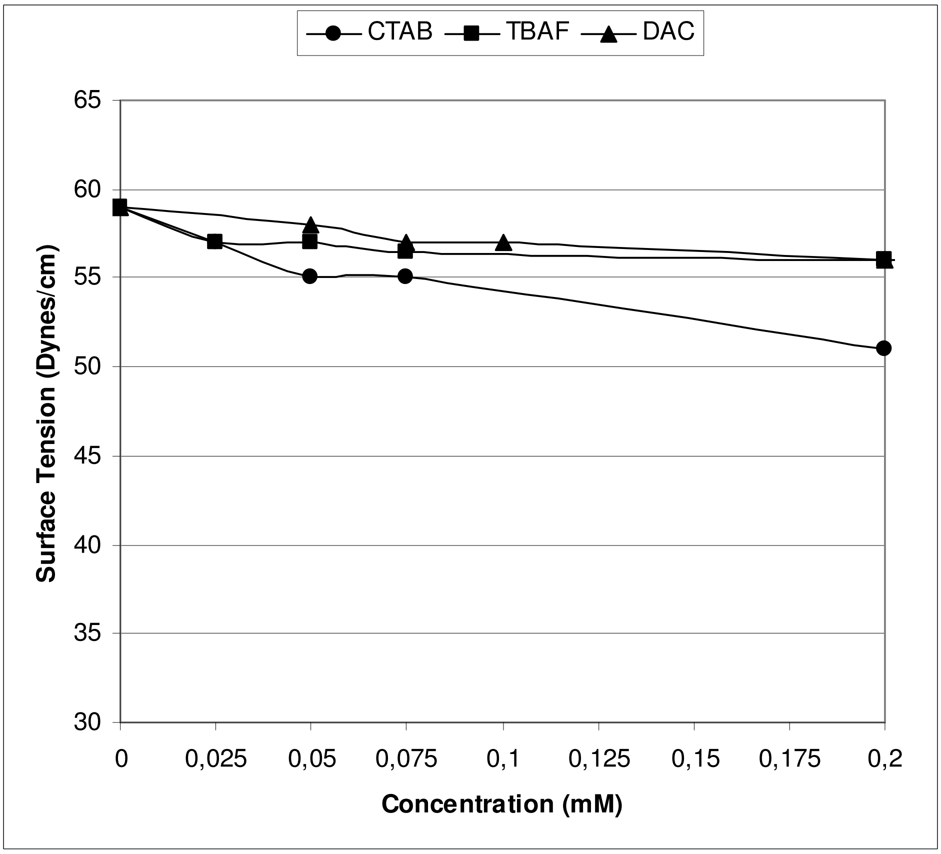


Figure 4.33: The change of surface tension of the polymer solutions (0.064 wt % HMPA in 50 % glycol) by addition of cationic surfactants

As it is stated above, none of the cationic surfactants is capable of reducing the surface tension of polymer solutions near to desired values. Notably, significant polymer-surfactant association still occurs even if the surfactant ion and the ionic group of the HMPA polymer are of the same charge, indicating that the hydrophobic effect is the driving force in these interactions.

4.2.2.3.4.3 The effect of nonionic surfactant "Triton X-100"

The nonionic surfactant, p-tert-octylphenoxy polyethylene ether (Triton X-100) is selected because of its extensive use in industrial and pharmaceutical formulations and in biochemical research [50]. The effect of Triton on solution rheology is similar to the anionic and cationic ones as can be seen from Figure 4.34.

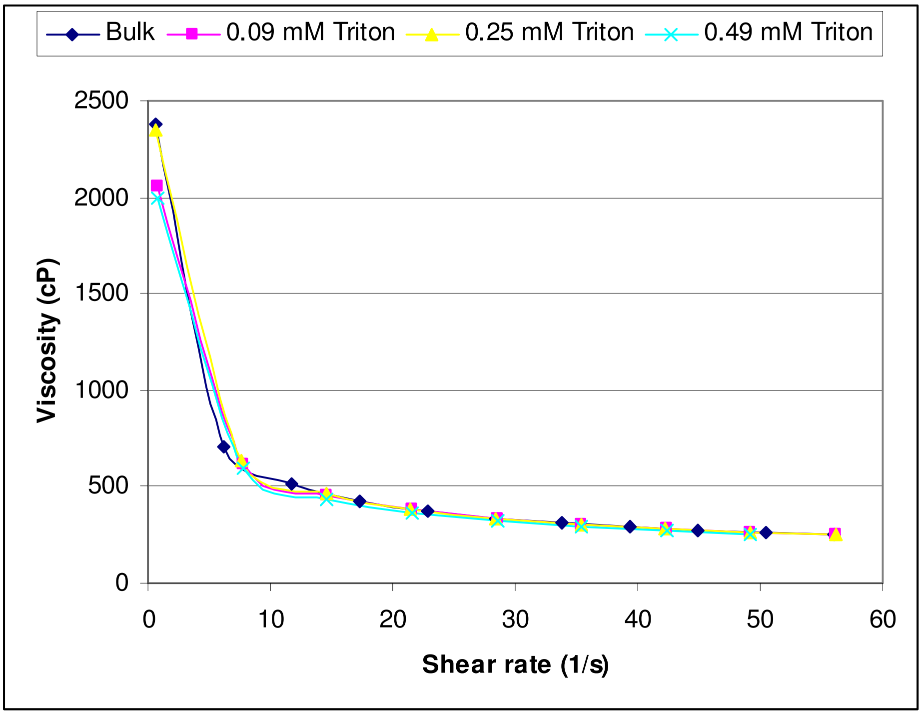


Figure 4.34: The rheological behavior of polymer solutions (0.067 wt % HMPA in 50 % glycol) with the addition of Triton X-100

It can be observed that after 0.25 mM Triton concentration, the viscosity of the solution starts to decrease. The surface activity of the Triton can be observed in Figure 4.35. It is seen that, Triton is not successful in decreasing the surface tension of the polymer solutions.

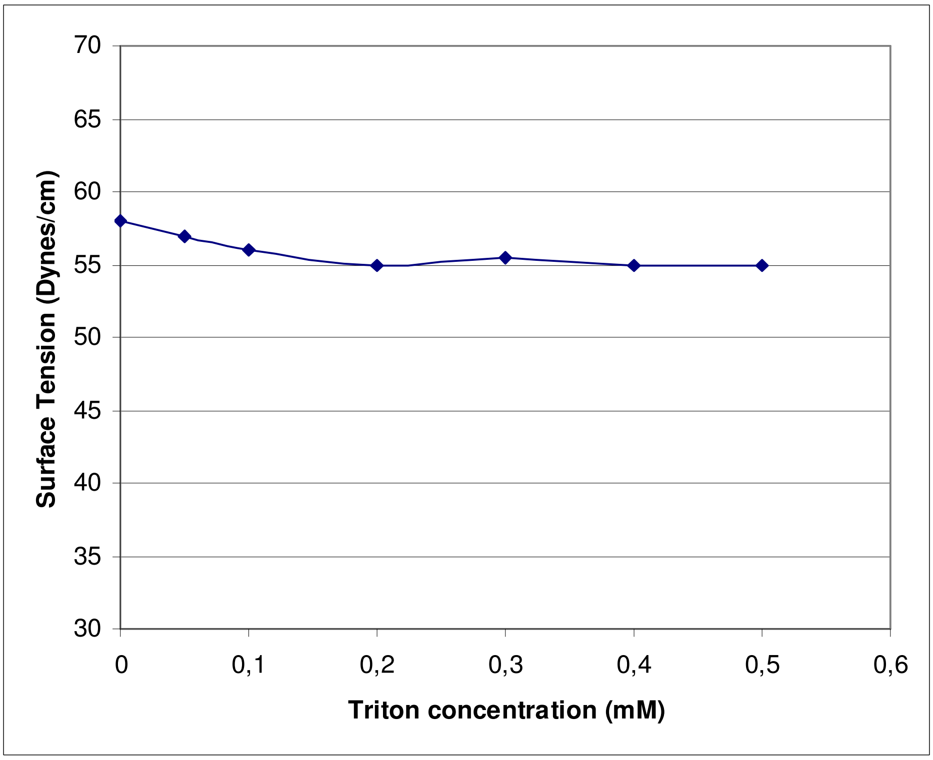


Figure 4.35: The change of surface tension of the polymer solutions (0.064 wt % HMPA in 50 % glycol) by addition of Triton

4.2.2.3.5 The effect of corrosion inhibitor on solution rheology

Benzotriazole (BT) not only reduces the corrosive effect of de/anti icing solutions but also it decreases the low shear viscosity of the solutions. This decrease may be forced by the broken network structure of polymer chains in the solution due to the interaction of the aromatic group of the BT with the hydrophobic domains in the network. The decrease in the solution viscosity by the increase of BT concentration in the solution can be observed in Figure 4.36.

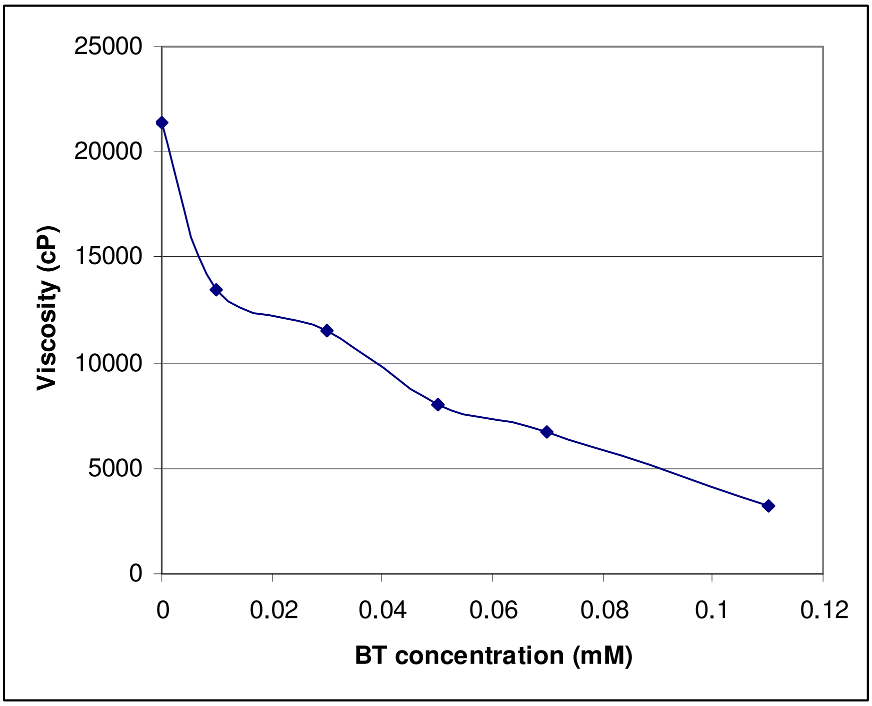


Figure 4.36: The effect of BT concentration on low shear viscosity of 0.08 % HMPA solutions composed of 50 % water and 50 % glycol

4.2.2.3.6 The effect of temperature on solution rheology

The viscosity of the HMPA solutions increases with decreasing temperature as expected. The rheological behavior of the polymer solutions at three different temperatures can be observed in Figure 4.37. Indeed, the low shear viscosity of the solutions steadily increases by decreasing temperature.

The interesting point here is the change of pH with the temperature. As the temperature decreases, the ionization of polyacrylic acid decreases and so the pH of the solution increases. As it is shown in Figure 4.15, the viscosity of the solutions decreases rapidly after it reaches maximum at certain pH. Therefore, if the solution is prepared at a pH value corresponding to the maximum viscosity at certain polymer concentration, the further decrease in temperature will tend to decrease the viscosity, while the reduction in the mobility of the chains will tend to increase the viscosity of the solutions. The outcome of these two contradicting effects will give the resulting polymer viscosity.

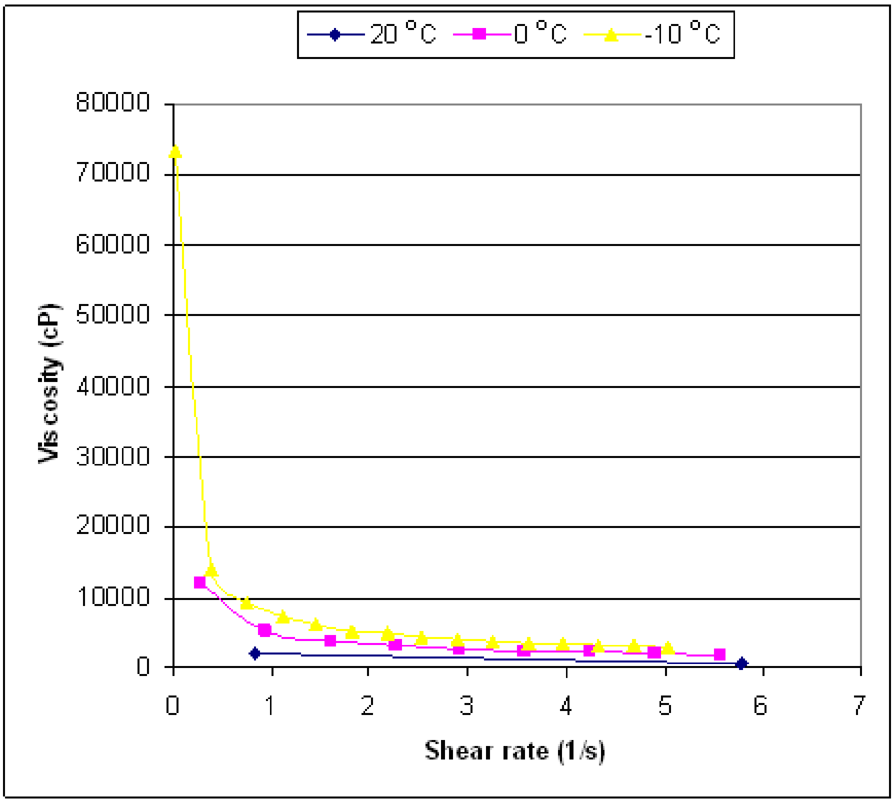


Figure 4.37: The change of viscosity of HMPA solutions (0.067 wt %, 50 % water- 50 % glycol) with increasing temperature.

4.2.2.3.7 Corrosion Tests

These tests are applied on the aluminum plates in order to predict whether the candidate de/anti icing solutions will cause any corrosion on aircraft surfaces. The aluminum plates are immersed into solutions at different benzotriazole concentrations at 88 ^oC under constant air flow. After 15 days, the loss of weight of the plates per area are calculated and tabulated in Table 4.11.

Table 4.11: Corrosion test results for anti-icing fluids

	1	2	*3*	*4*
Benzotriazole concentration	-	% 0.01	% 0.05	% 0.1
Weight of the aluminum before test (g)	6.5587	7.6435	6.0725	5.5487
Weight of the aluminum after test (g)	6.5577	7.6425	6.0725	5.5487
Loose of weight in g/m^2	0.48	0.27	0	0

It can be seen from Table 4.11 that, even in the case where 0.01 % BT is used in the solutions, the corrosion rate is too low, around 0.27 g/m^2. The maximum allowable corrosion is 4 g/m^2 as mentioned in Aerospace Material Specifications 1375. If the BT concentration is further increased, no corrosive effect is observed in the plates.

After the corrosion tests applied for the anti-icing solutions, the same procedure is followed for the de-icing fluid solutions containing 0.01 % benzotriazole. In this case only 0.23 g aluminum metal is lost for 1m^2 in 15 days. This result is also considered to be lower than the standards.

4.2.2.3.8 Freezing point tests

The freezing point of anti-icing fluids strictly depends on glycol content of the solutions. The presence of solutes in the solution lowers the freezing point further. Therefore, the freezing points tabulated in the literature for glycol-water mixtures are useful to have a guess of the actual freezing points of anti-icing fluids. The following table shows the freezing points of glycol-water mixtures at different concentrations.

Table 4.12: The freezing points of ethylene glycol-water mixtures [51]

Ethylene Glycol Concentration (wt %)	*Freezing Point (^oC)*
0	0
10	- 4
20	- 7
30	- 15
40	- 23
50	- 34
60	- 48
70	< - 51
80	- 46
90	- 29
100	- 12

Experiments to measure the freezing point of the solutions are conducted by using a refrigerator. The experimental results for anti-icing solutions are shown in Table 4.13. The results agree well with those shown in Table 4.12.

Table 4.13: The freezing point test results of anti-icing solutions containing polymer, surfactant and corrosion inhibitor

Ethylene Glycol Concentration (wt %)	*Freezing Point (^oC)*
50	- 36
60	< - 40
70	< - 40

The freezing tests of de-icing solutions are conducted by preparing the mixtures of 50 % water and 50 % de-icing solutions as it is used in the aviation. The results are listed in Table 4.14.

Table 4.14: The freezing point test results of de-icing solutions containing surfactant and corrosion inhibitor

Ethylene Glycol Concentration (wt %)	*Freezing Point (^oC)*
50	- 12
60	- 17
70	- 21

4.2.2.3.9 Stability test

The stability test is simply made for measuring the shelf life of the anti-icing fluids. Because of the limited time of the study, the solutions can be aged only for 106 days at room temperature while protected from sunlight. The rheological behavior and surface tension of a water-glycol solution containing both polymer, surfactant and corrosion inhibitor is measured and compared. The surface tension of the solution is measured as 39 Dynes/cm before and after the test. In Figure 4.38, the change of the rheology of the old and new polymer solutions can be observed.

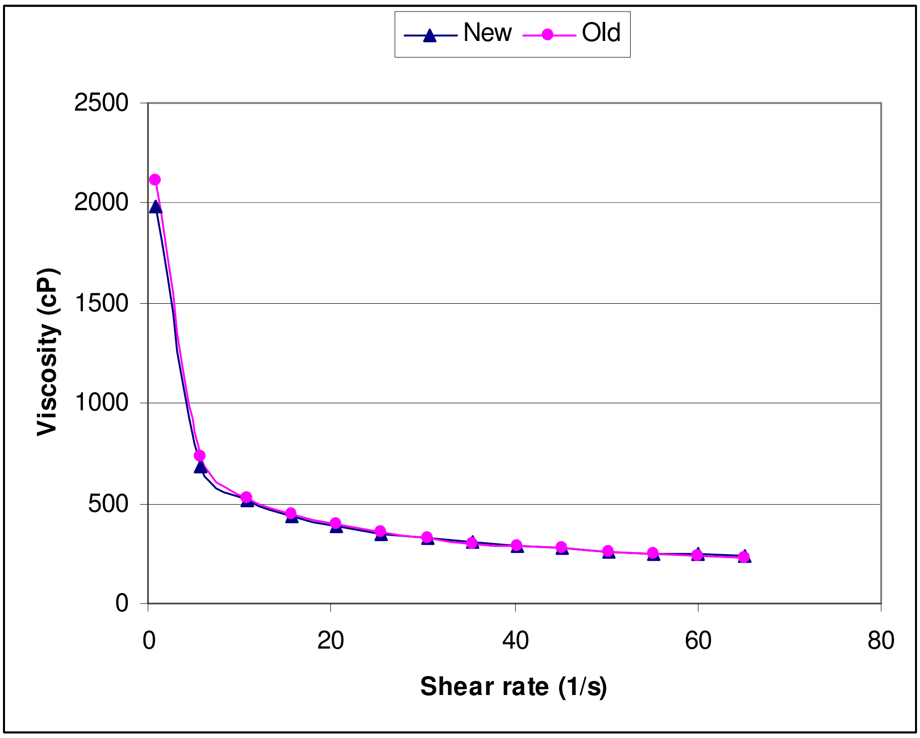


Figure 4.38: The comparison of the new and 106 days old anti-icing solution.

It is clearly observed that the old and new polymer exhibit the same rheology so that we can conclude that the physical properties of the polymer solutions are not affected with duration of more than 3.5 months. However, the actual case can be observed only by performing the stability test for adequate time mentioned in SAE AMS 1424-1428 standards which is 12 months.

4.2.2.4 The synthesis of hydrophobically modified polyacrylic acids

According to the satisfying results acquired from the crosslinked polyacrylic acids, the synthesis of a hydrophobically modified and slightly crosslinked polyacrylic acid is made in scope of the study. This synthesis is performed with direct synthesis method by using solution polymerization technique. Maleimide is chosen as a hydrophobic monomer, because it would also be synthesized in the laboratory. There are few sources about this reaction cited in the literature. In one of them, the reaction is conducted in dioxane as a solvent **[52]**, and the other one these monomers were used to synthesize a terpolymer **[53]**. A synthesis reaction of these monomers in alcohol as a solvent is never performed before.

The hydrophobic monomer maleimide is named by its long alkyl groups attached to it. In this study, two alkyl amines are utilized, as dodecyl amine and hexadecyl amine. The reaction procedures of maleimide and the resulting polymer are given in experimental part.

Unfortunately when this polymer is dissolved in water and the rheological behavior of the solutions is tested, no shear-thinning behavior is obtained even at high polymer concentrations. It is thought that, the synthesis reactions must be repeated again and the possible experimental errors must be eliminated in order to have a working polymer. However, these studies may be handled in another study because they are not directly related with the objective of this thesis work.

CHAPTER 5

CONCLUSIONS

The aim of this study is to produce and develop de and anti icing fluids for aircraft. To fulfil this objective, the relations between the functional chemicals inside a typical de/anti icing fluid are investigated and the effects of these chemicals on the basic physical properties of the solutions such as viscosity, surface tension, freezing point etc. are clarified. The following conclusions are drawn:

For Type-1 fluids;

- The effect of functional chemicals on physical properties of type-1 fluids is found to be strictly dependent on glycol water concentration except for the surface tension. To reduce the surface tension to 40 Dynes/cm, ethoxyphenol, tributyl amine and sodium oleate are utilized as surfactants. Benzotriazole is chosen as a corrosion inhibitor and in corrosion tests, aluminum plates lose 0.23 g/m^2 in solutions containing 0.01 % benzotriazole in 15 days.

For Type-2 fluids;

- Water-glycol mixture is chosen as a raw material in the anti icing solutions because of its very low freezing point. 50 % water-50 % glycol mixtures exhibit -37 ^{o}C freezing point. It is experimentally observed that the water content in the solution increases the solution viscosity due to the higher hydrogen-bonding capability of water.
- Various polymers are used in order to enhance the rheologhy of the solutions such as acrylic and acrylamide based polymers. Some of these polymers are synthesized in the laboratory, like poly(DADMAC-co-vinyl pyyrolidone) and some of them are purchased, like crosslinked polyacrylic acids. Among

these polymers, slightly crosslinked hydrophobically modified polyacrylic acid (HMPA) is chosen as a thickener due to its superior performance in enhancing the solution viscosity and shear thinning behaviour. By changing the polymer concentration, pH of the solution, surfactant concentration, corrosion inhibitor concentration, glycol-water content, and temperature, the rheologhy of polymer solutions can be adjusted. To emphasize, the viscosity of HMPA solutions is found to be strictly dependent on the solution pH. For example the low shear viscosity of a polymer solution containing 0.075 wt % HMPA can vary between 10 cP to 12000 cP at different pH values. The maximum viscosity is obtained at pH=6 with a 40 % NaOH concentration of the HMPA concentration.

- Sodium oleate is the most effective surfactant in reducing the surface tension of the solutions. Surfactants are found to enhance the viscosity of the solutions up to a certain concentration, after that, they decrease the viscosity. Anionic surfactants have better performance in reducing the surface tension, for example sodium oleate reduces the surface tension of 50-50 % water-glycol mixtures to 32 cP at 0.8 mM concentration. The non-ionic surfactant Triton X-100 does not show significant surface activity and surface tension of the glycol-water solutions does not change remarkably.
- Benzotriazole is chosen as a corrosion inhibitor due to its high protection against corrosion of the aircraft surfaces, besides its reducing effect on solution viscosity. In the corrosion tests, the aluminium plates lose 0.27 g/m^2 for the anti-icing fluid solutions

Besides the investigation carried on the relations between the chemicals in de/anti icing fluids, an invention of a new polymer namely poly(DADMAC-co-vinyl pyyrolidone) is made and the characterization and performance tests of this polymer are performed. It is concluded that such a copolymer having anti-bacterial effect induced by DADMAC segments and biocompatibility of NVP component would be of interest in medicine or other biorelated areas.

REFERENCES

[1] R. Hornig, Development of an International Standard for Safe Winter Operation, Journal of Aircraft, Vol.30, No.1, 14-18, Jan.-Feb. 1993.

[2] Association of European Airlines, Training Recommendations and Background Information for De-Icing/Anti-Icing of Aircraft on Ground, 2nd Edition, September 2005.

[3] Eugene G. Hill, Thomas A. Zierten, Aerodynamic Effects of Aircraft Ground De/Anti-Icing Fluids, Journal of Aircraft, Vol.30, No.1, 24-34, Jan.-Feb. 1993.

[4] J. F. Ross, J.T. Connolly, Contrasting Requirements for Type-II De/Anti-Icing Fluids, Journal of Aircraft, Vol.30, No.1, 10-13, Jan.-Feb. 1993.

[5] Development of Holdover Time Guidelines for Type-III Fluids, TP 14379 E, Final Version 1.0,November 2004.

[6] A. Beisswenger, G. Fortin, J. L. Laforte, Investigations of Type-II and Type-IV Aircraft Ground Anti-Icing Fluid Aerodynamic Certification Performance, DO/AR-03/55, July 2003.

[7] Guidelines for Aircraft Ground Icing Operations, 2nd Edition, April 2005.

[8] John J. Reinmann, Aerodynamic Effects of Deicing and Anti-Icing Fluids, Journal of Aircraft, Vol.30, No.1, 8-9, Jan.-Feb. 1993.

[9] UCAR Ultra Type-IV Fluid, Form No. 183-00003-1004AMS, October 2004.

[10] UCAR Flight Guard AD 480 Type-IV Fluid, Form No. 183-00043-0506AMS, May 2006.

[11] Rene Salvador, Josef Kapfinger, Erich Leidl, De-icing and anti-icing agent for aircraft, Patent no 4,744,913, May 17, 1988,

[12] Richard J. Tye, George E. Lauterbach, Philip R. Standel, Aircraft anti-icing fluid containing carrageenan, Patent no 4,698,172, October 6, 1987,

[13] Stephan K. Chan, Gale L. Hubred, Harold E. Todd, Deicer/anti-icer composition for aircraft, Patent no 5,435,930, July 25, 1995

[14] Richard D. Jenkins, David R. Bassett, Richard H. Lightfoot, Mehmut Y. Boluk, Aircraft anti-icing fluid, Patent no 5,461,100, October 24, 1995,

[15] Richard D. Jenkins, David R. Bassett, Richard H. Lightfoot, Mehmut Y. Boluk Aircraft anti-icing fluids thickened by associative polymers Patent no 5,681,882, October 28, 1997

[16] Charles Hobert Carder, Daniel Christopher Garska, Richard Duane Jenkins, Mark Joseph McGuiness, Aircraft deicing/anti-icing fluids thickened by associative polymers Patent no 5,708,068, January 13, 1998,

[17] Joseph Zhen U, John Wakelin, Arnold Wiesenfeld, Deicing and anti-icing composition for aircraft, Patent no 5,817,252, October 6, 1998,

[18] Schulz, D.N., Bock, J.. Synthesis and fluid properties of associating polymer systems. J. Macromolecules Sci. Chem. A 28 (11-12), 1235-1243, 1991

[19] Shuhui Wu, Robert A. Shanks, Gary Bryant, Properties of hydrophobically modified polyacrylamide with low molecular weight and interaction with surfactant in aqueous solution, Journal of applied polymer science, Vol. 100, 4348-4360, 2006

[20] Yujun Feng, Laurent Billon, Bruno Grassl, Abdel Khoukh, Jeanne François, Hydrophobically associating polyacrylamides and their partially hydrolyzed derivatives prepared by post-modification. 1 synthesis and characterization, Polymer vol.43, 2055-2064, 2002

[21] Kevin C. Taylor, Hisham A. Nasr-El-Din, Water-soluble hydrophobically associating polymers for improved oil recovery: A literature review, Journal of petroleum science and engineering 19, 265-280 1998

[22] Glass, J.E., Poymers in aqueous media, performance through association. Advances in Chemistry series No: 223, American Chemical Society, Washington, DC, pp. 151-164,1989

[23] Bock J, Siano DB, Schulz DN, Turner SR, Valint Jr. PL. Pace SJ, Polym. Material Science Angineering; 55:355, 1986

[24] Stanley Jr FW Water-in-oil emulsions of hydrophobe association polymers, Patent no: 4524175, 1985

[25] Turner SR, Siano DB. Bock J. Microemulsion process for producing acrylamide-alkyl acrylamide copolymers, Patent no: 4521580, 1985

[26] Stephen A. Ezzellt and Charles L. McCormick, Water-Soluble Copolymers. 39.Synthesis and solution properties of associative acrylamido copolymers with pyrenesulfonamide fluorescence labels, Macromolecules 25, 1881-1886, 1992

[27] Peer WJ. Polymers in aqueous solution: performance through association, Advances in chemistry series 223. Washington, DC: American Chemical Society. p381, 1989

[28] Edgar Volpert, Joseph Selb, and Françoise Candau, Influence of the Hydrophobe Structure on Composition, Microstructure, and Rheology in Associating Polyacrylamides Prepared by Micellar Copolymerization, *Macromolecules*, 29 (5), 1452 -1463, 1996.

[29] Ahmed A. Abdala, Wenjun Wu, Keith R. Olesen, and Richard D. Jenkins, Alan E. Tonelli, Saad A. Khan, Solution rheologhy of hydrophobically modified associative polymers: Effects of backbone composition and hydrophobe concentration, J of Rheologhy. 48(5) 979-994 September/October 2004

[30] Samuels,William D. Conkle, Nicholas H. Monzyk, Bruce F. Simmons, Kevin L Frye Jr., JohnG. Werpy, ToddA. Kuczek, SaraF. Chauhan, Satya P. De-icing/anti-icing fluids Patent no: 7,105,105 B2, September 12, 2006,

[31] Wiesenfeld, Arnold Meyers, Alex Leicht, Robert; De-icing and anti-icing concentrated composition for aircraft Patent no: 5,935,488, August 10, 1999,

[32] UCAR Concentrate “55/45” Type-I Fluid, Form No. 183-00024-0704AMS, July 2004

[33] Kilfrost ABC-S Material Safety Data Sheet, Revised: 4/2005

[34] Kilfrost ABC-3 Technical Data, March 2000

[35] Killfrost df plus certificate of Analysis, November 2004

[36] D. A. Topchiev, A. I. Martynenko, E. Yu. Kabanova, V. D. Oppengeim, Yu. I~. Kirsh, and T. M. Karaputadze, Copolymerization of N-Vinylpyrrolidone with N,NDimethyl-N,N- Diallyammonium Chloride, Plenum Publishing Corporation, 1991

[37] W. Jaeger, Regular Polyelectrolytes with Pyrrolidinium Units, Novel Precursors for Complexes of Charged Polymers, *0-14513 Teltow, Germany*

[38] Duygu Avci1, Nuri Mol, Levent Dagasan, New cationic polyelectrolytes for flocculation processes of baker’s yeast waste water, Polymer Bulletin 48, 353-359 2002

[39] Tararuj Christopher, Donahue Patrick, Katz Robert E.Deschryver, David Weiser Robert Product sampler Patent no: 20010023017, Eylül 20, 2001

[40] Amended final report on the safety assessment of polyacrylamide and acrylamide residues in cosmetics, International journal of toxilogy,;24 Suppl 2:21-50, 2005

[41] U. Käistner, H. Hoffmann, R. Dönges and J. Hilbig, Structure and solution properties of sodium carboxymethyl cellulose, Colloids Surf*., A* 123-124 307-328, 1997

[42] Biggs, S.; Salb, J.; Candau, Copolymers of acrylamide and N-alkyl acrylamide in aqueous solution: the effect of hydrolysis on hydrophobic interactions. F. *Polymer 34*, 580. 1993

[43] Copolymerization of acrylamide and a hydrophobic monomer in an Aqueous Micellar Medium: Effect of the Surfactant on the Copolymer Microstructure J. Phys. Chem. 96, 1505-1511, 1992

[44] R. Nagarajan1 AND Chien-Chung Wang Solution Behavior of Surfactants in Ethylene Glycol: robing the Existence of a CMC and of Micellar Aggregates, Journal of Colloid and Interface Science 178, 471–482, 1996

[45] Effing, J. J.; McLennan, I. J.; van Os, N. M.; Kwak, J. C. T. lH NMR Investigations of the Interactions between Anionic Surfactants and Hydrophobically Modified Poly(acry1amide)s *J Phys. Chem*., *98*, 12397, 1994

[46] Howley, C.; Marangoni, D. G.; Kwak, J. C. T. Association and phase behavior of hydrophobically modified photoresponsive poly(acrylamide)s in the presence of ionic surfactant *Colloid Polym. Sci*., *275* (8), 760, 1997

[47] Chang, Y.; Lochhead, R. Y.; McCormick, C. L. Water-Soluble Copolymers. 50. Effect of Surfactant Addition on the Solution Properties of Amphiphilic Copolymers of Acrylamide and Dimethyldodecyl(2-acrylamidoethyl)ammonium Bromide *Macromolecules*, *27*, 2145, 1994

[48] Kopperud, H. M.; Hansen, F. K.; Nystrom, B. Effect of surfactant and temperature on the rheological properties of aqueous solutions of unmodified and hydrophobically modified polyacrylamide *Macromol. Chem. Phys*., *199*, 2385, 1998

[49] S. Biggs, J. Selb, and F. Candau Effect of Surfactant on the Solution Properties of Hydrophobically Modified polyacrylamide, , *Langmuir*,8, 838-847, 1992

[50] C. Carnero Ruiz,* J. A. Molina-Bolı´var, and J. Aguiar, Thermodynamic and Structural Studies of Triton X-100 Micelles in Ethylene Glycol-Water Mixed Solvents, *Langmuir 17,* 6831-6840, 2001

[51] D.R. Cordray, L.R. Kaplan, P.M. Woyciesjes and T.F. Kozak, "Solid-Liquid Phase Diagram for Ethylene Glycol + Water" Fluid Phase Equilibria 117, pp. 146-152, 1996.

[52]Lianjun Shi, Sheng Chen, Junlian Huang, Radical copolymerization of α-(n-propyl)acrylic acid with maleimide in dioxane European Polymer Journal, vol. 36, no:2, pp. 365-372, 2000

[53] Chen X, Cindy Hurditch, Rodney "Alkaline soluble maleimide-containing polymers" US Patent 6586560, July 1 2003,

[54] 1- Butler, G. B.;. Ingley, P. L .J. Preparation and compound II. polymerization of unsaturated quatemary ammonium, J. Am. Chem. Soc. 1951, 73, 895.

[55] Gehr, R.; Henry, J. G., Adsorption behavior of cationic polyelectrolytes in dissolved air flotation, Water Sci. Tecnol. 1982,14, 689.

[56] Ginsburg, Cationic polyelectrolytes: a new look at their possible roles as opsonins, as stimulators of respiratory burst in leukocytes, in bacteriolysis, and as modulators of immune-complex diseases (a review hypothesis). I. Inflammation Vol. 11, Issue 4, Pages 489-515, 1987

[57] Montgomery, D. D.; Anson, F.C., Stable composite polyelectrolyte electrode coatings with morphologies that yield large ion-exchange capacities and high cross-coating charge propagation rates J. Am. Chem. Soc.,107, 3431, 1985

[58] Fineman, M.; Ross, S.D., Linear method for determining monomer reactivity ratios in copolymerization J. Polym. Sci., 5, 259., 1950

[59] Jaeger, W., Hahn, H., Lieske, A. and Zimmermann, A., Polymerization of water soluble cationic vinyl monomers. *Macromolecular Symposia* 111, pp. 95–106., 1996.

[60] Fuoss, R. M.; Strauss, U. P., Electrostatic interaction of polyelectrolytes and simple electrolytesJ. Polym. Sci. 3, 602, 1948

[61] Buchholz F.L. Keeping dry with super absorbent polymers. In, Buchholz F.L, Peppas N. A. Eds; Super absorbent polymers: Science and Technology. ACS symposium series. p.38-43, 1994

[62] Omidian H. Hashemi S.A.,. Sammes P.G,. Meldrum I.G. Modified acrylic-based superabsorbent polymers. Effect of temperature and initiator concentration. Polymer 39 (15), 3459-3466, 1998.

[63] Hirose H. , Shibayama M., Kinetics of volume phase transition in poly (N-isopropylacrylamide-*co*-acrylic acid) gels. Macromolecules 31(16), 5336–5342, 1998.

[64] Moriyoshi A., Fukai I., Takeguchi M., A composite construction material that solidifies in water. Nature 344(6263), 230–232,1990.

[65] K. S. Kazanskii and S. A. Dubrovskii, Chemistry and physics of agricultural hydrogels. Adv. Polym. Sci. 104, 97–133, 1992.

[66] T. Shimomura and T. Namba, in F. L. Buchholz and N. A. Peppas, eds., Superabsorbent Polymers, Science and Technology (ACS Symposium Series 573), American Chemical Society, Washington, D.C., pp. 112–115, 1994

[67] Sawahata K., Gong J. P., Osada Y.; Soft and wet touch-sensing system made of hydrogel. Macromol. Rapid Commun. 16(10), 713–716, 1995

[68] Mark J. E, Erman B.; Rubberlike Elasticity, A Molecular Primer, John Wiley & Sons, Inc., New York, 1988.

[69] Baker J.P, Hong L.H, Blanch H.W, Praustnitz J.M. Swelling properties acrylamide-based ampholytic hydrogels: Comparison of experiment with theory. Polymer 36 (5), 1061-1069, 1995.

[70] Okay O, Sariisik S.B. Swelling behavior of poly (acrylamide-co- sodium acrylate) in aqueous salt solutions: theory versus experiments. Eur. Polym. J. 36, 393-399, 2000.

[71] Seetharaman V., Kalyanasundaram S., Gopalan A. Quantitative study of interaction of vinyl polymers by ultrasonic method. J. Molecular Liq. 121 156–159, 2005

[72] Omidian H, Hashemi S.A, Sammes P, Meldrum I. G. A model for the swelling of superabsorbent polymers. Polymer 39 (26), 6697-6704, 1998.

[73] Buchholz F. L., in *Absorbent Polymer Technology*, L. Brannon-Peppas and R. Harland, eds., Elsevier Science Publishers, New York, , pp. 233–247, 1990

[74] Jeon C. H, Makhaeva E. E, Khokhlov A. Swelling behavior of polyelectrolyte gels in the presence of salts. Macromol. Chem. Phys. 199**,** 2665–2670, 1998.

APPENDIX A

MINOR RESULTS of the LABORATORY WORK

During the experiments conducted in the laboratory in order to find a suitable polymer for an anti-icing solution, the synthesis of a new polymer namely Poly(Diallyldimethyl ammonium chloride-co-vinyl pyyrolidone) (DCVP) is made. The studies about this new polymer are handled in two parts, in one of which the characterization of the polymer is made and several tests are applied. During the synthesis studies the polymer exhibites some characteristics that are in parallel with water superabsorbants. Therefore, this potential application is explored although this piece of work is not directly relevant to this study. In the second part, the results of performance tests of superabsorbant are reported.

A.1 The characterization of the Poly(DADMAC-co-vinyl pyyrolidone) (DCVP)

Since discovery by Butler and Ingley [54] in 1951, cyclopolymers and copolymers of dialkyl diallyl ammonium halides have gained great interest. Polymerization of these monomers takes place by cyclization to give polymers with five membered pyrrolidinium rings in the main chain. To date N, N-dimethyl, N, N-diallylammonium chloride, DADMAC, is one of the most important precursors for cationic polyelectrolytes, probably due to its high charge to mole ratio. These polymers have found extensive use in sludge dewatering [55], bacteria killing [56] and antistatic formulations [57].

Combination of the physical and chemical properties of polyDADMAC with those of PNVP by copolymerization seemed to be interesting. It was concluded that such a copolymer having anti-bacterial effect induced by DADMAC segments and biocompatability of NVP component would be of interest in medicine or other bio related areas.

Synthesis of DADMAC-NVP copolymers was reported by Topchiev and coworkers in 1990 [36]. This is the only report dealing with the subject. However structure and copolymerization data given seemed to be ill defined. Based on the reactivity ratios, $r_1 = r_2 = 1$ and absence of some typical ^{13}C and proton signals of the homopolymers, the copolymerization has been erroneously assigned to “azeotropic copolymerization” instead of “ideal copolymerization”. In this part of the study radical copolymerization of DADMAC with NVP in concentrated aqueous solution is re-investigated using 2, 2’-azo bis-(2-methyl propionamidine) dihydrochloride as initiator. Reactivity ratios of the monomers are determined based on chlorine analysis of the resulting copolymers. Structural characterization of the copolymers is carried out by HNMR and analytical measurements. The copolymerization procedure is explained in the experimental part.

A.1.1 Determination of the Reactivity Ratios of the Monomers

To inspect the copolymerization reactivity ratios of the monomers, a series of small scale batch polymerizations are performed using various DADMAC (monomer-1) to NVP (monomer-2) ratios in the same conditions. The polymerizations are terminated after 30 min by precipitation in acetone to attain low conversions (22.7-60.5 %). DADMAC contents of the resulting copolymers are assigned by analysis of chloride ions and data is collected in Table A.1.

Table A.1: Characteristics of the copolymers obtained by initiation with ABP in aqueous solutions with various monomer ratios (Conditions; total monomer conc. 40.0 % w / w, ABP /[Monomers] = 1 / 100, at 60 °C).

Total monomer concentration % (w / w)	f_1	*Chlorine content (mmolg^{-1})*	F_1	$\left(\frac{1}{1-f_1}\right)^2 \times \left(\frac{1-F_1}{F_1}\right)$	$\left(\frac{f_1}{1-f_1}\right) \times \left(\frac{2F_1-1}{F_1}\right)$
30	0.25	1.92	0.2363	0.3591	- 0.744
	0.40	2.72	0.3475	0.8345	- 0.585
	0.5	3.13	0.4132	1.420	- 0.420
	0.6	3.65	0.4974	2.2735	- 0.016
	0.75	4.26	0.6040	5.9006	1.033
40	0.4	2.86	0.3710	0.2914	-0.4636
	0.5	3.64	0.4954	1.0186	-0.0186
	0.6	4.07	0.5700	1.6974	0.3684
	0.8	5.18	0.7790	4.5392	2.8652

The resulting data are evaluated by Finemann-Ross method [58] based on so called "copolymerization equation" where, r_1 and r_2 are the reactivity ratios of the monomers, respectively for DADMAC. F_1 and f_1 denote molar ratios of DADMAC in the copolymer and in feed composition, respectively.

A plot of the left term of the equation versus coefficient of r_1 on the right hand side gives straight line (See Figure A.1). From the slope and intercepts of the plot the reactivity ratios are found; r_1=0.79 and r_2 = 0.82, for the copolymerization with 40 % total monomer concentration. This result can be ascribed to high tendency of the monomers to the copolymerization. However, in the case of 30 % of the total monomer concentration, chloride analyses of the copolymers reveal significantly different reactivity ratios, r_1 = 0.32 and r_2 = 0.84. Such an unusual result implies concentration dependency of the reactivity ratio of DADMAC component. This is not surprising because copolymerization of this monomer with acrylamide was also reported to be concentration dependent [59]. This result implies less preference of the growing radical with DADMAC end units to the same monomer in dilute conditions, due to Coulombic repulsion between the quaternary ammonium groups.

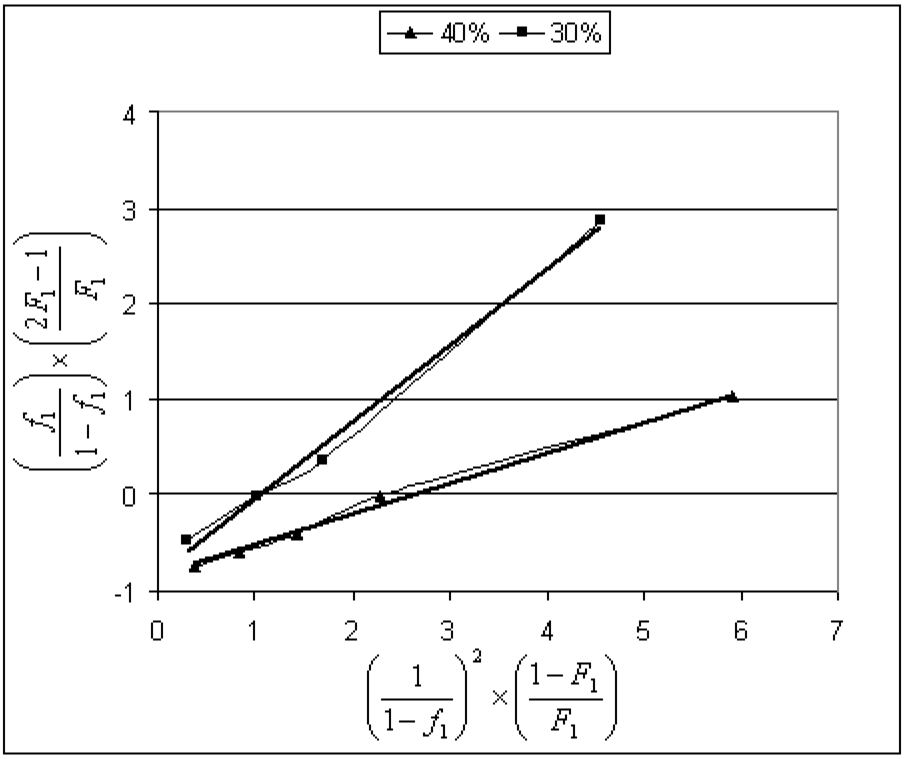


Figure A.1: Finemann-Ross plot for the copolymerization of DADMAC with NVP, in aqueous solutions, with 30 % (upper curve) and 40 % (lower curve) total monomer concentration

A.1.2 H-NMR spectra of the polymers

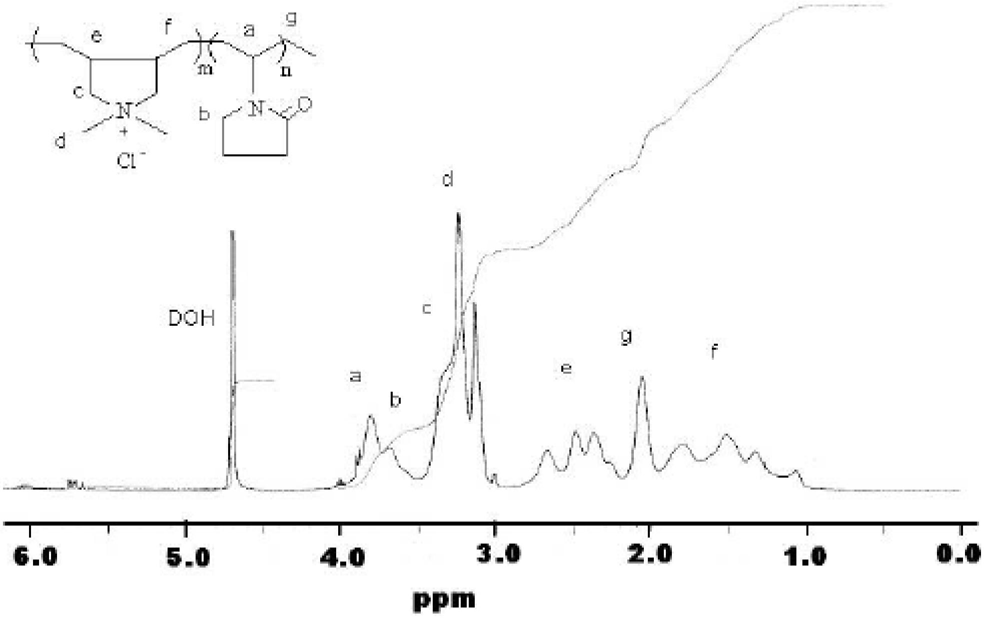


Figure A.2: H-NMR spectrum of copolymer obtained by polymerization equimolar DADMAC-NVP mixture in concentrated aqueous solution (40 % w/w).

H-NMR spectrum of the copolymer (See Figure A.2) represents pyrrolidinium and pyrrolidone units in the structure. The down field signal at 3.8 ppm is associated with methyne protons of PNVP component. Protons of the methylene and methyl groups attached to the quaternary nitrogen in poly (DADMAC) segment represent broad signal in 3.1-3.4 ppm range. Other aliphatic proton signals lie below 2.7 ppm. The signal at 4.7 ppm indicates DOH originating from extremely high hygroscopic nature of the copolymer. The peaks in 1-1.4 ppm range are absent in the spectra of the homopolymers. These signals can be ascribed to main chain methylene protons at the connecting points of alternating monomers. Integral ratio of a and b signals to those below 3.5 ppm indicates a molar ratio of 0.489 DADMAC in the copolymer, which is slightly lower than that of the feed composition (See Table A.1). Similarly DADMAC ratios of the copolymers are somewhat less than those of the feed compositions. However, the molar compositions fairly match with those predicted by the chlorine analyses as shown in Table A.2.

Table A.2: Compositions and copolymerization parameters of DADMAC-NVP copolymers, estimated based on chlorine analysis.

DADMAC/ NVP molar ratio	*Reac. time*	*Yield (%)*	$[\eta]$ (dlg^{-1})	*Chlorine Content* $(mmolg^{-1})$	*Molar ratio of DADMAC*		*GPC*	
					by chlorine analysis	*by NMR*	*Mn*	*Mw*
1/3	1 h	90.6	13.5	2.00	24.7 %	24.2 %	13900	16000
1/1	1 h	78.8	9.2	3.70	50.6 %	48.9 %	11000	14700
3/1	1 h	87.0	5.1	5.04	57.1	74.2 %	9600	11500

A.1.3 Concentration-viscosity relation of the polymer solutions

It is not surprising that aqueous solutions of the copolymers do not show linear viscosity concentration relationship, i.e. specific viscosities do not reduce by dilution. Instead the data obey Fuoss-Strauss equation (See Equation A.1) indicating typical polyelectrolyte behaviour of the copolymers in aqueous solution [60].

Fuoss-Strauss equation: $$\frac{\eta_{sp}}{C} = \frac{A}{1 + B\sqrt{C}} \qquad \text{(A.1)}$$

Indeed η/C versus $\sqrt{C}$ plots give straight lines which are characteristics of polyelectrolytes. Here A is intrinsic viscosity and B is a factor associated with electrostatic interaction of polymer with the solvent. All the copolymer samples with different DADMAC contents show linear plots. Figure A.3 shows Fuoss-Strauss plot of the copolymer with low DADMAC content (24.7 %). Linearity of the plot must be due to complete ionization of the quaternary ammonium groups involved.

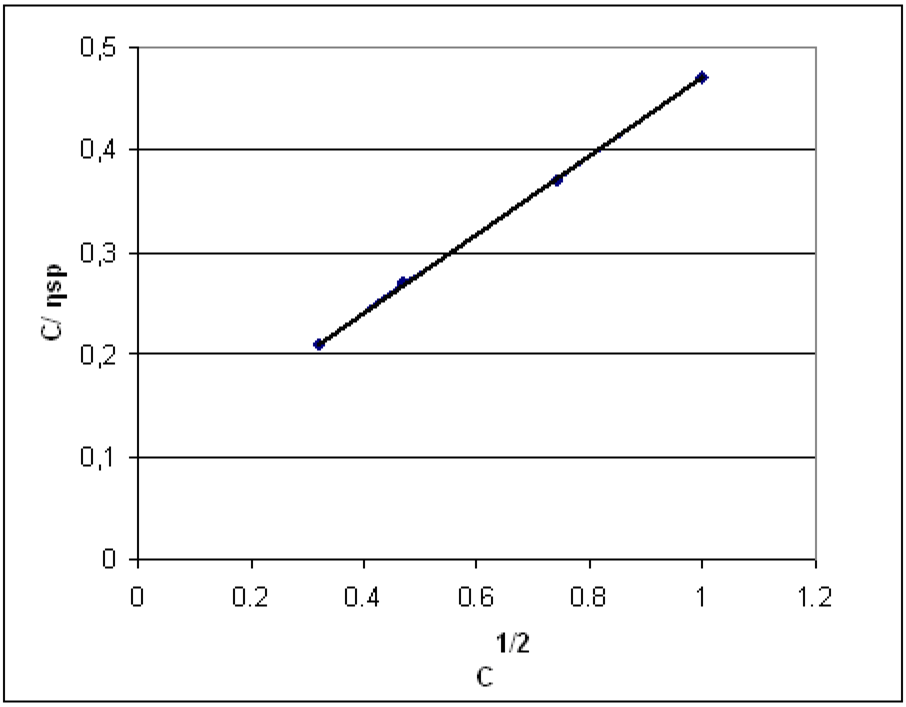


Figure A.3: Typical Fuoss-Strauss plot for aqueous solution of the copolymer with DADMAC / VNP: 1/3.

A.1.4 Polymerization rate

The copolymerization proceeds rapidly in concentrated solutions and reasonably high conversions (up to 70 %) are attained within 80 minutes for the case of 30 % (w/w) total monomer concentration, as shown in the conversion-time plot in Figure A.4-a. These data give linear semi-logarithmic plot in Figure A.4-b indicating first order kinetics with a rate constant of $2.48 \cdot 10^{-4}$ s^{-1}, for the copolymerization of 1/1 mixture of the monomers at 60°C.

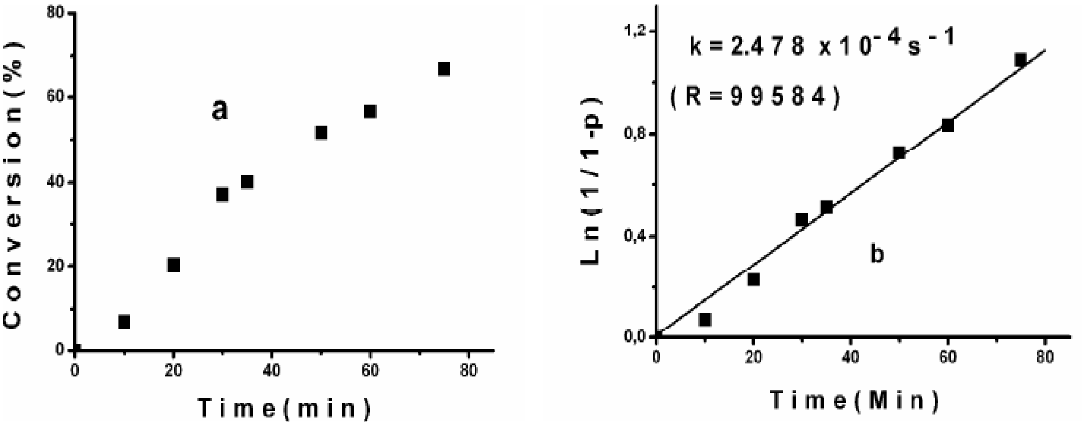


Figure A.4: Conversion-time plots for the copolymerization of DADMAC-NVP mixture (1/1) (a) and its relevant first order kinetics plot (b).

A.1.5 Gel permeation chromatography of the polymer

GPC traces of the copolymer samples show unimodal curves indicating copolymer formation. Figure A.5 shows chromatogram of the 1/1 copolymer as a representative example. The GPC traces indicate weight average molecular weights in 11.500-16.000 range depending on the reaction time and monomer ratios (See Table A.2).

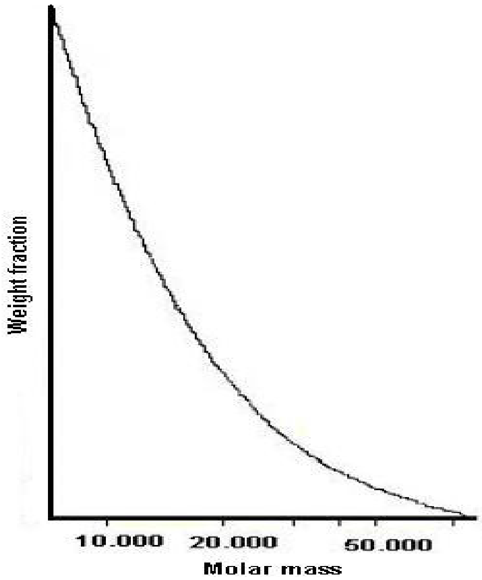


Figure A.5: GPC trace of DADMAC-NVP (1:1) copolymer in water.

A.2 Production of superabsorbent hydrogels

Superabsorbent hydrogels are crosslinked polymers exhibiting unusually high water uptake abilities [61]. These materials have found extensive use mostly in manufacturing of baby diapers [62] and sanitary napkins [63] etc. These have been used also in agriculture to retain moist in the soil [64] and in construction to protect buildings from water drainage [65]. Humidity control in food packaging [66] and pressure sensitive switching in electronics [67] are other applications of super absorbents. Commercial super absorbent hydrogels are almost confined to crosslinked poly (acrylic acid). Swelling of this polymer depends on pH of the solution and ionization degrees of the carboxyl group involved [68]. Although water sorption behavior of the crosslinked quaternary ammonium polymers (polyquats) is well known, there is yet no study dealing with super absorbency of the hydrogels with cationic charges.

Theoretical models on the gel swelling assume equilibrium between elastic, osmotic and polymer-solvent interaction forces [69]. In the case of charged hydrogels, the latter is negligible compared with the osmotic forces. Since contribution of osmotic forces to the swelling depends on ionization degrees of the charged groups, logically fully ionized nature of the quaternary ammonium groups is expected to give poly (DADMAC) hydrogels with super water sorption abilities, if sufficient elasticity is imparted.

Here, the synthesis of superabsorbent DADMAC-NVP copolymer gels and performance tests thereof are made, using N,N, N',N'-tetraalyl piperazinium dichloride as a crosslinker.

Using the procedure explained in section 3.2.4, a series of gel samples with varying comonomer ratios and crosslinker contents is prepared.

In the first series mol fraction of the crosslinker (TAP) is kept constant at 1 % and molar ratio of DADMAC component is changed to be 0, 0.3, 0.5, 0.7 and 0.995. In the second series, equimolar DADMAC-NVP mixtures are polymerized in the presence various amounts of TAP (in 0.5 %, 1 %, 2 %, 5 % molar ratios). In the third series, poly (DADMAC) gel with 0.5 % and 1 % mol crosslinker is prepared.

A.2.1 Swelling Measurements

Swelling of the gel samples were followed gravimetrically at room temperature. A weighed amount of dried gel (usually 0.1 g) is taken in a pouch and soaked into distilled water in a beaker. The pouch was removed at specific time intervals and left to suspend for a while (usually 30 min) for drainage of excess water. The bag was dried by a soft paper and weighed. Net weight of the swollen gel was assigned by subtracting wet weight of the bag. Wet weight of the bag was determined separately by the same way. Swelling ratio of the gel, q is defined as; water uptake per gram of dry polymer.

$$q = \frac{Q_s - Q_{dry}}{Q_{dry}} \qquad \text{(A.2)}$$

Q_S and Q_{dry} are weights of the swollen and dry gels respectively. The equilibrium swelling values were determined based on weights of the samples after contacting with water for 16 h. Average of three measurements was used to assign the swelling ratios.

The effect of salt or acid on the water uptake capacity was studied similarly, except the gel samples were allowed to swell in NaCl and HCl solutions in appropriate concentrations (0.017-6.85 M).

The same procedure was followed in the kinetic experiments. To make precise assignments measurements were performed as soon as possible, in which final weights of swollen gels were determined after rapid suction.

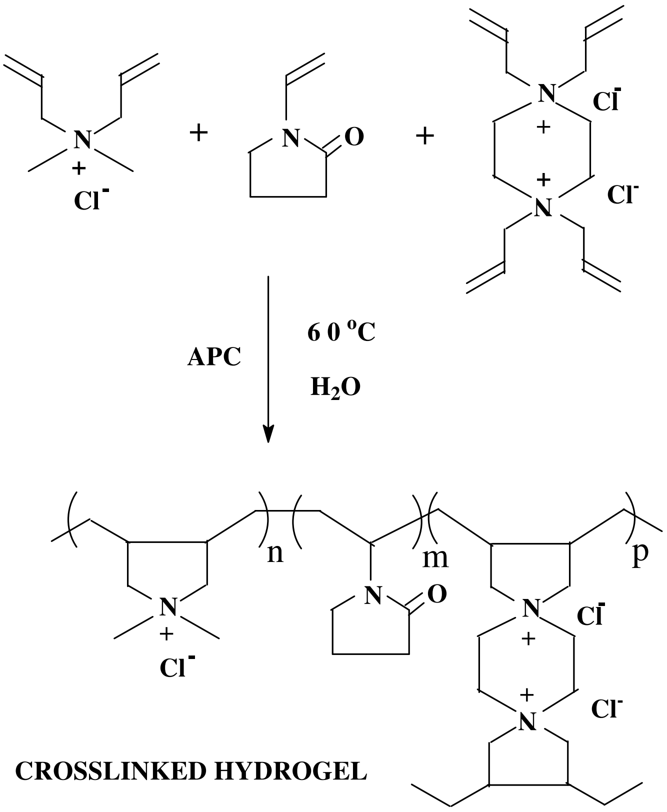


Figure A.6: Crosslinking terpolymerization of DADMAC with NVP and TAP.

The reactions, under these conditions, result in gelation within 15-75 min, depending on concentration of the crosslinker, TAP (See Figure A.6). This procedure result in hard and transparent gels in high yields (> 92%).

Since polymerization or copolymerization of diallylammonium monomers takes place mostly via five-membered ring formation, structures of the gels obtained in this work must contain pyrrolidinium units in the main chain, as depicted in Figure A.6.

A.2.2 Swelling Characteristics of the Gels

Swelling of dry gel samples are assigned by weight gains in the swollen state. Figure A.7 shows that the swelling ratio of the gel sample 1 % mole of TAP increases monotonically by increasing DADMAC content.

In the case of the gel consisting of DADMAC and TAP (1 % mole), the equilibrium volume swelling ratio rises up to 150, whereas this ratio is around 21 for the case of crosslinked PNVP gel. This reveals that incorporation of NVP comonomer segments into gel structure does not bring significant enhancement in the swelling ratios. Moreover the gels having NVP are also brittle. It is obvious that, presence of this component does not provide any elastic contribution to accommodate more water in the crosslinked polymer matrix.

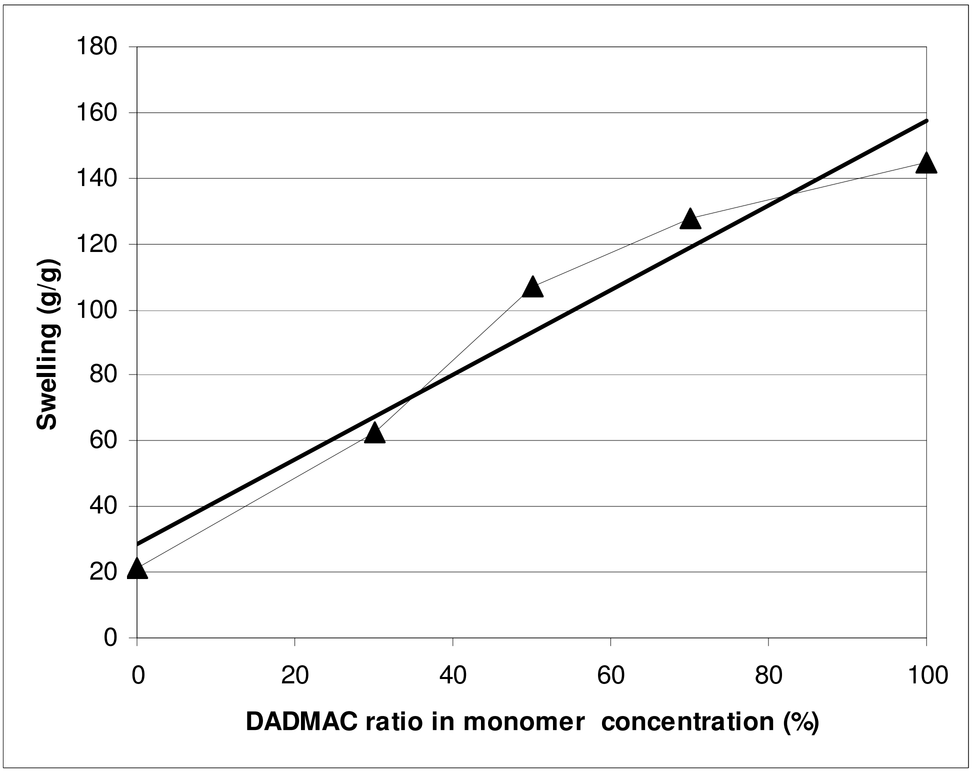


Figure A.7: Effect of DADMAC content on volume swelling ratio of the gels with 1 % (mol/mol) crosslinker.

Although swelling ratio of any super absorbent polymer is known to be strictly depending on the crosslink density, we have also studied the effect of the crosslinker content on the swelling ratio due to its double cationic group. Figure A.8 shows the equilibrium swellings versus crosslinker molar ratio of the gel with 1/1 - DADMAC/ NVP molar ratio.

It is shown that, increasing TAP content of 1/1 - DADMAC/ NVP gel from 0.5 % to 5 % decreases its swelling ratio from 205.3 to 27. Most probably, herein the actual cross-link density differs from the stoichiometry of TAP employed on account of its inefficient incorporation. To inspect the crosslinking efficiency of TAP, the crosslink densities are estimated by Flory-Rehner equation (See Equation A.3) [70] based on the swelling data in Figure A.8.

$$\ln(1 - v_2) + v_2 + \chi v_2^2 + N^{-1}\left[v_2^{1/3}\left(v_2^0\right)^{2/3} - v_2/2\right] - V_1 \frac{f}{\overline{V_r}} v_2 = 0 \qquad \text{(A.3)}$$

where, v_2 is the volume fraction of polymer in the swollen state, χ is polymer-solvent interaction parameter, N is average number of repeating units between two crosslink points, v_2^0 is volume fraction of the polymer after preparation. V_1 is molar volume of solvent and $\overline{V_r}$ is molar volume of the polymer repeating unit.

Using average density of the polymer as 1.12, $v_2^0 = 0.377$ and average molar volume of the polymer, $\overline{V_r} = 130 cm^3 g^{-1}$, number of the repeating units between the crosslink points, N was calculated for each sample.

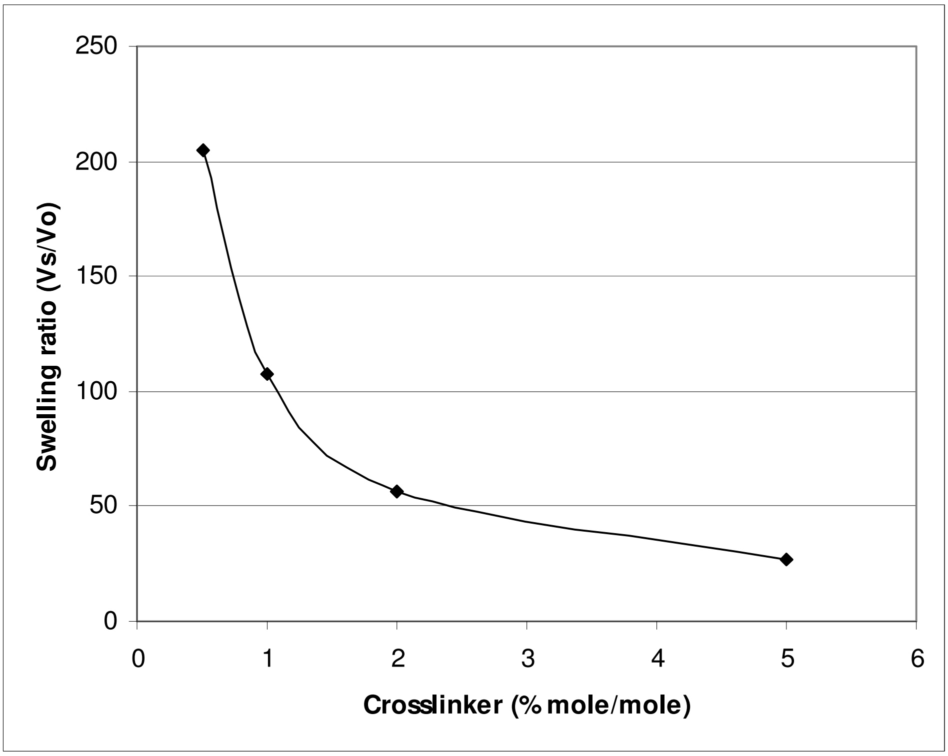


Figure A.8: Volume swelling ratios of 1/1 DADMAC/ NVP gel with varying TAP (0.5-5 %) contents.

Poly (DADMAC)-water interaction parameter χ was taken as 0.038 by extrapolation of the data given by Seetharaman et al [71]. Here the quaternary ammonium groups in DADMAC and TAP segments are assumed to be fully ionized at all concentrations. Therefore, mol fractions of the charged segments, f in these gels are taken as molar ratios of the cationically charged groups of the monomers. Accordingly the f parameter is in 0.50-0.525 range.

Table A.3: Swelling and crosslinking characteristics of 1/1 DADMAC-NVP gels with various crosslinker contents.

[TAP] /[Monomers]	*Volume swelling ratio*	*N (Expected)*^{a}	*Crosslink (Density)* ^{b}	***N (Calculated)***^{c}
5 / 100	26.9	20	0.0195	51
2 / 100	56.8	50	0.0100	99
1 / 100	107.3	100	0.0061	164
0.5 / 100	206.0	200	0.00376	265

(a) : Moles of monomers used per mole of the crosslinker. (b): In mol/mol, calculated from Flory-Rehner equation. (c) : calculated from Flory-Rehner equation

The resulting N values were compared with those theoretically predicted from stoichiometries of the gel formulations. Table A.3 shows that the Flory-Rehner equation indicates higher repeating units than those of the shoichiometry, which implies less efficiency of the crosslinker. For instance, 5 % (mol / mol) crosslinker employed corresponds to 20 repeating units, whereas the equation indicates 51 repeating units. However, at lower crosslink densities these values come closer. The equation implies 265 repeating units instead of 200 for a half percent of the crosslinker. Significant differences between the practical and theoretical numbers of the repeating units can be ascribed to strong electrostatic repulsion between TAP molecules with two positive charges. Dilution of the crosslinker reduces intermolecular forces and practical N value approaches to the theoretical value.

The highest swelling ratio, 360 was observed for poly (DADMAC) gel with 0.5 % TAP. Although there is no commonly approved lower limit for the super-absorbency, the highest swelling ratio, 360 attained in this work falls in 200-1000 range which was reported for poly (acrylic acid)-based superabsorbents [72]. In this study, it is also attempted to prepare gels with even lower crosslinker contents. Unfortunately, we were not able to obtain any gel using TAP lower than 0.5 % in the same polymerization conditions. This must be due to repulsion of its quaternary groups.

A.2.3 Swelling Kinetics of the Gels

All the gel samples show unusually fast swellings in distilled water. Figure A.9 shows swelling ratio-time plots of gel samples with different DADMAC and crosslinker contents. The curves A and B at the bottom represent swelling of the crosslinked (1 %) hydrogels with 70 % and 99.5 % DADMAC respectively. The upper curve (Curve-C) is for the poly (DADMAC) gel with 0.5 % crosslinker. In all cases, the swelling curves exhibit sudden jumps within 2 minutes and level off beyond that.

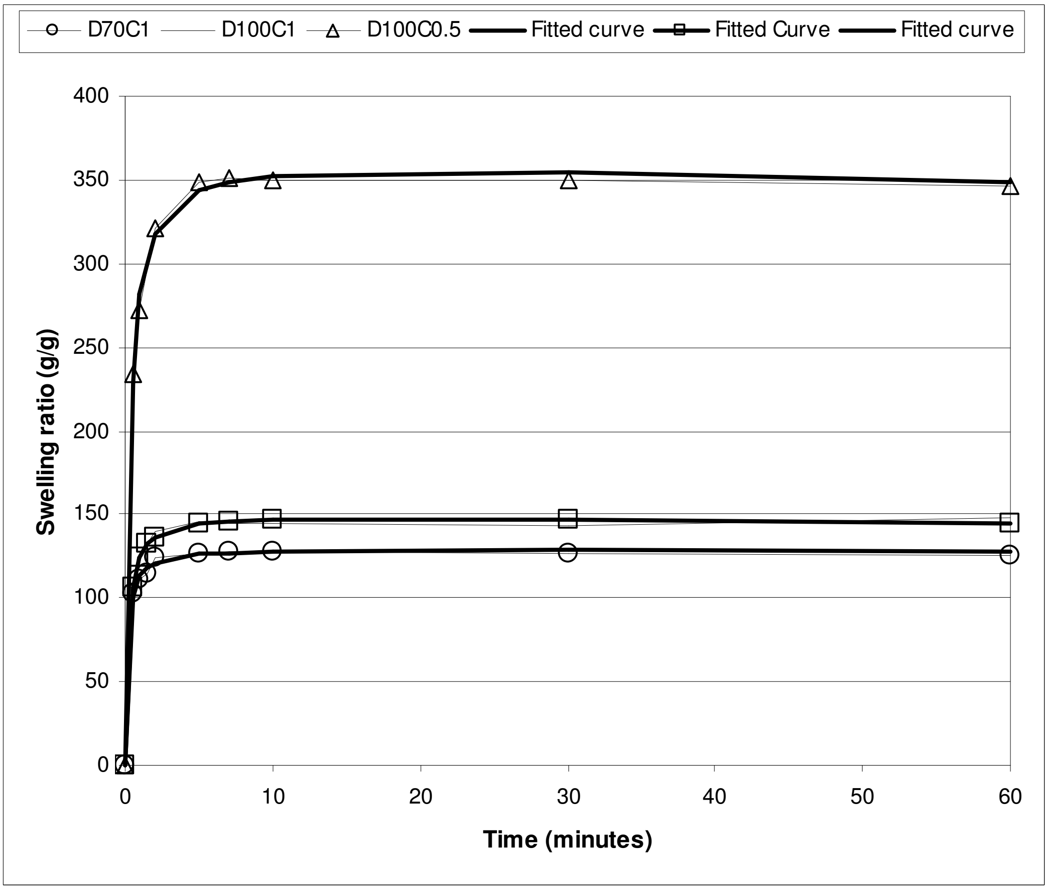


Figure A.9: Swelling ratio-versus time plots for the gels with 70 % DADMAC and 1 % TAP(A), 99 % DADMAC and 1 % TAP (B) and 99.5 % DADMAC and 0.5 % TAP (C).

Swelling kinetics of polyelectrolyte gels is defined by the following differential equation [73];

$$\frac{dQ(t)}{dt} = k\left[Q_{max} - Q(t)\right] \tag{A.4}$$

where, k is the “swelling exponent”.

Integration of this equation gives, $$k = -\frac{1}{t}\ln\left[1 - \frac{Q(t)}{Q\max}\right] \tag{A.5}$$

Using the swelling kinetic values in Figure A.9, $\ln\left[1 - \frac{Q}{Q_{max}}\right]$ versus t plots is drawn in 0-2 min time range. From the slopes of the straight lines, the swelling exponents are estimated to be k= 2.72×10^{-2}, 2.80×10^{-2} and 2.86 $\times10^{-2}$ s^{-1} for the curves A, B and C respectively.

Obviously sharp rise of the curves is due to fast flow of water into the gel matrices to compensate the osmotic pressure between inside and outside of the gel particles.

A.2.4 The Salt Effect

Swelling ratios are shown to be greatly reduced by NaCl in water. This reveals typical “salt effect” on poly (DADMAC) gels as reported by Khokhlov and his coworkers [74] on DADMAC-methylene bisacrylamide gels.

Figure A.10 shows that swelling ratio of poly (DADMAC)-TAP (1%) gel is reduced from 145 down to 30 in 2 M NaCl solution and further increase in concentration of brine does not change the swelling ratio.

Molar concentration of the quaternary ammonium group at this point can be calculated by,

$$\frac{1/161.5}{30\times10^{-3}} = 0.206\,\mathrm{M}$$

Here 1 gr of polymer is absorbed by 30 gr of water.

This value fairly matches with the concentration of NaCl (~0.25 M) at the inflection point of the swelling curve. Sharp decrease in the swelling by NaCl is clear evidence for the effect of salt on the cationic gels.

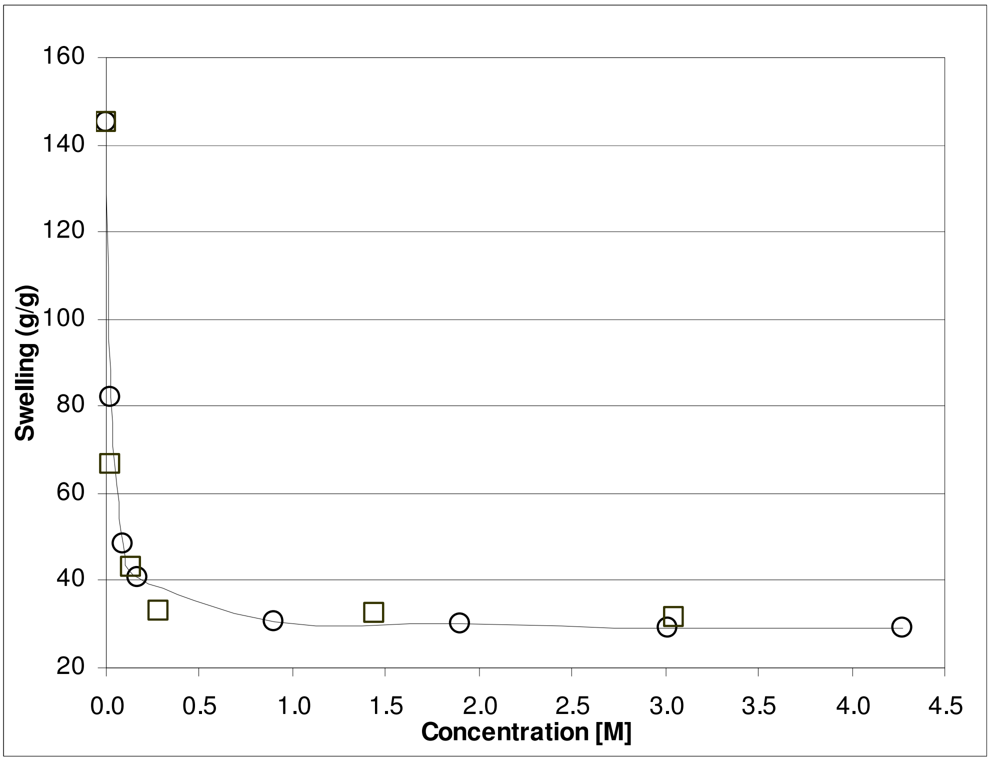


Figure A.10. Swelling ratio of poly (DADMAC) gel with 1 % (mol / mol) TAP, as a function of NaCl (○) and HCl (□)concentration.

Similar shrinking effect was observed in the presence of HCl. Having neither proton releasing nor proton accepting group, poly (DADMAC) segments are not sensitive to pH changes. Therefore, effect of HCl is due to its ions rather than its acidity. Indeed in the presence of HCl the swelling ratio-concentration curve exhibits almost the same trend as in the case of NaCl (See Figure A.10). The same shrinking effect of NaCl is also observed in other gel samples containing NVP.