Surface characterization of amphoteric and anionic membranes

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Thesis for the Master`s degree in chemistry

60 study points

Department of Chemistry

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UNIVERSITY OF OSLO

May 2016

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ACKNOWLEDGEMENTS

First and foremost, I would like to express my deepest gratitude to my prof. Finn Knut Hansen for guiding me all the way from the start up to the end of my thesis work. Without his extreme patience and persistent help, this study would not have been possible. His constructive comments and valuable explanations have immensely contributed to the completion of my experiments and thesis manuscript.

My heartfelt thanks also goes to my co-advisor Prof. Jaan Erik Roots for his support in the laboratory work. He was very passionate in delivering the necessary instructions, guidance and discussions of the experimental results. On top of that, he was the first person (from the department) who accepted me while commencing my study in this master's program.

Apart from that, I want to extend my special thanks to a Norwegian quota scheme program for the financial support. I cannot forget the significant financial backing that I got when I arrived in Norway as a quota student.

My family has been on my side not only on the joyous occasions, but also on the frustrating and critical times that threatened my very survival. So I could not find terminologies to describe my best thanks to my lovely wife Awetash Kiros, my son Robel and my daughter Solyana. They always make my life meaningful and colorful.

Above all, I am very much indebted to the Norwegian people and the government which extended my life. Your generous donation was a life changer. I am enjoying life because of you. I will always be grateful for your best gift which changes my situation from death to life. During my repeated visit to the hospitals in Oslo, the doctors, nurses and other staff members were all very caring. Hence, they deserve much appreciation for their humanity and professional ethics.

Finally, I wish to thank my friends Yemane, Ginbo, Hailay, Tewelde, Sahle, Tesfahunegn and others for their friendship and support in my trying times.

LIST OF ABBREVIATIONS AND SYMBOLS

Abbreviation	**Description**
BN66A	Blotting nylon 6,6, type a
CA	Contact angle
CQ	Camphorquinone
MMA	Methyl methacrylate
MAA	Methacrylic acid
DEGDA	Diethylene glycol diacrylate
DMAEMA	Dimethyl amino ethylene methacrylate
MEHQ	Methyl ether hydroquinone
DEGDA	Diethylene glycol diacrylate
PMPIP	Pentamethylpiperidine
LDPE	Low density polyethylene
POM	Polyoxymethylene
SEM	Scanning electron microscopy
XPS	x-ray photoelectron spectroscopy
PI	Isoelectric point
CA	Contact angle (degree)
σ	Standard deviation
$\bar{x}$	Average

CMC	Critical micelle concentration
UV	Ultraviolet
pKa	Logarithm of the acid dissociation constant
T	Absolute temperature
ΔG_{ads}	Free energy of adsorption
ΔG_{elec}	Electrical adsorption energy
ΔG_{spec}	Specific adsorption free energy
ΔP	pressure difference
ζ	Zeta potential
pH	Potential of hydrogen
Ceq	Equilibrium concentration
µL	Microliter
µM	Micrometer
mM	Millimolar
γ	Surface tension
Ɵ	Theta
Mw	Molecular weight (g/mol)
^{o}C	Degree celsius
CFu	Colony forming unit
ppb	parts per billion (10^{-9})
µS/cm	micro-Siemens/centimeter

ABSTRACT

In recent years, the physical and chemical properties of hydrophilic surfaces been exploited in a number of novel applications. Especially, amphoteric membranes were the focus of many theoretical studies since they have a wide range of applications particularly in bio separation techniques. This particular study sought to determine surface characteristics of amphoteric and acidic membranes. Simple and reliable surface characterization method is important for understanding of membrane surface chemistry, separation performance and fouling resistance. Surface properties such as acid-base, hydrophilicity and hydrophobicity in which the performance of the polymer membranes is dependent on, were determined by contact angle using the immersion method.

First, the surface properties of model commercial amphoteric membranes were characterized followed by lab-made amphoteric and acidic surfaces were investigated. A typical commercial amphoteric Blotting Nylon 6, 6, Type A membrane, plates of Polyoxymethylene modified by chromic acid as well as methyl acrylate based lab-made acidic and amphoteric membrane were examined. These new membranes were prepared using methyl methacrylate as monomer, di (ethylene glycol) diacrylate as cross linker, anionic methacrylic acid and cationic 2-(N, N-dimethyl amino) ethyl methacrylate as functional monomers. The syntheses were made by means of photo induced radical polymerization via camphorquinone/amine initiator. The contact angle titration curve for each membrane immersed in aqueous solution shows that the contact angle is sensitive to the degree of ionization of the surface functional groups. Moreover, surfactant adsorption property of the surfaces were determined using ceryl trimethylammonium bromide and sodium dodecyl benzene sulfonate (well below their critical micelle concentration) solutions as a function of pH.

The contact angle titration curve in the presence of these surfactants describes the surface can go from hydrophilic to hydrophobic upon the adoption ionic surfactant depending on the pH, surface charge density and surfactant concentration. Furthermore, scanning electron microscopy (SEM) has been used to characterize surface morphology of the amphoteric and acidic surfaces. The SEM image of the commercial surface showed that, the surface has high porosity, rough,

uneven, and the pore size and hydrophobicity increase upon the adsorption of ionic surfactant. However, polyethylene surface did not show any visible changes after treatment. In addition, SEM image of the synthesized amphoteric surface was also analyzed.

From the results of this study, it can be concluded that the change in contact angle as a function pH is sensitive to the degree of ionization of surface functional groups. The adsorption of ionic surfactant is dependent on the membranes acidity, basicity and surfactant concentration as functions of pH. Besides, synthesis of membranes by photo polymerization of acrylate based monomers can be used for the preparation of functionalized surfaces. On top of that, based on the experiments done in this thesis, it can be concluded that the hydrophilicity, acidic and basic of surface groups can be determined using the immersed contact angle method. Therefore, it could be possible to suggest that determination of surface properties of anionic and/or basic surfaces using contact angle immersed method should be given emphasis for the development functionalized membranes.

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1. INTRODUCTION

1.1 Background

In recent years membranes have gained especial interest in the development of chemical technology. There are widely used in many industrial production systems due to the fact that they have relatively high efficiency, good operational simplicity, high selectivity, good strength under wide range operating situations and ecofriendly compatibility[1]. The processes of separation and identification through membranes are driven based on several factors such as molecular size, charge on individual component, pressure and a concentration gradient [2, 3].

Membranes can be classified as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) depending the pore size and molecular weight of solute it can filter[4]. They can also be classified as acidic, basic and amphoteric membranes according to their surface functional group[4].

Amphoteric membranes are polymers made up of weak acid-weak base, strong acid -weak base, weak acid-strong or strong acid-strong base functional monomers on their pore surface[5]. These membranes are commonly used in biomedical areas because of their high hydrophilicity leads to effect interaction between hydrophilic pores, surface and proteins or cells[6]. The surface net charge and the charge distribution on the surface are controlled by changing the pH the medium [5, 7, 8].

Characterization of amphoteric membrane is very difficult due to the complexity of the ions within the membrane and limit analytical methods. However, it is useful to determine surface property by contact angle analysis [9, 10], electro kinetic measurement[6], light microscopy[11], X-ray photoelectron spectroscopy (XPS) [12], fourier-transform infrared spectroscopy (FTIR)[13], Scanning Electron Microscopy (SEM) [11, 14] and scanning probe/atomic force microscopy (SPM, AFM) [15-17] are most common surface analysis techniques. Of these methods dealt in this study are mainly by goniometry contact angle analysis in immersion method for the determination of hydrophilicity/hydrophobicity and acid base properties of surfaces. In addition, SEM was used to study the surface morphology of selected membrane samples.

1.2 Objective of this study

The objectives of this study are:

- Surface characterization of commercial amphoteric membrane
- Surface treatment and characterization of hydrophobic surface
- Synthesis and characterize new amphoteric and acidic surface membranes using photo polymerization
- Studying the effects of ionic surfactant adsorption on amphoteric and acidic surfaces as a function of pH
- Applying contact angle immersion method in order to characterize surface hydrophilicity and acid-base properties
- Determination of surface morphology of using scanning electron microscopy (SEM) technique

2. LITERATURE REVIEW

2.1 Amphoteric and anionic membranes

Amphoteric membranes have a random distribution of acidic and basic functional groups on the pore surface. They are widely applicable as ion-exchange in several fields [18, 19]. They are mostly used for desaltation, ultrafiltration, drug delivery, and for protein separation and purification. Essentially, in protein adsorption process in dialysis as well as ultrafiltration membranes. The process of adsorption and filtration is supported by the interaction between the charged protein molecules and charged pore surface has significant importance. This, in turn enable to develop blood purification apparatuses and artificial kidney [5, 20].

Amphoteric membrane surfaces have random distribution cationic groups (basic sites) which are chemically bonded to the membrane`s pore surface[9]. For example, basic groups such as amine (-NH2), hydroxide (-OH) and acidic groups like carboxylic acid (-COOH), phosphoric acid (-PO_4) and sulfonate (-R-SO3-) on their surfaces. Due to the presence of acidic and basic sites on their surface, amphoteric membranes are applicable in a wide range of adsorption and separation process[21]. Whereas, anionic membranes have only acidic functional groups on their pore surfaces and they are predominantly used as a cation exchange membrane[22].

2.2 Preparation of amphoteric membranes

In process of membrane preparation, there are several criteria that should be considered. For example, the membrane has to be insoluble and have fixed charged groups on the membrane`s pore surface[22]. There are various types of amphoteric membrane preparations based on the way how the functional monomers are introduced. Among these:

(i) Copolymerization membrane preparation in which functional (anionic and cationic) monomers arranged at random during the preparation process[22]. For example, copolymerization of styrene, 2-methyl-5-vinyl pyridine and divinylbenzene and then the functionalization is done by sulfonation and quaternization gives amphoteric membrane with cationic amine and anionic sulfonic sites [23, 24]. Another example of this method is the aqueous polymerization of *N*-carboxyl methyl- *N*, *N*-dimethyl-*N*-allyl ammonium (CDMA) and acrylic acid (AA) monomer solution to prepare the amphoteric copolymer of CDMA/AA in the presence of cross-linker *N*, *N*-methylene bisacrylamide (NMBA)[25].

(ii) Grafting of functional monomers to the existing surface[26]. For instance, graft polymerization of acrylic acid (AA) and N, N-dimethyl aminopropyl acrylamide (DMAPAA) monomers to low density polyethylene (PE) offers to amphoteric surface[27].

2.3 Modifications of surfaces

The surface properties of materials such as hydrophilicity, acid-base and adhesion properties in which the performance of a material is dependent on can be improved through surfaces treatment. Modification of surface through wet chemical reaction[28], UV-grafting of functional monomers[29], and plasma treatment and radiation[30] are the most known surface modification methods. These methods give great advantages as they are low cost and they can be applied to pre-existing membranes in order to improve performance of the material. Surface treatment involves the physicochemical interaction change on the surface at a molecular level. Biomaterials such as ceramic and polymer composites are among the most common practices to improve the performance of the surfaces [31, 32].

Wet chemical method has also been used for treatment involves formation of functional groups on the surfaces of materials [28]. For example, low density polyethylene (LDPE) has very poor adhesive due to the non-polar structure, its application is limited where good adhesive properties are required. However, the hydrophilic property of LDPE membrane has been improved by modifying the surface through chemical treatment via nitric acid or chromic acid solution [33]. Etching the surface of LDPE with acid helps to create functional groups like ether, alcohol, ester or hydroxide on the surface so that to improve the adhesive property and chemical performance [33]. Another method for wettability improvement is plasma treatment used to improve the performance of polypropylene (PP), which is mainly used for separation in a variety of industrial applications like wastewater treatment, desaltation and blood filtration [30].

Polyoxymethylene (POM) typical thermoplastic material used in many applications, for instance in automotive hardware and other appliance parts. POM can be synthesized from the reaction of polyformaldehyde and acetic acid through condensation reaction [34]. It can be also produced through cationic polymerization 1,3,5 tioxane and cyclic ether [35]. POM has a high degree of polymer chain arrangements and hydrogen pairing on the surface due to the presence of acetyl group (Fig. 1). This provides the surface to have poor adhesive property, mechanically strong, resistance to alkali, hot water and long lasting at high temperature [35]. However, POM is sensitive to acidic solution. When it reacts with the acid, it leads to the formation of functional groups such as aldehyde, ketone and carboxylic acid [28]. The formation of functional groups on the surface through acidic reaction improves hydrophilicity of surfaces. Moreover, treatment surface by acid not only create functional groups, but also creates cavities on the etched site or treated surfaces that contribute to the hydrophilicity improvement [36].

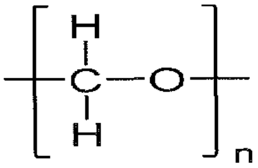


Figure 1: Chemical structure of polyoxymethylene

Etching of polymer surfaces by acid solution is a common industrial practice used to improve the hydrophilicity or wettability of surfaces [28].

2.4 Membrane preparations by photo polymerization

Photopolymerization is environemental friendy means of converting monomers into their desired product with high conversion rate, low energy consumption and relativey without volatile organic compound release [37, 38]. It can be used for material preparation for the application like biodegradable polymer hydrogels for drug delivery[37] . It is common in dentists where preparation of hydrogels can be irradiating with blue visible light. Photo induced polymerization is the process of converting initiator molecules into free radicals. The free radical reaction with monomers having double bond and form polymers.

Camphorquinone (CQ) (2,3-Bornanedione) is one of the most common commercially available photoinitiator. The conversion rate is inefficeient, when using only CQ alone. Therefore, reducing agents for instance, tertiary amines are added as a coinitiators to increase the efficiency of the photoinitaition reaction[26, 39]. Phopolymerization using a combination of CQ initiator and amine is coinitiator are commonly used for polymerization of acrylate based monomers [26, 38, 39]. Initiator CQ has a yellor color due to the absorption of visible light region (400-500nm) with maximum absorbance at 468nm and it can also absorb at UV-region between 200-300nm[37, 39].

Figure 2 shows that the reaction mechanism of initiator CQ and coinitiator in photoinitialtion system. The absorption of UV by initiator CQ resulted to the formation of two exited state the first is, the creation of singet state(S1) which leads to the formation of triplet state(T1) which is used for the formation of photochemical reactions. The trilpet state CQ reacts with amine molecules to produce an exited state molecule complex. In the complex reaction of initiators and monomers, the initiator CQ abstracts hydrogen from tertiary amine causing the formation of free radicals CQ-radical and amino alkyl radical through electron and proton transfer. In a reaction mixture containing monomers, initiator CQ and coinitiator amine, the abstraction of hydrogen atom by triplet CQ is much earlier than the reaction with the monomer. This is due to tertiary amine have low oxidation potential than other proton donor molecules[39].

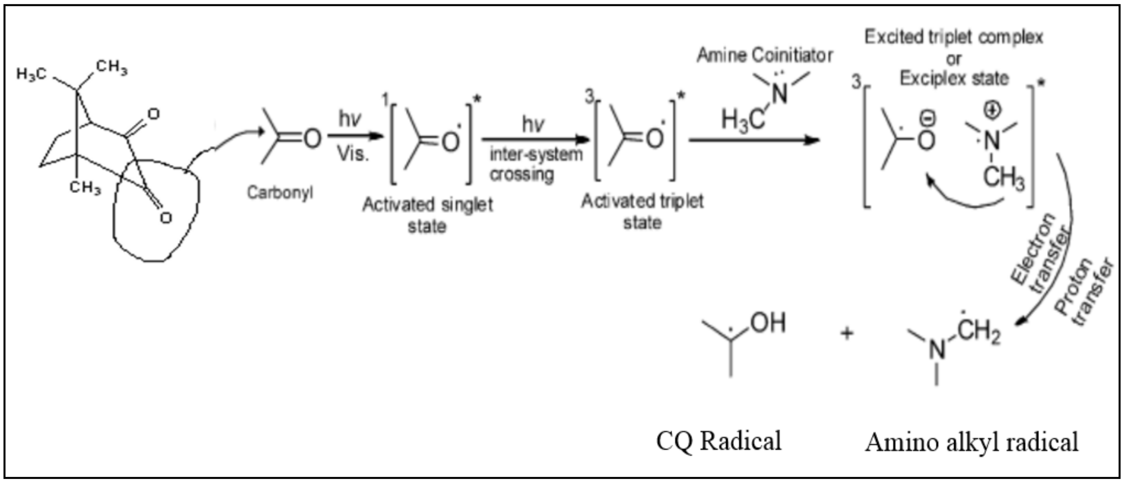


Figure 2: Reaction mechanism of photoinitiator system containing photoinitiator (CQ) and electron donor anime initiator[39]

There are several factors that affect the photochemical reaction using CQ as initiator. The first thing to consider is, the yellow color of CQ initiator by itself can hinder the reaction mechanism by blocking the irradiation light from enterring in the bulk solution resulting in more unreacted photoinitiator. Another factor such as viscosity, amount of initiator and heat formed as a result of irradiation are also among the factors influencing the applicability of photoinduced polymerization[38].

2.5 Factors affecting the membrane surface

2.5.1 Effect of pH

Amphoteric membranes contain a random arrangement of weak acids (negatively charged) and weak base (positively charged) groups. For example, modified Chitosan, which is commonly used for separation of proteins have amphoteric nature. This is because of the presence of weak acid carboxylic acid (-COOH) and weak base amine ($-NH_2$) on the structure (Fig.3). The net charge can be positive or negative depending on the environmental strength of the solution[5, 40].

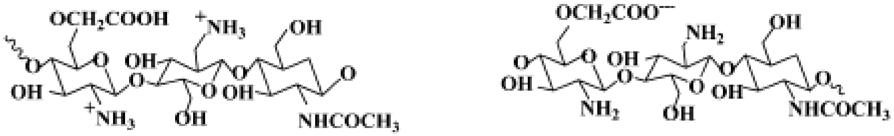


Figure 3: pH dependency of the modified structure of chitosan at low pH (left) and at high pH (right) [40]

2.5.2 Isoelectric point (pI)

Amphoteric membranes have a characteristics property called isoelectric point (pI)[41]. It is the pH at which a particular molecule carries no net electrical charge. The different types amino acids, which are the building blocks of protein in our body can be separated by electrophoresis in a pH gradient using isoelectric focusing method according to the isoelectric points [42, 43].

Figure 4 shows that as pH of the medium increase from acidic to basic solution the charge on the molecule changes. Above the dissociation constant pKa_1 value, the carboxylic acid group releases hydrogen atom and becomes negatively charged molecules. On the other hand, the amine group starts to gain hydrogen ion as the solution becomes acidic (below pKa_2) and they will be protonated. At a certain pH or at isoelectric point (pI), the carboxylate ($-COO^-$) and ammonium ($-NH3^+$) ions or will be equal to the molecule exist in its zwitterion. At pI there are equal number of positive and negative ions they will cancel each other and become a neutral charge[44, 45].

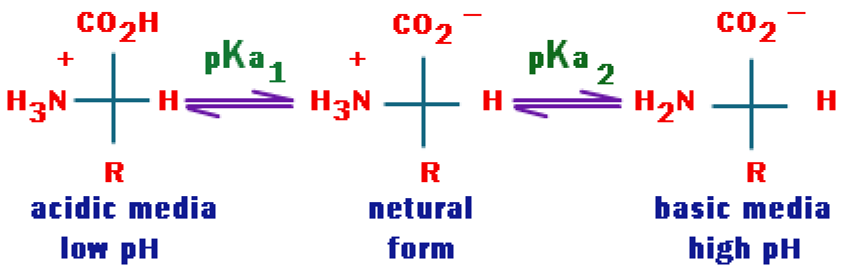


Figure 4: Influence of pH on amphoteric substances[46]

The acid-base equilibrium of dissociable groups is described by Henderson-Hasselbalch equation [5].

$$pH = pK`_a + n\log(\alpha/1- \alpha) \tag{2.1}$$

$$pH\ pK`_b + n\log(1-\beta/ \beta) \tag{2.2}$$

Where $pK`_a$ and $pK`_a$ are the apparent dissociation constant of the acid and basic groups respectively and α and β are degree of ionization of acidic and basic groups. This equation is used (i) for the determination of the pH buffer system; (ii) to find the ratio of conjugated base to conjugated acid or vice versa[5]; and for the determination of pI values. For example, different types amino acids, which are the building blocks of protein in our body can be separated by electrophoresis in a pH gradient using isoelectric focusing method according to the isoelectric points [42, 43].

The degree of dissociation of carboxylic acids is dependent on the groups in which they are attached. Most carboxylic acids in different molecules and surfaces have pKa vales ranges from 2 to 5[44]. For anionic surface, the effect of pH is high above the pKa values the acidic groups. However, unlike the amphoteric membrane acidic membranes have a stable surface at low pH (below pKa). This is because acidic membranes have only acidic sited and form hydrogen membrane on the surface. A typical acidic monomer (3-mercaptopropinic) coated on gold surface shows (Fig.5) shows the surface is stable at low pH[47].

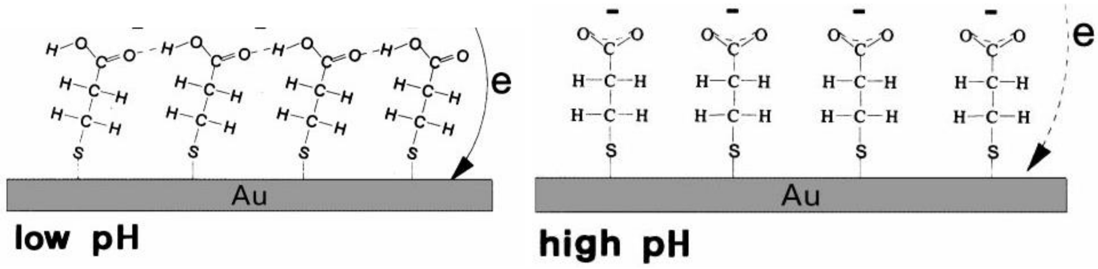


Figure 5: Carboxylic acid group surface structure: The formation of Hydrogen bond (left) and negatively charged carboxylic acid (right)[47]

2.5.3 Effect of electrolyte

The interaction between electrolyte solution and amphoteric membrane can be determined by membrane potential and membrane conductance. The presence of cationic and anionic sites on the amphoteric membrane has different electrostatic attractions based on the type of electrolyte solution present in the bulk solution. For example, the presence of trivalent (such as $LaCl_3$) cations in a solution has strong electrostatic interaction with negative site of the amphoteric membrane than univalent cation (e.g. NaCl) [48]. Furthermore, the adsorption of ionic surfactants on amphoteric membrane surfaces is also affected by the presence of electrolyte solution. The ionic effect on membrane surface is usually described by the ionic strength of the solution. The presence of effective electrolyte counter ions in the bulk solution facilitates adsorption of anionic surfactants on a negatively charged interface [15, 49]. At low concentration (below the critical micelle concentration) of surfactants, increasing the ionic strength will decrease the adsorption of ionic surfactants over the oppositely charged surface. This is due to the fact that, screening of Columbus attraction between polar head of the surfactant and the surface. However, the adsorption of low concentration of surfactant facilitates by adding a small amount of electrolyte [15, 50, 51].

2.5.4 Adsorption of surfactants

Surfactants have a special tendency to adsorb on an interface due to their surface active characteristics. They are surface active amphiphilic molecules consists mostly polar head groups having functional groups such as amine, amide, phosphate alcohols, and sulfonate. On the other side, they have non-polar tail contains hydrocarbons (lipophilic) chain such as alkyl or alkyl benzene type. The polar part or hydrophilic part of the molecules have a strong affinity towards polar solvents like water while the non-polar tail or hydrophobic part tends to arrange themselves away from the polar solution[52].

Adsorption refers to the migration of surfactant molecules from the bulk solution to the surface or interface. The interaction of surfactant and surface in bulk solution has a key role in a wide range of applications such as in drug delivery[20, 32, 53] oil recovery[54], refining and decontamination [52, 55], mineral proceeding and consumer products[56], wettability modification[55], as emulsifiers, adhesives, household detergents, paints and in other industrial applications [57, 58] this is due to their special characteristics of lowering the surface and interfacial properties.

There are several mechanisms in which surfactant molecules adsorb from aqueous solution to solid surface/interface. For example, as ion exchange**:** **-** in which counter ions adsorbed on a surface are replaced by similar charged surfactant ions, as electrostatic**:** **-** when cationic/ anionic surfactant adsorbed on oppositely charged hydrophilic surface [15, 59] and as hydrophobic:- bonding is the driving force for the adsorption of surfactant molecules on hydrophobic solid where both hydrophobic surface and alkyl group of the surfactant are attached at the interface while, the polar heads oriented to the bulk solution [15, 52].

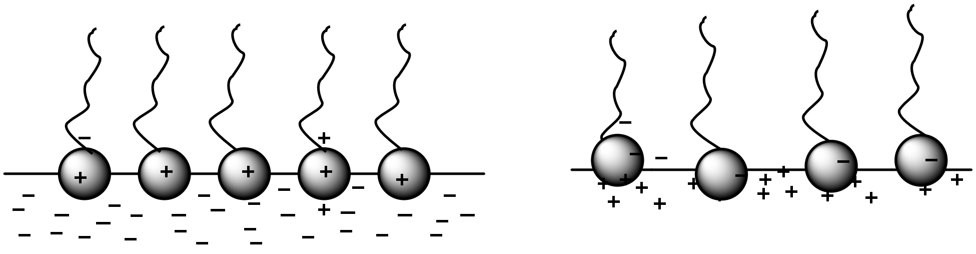


Figure 6: Illustration of adsorption cationic and anionic surfactants on negatively charged and positively charged surface respectively

The adsorption of surfactant molecules on membrane surfaces is dependent on the types of surfactant. The electrostatic and hydrophobic attraction between surfactant molecules play an important role for surfactant molecules to be attached on a hydrophilic surface. Cationic surfactants are best adsorbed on negatively charged surface whilst, the anionic are adsorbed on positively charged surfaces (Fig.6). This is due to the electrostatic attractions between oppositely charges molecules[55] which leads to the formation of electrical double layer at the interface that is an important property for the adsorption of ionic surfactant on a charged surface[15, 60]. The rate of adsorption is dependent on the surfactant type. anionic and non-ionic have almost similar rate of adsorption whereas, cationic surfactants have higher rates of adsorption.[61].

2.5.5 Adsorption isotherm of ionic surfactant on surface

The adsorption mechanism of ionic surfactants on charged surface/interface is described by the free energy adsorption ΔG^{o}_{ads}. The free energy adsorption is the summation of electrical and non-electrical adsorption systems [15]. It is represented by the equation below:

$$\Delta G^{o}_{ads} = \Delta G^{o}_{elec} + \Delta G^{o}_{spec} \qquad (2.3)$$

Where ΔG^{o}_{elec} is the electrical adsorption energy and ΔG^{o}_{spec} is the specific adsorption free energies. The adsorption energy can be calculated by the Stern-Grahame equation[15] as follows:

$$\Gamma = rCeq \exp(\Delta G^{o}_{ads/}RT) \qquad (2.4)$$

Where r is the radius of adsorbed ion and C_{eq} is the equilibrium concentration.

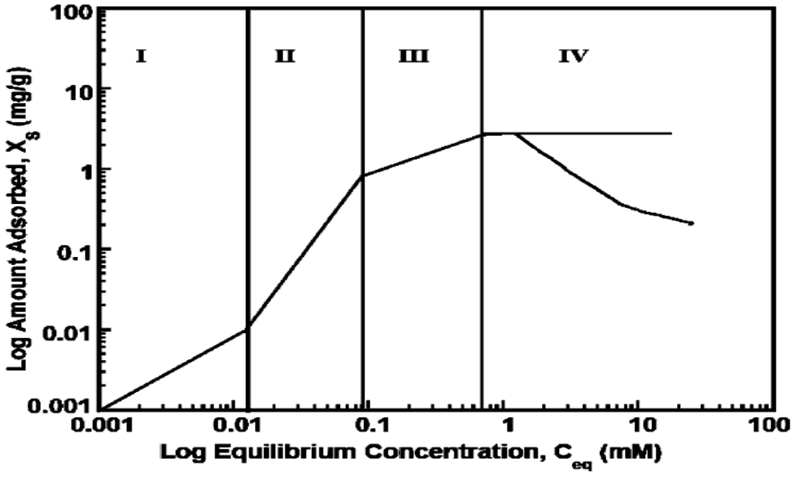


Figure 7: Adsorption isotherm: amount of ionic surfactant adsorbed versus equilibrium concentration of surfactant in bulk solution [15]

Generally, the amount of surfactants adsorbed on the solid-liquid interface is directly proportional to the concentration of surfactants in the bulk solution. Figure 7, region I, shows that at low concentration the rate of adsorption increase as the concentration of surfactants increase. In this region, the activity of surfactant is very high and the driving force for adsorption is in this case electrostatic force. And the rate of adsorption will increase faster as surfactants form of aggregate due to lateral interaction (region II). Above the critical micelle concentration region II and III surfactants form micelle and the rate will decrease and become constant due to the restricted activity of surfactant molecules [15, 21, 50, 57, 62].

2.5.6 Surfactant structure

Adsorption of surfactants on hydrophilic surface is affected by the surfactants chain length. Even though the adsorption of surfactant on a surface is highly dependent on the hydrophilic head, the structure of the attached molecular chain may alter the interaction with the surface[63]. The longer the hydrophobic tail of surfactants molecules has a high efficiency of adsorption. And surfactant with branched hydrophobic tail have a relatively more efficiency than its single tail isomer whenever the interaction between the hydrophobic repulsive is strong enough[64]. A surfactant molecule with long alkyl tail adsorbs more because they have hydrophobic tail interaction with the surface in addition to the strong electrostatic attraction[55].

2.5.7 Surfactant concentration

As described by adsorption isotherm, the amount of adsorbed surfactant molecules per unit area of surfaces is depending on the concentration of surfactant in a solution[55]. The amount of surfactant adsorbed on a membranes surface increase with increasing surfactant concentration even above the critical micelle concentration[58]. For example the electrostatic force between cationic surfactant and negatively charged surface leads to the adoption. As the surfactant concentration increase, the amount surfactant adsorbed also increase, i.e. more and more surfactant attached to the surface and orientates the polar heads attached to the membrane surface and non-polar head side with the solution forming monolayer and double layer depending on the surfactant concentration [58, 65].

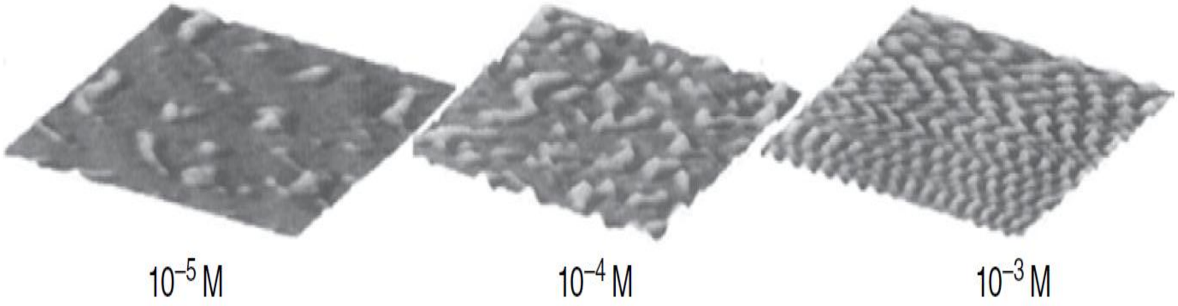


Figure 8: Image of atomic force microscopy AFM showing the adoption of cationic surfactant CTAB on mice at different concentrations

The adsorption of CTAB surfactant on mica at different concentrations (Fig. 8) clearly shows the growth of surfactant molecules increase on the surface as concentration increase. The hydrophobicity of the surface increase as more and more surfactant molecules are adsorbed until the surfactant forms monolayer. Otherwise, the hydrophilicity will increase as the molecules are forming a double layer above the critical micelle concentration [15, 66].

2.6 Critical micelle concentration

In order to study the effect of surfactants on a membrane surface, it is important to know the key characteristics of surfactants called critical micelle concentration (CMC). CMC is the concentration of surfactants at which surfactant molecules aggregate of tensile molecules called micelle starts to form. The formation of micelle is due to the principle that molecules by nature arrange themselves to minimize energy. The non-polar part of the surfactant molecules tends to hide from interaction with polar molecule of water. Therefore, the polar heads of the surfactant molecules attracted to water molecules and the non-polar tail arrange themselves away from water molecules. The polar heads have large surface area and form a spherical shape in solution and double layer above polar surfaces [57]. As the concentration of surfactant molecule increases, the surface tension between the molecules will decrease and above CMC the surface tension is independent of concentration.

2.6.1Methods for CMC determination

The CMC of surfactants can be measured using various kinds of methods such as surface tension, interfacial tension, osmotic pressure and UV-visible spectrophotometry[67]. The surface tension pendent drop method is selected as the most common and simple method to investigate the CMC of cetyltrimethylammonium bromide (CTAB) and sodium dodecyl benzenesulfonate (SDBS). The CMC of surfactant solution can be determined through measuring surface tension of pendent drop as a function of log concentration (Fig.9).

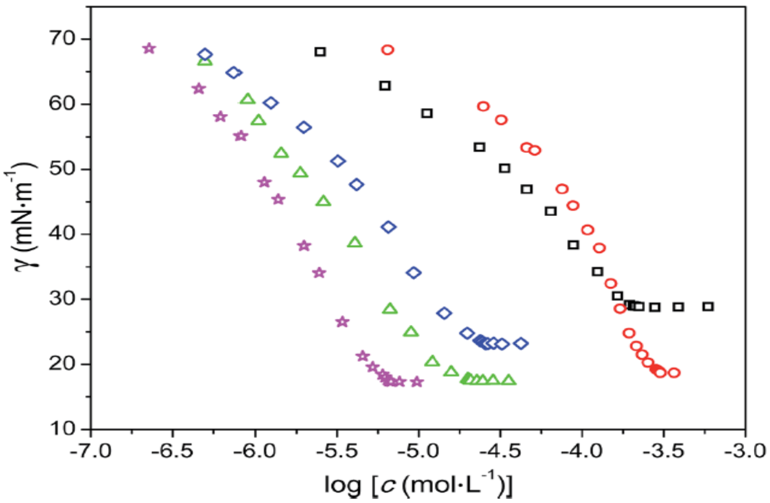


Figure 9: Surface tension versus surfactant concentration. As concentration increase, the surface tension lowers and after CMC the surfaces tension is almost independent ion the surfactant molecules in the solution [68].

2.7 Characterizations of membrane surfaces

Determination of surface properties such as physicochemical, adsorption properties, wettability or hydrophilicity and fouling resistance is essential for the desired use[17]. Amphoteric surface properties are usually characterized by several techniques. For example, measuring ion-exchange capacity[69], water uptake[70], electrical conductivity, charge density, and membrane charge potential using ζ potential as a function of pH [7, 61]

The interaction of surface with other surface materials is dependent on the chemical composition, hydrophilicity/hydrophobicity, morphology and biocompatibility of membrane surfaces [45, 71]. Membrane surface can be characterized using many types of characterization techniques. Contact angle measurement, scanning electron microscopy (SEM), x-ray photoelectron spectroscopy (XPS) and others can be used for characterizing surface properties of materials.

2.8 Characterization of surfaces by Contact angle

2.8.1 Contact angle in immersed method

The wettability of the liquid on a solid surface is dependent on the chemical and physical nature of the solid and the surface tension of liquid. The interaction between the liquid molecules and the solid surface is dependent on polar and non-polar interactions. It can be used in application such as coating, polymer development and biological research activities.

Contact angle measurement using immersed method involves, a general system having a sessile drop of neural organic liquid which is immiscible with water placed on a surface immersed in aqueous solution (Fig.11). However, in immersed solution the of contact angle of sessile oil droplet or captive bubble the angle will be the supplementary angle figure 10.

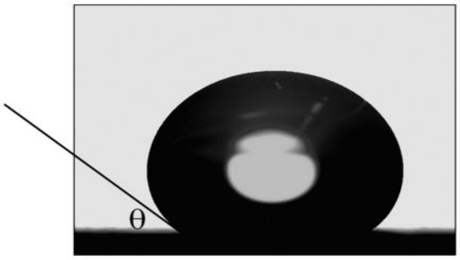


Figure 10: Contact angle of liquid droplet immersed in aqueous solution

Other immersed contact angle measurement system is a captive bubble method in this contact angle of air bubble placed up-side down on a solid surface can be used; but this a method needs more sophisticated instrument in order to keep the membrane suspended over the immersed liquid[9, 72].

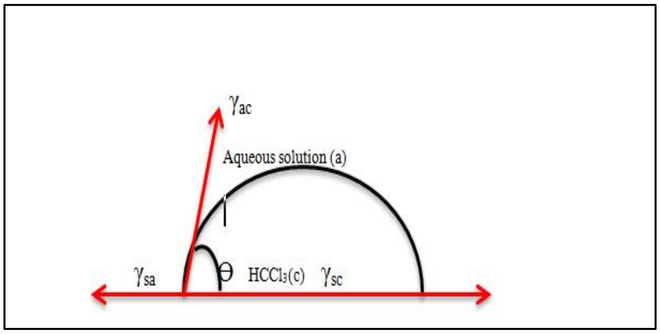


Figure 11: Young's Model sessile droplet of chloroform showing the relationship between interfacial tensions

The force balance at the equilibrium contact angle is young-Dupree equation (equ. 2.6):

$$\gamma_{ac}\cos\Theta=\gamma_{sa}-\gamma_{sc} \qquad (2.6)$$

Where γ_{ac} is the interfacial tension between the aqueous solution and chloroform, γ_{sa} is the interfacial tension between the surface and the aqueous solution, γ_{sc} is the interfacial tension between the surface and chloroform.

Determination of surface properties by contact angle using immersed in aqueous solution by Appling young-Dupree equation is based on assumptions that; (i) the aqueous solution and the surface are in thermodynamically equilibrium; (ii) the surface is flat and homogenous; (ii) the liquid droplet is surrounded by a well-defined three-face in which it is immiscible with the aqueous solution; and (iv) the absorption of liquid droplet by the surface is negligible[9, 73].

Contact angle in immersed method has been developed by Hamilton to characterize the magnitude of polar interaction between immiscible liquid (n-octane) droplet and solid surface immersed in water[74]. This method has been used for the determination of acid-base properties surface and the adsorption of cationic surfactant on acidic and amphoteric membranes. The results showed that the contact angle of carbon tetrachloride is sensitive to the ionization of acidic and basic functional groups in solid-liquid interface[9].

Understanding the acid-base property of an amphoteric and acidic surface at solid-liquid interface helps to understand the phenomena's in many applications such as the polarity of solid colloids, fouling of proteins and the mechanism of catalyst by enzymes[73]. Furthermore, this helps to develop surface having of amphoteric nature. For example, the formation of carboxylic acid, ketone and aldehyde on the low density polyethylene surface as a result of chromic acid treatment, has been characterized by contact angle measurement as a function of pH. The titration curve showed that the contact remains constant below pH 5 and then decreased until pH11. This shows the surface has acidic groups and the dissociation constant pKa is the pH value midway between the maximum and minimum contact angle (Fig.12).

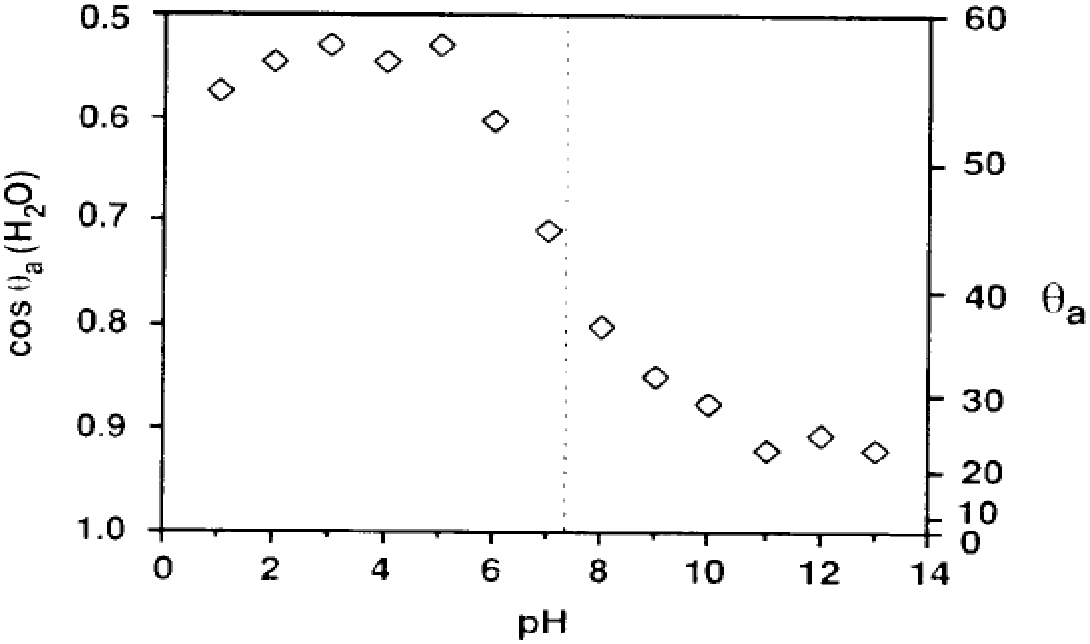


Figure 12: Advancing contact angle versus pH with sessile droplets of water on the surface of anionic PE-CO2H air. Where the dashed line is the pKa of the acdidc surafce group [73].

Whereas, for surface which have an ionisable basic functional group such amine on their surface, the contact angle increases as a function of pH due to the deprotonation the ammonium ions[73].

Membranes having basic and/or acidic groups immersed in surfactant solutions, the adsorption of ionic surfactant is dependent on the surface charged and pH [15]. As the pH of the solution increase anionic groups will protonated and the surface becomes negatively charged. Therefore, cationic surfactants which have positively head groups will adsorb on the negatively charged surface and the reverse is true for anionic surfactant on the positively charged surface. The contact angle titration curve (Fig.13) shows the acid-base interaction properties and hydrophilicity membranes. As pH increases, the ionization of anionic surface groups increase and more surfactant molecules are adsorbed electrostatically and the alkyl tail of the surfactant oriented to the bulk solution resulting in hydrophobic interface. High contact angle at high pH illustrates, there is strong acidic behavior of the membranes[9].

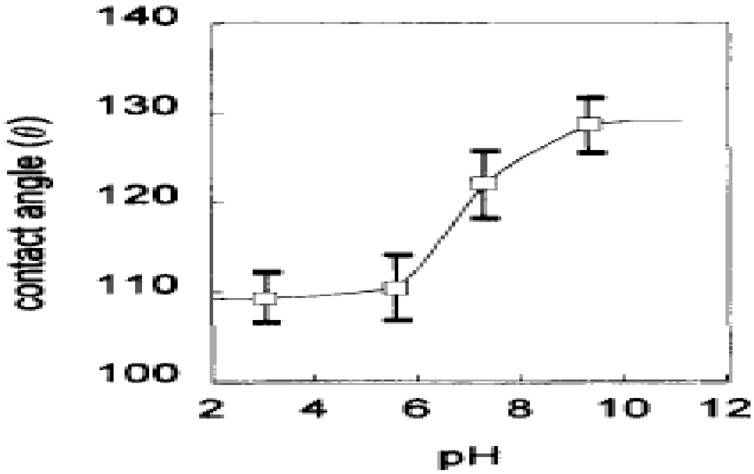


Figure 13: Advancing contact angle of carbon tetra chloride droplet on the membrane surface immersed in a cationic surfactant as a function of pH values for amphoteric membrane[9]

2.8.2 Advantages of contact angle measurement by immersed method

Amphoteric surfaces have high energy surfaces due the presence of polar, hydrogen bonding or ionized groups. Characterization of those surfaces by measuring contact angle in an immersed water solution is preferable. The system prevents the membrane surface from drying and keeps the membranes in wet condition the same as in their applications. Amphoteric membranes are applicable in filtrations in which the membranes are immersed in liquid solutions. High energy surfaces in air form low energy under water. Hydrophilic membranes are high energy surfaces, hence they can be easy contaminated in air. Therefore, keeping under water solution will lower their surface energy so less affinity toward other molecules therefore it minimizes interacting with external molecules[9].

2.8.3 Considerations in contact angle measurements

Contact angle measurement has many drawbacks especially for characterization of hydrophilic surfaces. Young`s equation define only in an ideal condition surface like smooth and no absorption by the solid surfaces. The following factors should be considered while charactering surfaces by contact angle.

Liquid contamination: The contact angle measurement has three phases the solids surfaces, liquids droplet and air/liquids surround. Contamination at any of the three conditions can alter the contact angle measurement.

Surface roughness: Surface roughness affect contact angle. The influence is dependent on surface hydrophilicity. Contact angle increase as the surface roughness factor increase for hydrophobic surfaces and decrease for hydrophilic surfaces[45].

Absorption of liquid by the solid surfaces: When Liquid molecules penetrating the surface and filled the pores the membrane hydrophilicity will change because the liquid molecules will be part of the membrane so it does affect the hydrophilicity and performance of [75]membranes.

Drop volume and effect of gravity: Contact angle also depends on drop size. Generally small angle will minimize the effect due to gravitational force. But on the rough surface and high energy surface the contact angle is highly dependent on droplet size and larger sessile drop volume have less error depending on the surface energy [72].

2.9 Scanning electron microscopy (SEM) analysis

Scanning electron microscopy is the most common method for surface morphology characterization. SEM used beams of electrons to create an image of spacemen. Figure 14 shows that the schematic diagram of SEM used in this work. The electrons bombarded by the electron gun will reflect with two types of electron as secondary and backscattered electron hitting the spacemen. The secondary electron comes back after hitting the atoms of the spacemen and the atoms will release their own electron from the surface atoms call the secondary electrons. Those electrons are collected by the secondary electron detector and the detector uses the information to convert as an image. The image obtained from secondary electron uses to get information about the morphology of the surface. While the back scattered electrons come from a reflected electron from deep part of the spacemen and uses for elemental analysis when there is x-ray detector. This can be used for surface characterization amphoteric and acidic membranes [14, 27, 76]. In this study, SEM was applied for surface morphology characterization of the selected amphoteric and acidic sample was characterized.

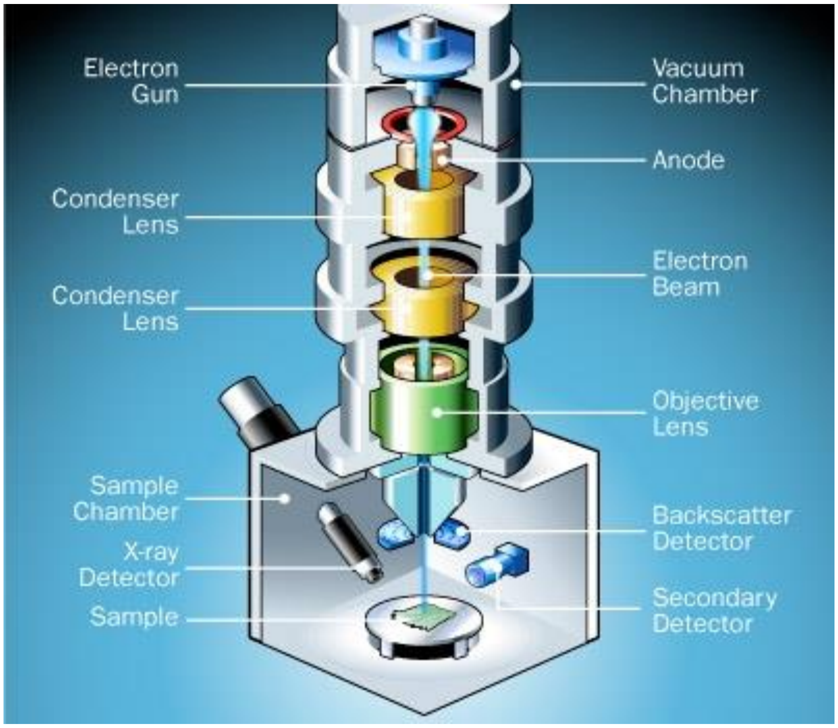


Figure 14: Schematic diagram of scanning electron microscopy (SEM)[77]

3. MATERIALS AND METHODS

3.1 Membranes

3.1.1 Blotting Nylon 6, 6 Type A

Commercial membrane blotting-nylon 6, 6 membranes, type A (BN66A) was obtained from Sigma Aldrich. The membrane has 50% amino and 50% carboxylic acid polar groups supported by polyester. Some of the characteristics of this membrane are listed under Table 1.

Table 1: Characteristics of BN66A membrane [78]

Form	Foil (round)
Diameter	82mm
Surface coverage	50% amino group 50% carboxyl group
Pore size	0.2 μm pore size

3.1.2 Polyoxymethylene (POM)

Commercial plates of POM were used to improve the surface hydrophilicity by treating it with chromic acid solution. Several pieces of POM Plates with approximately dimension of 2 x 1.5 x 0.6 cm were obtained.

3.3 Chemicals

3.3.1 Surfactants

Cationic surfactant N-cetyl-N, N, N-trimethyl ammonium bromide (CTAB) with chemical formula ($C_{19}H_{42}NBr$ Mw=364.45g mol^{-1}) and anionic surfactant sodium dodecyl benzene sulfonate (SDBS) with chemical formula ($CH_3(CH_2)_{11}C_6H_4SO_3Na$ Mw=348.48g mol^{-1}) both obtained from Aldrich were used for the adsorption study on amphoteric and acidic surface without any purification. The chemical structure of SDBS and CTAB surfactants are given in figure 15 and 16 respectively.

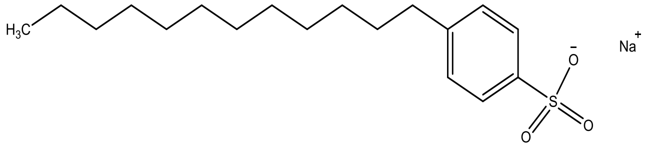


Figure 15: Chemical structure of Sodium dodecyl benzene sulfonate

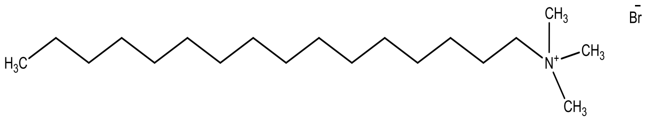


Figure 16: Chemical structure of Cetyl –trimethyl ammonium bromide

3.3.2 Reagents

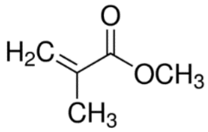
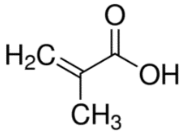
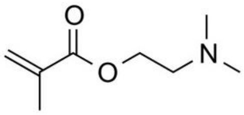
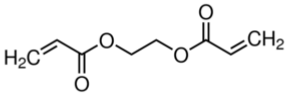
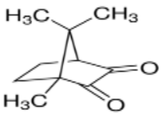
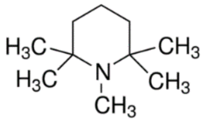
Sodium hydroxide (chemical formula NaOH with 98% purity) supplied by Eka Nobel and Hydrochloric acid (chemical formula: HCl with 35% concentration) from VWR chemicals were used for adjusting the pH solution; Acetone (chemical formula CH_3COCH_3 Mw. 58,08g/mol of ≥99% purity) was used for cleaning purpose; Potassium chloride (chemical formulas: KCl and≥99% purity) obtained from sigma Aldrich were used to get constant ionic strength; Sulfuric acid H_2SO_4 (96%) and potassium dichromate $K_2Cr_2O_7$ (99%) both supplied from sigma Aldrich were used for chromic acid preparation which was used for surface treatment; and chloroform ($CHCl_3$) with 99.2% purity and density of 1.489 g/cm^3 supplied by sigma-Aldrich was used as a heavy organic liquid (oil droplets) for measuring contact angle.

3.3.3 Monomers

The following monomers, initiator and co-initiator were used for the synthesis of amphoteric and acidic surface membranes. Methyl methacrylate (MMA) (Molecular weight: 100.12g/mol) with 99% purity (contains an inhibitor ≤ 30 ppm of mono methyl ether hydroquinone (MEHQ)) was used as a main monomer. Methacrylic acid (MAA) (with molecular weight: 86.09g/mol of 99% purity contains impurity of 250 ppm MEHQ as inhibitor was used as an anionic functional monomer. In addition, 2-(N, N-Dimethyl amino) ethyl methacrylate (DMAEMA) (Molecular weight: 157.2g/mol and 99% purity was used as a cationic functional monomer. Whereas, di (Ethylene glycol) di acrylate (DEGDMA) (Molecular weight: 214.22g/mol technical grade75% purity was used as cross linker. Moreover, camphor quinone (CQ) (Molecular weight:

166.22g/mol ((±) camphor quinone, 2, 3-bornanedione) with 97% purity and 1, 2, 2, 6, 6-pentamethylpiperidine (PMPIP) (Molecular weight: 155.28g/mol of purity level ≥ 99.0%) were used as photoinitiator and co-initiator respectively. All chemicals were obtained from Sigma-Aldrich and their chemical structures are presented in table 2.

Table 2: Monomers and their corresponding chemical structure

No	Name	Structure
1	Methyl methacrylate (MMA)	
2	Methacrylic acid (MAA)	
3	2-(N,N-Dimethyl amino)ethyl methacrylate (DMAEMA)	
4	Di(ethylene glycol) diacrylate (DEGDA)	
5	Camphorquinone (CQ)	
6	1, 2, 2, 6, 6-pentamethylpiperidine (PMPIP)	

3.4 Instruments and Methods

3.4.1 Instruments

(i) Ramé-hart contact angle goniometer instrument (Fig17) with DROPimage advanced edition software version 2.8.02 (developed by Professor Finn Knut Hansen at the University of Oslo) was used to measure surface tension and contact angle. The instrument equipped with a video camera for recording the drop image formed and transmitted to the computer where the contact angle of sessile droplet is measured.

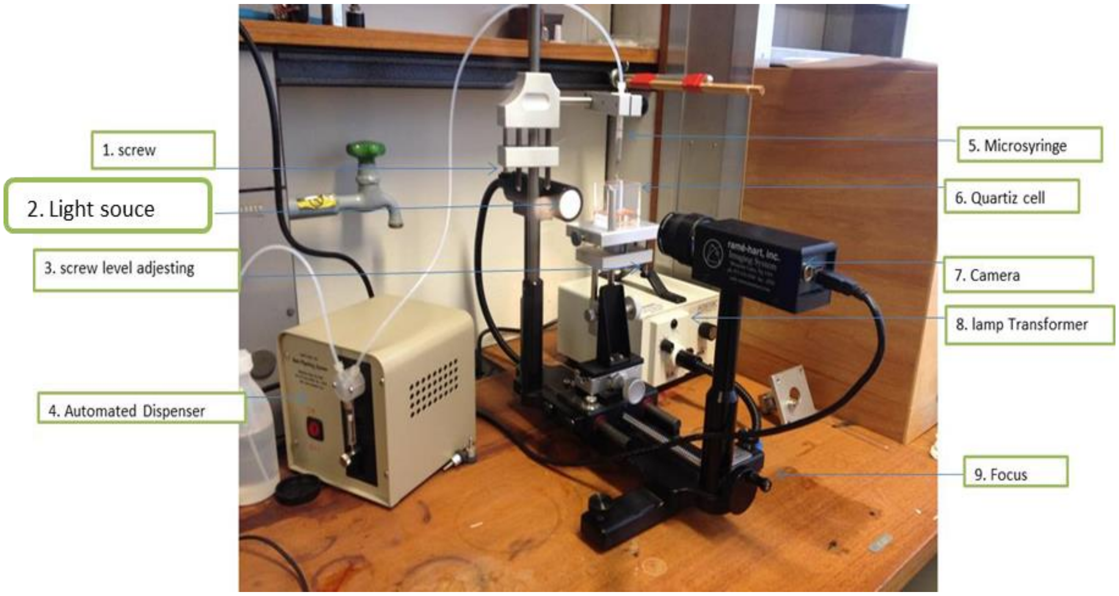


Figure 17: A basic experimental setup of Ramé hart Goniometry instrument

(ii) PH-meter 827 pH lab supplied by Metrohn Swiss was used for measuring pH.

(iii) Philips 500 W lamps (type PF 318 E/49) obtained from Philips was used for photo polymerization reaction. The lamp produces visible light radiation over 400nm with a total intensity of 60mW/cm^{-2}. This range is suitable since the initiator CQ absorbs 400 to 510nm with a wavelength maximum peak at 468nm and

(iv) Scanning electron microscope (SEM) model FEI Quanta 200 FEG-ESEM was used characterization of surface topography.

3.4.2 Methods

3.4.2.1 Determination of Critical micelle concentration (CMC) Pendent drop method

Ramé hart Goniometry instrument (Fig. 17) was used for determination of CMC using the pendent drop method.

The interfacial tension measurement using pendent drop is relatively simple. But, there are factors to be considered in order to get good image quality for precise measurement. The light source was focused to get sufficient light and diffused to ensure no optical deviation occurs at the drop margin. The setup was placed where no other light (overhead light) interference. A typical pendent drop image that is well appropriate for fitting is given in the figure below (Fig. 18).

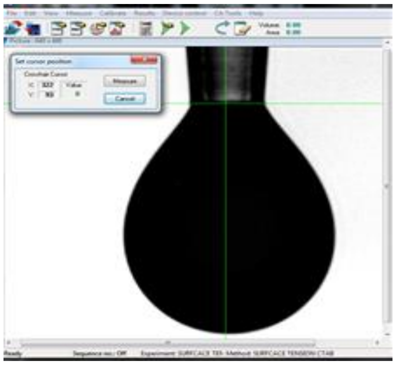


Figure 18: A typical Pendent drop Image as acquired by the digital camera

A micro syringe was adjusted to be in a vertical position to get the required asymmetric and placed in a stable stage where there is no oscillation of pendent drop due to vibration. A sufficient amount of chloroform was injected through the automatic dispenser. However, there was liquid wetting on the polyethylene micro syringe, for this reason, the tip of the polyethylene was designed and replaced by a glass tip to avoid wetting of chloroform (Fig.19).

Figure 19: Polyethylene micro syringe (right) modified to a have glass tip (left)

DROPimage advanced program measures the interfacial tension from the shape of pendent drop hanging at the tip of the glass micro syringe. To determine the CMC surfactants (CTAB and SDBS), a stock solution of each surfactant were prepared. One liter of CTAB solution was prepared by dissolving 0.8098 grams of CTAB in distilled water liter to get final concentration of 1.472mM. The same way, one liter of 1.08mM SDBS solution was prepared by dissolving 0.377grams of SDBS in distilled water. Then, from the stock solution, a series of CTAB and SDBS concentrations were prepared by diluting with distilled water as given in tables 3 and 4 respectively.

Table 3: Dilutions and concentrations of CTAB in distilled water

Solution number	CTAB added (mL)	Water added (mL)	Final volume (mL)	Final CTAB concentration (mM)
1	5	45	50	0.147
2	10	40	50	0.294
3	15	35	50	0.442
4	20	30	50	0.589
5	25	25	50	0.736
6	30	20	50	0.883
7	35	15	50	1.031
8	40	10	50	1.178
9	45	5	50	1.325
10	50	0	50	1.472

Table 4: Dilutions and concentrations of SDBS in distilled water at room temperature (23^{o}C)

Solution number	SDBS added (mL)	water added (mL)	Final volume (mL)	Final CTAB concentration (mM)
1	5	45	50	0.108
2	10	40	50	0.216
3	15	35	50	0.324
4	20	30	50	0.432
5	25	25	50	0.541
6	30	20	50	0.648
7	35	15	50	0.756
8	40	10	50	0.864
9	45	5	50	0.972
10	50	0	50	1.081

The interfacial tension pendent drop for each of the diluted surfactant solution was measured using the standard operating procedure for the DROPimage advance program. The measurement was repeated at least three times for each concentration in order to get reproducibility.

3.4.2.2 Characterization of Blotting-nylon 6, 6 membranes, Type A (BN66A) by Sessile Drop method in immersed technique

Contact angle measurement by sessile drop method in immersed aqueous solution was applied. The experiments were carried out to determine the hydrophilicity as a function the influence of pH gradient, acid-base property and effect of cationic and anionic surfactant solution on the surface membrane. Contact angle results are subjected to errors due impurity and care was taken to minimize any contamination from the quartz cell cuvette. The quartz cell was soaked with a chromic acid solution and then rinsed with distilled water and dried at room temperature.

3.4.2.2.1 Membranes preparation

BN66A membrane was used as received and several pieces of membrane approximately 1.5 x 2.5cm were predated and a glued to a glass by double sided tape in order to immerse into the bottom of the solution (Fig.20).

3.4.2.2.2 Solution preparation

For this experiment, the chemicals listed in table 5 were prepared using distilled water and well cleaned volumetric flasks.

Table 5: List of chemicals and concentration prepared in water

Solution No	Chemical	Weight/volume	Total volume (L)	Concentration (M)
1	HCl	4.4ml	0.5	0.1
2	NaOH	2.06 gram	0.5	0.1
3	KCl	0.74 gram	1.0	0.01
4	SDBS	0.037gram	1.0	$0.105x10^{-3}$
5	SDBS	0.065gram	1.0	$0.190x10^{-3}$
6	CTAB	0.016gram	1.0	$0.042x10^{-3}$
7	CTAB	0.160gram	1.0	$0.420x10^{-3}$

3.4.2.2.3 Contact angle measurement

Immersed method measuring contact angle was made by two-liquid phases, immiscible liquids of chloroform and water solution and solid surface. The experiment was carried out by measuring contact angle of a sessile droplet of liquid chloroform on a membrane sample immersed in water solution. To evaluate the contact angle of liquid chloroform droplet on a solid surface as follows.

i. **Calibration**: the magnification of the goniometry instrument was calibrated before measurement.
ii. **pH adjustment:** The pH meter was calibrated using buffer solutions before use. Then Approximately 80% of the volume of quartz cell was filled with water solution. After that after the pH of the solution was recorded by pH-meter.
iii. **Fluid loading:** The micro syringe was filled with approximately 100 to 100 µL of chloroform.
iv. **Membranes wetting:** The membranes already prepared were inserted in to the aqueous solution with predetermined pH. In order to get equilibrium between the interaction of the solution and membrane surface the membrane was immersed for at least 3 to 5 minutes to get equilibrium between the membrane surface and solution (Fig.20).

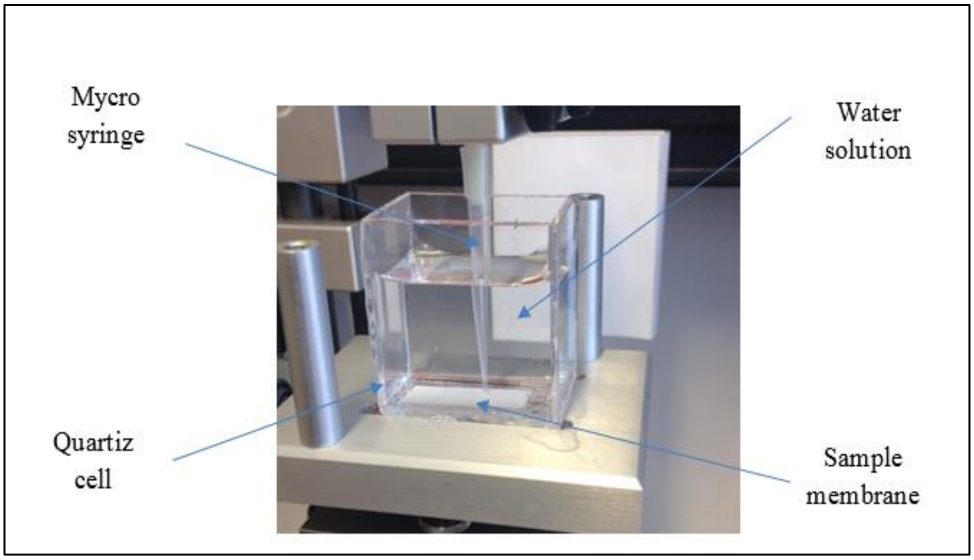


Figure 20: Image of Quartz cell containing aqueous solution, sample membrane and macro syringe

v. **Visualizing the drop image**: The live image of micro syringe and sessile droplet of chloroform immersed in water solution (Fig.21). The micro syringe, sessile drop and membrane surfaces focused by the camera to get a clear image.

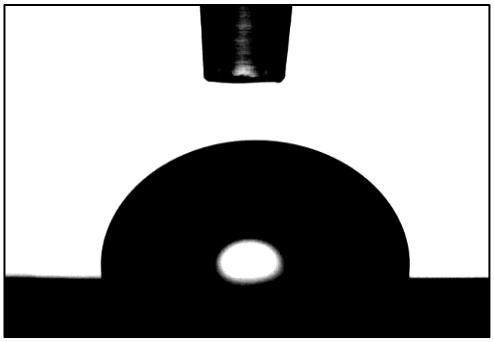


Figure 21: Live image of quartz cell making sessile droplet of chloroform over BN66A membrane surface.

i. Drop dispense: initially about 5µL liquid chloroform droplet was dispensed by lowering the micro syringe tip near to the surfaces of the membrane.
ii. The contact angle measurements were done after 3 to 5 minutes of deposition time and gradually increase the drop volume up to approximately 25µL while measuring the contact angle for each µL.
iii. The advancing contact angle of the sessile drop was determined by measuring the contact angle for each µL of chloroform droplet increase (Fig.22).

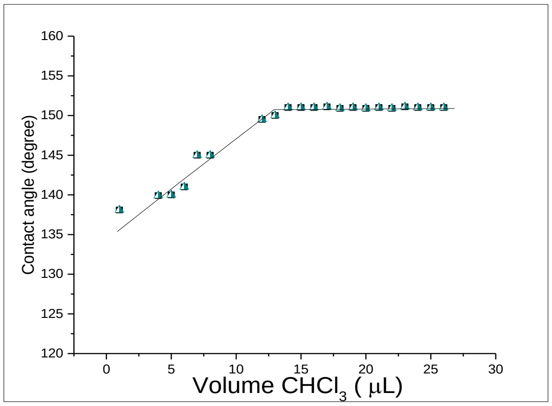


Figure 22: Advancing contact angle of chloroform droplet over the BN66A membrane surface immersed in water solution as a function of volume increase (µL) at room temperature after 3-5 min of drop deposition.

As shown in figure 22, the contact angle is independent on the drop size after approximately 12µL. Therefore, the average contact angle above the break line was taken for analysis.

The measurement was repeated at least three times by choosing a different location on the same surface. Contact angles of chloroform droplets in immersed solution were made at different aqueous solution. (i). in the presence of potassium chloride solution**.** The quartz cell is filled with a solution of 0.01M KCl. The pH of the solution was adjusted by adding drops 0.1MHCl and 0.1MNaOH through a pH range 2 to 12 with approximately 0.5 intervals. The contact angle of chloroform droplet was measured at each interval for each new sample membrane; (ii) in the presence cationic surfactant (CTAB) and Anionic surfactant (SDBS). The contact angle of chloroform on BN66A membranes was measured as a function of pH and at different concentrations (table 5 solution numbers 4 to 7) of CTAB and SDBS surfactants.

3.5 Surface modification of Polyoxymethylene (POM)

3.5.1 Chromic acid preparation

A solution of chromic acid was prepared by diluting 20 g of potassium dichromate into 300mL of sulfuric acid in one liter volumetric flask. The reaction between sulfuric acid and water is highly exothermic therefore care was taken. The reaction was done under a fume hood and by wearing eyeglass and glove for safety. First, 20 grams of potassium dichromate was added to one liter volumetric flask and dissolved with approximately 500 ml distilled water. Then, concentrated sulfuric acid is added with great care. The solution was allowed to cool down to room temperature and filled with distilled water up to the mark. From this stock solution, a series of five concentrations of chromic acid solutions were prepared and labeled as 1M, 2M, 3M, 4M and 5M according to their concentrations (tab.6).

Table 6: Standard solutions of chromic acid in water

Solution number	5.4M chromic acid (mL)	Water added (mL)	Final volume (mL)	Final chromic acid concentration (M)
1	9.3	40.7	50	1
2	18.5	31.5	50	2
3	27.7	22.3	50	3
4	37.0	13.0	50	4
5	46.3	3.7	50	5

3.5.2 POM membrane modification

Several Pieces of POM Plates were cut into dimensions approximately 2 x 4 cm. these pieces were taken for analysis. A total of six POM plates (Fig.23) was taken for analysis in which five were treated with chromic acid at different concentrations (Fig.24). The plates were immediately washed with acetone followed by rinsing with distilled water and dried at room temperature before contact angle measurement.

Figure 23: Image of POM place used for modification

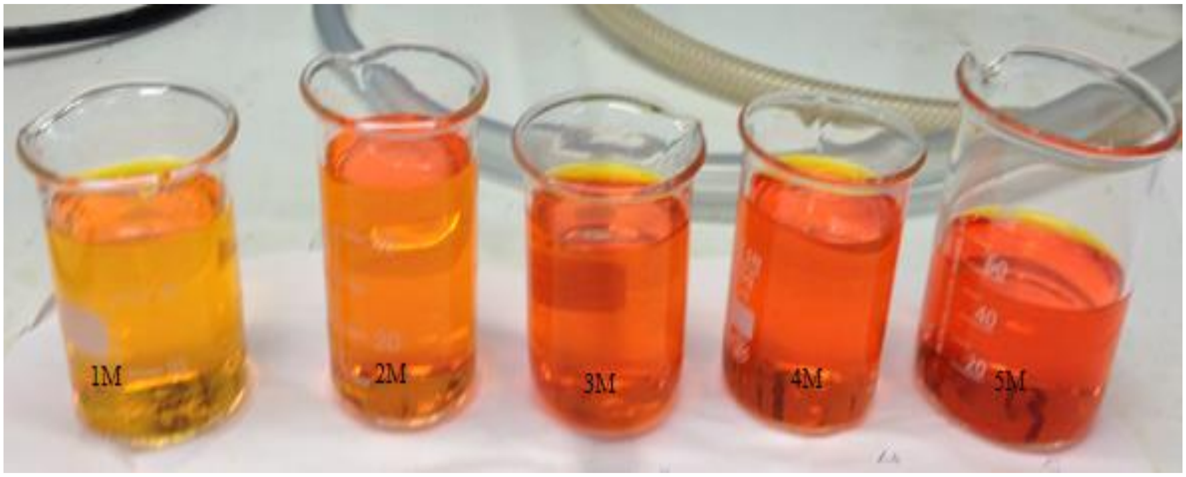


Figure 24: Image of different concentration of chromic acid where POM Plates were treated

3.5.3 POM surface characterization by immersed contact angle method

Treated POM plates were washed with acetone and rinsed with distilled water to remove impurities and chromic acid from the surface. Then they dried at room temperature before contact angle measurement. The contact angle of chloroform droplet immersed in distilled water of pH 6.5 on each POM surface was measured. The measurement was repeated at different time intervals at 1, 10, and 60 minutes and at a longer time after 13 hours. In addition the contact angle of the untreated POM surface was also measured for comparison. The contact angle was measured at least in three different spots of each sample to get reproducible data.

3.5.4 Effect of pH on treated POM surfaces

After treatment, it is expected that the POM surface has acidic functional groups. In order to characterize acidic property of treated POM membranes, the contact angle of sessile droplets of chloroform droplet was measured in immersed solution containing 0.01MKCl as a function of pH. POM Plate which was treated with 4M chromic acid was taken for contact angle measurement after washing with acetone and distilled water. The contact angle was measured across the pH range 2 to 12 within the intervals approximately of 0.5.

3.5.5 The effect of cationic surfactant on treated POM membrane surfaces

To determine the influence of surfactant solution on treated POM Surface, CTAB solution was used. The contact angle of chloroform on treated 5M chromic acid POM (5M) surface in immersed 0.413mM CTAB solution was measured as a function of pH. The pH ranges were between 2 and 12 with an interval of 0.5 the same in all experiments.

3.6 Synthesis membrane by photo polymerization

3.6.1 Acidic membrane

In this experiment amphoteric membranes were synthesized through Photo-polymerization reaction. Methyl methacrylate (MMA) was used as monomer; Di (Ethylene glycol) di acrylate (DEGDMA) used as cross linker. Functional monomers Methacrylic acid (MAA) as a anionic monomer and 2-(N, N-Dimethyl amino) ethyl methacrylate (DMAEMA) as a cationic were used for functionalization. Photo polymerization initiator camphor Quinone (CQ) together with co-initiator tertiary amine 1, 2, 2, 6, 6-Pentamethylpiperidine (PMPIP) was used. All the above chemicals were used as received without any purification. Methyl methacrylate (MMA) and methacrylic acid (MAA) were purified by passing through alumina oxide column three times in order to remove the inhibitor mono methyl ether hydroquinone (MEHQ) before use. Otherwise, all chemicals were used as received. Table 7 shows, chemical compositions of monomers and initiators taken for the photo polymerization of acidic membrane.

Table 7: Composition of monomers and initiators used for preparation of anionic membrane

Name	Mass(gram)	Composition (%)
MMA	12.95	70.88
MAA	2.16	11.79
DEGDA	2.23	12.17
CQ	0. 28	3.82
PMPIP	0. 70	2.75

All the above chemicals were mixed in a 50ml glass bottle vial covered with aluminum foil to prevent premature polymerization. The solution was stirred for one hour in order to get the homogenous solution and was kept under nitrogen flow for another one hour to remove dissolved oxygen which is inhibitor for the photochemical reaction. Approximately 10ml of the mixture was taken and poured into a petri dish with approximately 1 to 2mm thickness. This solution was irradiated with Philips 500 Watt lamp (Fig.25) at a distance of approximately 5 to 10 cm from the source. It took about 5 minutes to nearly complete the polymerization. The product was cooled to room temperature before it was washed with acetone and distilled water for removing unreacted monomers.

3.6.2 Amphoteric membrane

The chemicals listed under table, with the addition of cationic functional monomer DMAEMA were used for the preparation of amphoteric membrane as given in table 8.

Table 8: Composition of monomers and initiators used for preparation of amphoteric membranes

Name	mass (gram)	Composition (%)
MMA	16.70	68.23
MAA	2.50	10.22
DMAEMA	0.70	2.86
DEGDA	3.70	15.1
CQ	0.25	1.02
PMPIP	0.62	2.53

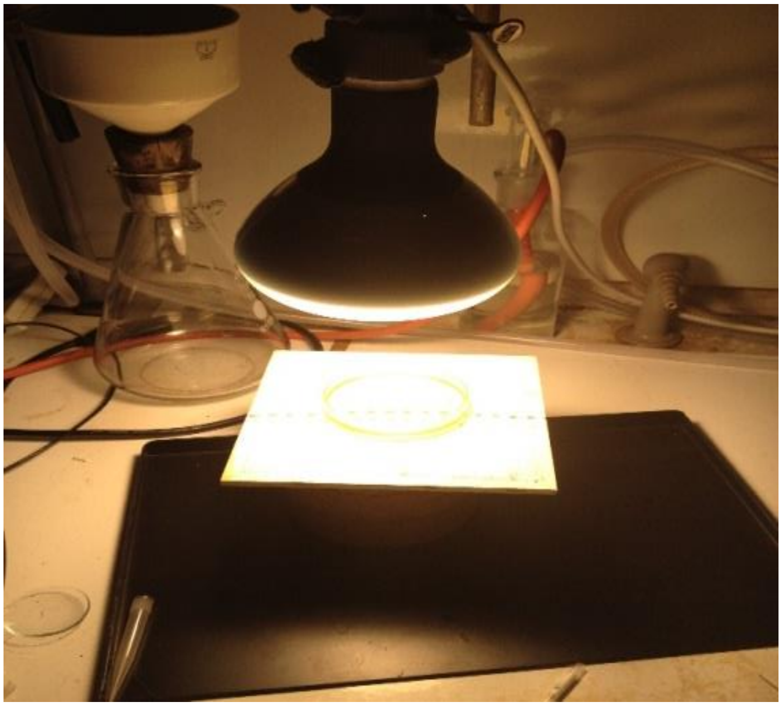


Figure 25: Philips lamp irradiating sample mixture

The rate of photo polymerization for preparation of amphoteric membranes is much slower than for the synthesis of acidic membranes. It took approximately 25 minutes to get a well polymerized amphoteric membrane.

3.6.3 Influence of pH and surfactant on synthesized membrane

After the membranes were polymerized, the products were cooled to room temperature. The membranes were soaked in acetone for six hours and to remove unreacted monomers and initiator, and washed with distilled water and dried at room temperature.

The acid-base, hydrophilicity and the interaction with ionic surfactant of the photo polymerized membrane were characterized by measurement of chloroform contact angle in immersed aqueous solution. The synthesized amphoteric membranes were characterized by contact angle titrating methods in the immersion aqueous solution of pH range 2 to 12 and in the presence of 0.413mM CTAB and 0.19mM SDBS surfactant solutions. The synthesized acidic membrane experiment was carried out at different pH and 0.413mM CTAB surfactant solution.

3.7 Surface characterization by scanning electron microscopy (SEM)

Scanning electron microscope (SEM) model FEI Quanta 200 FEG-ESEM was used to see the detail structural topography of membranes. Surface imaging using SEM is highly affected by the presence of impurities on the surface. Therefore, specimen of BN66A, treated POM and lab-made acidic and amphoteric membranes were washed with acetone, followed by distilled water and finally dried at room temperature before SEM Images were taken. The morphology of membranes was observed using the standard operating procedure of SEM.

4. RESULTS AND DISCUSSION

4.1 Measurement of Critical micelle concentration (CMC)

In order to study the effect of surfactant adsorption on surfaces, current CMC of surfactant should be determined before analysis. Many researches show that the interaction between ionic surfactant and charged membrane surface is highly dependent on several factors. These factors are: concentration of surfactant molecules in the bulk solution [9], temperature [62] and the presence of electrolytes [49]. It must be noticed that the concentration level of surfactant should be well below the CMC so that the interaction between surfactant molecules can be negligible [9]. This helps to determine only the effect of surfactant molecules on the hydrophilic surface. Since all the experiments were carried out at room temperature, the effect temperature was considered negligible. Furthermore, the influence of electrolyte concentration is very low, as the surfactants were prepared using distilled water.

At very low surfactant concentration the interaction between surfactant molecules is insignificant. Water molecules have high surface tension (72mN/m) due to the high intermolecular force of hydrogen bond. As a result, the surface tension at low concentration surfactant is dominated by water molecules. As shown in section 3.4.2 the CMC of CTAB and SDBS was determined by surface tension measurement using the pendant drop method.

CTAB and SDBS have polar groups and non-polar group. At the surface of the pendant drop, the polar head of the surfactant molecules attracts with water molecules and the non-polar tail oriented to the air. As the concentration of CATB and SDBS increase, there will be more surfactant molecules on the surfaces replacing the water molecules. Further increase in concentration of surfactant molecules causes to decrease the surface tension. At a certain point, surfactant molecules start to form micelle and the surface tension becomes independent of the concentration. The CMC value of the surfactants is the intersection between the decline and the base line of minimum surface tension [66].

Figures 26 and 27 represent the variation of surface tension versus log concentration of CTAB and SDBS surfactants respectively. The results of surface tension versus log Concentration graph showed a decreasing in surface tension with negative slope until it reaches the minimum value of 10mN/m for CTAB and 2mN/m for SDBS. This region is the concentration below the CMC.

After CMC the surface tension remains almost constant. Due to the aggregate formation, the activity of the surfactant molecules is restricted. This, in turn, causes the surface tension to remain independent of the surfactant concentration.

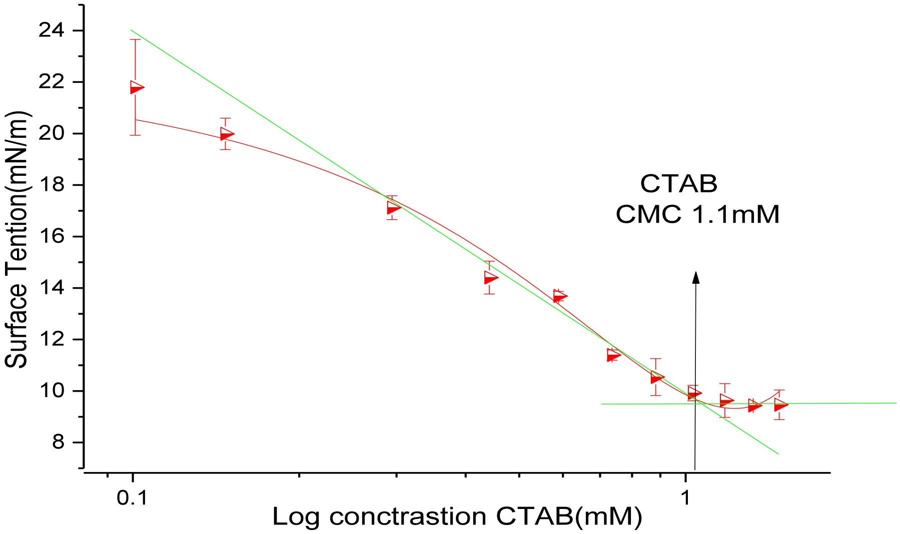


Figure 26: Surface tension of CTAB as a function of concentration diluted in distilled water at room temperature (23^{o}C) using the pendant drop method.

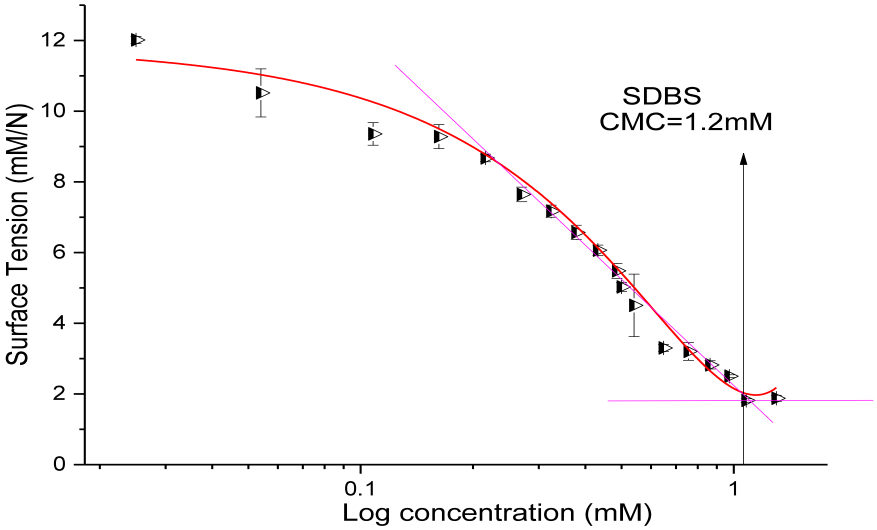


Figure 27: Surface tension versus SDBS concentration diluted in distilled water at room temperature (23^{o}C).

From the figures 26 and 27 the values of CMC for CTAB and SDBS is about 1.10 and 1.21mN/m respectively. These values indicate there is consistent with results obtained by others as shown in table 9.

Table 9: Comparison of CMC values of this work with others at room temperature

Surfactant	CMC value (mM)	Method	reference
CTAB	1.01	Conductivity	[79]
	1.10	Densitometry	[79]
	1.10	Surface tension	(Fig.26)
SDBS	1.23	Surface tension	[80]
	1.21	Surface tension	(Fig.27)

4.2 Measurement of contact angle

The experimental results from the amphoteric and acidic surfaces of different data point between measurements indicated that the methods is reproducible with maximal deviation values of 7 (appendix. C-F). These values are in agreement with values reported from literatures [81] or even less value with other literatures [82]. For hydrophilic surface, relatively large deviation up to 20 degree is expected [83].

4.2.1 Effect of pH on BN66A membrane

The pH and the ionic strength should be controlled when characterizing of materials in aqueous solution. The importance of working in 0.01MKCl solution is to get constant ionic strength. When there are changes in both pH and activity coefficients, there will be change in the ratio of acids and their conjugated bases. This, in turn, changes the reaction kinetics and equilibrium leads to irreproducible in experimental results [84].

The contact angles of chloroform droplet on the BN66A membrane surface versus titration graph is given in figure 29. The graph shows that the membrane surface remains hydrophilic (less than 90) across the pH with average contact angle of 27±10. However, the results, as presented in the figure 29, indicate that the degree of hydrophilicity changes throughout the pH range. This might be due to the acid-base interaction. Acid-base interaction arises from the reaction of acid sites of the membranes when it interacts with basic site of the bulk solution. The basic sites of the surface interact with acidic sites of the bulk solution at different rates [9]. Presence of ionisable and high energy groups of amine (-NH_2) and carboxylic acid (-COOH) (Fig.28) on the surface of BN66A leads to hydrophilicity and acid/base characteristics (Fig.29).

The contact angle titration curve for this membrane is the combination of the acidic and basic functional groups of the surface. The curve for the acidic group (carboxylic acid) is independent of pH at low pH. It decreases as the pH increases. While contact angle titration curve for basic (amine) groups increase, the pH increases and become independent of pH [73].

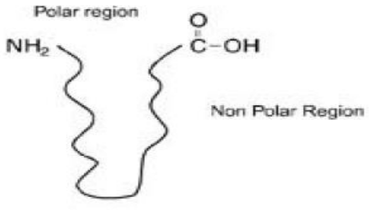


Figure 28: The possible structure of Nylon 6, 6 with amino and carboxylic acid terminal ends [85].

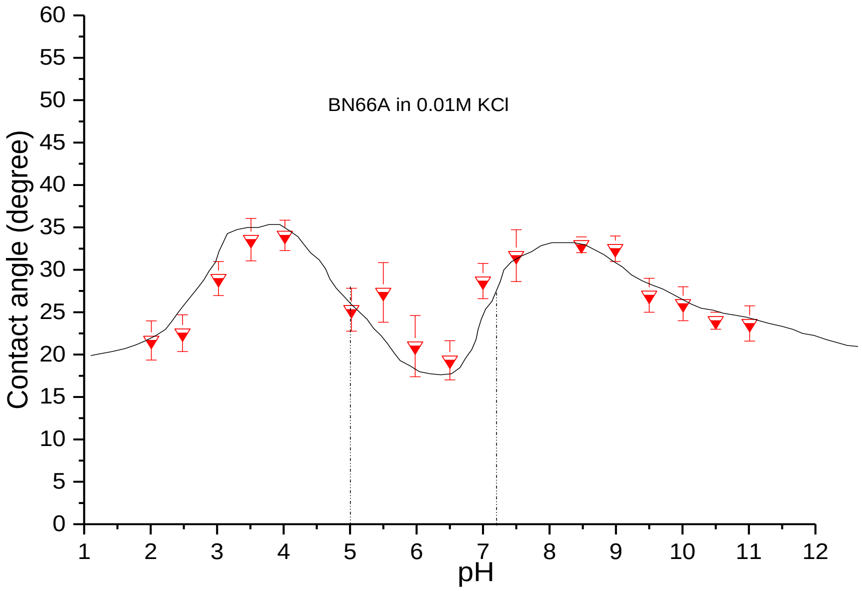


Figure 29: Advancing contact angles of chloroform droplets on BN66A immersed in water solution of 0.01M KCl as a function of pH after 3-5 min deposition time at room temperature 23^0C. The dashed lines indicate the value of pKa of surface carboxylic and amine group respectively

The constant angle of chloroform on BN66A surface below the Plateau pH 3 decreases from 35 to 18 degrees. In this pH range, there is no dissociation of carboxylic acid group due the absence of acid base reaction. The unionized carboxylic acid groups are surrounded by ammonium ions. As a result, the surface has high positive surface charge of ammonium ions. As pH becomes more acidic, the concentration of charged ammonium ions on the surface increases; this leads to decrease in contact angle or increases in wettability.

The low contact angle at around pH 6 refers to the isoelectric point (PI) value of the membrane. This is the point where the membrane exists in its highest hydrophilicity. At this pH value, the membrane has equal number of carboxylate ($-COO^-$) and ammonium ($-NH_3^+$) ions. In other words, the surface is in its highest zwitterions. Hence, the net charge on the membrane surface is zero. The pI value is within the expected pH range (6-7). This is an evidence that the experimental pI value is almost similar with value (6.5) given by the manufacturer [85]. The more hydrophilicity at around pI vales is therefore due to the presence of high negative and positive surface charges.

The decrement of the contact angles (Fig.29) from approximately pH values 3 to 6 indicates that the carboxylic acid group of the membrane is at its highest dissociation rate. At this range, half of the carboxylic acid group dissociates to form carboxylate ions. This curve has similarities with carboxylic acid titration curve obtained by others [73]. On the other hand, it can be explained that there is protonation of the amine group. Below pH 4, the hydrophilicity decreases with increasing pH. This is because the rate formation of carboxylate ions is more dominant than the rate formation of ammonium ions on the surface.

The dissociation constant pKa value of the acidic groups is determined from halfway between the contact angles of the highest and lowest values [73]. Therefore, as indicated by the vertical dashed line (Fig.29) it is observed that the estimated pKa value of carboxylic acid is at pH 5. On the same way the estimated dissociation constant for the amine group is around pH 7.3 as indicated by the dashed line (Fig.29).

The contact angle increases from about pH 6 to 8.5 (Fig.29) indicates more and more ammonium ions loss their hydrogen atom and become amine group. At this pH gradient, as the pH values increases, the hydrophilicity decreases. This is because the surface is dominated by the rate of the formation of ammonium ions than the formation of carboxylate ions. Above the plateau pH 9, the contact angles start to decrease. In this pH range, the formation of polar carboxylate (-COO-) ions is responsible for the increasing hydrophilicity of the surface. Most carboxylic acid groups are dissociated 100% at around pH 11[9]. In addition, the membranes may be subjected to formation of cavity or increase its porosity due to high basic solution. This may influence to increase the hydrophilicity of the membrane as it can be seen from the light microscopy image in appendix G-2.

4.2.2 Effect of SDBS solution on BN66A membrane

Figure 31 represents the titration curve of BN66A membrane. The contact angle decreases until it reached pH 4 at 0.19mM and pH 3 at 0.10mM SDBS concentrations and then becomes independent on pH solution. The adsorption of SDBS onto the surface is dependent on several factors: First, it is highly dependent on the surface net charge [60]. At low pH values, less than the pI value of the surface functional groups, the net charge is positive and above pI the overall charge of surface is negative. Since SDBS has a negatively sulfonate head, the adsorption mechanism is highly dependent by electrostatic interaction when the surface is positive charge[86].

There is a dramatic decrease in contact angle as the pH increases from pH 2 to 4 at 0.19mM, and from pH 2 to 3 at 0.10mM SDBS concentrations (Fig.31). The following conclusions can be given for the rapid decrease in contact angle:

(i) The adoption of negatively charged SDBS molecules is dependent on the surface charge. At very low pH value, most amine groups of the BN66A surface protonated to ammonium ions[9]. As a result SDBS ions are adsorbed on the surface in which the negative sulfonate heads of SDBS attached to the positive charge on BN66A surface amine groups the hydrophobic tail oriented to the bulk solutions (Fig.30). Thus, the contact angle becomes higher (Fig.32 left) and the surface becomes hydrophobic as more SDBS molecules are adsorbed on the surface [60, 86].

(ii) The hydrophobicity changes differently when the concentration of surfactant changes. This indicates that the effect of surfactant is not only dependent on the density of the positive amine group, but also dependent on the concentration of SDBS solution in the bulk solution[86].

(iii) The steep lines indicate that the density of the SDBS molecules adsorbed on the surface are not on the stages of forming monolayer. It will be a straight line when there is a formation of a monolayer layer at low pH[51]. This shows that the concentration of surfactant used is well below the CMC.

The contact angle remains almost constant and hydrophilic surface and above pH 4 in 0.19mM and 3 in 0.10mM SDBS solution. In this pH range, the effect of surfactant molecules on the hydrophilicity of the surface is not significant. The negatively charged SDBS may not get enough positive counter (ammonium) ions on the BN66A surface at pH> 4 in 0.19mM and pH >3 in 0.10mM SDBS. Therefore, low the contact angle between chloroform and the surface remain hydrophilic (Fig.32 right). However, the surface gets relatively more hydrophobic nature at higher SDBS concertation. The driving force for the adsorption of SDBS molecules is both electrostatic, until it reached pKa of the amine group and hydrophobic interactions. Relatively higher hydrophobicity at 0.19mM than at 0.01mM SDBS concentration is the result of more

SDBS molecules adsorb onto the surface to some extent at higher concentrations than at lower concentration [15].

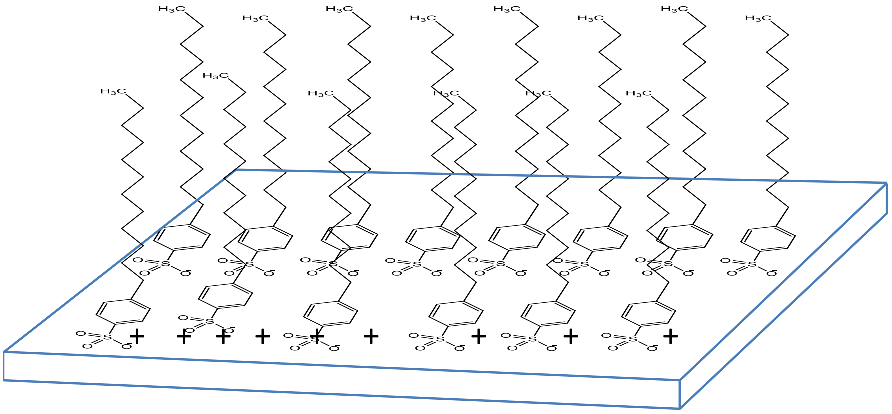


Figure 30: Schematic diagram of SDBS configuration on positively charged surface at low pH[15]

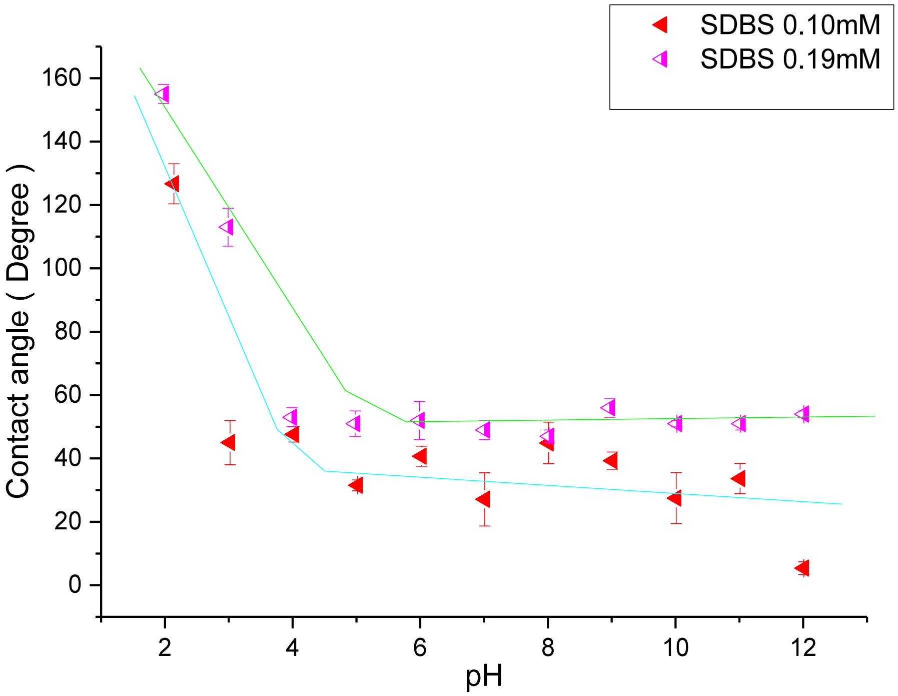


Figure 31: Advancing contact angle of chloroform droplet over BN66A membrane as a function of pH in anionic surfactant (SDBS) concentration at 0.10mMmM and 0.19mM of SDBS solution 3-5 min deposition time at room temperature 23^{o}C.

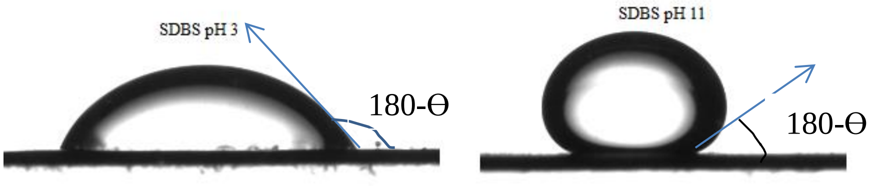


Figure 32: Images of chloroform droplet on BN66A membrane immersed in 0.19mM solution of SDBS at pH 3 and 11 after 3-5 minutes deposition time. At pH=3 the membrane surface is positive and the surfactant has negative charged: at pH=11 the surface and the surfactant has the same charge.

The titration curve also gives further evidence for the dissociation constant of the acidic groups [9]. However, the curve breaks at pH 3 and 4 in the presence of 0.10 and 0.19mM SDBS solutions respectively. This indicates that the presence of relatively higher surfactant concentration provides more chance of determine the pKa value.

4.2.3 Effect of CTAB solution on BN66A membranes

The opposite trend was observed when anionic SDBS surfactant was replaced by cationic CTAB surfactant. The curve has similar style with the contact angle titration curve obtained on the acidic membrane surface[9]. In the presence of 0.413mM CTAB, Contact angle of chloroform droplet remains constant until it reaches pH 5 and then increases with positive slop after pH 10 (Fig. 33). Above pI value, surface net charge is negative and the interaction between the surfactant molecules and the surface is dominated by electrostatic interaction leads to the more hydrophobic interface[15].

As expected, the influence of surfactant at low pH value remained unchanged. This shows that there is week adsorption due to lack of ionized acidic group. As the membrane goes to more basic solution, more and more carboxylic acid are ionized as a result more CTAB molecules are adsorbed. The concentration of CTAB molecules on the surface increase as pH increase leads to high contact angle (Fig.33) or high hydrophobic surface. Whereas, the constant angle remains almost constant when the CTAB diluted ten times (0.0413mM). This shows that the presence of low surfactant concentration has no significant effect on the surface hydrophilicity across the pH range even at high pH when surface ionized to highly negative charged.

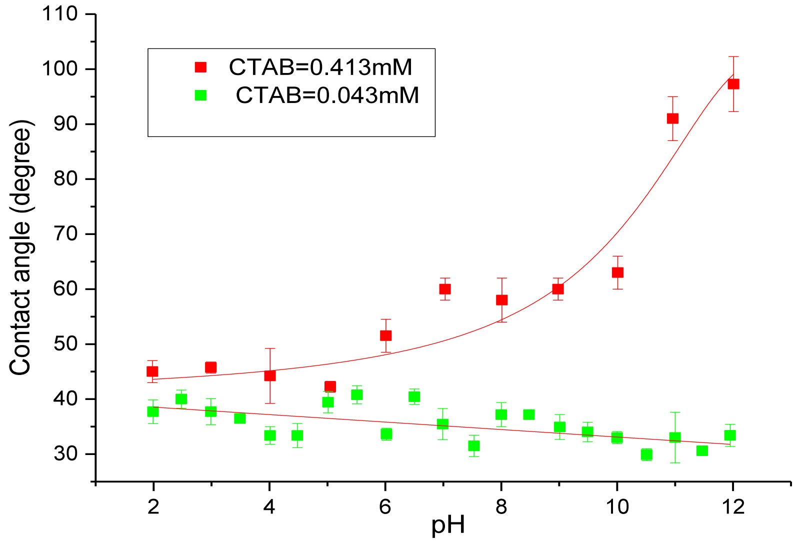


Figure 33: Advancing contact angle of chloroform droplet over BN66A surface as a function of pH in the presence of cationic surfactant (CTAB) at concentration at 0.415mM and 0.043mM of CTAB solution after 3-5 deposition time at room temperature 23^{o}C.

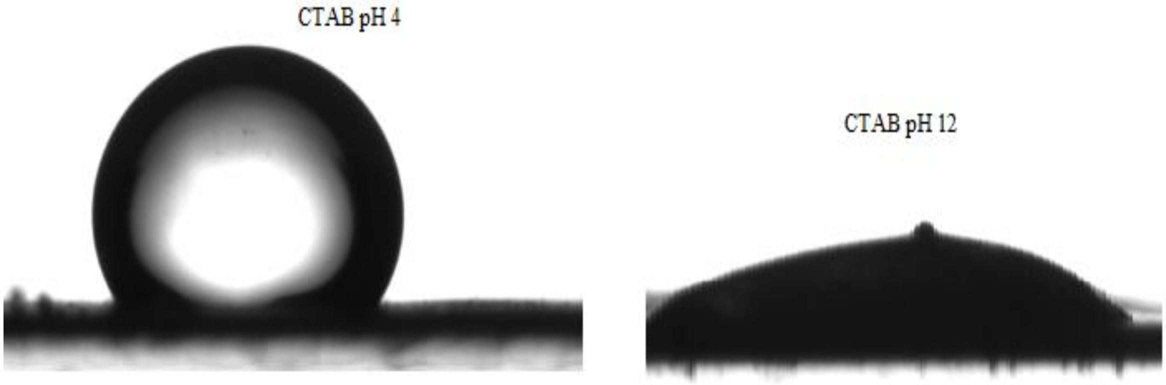


Figure 34: Images of chloroform droplet on BN66A membrane immersed in CTAB surfactant solution (0.415mM) at pH 4 hydrophilic the surface and at pH 12 hydrophobic surface at room temperature after 3-5 minutes deposition time.

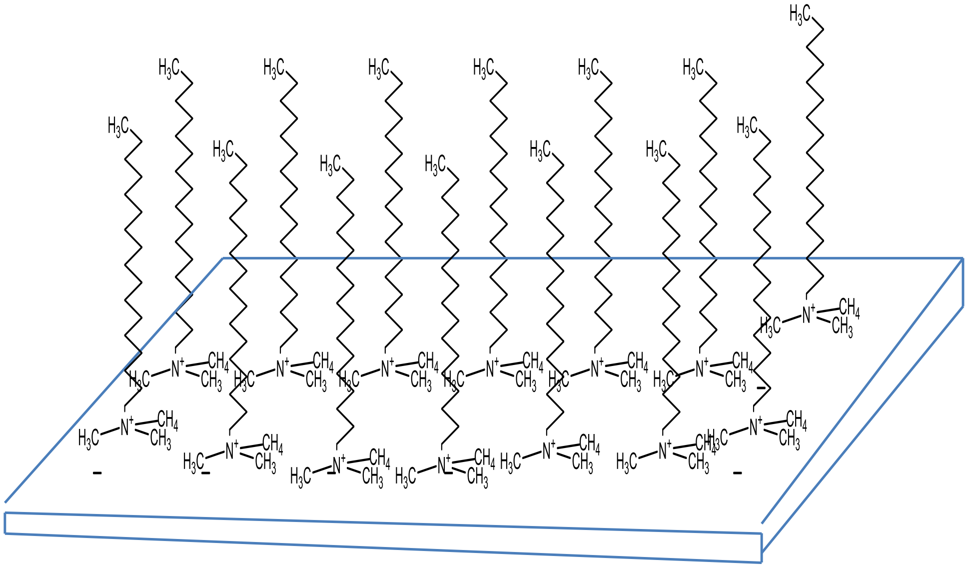


Figure 35: Schematic diagram of CTAB configuration on negatively charged surface at high pH

Unlike in the presence of SDBS, the contact angle begins to increase after the approximately above the pI value (Fig.33). This may indicate that the concentration of CTAB was higher than SDBS with respect to CMC of each surfactant. This illustrates, the presence of relatively higher concentration of surfactant has more chance of interacting with the acidic groups even at their early stage of dissociation. Furthermore, as the pH of the medium increase, the adsorption positively charged CTAB molecules increases. This leads to increase high concentration of surface on the surface as a function of pH. The high hydrophobicity (Fig.33 right) at high pH indicates that the surface has high concentration of acidic group. Most surface carboxylic groups dissociates 100% at around pH 11[9]. As a result more cationic CTAB surfactants are adsorbed at the surface electrostatically (Fig.35).

4.3 Modification of POM Surface

4.3.1 Effect of chromic acid solution on POM surface

The treated POM surfaces did not show any visible changes, but the chloroform contact angles of the surfaces gradually decreased as a function of time and concentration (Fig.36). The decrease in the contact angles (increase in hydrophilicity) with respect to concentration and time may be due to the formation of polar functionalities as a result of treatment. The wet chemical treatment of the surface produces functional groups such as carboxylic acid, formaldehyde, formic acid ketone, ether, etc. [36]. The contact angle decreases rapidly at the beginning and then decreasing linearly with negative slop with time and concentration. This suggests a desired level of hydrophilicity on the POM surface can be obtained by controlling the concentration of the acid and time of treatment. The hydrophilicity improvement is the result formation of new functional groups. The creation polar groups may lead to the hydrophilicity improvement. The hydrophilicity increase is directly proportional to: (i) time of treatment, i.e. the reaction between the acid and the surface takes time for the formation new acidic groups on the surface: (ii) The acidic functionality of POM surface increase as the concentration of the acid increase increases.

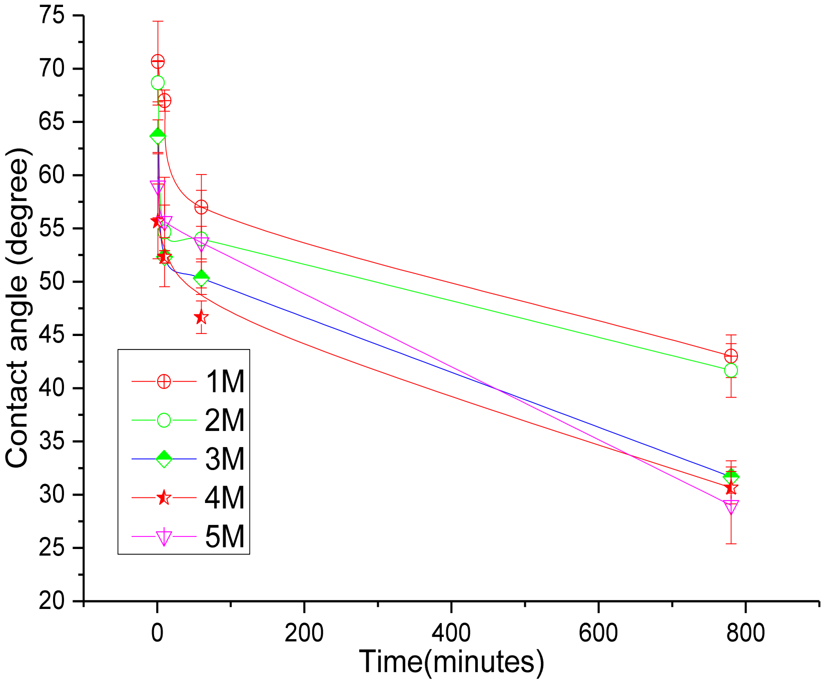


Figure 36: Advancing contact angle of chloroform droplet on POM surface immersed in aqueous solution as function of time of treatment and 3-5 min deposition time at room temperature 23^{o}C.

The effect of concentration and time becomes more visible after about ten minutes treatment. High hydrophilicity is observed at higher concentration, especially at 3, 4 and 5M solution than at 1 and 2M chromic acid solution. However, the effect of concentration becomes insignificant as a function of time.

Table 10: Contact angle of chloroform droplet on POM surfaces at different conditions at pH 6.5

Sample name	Average Contact angle $^o\Theta$ in air	Sample name	Average Contact angle Θ in water solution after 13Hours
Untreated	68±3	After treated (4M)	31±3
After treated (4M)	~0	After treated (5M)	29±2

Table 10 summarizes the changes in hydrophilicity of POM surfaces before and after treatment with chronic acid solution. The average contact angle values obtained after treatment with 4M and 5M are almost similar with 31 and 29 degree respectively. This indicates that the longer the time of treatment the better the wettability of the surfaces become. Since chromic acid is highly oxidizing agent, even at low concentration can be effective and economical for surface treatment. Dramatic change in contact angle in air from 68 to 0 degree clearly shows POM the surface has been effectively functionalized [31].

4.3.2 Effect of pH on treated POM surface

After POM was treated, the presence of anionic functionalities was tested by chloroform contact angle on the surface as a function of pH. Therefore, the contact angle of POM surface, which was treated under (5 M) chromic acid solution was measured as a function of pH (Fig.37). The graph shows, the contact angle of chloroform droplet over treated membrane surface is less than 90^0 with average contact angle 34±8 degree (the surface is hydrophilic) throughout the pH gradient. The peak at about pH 5 has similarity with titration of polyethylene membrane having functionalized with carboxylic acid and ketone active layer [87]. Therefore, the treated POM surface may have carboxylic acid and ketone as predominant dominant anionic functional groups. The contact angle decreases slightly above pH 5, however, the contact angle below pH 5 contradicts with the theory. It should have been independent on pH or a slight increase until pH5 [73]. This may arise from experimental error or there may be chromate or sulfonate anion groups remained attached on it [48].

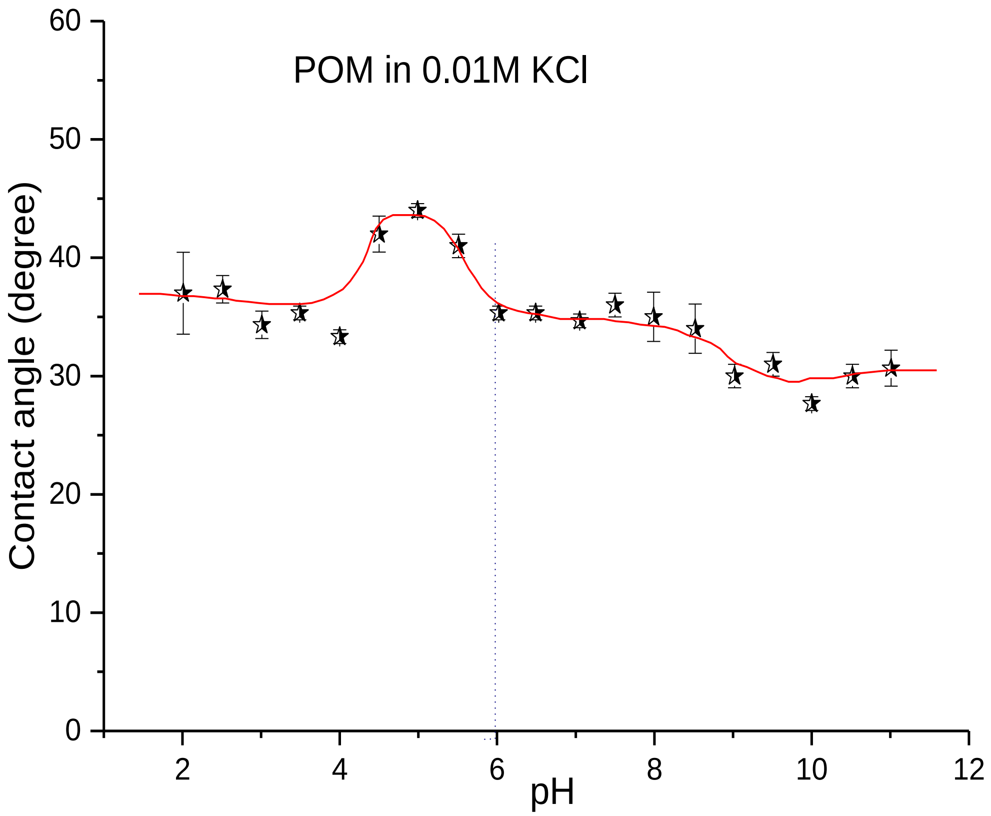


Figure 37: Advancing contact angle of chloroform droplet as a function of pH in of 0.01KCl solution at room temperature 23 ^{o}C after 3-5 min deposition time. The dashed lines indicate the value of pKa of acidic groups.

The contact angle decreased with relatively high negative slop between pH 5 and 6.3 and the estimated pKa value of the acidic group is will be at about pH 6 indicated by the dashed line. The relative low contact angle above pH value of 9 indicates the surface has some acidic groups[35]. However, the decrease in contact angle after pH 5 is not significant. This may explain the concentration of generated carboxylic and ketone functionalized on the surface are very low.

4.3.3 Effect of CTAB on POM surface

The contact angle of chloroform on treated POM surface increases from 20 to up to 33 degrees with increasing pH solution (2 to 11) in the presence of 0.413mMCATB solution (Fig. 38). The increase in contact angle is additional conformation in the presence of anionic groups after treatment. As the pH of the medium increase, the acidic groups are subjected to more basic solution resulting in ionization to negatively charged surface. As more and more acidic groups are ionized across the pH gradient, more positively charges CTAB molecules are adsorbed on negatively charge POM surface. This resulted in increasing contact angle as more CTAB surfactant molecules adsorbed in such a way that the alkyl chain away from the POM surface leads to more hydrophobic interface between the adsorbed CTAB and the bulk solution[9].

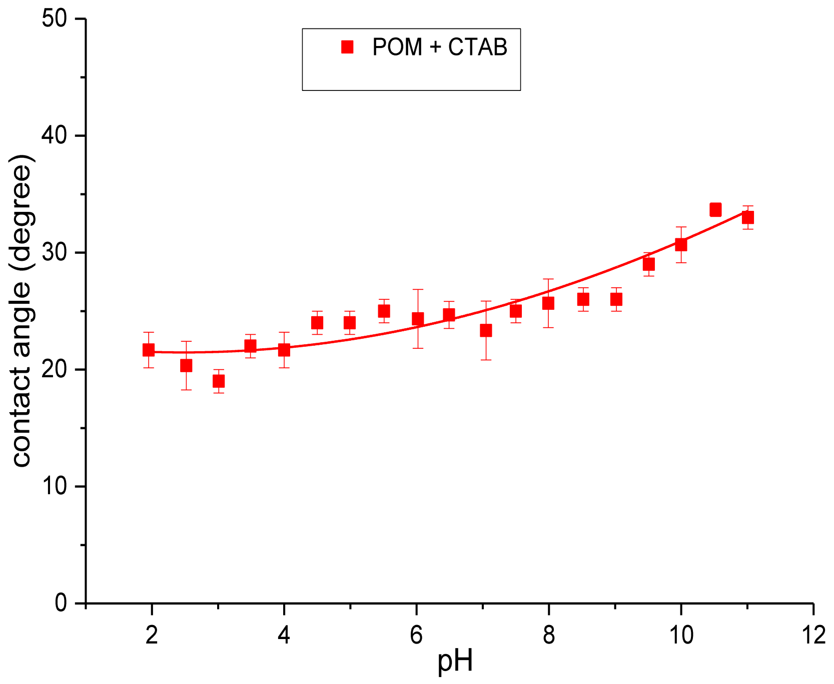


Figure 38: Advancing contact angle of chloroform droplet over treated POM surface immersed in CTAB (0.413mM) solution as a function of pH at room temperature after 3-5min deposition time.

The contact angle still remains in the hydrophilic surface with a maximum contact angle of 35 degrees, unlike the BN66A surface (Fig.33) even though; both are immersed in the same CTAB concentration. This indicates BN66A has more dissociable acidic groups than the treated POM surface. In addition, the low porosity of POM surface than BN66A surface may lead to low adsorption. Furthermore, the hydrophilicity only slightly increases above pH 5 as a function of pH (Fig.38). Therefore, there is clear indication why the hydrophilicity change in the presence of CTAB surfactant does not significantly. That means, the adsorption of ionic surfactants is not dependent only the concentration in the bulk solution but also dependent on concentration and counter ions on the surface [49].

4.4 Synthesis of membranes by photo polymerization reaction

The polymerization of monomers methyl methacrylate (MMA) using Camphorquinone/ amine initiator using di (ethylene glycol) diacrylate (DEGDA) as a cross linker was successfully polymerized by photo induced radical polymerization.

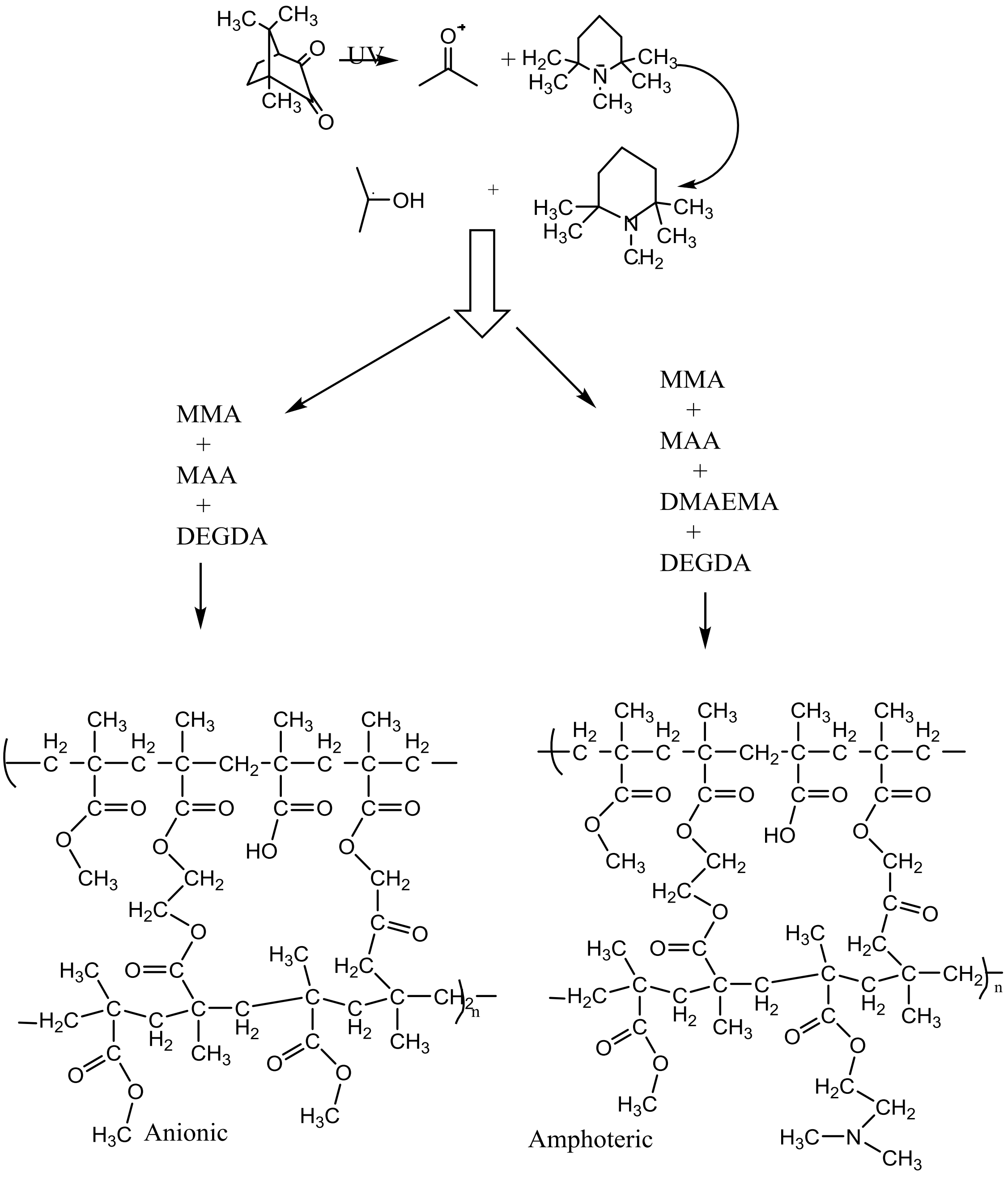


Figure 39: Reaction mechanism of photo induced radical polymerization of MMA, MAA, DMAEMA and DEGDA using CQ/amine Initiator

The functionalization was made by adding Methacrylic acid (MAA) to get an acidic site on the surface and both methacrylic acid (MAA) and 2-(N,N-Dimethyl amino) ethyl methacrylate (DMAEMA) to get amphoteric membranes surface. The reaction mechanism and the probable structure of the membranes are illustrated in figure 39. The membranes were stable during process of washing with acetone and distilled water. The compositions of the initiator and co-initiator were taken about 1% for CQ and for the co-initiator almost double the amount of initiator CQ as described in other literatures [37, 39].

4.4.1 Limitation of photo polymerization

There are several factors which affect the photo polymerization process and overall final structure the membrane[38]. The rate of monomer conversion, temperature, distance from the UV source, thickness of sample taken, composition of cross linker[88], the amount of initiator and co-initiator affects the final structural, morphological and molecular weight of the membrane[39]. During this experiment, the rare of conversion of monomers and was not monitored. However, the formations of polymerized solid membrane were dependent on of irradiation time, sample thickness and distance from the lamp. As the sample getting closer and closer to the UV lamp rapid polymerization reaction, more bubble and high temperature of the sample was observed. It was quite difficult to optimize the irradiation time, system temperature and the suitable distance from the UV source. However, at around 10 to 15 CM from the lamp, well polymerized membranes were obtained without bubble formation. The irradiation time taken for polymerization of acidic membranes was around 5 minutes, whereas for amphoteric membrane takes longer time around 25 minutes. This shows the basic functional monomer DMAEMA has an inhibitory effect on the photo polymerization reaction. At high DMAEMA monomer composition, makes it very difficult to polymerize the mixture even after long time. Appendix G-1 figure (b) illustrates the addition of 3.5% of DMAEMA functional monomer after one hour of irradiation time.

4.4.2 Effect of pH on lab-made anionic membrane

The presence of anionic and/or basic functional groups on the membrane surfaces can be by measuring contact angle as a function of pH. Therefore, the photo polymerized acidic and amphoteric membranes were characterized by measuring the contact angle of chloroform sessile droplet immersed in aqueous solution as a function of pH. In addition the influence of cationic surfactant CTAB on the acid membrane and the effect of anionic SDBS and cationic CTAB solution were also determined. The synthesized anionic membrane prepared is hydrophilic with average contact angle 26±6 degree (fig.40). The membrane`s high hydrophilic property may be due to the presence of anionic carboxylic acid groups on the surface membranes. The contact angle titration curve decreases as pH increases above pH 4.5 this curve has similarity with other carboxylic acid surface contact angle anionic titration curves[73]. At low pH, the contact angle is independent of the pH change. However, the contact angle increases as the pH increase below pH 4.5 is not the characteristics of anionic surface [9, 73]. Since both the surface and bulk solution has acidic character (surface carboxylic acid groups are surrounded by hydrogen ions), the contact angle should have been constant until the carboxylic acid begins to ions (pH4.5). The deviation from the theoretical may due to several factors such as; (i) since the surface is surrounded by high acidic medium, the absorption of hydrogen ions can create a hydrophilic surface and hydrophilicity increase as acidic character increase; (ii) the membrane was photo polymerized is not stable under extreme pH; and (ii) this may be due to inefficiency of the cross linker or formation of low molecular weight due to immature termination reaction.

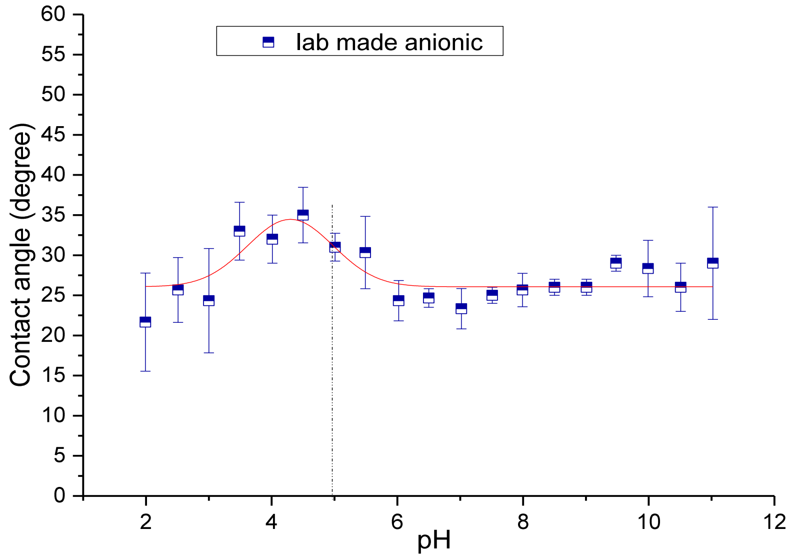


Figure 40: Advancing contact angle of chloroform droplet over lab-made anionic surface immersed in 0.01M KCl solution as a function of pH at room temperature after 3-5min deposition time. The dashed line indicates value pKa of acidic the group.

4.4.3 Effect of CTAB solution on lab–made anionic membrane

Figure 41 shows the result of contact angle as a functional of pH in the presence of 0.413mM CTAB solution. The graph shows that the contact angle increases from 25 to 108 degrees as the pH increase from 2 to 11 respectively. This result showed the membrane adsorption CTAB molecules based on the relative ionization of the acidic group on the resurface.

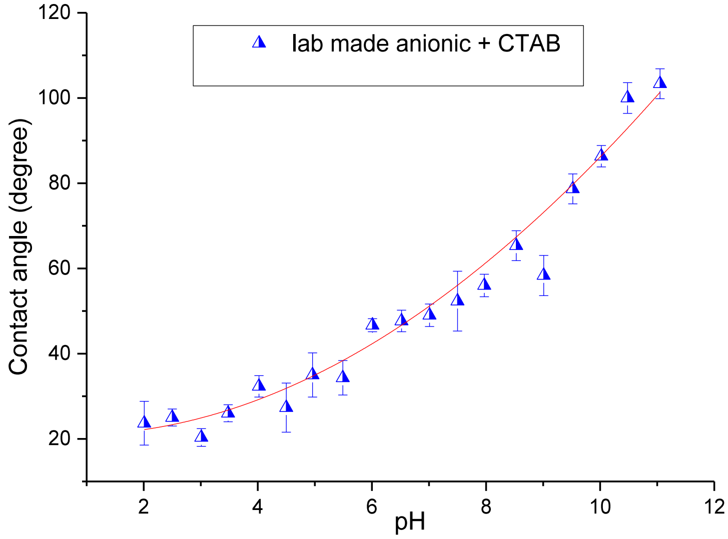


Figure 41 Advancing contact angle of chloroform droplet over lab-made anionic surface immersed in CTAB (0.413mM) solution as a function of pH at room temperature after 3-5min deposition time.

The hydrophilicity of the anionic membrane decrease as more cationic CTAB surfactant is adsorbed over a negatively charged membrane above the pKa value. At low pH, below the dissociation constant of Carboxylic acid the membranes the carboxylic acid groups are not ionized so that there is no electrostatic interaction between surfactant and the surface and therefore the membrane remains hydrophobic. But, as more negatively charged carboxylic acid groups are created due to the abstraction of hydrogen by the hydroxide ions, more and more carboxylate ($-COO^-$) ions are formed. High contact angle or hydrophobic interface at high pH is the result more CTAB molecules are adsorbed electrostatically between negative surface and positive heads of the surfactant.

4.4.4 Effect of pH on lab-made amphoteric membrane

Figure 42 is the result of contact angle of chloroform on lab-made amphoteric membranes immersed in aqueous solution as a function of pH. The graph has similarity with amphoteric BN66A membrane with high contact angle at around 5.8 and 8.5 indicated that the membrane has an acid/ base properties due to the carboxylic and amine functional groups added during the polymerization process.

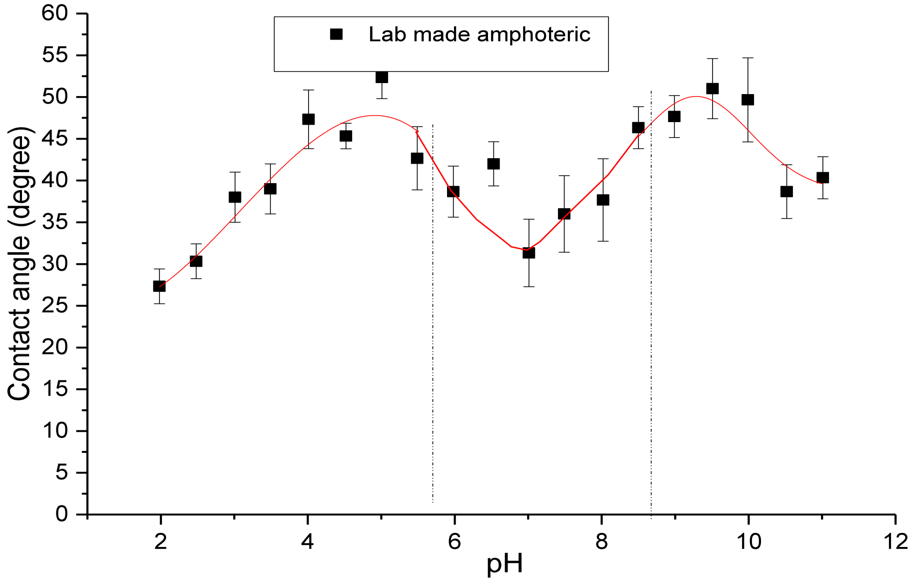


Figure 42: Advancing contact angle of chloroform droplet over lab-made amphoteric surface immersed in water as a function of pH at room temperature after 3-5min deposition time. The dashed line indicates value pKa of acidic and basic groups respectively.

4.4.5 Influence of cationic and anionic surfactants on the amphoteric membrane

Figure 43 shows the membrane surface changed from hydrophilic surface 20 degree at low pH to hydrophobic surface 118 degree. This indicates the membrane is negatively charged at high pH, which can adsorb positively charged surfactant molecules. But at low pH the membrane has positively charged group from ionization of an amine group to ammonium ions and therefore the interaction between positively charged surfactant and positively charged membranes creates a repulsion force and the effect of surfactant molecules is negligible. As a result the hydrophilicity remains an affected.

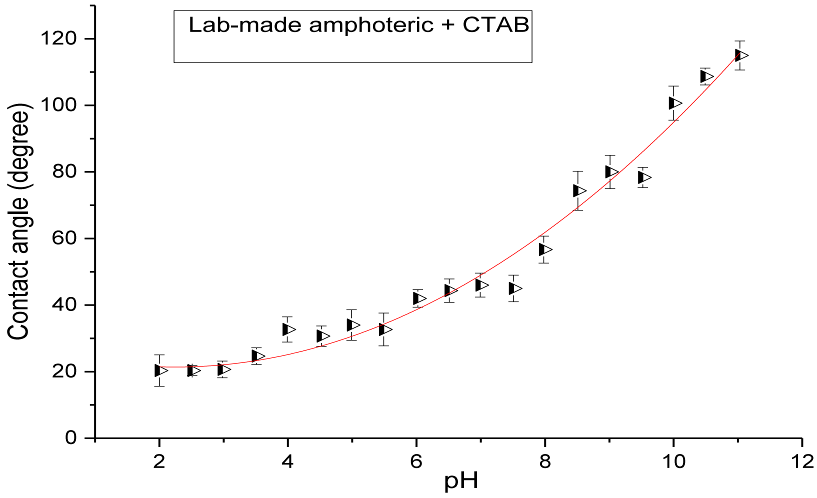


Figure 43: Advancing contact angle of chloroform droplet over lab-made amphoteric surface immersed in CTAB solution

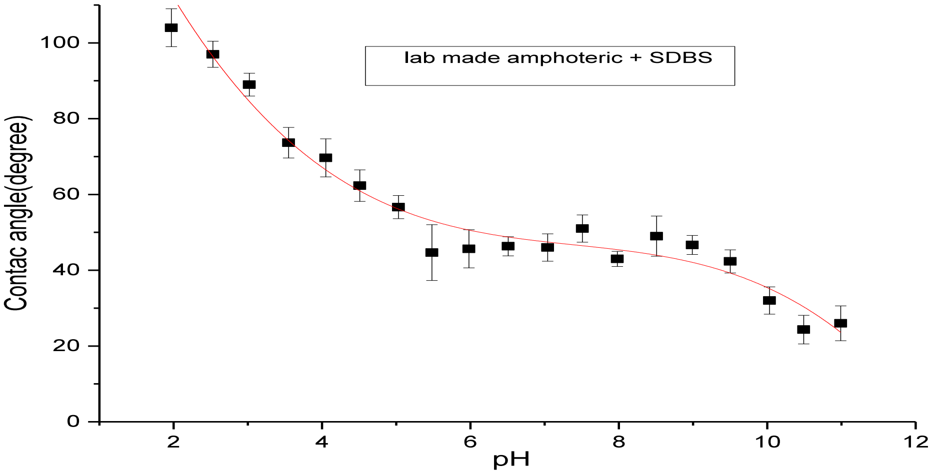


Figure 44: Advancing contact angle of chloroform as a function of pH SDBS solution at room temperature after 3-5min deposition time.

The opposite is true when the new amphoteric membrane is in anionic surfactant (SDBS) solution (Fig. 44). As discussed above, this membrane may have positively charged surface at low pH due to the amine group from DMAEMA monomer. So, the interaction between oppositely charged group anionic surfactant SDBS and cationic surface amine (-NH3$^+$) results in electrostatic attraction so that the non-polar tail of anionic oriented away from the surface to give high hydrophobic surface and high contact angle. However, the contact slightly decreases above pH 9 this indicates that the surface is unstable at this pH ranges, i.e. the high pH may damage surface leads to high hydrophilicity.

4.5 Characterization of surface morphology by SEM

The morphology of commercial membrane BN66A, POM and amphoteric and acidic membranes prepared by photo polymerization were examined using a high resolution scanning electron microscopy. SEM photographs of surface images of these membranes are shown in figure 45.

From figures 45-a and b, it can be seen that the BN66A has pores, uneven and rough surface. A change in the surface morphology was observed from the adoption of the SDBS surfactant solution (Fig. 45-b). The surface becomes smoother, more crystalline structure and less pores surface. This indicates that the adsorption of surfactant onto amphoteric BN66A membrane surface has an effect on surface structure and hydrophilicity. The increase in contact after the immersion in a surfactant solution (Fig.33) is, due to the change in pore shape and morphology of the surface[89].

SEM results of POM are shown in figures 45-c and 45-d the change in morphology is not visible after the surface was treated with chromic acid solution. Even though POM surface has high resistance to acid oxidation, under high concentration of chromic acid solution POM surface can be decomposed to their monomers [35]. However, the contact angle measurement indicates the hydrophilicity increases as a result of treatment without changing the physical structure of the surface (Fig.36). This may be due to the formation of negatively charged groups on the surface as a result of oxidation without significant change on surface chemical structure[30].

SEM micrographs of the photo polymerized membranes were also taken. The images of the acidic lab-made membrane as shown in figure 45-e, has a smooth and crystalline structure. On the other hand, the lab-made amphoteric membrane was melted upon heat from the electron beam. This shows that the membrane didn't cross linked well and additional conformation for the basic functional monomer (DMAEMA) inhibits the photo polymerization reaction.

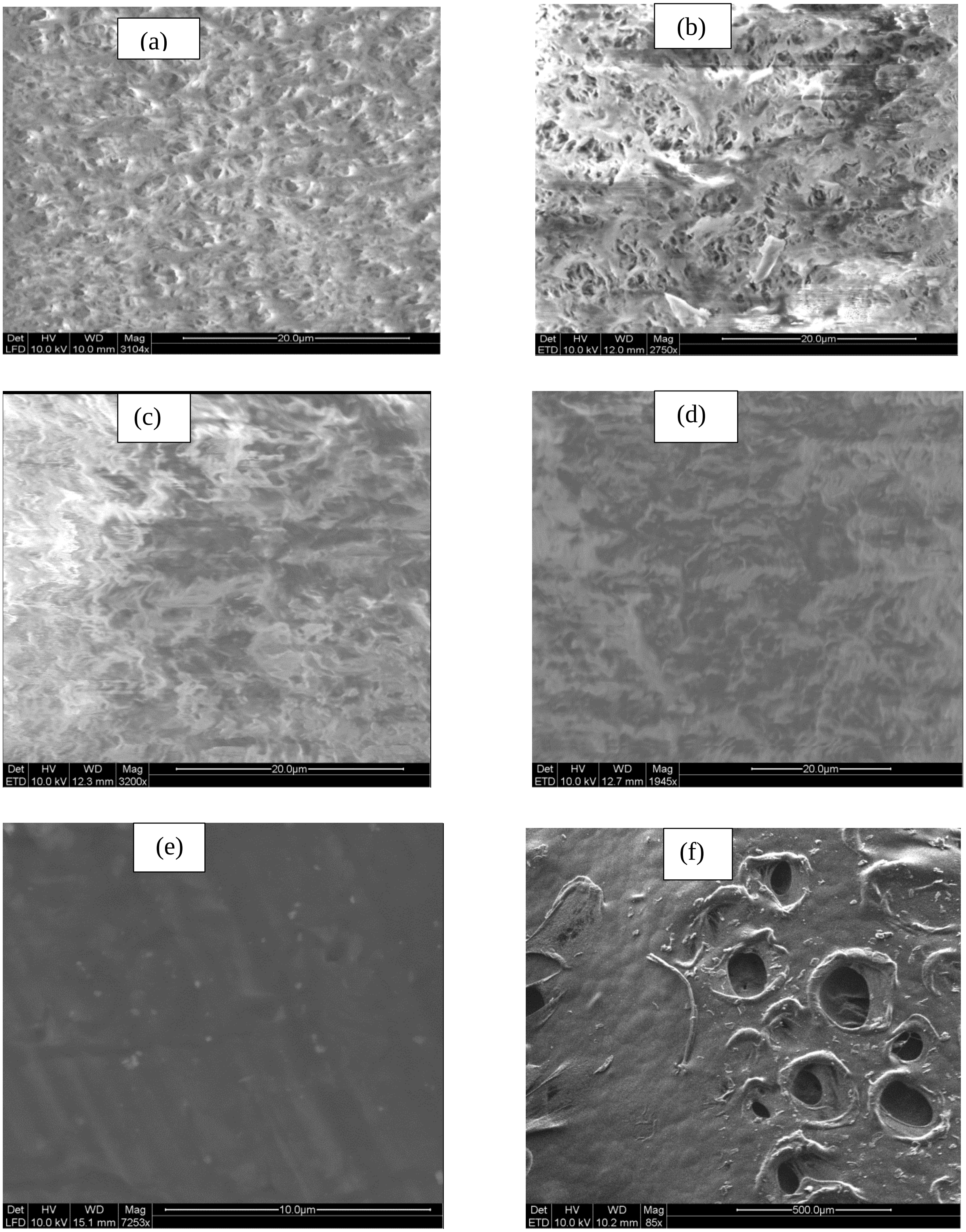


Figure 45: SEM pictures of (a) BN66A membrane immersion; (b) BN66A membrane after immersed in 0.413mM CTAB solution for 5 minutes at pH 9; (c) POM plate before modification; (d) POM plate after treatment in 4M chromic acid for 13 hours; (e) lab-made acidic membrane and (f) lab-made amphoteric membrane.

5. CONCLUSION AND RECOMMENDATION

5.1 Conclusion

Through the experiments done in this thesis, it can be determined that the hydrophilicity, acidity and basicity of surfaces can be determined using immersed contact angle method. Since the measurements were done under aqueous solutions, this helps to see the interactions between the surface and the bulk solution similar condition as practical applications. Generally, the main conclusions of this work can be drawn as follows:

I. By changing the pH of aqueous solution, it can be seen that:
   a. The surface charge on functional membranes can be controlled by changing pH.
   b. Hydrophilicity of the surfaces can be changed as a result of ionization of functional groups.
   c. As the pH increases, the net surface charge can go from positive to negative values.
   d. Degree of ionization of functional groups can be estimated from the contact angle titration curve.
   e. From the contact angle titration curve, the dissociation constant (pKa) and isoelectric point (pI) of the surface can be determined.

II. By adding ionic surfactant to the aqueous solution, it can be observed that:
   a. Membrane surfaces can be changed from hydrophilic to hydrophobic as a result of ionic surfactant adsorption.
   b. A change in contact angle upon adsorption of ionic surfactant is dependent on factors such as: - surface charge, pH, types of surfactant and its concentration in the bulk solution.

III. Hydrophilicity of polyoxymethylene can be improved through wet chemical reaction of chromic acid.

IV. Functionalized membrane surfaces can be synthesized from acrylate based monomers via camphorquinone/amine induced radical photo polymerization.

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5.2 Recommendation

This study tried to observe the nature of acidic and basic functional groups on amphoteric and acidic membrane surfaces as a function of pH and the interaction with surfactant molecules. However, this work still has limitations that need to be considered in further studies.

I. The contact angle measurement by immersion method provides surface chemical properties such as hydrophilicity and acid-based characteristics. However, since the titration curve was obtained by measurement, the pH followed by contact angle measurement for every single pH interval, this method is too tiresome for large sample analysis. Contact angle measurement using an automatic analytical technique may be required when there is a need for large sample analysis and more accuracy.
II. Contact angle experiments using immersed solution should be performed with great care and precision, as the hysteresis and impurities create large differences in the results.
III. BN66A membrane was very difficult to immerse to the bottom of the solution due to its low density and easy removed from the attached surface. This resulted in inaccuracy on the result and makes this method less relevance for thin surfaces.
IV. The photo polymerization was made by taking random composition of monomers. In order to synthesis well polymerized with known chemical structure and fixed functionalities for a specific applications. The compositions and reaction rate, well as other monitoring methods should be involved.

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Appendices

Appendix-A

Table A Type of distilled water used water

The following table describes the types distilled water used in the preparation of reagents according to the Millipore purification specifications

Parameter	Type II
Conductivity µS/cm at 25 °C	< 1.0
TOC(ppb)	< 50
Sodium (ppb)	< 5
Chloride (ppb)	< 5
Silica (ppb)	< 3
Bacteria (CFu/ml)	<100

Appendix-B

Table B-1

Results of surface tension versus concentration of SDBS solution at room temperature

Concentration of SDBS (mN/m)	Surface tension (mN/m) pendent drop 1	drop 2	drop 3	$\bar{x}$	σ
0.025	12.10	11.90	12.04	12.01	0.10
0.054	10.08	10.17	11.3	10.52	0.68
0.108	9.03	9.37	9.67	9.36	0.32
0.162	9.18	9.66	9.00	9.28	0.34
0.216	8.77	8.70	8.56	8.68	0.11
0.270	7.88	7.55	7.50	7.64	0.21
0.324	7.15	7.01	7.35	7.17	0.17
0.378	6.53	6.39	6.79	6.57	0.20
0.432	5.91	6.20	6.09	6.07	0.15
0.486	5.45	5.29	5.71	5.48	0.21
0.500	5.13	4.88	5.07	5.03	0.13
0.540	3.50	4.87	5.15	4.51	0.88
0.648	3.20	3.40	3.30	3.30	0.10
0.756	3.02	3.49	3.10	3.20	0.25
0.864	2.72	2.80	2.95	2.82	0.12
0.972	2.14	2.10	2.05	2.10	0.05
1.080	1.81	1.88	1.98	1.89	0.09
1.300	1.80	1.97	1.86	1.88	0.09

Table B-2

Results of surface tension versus concentration of CTAB solution in water at room temperature

Concentration of CTAB (mM)	Surface tension (mN/m) Pendent drop 1	drop 2	drop 3	$\bar{x}$	σ
0.101	22.6	19.67	23.12	21.80	1.86
0.147	19.57	20.69	19.7	19.99	0.61
0.2944	16.79	17.65	16.92	17.12	0.46
0.4416	14.88	14.66	13.68	14.41	0.64
0.5888	13.86	13.5	13.7	13.69	0.18
0.736	11.6	11.2	11.39	11.40	0.20
0.8832	11.36	10.02	10.25	10.54	0.72
1.0304	10.2	9.96	9.6	9.92	0.30
1.1776	9.15	9.37	10.38	9.63	0.66
1.3248	9.51	9.42	9.37	9.43	0.07
1.4772	9.86	8.81	9.73	9.47	0.57

Appendix C

Table C-1

Contact angle of chloroform on Blotting Nylon 6, 6 Type A amphoteric membrane as a function of pH in the presence of electrolyte 0.01KCl

pH	CA				$180-\bar{x}$	σ
2.01	161	157	157	158	22	2
2.48	159	155	158	157	23	2
3.02	149	151	153	151	29	2
3.51	149	144	146	146	34	3
4.02	145	148	145	146	34	2
5.02	152	155	157	155	25	3
5.50	153	149	156	153	27	4
5.98	157	152	159	156	24	4
6.50	158	162	162	161	19	2
7.00	149	152	153	151	29	2
7.50	151	149	145	148	32	3
8.48	148	146	147	147	33	1
8.99	146	148	149	148	32	2
9.50	155	153	151	153	27	2
10.01	154	156	152	154	26	2
10.50	157	155	156	156	24	1
11.01	154	157	158	156	24	2

Table C-2

Contact angle of chloroform on Blotting Nylon 6, 6 Type A amphoteric membrane as a function of pH in the presence of CTAB (0.43mM)

pH	$\bar{x}$	180- $\bar{x}$	σ
1.98	135	45	2
2.99	134	46	1
4.01	136	44	5
5.05	138	42	1
6.01	128	52	3
7.03	120	60	2
8.01	122	58	4
8.98	120	60	2
10.01	125	63	3
10.96	89	91	4
12.01	83	97	5

Table C-3

Contact angle of chloroform on Blotting Nylon 6, 6 Type A amphoteric membrane as a function of pH in the presence of SDBS (0.19mM)

pH	CA	180- $\bar{x}$	σ
1.98	25	155	3
2.99	67	113	6
3.99	127	53	3
4.98	129	51	4
5.99	128	52	6
7.01	131	49	3
8.02	133	47	2
8.97	124	56	3
10.02	129	51	1
11.02	129	51	2
12.01	126	54	1

Appendix D

Table D-1

Contact angle of sessile droplet on treated POM surface as a function of time and chromic acid concertation

Concentration (M) chromic acid	Time(minutes)	CA			180 $\bar{x}$	180-$\bar{x}$	σ
sample 1M							
	1	105	111	112	109	71	4
	10	123	124	123	123	57	1
	60	134	130	133	132	48	2
	780	141	139	137	139	41	2
sample 2M							
	1	109	112	113	111	69	2
	10	124	131	121	125	55	5
	60	125	122	131	126	54	5
	780	141	136	138	138	42	3
Sample 3M							
	1	116	115	118	116	64	2
	10	128	127	128	128	52	1
	60	130	128	131	130	50	2
	780	147	148	150	148	32	2
Sample 4M							
	1	124	121	128	124	56	4
	10	128	128	127	128	52	1
	60	132	135	133	133	47	2
	780	149	151	148	149	31	2
Sample 5M							
	1	121	118	124	121	59	3
	10	126	123	124	124	56	2
	60	125	126	128	126	54	2
	780	150	155	148	151	29	4

Table D-2

Contact angle of chloroform on treated POM (5M) surface as function of pH in the presence of electrolyte (0.01KCl) at 3-5 deposition time

pH	CA			$\bar{x}$	180-$\bar{x}$	σ
2.01	145	145	139	143	37	3
2.51	144	143	141	143	37	1
3.01	145	145	147	146	34	1
3.49	145	144	145	145	35	1
4.00	147	147	146	147	33	1
4.50	143	142	145	143	42	2
4.99	144	144	143	144	44	1
5.51	144	145	146	145	41	1
6.02	145	144	145	145	35	1
6.49	145	144	145	145	35	1
7.05	145	146	145	145	35	1
7.50	140	142	141	141	36	1
7.99	134	135	138	136	35	2
8.52	142	139	138	140	34	2
9.02	149	150	151	150	30	1
9.51	150	148	149	149	31	1
10.00	152	153	152	152	28	1
10.52	149	150	151	150	30	1
11.01	148	149	151	149	31	2

Table D-3 Contact angle of chloroform on treated POM surface as a function of pH in the presence of 0.413mm CTAB at 3-5 deposition time

pH	CA			$\bar{x}$	180- $\bar{x}$	σ
1.99	153	157	165	158	22	6
2.51	155	150	158	154	26	4
3.00	156	149	162	156	24	7
3.49	150	148	143	147	33	4
4.01	145	148	151	148	32	3
4.50	143	149	143	145	35	3
5.01	150	150	147	149	31	2
5.49	150	145	154	150	30	5
6.02	153	158	156	156	24	3
6.50	154	156	156	155	25	1
7.02	159	157	154	157	23	3
7.51	155	154	156	155	25	1
7.99	156	155	152	154	26	2
8.50	154	153	155	154	26	1
9.01	153	154	155	154	26	1
9.48	151	152	150	151	29	1
9.99	155	148	152	152	28	4
10.51	157	151	154	154	26	3
11.02	159	146	148	151	29	7

Appendix E

Table E-1: Contact angle of chloroform on new anionic membrane as a function of pH in presence of 0.01MKCL at 3-5 deposition time.

pH	CA			$\bar{x}$	180- $\bar{x}$	σ
1.99	153	157	165	158	22	6
2.51	155	150	158	154	26	4
3.00	156	149	162	156	24	7
3.49	150	148	143	147	33	4
4.01	145	148	151	148	32	3
4.50	143	149	143	145	35	3
5.01	150	150	147	149	31	2
5.49	150	145	154	150	30	5
6.02	153	158	156	156	24	3
6.50	154	156	156	155	25	1
7.02	159	157	154	157	23	3
7.51	155	154	156	155	25	1
7.99	156	155	152	154	26	2
8.50	154	153	155	154	26	1
9.01	153	154	155	154	26	1
9.48	151	152	150	151	29	1
9.99	155	148	152	152	28	4
10.51	157	151	154	154	26	3
11.02	159	146	148	151	29	7

Table E-2: Contact angle of chloroform on new anionic surface as a function of pH in the presence of 0.413mm CTAB at 3-5 deposition time

pH	CA			Av	180- $\bar{x}$	σ
2.01	162	155	152	156	24	5
2.50	157	153	155	155	25	2
3.01	159	158	162	160	20	2
3.48	154	156	152	154	26	2
4.02	145	150	148	148	32	3
4.50	146	156	156	153	27	6
4.96	142	151	142	145	35	5
5.49	150	142	145	146	34	4
6.01	133	132	135	133	47	2
6.52	130	135	132	132	48	3
7.01	132	128	133	131	49	3
7.50	135	127	121	128	52	7
7.97	126	125	121	124	56	3
8.53	118	111	115	115	65	4
9.01	127	118	120	122	58	5
9.52	101	98	105	101	79	4
10.02	96	91	94	94	86	3
10.48	81	76	83	80	100	4
11.05	80	77	73	77	103	4

Appendix F

Table F-1: Contact angle of chloroform on new amphoteric membrane as a function of pH (0.01MKCl) 3-5 deposition time.

pH	CA			$\bar{x}$	180-$\bar{x}$	σ
1.98	155	151	152	153	27	2
2.48	148	152	149	150	30	2
3.01	142	139	145	142	38	3
3.49	138	141	144	141	39	3
4.01	133	129	136	133	47	4
4.52	136	135	133	135	45	2
5.01	125	128	130	128	52	3
5.49	139	140	133	137	43	4
5.98	144	142	138	141	39	3
6.53	136	137	141	138	42	3
7.01	145	148	153	149	31	4
7.49	148	145	139	144	36	5
8.02	140	148	139	142	38	5
8.50	131	134	136	134	46	3
8.99	135	132	130	132	48	3
9.51	130	125	132	129	51	4
9.99	135	131	125	130	50	5
10.52	140	145	139	141	39	3
11.01	137	140	142	140	40	3

Table F-2: Contact angle of chloroform on new amphoteric membrane as a function of pH in the presence of 0.413mM CTAB 3-5 deposition time

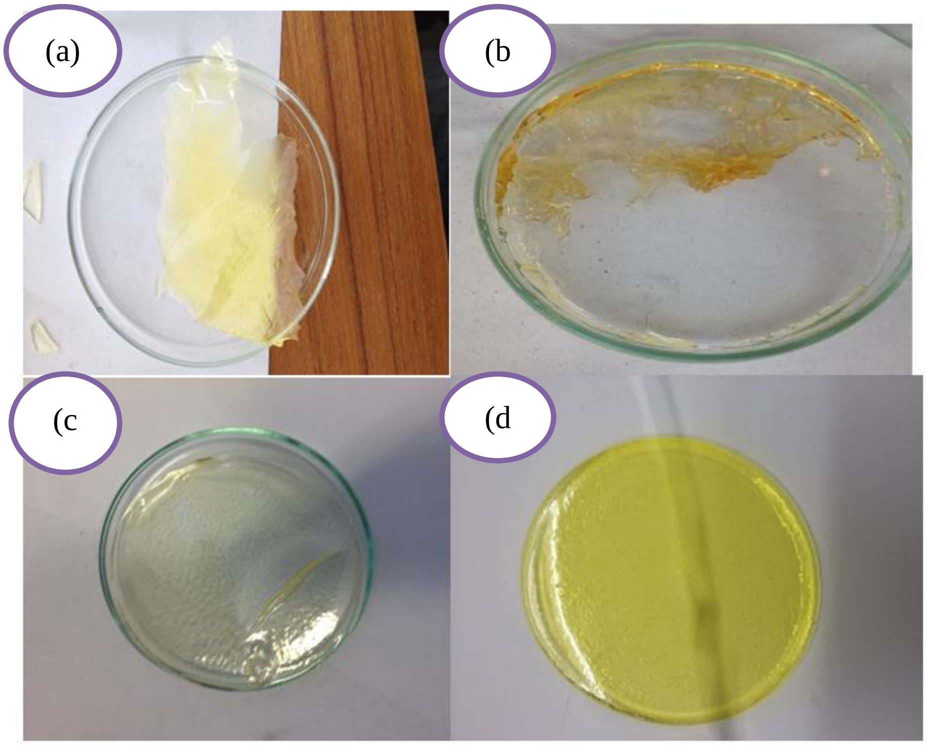
pH	CA			$\bar{x}$	$180-\bar{x}$	σ
2.10	165	158	156	160	20	5
2.51	158	160	161	160	20	2
2.98	162	157	159	159	21	3
3.51	153	155	158	155	25	3
3.99	143	150	149	147	33	4
4.52	146	150	152	149	31	3
4.99	142	151	145	146	34	5
5.49	153	144	145	147	33	5
6.02	135	139	140	138	42	3
6.51	132	139	136	136	44	4
6.99	137	135	130	134	46	4
7.51	133	126	128	129	51	4
7.98	121	128	121	123	57	4
8.51	100	108	110	106	74	5
9.01	115	112	109	112	68	3
9.52	99	105	101	102	78	3
10	78	85	75	79	101	5
10.49	69	74	71	71	109	3
11.03	63	62	70	65	115	4

Table F-3: Contact angle of chloroform on new amphoteric membrane as a function of pH in the presence of 0.19mM SDBS at 3-5 deposition time

pH	CA			$\bar{x}$	180-$\bar{x}$	σ
1.97	71	76	81	76	104	5
2.53	85	79	85	83	97	3
3.02	88	94	91	91	89	3
3.55	102	107	110	106	74	4
4.05	115	111	105	110	70	5
4.51	121	119	113	118	62	4
5.03	126	124	120	123	57	3
5.48	138	127	141	135	45	7
5.98	135	139	129	134	46	5
6.51	131	134	136	134	46	3
7.04	137	135	130	134	46	4
7.51	133	126	128	129	51	4
7.98	135	137	139	137	43	2
8.51	129	137	127	131	49	5
8.99	131	136	133	133	47	3
9.5	135	141	137	138	42	3
10.03	147	152	145	148	32	4
10.49	153	154	160	156	24	4
10.99	155	149	158	154	26	5

Appendix G

Pictures G-1: Images of photo polymerized membranes at different composition thickness: (a) and (d) has the same composition but different thickness: (b) addition 3.5% functional monomer 2-(N,N-dimethyl amino)ethyl methacrylate(DMAEMA); (c) high composition of cross linker (25%) di (ethylene glycol) diacrylate (DEGDA).



Pictures G-2

The following images were taken by Light microscope images for comparison on influence of pH on BN66A surface: (a) before immersion and (b) after the membrane was immersed in basic medium after approximately 5 minutes immersion time at pH 12.