Development of Osmotic Membrane For The Reverse Osmosis Process.

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PREFACE

Since long, the Cellulose Acetate membranes have been recognized as unique for their semipermeability. The need to modify them chemically or physically is widely felt due to some inherent drawbacks present in them. These are : 1) membrane hydrolysis, 2) membrane compaction under pressure, and 3) Microbial degradation, which reduce the life of the membrane. Most of the modifications suggested for Cellulose acetate membranes have been primarily aimed at eliminating these drawbacks.

It was considered that the physical blending of Cellulose acetate & PMMA, Poly (Methyl Methacrylate) may improve the characteristics of the membrane prepared therefrom.

The cellulose diacetate - Poly (Methyl methacrylate) blend system, first time developed during this investigation offers a good scope for the desalination of brackish water.

A very immediate aim of the present investigation is to evaluate the indigenous materials (CA & PMMA) for membrane preparation that would yield reverse osmosis membranes of relatively better osmotic properties than the cellulose diacetate membrane, with respect to the membrane strength and performance for desalination of saline water by R.O.

A major effort was devoted to the optimization of the polymerization of methyl methacrylate monomer, of formulation of the composition of the blend of cellulose diacetate and Poly (methyl methacrylate), of the flat membrane casting conditions and also the characterization of the flat blend membrane on a laboratory scale; on the basis of which qualitative criteria were established for the tubular membrane preparation from the blend composition.

It is felt that the study reported here has been helpful in obtaining an improved semipermeable membrane for the R.O. Process.

STATEMENT 1

I hereby declare that the work incorporated in the Thesis is original and has not been submitted earlier to any University for the award of a Diploma or Degree.

STATEMENT 2

The sources on which this investigation is based have been reviewed through the text and also systematically indicated in the work and interpretation of the results and discussions thereon are entirely original and are based on the work carried out by me.

B. J. Narola.
Signature of the Candidate

M. V. Chandarikar.
Signature of the Guide

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CHAPTER - I

INTRODUCTION

1.1 Water picture in the World

Earth is considered to be water rich planet of our solar system. It contains inexhaustible quantity of water without which life cannot exist. Water is intimately associated with our evolution, civilization and clesting. It has a very great role to play in all the phases of animal and vegetable life. Abundant and good quantity of water invites settlement, agriculture pursuits and industrial activities. It also promotes trade and provides power. Though at present, supply of fresh water can meet the demand of earth population, problems of good water supplies are going to arise in near future due to fast growing population, progressive industrialization, expansion of irrigation, agriculture and rehabilitation of arid area. To obviate this water shortage, considerable amount of research and development funds and facilities have been extended to creative Scientists and technologists of various well-developed countries like United States of America, France, Canada, United Kingdom, Israel, etc. to carry out this research and development work. This includes purely basic research and development of desalination technique to the level of commercial plants and commercial units, processing millions of gallons of saline brackish or sea water every day to obtain potable water.

1.2 Desalination

Desalination is one of the oldest method known for separating fresh water from salt water solution. Desalination of saline water can be described in several ways. Some of these techniques are well-known and have been put to commercial use. Some others which were known in concept in past and are now being investigated and have reached to pilot plant and semi-commercial stage, while some others are still under study in laboratory. The known desalination techniques can be classified as under :

A. Distillation :

- i) Long-tube vertical
- ii) Flash distillation
- iii) Vapour compression
- iv) Multi-effect Multi-stage

B. Membrane Process :
    i) Reverse Osmosis
    ii) Electrodialysis
    iii) Transport depletion

C. Freezing Process :
    i) Direct Freezing
    ii) Secondary refrigerant

D. Humidification Process :
    i) Solar
    ii) Diffusion

E. Chemical Process :
    i) Hydrates
    ii) Ion Exchange

In distillation processes, water is first boiled and the steam or water vapour is cooled.

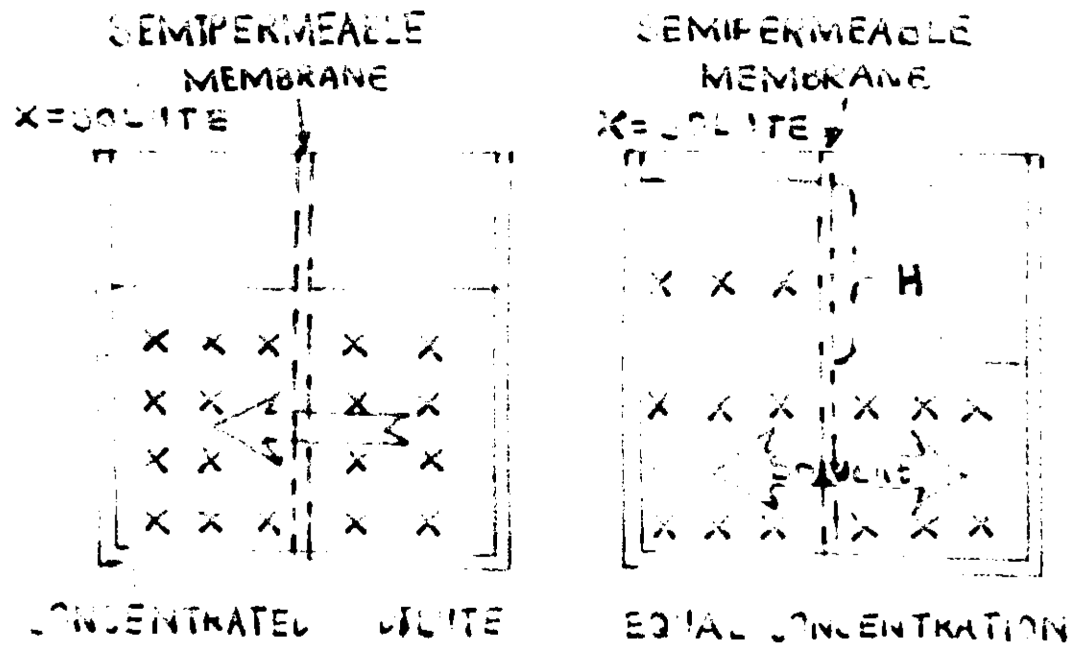
Reverse Osmosis is classified under membrane process in which semi-permeable membrane supported on a suitable porous or perforated support is used.

The freezing process is based on the fact when salt water freezes, fresh water ice crystals form, and the salt remains in solution in the unfrozen water. The pressure gradient either the mechanical or electrical is employed in the separation of fresh water from saline water.

1.3 Reverse Osmosis

When pure water and salt solution are placed on opposite sides of an ideal semipermeable membrane, fresh water passes through the membrane and dilutes the salt solution due to the osmotic pressure of salt solution. This process is known as Osmosis. If pressure is applied to the salt solution in excess of its osmotic pressure, fresh water flows through the membrane in the opposite direction to normal osmotic flow. This process is known as "Reverse Osmosis" or "Hyperfiltration". It is shown in Fig. 1.

This process is an excellent recent development in the field of separation, concentration and fractionation of liquids or gaseous substances. As a result of intensive efforts centred on Cellulose Acetate semipermeable membrane, the Reverse Osmosis desalination system has been advanced to the pilot plant scale. Recently, a hypothesis is put forward by Professor Leven Spiegl and Nevers[1] who have suggested the possibility of an "Osmotic Pump" which would yield fresh water from

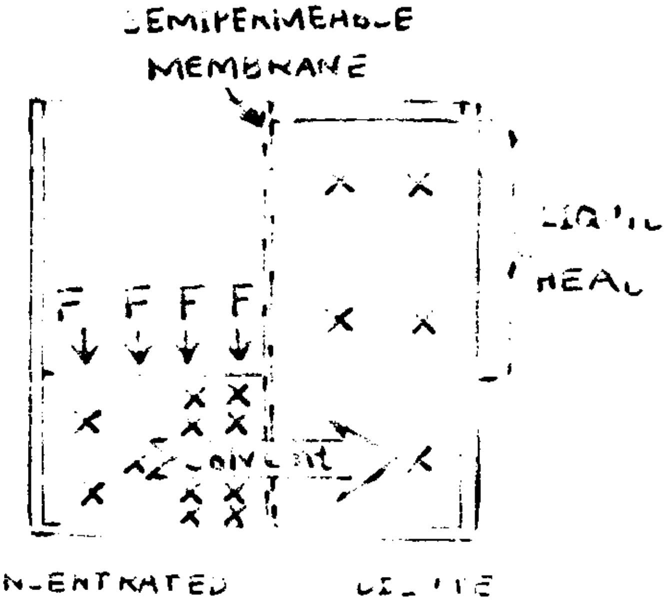


DIRECT OSMOSIS

H=LIQUID HEAD=OSMOTIC PRESSURE DIFFERENCE

(1)

(2)



F=OSMOTIC PRESSURE + LIQUID HEAD

REVERSE OSMOSIS

(3)

SCHEMATIC DIAGRAM OF OSMOTIC PROCESS

FIG. 1.

sea water at no expenditure of energy and of its corollary an "Osmotic Power Plant" which would be extracted work from the ocean.

1.4 Theory of Semi-permeability

Several mechanisms have been put forward to explain the action of semipermeability and each of them is valid for the same system.

i) Sieve Mechanism

According to this mechanism, the membrane is regarded as containing pores so tiny that only the water molecules can pass through them, while the bigger solute molecules can be retained over it. However, the size of the ions is very near to that of water molecules, so that this theory has gained no ground, but this is most obvious for removal of some larger diameter molecules in ultrafiltration[2].

ii) Distillation Mechanism

Callender[3] suggested that the membrane is assumed to contain non-wettable pores through which solvent passes as a gas. Such mechanism is obviously excluded because water can exist as a gas only at higher temperatures and pressures and it is not possible to dry the pores in the membrane.

iii) Adsorption Theory

This process is governed by surface phenomena in which membrane surface is porous and homogeneous and the transport of the preferentially sorbed water[4,5,6] and aqueous solution occurs through the capillary pores on the membrane surface. Though the existence of pores of appropriate size on the area of the active porous film at the interface is not possible, it is of prime importance for the practical success of this separation process. The separation and the product rate characteristics of a membrane depend on the extent of the negative adsorption of the solute, the membrane solution interface, osmotic pressure of the solution and other factors governing the transport of materials.

The application of above theory for a given separation problem involves essentially the problem of choosing the appropriate chemical nature of the film surface and developing techniques for making film containing the largest number of pores of the required size on the area of the film at the interface.

iv) Hydrogen Bonding Theory

If the membrane is supposed to be a porous body and the solvent molecules are adsorbed on the pore wall in such a way that there is no room for the passage of solute molecules than solvent molecules can pass through by successive transfer from one adsorption site to another.

Reid C.E., and Breton[7] developed the mechanism regarding Cellulose Acetate semipermeable membrane, the most widely studied material for desalination. In this case, permeation occurs in non-crystalline portion of the membrane via hydrogen bonding. Water in this region is postulated to be mostly "bound" by hydrogen bonds and salt leakage is pictured as taking place at imperfection holding "Capillary" water.

1.5 History of Development of Reverse Osmosis

The historical development of Reverse Osmosis process had been studied by Yuster et al[4] who first suggested the possibilities of desalinating saline water by skimming out surface layer of pure water from that of sodium chloride solution. This suggestion was perhaps starting point of investigation on the subject at University of California, Los Angeles and simultaneously at University of Florida in U.S.A. in 1956.

Knowledge of osmotic phenomenon is about two centuries old when Abbe Nollet published his first maiden paper on diffusion through animal membrane.

Later on Traube made successful experiment on osmosis using artificially prepared membrane. Pfeffer made first quantitative measurement of osmotic pressure using membrane consisting of copper ferrocyanide precipitated in porous porcelain, while the perfection of preparation and handling of the membrane was studied by Mores, Berkeley and Hartley. Theoretical development started with Vant Hoff and thermodynamic treatment was developed largely through sound theoretical understanding of the osmosis phenomenon.

Flow through an osmotic membrane has been expressed mathematically by the following general equation[8]

$$F = A(\Delta P - \Delta \pi) \qquad \text{----} \qquad (1)$$

where,

F = Fresh water flux through the membrane

A = Membrane constant

ΔP = Pressure gradient across the membrane

$\Delta \pi$ = Osmotic pressure difference between the feed and product.

According to above equation, the driving force for flow through osmotic membranes is the difference between the applied pressure across the membrane and the osmotic pressure of the solution at the solution membrane interface. In other words, the applied pressure on the brine side tends to push the water through the membrane to the fresh water side, while the osmotic pressure of the solution tends to push the water through the membrane in the opposite direction i.e. back to the brine side. Hence, to get water from the solution, the pressure applied (P) on the solution side of the membrane should be greater than the osmotic pressure (ΔP) of the solution. Greater the ΔP, lower the $\Delta\pi$ (which is dependent on the concentration of the solution) greater will be the flux, i.e. the output of pure water. This again depends upon the membrane constant "A" which determines the quality of the membrane.

Mathematical models for analysing the flow of water through osmotic membranes have been presented by Lonsdale and Merton[9]. The yield and purity of the product water therefore depends upon, 1) salinity, 2) applied pressure, 3) physical and chemical nature of semipermeable membrane. For utilizing reverse osmosis technique for desalination, separation or concentration, one must prepare suitable semi-permeable membrane which must mainly meet the following three requirements :

1) It must desaline a given saline feed water adequately.
2) It should provide adequate desalinized water flux at reasonable pressure.
3) It should maintain the above two characteristics for reasonable length of time.

1.6 Application of Reverse Osmosis

Reverse Osmosis provides a new valuable tool that can be applied towards the solution of a diverse spectrum of treatment and concentration problems. During the reverse osmosis process, feed is divided into two streams viz. the diluted stream and the concentrated stream. Accordingly, in this process, either the diluted stream (reverse osmosis as a desalination process) or the concentrated stream (reverse osmosis as a concentration process) can be useful as the product, as mentioned below :

Various applications of Reverse Osmosis as a desalination process are :

i) For brackish water desalination
ii) For producing boiler feed water
iii) For producing pharmaceutical grade water (the product from this process is free from bacteria and virus).

iv) For sewage treatment
v) For purification of industrial effluents
vi) For producing quality water for beverage, electrical and other industries.

Similarly, as a concentration process, it is useful :

i) For concentration of fruit juices
ii) For concentration of liquid food products
iii) For concentration of dairy products
iv) For concentration of pharmaceutical properties
v) For polymer emulsion concentration
vi) For reclamation of valuable materials from plating industries
vii) For separation of chemicals

1.7 Advantages of Reverse Osmosis

i) It is an ambient temperature process and separation of salt from saline water is achieved without a phase change.
ii) The process in addition to desalting removes bacteria and viruses from feed water.
iii) The energy consumption is low when compared to other desalination processes.

iv) The same plant can be used for brackish water of different salinities (between 2,000 to 10,000 ppm of total dissolved solids) as the process is not very sensitive to the salinity.

v) Equipment can be built and operated with local materials and manpower and no elaborate shop fabrication facilities are needed to manufacture reverse osmosis plant.

vi) Maintenance costs are low as excepting for the high pressure pumps, there are no other mechanical or electrical devices that require frequent maintenance.

1.8 Background of Development of Cellulose Acetate Membranes

In the history of membrane technology over the past twenty years, two milestones are now apparent. The first is the work by C.E. Reid and Breton[7] which demonstrated that the reverse osmosis process offered a viable alternative of distillation for water desalination and thereby stimulated further exploration of membrane separation process. They suggested that the membrane material should have hydrophylic nature.

The second milestone of course, is discovery of Loeb-Sourirajan[10] of assymetric cellulose acetate membrane. Their work which has also directed towards water desalination by reverse osmosis produced a quantum jump in the intensity of applied research and development which persists to the present day. Many of the advances in membrane science and technology in the past decade viz. Ultrafiltfation, hemodialysis and other biomedical applications of membrane in addition, of course, to reverse osmosis were stimulated by the pioneering work of Reid, Loeb and Sourirajan.

Yuster, Sourirajan and Bernstein[4] studied several cellulosic derivatives and found suitability of C.A. film. Later on Mahon[11] tried cellulose triacetate membrane in the form of fine tubes.

However, above investigators could get only low flux C.A. membrane having rather good salt rejection. Loeb and Sourirajan[12] attempted to increase the flux through the use of Scheichner and Schuell type (S&S) commercial membrane. They could get good desalination by heating the membrane in hot water bath. From that they concluded that the degree of desalination is directly and water flux is inversely proportional to heating temperature. They also studied in full detail the characterization of S & S type cellulose acetate membrane regarding the effect of heating temperature, pH and drying of the membrane[13, 14, 15] etc. and finally developed their own technique for making porous cellulose acetate membrane. Loeb and Sourirajan came across an article by Dobry[16] in which she had suggested the use of saturated aqueous magnesium perchlorate as a solvent for cellulose acetate in the preparation of ultrafiltration membrane.

In 1965, Sourirajan and Govindan[17] used a solution of 17% cellulose acetate, 68% acetone and 1.5% magnesium perchlorate and 13.5% water referred to as perchlorate system cast at -10°C with 4 min. evaporation time. This system afforded higher water flux at a given level of salt rejection than the original Loeb-Sourirajan formula and indicated that the earlier method was not optimised with respect to casting solution composition.

Manjikian, Loeb and McCutchan[18] reported an advance which yielded identical performance to above by a method which allows room temperature casting. A 25% cellulose acetate, 30% formamide, 45% acetone solution referred to as a formamide system was cast under ambient conditions with 30 seconds evaporation time. Films made by latter method, because of its ease of execution, have become the membranes of choice in reverse osmosis.

Saltonstall et al[19] have achieved improvement in membrane performance by blending various cellulose acetates of different degree of substitution.

1.9 Limitation of Cellulose Acetate Membrane

Cellulosic membranes which are currently in use suffer from a number of limitations. Most are attributed to the polymeric properties. They can be used only with aqueous solutions since organic solvents either dissolve the membrane or plasticize it sufficiently to cause its collapse. Most of them must be kept water wet. If they are allowed to dry out, they irreversibly consolidate and lose their permeability because of the rather low glass transition temperature of cellulose acetate. These membranes cannot be operated at temperatures above 50° to 60° since they collapse, consolidate and become impermeable. Because the polymer is both a poly glucose and ester, it is sensitive to hydrolysis at low and high pH and to enzyme and microorganism attack.

1.10 Utility of Cellulose Acetate Methacrylate Membrane

The solution of this polymer in volatile solvent finds use as special adhesives. Upon evaporation of the solvent, transparent, strong and flexible films are formed. They are resistant to chemicals.

The acrylate ester in copolymers produced[20] an "Internal Plasticization" of the polymers resulting in improved toughness, increased tensile strength, increased tear and impact strength and improved processibility. Poly (Methyl Methacrylate) has certain electrical properties that make it a unique material for many applications. Its surface resistivity is higher than for most plastic materials. Poly (Methyl methacrylate) is extremely resistant to alkaline saponification and is relatively unaffected by inorganic and organic acids.

Cellulose Acetate (I), Poly (methyl methacrylate) (II) blends have practically the same properties as cellulose acetate methacrylate graft copolymer (III) prepared with the same monomer[21] ratio as the I and II in the blend. Films made of I-II blend or III have globular structure. When the amount of II in the blend or number of II unit in III are increased upto 50%, the tensile strength of the film decreases until it remains constant in the 50-90% II concentration range. When the concentration of II is increased from 40-90%, the elasticity of the film is increased from 10% to 900%. The brittle point of the film increases when the amount of II is increased upto 40% and it remains constant at $\sim$ 20% when the amount of II is increased from 40% to 90%.

Incorporation of cross-linked cellulose acetate methacrylate (CAM) membrane[22] in Reverse Osmosis equipment should serve to improve the efficiency of the process in desalination of brackish water due to their high flux and excellent flux stability. Adaption of the membranes for 99.5% salt rejection, currently under study, would be similarly advantageous in the single pass desalination of sea water. In subsequent studies[23] CA, CAB and CAM with degree of substitution between 2.5 to 2.7, all proved to yield membrane with salt retention satisfactory for sea water desalination.

Cellulose Acetate Methacrylate Membrane

Annealing Temp.	Flux (56 Kg/cm^2) m^3/m^2 day	Flux Decline Slope m	NaCl % Retention
80	2.0	- 0.04	86
80*	2.7	- 0.02	77
83	1.4	- 0.04	90
83*	2.1	- 0.02	83
86	1.6	- 0.05	91
86*	1.7	- 0.01	90

* Cross-linked

As expected, high flux membranes of greatly superior stability resulted from the employment of CAM as the membrane polymer and cross-linking the membrane prior to high pressure testing.

Cross-linked CAM Membrane

Annealing Temp.	Flux (56 Kg./cm^2) m^3/m^2 day	Salt Retention % NaCl	Salt Retention % Na_2SO_4
80*	3.3	81	-
	3.9	-	98
83*	2.3	88	-
	3.0	-	99

* Cross-linked

It is noteworthy that in each case, the cross-linked specimen exhibited a lower salt rejection and a higher flux than the uncrosslinked. This is believed to result from the very rapid compaction of polymer in the uncrosslinked membranes acting to reduce the flux and at the same time, producing a barrier more resistant to the passage of salt. The crosslinked membrane resists both these changes.

Progress is reported[24] in utilization of a commercial cellulose acetate (E-383-40) in the production of tubular cellulose acetate methacrylate (CAM) with methacrylate substitution of 0.33. Reverse osmosis membrane with >90% insoluble in Me_2Co, and initial flux of <51% gfd yielded a constant NaCl rejection of 91.5% at 800 psi, a flux decline parameter (m), 0.041 and projected mean first year flux of 33 gfd. Flat sheet CAM membrane cross-linked <90% yielded initial fluxes of 37-49 gfd, a constant NaCl rejection of 96-97% and m = 0.00 - 0.01 at 800 psi. The long term performance of membrane from CAM ds 2.62 was outstanding. The log-log slope of flux decline was 0.01 which is a large improvement over the present cellulose acetate. The salt rejection remained above the required minimum of 99.5% during the entire test. The CAM membranes of ds 2.52 has a slope of 0.059 which is also an improvement over cellulose acetate membrane from E-398-3 but is clearly inferior to the higher ds polymer.

Cross-Linking of CAM (E-398-3)

Sample	Cross-linking Dry Wt. 3 gm. of membrane in 4% solution[b]	Gel Function %	2 hrs. R.O. Results		
			Flux gfd.	% Rej.	Test Sample
CAM ds 2.52 (Centroll)	None	0	10.33 ±0.4	99.0 ±0.04	.3
CAM* ds 2.52	@ 2 min. 90°C	53.0	10.28 ±0.16	99.0 ±0.03	6
CAM ds 2.62 (Centroll)	None	0	9.42 ±0.76	99.0 ±0.49	3
CAM* ds 2.62	35 min. @ 90°C	-	9.43 ±0.98	99.4 ±0.4	9

@ All samples heat treated : 3 min. at 90°C

b Redox solution : 1.85×10^{-2} M. $K_2S_2O_8$

1.92×10^{-3} M. $NaHSO_3$

* Cross-linked

1.11 Aim and Object of Development of Cellulose Acetate Methacrylate Membrane

One of the major tasks of this programme is the development of membrane capable of very high salt rejection with improved useful operating life. Such membrane properties are indispensable to the successful operation of single pass reverse osmosis desalination of sea water. Membranes of long useful life are also available to the ultimate economic success of any of the application of reverse osmosis.

The combined objective of incorporating high retention and long life in a simple membrane is the ultimate goal of this programme. The intermediate individual goal of high retention membranes and membranes of improved life were approached separately and each phenomenon is studied. It is subsequently shown in the case of the programme that both properties can be combined in membrane with high flux range. From the early work on the use of cellulose acetate in reverse osmosis[25,26] and discovery of high flux membrane by Loeb and Sourirajan[27], the research on new polymeric membrane for reverse osmosis has progressed considerably to solve the problem of finding new materials having analogous properties to cellulose acetate and simultaneously allowing the synthesis of high flux high rejecting membrane.

Other objective of the work is the development of blended/grafted copolymer CA + PMMA/CAM composition that would yield reverse osmosis membrane superior to cellulose acetate membrane in reverse osmotic properties and its chemical stability.

p.35

In the present work, membranes prepared from the blend of Cellulose Acetate + Poly (Methyl Methacrylate) have been studied using acetone benzene solvent system and formamide as additive material. This solvent has been selected because of better solubility of CA + PMMA in Acetone-Benzene solvent mixture than a single solvent or solvent mixture. Thus making blending system more simple and efficient for membrane preparation.

Blended formulations have been studied with a view to establish the final casting composition on laboratory scale experiments. After selection of suitable casting formulation, membrane casting conditions were optimised with respect to the solvent evaporation time, heat treatment, membrane thickness etc. Effect of blend composition has been studied by taking different proportions of cellulose acetate and Poly (Methyl Methacrylate) in casting composition and suitable membrane was selected for the long term running of 5000 ppm sodium chloride solution at 600 psi pressure. A parallel study on cellulose diacetate membrane under similar conditions as these for the blend membranes has been conducted to compare the results of blended (cellulose acetate Poly (Methyl Methacrylate) membranes whenever it was necessary.

Assymetric membranes have been characterised by determining the total water content at different casting conditions and these were correlated with the performance properties of respective membranes.

To develop the (CA:PMMA) blended system on a large scale, pre-established conditions for flat membranes have been examined on a tubular configuration.

Consistent Approach

Monomers i.e. Methyl Methacrylate and Cellulose Acetate are easily available in India. Though monomer and poly (Methyl Methacrylate) are also imported from abroad.

Optimization of polymerization of monomer has been studied using different initiators and catalysts. One polymer which was prepared in laboratory was characterized and was compared with commercial PMMA. The characteristics which were studied were :

1) Molecular weight data
2) Softening point
3) Bulk density

4) Solubility in different solvents
5) Moisture Sorption - Desorption

After characterization of lab. scale product which was used for blending of (CA + PMMA), the optimization of CA:PMMA proportion was carried out for preparing the solution and the blended membrane was prepared which was optimised and characterised.

Optimization of graft copolymerization of CA with PMMA was studied and its characterization was carried out. The assymetric graft osmotic membranes were prepared and their preparation conditions were optimized.

Comparison of characteristics of CA:PMMA and CAM (grafted) membrane was studied. Moreover, comparison study of characteristics of osmotic membranes of CA (CA + PMMA) blend and CAM (grafted) was carried out.

From the above characterization studies, it was found that there was scope to study the possibility of developing high rejecting CAM membrane of better physico-chemical properties.

CHAPTER - II

MATERIALS, METHODS & EQUIPMENTS

2.1 MATERIALS

2.1.1 Methyl Methacrylate (MMA) Monomer :

It is a colourless liquid. B.P. 100-101°C, $d^{25} = 0.939$, $n_D^{25} = 1.4119$, Inhibitors are MEHQ (50-100 ppm), or H.Q (25-60 ppm).

2.1.2 Poly (Methyl Methacrylate) (PMMA) :

The methyl methacrylate monomer was polymerized in laboratory and the product was characterized.

1) Specific gravity : 1.19
2) Tensile strength of film of 0.1 mm thickness : 1100 psi
3) Water absorption (% wt. gain 24 hrs) : 0.6
4) Bulk Density : 0.1384 gm/cc.
5) Molecular Weight : 8-9 lakhs
6) Solubility : Soluble in hydrocarbons and chlorinated hydrocarbon.

2.1.3 Secondary Cellulose Acetate : Secondary Cellulose Acetate manufactured by Mysore Cellulose Product was used and characterized.

1) Acetyl content (%) : 39.85
2) Moisture Content : 4.0
3) Ash Content : 0.08
4) Relative Viscosity : 1.32
5) Melting Point : 240°C
6) Molecular Weight : 45000

2.1.4 Cellulose Acetate Poly (Methyl Methacrylate) Blend :

Cellulose acetate 80 and poly (methyl methacrylate) 20, i.e. 80:20% by weight was mixed.

2.1.5 Cellulose Acetate Methacrylate (CAM), Graft Copolymer:

The above product was prepared in the laboratory and was characterized.

1) Solubility : Soluble in ketone, ester, hydrocarbon, and mixed solvent e.g. Acetone, Benzene.
2) Total Ester as % Acetyl : 41.7
increase in D.S. : 0.1 - 0.2

1% graft

2.1.6 Ceric Ammonium Sulphate :

Molecular Formula – $(NH_4)_4Ce(SO_4)_4.2H_2O$

Molecular Weight : 632.56

Assay : 90% to 105%

Other rare earth (as sulphate) : 2%

Nitrate : 0.1%

2.1.7 2.2-Bis Azo Isobutyronitrile (AZBN) :

White powdery substance, chemically pure.

2.1.8 Benzoyl Peroxide :

It is an odourless, tasteless, rhombic crystalline solid $(C_6H_5CO_2)_2O_2$, formula weight : 242.2 Melting point : 103-105°C, & $n_D^{20} = 1.545$

It is insoluble in water and slightly soluble in petroleum solvents, alcohol and Vegetable oils. It is more soluble in aliphatic ketones, aromatic hydrocarbons and chlorinated solvents.

2.1.9 Sodium Hydroxide CP was used having following contents:

Molecular formula : NaOH

Formula Weight : 40.01

It is corrossive to skin, very soluble in water and strongly alkaline. M.P. : 318.4, B.P. : 1390°C, Density : 2.130 gm/cm^3.

2.1.10 Acetone

CP grade of Acetone was used having the following characteristics :

Molecular formula : CH_3COCH_3
Molecular weight : 58.08
Specific Gravity : 0.790
Boiling range : 55-57°C
Minimum assay : 99%

It is miscible with water.

2.1.11 Formamide

It is a colourless, odourless liquid.

Molecular formula : $HCONH_2$
Molecular weight : 45.04
Specific gravity : 1.131 to 1.134 at 20°C
Boiling range : 210°C (decomposition)

It is miscible with water.

Minimum assay : 98%
Minimum limit of impurities
Ammonium formate : 1%
Formic acid : 0.1%

2.1.12 Benzene

CP grade of Benzene was used having the following characteristics :

It is an organic solvent having

Molecular formula : C_6H_6

Molecular weight : 78.11

Specific gravity : 0.875

B.P

2.1.13 Glycerol

It is a colourless liquid of molecular

Formula : $OHCH_2CHOH.CH_2OH$

Molecular weight : 92.09

Boiling range : 290°C

It is miscible with water.

2.1.14 Sulphuric Acid

Sulphuric acid CP was used having the following characteristics :

Molecular formula : H_2SO_4

Molecular weight : 98

Specific gravity : 1.855

Max. impurities(%)

HCl : 0.0005

HNO_3 : 0.0005

SO_2 : 0.015

NH_3 : 0.001
AS_2O_3 : 0.00005
Fe : 0.015
Pb : 0.005

2.1.15 Nitrogen gas used for inert atmosphere

Gaseous nitrogen condensed to a colourless liquid at -195.8, Density of gas at 0°C and 1 atm. = 1.2506 gm/lit.

Slightly soluble in water, 0.023 volume of nitrogen being absorbed by 1.0 volume of water at 0°C.

2.2 METHODS

2.2.1 Removal of Stabilizer from Methyl Methacrylate Monomer:

Removal of stabilizer[28] from methyl methacrylate monomer was carried out by treating the monomer with NaOH solution of known concentration by a separating funnel. The treatment was given for 3-4 times till the coloured solution layer had disappeared. Then the monomer was used for polymerization.

2.2.2 Polymerization of Methyl Methacrylate Monomer

All polymerization of acrylic esters are carried out[29] by free radical processes. These remain the predominant synthetic route in industrial manufacture. The polymerization can be performed in homogeneous media either in bulk or in solution, or in heterogenous media, either emulsion or suspension.

It is convenient to discuss the free radical polymerization of acrylic esters in accordance with the preparative systems.

The principle uses of methacrylic ester monomers are in the preparation of their polymers. They polymerize[30] readily under the influence of heat, light and oxygen and oxygen yielding substances such as acetyl or benzoyl peroxide, H_2O_2, tert-butyro hydroperoxide, tert-butyl perbenzoate ammonium or potassium persulphate.

The polymerization may be carried out 1) in Mass (casting), 2) in Suspension (moulding powder), 3) in emulsion, and 4) in solution.

The choice of catalysts depends upon the monomer and on the type of polymerization.

Solution polymers are readily prepared by carrying out polymerization in a solvent in which both the monomer and polymer are soluble. Typical solvents include aromatic hydrocarbons, chlorinated hydrocarbons, esters, ketones, and nitroparaffins.

The behaviour of a polymerization reaction and properties of the resulting polymer can vary greatly according to the nature of physical system in which the polymerization reaction is carried out[31]. The following types of physical systems are considered briefly :

1) Bulk polymerization
2) Solution polymerization
3) Suspension polymerization
4) Emulsion polymerization
5) Precipitation polymerization
6) Gas polymerization
7) Solid state polymerization

If a polymer is insoluble in its own monomer or in a particular monomer solvent combination, it will precipitate out as it is formed. If the polymer precipitates out in the form of compact small spheres while still containing a line radical end group, an increase in the rate of polymerization will be observed, because the line end groups become burried in the spheres and termination between two growing polymer chains becomes extremely difficult or improbable. The phenomenon is termed precipitation polymerization, and in emulsion polymerization, the rate of polymerization follows kinetic relationships considerably different from those for a homogeneous bulk polymerization reaction[32].

Polymerization in which this phenomenon is believed to occur includes methyl methacrylate in water[33] and others[34,35,36,37].

Polymerization of methyl methacrylate monomer can also be carried out by using :

1) Ceric ammonium sulphate/Nitrate as initiater[38]
2) Potassium permanganate and oxalic acid[39,40]
3) Ferric chloride as initiater[41]
4) Irradiation method[42] using Benzoyl peroxide as initiater and Azo-bis isobutyronitrile.

Out of all the above methods, polymerization of methyl methacrylate monomer was found suitable by using Ceric ammonium sulphate as initiater and the product was found suitable and comparable with commercial product, imported from USA, manufactured by Kodak.

method!

Comparison between imported and lab. scale prepared poly (methyl methacrylate) is as follows :

		Imported	Lab. Product
1.	Colour & Phase	White powder	White powder
2.	Solubility	Soluble in Benzene	Soluble in Benzene
3.	Molecular Weight	4-5 x 10^5	4-5 x 10^5
4.	Softening Point	125°C	123°C - 125°C

2.2.3 Characterization of Poly (Methyl Methacrylate) :

a) Solubility

Solubility of PMMA was determined employing the following different solvents.

In each test tube, 10 ml of chemically pure solvent was taken and about 1 gm. of PMMA was added in each test tube, mixed well and left for 24 hours. The following observations were obtained :

	Solvent	Observations
1.	Acetone	Fairly soluble
2.	Benzene	Completely soluble
3.	Chloroform	Fairly soluble
p 22 { 4.	Dimethyl formamide	Insoluble
5.	Methyl Ethyl Ketone	Insoluble
6.	Dioxane	Insoluble
7.	Methylene dichloride	Insoluble
8.	Ethanol	Insoluble
9.	Carbon tetra chloride	Insoluble
10.	Dimethyl Sulphoxide	Insoluble

From the above observations, it was concluded that Benzene is the best solvent for the same product.

b) Molecular Weight Determination

The molecular weight of high polymers can be determined by various methods[43] each of which is applicable within the molecular weight range indicated below :

1.	End group assay	upto $3x10^4$
2.	Ebullioscopy, Cryoscopy, Isothermal distillation	upto $3x10^4$
3.	Osmometry	10^4 to 10^5
4.	Light scattering	10^4 to 10^7
5.	Sedimentation in ultra-centrifuge & diffusion	10^4 to 10^7

All these methods except for the end group assay are based on the determination of the properties of polymer solutions. Since the properties of the solutions of high polymers differ from those of ideal solutions, all experimental results must be extrapolated to zero concentration. However, determination of molecular weight by all these methods requires complicated apparatus and is time consuming. For this reason, the viscometric method is generally used in the laboratory practice and the molecular weight is calculated from the viscosity of the solution[44,45,46].

To find the molecular weight from the viscosity data, it is necessary to use empirical equations which give viscosity as a function of the molecular weight. These equations are set up with the aid of any suitable absolute method, for the determination of molecular weight.

To calculate the molecular weight of a polymer, its intrinsic viscosity (n) in a given solvent must be known. The value (n) is obtained by graphical extrapolation of n/c reduced or nsp/c as function of "c". It follows that the determination of the intrinsic viscosity amounts to the determination of relative viscosities of dilute polymer solutions at various concentrations.

$\{\eta\}$

η

When it is intended to calculate the molecular weight from the empirical equation

[η]

$$(n) = K.M.^{a}$$

(n) must be determined in the solvent for which this empirical equation has been established. Moreover, the solvent should be easily purified, should not easily absorb atmospheric moisture and should not be very volatile. A solution of the polymer is prepared as follows :

0.25 - 1.0 gm. polymer sample is placed in a 100 ml volumetric flask. About 60 ml of solvent is added. When the polymer has completely dissolved, the flask with the solution is placed in a thermostat and filled up to the mark with the solvent. As a rule, the polymer dissolves very slowly so it is kept for 24 hours.

Determination of the effluxe time of the Solvents : The viscosity of polymer solution is usually determined at a temperature within 25°C-30°C range. When a constant temperature is attained the viscometer is fixed in the thermostat in vertical position so that bulb "f" is fully immersed in water as shown in fig. 2.

η)

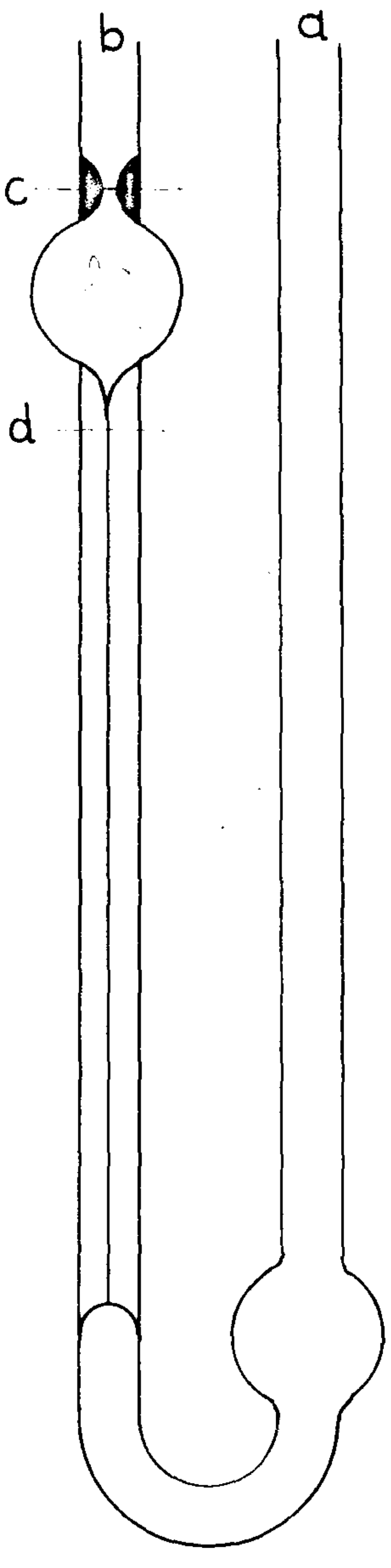


FIG : 2. OSTWALD VISCOMETER

Then 11 ml of pure solvent is introduced into the tube through a no. 2 filter and the effluxe time of solvent is determined. Similarly efflux time of solute is also determined as described[47]. The data are collected and the graph of $\frac{nsp}{c}$ vs c is plotted as shown in fig. 3 from which the intrinsic viscosity (n) was found out and the value of molecular weight was calculated for PMMA using the relation (n) = KM^a where K and a are constant as described[48].

c) Moisture Sorption Desorption

The quantity of moisture sorbed by PMMA was determined at different relative humidities by means of the desiccator method as described by Lonsdale et al[49]. Samples were dried in a vacuum oven at 40°C for 5 to 6 hours. Desired relative vapour pressures were acquired in the air tight desiccator system using different dilutions of sulphuric acid water mixture[50]. Samples were exposed at different relative humidities and allowed to attain the equilibrium till no change in weight occurred. The desiccator was kept in a closed wooden chamber at a constant temperature, the temperature in the chamber being controlled by a toluene mercury regulator system. By knowing the increase in weight at any particular relative humidity, the percent sorbed water in the given sample was calculated using the following formula :

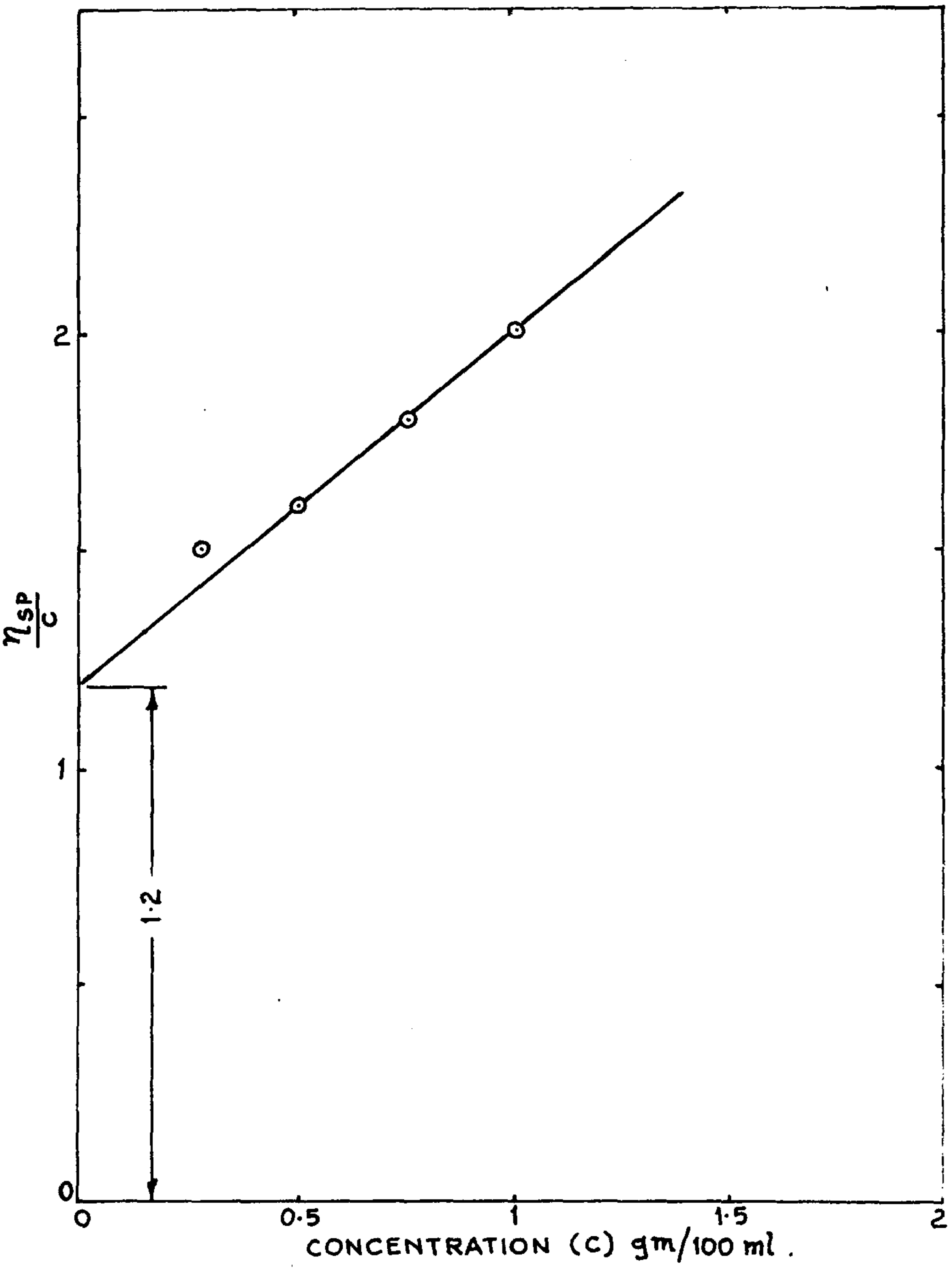


FIG: 3. MOLECULAR WEIGHT DETERMINATION.

$$\% \text{ sorbed water} = \frac{W_1 - W_2}{W_2} \times 100$$

Where, W_1 = Weight of sample after equilibrium water sorption in gms.

W_2 = Initial weight of sample in gms.

d) Softening Point

Softening Point of PMMA was determined by taking the polymer in a capillary tube and heating it in a paraffin bath till the product was found to be softened. It was found in the temperature range of 120-125°C.

e) Determination of Saponification Number

Saponification number of the polymer was determined by taking one gm. of sample, adding 25 ml of alcoholic KOH solution and adding Phenalphthalein as indicator. Then it was left aside for an hour and back titrated with 0.5N.HCl.

Saponification Number :

(Blank - Back titrating Reading) x 0.02805 = saponification in m. gms.

f) Tensile Strength

Tensile strength of the polymeric film was determined by the method ASTM[51] - D638.

what is relevance ?

g) Bulk Density

Bulk density of the polymer was determined by taking 50 gms. of polymer in a measuring cylinder of capacity 250 cc and strokes were given at regular periods. Volume was measured after 50 strokes. Bulk density was calculated as :

$$\frac{\text{Wt. taken}}{\text{Volume after strokes}} = \qquad \text{gm/cc.}$$

2.2.4 Characterization of Secondary Cellulose Acetate

The methods described below for analysis of secondary cellulose diacetate were adopted by following the ASTM methods[52].

a) Moisture Content

About one gm. of the sample was taken in a weighing bottle, dried in an oven at 105°C for two hours and reweighed after cooling it in a desiccator till the constant weight was obtained. The percent moisture content was calculated using the relation

$$\text{\% Moisture Content} = \frac{\text{Weight loss on heating}}{\text{Weight of sample taken}} \times 100$$

b) Ash Content

About 10 gm. of powder was taken in a weighing bottle and dried at 105°C for two hours to make it free from moisture. From this, one gm. of the powder was taken in a silica crucible and heated in a muffle furnace at 550°C for four hours. The crucible was allowed to cool at room temperature and weighed, till constant weight was obtained. The percent ash content was calculated adopting the relation :

$$\%\text{ Ash Content} = \frac{\text{gm. of Ash}}{\text{gm. of Sample taken}} \times 100$$

c) Acetyl Content

The estimation of acetyl content was carried out according to Etard's method, using aqueous sodium hydroxide solution to hydrolyze the cellulose acetate and back estimating the excess sodium hydroxide with standard hydrochloric acid solution.

Exactly weighed (one gram) Cellulose Acetate secondary was taken in an iodine flask and swollen in 40 ml solvent mixture prepared by mixing 300 ml of absolute alcohol, 100 ml of acetone and 50 ml of distilled water. The flask was warmed at 50-55°C for 30 minutes with slow stirring. Then exactly 40 ml of

0.5 normal sodium hydroxide solution was added into the flask to hydrolyze the cellulose acetate, and warmed at 45°C for 15 minutes. Afterwards the flask was kept for 48 hours to complete hydrolysis at room temperature. During this time, it was stirred slowly, manually and intermittently. Then excess of sodium hydroxide was back titrated against 0.5 normal hydrochloric acid solution using phenalphthalein as an indicator. Blank reading without addition of cellulose acetate was also taken to determine the exact quantity of sodium hydroxide solution used in the hydrolysis. percent acetyl content was calculated as shown below :

p. 26
grafted CA

$$\% \text{ Acetyl Content} = \frac{(A-B) \times N \times 4.3}{W}$$

Where, A = Blank reading

B = Back reading

N = Normality of the acid

W = Weight of the sample taken

4.3 = Factor to calculate percent acetyl equivalent weight 43. If percent acetic acid is required, a factor of 6.0 is used.

d) Molecular Weight Determination

[illegible]

Molecular Weight determined as mentioned in 2.2.3 (b).

e) Softening Point

Softening Point of secondary cellulose acetate was determined as described in 2.2.3(c).

f) Tensile Strength

Tensile strength of secondary cellulose acetate film was calculated as mentioned in 2.2.3(f).

g) Determination of Percent Acetyl of Membrane

Same way the percent acetyl of blended membrane was determined by drying the membrane at 105°C and making the membrane in powdery form. The same powder of the membrane was taken for determination of percent acetyl.

The observations have been tabulated in Table 25-A of Chapter IV.

2.2.5 Dense Membrane Preparation

a) Preparation of Dense Membrane of Cellulose Acetate

1) Preparation of Solution : Casting solution of cellulose diacetate was prepared from 20:30:50 weight percent cellulose acetate, formamide and acetone respectively reported by Chandorikar et al[53]. After adding the three components, the entire mass was rolled in a ball-mill for 24 hours.

2) Dense Membrane Preparation : The dense membrane of cellulose diacetate was prepared by spreading the casting solution on an extra smooth surface of glass plate by a stainless steel blade, having the required clearance between the two ends to form a uniform film layer. Solvent was allowed to evaporate completely in a dust-free atmosphere. After 24 hours, it was vacuum dried at 40°C for 3 hours to remove completely the solvent from the polymer film. It was then easily peeled off from the glass plate. Care was taken to dry the film completely. Thickness of the dense film was measured by micrometer. Dense films were preserved in a clean dustless box.

b) Preparation of Dense Membrane of PMMA :

In general, this membrane was prepared on the same line as mentioned in a-2) but the solution was prepared taking 25% weight percent of PMMA in Benzene and mixed well.

2.2.6 Preparation of CA:PMMA Blended Membrane

a) Preparation of Casting Solution for the blended Membrane

The casting solutions for blended membranes consist of cellulose diacetate and PMMA as polymer and acetone and benzene as solvents and formamide as additive.

First cellulose diacetate solution was prepared from 20:30:50 weight percent cellulose acetate:formamide and acetone respectively. After adding the three components the entire mass was rolled in a ball mill for 24 hours.

Similarly, PMMA solution was prepared from 25% weight percent PMMA in Benzene and after addition, the mass was rolled in a ball mill foe 24 hours.

Afterwards, both the solutions of Cellulose Acetate and PMMA were mixed in 80:20 proportion respectively and the whole mass was rolled in a ball mill for 6 hours.

The viscosity of the casting solution was measured by Brookefield Synchrolectric viscometer at room temperature.

devise n¶

b) Preparation of Reverse Osmosis Membrane

The membranes were cast in the form of flat sheet throughout the duration of these experiments according to the method described by Loeb-Sourirajan[54]. The glass plate was selected having a fine smooth surface and dimension of 50 x 30 square centimetres. Membranes were cast by spreading the casting solution with the help of the Shandon spreader on to a glass plate. It was absolutely necessary that the surface of the plate must be smooth and clean to avoid formation of blister-like impression on the surface of the membrane. Hence, the glass-plate was carefully cleaned with acetone and subsequently with ether before casting the membranes. After definite period of the solvent evaporating the membrane was immersed in an ice-cold water bath maintained at 0-2°C. After one hour, the immersed glass plate was removed from the cold water. The membrane was easily peeled off from the glass plate. It was heated in a constant temperature water bath at a definite temperature for 15 minutes. The membrane so prepared was generally milky white and opaque in appearance. Thickness of the membrane was measured by means of micrometer having the accuracy within the limit of 0.002 mm. The membrane was preserved in distilled water containing 0.2% formalin before using it for performance test.

2.2.7 Determination of Bound Water Content of the Membrane

Method reported by Vincent et al[55] was followed with necessary modification. The membrane samples were blotted to remove adhering water and weighed in weighing bottles, then the membrane samples were immersed in 20 percent cobaltous chloride hexahydrated solution for overnight. They were removed and adhering solution was removed by pressing between filter paper. The blotted pink coloured samples were exposed to atmosphere and when turned to lavender colour weighed quickly in tared weighing bottle. These samples were then dried in oven at 105 ± 1°C till they turned bright blue in colour to a constant weight. The leached weights of the samples were obtained by leaching samples with distilled water and dried at 105 ± 1°C. By knowing wet lavender and blue weights of the membrane the percent bound water was calculated by following equation :

$$\frac{(\text{Lavender} - \text{blue}) - 0.122\ (\text{blue} - \text{leached})}{\text{leached}}$$

$$= \frac{\text{gram bound water}}{\text{gram polymer}}$$

$\therefore$ Considering percent acetyl of CA:PMMA blended - glycerol treated membrane = 35.49 - 0.37 = 35.12

$\therefore$ Degree of Substitution :

$$\frac{380 \times 35.12}{102.4 - 35.12} = 2.017$$

$\therefore$ Molecular weight of 2.017 D.S. of Cellulose Acetate = Glucose molecules

= 2.017 OAC : 119

0.983 OH : 16.7

CH_2 : 14.0

2CH : 26.0

3C : 36.0

2O : 32.0

2H : 2.0

245.7

$$\therefore \frac{\text{Moles } H_2O}{\text{Moles OH}} = \frac{\frac{\text{Gm. bound water}}{18}}{\frac{\text{Gm. Polymer}}{245.7} \times 0.98}$$

$$= \frac{\text{Gm. bound water}}{\text{Gm. polymer}} \times \frac{245.7}{18 \times 0.98}$$

$$= \frac{\text{Gm. bound water}}{\text{Gm. polymer}} \times 13.87$$

$$\therefore \frac{\text{Gm. bound water}}{\text{Gm. Polymer}}$$

$$= \frac{13.87 \text{ (Lavender - blue)} - 0.122 \text{ (blue - leached)}}{\text{leached}}$$

Where, 0.122 = factor of dehydration of $Cocl_2.2H_2O$ to $Cocl_2H_2O$ at the time of lavender to blue colouration.

$$\therefore \frac{\text{Weight of } CoCl_2.H_2O}{147.9} \times 18$$

$$= 0.122 \text{ (blue - leached)}$$

Illustration

$$\frac{\text{Gm. Bound Water}}{\text{Gm. Polymer}}$$

$$= \frac{13.87\ (0.0259) - 0.122(0.0388)}{0.1347}$$

$$= 2.63$$

Where, lavender-blue : 0.0259 gms.

blue-leached : 0.0388 gms.

The above data for CA:PMMA blended optimized flat membrane have been tabulated in Table 26 of Chapter IV.

2.2.8 Graft Copolymerization of PMMA with Secondary Cellulose Acetate

Graft copolymerization of PMMA with secondary cellulose acetate was carried out using ceric ammonium sulphate as initiater[56].

In a three-necked round bottom flask, known amount of secondary cellulose acetate was taken in which previously prepared ceric solution was added. Moreover, calculated amount of Benzoyl peroxide and azo-bis isobutyronitrile were added. Stirring of the above mixture was carried out at a fixed temperature and time. Then a calculated amount of methyl methacrylate monomer was added and the reaction was carried out for a known time. The final product was extracted with Benzene to remove homopolymer and then by acetone to remove cellulose acetate by Soxhlet extracting unit.

Finally the grafted product was obtained which was characterized.

% grafting
p-147

2.2.9 Characterization of Cellulose Acetate Methacrylate (CAM)

Estimation of acetyl content of CAM was carried out as described in 2.2.4(c).

2.2.10 Preparation of CAM Membrane

a) Solution Preparation

Solution of cellulose acetate methacrylate was prepared in acetone benzene mixed solvent in known preparation, mixed well by ball-mill rotations for 24 hours.

b) Membrane Preparation

Preparation of the said membrane was carried out as described in 2.2.6(b).

2.3 EQUIPMENTS

2.3.1 Equipment for Polymerization of Methyl Methacrylate

Polymerization of methyl methacrylate was carried out in a round-bottomed flask.

Ceric ammonium sulphate of known concentration and known volume was added in the flask and was kept on heating mantle at a fixed temperature. Methyl methacrylate of known volume was added and heated for fixed time and left for some time at room temperature as shown in fig. 4.

Solvent Condition

2.3.2 Description of "Shandon Spreader for Flat Membrane Preparation

Casting of flat membrane was carried out as described in 2.2.4 using shandon spreader - fig. 5.

The latter (fabricated from aluminium sheet at this institute) consists of a rectangular cup which holds the casting solution and can be covered with an aluminium lid. At the bottom of this cup, along with its one long

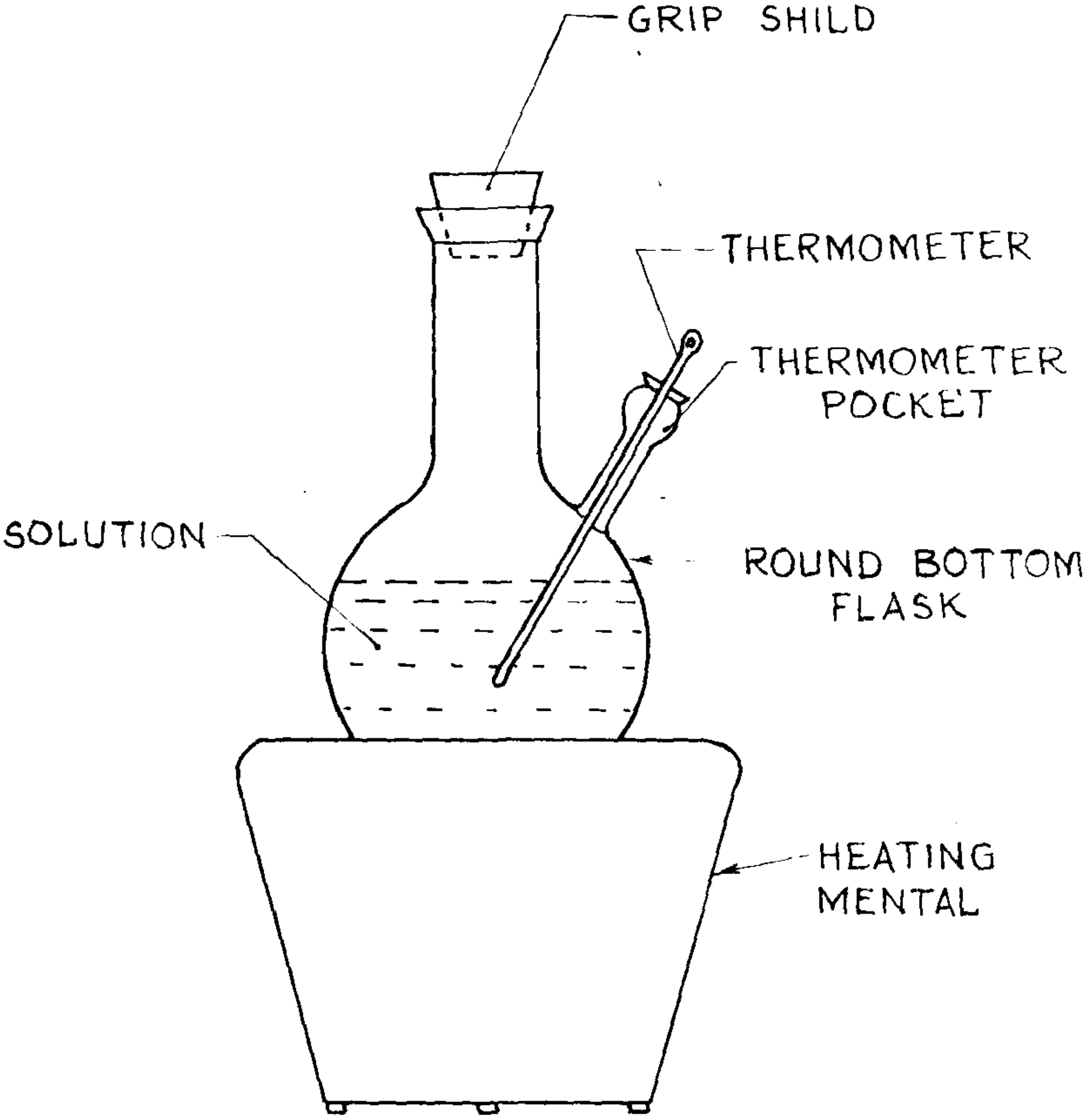


FIG: 4. POLYMERISATION UNIT.

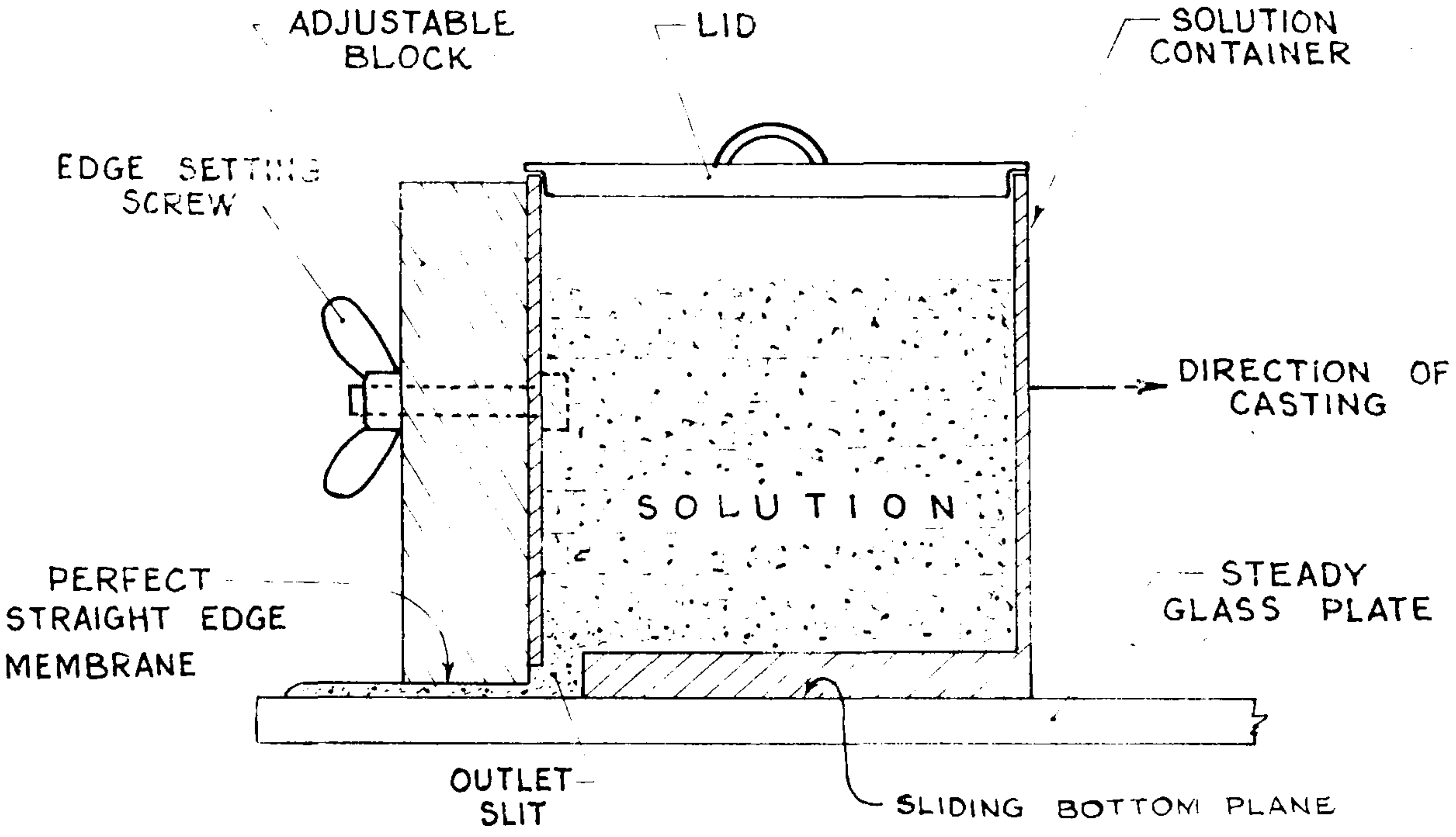


FIG : 5 . SHANDON SPREADER .

itudinal edge, there is a rectangular slit with a sufficient width which allows sufficient flow of the casting solution to drain outside on the casting surface during the membrane casting. In front of the slit, on the outside of the wall of this cup, there is an arrangement to vertically hold an aluminium casting blade with two screw-clamps so that the required gap can be accurately arranged between this blade's bottom surface and casting surface which allows to fix the as-cast thickness of the membrane. At the two bottom ends of the rectangular cup, two supports (from PVC sheet) have been fixed by an adhesive, the bottom surfaces of them being made sufficiently smooth. Two hand-grips have been provided to the rectangular cup, one at each edge of the cup.

2.3.3 Conductivity Bridge

Conductance measurements were carried out on conductivity bridge supplied by M/s. Toshniwal Co.Ltd., type CL01/024, Sr. No. 319, consisting of a valve oscillator, wheatstone bridge arrangement, amplifier, detector and magic eye. The bridge had working test frequency of 3 KC/S and 50 C/S. The conductance system under measurement was connected between the cell terminal which forms one of the terms of wheatstone bridge. The balancing point was indicated by means of a sensitive magic eye.

2.3.4 Reverse Osmosis Test Unit

Reverse Osmosis performance data of the membranes were collected using a laboratory test unit, supplied by M/s. Universal Water Corporation, California, U.S.A. It consisted of feed water tank (G), pressurizing pump (F), Pressure Accumulator (E), By-pass valve (D), and stainless steel high pressure test cell (D). This unit is schematically shown in fig. 6 and the high pressure test cell is shown separately in fig. 7.

Feed water is circulated by high pressure pump of pressure range 0 to 1500 psig. The pump was a variable strokes positive displacement diaphragm coupled with a 0.75 H.P. motor and a pumping capacity of 600 ml/min. Any pulse due to pumping was eliminated by a green placar accumulator. The inlet pressure in the system was controlled by adjusting the spring loaded back pressure regulator provided in the by-pass line. Water from the back pressure regulator was usually returned to the feed water tank and recycled.

Operating procedure for Reverse Osmosis test Unit : Feed Water tank (G) of six litres capacity was filled with a known concentration of pure sodium chloride solution. Desired pressure in the back pressure regulator was fixed by filling nitrogen gas in it. Oil level in the pump was checked before starting any operation. Membrane of about

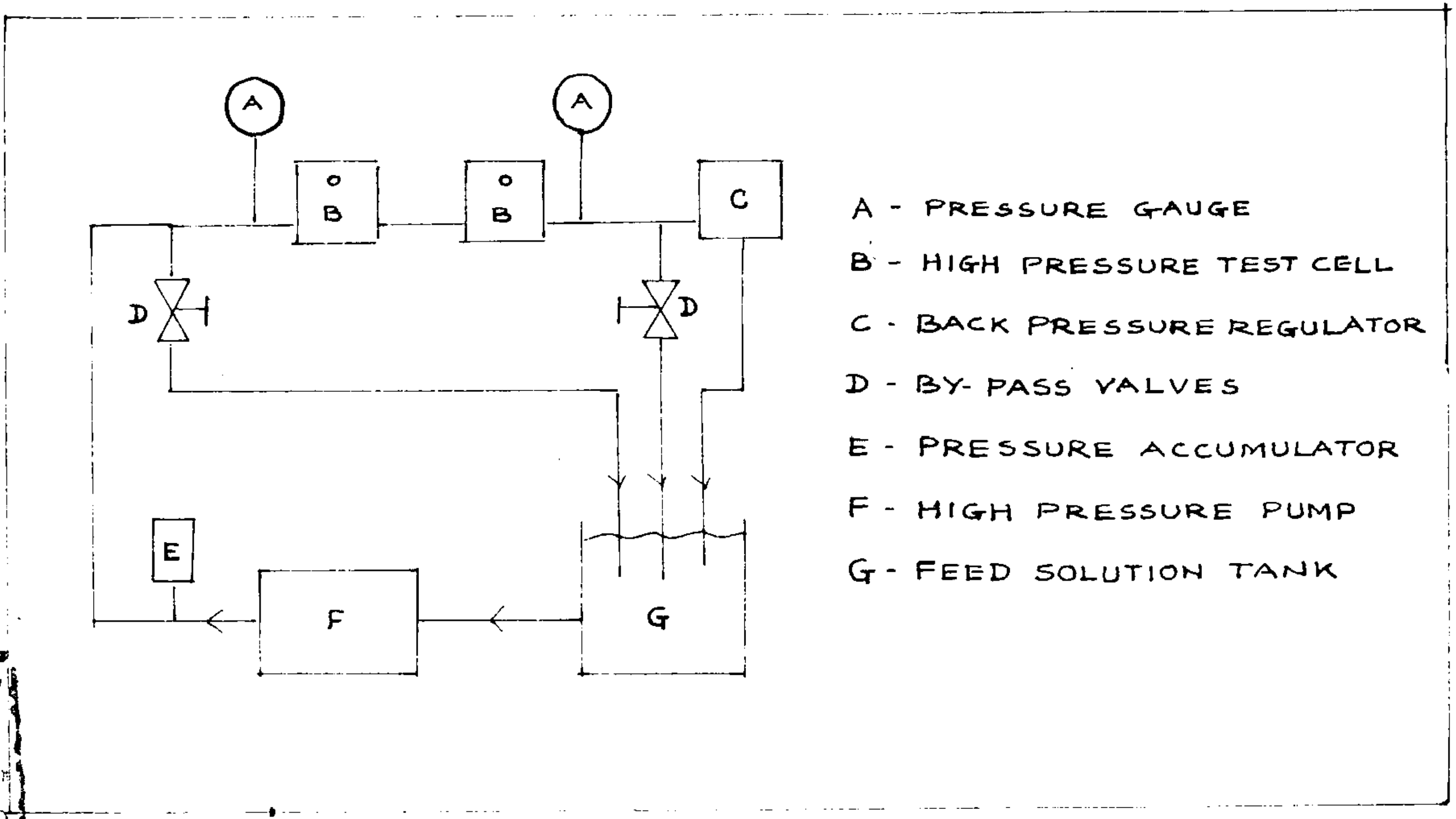


FIG: 6 DIAGRAMATIC PRESENTATION OF THE R.O. ASSEMBLY.
(FLAT MEMBRANE)

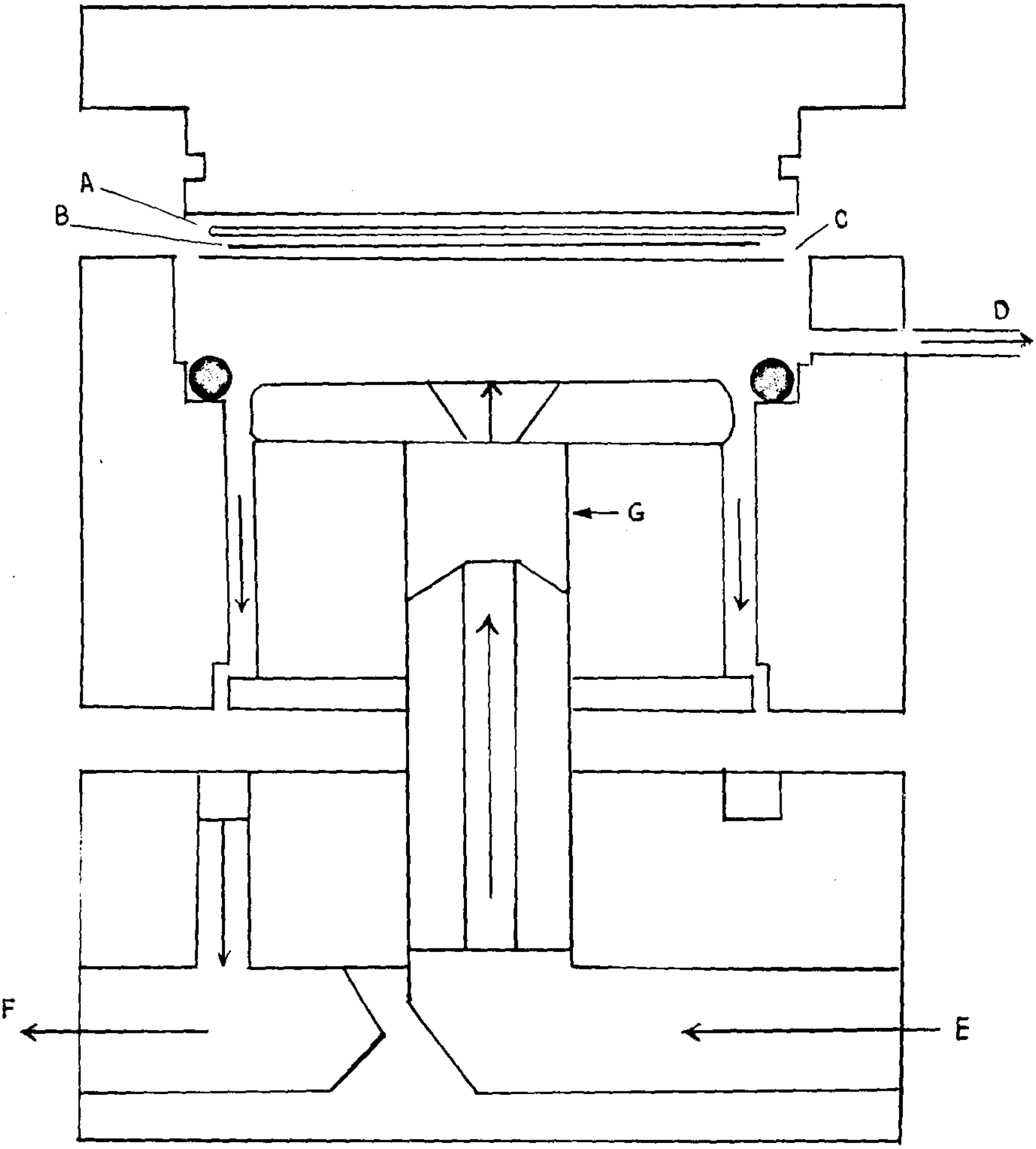


FIG: 7. HIGH PRESSURE TEST CELL

A – Porous s.s. plate
B – Filter paper
C – Membrane - active Surface facing brine
D – Product outlet
E – Feed inlet
F – Brine outlet.
G – Feed channel.

18.6 sq.cm. area, together with a filter paper and a porous disc were placed in the test cell and assembled as shown in diagram. The pump was started, keeping the by-pass valve open. Care was taken to avoid any air bubble in the feed water for smooth operation of the unit. The by-pass valves were slowly closed so as to get the desired pressure as adjusted in the back pressure regulator valve. The product water coming out through the membrane was collected in a flask. The volume of product water after a regular time intermal was measured and this was then converted to gfd.

2.3.5 Brooke Field Synchroelectric Viscometer

For the measurement of the viscosity of the sample, a synchroelectric viscometer (Model LVF) was used. It rotates a cylinder or a disc in a field and measures the torque necessary to overcome the viscous resistance to the induced movement. That is accomplished by driving the immersed spindle through a berrylium copper spring. The degree to which the spring is wound, indicated by the position of the red point on the viscometer dial, is proportional to the viscosity of the fluid for any given speed and spindle. It has an accuracy of 1 percent and reproducibility of 2 percent. The solutions of the cellulose acetate, cellulose acetate PMMA blend, and cellulose acetate methacrylate grafted were transferred to a six centimeter diameter cylinder which was kept in constant temperature bath during the measurement. Using the spindle no. 4 and a speed of 6, 12 and 30 rotations per minute, the viscosities of the solutions were directly measured on the viscometer dial in centipoise.

CHAPTER - III

EXPERIMENTAL

3.1 POLYMERIZATION OF MONOMER METHYL METHACRYLATE (MMA)

This polymerization study was carried out utilizing the method as outlined in (2.2.2) studying the following variable parameters:

i) The amount of the initiator, ceric ammonium sulphate.
ii) The reaction temperature
iii) The reaction period - the amount of the monomer (MMA) was kept constant.

3.1.1 Variable Parameter Studied

The amount of the initiator Ceric ammonium sulphate: Constant experimental conditions :

i) Reaction temperature : 60°C
ii) Reaction period : 45 min.

A series of laboratory experiments were carried out varying the amount of ceric ammonium sulphate from 0.1 N to 0.0025 N. The results are described in Table 1.

3.1.2 Variable Parameter studied

The Reaction Temperature :

Constant Experimental Conditions :

i) Amount of Ceric ammonium sulphate 0.0025N - 30 ml.
ii) Reaction Period : 45 min.

The polymerization of methyl methacrylate monomer (MMA) was carried out at different temperatures ranging from 40°C to 60°C. Data was collected as shown in Table 2.

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3.1.3 Variable Parameter studied

Reaction period :

Constant Experimental Conditions :

i) Amount of ceric ammonium sulphate : 0.0025N - 30 ml.
ii) Reaction Temperature : 60°C

The homopolymerization of MMA was carried out for different reaction periods ranging from 30 min. to 60 min. Data was collected and tabulated in Table 3.

The studies from 3.1.1 to 3.1.3 have led to the optimized conditions of homopolymerization of methyl methacrylate (MMA) monomer which is shown in Table 4.

3.1.4 Bench Scale Homopolymerization of Methyl Methacrylate Monomer (MMA) under the optimized conditions

1
123

Employing the above-mentioned optimized conditions, bench scale experiments were carried out for homopolymerization of the monomer MMA; Each time in a 10 litre capacity round-bottomed flask, 300 ml of the monomer (MMA) was utilized for polymerization using monomer 0.0025 N ceric ammonium sulphate equal to 1:30 by volume. Table 5 contains the results.

The product poly methyl methacrylate (PMMA) from bench scale polymerization was also characterized as shown in Table 6.

3.2 CHARACTERIZATION OF PMMA

The following characteristics were studied for PMMA :

3.2.1 Softening Point

Softening point of PMMA was carried out as described in 2.2.3.d.

3.2.2 Moisture Adsorption-Desorption of PMMA

Adsorption-desorption of PMMA was studied as described in (2.2.3.c) and the data were collected as tabulated in Table 7.

3.2.3 Determination of Molecular Weight of PMMA

Molecular weight determination of PMMA was carried out by the method as described in (2.2.3 b) and the data were collected in Table 8.

p.77

3.2.4 A sample of PMMA obtained from Eastman Kodak Co., USA, was characterized on similar lines and its characteristics were compared with the laboratory prepared product - Table 9.

3.3 OPTIMIZATION OF THE BLEND PROPORTION OF CA:PMMA FOR OBTAINING A SUITABLE FLAT OSMOTIC MEMBRANE

For this study, the cellulose diacetate solution was utilized in the proportion, Cellulose diacetate: Formamide:Acetone::20:30:50 % by weight, and the Poly Methyl Methacrylate (PMMA) as 25% by weight benzene solution.

The membrane casting solutions were prepared in the following blend proportion :

i) 80:20, ii) 60:40, iii) 40:60, iv) 20:80 as CDA:PMMA % by weight respectively. The constant membrane preparation parameters were as follows :

Post-cast evaporation period : 20 sec.
As-cast thickness : 0.25 mm.
Annealing temperature : 92°C.
Gelling bath temperature : 0-2°C
Experimental % R.H. : In the range of 65-70

These membranes were one by one applied to the Reverse Osmosis cell and their operational data were recorded at the end of 6 hours operation. These data are reported in Table 10.

Illustration :

Constant Operational Conditions :

i) Pressure : 40 atm.
ii) Feed rate : 800 ml/min.
iii) Operational period : 6 hrs.
iv) Feed concentration : approx. 5000 ppm NaCl soln.
v) Feed Temperature : 30-32°C
vi) Effective membrane area : 18.6 cm^2

Membrane Performance :

Product Water flux : 490 lmd p. 79 ?
Percent salt rejection : 98%

This study has led to the optimized blend composition of CA:PMMA for the preparation of a useful Reverse Osmosis flat membrane.

3.4 OPTIMIZATION OF FLAT MEMBRANE PREPARATION USING OPTIMIZED BLEND CA:PMMA SOLUTION

Using the optimized CA:PMMA blend solution, four types of membranes were prepared under the following membrane preparation parameters :

Membrane Type	Constant Parameters	Varied Parameter
1.	Post-cast evaporation time:20 sec. Annealing temperature : 92°C	As-cast thickness 0.18, 0.24, 0.3, 0.36 mm.
2.	As-cast thickness : 0.25 mm. Annealing temperature : 92°C	Post-cast evaporation period : 20, 40, 60, 90, 120 sec.
3.	Post-cast evaporation time:20 sec. As-cast thickness : 0.25 mm.	Annealing temp. : 86, 88, 90, 92, 94°C.
4.	Post cast evaporation period:20sec As-cast thickness : 0.25 m Annealing temp. : 92°C	Cross-linking during annealing using $K_2S_2O_8$ and $NaHSO_3$.

The Reverse Osmosis operational data of these membranes are noted in Table Nos. 11, 12, 13, 13A, and 14.

p. 85 It was attempted to reproduce the optimized flat CA:PMMA blend membrane several times. Table 15 contains the Reverse Osmosis performance data. This flat membrane indicated some minute pores, while making visual observation. It is probable that most of these pores were self-sealing under high pressure and this is supported by the virtual disappearance of the hydraulic flow of salt solution.

It was thought useful to prepare cellulose acetate flat membrane (casting solution composition cellulose acetate:Formamide:Acetone::20:30:50 % by wt) under identical membrane preparation parameters as employed in the optimized flat CA:PMMA blend membrane and to collect its reverse osmosis performance data under the identical operational conditions as employed for the latter membrane. These data are tabulated in Table 16.

Illustration, utilizing CA membrane :

Product Water flux	:	440 lmd
% Salt rejection	:	92.0%
Effective membrane area	:	18.6 cm^2

3.5 FURTHER DEVELOPMENT OF OPTIMISED FLAT CA:PMMA BLEND MEMBRANE

It has been reported[57] that heating cellulose acetate membrane in aqueous glycerol solution and drying at < 50°C increase its product water flux and desalination capacity. Keeping this in view, CA:PMMA blend optimized membrane and also cellulose acetate flat membrane prepared as mentioned in (2.2.6) were annealed in 30% aqueous glycerol bath at different temperatures. Their reverse osmosis performance data were collected as mentioned in Table 17.

3.6 TUBULAR MEMBRANE FROM CA:PMMA BLENDED OPTIMISED CASTING SOLUTION

A gravity drop method of Loeb[58]∠modified and ∠was adopted for casting the tubular membrane. At the Central Salt and Marine Chemicals Research Institute, casting of tubular membrane has been developed[59] for brackish water desalination in which a separate solution container has been provided for this arrangement (fig. 8). This arrangement helps in two ways :

a) Loss of casting solution is minimized

b) A batch casting tubular membrane is easily accomplished.

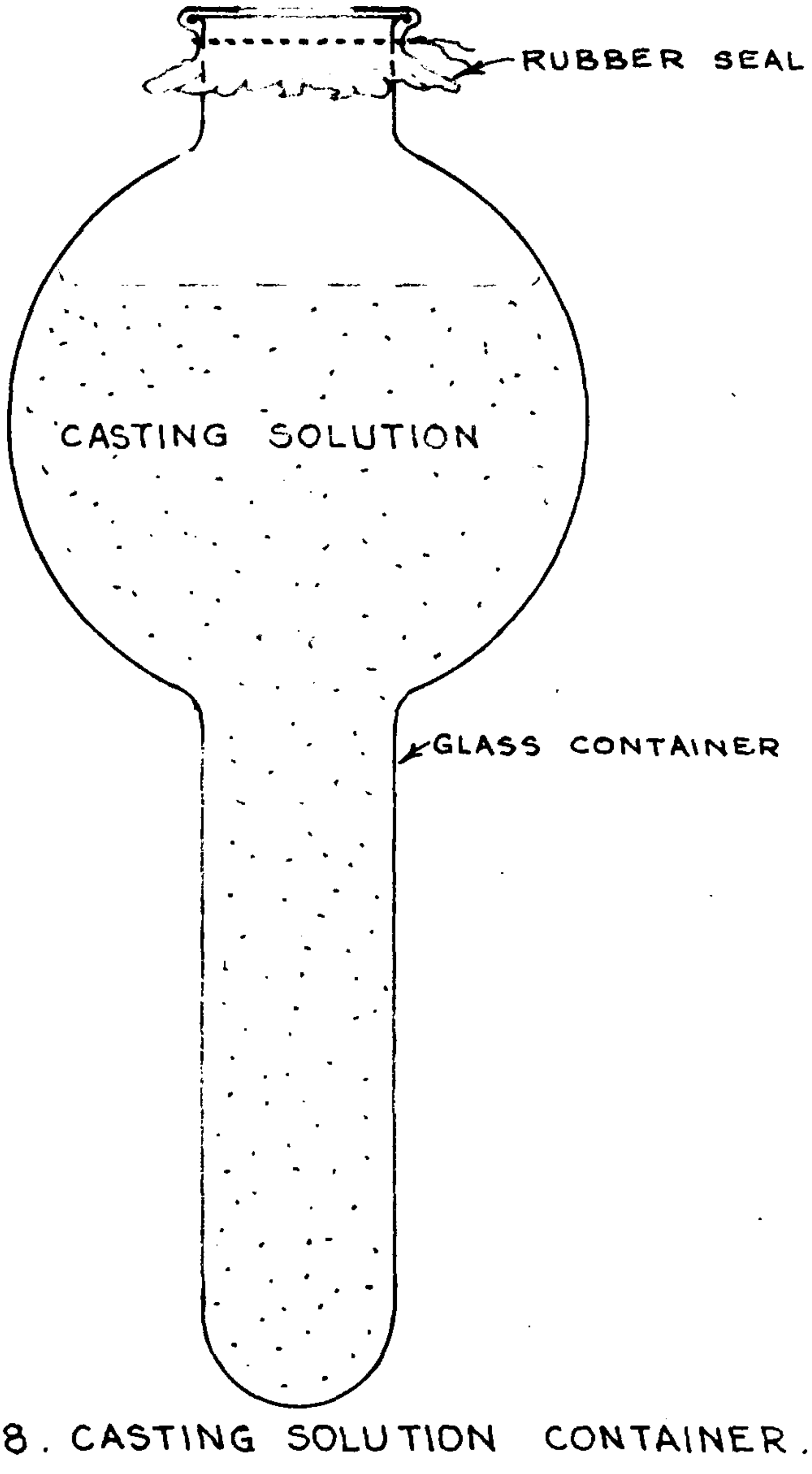


FIG: 8. CASTING SOLUTION CONTAINER.

This modified process is described below in detail: The membrane was batch-cast using equipment as shown in fig. 9. This consists of 1) a glass container as shown in fig. 6, a bob of 1.75 cms. diameter as shown in fig. 10. The intercepting conical section of the bob provides a smooth flow of casting solution between the casting tube and the bob.

3.6.1 Casting Tube

The solution was slowly filled in the glass container while the bob was inside. Then the casting tube previously cleaned and washed with acetone is held by a side screw available at the bottom-most 3rd guide. The three guides, fixed at definite spacing allow the centering of the casting tube. Afterwards, the screw is loosened and the casting tube is immersed in the casting solution in the glass con-tainer upto a pre-fixed depth (fig. 11) so that the casting solution gradually finds its way inside the casting tube. After clamping the casting tube in this position, the glass container is slowly lowered and removed away from the bottom end of the casting tube during which the casting solution adhering to the outer surface of the lower end of the casting tube is scrubbed out inside the glass container by the centrally-holed rubber diaphram attached to the neck of the glass container. During the gravity drop of the casting tube, the solution was dragged out along with the bob, but there is an annular space between the bob

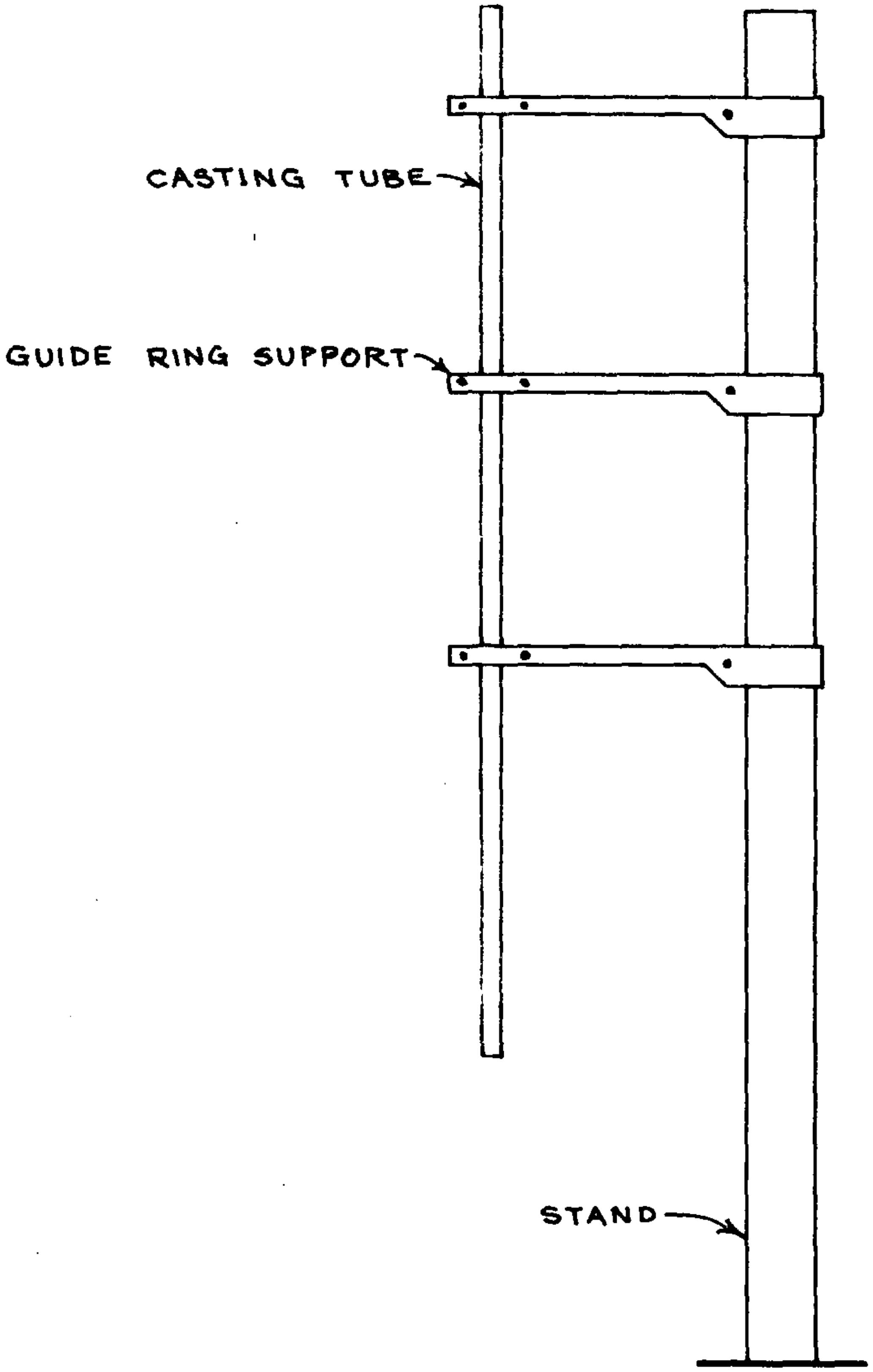
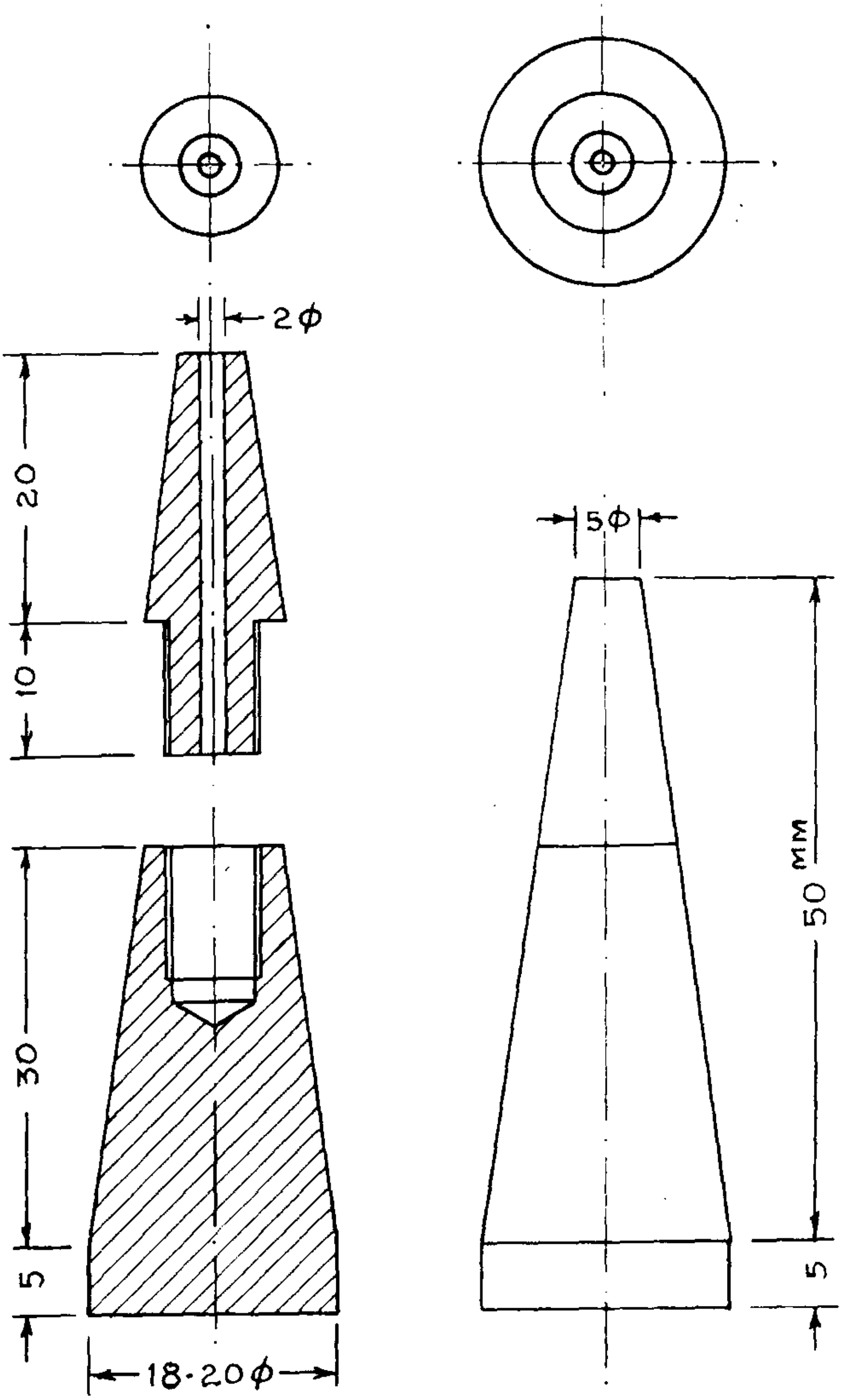


FIG: 9. CASTING STAND



CASTING BOB

FIG. 10.

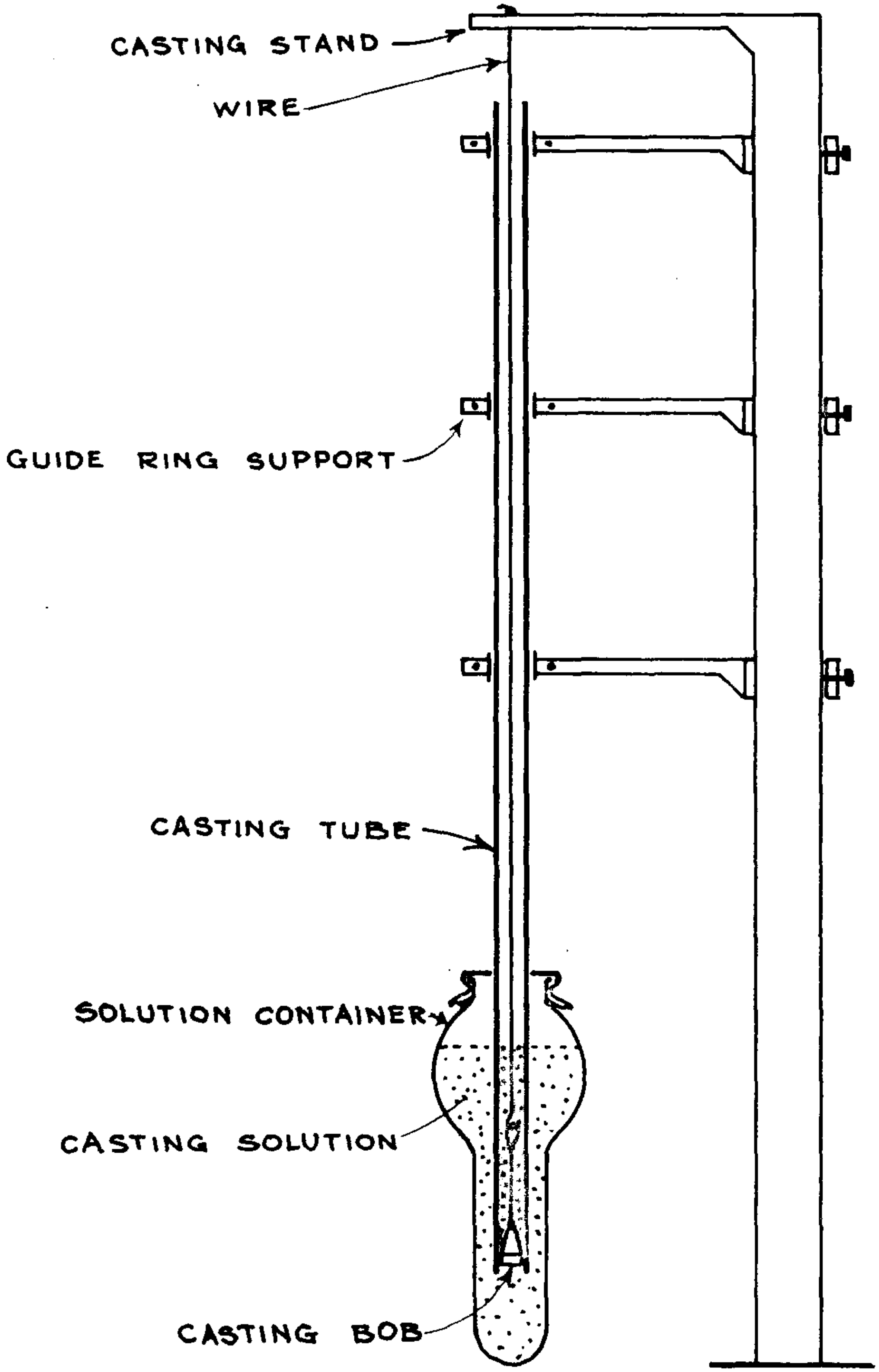


FIG: 11. CASTING TUBE IN SOLUTION CONTAINER and the casting tube, a small quantity of the solution remained adhered to the inner surface of the casting tube in the form of the tubular film. It took about 25-30 seconds to complete this operation. The casting tube along with the nacent membrane inside was given some time for solvent evaporation known as post-cast evaporation time. A part of the solvent had evaporated during this operation. It was then slowly immersed in a container filled with ice-cold water (0-2°C) and allowed to gel for an hour. During this gelation process, the remaining acetone, benzene and formamide were leached out, the film got shrunk which helped in its easy removal from the casting tube (photograph 1).

3.6.2 Insertion of the Membrane into Perforated Tube

After gelation, the membrane was removed from the casting tube, wrapped with fine nylon cloth prior to its insertion in the perforated anodized aluminium tube. The wrapping of nylon cloth provided a path of least resistance for the flowing out of desalinized water permeated from the membrane. Usually for wrapping the membrane, one and a half turns of nylon cloth was sufficient. After the insertion of the membrane, the protruding ends were cut with a sharp razor blade. The rubber seals were now introduced to both the ends of

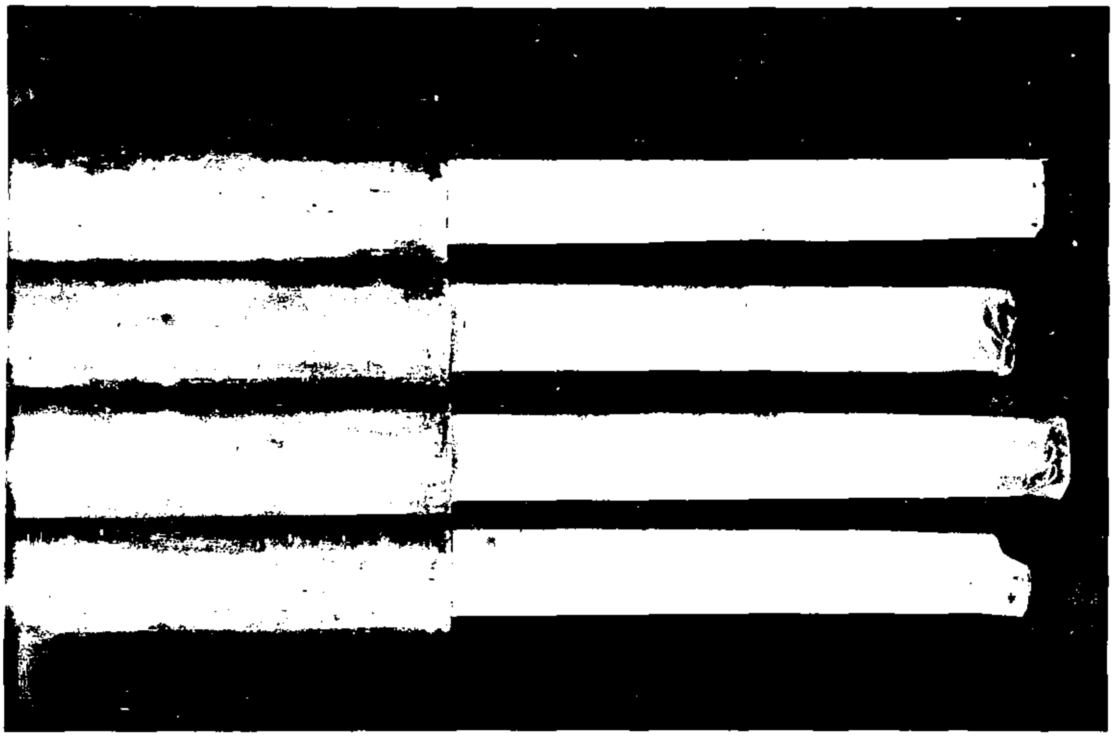


Plate 1 : Membranes drawn out a little from casting tubes

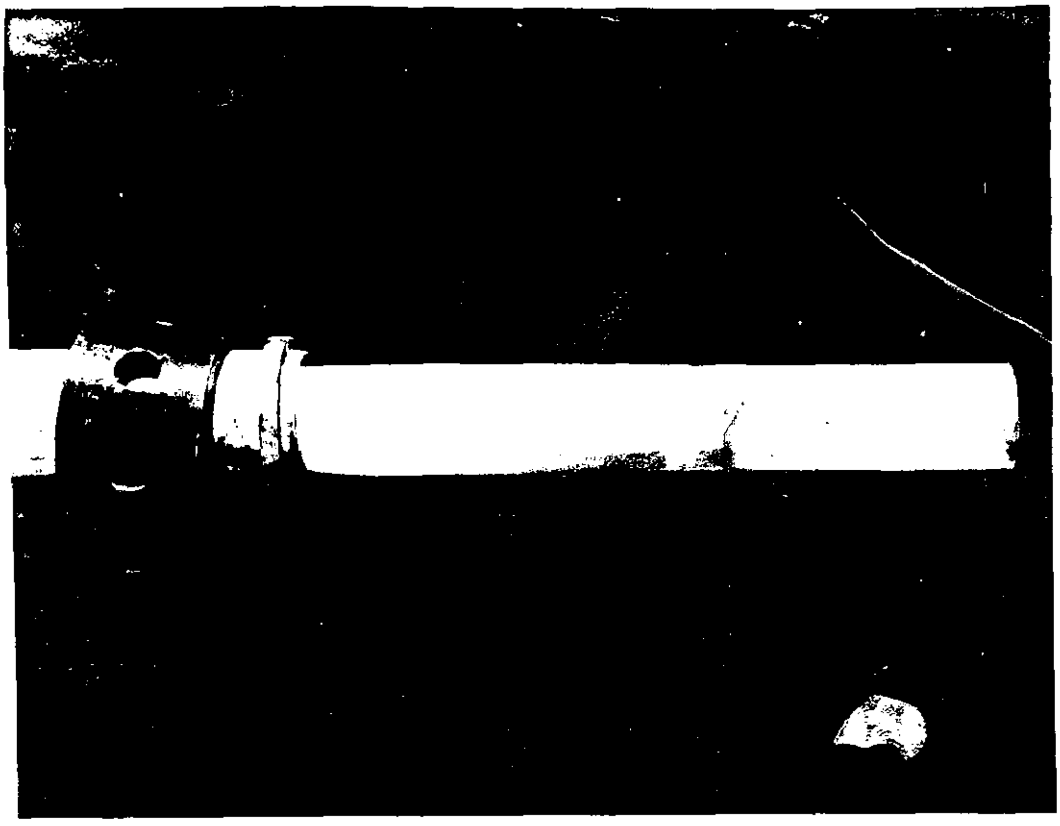


Plate 1A : Support cloth wrapped membrane inserted into a perforated tube the tube as shown in fig. 12 and then tapered metallic hollow expanders were fixed over the rubber seal (photograph 2). The membrane was now ready for the annealing treatment and the end pieces of the membrane were preserved for studying other properties.

3.6.3 Annealing Treatment and Module Assembly

Sealed tubular membranes were assembled in the series system, Fig. 13. water was heated to a required temperature and was circulated in the tube with a centrifugal pump for 15 minutes at a known flow rate and at 0.5 atmospheric pressure. The pressure was regulated by providing needle valve at the outlet of the assembly. Water at room temperature was then circulated with the same pump at slightly elevated pressure 0.7 atm. till the system attained ambient temperature. The annealed membranes were now ready for reverse osmosis application.

The membrane support tubes along with the membranes were then detached from the annealing treatment assembly and assembled again in series connected by specially designed 'U' type anodized aluminium header (fig. 14).

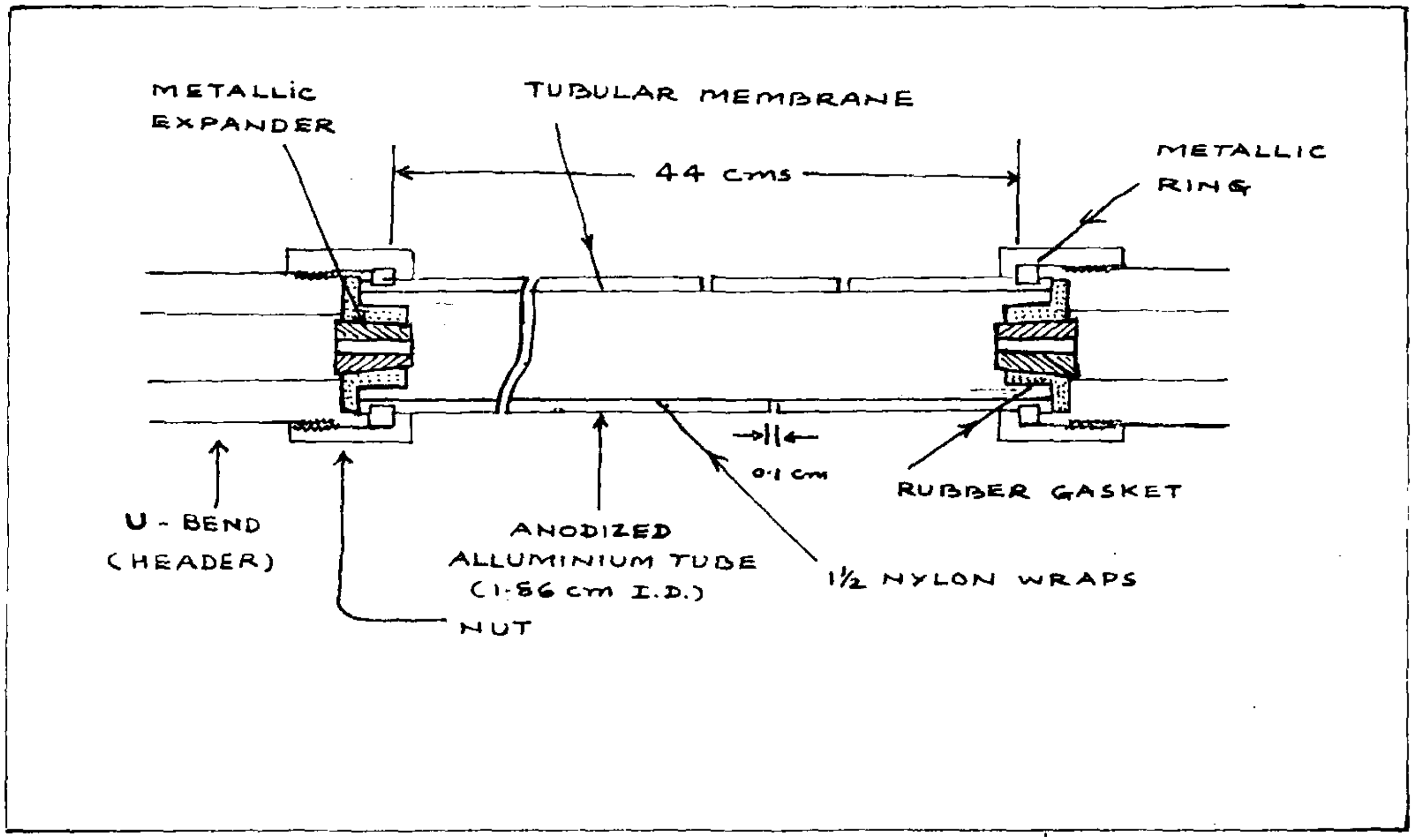


FIG:12. CROSS SECTION OF TUBULAR ASSEMBLY.

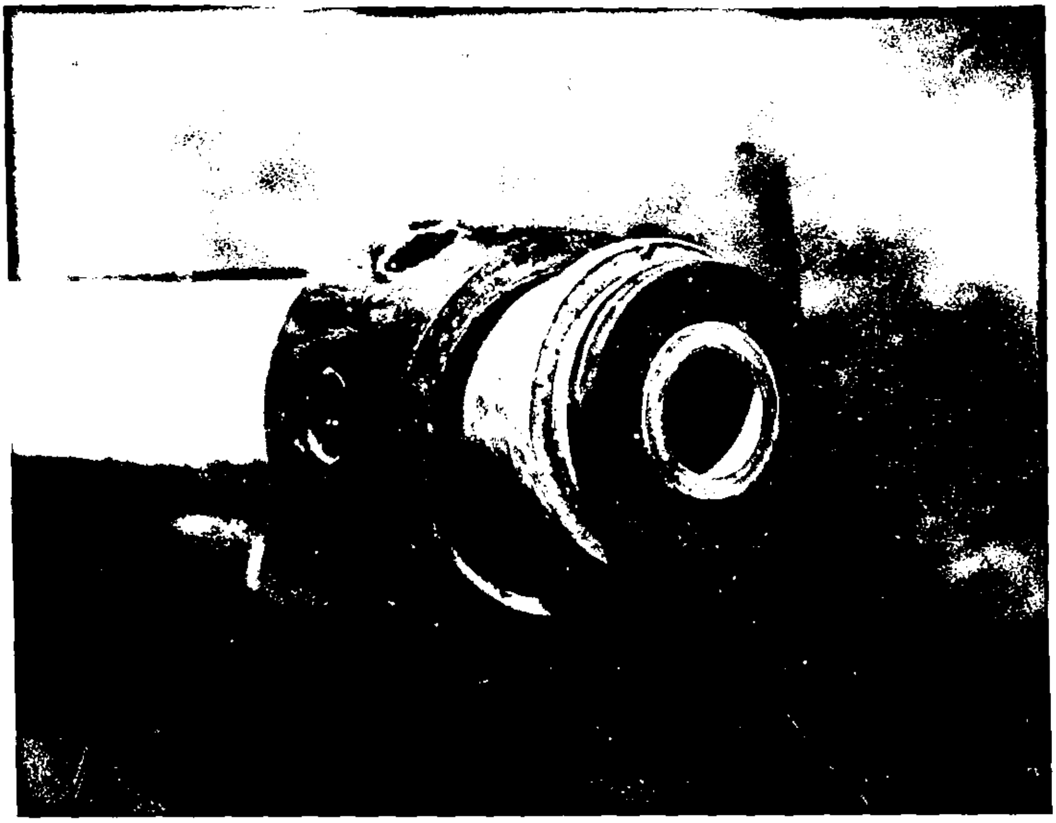
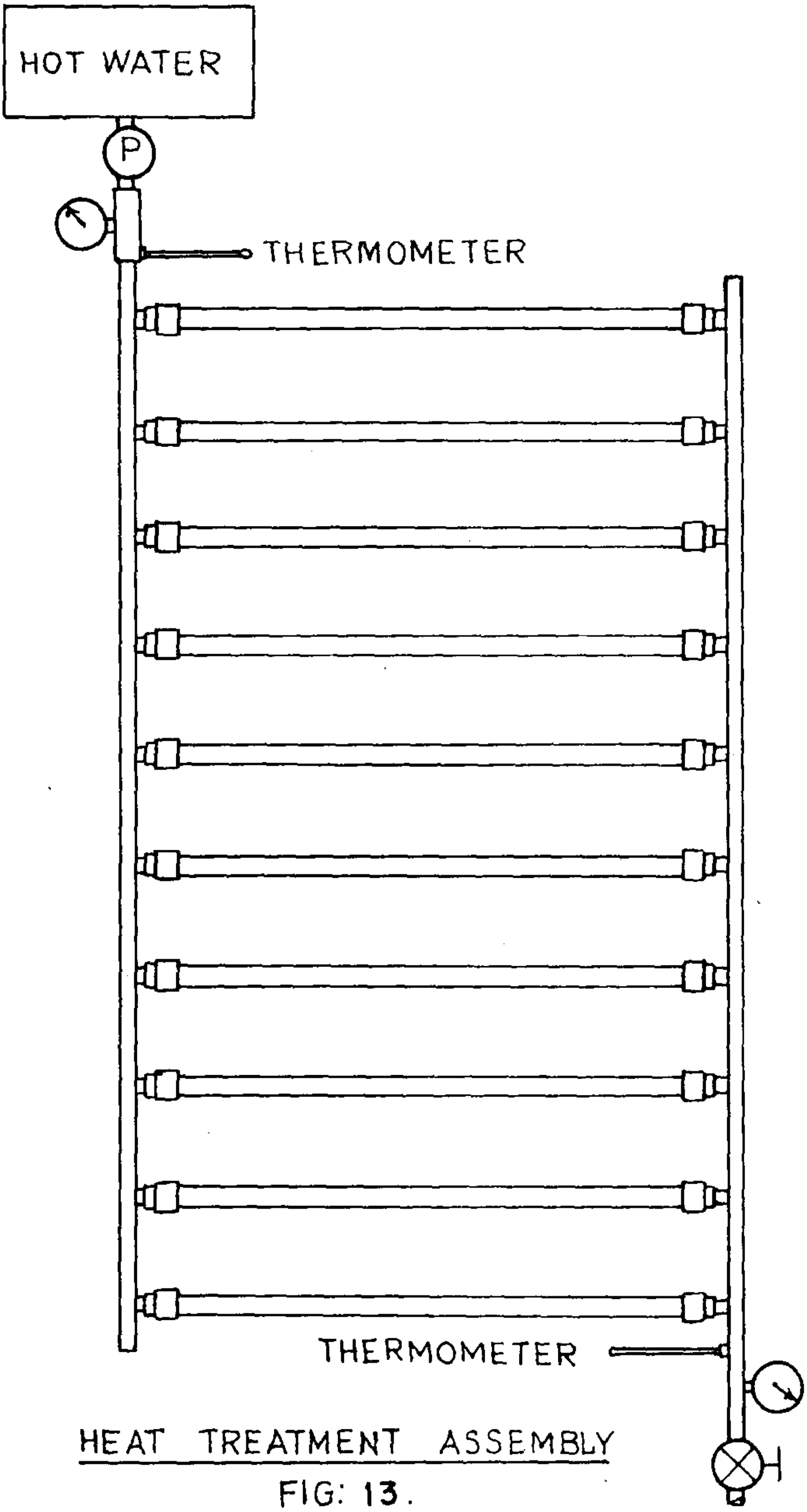
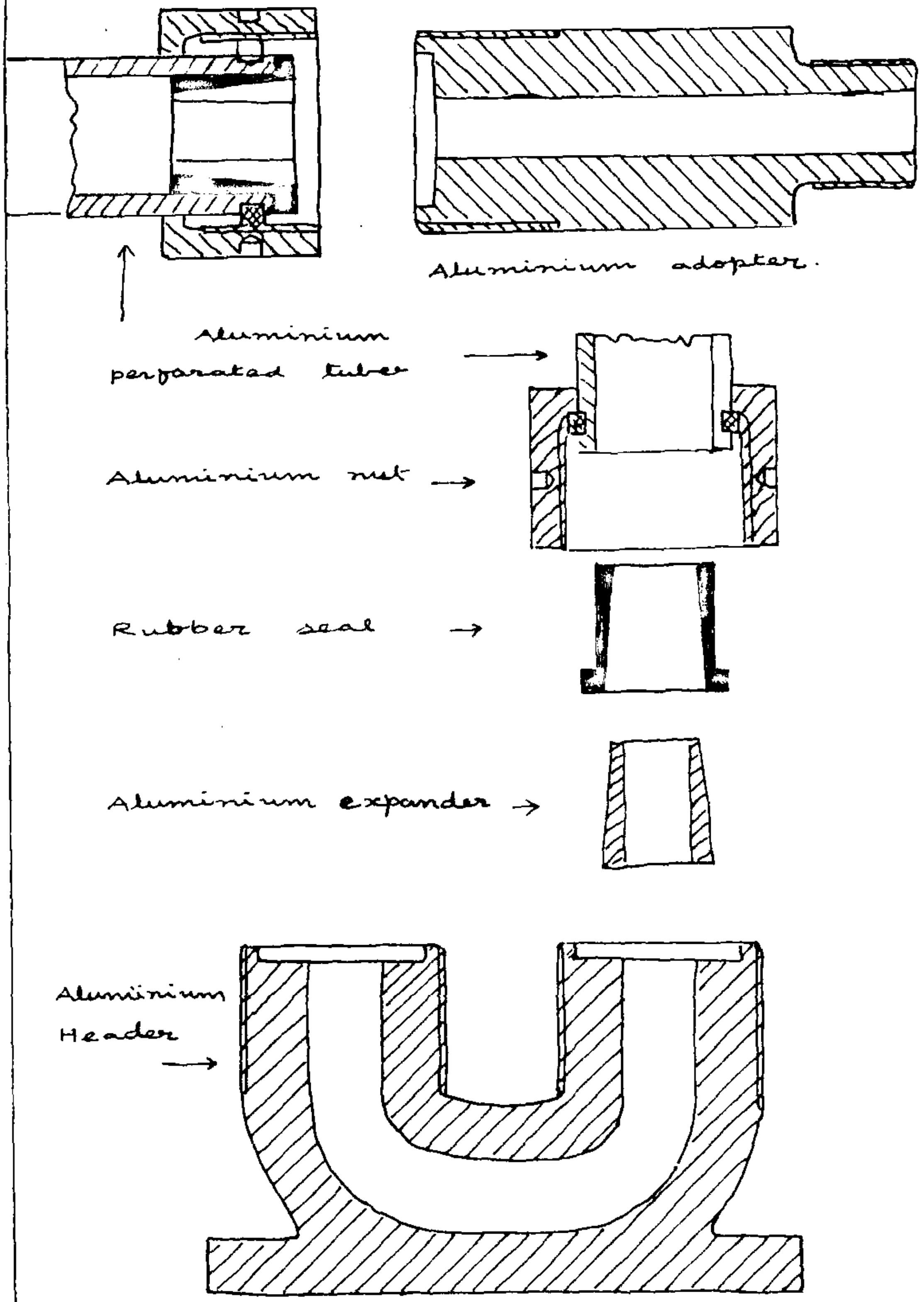


Plate 2 : A sealed end of the membrane element.



HEAT TREATMENT ASSEMBLY

FIG: 13.



FIG; 14. END CONNECTION DETAILS

3.6.4 Performance of the Tubular Assembly for various Parameters

brine circulation?

The membranes assembled (fig. 15) were connected on one side with the feed tank (F) through an accumulator (A) and they were connected with back pressure regulating valve (V) and by-pass arrangement (B). The high pressure pump (P) drives the feed solution through the accumulator to the membrane module at a definite feed rate and a definite pressure. The pressure in the assembly was regulated and controlled by back pressure regulator. During the performance study it was necessary to characterize the membrane by determining its flux and salt rejection. The flux was measured by collecting the permeate of the individual membrane in a suitable container for definite time interval under fixed conditions of pressure, feed, velocity, and salinity. From the amount of the product collected, the flux in litres per square meter per day (LMD) was calculated.

The other significant membrane characteristic is its salt rejection capacity. This was determined by measuring the electrical conductivity of the feed and the permeate when the other conditions were constant. This is given by the following equation :

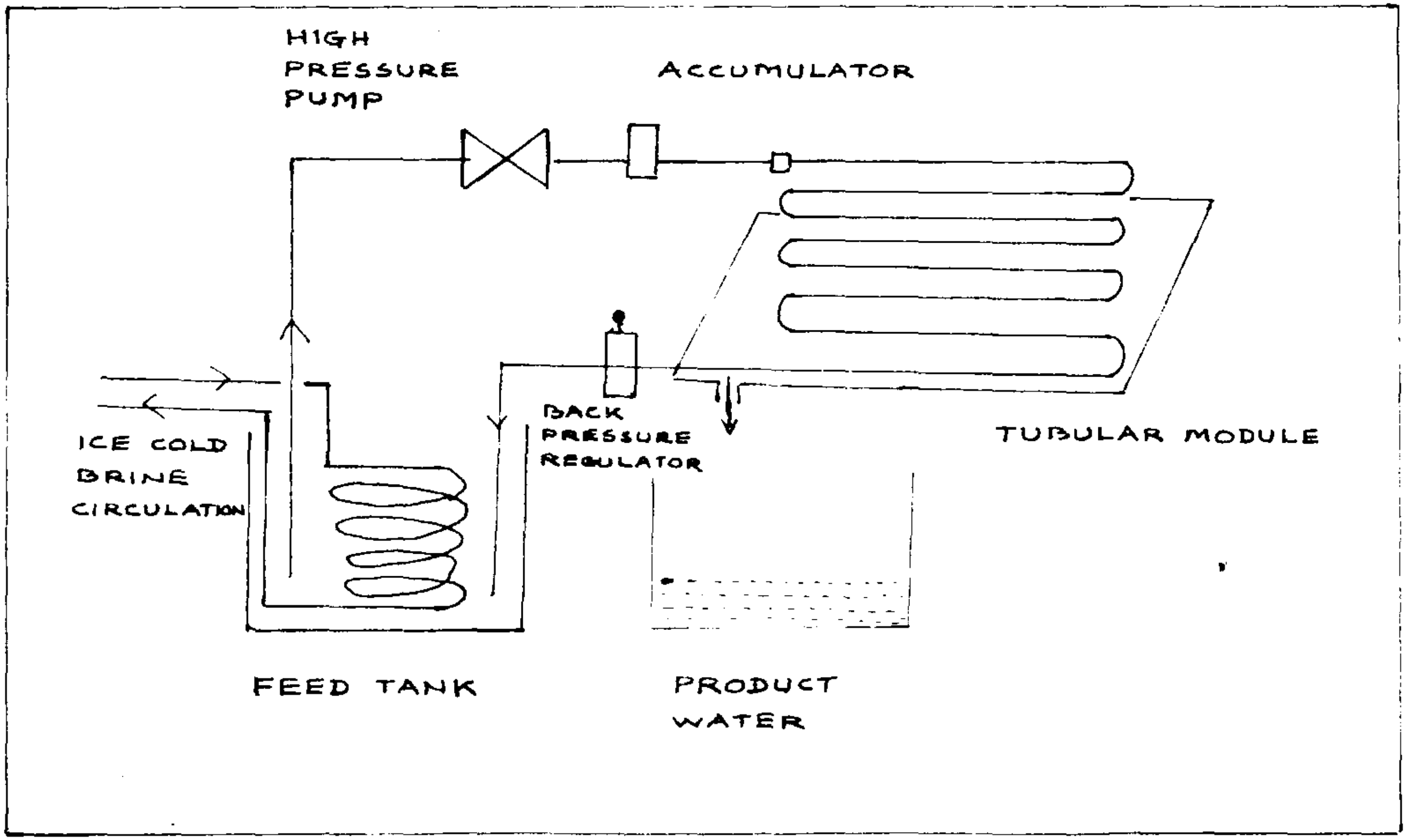


FIG: 15. FLOW DIAGRAM OF TUBULAR ASSEMBLY.

Percent Salt Rejection :

$$\frac{\text{Conductivity of Feed} - \text{Conductivity of Product}}{\text{Conductivity of Feed}} \times 100$$

The results are tabulated in Table 18.

On similar lines as mentioned above, tubular membranes were prepared but annealed with aqueous glycerol bath. Table 19 contains their reverse osmosis performance data.

Similarly, cellulose acetate tubular membranes were annealed in aqueous glycerol bath and their reverse osmosis performance data have been collected as mentioned in Table 20.

3.7 FLAT MEMBRANE FROM (CAM) CELLULOSE ACETATE METHACRYLATE GRAFT COPOLYMER

The casting solution composition was CAM: Formamide:Acetone::20:30:50 % by weight, but in the calculated acetone requirement 10% by weight benzene is utilized along with acetone. The membrane preparation parameters were the same as for the optimized flat CA:PMMA blend membrane. Its reverse osmosis performance data is incorporated in Table 21.

3.8 AN APPLICATION STUDY OF THE OPTIMIZED FLAT CA:PMMA BLENDED MEMBRANE

It has been observed by other research workers[60] that with cellulose acetate membrane in Reverse Osmosis in compavition to other anions or radials generally present in brackish water (e.g. Cl', SO_4'', HCO_3'') the level of rejection of radicals like NO_3', NO_2', NH_4' and of urea etc. remains quite low. Keeping this in view CA:PMMA flat blended membrane and cellulose acetate flat membrane prepared under the identical optimised conditions were employed in the Reverse Osmosis cell using synthetic urea aqueous solution (F) as feed or (II) as with 0.5% NaCl solution as feed. Table 22 contains their reverse osmosis performance data.

TABLE 1

Polymerization of Methyl Methacrylate Monomer using different Concentrations of Ceric Ammonium Sulphate

Experiment No.	Concentration of Ceric Ammonium Sulphate (Normality)	% yield based on the weight of Monomer
1	0.1	35
2	0.01	55
3	0.005	60
4	0.0025	65

Proportion of Ceric Ammonium Sulphate Solution:Monomer is 30:1 by Volume.

TABLE 2

Polymerization of Methyl Methacrylate Monomer at different Temperatures

Experiment No.	Reaction Temperature °C	% yield based on the weight of Monomer
1	40	30
2	45	45
3	50	50
4	55	55
5	60	65
6	65	60

TABLE 3

Polymerization of Methyl Methacrylate Monomer for different Reaction Periods

Experiment No.	Reaction Period in Minutes	% yield based on the weight of Monomer
1	30	45
2	40	65
3	50	65
4	60	65
5	70	65

TABLE 4

Optimized Conditions of Polymerization of Methyl Methacrylate Monomer

	Optimized Conditions	% yield based on weight of Monomer
1)	Concentration of Ceric Ammonium Sulphate 0.0025 N - 30 ml for 1 ml. Monomer	65
2)	Reaction Temperature 60°C	65
3)	Reaction Period 40 minutes	65

TABLE 5

Bench Scale Preparation of Poly
(Methyl Methacrylate)

Experiment No.	% yield based on weight of Monomer
1	65
2	66
3	65
4	65
5	65
6	66
7	67
8	65
9	65
10	65

Experimental Conditions :

1) Amount of Monomer : 300 ml.

2) Concentration of Ceric Ammonium Sulphate & Volume : 0.0025 N of 9000 ml.

3) Reaction Temperature: 60°C

4) Reaction Period : 40 minutes

TABLE 6

Characterization of Poly (Methyl Methacrylate)

	Characteristics	Average Value of 3 Experiments
1)	Molecular Weight	700000 - 800000
2)	Softening Point	123 - 126°C
3)	Bulk Density	0.3123 gm/cc.
4)	Moisture Adsorption-Desorption (%)	0.4

TABLE 7

Moisture Adsorption-Desorption Data of Poly (Methyl Methacrylate)

		Humidity			
	100%	80%	60%	40%	20%
A) LABORATORY PRODUCT					
1) % D	4.297	2.546	1.054	0.5676	0.09731
S	4.297	2.838	2.027	0.6811	0.1460
2) % D	4.374	2.594	1.307	0.4324	0,2011
S	4.374	3.108	1.458	0.5732	0.3017
B) IMPORTED PRODUCT					
3) % D	3.398	1.845	1.099	0.2223	0.02064
S	3.398	2.744	1.199	0.4254	0.04033
4) % D	3.205	1.257	1.136	0.4464	0.01729
S	3.205	1.490	1.460	0.5476	0.04254
5) % D	3.116	1.558	0.8714	0.3808	0.04008
S	3.116	1.827	0.9915	0.3828	0.09015

RESULTS

1) From the above data, it is shown that the Maximum Sorption of the product is about 4.0%.
2) The Imported Product is comparable with Lab. Product.
3) At 60 & 40% humidity both, imported and lab. product, gave sorption % in a comparable range.

TABLE 8

Molecular Weight Determination of Poly (Methyl Methacrylate)

Experiment No.	Molecular Weight
1	780000
2	800000
3	786000
4	818000
5	800000

Experimental Conditions :

Room Temperature : 26–27°C

Solvent : Benzene

Constant : $K = 9.6 \times 10^{-5}$

$a = 0.69$

TABLE 9

Comparison of the Characteristics of Eastman Kodak PMMA and Lab. Product

Characteristics	Eastman Kodak PMMA	Lab. Product PMMA
	Average Value of 3 Experiments	
1) Molecular Weight	800000-900000	700000-800000
2) Softening Point	125°C	122-123°C
3) Moisture adsorption desorption (%)	0.4%	0.4%

Table 7
4%

TABLE 10

Optimization of the Blending Proportion of Cellulose Diacetate:Poly(Methyl Methacrylate)

	CA:PMMA	% S.R.	Flux (lmd)
1)	80:20	98.0	503.8
2)	60:40	60.0	980.0
3)	40:60	Flat membrane is not possible	
4)	20:80	- do -	

St. CA ?

p. 6c

Operational Conditions :

1) Applied Pressure : 40 atm.
2) Feed Rate : 800 ml./minute
3) Operational Period : 6 hours
4) Feed Temperature : 30-32°C
5) Feed Concentration : Approx. 5000 ppm. of NaCl soln.
6) Effective Membrane Area : 18.6 cm^2.

TABLE 11

Flat CA:PMMA Blended Membrane Performance Data at different As-Cast Thickness

As-Cast Thickness	Readings at the end of 6 hours Operation	
	% S.R.	Flux (lmd.)
1) 0.36 mm.	20	1666
2) 0.3 mm.	88	314
3) 0.24 mm.	98	503.8
4) 0.18 mm.	57	1570

Operational Conditions :

1) Applied Pressure : 40 atm.
2) Feed Rate : 800 ml/min.
3) Feed Concentration: About 5000 ppm. of NaCl soln.
4) Feed Temperature : 30-32°C
5) Operational Period: 6 hours
6) Effective Membrane Area : 18.6 cm^2

TABLE 12

Flat CA:PMMA Blended Membrane Performance Data giving different Evaporation Periods

Evaporation Period Sec.	Reading at the end of 6 hours operation	
	% S.R.	Flux (lmd)
1) 20	98.0	503.8
2) 40	96.0	357.7
3) 60	94.0	294.0
4) 90	88.0	250.0
5) 120	90.0	166.6

Operational Conditions :

1) Applied Pressure : 40 atm.
2) Feed Rate : 800 ml/min.
3) Operational Period : 6 hours
4) Feed Concentration : Approx. 5000 ppm of NaCl soln.
5) Feed Temperature : 30-32°C
6) Effective Membrane Area : 18.6 cm^2

TABLE 13

Flat CA:PMMA Blended Membrane Performance Data at different Annealing Temperatures

Annealing Temp. °C	Reading at the end of 6 hours operation	
	% S.R.	Flux (lmd.)
1) 86	86.0	711.5
2) 88	94.5	637.0
3) 90	96.0	545.0
4) 92	98.0	503.8
5) 94	96.0	421.0

Operational Conditions :

1) Applied Pressure : 40 atm.
2) Feed Rate : 800 ml/min.
3) Feed Concentration : Approx. 5000 ppm of NaCl soln.
4) Feed Temperature : 30-32°C
5) Operational Period : 6 hours
6) Effective Membrane Area : 18.6 cm^2

TABLE 13-A

Optimised Flat Membrane preparation parameters for the CA:PMMA (80:20) Blended Membrane

Sr. No.	Parameter	Optimum Value
1.	As-Cast thickness	0.24 mm.
2.	Evaporation Period	20 sec.
3.	Annealing Temperature	92°C

TABLE 14

Flat Cross-Linked CA:PMMA Membrane Performance Data

Experiment No.	Variation in Cross-linking Technique	Readings at the end of 6 hours operation	
		% S.R.	Flux (lmd)
1.	0.2% $K_2S_2O_8$ + 0.2% $NaHSO_3$ soln. - 3 min.	94.0	580.0
2.	0.2% $K_2S_2O_8$ + 0.2% $NaHSO_3$ soln. - 15 min.	95.0	525.0
3.	0.4% $K_2S_2O_8$ + 0.4% $NaHSO_3$ soln. - 3 min.	96.0	320.0
4.	0.4% $K_2S_2O_8$ + 0.4% $NaHSO_3$ soln. - 15 min.	92.0	630.0

Operational Conditions :

1) Applied Pressure : 40 atm.

2) Feed Rate : 800 ml/min.

3) Feed Concentration : Approx. 5000 ppm of NaCl soln.

4) Feed Temperature : 30-32°C

5) Operational Period : 6 hours

6) Effective Membrane Area : 18.6 cm^2

TABLE 15

R.O. Data of Optimized Flat CA:PMMA Blended Membrane (80:20)

Experiment No.	Reading at the end of 6 hours operation	
	% S.R.	Flux (lmd)
1	98.0	503.8
2	97.97	514.8
3	98.01	503.0
4	98.66	490.0
5	97.66	534.0
6	98.5	514.0
7	98.2	494.9
8	98.0	503.8
9	98.1	514.0
10	98.0	513.8
Avarage	98.0	503.8

Operational Conditions :

1) Applied Pressure : About 40 atm.
2) Feed Rate : 800 ml/min.
3) Operational Period : 6 hours
4) Feed Concentration : Approx. 5000 ppm of NaCl soln.
5) Operational Period : 6 hours
6) Effective Membrane Area : 18.6 cm^2

TABLE 16

Performance of Cellulose Diacetate Membrane prepared under the optimized conditions of Flat CA:PMMA Blended Membrane

Experiment No.	Readings at the end of 6 hours operation	
	% S.R.	Flux (lmd)
1	92.0	440.0
2	94.8	408.0
3	93.0	490.0

Operational Conditions :

1) Applied Pressure : 40 atm.
2) Feed Rate : 800 ml/min.
3) Feed Concentration : Approx. 5000 ppm of NaCl soln.
4) Feed Temperature : 30-32°C
5) Operation Period : 6 hours
6) Effective Membrane Area : 18.6 cm^2

TABLE 17

Membrane Performance of CA:PMMA Blended and CA Flat Membrane with Glycerol Annealing Treatment

Type of Membrane	Experiment No.	Annealing Temp. °C	Readings at the end of 6 hours operation	
			% S.R.	Flux (lmd)
CA:PMMA	1	88	88.3	1960
	2	90	89.2	1764
	3	92	94.4	1560
Cellulose Diacetate	1	90	90.0	1225
	2	92	91.6	980

Operational Conditions :

1) Applied Pressure : 40 atm.
2) Feed Rate : 800 ml/min.
3) Feed Temperature : 30-32°C
4) Feed Concentration : Approx. 5000 ppm of NaCl soln.
5) Operational Period : 6 hours
6) Effective Membrane Area : 18.6 cm^2

TABLE 18

Performance of Tubular Assembly from CA:PMMA Blended Membrane

Experiment No.	Readings at the end of 6 hours operation	
	% S.R.	Flux (lmd)
1	90.0	540
2	92.0	514
3	88.0	588
4	89.0	546

Operational Conditions :

1) Applied Pressure : 40 atm.
2) Feed Rate : 4.5 lit./min.
3) Feed Temperature : 32-35°C
4) Feed Concentration : Approx. 5000 ppm of NaCl soln.
5) Operational Period : 6 hours

Fig 15 ice cold brine

eff. area ? !

TABLE 19

Tubular Membrane Performance CA:PMMA Blended with Glycerol Annealing Treatment

Experiment No.	Readings at the end of 6 hours operation	
	% S.R.	Flux (lmd)
1	80.0	1078
2	82.0	980

Operational Conditions :

1) Applied Pressure : 40 atm.
2) Feed Rate : 4.5 lit./min.
3) Feed Concentration : Approx. 5000 ppm of NaCl soln.
4) Operational Period : 6 hours
5) Feed Temperature : 30-33°C

TABLE 20

Tubular Membrane Performance of Cellulose Diacetate with Glycerol Treatment

Experiment No.	Readings at the end of 6 hours operation	
	% S.R.	Flux (lmd)
1	76	750

Operational Conditions :

1) Applied Pressure : 40 atm.
2) Feed Rate : 4.5 lit./min.
3) Feed Concentration : Approx. 5000 ppm of NaCl soln.
4) Operational Period : 6 hours
5) Feed Temperature : 30-33°C

TABLE 21

Performance of Flat Membrane from Cellulose Acetate Methacrylate Graft Copolymer

Experiment No.	Readings at the end of 6 hours operation	
	% S.R.	Flux (lmd)
1	95.0	580
2	96.0	540
3	95.5	545
4	95.0	575

Operational Conditions :

1) Applied Pressure : 40 atm.
2) Feed Rate : 800 ml/min.
3) Feed Concentration : Approx 5000 ppm of NaCl soln.
4) Operational Period : 6 hours
5) Effective Membrane Area : 18.6 cm^2
6) Feed Temperature : 30-32°C

TABLE 22

Flat Membrane of CA:PMMA Blended & Cellulose Diacetate applied for specific use, i.e. Urea Rejection

Experiment No.	Type of Membrane	Feed	Reading at the end of 6 hours operation		% Urea Rejection.
			% S.R.	Flux(lmd)	
			Average of 3 Experiments		
1	CA:PMMA	5000 ppm NaCl +2000 ppm Urea soln.	97.97	514	75.0
2		3000 ppm Urea soln.	-	-	80.0
3		2000 ppm Urea soln.	-	-	84.0
4	CA	5000 ppm NaCl 2000 ppm Urea soln.	90.0	490	10-12
5		2000 ppm Urea soln.	-	-	10-12

Operational Conditions :

1) Applied Pressure : 40 atm.
2) Feed Rate : 800 ml/min.
3) Operational Period : 6 hours
4) Feed Temperature : 30-32°C
5) Effective Membrane Area : 18.6 cm^2

CHAPTER IV

MEMBRANE CHARACTERIZATION AND MASS TRANSFER

4.1 At each phase of the optimization of the different types of membranes studied during this investigation, each type of the optimized flat membrane was characterized for its physico-chemical properties as mentioned below :

I) Specific Water Content

It has been realized from the very inception of the studies on the Reverse Osmosis membrane and its water content that some close relationship exists between the transport properties (i.e. product water flux and salt rejection) of the reverse osmosis membrane and its water content.

The water content of the membrane comprises of free or capillary water and bound water. The latter cannot be easily detached or expelled off from the membrane and generally forms as an undetachable part of the polymer. As bound water H-OH as a hydronium ion is bound directly to the specific group of the polymer.

The existence of bound water in cellulose acetate was first reported by Vincent et al[61]. This was previously postulated by Reid & Breton[62]. It has been attempted to utilise the data on the membrane specific water content for predicting product water flux and salt rejection of reverse osmosis membrane. It is anticipated that for a better reverse osmosis membrane, dispersion of the water should be uniform throughout the structure[63].

The estimation of the specific water content of different types of membrane i.e. CA:PMMA blended, CA, CAM grafted, and CA:PMMA Blend with glycerol treatment was carried out as follows :

The small pieces of known area of different membranes were cut. The superficial water was carefully removed with blotting paper, then quickly placed in previously weighed weighing bottles. These were then weighed and dried at 105°C till constant weight was attained. From the difference of wet and dried weight, the specific water content was calculated as follows :

$$\text{Specific Water Content} = \frac{\text{Wt. of wet membrane} - \text{Wt. of dried membrane}}{\text{Area of Membrane}}$$

$$= \text{gm./cm}^2$$

The results of the specific water content of different types of membranes were calculated and tabulated in Table 23.

II) Salt Adsorption by Immersion

The above characteristic of the optimised CA:PMMA flat membrane was studied as under :

The CA:PMMA flat membrane was cast at the optimised conditions and two circles of known area were cut and the same were immersed in known concentrated NaCl solution for 24 hours. The same pieces were taken out from the NaCl solution and were further immersed in distilled water for few moments and then immediately were blotted between the two sheets of filter paper.

After blotting, the samples were transferred to two vials containing a known volume (100 ml) of distilled water at room temperature and kept immersed for 24 hours. Afterwards the leached NaCl was calculated by titrating the same solution with standard $AgNO_3$ solution.

Equation :

Leached out NaCl = Reading x Normality of $AgNO_3$ solution x 0.0585, from the total salt absorption by unit area of the membrane was calculated as under :

$$\frac{\text{NaCl leached out}}{\text{Area of the membrane x Thickness of the membrane}} = \frac{\text{gm.}}{\text{cm}^3}$$

The data for the different types of membranes are tabulated in Table 24.

III) Direct Osmosis

The optimised flat CA:PMMA blend membrane was employed for direct osmosis as follows :

The osmotic cell made from stainless steel consists of two compartments (fig. 16), one corresponding to equal dimensions as the other. The osmotic membrane can be fixed in-between the two circular slits of equal diameter in each of the facing walls of these compartments and can be firmly fixed by clamping tight these two compartments. Each compartment has an outlet at a fixed higher level from its bottom from which the excess liquid can drain out and the compartment can be filled with liquid upto this draining level; and at that time each compartment can hold about 3.5 litres liquid.

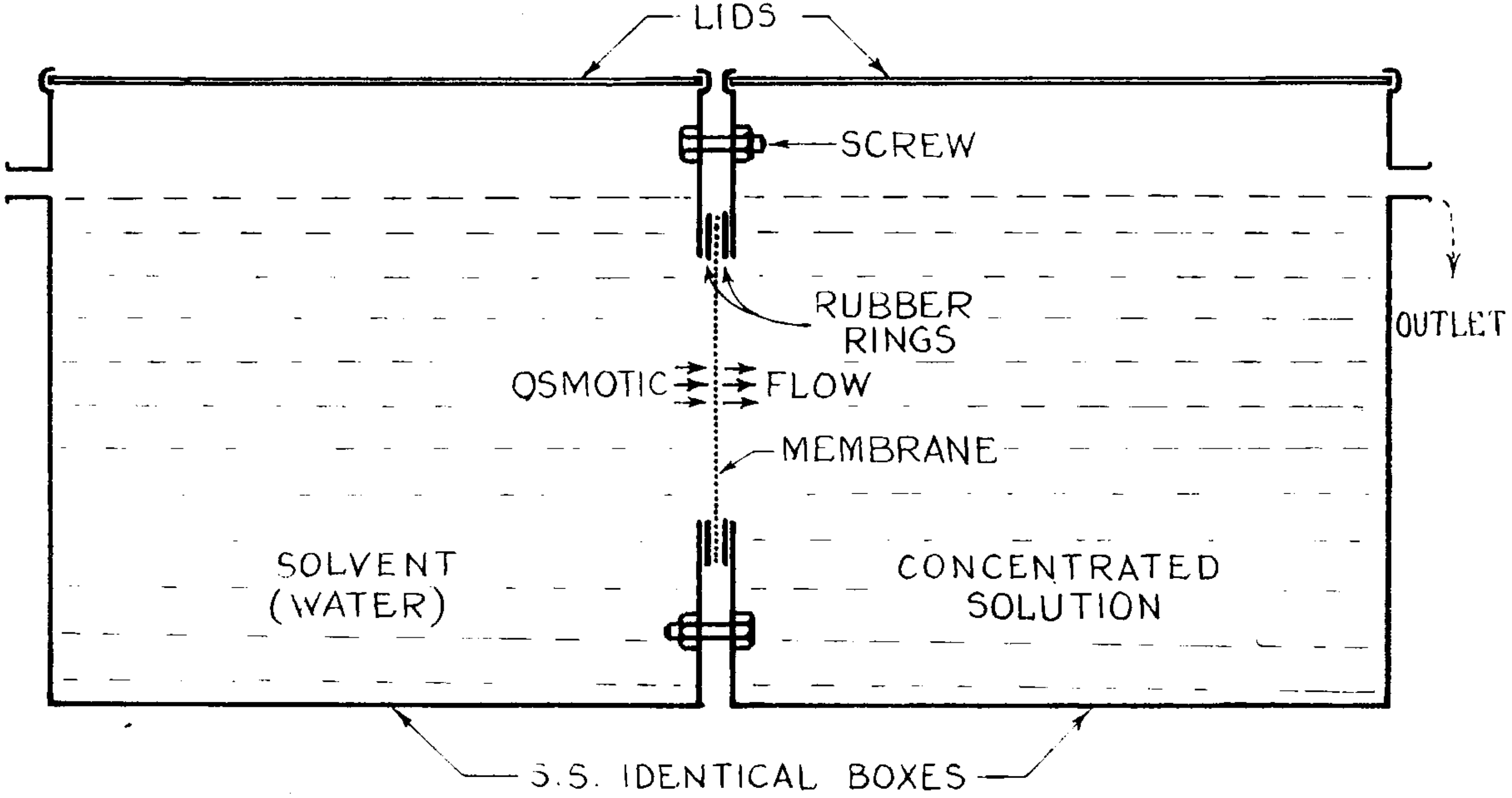


FIG : 16 . DIRECT OSMOSIS UNIT

?|

Having fixed the membrane and having levelled the osmotic cell, the compartment (L) towards which the active surface of the membrane is facing is filled with distilled water upto the draining level during which the membrane would bulge to some extent on the empty compartment side. Next, the other compartment (R) is filled with approximately 3.5 litres NaCl solution upto the draining level and the membrane bulging is apparently nullified during which some small amount of distilled water drains out and again this compartment remains filled upto its draining level.

As soon as both the compartments are filled with respective liquids Osmosis sets on. Depending upon the osmotic properties of the membrane, pure water from (L) will flow through the membrane to (R) which would drain out, can be collected and measured. Similarly, some salt may diffuse through the membrane from (R) to (L) thus increasing the salinity of water in (L). Initially, this phenomena rate may be more which would gradually decrease and cease at which the whole time interval is noted. From the collected solution which has drained through (R), the water transported can be made out. Knowing the initial and final salinity of water in (L) the salt transported can be calculated. Initial and final temperature of the solutions in both the compartments are also noted. The salinity is ascertained by Mohr's titrimetric method.

Illustration

i) Initial NaCl content of (L) compartment : Nil

Final NaCl content of (L) compartment : 0.31 gm.

.˙. Amount of NaCl transported : 0.31 gm.

Total period of observation : 5 hrs.

Membrane area : 82.52 cm^2

$$\therefore \text{Solute Flux} = \frac{\text{Amount of NaCl transported}}{\text{Membrane area x Time in sec.}}$$

$$= \frac{0.31}{82.52 \times 5 \times 3600}$$

$$= 0.1662 \times 10^{-7}$$

ii) Volume of water drained out through (R) = 75 ml.

$$\therefore \text{Solvent Flux} = \frac{\text{ml. of water drained out}}{\text{membrane area x time in sec.}}$$

$$= \frac{75}{82.52 \times 5 \times 3600}$$

$$= 4.021 \times 10^{-5} \text{ ml/cm}^2\text{.sec.}$$

The data for the different types of membranes were collected and shown in Table 25.

Material Balance of NaCl

	NaCl Initial	NaCl Final
(L)	Nil	0.31
(R)	124.7	120.4
Drained	Nil	2.66
Total	124.7 gm.	123.37 gm.

$$\% \text{ Deviation} = 124.7 - 123.37 = 1.33$$

$$= \frac{1.33 \times 100}{124.7}$$

$$= 0.1067\%$$

IV) A) Membrane Resistance Measurement, B) Membrane Average Pore Diameter.

A) The measurement of the resistance of the flat CA:PMMA membrane was carried out as follows :

The diffusion coefficient of sodium chloride in the membrane was determined by adopting the method evaluated previously by Saltonstall et al[64] and recently modified by J.B. Craig[65], The electric conductance of the membrane was measured as a function of time until an equilibrium stage is reached where the salt concentration in the membrane and concentration of surrounding solution is in equilibrium. A plot of Log Q versus time gives straight line (as shown in fig. 17) from which slope of line is obtained. The diffusion coefficient and distribution coefficient were calculated using equation as shown under :

$$D_2 = \frac{\text{Slope in tan Q} \times t^2 \times 2.303}{\pi^2}$$

where D_2 = diffusion coefficient of NaCl in cm^2/sec.

t = thickness of membrane in cm.

$$D_2K = \frac{Rsp \times D_2 0 \times t}{Rm \times A}$$

where, D_2K = distribution coefficient of sodium chloride in cm^2/sec.

Rsp = Specific resistance of 0.1 M sodium chloride solution.

D_2° = Self diffusion coefficient for 0.1 M sodium chloride solution.

A = Area of the film : 1.77 cm^2

Rm = Membrane resistance at equilibrium state.

Illustration

$$\tan Q = 2.92 = \frac{\pi^2 D_2}{2.303 \times t^2}$$

$$\therefore \quad \pi = 3.142$$

$$t = 0.02$$

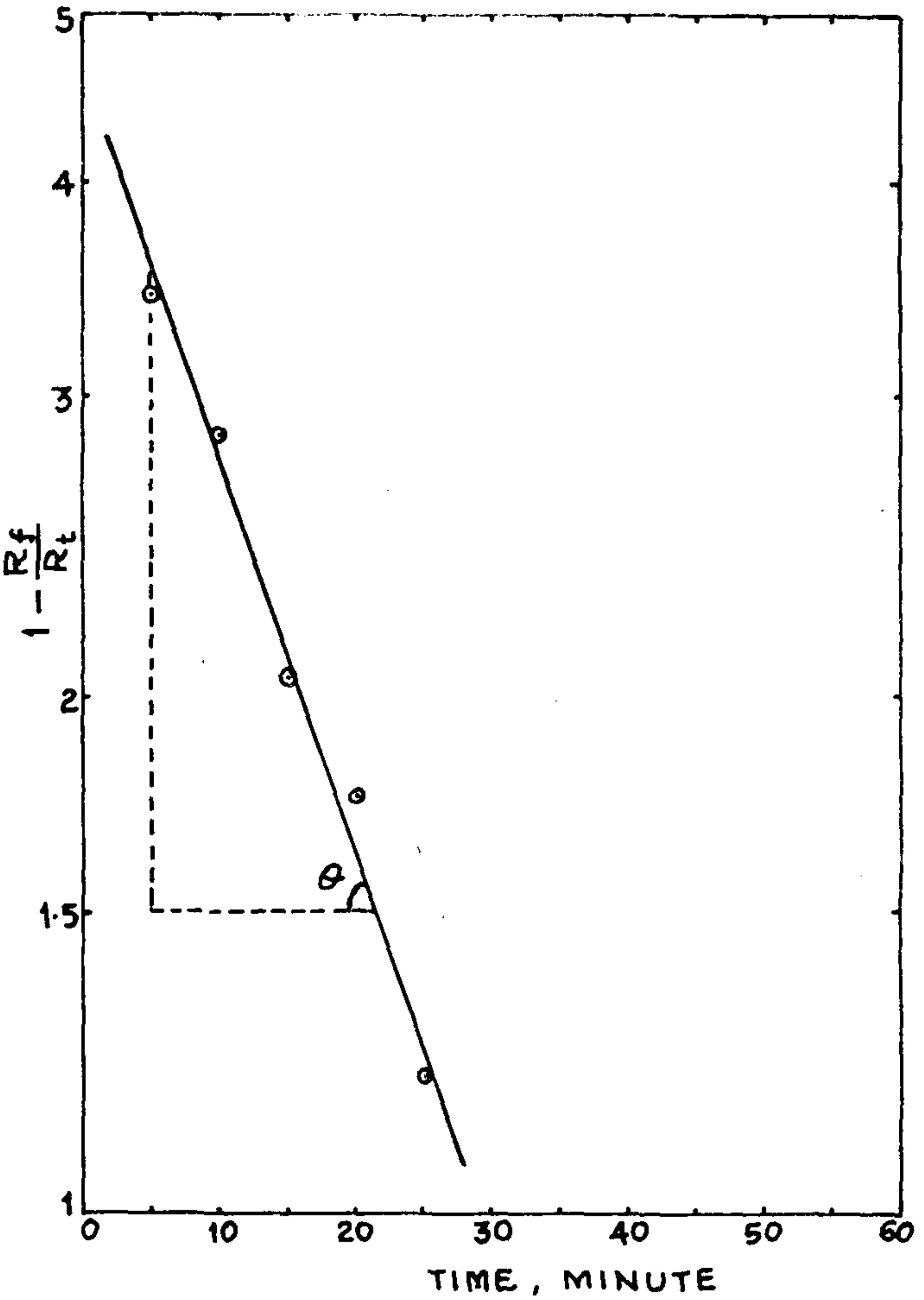


FIG: 17. Log θ Vs TIME.

$$\therefore \quad \text{i)} \quad D_2 = \frac{2.303 \times 0.0004 \times 2.92}{(3.142)^2}$$

$$= 2.727 \times 10^{-4} \ \text{cm}^2/\text{sec.}$$

$$\text{ii)} \quad D_2K = \frac{D_2^\circ \times Rsp \times t}{R_m . \pi r^2}$$

$$= \frac{1.475 \times 10^{-5} \times 0.27 \times 10^{-3} \times 0.02}{4000 \times 1.77}$$

$$= 1.125 \times 10^{-8} \ \text{cm}^2/\text{sec.}$$

Where, $D_2^\circ = 1.475 \times 10^{-5}$

$Rsp = 0.27 \times 10^{-3}$

$R_m = 4000$

Area of circle $= \pi r^2 = 1.77 \ \text{cm}^2$

$$\text{iii)} \quad K = \frac{1.125 \times 10^{-8}}{2.727 \times 10^{-4}} = 4.125 \times 10^{-5}$$

B) The Average Pore Diameter of the flat membrane was calculated using the following equation :

$$J = (\text{Pore Diameter})\, 2r = 4\left[\frac{2VNL}{SAPT}\right]^{1/2}$$

$$= 4\left[\frac{2 \times 32 \times 0.01 \times 0.02}{0.8995 \times 186 \times 3600 \times 600 \times 68900}\right]^{1/2}$$

$$= 28.34 \ \text{A}^\circ$$

Where, V = pure water permeability, ml/hr.
n = viscosity of pure water
L = thickness of membrane
S = specific water content
A = effective membrane area
P = pressure in atmosphere
t = time in seconds

The data of different types of membranes are given as shown in Table 26.

The apparatus utilised for the membrane resistance measurement is shown in Fig. 18.

V) Tensile Strength

The determination of the tensile strength of the CA:PMMA blend membrane was carried out as discussed in 2.2.3F[51]. The apparatus for this determination is shown in phtg. 13. The data for the different types of membranes are tabulated in Table 27.

Illustration

i) Wt. at yield point : 1550 gm.
487 dead weight
2037 gm.

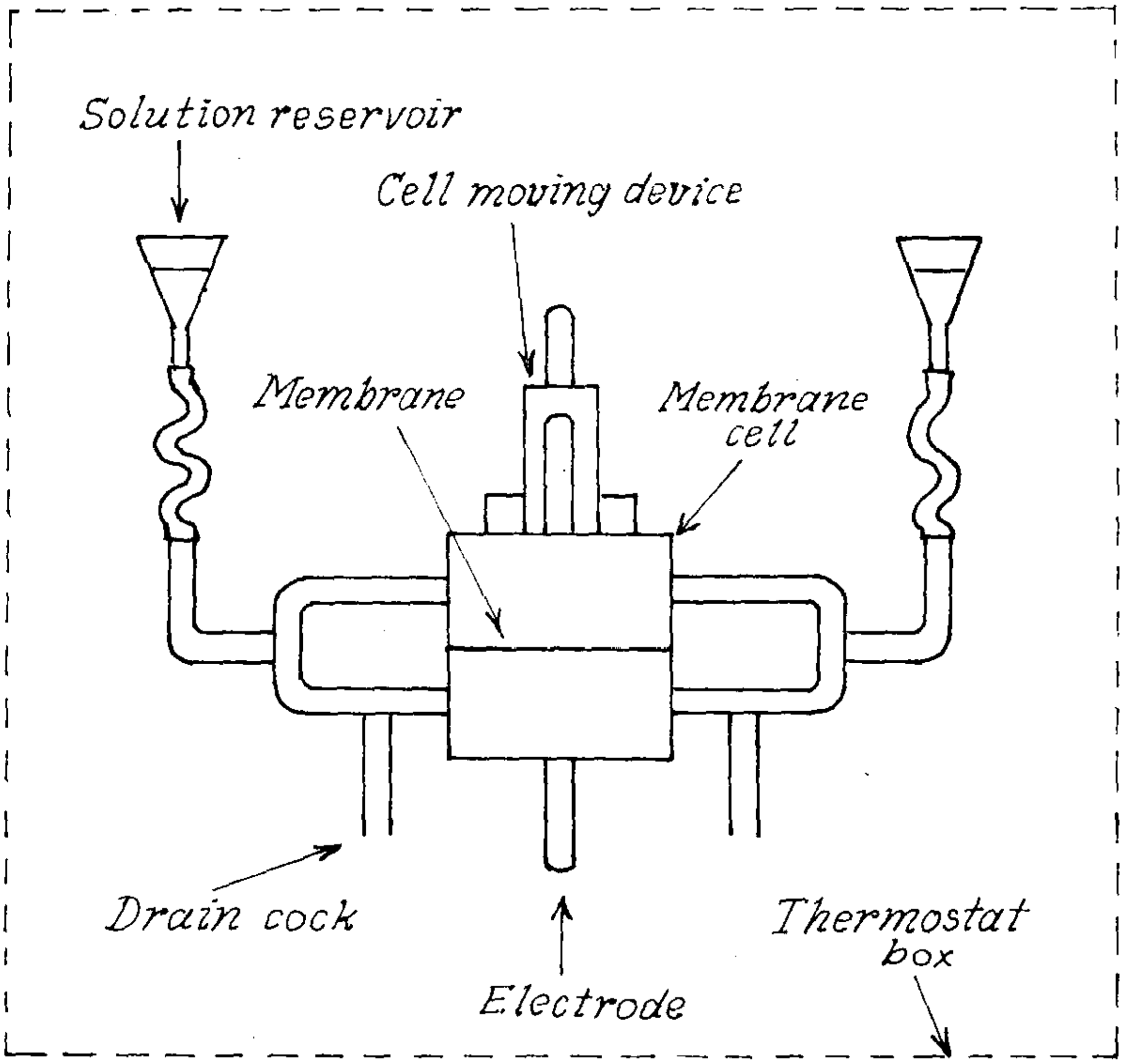


Figure: 18. Membrane conductance apparatus

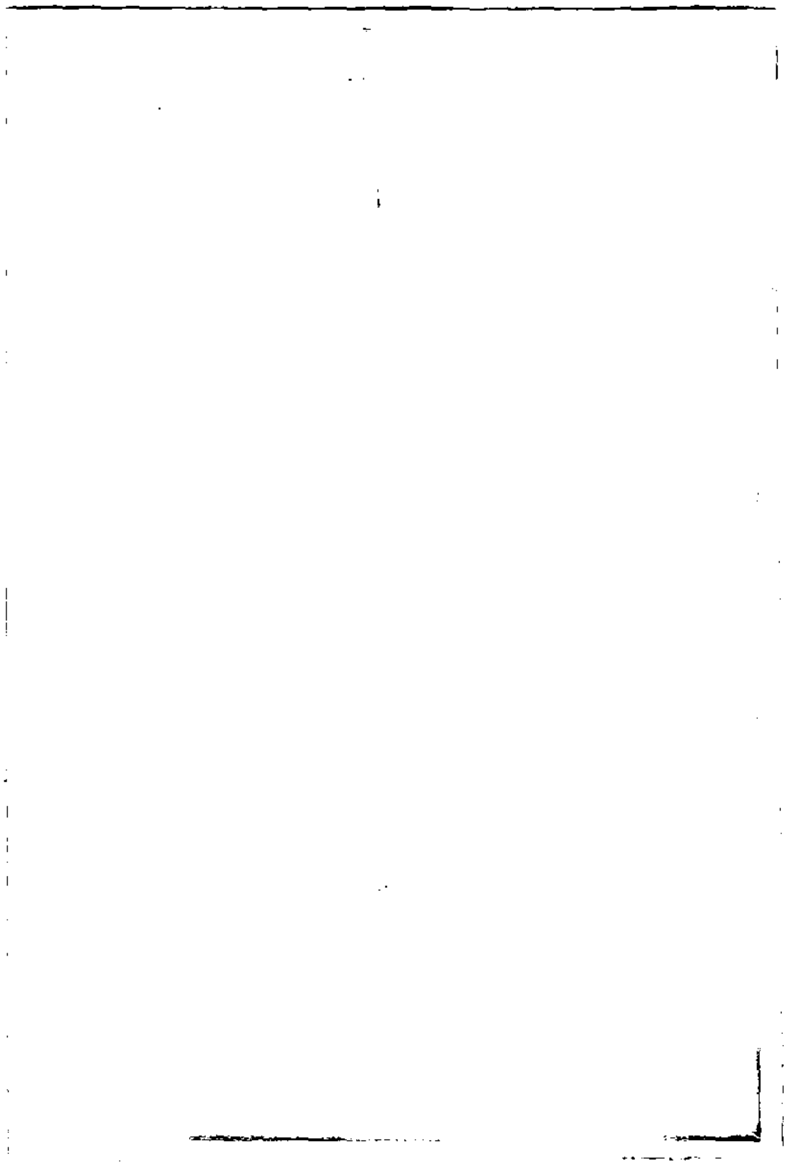


Plate 3 : Tensile Strength Measurement Unit

ii) Membrane Area : Width x Thickness

$$1 \times 0.018$$

$$= 0.018 \text{ cm}^2$$

iii) Tensile Strength (psi)

$$= \frac{980665 \times 2.037 \times 1.450 \times 10^{-5}}{0.018}$$

$$= 1614 \text{ psi.}$$

4.1.2 Utilizing the methods described in 4.1 (I to V), the physico-chemical characteristics of the following types of the optimised flat membrane were determined:

i) The membrane from CA:PMMA blend as shown in Table 28.

ii) Secondary cellulose acetate flat membrane as tabulated in Table 29.

iii) Cellulose acetate methacrylate grafted as described in Table 30.

iv) Cellulose acetate Poly methyl methacrylate CA:PMMA blended (glycerol treated) flat membrane as shown in Table 31.

4.1.3 Determination of Bound Water Content of the Flat Membrane

Determinations of Bound Water Content of flat membrane of CDA and CA:PMMA blend have been described in 2.2.7 and the data are tabulated in Table 27-B.

4.1.4 Determination of Acetyl Content of Flat Membrane

Determinations of acetyl content of flat CDA and CA:PMMA blend membranes have been described in 2.2.4g and the data are tabulated in Table 27-A.

4.1.5 Characterization of Dense Flat membranes of CA:PMMA Blend and CDA

These membranes were characterized on the same lines as mentioned earlier and the results are incorporated in Table 27-C.

4.2 It was considered interesting and useful to characterize the aforesaid membranes with regards to the mass transfer taking place during their reverse osmosis application. These studies were carried out on similar lines as mentioned in 66, 67.

4.2.1 During the investigation of the Mass Transfer characteristics of these membranes, the following factors were determined :

I) Pure water permeability (JD):LMD

II) Membrane Constant [Lp]: $\frac{gm.mole}{cm^2.sec.atm.}$

III) Solvent flux : (JV):LMD

IV) Membrane wall concentration (CW):Molar

V) Product water concentration (Cp):Molar

VI) Feed water concentration (Cb):Molar

VII) Concentration polymerization ratio Cw/Cb

VIII) True Salt Rejection : Ri

IX) Observed salt rejection : Ro

X) Solute permeability $Ps(\bar{D})$:LMD

XI) Mass Transfer coefficient (K):LMD

4.2.2 The different factors evaluated in the study of mass transfer characteristics were determined as follows :

I) Pure Water Permeability (PWP):LMD

The pure water permeability of the optimised flat CA:PMMA blended membrane was determined by employing two circles (of the membrane) of known area in the reverse osmosis kit as described in 2.3.4

Taking distilled water as feed, reverse osmosis cell is operated at an accurately known pressure about 40 atmospheric pressure and the readings for the product flux are noted at regular intervals of time until the consecutive two readings of the flux are obtained, nearly constant, indicating the establishment of equilibrium. At this juncture, the feed temperature is also carefully noted. The final flux reading (ml/hour) leads to the calculation of flux in IMD as mentioned below :

Equation

$$\text{PWP in IMD} = \frac{\text{ml}}{1000} \times \frac{10^4 \times 24}{\text{membrane area in cm}^2}$$

Illustration

Flux = 32 ml/hr.

Membrane Area = 18.6 cm^2

$$\therefore \text{Flux in IMD} = \frac{32 \times 10^4 \times 24}{1000 \times 18.6}$$

$$= 533.1 \text{ IMD.}$$

Table 32 contains the results for the different types of membranes.

II) Membrane Constant (Lp)

The Membrane constant of the CA:PMMA blended flat membrane was calculated by employing the following equation:

$$\text{Membrane Constant (Lp)} = \frac{J_D}{\Delta P - \Delta \pi}$$

where, J_D = Pure water permeability

ΔP = Effective applied pressure

$\Delta \pi$ = Difference of osmotic pressure between that of feed and product water, which in this case is equal to zero because pure water is as feed.

Illustration

$$Lp = \frac{J_D}{\Delta P - \Delta \pi}$$

where, $PWP = J_D = \text{ml/hr.} = \frac{32}{3600}$

$$\Delta P = \frac{600}{14.7} \text{ atmosphere}$$

Membrane Area = 18.6 cm^2

$$Lp = \frac{32 \times 14.7}{3600 \times 600 \times 18.6}$$

$$= 1.170 \times 10^{-5} \text{ gm/cm}^2\text{.sec.atm.}$$

Similar determinations were carried out for different types of membranes which have been shown in Table 33.

III) Solvent Flux (JV):LMD

The solvent flux of the optimised CA:PMMA blended flat membrane was determined as follows :

The membrane pieces which had been previously utilized for the determination of membrane constant were further employed in the same reverse osmosis kit for desalination of aqueous synthetic sodium chloride solution of known salinity (approx. 5000 ppm) at known outlet pressure. The reverse osmosis operation was continued until the two consecutive readings for the product water flux and the percent salt rejection were nearly constant. During this operation, the readings were periodically noted at a regular time interval.

While noting the final reading, the samples of the feed and product water were also collected for the titrimetric estimation of their chloride content so as to assess the percent salt rejection more accurately and also to compare it with the results obtained by the conductivity measurement.

Also the feed temperature was accurately noted at this juncture. The observed flux was calculated as follows :

Illustration

Product flux in lmd : $\frac{ml}{hr} = 32$

Membrane Area = 18.6 cm^2

$$\frac{ml}{\frac{hour}{1000}} \times \frac{10^4}{\text{membrane area}} \times 24$$

$$\therefore \frac{32 \times 10^4 \times 24}{600 \times 18.6}$$

$$= 526.4$$

The theoretical product flux was calculated as follows :

Illustration

$$JV : Lp\ (\Delta P - \sigma \Delta \pi)$$

where, JV = Solvent flux in lmd.

Lp = Membrane constant = 1.170×10^{-5} $gm/cm^2.sec.atm.$

ΔP = Applied Pressure = 40 atm.

σ = Reflection coefficient (taken as unity as tight type of membrane)

$\Delta\pi$ = Osmotic pressure difference between feed and product.

$= \pi b - \pi p = 1$ atm.

$\therefore JV = 539.8$

The results for the different types of membranes were tabulated in Table 34.

IV) Determination of Solute Concentration of Membrane Wall Cw, in the product water, Cp, and in the Bulk solution, Cb

For these estimations, the following equations were made use of :

i) $$Cw = \frac{\Delta P}{\sigma \pi b}\left(1 - \frac{J_V}{J_D}\right) + Cp$$

where, ΔP = Effective applied pressure in atmosphere

σ = Reflection coefficient taken, unity in this case.

πb = Osmotic pressure in atmosphere of the bulk solution[68]

J_V = Solvent flux in lmd

J_D = Pure water permeability in lmd.

Cp = Product water concentration in molar.

ii) $$Cp = \frac{\text{Amount of NaCl in one litre product}}{58.5}$$

iii) $$Cb = \frac{\text{Amount of NaCl in one litre bulk solution}}{58.5}$$

For the given membrane J_V and J_D are known. ΔP is noted during reverse osmosis operation and Cp and Cb are also determined titrimetrically.

Table 35 contains the results for the different types of membranes.

Illustration

$$Cw = \frac{\Delta P}{6 \pi b}\left[1 - \frac{J_V}{J_D}\right] + Cp$$

$$\Delta P = \frac{600}{14.7} \text{ atm.}$$

$$\sigma = 1$$

$$J_V = 526.46$$

$$J_D = 533.1$$

$$Cp = 0.0014$$

$$\pi b = 49$$

$$\therefore Cw = \frac{600}{49}\left(1 - \frac{526.46}{533.1}\right) + 0.0014$$

$$= 12.5\ (0.0127) + 0.0014$$

$$= 0.1556 \text{ molar}$$

V) Concentration Polarisation Ratio $\frac{Cw}{Cb}$

For a given membrane Cw and Cb can be determined as mentioned in (4.2.2.iv). This helps to calculate the concentration polarization ratio Cw/Cb. Table 36 contains the concentration polarization ratio data determined for different types of membranes :

Illustration

$$\frac{Cw}{Cb} = \frac{0.1556}{0.07196} = 2.163$$

VI) True Salt Rejection (Ri) and Observed Salt Rejection (Ro)

True salt rejection and observed salt rejection have been determined by use of the following two equations:

$$\text{i)} \quad Ri = 1 - \frac{Cp}{Cw}$$

$$\text{ii)} \quad Ro = 1 - \frac{Cp}{C_b}$$

Where Cw, Cb and Cp have been the same symbol explanation as mentioned previously.

Illustration

For a given membrane under reverse osmosis application :

$Cw = 0.1556$ molar

$Cb = 0.07196$ molar

$Cp = 0.0019$ molar

$$\therefore Ri = 1 - \frac{0.0019}{0.1556} = 0.9972 = 99.72\%$$

$$Ro = 1 - \frac{0.0019}{0.07196} = 0.9766 = 97.66\%$$

The Ri and Ro data for the different types of membranes have been incorporated in Table 37.

VII) Solute Permeability $Ps(\bar{D})$:(LMD)

The following equation was utilised for the determination of the solute permeability of the given membrane during its reverse osmosis application:

Equation

$$Ps(\bar{D}) = \frac{J_V \times Cp}{Cw - Cp}$$

where, the symbols have the same explanations as previously mentioned.

Illustration

$$Ps(\bar{D}) = \frac{Jv.Cp}{Cw-Cp}$$

$$J_V = 526.46$$

$$Cp = 0.0014$$

$$Cw = 0.1556$$

$$\therefore Ps(\bar{D}) = \frac{526.46 \times 0.0014}{0.1556}$$

$$= 4.741 \text{ lmd.}$$

In Table 38, the solute permeability data for the different types of membranes are tabulated.

VIII) Mass Transfer Coefficient K:(LMD)

Mass transfer coefficient of the flat blended CA:PMMA membrane was calculated using the equation :

$$K = \frac{J_V}{\ln \dfrac{\frac{Cw}{Cb} - (1 - RO)}{RO}}$$

$$J_V = 526.4 \text{ lmd.}$$

$$\frac{Cw}{Cb} = 2.163$$

$$RO = 0.9766$$

$$\therefore K = \frac{526.4}{\ln \frac{2.163 - (1-0.9766)}{0.9766}}$$

$$= 681.6 \text{ lmd.}$$

Similarly, the Mass Transfer Coefficient for the different types of membranes were determined, and the results are tabulated in Table 39.

4.2.3 Summary of the Membrane Mass Transfer Data

Table 40 contains the complete mass transfer data for each type of the following membranes :

i) CA:PMMA optimised blended flat membrane
ii) CA:PMMA optimised blended flat membrane (glycerol treated)
iii) Cellulose diacetate membranes
iv) Cellulose acetate methacrylate grafted membranes

TABLE 23

SPECIFIC WATER CONTENT

	Types of Membranes	Expt. No.	Specific Water Content gm/cm^3
1)	CA:PMMA	1	0.7279
	(80:20) blended	2	0.7030
		3	0.7195
2)	CDA	1	0.6921
		2	0.6720
		3	0.6888
3)	CAM Graft Copolymer	1	0.6776
		2	0.6690
		3	0.6640
4)	CA:PMMA (80:20)	1	0.7835
	blended	2	0.7789
	(glycerol treated)	3	0.7735

TABLE 24

SALT ABSORPTION BY IMMERSION

Types of Membranes	Expt. No.	Salt Absorption gm/cm^3
1) CA:PMMA (80:20)	1	0.7833×10^{-2}
blended	2	0.7783×10^{-2}
	3	0.7739×10^{-2}
2) CDA	1	0.8225×10^{-2}
	2	0.8335×10^{-2}
	3	0.8215×10^{-2}
3) CAM graft Copolymer	1	0.7691×10^{-2}
	2	0.7583×10^{-2}
	3	0.7682×10^{-2}
4) CA:PMMA (80:20)	1	0.7588×10^{-2}
blended	2	0.7381×10^{-2}
(glycerol treated)	3	0.7601×10^{-2}

TABLE 25

DIRECT OSMOSIS

	Types of Membranes	Expt. No.	Direct Osmosis	
			Solute Flux $gm/cm^2.sec.$	Solvent Flux $gm/cm^2.sec.$
1)	CA:PMMA (80:20) Blended	1	1.662×10^{-8}	5.049×10^{-5}
		2	1.659×10^{-8}	5.113×10^{-5}
		3	1.661×10^{-8}	5.010×10^{-5}
2)	CDA	1	10.94×10^{-8}	12.83×10^{-5}
		2	10.88×10^{-8}	12.88×10^{-5}
		3	10.99×10^{-8}	12.80×10^{-5}
3)	CAM graft Copolymer	1	2.849×10^{-8}	7.727×10^{-5}
		2	2.901×10^{-8}	7.810×10^{-5}
		38	2.859×10^{-8}	7.747×10^{-5}
4)	CA:PMMA (80:20) Blended (Glycerol treated)	1	23.03×10^{-8}	13.15×10^{-5}
		2	22.95×10^{-8}	13.01×10^{-5}
		3	22.89×10^{-8}	12.98×10^{-5}

TABLE 26

MEMBRANE RESISTANCE MEASUREMENT

Types of Membranes	Expt. No.	Salt Diffusion Coefficient D_2 $cm^2/sec.$	Salt Permeability D_2K $cm^2/sec.$	Salt Distribution Coefficient K	Average Pore Diameter J A°
1) CA:PMMA (80:20)	1	$2.727x10^{-4}$	$1.125x10^{-8}$	$4.125x10^{-5}$	28.34
Blended	2	$2.80 \ x \ 10^{-4}$	$1.130x10^{-8}$	$4.035x10^{-5}$	32.34
	3	$2.78 \ x \ 10^{-4}$	$1.21 \ x10^{-8}$	$4.389x10^{-5}$	32.05
2) CDA	1	$1.523x10^{-4}$	$1.295x10^{-8}$	$8.507x10^{-5}$	25.16
	2	$1.521x10^{-4}$	$1.290x10^{-8}$	$8.505x10^{-5}$	25.23
	3	$1.522x10^{-4}$	$1.293x10^{-8}$	$8.500x10^{-5}$	25.21
3) CAM Graft	1	$1.614x10^{-4}$	$1.248x10^{-8}$	$7.920x10^{-5}$	32.8
Cppolymer	2	$1.615x10^{-4}$	$1.250x10^{-8}$	$7.940x10^{-5}$	32.78
	3	$1.614x10^{-4}$	$1.249x10^{-8}$	$7.930x10^{-5}$	32.82
4) CA:PMMA(80:20)	1	$1.494x10^{-4}$	$1.591x10^{-8}$	$13.41x10^{-5}$	41.2
Blended	2	$1.510x10^{-4}$	$1.589x10^{-8}$	$13.42x10^{-5}$	41.28
Glycerol treated	3	$1.520x10^{-4}$	$1.589x10^{-8}$	$13.42x10^{-5}$	41.3

TABLE 27

TENSILE STRENGTH OF THE MEMBRANE

Types of Membranes	Expt. No.	Tensile Strength Psi.
1) CA:PMMA (80:20)	1	1500
Blended	2	1600
	3	1400
2) CDA	1	1036
	2	1080
	3	1000
3) CAM Graft	1	1100
Copolymer	2	1055
	3	1050
4) CA:PMMA (80:20)	1	1500
Blended	2	1400
(Glycerol treated)	3	1380

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TABLE 27-A

Types of Membranes	% Acetyl
1) CA:PMMA (80:20) Blended	36.24
2) CA:PMMA (80:20) Blended (glycerol-treated)	35.39

TABLE 27-B

Types of Membranes	Percent Bound Water Content
1) CA:PMMA (80:20) Blended	2.63
2) CA:PMMA (80:20) Blended (glycerol-treated)	2.474

TABLE 27-C

CHARACTERIZATION OF DENSE CDA AND CA:PMMA BLEND FLAT MEMBRANE

	Characteristics	Types of Membranes	
		CDA	CA:PMMA (80:20) Blended
1)	Specific Water Content gm/cm^3	0.2097	0.1879
2)	Salt absorption by immersion gm/cm^3	0.2517x10^{-2}	0.1888x10^{-2}
3)	Average Pore Dia. (J) A°	2.87 A°	2.7 A°
4)	Tensile Strength (psi)	2582	2720

Table 28

TABLE 28

CHARACTERISTICS OF FLAT OPTIMISED BLENDED CA:PMMA (80:20) MEMBRANES

1)	Specific water content	: 0.7195 gm/cm^3
2)	Salt absorption by immersion	: 0.77 x 10^{-2} gm/cm^3
3)	Direct Osmosis	
	i) Solute flux	: 1.662x10^{-8} gm/cm^2.sec.
	ii) Solvent flux	: 5.049x10^{-5} gm/cm^2.sec.
4)	Membrane Resistance Measurement	
	i) Salt Diffusion Coefficient D_2	: 2.72 x 10^{-4} cm^2/sec.
	ii) Salt Permeability D_2K	: 1.125x10^{-8} cm^2/sec.
	iii) Salt Distribution Coefficient K	: 4.125x10^{-5}
	iv) Average Pore Dia. J	: 28.34 A°
	v) Tensile Strength	: 1500 psi.

TABLE 29

CHARACTERISTICS OF OPTIMISED CDA MEMBRANES

1)	Specific Water Content	0.6921 gm/cm^3
2)	Salt absorption by immersion	0.8225×10^{-2} gm/cm^3
3)	Direct Osmosis	
	i) Solute flux	10.94×10^{-8} $gm/cm^2.sec.$
	ii) Solvent flux	12.83×10^{-5} $gm/cm^2.sec.$
4)	Membrane Resistance Measurement	
	i) Salt diffusion Coefficient D_2	1.523×10^{-4} $cm^2/sec.$
	ii) Salt permeability D_2K	1.295×10^{-8} $cm^2/sec.$
	iii) Salt distribution coefficient K	8.507×10^{-5}
	iv) Average Pore Diameter J	25.16 A°
	v) Tensile Strength	1000 psi.

TABLE 30

CHARACTERISTICS OF CAM GRAFT COPOLYMER MEMBRANES

1)	Specific water content	: 0.6690 gm/cm^3
2)	Salt absorption by immersion	: 0.7691×10^{-2} gm/cm^3
3)	Direct Osmosis	
	i) Solute flux	: 2.849×10^{-8} gm/cm^2.sec.
	ii) Solvent flux	: 7.72×10^{-5} gm/cm^2.sec.
4)	Membrane Resistance Measurement	
	i) Salt diffusion Coefficient D_2	: 1.614×10^{-4} gm^2/sec.
	ii) Salt permeability D_2K	: 1.248×10^{-8} cm^2/sec.
	iii) Salt distribution coefficient K	: 7.920×10^{-5}
	iv) Average Pore Diameter J	: 32.8 A°
	v) Tensile Strength	: 1100 psi.

TABLE 31

CHARACTERISTICS OF CA:PMMA (80:20) BLENDED (GLYCEROL-TREATED) MEMBRANE

---

1) Specific water content : 0.7835 gm/cm^3

2) Salt absorption by immersion : 0.7588×10^{-2} gm/cm^3

3) Direct Osmosis

   i) Solute flux : 23.03×10^{-8} $gm/cm^2.sec.$

   ii) Solvent flux : 13.15×10^{-5} $gm/cm^2.sec.$

4) Membrane Resistance Measurement

   i) Salt diffusion coefficient D_2 : 1.494×10^{-4} $cm^2/sec.$

   ii) Salt permeability coefficient D_2K : 1.591×10^{-8} $cm^2/sec.$

   iii) Salt distribution coefficient K : 13.41×10^{-5}

   iv) Average Pore Diameter J : 41.2 A°

   v) Tensile Strength : 1450 psi.

TABLE 32

Types of Membranes	Expt. No.	Pure Water Permeability (PWP) lmd.
1. CA:PMMA (80:20)	1	533.1
blended	2	538.8
	3	531.1
2. CDA	1	499.8
	2	490.0
	3	493.8
3. CAM Graft	1	492.0
Copolymer	2	488.0
	3	491.0
4. CA:PMMA 980:20)	1	1999.2
Blended	2	2021.0
(glycerol treated)	3	2058.8

TABLE 33

MEMBRANE CONSTANT (Lp):Gm/cm^2.sec.atm.

Types of Membranes	Expt. No.	Membrane Constant (Lp):gm/cm^2.sec.atm.
1. CA:PMMA (80:20)	1	1.171×10^{-5}
blended	2	1.176×10^{-5}
	3	1.172×10^{-5}
2. CDA	1	1.097×10^{-5}
	2	1.098×10^{-5}
	3	1.096×10^{-5}
3. CAM Graft	1	1.087×10^{-5}
copolymer	2	1.083×10^{-5}
	3	1.091×10^{-5}
4. CA:PMMA (80:20)	1	3.659×10^{-5}
blended	2	3.651×10^{-5}
(glycerol treated)	3	3.661×10^{-5}

TABLE 34

SOLVENT FLUX (J_V) LMD

Types of Membranes	Expt. No.	Solvent Flux (JV) Lmd. Experimental Value	Calculated Value	% deviation of av.exptl. value from calculated value
1) CA:PMMA	1	526.4		
(80:20)	2	525.4	539.4	(-) 2.62
Blended	3	527.4		
2) CDA	1	488.4		
	2	487.5	508.0	(-) 4.61
	3	489.8		
3) CAM Graft	1	480.0		
Copolymer	2	475.0	493.8	(-) 3.0
	3	478.0		
4) CA:PMMA	1	1660		
(80:20)	2	1659	1715.0	(-) 3.5
Blended	3	1666		
(glycerol-treated)				

TABLE 35

DETERMINATION OF SOLUTE CONCENTRATION AT MEMBRANE WALL Cw, IN PRODUCT WATER Cp, & IN BULK SOLUTION Cb

Types of Membranes	Solute Concentration (Molar) Average of 3 experiments		
	Membrane Wall Cw	Product Water Cp	Bulk Solution Cb
1) CA:PMMA (80:20) Blended	0.1556	0.0014	0.07196
2) CDA	0.1660	0.0016	0.07303
3) CAM Graft Copolymer	0.2868	0.0018	0.08316
4) CA:PMMA (80:20) Blended (Glycerol treated)	0.1852	0.0039	0.06944

TABLE 36

CONCENTRATION POLARISATION RATIO Cw/Cb

	Types of Membranes	Expt. No.	Concentration Polarization Ratio Cw/Cb
1.	CA:PMMA	1	2.163
	(80:20)	2	2.159
	Blended	3	2.161
2.	CDA	1	2.273
		2	2.271
		3	2.276
3.	CAM Graft	1	3.451
	Copolymer	2	3.449
		3	3.452
4.	CA:PMMA (80:20)	1	2.667
	Blended	2	2.669
	(Glycerol treated)	3	2.668

TABLE 37

Types of Membranes	Expt. No.	True Salt Rejection % Ri.	Observed Salt Rejection % Ro
1. CA:PMMA	1	0.9972	0.9766
(80:20)	2	0.9977	0.9801
Blended	3	0.9993	0.9797
2. CDA	1	0.9884	0.9688
	2	0.9894	0.9778
	3	0.9934	0.9684
3. CAM Graft	1	0.9948	0.9737
Copolymer	2	0.9984	0.9747
	3	0.9933	0.9727
4. CA:PMMA(80:20)	1	0.9772	0.9166
Blended	2	0.9762	0.8986
(glycerol treated)	3	0.9782	0.8870

TABLE 38

SOLUTE PERMEABILITY PS($\bar{D}$) LMD

	Types of Membranes	Expt. No.	Solute Permeability Ps($\bar{D}$) lmd
1)	CA:PMMA	1	4.778
	(80:20)	2	4.768
	Blended	3	4.787
2)	CDA	1	4.753
		2	4.743
		3	4.766
3)	CAM Graft	1	3.031
	Copolymer	2	2.882
		3	2.805
4)	CA:PMMA (80:20)	1	35.73
	Blended	2	35.42
	(glycerol treated)	3	35.84

TABLE 39

MASS TRANSFER COEFFICIENT K (LMD)

	Types of Membranes	Expt. No.	Mass Transfer Coefficient K Lmd
1)	CA:PMMA	1	670.8
	(80:20)	2	673.0
	Blended	3	676.6
2)	CDA	1	582.5
		2	585.8
		3	582.9
3)	CAM Graft	1	382.6
	Copolymer	2	369.8
		3	365.9
4)	CA:PMMA (80:20)	1	1601.0
	Blended	2	1580.0
	(glycerol-treated)	3	1574.0

TABLE 40

MASS TRANSFER DATA

Type of Membranes	Pure Water Permeability PWP lmd	Membrane Constant (L_p) gm/cm^2.sec.atm.	Solvent Flux (J_v) Lmd.	Solute Concentration Molar			Concentration Polarization ratio Cw/Cb	True Salt Rejection % Ri	Observed Salt Rejection % Ro	Solute Permeability Ps($\bar{D}$) lmd.	Mass Transfer Coefficient K lmd.
				Membrane Wall Cw	Product Water Cp	Bulk solution Cb					
1) CA:PMMA (80:20) Blended	533.1	1.171×10^{-5}	526.4	0.1556	0.0014	0.07196	2.163	0.9972	0.9763	4.778	673.5
2) CDA	499.8	1.097×10^{-5}	488.4	0.1660	0.0016	0.07303	2.273	0.9884	0.9688	4.754	583.6
3) CAM Graft Copolymer	492.0	1.087×10^{-5}	486.0	0.2868	0.0018	0.08316	3.451	0.9948	0.9737	3.031	373.0
4) CA:PMMA (80:20) Blended (Glycerol-treated)	1999.2	3.659×10^{-5}	1715.0	0.1852	0.0039	0.06944	2.667	0.9770	0.9166	35.66	1585

CHAPTER - V

DISCUSSIONS OF THE RESULTS AND CONCLUSIONS

5.1 Poly (Methyl Methacrylate)

The optimization conditions for polymerization of methyl methacrylate are tabulated in Table 4 of Chapter III. Conditions for bench scale preparation of Poly (methyl methacrylate) have also been optimized. Table 5 of Chapter 3 contains the results for the same. The comparison for the above two Tables indicates that the laboratory scale results are reproducible at bench scale. The Table 6 of Chapter III contains the characteristics of the laboratory produced poly (methyl methacrylate). It is also indicated from Table 9 of Chapter III that the characteristics of the laboratory prepared poly (methyl methacrylate) favourably compares with imported (Eastman Kodak) poly (methyl Methacrylate).

5.2 Physical blending of Cellulose Diacetate (CDA) with Poly (Methyl Methacrylate) PMMA

As mentioned in paragraph 3.3, physical blending of PMMA with CDA was attempted with the solution composition and the membrane preparation parameters as mentioned therein. Table 10 of Chapter III contains the performance results of the flat membrane prepared from these blended casting solution compositions. It is indicated from these results that the membrane prepared from (80:20) CA:PMMA physical blend produced encouraging results, (503.8 lmd flux and 98.0% salt rejection). In this optimum casting solution composition from CA:PMMA blended mixture, the ratio of volume of Acetone + Formamide : Benzene is about 6.74:1 i.e. volume proportion of Benzene is considerably small.

It is evident from the experimental results that though benzene is water immissible, but as its proportion in the casting solution is very small, useful Reverse Osmosis membrane from CA:PMMA (80:20) blend mixture has been possible to obtain inspite of the presence of Benzene as one of the solvents.

5.3 Optimized Flat Membrane from CA:PMMA (80:20) Blended solution

Utilizing the optimized CA:PMMA casting solution composition, the following flat membrane preparation parameters were optimized:

1) As-Cast thickness
2) Evaporation period
3) Annealing temperature

Tables 11, 12, and 13 of Chapter III respectively contain the results. Moreover, Table 13A of IIIrd Chapter contains the optimized membrane preparation parameters.

A series of the optimized flat CA:PMMA membrane was prepared and their reverse osmosis performance data were collected. (Table 15, Chapter III). It is indicated that their reverse osmosis performance data are fairly reproducible and on an average, this membrane produces about 98% salt rejection at a product flux rate about 503.8 lmd under the operational conditions as mentioned under the same Table.

Several optimized CA:PMMA flat membranes were prepared and it was attempted to cross-link them by employing the redoxe-system using different amounts of potassium persulphate ($K_2S_2O_8$), and sodium hydrogen sulphite ($NaHSO_3$). Also the period for cross-linking was varied as shown in Table 14, Chapter III. It is Indicated that the reverse osmosis performance of these membranes is not better than that of the non-cross-linked optimized CA:PMMA flat membrane. It may be inferred from this that the cross-linking step has not induced any favourable membrane structurization which may help to obtain better performance.

Phy prop?

5.4 Comparison of Reverse Osmosis performance of Flat CA:PMMA blended membrane with that of the Cellulose Diacetate flat membrane

These two types of membranes were prepared under identical membrane preparation parameters and were tested under identical operational parameters as shown in Table 15 and 16 of Chapter III.

The average performance of these membranes is as follows :

Membrane Type	Flux lmd	% Salt Rejection
1) CA:PMMA	503.8	98.0
2) CDA	446.0	93.0

It shows that the flat CA:PMMA membrane on an average produces 12.5% more flux and 5.3% more salt rejection.

The increased salt rejection produced by CA:PMMA flat membrane may indicate finer porosity of its active surface than that of the CDA flat membrane.

As CDA and PMMA both possess comparably low dielectric constant value and also as the proportion of PMMA in blend is small, hence this characteristic of these two materials would not significantly add to the high percent salt rejection produced by CA:PMMA flat blènded membrane. A comparatively little more product flux produced by CA:PMMA blend membrane may indicate either greater number of fine pores on its active surface and/or its slightly thinner active surface.

5.5 Performance of CA:PMMA blend and Cellulose Diacetate (CDA) Flat Membrane given glycerol annealing treatment

As mentioned in Table 17 of Chapter III, the average performance of these two types of flat membranes is as follows :

	Membrane Type	Flux lmd.	Percent Salt Rejection
1)	CA:PMMA	1760	90.6
2)	CDA	1100	90.8

The above-mentioned data show the following extent of improved performance as regards the product flux than that of the membranes given annealing treatment in plain water.

	Membrane Type	Percent Excess Product Flux	Decline in Percent Salt Rejection
1)	CA:PMMA	250	7.4
2)	CDA	147	2.2

Glycerol, a trihydric alcohol (Bp. 290°C at 760 mm. pressure, vapour pressure 0.195 mm at 100°C) is a hygroscopic liquid which is extensively used as a softener or a plasticizer[69,70].

Cellulose triacetate can be hydrolyzed in alcohols or glycerols at atmospheric pressure or higher pressure at temperature upto 445°F.[71]

Schoep was responsible for the use of glycerol, a non-volatile swelling agent, to control the gel structure. Brown produced a graded series of collodion membranes by swelling initially dense film in varying concentrations of alcohol-water[72].

Water permeability increases with the extent of de-esterification both because hydroxyl groups are more hydrophilic than the ester group they replace, and because (in the case of the partial hydrolysis), the ester group occupies large volume which is subsequently replaced by the hydrolytic medium[73].

The membrane that appears on completion of Sol-to-gel transition is referred to as primary gel structure. Such a species can be physically modified by additional treatment to produce secondary gel structure exhibiting altered performance characteristics. These alterations are attributable to change in both swelling and order within the primary gel.

The degree to which the primary gel is swollen, can be either increased or decreased. The films are immersed in the suitable swelling medium in which the polymer solvent interaction is sufficient to overcome the same, but not all of the secondary valency forces that constitute the polar inter molecular cross-linked opposing solution.

In case of swollen asymmetric cellulose acetate membrane, it is usually desirable to de-swell the already comparatively unswollen surface layer of the primary gel still further in order to increase perm selectivity. The aqueous annealing treatment serves this purpose.

Trudelle and Nicohal[73] have recently shown that the thermal treatment of cellulose acetate reverse osmosis membranes decreases the water content of surface layer (from 46 to 38.6%) to a much greater extent than it does in that of substructure (from 63 to 61.8%).

Considering whatever has been mentioned above, the already mentioned differences in the performance of the membranes that are either annealed in 1) Aqueous glycerol bath, or 2) Plain water bath, may be explained as under :

i) Swelling of active surface
ii) Partial hydrolysis of active surface
iii) Because of its high B.P., low vapour pressure, and hydrogen-bonding capacity, the glycerol may be comparatively less squeezed out than capillary water during the swelling of the membrane by the annealing treatment.

All the above-mentioned factors can produce a high water permeability in a flat membrane at the cost of some extent of decline in perm-selectivity.

It is reported[74] that when a membrane is brought into contact with an aqueous solution of a poly valent alcohol, a sufficient and continuous exchange of water imbibed in the membrane with the poly valent alcohol can take place. During the same reported investigation, the following observations have been given; While investigating the performance of two types of cellulose acetate membranes, one given a plain water annealing treatment, while the other aqueous glycerol annealing treatment, the rest experimental condition remains constant.

	Membrane Type	Annealing Temp. °C	Flux lmd.	% S.R.
1.	Plain water annealing treatment	84	580	96.3
2.	Aqueous glycerol annealing treatment	a) 84	1600	64.0
		b) 90	560	96.2

It is reported as a conclusion that for obtaining similar performance, an aqueous glycerol annealed and dried membrane must be annealed at above 5°C high temperature when it is used in the usual manner in the order to obtain a wet desalting membrane.

The above data indicate that an aqueous glycerol treated membrane when annealed at the same temperature as in the case of plain water annealing treatment possesses comparatively bigger pore diameter on its active surface and to decrease these pore diameters to the desired extent, it requires comparatively higher annealing temperature.

During the above referred investigation, the extent of the effect of glycerol content of the annealing bath of 90°C has been given as below :

Glycerol Content %	Flux lmd.	% S.R.
20	410	97.3
25	500	96.5
30	560	96.2
35	770	90.9

This data indicates that as the per cent glycerol content of the annealing bath increases, the product flux of the membrane also increases but the per cent S.R. decreases. This may be attributed to glycerol as a plasticizing/swelling agent and also a mild hydrolyzing agent.

A comparable study on the same lines, a little has been reported[75].

Dry semi-permeable cellulose acetate (I) membranes of good stability are prepared as follows :

A flat membrane consisting of an active separatary layer and a porous supporting layer was prepared by pouring (I),(ACo group content 39.8%) 25, $HCONH_2$ 30 and Me_2CO 45 parts on an even support, keeping 10 seconds at R.T. for Me_2CO evaporation, immersion in water at 20°C for 5 minutes, removing (I) layer from the support and immersion in water at 82°C for 5 minutes. ~~This~~

gave a semipermeable (I) membrane of water permeability 830 lmd and per cent S.R. 92.3. But if this membrane is further immersed in HA$\bar{c}$ 5, glycerol 30, and H_2O 65% at R.T. and dried at 60°C for 5 minutes, it produces water permeability 920 lmd and per cent S.R. 95.9 for 0.5% NaCl solution at 40 atmospheric pressure.

The acetyl content value of the membrane samples obtained from same piece of flat(CA:PMMA) blend membrane indicates that this value for the membrane sample given aqueous glycerol annealing treatment is slightly lower than that of the membrane given plain water annealing treatment which may indicate the probability of a little hydrolyzing effect of glycerol during the annealing treatment.

The determination of bound water content of the same type of membrane sample does not indicate a significant differente in the value.

5.6 Performance of flat membrane from CAM graft Copolymer

On an average, this membrane produces 560 lmd product flux with 95.4 per cent salt rejection as shown in Table 21 of Chapter III. This performance is not significantly better than that of the optimized flat CA:PMMA blend membrane which indicates that the grafted material has not proved to be a better membrane material than the blended one.

It may be noted as mentioned earlier, the way the grafting of PMMA on cellulose diacetate was effected, the product indicated a major proportion of PMMA as the homopolymer.

grafting not
proper -
g. PMMA →
same blend?

5.7 Treatment of Urea containing Feed with the optimized CA:PMMA Blend Flat Membrane & Cellulose Diacetate Flat Membrane

The results in Table 22 of Chapter III indicate:

1) With CA:PMMA blend membrane appreciable rejection of urea from either aqueous urea feed solution or NaCl containing urea feed solution.

2) With Cellulose diacetate membrane, insignificant rejection of urea from either aqueous urea feed solution or NaCl containing urea feed solution.

This indicates that the pore diameter of the active surface of the former membrane is comparatively smaller than that of the active surface of the later membrane. A similar observation has been reported[76] that as Na^+ and CI^- ions are dominant in the water, the maximum diameter of pores in the membranes should not exceed 7 A°. For high degree desalination (removal of NO_3^- and CI^-) and for separation of low molecular weight organic compound (e.g. MeOH, urea,etc) the membrane should have pores with diameters of 2.5-3.5 A°.

5.8 Tubular Membrane from CA:PMMA blend & Cellulose Diacetate

Table 18 and 19 of Chapter III respectively contain the performance data of tubular membranes from CA:PMMA blend, given plain water and aqueous glycerol annealing treatment. Their average performance is as follows :

Mode of Annealing Treatment	Flux lmd.	Percent Salt Rejection
1) Plain water	547	69.8
2) Aqueous glycerol	1029	81.0

Compared to the performance of similar type of CA:PMMA blend flat membranes, a significant decline in per cent salt rejection is observed while maintaining a reasonable extent of flux.

During the fabrication of these tubular membranes, it has been observed that a number of these membranes show numerous fountains during the initial stage of annealing which disappear to a great extent as the annealing treatment proceeds.

A similar observation is made during the high pressure testing of these annealed tubular membranes. In the initial stage of pressurising these membranes during reverse osmosis testing, a number of them show several fountains which gradually decline, and disappear as the high pressure testing proceeds.

The above-mentioned performance and behaviour of CA:PMMA blend tubular membrane can be explained as follows :

It has been observed[77] that voids and large cavities similar in shape to the finger-like protrusions are commonly found in tubular (internal flow) cellulose acetate membranes prepared from the modified Loeb-casting solution. It has been reported that if the possibility of free shrinking of the polymeric phase, accompanying phase, Separation is eliminated, voids will be occluded in the precipitate. While the sheet membrane is free to shrink through reduction of its thickness, the interfacial precipitates in the tubular membrane is immobilized. In the tubular membrane situation, the resistance of the solidified internal surface to stretching inhibits free shrinking of the cast tubular film and thereby induces cavity formation.

In short, tubular membranes are more susceptible to occlude voids in their matrix than sheet membranes.

This is because the tubular membranes are not as free as sheet membranes to shrink during their precipitation.

Moreover CA:PMMA blend membrane is a two phase polymer matrix wherein PMMA has a globular structure. Because of this it is very likely to develop some physical flaws like minute pores on its active surface during its gelling. As mentioned earlier, some minute pores are visible on a similar flat membrane. It is probable that a number of these pores might be sealing due to plasticization during annealing treatment and more so during the high pressure treatment as it is reported[78] that holes as large as 30-100 μ in a membrane appear to be completely self-sealing. This is supported by the virtual disappearance of the hydraulic flow of salt solution and also the disappearance of the fountains.

The performance of cellulose diacetate tubular membrane given aqueous glycerol annealing treatment (shown in Table 20 of Chapter III) shows also a similar decline in per cent salt rejection. It is observed that these membranes which have a homogenous matrix of single polymer usually do not exhibit the fountains either during annealing treatment or during high pressure testing.

5.9 Membrane Specific Water Content

Table 23 of Chapter IV contains the specific water content data of the different types of flat membranes. The average value of the specific water content of each type of these membranes has been co-related with the average value of the experimental solvent flux (taken from Table 34 of Chapter IV) by plotting the specific water content value versus solvent flux (J_V) in fig. 19

The fig. 19 indicates that the membrane solvent flux is in a direct variation with the membrane specific water content and beyond a critical value of specific water content there takes place a steep rise in the value of the solvent flux with a small increase in the specific water content value. This also indicates that the specific water content values of different membranes can be a pointer to suggest their solvent fluxes under identical operational condition.

It is reported[79] that during the gelling of the membranes which are cast from solution containing swelling agents or additives, the gellation is retarded to a large stage in the dissolution process. The ultimate result is the increased membrane water content and the decreased resistance of the membrane to get to the material transport.

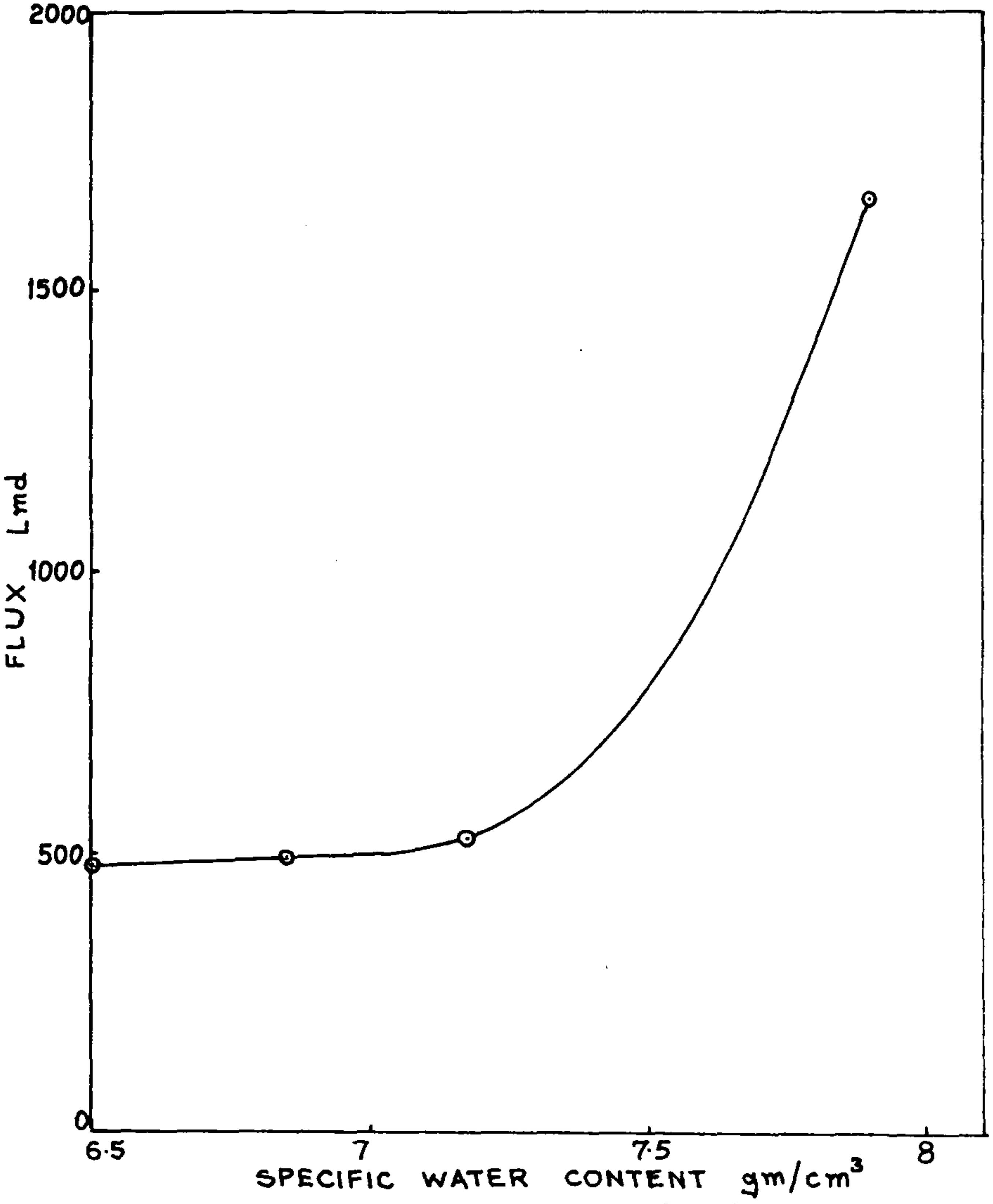


FIG: 19. SPECIFIC WATER CONTENT Vs FLUX (Jv).

It is reported[80] that the flux of water through a membrane increased with the membrane water content. For any given pressure there exists in the water flux versus per cent water in the membrane relation, a water content above which the flux increases sharply. This may be explained on the basis of a change in the mechanism from solution transport in viscous flow.

The performance of aqueous glycerol annealed CA:PMMA flat membrane fairly supports the above-mentioned observation.

5.10 Salt Absorption by Immersion

The data in Table 24 of Chapter IV shows that the salt absorption values of the different types of membranes are nearly equal within a narrow range which indicates a nearly equal capability of salt absorption by the membrane matrix, because all these membranes are Loeb-type asymmetric porous membranes. These immersion type experiments would only be useful to indicate solute transport through the membrane if dense membranes have been handled.

5.11 Direct Osmosis

The solvent flux and the solute flux of different types of flat membranes as shown in Table 25 of Chapter IV obtained by direct osmosis experiments have been plotted as the former versus the latter (fig. 2). The inference from fig. 2 is that the solvent flux is in a direct variation within the solute flux and beyond a threshold value of the solvent flux, the solute flux value shows a steep rise.

Because the direct osmosis experiments are performed at zero pressure, any physical flaws in the membrane would not significantly interfere with the observation made and hence this seems a practicable and suitable approach to characterize the behaviour of an osmotic membrane.

5.12 Membrane Salt Permeability D_2K

The average values of salt permeability of different types of flat membranes (as shown in Table 26 of Chapter IV) have been plotted against their average values of specific water content and per cent salt rejection (fig.23) from which it is inferred that the specific water content values and the per cent

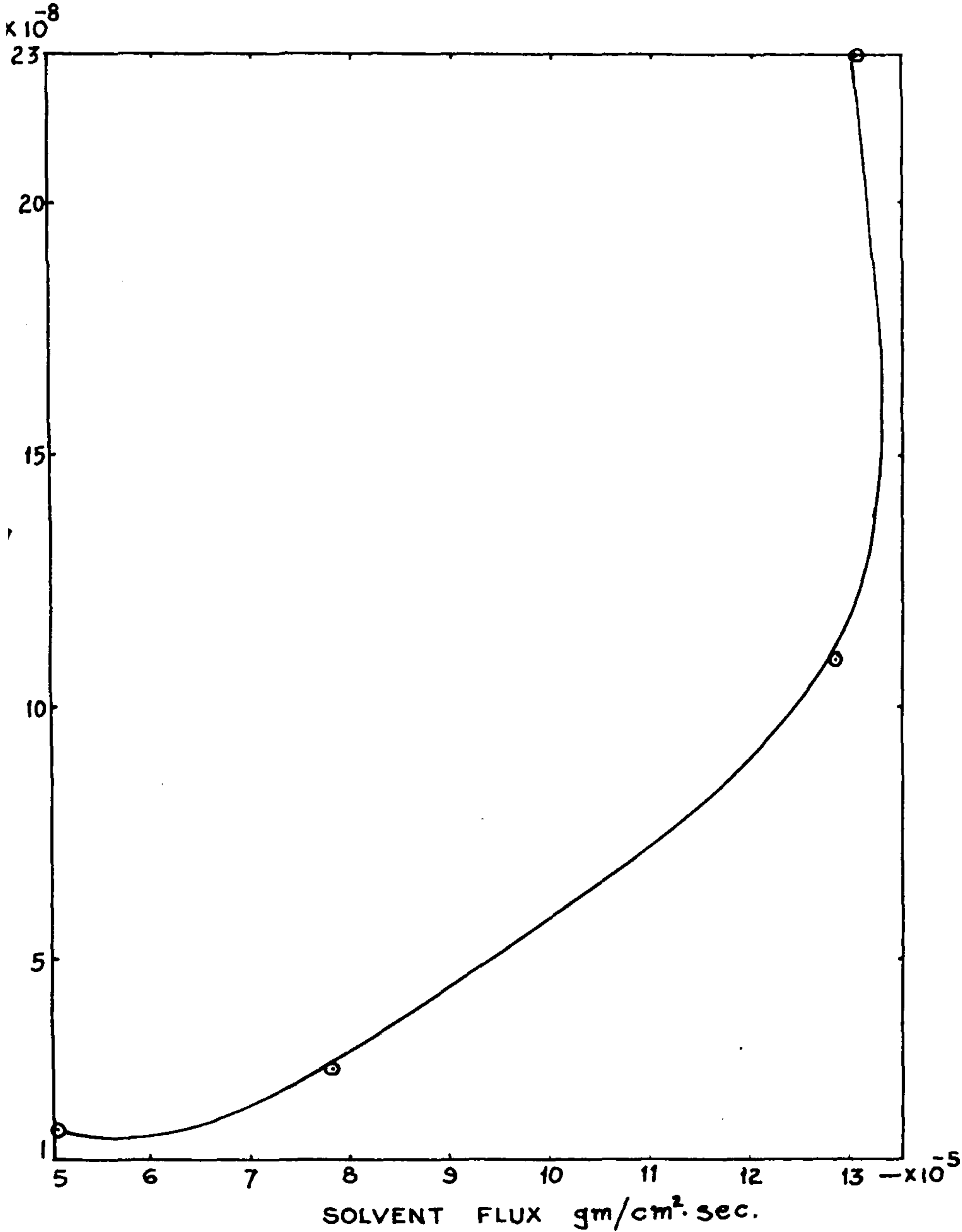


FIG: 20. SOLVENT FLUX Vs SOLUTE FLUX.

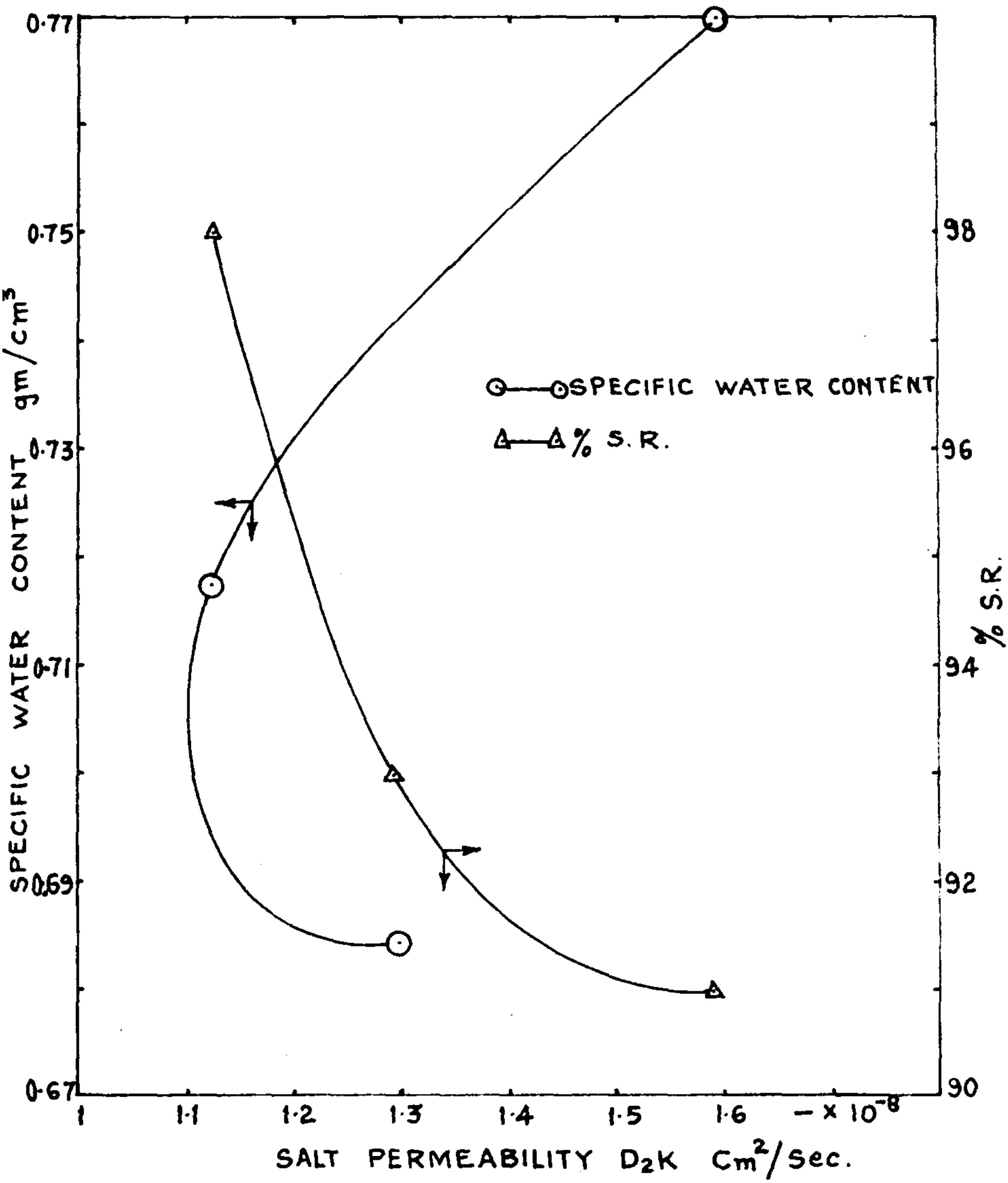


FIG: 21. SALT PERMEABILITY Vs SPECIFIC WATER CONTENT AND % SALT REJECTION.

salt rejection values for these membranes are in a direct and an inverse variation respectively with the salt permeability values of these membranes.

Similar observations have been reported for Cellulose acetate and Cellulose acetate methacrylate membranes[81,82].

It is observed from the values of average pore diameter of different types of flat membranes (mentioned in the same table) that these values are nearly equal within a small range of 25-40 A°, and hence they are not immediately useful in the characterization of an asymmetric porous membrane but can be quite useful in the characterization of a dense membrane.

5.13 Tensile Strength of the Membrane

From the Table 27 of Chapter IV, it is observed that the tensile strength of CA:PMMA blend flat membrane is significantly higher than that of cellulose diacetate flat membrane; hence the former membrane would have better useful life than the latter membrane.

As mentioned below, similar tensile strength values have been reported[82] :

Membrane Type	Tensile Strength psi
Cellulose diacetate E-398-3	800-1100
Cellulose Acetate Methacrylate	
a) Uncross-linked	1400
b) Cross-linked	1540

Boyer graphs p.147

Tables 28 to 31 of Chapter IV contain the characteristics already discussed of different types of flat membranes.

As mentioned in Table 27-C of Chapter IV, several characteristics (viz. specific water content, salt absorption by immersion and average pore diameter) of the dense membranes of CA:PMMA blend and CDA are significantly lower than those of the corresponding asymmetric membranes. These observations are generally expected from a dense membrane.

The values of the above mentioned characteristics of the CA:PMMA blend dense membranes are comparatively lower than those of the CDA dense membranes. These observations fairly support the previously stated experimental performance of the asymmetric membranes of CA:PMMA blend and CDA.

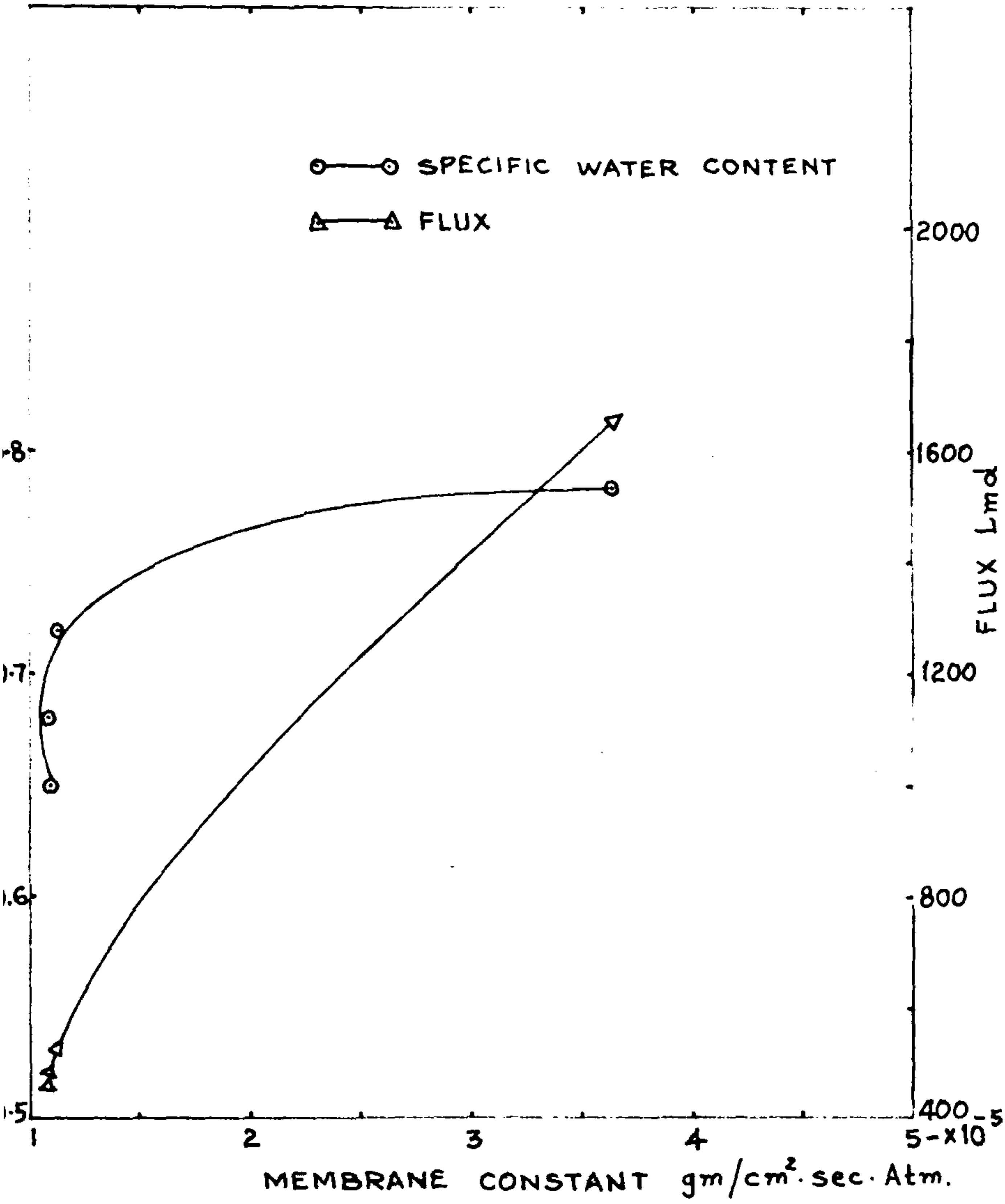
The value of the Tensile Strength of CA:PMMA flat dense membrane is higher than that of the CDA flat membrane. Similar observations have been previously stated for the Tensile Strength value for the asymmetric flat membrane of CA:PMMA blend and CDA membrane.

5.14 Membrane Pure Water Permeability (PWP) and Membrane Constant

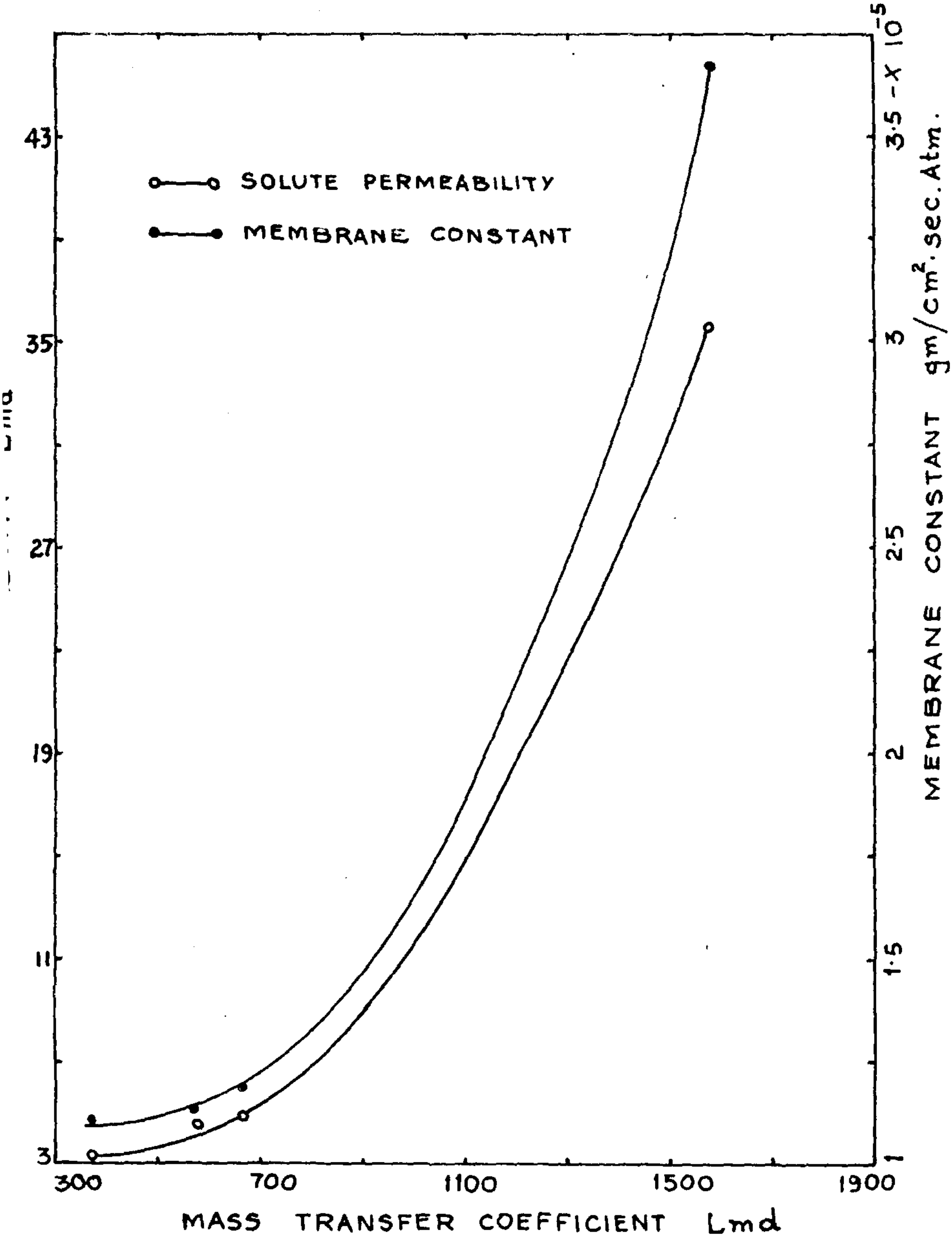
These data for different types of flat membranes are incorporated in Table 32 and 33 of Chapter IV respectively. The membrane constant values of these membranes have been plotted against their respective specific water content values and their respective solvent flux values (fig. 4).

It is reported[83] that the membrane constant is a measure of overall porosity of the film, given in terms of the permeation rate of pure water for which the membrane material has a preferential sorption from aqueous solution in reverse osmosis. The membrane constant corresponds to conditions of zero concentration polarization and it is independent of any solute under consideration.

The following two similar observations from fig.24 have been arrived at :



IG: 22. MEMBRANE CONSTANT Vs SPECIFIC WATER CONTENT AND FLUX.



IG: 23. MASS TRANSFER COEFFICIENT Vs SOLUTE PERMEABILITY & MEMBRANE CONSTANT.

1) Within a small range of specific water content, the membrane constant values remain fairly constant and beyond that range of specific water content, the membrane constant value shows the steep rise.

2) The solvent flux is in a direct variation with the membrane constant.

Data in Table 34 of Chapter IV show that the percent deviation between the experimental and the calculated values of the solvent flux of different types of flat membrane is within a reasonable extent of experimental errors.

5.15 Concentration polarisation ratio and True and Observed Salt Rejection

The concentration polarization ratio values for the first three types of flat membranes as mentioned in Table 36 of Chapter IV have been correlated with the respective product water flux and per cent salt rejection as mentioned below :

Membrane Type	Concentration polarization ratio	Average product flux lmd	Average observed % salt rejection
1. CA:PMMA blend	2.16	527.0	97.9
2. Cellulose diacetate	2.27	489.0	97.2
3. CAM graft copolymer	3.45	478.0	97.4

It is observed that as the concentration polarization ratio increases correspondingly the product flux and per cent salt rejection decreases, the only anamolous point being a very small rise in per cent salt rejection of graft copolymer membrane which may be attributed to an experimental error.

The data for the aqueous glycerol annealed CA:PMMA blended membrane are :

Cw/Cb = 2.27
J_V = 1662 lmd
Per cent Salt Rejection = 90%

It is observed that inspite of there being a considerable rise in the solvent flux, the Cw/Cb value has not correspondingly increased, indicating that there is a simultaneous increase in the solute transport which is borne out by the value of the observed salt rejection.

According to Table 37 of Chapter IV, the difference between the true salt rejection (Ri) and the observed salt rejection (Ro), for the first three types of flat membranes are quite narrow and fairly constant. In the case of aqueous glycerol annealing CA:PMMA flat membrane, this difference is considerably large which can be attributed to the acceptance of the reflection coefficient value 'σ' equal to unity, while calculating the Cw and J_V values for the said membrane. As this membrane produces less than 95 per cent observed salt rejection, according to the previously cited references, the 'σ' value for this type of membrane should be less than unity, and for its correct value determination, an attempt has not been made during this investigation.

From the data in Table 35 of Chapter IV, it is observed that with nearly the minimum value of Cb as compared to those for the rest three types of membranes, the Cp value for this membrane is maximum so according to the equation $Ri = 1-\frac{Cp}{Cw}$; the Ri value should be comparatively much smaller than those for the rest of the membrane. This indicates the necessity of employing the correct value of 'σ' in the calculation of Cw of this type of membrane.

5.16 Solute Permeability and Mass Transfer Coefficient

Tables 38 and 39 of Chapter IV contain the membrane salt permeability and membrane mass transfer coefficient data respectively. In fig. 5, the membrane mass transfer coefficient is plotted as abcissa and the salt permeability and the membrane constant as the coordinate.

The membrane constant value is based on the membrane pure water permeability and hence reflects its solvent flux also. According to fig.25, it is seen that as the mass transfer coefficient value goes on increasing, the solute permeability value and the membrane constant value, both, go on increasing, and beyond some threshold value of the mass transfer coefficient, both the latter values show a steep rise. This indicates that with the types of membrane under this investigation there can be an optimum value of the membrane constant beyond which the membrane solute permeability value would be so high as the membrane may not produce an acceptable level of salt rejection. The complete mass transfer data of each type of flat membrane under investigation is incorporated in Table 40 of Chapter IV.

5.17 Conclusions

1) A new membrane from CA:PMMA blend is developed and characterised. This flat membrane produces 98 per cent salt rejection at a product flux rate of 503.4 lmd with 0.5 per cent sodium chloride (NaCl) solution as feed at an outlet pressure of 40 atmosphere.

2) The new CA:PMMA blend flat membrane is found superior to the conventional cellulose diacetate flat membrane prepared under identical condition in the following aspects :

a) Per cent salt rejection
b) Tensile strength
c) Urea rejection

3) The new CA:PMMA blend flat membrane has been further modified by aqueous glycerol annealing treatment so that this modified membrane produces about threefold product flux compared to the unmodified membrane and maintaining a useful level of salt rejection (about 90 per cent) so that this modified membrane can be very useful in brackish water desalination.

4) A small portion of Benzene has been first time successfully incorporated with Formamide and Acetone to obtain CA:PMMA blend useful flat reverse osmosis membrane.

5) The laboratory product homopolymer PMMA compares favourably with Eastman Kodak product PMMA.

6) A correlation between the membrane specific water content and its product flux has been evaluated.

7) The results of the direct osmosis experiments indicate this technique to be suitable and simple either to characterize a reverse osmosis membrane or the membrane material. When used along with the comparison of a conventional cellulose acetate flat membrane, prepared under identical conditions, this technique can be very useful to evaluate an unknown membrane by working at zero pressure.

8) A correlation has been evaluated between the specific water content of the membrane and its salt permeability as determined by the conductivity cell experiment and also its per cent salt rejection as found by the reverse osmosis experiments.

9) A correlation between the membrane specific water content and the membrane constant has been established.

It has been shown that the calculated product flux of the membrane is fairly coinciding with the experimental value.

10) The concentration polarization ratio for the different types of membranes under investigation have been obtained and also have been correlated with the product flux and per cent salt rejection of the respective membrane.

11) Assuming the reflection coefficient value 'σ' equal to one for the membrane producing 95 per cent or above salt rejection, the membrane true salt rejection has been successfully worked out and compared with the observed rejection for the respective membrane.

It has also been brought out that for the membrane producing less than 95 per cent salt rejection the 'σ' value equal to one does not stand good.

12) The complete mass transfer data for each type of membrane investigated have been obtained and also have been correlated with the membrane semipermeability and the membrane constant of the respective membrane.

13) An attempt has been made to translate the CA:PMMA flat membrane preparation parameters into CA:PMMA tubular membrane.

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