STUDIES IN CELLULOSE : MODIFICATION OF CELLULOSE ESTER FOR USE IN DESALINATION

A THESIS
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TO MY PARENTS

FORM 'A'

Certified that the work incorporated in thesis "STUDIES IN CELLULOSE : MODIFICATION OF CELLULOSE ESTER FOR USE IN DESALINATION", submitted by Shri M.B. Sabne was carried out by the candidate under my supervision. Such material as has been obtained from other sources has been duly acknowledged in the thesis.

[N.D.Ghatge]
Supervisor

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MBSabne

M.B. SABNE

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June, 1984.

GENERAL REMARKS

1. The figure (graphs, spectra, etc.) numbers, reference numbers etc. are given in each part refer to particular part only. The references are given at the end of each part.
2. The temperatures are given in centigrade scale and wherever it was necessary to have the temperature to be constant, thermostatic bath was used.
3. All solvents were distilled before use and were dried wherever necessary.
4. The IR spectra of the polymer samples were recorded by casting the film by evaporation of the solution in a suitable solvent.
5. The IR spectra were recorded on Perkin-Elmer, Model E 137.
6. The concentration of sugar solutions were determined on JASCO DIP-181 Digital Polarimeter (Japan)
7. All melting points are uncorrected.
8. Elemental analysis of polymers is carried out by microanalytical procedures for carbon, hydrogen, nitrogen.
9. The accuracy of % Salt Rejection, % Solute Rejection is within 1% and that of pure water permeability, water flux is within 3%.

PART I

GENERAL INTRODUCTION

INTRODUCTION

Fresh and pure water is the basic requirement of life, but available water from natural sources is generally contaminated with dissolved, dispersed and suspended impurities. A large portion of available water on our planet is in the form of saline water which cannot be used directly. This is where the 'Desalination' comes into picture. With increasing growth of population and industrialization of the world, the total potable water sources in nature will be insufficient. Thus realising the situation of potable water, advanced countries like USA, Japan, Denmark, Israel etc. have taken up the projects of converting the saline waters to potable water employing various desalination techniques using different polymeric membrane materials.

Desalination Techniques

Desalination process can be described as one of the separation processes which converts saline water into potable water by the application of external energy. There are several techniques for desalting the saline water and they are classified as follows

Processes using a phase change of water :

i) Distillation
ii) Freeze separation
iii) Hydrate separation

Processes utilizing properties of membranes :

i) Electrodialysis

ii) Reverse osmosis

Processes utilizing ion selective properties of solids and liquids :

i) Ion exchange

ii) Solvent extraction.

Of these techniques that are of current importance, electrodialysis and reverse osmosis are best adapted to the desalination of brackish water. Of the two, reverse osmosis is one which can effect efficiently for purification, separation and concentration of the dissolved solids from their aqueous solutions, under suitable process conditions and therefore it is regarded as a versatile process[1].

For more than ten years, polymers such as cellulose acetate and more recently polyamides, polyamidehydrazides or polybenzimidazolone[2,3] have been used as membrane materials for desalination.

Reverse Osmosis

Reverse osmosis is a process in which an applied pressure is used to reverse the normal osmotic flow of water across a semipermeable membrane. According to Fig.1, the normal direction of water flow across membrane from a solution of lower solid concentration to a solution of higher solid concentration. If a pressure ($\triangle P$) is applied

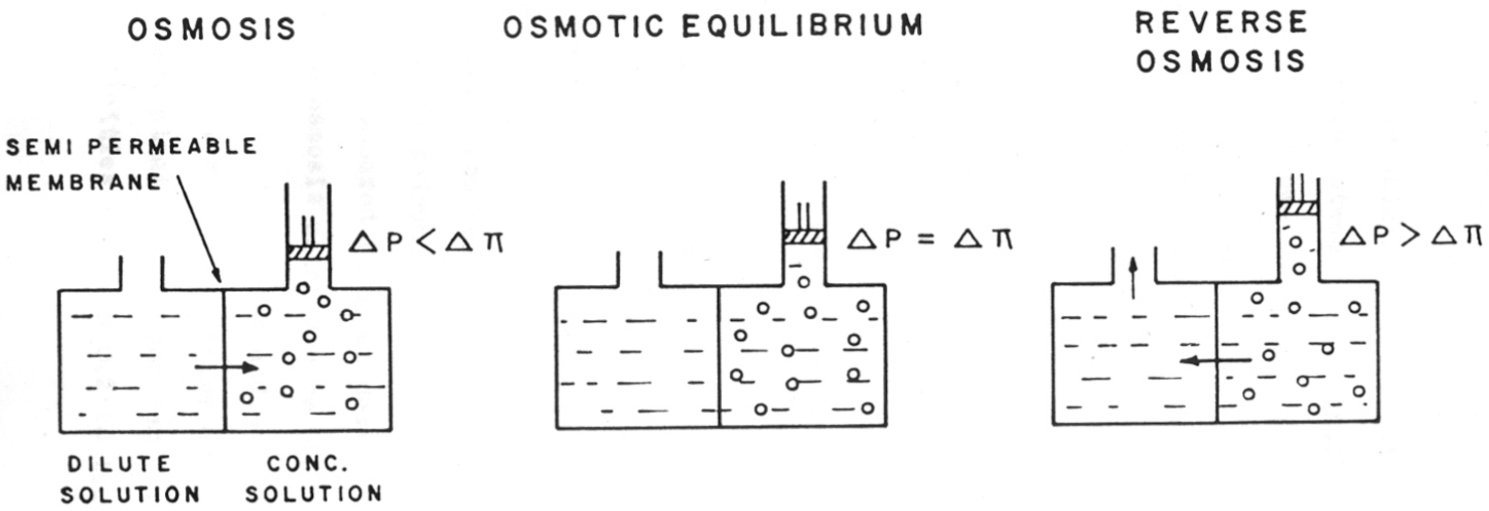


FIG.1 OSMOTIC PHENOMENA

to the concentrated solution just equal to the osmotic pressure difference between the two solutions ($\Delta \pi$), water flow ceases and is known as osmotic equilibrium. At a higher pressure ($\Delta P > \Delta \pi$), water will flow from concentrated to the dilute solution. If the membrane is sufficiently semipermeable, this process can be used to desalt the concentrated solution.

The sucess and the acceptibility of the process is associated firmly with the type of the semipermeable membrane and thus the improvement of cellulose acetate membranes have resulted in the advancement of the process to a pilot plant scale with respect to brackish water desalination.

Advantages of Reverse Osmosis

1) Separation of salt from saline water is achieved at ambient temperature without phase change.

2) The process in addition to desalination removes bacteria and virus from feed water.

3) The energy consumption, operation and maintenance cost is low when compared to other desalination processes.

4) Reverse osmosis plant can be built and operated with locally available materials and manpower and no elaborate shop fabrication facilities are required.

5) The same plant can be used for brackish water of different salinities (between 0.2 to 1.0% of total

dissolved solids) as the process is not very sensitive to the salinity.

Theory of Semipermeability

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

i) Sieve Mechanism[4]

According to this mechanism, the membrane contains tiny pores through which only the water molecules can pass through, while the bigger solute molecules or ions of the solute can retained over it. However, the size of the small inorganic ions is very near to that of water molecules. Therefore this mechanism has limitations.

ii) Distillation Mechanism

According to Callender[5] the osmotic transport proceed by distillation in cases where the solute is not volatile. Porous films could act as osmotic membranes if the liquid is kept out of the pores by surface tension, the solvent alone passes through them as vapour. Still there are doubts regarding this mechanism.

iii) Adsorption Theory[6-8]

This theory is based on a surface (interfacial) phenomenon. The surface layer of the membrane is microporous and heterogeneous. If only the surface of the porous membrane in contact with the solution has a preferential adsorption or repulsion for one of the constituents of the mixture, then a steep concentration gradient come into existence at the membrane solution interface. In this way the interfacial fluid layer gets enriched in one of the constituents of the feed solution. A continuous removal of this interfacial layer by flow under pressure through the membrane capillaries results in a product solution whose composition defers from that of feed solution.

The application of above theory for any separation problem involves the selection of appropriate chemical nature of film surface containing maximum number of pores of appropriate size at the interface.

Since some of the experimental results cannot be explained on the basis of the above theories, they are not acceptable totally. One of the latest theories proposed and generally accepted is the Hydrogen bonding theory postualated by Breton[9] while studying the solvent-solute transport mechanism in cellulose acetate membrane.

Hydrogen Bond Theory[9]

According to this theory, the pure water which passes through the 'perfect' portion of the membrane's active layer, is transported by successive forming and breaking of hydrogen bonds between the water molecules and the active sites. Under the driving force of the applied pressure, the water molecule, approaches a membrane site at which one or more water molecules are already bound. The next approaching water molecule forms a new bond at the active site, displacing the previously bound water molecule. The feed water molecule moves immediately downstream to approach another active site. By a succession of such transfer from site to site bound water 'diffuses' through the surface layer in the 'body' or the porous structure of the membrane. The membrane is swollen and the qnautity of capillary water is so large that the movement of water is same as through the huge pores.

The hydrogen bonding mechanism does not exclude the Sieve-mechanism. The size of the holes that are continuously appearing and disappearing plays a secondary role. The rates of diffusion of solutes that cannot enter into hydrogen bonding depend upon pore size. However, in the case of ions and molecules that can enter into hydrogen bonding, the permeability depends upon their ability to fit into the icelike structure of the membrane.

The solute-solvent transport mechanism of the cellulose acetate membrane has been shown in Fig. 2a, 2b.

Though hydrogen bond theory has been considered as one of the reasonable and logical approaches for the explaining the solute-solvent transport through asymmetric membranes, other approaches also play a significant role. Such approaches have thus produced the following two theories on the basis of diffusion and thermodynamics principles.

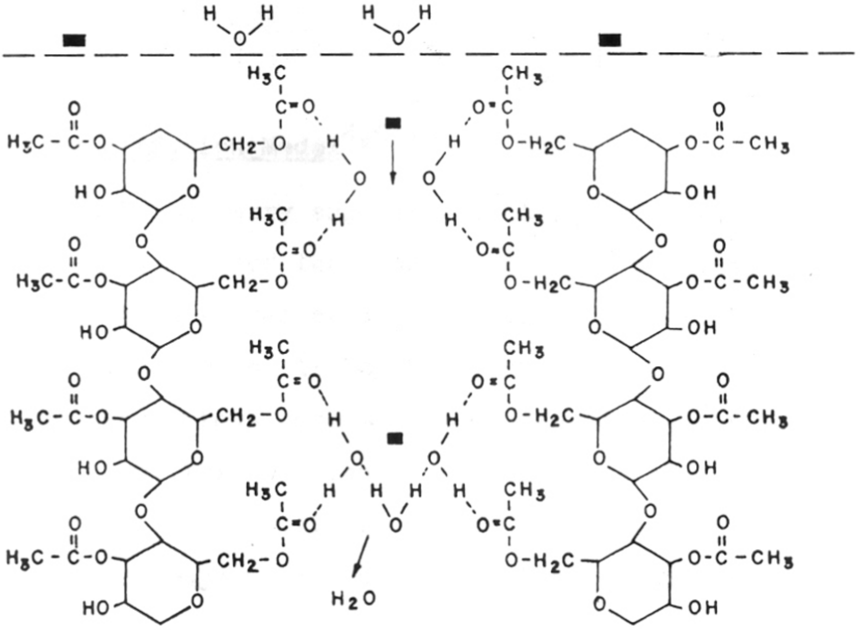


FIG. 2a PERMEATION OF SALT [▬] AND WATER
NON ANNEALED MEMBRANE

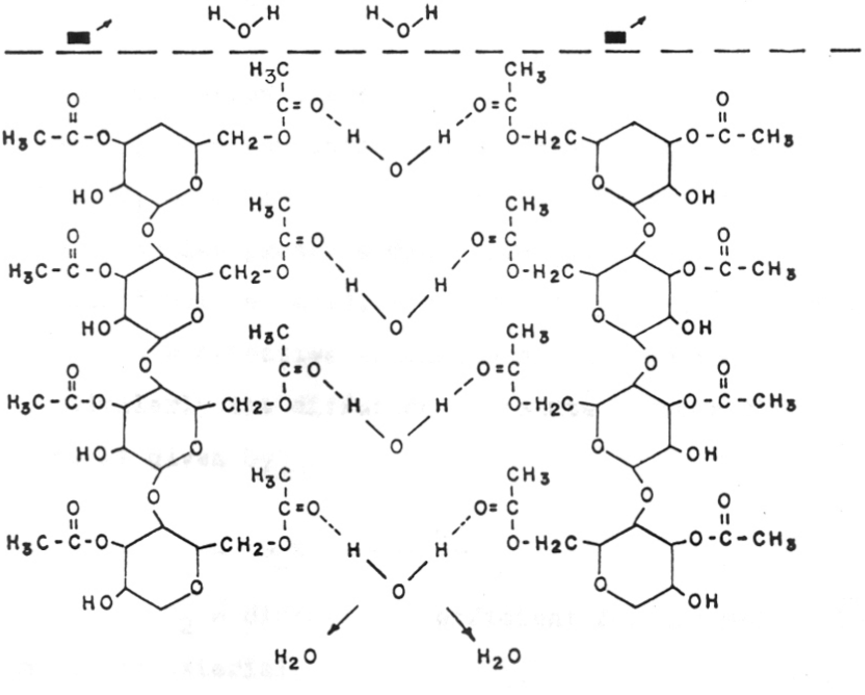


FIG. 2b ANNEALED MEMBRANE

Solution Diffusion Model[4,6,10]

In 1885, Ferry suggested that ultrafiltration, a very closely related technique to reverse osmosis, may occur by a mechanism termed as the 'solution diffusion mechanism'. While explaining the transport by the aid of this model, certain assumptions were made and accordingly the transport through asymmetric membranes have been explained.

The solution diffusion model for the transport through the membrane could be explained by the following equation :

The water flux F_1 is given by

$$F_1 = \frac{D_1C_1V_1}{RT} \quad \frac{\Delta P - \Delta \pi}{\lambda}$$

where D_1 = diffusion coefficient of water in the membrane ($cm^2\ sec^{-1}$), C_1 = concentration of water in the membrane ($g\ cm^{-3}$), V_1 = partial molar volume of water in membrane, $\Delta P - \Delta \pi$ = applied pressure minus osmotic pressure difference across the membrane (atm), R = gas constant, T = temperature (°K) and λ = effective thickness of the membrane (cm).

Similarly the diffusion of solute through the membrane is given by

$$F_2 = D_2K \quad \frac{\Delta C_2}{\lambda}$$

Where D_2 = diffusion coefficient for the solute in the membrane material.

K = distribution coefficient constant

$\triangle C_2$ = concentration difference across the membrane

λ = effective membrane thickness (cm).

However, for any other system than NaCl - H_2O, the equation may have to be modified, taking into consideration the chemical potential gradient for those particular systems under investigations.

Irreversible Thermodynamics

(The thermodynamic approach for the transport)

It is known that flow of matter from one region to another determined by a property called the chemical potential. Any kind of matter, such as water, flows in the direction in which its chemical potential decreases, exactly as heat flows in the direction of decreasing temperature. Such a chemical potential especially of the solvent should be same on both sides of the osmotic membrane for the osmotic equilibrium. This condition is considered as the principal requirement for attaining the equilibrium in a system, however, no such condition is imposed on the solute, since the membrane prevents its passage.

The chemical potential is defined by Gibb's equation :

$$dU = TdS - PdV + \sum_i \mu i dNi$$

where U is the energy, T the temperature, S the entropy, P the pressure, V the volume and μi and Ni are the chemical potential and number of moles respectively of component i. This equation is finally correlated with the osmotic pressure (π) arriving at the final form as expressed by

$$\pi V_1 = RT \ lN \ (P_1^*/P_1)$$

Where V_1 is the partial molar volume of solvent, P_1 and P_1^* are the vapour pressure of the solution and pure solvent respectively. R is the gas constant and T the temperature.

The distinct differences of this concept with that of the solution diffusion model are

i) The transport of both the solvent and the solute can easily be explained for all the membranes.

ii) No assumption for the membrane 'perfection or imperfection' is required to be considered while explaining the transport.

iii) The solvent may be anything and not necessary water as required in the solution diffusion model.

iv) This concept recognises the possibility of the coupled flow, employing an additional factor, the 'reflection coefficient' (σ), which is a correction factor compensating for the fact that most practical membranes are not strictly semipermeable but do pass some solutes. For a strictly semi permeable membrane, σ approaches unity.

Development of Reverse Osmosis

The historical development of reverse osmosis process has been studied by Yuster et al[11] who first suggested the possibility of desalinating saline water by skimming out surface layer of pure water from that of sodium chloride solution. This suggestion was perhaps the starting point of research on the desalination at University of California and simultaneously at University of Florida, USA in 1956.

The phenomenon called osmosis, was first reported by the Abbe' Nollet in 1748, using animal membranes. Later on in 1867 Traube made an artificial membrane for osmosis. In 1877, Pfeffer[6,12] made the first quantitative measurements, using a membrane consisting of copper ferrocyanide precipitated in the pores of porcelain. The perfection of the difficult techniques for preparing and handling of the membranes was done by Morse, Berkeley and Hartley[13]. The theoretical development started with Von't Hoff and thermodynamic treatment was developed largely through sound theoretical understanding of the osmosis phenomenon by Gibb's.

Flow through an osmotic membrane has been expressed mathematically by the following general equation[10].

$$F_1 = A(\triangle P - \triangle \pi)$$

where F_1 = fresh water flux through the membrane (g/cm^2-sec)

A = Membrane constant (g/cm^2-sec-atm)

$\triangle P$ = Pressure drop across the membrane (atm)

$\triangle \pi$ = Osmotic pressure of the feed (atm)

Greater the $\triangle P$, lower the $\triangle \pi$ (which is dependent on the concentration of the solution), higher will be the output of pure water (i.e. flux). This also depends upon the membrane characteristic (i.e. 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 Merten[6]. For employing reverse osmosis technique for desalination, separation or concentration a suitable semipermeable membrane must meet the following requirements,

1) It must desalinize a given saline feed water adequately,

2) It must have adequate desalinized water flux (flow rate per unit area of membrane) at reasonable pressure.

3) It must possess the above two characteristics for a reasonable length of time.

In reverse osmosis, perhaps more than in any other membrane application, innovation has played a key role over the last twenty years. The literature documentation clearly indicates that reverse osmosis is one of the most promising processes for the desalination of sea and brackish water in terms of economics and technical simplicity. Large scale reverse osmosis seawater desalination plants have recently gone on stream in Middle East[14].

Development of Membrane Materials

1) Cellulosic Membranes

Many polymeric materials have been scrutinised over twenty-twenty five years for the preparation of semipermeable membrane for use in reverse osmosis technique for desalination. Reid and Breton[9] reported cellulose acetate as a promising material for the preparation of membrane in comparison with other polymeric materials. The conclusions drawn by Sourirajan and Bernstein[11] were also similar to that of Reid.

Eventhough the salt rejection of Cellulose acetate membrane was on the higher side the water flux was low. Loeb and Sourirajan[15] attempted to increase the water flux through the use of Schleicher and Schuell type commercial membrane. They could improve the salt rejection, by heating the membrane in hot water for a period of 3 to 10 minutes. From their studies they concluded that the degree of desalination is directly proportional and water flux is inversely proportional to heating temperature. They also studied[16,18] the effect of heating temperature, pH, etc. on Schleicher and Schuell type cellulose acetate membranes and finally developed their own technique for making porous cellulose acetate membrane. By incorporating acetone as an additional component in the casting solution and by instituting a number of other changes from original Dobry method[19], Loeb and Sourirajan[15] found it possible to fabricate cellulose acetate membranes having improved water flux maintaining higher percent salt rejection.

In 1965, Sourirajan and Govindan[20] used a solution of 17% cellulose acetate, 68% acetone, 1.5 magnesium perchlorate and 13.5% water, referred as perchlorate system cast at -10°Cwith 4 minutes evaporation time. This system gave 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. Various additives in the membrane casting solutions have also been studied to modify and to improve the membrane performance[21].

Manjikian, Loeb and McCutchan[22] described a number of useful membrane casting solutions containing only nonelectrolytes which yielded identical performance to above by a method which allows room temperature casting (although the immersion water temperature should be in the range of 0-5°C). They have reported the composition consisting of cellulose acetate-formamide-acetone in the ratio 25 : 30 : 45 wt. % appeared to be optimum. It was also reported that the presence of formamide in cellulose acetate casting solution is responsible for the creation of pores in the resulting membrane. The average pore size in the membrane was independent of the amount of formamide but the number of pores in the membrane increases with increase in formamide in the casting solution. Several reverse osmosis membranes capable of giving 99% salt rejection with acceptable water flux (using feed solutions whose concentrations was comparable to seawater) have been reported from cellulose esters and mixed esters[6,23-27].

Loeb type cellulose acetate membranes have been most widely used membranes todate for desalination of brackish/ seawater by reverse osmosis technique. Eventhough these membranes are quite efficient they suffer from number of shortcomings. The most serious problems associated with these membranes are,

(1) High rate flux decline under operating conditions,

(2) Low specific water flux for maintaining adequate salt rejection.

(3) Since cellulose acetate is polyglucose and ester, it is susceptible to microbial degradation[29] at low and high pH, causing rapid loss of semi-permeability.

(4) They can be used only with aqueous solution since organic solvents either dissolve or plasticize it causing it's collapse. Secondly most of these membranes must be kept in wet conditions because if they are allowed to dry, they irreversibly consolidate and loose semipermeability.

(5) These membranes cannot be operated at higher temperature.

2) <u>Non Cellulosic Membranes</u>

Since cellulosic membranes possess certain drawbacks, considerable efforts have been made in recent years in the development of a number of polymeric materials which exhibit superior transport, mechanical, thermal, biological and chemical properties to those of cellulose acetate. Among the most promising polymers for membrane applications are aromatic polyamides, polyimides and nitrogen containing aromatic backbone polymers.

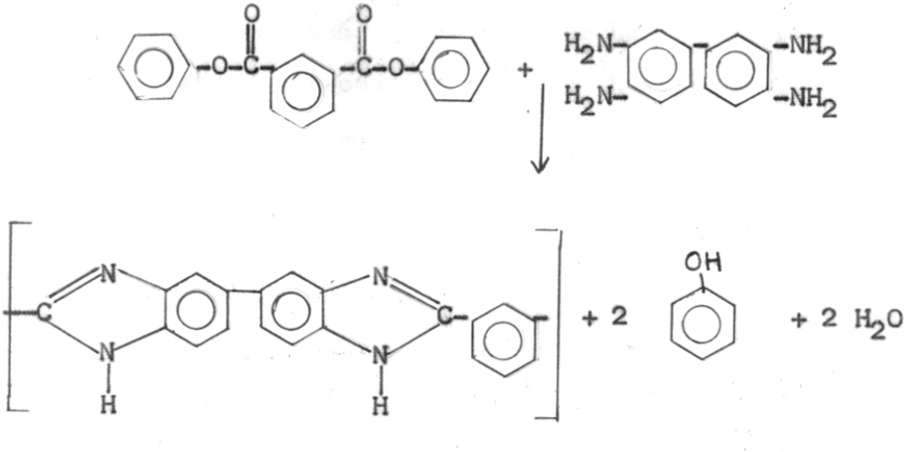
Polyamides

Aromatic as well as other polyamides can be obtained by two principal methods : the interfacial polycondensation and low temperature, homogenous solution polycondensation in the presence of a solvent which may function as an acid acceptor.

Techniques for the fabrication of asymmetric membranes for aromatic polyamides do not differ from those developed for cellulosic derivatives. Aromatic polyamides show better hydrolytic stability than the aliphatic polyamides such as nylon 6 and nylon 6-6. Wholly aromatic polyamides possess remarkable gamma radiation resistance. The outstanding radiation resistance property of these polymers has been utilised in solving the effluent problem from the atomic reactors and radioactive waste concentration and recovery.

Polybenzimidazole (PBI)

Polybenzimidazole (PBI) a class of polymers has been developed recently for reverse osmosis membrane applications[30]. Poly-2,2'-(m-phenylene)-5,5' bibenzimidazole (PBI) is prepared from 3,3'-diaminobenzidine and diphenylisophthalate according to the following scheme.



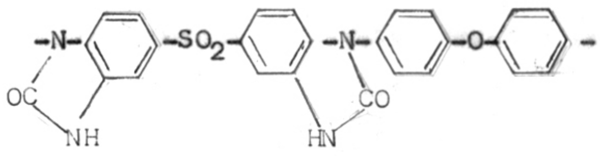
(PBI)

During this studies it was found that the PBI has very high moisture affinity about 13%. In addition to moisture affinity, PBI is known to possess outstanding thermal, physical and chemical stability over a wide range of pH. This polymer has solubility in dimethylacetamide. All these characteristics support PBI as a logical polymer as reverse osmosis membrane material. The membrane performance characteristics of PBI polymer are superior to those of cellulose acetate particularly at high temperatures and high pressures.

Polybenzimidazolone (PBIL)

Aromatic polymer containing benzimidazolone ring in the main chain has been found to show excellent performance as a R.O. membrane compared with cellulose acetate membranes[2,3].

PBIL polymer is synthesised by polycondensation reaction of aromatic diamine and dichloride, followed by ring formation reaction. PBIL polymer has a following polybenzimidazolone repeating unit in the backbone.



(PBIL)

The asymmetric membranes prepared from PBIL polymer exhibit higher salt rejection and higher water flux as compared to cellulose acetate membranes. According to the reports, Teijin Ltd., Japan, has successfully developed reverse osmosis plant[3] using PBIL membranes.

In addition to the above polymers, polyethyleneimine crosslinked by polyisocyanate, sulfonated polysulfone and polyphenylene oxide, and polypiperazineamide have shown promises in the R.O. applications.

Large Scale Application of Reverse Osmosis

Reverse osmosis has gained firm entry in recent years into industrial world for water treatment, separation and concentration of industrial liquids. The production of potable water from sea and brackish water is the largest application of reverse osmosis. The major related areas are

a) Production of boiler feed water.

b) Production of pharmaceutical water (The product from this process is free from bacteria and virus[31])

c) Sewage treatment.

d) Purification of industrial effluent such as[32-34] effluent from nuclear power plant etc.

e) Production of quality water for beverage, semi-conductor and other industries.

f) Concentration of fruit juices.

g) Concentration of liquid food products such as beet and sugarcane juice and tomato juice[35-39].

h) Concentration of dairy products[40,41].

i) Concentration of pharmaceutical products.

j) Reclamation of valuable materials from electroplating industries.

k) Water-alcohol separation[42].

As per the recent announcement the Japanese government is planning a ten year $ 45.6 milion development programme for new membrane applications, including water-alcohol separation, uranium recovery and others. A similar national programme in this area has been launched by Italian government also.

Future of Membrane Processes

Currently reverse osmosis, ultrafiltration and other membrane processes have been accepted as a very useful tools for the separation of molecular mixtures. The increasing applications of these membrane processes in producing potable water from sea and brackish water sources, to recover valuable products from industrial effluents and for concentration, purification and fractionation problems in chemical, food and drug industries demands the development of new membranes from cellulosic, non-cellulosic, combined cellulosic and non-cellulosic materials possessing excellent performance.

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PART II

MODIFICATION OF CELLULOSE ACETATE BY AROMATIC AND ALIPHATIC ISOCYANATES

INTRODUCTION

Polymer modification is a broad and rapidly expanding area of polymer science. The modification of existing synthetic and naturally occuring polymer is intended to improve some of their properties such as enhanced thermal stability, biological resistance, flexibility, rigidity, solubility etc. At the present time polymer modification can be approximately grouped in two ways :

a) Physical modification including entanglement, entrapment and radiation induced changes and,

b) Chemical modification where chemical reactions on the polymer are expected.

Numerous papers have appeared in the literature describing the reactions of various compounds with polymers in order to change the properties of the polymers[1,2].

Chemical Modification of Cellulose Acetate

Cellulose acetate is prepared from cellulose obtained from wood pulp or cotton linters by acetylation with acetic anhydride, acetic acid and a catalyst such as sulphuric acid. The partially hydrolyzed products of cellulose triacetate are known as secondary cellulose acetate. The degree of polymerization of commercially available products falls in the range of 100-300 and the molecular weight ranges from 25,000 to 80,000.

In the case of secondary cellulose acetate the ratio of free primary to free secondary hydroxyl groups depends upon the amount of water used during hydrolysis. The increase in the ratio of free primary to free secondary hydroxyl group has profound effect on the processing (solubility) of the polymer, and the end use characteristics of the membrane. The solubility of cellulose acetate is critical for the preparation of asymmetric membranes than for films or fibers, since the membranes are prepared from polymer solutions which must tolerate the incorporation of high concentration of relatively incompatible pore producing constituents.

Cellulose esters contain two functional groups : hydroxyl and ester. Either of these groups are capable of undergoing chemical reactions under proper conditions. An extensive literature is available on the modification of cellulose acetate for different end applications[3-10].

Phenyl isocyanate and α-naphthyl isocyanate react quantitatively with free OH groups of cellulose acetate without disturbing acetyl groups[11]. The phenyl carbamate groups in cellulose acetate has been found to be very stable towards hydrolysis. The reaction of aliphatic and aromatic isocyanates on cellulose acetate (low and high acetyl content) and cotton linters have been reported by Hearon et al[12]. The reaction products of cellulose acetate with phenyl isocyanate are white and fibrous in nature and are soluble in many common solvents normally known for cellulose esters.

Modified cellulose ion-exchange compounds have been prepared by reacting cellulose or its derivatives with excess of polyisocyanate and with aliphatic polyamines under anhydrous conditions[13].

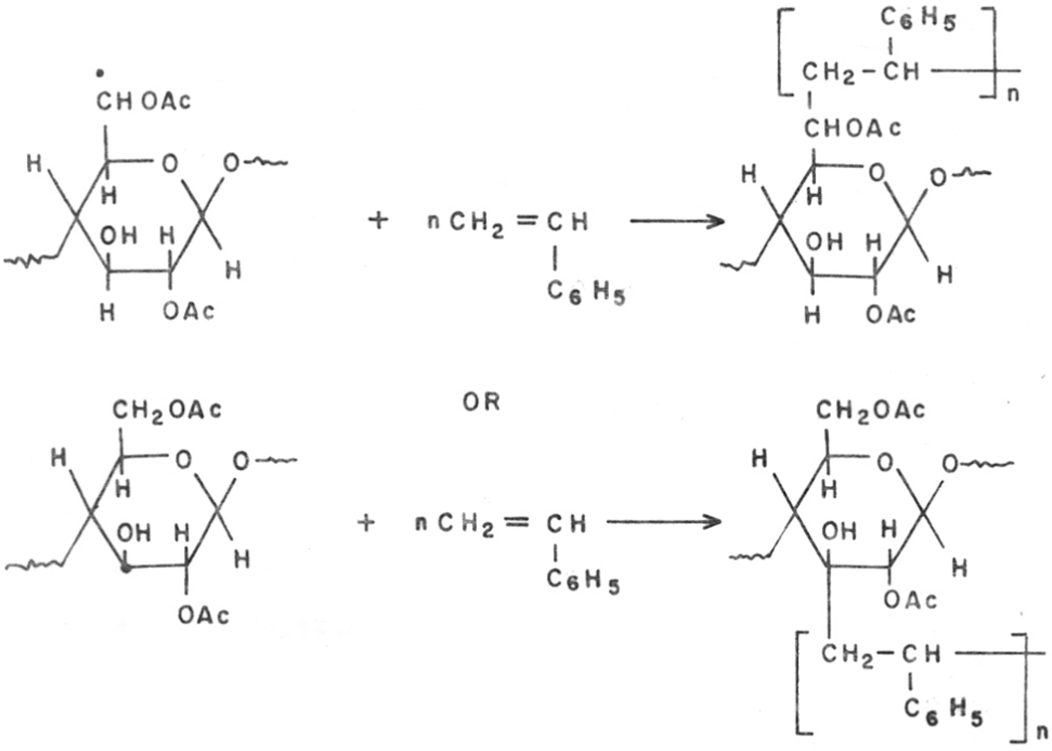
Surface modification of cellophane has been carried out by Matsunaga and Ikada[14] by reacting the hydroxyl groups from cellophane with different isocyanates. The enhanced hydrolytic stability was observed in these isocyanate modified cellophane. Membranes have been prepared from cellulose acetate - methyl carbamate polymer and the reverse osmosis data of these membranes has been compared with cellulose triacetate[15].

Improved composite reverse osmosis membranes have been prepared from crosslinked regenerated cellulose and with an ultrathin film of cellulose triacetate. The crosslinking of regenerated cellulose has been effected by toluenediisocyanate. This composite membrane has been found to exhibit slightly better creep resistance at high applied pressures than the Loeb-type membranes[16].

Dry reverse osmosis membranes have been prepared from cellulose acetate modified by using small amount of blocked isocyanates[17]. Monofunctional isocyanates are not as efficient as diisocyanates for carbamate formation. It has been reported that the cellulose acetate membranes containing neutral carbamate groups decrease the permeability but not the permselectivity.

Modification of Cellulose Acetate by Grafting

Graft copolymerization is an attractive method for modifying the base polymer since grafting results in the superposition of properties of the grafted chains on the backbone polymer. Generally grafting is initiated chemically, photochemically, or with ionizing radiation such as gamma rays from Cobalt-60 source or high electrons. Ionizing radiation is the cleanest method for grafting and has several distinct advantages such as 1) the rate of production of radicals is practically independent of temperature, 2) the rate of production of radicals does not decrease with time, 3) radicals are generated deep into the polymer structure and finally, 4) no catalyst residues are left in the product. Cellulose acetate has been grafted by styrene, by radiation method. The grafting takes place as per the scheme shown below.

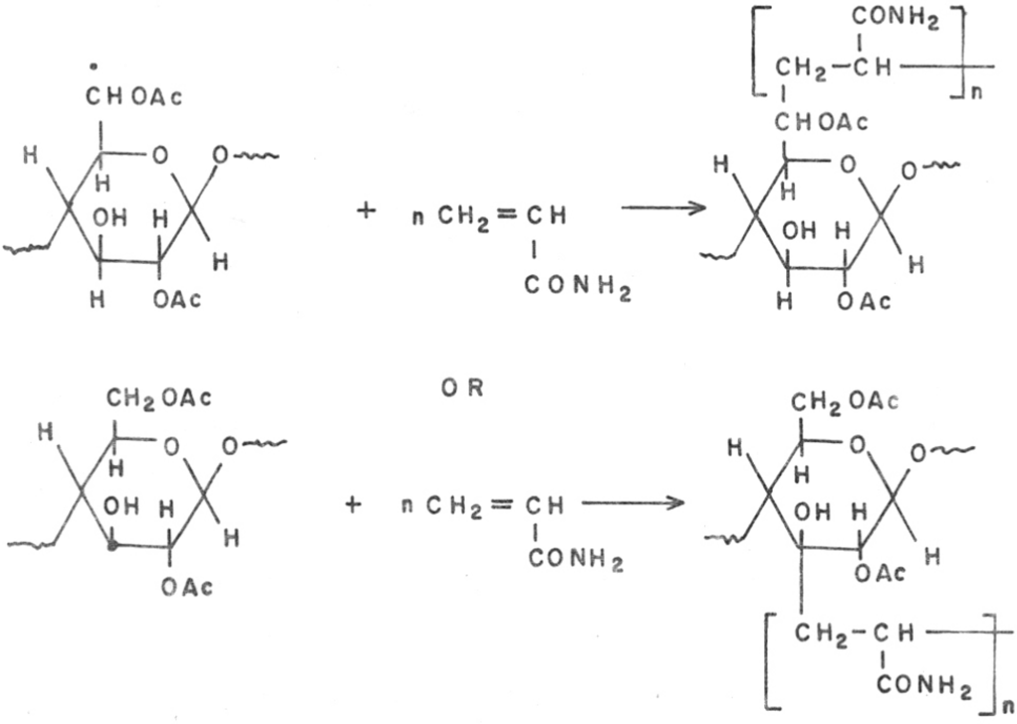


GRAFTING OF STYRENE ONTO CELLULOSE ACETATE

The effect of styrene grafting onto cellulose acetate by radiation has been studied as a possible technique for mechanically stabilizing cellulose acetate membranes[18,19]. This study was subdivided into four areas, 1) direct grafting of styrene to dense symmetrical cellulose acetate films and measurement of water transport and tensile creep behaviour of these modified films, 2) grafting of styrene to Loeb-Sourirajan type asymmetric membranes and measurement of the time-dependance, 3) preparation of purified styrene - cellulose acetate grafts and evaluation of dense membranes prepared from these graft copolymers, 4) preparation of asymmetric membranes by combined irradiation and casting technique. The above study clearly indicates that the graft polymer reduces the wet tensile creep, moreover, short chain grafting is significantly effective than long chain grafting.

In addition to the creep behaviour of styrene or α methyl styrene - cellulose acetate membranes, the water vapour sorption equilibria, sorption kinetics and related reverse osmosis behaviour have been studied[20,21]. The salt rejection for both styrene-cellulose acetate and α-methyl styrene - cellulose acetate system is identical upto a dose of 4 Mrad. At higher dose, the rejection reaches to zero for α-methyl styrene. Increased water flux is observed over a significant range of grafting of styrene or α-methyl styrene on cellulose acetate without altering the creep and salt rejection properties.

Acrylamide - cellulose acetate membranes prepared by radiation grafting have been used for reverse osmosis studies[22]. Radiation grafting of acrylamide on cellulose acetate takes places as shown below.



Extensive efforts are being made in grafting of vinyl and other monomers on cellulose acetate. The copolymer grafts of methyl methacrylate and 2-vinyl pyridine show similar results to that of styrene grafts. The methylmethacrylate series has excellent salt rejection accompanied by high flux as compared with styrene - cellulose acetate[21].

PRESENT INVESTIGATION, RESULTS AND DISCUSSION

The large scale research on reverse osmosis as an effective means of obtaining potable water from brackish and seawaters, controlling municipal and industrial water pollution, recovery of industrial waste and reusing water over again and again has shown that cellulose acetate (CA) membranes are extremely effective in desalting. This success of cellulose acetate membranes indicates that it is the material of choice in future reverse osmosis plants. Inspite of several good features of these membranes, they have some drawbacks such as poor chemical resistance and fast biodegradability, rapid flux decay due to membrane compaction under the high influent pressure, etc. Surely modification of cellulose acetate resulting improved performance such as better chemical, microbial, radiation and mechanical resistance etc. will make it more effective polymer in the preparation of reverse osmosis membranes for sea and brackish water desalination.

In the present work the residual hydroxyl groups of secondary cellulose acetate have been reacted partially with aromatic and aliphatic isocyanates. The modified polymers thus obtained have been characterized for molecular weight, softening point, thermal degradation etc. The work has been further extended to study the potentiality of these modified cellulose acetate polymers possessing urethane linkages as reverse osmosis membranes.

Modification of Cellulose Acetate by Isocyanates

Indigeneously available secondary cellulose acetate has been reacted partially with phenyl, propyl and butyl isocyanates in pyridine. The modified polymers have been isolated by precipitation with the addition of ethyl alcohol. Polymers obtained were in the form of whitish powder and were washed several times with ethyl alcohol. The modification of cellulose acetate has been effected by using different proportions of phenyl, propyl and butyl isocyanates. The modified polymers thus obtained have been designated as (i) CANCO (0.10), CANCO (0.050), CANCO (0.025), and CANCO (0.0125).

ii) CAPRO (0.10), CAPRO (0.075), CAPRO (0.050), CAPRO (0.025), and CAPRO (0.0125).

iii) CABNCO (0.10), CABNCO (0.075), CABNCO (0.050), CABNCO (0.025), and CABNCO (0.0125).

for phenyl, propyl, butyl isocyanate modified cellulose acetate polymers respectively. The numerical numbers stand for the molar quantities of each isocyanate used during the partial modification of cellulose acetate.

Characterization of Modified Cellulose Acetate Polymers

The characteristics of CANCO, CAPRO and CABNCO polymers along with CA characteristics have been shown in Tables 1,2 and 3.

IR Studies

The representative IR spectra of CANCO (0.050), CAPRO (0.050) and CABNCO (0.050) samples have been given in Figs.3,4.

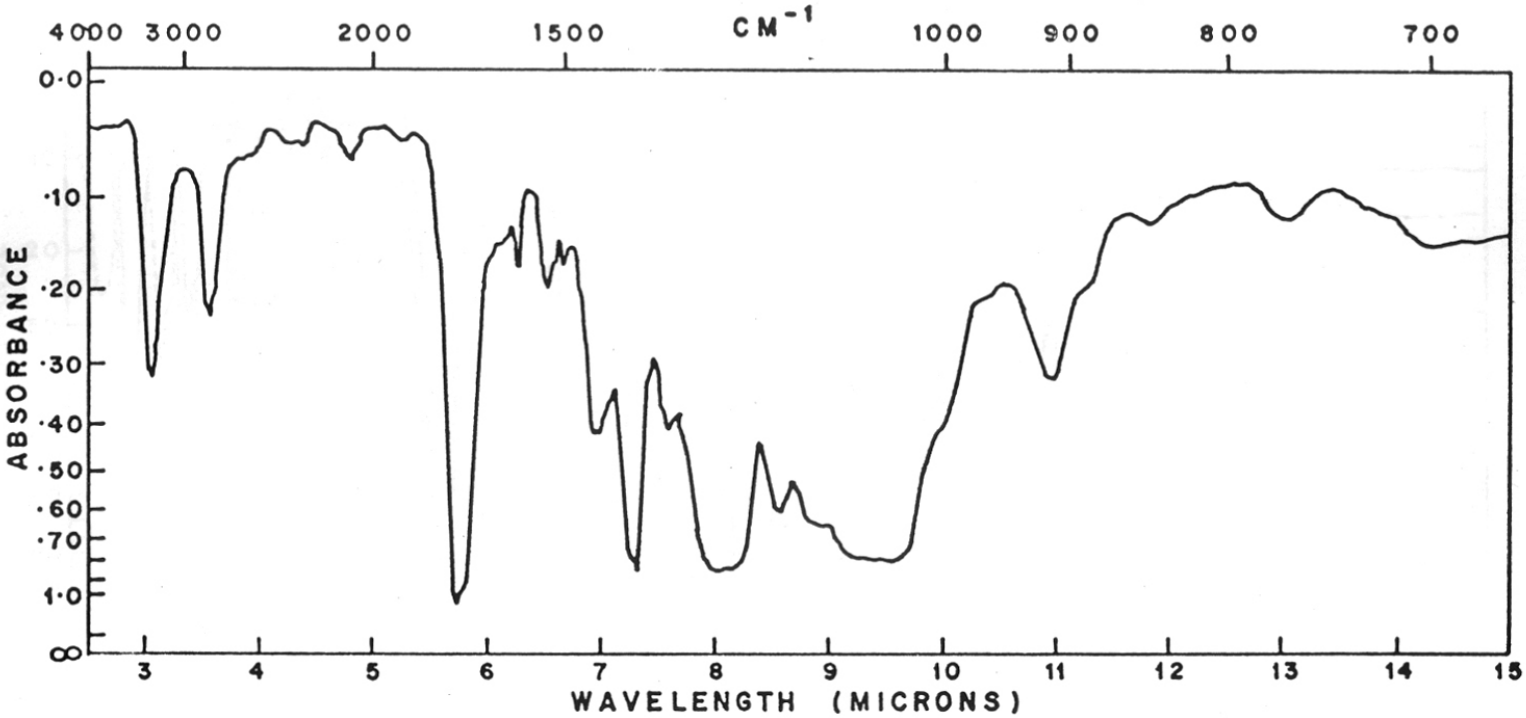


FIG. 3 IR SPECTRUM OF CANCO (0·050) SAMPLE

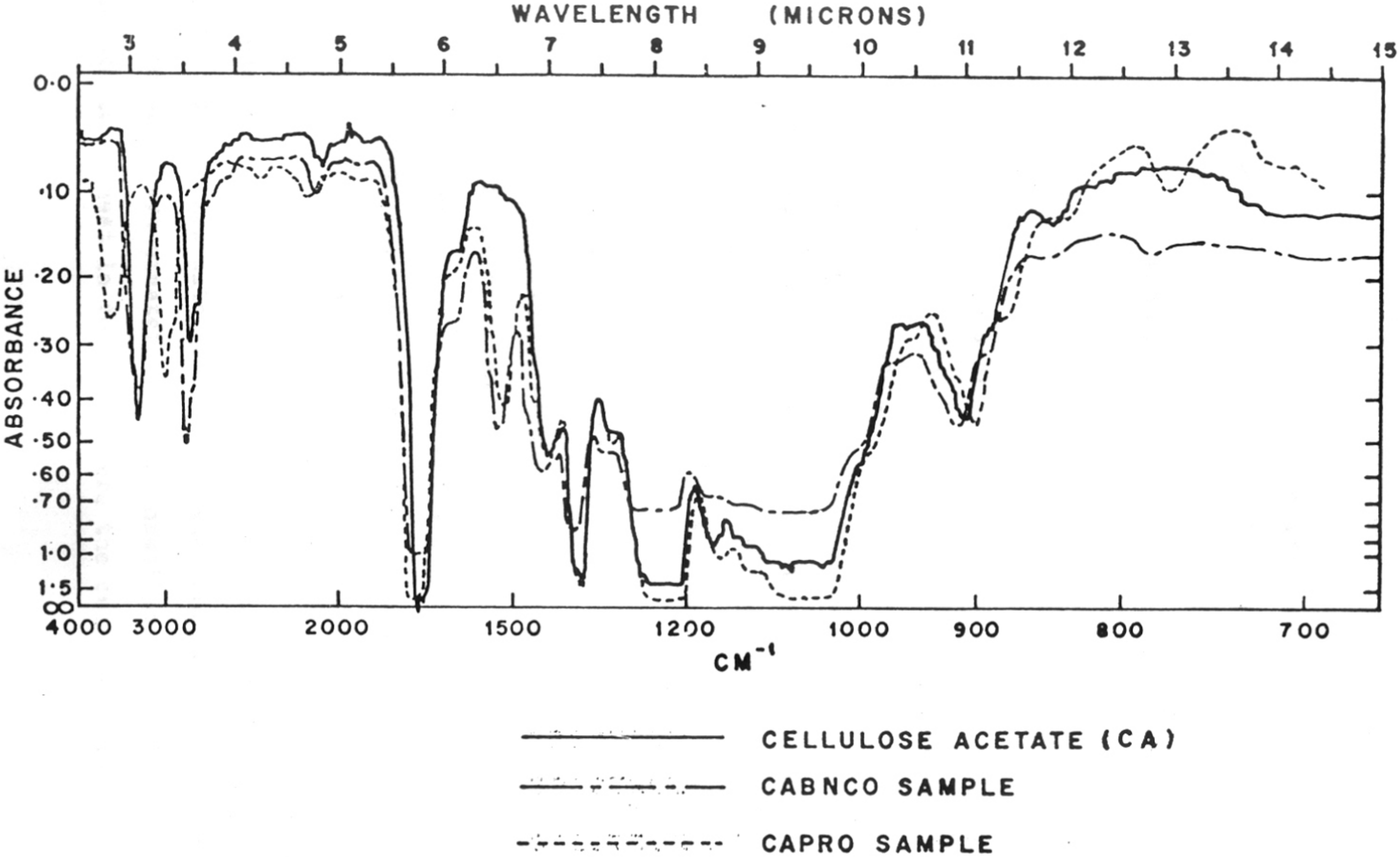


FIG. 4 IR SPECTRA OF CA, CABNCO AND CAPRO SAMPLES

The spectra are generally found to be identical with each other having characteristic bands at 3500 cm^{-1} (O-H group), 2940 and 2880 cm^{-1} (C-H group), 1750-1700 cm^{-1} (C=O group) and a broad band at 1400-1000 cm^{-1} (C-O group), 1650-1550 cm^{-1} for transamide group.

Softening point

The softening points of the polymers have been determined on Campbell Electronics (Bombay) melting point apparatus. The softening points of cellulose acetate polymers modified with propyl isocyanate ranges between 243-252°C whereas in the case of cellulose acetate modified with butyl isocyanate, the softening point range lies between 237-245°C. When cellulose acetate has been modified with phenyl isocyanate the softening point ranges from 232-242°C.

Molecular Weight and Tensile Strength

The molecular weights[23] have been determined at 30±1°C in acetone by viscosity method using intrinsic viscosity dL/g $[\eta] = KM^{\alpha}$ where $K = 1.56 \times 10^{-4}$ and $\alpha = 0.83$. The tensile strength measurements of the cast films have been determined on Scott Testing Machine. Molecular weights and tensile strength values have been given in Tables 1,2 and 3. From the tensile strength values it is observed that when cellulose acetate is modified with isocyanates the tensile strength is found to be always greater than the parent polymer. Tensile strength is highest in the case where the cellulose acetate has been modified with phenyl isocyanate. The tensile strength is found to increase with increasing amount of isocyanate in all the modified polymers. The higher tensile strength values in the case of cellulose acetate modified with phenyl isocyanate will surely improve its compaction resistance under high influent pressure. Percent nitrogen in the polymers has been determined from Dumas method and the values have been given in Tables 1,2 and 3. From % nitrogen the degree of substitution and apparent total % acetyl of the modified polymers were calculated. These values are reported in Tables 1,2 and 3 along with the values obtained from standard ASTM method[24].

Transport Properties

The transport properties of the membranes were tested for water flux and % salt rejection using reverse osmosis unit fabricated in our laboratory (photograph of the unit has been given in part IV), at operating pressures 600 and 900 psi with 5000 ppm sodium chloride solution as a feed. The % salt rejection by the membranes was evaluated by measuring the conductance of feed and permeate solutions. The transport properties of various membranes from modified cellulose acetate polymers have been given in Tables 4-15. The effect of urethane modification of cellulose acetate by phenyl, propyl and butyl isocyanate on % salt rejection and water flux has been shown in Figs. 5 and 6. It can be observed from these figures that the modification of cellulose acetate

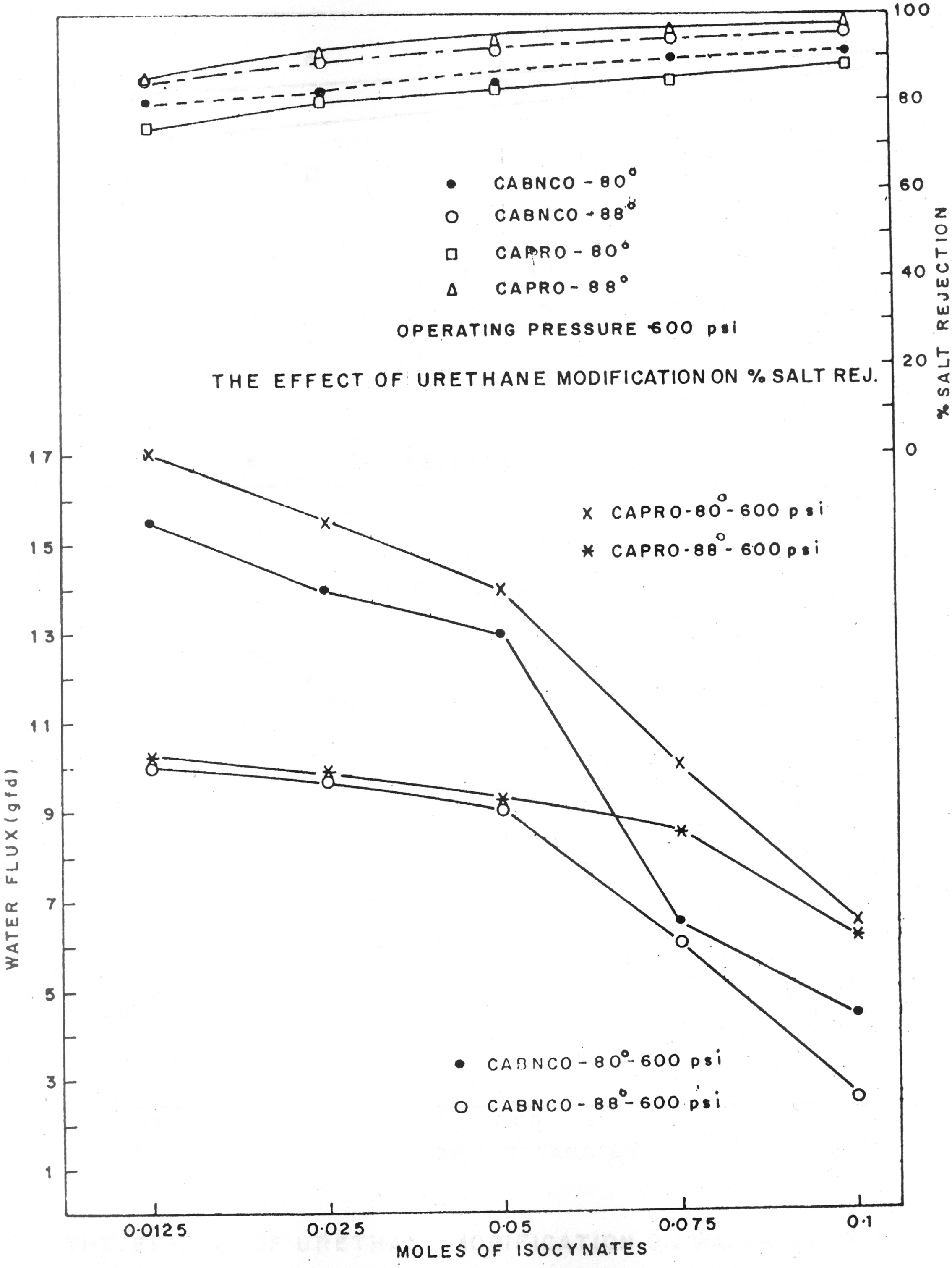
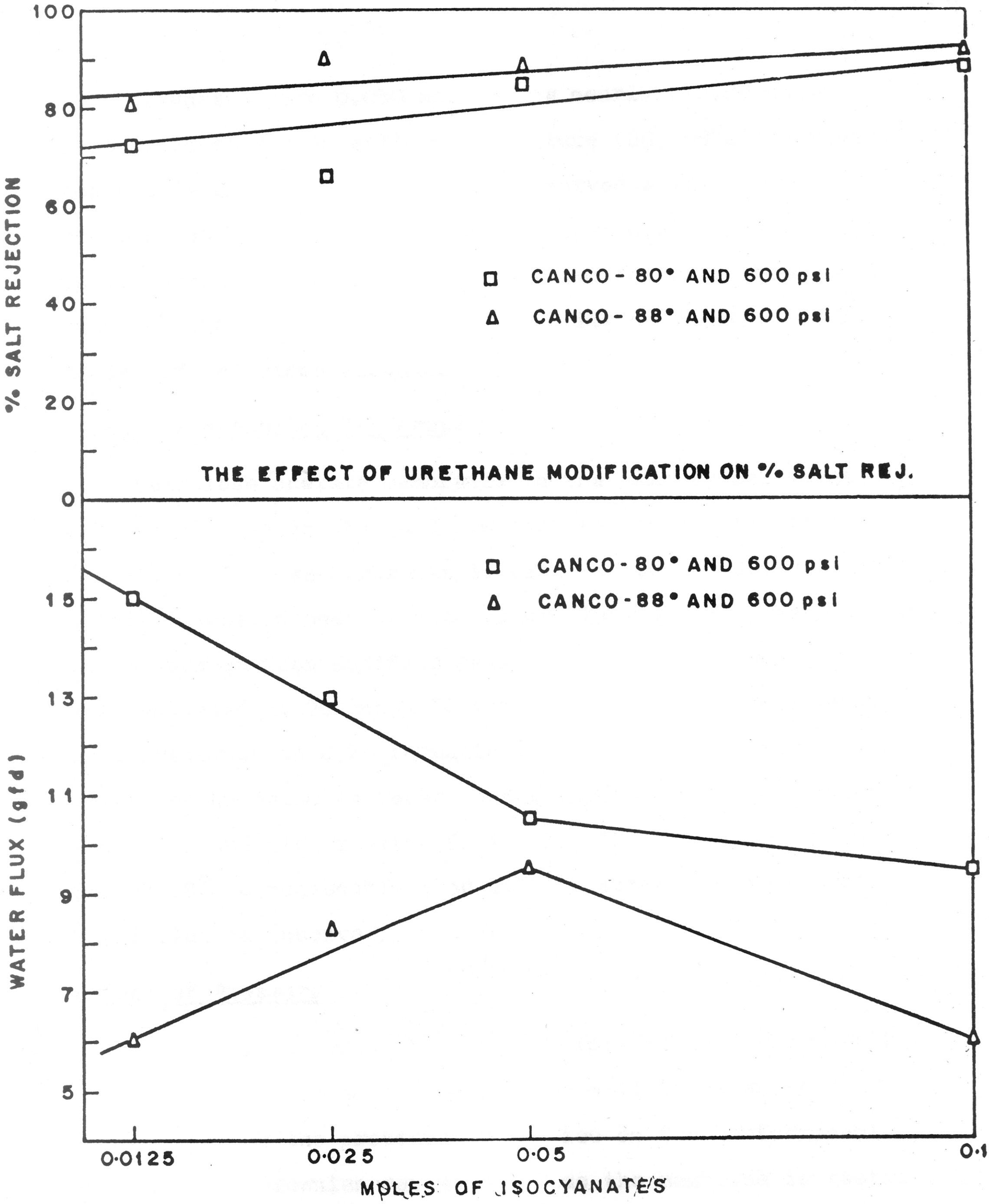


FIG. 5 THE EFFECT OF URETHANE MODIFICATION ON WATER FLUX



THE EFFECT OF URETHANE MODIFICATION ON WATER FLUX

FIG. 6

by isocyanates upto 0.050 moles show nearly steady water flux at different annealing temperature (80, 88°C), however, reasonable drop in water flux is observed where cellulose acetate has been modified with more than 0.050 moles of the isocyanates. A higher % salt rejection has been observed with the increase of isocyanate quantity used during modification of cellulose acetate.

Effect of Annealing Temperature

Cellulose acetate membranes in the primary gel stage exhibit high water flux and low salt rejection. Therefore annealing of these membranes is carried out to achieve higher % salt rejection and adequate water flux. In the present study the membranes from modified cellulose acetate polymers have been annealed at 80 and 88°C for 15 minutes. The membranes were preserved in 0.2% formalin solution after annealing. Membranes annealed at lower temperature exhibit low % salt rejection and higher water flux. When the annealing is carried out at 88°C a reasonably good salt rejection with reduced water flux is observed.

Effect of Pressure

The applied pressure on the semipermeable membrane has profound effect on salt rejection as well as on water flux[25,26]. As the pressure is applied on the semipermeable membrane the Brownian movement inside the membrane is restricted and the polymer structure is compressed. The water within the amorphous region of the polymer becomes more tightly bound making the membrane as an impermeable barrier to sodium chloride. In the present study two operative pressures (600 and 900 psi) have been used to study the effect of applied pressure on the membranes prepared from modified cellulose acetate polymers. In most of the cases it has been observed that the higher operative pressure (900 psi) improves the water flux of the membranes with marginal increase in salt rejection.

The membrane characteristics such as specific water content, membrane constant, average pore diameter are given in Tables 16-21. The specific water content of the membrane and the rate of water transport across the semipermeable membrane has been explained on the basis of solution transport mechanism[27,28]. The water flux through the membrane increases with increase in water content of the membrane. Membrane constant and average pore diameter of all the membranes studied are lower as compared to membrane constant and average pore diameter for cellulose acetate membranes. The decrease in specific water content, membrane constant, average pore diameter has been observed with the increase of amount of isocyanate used during the modification of cellulose acetate. The specific water content values of the membranes prepared from modified cellulose acetate polymers are lower than the specific water content in CA membranes indicating that these membranes will have lower water flux. This observation is confirmed from the experimental data obtained for water flux.

Thermal Stability

Thermal stability of cellulose esters have been studied in the past[29-31] and the data is available in the literature. In the absence of such data for partially modified cellulose acetate with phenyl, propyl and butyl isocyanates, the present work was extended to study the thermal stability of these modified CA polymers in dry state by thermogravimetric analysis (TGA) method. The thermogravimetric analysis experiments were made in air at a heating rate of 10°C/min with MOM-BUDAPEST DERIVETOGRAPH. The thermogravimetric curves have shown in Figs. 7-9. Loss of weight of polymers at different temperatures was determined from TGA curves and has been presented in Tables 22-24.

The results from Tables 22-24 indicate that the presence of phenyl ring and urethane group on cellulose acetate backbone improves the thermal stability. The modified CA polymers are fairly stable upto 300°C in air, however, a further increase in temperature causes rapid decomposition of the modified CA as has been observed in the case of cellulose acetate.

γ Irradiation Effect

In selecting a particular polymer for the preparation of membrane material for any specific use in radiation environment, a knowledge of its radiation stability is essential. Therefore one of the modified cellulose acetate

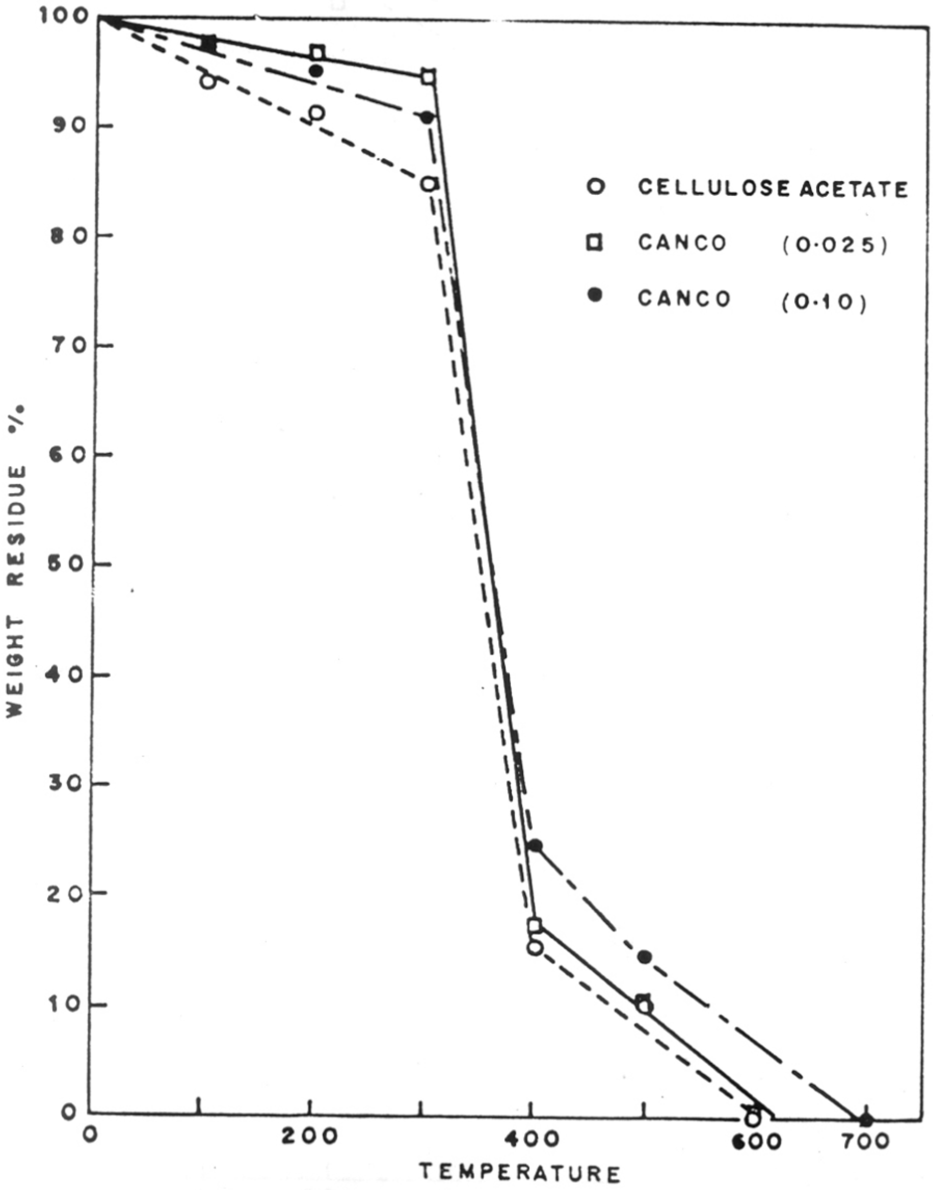


FIG. 7 TG CURVES IN AIR AT 10°C/min. FOR CANCO SAMPLES

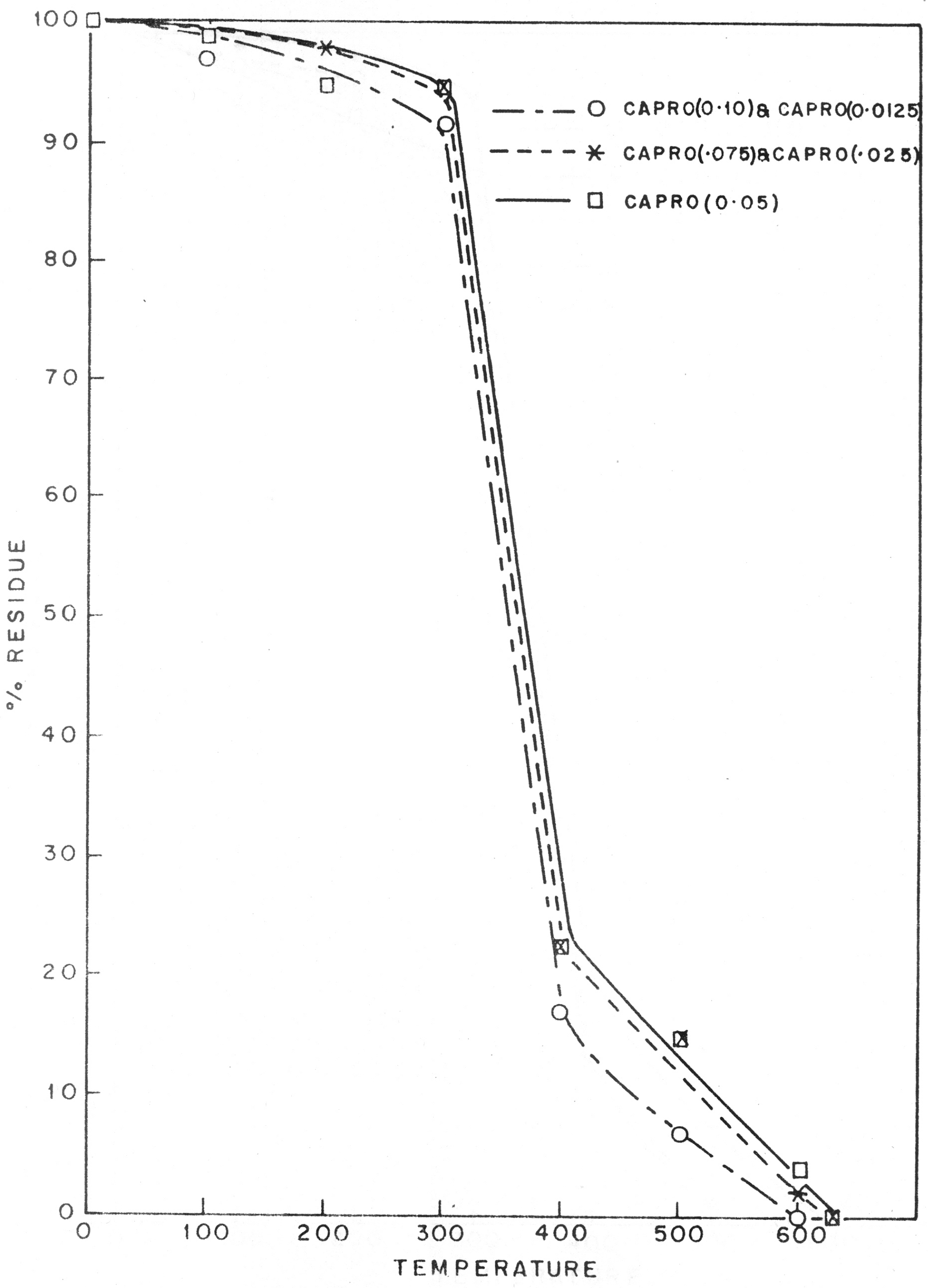


FIG. 8 T G CURVES IN AIR AT 10 °C / MIN FOR CAPRO SAMPLES

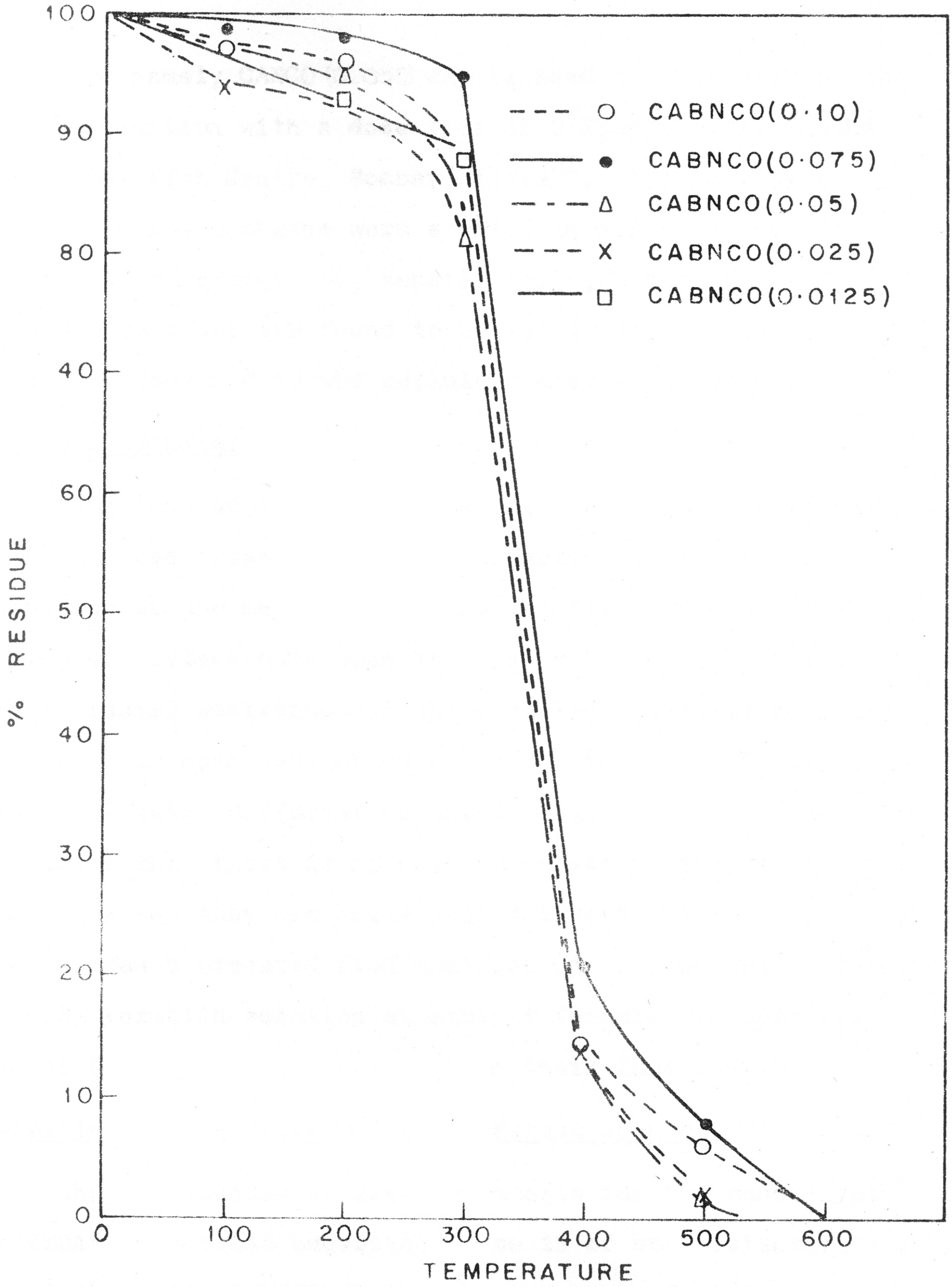


FIG. 9 T.G. CURVES IN AIR AT 10 °C / MIN FOR CABNCO SAMPLES

membranes namely CANCO (0.050) was exposed to Cobalt-60 source in wet condition with a dose rate of 8 Krad/min. at Bhabha Atomic Research Centre, Bombay, India[32]. The radiation effects on the membrane were studied in terms of changes in the transport properties, tensile strength etc. The CANCO (0.050) membranes are found to be relatively stable upto 1 Mrad as compared to the cellulose acetate membrane.

Microbial Studies

Cellulose acetate membranes are prone to biodegradation with many bacterias. The kinds of active bacteria and the stability of the membrane towards conditions favouring biological attack have been studied by Cantor et al[33]. The microbial resistance of the modified cellulose acetate polymers has been determined by ASTM designation D 1924-63 (1964) by using different cultures. The microbial study indicates that there is no adverse effect on any of the membranes and they are quite stable towards microbial attack. The membranes prepared from modified CA polymers were preserved in 0.2% formalin solution at ambient temperature upto six months and no change has been observed in their function.

Selectivity of Modified CA to Different Solutes

The application of reverse osmosis for the concentration of fruit juices and sugarcane juice is of both scientifically and technically important in recent years. In this part of the work few membranes (prepared from modified CA polymers) having optimum salt rejection and water flux were chosen for studying the selectivity of different solutes such as glucose, fructose and sucrose. The selectivity of the membranes have been studied on reverse osmosis unit at operating pressure of 600 psi and various concentration of the solute solutions as a feed. The results are given in Table 25.

In all the cases the % solute rejection and flux rates are at par with cellulose acetate membranes. Hence these modified membranes might be useful for concentration of different juices.

Some attempts have also been made to concentrate sucrose solution (10%) and concentration was found to increase to 16%. The initial and final concentrations were measured by JASCO DIP-181 Digital Polarimeter (Japan). In the case of sugarcane juice concentration, the rate of water flux decreases rapidly because of some deposition of colour and waxy material on the membrane.

Table-1 : Characteristics of CANCO Polymers and Cellulose Acetate

Sample No.	Sample	Softening point °C	[η] Intrinsic viscosity dL/g	Molecular weight	Tensile strength of the membrane Kg/cm^2	% N	Total DS	Apparent total % Acetyl **	% Acetyl*
1	CANCO (0.0125)	232-235	1.45	60,300	156	0.34	2.53	39.87	41.0
2	CANCO (0.025)	238-240	1.47	61,000	175	0.52	2.569	39.8	41.9
3	CANCO (0.050)	238-240	1.55	64,860	187	0.99	2.67	39.68	41.8
4	CANCO (0.10)	242-244	1.50	62,800	190	1.85	2.88	39.4	40.3
5	Cellulose Acetate	242-243	1.40	57,800	105	-	2.466	-	39.9

* As per ASTM method

** Calculated from total DS

Table-2 : Characteristics of CAPRO Polymers and Cellulose Acetate

Sample No.	Sample	Softening point °C	[η] Intrinsic viscosity dL/g	Molecular weight	Tensile strength of the membrane Kg/cm^2	% N	Total DS	Apparent total % Acetyl**	% Acetyl*
1	CAPRO (0.0125)	243-245	1.425	59,000	122	0.30	2.51	40.1	40.0
2	CAPRO (0.025)	248-250	1.45	60,200	150	0.50	2.56	40.2	39.8
3	CAPRO (0.050)	247-250	1.46	61,000	145	1.08	2.68	40.8	39.0
4	CAPRO (0.075)	248-250	1.475	61,400	162	1.43	2.77	40.9	38.7
5	CAPRO (0.10)	250-252	1.50	62,800	168	1.95	2.87	41.0	38.4
6	Cellulose Acetate	242-243	1.40	57,800	105	-	2.466	-	39.9

* As per ASTM method

** Calculated from total DS

Table-3 : Characteristics of CABNCO Polymers and Cellulose Acetate

Sample No.	Sample	Softening point °C	[η] Intrinsic viscosity dL/g	Molecular weight	Tensile strength of the membrane Kg/cm^2	% N	Total DS	Apparent total % Acetyl**	% Acetyl*
1	CABNCO (0.0125)	237–240	1.425	59,000	138	0.30	2.52	40.0	40.7
2	CABNCO (0.025)	245–247	1.55	64,800	134	0.38	2.54	39.9	41.0
3	CABNCO (0.050)	243–245	1.55	64,800	140	0.91	2.65	40.1	41.2
4	CABNCO (0.075)	240–242	1.6	65,920	134	0.99	2.67	40.2	41.0
5	CABNCO (0.10)	237–240	1.50	62,800	137	1.56	2.79	40.3	41.3
6	Cellulose Acetate	242–243	1.40	57,800	105	–	2.466	–	39.9

* As per ASTM method

** Calculated from total DS

Table-4 : Transport Properties of CANCO Membranes

Operating Conditions

1) Applied pressure ... 600 psi
2) Feed concentration ... 5000 ppm NaCl
3) Feed temperature ... 23-25°C
4) Operating period ... 6 hrs.
5) Membrane area ... 18.6 cm^2

Sample No.	Sample	Annealing temperature °C	Pure water permeability gfd	Water flux gfd	% Salt rejection
1	CANCO (0.0125)	80	20	15	72.5
2	CANCO (0.025)	80	21	13	66.0
3	CANCO (0.050)	80	13	10.5	85.0
4	CANCO (0.10)	80	11	9.0	89.0
5	Cellulose Acetate	80	24	20	70

Table-5 : Transport Properties of CANCO Membranes

Operating Conditions

1) Applied pressure ... 600 psi
2) Feed concentration ... 5000 ppm NaCl
3) Feed temperature ... 23-25°C
4) Operating period ... 6 hrs.
5) Membrane area ... 18.6 cm^2

Sample No.	Sample	Annealing temperature °C	Pure water permeability gfd	Water flux gfd	% Salt rejection
1	CANCO (0.0125)	88	7.5	6	81
2	CANCO (0.025)	88	12	8.30	90
3	CANCO (0.050)	88	11	9.5	88.2
4	CANCO (0.10)	88	7.5	6.0	92
5	Cellulose Acetate	88	14	10.5	83

Table-6 : Transport Properties of CANCO Membranes

Operating Conditions

1) Applied pressure ... 900 psi
2) Feed concentration ... 5000 ppm NaCl
3) Feed temperature ... 23-25^{o}C
4) Operating period ... 6 hrs.
5) Membrane area ... 18.6 cm^2

Sample No.	Sample	Annealing temperature ^{o}C	Pure water permeability gfd	Water flux gfd	% Salt rejection
1	CANCO (0.0125)	80	20	17	73
2	CANCO (0.025)	80	22.5	14.5	63
3	CANCO (0.050)	80	15	13	87
4	CANCO (0.10)	80	12	8.2	90
5	Cellulose Acetate	80	41	38	63

Table-7 : Transport Properties of CANCO Membranes

Operating Conditions

1) Applire pressure ... 900 psi
2) Feed concentration ... 5000 ppm NaCl
3) Feed temperature ... 23–25^{0}C
4) Operating period ... 6 hrs.
5) Membrane area ... 18.6 cm^{2}

Sample No.	Sample	Annealing temperature ^{o}C	Pure water permeability gfd	Water flux gfd	% Salt rejection
1	CANCO (0.0125)	88	9.5	8	84
2	CANCO (0.025)	88	12.5	9.60	94
3	CANCO (0.050)	88	13	11.50	91.5
4	CANCO (0.10)	88	9	7.60	94
5	Cellulose Acetate	88	15	13	84

Table-8 : Transport Properties of CAPRO Membranes

Operating Conditions

1) Applied pressure ... 600 psi
2) Feed concentration ... 5000 ppm NaCl
3) Feed temperature ... 23–25°C
4) Operating period ... 6 hrs.
5) Membrane area ... 18.6 cm^2

Sample No.	Sample	Annealing temperature °C	Pure water permeability gfd	Water flux gfd	% Salt rejection
1	CAPRO (0.0125)	80	20.5	17	74
2	CAPRO (0.025)	80	18	15.5	80
3	CAPRO (0.050)	80	16	14	82
4	CAPRO (0.075)	80	11.5	10	85
5	CAPRO (0.10)	80	9	7.5	88
6	Cellulose Acetate	80	24	20	70

Table-9 : Transport Properties of CAPRO Membranes

Operating Conditions

1) Applied pressure ... 600 psi
2) Feed concentration ... 5000 ppm NaCl
3) Feed temperature ... 23-25°C
4) Operating period ... 6 hrs.
5) Membrane area ... 18.6 cm^2

Sample No.	Sample	Annealing temperature °C	Pure water permeability gfd	Water flux gfd	% Salt rejection
1	CAPRO (0.0125)	88	13	10.2	85
2	CAPRO (0.025)	88	11.5	9.8	90
3	CAPRO (0.050)	88	11	9.2	93
4	CAPRO (0.075)	88	10.5	8.5	95
5	CAPRO (0.10)	88	8	6.2	96
6	Cellulose Acetate	88	14	10.5	83

Table-10 : Transport Properties of CAPRO Membranes

Operating Conditions

1) Applied pressure ... 900 psi
2) Feed concentration ... 5000 ppm NaCl
3) Feed temperature ... 23-25^{o}C
4) Operating period ... 6 hrs.
5) Membrane area ... 18.6 cm^{2}

Sample No.	Sample	Annealing temperature ^{o}C	Pure water permeability gfd	Water flux gfd	% Salt rejection
1	CAPRO (0.0125)	80	22	18	75
2	CAPRO (0.025)	80	19.5	16	80.3
3	CAPRO (0.050)	80	18	14.8	83
4	CAPRO (0.075)	80	14	12.5	85.5
5	CAPRO (0.10)	80	11	8.7	88.5
6	Cellulose Acetate	80	41	38	63

Table-11 : Transport Properties of CAPRO Membranes

Operating Conditions

1) Applied pressure ... 900 psi
2) Feed concentration ... 5000 ppm NaCl
3) Feed temperature ... 23-25^{o}C
4) Operating period ... 6 hrs.
5) Membrane area ... 18.6 cm^2

Sample No.	Sample	Annealing temperature ^{o}C	Pure water permeability gfd	Water flux gfd	% Salt rejection
1	CAPRO (0.0125)	88	14	11.5	85.5
2	CAPRO (0.025)	88	12.5	10.3	92
3	CAPRO (0.050)	88	11.5	9.8	94
4	CAPRO (0.075)	88	11	9.2	95.5
5	CAPRO (0.10)	88	9	7	96.0
6	Cellulose Acetate	88	15	13	84

Table-12 : Transport Properties of CABNCO Membranes

Operating Conditions

1) Applied pressure ... 600 psi
2) Feed concentration ... 5000 ppm NaCl
3) Feed temperature ... 23-25°C
4) Operating period ... 6 hrs.
5) Membrane area ... 18.6 cm^2

Sample No.	Sample	Annealing temperature °C	Pure water permeability gfd	Water flux gfd	% salt rejection
1	CABNCO (0.0125)	80	18.5	15.5	80
2	CABNCO (0.025)	80	16	14.0	82
3	CABNCO (0.050)	80	15.5	13.0	83
4	CABNCO (0.075)	80	9	6.5	90
5	CABNCO (0.10)	80	7	4.5	91
6	Cellulose Acetate	80	24	20	70

Table-13 : Transport Properties of CABNCO Membranes

Operating Conditions

1) Applied pressure ... 600 psi
2) Feed concentration ... 5000 ppm NaCl
3) Feed temperature ... 23–25^{o}C
4) Operating period ... 6 hrs.
5) Membrane area ... 18.6 cm^2

Sample No.	Sample	Annealing temperature ^{o}C	Pure water permeability gfd	Water flux gfd	% Salt rejection
1	CABNCO (0.0125)	88	13	10.0	85
2	CABNCO (0.025)	88	11.5	9.6	89
3	CABNCO (0.050)	88	11	9.0	93
4	CABNCO (0.075)	88	8.5	6.0	95
5	CABNCO (0.10)	88	6.7	3.5	96
6	Cellulose Acetate	88	14	10.5	83

Table-14 : Transport Properties of CABNCO Membranes

Operating Conditions

1) Applied pressure ... 900 psi
2) Feed concentration ... 5000 ppm NaCl
3) Feed temperature ... 23-25°C
4) Operating period ... 6 hrs.
5) Membrane area ... 18.6 cm^2

Sample No.	Sample	Annealing temperature °C	Pure water permeability gfd	Water flux gfd	% Salt rejection
1	CABNCO (0.0125)	80	20	17	81
2	CABNCO (0.025)	80	17.5	15	82.5
3	CABNCO (0.050)	80	16	14	84
4	CABNCO (0.075)	80	10	8	90.3
5	CABNCO (0.10)	80	8.5	6.3	91.5
6	Cellulose Acetate	80	41	38	63

Table-15 : Transport Properties of CABNCO Membranes

Operating Conditions

1) Applied pressure ... 900 psi
2) Feed concentration ... 5000 ppm NaCl
3) Feed temperature ... 23-25^{o}C
4) Operating period ... 6 hrs.
5) Membrane area ... 18.6 cm^{2}

Sample No.	Sample	Annealing temperature ^{o}C	Pure water permeability gfd	Water flux gfd	% Salt rejection
1	CABNCO (0.0125)	88	14.5	11.0	87
2	CABNCO (0.025)	88	13	10	90.5
3	CABNCO (0.050)	88	10.5	9.6	93
4	CABNCO (0.075)	88	9	7	94
5	CABNCO (0.10)	88	6.5	4.7	94
6	Cellulose Acetate	88	15	13	84

Table-16 : Characteristics of CANCO Membranes

Operating Conditions

1) Operating pressure ... 600 psi
2) Membrane area ... 18.6 cm^{-2}
3) Feed temperature ... 23–25^{o}C

Sample No.	Sample	Annealing temperature ^{o}C	Specific water content g/cm^3	Membrane constant x 10^5 g/cm^2-sec-atm	Av.pore diameter A^{o}
1	CANCO (0.0125)	80	0.68	2.10	31.50
2	CANCO (0.025)	80	0.66	2.30	32.00
3	CANCO (0.050)	80	0.65	1.40	26.80
4	CANCO (0.10)	80	0.495	1.2	26.00
5	Cellulose Acetate	80	0.72	2.60	32.20

Table-17 : Characteristics of CANCO Membranes

Operating Conditions

1) Operating pressure ... 600 psi
2) Membrane area ... 18.6 cm^2
3) Feed temperature ... 23–25°C

Sample No.	Sample	Annealing temperature °C	Specific water content g/cm^3	Membrane constant x 10^5 g/cm^2-sec-atm	Av.pore diameter A°
1	CANCO (0.0125)	88	0.59	0.82	21.20
2	CANCO (0.025)	88	0.64	1.30	24.00
3	CANCO (0.050)	88	0.63	1.20	22.80
4	CANCO (0.010)	88	0.490	0.80	20.20
5	Cellulose Acetate	88	0.7	1.50	23.80

Table-18 : Characteristics of CAPRO Membranes

<u>Operating Conditions</u>

1) Operating pressure ... 600 psi
2) Membrane area ... 18.6 cm^2
3) Feed temperature ... 23-25^oC

Sample No.	Sample	Annealing temperature ^oC	Specific water content g/cm^3	Membrane constant x 10^5 g/cm^2-sec-atm	Av. pore diameter A°
1	CAPRO (0.0125)	80	0.66	2.20	30.5
2	CAPRO (0.025)	80	0.64	1.97	28.9
3	CAPRO (0.050)	80	0.61	1.75	29.0
4	CAPRO (0.075)	80	0.54	1.26	26.6
5	CAPRO (0.10)	80	0.53	0.98	21.10
6	Cellulose Acetate	80	0.72	2.60	32.20

Table-19 : Characteristics of CAPRO Membranes

Operating Conditions

1) Operating pressure ... 600 psi
2) Membrane area ... 18.6 cm^2
3) Feed temperature ... 23-25°C

Sample No.	Sample	Annealing temperature °C	Specific water content g/cm^3	Membrane constant x 10^5 g/cm^2-sec-atm	Av.pore diameter A°
1	CAPRO (0.0125)	88	0.65	1.42	23.50
2	CAPRO (0.025)	88	0.63	1.26	23.00
3	CAPRO (0.050)	88	0.60	1.20	22.80
4	CAPRO (0.075)	88	0.58	1.13	20.20
5	CAPRO (0.10)	88	0.52	0.87	18.70
6	Cellulose Acetate	88	0.70	1.50	23.80

Table-20 : Characteristics of CABNCO Membranes

Operating Conditions

1) Operating pressure ... 600 psi
2) Membrane area ... 18.6 cm^2
3) Feed temperature ... 23-25°C

Sample No.	Sample	Annealing temperature °C	Specific water content g/cm^3	Membrane constant x 10^5 g/cm^2-sec-atm	Av.pore diameter A°
1	CABNCO (0.0125)	80	0.67	2.03	30.10
2	CABNCO (0.025)	80	0.64	1.75	28.30
3	CABNCO (0.050)	80	0.62	1.70	27.90
4	CABNCO (0.075)	80	0.56	1.20	23.80
5	CABNCO (0.10)	80	0.54	0.88	20.00
6	Cellulose Acetate	80	0.72	2.60	32.20

Table-21 : Characteristics of CABNCO Membranes

Operating Conditions

1) Operating pressure ... 600 psi
2) Membrane area ... 18.6 cm^2
3) Feed temperature ... 23-25°C

Sample No.	Sample	Annealing temperature °C	Specific water content g/cm^3	Membrane constant x 10^5 g/cm^2-sec-atm	Av.pore diameter A°
1	CABNCO (0.0125)	88	0.65	1.42	23.80
2	CABNCO (0.025)	88	0.60	1.26	23.60
3	CABNCO (0.050)	88	0.58	1.20	23.00
4	CABNCO (0.075)	88	0.52	1.15	22.00
5	CABNCO (0.10)	88	0.51	0.76	19.00
6	Cellulose Acetate	88	0.70	1.50	23.80

Table-22 : Percentage Weight Loss at Different Temperature for CANCO Polymer

Temperature °C	CANCO (0.0125)	CANCO (0.025)	CANCO (0.050)	CANCO (0.10)	Cellulose Acetate
100	3	3	2	2.5	6
200	3	3	3	3.5	7
300	5	5	5	8.5	15
400	85	82	85	75	85
500	90	90	90	85	92
600	100	100	100	88	100
700	-	-	-	100	-

Table-23 : Percentage Weight Loss at Different Temperature for CAPRO Polymer

Temperature °C	CAPRO (0.0125)	CAPRO (0.025)	CAPRO (0.050)	CAPRO (0.075)	CAPRO (0.10)	Cellulose Acetate
100	4	0	0	1.5	3	6
200	4	1	1	2	4.5	7
300	8	5	5	5	8	15
400	84	77	85	78	83	84
500	94	91	87	85	93	91
600	100	95	96	98	100	100
620	-	100	100	100	-	-

Table-24 : Percentage Weight Loss at Different Temperature for CABNCO Polymer

Temperature °C	CABNCO (0.0125)	CABNCO (0.025)	CABNCO (0.050)	CABNCO (0.075)	CABNCO (0.10)	Cellulose Acetate
100	6	2	4	1.5	3	6
200	7	2.5	5	1.8	4	7
300	12	7	9	5	12	15
400	86	80	85	79	84.5	84
500	98	90.5	96	92	94	91
600	100	100	100	99	100	100

Table-25 : Selectivity of Modified C.A. membranes to different solutes

Solute	CANCO (0.050)			CAPRO (0.050)			CABNCO (0.050)			Cellulose Acetate		
	Feed % Conc.	Flux gfd	% Rej.	Feed % Conc.	Flux gfd	% Rej.	Feed % Conc.	Flux gfd	% Rej.	Feed % Conc.	Flux gfd	% Rej.
Glucose	0.5	6.4	97.5	0.5	6.7	96.1	0.5	6.7	96.5	0.5	6.5	94.5
	1.5	5.6	97.5	1.5	5.6	96	1.5	5.5	96	1.5	6	95
	3	4	97.2	3	4.5	96.5	3	4.5	95	3	5	94.0
	5	3.4	97	5	3.5–4	95.2	5	3.5–4	95.8	5	4	92.5
Sucrose	5	3.6	97	5	4	95	5	3.8	95.5	5	4	95.0
Fructose	0.5	5	98	0.5	5.8	97.2	0.5	6	96.5	0.5	6	94.5

Operating pressure ... 600 psi
Operating temperature ... 23–25°C

EXPERIMENTAL

Materials

Secondary cellulose acetate (CA) (39.9% acetyl) was procured from M/s. Mysore Acetate, India.

Phenyl isocyanate (98% pure) was obtained from M/s. Fluka, West Germany.

Butyl and propyl isocyanates (98%) were obtained from M/s. Aldrich Chemical Co., USA.

Solvents such as benzene, pyridine, acetone, ethyl alcohol, and formamide were distilled prior to use.

Sodium hydroxide, hydrochloric acid, sodium chloride, sucrose, glucose and fructose used were of analytical grades.

Clarified sugarcane juice was procured from M/s. Yeshwant Sahakari Sakhar Karkhana, Pune, India.

Modification of Cellulose Acetate by Isocyanates

A mixture of 25 g moisture free cellulose acetate and 300 mL of dry pyridine was placed in a 500 mL round bottom flask fitted with a mechanical stirrer, a thermowell, a reflux condenser and a dropping funnel. The cellulose acetate was dissolved completely and then the required amount of appropriate isocyanate was added dropwise in 15 minutes time at 30-35°C with constant stirring. After the addition of isocyanate the temperature of the reaction mixture was raised to refluxing temperature (110°C) and refluxing was continued further for 4 hours with constant stirring. The reaction mixture was then cooled to ambient temperature and diluted with small amount of acetone. The modified cellulose acetate polymers were isolated by precipitation with the addition of ethyl alcohol. The polymers thus obtained were in whitish powdery form and were washed several times with ethyl alcohol.

The modification of CA has been effected by using different molar proportions of phenyl, propyl and butyl isocyanates. The modified CA polymers have been designated as CANCO (0.10), CANCO (0.050), CANCO (0.025), CANCO (0.0125), (Phenyl isocyanate), CAPRO (0.10), CAPRO (0.075), CAPRO (0.050), CAPRO (0.025), CAPRO (0.0125) (Propyl isocyanate) and CABNCO (0.10), CABNCO (0.075), CABNCO (0.050), CABNCO (0.025), CABNCO (0.0125) (Butyl isocyanate). The figures given in brackets show the molar quantities of each isocyanate used during the partial modification of cellulose acetate. All the modified polymers were dried in an oven at 100±5°C for 6 hours.

Infrared Spectra

Infrared spectra of the modified cellulose acetate films have been taken on Perkin-Elmer spectrophotometer model E 137.

Determination of Intrinsic Viscosity and Molecular Weight

1% solution of the polymer was prepared in acetone and was filtered through sinter funnel. The filtered solution was then transferred to Ubbelohde viscometer and the viscosity measurements were made at 30±1°C. The intrinsic viscosity was determined from the plots of $\eta_{sp/c}$ Vs concentration.

Determination of Acetyl Content (by ASTM Method)

The percent acetyl of the modified cellulose acetate polymers has been determined according to ASTM Designation D871-61T.

One gm of accurately weighed polymer was taken in 250 mL of Erlenmeyer flask with stopper and it was swollen in 40 mL of ethyl alcohol (75%). Then this loosely stoppered flask was warmed at 50-60°C for 30 minutes on a water bath with intermittent stirring. Then 40 mL of 0.5N NaOH solution was added to it and heating was continued further at 50-60°C for 15 minutes. Then the flask was allowed to stand for 72 hours. During this period also the flask was stirred intermittently. At the end of this period the excess of NaOH was back titrated against 0.5N HCl using phenolphthalein as an indicator. Then 1 mL excess of 0.5N HCl was added to the flask and was kept overnight. The disappearance of pink colour indicates the complete neutralization of NaOH.

Excess of HCl was titrated with 0.5N NaOH solution using phenolphthalein as an indicator. % acetyl was calculated as follows,

$$\% \text{ Acetyl content} = [\,(D-C)\,Na + (A-B)\,Nb\,]\,\frac{F}{W}$$

where, A = mL of NaOH required for titration of the sample.

B = mL of NaOH required for titration of the blank.

Nb = Normality of NaOH solution.

C = mL of HCl required for titration of the sample.

D = mL of HCl required for titration of the blank.

Na = Normality of HCl solution.

F = 4.305 for acetyl.

W = Weight of the sample taken.

The % acetyl as well as Degree of Substitution (DS) of the parent cellulose acetate polymer was also determined by the above procedure.

Determination of Urethane DS

The DS of the urethane group was determined from the percent nitrogen of the polymer by using the following formula.

$$\frac{14\,x}{265.4 + xM} = \frac{y}{100}$$

where M = Molecular weight of isocyanate used.

x = DS of urethane.

y = % N determined.

Apparent Total % Acetyl

With regard to the modified cellulose acetate polymers, the ASTM procedure (for determination of acetyl) will lead to the hydrolysis of both the acetyl groups as well as the urethane groups present, leading to an apparent total percentage acetyl value which depends on the values of the Degree of Substitution of both acetyl and urethane groups. The apparent total % acetyl thus determined is compared with the value computed from the known DS of acetyl and urethane of the modified cellulose acetate. This computation is made as given below :

$$\text{Apparent total \% acetyl} = \frac{100}{265.4 + xM} \times [(2.466+x)\ 43]$$

where M = Molecular weight of isocyanate.

x = DS of urethane.

The molecular weights of modified cellulose acetate samples were calculated from the equation[23].

$$[\eta] = KM^{\alpha} \text{ where } K = 1.56 \times 10^{-4} \text{ and } \alpha = 0.83.$$

Thermal Stability

The thermogravimetric experiments have been carried out in air at a heating rate of 10°C/minute with MOM-BUDAPEST DERIVETOGRAPH.

Preparation of Modified Cellulose Acetate Membranes

a) Casting solution : Casting solutions of different modified cellulose acetate polymers have been prepared using the proportion of polymer : formamide : acetone in 20:30:50 (weight ratio) respectively as reported by Rao et al[34]. After initial mixing of these components the entire mass was ball milled for 24 hours.

b) Membrane casting : The membranes were cast in the form of flat sheet as per the method described by Loeb and Sourirajan[35]. Film - 15 cm wide and 30 cm long - was cast on a clean, dry glass plate with multiple electric tapes (15 mm wide, 0.4 mm thick) as guide and a casting knife. After evaporation of solvent for 1 minute the membrane cast plate was immersed in a cold water bath (2-3°C) and after a period of 1 hour, the glass plate was removed and the membrane released from it. The membranes thus prepared were annealed at 80/88°C for 15 minutes and were preserved in 0.2% formalin solution.

Tensile Strength Measurements

The tensile strength measurements of different membranes have been carried out according to ASTM designation D882-52T on a Scott Testing Machine. The test specimens were consisted of strips of uniform width and thickness of at least 5 inch length.

Microbial Test

The microbial resistance of different membranes have been carried out by ASTM Designation D1924-63. The list of organisms used during the testing is given below.

1)	Aspergillus amstelodami	NCIM NO	1026
2)	Aspergillus niger	"	773
3)	Aspergillus niger	"	1074
4)	Aspergillus niger	"	1025
5)	Fusarium moniliforme	"	1103
6)	Penicillium Ochrochloron	"	1044
7)	Tricoderma Viride	"	992
8)	Chaetomium globosum	"	874
9)	Pullularia Pullulans	"	1048

The membrane pieces were placed separately on agar plate and in a conical flask. Afterwards 1 mL of spore suspension was spread on them. Then incubation was carried out at 30°C for 30 days. The microbial study reveals that there is no fungi growth on any of the membranes.

Determination of Transport Properties and Characteristics of the Membranes

The transport properties such as % salt rejection, water flux, pure water permeability etc. have been measured on the reverse osmosis unit fabricated in our laboratory. The details of the unit is given elsewhere.

Measurement of Pure Water Permeability

A circular membrane having area 18.6 cm^2 was cut from the flat membrane and was placed with a circular filter paper and a stainless steel porous plate having similar dimensions as a support in the reverse osmosis cell. The membrane surface which was in contact with air during casting was directed to the high pressure side of the feed solution (Distilled water). The feed water reservoir was filled with distilled water. The reverse osmosis cell was pressurized initially with low pressure to avoid any error in the permeate volume due to imperfection in the membrane. Then the cell was pressurized to a known pressure (600 and 900 psi) and the readings for the product flux were noted at regular interval of time till two cosecutive readings (nearly constant) of the flux were obtained. The final flux readings were converted into gallon ft^2-day (gfd).

Determination of Membrane Constant

The membrane constant 'A' was calculated from the pure water permeability data using the following equation and expressed as g/cm^2-sec-atm.

$$A = \frac{V}{a \times t \times \Delta P}$$

where V = Volume of permeate in time t

a = effective membrane area

t = time taken in collecting V mL of permeate in sec.

ΔP = applied pressure in atm.

Determination of Average Pore Diameter

Average pore diameter of the membrane was calculated by using the following equation[36].

$$\text{Average pore diameter } J = 2r = 4 \left[\frac{2V\eta L}{SAPT} \right]^{1/2}$$

where V = volume of the permeate collected in time t.

η = viscosity of pure water CPS.

L = membrane thickness (cm)

S = specific water content of the membrane

A = effective membrane area (cm^2)

P = applied pressure (atm)

T = time taken in collecting V mL of permeate in Sec.

% Salt Rejection (% SR)

The salt rejection from different membranes has been determined as per the procedure followed for pure water permeability of the membranes. The only difference is that the feed water reservoir was filled with 5000 ppm NaCl solution instead of distilled water.

The % salt rejection by the membrane was evaluated by measuring the conductance of feed and permeate solutions. The conductance of feed and permeate solution has been measured on conductivity meter. The % salt rejection was calculated as follows :

$$\% \text{ SR} = \frac{\text{Conductance of feed} - \text{Conductance of permeate}}{\text{Conductance of feed}} \times 100$$

Determination of Specific Water Content

The specific water content of the membranes was estimated by the method reported by Ferry[36]. A small piece of known area from the membrane was cut. The superfacial water was carefully removed with a pair of blotting paper by pressing. Then it was immediately placed in previously weighed weighing bottle and weighed accurately. Then the sample was dried at 105°C till constant weight. The specific water content was calculated as follows :

$$\text{Specific Water Content} = \frac{\text{Loss in weight of drying}}{\text{Membrane area X thickness of the membrane}}$$

$$= \text{g/cm}^3$$

γ Irradiation Studies

One of the membranes particularly CANCO (0.050) (where optimum water flux and % SR was observed) was exposed to Cobalt - 60 source for studying the effect of irradiation. These studies were conducted at Bhabha Atomic Research Centre, Bombay, India and the results have already been reported[32].

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PART III

MODIFICATION OF CELLULOSE ACETATE BY PROPYLENE OXIDE

PRESENT INVESTIGATION, RESULTS AND DISCUSSION

An extensive research has been carried out for modifying the existing polymers by grafting different monomers on them. Graft copolymers usually consists of a parent polymer to which few side chains are attached, therefore on the molecular scale little changes occur on the substrate polymer. The morphology of the polymer or membrane prepared from it normally does not alter much at low degree of grafting, however, with high degree of grafting the properties change towards those of side chains.

In the earlier work (Part II), the residual hydroxyl groups of cellulose acetate have been reacted partially with isocyanates. Isocyanates are known to be toxic in nature, therefore it was decided to modify cellulose acetate by propylene oxide which has practically no toxic effects.

Cellulose esters of high stability have been prepared by reaction of Cellulose Sulphate with ethylene oxide[1]. Ethylene oxide has also been grafted on CA by anionic graft polymerization[2]. Russian scientists have reported[3] the hydroxyl propylation of cellulose acetate but details regarding the reaction course has not been disclosed. So far, limited literature is available on polyaddition or grafting of ethylene oxide, propylene oxide on cellulose acetate and their use as reverse osmosis membranes.

In the present work dry cellulose acetate has been modified with propylene oxide without using any catalyst. The grafted polymers were isolated and have been characterized for inherent viscosity, thermal stability, softening point, scanning electron microscopy.

Membranes were cast from these polymers and after annealing at proper temperature for a particular period, they have been studied for their transport properties and other characteristics.

Characterization of Modified Cellulose Acetate (CAPO) Polymers

The characteristics of CAPO polymers along with CA characteristics have been given in Table 26.

Softening Point

The softening point of cellulose acetate modified with propylene oxide ranges between 260-270°C.

Inherent Viscosity and Tensile Strength

Inherent viscosity of the modified cellulose acetate polymers has been determined by using Ubbelohde viscometer in DMSO at 30± .1°C.. The tensile strength measurements of the cast films have been determined on Scott Testing Machine. Inherent viscosity and tensile strength have been given in Table 26. From the tensile strength values it is observed that when cellulose acetate is modified with propylene oxide the tensile strength is higher than the parent polymer. The tensile strength is found to increase with increasing amount of propylene oxide in all the modified polymers.

Transport Properties

The transport properties of the membranes were tested for water flux and % salt rejection using the reverse osmosis unit at operating pressure of 600 psi with 5000 ppm sodium chloride solution as a feed. The transport properties of different membranes from modified CA polymers have been given in Table 27. Propylene oxide modified cellulose acetate membranes show reasonably higher salt rejection, however, the water flux is lower as compared with CA membranes.

The membrane characteristics such as specific water content, membrane constant, average pore diameter are given in Table 27. Decrease in specific water content, membrane constant and average pore diameter has been observed with increasing amount of propylene oxide used during the modification.

Thermal Stability

Thermal stability of these modified CA polymers has been studied by TGA method as described in Part II. The TGA curves are shown in Fig.10. Loss in weight of polymers at different temperatures was determined from TGA curves and has been presented in Table 28. The TGA data indicates that the partial modification of cellulose acetate by propylene oxide has no adverse effect on its thermal

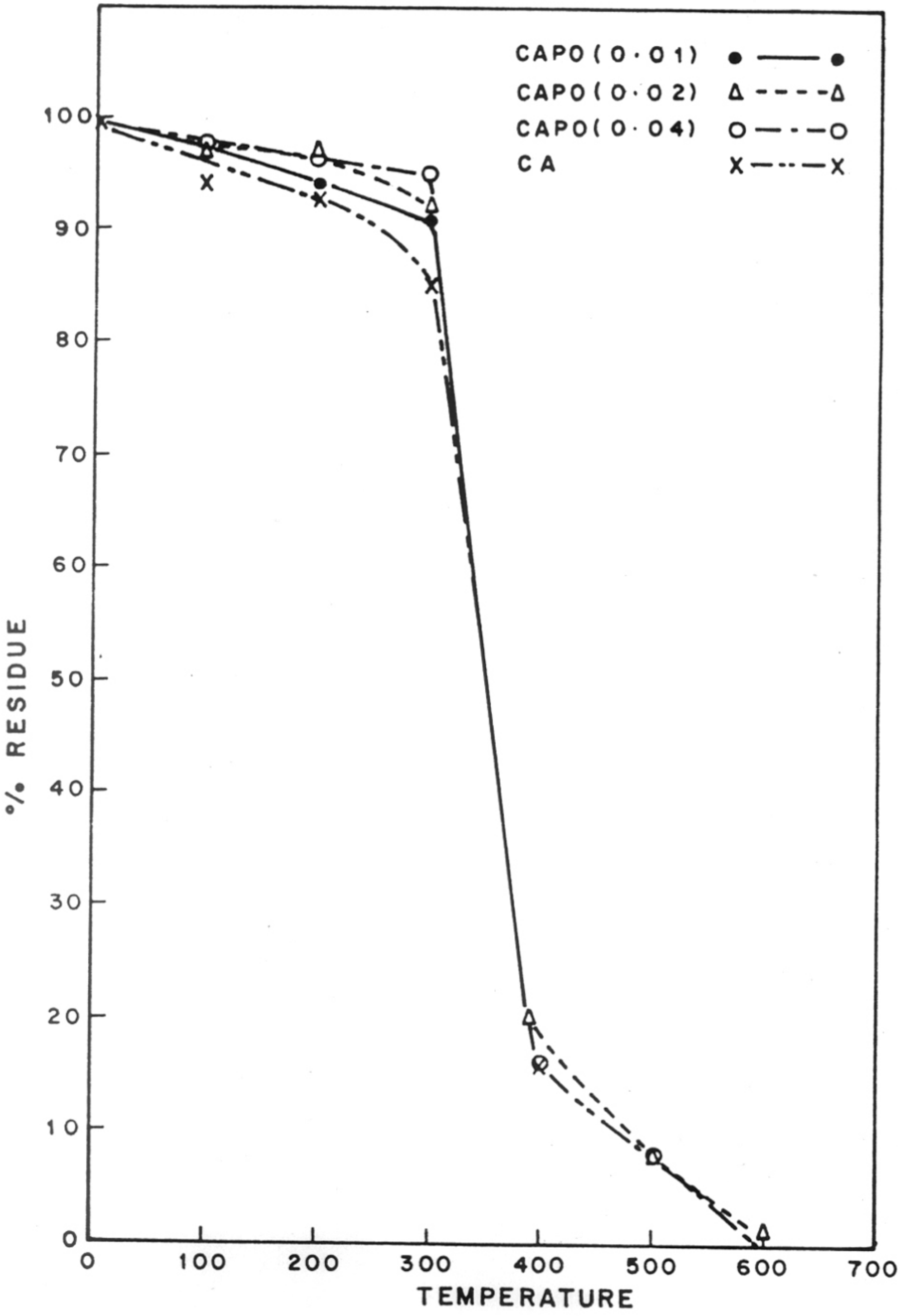

FIG.10 T. G. CURVES IN AIR AT 10°C/MIN FOR CAPO SAMPLES

stability upto 300°C in air, however, further increase in temperature, a rapid decomposition is observed in all the cases.

Scanning Electron Microscopy

The change in surface morphology of cellulose acetate after modification with propylene oxide by using different molar quantities could be seen from scanning electron micrograph, Figs.11, 11A and 12. X-ray diffractograms were also recorded on PW 1730 X-ray generator (PHILIPS) for CA and CAPO from 6^{o}-50^{o}. The X-ray diffractograms show unresolved broad structure resembling nearly amorphous nature of CA, however, it was not possible to draw any conclusions from the broad spectrum.

FIG. 11 SCANNING ELECTRON MICROGRAPH OF CAPO (0·02)

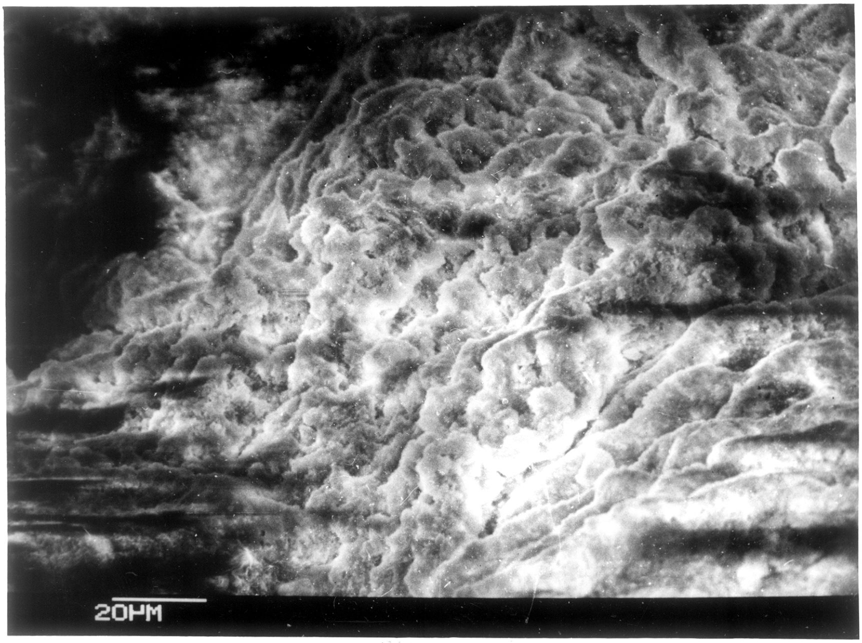

FIG. 11 a SCANNING ELECTRON MICROGRAPH OF CAPO (0·04)

FIG. 12 SCANNING ELECTRON MICROGRAPH OF CELLULOSE ACETATE

Table-26 : Characteristics of Modified Cellulose Acetate and Cellulose Acetate

Sample No.	Sample	Softening point ^{o}C	η_{inh} dL/g	Tensile strength of the membrane Kg/cm^2
1	CAPO (0.01)	260–262	1.41	112
2	CAPO (0.02)	263–264	1.42	120
3	CAPO (0.04)	270	1.49	125
4	Cellulose Acetate	242–243	1.40	105

Table-27 : Transport Properties and Characteristics of CAPO Membranes

Operating Conditions

1) Operating pressure ... 600 psi
2) Operating temperature ... 23-25°C
3) Feed concentration ... 5000 ppm NaCl
4) Operating period ... 6 hours
5) Effective Membrane Area ... 18.6 cm^2

Sample No.	Sample	Pure water permeability gfd	Water flux gfd	% Salt rejection	Membrane constant x 10^5 g/cm^2-sec-atm	Specific water content g/cm^3	Av.pore diameter A°
1	CAPO (0.01)	9.00	7.00	93.00	0.98	0.66	22.60
2	CAPO (0.02)	8.60	6.60	94.50	0.94	0.64	22.78
3	CAPO (0.04)	3.80	3.10	95.60	0.40	0.50	17.78
4	Cellulose Acetate	13.00	10.50	83.00	1.50	0.70	23.80

Table-28 : Percentage Weight Loss at Different Temperature for Modified Cellulose Acetate and Cellulose Acetate

Temperature °C	Modified Cellulose Acetate			Cellulose Acetate
	CAPO (0.01)	CAPO (0.02)	CAPO(0.04)	
100	3.5	3	3	6
200	6	3.5	3.8	7
300	8.5	8	5.0	15
400	80	80	84.0	85
500	92	91.5	92.0	92
600	100	100	100	100

EXPERIMENTAL

Materials

Secondary Cellulose acetate (CA) (39.9% acetyl) was procured from M/s. Mysore Acetate, India.

Propylene oxide was obtained from M/s. SISCO, Bombay, India and was distilled just before use.

Solvents such as cyclohexanone, dimethyl sulfoxide (DMSO), formamide, acetone and methyl alcohol were also distilled prior to use.

Modification of Cellulose Acetate by Propylene Oxide

Dry cellulose acetate 5 g was dissolved in 45 mL of dry and distilled cyclohexanone. The solution was then transferred into a 70 mL capacity stainless steel bomb. The required amount of distilled propylene oxide was added to it and the bomb was closed tightly. It was then kept in an oven at $105 \pm 1^{\circ}C$ for 18 hours with occasional shaking. At the end of the reaction period the bomb was cooled to ambient temperature and solution was transferred into a beaker. The modified polymer was isolated by precipitation with the addition of methyl alcohol. The polymer obtained was in the form of whitish powder and was washed several times with methyl alcohol.

The modification of cellulose acetate has been carried out by using different molar quantities of propylene oxide.

The modified polymers thus obtained have been designated as CAPO (0.01), CAPO (0.02) and CAPO (0.04). The numerical number in brackets is the molar quantity of propylene oxide used during the modification. All the modified cellulose acetate polymers were dried in an oven at $100\pm5^{\circ}C$ for 6 hours.

Determination of Inherent Viscosity

Measurements of inherent viscosity (η_{inh}) of all modified cellulose acetate polymers and CA were carried out in DMSO at $30\pm0.1^{\circ}C$ using Ubbelohde viscometer.

The inherent viscosity value is defined as follows :

$$\eta_{inh} = \frac{2.303 \log {}^{t}/_{t_o}}{C}$$

where t and t_o represents the flow time for polymer solution and solvent respectively. The solution concentration C was 0.5 g/100 mL.

Thermal Stability

The thermogravimetric experiments have been carried out in air at a heating rate of $10^{\circ}C$/minute with MOM BUDAPEST DERIVETOGRAPH.

Scanning Electron Microscopy

Scanning electron micrographs of modified cellulose acetate by propylene oxide and cellulose acetate were taken on Cambridge Stereo Scan 150, Scanning electron microscope.

Preparation of Modified Cellulose Acetate Membranes

a) Casting Solution : Casting solutions of different modified cellulose acetate polymers have been prepared using the proportion of polymer : Formamide : acetone in 20:30:50 (weight ratio) respectively. After initial mixing of these components the entire mass was ball milled for 24 hours.

b) Membrane Casting : Membranes were cast from these modified cellulose acetate polymers on a clean glass plate as per the procedure described in Part II. Membranes thus prepared were milky white and opaque in appearance. These membranes were then annealed for 15 minutes at 88°C and were preserved in 0.2% formalin solution.

Tensile Strength Measurements

The tensile strength measurements of different membranes have been carried out according to ASTM Designation D882-52T on a Scott Testing Machine.

Determination of Transport Properties and Characteristics of the Membrane

The transport properties such as % salt rejection, water flux, pure water permeability etc. have been measured on the reverse osmosis unit fabricated in our laboratory. The details of the unit are given in Part IV.

Measurement of Pure Water Permeability

A circular membrane having area 18.6 cm^2 was cut from the flat membrane and was placed with a circular filter paper and a stainless steel porous plate of similar dimension as a support in the reverse osmosis cell. The pure water permeability was determined as per the procedure described in Part II at 600 psi operating pressure.

Membrane constant and average pore diameter were calculated from pure water permeability as per the procedure described in Part II.

% Salt Rejection (% SR)

The sodium chloride (5000 ppm) was used as a feed for the reverse osmosis unit. The R.O. unit was operated at 600 psi and the product water was collected. Conductivity of feed and product water was measured. The % SR was calculated as per the procedure mentioned in Part II.

Specific Water Content

The specific water content of modified cellulose acetate membranes were determined according to the procedure given in earlier part.

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PART IV

FABRICATION OF REVERSE OSMOSIS LABORATORY TEST UNIT

The work of Breton and Reid in year (1959) at the University of Florida gave encouragement to the basic research on reverse osmosis membranes[1]. The pilot plant activity for making practical reverse osmosis unit began with the discovery of cellulose acetate membrane formulation by Loeb and Sourirajan[2] in 1960. A large amount of engineering is involved in fabricating pilot plant scale reverse osmosis modules. In about two decades, reverse osmosis has already become advanced technology[3], and the early problems of membrane fouling, concentration polarization, pre- and post-treatment procedures have been mostly solved.

Saline-water conversion plants are frequently divided into two classes, namely, for (1) seawater conversion, and (2) brackish water conversion. Brackish waters often require low operating pressure than for seawater conversion. The lower feed water salinities permit the use of higher permeability and less selective membranes than that is used for seawater. The pressure at which brackish water R.O. systems should be operated depend upon the quality of water to be treated as well as on the design of the plant. At present the R.O. plant for conversion of brackish water upto 600 psi and for seawater upto 2000 psi pressure are available.

Design of R.O. plant depends upon the quality of the product water required from the feed water stock, operating pressure and the membrane characteristics. The design of a R.O. unit must be judged on the basis of its effect on total product water cost.

Basic Requirements for R.O. Plant

Materials of Construction

The materials for the construction of reverse osmosis plant depend upon factors such as pressure, corrosion, economic requirements etc. R.O. systems are normally operated at ambient temperatures and at feed water pH range between 3 to 7. Because of relatively noncorrosive nature of brackish water carbon steel pipes and fittings are employed.

For seawater systems the alloys such as Mondel or 316 Stainless Steel are generally used. For systems where operating pressures of 500 psi or below is eployed, tubes of glass reinforced epoxy can be used. The glass fiber reinforced epoxy material has excellent corrosion resistance and considerable strength.

Chemical Pretreatment

Hydrolysis of cellulose acetate has adverse effects on desalination properties. Control of pH is most important in feed pretreatment. It is desirable to keep the pH between 3-7 because of membrane life time considerations[4]. It is also necessary to add acid in water to prevent the precipitation of calcium carbonate or magnesium hydroxide during the concentration of the feed stream within the membrane unit. pH of feed water is maintained between 5 to 6.

Periodic chlorination or other bactericide additions to the feed supply are necessary to reduce the growth of organism within the plant. Chlorine in small doses does not affect the CA membranes. It has been observed that the feeds with 1 to 2 ppm residual chlorine have been used for longer periods without any harm[5].

Clarification of Feed Water

The high clarity feed water circulation within the membrane unit is the first step of the design. The major problem appears to be the mechanical plugging of the brine flow channels. Fine particles, emulsion of greases and waxes, iron oxide ..etc. creates problem in reverse osmosis process. Replaceable catrige fitters are used to remove fine particles.

High Pressure Pump

The pressure pump is the most important part of the R.O. plant. Centrifugal pumps are generally used because of lower maintenance requirements. Piston pumps are used for lower capacity plant and for low pressure (i.e. 400 to 1000 psi) operation.

Reverse Osmosis Systems Configuration[3,5]

In selecting reverse osmosis system, the equipment, cost for replacement of membrane or modules and cost for operation and maintenance is taken into consideration.

Hence the efficient R.O. unit must be judged on the basis of its effect on total product water cost.

Plants are designed on the basis of the following requirements :

1) high membrane area - volume ratio,
2) no leakage with changing operating pressure,
3) low initial cost and minimum maintenance,
4) easy replacement of membranes and clean up,
5) uniform distribution of the processed water over the entire membrane surface.

There are different approaches to the assembly of the membrane units of R.O. system. Each of these differs in the method of assembly and support of the membrane material. The methods of assembly are termed as plate and frame, spiral wound module, tubular module and hollow fiber module.

(1) Plate and Frame Module

Plate and frame design is analogous to the conventional filter press as shown in the Fig.13. Circular sheets of membrane are placed on each side of a porous supporting disc. Many such discs, each with two membranes, are then stacked next to each other with a spacer washer around the periphery between each pair of discs. The whole assembly is held together by external tie bolts between sufficiently thick end plates. The system pressure is carried out by these tie bolts and by the disc rims and spacer rings. The brine flow takes place in the space between the discs, and the product-water flows,

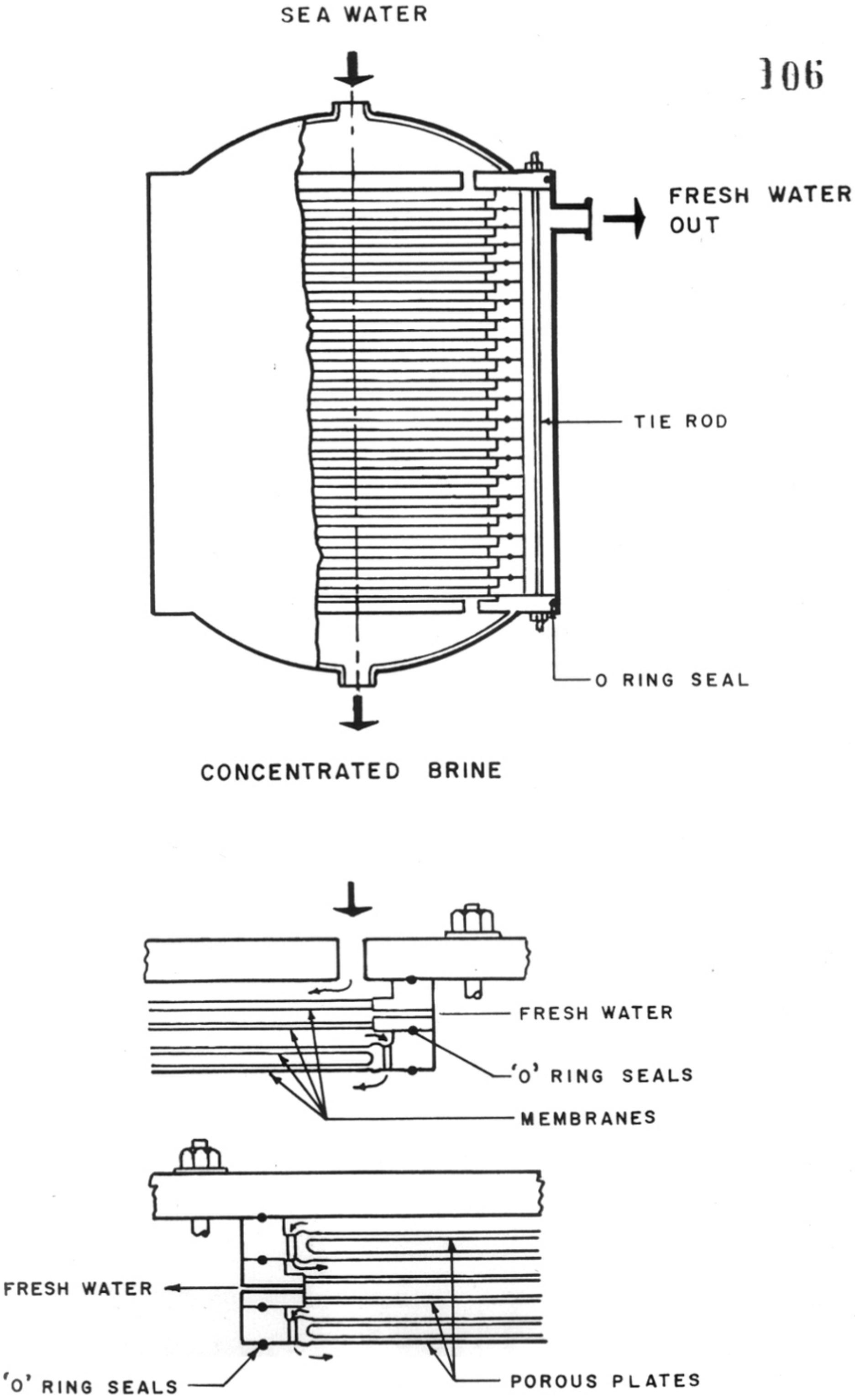

FIG. 13 PLATE-AND-FRAME MODULE DESIGN.

through the membrane into the porous supporting structure and readilly outward to a product-water outlet. This system is simple. It has an advantage that when membrane material fails only the membrane itself needs replacement. The membrane packing density in current designs ranges from 50 to 150 sq.ft/ft^3.

(2) Spiral-Wound Module

Spiral-wound module[5] configuration concept is made clear in Fig.14, which also shows the specific functional components of this configuration. A piece of membrane is folded over a porous product water side backing material and a perforated tube is placed between the two layers at the fold. The resulting sandwich is then sealed along both sides and one end as well as around the central tube where the tube leaves the sandwich. This unit is then simply rolled up by wrapping the leaf around the tube. The rolled up unit, called a module, is then placed in a pressure tube and sealed between the outer wrap of the module and the inside of pipe.

The brine is forced through the brine-side spacer in a direction parallel to the axis of the roll. The brine flows through the module, part of the water is forced through the membrane and into the porous product-water side backing material. Once it comes in the backing material it flows to the central tube and then out - through a sealing connection in the pressure-pipe end. The spiral wound design is compact, with membrane area packing densities

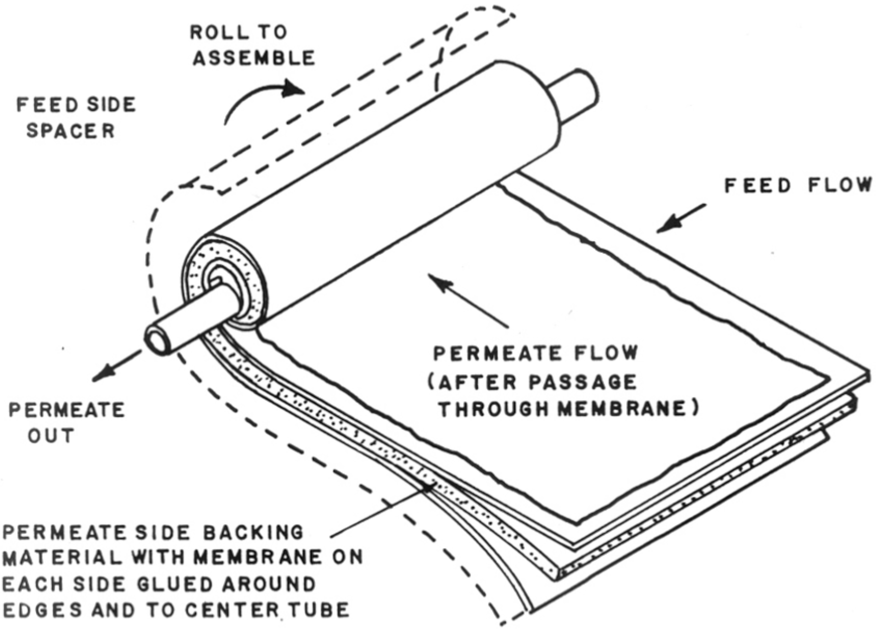

FIG 14 SPIRAL WOUND MODULE

ranging from 200 to 500 ft^2/ft^3. The design of such modules permits high product recoveries. The preassembled membrane catridge is treated as a replaceable component. Modern spiral-wound modules contain multi-leaf and more complex design. Nearly one-half of the R.O. desalting equipments in the world utilize this type of modules.

(3) Tubular Module

In the tubular module design a pressure substaining tubular support is utilized. The membrane can be inside or on the outside of the support tube and can be bonded to the support tube. The bonded membranes can be cast into a single tube and then these tubes assembled into a module as shown in Fig.15. Brine flow is axial inside the tube. Product water flow is through the membrane, to an outlet hole in the supporting tube wall and then through the porous wall. The water emerges at atmospheric pressure and is collected in the storage tank. Packing densities for tubular system are within the range from 10-100 ft^2/ft^3.

(4) Hollow Fiber Module

Hollow fiber modules contain a very large number of hollow tubes. The tube diameters are in the range of 5-100μ with diameter to wall ratios from 4 to 5. These tubes are arranged in bundles with the ends sealed in header by epoxy resin. This bundle is inserted into a cylindrical shell which serves as a pressure vessel. The hollow fiber walls serve as the semipermeable membrane. The brine flow is inside the

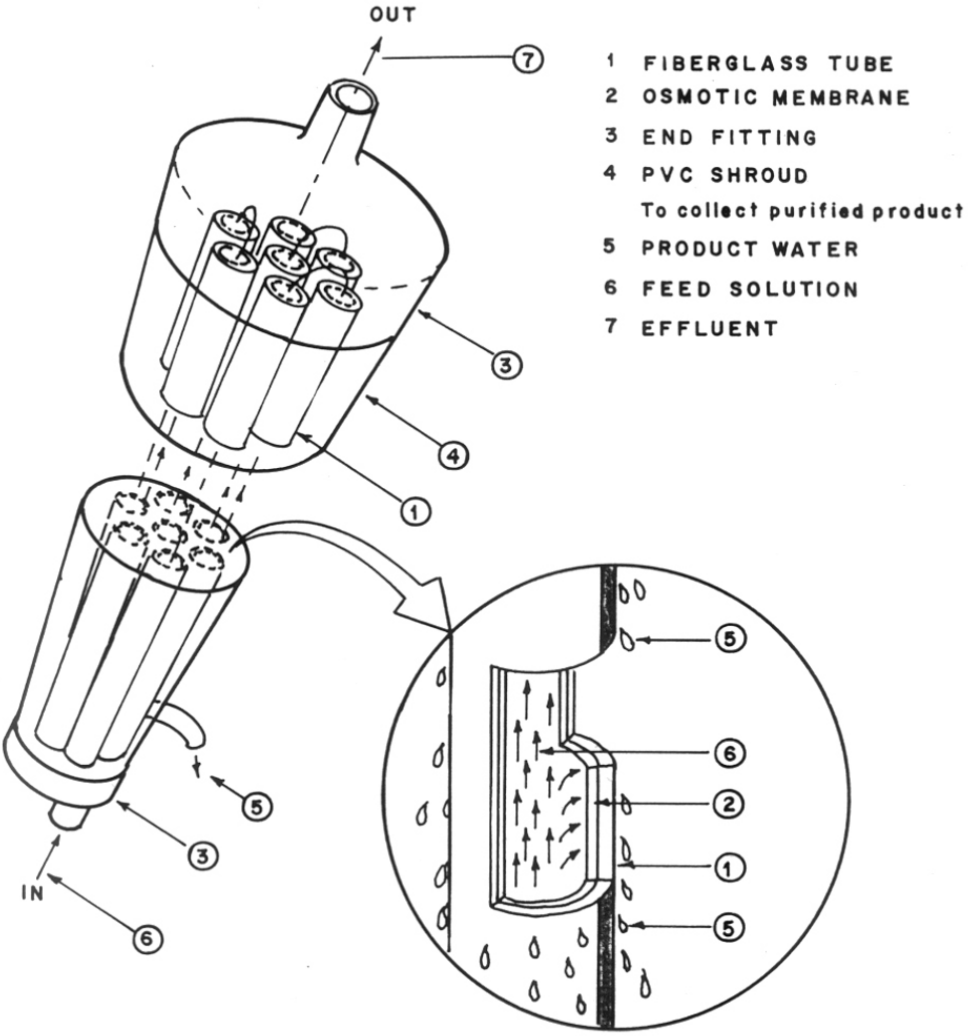

FIG. 15 TUBULAR MODULE DESIGN

tubes. The product water flows through the walls of the tubes and is collected at near atmospheric pressure in a storage tank. Schematic diagram of the hollow fiber in a R.O. unit is shown in Fig.16.

The advantages of hollow fiber modules are relatively high flux densities and elimination of membrane support media. However, this system requires efficient pretreatment.

Fabrication of Reverse Osmosis Laboratory Test Unit

Since laboratory reverse osmosis test unit was not easily accessible, a small R.O. test unit was fabricated in our laboratory using indegeneous raw materials. The photograph of the total unit is shown in Fig.17. This unit consists of high pressure pump, water accamulator, pressure gauge, stainless steel high pressure test cell and by pass volve. The schematic flow diagram of the unit is shown in Fig.18.

Materials Used During Fabrication :

1) Stainless steel plate (316 SS) $1\frac{1}{2}$ inch thick (2 Nos.)
2) Stainless steel pipe - 1/4 inch diameter, wall thickness 1/16 inch.
3) Water accumulator was prepared from stainless steel pipe 2 inch diameter, 2.5 inch in length and wall thickness - 1/16 inch.
4) Nut and bolts (M.S.) - 3/8 x 4 inch.
5) Pressure gauge 0-100 Kg/cm^2 obtained from M/s. J.N.Marshall Pvt.Ltd., Poona, India.

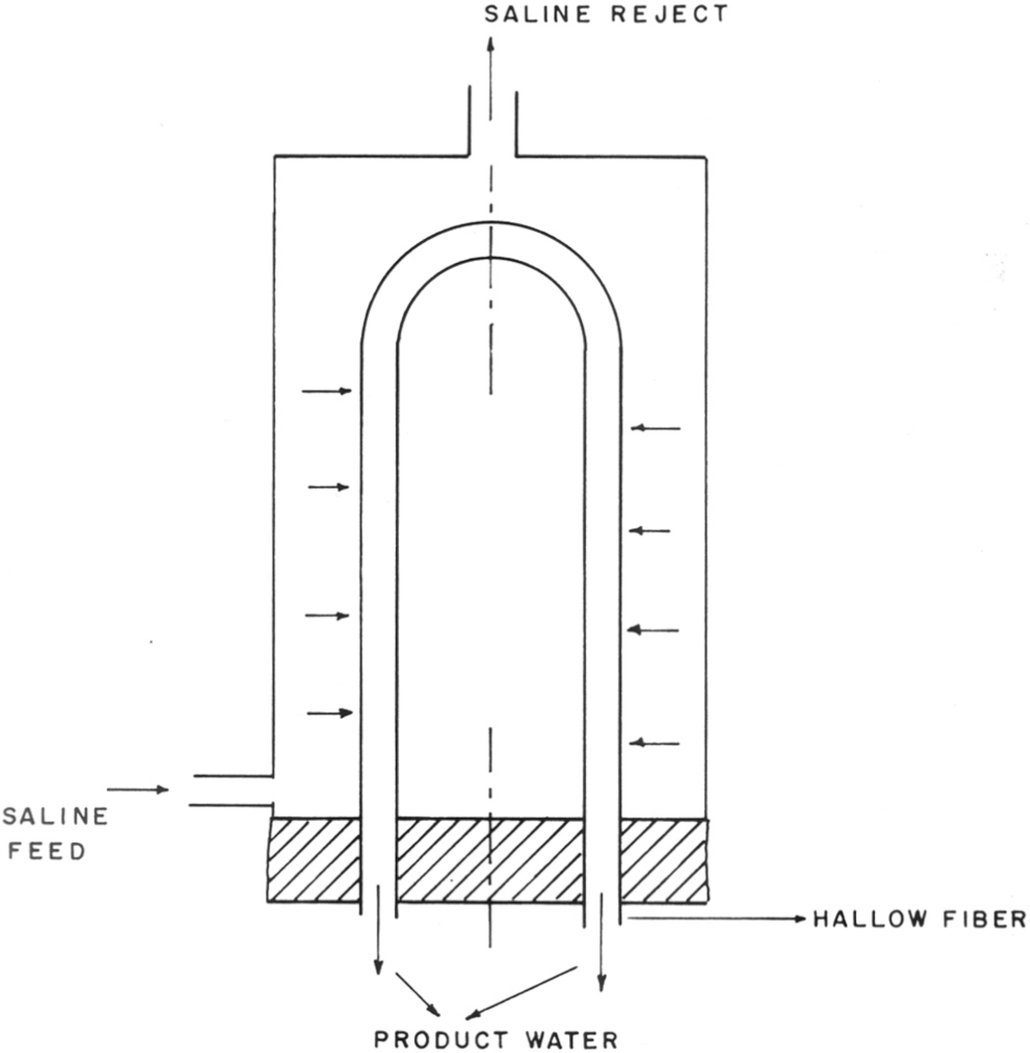

FIG. 16 SCHEMATIC OF THE HOLLOW FIBER IN R.O. UNIT, THE SINGLE END U-CONFIGURATION WITH AXIAL FLOW IS DEPICTED

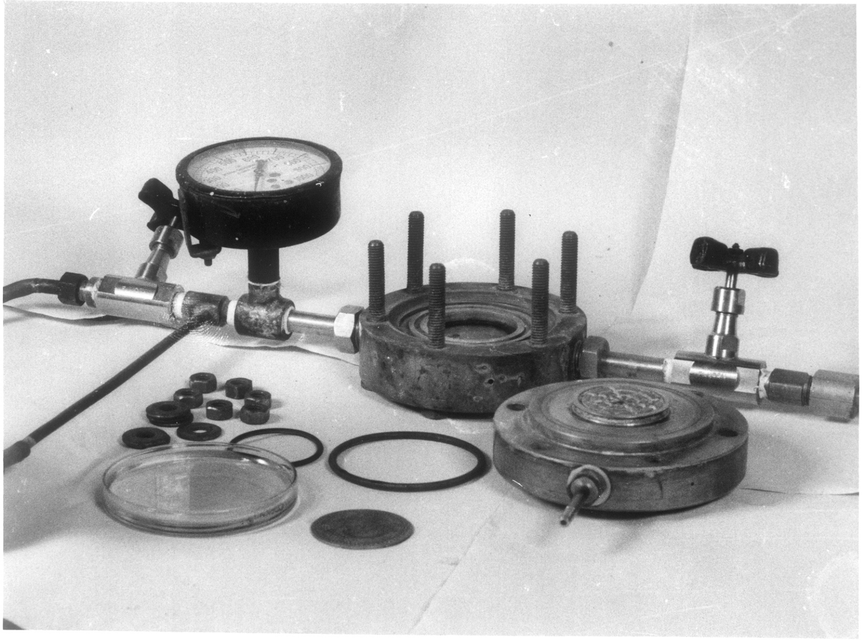

FIG. 17 REVERSE OSMOSIS TEST CELL

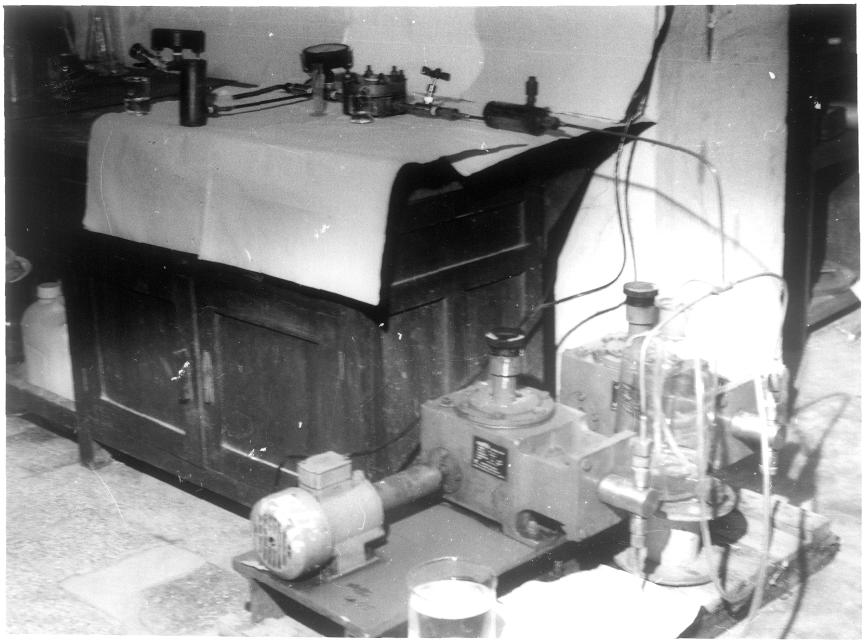

FIG. 17 REVERSE OSMOSIS UNIT FABRICATED IN NCL

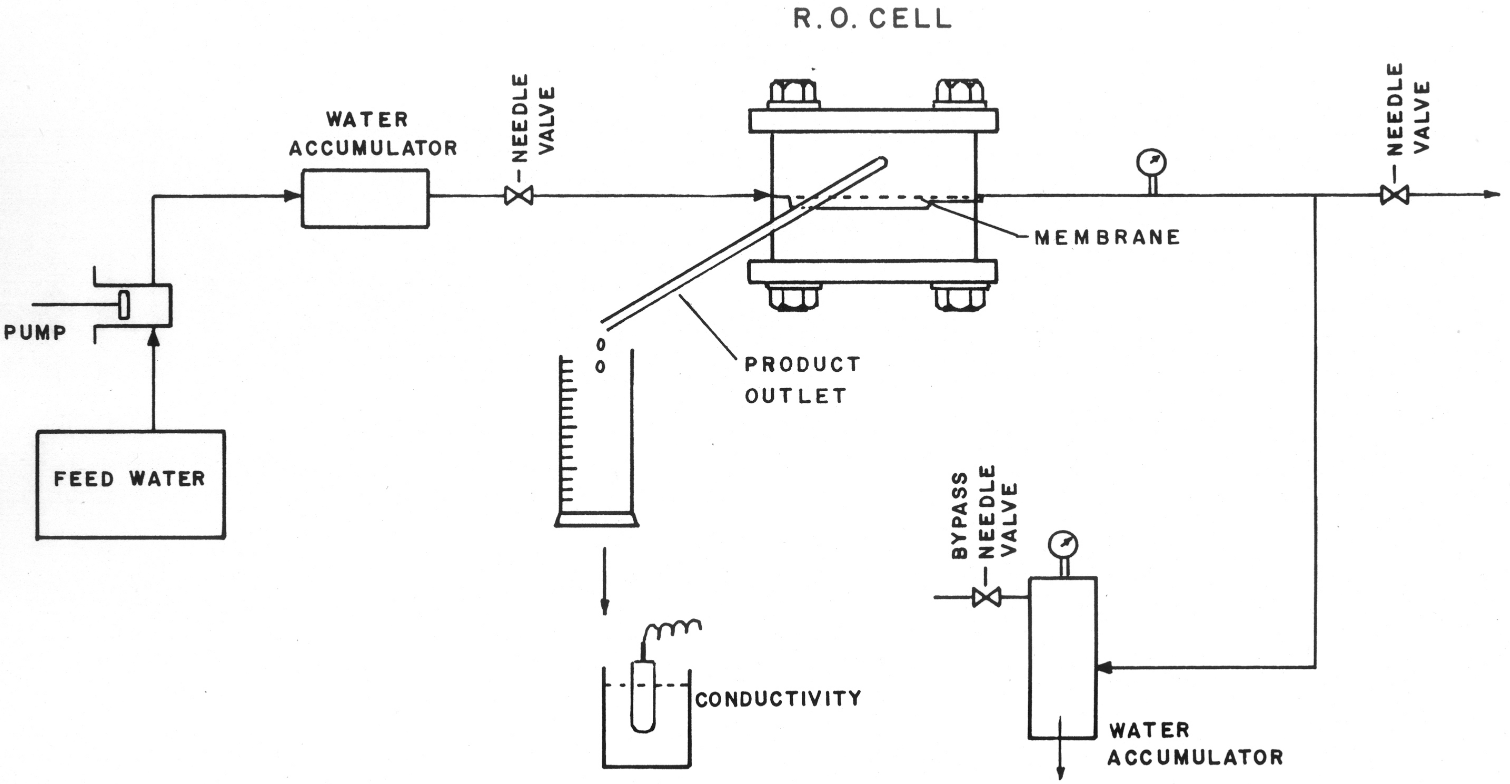

FIG. 18 FLOW DIAGRAM OF R.O. UNIT (FOR FLAT MEMBRANE)

6) Stainless steel porous disc.

7) Stainless steel needle valves.

8) High pressure pump., pressure pump was procured from M/s. V.K.Pump, Bombay, India with the following specifications :
   Multiflow dosing pump, model PR 120 (twin) with a capacity of 14 litres/hour.
   Lubricating oil 40 SAE was used as lubricating oil for the pump.

Preparation of R.O. Cell

Reverse osmosis cell was made by machining the stainless steel plates. Lower part of the cell was made hollow and provided with inlet and outlet connections. This plate was connected to the system containing water accumulator, pressure gauge, high pressure pump and a by-pass needle valve. The lower portion of the top plate was machined in such a way that it fits into the lower part of the cell. The top plate was then tighened with nut and bolts.

Working of High Pressure Pump

Feed water (pure or brine water) is circulated by high pressure pump. The pump had independent stroke adjustment coupled with a 0.5 HP electric motor. Any pulse due to pumping strokes were eliminated by water accumulator. The pressure in the system was controlled by adjusting the pump strokes and by a needle valve.

Operating Procedure

Feed water tank was of two litre capacity and was filled either with distilled water or saline water of known concentration. Oil level in the high pressure pump was checked before starting the operation. Rubber 'O' ring was placed in lower part of the cell to avoid saline water leakage. A circular flat membrane facing its air dried surface towards pressure side (effective area 18.6 cm^2) was placed, along with a circular filter paper and a stainless steel porous disc of similar dimension as a support. The top plate was placed on it and evenly tightened with nut and bolts.

The pump was started by opening the by-pass needle valve initially and as the air is displaced, the water is filled in the accumulator. The by-pass needle valve was slowly closed to get desired pressure in the system. The pressure was accurately maintained by adjusting the piston strokes.

The product water coming out through the membrane was collected at a regular interval of time. The volume of the water collected was measured and converted into gfd (gallon/ft^2-day).

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SUMMARY

Part-I INTRODUCTION

Pure and fresh water is the basic requirement of life. Water is one of the most essential products of nature, but available water from natural sources is generally contaminated with dissolved, dispersed and suspended impurities. A large portion of available water is in the form of saline water which cannot be used directly. This is where the 'Desalination' comes into picture. With increasing growth of population and industries, the total known potable water resources in nature are found to be insufficient which do not fulfil the demand of pure water. Thus realising the importance of pure water, many advanced countries have takem up projects of converting the saline waters to pure water by employing various desalination techniques.

Numerous processes have been proposed for the desalination of water, and a few of these have attained important commercial status. Distillation, electrodialysis and reverse osmosis are already applied to a variety of practical installation. Of the methods that are of current importance, electrodialysis and reverse osmosis are best adapted to the desalination of brackish waters while distillation is applicable to the entire range of salinities upto seawater as dense as 43,000 ppm. Water that is good enough to drink, when used untreated in many industrial applications, can seriously reduce equipment performance, increase maintenance, and lower quality of finished products. Reverse Osmosis (R.O.) offers many advantages and possibilities for the production of water of various qualities in chemical plant at low cost as compared to the other desalination processes. Reverse osmosis can effect efficiently for purification, separation and concentration of the dissolved solids from their aqueous solutions, hence it has a wide scope in the field of separation technology in Chemical Engineering processes.

Many polymeric materials such as esters of cellulose, mixed esters of cellulose, polyvinyl alcohol and polystyrene have been tried for the use of membranes by Reid and Breton[1]. In the course of surveying a number of cellulosic and non-cellulosic polymers for use as reverse osmosis membranes, cellulose acetate (CA) appeared to have high flux and high salt rejection than that of others. Recently polyamides, polybenzimidazole (PBI), polybenzimidazolone (PBIL) polymers[2,3] have been developed for reverse osmosis membranes.

The recent development in science and engineering of R.O. was due to CA membranes developed by Loeb and Sourirajan[4] in 1960. The features of CA membranes initiated a wide spread interest in R.O. as an economical method for the desalination of sea and brackish waters. Loeb and Sourirajan type CA membranes have been the most widely used membranes to date for reverse osmosis desalination because no other low cost membranes have been developed which have high flux rate and selectivities equal to those of cellulose acetate. Inspite of several good features of these membranes, they have some drawbacks such as poor chemical resistance and fast biodegradability[5], the rapid flux decay due to the membrane compaction under the high influent pressure etc. Modification of CA resulting in improved performance will make it more attractive polymer for use as R.O. membranes for sea and brackish waters. Some work has already been reported for mechanically stabilizing CA membranes by grafting of vinyl monomer[6] on CA.

The present work describes the modification of indigenously available CA by aromatic, aliphatic isocyanates and propylene oxide.

Part II Modification of CA by aromatic and aliphatic isocyanates

The residual hydroxyl groups of cellulose acetate have been reacted partially with phenyl[7], butyl and propyl isocyanates[8]. The modified CA urethane polymers were characterized for their physical and chemical properties such as softening point, intrinsic viscosity, molecular weight, acetyl content, thermal stability, infrared spectroscopy (IR), elemental analysis and microbial resistance. The radiation resistance of CA polymer modified by phenyl isocyanate has been studied. These modified CA polymers have been utilized for the preparation of membranes. The membranes were cast as per the procedure reported in the literature[9,10]. These membranes were annealed at different temperatures to study the effect of annealing temperature on their transport properties. The transport property data for water flux and % salt rejection was obtained using R.O.Unit fabricated in our laboratory.

The modification of CA with isocyanates results in stronger polymers which are more resistant to thermal and γ radiation[11] (incase of phenyl isocyanate modified CA) as compared with CA. The reverse osmosis experiments show reduced water flux and increase % salt rejection in comparison with CA membranes. Some of these membranes have been studied for the selectivity of different solutes such as glucose, fructose and sucrose.

Part III Modification of CA by propylene oxide

Graft copolymerization is an attractive means for modifying base polymer because grafting frequently results in the superposition of properties relating to backbone and pendant chains. Grafting of vinylmonomers on CA has been reported by many researchers for membrane purposes. The effect of styrene grafting to CA has been reported[6] as possible technique for mechanically stabilizing the membranes. Cellulose esters of high stability have been prepared by reaction with epoxides e.g. ethylene oxide[12]. Russian workers[13] have reported hydroxypropylation of cellulose acetate but the details regarding the reaction course has not been disclosed. According to U.S.Patent[14], the methyl hydroxypropyl cellulose acetate was reported by etherifying cellulose with propylene oxide and then esterifying with acetic anhydride.

In this part CA has been grafted by propylene oxide without using a catalyst. The grafted polymers were characterized for their mechanical strength, thermal stability, inherent viscosity, scanning electron microscopy, softening point etc. Membranes were cast from these polymers and after annealing the membranes for a specified time they were tested for transport properties such as waterflux and % salt rejection. In addition to their transport properties other characteristics of the membranes such as specific water content, membrane constant and average pore diameter have also been calculated.

Part IV Fabrication of Reverse Osmosis Laboratory Test Unit

The pilot plant activity began with the discovery of asymmetric porous cellulose acetate membranes by Loeb and Sourirajan[4] in 1960 for making practical reverse osmosis unit. Even though R.O. has been applied in few large scale plants, the published information on engineering aspects is still limited. The design of R.O. Plant depends upon the quality of the product water required from the characteristics of the feed, the operating pressure and membrane characteristics. The design of a R.O.unit is judged on the basis of its effects on total product cost.

Since laboratory R.O. test units were not easily accessable, a small test unit was fabricated in our laboratory. This unit consists of high pressure pump, water accumulator, pressure gauge and R.O.Cell. The material of construction of this unit is stainless steel. On this unit the transport properties of various flat membranes have been tested at different operating pressures.

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PUBLICATIONS

The following papers have been published based on the work presented in the thesis.

1. Modified Cellulose Acetate Membranes for Desalination.
   N.D.Ghatge, M.B.Sabne, K.B.Gujar and S.S.Mahajan,
   J.Appl.Polym.Sci. (in press)

2. Modification of Cellulose Acetate by Aliphatic Isocyanates for Reverse Osmosis Studies.
   N.D.Ghatge, M.B.Sabne, K.B.Gujar and S.S.Mahajan,
   Submitted to Third National Conference on Water Desalination, held at CSMCRI, Bhavnagar (India) on 10-12 Feb. 1984.

3. Modification of Cellulose Acetate by Propylene Oxide.
   S.S.Mahajan, M.B.Sabne, K.B.Gujar and N.D.Ghatge,
   Desalination (communicated)

FORM 3A
THE PATENTS ACT 1970
COMPLETE SPECIFICATION
(SECTION 10)

A PROCESS FOR THE PREPARATION OF MODIFIED CELLULOSE ACETATE POLYMERS SUITABLE FOR MAKING MEMBRANES FOR USE IN REVERSE OSMOSIS.

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH, Rafi Marg, New Delhi-110001, India, an Indian registered body incorporated under the Registration of Societies Act (XXI of 1860).

The following specification particularly describes and ascertains of this invention and the manner in which it is to be performed :

This is an invention by Nanasaheb Dattajirao Ghatge, Madhukar Bhagwant Sabne and Kantilal Balaram Gujar, Scientists of the National Chemical Laboratory, Pune, India and citizens of the Republic of India.

This invention relates to a process for the preparation of modified cellulose acetate polymers suitable for making membranes for use in reverse osmosis.

The modified cellulose acetate polymers are used for the making of membranes in the desalination of brackish water and effluent solutions by the technique called Reverse Osmosis.

As per known art cellulose acetate is used commercialy for the preparation of desalination membranes in reverse osmosis.

In spite of good permeability, waterflux and salt rejection of cellulose acetate membranes, they have certain disadvantages. These are as follows :

(i) cellulose acetate membranes do not stand for constant high pressure, temperature and pH,

(ii) Chemical and radiation resistance of these membranes is poor, and

(iii) these membranes are susceptible to biodegradation

The main object of our invention is to modify the cellulose acetate whose membranes will have improved resistance to high pressure, temperature, pH, chemical radiation and biodegradation for use in the desalination in the reverse osmosis process.

Our modified cellulose acetate polymer membranes have good water flux and salt rejection with improved chemical and radiation resistance. They stand for high temperature and pressure.

The main finding underlying the invention is the modification of OH group in cellulose acetate molecule by reacting them with isocyanate groups to create urethane linkages. These urethane linkages are responsible for the improved properties of the modified cellulose acetate membranes.

Cellulose acetate is commercially available with an acetyl content of 27-40 percent is used for the preparation of modified polymer.

The process of the present invention consists of preparation of modified cellulose acetate polymer product by reacting cellulose acetate with mono/diisocyanates to give desired properties of membranes prepared therefrom.

In the method of preparation of modified cellulose acetate polymer one mole of cellulose acetate was dried by azotropic distillation of benzene. It was dissolved in dry and distilled pyridine at temperature 60-70°C under nitrogen atmosphere. Then 0.5 mole of mono isocyanate was added slowly, dropwise at 60-70°C. The reaction mixture was refluxed for 4 to 6 hours.

Then reaction mixture was precipitated, washed till free of pyridine and dried. The final product was analyzed for nitrogen content, I.R., N.M.R., thermal analysis.

Accordingly this invention provides a process for the preparation of modified cellulose acetate polymers suitable for making membranes for use in reverse osmosis which comprises reacting cellulose acetate with an isocyanate compound in the presence of an organic solvent.

According to a feature of the invention the reaction is carried out at a temperature range of 25°C-200°C.

According to another feature of the invention the isocyanate compound used is a mono isocyanate like phenyl, methyl, ethyl, butyl or propyl isocyanate.

According to still another feature of the invention the isocyanate compound used is a diisocyanate like toluene diisocyanate, diphenyl methane diisocyanate, hexamethylene diisocyanate alone or admixed with a mono isocyanate.

According to a further feature of the invention the organic solvents used are such as acetone, pyridine, ethylene dichloride or dioxane.

According to another further feature of the invention the reaction is carried out at a temperature of 110°-120°C at normal pressure.

The membrane is prepared by casting solution which consists of 22.2 wt. percent of modified cellulose acetate, 1.1 wt. percent of magnesium perchlorate $Mg(ClO_4)_2$, 66.7 wt. percent of reagent grade acetone and the balance distilled water. The solution is cooled to 25°C and cast on cold glass plates in a deep freeze maintained at this temperature. The membranes were allowed to dry for 4 minutes after casting and were then immersed in ice water and kept there for at least 1 hour. Finally the membranes were annealed in 81°C water for 30 minutes.

The transport properties were measured by reverse osmosis. The properties like water flux, salt rejection, radiation resistance tensile strength, temperature stability are improved over that of unmodified membranes.

Comparison of properties of C.A. and M.C.A.

Properties	C.A.	M.C.A.
i) Water flux gfd.	10-15	15-20
ii) Percent salt rejection	90-95	90-96
iii) Tensile strength kg/Cm^2	85-90	100-110

Modified cellulose acetate product has good thermal stability than known cellulose acetate.

C.A.	250-270°C	(10 percent wt. loss)
M.C.A.	300-325°C	(10 percent wt. loss)

Modified cellulose acetate membranes have good radiation resistance.

	Waterflux $lm^{-2}d^{-1}$	Percent SR
Pre-irradiation	800-1100	85-92
Post-irradiation	800-1000	85-90

Dose : 1 Mrad gamma dose from CO-60 source. Pressure

$40\ kg/cm^2$. Feed 5000 ppm NaCl.

The process for the preparation of modified cellulose acetate thus consists of reacting cellulose acetate with isocyanates by using different molar ratios of the reactants. The acetyl content of cellulose acetate used ranges from 26 percent to 42 percent. A mono isocyanate, such as phenyl, methyl, ethyl, butyl propyl isocyanate may be used. The reaction is carried out with a toluene diisocyanate, diphenyl mathane diisocyanate, hexamethylene diisocyanate and mixed isocyanates and other mono isocyanate obtained by the modification of the diisocyanates by using solvents such as acetone, pyridine, ethylene dichloride and dioxane, etc. The polymers formed are used for the preparation of desalination membranes.

Modified cellulose acetate polymer are thus prepared by steps of the process, wherein first removal of moisture from cellulose acetate, is effected, cellulose acetate is dissolved in solvent, and then it is reacted with isocyanate. Polymeric membrane prepared from this modified cellulose acetate are very useful for desalination in reverse osmosis. The results obtained are better than with the known cellulose acetate membranes. The reaction of isocyanate with cellulose acetate can be carried out at temperature 25°C to 200°C and normal pressure. The optimum reaction condition for MCA are temperature of 110-120°C and normal pressure.

We claim :

1. A process for the preparation of modified cellulose acetate polymers suitable for making membranes for use in reverse osmosis

comprising reacting cellulose acetate with an isocyanate compound in the presence of an organic solvent.

2. Process as claimed in claim 1 wherein the reaction is carried out a temperature range of 25°C-200°C.

3. Process as claimed in claims 1 or 2 wherein the isocyanate compound used is a mono isocyanate like phenyl, methyl, ethyl, butyl or propyl isocyanate.

4. Process as claimed in any of the preceeding claims wherein the isocyanate compound used is a diisocyanate like toluene diisocyanate, diphenyl methane diisocyanate, hexamethylene diisocyanate alone or admixed with a mono isocyanate.

5. Process as claimed in any of the preceeding claims wherein the organic solvents used are such as acetone, pyridine, ethylene dichloride or dioxane.

6. Process as claimed in any of the preceeding claims wherein the reaction is carried out at a temperature of 110°-120°C at normal pressure.

7. A process for the preparation of modified cellulose acetate polymers for making membranes for use in reverse osmosis substantially as herein described.