Development of reverse osmosis membranes cast directly on various support materials
by Juin-yih Lai

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of MASTER OF SCIENCE in CHEMICAL ENGINEERING
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Abstract:
The reverse osmosis process is characterized by the use of pressure in excess of osmotic pressure to force fresh water at ambient temperature through a selective membrane capable of rejecting dissolved salts. It is a technically feasible process, with good thermodynamic efficiency, flexibility and simplicity.

The purpose of this work was to develop cellulose acetate membranes cast directly on various support materials and optimize the conditions.

Most variables that affect salt rejection and water flux of membranes have been considered in 239 runs. Sixteen different kinds of supports, several types of cellulose acetate, cellulose acetate contents, different ratios of acetone to formamide, heat treatment temperatures, evaporating times, and pressures were tested.

The olyvinyl chloride support is the most promising for cellulose acetate membranes. The type E398-10 cellulose acetate was the best for PVC supports. The best results always came when a casting solution with 21.9$ cellulose acetate content was used.

The acetone to formamide ratios were found not to be important.

By adjusting some other variables, such as evaporating time and heat treatment temperature, one can get the same results although the acetone-formamide ratios were different.

Most membranes are very sensitive to heat treatment. Decreasing the heat treatment temperature always increased the water flux and decreased the salt rejection for short evaporating time. It seems the shorter the evaporating time the better the results for cellulose acetate membranes. Membranes with PVC supports are less compressible under high pressure than other membranes.

A set of casting conditions for optimal membranes was found: casting environment: 70°F, 50% humidity; solvent evaporating time: 5 sec.; gelation: 0°C, 1 hour; heat treatment: 84°C, 4 min.; supports: PVC, ES, 2.0 microns, Millipore Corp.; solution: E398-10 cellulose acetate (21.9%)-formamide-acetone ternary solution.

The average water flux and salt rejection, based on 124 hour runs, was 23.5 GSFD and 95•7% respectively.

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ABSTRACT

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The acetone to formamide ratios were found not to be important. By adjusting some other variables, such as evaporating time and heat treatment temperature, one can get the same results although the acetone-formamide ratios were different.

Most membranes are very sensitive to heat treatment. Decreasing the heat treatment temperature always increased the water flux and decreased the salt rejection for short evaporating time. It seems the shorter the evaporating time the better the results for cellulose acetate membranes. Membranes with PVC supports are less compressible under high pressure than other membranes.

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The average water flux and salt rejection, based on 124 hour runs, was 23.5 GSFD and 95.7% respectively.

I. INTRODUCTION

The water problem - the problem of how to have water in adequate quantity and of adequate quality, available at a reasonable cost, when and where needed - is one of world-wide importance.

A new conventional source of water may be developed today for a cost of 13 cents to 70 cents per thousand gallons. It is estimated that by 1980 this cost will have risen to 20 cents to 90 cents per thousand gallons [(1)]. In terms of improvements in technology and/or equipment, there is little potential for savings in this respect. Clearly, desalination will be a part of the solution of the total water problem.

Many processes have been tried for desalination. Some of them have been used in actual large desalination plants in many countries. Those are: multistage flash distillation, longtube vertical distillation, electrodialysis (brackish water only), vapor compression distillation, direct freezing, and reverse osmosis.

Saline water conversion is still in its infancy, since the cost of desalination is still relatively high. But, in some areas desalination is even now competitive with other means of obtaining usable water.

It was reported that cost of fresh water obtained by small desalination plant (multi-stage flash evaporation) was about $.80 to $1.10 per thousand gallons, and for a large plant 20-40 cents per thousand gallons (50 million gallons per day products or more) with present technology [(1)].

Recently, reverse osmosis is one of the most interesting processes. Possibly the most important reason is the recent development of membranes which combine good salt rejection with moderately high water flux. Second, is the appealing conceptual simplicity of the method, which essentially consists of removal of salt by filtering it away from water under pressure.

Third, this process tends to avoid scaling problems and to minimize corrosion since it always operates at ambient temperature. Fourth, the energy requirements for the process are low. The theoretical minimum of work for desalting sea water at 25°C is 2.65 Kilowatt-hours per thousand gallons. The energy consumption of multistage flash distillation and long-tube vertical distillation, for example, is six times that of the reverse osmosis process(3).

The reverse osmosis process is characterized by the use of pressure in excess of osmotic pressure to force fresh water at ambient temperature through a selective membrane capable of rejecting dissolved salts. The process name is derived from the phenomenon whereby water under an applied pressure driving force flows in a reverse direction to the flow in an osmotic experiment where the driving force is the concentration gradient.

The most important part of reverse osmosis equipment is the membrane. The important membrane properties are water flux, salt rejection and membrane life. Flux is usually given in gallons/ft.^{2}-day (GSFD) and salt rejection is usually given as % salt rejection or salt reduction factor = 100/(100-percent rejection). Many kinds of membranes have been tried for reverse osmosis, some of them with high rejection but very low flux, such as ethyl cellulose-poly-acrylic acid membranes, and some of them with high flux but low rejection, such as poly-acrylonitrile membranes.

Cellulose acetate is the most promising membrane which provides high rejection and moderately high flux. The first recognition that salt rejection by membranes might be useful in desalination seems to have been by Reid at the University of Florida[3]. Reid and Breton obtained a maximum water flux of .945 GSFD and salt reduction facotr of 25 (96% salt rejection) from their cellulose acetate membranes.

Since then cellulose acetate membranes have been improved quite rapidly. Total cost for products by the reverse osmosis process, using cellulose acetate membranes, is still high. It is mainly caused by the low flux and short membrane life.

General Atomic Division of General Dynamics has proposed a design for a 1 million gallon per day reverse osmosis pilot plant. The minimum cost of fresh water produced by this pilot plant was estimated to be 75.5 cents per thousand gallons from sea water[6].

The water flux of their membranes is about 10 GSFD under 1440 psi. pressure. If the flux can be increased to 20 GSFD and keep the other conditions the same, for example, the cost of fresh water obtained from this pilot plant could be reduced to about 50 cents per thousand gallons[3].

In this pilot plant the cost of membrane replacement is about one third of the total cost. It is reported that the labor cost of membrane replacement would be much higher than the cost of the membrane itself. It is believed that the membranes cast directly onto porous supports could reduce the high labor cost of membrane replacement, as a shorter time and more simple procedure would be required to replace the membrane.

Donald Wang[5] has successfully investigated a membrane by using direct casting on porous supports. His membrane, cast from cellulose acetate (E-400 -25, 21.9%) formamide (31.2%) acetone (46.9%) ternary solution on rigid porous epoxy filled fiberglass supports (Gelman Versapor .9 micron), can provide an average water flux of 21 GSFD and 95% salt rejection.

The purpose of this work is to develop cellulose acetate membranes cast directly on other support materials and optimize the conditions.

Most variables that affect salt rejection and water flux of membranes have been considered in 239 runs. Different kinds of membrane support, casting solution composition, heat treatment temperature, solvent evaporating time and operating pressure are all important. Sixteen different kinds of supports, five types of cellulose acetate, six different cellulose acetate contents, five different ratios of formamide to acetone and several evaporating times have been tested in fabricating membranes. Several different heat treatment temperatures were used before the membranes were tested at three pressures.

In all processes for water desalination, the water and the salt to be separated must ultimately diffuse apart by molecular diffusion. Thus, at the phase boundary where the separation is effected there will be a salt-concentration boundary layer, the salt concentration at the phase boundary exceeding that in the bulk brine. This salt-concentration polarization is important in desalination by reverse osmosis. For simplicity, the film-theory was used for the turbulent flow. The boundary layer is idealized as a thin, liquid film in which eddy motion is assumed to be negligible and therefore mass transport takes place by molecular diffusion alone.

The following equation[4] expresses the film theory prediction for the salt concentration build-up at the membrane surface in terms of the permeation flux, the fluid mechanical parameters, and Schmidt number, N_{sc}, for salt diffusion. For a high salt rejection membrane, approaches unity.

$$\frac{C_2'}{C_2^b} = \frac{\exp[(v'/j_D\bar{U})\ N_{sc}^{2/3}]}{r + (1-r)\ \exp[(v'/j_D\bar{U})\ N_{sc}^{2/3}]}$$

where C_2' = salt concentration at membrane interface, g/cm^3

C_2^b = salt concentration in bulk solution g/cm^3

v' = product water flow velocity through the membrane, cm/sec.

j_D = Chilton-Colburn mass transfer j-factor

N_{sc} = Schmidt number for salt diffusion

$\bar{U}$ = average velocity over the cell, cm/sec.

r = salt rejection

II. EQUIPMENT AND PROCEDURE

A. MEMBRANE FABRICATION EQUIPMENT

A constant temperature and humidity chamber was used for membrane casting of all runs. The chamber was constructed with a fiber glass body, a safety glass window (10 1/2" x 32") in front of the chamber, and two 6" diameter rubber plate covered working holes on the front chamber door (40" x 10"). The chamber contains lights, a heater, cooler, fan, two salt solution containers and a thermoprobe connected to an electronic temperature controller. The temperature was kept at 24.5 ± 0.2°C and humidity was kept at 50% by using saturated $Ca(NO_3)_2 \cdot 4H_2O$ salt solution. A level aluminum surface with the dimensions of 8 inches by 5 inches was used for membrane casting in order to produce even membrane thicknesses.

B. TEST CELL

The test cells shown in Figure 4 were made of stainless steel 304 blank flanges with 4.5" outside diameter and a 2" diameter test area. The membrane was supported by a 1/8 inch porous stainless steel plate (Grade H, pore size 5 microns, Pall Corp.) which was mounted between the two halves of the cell. The salt water under pressure was circulated through the upper half.

C. MEMBRANE TEST SYSTEM AND FLOW DIAGRAM

The flow diagram is shown in Figure 5. The test system consisted of four test cells, a filter, two parallel test lines, and a plastic feed tank with stirrer and cooler. System pressure was controlled with backpressure regulators. A nitrogen cylinder was used to load the regulators.

The pressure used for all runs was 800 psi. except Runs 185, 186, 187, and 188. The temperature of the feed solution (1% NaCl) was kept at 25°C. Control of the cooling water rate can control the temperature of the feed solution. A maximum feed flow rate of 11.4 ml./sec. was used. The average volume of the test cells was 8.3 ml., so that the feed in the cell was replaced every 0.73 sec. and the average feed flow velocity across the cell was 7.9 cm./sec.

D. TEST PROCEDURE

The following is the membrane fabrication procedure used for this study. The support was fixed on the aluminum plate with masking tape which was about .005" thick. A glass rod was used to spread the solution smoothly onto the support, with the tape as a thickness guide, in a constant temperature and humidity chamber. The cast solution was evaporated as long as needed. The aluminum plate was immersed with the membrane in 0°C ice water for one hour. Then the membrane was heat treated with the aluminum plate in hot water which had been heated to the required temperature. The heat treatment time used was four minutes. The membrane was immersed in cold water until it was tested. It was cut to the dimension to fit the test cell when it was tested.

The membranes were firmly mounted in the test cells with the cellulose acetate film facing the high pressure side. The pump was started and the pressure gradually increased until 800 psi was reached. Cold water to the cooler was adjusted to keep the temperature of the feed solution at 25°C. The feed concentration was checked when every sample was taken. The sample was taken once every hour or two and most membranes were tested four to eight hours.

A conductivity bridge (Industrial Instruments Model RC-16 B-2) was used in conjunction with a conductivity cell to analyse the concentration of salt water and product water. The relationship between concentration and resistance can be approximately expressed as:

$$C_t = \frac{6.4 - (t-25) \times .1}{(R_t)^{1.0496}}$$

where C_t = salt water concentration, moles/liter

t = temperature of conductivity measurement, °C

R_t = resistance at temperature t, ohms

This equation was used to calculate concentration from different temperature and resistance to make a plot of concentration versus resistance at different temperatures. This plot, Figure 6, was used to convert the resistance of every sample to concentration. Periodically this curve was checked against standard NaCl solutions.

III. RESULTS

Two hundred and thirty-nine membranes have been made to optimize conditions among the variables which affect the salt rejection and water flux of membranes. The results of all of these tests are tabulated in Table XI.

A. SUPPORTS

The membrane support has an important effect upon the properties of the membrane. Possible membranes that were considered are shown in Table I.

Nine kinds of filter materials were studied: mixed esters of cellulose, nylon, Millipore proprietary, teflon, polyvinyl chloride, polyvinylidene fluoride, Gelman Versapor, cellulose triacetate and α-cellulose.

The range of pore size of the supports which were tested varied from .05 to 5.0 microns.

The first casting solution contained 21.9% E398-10 cellulose acetate, 31.2% formamide, and 46.9% acetone. In the evaluation of the supports, the following factors were kept constant: casting environment - 70°F, 50% relative humidity; solvent evaporating time - 5 seconds; gelation - 0°C, 1 hour; heat treatment - 86°C, 4 minutes.

Table II shows that polyvinyl chloride is the most promising material. Two different pore sizes of this material are promising. BD (.6 micron) gives the highest water flux (31.5 GSFD) and moderately high salt rejection (93%). BS (2.0 microns) gives the best salt rejection (97.3%) and a high water flux (21.3 GSFD).

Teflon gives very high water flux, 30.4 GSFD, but low salt rejection 76.5%.

For the same material, pore size near .6 micron seems to always give higher water flux than other pore sizes for the solution using E398-10 type cellulose acetate. It is true for polyvinyl chloride, as previously shown, and also true for Versapor, mixed esters of cellulose and Millipore proprietary filters.

Use of E400-25 type of cellulose acetate instead of E398-10 cast on different kinds of materials shows quite different results. These tests were made keeping solution composition and other variables the same. The results are shown in Table III. By using E400-25 cellulose acetate, Versapor can get best results, especially in the .9 micron size.

B. <u>CELLULOSE ACETATE TYPE</u>

Five different grades of cellulose acetate (E398-3, E398-10, E394-45, E394-60, E400-25) were studied. The acetyl contents of E398, E394, and E400 are 39.8, 39.4 and 39.9 percent respectively. The viscosities of E398-3, E398-10, E394-45, E394-60, and E400-25 are 1.8 to 3.9; 8.0 to 13.0; 39 to 52; 53 to 75 and 17 to 35 seconds, respectively. The melting point range of these cellulose acetates is from 230 to 260°C.

E400-25 cellulose acetate can give better results for Versapor support than E398-10, E394-3, E394-60, and E400-45. Versapor was the only support studied by Wang[4] when he considered the effect of type of cellulose acetate.

The author has studied the effect of type of cellulose acetate on other different supports, BD (PVC, .6 micron), BS (PVC, 2.0 micron) and VF6 (polyvinylidene fluoride, .45 micron).

Table IV shows how different cellulose acetates affect the water flux and salt rejection for BD supports with all variables except heat treatment temperature kept constant.

E398-10 gives highest water flux and rather high salt rejection, and E398-3 gives the highest salt rejection and a rather high water flux. It is obvious that E398 is the best type for BD (PVC, .6 micron) supports. When BS (PVC, 2.0 microns) was studied, only E398-10 and E398-3 were considered. The best results of 21.3 GSFD average water flux and 97.3% average salt rejection can be obtained by using E398-10 cellulose acetate.

Table V shows that E400-25 is the best cellulose acetate type for polyvinylidene fluoride supports among E398-10, E398-3, E394-60, and E400-45.

C. COMPOSITION OF SOLUTION

1. Ratio of Acetone and Formamide

With the cellulose acetate content at 20%, four different ratios of acetone to formamide, 1, 1.25, 1.75, and 2 have been studied.

The usual ratio used in most runs is 1.5. The purpose of this study is to see if there is any other ratio of acetone to formamide that can give better results than that of 1.5.

Table VI lists those different acetone-formamide ratios with different evaporating time. Three different evaporating times, 10, 20, and 30 seconds have been tested for ratio of 2 with the best results at 20 sec. and the best result at a ratio of 1.75 is when 10 seconds (among three different evaporating times 5, 10, and 20 seconds) evaporating time is used.

When evaporating time is kept the same, increase of the ratio always decreases the salt rejection. It was shown in salt rejection versus acetone-formamide ratio on Figure 1. Five seconds, 10 seconds, and 20 seconds of evaporating time have been plotted. Though ratios around 1.25 to 1.75 could give a little higher water flux, yet they still could not affect flux much. It is shown in water flux versus acetone-formamide ratio on Figure 2. When the evaporating time is kept the same, the flux only shows little differences though the ratios are different. It also shows that short evaporating time always gives higher water flux.

By adjusting the evaporating time and heat treatment temperature, almost the same results could be gotten, though the acetone and formamide ratios are different. For example, Runs 129 and 130, acetone and formamide ratio 2.0, evaporating time 20 seconds, heat treatment 84°C, gave almost the same results as Runs 94 and 95, ratios 1 and 5 seconds

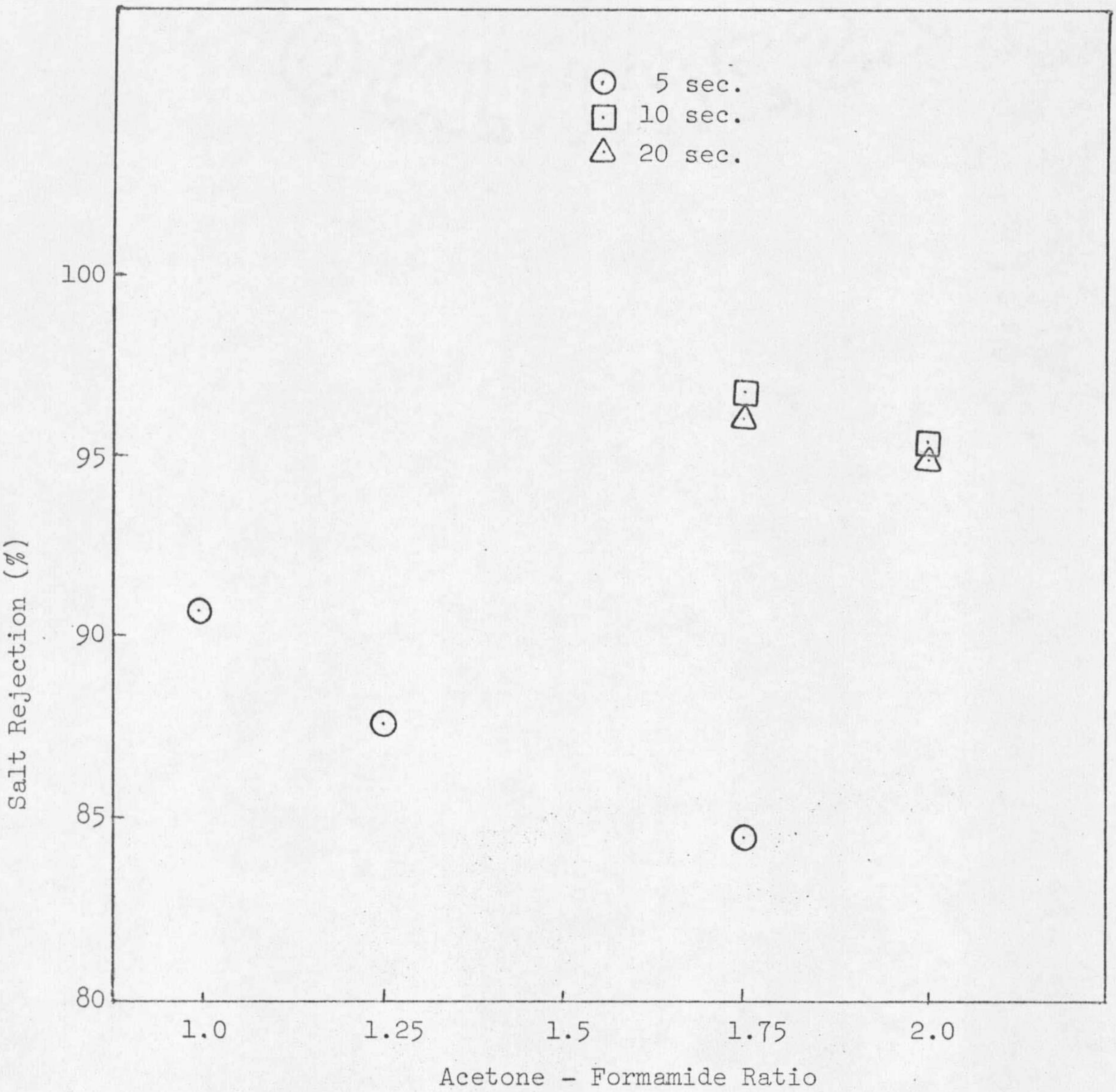

Figure 1. Effect of Acetone-Formamide Ratio and Evaporating Time on Salt Rejection.