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Optimization of the Fabrication Variables of Poly-2-vinylimidazoline Tubular Reverse Osmosis Membranes

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ABSTRACT

The fabrication of tubular poly-2-vinylimidazoline (PVI) composite reverse osmosis (RO) membranes is described. Self-directing optimization experiments were used to derive a formulation for these membranes. Two types of membranes were prepared from two different PVI precursors, each interfacially crosslinked with 3-(chlorosulfonyl)benzoyl chloride. Very good RO properties were exhibited by the "optimized" membranes: in one case 99.4% NaCl retention and a permeate flux of 500 $L/m^2/d$ were obtained. Conditions of evaluation were: 2 MPa, 20°C, 2 g/L NaCl feed, 1 m/s linear flow rate.

INTRODUCTION

Novel ultrathin film (UTF) composite reverse osmosis (RO) membranes were fabricated in situ by the interfacial polycondensation of poly-2-vinylimidazoline (PVI) precursors and the aromatic acid chloride crosslinking agents 3-(chlorosulfonyl)benzoyl chloride (X) or 1,3-benzenedicarbonyl dichloride (Y) upon a polysulfone (PS) support membrane (1).

Early test results of flat-sheet membranes revealed that these novel PVI

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membranes showed promise as low-pressure brack-water desalination membranes (2).

The process of fabricating UTF membranes involves the control of a large number of interrelated factors, all of which play roles in the integrity and RO performance exhibited by the resulting membranes.

Numerous flat-sheet membranes have been made by changing one variable at a time. Rather than using this one-variable-at-a-time approach to optimize the performance of UTF tubular membranes, it was decided to use a sequential approach: the simplex self-directing optimization (SDO) technique, in which all the factors involved are considered simultaneously. SDO is a relatively simple approach to optimization and requires little mathematical manipulation.

In the development of RO membranes from new and noncommercially available starting materials, difficulties can arise due to slight variations between different batches of both membrane-chemicals synthesized (purity and characteristics) and batches of PS support membranes fabricated. By means of SDO, which is a self-correcting sequential technique, an optimum can nonetheless be reached within a relatively short number of experiments.

The optimization experiments were initiated with the following assumptions:

1. A composite UTF membrane system, fabricated from a given set of crosslinking and precursor reagents, should show an intrinsic maximum salt-retention capability when operated at specific conditions.
2. An optimized UTF membrane is regarded as a membrane with the best combination of salt-retention and water permeability performance.

The intention of the SDO study was, first, to establish the potential of the membrane system, in the light of the above points, within the smallest possible number of experiments, and second, to determine the usefulness of the SDO approach to optimize membrane performance.

The intended use for the PVI UTF membrane was in low-pressure desalination. The RO performance, to determine the viability of the chemistry and system geometry for this application, was therefore tested under low-pressure conditions.

PVI, the amine-precursor, is a copolymer comprising 2-imidazoline repeat units and its hydrolyzed form, aminoethylamide repeat units. Two forms of PVI were synthesized (PVI I and PVI II) and used separately as precursors in the fabrication of membranes. (The differences between the two materials are noted in the Experimental Section.)

EXPERIMENTAL

Syntheses of Precursor Materials

PVI was synthesized by the amination of polyacrylonitrile with ethylenediamine (3); the details of the synthesis method are given in an earlier paper (1). The reaction was carried out by two different methods; this resulted in two different copolymeric products, PVI I and PVI II.

The PVI I material was obtained after reaction of PAN and ethylenediamine in *N*,*N*-dimethylformamide (DMF) solvent. The reaction product was isolated by precipitation in acetone, filtering, then drying under reduced pressure in a vacuum oven at 40°C. Upon exposure to the atmosphere, the PVI product, because of its hygroscopic nature, became very tacky and difficult to handle.

PVI II was obtained after reaction of PAN with an excess of ethylenediamine and isolation by freeze-drying. In this reaction, ethylenediamine was used both as reagent and solvent.

PVI III was obtained after partial extraction of ethylenediamine from PVI II by an acetone extraction.

Calculations from ^{13}C NMR analyses of both copolymeric PVI products indicated that PVI I contained up to 22% hydrolyzed repeat units and traces of DMF solvent. PVI II contained fewer hydrolyzed repeat units: an average of 13% for eight determinations. It also contained a quantity of the ethylenediamine reagent which had not been adequately removed during freeze-drying of the crude product.

1,3-Benzenedicarbonyl dichloride (Y), one of the crosslinking reagents used, was commercially available and recrystallized from petroleum ether. The preferred crosslinking agent, 3-(chlorosulfonyl) benzoyl chloride (X), was not commercially available and was synthesized according to the method of Imai and Okunoyama (4).

Fabrication of Tubular Membranes

The procedure for creating a PVI UTF composite RO membrane included the following steps:

1. Microporous tubular polysulfone (PS) substrate membranes were prepared from casting solutions containing either 12% PS (series 224) or 11.5% PS (series 225). The PS Udel 3500P was dissolved in a fixed-ratio mixture of solvents (NMP:dioxane = 3.5:1) (5). Membranes were made in lengths of 3, 1.2, or 0.6 m.
2. The UTF membrane was prepared, in situ, by depositing a thin layer of a dilute aqueous solution of PVI on the surface of the substrate

membrane and then contacting the polymer layer with a dilute hexane solution of the crosslinking agent (X or Y) to create a thin, crosslinked, semipermeable film. The substrate membranes were kept wet, and a 10 minute predraining time was allowed before the membranes were coated.

3. The membranes were dried in a tunnel oven at elevated temperature.

Triethylamine (TEA) and trisodium phosphate (TSP) were added to the aqueous precursor solution as acid acceptors to neutralize the HCl which was formed as a condensation product during the crosslinking reaction. The effect of using sodium lauryl sulfate (SLS) surfactant to facilitate the coating of the membrane with an even film of polymeric precursor and also to assist in the even drainage, was investigated. SLS, when required, was added to the aqueous precursor solution.

Membrane Evaluation

The salt-retention and water-permeability performances of the UTF membranes were evaluated in a closed-loop test system under the following operating conditions: temperature 20°C, linear velocity 100 cm/s, feed pressure 2 MPa, 2 g/L NaCl solution. Six membranes were evaluated simultaneously. The salt-retention and flux performance of each set of six membranes were measured individually, and the performance of the set was calculated as the arithmetic mean of the five best individual results. The mean salt retention and permeate flux of a set of membranes were used in the calculation of their overall performance, given by the A^2/B value.

A method which can be used to compare the RO performance of membranes with different salt retention and water permeability performances was derived from the rejection model and the theories of Lonsdale (6). This was achieved by comparing the pure water permeability coefficient (A) and the salt permeability coefficient (B) of the different membranes at similar operating conditions through the relationship A^2/B. The basic transport equations for these parameters, assuming that the fluxes are diffusional, are (7):

$$\text{Water flux:} \quad F_1 = A[\Delta P - (\pi_w - \pi_p)]$$

$$\text{Salt flux:} \quad F_2 = B(C_w - C_p)$$

where A membrane permeability coefficient for water
B membrane permeability coefficient for salt

ΔP	pressure difference across the membrane
π_w	osmotic pressure at the membrane–brine interface
π_p	osmotic pressure of the product water
C_w	salt concentration at the membrane–brine interface
C_p	salt concentration in the product water

Concentration polarization has an effect on membrane performance and should be incorporated into the above performance equation. For turbulent flow in tubular membranes the concentration polarization ratio is given by (8):

$$C_w/C_b = 1/D_r + (1 - 1/D_r) \exp (F_1 N_{Sc}^{0.67})/(U_b j_d)$$

$$D_r = D_b/D_p = 1/(1 - R)$$

where	C_w/C_b	concentration polarization
	C_w	salt concentration at membrane–brine interface (g/cm^3)
	C_b	salt concentration in bulk of flow (g/cm^3)
	D_r	ratio of bulk brine concentration to product concentration
	F_1	water flux (cm^3·cm^{-2}·s^{-1})
	N_{Sc}	Schmidt number for salt diffusion = ν/D
	U_b	bulk brine velocity (cm/s)
	j_d	Chilton–Colburn (dimensionless) mass-transfer factor
	R	membrane salt retention (%)
	ν	kinematic viscosity (cm^2/s)
	D	salt diffusion coefficient (cm^2/s)

The Chilton–Colburn mass transfer factor is

$$j_d = 0.023 N_{Re}^{-0.17}$$

where	N_{Re}	Reynolds number (dimensionless)
	d	tubular membrane inside diameter

expressed as

$$N_{Re} = U_b d/\nu$$

After the necessary assumptions and substitutions have been made, concentration polarization is incorporated into the two performance equations and the following relationships result by which the A and B coefficients can be obtained:

$$C_w/C_b = 1/D_r + (1 - 1/D_r) \exp (F_1 \upsilon^{0.5} d^{0.17})/(0.023 U_b^{0.83})$$

$$F_2 = F_1 C_p \text{ (neglect density differences)}$$

$$A = F_1/[\Delta P - \pi_b(C_w/C_b) + \pi_b/D_r]$$

$$B = F_2/C_b(C_w/C_b' - 1/D_r)$$

SDO Optimization

The intention of the optimization of the membrane was to determine what the upper limit in salt retention was and to establish the fabrication formulation of such a membrane. To achieve this, the simplex technique of SDO was used. This, in essence, is an easy approach to empirical optimization of a system involving multiple factors. The method does not become unmanagable when large numbers of variables are involved in the study; on the contrary, the method was designed specifically to accommodate such situations.

In this method a regular geometric figure (known as the base simplex) is used as the basis. To arrange the initial simplex, $n + 1$ trials (experiments) in n dimensions (n = number of factors) are set up in such a way that orthogonality between factors and their effects are ensured (9).

It is only necessary to set up the first simplex, as coordinates for the next simplex are generated from the previous set of trials.

The method progresses toward the optimum along the route of steepest ascent and converges reasonably rapidly. Movement from one simplex to the next is governed by the following rules (10):

1. In a simplex, discard the experimental trial(s) with the least acceptable response (i.e., in this case the lowest A^2/B value) and replace it (them) by its (their) mirror image. The coordinates of the new trial(s) are given by twice the average of the coordinates of the remaining trials, minus the coordinates of the rejected trial (see Table 1).
2. When a newly generated trial has the least acceptable response, care must be taken to ensure that when this trial is rejected, the new trial generated is not its mirror image.

DISCUSSION AND RESULTS

Self-Directing Optimization, PVI I RO Membrane Formulations

Some understanding of the UTF membrane-fabrication formulations was gained from experience with flat-sheet membranes (11), and these formulations allowed initial selections to be made of factors and their levels for the SDO program. However, it was not known to what extent fabrication conditions of the small (50 cm^2) flat-sheet membranes would be applicable to tubular membranes.

The 12 factors which were selected for investigation in the SDO study of the PVI membranes are shown in Table 1 (5). The experimental design or treatments, according to which the initial 14 sets of UTF PVI I membranes were fabricated, that is, trials I-1 to I-14, are shown in Table 2. The data in the table are those for the 3-m long membranes and are ranked according to their A^2/B response from the "best" (i.e., treatment combination I-12) to the "worst" (i.e., treatment I-5). These 14 trials were replicated three times. In each replicate, sets of membranes of different lengths were produced by either the fill-coating or the immersion-coating method. This allowed comparisons to be made of the performances of 3-m long membranes produced by fill-coating and the 0.6-m and 1.2-m long membranes produced by immersion-coating. The salt retention and flux performances of the sets of membranes of different lengths are given in Table 3. It was concluded that the average performance of the 3-m membranes prepared by the fill-coating technique appeared to be superior to that of the 1.2- and 0.6-m membranes prepared by dip-coating.

The new coordinates generated for the second simplex, by calculation (9), are illustrated in the lower half of Table 2. The optimum number of trials to discard was shown to be 10.

TABLE 1

Factor Levels for First SDO Experiment Conducted on the PVI I/X Membrane

Factor	Factor level Low	Factor level High
A Concentration PVI I (mass%)	0.8	3.0
B Surfactant [SLS] (mass%)	0	0.4
C Acid acceptor [TEA] (mass%)	0.1	0.5
D Acid acceptor [TSP] (mass%)	0	0.1
E Precursor contact time (min)	15	30
F Precursor draining time (min)	7	11
G Concentration X (mass%)	0.9	2.5
H Concentration Y (mass%)	0	0.4
J Crosslink reagent contact time (min)	3	6
K Post-crosslink air-drying time (min)	5	10
L Oven temperature (°C)	90	115
M Oven residence time (min)	7	12

TABLE 2
First Simplex Design Matrix, PVI I/X 3-m Membranes[a]

Trial	Factors[b]												A^2/B value
	A	B	C	D	E	F	G	H	J	K	L	M	
					Coordinate points for first simplex—"best" response								
I-12	3.0	0	0.5	0.1	15	7	0.9	0	6	5	114	11.67	2.56×10^{-5}
I-9	3.0	0	0.1	0	15	11	2.5	0	6	5	90	6.5	2.46×10^{-5}
I-11	3.0	0	0.5	0	30	7	2.5	0.4	3	5	115	7.0	2.39×10^{-5}
I-14	3.0	0.4	0.1	0.1	15	7	2.5	0	3	10	91	10.5	2.30×10^{-5}
Mean	3.0	0.1	0.3	0.05	18.8	8	2.1	0.1	4.5	6.25	102.5	8.92	
2 × Mean	6.0	0.2	0.6	0.1	37.5	16	4.2	0.2	9	12.5	205	17.84	
					Coordinate points for first simplex—"worst" response								
I-13	3.0	0.4	0.1	0	30	7	0.9	0.4	6	10	91	7.0	1.83×10^{-5}
I-4	0.8	0	0.5	0.1	30	11	2.5	0	3	10	92	7.0	1.75×10^{-5}
I-10	3.0	0	0.1	0.1	30	11	0.9	0.4	3	5	89	11.5	1.39×10^{-5}
I-1	0.8	0	0.1	0	30	7	0.9	0	3	10	116	7.5	1.21×10^{-5}
I-2	0.8	0	0.1	0.1	15	7	2.5	0.4	6	10	116	7.0	1.12×10^{-5}
I-3	0.8	0	0.5	0	15	11	0.9	0.4	6	10	84	12.0	1.04×10^{-5}
I-8	0.8	0.4	0.5	0.1	15	7	0.9	0.4	3	5	91	7.0	0.76×10^{-5}
I-6	0.8	0.4	0.1	0.1	30	11	0.9	0	6	5	115	7.0	0.54×10^{-5}
I-7	0.8	0.4	0.5	0	30	7	2.5	0	6	5	90	12.0	0.47×10^{-5}
I-5	0.8	0.4	0.1	0	15	11	2.5	0.4	3	5	116	15.0	0.33×10^{-5}

	New coordinate points generated for second simplex for the "worst" points of the first simplex												
I-15	3.0	0	0.5	0.1	7.5	9	3.3	0	3	2.5	114	10.84	From I-13
I-16	4.0	0.2	0.1	0	7.5	5	1.7	0.2	6	2.5	113	10.84	From I-4
I-17	3.0	0.2	0.5	0	7.5	5	3.3	0	6	7.5	116	6.34	From I-10
I-18	4.0	0.2	0.5	0.1	7.5	9	3.3	0.2	6	2.5	89	10.34	From I-1
I-19	4.0	0.2	0.5	0	22.5	9	1.7	0	3	2.5	89	10.84	From I-2
I-20	4.0	0.2	0.1	0.1	22.5	5	3.3	0	3	2.5	121	5.84	From I-3
I-21	4.0	0	0.1	0	22.5	9	3.3	0	6	7.5	114	10.84	From I-8
I-22	4.0	0	0.5	0	7.5	5	3.3	0.2	3	7.5	90	10.84	From I-6
I-23	4.0	0	0.1	0.1	7.5	9	1.7	0.2	3	7.5	115	5.84	From I-7
I-24	4.0	0	0.5	0.1	22.5	5	1.7	0	6	7.5	89	2.84	From I-5

[a] Absolute values have been taken where the signs of new points generated were negative.

[b] A = Concentration PVI I.
B = Surfactant [SLS].
C = Acid acceptor [TEA].
D = Acid acceptor [TSP].
E = Precursor contact time.
F = Precursor draining time.
G = Concentration X.
H = Concentration Y.
J = Crosslink reagent contact time.
K = Post-crosslink air-drying time.
L = Oven temperature.
M = Oven residence time.

TABLE 3
PVI I/X Membrane Performance: 0.6-m, 1.2-m, and 3-m Membrane Lengths (Simplex 1)

	3-m membranes, fill-coated		1.2-m membranes, immersion-coated		0.6-m membranes, immersion-coated	
Trial	Retention (%)	Flux (L/m^2/d)	Retention (%)	Flux (L/m^2/d)	Retention (%)	Flux (L/m^2/d)
I-12	86.7 ± 1.7	1000 ± 61	90.8 ± 1.1	590 ± 85	90.4 ± 1.0	430 ± 54
I-9	89.1 ± 1.4	790 ± 0.8	83.5 ± 0.8	720 ± 45	86.7 ± 0.5	610 ± 23
I-11	94.5 ± 1.2	400 ± 89	89.6 ± 1.0	270 ± 29	89.8 ± 0.3	190 ± 14
I-14	95.1 ± 0.7	230 ± 39	95.9 ± 0.4	250 ± 20	94.1 ± 1.7	180 ± 8
I-13	91.9 ± 0.9	430 ± 14	92.5 ± 1.0	400 ± 42	90.0 ± 0.3	360 ± 48
I-4	89.8 ± 1.2	520 ± 10	75.0 ± 1.8	820 ± 31	74.7 ± 4.1	810 ± 18
I-10	81.0 ± 0.8	790 ± 25	81.9 ± 2.7	840 ± 125	84.6 ± 1.5	750 ± 65
I-1	79.7 ± 0.8	740 ± 31	76.8 ± 1.1	900 ± 59	66.8 ± 1.5	1300 ± 105
I-2	81.0 ± 1.5	650 ± 67	76.5 ± 1.6	560 ± 18	75.8 ± 1.5	650 ± 93
I-3	75.9 ± 2.4	750 ± 19				
I-8	64.3 ± 2.5	850 ± 37	63.4 ± 3.0	920 ± 116	54.0 ± 1.8	1300 ± 82
I-6	76.0 ± 1.0	380 ± 59	78.1 ± 2.5	270 ± 48	78.9 ± 1.4	260 ± 67
I-7	68.8 ± 3.7	440 ± 5	55.4 ± 4.4	700 ± 84	44.1 ± 3.6	710 ± 141
I-5	33.7 ± 3.7	530 ± 190	49.8 ± 1.4	520 ± 50	39.2 ± 0.7	670 ± 202
Mean	79.4	596	77.6	597	74.5	632

Table 4 illustrates how the performances of membranes improved from simplex to simplex as the SDO experiment progressed. In this table, the performances of the three membrane sets with the "best" performance ratings obtained from each of the six simplexes conducted are shown. No further improvement could be obtained beyond Simplex 6, and the optimization study on PVI I membranes was terminated. The fabrication formulation, corresponding to the "best" trial, I-74, is listed in Table 5.

Two factors were excluded at an early stage from the study (Simplex 3), as there was an indication that they had a detrimental effect on membrane performance: these two factors were SLS (surfactant) and 1,3-benzenedicarbonyl dichloride (Y, crosslinking reagent). Omission of Y from the tubular membrane study confirmed earlier findings, based on work with flat-sheet membranes (1, 11), that PVI I/Y membranes were inferior to PVI I/X membranes.

The movement in the variable space as optimum membrane performance is approached for each of the remaining 10 factors investigated is

TABLE 4
Summary of Best Performances of PVI I/X Membranes

Trial	A^2/B value	Retention (%)	Flux (L/m^2/d)	Simplex
I-12	2.56×10^{-5}	86.7 ± 1.7	1000 ± 61	1
I-9	2.46×10^{-5}	89.1 ± 1.4	790 ± 46	
I-11	2.39×10^{-5}	93.9 ± 1.0	420 ± 78	
I-12	2.56×10^{-5}	86.7 ± 1.7	1000 ± 61	2
I-9	2.46×10^{-5}	89.1 ± 1.4	790 ± 46	
I-23	1.06×10^{-5}	86.4 ± 0.7	420 ± 27	
I-12	2.56×10^{-5}	86.7 ± 1.7	1000 ± 61	3
I-9	2.46×10^{-5}	89.1 ± 1.4	790 ± 46	
I-26	0.77×10^{-5}	81.6 ± 1.6	420 ± 24	
I-47	5.75×10^{-5}	96.1 ± 0.3	650 ± 46	4
I-41	3.21×10^{-5}	96.4 ± 0.5	330 ± 29	
I-46	2.49×10^{-5}	87.5 ± 0.9	920 ± 69	
I-61	6.37×10^{-5}	97.2 ± 0.2	500 ± 38	5
I-47	5.75×10^{-5}	96.1 ± 0.3	650 ± 46	
I-52	4.92×10^{-5}	97.1 ± 0.7	410 ± 19	
I-74	8.98×10^{-5}	97.1 ± 0.1	730 ± 24	6
I-65	7.88×10^{-5}	97.2 ± 0.1	620 ± 38	
I-66	7.87×10^{-5}	98.0 ± 0.2	440 ± 33	

TABLE 5
Optimum PVI I/X Membrane Fabrication Formulation (Trial I-74) and RO Performance

Factor	Level
A Concentration PVI I (mass %)	5.0
~~B Surfactant (SLS)~~	
C Acid acceptor [TEA] (mass%)	1.1
D Acid acceptor [TSP] (mass%)	0.14
E Precursor contact time (min)	43
F Precursor draining time (min)	1.5
G Concentration X (mass%)	4.5
~~H Concentration Y~~	
J Crosslink reagent contact time (min)	3
K Post-crosslink air-drying time (min)	10
L Oven temperature (°C)	95
M Oven residence time (min)	5.4
Performance: Retention	97.1 ± 0.1%
Flux	730 ± 24.1 L/m^2/d
A^2/B value	8.89×10^{-5}

indicated in Table 6. Here, the means of the variables for the three "best" membranes (Table 4) from each of the six simplexes are shown.

An interesting feature of the formulation shown for Trial I-74 (regarded as optimum) in Table 6 is the high precursor concentration (Factor A, 5% by mass) that originated from the SDO study. This concentration was regarded as being very high, especially when compared with solids levels indicated for the making of other UTF composite membrane systems based on polymeric precursors; these generally ranged from 0.7 to 2% by mass (12).

The active role played by the acid-acceptors in the formulation became manifest in the increase in concentration levels of both TEA and TSP (Factors C and D) above their respective starting values. This confirmed that the hydrochloric acid freed during the interfacial polycondensation reaction was detrimental to the fabrication of the membrane and to the eventual desalting barrier structure; neutralization of the acid was necessary to increase the extent of the crosslinking reaction.

At the average temperatures and residence times given in Table 6 for Simplexes 5 and 6 (Factors L and M) and for those of the final formulation (Trial I-74), the membranes were still damp when they were removed from the tunnel oven. This indicated that the membranes actually did not need high curing temperatures for optimum performance which, in turn, indi-

TABLE 6
Mean Trends in the Variable Space of Factors Investigated for the PVI I/X Membrane

	Factors									
Simplex	A	C	D	E	F	G	J	K	L	M
1	3.0	0.37	0.03	20.0	8.33	1.97	5.0	5.0	106	8.4
2	3.3	0.23	0.07	12.5	9.00	1.70	5.0	5.8	106	8.0
3	3.0	0.37	0.03	15.0	9.67	1.43	7.0	3.7	106	8.7
4	4.0	0.56	0.05	22.5	7.66	1.90	6.0	2.3	109	6.1
5	4.3	0.97	0.09	30.0	3.35	2.93	8.7	6.1	88	2.3
6	5.3	1.32	0.19	34.3	2.00	4.64	5.0	11.7	80	3.2
Trial I-74	5.0	1.10	0.14	43	1.5	4.5	3.0	10	95	5.4

Factors	Simplex 1 (base) Table 1
A Concentration PVI I (mass%)	1.9
C Acid acceptor [TEA] (mass%)	0.3
D Acid acceptor [TSP] (mass%)	0.05
E Precursor contact time (min)	22.5
F Precursor draining time (min)	9
G Concentration X (mass%)	1.7
J Crosslink reagent contact time (min)	4.5
K Post-crosslink air-drying time (min)	7.5
L Oven temperature (°C)	102
M Oven residence time (min)	9.5

cated that chemical crosslinking played a primary role in establishing the final PVI I/X membrane matrix, as opposed to thermally induced crosslinking which could take place between adjacent primary amines.

On the other hand, it is possible that excess thermal curing and consequent rapid loss of water from within their respective structures could induce stress in the brittle UTF due to substrate membrane densification or shrinkage of the UTF. As a result, microcracks could form in the UTF which, in turn, would cause leakage of salt, which would result in lower potential salt retention. (Microcracks were clearly observed by optical microscopy in films of PVI I/X produced on glass plates and cured at 110°C for 10 minutes.)

Self-Directing Optimization, PVI II RO Membrane Formulations

When the alternate PVI material, PVI II, became available, the SDO work on PVI I/X membranes had already progressed to the fourth simplex, with Trial I-47 (see Table 7) showing the best results. These fabrication conditions were duplicated and 0.6-m long UTF membranes were prepared, substituting the PVI II precursor for the PVI I material. No water permeated this PVI II/X desalting barrier under standard conditions of evaluation. By reducing the polymer concentration of the PVI II precursor solution (Factor A), the water permeability of the membrane was subsequently improved (the results are summarized in Table 8).

These preliminary results indicated what analysis later confirmed, namely, that the two PVI precursor materials were chemically different. Different precursor concentrations were required to fabricate PVI I/X

TABLE 7
Formulations for Trial I-47, PVI I/X Membrane
(chosen as first replicate for PVI II/X membrane)

Factor	Level
A Concentration PVI polymer (mass%)	4.0
C Acid acceptor [TEA] (mass%)	0.73
D Acid acceptor [TSP] (mass%)	0.07
E Precursor contact time (min)	22.5
F Precursor draining time (min)	6.33
G Concentration X (mass%)	2.17
J Crosslink reagent contact time (min)	8.0
K Post-crosslink air-drying time (min)	4.8
L Oven temperature (°C)	100
M Oven residence time (min)	1.9
Performance: Retention	96.1 ± 0.3%
Flux	650 ± 46 L/m²/d
A^2/B value	5.75×10^{-5}

TABLE 8
Results of First Experimental PVI II/X Membranes[a]

PVI II (mass%)	Retention (%)	Flux (L/m²/d)	A^2/B value
4.0	—	Nil	—
1.0	97.5 ± 0.5	370 ± 22	5.18×10^{-5}
0.5	68.6 ± 4.1	690 ± 146	0.72×10^{-5}

[a] Prepared according to the formulation for Trial I-47, see Table 7, except for the change in PVI II concentration.

and PVI II/X membranes of relatively similar RO performances. (From a practical point of view it was advantageous that low solids concentration of PVI II were required, because this meant that smaller quantities of material needed to be synthesized.)

PVI II UTF membranes were prepared according to formulations (first simplex) shown in Tables 9 and 10. Substrate membranes, similar to those used in the PVI I SDO study (Series 224), were used. The performances in the first simplex (PVI II/X membrane system) are summarized in Table 10 and ranked in decreasing order of their A^2/B values. A second simplex was generated from this data as shown in the lower half of Table 10.

Three SDO experiments were conducted in all. The performance of the four "best" membranes from each simplex are summarized in Table 11. There was no further improvement in the performance of the PVI II/X membranes after the second simplex, and the formulation of membrane II-14 was taken as optimum (Table 12).

SDO optimization of the PVI membranes clearly showed that the two membrane precursor starting materials differed, and that the final SDO formulation for the PVI I membrane (Trial I-74) was not suitable for the fabrication of PVI II membranes (Table 8). A further indication that the materials differed, and also of the suggested "superiority" of PVI II as a membrane precursor material, was that the first 99% salt-retention membrane was produced from this material (II-18, Table 11), as opposed to membranes with a maximum salt-retention of 98% made from the PVI I material (I-66, Table 4). A further observation was that the standard deviation of salt retention decreased as the salt retentions approached 99%.

TABLE 9
Factor Levels for First SDO Experiment Conducted on the PVI II/X Membrane

Factor		Factor level	
		Low	High
A	Concentration PVI II (mass%)	0.8	1.6
B	Acid acceptor [TEA] (mass%)	0.2	0.5
C	Acid acceptor [TSP] (mass%)	0.1	0.3
D	Precursor contact time (min)	15	25
E	Precursor draining time (min)	5	8
F	Concentration X (mass%)	1	2
G	Crosslink reagent contact time (min)	2	4
H	Post-crosslink air-drying time (min)	4	8
J	Oven temperature (°C)	95	105
K	Oven residence time (min)	2	8

TABLE 10
PVI II/X Membrane Formulation and Performance, First Simplex

	Factors[a]												
Trial	A	B	C	D	E	F	G	H	J	K	Retention (%)	Flux (L/m^2/d)	A^2/B value
II-11	0.8	0.2	0.3	15	8	2	4	4	95	2	98.4 ± 0.3	280 ± 28	6.25×10^{-5}
Mean	0.8	0.2	0.3	15	8	2	4	4	95	2			
2 × Mean	1.6	0.4	0.6	30	16	4	8	8	190	4			
II-10	1.6	0.2	0.1	25	5	2	4	8	95	2	98.4 ± 0.3	160 ± 46	3.51×10^{-5}
II-3	0.8	0.5	0.3	25	5	1	2	8	93	2	79.4 ± 3.8	730 ± 95	1.20×10^{-5}
II-6	1.6	0.2	0.1	15	8	1	2	8	96	8	65.0 ± 1.9	1300 ± 164	1.14×10^{-5}
II-7	0.8	0.2	0.1	25	5	1	4	4	102	8	92.0 ± 2.8	250 ± 97	1.09×10^{-5}
II-4	1.0	0.5	0.3	15	5	1	4	4	96	8	67.9 ± 1.2	880 ± 55	0.89×10^{-5}
II-9	0.8	0.5	0.1	15	8	1	4	8	102	2	76.8 ± 4.8	610 ± 97	0.89×10^{-5}
II-1	1.6	0.5	0.3	25	8	2	4	8	107	8	75.5 ± 8.3	260 ± 53	0.37×10^{-5}
II-2	1.6	0.2	0.3	25	8	1	2	4	104	2	66.9 ± 4.1	140 ± 23	0.15×10^{-5}
II-5	1.6	0.5	0.1	15	5	2	2	4	103	2	74.4 ± 6.9	73 ± 10	0.10×10^{-5}
II-8	0.8	0.2	0.3	15	5	2	2	8	107	8	76.4 ± 5.2	60 ± 23	0.09×10^{-5}

	Coordinate points generated for the second simplex									
II-12	1.2	0.2	0.5	5	11	2	4	3	95	2
II-13	0.8	0	0.3	5	11	3	6	3	97	2
II-14	1.2	0.2		0.5	185	3	6	3	94	4
II-15	0.8	0.2	0.5	5	11	3	4	4	88	4
II-16	0.6	0	0.3	15	11	3	4	4	94	4
II-17	0.8	0	0.5	15	8	3	4	3	88	2
II-18	1.2	0	0.3	5	8	2	4	3	83	4
II-19	1.2	0.2	0.3	5	8	3	6	4	86	2
II-20	1.2	9	0.5	15	11	2	6	4	87	2
II-21	0.8	0.2	0.3	15	11	2	6	3	83	4

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[a] A = Concentration PVI II.
B = Acid acceptor [TEA].
C = Acid acceptor [TSP].
D = Precursor contact time.
E = Precursor draining time.
F = Concentration X.
G = Crosslink reagent contact time.
H = Post-crosslink air-drying time.
J = Oven temperature.
K = Oven residence time.

TABLE 11
Summary of Best Performances of PVI II/X Membranes

Trial	A^2/B value	Retention (%)	Flux (L/m²/d)	Simplex
II-11	6.25×10^{-5}	98.4 ± 0.3	280 ± 28	1
II-10	3.51×10^{-5}	98.4 ± 0.3	160 ± 46	
II-3	1.20×10^{-5}	79.4 ± 3.8	730 ± 95	
II-6	1.14×10^{-5}	65.0 ± 1.9	1300 ± 164	
II-14	10.90×10^{-5}	98.2 ± 0.7	560 ± 150	2
II-18	9.96×10^{-5}	99.2 ± 0.1	220 ± 100	
II-17	8.83×10^{-5}	98.8 ± 0.4	310 ± 230	
II-20	8.61×10^{-5}	98.9 ± 0.2	260 ± 147	
II-14	10.90×10^{-5}	98.2 ± 0.7	560 ± 150	3
II-18	9.96×10^{-5}	99.2 ± 0.1	220 ± 100	
II-17	8.83×10^{-5}	98.8 ± 0.4	310 ± 230	
II-20	8.61×10^{-5}	98.9 ± 0.2	260 ± 147	

In comparison with the PVI I membrane system, fewer experimental trials were conducted on the SDO of PVI II formulations before the simplex converged to a solution. Possible reasons for this were that the performance of membranes produced by the fill-coating technique was more consistent, or that the base points of the first simplex were chosen closer to the respective maxima of the factors. (Ideally, another simplex should be generated at coordinates away from that of the solution, to determine whether a second SDO study would converge to the same solution.)

The concentrations of the acid acceptors included in the precursor solution were lower in the II-14 formulation than in the I-74 formulation. A possible explanation is the presence of unreacted ethylenediamine which was found to be present in the freeze-dried PVI II product. Ethylenediamine can both react as an acid acceptor and react with 3-(chlorosulfonyl) benzoyl chloride (X). At a stage in the crosslinking reaction when the mobility of PVI II is hindered due to the crosslinked network which has been formed, unreacted ethylenediamine retains its mobility and can diffuse toward the interface to participate in the crosslinking reaction. As 3-(chlorosulfonyl) benzoyl chloride and ethylenediamine are both difunctional, a linear polymer will result from a reaction between these two compounds. (Crosslinking results only if the end groups on the linear polymer chain react with the PVI II matrix.) This chemical modification of the desalting matrix is expected to, and did, result in lower salt retention.

A quantitative analytical technique was therefore devised to determine the relative concentrations of ethylenediamine in each batch of PVI II

TABLE 12
Optimum PVI II/X Membrane Fabrication Formulation (Trial II-14) and RO Performance

Factor	Level
A Concentration PVI II (mass%)	1.2
B Acid acceptor [TEA] (mass%)	0.2
C Acid acceptor [TSP] (mass%)	0.5
D Precursor contact time (min)	15
E Precursor draining time (min)	8
F Concentration X (mass%)	3
G Crosslink reagent contact time (min)	6
H Post-crosslink air-drying time (min)	3
J Oven temperature (°C)	95
K Oven residence time (min)	4
Performance: Retention	98.2 ± 0.7%
Flux	560 ± 150 L/m^2/d
A^2/B value	10.9×10^{-5}

synthesized (13), and only batches with an ethylenediamine content which was considered to be below an "acceptable" level (<20%) were considered for use in membrane making.

Initial PVI/X membranes, prepared from a PVI precursor with a reduced ethylenediamine content (PVI III) and fabricated according to Trial II-14 gave better RO performances than the optimized PVI II/X membrane, as is described in an earlier paper (14). This illustrates that an optimum formulation, aimed at by the SDO method, is obtained for a given system. Once the system is altered, the optimization must be repeated to find a new optimum fabrication formulation for that new system.

Substrate Membranes

The effect of different PS substrate membranes on the RO performances of PVI II/X membranes, produced according to their optimum formulation (Trial II-14), are shown in Table 13. The performances were recorded for 3-m fill-coated membranes.

CONCLUSIONS

The science of any membrane system includes an examination of a multitude of fabrication variables. Membrane research involves, there-

TABLE 13

Results of PVI II/X Membranes Made from Different Substrate Membrane Batches

Substrate lot code	Retention (%)	Flux (L/m^2/d)	A^2/B value
107T35S224	99.4 ± 0.1	500 ± 103	28.7×10^{-5}
108T35S225	99.4 ± 0.4	450 ± 88	26.6×10^{-5}
107T35S224	99.2 ± 0.2	490 ± 103	22.7×10^{-5}
108T35S225	99.2 ± 0.6	470 ± 76	19.5×10^{-5}
102T35S224	99.0 ± 0.1	340 ± 39	12.8×10^{-5}
103T35S224	98.5 ± 0.3	390 ± 169	9.8×10^{-5}

fore, a study of these variables and of their interactions in order to obtain a better understanding of the science involved.

Although the fabrication of membranes with good and consistent performance requires that many of these variables be controlled, it has been shown that it is possible to make membranes with good performances by controlling only a few. Using the SDO technique of optimization requires only a limited number of experiments to determine the formulation according to which membranes with inherent optimum performances can be made.

The optimization study of the PVI/X UTF RO membrane system therefore proved successful in two ways:

1. It was demonstrated that up to 12 membrane formulation variables could be studied simultaneously, in a self-directing optimization approach, to yield membranes with high salt retention and permeate flux (shown in Tables 5 and 12).
2. Tubular UTF composite membranes with very good RO properties can be fabricated from poly-2-vinylimidazoline crosslinked with 3-(chlorosulfonyl) benzoyl chloride. In an optimum case, a tubular membrane with a sodium chloride retention of 99.4 ± 0.1% and a permeate flux of 500 L/m^2/d (A^2/B value 28.7×10^{-5}) could be fabricated. Such results warranted the use of the PVI/X membrane as a commercial brack-water desalting membrane.

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