

# Studies on Cellulose Acetate-Carboxylated Polysulfone Blend Ultrafiltration Membranes. III

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**ABSTRACT:** Enhancement of the hydrophilicity in polymeric membrane materials results in membranes with higher flux and better membrane characteristics. Hence, polysulfone was carboxylated and ultrafiltration membranes were prepared from blends of cellulose acetate and carboxylated polysulfones having various degrees of carboxylation with a total polymer concentration of 20 wt % in casting solution and at different blend polymer compositions. The effects of degree of carboxylation on membrane characteristics such as compaction, pure water flux, and membrane hydraulic resistance ( $R_m$ ) have been investigated. The influence of the polymer concentration in the blend solution on the performance of blend membranes at various blend poly-

mer compositions has also been investigated and compared with that of blend membranes prepared from blends of cellulose acetate and polysulfone or carboxylated polysulfone with a total polymer concentration of 17.5 wt %. Further, the solute rejection performance of the membranes has also been investigated by subjecting the membranes to metal ion permeation studies using polyelectrolyte-enhanced ultrafiltration. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 97: 976–988, 2005

**Key words:** carboxylated polysulfone; degree of polymerization; cellulose acetate; blends; membranes; ultrafiltration

## INTRODUCTION

Membrane processes are gaining momentum in view of their wide application in various industries such as chemical, food, pharmaceutical, and metal finishing industries.<sup>1</sup> Even though membranes are normally fabricated from commercial polymers,<sup>2</sup> the adaptability of membrane processes to a wide range of applications stems from the development of new polymers or modifications of the existing polymers.<sup>3</sup> Although several methods are available for the preparation of ultrafiltration membranes, the phase inversion technique has been found to be versatile for making new types of modified ultrafiltration membranes, as the conditions of membrane formation can be varied widely to prepare membranes with desired morphology and pore structure. Hence, this technique has been applied and a series of membranes based on cellulose acetate and polysulfone has been prepared in the present investigation.

In view of the better performance of cellulose acetate,<sup>4,5</sup> polysulfone,<sup>6–10</sup> and carboxylated polysulfone<sup>11–13</sup> as membrane materials, these polymers have been chosen for the preparation of membranes in the

present investigation. Further, ultrafiltration membranes prepared by blending cellulose acetate with polysulfone have been found to exhibit better performance compared to membranes prepared from individual polymers.<sup>14–16</sup> Hydrophilic polysulfones containing pendant carboxylic acid groups have been prepared by chemical modification of polysulfone (Udel P-3500), by a process of metallation and subsequent carboxylation.<sup>17–20</sup> Carboxylated polysulfone (CPSU) acquires hydrophilicity through its carboxyl groups and its hydrophilicity is proportional to the degree of carboxylation, i.e., the number of  $-\text{COOH}$  groups per repeat unit.<sup>20</sup> Hence, flat-sheet, blend, ultrafiltration membranes based on blends of cellulose acetate (CA), polysulfone (PSU), and CPSU with a total polymer concentration of 17.5 wt % have been prepared by phase inversion technique in our earlier investigations and characterized in terms of pure water flux, water content, and membrane hydraulic resistance.<sup>21,22</sup> The membranes were also subjected to permeation of metal ions such as Cu(II), Cd(II), and Ni(II) to investigate the solute rejection performance. Polyelectrolyte-enhanced ultrafiltration with synthetic surfactants is a recently developed technique, which can remove heavy metal ions and other low-molecular-weight ions from aqueous waste streams at relatively lower cost and without a phase change.<sup>23–32</sup> Since several workers<sup>32–39</sup> have used polyethyleneimine with its better efficiency of separation, it was chosen as the complexing agent in the present investigation.

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The present study was conducted to investigate the effects of polymer concentration and degree of carboxylation of the blend polymer component, carboxylated polysulfone, on the performance of membranes. Blend membranes were prepared from polymer casting solutions of cellulose acetate and carboxylated polysulfones of 0, 0.14, 0.43, and 0.75° of carboxylation with total polymer concentration of casting solution of 20 wt % and at varied blend polymer compositions of 85/15, 80/20, and 75/25 wt % of CA/CPSU and characterized. The results were compared with the performance of membranes prepared in our earlier studies<sup>21,22</sup> with a total polymer concentration of casting solution of 17.5 wt % and the effects of degree of carboxylation of the blend polymer component and polymer concentration on membrane performance are discussed.

## EXPERIMENTAL

### Materials

Commercial grade MYCEL cellulose acetate procured from Mysore Acetate and Chemicals Company Ltd., Mysore, India, and commercial grade polysulfone, Udel P-3500, received as a gift sample from Amoco Polymers, were used as such. Carboxylated polysulfone of 0.14° of carboxylation was prepared by a two-stage process as reported earlier.<sup>18</sup> The degree of carboxylation of the prepared polymer was 0.14.<sup>40</sup> Carboxylated polysulfones of 0.43 and 0.75° of carboxylation were received from the National Research Council of Canada.

Analar grade *N,N*-dimethylformamide (DMF) was obtained from Qualigens Fine Chemicals, Mumbai, India, and sodium lauryl sulfate was procured from Glaxo India Ltd., Mumbai, India. DMF was sieved through molecular sieves (Type-4Å) for removing moisture and stored in dried conditions prior to use. Acetone procured from E-Merck, Germany, was used as received. Analar grades of copper sulfate, nickel sulfate, and cadmium sulfate were received from E-Merck, Ltd. (India), and used as such in the preparation of aqueous metal ion solutions. A 50% aqueous solution of polyethyleneimine of 600-1000 kDa molecular weight procured from Fluka AG, Switzerland, was used.

### Characterization of polymers

The thermal stability and the glass transition temperature of the polymers used in the investigation were studied by thermogravimetric analysis (Mettler, Model TA 3000) and differential scanning calorimetry (Dupont 2000, Model DSC 2910), respectively.<sup>22</sup>

TABLE I  
Membrane Formulations

No.	CA (wt %)	CPSU (wt %)	CPSU (DC)
1	100	0	0
2	0	100	0.75
3	85	15	0
4	80	20	0
5	75	25	0
6	85	15	0.14
7	80	20	0.14
8	75	25	0.14
9	85	15	0.43
10	80	20	0.43
11	75	25	0.43
12	85	15	0.75
13	80	20	0.75
14	75	25	0.75

Note. Polymer 20 wt %; Solvent 80 wt %.

### Preparation of blend membranes

Blend membranes of cellulose acetate and carboxylated polysulfone were prepared from polymer solutions with a total polymer concentration of casting solution of 20 wt % and at blend compositions of 85/15, 80/20, and 75/25 wt % of CA/CPSU. The membrane formulations used in this investigation are presented in Table I. The film casting conditions were maintained as in our earlier investigations.<sup>22</sup> The membrane-casting chamber was maintained at a temperature of  $24 \pm 1^\circ\text{C}$  and a relative humidity of  $50 \pm 2\%$ . The gelation bath of 2 L consisting of 2.5% (v/v) DMF (solvent) and 0.2 wt % surfactant, sodium lauryl sulfate in distilled water (nonsolvent), was maintained at  $12 \pm 2^\circ\text{C}$ . Although polysulfone and carboxylated polysulfones of lower degrees of carboxylation undergo phase separation at room conditions, CA/PSU, CA/CPSU blend membranes have been prepared at room conditions owing to the higher hydrophilicity.<sup>20</sup> The membranes were cast over a glass plate using a doctor blade. The thickness of the membranes was maintained at  $0.22 \pm 0.02$  mm and measured with a micrometer with a precision of 0.01 mm. The membrane sheets were subsequently stored in 0.1% formalin solution in distilled water to prevent microbial attack.

### Characterization of blend membranes

The membranes were cut into parts with effective membrane area of  $38.5\text{ cm}^2$  and fitted in the ultrafiltration stirred batch cell with a capacity of 450 mL, supplied by M/S Spectrum, Inc.. The membranes were compacted at a transmembrane pressure of 414 kPa prior to further characterization. The pure water flux (PWF) and hydraulic resistance of the membranes were determined and the influence of degree of car-

boxylation of polysulfone on the above membrane characteristics were evaluated. All experiments were conducted in triplicate and the mean values of the results are presented and discussed.

### Compaction

The membranes were washed thoroughly and loaded in the UF test cell connected to the pressurized reservoir filled with distilled water. The initial flux of the membrane was measured after fixing the membrane in the UF cell and pressurizing it at a transmembrane pressure of 414 kPa for 20 s. The water flux was measured at an interval of 1 h. The flux declined sharply in the earlier hours and reached a steady state after 3–4 h of compaction.<sup>41</sup> These compacted membranes, after steady-state water flux was obtained, were used in subsequent ultrafiltration experiments.

### Pure water flux

The membranes compacted at a transmembrane pressure of 414 kPa were then subjected to a transmembrane pressure of 345 kPa and the PWF was measured. The PWF of the membrane was calculated using the equation<sup>42</sup>

$$J_w = Q/A\Delta t,$$

where  $Q$  is the amount of permeate (L);  $J_w$  is the water flux ( $L\ m^{-2}\ h^{-1}$ );  $\Delta t$  is the sampling time (h); and  $A$  is the membrane area ( $m^2$ ).

### Membrane hydraulic resistance

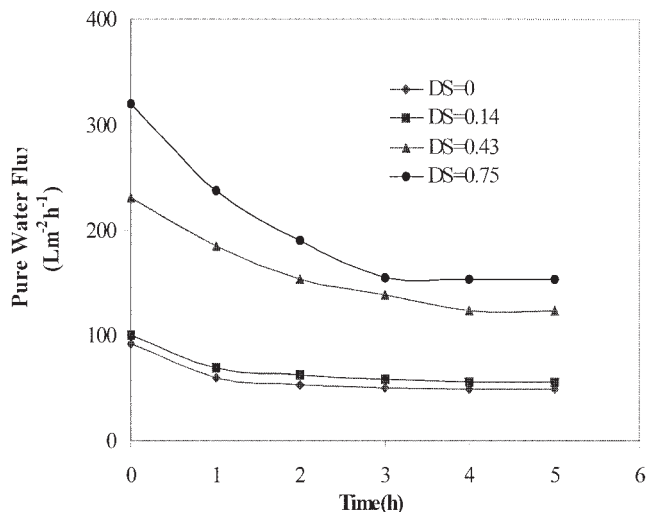
The pure water flux of the membranes at different transmembrane pressures, viz., 69, 138, 207, 276, 345, and 414 kPa, was measured. The hydraulic resistances of the membranes ( $R_m$ ) were evaluated from the slope of the plot of pure water flux versus pressure difference ( $\Delta P$ ) using the equation<sup>43</sup>

$$J_w = \Delta P/R_m,$$

where  $J_w$  is the water flux ( $L\ m^{-2}\ h^{-1}$ ),  $\Delta P$  (kPa) is the pressure difference, and  $R_m$  is the membrane resistance ( $kPa/L\ m^{-2}\ h^{-1}$ ).

### Metal-ion rejection

Aqueous solutions of Cu(II), Cd(II), and Ni(II) of 1000 ppm concentration were prepared independently in 1 wt % solution of polyethyleneimine (PEI) in deionized water. The pH of the solutions was adjusted to 6.25. Solutions containing PEI and metal ions were mixed and left standing for 5 days to complete binding.<sup>36–38</sup>



**Figure 1** Compaction of CA/CPSU (85/15 wt %) blend membranes of various degrees of carboxylation. Polymer concentration = 20 wt %.

Solute separation studies were carried out with the metal ion–PEI chelate solutions. The permeate flux was measured by collecting the permeate at a transmembrane pressure of 345 kPa over measured time intervals and the percentage solute rejection was determined by measuring the metal ion concentrations of the feed and the permeate of individual metal ion solutions using an atomic absorption spectrophotometer (Perkin–Elmer-2380) at  $\lambda_{max}$  of 280 nm.

The percentage solute rejection was calculated as

$$\% SR = (1 - C_p/C_f)100$$

where %SR is the solute rejection (%), and  $C_p$  and  $C_f$  are concentrations of the solute in the permeate and feed.

## RESULTS AND DISCUSSION

### Compaction of membranes

The compaction of membranes makes the membrane pores uniform and rigid and facilitates a steady flux. The membranes were compacted at a pressure of 414 kPa and the results are presented in Figures 1 to 3 for 85/15, 80/20, and 75/25 wt % CA/CPSU membranes, respectively.

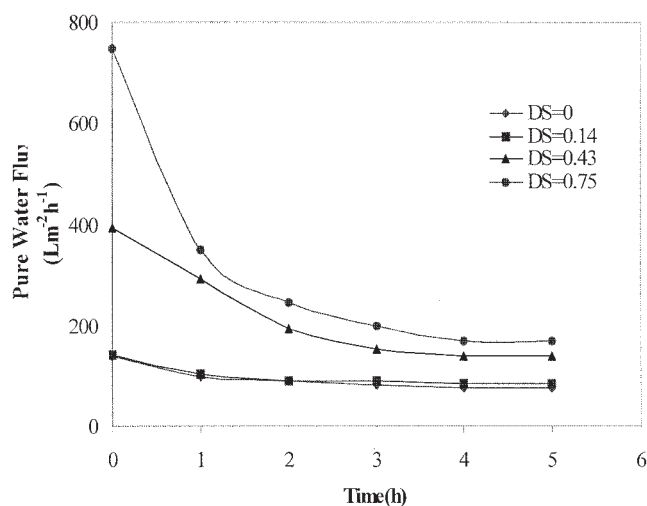
### Effect of degree of carboxylation on compaction

All blend membranes were observed to be compacted after 3 h of compaction. The steady-state pure water flux of the blend membrane (85/15 wt %) prepared from a casting solution of 20 wt % polymer concentration consisting of a blend of 85 wt % of cellulose acetate with 15 wt % of polysulfone of zero degree of

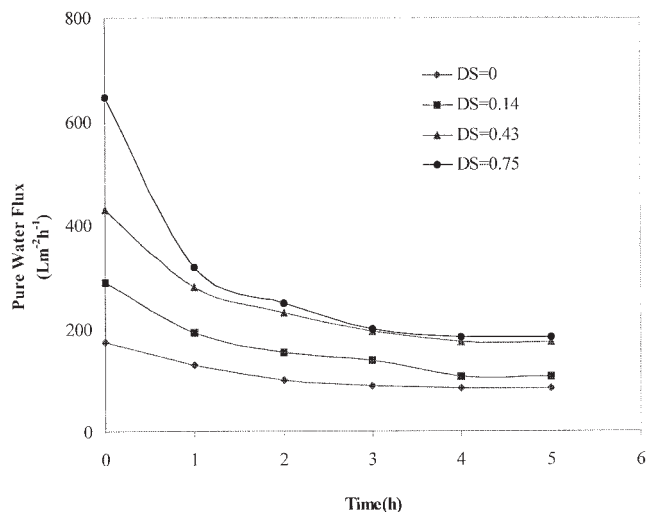
carboxylation as casting solution was observed to be  $48.31 \text{ L m}^{-2} \text{ h}^{-1}$  (Fig. 1). When the polysulfone in the blend was replaced with 15 wt % of carboxylated polysulfone of 0.14° of carboxylation (85/15 wt %), the steady-state flux was found to increase to  $56.10 \text{ L m}^{-2} \text{ h}^{-1}$ . This may be due to the fact that the carboxyl groups impart an increase in the hydrogen bonding and polar contributions,<sup>20</sup> resulting in an enhancement of the hydrophilicity of the resultant blend membrane, and leads to a comparatively higher steady-state pure water flux.

Further, when the degree of carboxylation of the blend component (CPSU) of casting solution of a particular blend composition of 85/15 wt % is increased, the steady-state flux of the blend membranes also keeps on increasing and the results are shown in Figure 1. Thus, an addition of carboxylated polysulfone of 0.43° of substitution up to 15 wt % in the casting solution of 20 wt % of total polymer concentration in the presence of cellulose acetate (85 wt %), enhances the flux to  $123.12 \text{ L m}^{-2} \text{ h}^{-1}$ , and a further increase in the degree of carboxylation to 0.75 increases the flux to  $152.73 \text{ L m}^{-2} \text{ h}^{-1}$ . This may be due to the fact that the hydrophilicity of carboxylated polysulfones increases with increase in the degree of carboxylation,<sup>13</sup> resulting in higher water flux in membranes with CPSU of higher degrees of carboxylation.

A similar trend of an increase in steady-state flux with an increase in the degree of carboxylation of the blend component, polysulfone, was found in blend membranes with CA/CPSU blend compositions of 80/20 and 75/25 wt % and are presented in Figures 2 and 3, respectively.



**Figure 2** Compaction of CA/CPSU (80/20 wt %) blend membranes of various degrees of carboxylation. Polymer concentration = 20 wt %.



**Figure 3** Compaction of CA/CPSU (75/25 wt %) blend membranes of various degrees of carboxylation. Polymer concentration = 20 wt %.

#### Comparison of the compaction of membranes with total polymer concentrations of 17.5 and 20 wt % in casting solution

Comparison of these observations with our earlier research work<sup>22</sup> on membranes prepared from casting solutions of 17.5 wt % as total polymer concentration indicates that an increase in concentration of pure cellulose acetate in casting solution from 17.5 to 20 wt % decreases the steady-state pure water flux of the membranes. The decrease in flux may be due to closer packing of the polymer segments, as the viscosity of the casting solution would be comparatively higher at higher concentrations of polymer in the casting solution.

The steady-state pure water flux of blend membranes with polymer concentrations of 20 wt % in casting solution was lower than that of membranes with a polymer concentration of 17.5 wt %, in the case of blend membranes with unmodified polysulfone and carboxylated polysulfone with a degree of carboxylation of 0.14.<sup>21,22</sup> However, as the degree of carboxylation of the blend polymer (CPSU) is increased to 0.43 and 0.75, the membranes showed a higher flux compared to those membranes prepared from a casting solution with a polymer concentration of 17.5 wt %.

This abnormal enhancement in flux at 20 wt % polymer concentration in casting solution may be due to the fact that, even though the polymer-polymer interactions in the blend decrease owing to the hydrophilic nature of the polymers (cellulose acetate and carboxylated polysulfone) as the degree of carboxylation increases, the incorporation of carboxylic groups is likely to lead to self-association of carboxylated polysulfone.<sup>44</sup> Also, an increase in hydrogen bonding and polar contributions in membranes with carboxy-

**TABLE II**  
**Membrane Characteristics**

No.	Blend polymer composition (wt %)		Membrane characteristics		
	CA	CPSU	CPSU (DS)	Pure water flux at 345 kPa ( $L m^{-2} h^{-1}$ )	Hydraulic resistance ( $kPa/L m^{-2} h^{-1}$ )
1	100	0	0	5.94	62.50
2	0	100	0.75	110.72	3.09
3	85	15	0	34.29	9.47
4	80	20	0	68.57	5.78
5	75	25	0	76.36	5.12
6	85	15	0.14	38.96	7.99
7	80	20	0.14	76.36	4.62
8	75	25	0.14	93.51	3.80
9	85	15	0.43	112.21	3.31
10	80	20	0.43	136.88	2.78
11	75	25	0.43	143.38	2.46
12	85	15	0.75	128.68	2.64
13	80	20	0.75	178.62	2.15
14	75	25	0.75	182.96	2.08

Note. Polymer concentration = 20 wt %.

lated polysulfones of higher degrees of carboxylation of 0.43 and 0.75 at higher polymer concentration (20 wt %) may result in a decrease in the dispersive forces in the presence of COOH groups,<sup>2</sup> resulting in an increase of the steady-state flux.

The steady-state flux of pure carboxylated polysulfone membrane with a degree of carboxylation of 0.75 of 20 wt % polymer concentration as casting solution was observed to be lower than that with a polymer concentration of 17.5 wt %, as expected.

### Pure water flux of membranes

Effect of degree of carboxylation on pure water flux

Membranes prepared from pure cellulose acetate with a polymer concentration of 20 wt % in casting solution exhibited a pure water flux of  $5.94 L m^{-2} h^{-1}$ , which was observed to be lower than the blend membranes (Table II).

The blend membrane prepared from a casting solution consisting of 85 wt % cellulose acetate and 15 wt % polysulfone exhibited a pure water flux of  $34.29 L m^{-2} h^{-1}$  and is shown in Table II. The flux increased to  $38.96 L m^{-2} h^{-1}$  when 15 wt % carboxylated polysulfone of 0.14° of carboxylation (85/15 wt %) was used as the blend component instead of unmodified polysulfone. The carboxylation results in the variation of the ratio of the hydrophilic moieties in the pendent group of polysulfone, leading to alteration of the chemical structure of the membranes with respect to their hydrophilic–hydrophobic balance, resulting in an enhanced flux.<sup>45</sup> Further, when the degree of carboxylation of the blend component (CPSU) of casting solutions of a particular blend composition of 85/15

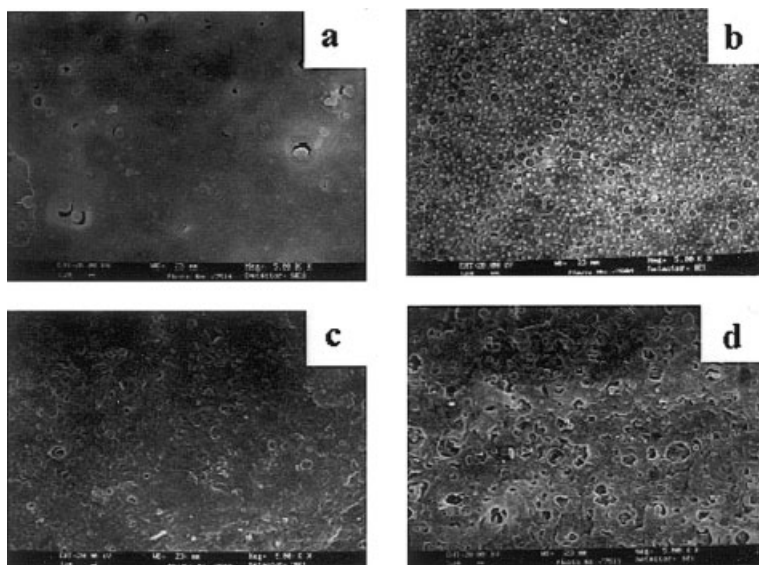
wt % was increased, the pure water flux of the blend membranes also continued to increase (Table II). This may be due to the increase in hydrophilicity of the blend membranes containing polysulfones of higher degree of carboxylation.

A similar trend of an increase in pure water flux with increase in degree of carboxylation of the blend component, polysulfone, was also observed in membranes with CA/CPSU blend compositions of 80/20 and 75/25 wt %, as shown in Table II.

### Comparison of the pure water flux of membranes with total polymer concentrations of 17.5 and 20 wt % in casting solution

It is evident from Table II that membranes prepared from 20 wt % cellulose acetate as casting solution exhibited a flux of  $5.94 L m^{-2} h^{-1}$ , while membranes prepared from 17.5 wt % cellulose acetate<sup>21</sup> had a flux of  $31.17 L m^{-2} h^{-1}$ . The reduction in flux at higher polymer concentration is due to closer segmental packing of the macromolecules at higher casting solution concentration.

Similar observations on pure water fluxes were also made in blend membranes prepared from (i) cellulose acetate and unmodified polysulfone and (ii) cellulose acetate and carboxylated polysulfone with a degree of carboxylation of 0.14 as the blend components. However, at higher degrees of carboxylation of 0.43 and 0.75 of polysulfone, the blend membranes exhibited higher fluxes at 20 wt % polymer concentration than at 17.5 wt %.<sup>21</sup> Thus, blend membranes with 80/20 wt % CA/CPSU with 0.43° of carboxylation had a pure water flux of 128.66 and  $136.88 L m^{-2} h^{-1}$  for 17.5 and



**Figure 4** Scanning electron micrographs of CA/CPSU (0.43) blend membranes with blend composition of 80/20 wt % and polymer concentrations of 17.5 and 20 wt %. (a) 17.5 wt % top surface; (b) 20 wt % top surface; (c) 17.5 wt % bottom surface; (d) 20 wt % bottom surface.

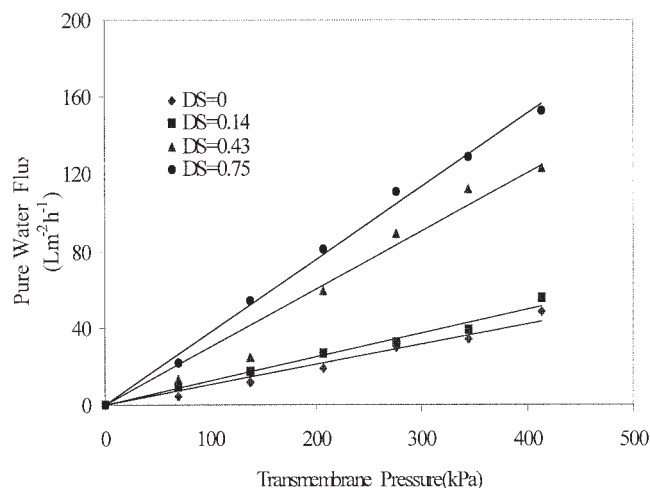
20 wt % of total polymer in casting solution, respectively. Similarly, for the above blend composition for 0.75° of carboxylation, the pure water flux was 137.14 and 178.62  $\text{L m}^{-2} \text{h}^{-1}$  for 17.5 and 20 wt % in casting solution, respectively. The higher flux of blend membranes containing polysulfones of higher degrees of carboxylation at high polymer concentration may be due to the fact that the hydrophilicity of CA/CPSU membranes, even though it increases with increase in carboxyl content in the membrane, hydrogen bonding is also expected to take place among the carboxylated polysulfone molecules<sup>20</sup> and with cellulose acetate. This may also lead to higher porosity, as evidenced by the scanning electron micrographs (Fig. 4) of CA/CPSU (80/20%) blend membranes with carboxylated polysulfone of 0.43° of carboxylation as the blend component, prepared from polymer solutions of 20 wt % polymer concentration, than that of 17.5 wt %. The effect of hydrogen bonding is strong in CPSUs of higher degrees of carboxylation and higher CPSU content in a blend leads to an enhanced flux in carboxylated polysulfones of higher degrees of carboxylation of 0.43 and 0.75 due to higher sorption of water in blend membranes of higher polymer concentration (20 wt %).

However, in the absence of cellulose acetate, the extent of hydrogen bonding is reduced, resulting in lower flux at 20 wt % polymer concentration. This is evidenced by the lower flux, 110.72  $\text{L m}^{-2} \text{h}^{-1}$ , exhibited by pure carboxylated polysulfone membranes with a degree of carboxylation of 0.75, at 20 wt % polymer concentration (Table II) compared to 17.5 wt % polymer concentration,<sup>22</sup> i.e., 135.06  $\text{L m}^{-2} \text{h}^{-1}$ . Similar observations of declines in pure water perme-

ability with increase in polymer concentration have also been reported by Stropnik et al.<sup>46</sup> in pure polysulfone membranes.

#### Hydraulic resistance of membranes

The pure water fluxes of the membranes were measured at different transmembrane pressures and the hydraulic resistances of the membranes were calculated as the inverse of the slope of the plots of pure water fluxes against the respective transmembrane pressures (Figs. 5–7).



**Figure 5** Pure water flux of CA/CPSU (85/15 wt %) blend membranes of various degrees of carboxylation at different transmembrane pressures. Polymer concentration = 20 wt %.

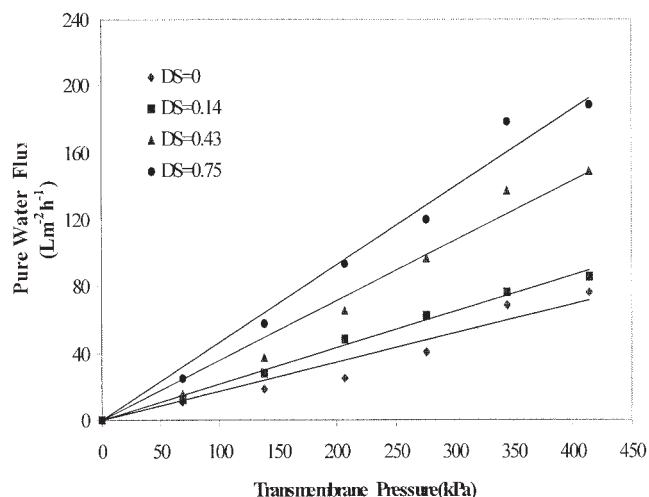
### Effect of degree of carboxylation on membrane hydraulic resistance

The hydraulic resistance of pure cellulose acetate membrane prepared from a casting solution of 20 wt % was observed to be  $62.50 \text{ kPa/L m}^{-2} \text{ h}^{-1}$  (Table II). The hydraulic resistances offered by the membranes prepared from a blend of 85 wt % cellulose acetate and 15 wt % polysulfone with different degrees of carboxylation as the blend component showed a decline in hydraulic resistance with an increase in the degree of carboxylation of the blend component as evidenced from Table II. Thus, the hydraulic resistance of the membrane (CA/PSU: 85/15 wt %) with unmodified polysulfone as the blend component was  $9.47 \text{ kPa/L m}^{-2} \text{ h}^{-1}$  and it was observed to decline to  $7.99 \text{ kPa/L m}^{-2} \text{ h}^{-1}$  when polysulfone was substituted with carboxylated polysulfone of 0.14 degree of carboxylation as the blend component. This was found to decline further to  $3.31 \text{ kPa/L m}^{-2} \text{ h}^{-1}$  and  $2.64 \text{ kPa/L m}^{-2} \text{ h}^{-1}$  when the degrees of carboxylation of the blend components were increased to 0.43 and 0.75, respectively. This decline in membrane resistance may be due to the incorporation of enhanced hydrophilicity imparted by the carboxylated polysulfones compared to their unmodified polysulfone precursor.<sup>47</sup>

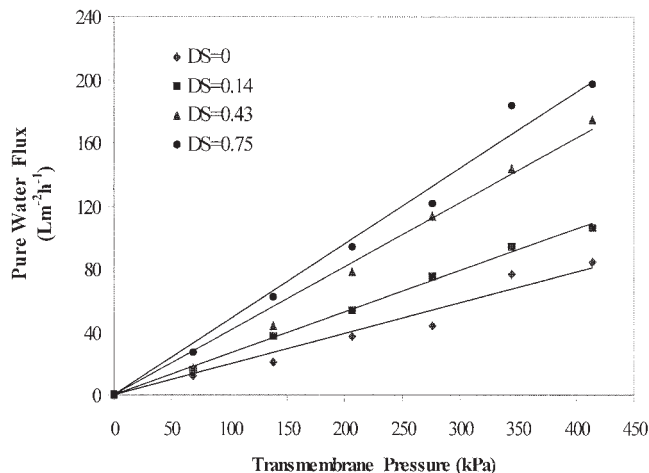
A similar trend of a decline in membrane hydraulic resistance with increase in degree of carboxylation of the blend component, polysulfone, was also observed in membranes with CA/CPSU blend compositions of 80/20 and 75/25 wt % (Table II).

### Comparison of the hydraulic resistance of membranes with total polymer concentrations of 17.5 and 20 wt% in casting solution

An increase in the polymer concentration of casting solution of pure cellulose acetate from 17.5 to 20 wt %



**Figure 6** Pure water flux of CA/CPSU (80/20 wt %) blend membranes of various degrees of carboxylation at different transmembrane pressures. Polymer concentration = 20 wt %.

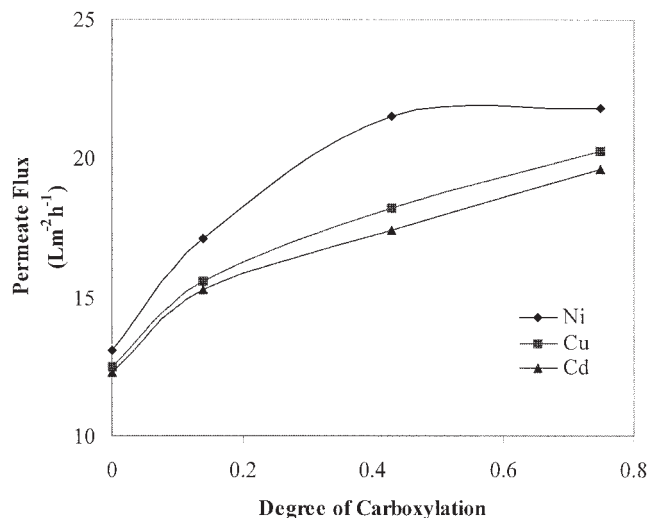


**Figure 7** Pure water flux of CA/CPSU (75/25 wt %) blend membranes of various degrees of carboxylation at different transmembrane pressures. Polymer concentration = 20 wt %.

induces an enhancement of the hydraulic resistance of the membrane from  $10.83^{22}$  to  $62.50 \text{ kPa/L m}^{-2} \text{ h}^{-1}$ . The increase in membrane hydraulic resistance with increase in polymer concentration may be explained by the fact that the viscosity of the casting solution increases with increase in polymer concentrations and resulted in closer segmental packing of the macromolecules, resulting in a decline in pore size of the membranes at higher casting solution concentration.

The hydraulic resistance of blend membranes with polymer concentrations of 20 wt % was higher than for membranes with a polymer concentration of 17.5 wt %, in the case of blend membranes with unmodified polysulfone and carboxylated polysulfone with a degree of carboxylation of 0.14, as expected.<sup>21,22</sup> However, the membranes showed a decline in hydraulic resistance when the degree of carboxylation of the blend polymer (CPSU) was increased to 0.43 and 0.75 compared with membranes prepared from a casting solution with a polymer concentration of 17.5 wt %.<sup>22</sup> Even though the hydrophilicity of CA/CPSU blend membranes is expected to increase with increase in carboxyl content in the membrane, hydrogen bonding also takes place among the carboxylated polysulfone molecules and cellulose acetate. Hence the effect of hydrogen bonding is strong in CPSUs of higher degrees of carboxylation<sup>20</sup> in the presence of cellulose acetate, leading to a higher affinity toward water. This resulted in reduced hydraulic resistance in blend membranes consisting of carboxylated polysulfones of higher degrees of carboxylation of 0.43 and 0.75 at higher polymer concentration (20 wt %).

The hydraulic resistance of pure carboxylated polysulfone membrane with a degree of carboxylation of 0.75 of 20 wt % polymer concentration was observed to be  $3.09 \text{ kPa/L m}^{-2} \text{ h}^{-1}$ , which was comparatively higher than that obtained with a polymer concentra-



**Figure 8** Metal chelate permeation flux of CA/CPSU (85/15 wt %) blend membranes. Polymer concentration = 20 wt %.

tion of 17.5 wt % ( $2.47 \text{ kPa/L m}^{-2} \text{ h}^{-1}$ ), as expected, in view of the reduced hydrogen bonding in the absence of cellulose acetate.

### Separation of heavy metal ions

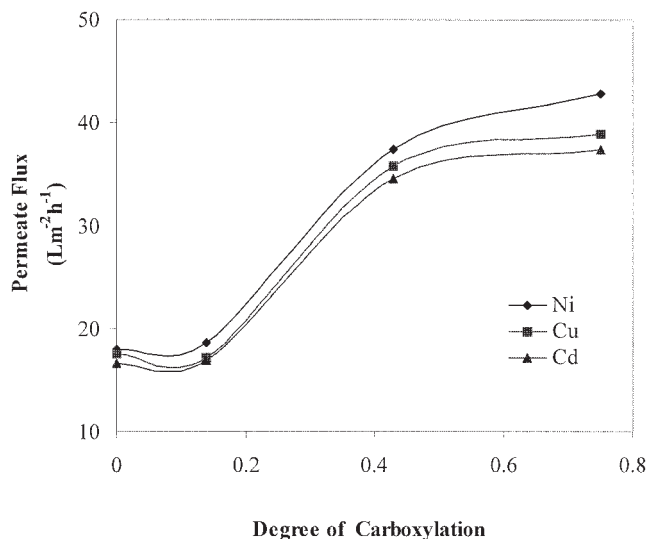
In the present investigation, the efficiency of membranes for the separation of metal ions such as nickel, copper, and cadmium from aqueous streams was studied by ultrafiltration of the respective complexes of the metal ions with PEI at a pH of  $6 \pm 0.25$  followed by the measurement of the concentration of these metal ions in the feed and the permeate using an atomic absorption spectrophotometer (Perkin-Elmer 2380). The percentage rejections of the metal chelates were calculated from the concentrations in the feed and permeate.

### Solute permeation flux of membranes

The metal ion permeation flux of membranes prepared from blends of cellulose acetate and carboxylated polysulfone of various blend compositions (85/15, 80/20, and 75/25 wt %) and total polymer concentrations of 17.5 and 20 wt % in the casting solution were measured to investigate the efficiency of the membranes. The variations in the permeation flux of the membranes with increase in the degree of carboxylation of the blend component (CPSU) are presented in Figures 8-13.

### Effect of degree of carboxylation on solute permeation flux

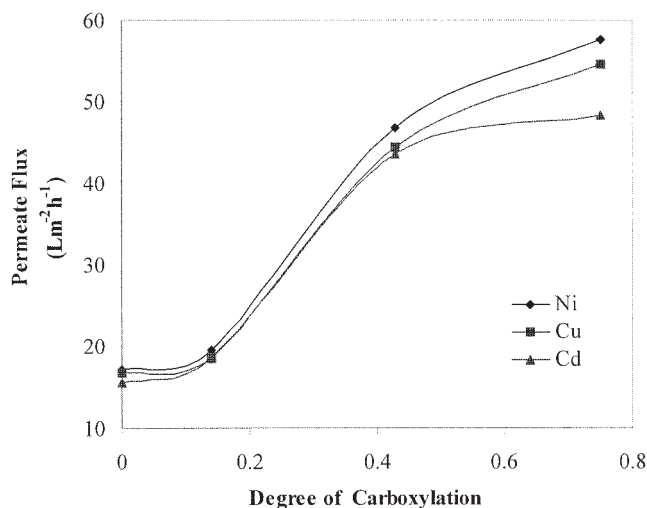
The nickel-chelate permeation flux of pure cellulose acetate membrane prepared from a polymer solution



**Figure 9** Metal chelate permeation flux of CA/CPSU (80/20 wt %) blend membranes. Polymer concentration = 20 wt %.

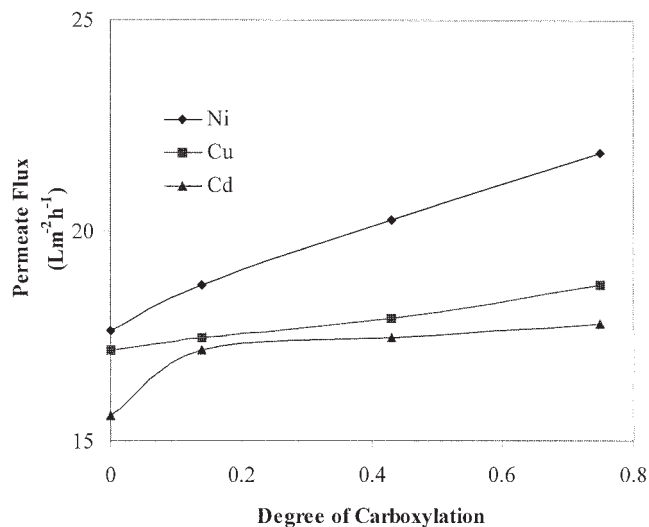
of 20 wt % concentration was  $3.82 \text{ L m}^{-2} \text{ h}^{-1}$ , which declined to  $3.31 \text{ L m}^{-2} \text{ h}^{-1}$  in the case of copper-chelate and decreased further to  $3.17 \text{ L m}^{-2} \text{ h}^{-1}$  for cadmium-chelate permeation.

The blend membrane prepared from a casting solution consisting of 85 wt % of cellulose acetate and 15 wt % of unmodified polysulfone exhibited a nickel-chelate permeation flux of  $13.09 \text{ L m}^{-2} \text{ h}^{-1}$ , which was observed to be comparatively higher than pure cellulose acetate membranes. The flux was found to increase slightly to  $17.14 \text{ L m}^{-2} \text{ h}^{-1}$  when 15 wt % of carboxylated polysulfone of 0.14 of carboxylation degree (85/15%) was used as the blend component in-



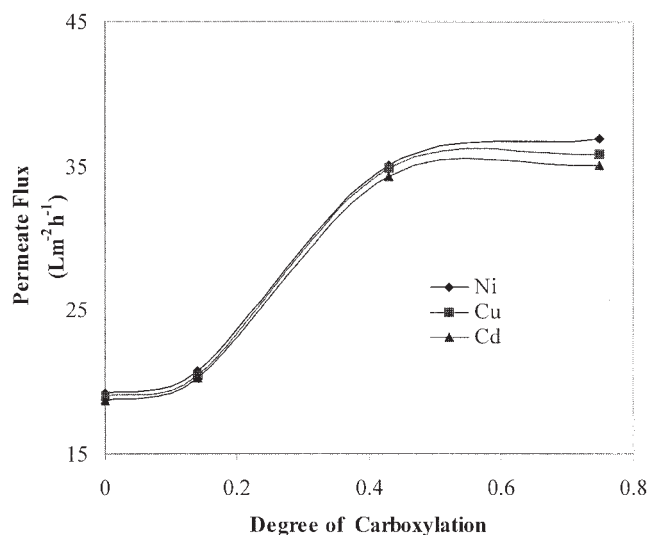
**Figure 10** Metal chelate permeation flux of CA/CPSU (75/25 wt %) blend membranes. Polymer concentration = 20 wt %.



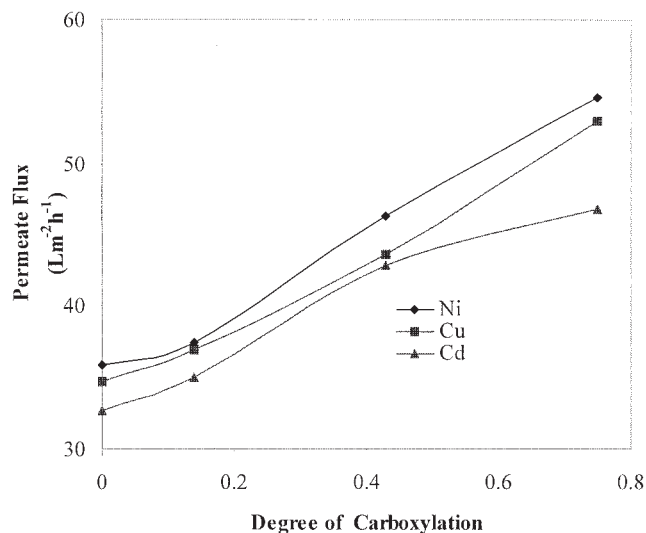


**Figure 11** Metal chelate permeation flux of CA/CPSU (85/15 wt %) blend membranes. Polymer concentration = 17.5 wt %.

stead of unmodified polysulfone. Introduction of the carboxyl moiety in the blend has resulted in the variation of the hydrophilicity of polysulfone, leading to alteration of the chemical structure of the membranes with respect to their hydrophilic–hydrophobic balance, resulting in an enhanced flux.<sup>44</sup> Further, when the degree of carboxylation of the blend component (CPSU) of casting solutions of a particular blend composition of 85/15 wt % was increased, the permeate fluxes of the blend membranes also continued to increase (Fig. 8). This may be reasoned by the availability of more carboxyl moieties for intermolecular interactions and hydrogen bonding in blends with carbox-



**Figure 12** Metal chelate permeation flux of CA/CPSU (80/20 wt %) blend membranes. Polymer concentration = 17.5 wt %.



**Figure 13** Metal chelate permeation flux of CA/CPSU (75/25 wt %) blend membranes. Polymer concentration = 17.5 wt %.

ylated polysulfones of higher functionality, resulting in membranes with higher porosity and pore density.

Similar trends of increase in permeate fluxes with increase in degree of carboxylation of the blend component were observed in blend membranes with higher compositions (80/20 and 75/20 wt %) of the blend component (PSU and/or CPSU), as depicted in Figures 9 and 10.

#### Comparison of the solute permeation flux of membranes with total polymer concentrations of 17.5 and 20 wt% in casting solutions

Variation of the metal ion permeation fluxes of the blend membranes prepared from total polymer concentration of 17.5 wt % in blend solution with increase in the degree of carboxylation of the blend component (CPSU) are presented in Figures 11–13.

The nickel-chelate permeation flux of pure cellulose acetate membrane prepared from 20 wt % concentration as casting solution was  $3.82 \text{ L m}^{-2} \text{ h}^{-1}$ , which declined to  $3.31 \text{ L m}^{-2} \text{ h}^{-1}$  in the case of copper-chelate and decreased further to  $3.17 \text{ L m}^{-2} \text{ h}^{-1}$  for cadmium-chelate permeation similar to membranes prepared from casting solutions of 17.5 wt % as polymer concentration. An increase in the polymer concentration of pure cellulose acetate from 17.5 to 20 wt % was observed to decrease the nickel-chelate permeation flux of the membranes from  $12.80$  to  $3.82 \text{ L m}^{-2} \text{ h}^{-1}$ , due to closer segmental packing of the macromolecules at higher casting solution concentration.

Similar observations of reduction in metal chelate permeation fluxes were noticed in blend membranes prepared from blends of cellulose acetate and unmodified polysulfone (CA/PSU) and cellulose acetate and

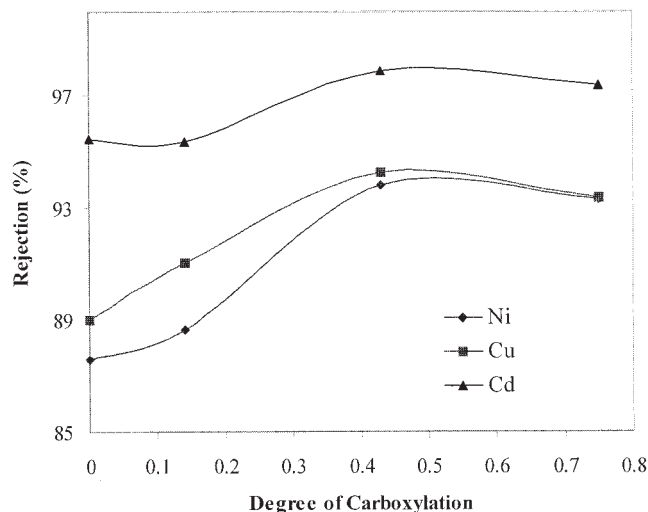
carboxylated polysulfone (CA/CPSU) with a degree of carboxylation of 0.14 as the blend component. However, blend membranes, having higher degrees of carboxylation of 0.43 and 0.75, of polysulfone as the blend component exhibited higher fluxes at 20 wt % polymer concentration than at 17.5 wt %.

The higher flux of blend membranes containing polysulfones of higher degrees of carboxylation at high polymer concentration may be due to the fact that hydrogen bonding takes place among the carboxylated polysulfone molecules<sup>20</sup> and also with cellulose acetate. The effect of hydrogen bonding is strong in CPSUs with higher degrees of carboxylation and at higher CPSU content in blend, leading to higher pore density and a resultant enhancement of flux in membranes with carboxylated polysulfones of higher degrees of carboxylation of 0.43 and 0.75 as the blend component.

However, in the absence of cellulose acetate, the extent of hydrogen bonding is reduced, resulting in comparatively lower flux at 20 wt % polymer concentration, as evidenced by the lower nickel-chelate flux,  $19.82 \text{ L m}^{-2} \text{ h}^{-1}$ , exhibited by pure carboxylated polysulfone membranes with a degree of carboxylation of 0.75, compared to 17.5 wt % polymer concentration, i.e.,  $28.05 \text{ L m}^{-2} \text{ h}^{-1}$ . Similar observations of a decline in permeability with increase in polymer concentration have also been observed for other metal chelates such as copper and cadmium for pure carboxylated polysulfone membranes.

### Solute rejection efficiency of membranes

The solute (metal chelate) rejection efficiency of membranes prepared from blends of cellulose acetate and carboxylated polysulfone of various blend composi-



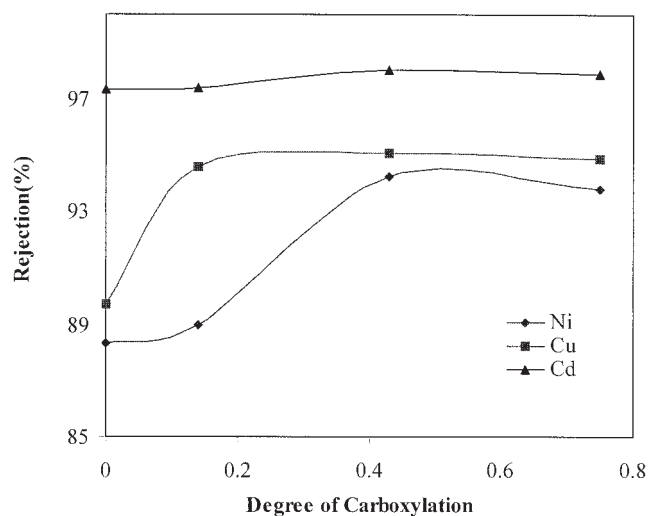
**Figure 15** Metal chelate rejection of CA/CPSU (80/20 wt %) blend membranes. Polymer concentration = 20 wt %.

tions and total polymer concentrations of 17.5 and 20 wt % in the casting solution was measured. The variations in solute rejection (%) of the membranes with increase in the degree of carboxylation of the blend component (CPSU) are presented in Figures 14–19.

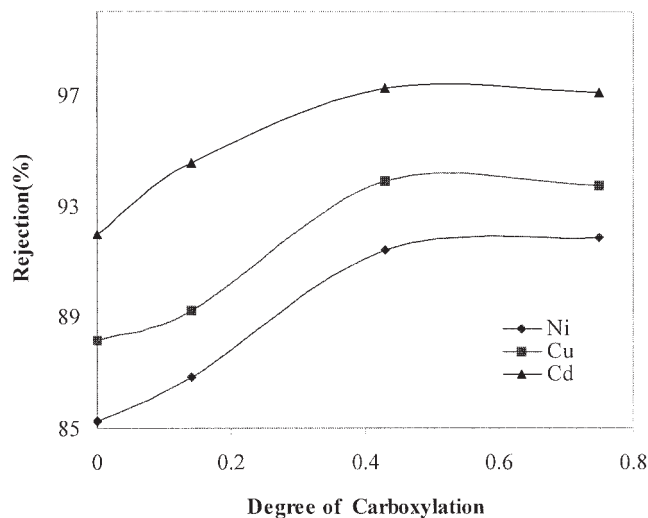
### Effect of degree of carboxylation on solute rejection

The nickel ion rejection by pure cellulose acetate membrane prepared from a polymer solution of 20 wt % concentration was 95.58%, which increased to 97.59% in the case of separation of cadmium ions.

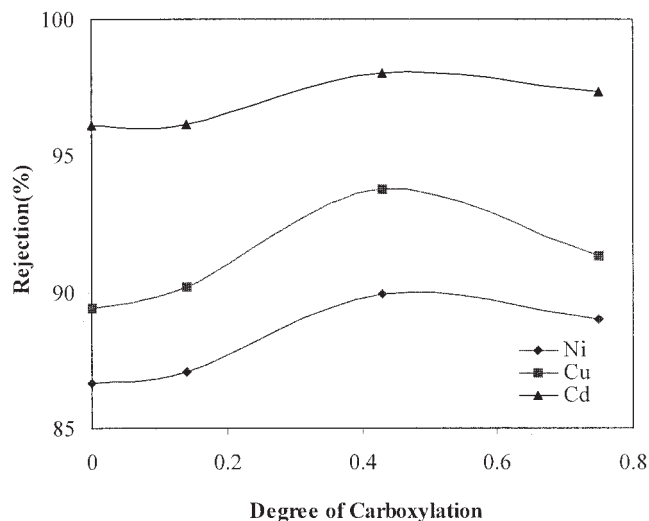
The blend membrane (85/15 wt %) prepared from a casting solution consisting of 85 wt % cellulose acetate



**Figure 14** Metal chelate rejection of CA/CPSU (85/15 wt %) blend membranes. Polymer concentration = 20 wt %.

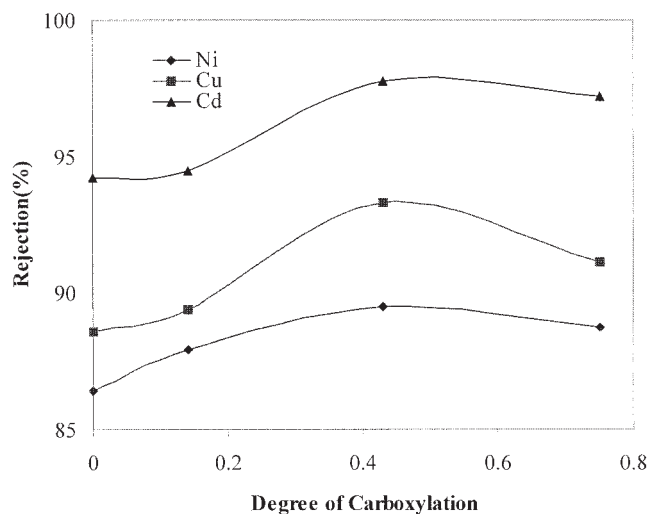


**Figure 16** Metal chelate rejection of CA/CPSU (75/25 wt %) blend membranes. Polymer concentration = 20 wt %.

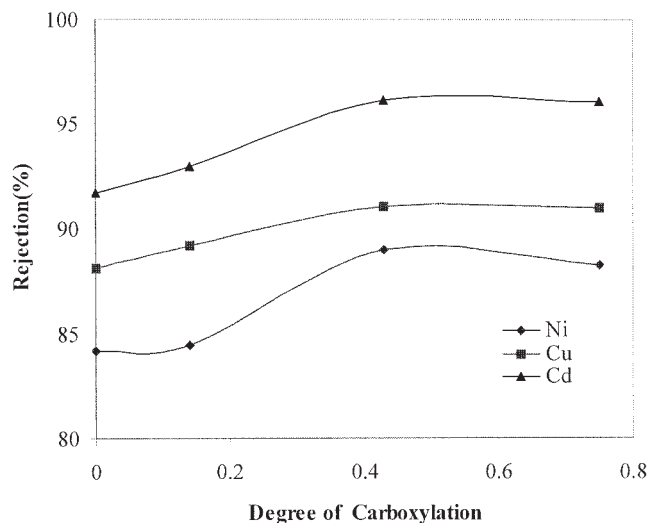


**Figure 17** Metal chelate rejection of CA/CPSU (85/15 wt %) blend membranes. Polymer concentration = 17.5 wt %.

and 15 wt % polysulfone rejected 88.36% nickel ions (Fig. 14). When 15 wt % of carboxylated polysulfone of 0.14° of carboxylation (85/15 wt %) was used as the blend component instead of polysulfone, the nickel ion rejection increased to 88.99%. This increase in metal ion rejection indicates a decline in pore size with increase in degree of carboxylation of the blend component. Further, when the degree of carboxylation of the blend component (CPSU) of casting solutions of a particular blend composition of 85/15 wt %, is increased, the metal ion rejection of the blend membranes also increased as expected and the results are shown in Figure 14. Thus, membranes prepared from blends of carboxylated polysulfone of 0.43° of substitution and cellulose acetate showed a considerably



**Figure 18** Metal chelate rejection of CA/CPSU (80/20 wt %) blend membranes. Polymer concentration = 17.5 wt %.



**Figure 19** Metal chelate rejection of CA/CPSU (75/25 wt %) blend membranes. Polymer concentration = 17.5 wt %.

higher nickel ion rejection of 94.25%. A further increase in the degree of carboxylation to 0.75 slightly decreased the nickel ion retention to 93.78%. Similar observations were also observed for all of the metal ion solutions. Thus, when the degree of carboxylation of the blend component, PSU, was increased from zero to 0.43, copper ion rejection increased from 89.72 to 95.08% and cadmium ion rejection increased from 97.35 to 98.03%.

However, when the degree of carboxylation of the blend component was increased further to 0.75, the copper and cadmium ion rejections were observed to slightly decline to 94.89 and 97.88, respectively. This decline in rejection percentage with increase in the degree of carboxylation of the blend component from 0.43 to 0.75 may be attributed to a slight increase in the pore size.

Similar results of increase in metal ion rejection with increase in degree of carboxylation of the blend component followed by a slight decline with increase in the degree of carboxylation of the blend carboxylated polysulfone component in the blend from 0.43 to 0.75 were also observed in blend membranes with polymer compositions of CA/CPSU 80/20 and 75/25 wt %, as illustrated in Figures 15 and 16.

#### Comparison of solute rejection efficiency of membranes with total polymer concentrations of 17.5 and 20 wt % in casting solution

An increase in the polymer concentration of pure cellulose acetate from 17.5 to 20 wt % was observed to elevate the rejection of nickel ions from 91.15 to 95.58%, owing to the closer segmental packing of the macromolecules at higher casting solution concentration, as expected. Likewise, the percentage rejections

of other metal ions were also enhanced when the polymer concentration of the casting solution was increased from 17.5 to 20 wt %. Thus, copper ion rejection increased from 95.15 to 96.46% and cadmium rejection increased from 96.80 to 97.59%.

Similar observations of increases in percentage of metal ion rejections were noticed in blend membranes of cellulose acetate and carboxylated polysulfone (CA/CPSU) of different degrees of carboxylation as the blend component. Further, it has been observed that the fluxes of blend membranes prepared from carboxylated polysulfones of 0.43 and 0.75° of carboxylation as the blend component also increased with increasing polymer concentration in contrast to pure cellulose acetate membranes, cellulose acetate-polysulfone blends, and cellulose acetate-carboxylated polysulfone (DS = 0.14) blend membranes. This trend of higher metal ion percent rejections accompanied by a higher rate of permeation is an added advantage of the blend membranes comprising CPSUs of higher degrees of substitution.

The high membrane performance of blend membranes containing polysulfones of higher degrees of carboxylation at high polymer concentration may be due to higher pore density in blend membranes with CPSUs having higher degrees of carboxylation (0.43 and 0.75). Further, blend membranes prepared from polymer solutions of 20 wt % polymer concentration have a slight increase in porosity compared to those prepared from 17.5 wt % (Fig. 4). This may be due to intermolecular forces existing between the component molecules with higher degrees of carboxylation.

The membranes prepared from pure carboxylated polysulfone of 0.75° of carboxylation also show a similar trend, i.e., the metal ion retention was found to increase with increase in the polymer concentration of the casting solution. Thus, nickel ion rejection increased from 88.63 to 93.27%. A similar trend of an increase in metal ion rejection was also observed in other metal ions such as copper and cadmium for pure carboxylated polysulfone membranes. This increase in metal ion rejection may be due to a decline in pore size brought about by the closer packing of the polymer segments in membranes prepared from polymer solutions of higher concentrations.

## CONCLUSION

Ultrafiltration membranes based on cellulose acetate and carboxylated polysulfones of various degrees of carboxylation were prepared. Phase separation occurs beyond certain blend compositions and suitable compositions were found to be 85/15, 80/20, and 75/25 wt % CA/CPSU. Blending of cellulose acetate with carboxylated polysulfone resulted in blend membranes with enhanced ultrafiltration membrane characteristics such as lower hydraulic resistance coupled with

higher water flux. The degree of carboxylation of the polysulfone component in the blend influences the membrane characteristics. Thus, as the degree of carboxylation of polysulfone in the blend was increased gradually, the pure water flux increased, while the hydraulic resistance of the membranes declined. Further, membranes prepared from carboxylated polysulfones of 0.43 and 0.75° of carboxylation as the blend component showed higher metal ion percentage rejections accompanied by higher rate of permeation, which would be an added advantage of blend membranes comprising CPSUs of higher degrees of substitution. Thus, carboxylated polysulfones of 0.43 and 0.75° of carboxylation could be efficiently used in the preparation of blend membranes based on cellulose acetate from casting solutions of 20 wt % polymer concentration with added advantages of higher flux rates and solute rejection. It has been concluded that the incorporation of the hydrophilic moiety (CPSU) in blend membranes plays a major role in improving the flux and performance of the membranes.

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