Identification of Optimum Synthesis Conditions for a Novel Anion Exchange Membrane by Response Surface Methodology

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ABSTRACT: The Response Surface Methodology (RSM) was employed for the optimization of the synthesis conditions of an anion exchange membrane. A novel chlorinated-polypropylene heterogeneous anion exchange membrane was made via phase inversion. A nonionic surfactant was incorporated into the composition as an additive to enhance the membrane properties. The membrane performance was measured in terms of ion exchange capacity (IEC) and permselectivity. An experimental design was used to quantify the effects of variables including the ratio of resin/polymer, the ratio of additive/total solid, and the ratio of solvent/polymer, on IEC and permselectivity. For each function, a quadratic model was developed to correlate the relationship between variables and the response. The results demonstrated the accuracy of the two models. The anion exchange membrane with the best combination of a high IEC and high permselectivity was synthesized with a solvent/polymer ratio of 18.63 (v/w), resin/polymer ratio of 1 (w/w), and additive/total solid ratio of 0.02 (w/w). © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 39888.

INTRODUCTION

Ion exchange membranes are used in various applications with either a difference in voltage (electrodialysis) or a difference in concentration (diffusion or Donnan dialysis) as the driving force, for cleaner production and environmental protection. Bipolar, anion, and cation exchange membranes are three different types of ion exchange membranes that have been utilized in various applications.[1–3] Desalination of brackish water, production of organic acids, concentration and separation of ionic species from nonionic ones, recovery and extraction of charged solutes from waste streams, production of chlor-alkali products, production of pure and ultra-pure water, and a number of other processes can be mentioned as different applications of these membranes.[4–7]

Ion exchange membranes contain fixed electrically charged groups on a polymer matrix, which allow permeation of counter-ions, and reject co-ions through the membrane matrix, based on the Donnan equilibrium law. According to the sign of the fixed charged group, these membranes are categorized into cation- and anion- exchange membranes, i.e., with negative and positive fixed charges, respectively. Furthermore, cation and

anion exchange membranes can be heterogeneous or homogeneous, based on their structure and heterogeneity.[8,9] Heterogeneous membranes have a better mechanical strength, an easier preparation procedure, and lower production costs in comparison with homogeneous ones. On the other hand, homogeneous membranes have better electrochemical properties but a lower mechanical strength.[9–13] Although most of the commercial membranes are homogeneous, the synthesis of inexpensive membranes using an easy method (heterogeneous) with superior properties, is a vital step in developing of these membranes for various applications.

The desired heterogeneous ion exchange membrane can be produced by selecting (a) the polymeric matrix, (b) considering the functional groups that are present (resin particles), (c) the hydrophilicity and hydrophobicity of the membrane, and (d) the use of various additives and synthesis conditions.[14–17] The preparation method and synthesis conditions, i.e., distribution of functional groups, ratio of resin/polymer, application of different additives, extent of the additive, solvent type and its ratio in the polymeric solution, have also significant influences on the properties and performance of the heterogeneous ion exchange membranes. High quality membranes can be synthesized by adjusting

the effective preparation variables. Determination of the effective variables, their interactions among each other, and system optimization becomes more important in a system that is affected by a larger number of independent variables. The interactions among variables cannot be evaluated by traditional optimization techniques. The effect of variables on the response and interactions among them can be investigated by experimental design methods such as Response Surface Methodology (RSM). RSM consists of mathematical and statistical techniques that are used for the modeling and analyzing of the problem. The objective is to optimize the response which is affected by several variables. RSM is the experimental strategy for exploring the variables, empirical statistical modeling to develop an adequate functional relationship between the response and variables, and optimization for determining the values of the variables for obtaining the desirable response. Through this technique, one can investigate the number of variables and their interactions. By using RSM, the effects of different variable factors, interactions among variables, and process optimization can be evaluated with a small number of experimental trials, in a cost-effective manner (in terms of both manpower and resources). The relationships of variables are described by polynomial fitting. The parameters of the polynomials are estimated by using the least squares method. The fitted surface can be used for response surface analysis. If the fitted surface is an adequate approximation of the true response function, then analysis of the fitted surface will be approximately equivalent to analysis of the actual system.[18–23]

Applications of ion exchange membranes can be improved by developing membranes with better properties. By enhancing the properties of an ion exchange membrane, electrodialysis (the most common application of the ion exchange membranes) can become one of the most promising techniques for water desalination and treatment. The chloride and sodium ions can be removed selectively from water by developing permselective anion- and cation-exchange membranes, respectively. There are several important parameters required for an ion exchange membrane: IEC, water content, fixed ion concentration (FIC), transport number, permselectivity, fixed group concentration, and conductivity, among others. These parameters work in opposite directions or in the same direction.[1,2] Therefore, finding a compromise among properties of the membrane is an outstanding problem in membrane synthesis. Some properties of ion-exchange membranes follow a similar or opposite trend and can predict the trend of other properties. For example, a membrane with a high conductivity requires a substantial water content (to assist the ionic migration). However, high water content weakens the membrane selectivity (permselectivity). Membrane with a high ionic conductivity generally have a low selectivity.[24] In other words, in some cases, it is not necessary to measure all the properties of the membrane, i.e., some parameters can be deduced from known ones.[25] By using RSM, a membrane with desired properties can be synthesized by choosing the most important properties (as a response parameter), to predict the trend of other properties, as a cost-effective method. One of the fundamental (IEC) and one of the diffusivity (permselectivity) properties of ion exchange membrane can be considered as objective functions to enhance the properties of the ion exchange membrane and determine the optimum synthesis conditions. The trend of other properties of the membrane, based on variable factors, can be predicted using IEC and permselectivity.

The application of RSM in biological and chemical processes has been investigated.[26–30] In the field of membrane science, RSM has been mainly used for the optimization of operating conditions in membrane processes.[31–35] The application of this technique has also been reported for the optimization of synthesis conditions of membranes.[36–40] However, to the best of our knowledge, the application of RSM for the estimation of optimum synthesis conditions in ion exchange membranes has not been reported yet. Investigation of the effects of more than one variable on the properties of the ion exchange membrane has not been reported. Only the effect of one variable, by fixing all other parameters, has been investigated.[10,14,40] The effect of solvent and of a nonionic surfactant (Triton X-100) even with fixing other parameters has not been reported yet.

This work introduces RSM as an effective technique for the optimization of ion exchange membrane properties. In this study, the optimum conditions for the synthesis of anion exchange membranes were identified. Chlorinated-polypropylene (CPP) heterogeneous anion exchange membranes were made via phase inversion, i.e., solvent evaporation and precipitation. Three of the most important and effective parameters determining the membrane properties were chosen as variables, i.e., ratio of resin/polymer, ratio of additive/total solid, and ratio of solvent/polymer. IEC and permselectivity were chosen as objective functions for optimization of the conditions of membrane synthesis. The trends of other properties were predicted based on variable factors using IEC and permselectivity. The predicted trends were compared with experimental results. The Box-Behnken design was carried out to correlate the synthesis variables to the responses. The Box-Behnken design is a spherical design (rotatable) that can be utilized for proposing three-level designs for fitting response surfaces. RSM showed as a cube and consists of a central point and the middle points of the edges. It is quite general and flexible design and has been used for optimization of various chemical and physical processes.[18,41,42] Quadratic models were obtained for IEC and permselectivity, by which the optimum conditions for the synthesis of anion exchange membranes were estimated.

EXPERIMENTAL

Materials

Chlorinated-polypropylene (CPP, $M_w = 100,000$) was supplied by Sigma-Aldrich Co., Japan. Toluene, which was used as solvent, obtained from Merck, Germany (used without further purification). Triton X-100 (nonionic surfactant) from Merck was used as an additive. An anion exchange resin (Amberlite IRA-400, a strongly basic anion exchange resin, Cl⁻ form) from Sigma-Aldrich Co. was used as reagent. Other chemicals (NaCl, NaNO₃, AgNO₃, and K₂CrO₄) were supplied by Merck.

Membrane Preparation

The polymeric solutions were prepared by dissolving specified quantities of CPP in toluene. Triton X-100 and powdered resin

particles were subsequently added to the solution. The anion exchange membranes were prepared by dispersing anionic resin particles in the polymeric solution, followed by solvent evaporation and precipitation. Anion exchange resins were first dried in an oven at 50°C for 24 h, and subsequently powdered in a ball mill and sieved. During the entire preparation process, the mixtures were agitated at room temperature by means of a mechanical stirrer. After obtaining a uniform distribution of particles in the solution, the mixture was sonicated using an ultrasonic homogenizer (Bandelin-LS8) for a better distribution and aggregation break-up for more than one hour. The mixture becomes more concentrated and homogeneous during the sonicated process. The mixture was casted on a dry and clean glass plate and was allowed to dry for 30 min (solvent evaporation). The product was then immersed in distilled water (solvent–nonsolvent exchange). The prepared membranes were finally treated by immersing in NaCl solution.

Membrane Morphology

The membrane structure as well as the distribution of functional groups was studied by scanning electron microscopy (SEM) (Nova 600 NanoLab).

Water Content

The membrane was immersed in distilled water for 24 h. Afterwards, the moisture was wiped off from the membrane surface by means of a filter paper and the membrane was weighted (W_w). The membrane was then dried until a constant weight (W_d) was achieved. The water content in the membrane was calculated using the following equation:[15,43]

$$Watercontent = \frac{W_w - W_d}{W_d} \qquad (1)$$

IEC Measurement

The IEC of the ion exchange membrane is defined as milliequivalent of ion exchange groups incorporated in 1 g of a dry membrane.[43] The IEC was determined by the Moher titration method.[15] In order to convert the ion exchange groups into Cl^- type, the membrane was immersed in a $1M$ NaCl solution for 24 h. The membrane was then removed and washed frequently with deionized water. The membrane was subsequently immersed in water for 24 h. In order to liberate the Cl^- ions, the membrane was immersed in a $1M$ NaNO$_3$ solution for 24 h. The dissolved Cl^- ions in the solution were measured with $0.01M$ AgNO$_3$ and a K$_2$CrO$_4$ indicator (**a** meq). The IEC was calculated as follows:[15,43]

$$IEC = \frac{a}{W_d} \qquad (2)$$

where W_d is the dry weight of the membrane.

The fixed ion concentration (FIC) can be calculated through the following equation:[15]

$$FIC = \frac{IEC}{Watercontent} \qquad (3)$$

Permselectivity Measurements

The membrane permselectivity, permeation of counter ions, and exclusion of co-ions, depends on the properties of both membrane and electrolyte solution. The permselectivity (between co-ions and counter ions) can be used as a quantitative expression

to show the difference between counter- (Cl^-) and co-ions (Na^+) permeability through the membrane. The permselectivity of the membrane was calculated based on the membrane potential and transport number. The membrane potential (algebraic sum of Donnan and diffusion potentials) was measured using a two-compartment cell. The cell was made from Pyrex glass and the compartments were separated by the membrane. The ratio of electrolyte concentrations (NaCl) in both sides (C_1/C_2) was kept constant at 10 ($C_1 = 0.1M$ and $C_2 = 0.01M$). For minimizing the effect of the boundary layer on the potential, both compartments were vigorously stirred by means of mechanical stirrers during the measurements. The developed potential across the membrane was measured using calomel electrodes and a digital multimeter (E_m). The transport number of counter ions (Cl^-) through the membrane was calculated from the measured membrane potential.[7,44,45] The permselectivity of the membrane is a function of the ion transport numbers in the membrane and in the solution. The permselectivity can be calculated by the following equation:[15,44]

$$P_s = \frac{t_- - t_0}{1 - t_0} \qquad (4)$$

where t_0 and t are the anion transport number in the solution and in the membrane, respectively. The charge of the membrane matrix (fixed group concentration (φ)) can be expressed in terms of permselectivity through the following equation:[15,44]

$$\varphi = \frac{2 P_s C_M}{\sqrt{1 - P_s^2}} \qquad (5)$$

where C_M is the mean concentration of electrolytes.

Conductivity Measurements

Measurements on membrane conductivity were carried out in a $0.5M$ NaCl solution. An equilibrated membrane was incorporated into the measurement cell. The cell was composed of two black graphite electrodes and a digital LCR meter (HEWLETT PACKARD, 4262A). The electrical resistance was measured in the presence of the membrane (R_1). In the next step, the membrane was removed and the electrical resistance was measured (R_2). The membrane resistance (R_m) was obtained as the difference between R_1 and R_2. The conductivity of the membrane was then calculated by the following equation:[44]

$$k = \frac{L}{A.R_m} \qquad (6)$$

where, k, L, and A are conductivity, thickness, and effective area of the membrane, respectively.

Experimental Design

RSM is a combination of mathematical and statistical techniques. It has four steps: experimental design, model fitting, model validation, and optimization.[31] The experimental design was carried out using Design Expert software version 7.0.1. The Box Behnken design with a quadratic model was employed to correlate the three independent synthesis variables (at three levels); ratio of resin/polymer, ratio of additive/total solid, and ratio of solvent/polymer to the responses, i.e., IEC and permselectivity. The relation between response and variables can be

expressed by a second-order polynomial function that consists of linear, quadratic, and interactive components, as follows:

$$Y = A_0 + \sum A_i X_i + \sum A_i X_i^2 + \sum A_i X_i X_j \qquad (7)$$

where Y, X, A_0, A_i, A_{ii} are the response variable, independent variables, intercept, linear, quadratic, and interaction constant coefficients, respectively.

Analysis of variance (ANOVA) has been used to check and justify the significance of the model. The F value and $P > F$ were employed to determine the statistical significance of the model. A significant model should have a high F value and a $P > F$ below 0.05. The accuracy of the model can also be estimated by determination the R-squared and adjusted R-squared.[30,39] The R^2 and R^2_{adj} show a measure of the variability in the response values and the fraction of variation of the response explained by the model adjusted for degrees of freedom, respectively.[23]

The variables with the coded and actual values are shown in Table I. Fifteen experiments were conducted at different combinations of variable factors by using the Box-Behnken design.

RESULTS AND DISCUSSION

Experimental Design and Model Fitting

Experimental values of the Box-Behnken design for IEC and permselectivity of the anion exchange membranes are shown in Table II.

The final regression equations for IEC and permselectivity in term of coded form and based on significant model terms were obtained as follows:

$$[IEC = +1.29 + 0.053 \times A + 0.180 \times C + 0.041 \times A \times C - 0.061 \times B^2 \\ + 0.0520 \times C^2]$$
$$(8)$$

$$[permselectivity = +0.97 + 0.028 \times A + 0.097 \times C - 0.11 \times C^2] \qquad (9)$$

The statistical significance of IEC and permselectivity model terms was examined via ANOVA and regression analysis. The fitting results of IEC and permselectivity equation models are shown in Tables III and IV, respectively. The reliability of the fitted models for IEC (Table III) and permselectivity (Table IV) can be confirmed by the high values of F and the very low values of probability. Furthermore, the values of R^2 and R^2_{adj}, are close to 1. Also the very small difference between R^2 and R^2_{adj} shows the accuracy of the models. For the IEC and permselectivity models, more than 98.86% and 97.12% of the total variation was attributed to the experimental variables studied so that only 1.14% and 2.88% of the total variance was not explained by the models. Meanwhile, the values of lack of fit confirm the

Table I. Levels and Codes of the Box-Behnken Experimental Design

Variable factor	Code level		
	−1	0	+1
A: Ratio of resin/polymer (w/w)	0.6/1	0.8/1	1/1
B: Ratio of additive/total solid (w/w)	0/100	3/100	6/100
C: Ratio of solvent/polymer (v/w)	10/1	15/1	20/1

Table II. Experimental Values of the Box-Behnken Design

Runs (sample)	Variable factors			Responses	
	A	B	C	IEC (meq/g)	Permselectivity
1	−1	−1	0	1.157	0.955
2	+1	−1	0	1.260	0.977
3	−1	+1	0	1.142	0.941
4	+1	+1	0	1.230	0.948
5	−1	0	−1	1.103	0.698
6	+1	0	−1	1.139	0.830
7	−1	0	+1	1.400	0.920
8	+1	0	+1	1.598	0.980
9	0	−1	−1	1.110	0.750
10	0	+1	−1	1.090	0.748
11	0	−1	+1	1.470	0.965
12	0	+1	+1	1.440	0.936
13	0	0	0	1.330	0.968
14	0	0	0	1.279	0.953
15	0	0	0	1.250	0.976

significance of the developed models for IEC and permselectivity ($P < 0.05$).

An analysis of the normal probability of the residual can be used to examine the accuracy of the model. The normal probability versus residual for IEC and permselectivity is shown in Figure 1. A residual distribution close to a straight line is an indicator of the accuracy of the model. If the residuals fall near a straight line, the errors are evenly distributed, which supports the adequacy of the least-square fit.[23,32,37] As can be seen in Figure 1(a,b), the residuals distribute normally close to a straight line.

The plots of the residuals versus predictions for IEC and permselectivity are shown in Figure 2. As shown, all points are scattered randomly within a constant distance of residuals across the graph, i.e., within the horizontal lines at a value of ±3.0. This shows the accuracy of the models and confirms the constant variance assumption.[40]

The plots of the actual responses versus the predicted values are presented in Figure 3. As shown, the points are close to the diagonal. This shows a high correlation between experimental and predicted values and confirms the reliability of the models to predict IEC and permselectivity.

Effects of Variables on IEC and Permselectivity

IEC of the Membrane. As can be seen in Table III, ANOVA results indicate that IEC is significantly affected by ratio of resin/polymer and ratio of solvent/polymer, the P values are below 0.05 (linear variables). On the other hand, the effect of solvent/polymer ratio on IEC is more significant than that of resin/polymer ratio. Among the quadratic variables, the ratio of solvent/polymer and the ratio of additive are significant and have effects on IEC. Among the interactive terms, the interaction

Table III. Analysis of Variance for the Regressive Model of IEC

Source	DF	SS	MS	F	P > F	Significance
A	1	0.0230	0.0230	29.870	0.0028	
B	1	0.00113	0.00113	1.490	0.2763	
C	1	0.2700	0.2700	355.400	0.0001	
A. A	1	0.00295	0.00295	3.910	0.1049	
A. B	1	0.000056	0.000056	0.0740	0.7959	
A. C	1	0.00656	0.00656	8. 680	0.0320	
B.C	1	0.000025	0.000025	0.0330	0.8628	
B. B	1	0.0140	0.0140	18.050	0.0081	
C. C	1	0.0099	0.0099	13.19	0.015	
Model	9	0.3300	0.0360	48.130	0.0003	Significant
Lack of fit	3	0.00049	0.00016	0. 10	0.9521	Not significant

$R^2 = 0.9886$; $R^2_{ADJ} = 0.9680$. Significant ($P < 0.05$); highly significant ($P < 0.01$).
DF, degree of freedom; SS, sum of squares; MS: mean of squares.

of resin and solvent ratios is significant. However, as the other *P* values of the interactive terms are larger than 0.05, the IEC of the membrane is not significantly affected by other interactions of variables.

Resin particles act as ionic sites and increase the resin ratio enhances membrane properties. SEM images of the membrane surface at different resin ratios are shown in Figure 4. The distribution of anion exchange resin particles can be clearly identified in this figure. A thinner surface was obtained by decreasing the resin ratio (other variables are constant). As a result, electrochemical properties of membranes are weakened by decreasing the amount of resin particles on the surface of the membrane. The images of three different solvent ratios are shown in Figure 4. As can be seen at all solvent ratios, a thicker surface can be obtained by increasing the resin ratio, which can enhance membrane properties.

The effect of solvent ratio on membrane morphology is shown in Figure 5. The viscosity of solution increases by decreasing the

solvent ratio. Therefore, in this solution and consequently at the casted film the compression of polymer chains and covering (isolation) of resin particles by polymer binder occurred and thus the accessibility to resin particles decreased. As can be seen, at low solvent ratio [Figure 5(a,b)] the resin particles were covered with polymer binder. Therefore, the accessibility to these sites decreases and as a result the IEC decreases. But with increasing solvent ratio [Figure 5(e,f)], the resin particles can be spread at membrane surface without any isolation or accumulation due to the low viscosity of the casting solution. Spaces between resin particles and polymer binder (not covering) enhance the ion exchange process by enhancing the accessibility to resin particles [Figure 5(e,f)]. As can be seen, the accessibility to resin particles is much higher in Figure 5(e,f) than Figure 5(a,b). Therefore, the membrane has a higher IEC at higher solvent ratio.

The nature and extent of the interactions between variable factors can be shown by the shapes of the interaction and contour plots. Elliptical and circular shapes of the contour plots indicate

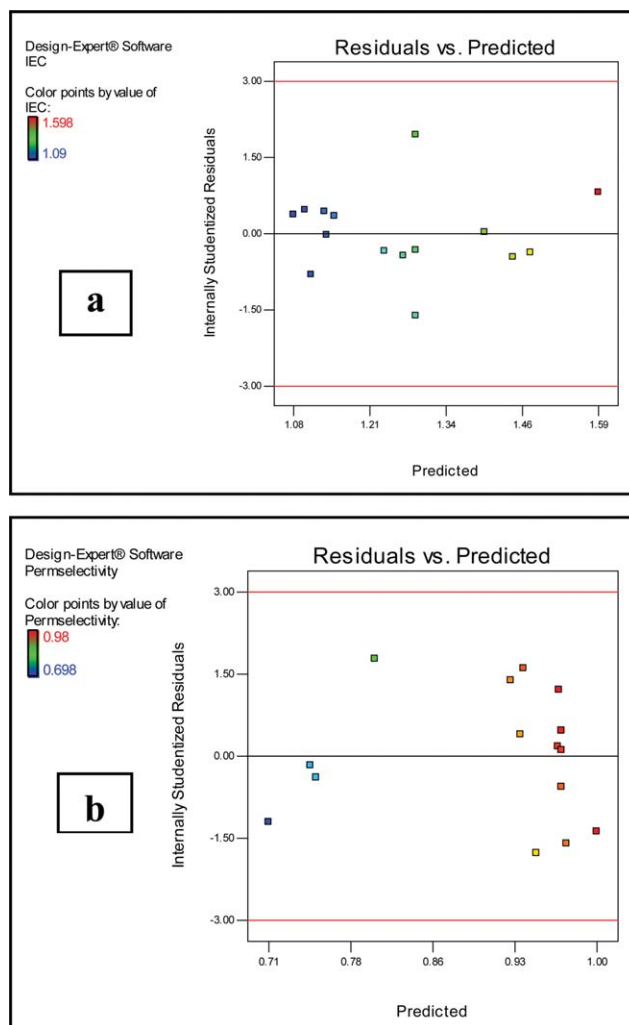**Table IV.** Analysis of Variance for the Regressive Model of Permselectivit

Source	DF	SS	MS	F	P > F	Significance
A	1	0.00610	0.00610	8.18	0.0354	
B	1	0.000684	0.000684	0.92	0.3822	
C	1	0.07500	0.07500	100.59	0.0002	
A. A	1	0.000009	0.000009	0.012	0.9157	
A. B	1	0.000056	0.000056	0.075	0.7947	
A. C	1	0.00129	0.00129	1. 74	0.2447	
B.C	1	0.000182	0.000182	0.24	0.6421	
B. B	1	0.000288	0.000288	0.39	0.5616	
C. C	1	0.042	0.042	56.73	0.0007	
Model	9	0.13	0.014	18.74	0.0024	Significant
Lack of fit	3	0.0034	0.00123	8.46	0.1076	Not significant

$R^2 = 0.9712$; $R^2_{ADJ} = 0.9194$. Significant ($P < 0.05$). Highly significant ($P < 0.01$).
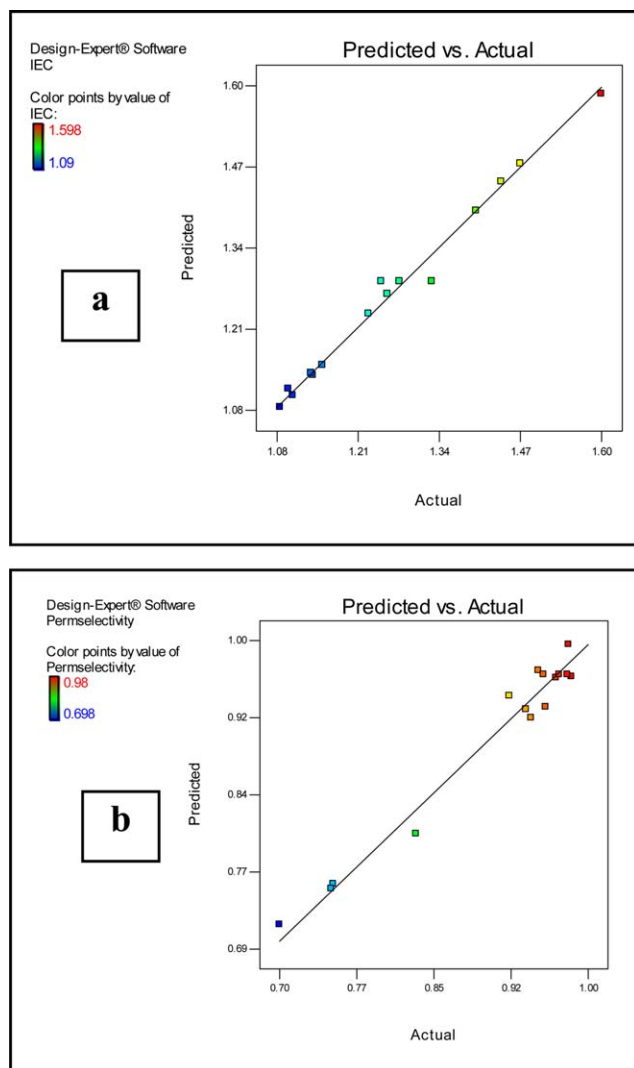DF, degree of freedom; SS, sum of squares; MS, mean of squares.
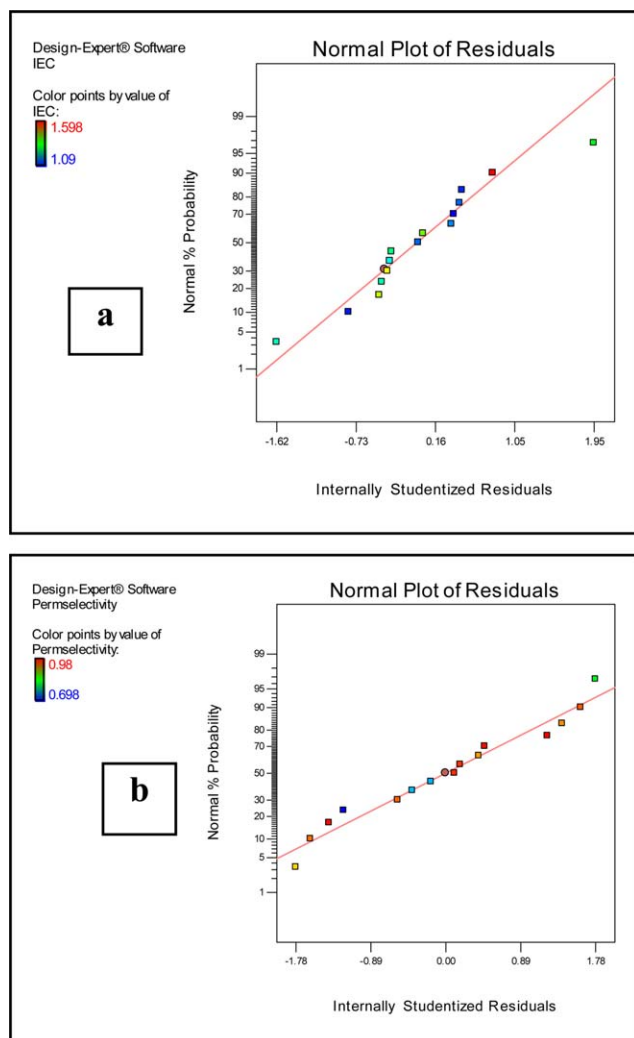
Figure 1. Normal plot of residuals for (a) IEC and (b) permselectivity. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 2. Plot of studentized residual vs. predicted for (a) IEC and (b) permselectivity. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

prominent and negligible interactions, respectively.[32] The interaction graphs and counter plots of IEC are shown in Figure 6. The interaction effect between resin ratio and additive ratio [Figure 6(a)] indicates that IEC can be improved by increasing the resin ratio. The IEC enhancement by increasing resin ratio is larger at lower additive ratios. In other words, increasing the resin ratio is more effective for the improvement of the IEC at a lower additive ratio than that at higher additive ratios. Surfactants (additive, Triton X-100) can decrease the surface tension of its contacted molecules. Therefore, the uniform distribution of resin particles can be obtained at appropriate additive ratio by decreasing the surface tension of solution. Triton X-100 has a hydrophilic polyethylene oxide chain and an aromatic hydrocarbon lipophilic or hydrophobic group (amphiphilic properties). Because of the hydrophobic properties of the solvent (toluene), a layer of surfactant molecules forms on the surface of the casting film at higher additive concentrations. This layer increases the membrane formation time. Thus, accumulation of resin particles occurs and the uniformity distribution of resin

particles as well as membrane homogeneity is decreased.[46] The latter weakens the membrane properties, i.e., IEC and permselectivity. But, appropriate amount of additive enhance the distribution of resin particles in solution and subsequently at the casted film (by decreasing the surface tension of the solution). IEC showed a peak of approximately 1.312 at a resin ratio of 1, an additive ratio of 0.03 and a solvent ratio of 15. The interaction effect between resin ratio and solvent ratio [Figure 6(b)] indicates that IEC can be improved by increasing the solvent and resin ratios. Increasing the resin ratio is more effective on IEC at higher solvent ratios. As can be seen, the accessibility to resin particles is much higher in Figure 5(e,f) than that in Figure 5(a,b). Therefore, the membrane has a higher IEC at higher solvent ratio. At an additive ratio of 0.03, by increasing the resin ratio from 0.6 to 1, IEC increases from 1.114 to 1.139 at a solvent ratio of 10, and from 1.399 to 1.586 at a solvent ratio of 20. Concentrated polymeric solutions are obtained at low solvent ratios. In membrane that synthesis with such solution, the accessibilities to resin particles decrease by covering (isolation) of resin particles with polymer binder [Figure 5(a,b)].

Figure 3. Plot of actual (a) IEC and (b) permselectivity vs. predicted values. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
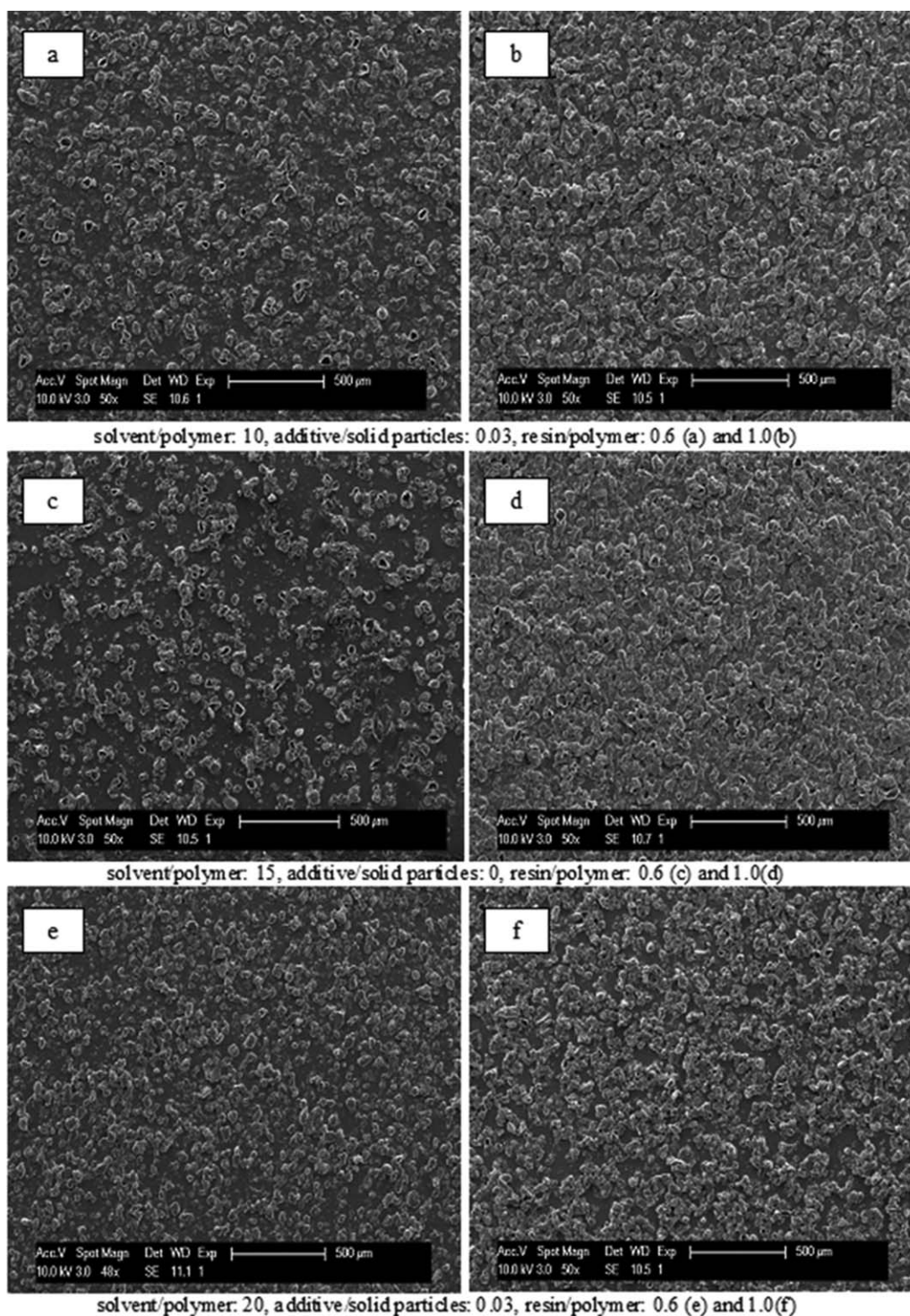
The plotted response surface graphs between two independent variables, where the other independent variables were kept at the centre point, are shown in Figure 7. These curves were used to investigate the interaction of the variables and to determine the optimum level of each variable for a maximum response.[30] A similar trend to Figure 6 can be seen in Figure 7. Figure 7(a–c) shows that the IEC is always enhanced by increasing the ratio of resin and solvent. Triton X-100 is a non-ionic surfactant. As such, by adding this additive, the solution's surface tension decreases and causes a uniform distribution of resin particles in the solution, and consequently in the casting film. The uniform distribution of resin particles at different solvent ratios and an additive ratio of 0.03 can be seen in Figure 8. Electrochemical properties of membranes are enhanced by a uniform distribution of resin particles. The effect of additive ratio at a solvent ratio of 15 can be seen in Figure 9. The membrane in Figure 9(b) was synthesized with a resin ratio of 0.8, but it was found to have a similar morphology to those of Figure 9(a,c), synthesized with a resin ratio of 1. The IEC of the membrane in Figure 9(b) (1.28) is higher than those of Figure 9(a) (1.26) and Figure 9(c) (1.23).

At higher ratios of additive (because of increasing membrane formation time and accumulation of resin particles) and lower ratios of solvent (compression of polymer chains and isolation of resin particles), resin particles become covered with polymer binder (decrease the accessibility of ion exchange groups in the membrane). The low IEC at low solvent and high additive ratios is attributed to this phenomenon. As a result, the accessibility of resin particles decreases by their covering with polymer binder and subsequently weakens the IEC of the membrane. A high IEC cannot be obtained at low solvent to polymer ratios, even at high resin and appropriate additive ratios [Figure 5(b)]. Generally, the high resin ratio and appropriate additive ratio are necessary for obtaining a high IEC. But the most important and effective parameter in obtaining high IEC is the ratio of solvent, which determines the accessibility to resin particles in the membrane matrix. Decreasing the accessibility to resin particles because of compression of polymer chains and covering the resin particles with polymer binder can be mentioned as a reason of the relatively low IEC at low solvent ratio.

Membrane Permselectivity. The ANOVA results confirm that the permselectivity is significantly affected by linear variables, i.e., ratio of resin to polymer and ratio of solvent to polymer. Among the quadratic variables, the ratio of solvent to polymer is significant and has a great effect on the permselectivity of the membrane.

During the membrane formation process the solvent can be removed easier from a thinner casted film.[24] when two membranes were casted by the same thickness on clean glass plate, a thinner film is obtained with a low viscous mixture. After casting the solution, the membrane is dried for 30 min (solvent evaporation) and then immersed in distilled water (precipitation). The membrane casted with a more viscous polymeric solution (lower solvent ratio and higher resin ratio) cannot be dried completely during 30 min, solvent cannot removed completely from the concentrated casted film, and the remaining

Meanwhile, IEC cannot be improved significantly even with increasing the resin ratio. At high solvent ratios, relatively enough spaces around resin particles enhanced the ion exchange possibilities. This means that resin particles do not become covered with polymer binder [this point can be clearly observed in Figure 5(e,f)]. Therefore, IEC is significantly improved with increasing the resin ratio at high solvent ratio. IEC had a peak of approximately 1.586 at a resin ratio of 1, a solvent ratio of 20, and an additive ratio of 0.03. The interaction effect between additive ratio and solvent ratio [Figure 6(c)] indicates that, the IEC can be improved by increasing the additive ratio up to 0.03, a further increase of the additive ratio decrease the IEC again. The IEC enhancement is larger at higher solvent ratios. The IEC shows a peak of approximately 1.52 at a resin ratio of 0.8, a solvent ratio of 19.90 and an additive ratio of 0.03. The uniform distribution of resin particles, due to the presence of appropriate amount of additive, improves the IEC of the membrane.

solvent/polymer: 10, additive/solid particles: 0.03, resin/polymer: 0.6 (a) and 1.0(b)

solvent/polymer: 15, additive/solid particles: 0, resin/polymer: 0.6 (c) and 1.0(d)

solvent/polymer: 20, additive/solid particles: 0.03, resin/polymer: 0.6 (e) and 1.0(f)

Figure 4. SEM images of membranes (×100 magnification) with different resin ratio.

part of the solvent should be removed via a solvent-non solvent exchange process (precipitation). Therefore, the resulting membrane has some pores [Figure 5(b)]. Furthermore, this membrane has a very compact structure and resin particles are covered with the polymer matrix (also compression of polymer chains). A porous structure and covering of resin particles with polymer binder decreases the permselectivity of the membrane.

However, at high solvent ratio, the solvent can be removed almost completely in 30 min and the membrane does have more significant dense structure than latter [Figure 5(f)]. The Donnan exclusion becomes effective for the membrane with less porous structure.[24] In this membrane only anions (the membrane has positive fixed sign) can pass through the membrane. A more selective membrane would therefore be less conductive,
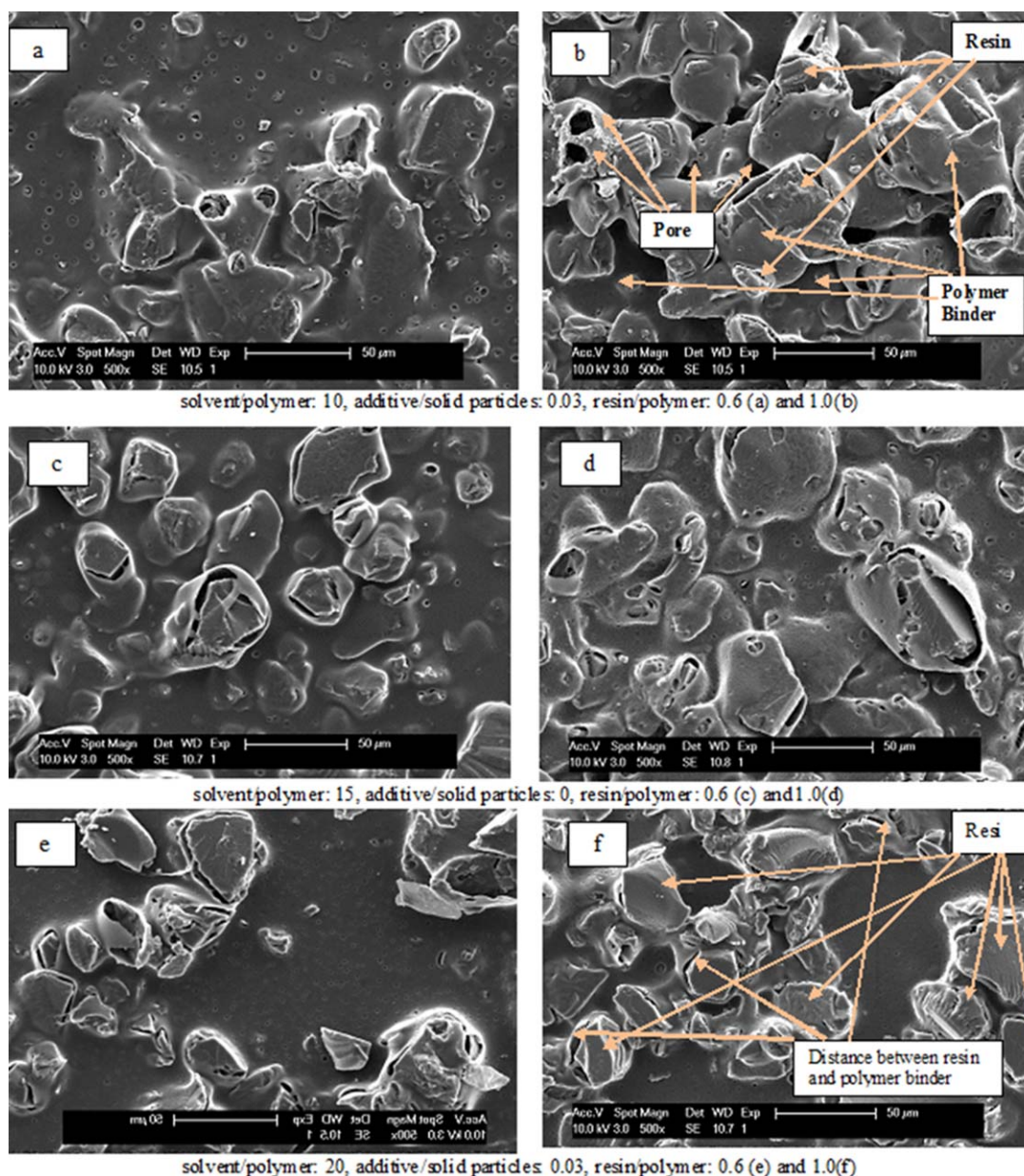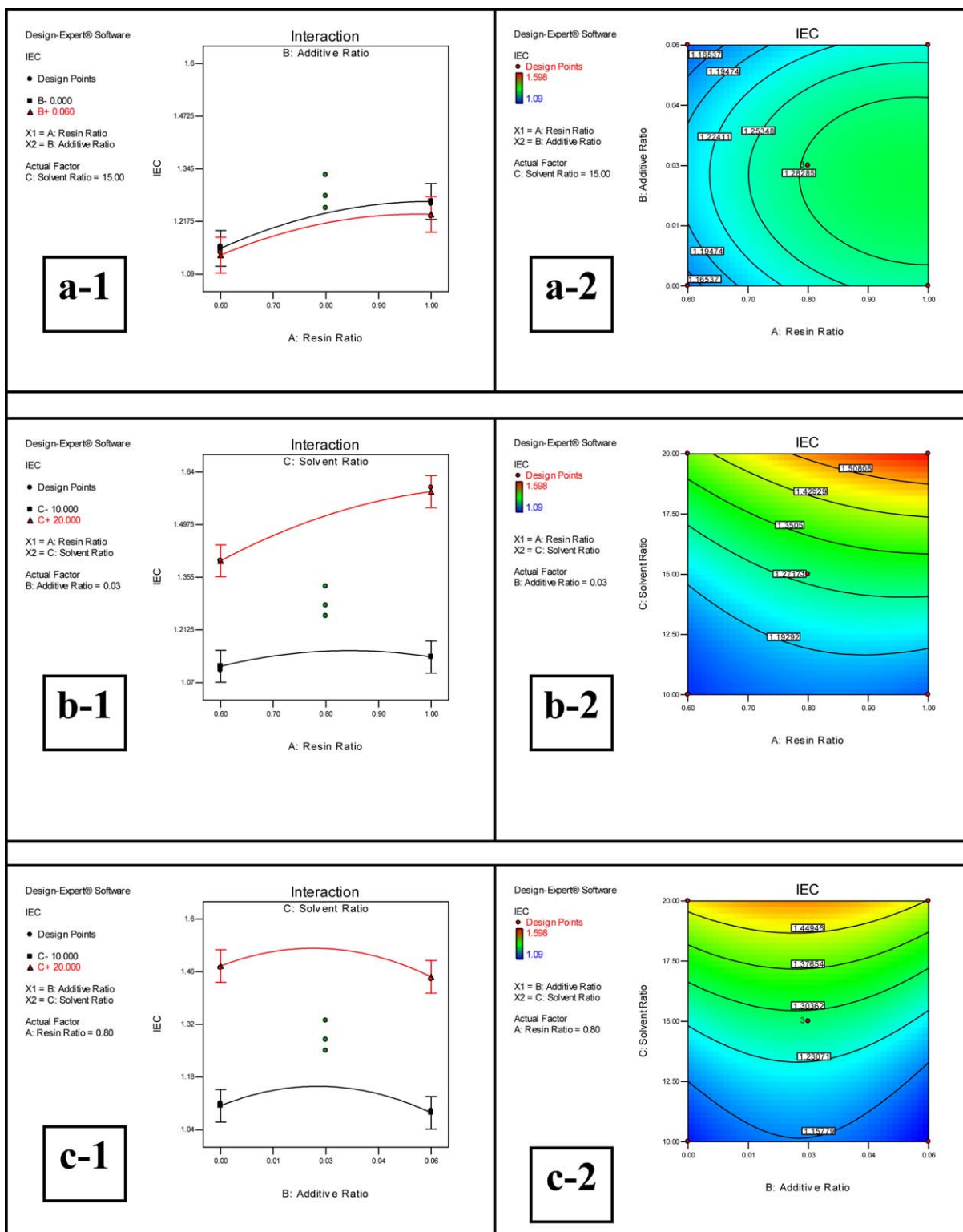
Figure 5. SEM images of membranes (×500 magnification) with different solvent ratio. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

because of non-porous structure. On the other hand, Donnan exclusion becomes less effective with increasing membrane porosity. Membranes with porous structures show a lower selectivity than dense membranes. However, porous membranes have lower resistances, higher conductivity and higher permeabilities than dense membranes.[24]

The interaction graphs and counter plots of permselectivity are shown in Figure 10. The interaction effect between resin ratio and additive ratio [Figure 10(a)] indicates that permselectivity can be enhanced by increasing the resin ratio. The permselectivity enhancement versus resin ratio is larger at lower additive ratios. The maximum value of permselectivity (0.994) was

obtained at a resin ratio of 1 and an additive ratio of 0.01 (solvent ratio was 15). The high additive ratio has negative effect on permselectivity of the membrane. Accumulation of resin particles (decrease of uniform distribution of resin particles) because of longer membrane formation time at high additive ratio has been occurred due to formation of additive layer on surface of the casting film. This layer decreases the rate of solvent evaporation.[46] Therefore, the most parts of solvent should be removed by solvent- non solvent process instead of solvent evaporation process. As a result, the obtained membrane has some pores in its structure. As described earlier, the Donnan exclusion becomes less effective due to the presence of these pores [Figure 9(c)]. The interaction effect between resin
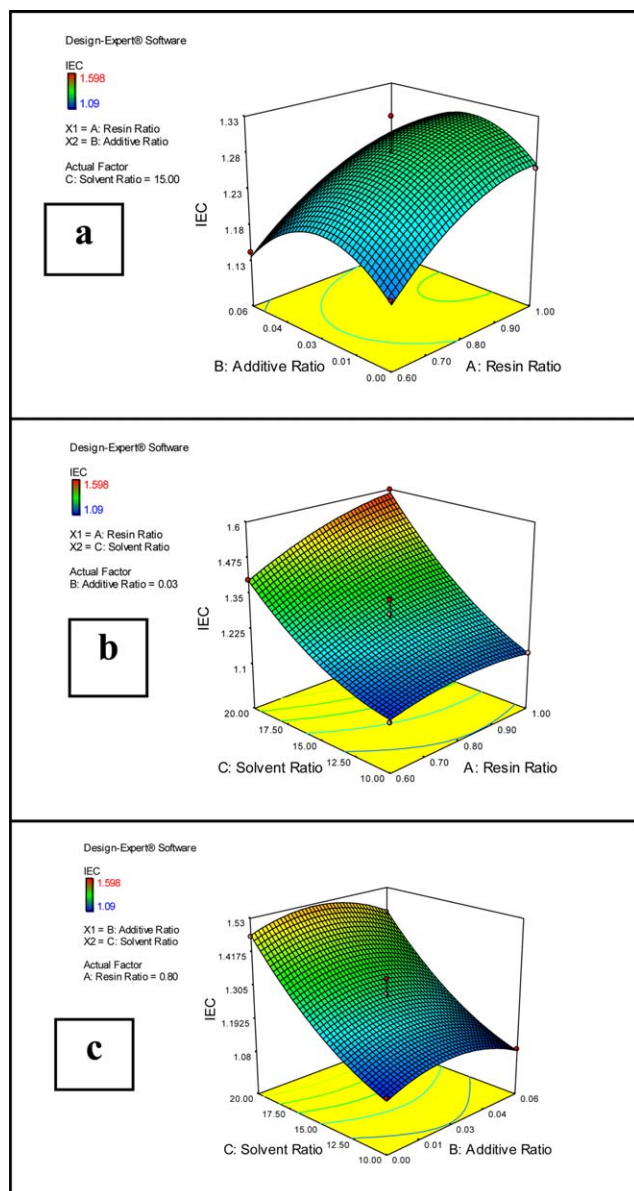
Figure 6. Interaction graphs (a1-c1) and counter plots (a2-c2) of IEC. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

ratio and solvent ratio [Figure 10(b)] indicates that, permselectivity can be improved by increasing the resin ratio. At a solvent ratio of 10 and an additive ratio of 0.03, the permselectivity increased from 0.69 to 0.83 by increasing the resin ratio from 0.6 to 1.0. Because of compression of polymer chains and covering of resin particles with polymer binder the low permselectivity obtained at a resin ratio of 0.6 and a solvent ratio of 10 [Figure 5(a)]. With increasing the resin ratio, increasing the

Figure 7. Response surface plots vs. IEC. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

charged site of the membrane, but because of the presence of some pores in the membrane structure a high permselectivity cannot be obtained [Figure 5(b)]. At a solvent ratio of 20, the permselectivity increased from 0.92 to 0.98 by increasing the resin ratio from 0.6 to 1.0 [good accessibility and relatively dense structure at 1 resin ratio, Figure 5(f)]. A membrane with high permselectivity should have a relatively dense structure. The structures of membranes have been studied using SEM images with high magnification (500×). It is verified that the membrane with high permselectivity [0.98; Figure 5(f)] has a significantly more dense structure than membrane with low permselectivity [0.82; Figure 5(b)]. On the other hand, Donnan exclusion becomes less effective with increasing membrane porosity. Membranes with porous structures show a weaker performance, i.e., lower permselectivity, than dense membranes. It was verified that the fixed charge density of membranes increased with reduced pore size and porosity.[24] The membrane with high IEC and relatively dense structure has high fixed charge density. The membrane in Figure 5(f) has a charge density of 3.591 meq/cm^3. As can be seen in Figure 11, permselectivity increases significantly with increasing the solvent ratio. The maximum value of permselectivity can be obtained at solvent ratios in the range of 16 to 18 (at a resin ratio of 1 and an additive ratio of 0.03). At a constant resin ratio, the surface of the membrane becomes thinner with increasing solvent ratio [Figure 4(b,d,f)]. At high resin and solvent ratios [Figure 4(f)] the distribution of resin particles on the surface of the membrane is thinner than that of low solvent and high resin ratios [Figure 4(b)]. The thin distribution of resin particles decreases the permselectivity of the membrane. The dense structure and uniform distribution of resin particles are necessary for obtaining a high permselectivity. Figure 10(c) indicates that the permselectivity can be increased by increasing the additive ratio up to 0.02, a further incorporation of additive decreases the permselectivity. The rate of solvent evaporation during the membrane formation decreases by the formation of an additive layer on the casted film (at higher additive ratios). Therefore, the accumulation and isolation of resin particles and presence of pores in the membrane structure decrease the permselectivity of the membrane [Figure 9(c)].

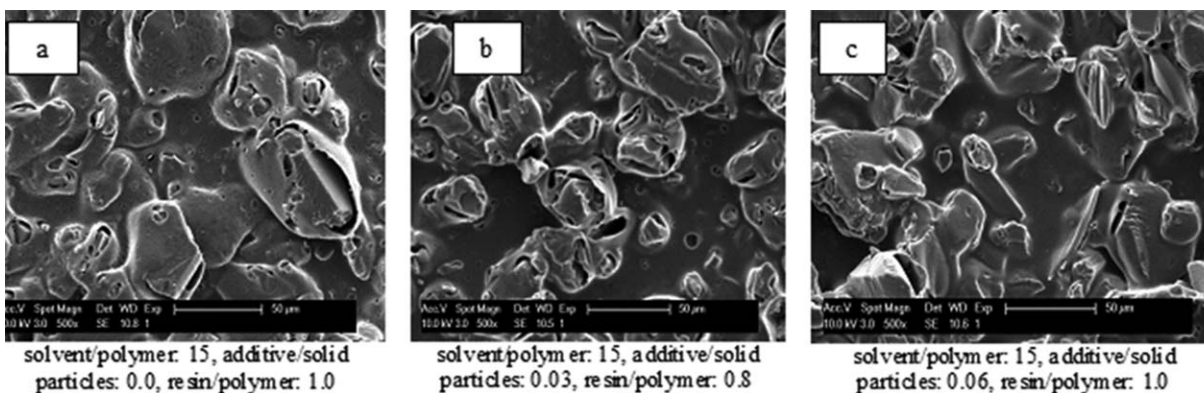**Figure 8.** Effect of additive addition on distribution of resin particles (×100 magnification).

solvent/polymer: 15, additive/solid
particles: 0.0, resin/polymer: 1.0

solvent/polymer: 15, additive/solid
particles: 0.03, resin/polymer: 0.8

solvent/polymer: 15, additive/solid
particles: 0.06, resin/polymer: 1.0

Figure 9. Effect of additive ratio on isolation of resin particles (×500 magnification).

The plotted response surface graphs between two independent variables, where the other independent variables were kept at its centre point, are shown in Figure 12. The effect of resin and additive ratios on the permselectivity is shown in Figure 12(a) (solvent ratio at its zero coded level). As it can be seen, similar to Figure 10(a), the permselectivity increases by increasing the resin ratio. Increasing the additive ratio initially improved the membrane permselectivity; however, a further increase in additive decreases the membrane permselectivity. The membrane permselectivity was improved by increasing the resin ratio at all additive ratios. A uniform distribution of functional groups and therefore effective Donnan exclusion can be obtained using higher resin and appropriate additive ratios. The SEM images of membranes with different magnification (500×, 200×, and 50×) for membrane with a resin ratio of 1, a solvent ratio of 20, and an additive ratio of 0.03 are shown in Figure 13. As can be seen, high permselectivity was obtained due to the uniform distribution of resin particles and relatively dense structure. Also, uniform distribution of resin particles at different solvent ratios and 0.03 additive ratio can be seen in Figure 8.
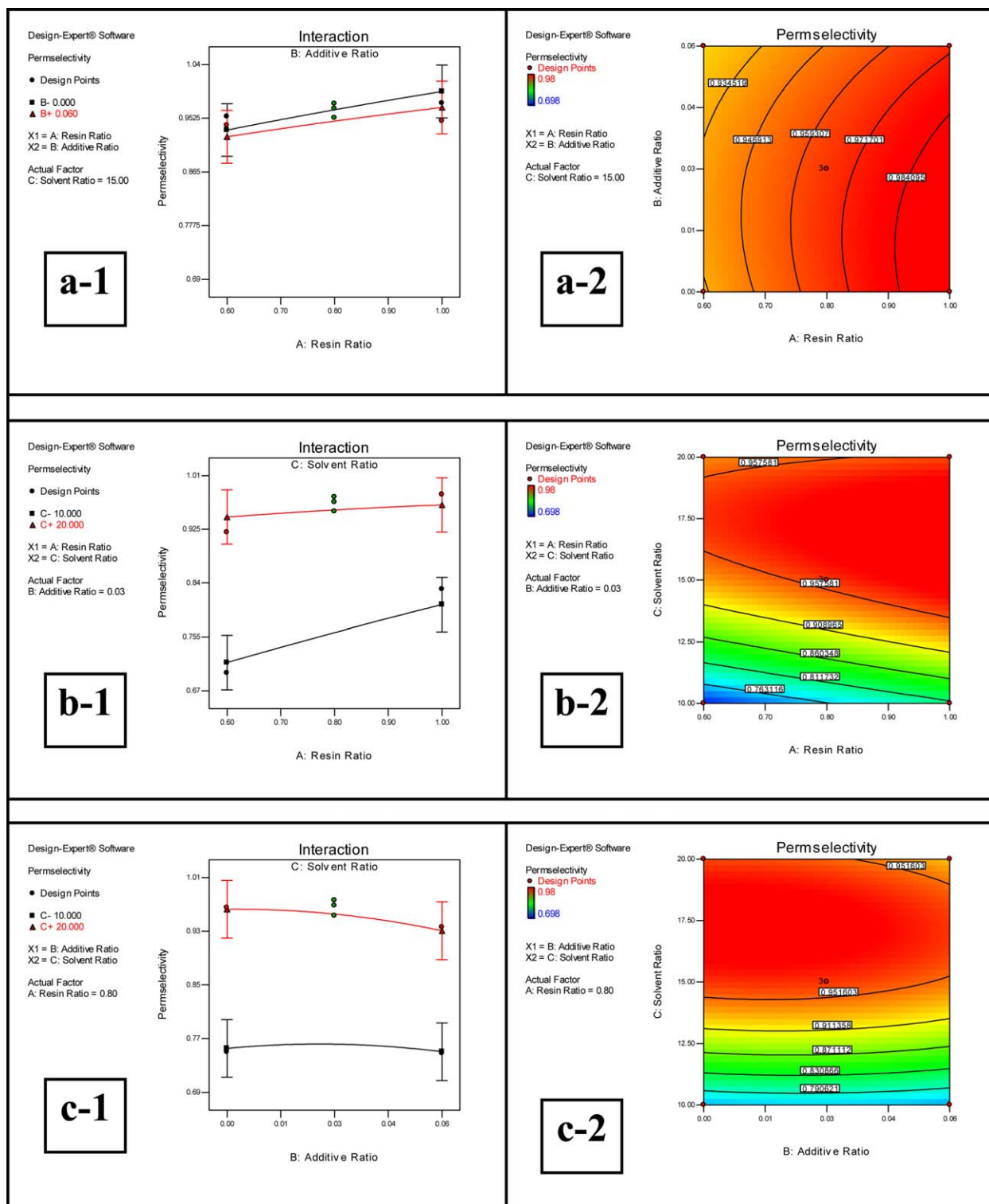
The membrane's permselectivity can be enhanced by increasing the solvent and resin ratios [Figure 12(b)]. As described earlier, covering of resin particles and presence of some pores in the membrane structure decreases the permselectivity of the membrane at lower solvent and higher additive ratios [Figure 5(b)]. At a constant resin ratio, an appropriate ratio of additive can enhance the membrane permselectivity at higher solvent ratios [Figure 12(c)]. However, that does not have a significant effect on the permselectivity at lower solvent ratios.

PREDICTION OF OTHER PROPERTIES OF THE MEMBRANE

In this study the effects of variable parameters on properties of the membrane are determined in a time saving method with a small number of experimental trials. As described, the properties of the ion exchange membrane work in the opposite or the same direction. Therefore, some properties can be predicted based on the other properties. In this study, the IEC and permselectivity of the membranes were measured experimentally. It was found that the solvent to polymer ratio and resin to polymer ratio are the most effective variables influencing the IEC and permselectivity. The trend of other properties of the membrane can be determined based on these variables.

• Conductivity and water content: It was shown that based on the membrane structure, by decreasing the membrane porosity, the permselectivity increases but the water content and conductivity decrease.[24] Thus, it is expected that a membrane with some pores in its structure has a lower permselectivity, a higher conductivity and a higher water content than a membrane with relatively dense structure. On the other hand, the electrochemical properties of the membrane are always enhanced with increasing resin ratio (as charged sites of membrane). Sample 6 [show in Figure 5(b)], sample 2 [Figure 5(d)], and sample 8 [Figure 5(f)] have a resin ratio of 1 and different solvent-to-polymer ratios (Table II). Figure 5 shows that the amount of pores in membrane structure reduces with increasing solvent ratio. Sample 8 has a relatively dense structure and has a high permselectivity (0.980), sample 6 has a porous structure and a lower permselectivity (0.830); sample 2 has a permselectivity between the two other samples (0.972). Therefore, according to their permselectivities and structures it is expected that the conductivity and water content of these membranes show opposite trends of permselectivity. This prediction was verified by measuring the conductivity and water content. Samples 8, 2, and 6 have 28.10, 34.37, and 38.46 water content and 5.2, 6.3, and 11.5 (mS cm^{-1}) conductivity, respectively. The solvent ratio resulted in some changes in membrane structure (porosity). The water content increases with increasing porosity of the membranes (due to water accumulation in membrane pores). The conductivity has a similar trend because the mobility of ions enhances due to the presence of continuous water channels. At the same solvent ratio, the conductivity and water content increase with increasing resin ratio. Water can be absorbed by resin particles and also at distances between resin particles and polymer binder. The increasing conductivity and water content with resin ratio was observed for samples 5 [Figure 5(a)] and 6 [Figure 5(b)], samples 1 [Figure 5(c)] and 2 [Figure 5(d)] and samples 7 [Figure 5(e)] and 8 [Figure 5(f)]. Samples 5 and 6 show a permselectivity of 0.698 and 0.830, respectively. The conductivity (4.1 (mS cm^{-1})) and water content (26.65) of sample 5 are lower than the conductivity (11.5(mS cm^{-1})) and water content (38.45) of sample 6. The electrochemical properties of the membrane improve with an increasing amount of charged sites (resin

Figure 10. Interaction graphs (a1-c1) and counter plots (a2-c2) of permselectivity. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

particles) on the membrane surface. However, this improvement is different at different solvent ratios. At a solvent ratio of 20, the conductivity and water content increase from 3.9 to 5.2 (mS cm^{-1}) and from 26.30 to 28.10 by increasing resin ratio from 0.6 to 1, respectively. At a solvent ratio of 10, the conductivity and water content increase from 4.1 to 11.5 (mS cm^{-1}) and from 26.65 to 38.45, respectively, by increasing the resin ratio from 0.6 to 1. Therefore, at lower solvent ratio,
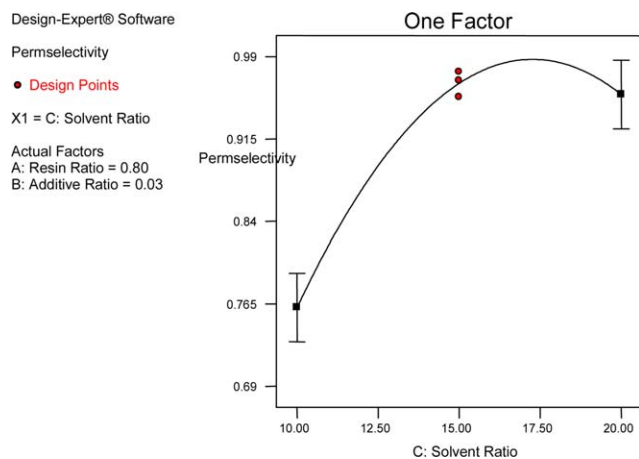
Figure 11. Permselectivity verse solvent ratio at a resin ratio of 1 and an additive ratio of 0.03. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

increase of the water content by increasing the resin ratio is higher than that at higher solvent ratio because of the difference in membrane structure of the membrane (more increasing in membrane porosity at 10 solvent ratio) [Figure 5(a,b)]. This trend is observed at a solvent ratio of 15 (sample 1 [Figure 5(c)] and 2 [Figure 5(d)]).

- Transport number and fixed group concentration: The membrane with high permselectivity has high transport number and high charge of the membrane matrix (fixed group concentration) [eqs. (4) and (5)].
- Fixed ion concentration: The fixed ion concentration (FIC) is another important property of the membrane. The FIC increased with increasing IEC and decreasing water content [eq. (3)]. The IEC increases with increasing solvent and resin ratio and water content increase with increasing resin ratio and decreasing solvent ratio. Therefore, improvement of FIC depends on the amount of increase of the IEC and decrease of the water content. By increasing the resin ratio, at low solvent ratio, the increase of water content is more significant than the increase of the IEC. Therefore, the FIC decreases with increasing resin ratio. The FIC of the membrane decreases from 4.13 meq/g (sample 5) to 2.96 meq/g (sample 6) by increasing the resin ratio from 0.6 to 1. This can be explained by increase of the porosity of the membrane. However, at high solvent ratio, FIC of the membrane increases from 5.32 meq/g (sample 7) to 5.686 meq/g (sample 8) by increasing the resin ratio from 0.6 to 1. At a high solvent ratio, the increase of the IEC is more significant than the increase of the water content. The membrane with the high IEC, i.e., sample 8, has high FIC (5.686).

The effect of solvent and resin ratios on the properties of ion exchange membranes are schematically shown in Figure 14

The permselectivity, transport number, IEC, and fixed group concentration increase with increasing resin and solvent ratios. However, the conductivity and water content increase with increasing resin ratio and decreasing solvent ratio.It should be mentioned that a membrane with a more dense structure can be synthesized with increasing solvent evaporation period
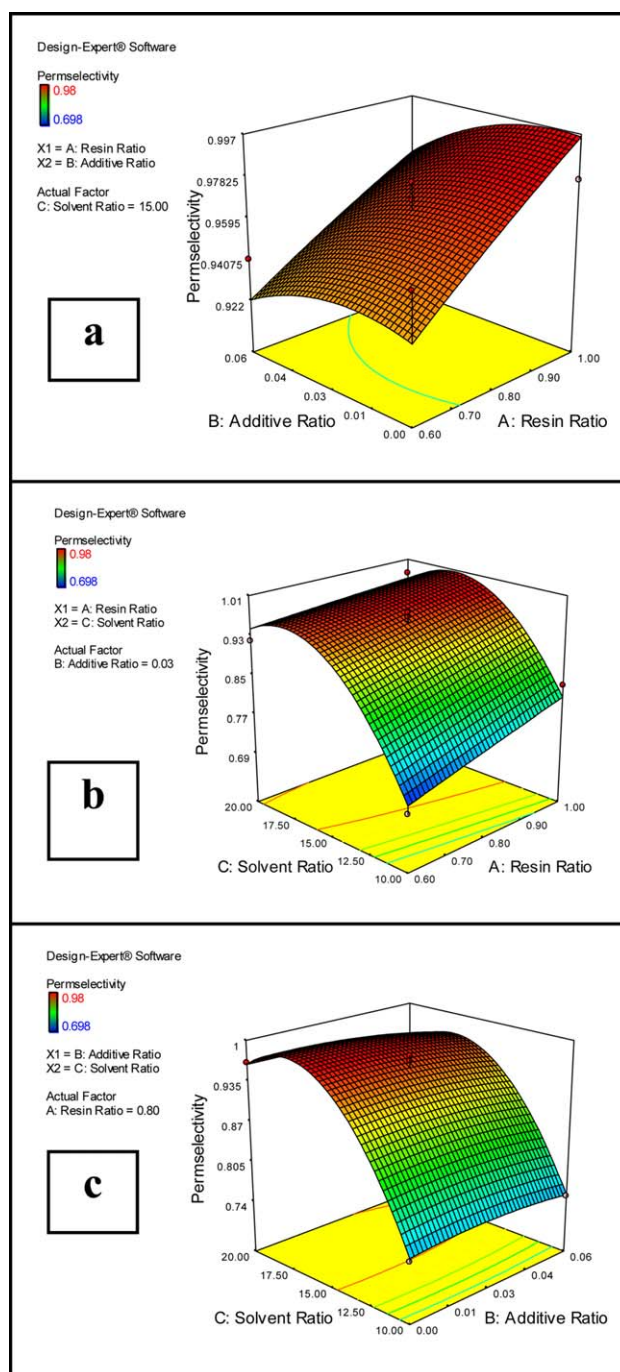

Figure 12. Response surface plots vs. permselctivity. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

(during the membrane formation process). In other words, the porosity of the membrane can be reduced with increasing drying time.[24] Therefore, by increasing the drying time (more than 30 min) a membrane with less porous structure can be obtained at lower solvent ratio.

OPTIMUM CONDITIONS

The maximum IEC and permselectivity were set as criteria for obtaining optimum condition for membrane synthesis. To verify
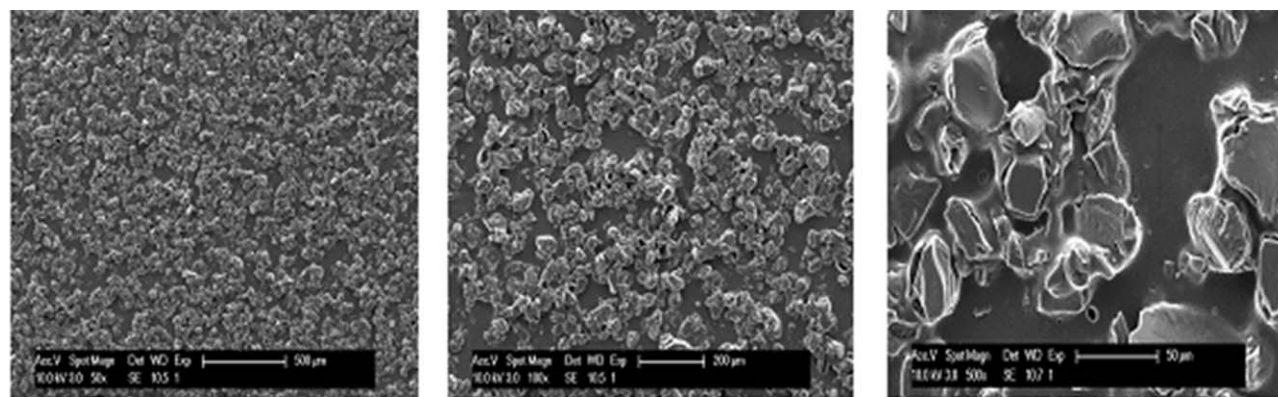
Figure 13. SEM images of distribution of functional group at a solvent ratio of 20, resin ratio of 1 and an additive ratio of 0.03.

the adequacy of the model, the IEC and permselectivity of the optimum point (maximum IEC and permselectivity) that predicted with model were measured experimentally. The predicted values for IEC and permselectivity with a solvent/polymer ratio of 18.63 (v/w), resin/polymer ratio of 1 (w/w) and additive/total solid ratio of 0.02 (w/w) are 1.495 and 0.998, respectively. The actual experimental values are 1.510 and 0.991, respectively. This was considered a fair and useful prediction.

CONCLUSIONS

In this study, optimum conditions for obtaining high IEC and high permselectivity of anion exchange membranes was investigated by using RSM technique. It was observed that the ratios of solvent/polymer and resin/polymer have significant effects on the IEC and permselectivity of the membrane. However, the ratio of solvent/polymer was the most significant variable.

It is necessary to find the optimum conditions as a compromise between a higher IEC and a higher permselectivity. Three variable factors were optimized simultaneously to identify the anion exchange membrane with maximum permselectivity and IEC. It was found that the optimum values of the variable factors should be adjusted at 18.63 (v/w) for solvent/polymer ratio, 1 (w/w) for resin/polymer ratio and 0.02 for the additive/total solid ratio. The predicted values for IEC and permselectivity were confirmed experimentally while only a limited deviation from the predicted values was observed.

The trends of properties of the membrane were predicted based on the most effective variable factors. The permselectivity, trans-

port number, IEC, and fixed group concentration increase with increasing the resin and solvent ratios. However, the conductivity and water content increase with increasing the resin ratio and decreasing the solvent ratio.

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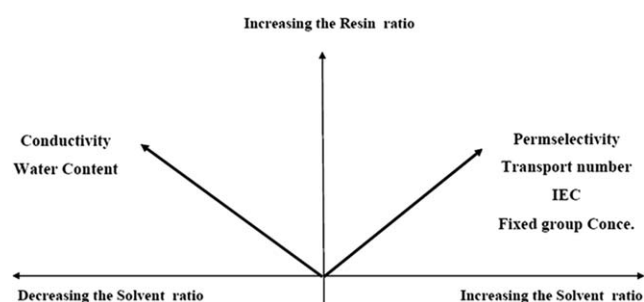
Figure 14. Schematic diagram of membrane properties base on variation of variable factors.

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