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Modification of a heterogeneous anion exchange membrane via amination process

T. Kikhavani[a], M. Ghavami[b], M. Namdari[b], S.N. Ashrafizadeh[b,*]

[a]*Chemical Engineering Department, Faculty of Engineering, Ilam University, Ilam 69315-516, Iran, Tel. +98 8432227026, email: kikhavani@iust.ac.ir*
[b]*Department of Chemical Engineering, Research Lab for Advanced Separation Processes, Iran University of Science and Technology, Narmak, Tehran 16846-13114, Iran, Tel. +98 21 77240496; Fax: +98 21 77240495; emails: ashrafi@iust.ac.ir (S.N. Ashrafizadeh), morteza_ghavami_66@yahoo.com (M. Ghavami), mhs.namdari@gmail.com (M. Namdari)*

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ABSTRACT

Heterogeneous anion exchange membranes were modified via amination process using dipropylamine solution as a new method. The response surface methodology was used for the optimization of amination process to correlate the relationship among variables, that is, amination time, amination temperature, concentration of the amine solution, and responses, that is, the selectivity between coions/counterions (permselectivity) and the selectivity between two counterions. The selectivities were enhanced by increasing the concentration and amination time, as well as decreasing the temperature. The highest selectivities were obtained at amination duration of 36 h, temperature of 25°C and concentration of amination solution of 35 wt%. After modification, the permselectivity and selectivity increased by 16.7% and 34.4%, respectively. Furthermore, the effect of solvent type on the amination process was investigated and methyl acetate was chosen as the most appropriate solvent for amination process versus ethanol.

Keywords: Heterogeneous anion exchange membrane; Amination; Selectivity; Modification; Response surface methodology

1. Introduction

Ion exchange membranes have numerous applications in many separation processes such as dialysis, production of organic acids, fuel cells, electrodialysis (ED), electrolysis, and a number of other processes [1–3]. An effective ion exchange membrane must have good electrochemical properties as well as satisfactory mechanical, chemical, and thermal stabilities [4–9]. Permselectivity and selectivity between different counterions are two crucial electrochemical parameters in the design of ion exchange membranes determined by the ion exchange membrane potential [10]. As such, high transport number of counterions as well as a high retention of coions, directly linked with high membrane potential, is desired for an ideal ion exchange membrane. This is particularly useful in the applications where high selectivity between counterions (between monovalent and divalent ions or even between ions with similar charge numbers, i.e., NO_3^- and Cl^-) is required. For instance, in water desalination process for production of potable water, complete demineralization of water is not desirable as it can cause serious health risks [10,11]. By utilizing ion exchange membranes with high selectivity and permselectivity between coions and counterions in this process, obtaining potable water with the eligible amount of minerals could become feasible [10,12].

Selectivity of ion exchange membranes can be defined in two ways [10]:

- Permselectivity: high retention of coions and transport of counterions
- Selectivity: selectivity between different counterions (between monovalent and divalent ions or even between ions with similar charge numbers, i.e., NO_3^- and Cl^-).

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* Corresponding author.

In order to improve the selectivity and permselectivity of an ion exchange membrane, several modification methods have been proposed in the literature [6,7,13–19]. It is shown that not only incorporating specific ion exchange groups significantly enhances the selectivity but also the distribution state of these functional groups has an effective role on the membrane electrochemical properties including the membrane transport number and consequently the membrane permselectivity. This is particularly important for heterogeneous ion exchange membranes where, unlike homogeneous membranes, the particles containing functional groups are not distributed uniformly along the polymeric matrix [1]. This issue once coupled with the disability of neutral polymeric segments within heterogeneous ion exchange membranes in transferring ionic species, causes remarkable reduction of the efficiency of the membranes. Thus, one way to significantly improve the heterogeneous ion exchange membrane efficiency is to employ a fabrication method which ensures uniform dispersion of resin particles accompanied by introducing functional agents to the polymeric matrix. Another important consideration in design of membranes is the interfacial properties of membranes which define the amount of Gibbs hydration energy of ions hence affecting the affinity of an ion toward membranes and the membrane selectivity. For instance, hydrophobic membranes have more affinity toward ionic species with less Gibbs hydration energy. As a result, by increasing the membrane hydrophobicity, its selectivity for ions with low Gibbs hydration energy could be improved.

In this research, a heterogeneous anion exchange membrane (AEM) was prepared with the aim of having high permselectivity and selectivity toward nitrate ions in water treatment process. This is motivated by the fact that nitrate can have inverse effects on human health. Excess amount of nitrate in human body could cause cancer due to nitrosamides or nitrosamines Therefore water contamination by nitrate is a serious problem in urban water networks. As nitrate ions have low hydration energy, a hydrophobic membrane will result in higher selectivity. Chlorinated polypropylene (CPP) is a hydrophobic material selected for this study. This polymer reacts with amine groups due to the presence of chloride agents in its chains [20] leading to the enhancement of electrochemical properties of AEM by introducing functional agents to the neutral polymeric segments. It is essential to use amines with long alkyl chains so the hydrophobicity of the membrane matrix could be further enhanced [20,21]. Another advantage of employing amination reaction is its ability to strengthen the mechanical properties of membrane matrix by the development of crosslinks throughout the matrix [20,22]. The key consideration to achieve high success in application of amination process, however, is to control various operational variables in the process. Response surface methodology (RSM) was used as an experimental design method to investigate the effect of different variables and their interactions in the process and optimize the response with the minimum number of experimental trials. Polynomial function expresses the relationship between different variables, which presented in 3D surfaces called fitted surfaces [23–27]. The parameters that affect the amination reaction are temperature, reaction time and concentration of the amine solution [7,14,20,28–33]. The central composite design (CCD) was applied to correlate these reaction variables to the responses. The concentration potential was used to calculate the membrane permselectivity between coions/counterions, and the bi-coionic/bi-counterionic potential was used for calculating the selectivity between two coions (nitrate and chloride) [34]. To the best of the author's knowledge, using amination process for modification of a heterogeneous AEM has not been reported yet.

2. Experimental

2.1. Materials

Chlorinated-polypropylene (CPP, M_w = 100,000 g/mol) was supplied by Sigma-Aldrich Co., Japan. Toluene was obtained from Chem-Lab Co., Belgium and used as solvent. Dipropylamine, ethanol, and methyl acetate were obtained from Merck. An anion exchange resin, Lewatit® Sybron Ionac® SR-7, Germany (92642 Fluka), from Sigma-Aldrich was used as ion exchange reagent. Other chemicals (NaCl and $NaNO_3$) were obtained from Merck.

2.2. Membrane preparation and modification

2.2.1. Synthesis of a heterogeneous anion exchange membrane

The heterogeneous AEM was prepared via dispersing anion exchange resin particles in the polymeric solution, followed by solvent evaporation. First of all, anion exchange resins dried in an oven at 50°C for 24 h, powdered in a ball mill and sieved to the −300 + 400 mesh. The polymeric solution was prepared by dissolving CPP in toluene (solvent) as well. When a homogeneous solution was obtained, the powdered resin particles were added to the polymeric solution, and the mixture was agitated at room temperature using a mechanical stirrer. The ratio of resin to polymer was kept at 1/1 (w/w). After obtaining a uniform dispersion of particles in the solution, the mixture was cast on a dry and clean glass plate and allowed to completely dry at ambient temperature (solvent evaporation). The synthesized AEM was treated by immersing in 1 M sodium nitrate solution. This membrane was named M_1.

2.2.2. Modification of the synthesized membrane by amination process

In order to initiate the amination process, the lab made heterogeneous AEM was immersed in a solution of dipropylamine. Amination reaction was carried out at different concentration of amine solution and different reaction temperature for particular time intervals in a sealed container at a shaker incubator (Teb Azma, Iran). In addition, ethanol and methyl acetate were used as solvent for amination reaction.

2.3. Experimental design

The Design Expert software (Stat-Ease Inc., Minneapolis) was used for experimental design. The CCD with a quadratic model was employed to correlate the variables to the responses. Three independent variables are amination temperature, amination time (duration), and concentration of amine solution. The responses are selectivity between coions/counterions (permselectivitiy) and selectivity between two counterions (nitrate and chloride). A second-order polynomial function that consists of linear, quadratic, and interactive components is applied to show the relation between response and variables:

$$Y = A_0 + \sum A_i X_i + \sum A_{ii} X_i^2 + \sum A_{ij} X_i X_j \tag{1}$$

where Y is the response variable; A_0, A_i, A_{ii}, and A_{ij} are the intercept, linear, quadratic, and interaction constant coefficients, respectively; X_i and X_j (i = 1–3; and j = 1–3) represent the independent variables [24,35].

Analysis of variance (ANOVA), the F value and p-value, is used to determine the statistical significance of the model. A desirable model should have a high F value and a p-value below 0.05. The accuracy of the model is determined by R-squared and adjusted R-squared. The R^2_{adj} and R^2 show the fraction of the response variation explained by the model adjusted for degrees of freedom and measure of variance in the response values, respectively [24]. The variables with the coded and actual values are shown in Table 1.

As mentioned hereinbefore, ethanol and methyl acetate were used as solvent for the modification of a membrane with dipropylamine to investigate the effect of solvent type on the amination process. Seventeen experiments were conducted at different combinations of variables for each solvent. However, because of low boiling point of methyl acetate (56.9°C), the amination process at the code level of +1 for factor B cannot be conducted. Therefore, eight experiments were conducted with methyl acetate as solvent (MA$_1$–MA$_8$). Conditions of amination experiments with ethanol and methyl acetate as solvents are shown in Table 2.

2.4. Membrane characterization

2.4.1. Amination degree

The degree of amination is calculated by using the results of elemental analysis according to Eq. (2) [20]:

$$\text{Degree of amination } (\%) = \frac{C_1 - C_2}{C_1} \times 100 \tag{2}$$

where C_1 and C_2 are the chloride contents (mmol/g) of the membrane before and after amination process, respectively.

2.4.2. Membrane morphology and chemical composition

The structure of the membranes is studied by scanning electron microscopy (SEM) (TEScan, Czech Republic). The samples were cut into the desired size and were mounted on a holder to be coated with a gold layer. After gold coating, the samples were ready for taking SEM images.

The chemical composition of the membranes is investigated by attenuated total reflectance (Shimadzu Model 8400S). The analysis was carried out in the spectrum range from 3,500 to 500 cm^{-1} to determine the structural changes in the membrane after surface modification, that is, amination process.

Table 1
Levels and codes of the CCD experimental design

Variable factor	Code level				
	$-\alpha$*	−1	0	+1	$+\alpha$
A: Amination time duration (h)	3.82	12	24.0	36	44.18
B: Amination temperature (°C)	11.36	25	45.0	65	78.64
C: Concentration of amine (wt%)	1.48	10	22.5	35	43.52

*α is star or axial point for orthogonal CCD in the case of three independent variables.

Table 2
Amination conditions in ethanol and methyl acetate

Ethanol as solvent				Methyl acetate as solvent			
Runs (sample)	Factors			Runs (sample)	Factors		
	A	B	C		A	B	C
E_1	12	25	10.0	MA$_1$	12	25	10.0
E_2	44	45	22.5				
E_3	12	65	35.0	MA$_2$	44	45	22.5
E_4	36	25	10.0				
E_5	24	45	22.5	MA$_3$	36	25	10.0
E_6	36	65	35.0				
E_7	4	45	22.5				
E_8	12	25	35.0	MA$_4$	24	45	22.5
E_9	12	65	10.0				
E_{10}	24	75	22.5				
E_{11}	36	25	35.0	MA$_5$	4	45	22.5
E_{12}	24	45	22.5				
E_{13}	24	15	22.5	MA$_6$	12	25	35.0
E_{14}	24	45	22.5				
E_{15}	24	45	43.5	MA$_7$	36	25	35.0
E_{16}	36	65	10.0				
E_{17}	24	45	1.5	MA$_8$	24	45	22.5

2.4.3. Permselectivity

When an AEM separates tow electrolyte solutions with different concentrations, a potential difference is established across the membrane (algebraic sum of Donnan and diffusion potentials) which is called the membrane potential. The magnitude of this concentration potential depends on the electrochemical characteristic of the membrane as well as the nature and concentrations of electrolyte solution. In ED process, the external electric field acts only as a driving force and intensifies the transport of ions through the ion exchange membrane. Transporting the counterions and hindering the coions (membrane permselectivity) was occurred due to the Donnan repulsion based on membrane properties. The effectiveness of Donnan repulsion depends on the membrane properties (potential, transport number, permselectivity, etc.). When both surfaces of an AEM are in contact with electrolyte solutions, that is,

$NaNO_3$ of different concentrations, then NO_3^- ions diffuse from a high-concentration side to the low-concentration side, however, the diffusion of Na^+ ions in this system is rather restricted. These phenomena make the spheres in the low-concentration side to be charged negatively and the spheres in the high-concentration side positively and generate a potential difference (membrane potential) which hinders further diffusion of NO_3^- ions. It assumed that an electric potential difference (dE) to be applied to a very small part in the membrane by transferring one Faraday of an electric current. The energy consumed (FdE) is equal to the free energy change (reversible changes) [36]:

$$dG = -FdE \tag{3}$$

F is the Faraday constant. The change of chemical potential is equal to the change of free energy. The chemical potential change can be created by ionic movement [36]:

$$dG_i = \frac{t_i}{z_i} d\mu_i = \frac{t_i}{z_i} RTd \ln a_i \tag{4}$$

where t_i, z_i, μ_i, a_i, R, and T are the transport number, charge number, chemical potential, activity of ions i, gas constant, and temperature, respectively. The Nernst equation can be obtained using Eqs. (3) and (4):

$$E = -\frac{RT}{F}\int \sum \frac{t_i}{z_i} d\ln a_i \tag{5}$$

When both surfaces of an ion exchange membrane are in contact with solution 1 and solution 2, Eq. (5) becomes as follow:

$$E = -\frac{t_+}{t_-}\frac{RT}{F}\ln\frac{(a_+)_2}{(a_-)_1} + \frac{t_-}{t_+}\frac{RT}{F}\ln\frac{(a_-)_2}{(a_+)_1} \tag{6}$$

where, t_+ and t_- are the transport number of cations and anions in the membrane, respectively. $(a_+)_2/(a_+)_1$ and $(a_-)_2/(a_-)_1$ are the activity ratio of cations and anions between both solutions, respectively. In case of using $NaNO_3$ ($(a_+)_2/(a_+)_1 = (a_-)_2/(a_-)_1$); the Eq. (6) becomes as follow [36]:

$$E = -(t_+ - t_-)\frac{RT}{F}\ln\frac{a_2}{a_1} = (2t_- - 1)\frac{RT}{F}\ln\frac{a_2}{a_1} \tag{7}$$

In order to measure the change in potential difference across the ion-selective membrane, the membrane potential was measured using a two-compartment cell. This cell that was acting such as a typical potentiometric cell is made of Pyrex glass and its compartments were separated by the AEM [37]. The ratio of electrolyte ($NaNO_3$) concentrations in both sides (C_1/C_2) was kept constant (C_1 = 0.1 M and C_2 = 0.01 M) and the solution stirred vigorously during the experiment. The potential was measured using two calomel electrodes and a digital auto multimeter (Em). Because the junction potential and the potential of the two calomel electrodes are constant, any change in potential is a result of a change in the membrane's potential [37]. The transport number of counterions through the membrane was calculated from the measured potential using Eq. (7) [13,24].

The permselectivity can be calculated by the following equation [10,13,24]:

$$P_S = \frac{t_i^m - t_0}{1 - t_0} \tag{8}$$

where t_0 is the transport number of the counterions in solution.

2.4.4. Selectivity between counterions (nitrate and chloride)

The selectivity between counterions was obtained from bi-coionic/bi-counterionic potential value [36]. This potential can be measured by two electrolyte solutions with the same ionic strength but different counterions or coions. At the beginning, both compartments were filled with 100 mL of 0.01 M $NaNO_3$ solution. After equilibration, 0.2 mL of 1 M NaCl solution and an equal amount of distilled water were added to the left and right compartments, respectively. The obtained potential (recorded by the digital multimeter) and concentration ratios of $NaCl/NaNO_3$ in the left compartment were used to calculate the selectivity ($P_{Cl}^{NO_3}$) [13,17,38]:

$$\exp\left(\frac{zF(-\Delta V)}{RT}\right) - 1 = P_{Cl}^{NO_3}\frac{C_{NaNO_3}}{C_{NaCl}} \tag{9}$$

where ΔV is the potential between the left and right compartments.

Using Eq. (9), selectivity between counterions can be evaluated by practically simple and cost-effective method in terms of both manpower and resources. The estimated selectivities for mono-valence anions using Eq. (9) are in coordination with results of practical ED using a heterogeneous AEM [38]. However, the selectivity calculated by this equation can be compared with ED with zero current and infinite flux (ideal case) [38].

2.4.5. Ion exchange capacity and fixed ion concentration

To measure the ion exchange capacity (IEC), membranes were initially placed in 1 M NaCl solution to ensure the conversion of all the exchange groups to Cl^-. Then, the membranes were washed and kept in water for 24 h. After that, the membranes were immersed in 1 M $NaNO_3$ solution for 24 h. Cl^- ions were replaced by NO_3^- ions in the solution. The amount of Cl^- ions in the solution which determined by the IC method represented the membrane IEC (the amount of Cl^- ions in 1 g of dried membrane) [10,24].

Fixed ion concentration (FIC) is directly determined applying Eq. (10):

$$\text{FIC} = \frac{\text{IEC}}{W_c} \tag{10}$$

where W_c is the membrane water content.

In order to measure the membrane water content, it was immersed in distilled water for 24 h. After that, the membrane surface was wiped off with filter paper and the membrane was weighted (BEL Digital Weighting Equipment Co., Italy). Next, the membrane was dried at a temperature of 40°C in an oven for 24 h. The membrane water content was calculated by Eq. (11) [10,13,24]:

$$W_c\% = \frac{\left(W_{\text{wet}} - W_{\text{dry}}\right)}{W_{\text{dry}}} \times 100 \tag{11}$$

2.4.6. Membrane electrical resistance

The electrical resistance was measured by applying the cell used for measuring the membrane potential. Both cell compartments, which were separated by a membrane, were filled with 0.5 M $NaNO_3$ solution at 25°C. Electrical resistance was measured by establishing an alternating current bridge with external voltage of 50 mV and constant frequency of 1,000 Hz across the cell with (R_1) and without membrane (R_2) (Audio signal generator JSG-106HD, Electronic Afzar Azma, Iran). Then the membrane resistance is calculated using the difference between the two resistances ($R_m = R_1 - R_2$). The electrical resistance of the membrane is expressed as follows [10,13,24]:

$$r\left(\Omega\,\text{cm}^2\right) = R_m \times A \tag{12}$$

where A is the surface area of the membrane.

3. Results and discussion

3.1. Heterogeneous membrane properties before amination

3.2. Amination reaction

During the amination process, a nucleophilic substitution occurs and the chlorinated bonds (chloride loading: 26 wt. %) of the CPP react with dipropylamine molecules which result in chloride replacement with dipropylamine. In the substitution reaction (Fig. 1(a)), amine molecules attack chloride with their nitrogen head. In order to be replaced in the polymer structure, size of the amine molecules should be small enough. Moreover, according to the kinetics of the reaction, the reaction rate increases with temperature. However, it should be noted that at high temperatures an elimination reaction is likely to occur instead of substitution reaction [20,32]. In the elimination reaction (Fig. 1(b)), carbon element, which is bonded to chloride, is space crowded. Therefore, dipropylamine molecules attack the carbon–hydrogen bonds in the methyl groups instead of carbon–chloride bonds. In such a case, dipropylamine acts as a catalyst. The product of this reaction has a double bond of carbon-carbon, which increases the hydrophilic characteristic. Increasing hydrophilicity, due to the elimination reaction, has a negative effect on membrane selectivity toward nitrate and decrease selectivity. The hydrophobic membrane has higher affinity to nitrate than chloride [10].

The FTIR spectrums of CPP before and after amination are shown in Fig. 2 [20]. The peaks at 3,303–2,782 cm^{-1} are attributed to the C–H stretching vibrations. The absorption bands at 2,950–2,840 cm^{-1} are assigned to the C–H stretching vibrations. The peaks at 1,455 and 1,378 cm^{-1} are attributed to bending of C–H and stretching of C–C bonds. The bond at 973 cm^{-1} arises from CH_2 vibration. The absorption bands at 723–682 cm^{-1} arise from stretching vibrations of C–Cl bonds [17,20,33]. Comparison between the spectra shows new peaks appearing at 3,419, 2,352, 1,604, and 1,268 cm^{-1}. The peak at 3,419 cm^{-1} is attributed to the symmetrical and asymmetrical stretching vibrations of NH and NH_2. The stretching vibrations of C–N–H or C=N observed at 1,604 cm^{-1} and the peak at 1,268 and 1,221 cm^{-1} is due to vibration of the C–N bond. The new peak at 2,352 may be due to C≡C or C≡N vibrations [17,32]. All these new peaks indicate the presence of the nitrogen bond in the membrane structure verifying the amination process. It can be concluded that after the amination process the neutral segments of the heterogeneous membrane will be charged and act as functional agents.

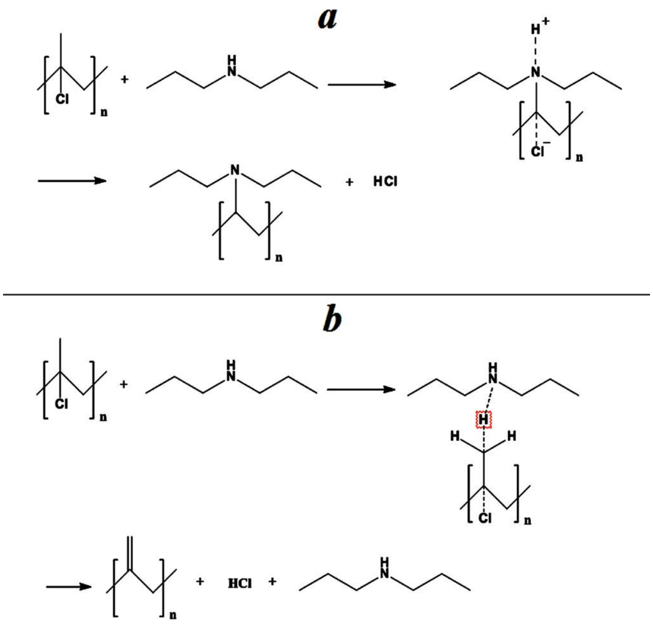

Fig. 1. Schematic diagram of substation (a) and elimination (b) reaction of CPP and dipropylamin.

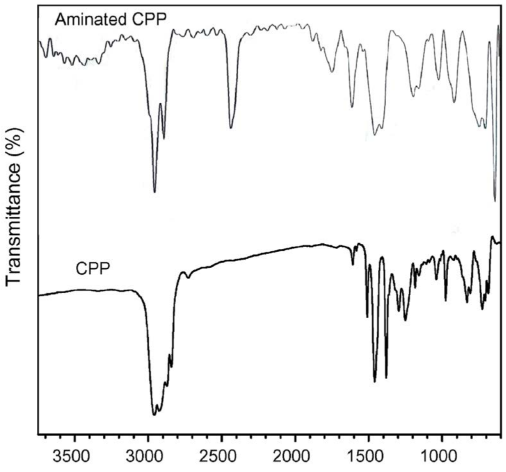

Fig. 2. FTIR spectrum for CPP and aminated CPP.

This also translates into an increase in the number of functional groups via amination reaction.

The effect of amination reaction on the membrane surface was also studied by SEM. SEM images were taken before and after amination and are shown in Fig. 3. The amination process could change the roughness of the membrane surface [14,39]. As can be seen, before amination (Fig. 3(a)) surface of the CPP film without resin is almost smooth, but after amination (Fig. 3(b)) the roughness of the membrane surface is changed. In heterogeneous AEM, the parts of the membrane without resin particles are clearly changed after amination (Figs. 3(c)–(d)). For example, a space resembling a puffy structure was formed between resin particles after amination. It can be argued that the functional groups of the membrane are increased after amination and the membrane electrochemical properties were subsequently enhanced. SEM images represent the effect of amination reaction on the membrane structure and confirm the amination reaction.

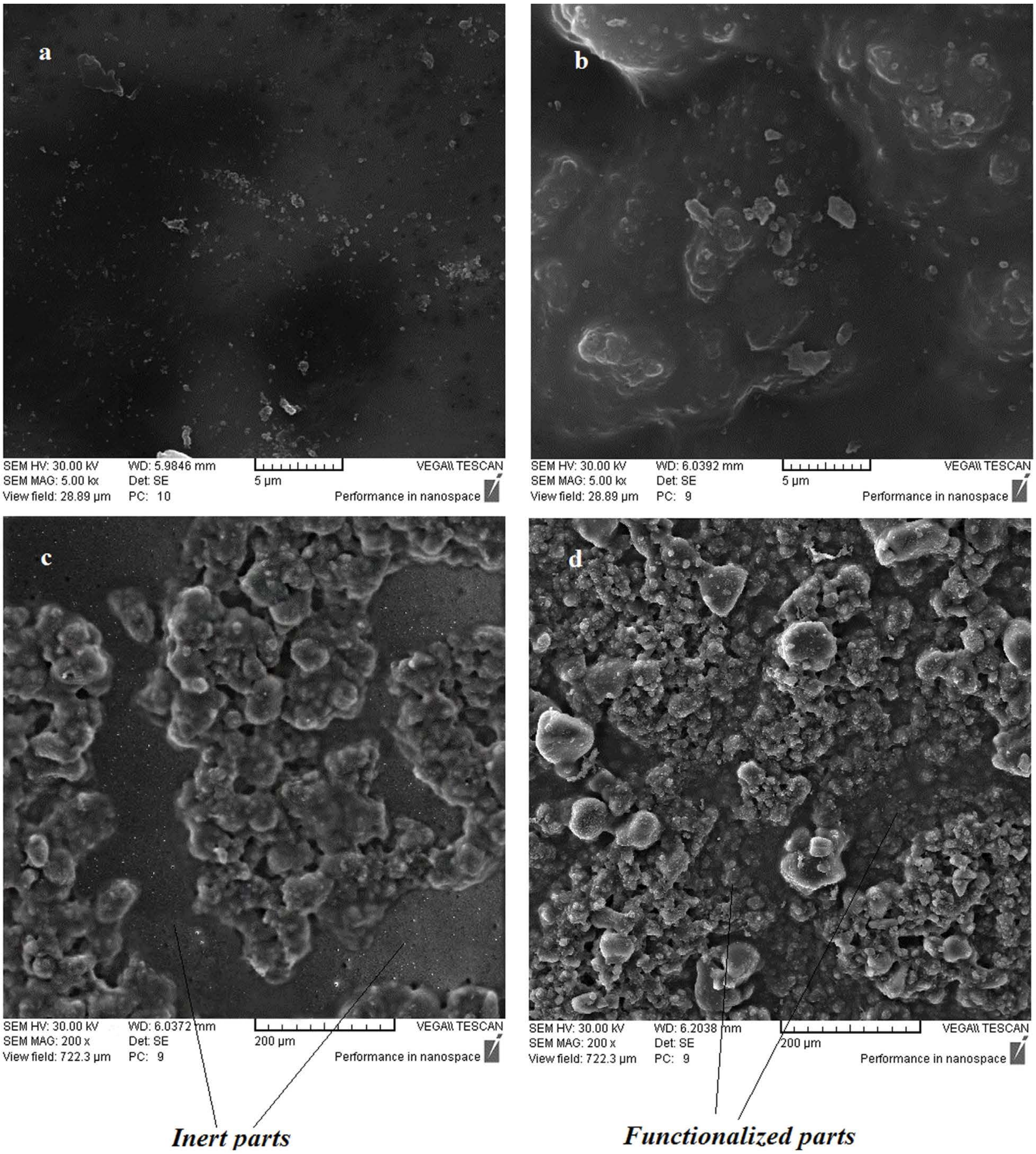

Fig. 3. SEM images for CPP (before (a) and after amination (b)) and heterogeneous membrane (before (c) and after amination (d)).

3.3. Amination degree

The elemental analysis results are presented in Table 3. The amination reaction can be confirmed by monitoring the variations in the amounts of nitrogen and chloride elements. In other words, increasing the amount of nitrogen and decreasing the amount of chloride verify the substitution of nitrogen of dipropylamine with chloride in the CPP structure. The chloride content of the membrane without resin before and after amination is 0.66 and 0.30 mmol/g, respectively. The content of nitrogen after amination process in a CPP membrane is 0.66 mmol/g. Furthermore, it was found that the amination rate, which is directly related to the amount of nitrogen, rises by increasing the amination time at constant temperature and concentration by comparing E_1 (Cl content of 0.45 mmol/g) to E_4 (Cl content of 0.44 mmol/g) and also E_8 (Cl content of 0.42 mmol/g) to E_{11} (Cl content of 0.40 mmol/g). At constant temperature and time, E_1 versus E_8, E_4 versus E_{11}, and E_{14} (Cl content of 0.42 mmol/g) versus E_{15} (Cl content of 0.39 mmol/g), the amination rate was enhanced by increasing the amine concentration. According to these results, the effect of concentration on the amination rate is more significant than that of amination time. On the other hand, the rate of amination decreases by increasing the amination temperature, decreasing the amination time and decreasing the amine concentration (E_{14} vs E_{11}). Moreover, at similar amination conditions, the MA_1 (Cl content of 0.35 mmol/g) has a higher amination rate in comparison with E_1 (Cl content of 0.45 mmol/g). The effect of solvent nature on the content of nitrogen is also indicated in Table 3. By using methyl acetate, the content of nitrogen will be higher than using ethanol.

After the amination, the amount of anion exchange groups of the membrane increase due to the substitution reaction. The elimination reaction between Cl and its adjacent H causes additional Cl loss, which could be perceived by a comparison between the Cl content before and after amination and the N content of the aminated CPP membranes. Moreover, the crosslinking of polymer chains is likely occurred due to the elimination reaction during the amination. The double bond of carbon-carbon, which can be obtained by this reaction, increases the hydrophilic characteristic of the membrane that has a negative effect on the membrane selectivity toward nitrate.

Generally, it can be concluded that the chlorinated polymer was successfully functionalized by amination reaction. The amination degree was changed between 27%–37% for amination in ethanol and 43%–44% for amination in methyl acetate as solvent.

3.4. Experimental design and model fitting

3.4.1. ANOVA analysis

The surface modification of membrane was carried out through the reaction of membrane matrix (CPP) with a solution of dipropylamine in ethanol. The experimental data of CCD for the permselectivity (P_S) and the selectivity between counterions ($P_{Cl}^{NO_3}$) are summarized in Table 4.

The final regression equations for P_S and $P_{Cl}^{NO_3}$ in terms of coded form and based on the significant model terms were obtained as follows:

$$\begin{aligned}P_S &= 0.93 + 0.023\times A - 0.004\times B + 0.022\times C + 0.007\times AB \\ &\quad - 0.003\times BC + 0.002\times A^2 - 0.004\times B^2 + 0.007\times C^2\end{aligned} \tag{13}$$

$$\begin{aligned}P_{Cl}^{NO_3} &= 2.41 + 0.13\times A - 0.068\times B + 0.18\times C + 0.020\times AB \\ &\quad + 0.004\times AC + 0.059\times BC - 0.011\times A^2 - 0.054\times B^2 \\ &\quad + 0.028\times C^2\end{aligned} \tag{14}$$

The statistical significance of P_S and $P_{Cl}^{NO_3}$ model terms was examined via ANOVA and regression analysis. The obtained results for P_S and $P_{Cl}^{NO_3}$ through fitting the model equations are given in Tables 5 and 6, respectively. The reliability of the fitted models for P_S (Table 5) and $P_{Cl}^{NO_3}$ (Table 6) can be confirmed by the high values of F in addition to the very low values of probability. Furthermore, the values of R^2 and R^2_{adj}, should be close to 1 and the very small difference between R^2 and R^2_{adj} supports the accuracy of the models. For the P_S and

Table 3
Elemental analyses of modified membranes

Solvent	Sample	C (%)	H (%)	O (%)	Cl (%)	Cl (mmol/ g)	N (%)	N (mmol/g)	Amination rate (%)
–	cpp	56.54	18.46	1.47	23.53	0.66	<0.1		
–	Aminated cpp	51.58	19.37	9.33	10.48	0.30	9.24	0.66	55
–	M_1 (cpp+ resin particles)	53.45	18.65	0.57	21.72	0.61	5.61	0.40	
Ethanol	E_1	48.58	18.87	7.53	15.78	0.45	9.24	0.66	27
	E_4	46.67	18.93	7.98	15.51	0.44	10.91	0.78	29
	E_6	48.33	18.24	8.03	13.73	0.39	11.67	0.83	37
	E_8	47.97	19.22	7.75	14.82	0.42	10.24	0.73	32
	E_{11}	48.08	18.77	7.89	14.32	0.40	10.94	0.78	34
	E_{14}	47.69	19.11	8.01	15.01	0.42	10.18	0.73	31
	E_{15}	48.11	18.56	7.97	13.87	0.39	11.49	0.82	36
Methyl	MA_1	46.76	18.32	11.87	12.3	0.35	10.75	0.77	43
acetate	MA_4	45.82	19.23	11.41	12.2	0.34	11.34	0.81	44

Table 4
Experimental values of the CCD

sample	Run	Variable factors			Responses	
		A	B	C	P_S	$P_{Cl}^{NO_3}$
E_1	1	–1	–1	–1	0.898 ± 0.006	2.227 ± 0.009
E_2	2	+α	0	0	0.977 ± 0.004	2.579 ± 0.018
E_3	3	–1	+1	+1	0.912 ± 0.005	2.392 ± 0.024
E_4	4	+1	–1	–1	0.943 ± 0.006	2.456 ± 0.035
E_5	5	0	0	0	0.925 ± 0.008	2.441 ± 0.046
E_6	6	+1	+1	+1	0.991 ± 0.007	2.717 ± 0.021
E_7	7	–α	0	0	0.886 ± 0.005	2.126 ± 0.057
E_8	8	–1	–1	+1	0.964 ± 0.003	2.474 ± 0.023
E_9	9	–1	+1	–1	0.902 ± 0.004	1.981 ± 0.060
E_{10}	10	0	+α	0	0.906 ± 0.007	2.103 ± 0.012
E_{11}	11	+1	–1	+1	0.970 ± 0.002	2.645 ± 0.005
E_{12}	12	0	0	0	0.927 ± 0.006	2.438 ± 0.020
E_{13}	13	0	–α	0	0.921 ± 0.003	2.360 ± 0.034
E_{14}	14	0	0	0	0.941 ± 0.005	2.354 ± 0.012
E_{15}	15	0	0	+α	0.989 ± 0.001	2.778 ± 0.019
E_{16}	16	+1	+1	–1	0.933 ± 0.008	2.219 ± 0.031
E_{17}	17	0	0	–α	0.907 ± 0.006	2.145 ± 0.041

$P_{Cl}^{NO_3}$ models, more than 91.23% and 97.97%, respectively, of the total variation was attributed to the experimental variables studied. It means R^2 value for P_S and $P_{Cl}^{NO_3}$ models is 0.9123 and 0.9797, respectively. Moreover, the value of R^2_{adj} for P_S and $P_{Cl}^{NO_3}$ models, which is 0.8732 and 0.9535 respectively, shows that models can predict experimental values virtually accurate. The obtained values for R^2 and R^2_{adj} exhibit acceptable errors by the models.

An analysis of the normal probability of the residual can be used to investigate the accuracy of the model. The normal probability versus residual for P_S and $P_{Cl}^{NO_3}$ are shown in Fig. 4. 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 [24]. As can be seen from Figs. 4(a) and (b), the residuals normally distribute close to a straight line.

The plots of the residuals versus predictions for P_S and $P_{Cl}^{NO_3}$ are shown in Fig. 5. As can be seen, all points are randomly scattered within the horizontal lines at a value of ±4.0. This shows the accuracy of the models and confirms the constant variance assumption.

The plots of the actual responses versus the predicted values are presented in Fig. 6. As shown, the points are close to the diagonal. This correlation between experimental and predicted values confirms the reliability of the models to predict P_S and $P_{Cl}^{NO_3}$.

3.4.2. The effects of variables on P_S and $P_{Cl}^{NO_3}$

Permselectivity (P_S): The ANOVA results (Table 5) confirm that the permselectivity is significantly affected by linear variables which are amination time (*t*) and concentration of amine solution (C). The *p* values are below 0.05 among linear variables. On the other hand, the effect of amination time on P_S is more significant than that of amine concentration; although the *p* values for other variables are greater than 0.05. Among the quadratic variables, the concentration of amine solution and among the interactive terms, the interaction of amination duration and amination temperature (*T*) seems to have a more significant effect on permselectivity. However, since the other *p* values of the interactive terms are much greater than 0.05, the P_S of the membrane is not affected by other variables interactions significantly. Moreover, amine concentration and amination duration have a more effective role to introduce activated sites to the membrane and enhance permselectivity rather than that of temperature.

As mentioned earlier, the functional groups of the membrane were increased due to the amination reaction; therefore, the modified membrane can pass counterions and reject coions better than a nonmodified membrane. Consequently, higher P_S can be obtained at higher amine concentrations and time durations, but also at low or moderate temperatures.

Table 5
Analysis of variance for the regressive model of P_S

Source	DF	Sum of squares	Mean square	*F* value	*p* value	
A	1	0.00723	0.00723	33.2437	0.00069	
B	1	0.00028	0.00028	1.27568	0.29592	
C	1	0.00655	0.00655	30.1036	0.00092	
AB	1	0.00043	0.00043	1.97418	0.20280	
AC	1	7.9983×10^{-6}	7.9983×10^{-6}	0.03674	0.85344	
BC	1	7.5315×10^{-5}	7.5315×10^{-5}	0.34592	0.57491	
A^2	1	4.0515×10^{-5}	4.0515×10^{-5}	0.18609	0.67917	
B^2	1	0.00021	0.00021	0.96639	0.35833	
C^2	1	0.00071	0.00071	3.25632	0.11413	
Model	9	0.01585	0.00176	8.09149	0.00582	significant
Lack of fit	5	0.00137	0.00027	3.51869	0.23599	not significant

$R^2 = 0.9123$ and $R^2_{adj} = 0.7996$. Significant ($p < 0.05$). Highly significant ($p < 0.01$).

Table 6
Analysis of variance for the regressive model of $P_{\mathrm{Cl}}^{\mathrm{NO_3}}$

Source	DF	Sum of squares	Mean square	F value	p-value	
A	1	0.21784	0.21784	92.6442	< 0.0001	
B	1	0.06268	0.06268	26.6566	0.00130	
C	1	0.42514	0.42514	180.799	< 0.0001	
AB	1	0.00332	0.00332	1.41238	0.27341	
AC	1	0.00010	0.00010	0.04471	0.83857	
BC	1	0.02797	0.02797	11.8932	0.01071	
A^2	1	0.00133	0.00133	0.56728	0.47590	
B^2	1	0.03246	0.03246	13.8034	0.00750	
C^2	1	0.00862	0.00862	3.66785	0.09702	
Model	9	0.79322	0.08814	37.4814	< 0.0001	Significant
Lack of fit	5	0.01158	0.00232	0.94974	0.58467	Not significant

$R^2 = 0.9797$ and $R^2_{\mathrm{adj}} = 0.9535$. Significant ($p < 0.05$). Highly significant ($p < 0.01$).

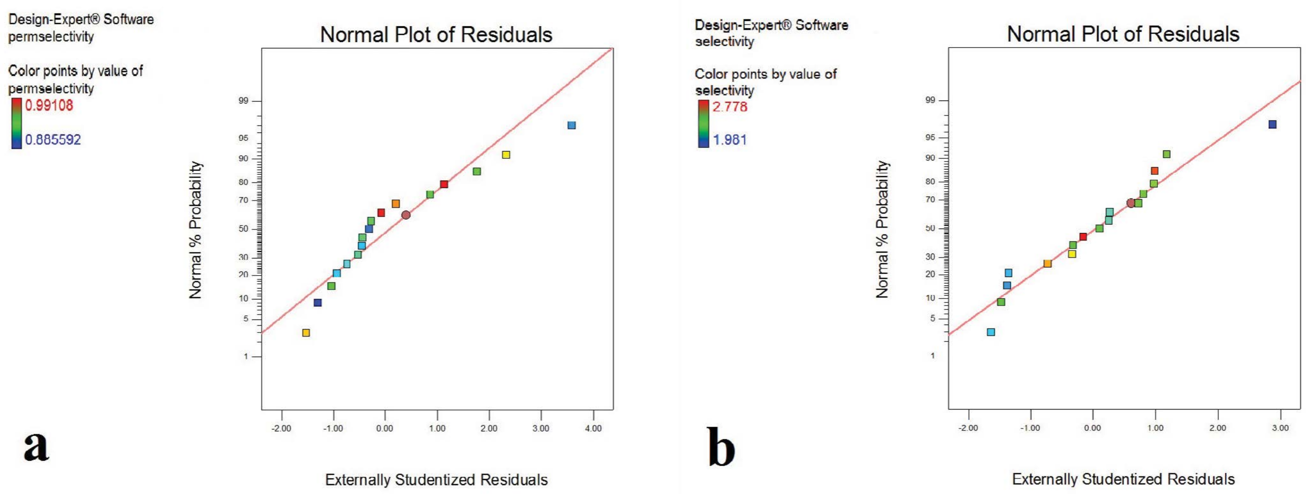

Fig. 4. Normal plot of residuals for P_S (a) and $P_{\mathrm{Cl}}^{\mathrm{NO_3}}$ (b).

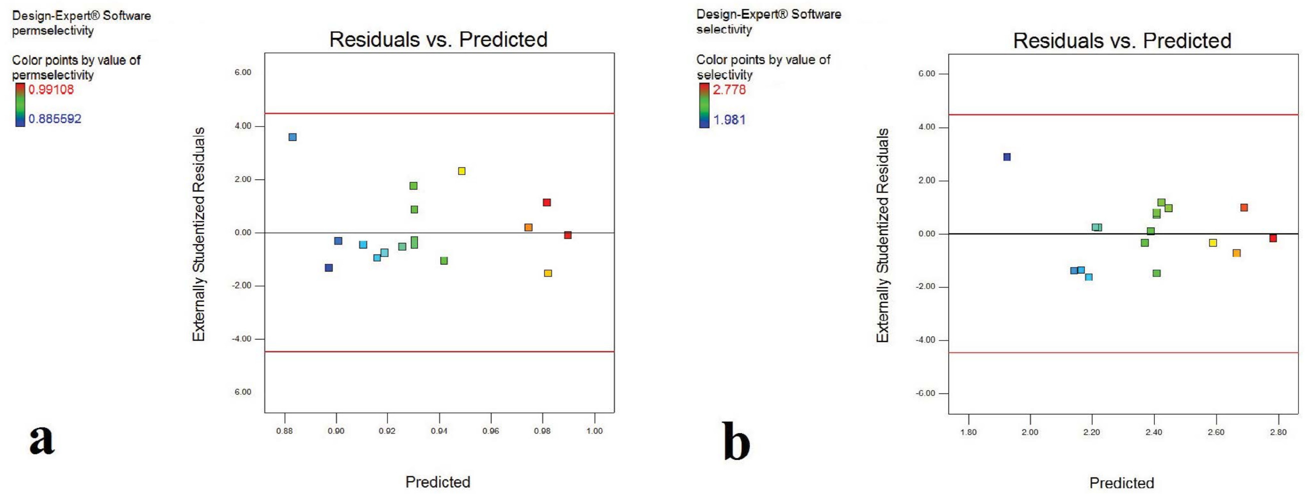

Fig. 5. Plot of studentized residual versus predicted for P_S (a) and $P_{\mathrm{Cl}}^{\mathrm{NO_3}}$ (b).

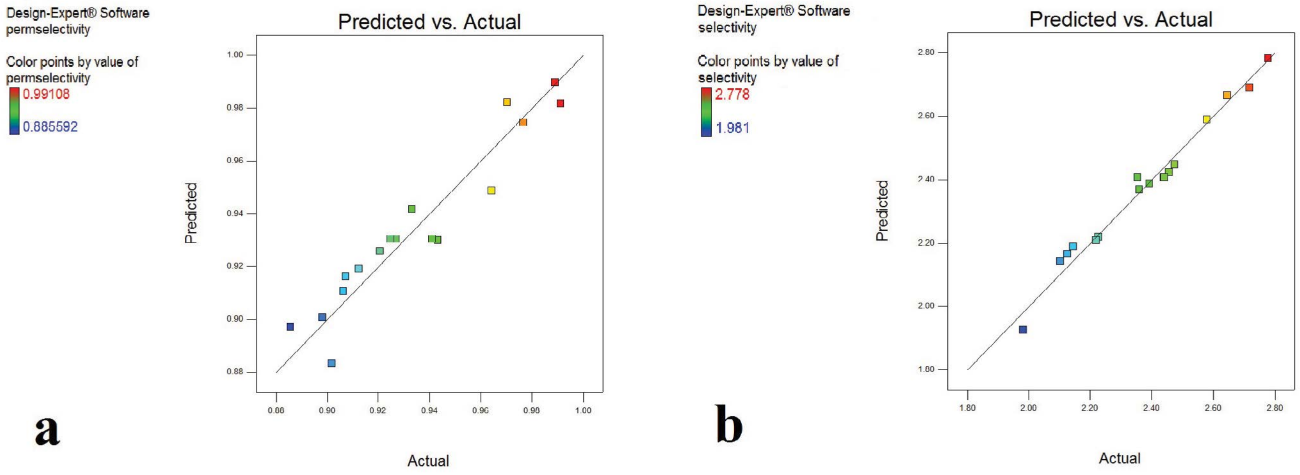

Fig. 6. Plot of actual P_S (a) and $P_{\mathrm{Cl}}^{\mathrm{NO_3}}$ (b) versus predicted values.

The shape of the interaction and contour plots can show the nature and extent of the interactions among variable factors. Prominent and negligible interactions can be shown by elliptical and circular shapes, respectively [24]. The interaction graphs and contour plots of P_S are shown in Fig. 7. The interaction effect between amination duration and amination temperature (Fig. 7(a)) indicates that P_S can be improved by increasing the amination duration. Furthermore, the P_S enhancement by increasing amination duration is further at higher amination temperatures. In other words in order to improve P_S, increasing the amination duration is more effective at higher amination temperatures. Although higher temperature increases the reaction rate, it increases the probability of undesirable reactions such as elimination reaction nevertheless. Moreover, the interaction between amination duration and concentration (Fig. 7(b)) indicates that P_S can be improved by increasing both variables. Increasing the amination time affect P_S at all concentrations and vice versa. As amination reaction takes place in a short period, investigation on longer time periods was not necessary. In addition, the interaction effect between amination temperature and concentrations (Fig. 7(c)) indicates that P_S can be enhanced by increasing the concentration and decreasing the temperature. However, at higher temperatures, the effect of concentration is more significant. The temperature has an almost negligible effect at lower concentrations.

The plotted response surface graphs between two independent variables, where the other independent variables were kept at the center point, are shown in Fig. 8. The interaction of the variables and optimum level of each variable can be studied by these curves [24]. Figs. 7 and 8 have similar trends. By these response surface graphs, it is clearly obvious that amination time and concentration of dipropylamine have a positive effect on P_S.

Resin particles that act as functional groups are heterogeneously distributed on the surface of the membrane. The parts of the membrane without resin particles cannot take part in transferring anion. Dipropylamine can react with these parts of the membrane. Therefore, the inert parts of the membrane can become activated by amination reaction. As a result, the electrochemical properties of the heterogeneous AEM can be enhanced by increasing functional groups of the membrane due to the amination reaction. This postulation is confirmed by SEM images (Fig. 3).

All in all, response surface graphs of P_S show that the permselectivity of AEM can be enhanced by increasing the concentration of dipropylamine and amination time. Also, better properties can be obtained at lower temperatures of amination reaction.

Selectivity between two counterions (nitrate and chloride $P_{\mathrm{Cl}}^{\mathrm{NO_3}}$): Results of ANOVA for the selectivity between nitrate and chloride indicate that all linear variables have significant effects on $P_{\mathrm{Cl}}^{\mathrm{NO_3}}$, and have p values below 0.05; in return, the p values for other variables are greater than 0.05. Amination temperature shows the most significant effect among the quadratic variables. Investigation on the interactive terms and their effect on $P_{\mathrm{Cl}}^{\mathrm{NO_3}}$ is shown in Fig. 9. Among the interactive terms, the interaction of amination temperature and concentration is the significant term. The interaction effect between amination temperature and duration (Fig. 9(a)) shows that amination duration can enhance $P_{\mathrm{Cl}}^{\mathrm{NO_3}}$. The $P_{\mathrm{Cl}}^{\mathrm{NO_3}}$ enhancement is more pronounced at higher amination temperatures. On the other hand, the high temperature has a negative effect on $P_{\mathrm{Cl}}^{\mathrm{NO_3}}$. Higher temperatures increase the chance of undesirable elimination reaction. As mentioned earlier, higher temperatures cause the production of double bond of carbon-carbon, which increases hydrophilic characteristic of the membrane.

The interaction effect between amination duration and concentration (Fig. 9(b)) indicates that $P_{\mathrm{Cl}}^{\mathrm{NO_3}}$ can be improved by increasing both variables. Increasing the amination duration affect $P_{\mathrm{Cl}}^{\mathrm{NO_3}}$ at all concentration values and vice versa, such as the effect of amination duration on P_S. Higher concentration and amination time have considerable impacts on hydrophobicity of the membrane by using a hydrophobic amine such as dipropylamine. $P_{\mathrm{Cl}}^{\mathrm{NO_3}}$ increases from 1.98 to 2.77 for the lowest concentration and duration to the highest values, respectively.

The interaction effect between amination temperature and concentration (Fig. 9(c)) demonstrates that the $P_{\mathrm{Cl}}^{\mathrm{NO_3}}$ can be enhanced by increasing the concentration and reducing the amination temperature. It should be noted that at higher concentrations $P_{\mathrm{Cl}}^{\mathrm{NO_3}}$ improves by increasing the temperature

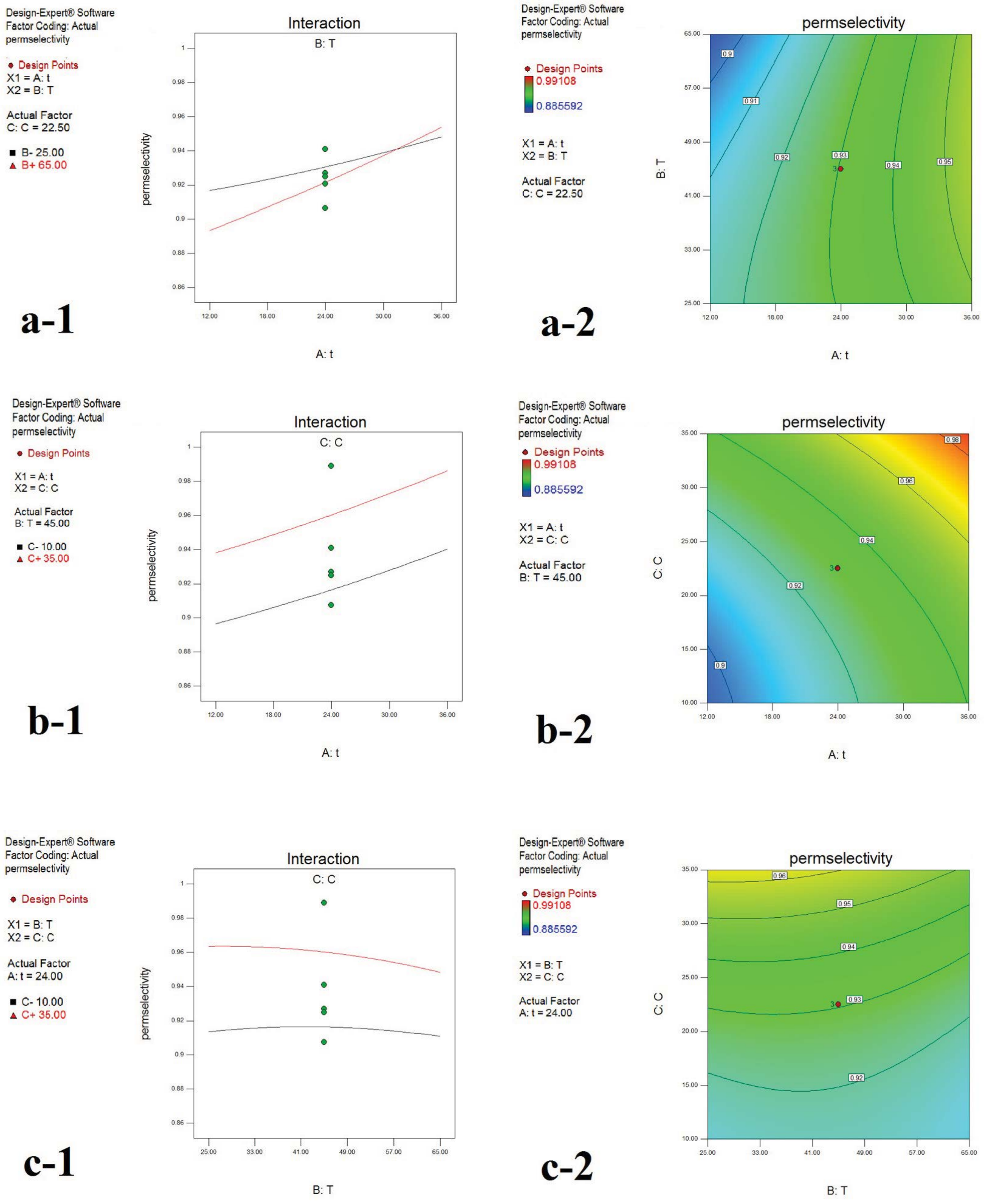

Fig. 7. Interaction graphs (a$_1$–c$_1$) and counterplots (a$_2$–c$_2$) of P_S.

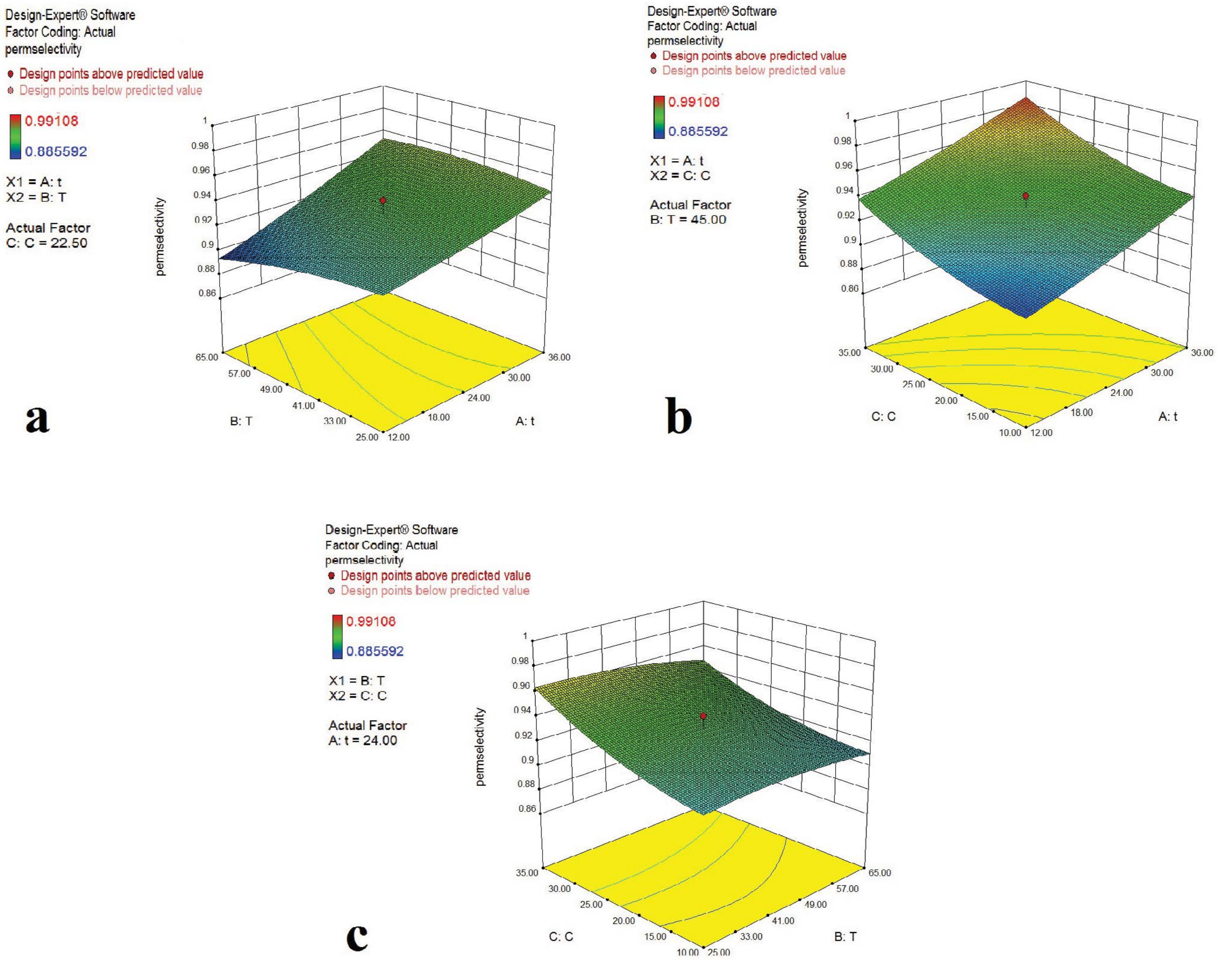

Fig. 8. Response surface plots versus P_S.

up to 45°C. However, by increasing the temperature beyond 45°C the $P_{\mathrm{Cl}}^{\mathrm{NO_3}}$ is decreased. Therefore, at intermediate temperatures and high concentrations conditions higher values of $P_{\mathrm{Cl}}^{\mathrm{NO_3}}$ will be obtained. In these conditions and at amination time of 24 h $P_{\mathrm{Cl}}^{\mathrm{NO_3}}$ has a value of 2.6. These results also confirm the effective roles of concentration and time duration on the amination of the membrane.

The plotted response surface graphs between two independent variables, where the other independent variables were kept at their center points, are shown in Fig. 10. The effect of amination duration and amination temperature on $P_{\mathrm{Cl}}^{\mathrm{NO_3}}$ is shown in Fig. 10(a) (solution concentration at its zero coded level). Increasing the duration as well as decreasing the temperature, increase $P_{\mathrm{Cl}}^{\mathrm{NO_3}}$. Also, the effect of concentration on improving $P_{\mathrm{Cl}}^{\mathrm{NO_3}}$ is shown in Figs. 10(b) and (c) (temperature and time are at their zero coded level). It is remarkable that all three variables have almost a similar effect on both P_S and $P_{\mathrm{Cl}}^{\mathrm{NO_3}}$. Moreover, amination with a hydrophobic amine, that is, dipropylamine, increases the hydrophobicity of the membrane hence improving $P_{\mathrm{Cl}}^{\mathrm{NO_3}}$. In conclusion, amination by an appropriate amine could improve the desirable characteristics of the membrane.

3.4.3. Optimum Conditions

The maximum quantities of P_S and $P_{\mathrm{Cl}}^{\mathrm{NO_3}}$ have been considered as the optimum conditions for modification of a heterogeneous AEM by amination. To verify the adequacy of the model, P_S and $P_{\mathrm{Cl}}^{\mathrm{NO_3}}$ of the optimum point (maximum values) which are predicted by the model, were measured experimentally as well. The predicted values for P_S and $P_{\mathrm{Cl}}^{\mathrm{NO_3}}$ with an amination duration of 36 h, amination temperature of 25°C and concentration of amine solution of 35 wt% were 0.982 and 2.669, respectively. The corresponding experimental values are 0.970 and 2.645, respectively. These results confirm viability and usefulness of the prediction.

The experiments were also repeated by using methyl acetate as a solvent. Since the boiling point of methyl acetate is relatively low (56.9°C–57.5°C), the modification process at temperatures higher than the boiling point of methyl acetate cannot be conducted. Therefore, the modification process with methyl acetate, as the solvent, was carried out at eight different conditions. The results of these modifications are given in Table 7.

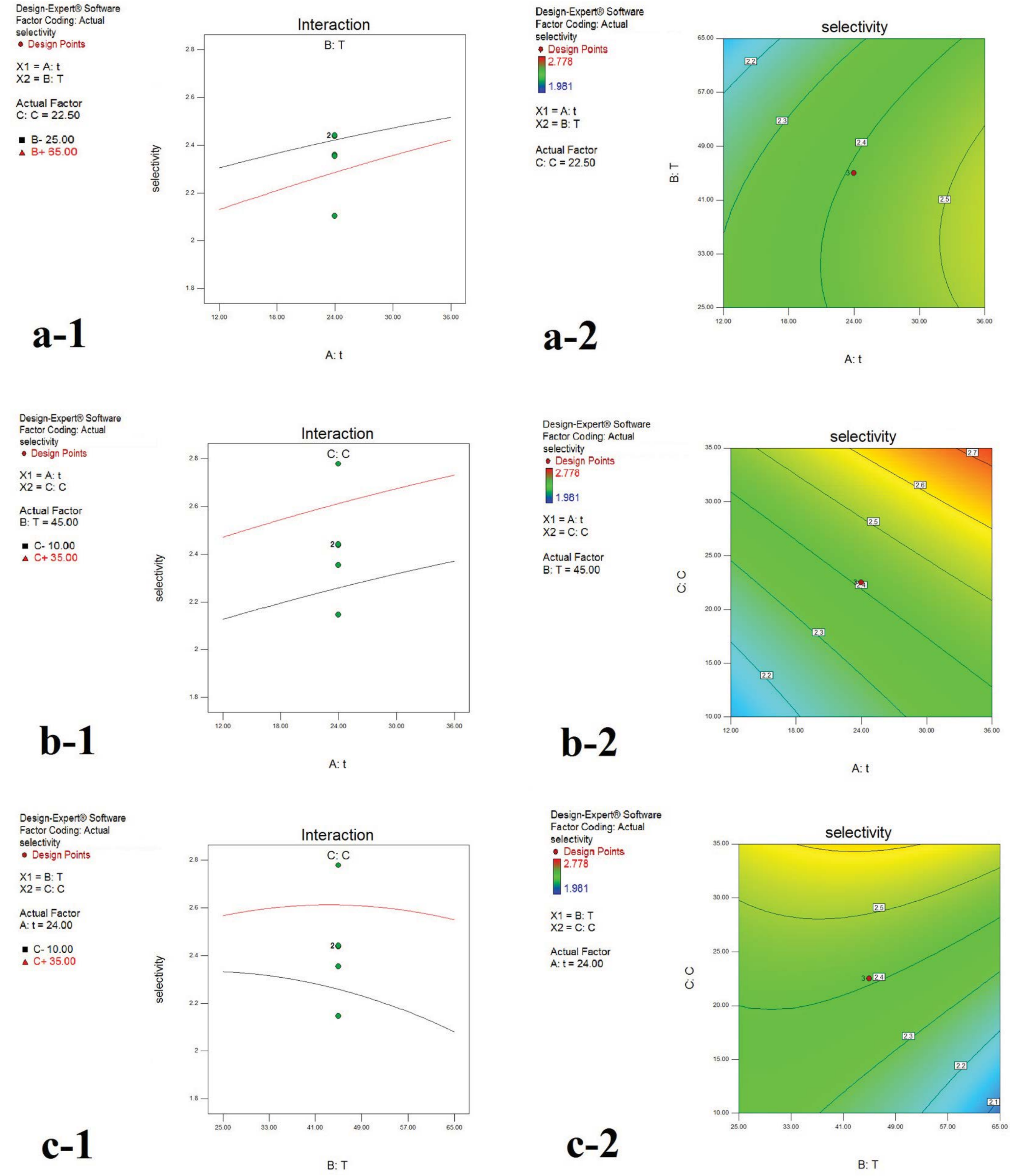

Fig. 9. Interaction graphs (a$_1$–c$_1$) and counterplots (a$_2$–c$_2$) of $P_{\text{Cl}}^{\text{NO}_3}$.

3.5. IEC, FIC, and membrane resistance

The effects of amination conditions on IEC and FIC of E$_1$–E$_{17}$ membranes are shown in Table 8. Amination process can increase the amount of ionic sites and improve transportation of the anions through the membrane. The modified membranes with high amine concentration (E_6, E_{11}, and E_{15}) show higher IEC. The concentration of amine solution and amination time has positive effects on IEC by increasing the rate of amination reaction. Therefore, IEC is improved after

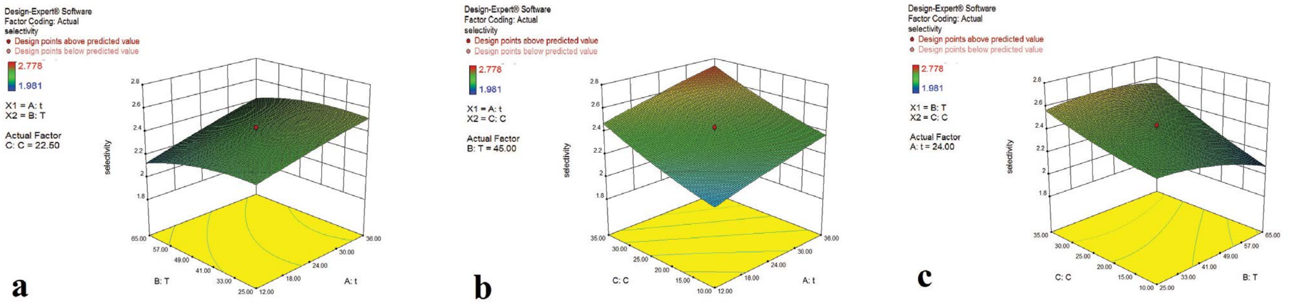

Fig. 10. Response surface plots versus $P_{\text{Cl}}^{\text{NO}_3}$.

modification due to increased ionic sits of the membrane. High temperature, on the other hand, has a negative effect on IEC (E_{16} and E_{17}).

The FIC value depends on IEC and water content (Eq. (6)). This parameter can be increased with increasing IEC and decreasing water content. As dipropylamine with moderate length of chain has hydrophobic nature, water content decrease with increasing amine concentration and amination time (E_6, E_{11}, and E_{15}). As E_6, E_{11}, and E_{15} also show high IEC, this combined effect translates into these membranes having high FIC as well.

The membrane resistance can be decreased after modification via amination process (Table 9). By increasing the amount of ionic sites on the membrane surface, a more uniform distribution of current occurs. Thus the membrane electrical resistance decreases. On the other hand, at high amination temperatures membrane crosslinking can occur due to the elimination reaction. Crosslinking can be intensified at high amination times. Therefore, at high temperature and amination duration, the membrane resistance decreases due to the negative effects of crosslinking on transferring ions through the membrane (E_2).

P_S and $P_{\text{Cl}}^{\text{NO}_3}$ of the unmodified heterogeneous membrane were 0.831 and 1.968, respectively. At optimum conditions these values were increased 16.7% and 34.4%, respectively (0.970 and 2.645, respectively). These increments can verify the significant improvement of the membrane properties by amination process.

The comparison of lab-made membrane (before and after amination) with the results of other research works is shown in Table 10. The permselectivity and selectivity of the modified lab made membrane are significant compared with those of other homogeneous membranes shown in the table. The permselectivity of modified membrane at optimum condition is 0.970, which is higher than all reported permselectivities. The selectivity between nitrate and chloride of

Table 7
Characterization results for MA_1–MA_8 membranes

Run	*t* (h)	*T* (K)	*C* (wt%)	P_S	$P_{\text{Cl}}^{\text{NO}_3}$
MA_1	12	25	10.0	0.912 ± 0.030	2.475 ± 0.014
MA_2	44	45	22.5	0.972 ± 0.003	2.749 ± 0.025
MA_3	36	25	10.0	0.906 ± 0.012	2.595 ± 0.056
MA_4	24	45	22.5	0.964 ± 0.016	2.386 ± 0.029
MA_5	4	45	22.5	0.933 ± 0.036	2.314 ± 0.017
MA_6	12	25	35.0	0.944 ± 0.008	2.496 ± 0.027
MA_7	36	25	35.0	0.983 ± 0.004	2.633 ± 0.038
MA_8	24	45	22.5	0.927 ± 0.010	2.531 ± 0.041

Table 8
Characterization results for E_1–E_{17} membranes

Sample	*t* (h)	*T* (°C)	*C* (wt%)	IEC (meq/g)	FIC (meq/g)
E_1	12	25	10.0	1.35 ± 0.012	3.007 ± 0.028
E_2	44	45	22.5	1.59 ± 0.009	3.958 ± 0.027
E_3	12	65	35.0	1.64 ± 0.003	3.864 ± 0.022
E_4	36	25	10.0	1.57 ± 0.010	3.721 ± 0.007
E_5	24	45	22.5	1.73 ± 0.021	3.836 ± 0.029
E_6	36	65	35.0	2.13 ± 0.031	5.471 ± 0.079
E_7	4	45	22.5	1.61 ± 0.028	3.672 ± 0.063
E_8	12	25	35.0	1.37 ± 0.018	3.020 ± 0.040
E_9	12	65	10.0	1.42 ± 0.020	2.999 ± 0.042
E_{10}	24	75	22.5	1.48 ± 0.017	3.167 ± 0.036
E_{11}	36	25	35.0	1.96 ± 0.004	4.771 ± 0.010
E_{12}	24	45	22.5	1.66 ± 0.007	3.856 ± 0.016
E_{13}	24	15	22.5	1.84 ± 0.002	4.103 ± 0.004
E_{14}	24	45	22.5	1.29 ± 0.013	2.945 ± 0.030
E_{15}	24	45	43.5	1.92 ± 0.025	5.188 ± 0.067
E_{16}	36	65	10.0	1.18 ± 0.034	2.621 ± 0.075
E_{17}	24	45	1.5	1.20 ± 0.009	2.516 ± 0.019

Table 9
Membrane electrical resistance

Sample	*t* (h)	*T* (K)	*C* (wt.%)	r_m (Ω.cm²)
M_1	–	–	–	2.54 ± 0.15
E_2	44	45	22.5	4.48 ± 0.02
E_5	24	45	22.5	3.36 ± 0.09
E_7	4	45	22.5	2.44 ± 0.05
E_9	12	65	10.0	2.54 ± 0.02
E_{12}	24	45	22.5	2.95 ± 0.01
E_{15}	24	45	43.5	4.17 ± 0.02
E_{17}	24	45	1.5	2.14 ± 0.01

Table 10
Comparison between the electrochemical properties of modified membrane (lab-made) and commercial anion exchange membranes

Sample	Type	r_m (Ω.cm²)	P_S	IEC (meq/g)	$P_{\mathrm{Cl}}^{\mathrm{NO_3}}$
Unmodified heterogeneous lab made membrane		2.54 ± 0.15	0.831 ± 0.013	1.33 ± 0.07	1.968 ± 0.038
Modified heterogeneous lab made membrane at optimum condition		4.41 ± 0.03	0.970 ± 0.007	1.96 ± 0.02	2.645 ± 0.044
Selemion AMV [18]	Homogeneous	2.8–3.9	0.966	1.85	–
AMX [18,40]	Homogeneous	2.1	0.782	2.0	1.4–2.1
AFN [40]	Homogeneous	0.4–1.5	0.806	2.0–3.5	–
ACS [40]	Homogeneous	2.0–3.5	0.903	2.0–2.3	–
ACM [40]	Homogeneous	5–10	0.830	1.1–1.3	–
MA-40 [40]	Heterogeneous	5.0	0.952	0.6	–
PE3362 [40]	Homogeneous	13.1	0.734	1.8–2.0	–
DF1133 [40]	Homogeneous	2.0–3.0	0.879	2.0–2.5	–
S203 [40]	Homogeneous	5.0–8.0	0.758	1.0–1.3	–
PPO-TEA [7]	Homogeneous	2.2–13.0	–	0.23–1.88	1.4–2.3
PPO-DMEA [29]	Homogeneous	30	–	1.5	1.0–1.4
BPPO-pyridine [14]	Homogeneous	10–90	0.806–0.879	0.3–1.3	–
BPPO-TMA [14]	Homogeneous	5–32	0.830–0.927	0.5–1.6	–
BPPO-4-vinylpyridine [17]	Homogeneous	12–33	–	0. 3–1.1	1.67–4.13
CPP-EDA [20]	Homogeneous	–	–	0.6–1.5	–
CPP-PEI [20]	Homogeneous	–	–	1.2–2.0	–

modified membrane is higher than that of other reported values in literatures as well except the value reported in Ref. [17]. Moreover, it should be mentioned that the modified membrane has very lower resistance and higher IEC in compare with homogeneous membranes.

4. Conclusions

Modification of a heterogeneous AEM was investigated. The modification was carried out by immersing the membrane into the amine solution. The effects of amine concentration (C), reaction temperature (T), and reaction duration (t) on the membrane selectivity between coions/counterions (permselectivity) as well as between counterions (nitrate and chloride) were studied by using RSM technique. In addition, the optimum conditions for membrane modification were investigated. It was observed that the amination duration and concentration of dipropylamine have significant effects on the both selectivities. However, the temperature has a negative effect on the selectivity. This is linked with the fact that high temperature can enhance the occurrence of elimination reaction. It follows that the temperature should be kept close to ambient temperature. It was found that the optimum values of the variables are 25°C for temperature, a concentration of 35 wt% and reaction time of 36 h. The effect of solvent type for dipropylamine solution was investigated, as well. Higher selectivities were obtained by using methyl acetate as solvent.

Other electrochemical properties of the membrane (IEC, FIC, and resistance) were measured before and after modification. The results verified that the amination can increase the membrane IEC, FIC, and decrease the resistance of the membrane.

Symbols

A — Membrane area, cm²
a — Solution electrolyte activity
C — Concentration, mol/L, mg/mL, mmol/g
E — Membrane potential, mV
F — Farady constant, A/s/eq
FIC — Fixed ion concentration, meq/g dry membrane
IEC — Ion exchange capacity, meq/g dry membrane
IEM — Ion exchange membrane
$P_{\mathrm{Cl}}^{\mathrm{NO_3}}$ — Selectivity between nitrate and chloride ions
P_S — Permselectivity
R — Gas constant, J/mol/K
r — Membrane resistance, Ω.cm²
T — Temperature, K, °C
t — Time duration
t_m — Transport number of the counterions in membrane
t_0 — Transport number of the counterions in solution
W_c — Water content
Z — Electrovalence of counterion, eq

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