

Preparation of Self-Standing Polyaniline-Based Membranes: Doping Effect on the Selective Ion Separation and Reverse Osmosis Properties

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Received 13 November 2006; accepted 11 February 2007

DOI 10.1002/app.26377

Published online 11 May 2007 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The selective ion transport of aqueous salt solutions including mono-, di-, trivalent cations across both doped and undoped polyaniline (PAni) membranes was described. PAni-based asymmetric membranes were prepared by the phase inversion method from the casting solution containing *N*-methyl pyrrolidone. It was found that the permeation rates (P_R) decline in the sequence of $P_R(\text{NaCl}) > P_R(\text{MgCl}_2) > P_R(\text{LaCl}_3)$. HCl-doped PAni membrane exhibited higher permeation rates for the salts than undoped one due to its more hydrophilic nature. In reverse osmosis (RO) applications, it was observed no water permeation through undoped PAni due to less permeable and hydrophobic nature, under even at 40 bar pressure. Concerning HCl-

doped PAni, this membrane showed very low water flux (J_w) and it was found as $1.01 \text{ L m}^{-2} \text{ h}^{-1}$ under 40 bar pressure. On the other hand, the J increased linearly with the applied pressure. Furthermore, typical separation factor (α) values calculated from permeation rate ratios were found to be as 6.3 and 39 for $\text{Na}^+/\text{Mg}^{2+}$ and $\text{Na}^+/\text{La}^{3+}$ for HCl-doped PAni, respectively. Especially, HCl-doped PAni membrane can be used for removing rare-earth metal salts due to its high separation efficiency in high temperature applications. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 2640–2645, 2007

Key words: polyaniline; membrane; ion separation; ion permeability; reverse osmosis

INTRODUCTION

The use of polymers for separation applications has grown rapidly during the past two decades.^{1,2} Polymeric membranes are mainly useful in separation of gases,^{3,4} inorganic ions under nanofiltration and reverse osmosis conditions,^{5–7} and alcohol/water mixtures under pervaporation conditions.⁸

Since the discovery of conducting polymers in the late 1970s many works have been published on the commercial applications such as electrochromic displays, lightweight batteries, and sensors.^{9,10} On the other hand, some works have been reported on the separation of various ion or liquid mixtures by using these conjugated polymeric membranes. First work was reported by Burgmayer and Murray on the use of electrochemically synthesized polypyrrole as an "ion gate" membrane.¹¹ Subsequently, Feldheim and Elliot reported a study on the separation of neutral solutes by using poly(3-methyl thiophene) and poly(*N*-methyl pyrrole)-based conducting polymers over porous polycarbonate (Celgrad) support.¹² At the beginning, interest in polyaniline (PAni) as a ma-

terial for membrane separation systems was due to its high selectivity toward gases^{13,14} and later on Illing et al. studied gas separation properties of the PAni-based membranes.^{15,16} Since most liquids are rare in the same size as gases (2–10 Å) PAni can be used for liquid separations as well.⁸ Recently, pervaporation studies with PAni membranes were published by Ball et al.⁸ PAni can be prepared either in doped or undoped state. In the doping process, where counter ions are added uniformly throughout the material on a molecular level, was found to decrease the permeability of all gases, while undoping was found to increase gas permeability. Among the conjugated polymers, PAni has attracted great attention due to having different chemical characters and high thermal stability up to 425°C in nitrogen.⁸ For example, the doped form of PAni is hydrophilic while the undoped form is hydrophobic.

Selective ion separation, reverse osmosis, and pervaporation studies were mainly carried out by Tieke and coworkers.^{17–19} They reported many works on composite membranes, which were prepared successfully through layer by layer (LBL) technique,^{17–21} showing high selective ion permeation and separation factor. In these works, preparing composite membranes consisting of a very thin, dense separating layer and a thick highly porous membrane was described as a suitable method.¹⁹ Several studies have shown that the LBL assembly of electrolytes is well

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Contract grant sponsor: Research Fund of Istanbul University; contract grant number: BYPF-7-11/270706.

suitable for the preparation of composite membranes with an organized, dense separation layer of controlled thickness in the nanometer range.

Reverse-osmosis (RO) properties aromatic polyamide²² and polysulfone membranes were reported earlier in nanofiltration applications.²³ During the last few years, extensive efforts have been made to synthesize membrane grade polymers as an economical substitute for the cellulose acetate which is routinely used in the preparation of membranes for desalination in the RO technique. With the discovery of aromatic membranes by Richter and Hoehn, a number of useful aromatic polyamide-based membranes have been developed.²⁴ Aromatic polyamide membranes based on piperazine showed high compaction on use at high pressure and showed a significant reduction in the solvent flux. On analyzing both the experimental data reported in the literature and mechanism of the transport of the solvent through the membranes, it has been concluded that the polymeric material with hydrophilic group would be of improved quality to develop RO membranes. In the view of these observations, efforts have been made to prepare polymeric membranes including hydrophilic group.

However, up to now, very few studies were concerned with ion permeability, ion rejection, and RO properties of the self-standing polymeric membranes. Moreover, a limited number of studies have been reported on the doping effect. HCl-doped PANi exhibits a dense membrane with positively charged surface; it was of our interest to compare its ion transport behavior across the membrane with both undoped and HCl-doped self-standing PANi membrane. For this purpose, selective ion permeation properties (permeation rate and separation factor) of the membranes were determined by using mono, di, and trivalent metal containing alkaline salts. Furthermore, preliminary results on the reverse osmosis properties of these membranes were investigated in conjunction with the membrane's hydrophilicity and surface charge (doping effect). Finally, all results were compared with poly(ethersulfon)-based commercial product.

EXPERIMENTAL

Materials

Aniline (ANi), ammonium peroxydisulfate (APS), *N*-methyl pyrrolidone (NMP), and hydrochloric acid were all supplied in reagent grades from Fluka. Milli Q water (resistance $\geq 18\text{M}\Omega\text{ cm}^{-1}$) was used as solvent in the ion separation experiments. NaCl, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, and $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$ (analytical grade) were purchased from Fluka and used without further purification.

PAni synthesis and membrane preparation

Polyaniline

PAni exhibits lots of outstanding properties such as oxidative and environmental stability, and excellent conductivity properties.^{9,10} Protonated PANi converts to a nonconducting blue emeraldine base when treated with ammonium hydroxide. PANi can be prepared by both chemical^{10,25,26} and electrochemical methods. In the study, PANi was prepared by chemical methods as described in the literature.^{10,25,26} The chemical structures of both HCl-doped and undoped PANi are given in Figure 1(a,b), respectively.

Polyaniline synthesis

Freshly distilled (14.6327 g : 0.154 mol) ANi was placed into the reactor and 300 mL of 0.2M of HCl was added subsequently and then it was strongly stirred for 30 min. Then (36.2900 g : 0.159 mol) APS solution in 200 mL of 0.2M of HCl was added by using dropping funnel. The reaction temperature was not allowed to exceed 5°C. Then the mixture was allowed to react overnight. After 24 h, the dark green precipitates of PANi were successfully filtrated and afterwards it was washed four times with 100 mL of 0.2M HCl and four times with 100 mL of acetone to remove impurities such as nonreacted monomer and APS. After the washing step, a dark green powder was collected and firstly dried at room temperature and later in a vacuum desiccator for 48 h. The yield was 98.4% (14.3968 g). The flow diagram for the preparation of the PANi-emeraldine salt (PANi-ES) is depicted in Scheme 1.

Membrane preparation

Preparation of HCl-doped PANi membrane

HCl-doped PANi membrane was formed from a dispersion of the emeraldine form of ANi in NMP by

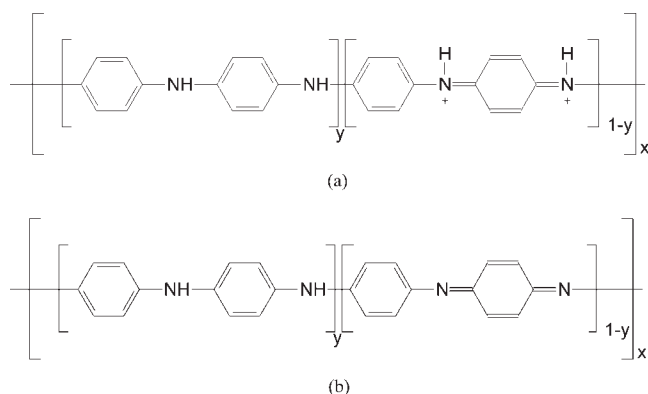
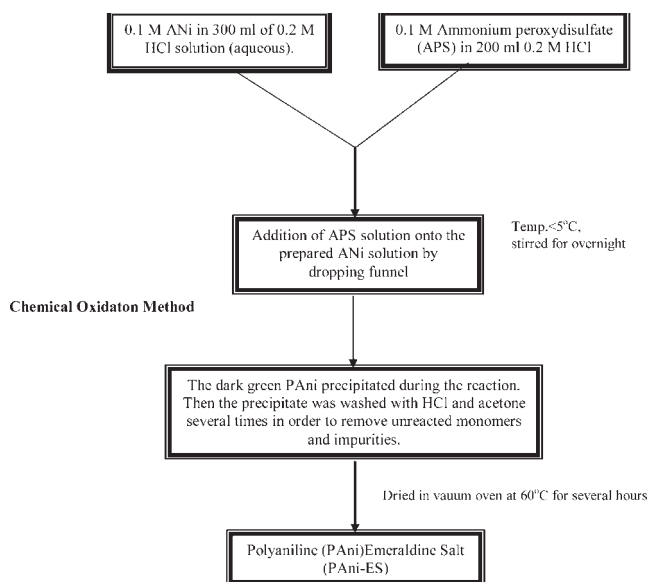


Figure 1 (a) HCl-doped polyaniline emeraldine salt (PANi-ES) (green) (b) Undoped polyaniline-base salt (PANi EB).



Scheme 1 The flow diagram for the preparation of the polyaniline-emeraldine salt (PANI-ES).

firstly grinding in a mortar and pestle. Afterward, this viscous dispersion was mold in a petridish and heat cured at 80°C for 12 h and 100°C for overnight to remove solvent completely. After cooling to room temperature, the membrane was removed from the glass by soaking in cold water. The chemical structure of the HCl-doped PANi is depicted in Figure 1(a).

Preparation of undoped PANi membrane

About 0.7 g PANi emeraldine salt (green form) was treated and stirred with 50 mL of NH_4OH for 24 h. Then the PANi was obtained in the base form, which was depicted in Figure 1(b), in blue color. Subsequently, PANi emeraldine base (PANI-EB) form was dispersed in NMP solvent (3 wt %). Afterward, this viscous dispersion was mold in a petridish and heat cured as described above. This procedure results in fully dense-free standing undoped PANi film which was purple-bronze in color. The thickness of the membrane is in the range of 40–60 μm .

Analysis

Ion permeation experiments

Ion permeation measurements were carried out by using a home-made apparatus which is shown in Figure 2. The membrane area $A = 4.52 \text{ cm}^2$ was placed between two chambers with a volume of 60 mL each. One of the chambers consists of salt solution with 0.1M salt concentration and the other chamber is pure water. The initial increase of conductivity $\Delta\Lambda/\Delta t$ was measured under constant stirring rate in all experiment to determine the permeation rate (P_R) of self

standing polymeric membranes.

$$P_R = (\Delta\Lambda/\Delta t) \cdot \Lambda_m^{-1} \cdot V \cdot (Ac)^{-1}$$

where Λ_m is the molar conductivity of the corresponding salt solution and V ($V_0 - \Delta V$) being the volume in chamber two after correction of the osmotic flow. The theoretical separation factor (α) simply the ratio of the permeation rates of NaCl and MgCl_2 and is shown as

$$\alpha(\text{NaCl}/\text{MgCl}_2) = P_{R(\text{NaCl})}/P_{R(\text{MgCl}_2)}$$

The successive permeation of different salts across the same membrane was studied thoroughly cleaning the membrane after each permeation measurement. For cleaning, the membrane was immersed several times in water until no conductivity changes (increase) could be detected.

Reverse osmosis experiments

Reverse osmosis measurements were carried out using a home-made apparatus working under constant stirred conditions (rotating speed = 700 rpm), and the actual cell containing the membrane (area $A = 36.8 \text{ cm}^2$). This apparatus includes a temperature controlled pressure chamber made of stainless steel with 1.8 L/vol. The maximum pressure that can be applied is 40 bar. At the bottom, the cell is equipped with an outlet for permeate solution. The reverse osmosis experiments were carried out for both HCl-doped PANi and undoped PANi membranes, the chamber was filled with 1.8 L of pure water and the pressure was adjusted with nitrogen gas from a pressurized bottle. At the second step, the fluxes for pure water and alkaline salt solutions were determined at

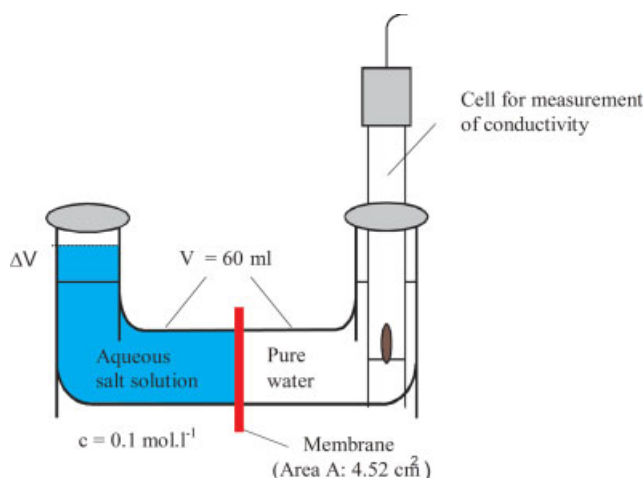


Figure 2 Apparatus for measurement of ion permeation. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

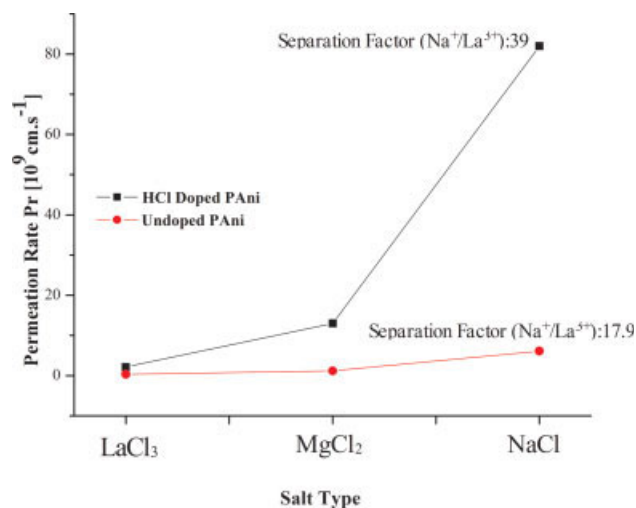


Figure 3 Permeation rates of various salts across doped and undoped PANi membranes. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

20, 30, and 40 bar by collecting the permeated water in a beaker.

Determination of flux

The permeation flux (J) was calculated from the measured volume V of the permeate, which was flowing across the membrane of area A in the time period Δt ,

$$J = V/A \cdot \Delta t (\text{L/m}^2 \text{ h})$$

RESULTS AND DISCUSSION

Selective ion separation

In this work, selective ion permeation properties of aqueous NaCl, MgCl₂, and LaCl₃ solutions across self-standing PANi-based membranes were investigated. When measuring the ion permeation, the membrane was placed between two chambers, one of them filled with pure water and the other one with a salt solution. The ion permeation across the membrane was determined by measuring the increase of ion conductivity per unit time and calculating the permeation rate (P_R) as outlined in the experimental part. Permeation rates and separation factors versus various metal alkali salts are shown in Figure 3 and Table I. Significantly, different P_R values of the salts

were found to be in the increasing order of P_R (NaCl) > P_R (MgCl₂) > P_R (LaCl₃). As one can see from Table I and Figure 3, the ion permeation value of the alkaline metal earth chloride being significantly smaller than those of the alkali salts. Clearly, the salt with small size (NaCl) facilitates higher permeation rates than salts with larger sizes (MgCl₂ and LaCl₃). In the case using undoped PANi membrane, it was observed nearly 6–14 times lower permeation rates than HCl-doped one. This phenomenon can be explained by the fact that undoped PANi has very dense and hydrophobic structure.²⁷ Thus, undoped PANi's hydrophobic nature reduces the solubility of water and lowers the overall permeability in undoped PANi membrane. With doping treatment of PANi membrane it was expected to improve the hydrophilicity of the membrane structure which results in more permeability. As expected, HCl-doped PANi membrane has significantly exhibited higher permeation rates. While the membrane is hardly permeable to inorganic ions in the undoped state; after HCl-doping the membrane exhibited higher permeation rates and this can be explained by the fact increase in the hydrophilicity of the membrane. This result is in good agreement with earlier reported work.²⁸

On the other hand, it was observed that di- or trivalent containing metal salts are highly rejected than monovalent salt. This can be explained due to the fact that di- or trivalent cations receive much stronger repulsive forces from the doped PANi membrane which can be considered that have a positively charged layer. This effect is called as Donnan effect and same result was reported before for PANi-based doped membranes.²⁹ In Donnan effect, trivalent ions receive much stronger repulsive forces from the equally charged layers (Donnan exclusion) and stronger attractive forces from the oppositely charged layers than the monovalent ones (Donnan inclusion). The lowest rejection rates for a salt with monovalent cation (sodium), but there are high rejection rates for salts with divalent and trivalent cations. Consequently, it can be concluded that PANi membranes can successfully separate alkaline metal ions and alkaline rare-earth metals summarized as above.

Furthermore, when using undoped PANi membrane, typical separation factor (α) values were found to be 5.11 and 17.9 for α (Na⁺/Mg²⁺) and α (Na⁺/La³⁺), respectively. While HCl-doped PANi was used

TABLE I
Permeation Rates and Separation Factors for the Poly(ether sulfon) and PANi-Based Membranes

Membrane	P_R (NaCl) (cm s ⁻¹)	P_R (MgCl ₂) (cm s ⁻¹)	P_R (LaCl ₃) (cm s ⁻¹)	α (Na ⁺ /Mg ²⁺)	α (Na ⁺ /La ³⁺)
Poly(ethersulfon) based	8.3×10^{-6}	5.7×10^{-6}	2.3×10^{-6}	1.46	3.61
Undoped PANi	6.1×10^{-9}	1.2×10^{-9}	3.4×10^{-10}	5.11	17.89
Doped PANi	8.2×10^{-8}	1.3×10^{-8}	2.1×10^{-9}	6.3	39

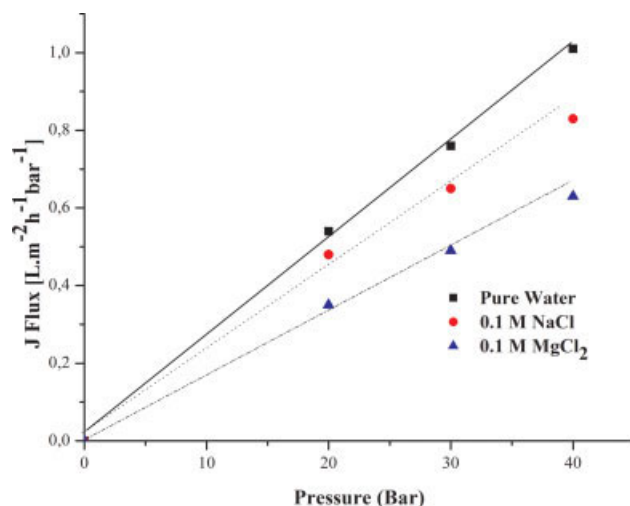


Figure 4 Flux values versus the pressure for HCl-doped PANi membrane. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

as separating membrane, it was found α ($\text{Na}^+/\text{Mg}^{2+}$) and α ($\text{Na}^+/\text{La}^{3+}$) to be 6.3 and 39, respectively. As one can see from Table I, the separation factor for ($\text{Na}^+/\text{La}^{3+}$) were improved from 17.9 to 39 in the case of using doped PANi membrane. This is the result of more rejection of trivalent cation from positively charged membrane.

For comparison, ion permeability and separation factor of poly(ethersulfon)-based commercialized membrane were also determined. While poly(ethersulfon)-based membrane showed roughly 1000 times higher permeation rates than HCl-doped PANi, the separation factor (α) values were very poor based on the permeation rates of the individual salts through this membrane (α ($\text{Na}^+/\text{Mg}^{2+}$) and α ($\text{Na}^+/\text{La}^{3+}$) are 1.46 and 3.61, respectively).

Reverse osmosis properties

The RO properties were determined by measuring the permeate collected in a definitely time interval and flux (J) was calculated as outlined in the experimental part. Schematic representation of the RO sys-

tem, which was used in the study, was depicted in the recently published paper.³

In this contribution, preliminary results of RO properties of the PANi-based membranes were studied and depicted in Figure 4 and Table II. Both doped and undoped PANi membranes were very dense and free of defects. In Figure 4, flux values are plotted as a function of the operating pressure (Δp). The operating pressure represents the difference between the applied pressure (p) and the osmotic pressure (π) of the feed solution. The pressure dependency of the flux of pure water across the membrane is showed.

Concerning the RO properties of undoped PANi membranes, the water flux of this membrane is too low for commercial application purposes due to its hydrophobic nature and less-permeable structure. At even 40 bar pressure, no permeation of water across undoped PANi membrane was observed. This result was in good agreement with the study of Ball et al.⁸ After this result, it is believed and tried to improve the hydrophilicity of the membrane structure which will result in high flux values. As is well known from the earlier works, in RO technique, these membranes are more suitable which are hydrophilic but not highly porous, otherwise the solvent ion rejection performance would be low. In addition, it is known that doped PANi can be considered as positively charged nanofiltration membrane. As we expected, it was observed the higher flux values for HCl-doped PANi than undoped one.

On the other hand, reverse osmosis properties of poly(ethersulfon)-based bare supporting membrane was measured for comparison and it was found that the flux values for both the poly(ethersulfon)-based and HCl-doped PANi membranes increase with increasing operating pressure (see from Fig. 4). While pure water flux (J_w) is 286.9 [$\text{L}/\text{m}^2 \cdot \text{h}$] and 404.3 [$\text{L}/\text{m}^2 \cdot \text{h}$] at 20 and 40 bar, respectively, for poly(ethersulfon)-based membrane, 0.54 [$\text{L}/\text{m}^2 \cdot \text{h}$] and 1.01 [$\text{L}/\text{m}^2 \cdot \text{h}$] flux values were found for HCl-doped PANi at corresponding pressures. Thus, poly(ethersulfon)-based bare supporting membrane showed nearly 400 times higher flux values. It was also tried to find flux values for NaCl and MgCl_2 in the RO experi-

TABLE II
Reverse Osmosis (RO) Properties of the Poly(ether sulfon) and PANi-Based Membranes

Membrane type	Fluxes ($\text{L m}^{-2} \text{ h}^{-1}$)								
	Pure water			0.1M NaCl			0.1M MgCl_2		
	20 bar	30 bar	40 bar	20 bar	30 bar	40 bar	20 bar	30 bar	40 bar
Poly (ethersulfone) based	286.9	365.2	404.3	231.5	326.1	384.8	130.4	179.4	222.8
Undoped PANi	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Doped PANi	0.54	0.76	1.01	0.48	0.65	0.83	0.35	0.49	0.63

n.d., not detected.

ments and the results were given in Table II. As it is seen from Table II, $MgCl_2$ has the lowest flux values. This trend can be explained by both receiving more repulsive forces and the effective diameter of those metal ions. The lowest rejection rate is for a salt with monovalent cation (sodium).

CONCLUSIONS

Self-standing HCl-doped and undoped PANi membranes were prepared successfully from NMP solution. HCl-doped PANi displayed better results in the selective transport of mono, di, and trivalent alkali metals than that of undoped PANi membrane. The ion permeability of larger metal containing salts and less hydrophilic materials is lower than small ones. The permeation rate of the lanthanide salts is especially low and good separation factors ($NaCl/LaCl_3$) up to 39 are found while using HCl-doped PANi membrane which exhibited higher permeation rates than undoped one due to hydrophilic nature. In addition, it was found that di-, trivalent metal salts are highly rejected than monovalent salt from the positively charged surface of the membrane. This can be explained due to Donnan effect. In RO application, poly(ethersulfon)-based bare supporting membrane showed nearly 400 times higher flux values than PANi-based self standing membranes. $MgCl_2$ has the lowest flux values. This trend is can be explained by both receiving more repulsive forces and the effective diameter of those metal ions. The lowest rejection rate is for a salt with monovalent cation (sodium).

The strong rejection of the lanthanides renders the HCl-doped PANi membrane useful materials for enrichment of rare earth metal ions and related ions such as Lanthanide(III) salts from aqueous solution.

The author sincerely thank Prof. Dr. Bernd Tieke from Universität zu Köln, Germany for all support during his postdoctoral staying.

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