

Solvent-Resistant Nanofiltration Membranes Based on Multilayered Polyelectrolytes Deposited on Silicon Composite

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ABSTRACT: Alternating deposition of oppositely charged polyelectrolyte complexes (PECs) on inorganic–organic composite membranes can efficiently overcome the drawback of microcracks induced by inorganic particles. Different bilayers of Poly (diallyldimethylammonium, chloride)/sulfonated poly(ether ether ketone) (PDDA/SPEEK) were first deposited on the charged silicon composite with hydrolyzed polyacrylonitrile (PAN-H) support and evaluated for solvent resistant nanofiltration membranes (SRNF) application. The morphology of the membranes was studied in detail via SEM and AFM. Because of Donnan exclusion, the multilayered PEC silicon composite membranes showed very high retentions up to 99% for negatively charged solutes (Rose Bengal (RB), 1017 Da) in the pressure driven filtration of isopropanol (IPA) solutions. For the first time, PEC-based silicon composite membranes were also applied in the filtration of organic solvents, where they were found to combine a remarkable stability in polar solvents with high fluxes and retentions. Compared with silicon composite membranes, the introduction of multilayered PDDA/SPEEK can efficiently improve the membrane performance and overcome the drawback induced by inorganic fillers. PEC-based silicon composite membranes thus show excellent prospective use in SRNF. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 129: 3156–3161, 2013

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INTRODUCTION

Nanofiltration (NF) is a pressure-driven membrane process (5–20 bars). Large scale applications are mostly focused on waste water treatment and drinking water production.^{1–3} One of the most challenges in NF at this time is to broaden the range of applications from aqueous to organic feeds.^{4,5} A more widespread use requires that membranes preserve their separation characteristics under more aggressive conditions of strongly swelling solvents and elevated temperatures.

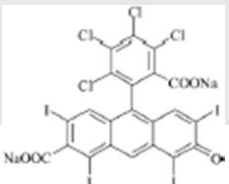
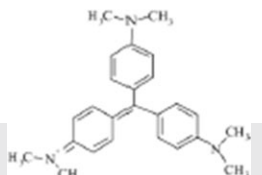
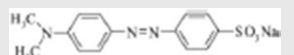
Solvent stable polymers normally contain quite rigid aromatic structures or special crosslinkable functional groups.^{6,7} Up to now, few commercial SRNF-membranes are currently available in the medium of apolar solvents. The performance of a membrane depends primarily on the structure and characteristic of the membrane material. Generally, several layers are included in NF membranes, where the toplayer mostly determine their selectivity, and the macro porous support layer provides the membrane with mechanical stability.^{8,9} Organic–inorganic polymer hybrids constitute now an emerging research field, which has opened the possibility of tailoring new materials, combining properties of inorganic glasses and organic polymers.^{10–12} For membrane application, the inorganic filler can provide

membranes with better mechanical, thermal, and chemical stability, which makes them attractive for separation at high temperatures and in aggressive environment especially in the solvents. For example, membranes containing silica nanoparticles were prepared by Nunes et al. to decrease swelling during separation of butane and methane.¹² Although the organic–inorganic hybrids were widely researched in membranes field, the brittleness of the inorganic layer which probably leads to the microcracks and further low retention, which limited their applications in NF.¹²

The layer-by-layer (LBL) deposition of polyelectrolytes (PEs) is regarded as a versatile and inexpensive method for the construction of polymeric thin films with specific surface properties. This is normally done via the alternating exposure of a charged substrate to solutions of positive or negative PEs.^{13–16} PEs have unique properties due to their strong internal Coulomb interactions and the possibility to tune their electrostatic nature by the composition and the characteristics of the individual PE constituents.^{17–19} Recently, PEC films were reported to have excellent stability in apolar solvents and therefore quite good potential in SRNF applications by Li et al.¹⁹

In this article, to combine the good thermal and chemical stability of inorganic fillers and overcome the shortcoming of

Table I. Solutes Properties

Component (MW) (g mol ⁻¹)	Structure	Charge	Molar volume (cm ³ mol ⁻¹)
Rose bengale (RB) (1017)		-	272.8
Crystal violet (CV) (407.99)		-	160
Methyl orange (MO) (327.3)		+	231

inorganic composite membranes, multilayered polyelectrolytes were first introduced on the inorganic nanoparticles-based membrane support and evaluated for SRNF application. The inorganic fillers will provide thermal mechanical and chemical stability of membranes as well as some selectivity on the solutes. The super thin multilayered polyelectrolytes will compensate the drawbacks of microcracks induced by inorganic particles, together with the good retention of charged solutes resulted from charged polyelectrolytes.

EXPERIMENTAL

Materials

Polyacrylonitrile (PAN) was purchased from scientific polymer product inc. Poly (diallyldimethylammonium, chloride), PDDA ($M_w = 200,000\text{--}350,000$) was obtained from Aldrich as a 20 wt % aqueous solution. Sulfonated poly (ether ether ketone), SPEEK, was prepared by direct sulfonation of PEEK (Vitrex) with sulfuric acid at 80°C for 3 h. The degree of sulfonation (the number of SO₃H groups per repeating unit), as obtained by ¹H NMR, is 0.89.²⁰

PAN and Hydrolyzed PAN Support (PAN-H) Preparation

The PAN and PAN-H supports were prepared by following the method reported via Vankelecom et al.¹⁹ The PAN fibers were dissolved in DMSO with 15 wt % solutions. The polymer solution was cast on a polypropylene support and then immersed in deionized water. The PAN-H support was obtained by immersing the PAN support in 12 wt % NaOH at 50°C for 45 min. The remaining NaOH was removed by washing water and then immersed in HCl for 4 h to convert -COONa into -COOH groups.

Preparation of Silicon Composite Membrane Support (PAN-H/Si)

To ensure the stability and uniformity of silicon particles in the membranes, the silicon dioxide was introduced in the membranes by *in situ* hydrolysis. One layer of PDDA was first

introduced on the PAN-H support to make sure the uniformly distribution of tetramethylorthosilicate (TMOS) on the PAN-H support. Then a layer of TMOS (4.1 g/50 mL ethanol) was introduced on the surface of PAN-H support via simple adsorption. Finally the PAH-H support with TMOS monomer was put in the ammonia solution for 24 h to induce the TMOS hydrolysis to form silicon particles.²¹ The formed PAN-H/Si composite membrane then was rinsed by water for layer by layer experiment.

Multilayered Silicon Composite Membrane Preparation

Polyelectrolytes were dissolved in aqueous medium with a concentration of 0.3 wt %. For adsorption of each layer, the PAN-H/Si support was immersed in the solution of the cationic polyelectrolyte (PDDA), followed by a rinsing step in water, then immersed in the solution of the anionic polyelectrolyte (SPEEK) and again rinsed by water. The described procedure

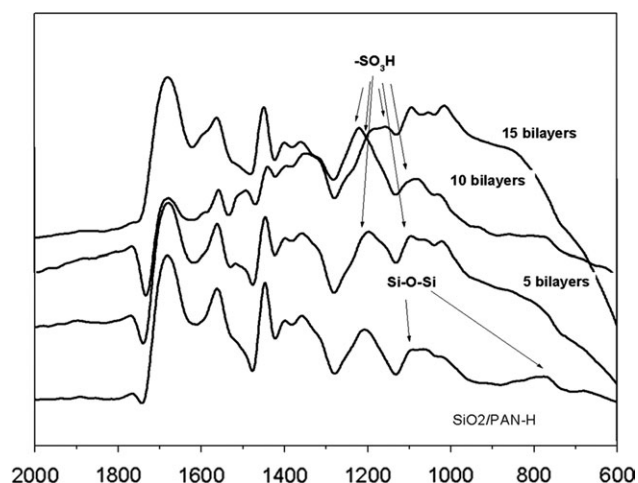


Figure 1. ATR-IR spectra of multilayered PAN-H/Si and PAN-H/Si membranes.

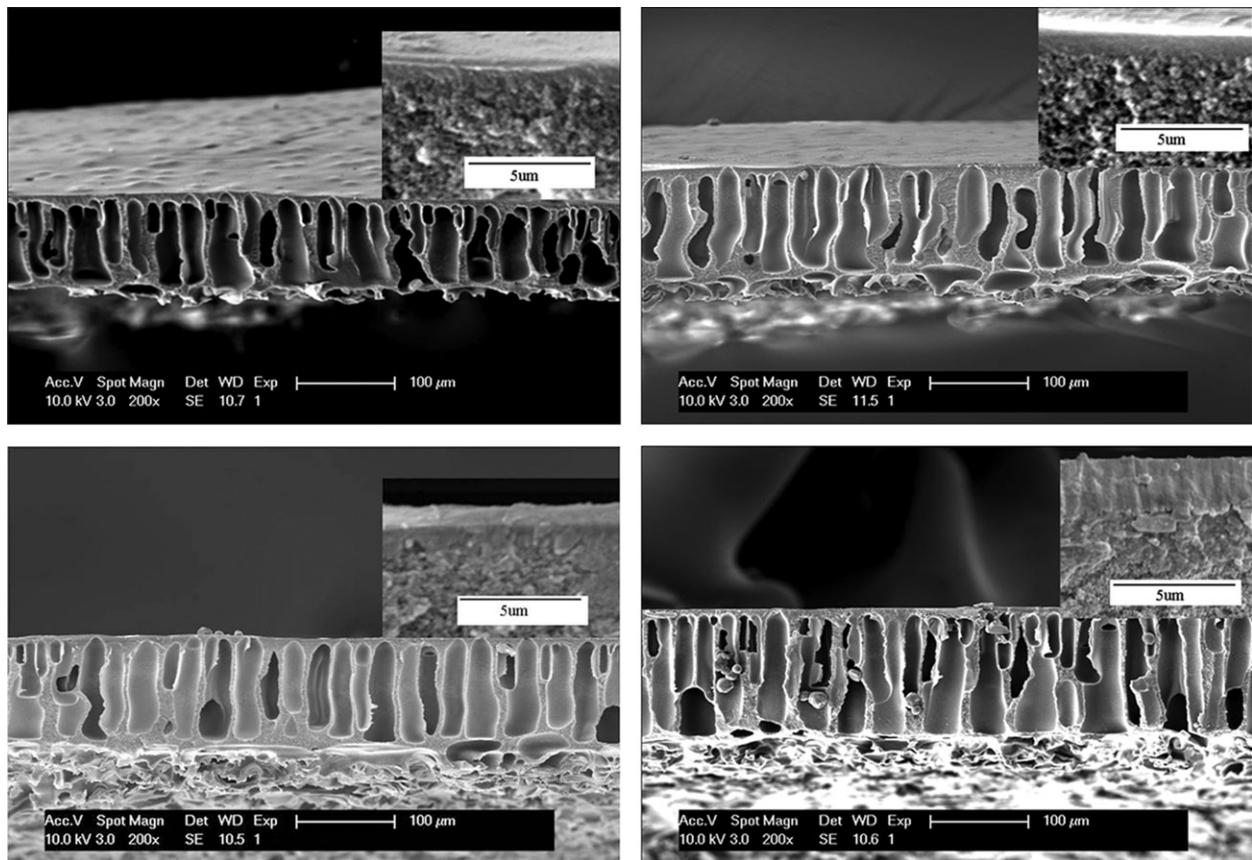


Figure 2. The cross section of multilayered PAN-H/Si and PAN-H/Si membranes.

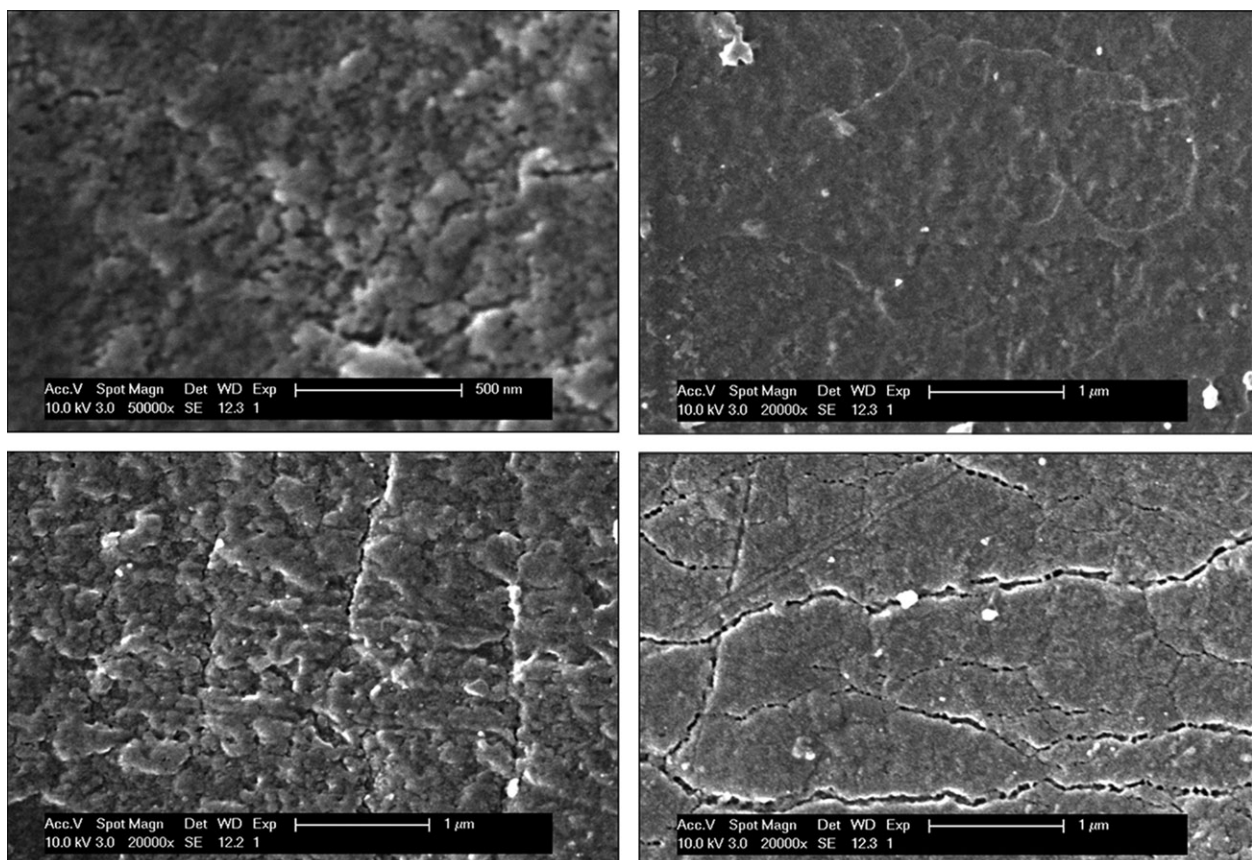


Figure 3. The surface structures of multilayered PAN-H/Si and PAN-H/Si membranes.

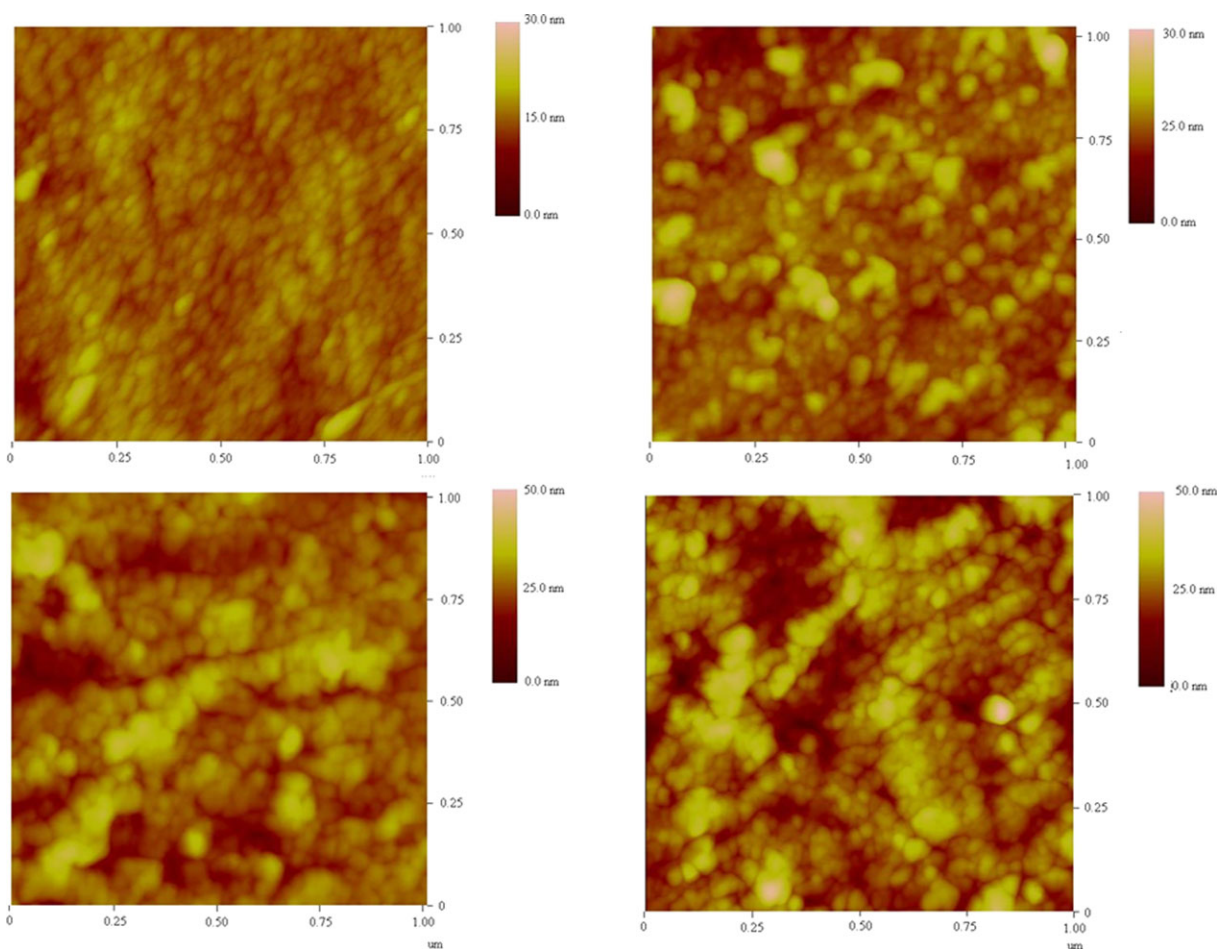


Figure 4. Topography images of multilayered PAN-H/Si membranes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

was repeated until a maximum 15 pairs of polycation/polyanion layers were adsorbed. Immersion time in the individual solutions was 10 min.

Attenuated Total Reflectance (ATR-IR) Infrared Spectra and UV-vis Spectroscopy

Attenuated total reflectance (ATR-IR) infrared spectra were acquired using a Bruker IFS66V/S spectrophotometer. A UV-vis spectrum was recorded on a Perkin-Elmer Lambda 12 double-beam spectrophotometer.

Scanning Electron Microscope (SEM)

SEM (JEOL 6360LV, Japan) was carried out to study the cross-section and surface structure of the membranes. The cross-section was obtained after breaking the membranes in liquid nitrogen.

Atom Force Microscope (AFM)

Tapping mode AFM was conducted at ambient conditions using a SPA-300HV with a SPI3800N controller (Seiko Instruments Industry, Japan). Both height and phase images were recorded simultaneously using the retrace signal. Etched Si tips with a resonance frequency of ~ 70 kHz and a spring constant of about 2 N m^{-1} were used, and the scan rate was in the range from

1.0 to 2.0 Hz. Each scan line contains 256 pixels, and a whole image is composed of 256 scan lines.

The average roughness R_a and the root-mean-square value (R_{MS}) were calculated by eq. (1).

$$R_a = \frac{1}{N} \sum_{i=1}^N |z_i - \bar{z}| \quad \text{and} \quad R_{ms} = \sqrt{\frac{1}{N} \sum_{i=1}^N |z_i - \bar{z}|^2} \quad (1)$$

Filtration Test

Filtrations were done in a stainless steel dead-end pressure cell with 10 cm^2 membrane area. The feed solution was poured in the cell, which was pressurized with nitrogen to $20 \times 10^5 \text{ Pa}$ (20 bar). During filtration, the feed solution was stirred to avoid

Table II. The Surface Roughness of Multilayered PAN-H/Si and PAN-H/Si Membranes

	0	5 bilayer	10 bilayer	15 bilayer
R_{ms}	2.22	4.66	5.03	3.60
R_a	1.71	3.46	3.97	2.84

Table III. NF Properties of Multilayered PAN-H/Si and PAN-H/Si Membranes for Different Charged Solutes from IPA Solutions

Solute	Permeability (L m ⁻² bar ⁻¹ h ⁻¹)					Retention (%)				
	PAN-H	PAN-H/Si	5	10	15	PAN-H	PAN-H/Si	5	10	15
RB	11.5	5.54	0.1	0.3	0.14	50	70	99	95	94
CV	47.6	10.3	5.16	9.42	6.33	11	12	18	27	14
MO	46.7	13.9	0.95	1.47	1.26	42	43	36	42	49

concentration polarization. Permeate samples were collected as a function of time, weighed and analyzed. The retention values were calculated with the permeate concentration and the concentration of the original feed solution according to formula (2)

$$R(\%) = (1 - C_p/C_f) \times 100 \quad (2)$$

The permeation was stopped when the retention reached a constant value. The characteristics of the solutes used in this article are listed in Table I. All the measurements were based on at least three samples, and the average values were used. The standard deviation on the measurements is about 5%.

RESULTS AND DISCUSSION

The method used for assembly of multilayered polyelectrolytes on spherical colloids is based on the interaction of oppositely charged polymers. The started charged support used in this article is negatively charged PAN-H support. Before introducing the silicon oxide on the support, the support was first coated with a layer of PDDA, the interaction between PDDA and TMSO could ensure the uniformly distribution of TMOS on the membrane surface. Afterward the PAN-H/Si composite membranes (PAN-H/Si) can be obtained by hydrolysis. Then multilayered PDDA/SPEEK films were introduced on the PAN-H/Si by layer-by-layer method. ATR-FTIR in Figure 1 shows spectra of PAN-H/Si and multilayered PEC membranes deposited on the PAN-H/Si. The peak at about 1100 cm⁻¹ is attributed to the typical Si—O—Si asymmetric stretching vibration. And the peak at about 800 cm⁻¹ is attributed to the Si—O—Si bending vibration band.²² For the multilayered PEC membranes, the bands at about 1080 and 1220 cm⁻¹ are attributed to the SO₃H groups, confirming the incorporation of SPEEK into the multilayered structure. After introduction of multilayered PDDA/SPEEK on silica composite membranes banding at 800 cm⁻¹ for Si—O—Si is disappeared, confirming the successfully formation of multilayered PDDA/SPEEK on the PAN-H/Si support. The cross section of the membranes was detected by SEM (Figure 2). Clearly, the support layer of all the

membranes show very open structures and finger like pores. A thin skin layer was clearly found. The thickness of the skinlayer increases with the bilayer number of PDDA/SPEEK increasing, which is a strong evidence for the layer growth. The surface of membranes was shown in Figure 3. The silicon particles were clearly detected in the silicon composite membranes. After introduction of multilayered polyelectrolyte, the roughness of the membranes surface changes dramatically. The membranes with 10 bilayers of PDDA/SPEEK show the roughest structure. While, when the bilayer number extends to 15, the membrane shows relatively smooth structures. Tapping mode AFM was performed on the different multilayered PEC membranes to detect their surface morphology. Figure 4 shows the height images of the multilayered PEC membranes deposited on PAN-H/Si support for a 1 × 1 μm² scale. Nanoparticles were clearly seen on the surface from the AFM results in Figure 4. The size of the particles increased after coating of bilayers of PDDA/SPEEK. With increasing PDDA/SPEEK layers, the particles gradually connected together. The roughness of the membranes in Table II showed that: with the introduction of the PDDA/SPEEK layers, the roughness first increases then decreases when the bilayer number reached 15, which is well in agreement with the SEM results.

Table III shows the filtration data of the multilayered silicon composite membranes with different bilayer of PDDA/SPEEK. Three different dyes with negative (Bengal rose B (RB) and Methyl Orange (MO)) and positive charge (Crystal violet (CV)) were selected for the filtration test to study the solute charge influence on the membrane separation properties. All the membranes show the highest retention on the negatively charged RB. After the introduction of silicon oxide on the PAN-H support, the retention of RB increases from 50 to 70%, which is relatively low due to the defects induced by the inorganic particles. After introduction of multilayered PDDA/SPEEK bilayers on the silicon composite membrane, the retention of negatively charged RB increased from 70 to about 90%, which indicates that: the multilayered PEC can successfully compensate the defects in the membranes. For the positively charged CV, the

Table IV. SRNF Properties of Multilayered PAN-H/Si and PAN-H/Si Membranes for RB from Different Organic Solvents

	Permeability (L m ⁻² bar ⁻¹ h ⁻¹)					Retention (%)				
	PAN-H	PAN-H/Si	5	10	15	PAN-H	PAN-H/Si	5	10	15
IPA	6.81	0.97	0.1	0.13	0.15	50	70	99	95	94
DMF	0.14	0.15	0.09	0.13	0.07	68	85	88	88	89
THF	218	127	7.23	10	13.9	87	95	97	99	98

retention is much lower than negatively charged RB. To clarify the role of charge and molecular size effect on the membrane selectivity, another dye with negative charge (MO) was selected for study that with a much smaller size ($160 \text{ cm}^3 \text{ mol}^{-1}$). All the membranes show lower retention on MO than RB. Obviously the bilayers charge density is too low to prevent the smaller MO molecule to permeate. Although MO has a smaller molar volume than CV, the retention of the negatively charged MO is higher than that of the positively charged CV clearly proving the important role of the charge of the ultimately deposited PEC. The negatively charged surface of the membranes, due to the SPEEK on the surface, creates a Donnan exclusion or repulsive forces between the sulfonic acid groups and the negative solute charges leading to the high retentions of the negatively charged dyes.²³

Table IV shows the filtration data of the membranes with RB as solute in different organic solvents. All the multilayered PEC silicon composite membranes show good or excellent retentions for RB in different solvents, tested THF, DMF, and IPA etc. The solvent fluxes differ greatly for the different solvent systems. The membrane performance is efficiently improved after the introduction of multilayered PDDA/SPEEK bilayers. All the membranes show the highest flux for THF and the lowest for DMF, which may be due to the different physical properties of solvents or the interaction between the membrane and solvent. Compared with reported multilayer PEC system, the prepared membranes show similar retention and relatively lower fluxes.¹⁹

CONCLUSION

Multilayered PDDA/SPEEK was successfully deposited on the silicon composite PAN-H membranes to overcome the drawbacks induced by inorganic fillers. The membranes deposited with 5, 10, and 15 bilayers of PDDA/SPEEK were successfully prepared. The morphology of the membranes was studied in detail by SEM and AFM. Because of Donnan exclusion, the multilayered PEC silicon composite membrane shows the highest selectivity on solutes with the same charge as the surface of the multilayered PEC membranes. For the first time, PEC-based PAN-H/Si membranes were also applied in the filtration of organic solvents. Compared with PAN-H/Si membranes, the introduction of multilayered PDDA/SPEEK can efficiently improve the membrane performance and overcome the drawbacks induced by inorganic fillers. PEC-based PAN-H/Si membranes thus show excellent prospective use in SRNF, especially in polar aprotic solvents, like dimethylformamide (DMF) and tetrahydrofuran (THF), which have been the biggest challenge so far for most existing SRNF membranes.

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