Efficacy of polyethylene interpolymer membranes for the fluoride and arsenic ions removal during desalination of water via electrodialysis

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Preparation of the PE-PSt and PE/P4-MS inter-polymer Film

The PE/PSt and PE/P4-MS inter-polymer films are prepared by two steps processes. First step is the preparation of PE/PSt and PE/P4-MS inter-polymer pellets, second step is the blow film extrusion of these pellets in an extruder to respective films. The inter-polymer pellets of PE/PSt and PE/P4-MS were prepared by free radical polymerization of Styrene (St)/4-methyl styrene (MS), divinyl benzene (DVB) and benzoyl peroxide (BPO) in presence of mixture of xylene and toluene as solvent at temperatures between 90 to 100 ^{0}C, by melt-process method. The PE (mixture of high density polyethylene and linear low density polyethylene (80:20 w/w for PE/PSt interpolymer preparation and 90:10 w/w for PE/P4-MS interpolymer preparation) was added into the reactor under stirring condition along with the slow addition of xylene (500 mL). Once the PE is observed to be melted in the reactor forming homogeneous dough, the additional toluene (~3 L) was added slowly and the temperature of the reactor was allowed to drop to ~ 95 ^{0}C. The monomer mixture (St/4-MS + DVB + BPO) was added into the molten mixture of PE. 1wt% DVB and 1wt% of BPO with respect to monmer (St/4-MS) was next added and the polymerization was carried out for 3.5 h at ~95 ^{0}C. At the end of the reaction, the reactor temperature was increased to 150 ^{0}C and the solvent is distilled out (2.5 L) through the condenser outlet. Next, the interpolymer strands were extruded and pelletized with the help of pelletizer. The pellets were throughly washed with methanol to remove unreacted monomer and dried in oven at 80 ^{0}C for 72 h. The inter-polymer composition in terms of PSt/P4-MS loading is determined by gravimetric method. For the production of the inter-polymer film, a blow-film extruder was used. The extrusion was carried out at 210-220 ^{0}C. Final thickness of inter-polymer film was 200 μm.

Characterization of Ion-Exchange Membranes

FT-IR spectra of CEM$_{inter}$ and AEM$_{inter}$

FT-IR spectra of the CEM$_{inter}$, AEM$_{inter}$ were recorded in a Perkin Elmer FT-IR Instrument at room temperature. Figure 1S shows the FT-IR spectra of CEM$_{inter}$ and AEM$_{inter}$ respectively. The appearance of absorption bands at 3406 cm^{-1} and 2964 cm^{-1} in the spectrum of CEM$_{inter}$ is due to the stretching vibrations of OH of SO$_3$H and CH stretching of aromatic protons of PStSO$_3$H part. The bands appeared at 1244–1177 cm^{-1} and 1043 cm^{-1} were assigned to the stretching vibrations for S=O and O=S=O, respectively. In the spectrum of AEM$_{inter}$ absorption bands appeared at 1642 cm^{-1} and 1458 cm^{-1} due to aromatic ring stretching vibration. The absorption band appeared at 3385 cm^{-1} was due to quaternary ammonium moiety.
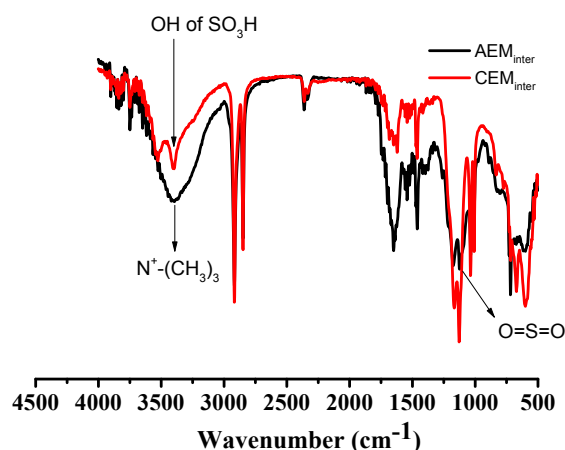
Fig S1: FT-IR spectra of CEM$_{inter}$ and AEM$_{inter}$.

Physicochemical and electrochemical properties of different membranes:

The physicochemical properties such as water uptake (%), the electrochemical properties such as ion-exchange capacity (IEC), ionic conductivity (K^m), transport number (t) of all the membranes used in this work has been measured.

For the determination of water uptake (%), known weight of dry membrane samples (m$_d$) previously kept in a vacuum oven at 60 ^{0}C for 48 h were immersed in distilled water for 24 h at 30 ^{0}C to ensure equilibrium water uptake by the membrane and weight (m$_w$) of membrane was recorded after the removal of surface water by blotting paper. The swelling of membranes in water was determined by the following equation:

$$S\,(\%) = \frac{(m_w - m_d)}{m_d}\mathrm{X}100 \quad (1)$$

Averages of at least four were taken.

The IEC, defined as the ratio between number of exchangeable ionic groups (equivalents) and the weight of dry membrane, was determined by the classical titration method. For example known weight of dry of membrane pieces were thoroughly washed with double distilled water and equilibrated in 50 mL of 0.10 M KNO$_3$ solution for 24 h. Equilibrated solution was titrated against 0.10 M silver nitrate solution using di-iododimethyl fluorescein solution in ethanol as indicator. The end point was detected by visualizing the colour change from orange to blue. Averages of 4-5 experiments were recorded.

The ionic conductivity of the membranes (K^m) were determined in a manually set up clip-on cell, composed of two black graphite electrodes fixed on acrylic plates. The active area of electrodes as well as of the membrane was 1.0 cm². Before determination of ionic resistance and conductivity, membranes were equilibrated with NaCl solutions (400 to 4000 mg/L) for 24 h. During the experiments, the wet membrane was tightly sandwiched between the electrodes and secured in place by means of set of screws. The membrane resistance (R^m) was measured with the help of digital conductivity meter (Model CC 601, Century, India) at ambient temperature. The thickness of the membrane was measured by a digital calibre, and membrane conductivity (K^m) was estimated by the following equation:

$$K^m = \Delta x / A R^m \quad (2)$$

where Δx is the thickness of the wet membrane and A is the effective membrane area.

For the determmination of transport number (t^+ or t^-) of the membranes used for this work, membrane sample of 9.0 cm² effective area was separated by sodium chloride solutions (NaCl) of concentration 0.1 mol dm⁻³ and 0.01 mol dm⁻³ respectively in a acrylic made cell. The potential difference across the membrane was measured using a multimeter (MECO, 81K-TRMS) which was connected to calomel reference electrodes. The transport number, t was calculated by the following equation

$$E_m = \frac{RT(2t-1)}{F} \ln \frac{C_1}{C_2} \quad (3)$$

where R is the gas constant, F is the Faraday constant, T is the absolute temperature (298 ^0K), C_1 and C_2 are the concentration of electrolyte solutions in the testing cell. Same procedure was followed for the measurement of transport number using sodium fluoride (NaF) as electrolyte.