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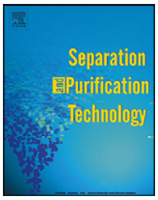

Investigation of electrochemical and morphological properties of S-PVC based heterogeneous cation-exchange membranes modified by sodium dodecyl sulphate

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ABSTRACT

Heterogeneous cation exchange membranes were prepared by solution casting technique using S-polyvinylchloride (S-PVC) and Styrene–Butadiene–Rubber (SBR) as binder and cation exchange resin as functional groups. In this research the effect of sodium dodecyl sulphate (SDS) on the selectivity, structure and electrochemical properties of potential driven membranes using this material in casting solution was evaluated. Totally the experiments revealed that SDS by revaluation in structure of membrane could change the membrane performance. The microstructures of prepared membranes were investigated by scanning optical microscopy (SOM). The images show that the enhancement in SDS ratio in the casting solution results in uniform distribution of functional groups. In order to investigate these prepared membranes, the oxidative stability and electrochemical properties tests were used. The measurements indicate that oxidative stability, ion exchange capacity, ion permeability, surface resistance, membrane potential, ionic flux, current efficiency, and selectivity parameters of prepared membranes have been improved by up to 2 wt% increase in SDS in the casting solution. Membrane with 2 wt% SDS loading exhibited higher efficiency and electrochemical properties in comparison with other prepared membranes in this research, while its water content was lower than other membranes.

1. Introduction

Electro-membrane processes are based on the selectivity of ion-exchange membranes. In such processes, the ions interactions with each other, a membrane or water will be happened in a complex fashion. There are cation- and anion-exchange membranes depending on the sign of the permeating ions [1–4]. These membranes contain electrically charged groups fixed into the polymer matrix and allow permeation of ions of opposite sign through the membrane under the influence of an electric field which separate ionic species from the aqueous solution and other uncharged components. Various requirements are enumerated for ion exchange membranes including: low electric resistance, high permselectivity, low diffusion of salt, high mechanical strength, high selectivity between the same charged ions, high chemical stability, low cost and so on [1–3]. Variation of functional groups, selection of different polymeric matrices, alteration of cross-link density, nature of surface layer and heterogeneity of the membranes are important tools to achieve superior membranes [5,6]. To assess the suitability of any membrane for any specific application two vital parameters, the main transport characteristics of the membrane and its structural properties, must be evaluated [5–10]. By the development of new ion exchange membranes with better selectivity, lower electrical resistance and improved thermal, chemical and mechanical properties, other applications of ion exchange membranes apart from the initial desalination of brackish water have recently gained a broader interest in food, drug, chemical process industry as well as biotechnology and waste water treatment nowadays [11–16].

It is well known that the slight change in the membrane fabrication process can affect the final membrane morphology and also the membrane performance. An important factor which determines the solution casting path of membrane forming system is the composition of the casting solution [17–24]. In some of previous works, surfactants have been applied to modify the surface of prepared membranes, enhancement of separation performance in ultrafiltration or reverse osmosis, change the monomer surface activity in the emulsion polymerization, prolong the stability of the separation performance in liquid membrane process and so on [25–32]. Also it has been shown that addition of surfactants in the casting solution can induce or suppress the formation of macrovoids [33].

The references quoted for the preparation of the membranes are all related to pressure driven membranes, not a single reference has been cited regarding the addition of surfactant in the casting solution of ion exchange membranes. This article is a continuation

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Nomenclature

S-PVC	S-polyvinylchloride
SBR	Styrene–Butadiene–Rubber
SDS	Sodium dodecyl sulphate
SOM	Scanning optical microscopy
wt%	Weight percent
THF	Tetrahydrofuran
W_{wet}; W_{dry}	Weight of wet membrane; dry membrane (g)
a	Milli-equivalent of ion exchange groups in membrane (mequiv.)
IEC	Ion exchange capacity
F.I.C.	Fixed ion concentration
$\bar{C}$	Ion concentration in membrane
C	Ion concentration in solution
E_{Measure}	Membrane potential (mV)
t_i^m; t_0	Transport number of counter ions in membrane phase; in solution
R	Universal gases constant (J mol^{-1} K^{-1})
T	Temperature (K)
n, Z_i	Electrovalence of ion
a_1, a_2	Ion electrolytic activities
P_s	Membrane ionic permselectivity
P	Diffusion coefficient of counter ions (m/s)
d	Membrane thickness (m)
N	Ionic flux (mol/m^2 s)
C, C_1, C_2	Cation concentration in the cell compartments (M)
A	Membrane surface area (m^2)
Q	Conductivity (μS)
t	Time (min)
r	Specific electrical resistance (Ω cm)
R	Electrical resistance (Ω)
Y	Concentration of fixed charge on the membrane surface
Δn	Number of transported moles through membrane potential (voltage, V)
V	Volume of each compartment in the used test cell
C.E.	Current efficiency
F	Faraday constant
I	Current intensity (A)
M_{w}	Molecular weight

of other activities to obtain more information about the effect of additives on the structure and the permeability of ion exchange membranes.

Sodium dodecyl sulphate (SDS) or sodium lauryl sulphate is a strong anionic surfactant which can decrease the surface tension of its contacted molecules. This surfactant can also improve hydrophilicity of membranes [17,18]. For this investigation heterogeneous cation exchange membranes were prepared by solution casting techniques using S-PVC/SBR blend as binder, cation exchange resin powder as functional group agent and tetrahydrofuran as solvent. Use of these polymers and their blends as membrane binders can offer special characteristics in the prepared membranes through combining the good support (strength and rigidity) of glassy polymers with toughness and high permeability of flexible rubbery ones. S-PVC is a flexible and durable polymer with suitable biological and chemical resistance [34]. SBR is a rubbery polymer with good permeability and appropriate abrasion resistance and aging stability [35].

In present research, SDS was selected as a strong anionic surfactant and the effect of this anionic surfactant as additive in the casting solution in preparing cation exchange membranes was investigated. Also it was tried to improve the membrane performance by adjusting the additive amount in the casting solution.

2. Materials and methods

2.1. Materials

Syndiotactic polyvinylchloride (S-PVC), supplied by BIPC, Iran, grade S-7054, Styrene–Butadiene–Rubber (SBR), Iran, grade 1502 (IR SBR. 1502) as binders, sodium dodecyl sulphate (SDS) or sodium lauryl sulphate as additive, tetrahydrofuran (THF) as solvent and cation-exchange resin (Ion exchanger Amberlite® 15, strongly acidic cation exchanger, H^+ form of capacity more than 1.7 mmol/ml) by Merck Inc., were used to prepare the membranes. All other chemicals were supplied by Merck Incorporation. Distilled water was used throughout this research.

2.2. Membrane preparation

Heterogeneous cation exchange membranes were prepared using solution casting technique. In the membrane preparation procedure, resin particles were dried in oven (Behdad Co., Model: oven 5) at 30 °C for 48 h and then pulverized into fine particles in a ball mill (Pulverisette 5, Fritisch Co.) and sieved to the desired particles size (−300 +400 mesh). The membranes were prepared by dissolving the polymers binder in THF solvent in a glass reactor equipped with a mechanical stirrer (Model: Velp Sientifica Multi 6 stirrer) for more than 4 h. This was followed by dispersing a specific quantity of grinded resin particle as functional group agents and SDS as additive in polymeric solution, respectively. The mixture was allowed to mix vigorously at room temperature in order to achieve uniform dispersion of particles in the polymeric solution. In addition, for better dispersion of particles and breaking up its aggregates, the solution was sonicated for 30 min using an ultrasonic instrument (Struers Metason 200 HT, by Struers, Copenhagen, Denmark) and it was allowed to mix for 15 min again by mechanical stirrer. Then the mixture was cast onto a clean and dry glass plate at 25 °C. The membranes were dried at ambient temperature and immersed in distilled water. As the final stage, the membranes were conditioned to Na^+ form by equilibrating in HCl and subsequently in NaCl solutions. The membrane thickness was measured by a digital caliper device (Electronic outside micrometer, IP54 Model: OLR) to maintain the membrane thickness around 80–120 μm.

For all of prepared membranes the ratio of polymers binder (S-PVC:SBR), ratio of solvent to binder, ratio of resin particle to binder, was 95/5 (w/w), 16/1 (w/w) and 1/1 (w/w) respectively. The ratios of SDS (additive/total solid) in samples 1–6 were: 0.0/100 (w/w), 0.5/100 (w/w), 1/100 (w/w), 2/100 (w/w), 4/100 (w/w), 8/100 (w/w) respectively.

2.3. Test cell

The test cell used in measuring transport number, specific electrical resistance, ion diffusion and other electrochemical properties is shown in our previous work [36]. Briefly the cell consists of two cylindrical compartments (vessel, each 150 cm^3) made from Plexiglas which were separated by the membrane. The membrane was fixed between rubber rings (the membrane area was 13.85 cm^2). One side of each vessel was closed by Pt electrode that supported with a piece of Teflon and its other side was equipped with a piece of porous medium to support the membrane. The top of each compartment contained two orifices for feeding or sampling. In order to minimize the effect of boundary layer during the experiments and also to establish the concentration polarization on the vicinity of membrane's surface, both sections were stirred vigorously by magnetic stirrers.