Available online at www.sciencedirect.com

Separation and Purification Technology 54 (2007) 61–70

Separation and Purification Technology

www.elsevier.com/locate/seppur

Effect of aging on the water sorption and ion exchange studies on Nafion and Dowex resins: Transition metal ions-proton exchange systems

Jayshree Ramkumar [a], Tulsi Mukherjee [b,*]

[a] Analytical Chemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400085, India
[b] Chemistry Group, Bhabha Atomic Research Centre, Trombay, Mumbai 400085, India

Received 13 March 2006; received in revised form 4 August 2006; accepted 16 August 2006

Abstract

Transition metal ion-H^+ exchanges on Nafion 117 membrane (pre-treated differently prior to use), Dowex 50W × 4 and Dowex 50W × 8 resins have been studied. The water sorption isotherms of these exchangers in different ionic forms generated over the entire range of water activity have been analyzed by the D'Arcy and Watt equation (DWE). The results show that the physical structure of the exchangers change due to long-storage or aging, and the amount of water sorbed becomes low. As a result, the counter-ions in the exchangers are not hydrated, resulting in discrepancies in the ion exchange studies. In the absence of any hydration of the transition metal ions in the resin phase, the driving force for the ion exchange reaction is the electrostatic interaction between the sulphonato group and transition metal ions. Pre-treatment of Nafion 117 membrane with boiling acid/water modifies the membrane structure and arrangement of the ionogenic groups. These modifications influence the state of water present in the Nafion 117 membrane and the ion exchange equilibria. The results obtained in the present study indicate that the ion exchangers lose their elasticity or swelling characteristics and therefore show poor water sorption characteristics.

Keywords: Nafion; Dowex resins; Transition metal ions; Water sorption; Ion exchange equilibrium; Aging

1. Introduction

Ion exchange resins with ionic content of 10-mol% known as ionomers, are of great importance because of their unique mechanical properties [1] caused due to the aggregation of ionic groups into clusters in the ion rich phase of the polymer. The most commonly used ionomer is perfluorosulphonate Nafion membrane (E.I. du Pont de Nemours and Co., USA). The transport and ion exchange property have been of great interest to rersearchers [2,3]. The formation of clusters depends on various factors like the water or solvent content, the number of the ionogenic groups and the counter-ion, the chemical nature of the polymer matrix, temperature, etc. [4]. The transport property of the ionomer membrane depends on the ion exchange selectivity and the mobility of the cation in the membrane phase [5–7].

The key role-played by the hydration of ions is evident in reactions both in the aqueous as well as non-homogeneous phases. Various models, proposed for explaining characteristics like swelling of ion exchangers, recognize the important role-played by ion–water interactions, both in the aqueous and the resin phases. The state of water present in an ion exchanger has been investigated by a variety of techniques to provide information regarding the nature of ion pair formation, ionic hydration, mobility of free water, etc. [8]. It has been concluded that in low and moderately cross-linked and fully swollen resins, water is present as a hydration sphere around the metal ion or as bulk water. The study of uptake of water is of importance both for Dowex resins and Nafion ionomer, with greater importance attached to the latter as it is used as an electrolyte in fuel cells [9] and it is observed that with decrease in the amount of water in the membrane phase, the conductivity decreases [10]. Thus, the water uptake characteristics of the membrane, specifically the balance between the sorption and desorption of water, plays a key role in determining the water content of the membrane [11]. Determining and analyzing the water sorption isotherms can provide very useful information on the ion–water interactions in the resin phase. For this purpose, many approaches have been used [12,13]. The analysis of the water sorption isotherms using the D'Arcy and Watt Equation (DWE) [14] gave realistic

---

[*] Corresponding author. Tel.: +91 22 25595234; fax: +91 22 25505331.
E-mail addresses: mukherji@barc.ernet.in, jrk@barc.ernet.in
(T. Mukherjee).

1383-5866/$ – see front matter © 2006 Published by Elsevier B.V.
doi:10.1016/j.seppur.2006.08.007

values of hydration numbers of the cations and also information on the structural differences in water present in different states/forms in the exchanger phase.

A complete understanding of ion exchange can be achieved only in terms of interactions at molecular level. Such an understanding of aqueous electrolytic solutions, which form a part of the ion exchange equilibrium system, has been achieved to a large extent. However, no direct information about the resin phase is available and therefore, various models have been proposed. The selectivity and related characteristics of the ion exchange resins based on polystyrene sulphonate cross-linked with divinyl benzene (PSS-DVB) have been fairly understood [15,16]. It is seen that the ionogenic groups (SO_3^-) are osmotically inactive and unhydrated and therefore in the absence of strong electrostatic interactions between $-SO_3^-$ and the counter-ion, the resin bead behaves like a container for counter-ions and water. The resin phase behave like single ion solutions and the properties of single ions can be studied over a wide range of concentration. Though Nafion is expected to show ion-exchange characteristics similar to that of the gel type PSS-DVB resins, the ion-exchange capacities of Nafion (eq.wt. ∼1100–1500) are smaller than those of PSS-DVB resins. These differences between these two ionomers could be due to the fact that Nafion unlike Dowex resins is not cross-linked and the phenomenon of clustering is expected to play an important role in determining the selectivity of Nafion. Further the effects of perfluoro and hydrocarbon backbones, present in Nafion and Dowex resins, respectively, on the binding of the sulphonate group with the counter-ion will be different.

In the present study, the water sorption isotherms of H^+ and the different cationic forms of the Nafion 117, treated differently, and Dowex 50W × 4 and Dowex 50W × 8 resins are generated over the entire range of water activity, a_w, and analyzed by the DWE. Nafion 117 membranes have been treated differently prior to their use in transport studies [17–23]. The most commonly used pre-treatment method is boiling the membrane in aqueous solutions. Such treatments alter the physical structure of the membrane and consequently the manner in which the ionogenic groups are ordered and can lead to variation in the water sorption and ion exchange properties. Steck and Yeager [17] has reported that the Nafion membrane treated with boiling water has lower selectivity as compared to the un-treated Nafion. With a view to understand the effect of such pre-treatments, Nafion 117 membranes are treated in different ways and used for the present investigations. The ion exchange equilibria of metal ion–H^+ systems using different transition metal ions have been studied using Nafion membranes and the results obtained have been compared with those obtained for Dowex resins.

2. Experimental

2.1. Preparation of air-dried ion exchangers

- Dowex 50W Resins: Dowex 50W × 4 and Dowex 50W × 8 resins after conversion to the H^+ form did not give the capacity values reported in the literature. Hence, the exchangers were treated using the procedure usually adopted to activate and regenerate the anion resin bed used in water treatment practices [24]. After washing the resin, it was treated with 2 M HCl to convert it to the H^+ form.
- Nafion 117 membrane: Nafion was pre-treated in different ways
  - (i) N: Nafion was immersed in cold 2 M HCl for 3 h.
  - (ii) AT: Nafion was refluxed with 1:1 HNO_3 for 1 h, and then boiled with distilled water (∼60 °C) for 0.5 h.
  - (iii) WT: Nafion was boiled with distilled water for 1 h, and immersed in cold 2 M HCl for 3 h.
  - (iv) nN and nAT: Nafion samples obtained relatively recently in comparison with the previous membrane and are treated as for the samples in (i) and (ii), respectively.

All the ion exchangers were washed free of acid and stored as air-dried material.

2.2. Capacity determination

- H^+ form: To a known weight of air-dried resin in the H^+ form, 10 ml of 0.1 M NaCl was added and the mixture titrated with standardized NaOH using phenolphthalein indicator. Knowing that the amount of alkali consumed is equal to the amount of H^+ liberated, the capacity of the air-dried resin was calculated. This was converted to the capacity/g of fully dried resin after determining the water content of the air-dried resin.
- Cationic forms: The H^+ forms of the resins were treated with a mixture of 0.2 M (MCl_2) solution (where $M = Cu^{2+}$, Ni^{2+}, Co^{2+}, Zn^{2+}) to convert it to the required ionic form. These resins were washed free of the salt and stored as air-dried samples. A known weight of the metal ion form of the resin was equilibrated repeatedly with a known volume of standard HCl solution. The equilibrated solutions were collected and made up to a known volume, including the washings of the resin. The H^+ concentration of this made up solution was estimated by titration using NaOH. The amount of hydrogen ion required to exchange with the metal ion in the resin was calculated and capacity is expressed as mequiv./g on a dry weight basis and are given in Tables 1 and 2.

2.3. Water content

- Air-dried sample: A known weight of the air-dried sample in the required ionic form was dried at 100 °C to a constant weight; the weight loss on drying being the water content of the sample, which can be converted to the dry weight basis.
- Fully swollen exchanger: Air-dried resin in the required ionic form was soaked in distilled water for 4 h. The sample was surface-dried. A known weight of the fully swollen exchanger was dried at 100 °C to a constant weight to estimate the water content.

2.4. Water sorption isotherms

The determination of water sorption isotherms is carried out using isopiestic measurements, at room temperature [25]. Determination of the isotherms requires the measurement of water