

Characterisation of Ion-Exchange Resins Under Thermal Loading

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ABSTRACT: The present work deals with the influence of temperature on the ion-exchange capacity of selected ion-exchangers. Technological operations running at elevated temperatures (drying, homogenization) can influence the lead or ion-exchange capability of ion-exchangers, which may affect values of the ion-exchange capacity. Several types of anion and cation-exchangers have been chosen for its application in practice. Samples of selected ion-exchangers were subjected to thermal stress in the temperature range of 75–160 °C at different times of exposure. It was shown that the

optimum processing temperature for anion and cation-exchange resins is in the range of 105–115 °C.

KEY WORDS: ion-exchange resins, ion-exchange capacity, thermal loading, anion-exchange resin, cation-exchange resin

1. INTRODUCTION

Porous types of ion-exchange resins are used in membrane processes such as ultrafiltration, nanofiltration or microfiltration. Gelatinous types of ion-exchange resins are used for processes such as reverse osmosis, electro membranes processes [1].

An ion-exchange resin is a high molecular substance (e.g. on the basis of copolymer of styrene-divinylbenzene (S-DVB) or polyacrylate) whose molecule contains functional groups capable of dissociation in an aqueous medium. Ion-exchange resins can be divided into anion resins (anion-exchange resin) and cation resins (cation-exchange resin) and ampholytic ion exchange-resins, which are able to exchange both anions and cations [2–3].

Anion-exchange resins themselves can be strongly basic, if the functional group is a quaternary ammonium group on the surface of copolymer. There are two types of strongly basic anion exchangers - type I which has a nitrogen atom bound to three methyl groups. Type II which has a nitrogen atom bound to different groups (two methyl groups and one hydroxyethyl group) [4–8]. The other group is represented by weakly basic anion-exchange resin which contain amino groups on their surface. Cation-exchange resin can be divided into strongly and weakly acidic types containing sulphonic and carboxyl groups, respectively [9–10].

The main characteristics of ion-exchange resins include ion-exchange capacity, pore size, nature of the counterions, ion charge, polarizability, and swellability. Ion-exchange resins can be used in many applications, e.g. deionisation, demineralisation or decarbonisation of water, selective removal of heavy metals [2, 11].

During the preparation of a ion-exchange membrane, ion-exchange resins pass through a number of technological operations during which their resins are thermally loaded. For example, temperatures about 110 °C are used for washing and drying, while homogenization of ion-exchange resins occurs around 140 °C. Operations taking place at elevated temperatures can influence the conductivity or the ion-exchange capability, thereby affecting the value of ion-exchange capacity and functionality of the ion-exchange resin.

Degradation by thermal loading in the case of cation-exchange resins with functional sulphonic groups is as follows: first, sulphonic acid is dehydrated and then decomposed into sulfur dioxide [12–13]. The thermal decomposition of anion-exchange resins with matrix of S-DVB with functional quaternary ammonium groups is shown in **Figure 1**. For OH⁻ form type I the thermal decomposition occurred at 60 °C, for Cl⁻ form the type I, the degradation was determined at 80 °C [14–15].

In this paper, ion-exchange resins were tested from the point of their thermal stability. As the ion-exchange resins (cation and anion) are frequently used as components of ion-exchange membranes that are subjected to thermal load during the processes of washing and drying, their thermal stability affecting the ion-exchange capacity plays the key role in their applicability.

2. EXPERIMENTAL

2.1 Materials

The tested samples of ion-exchange resins were tested in the H⁺ cycle and Cl⁻ cycle in a wet and dried state. Two types of cation-exchange resins and four types of anion-exchange resins were chosen, they are shown in **Table 1**, namely the macroporous and gel types [16]. From the viewpoint of the mechanical resistance, the ion-exchange resins of the gel type exhibit lower resistance than the macroporous ion-exchange resins which have a regular structure. Conversely, these ion-exchange resins have a smaller volumetric capacity. Before testing the ion-exchange capacity (IEC), the ion-exchange resins were subjected to conditioning.

Samples were subjected to thermal loading in the temperature range of 75–160 °C at different regimes, namely at 105 °C for 1 hour, at 140 °C for 1 and 4 hours, at 160 °C for 4 hours. Overview of the tested ion-exchange resins is shown in **Figure 2**. For samples of anion-exchange resins and cation-exchange resins, the ion-exchange capacity was determined as an indicator of the functionality of ion-exchange resins before and after thermal loading. Further, the residual moisture content, the particle size distribution and the water content were determined. Also, samples were characterized in terms of thermal behaviour using a thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC).

2.2 Used equipment

- laboratory thermo-balances KERN MRS 120-3 Moisture Analyser for measuring of the residual moisture
- dispersion unit Hydro 2000MU for determining particle size distribution in a wet state (Malvern Instrument, MasterSizer 2000)

- Titroprocessor 682 with 665 Dosimat for determining the exchange capacity
- electron microscope QUANTA FEG 450, the samples were chrome plating
- differential scanning calorimeter Mettler DSC 13E, the measurement was carried out in the temperature range of 25–400 °C and with a heating rate of 5 °C/min
- thermogravimetry was performed on a device assembled from a computer, oven and Sartorius BP210E S balance. Measurements were performed in quartz ampoules in the temperature range 25–950 °C at a heating rate of 5 °C/ min.

2.3 Conditioning of ion-exchange resins

Samples of commercially available ion-exchange resins were first kept in demineralised water to swell for 8 hours. Samples were conditioned, i.e. 5 g of cation-exchange resin material and 10 g of anion-exchange resin material. Samples were grouted with 1 M NaOH solution and left on a shaker for 8 hours at room temperature. After that the samples were rinsed with demineralised water and added into 1 M HCl solution for 12 hours. After being infused in to 1 M HCl solution, the samples were thoroughly rinsed. A half of each ion-exchange resin sample was then dried at 75 °C.

The ion-exchange resins (before and after heat loading) were determined particle-size distribution (before heat loading), water content (before and after heat loading) and used to the electron microscope images (before and after heat loading). The thermal behaviour of ion-exchange resins was characterized using thermogravimetry (TGA) and differential scanning calorimetry (DSC).

2.4 Determination of ion-exchange capacity

After conditioning in H⁺ cycles, the ion-exchange capacity of cation-exchange resins was investigated out in the following manner: 0.5 g of the cation-exchange resin sample was grouted with 50 mL of 0.1 M NaOH, then the sample was left on a shaker for 1 hour at room temperature. Thereafter, for the actual determination, 10 mL of the solution was pipetted and diluted to 30 mL with demineralised water. Subsequently, a magnetic stirrer and a glass electrode were inserted into the solution, being continuously stirred, the sample was titrated with 0.1 M HCl and the equivalence point was determined using a titroprocessor. The ion-exchange capacity of the cation-exchange resins per gram of dry matter was calculated from the decrease of sodium hydroxide using the relation:

$$IEC_{c.resin} = \frac{\left(c_{NaOH} - \left(\frac{c_{HCl} \times V_{HCl}}{V_{NaOH}^I} \right) \right) \times V_{NaOH}}{m_{c.resin}}$$

where:

C_{NaOH} - concentration of the NaOH solution added (g/mol)

C_{HCl} - concentration of the HCl titrant (g/mol)

V_{NaOH}^I - amount of the NaOH solution taken for titration (10 mL)

V_{NaOH} - amount of 0.1 M NaOH added (50 mL)

$m_{c.resin}$ - weight of dried cation resin (g)

After conditioning in Cl⁻ cycles, the ion-exchange capacity of anion-exchange resins was carried out in the following manner: 1 g of the anion resin sample was grouted with 50 mL of 4% NaNO₃, then the sample was left on a shaker for 1 hour at room temperature. Thereafter, for the actual determination, 10 mL of solution was pipetted into a 50 mL beaker and diluted to 30 mL with demineralised water.

Subsequently, 5 drops of the indicator K_2CrO_4 were added to the solution. The prepared sample is titrated with 0.1 M solution of $AgNO_3$ until the colour changed from yellow to orange by adding one superfluous drop of silver nitrate. The ion-exchange capacity of the anion-exchange resins per gram of dry matter was calculated from the decrease of sodium hydroxide using the relation:

$$IEC_{a.resin} = \frac{\left(\frac{c_{AgNO_3} \times V_{AgNO_3}}{V_{NaNO_3}^I} \right) \times V_{NaNO_3}}{m_{a.resin}}$$

Where:

V_{AgNO_3} - concentration of the $AgNO_3$ solution added (g/mol)

c_{AgNO_3} - concentration of the HCl titrant $AgNO_3$ (g/mol)

$V_{NaNO_3}^I$ - amount of the solution taken for titration (10 mL)

V_{NaNO_3} - amount of 0.1 M $NaNO_3$ added (50 mL)

$m_{a.resin}$ - weight of dried anion resin (g)

2.5 Determination of water content

The determination of water content was carried out as follows: samples of the ion-exchange resins were left for 12 hours to swell in demineralised water, and then and then the samples were dried in a temperature regime in one hour at 75 °C, 4 hours at 105 °C and then the amount of absorbed water was weighed. The entire volume of the measuring cylinder was then transferred to a filter paper and dried in an oven to a constant weight (1 hour at 75 °C, then at 105 °C for 4 hours).

2.6 Determination of particle-size distribution

For the initial samples of ion-exchange resins, the particle size distribution was determined in a wet state using the dispenser Hydro 2000MU.

2.7 Thermogravimetry

Thermogravimetry was performed on the device consisting of the computer, oven and Sartorius balance BP210E S. It was measured in a quartz ampoule in the temperature range of 25–950 °C at a heating rate of 5 °C/min. The samples were measured before thermal loading.

2.8 Differential scanning calorimetry

The commercially supplied samples of ion-exchange resins were subjected to differential scanning calorimetry where the samples were measured in the atmosphere under aerobic conditions, at a heating rate of 5 °C/min in the temperature range 35–220 °C. For comparison, the samples were measured before and after thermal loading.

3. RESULTS AND DISCUSSION

3.1 Determination of ion-exchange capacity

To evaluate the functionality of selected cation resins, the ion-exchange capacity was chosen as an evaluative property. The ion-exchange capacity refers to a number of ions that the system is able to bind [17]. The ion exchange capacity was also determined for the initial samples without thermal loading. The results are shown in **Table 2**. Also, the ion-exchange capacity was determined for ion-exchange resins in the H⁺ cycle and Cl⁻ cycle after thermal loading. The results are shown in **Table 3** and **Table 4**.

The results show that the IEC values decrease for the cation-exchange resins in the H^+ cycle with increasing thermal load, which is caused by degradation of the functional groups $-CH_2-NH-CH_2-PO_3Na_2$ and $-CH_2N(CH_2COOH)_2$ in the structure of the cation-exchange resin. As expected, IEC values for anion-exchange resins in the Cl^- cycle decrease with increasing heat load too, according to the expected Hoffman mechanism of degradation induced by thermal load [18]. The results of IEC values for Amberlite IRC 747 and Amberlite 748 indicate that thermal stress at 140 °C for 1 hour occurs probably to the accessing all functional groups consisting crosslinked copolymer based S-DVB. This effect was reflected by increasing the IEC values. For anion-exchange resins, this effect is not so obvious. Conservation of IEC for cation-exchange resins after heat loading 160 °C for 4 hours was in the range 50–60 %. Conservation of IEC for anion-exchange resins after heat loading 160 °C for 4 hours was in the range 58–99 %.

3.2 Determination of water content

Determination of water content is of great importance in terms of applicability of the ion-exchange resin. With a higher water content value we can also expect higher conductivity values, which is associated with higher levels of affinity to ions [2]. The determination of water content was carried out both for samples thermally unloaded and for samples after thermal load at 160 °C for 4 hours. There is a theoretical assumption that there should be a decrease the water content after thermal load due to the reduced number of functional groups that have higher affinity to water molecules compared with the molecular structure of DVB or acrylic matrix [17].

Table 5 shows that the best determination of water content can be seen with the anion resin Amberlite IRA 478 Cl^- and Amberlite IRA 900 Cl^- that exhibit 98 % of

maintaining the ability to water content after thermal load at 160 °C for 4 hours. Conversely, the lowest maintaining the ability to water content can be seen in the case of the cation-exchange resin Amberlite IRC 747 which exhibits nearly 80 % of maintaining the ability to water content after thermal load. The results of the maintaining the ability to water content for anion-exchange resin indicate the same trend as the results of conservation of IEC. Conversely, for cation-exchange resin the results differ.

3.3 Determination the particle-size distribution

The results from **Table 6** for each commercially available ion-exchange resin allow us to state that the area capable of the ion exchange is similar. At the same time, the results of the determination of particle size distribution are in accordance with the values declared by the manufacturers. Particle size distribution for all ion exchange resins was from about 530 µm to about 1000 µm. Range of maximum and minimum of particle size for every ion exchange resin was measured about 250 – 300 µm. Any ion exchange resin was not monodisperse.

3.4 Examining particles using a scanning electron microscope

To compare the ion-exchange resins (after chrome plating) before and after thermal load (160 °C/4 hours), images were made using an electron microscope and they are shown in **Table 7**. On the surface of ion-exchange resins after thermal load we can observe slight deformations that, as assumed, are related to the degradation of functional groups in the polymeric structure of the ion-exchange resin leading to decrease water content. Slight deformities may be related to phenomena to heat loading, such as cleavage of small molecules, the formation of bridges.

3.5 Examining degradation curves by thermogravimetry

To characterize the ion-exchange resins in terms of thermal loading, a thermogravimetric analysis was performed. Record of TG analysis for samples of cation and anion-exchange resins are shown in **Figure 3** and **Figure 4**. It is evident that degradation of cation and anion-exchange resins proceeds in several steps. At temperatures below 200 °C, there is a first weight loss associated with the degradation of functional groups in the polymeric structure and water evaporation. In the next step was degradation of the matrix. It can be observed from the results given in **Table 8** that the cation-exchange resin Amberlite IRC 747 exhibits the highest onset of degradation (420 °C). In the case of the samples of anion-exchange resins, the onset of degradation can be observed at about 270 °C.

3.6 Differential scanning calorimetry

The results of differential scanning calorimetry show that thermal loading induces an endothermic decomposition of functional groups in the tested cation and anion-exchange resins, which can be observed from the measuring results which they are shown in **Table 9**. The results of conservation of functional groups are shown in Table 9.

In the **Table 10** compares the results conservation of functional anion and cation-exchange resins after thermal loading 160 °C/4 hours using conservation values of ion-exchange capacity, conservation of the swelling fiction and conservation enthalphy of functional groups. As the most accurate indicator of evaluating the functionality used measurement of the ion-exchange capacity and DSC.

4. CONCLUSION

We can conclude that the selected commercially available types of cation-exchange resins with functional groups $-\text{CH}_2\text{-NH-CH}_2\text{-PO}_3\text{Na}_2$ and $-\text{CH}_2\text{N(CH}_2\text{COOH)}_2$ lose their ion-exchange ability as a result of thermal loading. This fact can be attributed to the degradation of functional groups. It was shown that the ion-exchange capacity of cation-exchange resins was maintained up to temperatures of about 105 °C. When compared to cation-exchange resins, anion-exchange resins after thermal loading at 160 °C for 4 hours exhibit a higher conversation of the ion-exchange capacity. On the surface of ion-exchange resins after thermal load we can observe slight deformations that are probably related to the degradation of functional groups in the polymeric structure of the ion-exchange resin leading to decrease in water swelling.

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