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Separation of HCl from the mixture of KCl and HCl using membrane distillation

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Membrane distillation (MD) was applied for the concentration of solutions containing hydrochloric acid and potassium chloride. The studies of the concentration and separation of HCl through the hydrophobic membrane were performed. In the investigations plate and frame or capillary modules, equipped with membranes from polytetrafluoroethylene and polypropylene were applied, respectively. The feed temperature amounted to 333 K or 343 K and permeate 293 K at the inlet of the module. Under the MD operation conditions the transfer of water vapour and hydrogen chloride from potassium chloride and hydrochloric acid solutions through the hydrophobic membranes took place, whereas the potassium chloride as a non-volatile component underwent concentration in the feed. The influence of acid concentration and salt presence in the feed on the HCl molar flux through the membrane was systematically studied. The increase of the temperature and salt concentration in the feed caused higher partial pressure volatile of HCl and the resultant HCl Flux through a membrane was higher.

During MD for the initial concentration in the feed equal 50 g KCl/dm^3 and 40g HCl/dm^3, at the feed temperature 343K, the permeate flux decreased from 353 dm^3/m^{2}d to 289 dm^3/m^{2}d, whereas the HCl flux increased to 6 mol/m^{2}d for the capillary module. At higher KCl concentration in the feed, amounting to 100g KCl/dm^3 and under the same operation conditions, the permeate flux decreased to 285 dm^3/m^{2}d, but the molar flux HCl increased to 18 mol/m^{2}d. The results were compared with the data obtained for the plate and frame module.

Keywords: HCl separation, membrane distillation.

INTRODUCTION

The membrane distillation (MD) process occurs when aqueous liquids with different temperature are separated by a hydrophobic membrane[1].

The mechanism of separation in the MD process is associated with the equilibrium of the system feeding solution – vapour. The selectivity of the process depends on the vapour pressure of the components of the feed under the operation conditions. This means that the component with higher vapour pressure will diffuse faster through the membrane[1]. The driving force of the process is supplied by a vapour pressure difference through a microporous membrane caused by the gradient of the temperature and the composition of the layers adjacent to the membrane[2 – 5].

Till now MD has been investigated mostly in aqueous solutions of sodium chloride with the purpose of obtaining potable water from the seawater and for the production of the high purity water. On the other hand, the MD process can also be applied to the concentration of the solutions up to the supersaturate state[2 – 6].

The results of our work have shown a perspective for the MD application for the recovery of volatile hydrochloric acid from its solutions[3 – 4]. The aim of the present work was to study the influence of salt concentration in HCl solutions on the separation of hydrochloric acid during membrane distillation. The presented study is part of the investigation on the KCl conversion with H_2SO_4 to $KHSO_4$. During the process HCl is formed.

EXPERIMENTAL

The MD installation (described earlier[2]) consisted of two thermostated loops, feed and distillate, which were connected to the membrane modules. The modules were equipped with capillary membranes, (Accurel) PP S6/2, made from polypropylene (PP). During all the experiments a feed flowed inside the capillaries, whereas the distillate flowed through the intercapillary space in a co-current mode. The diameters of the PP membrane, the nominal pore diameter and the porosity were d_{out}/d_{in} = 2.6/1.8mm, 0.22 μm and 73%, respectively. The working area for a flat-sheet membrane was 0,0105 m^2, and for the capillary module 0,0112 m^2. The initial volume of KCl – HCl solutions used as a feed was 3000 cm^3. The experiments were carried out at the inlet feed temperatures of 333 or 343 K. The inlet temperature of the cold distillate was kept at 293 K for all the experiments. The studies were performed using as a feed model solution containing KCl in hydrochloric acid solutions. The initial acid concentration in the feed was about 50 g/dm^3 and the salt concentration was 40 or 110 g/dm^3. During the MD of the solutions, the water vapour and hydrogen chloride were transported through the pores of the membrane. The vapour was condensed directly in the solution (distillate) in the cold compartment and HCl was then dissolved. The feeding solutions were concentrated close to the saturated state, when crystals were precipitated from the solution after cooling. The cold system was initially supplied by 500 cm^3 of distilled water.

The changes of cold distillate volume were measured every hour, for the calculation of the volume permeate flux. The distillate is the solution in the cold system. The HCl flux (J_{HCl}) was calculated from the material balance of HCl in the distillate every hour, taking into account the changes of the volume and the acid concentration in the distillate, according to the following equation:

$$J_{HCl} = \frac{(c_{t+1}V_{t+1} - c_tV_t)24}{AMt} \, [\frac{\mathrm{molHCl}}{\mathrm{dm}^3 \cdot d}]$$

where c_t and c_{t+1} are the distillate concentration at time t and $t+1$, V_t and V_{t+1} are the volume of the distillate at time t and $t+1$, A is the membrane area inside the capillaries or the working area of the flat sheet membrane, M is the molar weight of HCl, and t is the time between the successive measurements.

RESULT AND DISCUSSION

HCl is a volatile compound, hence, in accordance with the liquid/vapour equilibrium the vapour composition is affected by both the hydrochloric acid concentration in the feed and its temperature. During the MD of the volatile species solutions, both the water vapour and the volatile substances are transferred from the warm feed solution through the pores of the hydrophobic membrane to the permeate. The presence of KCl in the feed containing HCl varies in the amounts of HCl transferred and the results of the MD due to the changes of the vapour compositions. The salt in the feed decreases the solubility of the gas, causing vapour enrichment (the desalting out effect). Under the conditions of the MD operation a transfer of the water vapour and volatile hydrogen chloride from mixture of chloride potassium and hydrochloric acid by the hydrophobic membrane took place whereas the chloride potassium as a non-volatile component was concentrated in the feed. We have found that a high salt concentration causes HCl separation at acid concentration in the feed significantly lower than without the salt. For example, for the solution without salt, a significant molar HCl flux was observed when acid concentration in the feed was about 190 g/dm^3 [3], when salt was present in the feed as well, the HCl separation was observed at the feed containing 77.64 g HCl and 97.66 g KCl per litre (Fig. 1) for the capillary module. The presence of the acid in the distillate was observed at the 15th h. The KCl crystals in the feed appeared at 18 h of the process duration when the concentration of the salt and acid in the feed amounted to the KCl 126.74 g/dm^3 and HCl 94.77 g/dm^3, respectively. It follows from Fig.2 that the presence of KCl in the feed causes an increase in the molar flux. At acid concentration in the feed amounting to 50 g/dm^3 and the feed temperature of 333 K and salt concentration about 40 g KCl/dm^3, it was found that the molar HCl flux was increased to 9.84 mol HCl/m^{2}d for the capillary module in comparison with the solution without salt[3]. The vapour is condensed directly in the cold permeate and the volatile compounds are then dissolved in the distillate. In the course of concentration of the model solution, the values of the permeate flux gradually decrease[2 – 5]. The MD process of HCl separation was presented in Fig.3. As it can be seen, the permeate flux decreased from 216.79 to 155.93 dm^3/m^{2}d, for the initial concentration of 50 g HCl/dm^3 and 40 g KCl/dm^3 in the feed and at the feed temperature of 333 K.

When the feed temperature was elevated to 343 K, at the acid concentration in the feed amounting to 40.07 g/

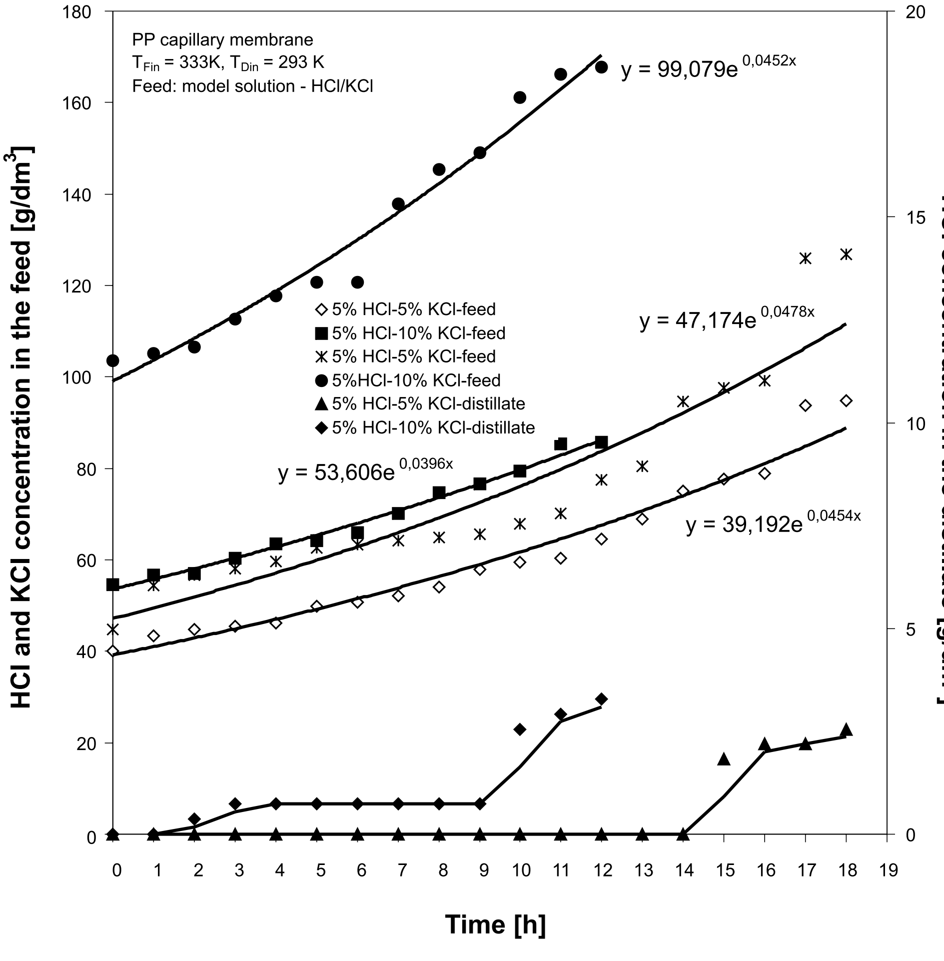

Figure 1. Gradual concentration of HCl/KCl model solution by MD at the eed temperature 333 K

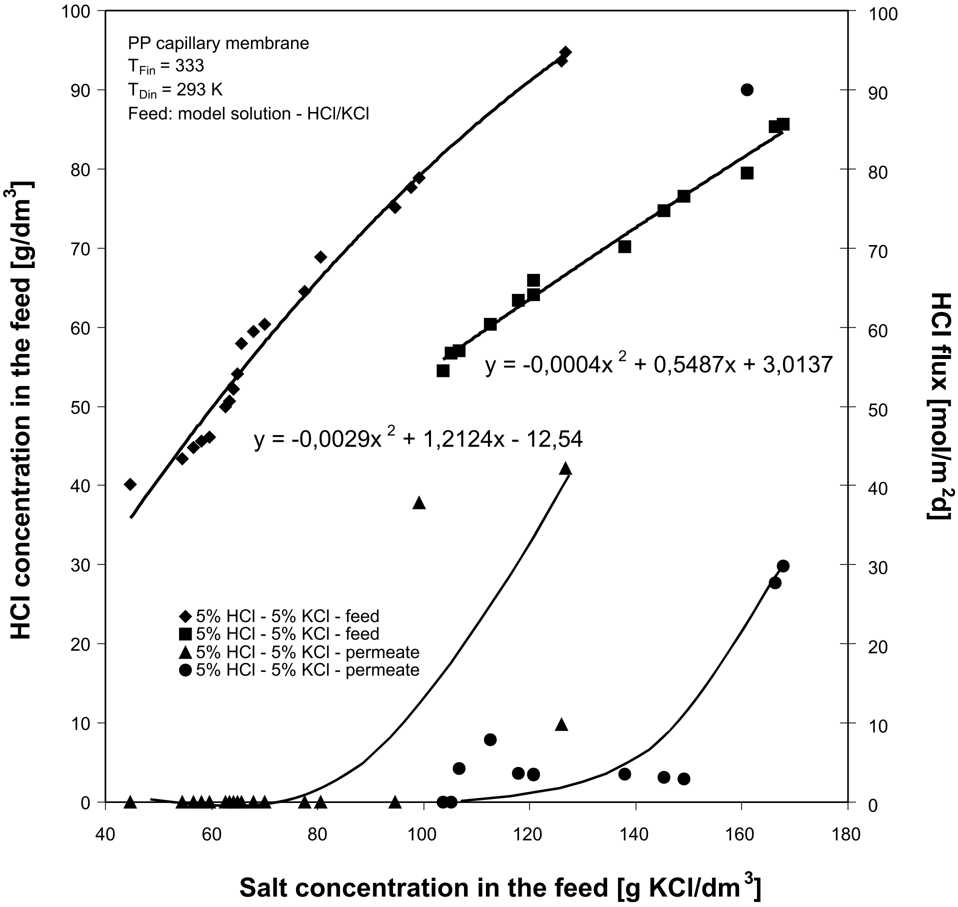

Figure 2. The influence of the feed composition on the HCl flux at the feed temperature 333 K

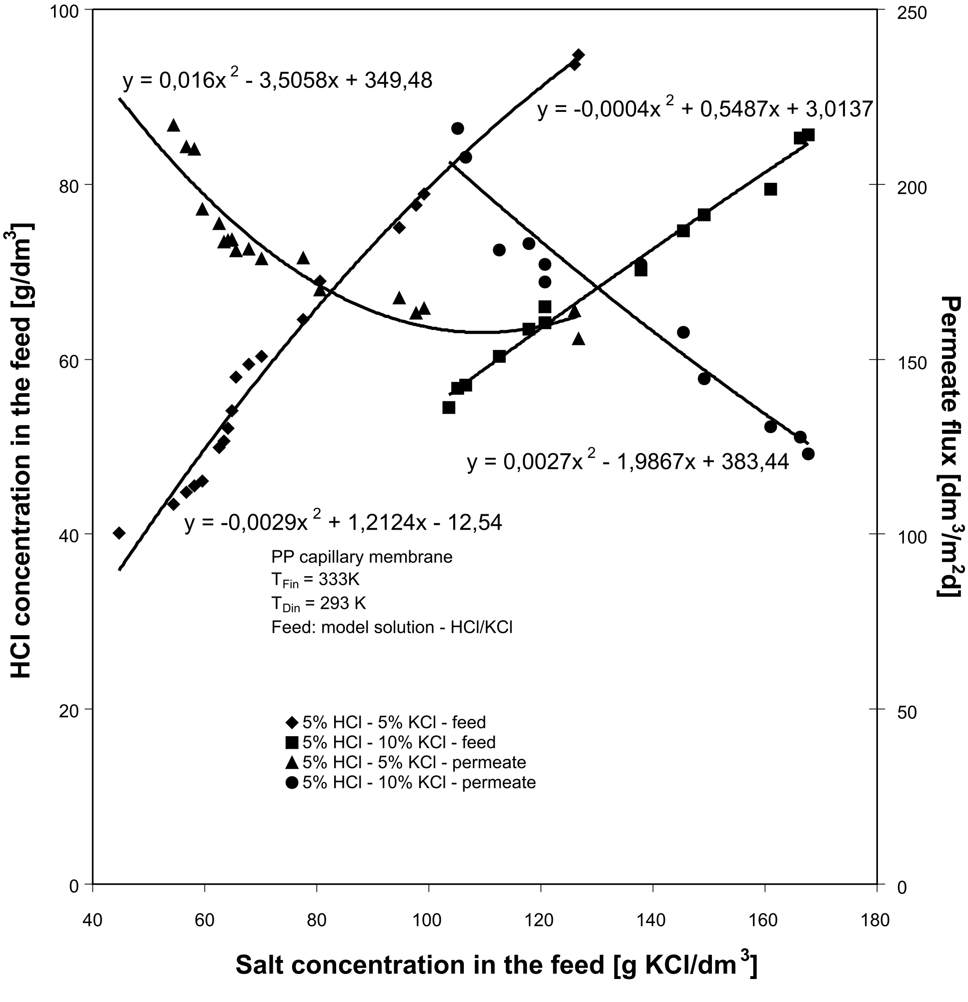

Figure 3. The influence of the feed composition on the volume permeate flux through a hydrophobic membrane during MD at the feed temperature of 333 K

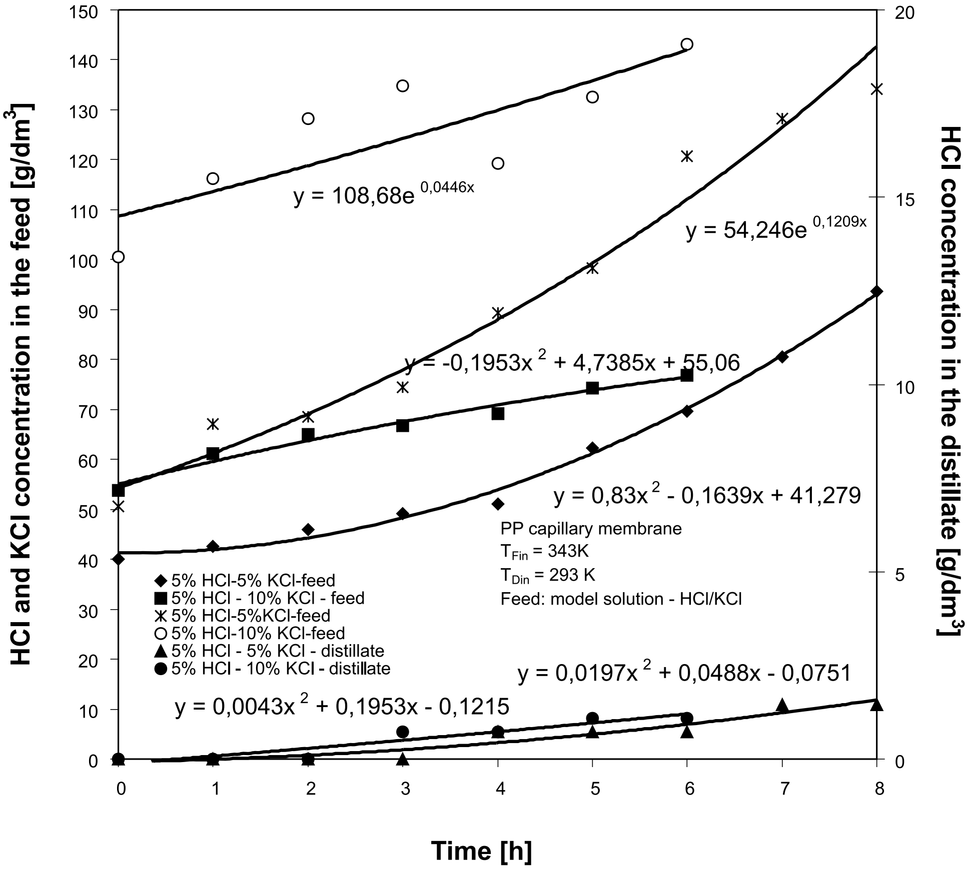

Figure 4. Gradual concentration of HCl/KCl model solution by MD at the feed temperature 343 K

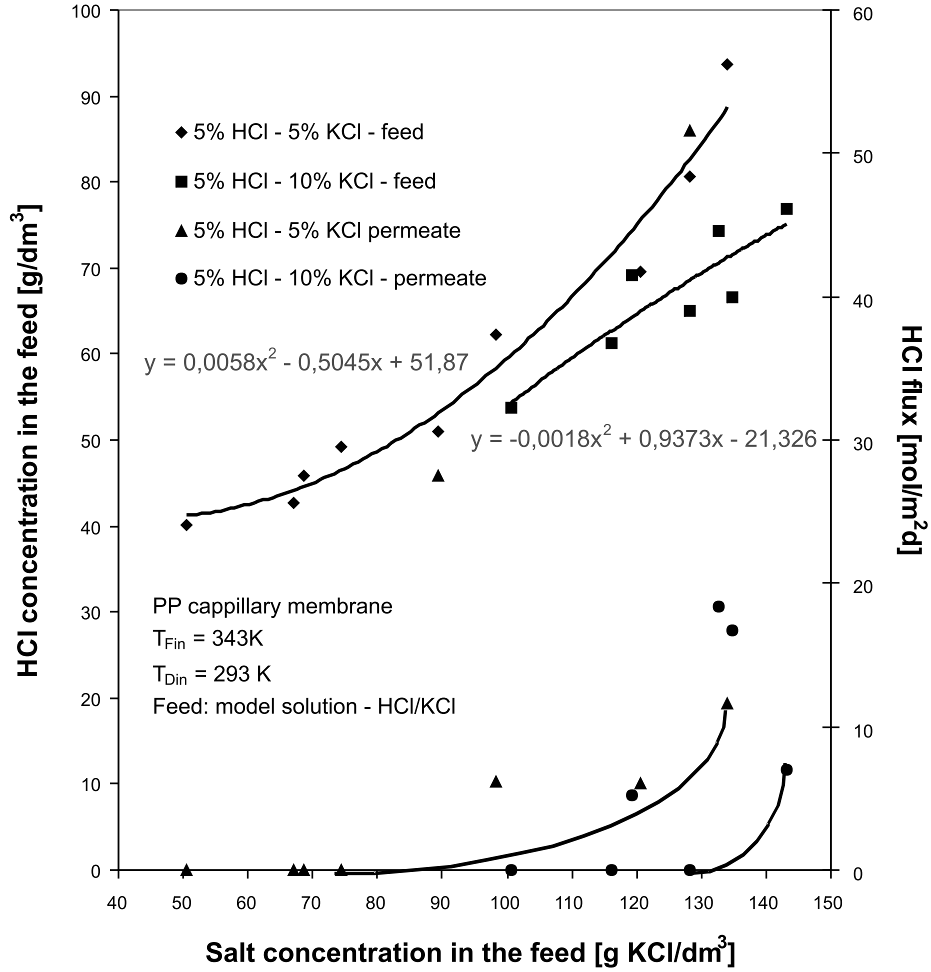

Figure 5. The influence of the feed composition on the HCl flux at the feed temperature 343 K

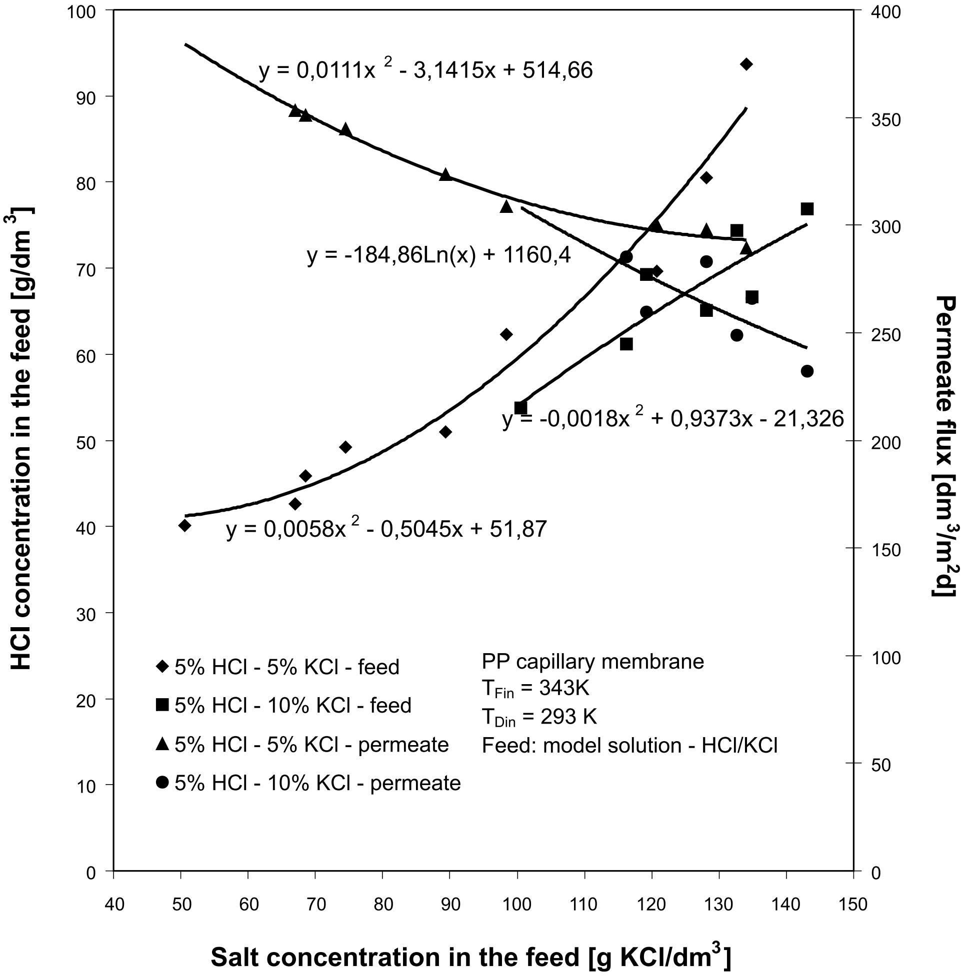

Figure 6. The influence of the feed composition on the volume permeate flux through a hydrophobic membrane during MD at the feed temperature of 343 K

dm^3 and the salt concentration was 50.61 g KCl/dm^3, faster separation of HCl separation was observed. The HCl diffusion was noticed for the feed containing 51.01 g HCl and 89.38 g KCl per litre. The HCl on the distillate side was observed after 4 h and the KCl crystal appeared in the feed at the 8th hour of the process duration when the salt and acid concentration in the feed amounted to 134 g KCl/dm^3 and 93 g HCl/dm^3, respectively. The increase of the feed temperature had an influence on both the molar and the permeate flux. The increase of the feed temperature from 333 K to 343 K, increased the molar and permeate flux to 60 mol HCl/m^{2}d and 353 dm^3/m^{2}d, respectively. However, during the concentration process the permeate flux decreased to 289.43 dm^3/m^{2}d.

The increase of the salt concentration from 44.73 g KCl/dm^3 to 103.62 g KCl/dm^3 in the feed at the feed temperature of 333 K, caused faster HCl diffusion to the distillate. The HCl on the distillate side was observed already in the 2nd h when the KCl concentration in the feed carried out 106.61 g/dm^3 (Fig. 1). Under these conditions the whole process lasted 12 hours. Under the same process conditions, the molar and permeate flux decreased to 29.81 mol HCl/m^{2}d and 122.91 dm^3/m^{2}d (Figs. 2 – 3), respectively.

However, the increase of the feed temperature to 343 K and at the feed containing 53.76 g HCl/dm3 and 100.64 g KCl/dm^3 had an influence on the change length – the time of the process. The dissolution of HCl was observed in the 3rd h when the HCl and KCl concentration in the feed was as follows: 73.99 g HCl/dm^3 and 136.66 g/dm^3. The KCl crystals in the feed were in the 6th h of the MD process. The change of the temperature to 343 K caused a decrease of the molar flux to 18 mol HCl/m^{2}d, in comparison to 333 K. Under these conditions the permeate flux in the feed decreased from 283.07 to 228.12 dm^3/m^{2}d.

The experiments of the HCl separation were also studied with the use of the plate and frame module. Moreover, the effect of the feed temperature and KCl concentration in the feed on the HCl diffusion to the distillate was determined. These results were shown in Figs.4 – 6. As it can be seen, the temperature and concentration affected the rate of the process. The HCl on the distillate side was observed at 333 K and the initial concentration of 41.17 g HCl/dm^3 and 49.13 g KCl/dm^3 in the feed after 11 h. The process was completed when the feed contained 84.18 g HCl/dm^3 and 184 g KCl/dm^3 (Fig. 4). The concentration of KCl in the feed caused the decrease of the vapour pressure being in equilibrium with the feed solution. The influence of KCl concentration in the feed on HCl molar flux through the membrane was systematically studied. When the initial concentration of KCl in the feed was 41 g/dm^3, at the feed temperature of 333 K, the molar flux increased to 12 mol HCl/m^{2}d (Fig. 5). When the KCl concentration in the feeding solution was increased from 40 g/dm^3 to 100 g/dm^3 (HCl concentration equal to 50 g/dm^3) (Fig. 5) it was found that the molar flux of the HCl increased to 36 mol/m^{2}d. However, the molar flux increased to 277 mol HCl/m^{2}d, along with an increase in the temperature to 343 K for the initial concentration of KCl in the feed, equal to 52.11 g/dm^3. When the initial concentration of KCl in the feed increased to 100 g/dm^3, then the molar HCl flux decreased to 65 mol/m^{2}d. This result demonstrated that the higher concentration of salt in the feed caused a decrease of the water vapour pressure, thereby a lower molar flux was obtained.

During the MD process the values of the permeate flux gradually decrease. The MD process of the HCl solutions at different initial concentrations is presented in Fig. 5. As it can be seen, the permeate flux decreased from 124 to 38 dm^3/m^{2}d (Fig. 6) for the plate and the frame module at the concentration of 41 g HCl/dm^3 and 49 g KCl/dm^3 in the feed and the feed temperature 333 K. The increase of KCl concentration in the feed from 40 g/dm^3 to 100 g/dm^3 (HCl concentration equal to 50 g/dm^3) caused a decline of the volume permeate flux from 109 dm^3/m^{2}d to 37 dm^3/m^{2}d (Fig. 6). When the feed temperature was higher (343 K) and for the feed composition including 49 g KCl and 41g HCl, the volume permeate flux was increased to the value of 250 dm^3/m^{2}d. The increase of the salt concentration in the feed to 100 g KCl/dm^3 caused a decrease of the volume permeate flux, from 213 to 151 dm^3/m^{2}d.

The salt retention in the MD process was 100%, therefore the distillate was pure hydrochloric acid. The performed studies demonstrated the possibility of the MD utilization for the concentration of acid solutions of salts and for the separation of hydrochloric acid and its recovery.

CONCLUSIONS

Membrane distillation was successfully applied for the concentration of non - volatile salt solutions. The KCl presence in the feed favours the HCl separation. MD could be a promising method of the separation of pure hydrochloric acid from the solutions of salts. The results of the experiments showed that the MD process could be applied for the separation of HCl from the spent solutions or for the separation of the volatile acid from a reaction mixture (e.g. during the conversion of KCl and H_2SO_4).

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