

Investigation on purification of hydrochloric acid by membrane method

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Received 27 June 2000; accepted 11 July 2000

Abstract

A process of hydrochloric acid transfer through an anion exchange membrane at its regeneration from acid wastewaters has been studied. An equation describing the diffusion process of components in the examined membrane system has been derived and experimentally tested. General mass transfer coefficients of hydrochloric acid and molecules of NaCl, CdCl₂, NiCl₂, and ZnCl₂ through the anion exchange membrane have been determined.

Keywords: Anion exchange membrane; Wastewater; Hydrochloric acid; Diffusion process; Electrodialysis; Current density

1. Introduction

Processes with the use of ion exchange membranes are most economical and promising for conversion of industrial wastewaters, natural water purification and synthesis of various chemicals [1,2]. They are also used for regeneration of mineral acids from process solutions. Usually an electrodialysis process combining different types of the ion exchange membranes [2,3] is used. But a scarce selectivity of anion exchange membranes results in a hydrogen ion

transfer from the acid solution into the salt solution. This decreases current efficiency of the acid and increases energy consumption of the process. To eliminate this, the electrodialysis process is carried out in cameras with combination and bipolar membranes [3,4]. Besides, works aimed at raising the selectivity of the anion exchange membranes are executed [5]. Meanwhile, an ability of hydrogen ions to pass across the anion exchange membranes may be used for purification of acid solutions from impurities. Anion exchange membranes are usually characterized by high selectivity in relations to cations of metals. Therefore, if anion

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exchange membrane is used for separation of a foul acid solution in one cell of the electro-dialysis out of clean water in other cell, then, because of a high mobility of hydrogen ions, the acid will begin to pass into the water. The acid solution that will be created in the second cell of the electro-dialysis, will have considerably less impurities than the initial one (the foul acid solution). The process is not only of practical, but also of theoretical interest since the kinetics of such acid transfer (unlike the salt transfer), as far as we know, was not yet studied.

2. Experimental

A laboratory rig consisted of a three-cell electro-dialysis. A center compartment of the electro-dialysis was separated from the electrode cells by two anions exchange membranes. There was a graphite anode and a non-corrosive steel cathode in the side compartments of the electro-dialysis. At first of every run a deluted solution of hydrochloric acid (0.18 mol/l) was poured into the center cell of the electro-dialysis. A solution imitating industrial acid wastewater was poured into the side compartments. The solution had the following chemical composition, in mg/l: Na^+ –1400, K^+ –154, Ca^{2+} –650, Cu^{2+} –90, Fe^{2+} –170, Ni^{2+} –380, Cd^{2+} –560, Sn^{2+} –126, Bi^{2+} –12, Pb^{2+} –4, Cr_{total} –116.6, Zn^{2+} –200, H^+ –1686, Cl^- –66,900. The colour of the solution was deep green. The solution imitates eluate composition after the regeneration hydrogen filters in plating industry. It was prepared from clean hydrochloric acid, appropriate salts, and distilled water. The circulation of the solutions through the cells of the electro-dialysis was kept by a peristaltic pump. Russian serial anion exchange membranes HMAK-2 and MAK-2 were used [6]. The transport numbers of chloride ions in 0.01–0.02 N NaCl solutions for these membranes are no less than 0.95 and 0.94 (fractions), respectively [6]. Before the runs, the membranes were kept in 0.5 M HCl for two days. The control

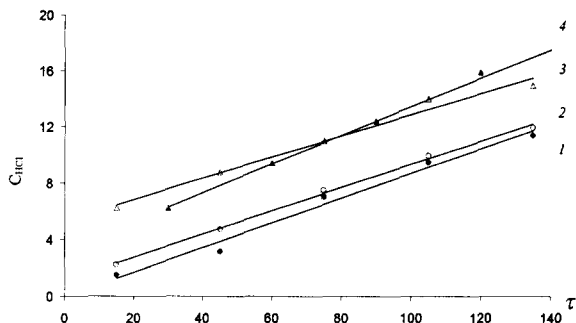


Fig. 1. Kinetics of the hydrochloric acid concentration C_{HCl} growth in the center cell of the electro-dialysis. The circulation rate of the solutions through the rig was 7.5 cm^3/s . τ is time (min) here and in Fig. 2. Current density I (A/m^2): 1, 70; 2, 140; 3, 210; 4, 0.

of the electro-dialysis process was effected by removing the samples of the acid solution from the center cell of the rig. The changes in the acid concentration with time were noted. Besides, at the end of the runs a chemical analysis of the solution from the center cell of the electro-dialysis was carried out. The main impurities were defined. These impurities could catch into the center compartment of the rig from the foul acid solution in the side cells of the electro-dialysis.

The first experiments were conducted with the anion exchange membranes HMAK-2 and current density 70–120 A/m^2 . From lines 1–3 in Fig. 1 can be seen that the increase in the current density of the electro-dialysis process from 70 to 120 A/m^2 does not result in transfer rate of hydrochloric acid across the anion exchange membrane (the slope of the lines is the same). This may be interpreted only by diffusion transport of hydrochloric acid. The hydrogen ions formed in the anode compartment of the electro-dialysis pass across the anion exchange membranes, the center cell of the rig, and discharge in the cathode. Hence, a change of the electro-dialysis current density practically does not influence the

Table 1
Chemical analysis results of the solutions from the center cell of the rig

| Run № | I, A/m ² | Length of run, min | Type of membrane | Concentration of ions, mg/l | | | |
|-------|---------------------|--------------------|------------------|-----------------------------|------------------|------------------|------------------|
| | | | | Na ⁺ | Cd ²⁺ | Ni ²⁺ | Zn ²⁺ |
| 5 | 70 | 135 | HMAK-2 | 11.7 | 2.1 | 1.2 | 2.0 |
| 6 | 140 | 135 | HMAK-2 | 12.5 | 2.5 | 1.2 | 4.5 |
| 7 | 210 | 135 | HMAK-2 | 15.8 | 10.5 | 1.8 | 17.3 |
| 18 | 0 | 420 | MAK-2 | 50.0 | 9.4 | 6.0 | 30.0 |
| 20 | 0 | 420 | MAK-2 | 29.2 | 17.1 | 5.6 | 15.3 |

acid transport rate. It may be expected that in the case of the process without of missing of current through the solution, the acid transport rate will be higher, since an ejection of the hydrogen ions from the center compartment of the electro dialysis due to electric field will be absent. The conducted experiment has confirmed this (see Fig. 1, line 4). It can be seen that the slope of the line 4 is higher, than that one of the lines 1–3.

The chemical analysis of the solutions from the center cell of the rig has shown a fairly low impurity concentration there (Table 1). A visual examination also confirmed this. If the solutions of the side compartments were deep green, the acid solution of the center cell of the rig was colorless.

A time reckoning in these runs was started when a circulation rate of the solutions through the rig had reached a fixed level. This explains a vertical displacement of the lines with respect to each other in Fig. 1.

Further, more prolonged experiments were carried out without the current through the solution. During the runs it was established that the anion exchange membranes HMAK-2 partly passed the solution across themselves: the measurements of volumes of the acid solutions in the compartments of the electro dialysis at the end of the each experiment showed that the common acid volume in the side cells of the rig

had decreased, and the acid volume of the center compartment had risen for adequate value. In order to clarify whether it was caused by osmotic or similar phenomena, experiments were conducted in the course of which ordinary distilled water circulated in all electro dialyzer cells. Nevertheless, the result of these runs was the same. Therefore, the solution flow from the side cells of the rig into the center one was caused only a mechanical passing of the solution by the anion exchange membranes HMAK-2. Subsequent experiments were carried out with the anion exchange membranes MAK-2 (the preliminary runs with distilled water had shown that these membranes did not pass a solution). Results some of these experiments is shown in Fig. 2, and data of the impurity concentrations in the acid solution from the center compartment of the electro dialysis is shown in Table 1.

3. Discussion

To analyze the experimental results let us consider the kinetics of hydrochloric acid transfer through an anion exchange membrane. The first experiments have shown (Fig. 1) that the acid transfer across the membrane is due to only diffusion transport. Hence, there is a concentration distribution of the diffusing substance (solute) close by the membrane surface. The

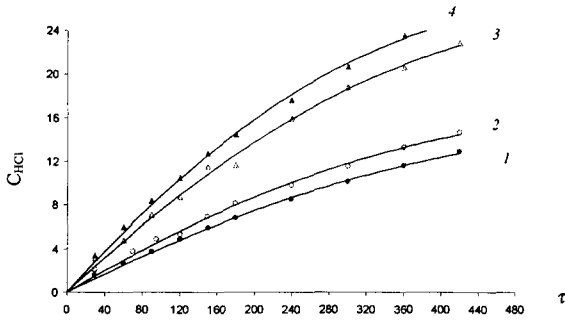


Fig. 2. Kinetics of the hydrochloric acid concentration C_{HCl} (g/l) growth in the center cell of the rig in the experiments without the current through the solution. 1, run 21; 2, run 20; 3, run 19; 4, run 18.

scheme of the distribution at the stationary conditions is shown in Fig. 3. The solute (in our case this is hydrochloric acid) with concentration C_1 diffuses through the membrane from the cell of volume V_1 into the cell of volume V_2 where the solute concentration is lower and is C_2 . Nearby the membrane surface, the solute concentrations are C_1^1 and C_2^1 , respectively. The distribution of the solute within the membrane is not shown in Fig. 3.

When the diffusion process is stationary, the transfer of the solute across the membrane may be described by equations:

$$\begin{cases} \frac{1}{S} \frac{dm}{d\tau} = K_1(C_1 - C_1^1) & (1) \\ \frac{1}{S} \frac{dm}{d\tau} = \beta(C_1^1 - C_2^1) & (2) \\ \frac{1}{S} \frac{dm}{d\tau} = K_2(C_2^1 - C_2) & (3) \end{cases}$$

where S is the area of the membrane (m^2); β is the mass transfer coefficient of the solute across the membrane (m/s); τ is time (s); m is the mass of the solute (g); K_1 is the mass transfer coefficient of the solute from the solution volume V_1

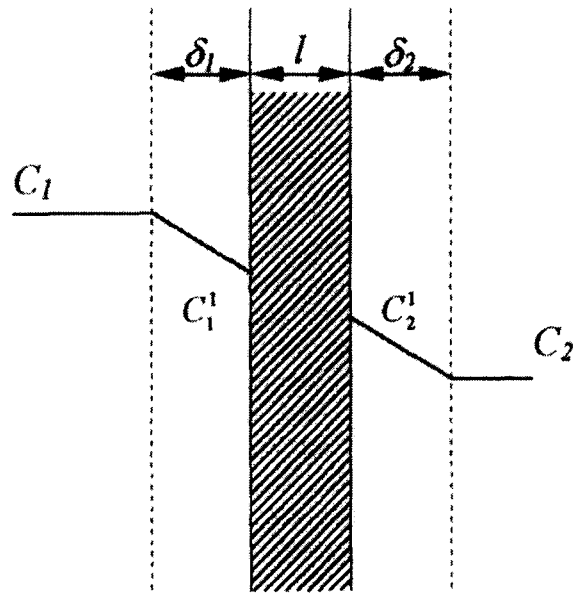


Fig. 3. Scheme of the concentration distribution of the diffusing substance solute near by the membrane surface when the diffusion process is stationary. l is the membrane thickness; δ_1 , δ_2 are the thicknesses of nonmixed layers of the solution.

to the surface of the membrane (m/s); K_2 is the mass transfer coefficient of the solute from the membrane surface into the solution volume V_2 (m/s).

One can solve simultaneously the equations (1)–(3) and then obtain an expression for the solute concentration near the membrane surface in the cell of volume V_2 :

$$C_2^1 = \frac{K_1\beta C_1 + K_1K_2C_2 + K_2\beta C_2}{K_1\beta + K_1K_2 + K_2\beta} \quad (4)$$

Substitution of Eq. (4) into expression (3) gives an equation describing the diffusion transfer of the solute across the membrane:

$$\frac{1}{S} \frac{dm}{d\tau} = K(C_1 - C_2) \quad (5)$$

where

$$K = \frac{1}{\frac{1}{K_1} + \frac{1}{K_2} + \frac{1}{\beta}} \quad (6)$$

When Nernst's non-mixed diffusion layers conception is used (Fig. 3), then K_1 and K_2 are equal to

$$K_1 = D/\delta_1 \quad (7)$$

$$K_2 = D/\delta \quad (8)$$

where δ_1 and δ_2 are the thicknesses of non-mixed layers (m).

Similarly, from the first Fick's diffusion law follows that

$$\beta = Dm/l \quad (9)$$

where D is the solute diffusion constant in the solution (m^2/s); D_m is the solute diffusion constant in the membrane substance (m^2/s); l is the membrane thickness (m).

Taking into consideration that

$$dm = V_2 dC_2 \quad (10)$$

$$C_1 = C_1^0 - \frac{V_2}{V_1} (C_2 - C_2^0) \quad (11)$$

after integration of Eq. (5), one can obtain finally

$$\ln = \frac{C_1^0 - C_2^0}{C_1^0 - \left(\frac{V_2}{V_1} + 1\right) C_2^0 + \frac{V_2}{V_1} C_2^0} = K \left(\frac{V_2}{V_1} + 1\right) \frac{S}{V_2} \tau \quad (12)$$

where C_1^0 , C_2^0 are the initial solute concentrations in the cells of volume V_1 and V_2 , respectively; K is a general mass transfer coefficient (m/s).

The equation coinciding with Eq. (5) and describing a dialysis process is given in work [7] without deduction. In [8], an equation is derived analogous to Eq. (12), but its derivation was made without consideration diffusion difficulties for the solute transfer in the solution. Besides, it was assumed that the solubility of the diffusing substance (solute) in the membrane material was a linear function of the diffusing substance (solute) concentration in the solution. Also, integration in [8] was carried out with an error so the derived equation was incorrect [8, p.60].

In work [9], the derivation of the equation analogous to Eq. (5) was made, as well as in [8], without account of the diffusion difficulties for the solute transfer in the solution. Thereto, it was supposed that the solute was adsorbed by the membrane surface in accordance with Henry's law. It should be noted that in the above derivation of Eqs. (5),(12), the assumptions about the solute adsorbtion, or the solute distribution and solubility in the membrane material were not made.

In [10], the experimental data on the diffusion of ammonium hydroxide across an anion exchange membrane were calculated on the equation similar to Eq. (12) which was given without deduction. Its distinction from Eq. (12) is that $V_1=V_2$ and $K=D_m/l$. Therefore, the influence of the diffusion transfer of the solute from the solution volume to the membrane surface on the general kinetics of the process again was not taken into account.

Computing of the data presented in Fig. 2 showed that they were approximated well by Eq. (12) (the correlation factor was in the range of 0.998–0.999). The calculated general mass transfer coefficients K of hydrochloric acid through the examined membrane are presented in Table 2. They clearly demonstrate that Eqs. (5),(12) can be used for description of the kinetics of the electrolyte (in our case this is hydrochloric acid) transfer process across the ion exchange membrane. As in the runs 18 and 20

Table 2

Calculated results of the general mass transfer coefficient K of the hydrochloric acid through the anion exchange membrane MAK-2

| Run № | Circulation rate of the solutions through the rig, cm^3/s | V_1 , m^3 | V_2 , m^3 | S , m^2 | $K \cdot 10^7$, m/s | $S_n \cdot 10^7$, m/s | n |
|-------|---|----------------------|----------------------|--------------------|-------------------------------|---------------------------------|-----|
| 18 | 7.5 | 0.0011 | 0.00055 | 0.02862 | 4.786 | 0.058 | 10 |
| 19 | 0.4 | 0.0011 | 0.00055 | 0.02862 | 4.105 | 0.089 | 10 |
| 20 | 7.5 | 0.0006 | 0.00055 | 0.01431 | 4.683 | 0.060 | 10 |
| 21 | 0.4 | 0.0006 | 0.00055 | 0.01431 | 3.987 | 0.035 | 10 |

the circulation rate of the solutions through the rig was $7.5 \text{ cm}^3/\text{s}$, the area S of the membranes was different in two times, solution volumes V_1 of the side cells were also different in two times, but calculated general mass transfer coefficients K of hydrochloric acid in these experiments were equal. Analogous equality of the general mass transfer coefficients of hydrochloric acid takes place in the runs 19 and 21. And when the circulation rate of the solutions is low then the general mass transfer coefficient K is low too (Table 2). It should be noted that the experimental data found here (in this study) do not confirm the equation for the diffusion transfer of the electrolyte across an ion exchange membrane that was given in [9] (the equation supposes that the diffusion flux of the solute must be in direct proportion to difference of two squares of the solute concentration on the different membrane sides).

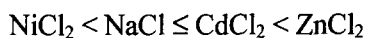
The general mass transfer coefficients of the impurity molecules in runs 18, 20 calculated by Eq. (12) (using the data of Table 1) are presented in Table 3. As can be seen, in two cases (CdCl_2 and NiCl_2) values K , calculated on the experimental data of the runs 18 and 20, were not equal. It may be caused by a chemical analysis error. At large, the general mass transfer coefficients of the impurity molecules through the anion exchange membrane were in order of magnitude below than that one of hydrochloric

Table 3

Calculated results of the general mass transfer coefficients of the impurity molecules through the anion exchange membrane MAK-2

| Run № | $K \cdot 10^8$, m/s | | | |
|---------|-------------------------------|-----------------|-----------------|-----------------|
| | NaCl | CdCl_2 | NiCl_2 | ZnCl_2 |
| 18 | 2.80 | 1.30 | 1.22 | 12.96 |
| 20 | 3.20 | 4.80 | 2.28 | 12.62 |
| Average | 3.00 | 3.05 | 1.75 | 12.79 |

acid. This allows using the process for regeneration of hydrochloric acid from acid wastewaters. On the basis of the data in Table 3, the exanimate molecules of impurities may be arranged in order of magnitude in accordance with the ability to transfer through the anion exchange membrane (the mass transfer rate of the impurity molecules across the anion exchange membrane increases from left to right):



Comparison of the results obtained with the data of other authors [8,10–14] is difficult because theirs studies were carried out with other types of ion exchange membranes. Besides, it is not always clear what regime, outer diffusion process (the general rate of the process is directed by transfer of solute from the bulk of

solution to the surface of the membrane), or inside diffusion process (the general rate of the process is directed by diffusion of the solute across the membrane), the measurements were made.

Nevertheless, the results obtained allow making approximate design of apparatus and parameters of the purification process of hydrochloric acid at its regeneration from acid wastewaters.

4. Conclusions

1. In the experimental conditions examined, hydrochloric acid transfer through the anion exchange membrane is realized by diffusion, and is independent of the current density at the electro dialysis process.
2. The general mass transfer coefficient of hydrochloric acid across the anion exchange membrane is in order of magnitude above than those ones of molecules of NaCl, CdCl₂, NiCl₂, and ZnCl₂ at the same experimental conditions. This allows using the process for regeneration of hydrochloric acid from acid wastewaters.
3. In accordance with the ability to transfer through the anion exchange membrane the exanimate molecules of the impurities may be arranged in order of magnitude (the mass transfer rate of the impurity molecules across the anion exchange membrane increases from left to right):
NiCl₂ < NaCl ≤ CdCl₂ < ZnCl₂

5. Symbols

C_1, C_2 — Solute concentrations in the cells of volume V_1 and V_2 , respectively
 C_1^0, C_2^0 — Initial solute concentrations in the cells of volume V_1 and V_2 , respectively

C_1^l, C_2^l — Solute concentrations near the membrane surface in the cells of volume V_1 and V_2 , respectively
 C_{HCL} — Concentration of hydrochloric acid, g/l
 D — Solute diffusion constant in solution, m²/s
 D_m — Solute diffusion constant in the membrane substance, m²/s
 I — Current density, A/m²
 K — General mass transfer coefficient, m/s
 K_1 — Mass transfer coefficient of the solute from the solution volume V_1 to the surface of the membrane, m/s
 K_2 — Mass transfer coefficient of the solute from the membrane surface into the solution volume V_2 , m/s
 L — Membrane thickness, m
 M — Mass of the solute, g
 N — Number of measurements of K
 S — Area of the membrane, m²
 S_n — Standard deviation of K , m/s
 V_1, V_2 — Solution volumes of the side cells of the rig, m³

Greek

β — Mass transfer coefficient of the solute across the membrane, m/s
 δ_1, δ_2 — Thicknesses of nonmixed layers, m
 τ — Time, s

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