Mechanism of isotope exchange of hydrogen with water in membrane contact devices

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Abstract. The article presents the results of an experimental study of the isotope exchange process between hydrogen and water in membrane contact devices with a Nafion-type membrane and a platinized heterogeneous RCTU-3SM catalyst. A mathematical description of the mechanism of mass transfer in a membrane contact device is proposed. The design of the presented membrane contact devices makes it possible to create countercurrent separation units that do not require a vertical arrangement.

1. Introduction
Separation of hydrogen isotopes is possible using different physicochemical methods, one of which is chemical isotope exchange (ChIE) in the water-hydrogen system.

In the presence of a heterogeneous catalyst, isotope exchange in this system occurs in two stages, the first of which is catalytic isotope exchange (CIE), and the second is phase isotope exchange (PhIE) of water:

\[
\begin{align*}
H_2O_{(v)} + HX_{(g)} &\xrightarrow{\text{Cat}} HXO_{(v)} + H_2(g), \quad \text{(CIE)} \quad (1) \\
HXO_{(v)} + H_2O_{(l)} &\xrightarrow{\text{Cat}} H_2O_{(v)} + HXO_{(l)}, \quad \text{(PhIE)} \quad (2) \\
H_2O_{(l)} + HX_{(g)} &\xrightarrow{\text{Cat}} HXO_{(l)} + H_2(g), \quad \text{(ChIE)} \quad (3)
\end{align*}
\]

where \(X\) is a heavy isotope of hydrogen (deuterium (D) or tritium (T)).

Traditional contact devices of the packed type used in countercurrent separation plants for isotope exchange in the water-hydrogen system are a layer-by-layer loading or a uniform mixture of a hydrophobic catalyst and a hydrophilic packing. To implement this process in a number of countries of the world (Canada, Japan, Russia, Belgium, Romania, etc.), platinized hydrophobic catalysts have been created that do not lose their activity upon contact with liquid water [1-4]. It should be noted that such contact devices, due to the hydrophobic properties of the catalyst particles, have a low throughput, which limits the application of ChIE technology to relatively small-scale tasks of separating hydrogen isotopes, and also require a vertical arrangement of separation columns with a height of about ten meters [1, 4].

In the D. Mendeleev University of Chemical Technology of Russia in recent years, a membrane contact device (MCD) has been developed, in which the spatial separation of the catalyst from the liquid
flow is realized with the help of a membrane permeable to water vapor. Thus, the catalyst is in contact only with a mixture of hydrogen with water vapor [5-7]. In this case, the CIE stage occurs in the vapor-gas space, and the PhIE - on the membrane surface. Structurally, this is solved using a membrane containing liquid water in its body, held by hydrogen bonds and impermeable to liquid water. This design of the contact device allows for high throughput and does not require a vertical arrangement of contact devices to organize a countercurrent separation process.

2. Experimental setup and data processing
We used two types of membrane contact devices: with flat (MCD) and tubular (MCD-TM) membranes, the schematic diagrams of which are shown in figure 1.

![Figure 1. Membrane contact device: a – with a flat membrane; b – with a tubular membrane; c – countercurrent separating module with MCD.](image)

In these contact devices, perfluorinated sulfonic cationite membranes MF-4SK and TF-4SK were used, which are the Russian analog of the Nafion membrane [8]. In this series of experiments, we used the Russian platinized hydrophobic catalyst RCTU-3SM [3], which is spherical granules of styrene-divinylbenzene copolymer 0.5–0.8 mm in diameter with supported platinum in an amount of 0.8 wt%.

The experiments were carried out at a pressure of 0.1 MPa and temperatures of 323–353 K.

According to the results of the experiment, the number of transfer units ($N_y$) and the mass transfer coefficient ($K_{oy}$) were calculated using the following formulas:

$$N_y = \int \frac{dy}{y_0 - y} = \frac{y - y_0}{\Delta y_{av}},$$  \hspace{1cm} (4)

$$\Delta y_{av} = \frac{(y^* - y)(y_0^* - y_0)}{\ln\frac{y^*}{y_0^*}},$$  \hspace{1cm} (5)

$$K_{oy} = \frac{G_{vg} \cdot N_y}{S_M},$$  \hspace{1cm} (6)

where $\Delta y_{av}$ is the average driving force; $y^*$ and $y_0^*$ are the equilibrium concentrations of deuterium or tritium in hydrogen in relation to their concentration in the liquid in the upper and lower sections of the column or MCD; $G_{vg}$ is the flow of the vapor-gas mixture passing through the catalytic space of the MCD under the experimental conditions (m$^3$/s); $S_M$ is the geometric surface area of the membrane in the MCD.
The number of theoretical separation stages \((N)\) was determined with the usage of the McCabe-Thiele method.

3. Results and discussion
To describe the process of mass transfer in MCD, a model based on the additivity equation of resistances to mass transfer was proposed earlier [9], which adequately describes the process of isotope exchange only in contact devices with a flat membrane in the H-form. It should be noted that Nafion-type membranes during operation can be contaminated with metal ions, which leads to a decrease in their water permeability, as a result of which there is a deterioration in the efficiency of the isotope exchange process in MCD, and its subsequent regeneration leads to an increase in these characteristics [10].

Based on the results of additional studies, the previously developed algorithm was corrected, which made it possible to take into account the effect of the type and state of the membrane on the efficiency of mass transfer in MCD. Thus, the process of isotope transfer into MCD can be described by the following stages:

1) the reaction of isotopic exchange between hydrogen and water vapor at active sites of the catalyst (CIE) and internal diffusion of hydrogen and water vapor in the catalyst pores;
2) diffusion of water vapors exchanged on the catalyst with hydrogen from the catalyst grain to the membrane surface in the gas-vapor space of the MCD;
3) phase isotope exchange on the membrane surface;
4) diffusion of water molecules through the membrane;
5) diffusion of water molecules from the membrane surface into the liquid flow in the MCD.

Based on the experimental data, when developing the technique, it was assumed that the CIE stage, diffusion processes in the catalyst grain, and mass transfer in the liquid phase affect the overall process of mass transfer in the MCD, and the CIE process in MCD is limited by diffusion processes taking place in the vapor-gas space and in the membrane body. As a result, an equation of the following form was proposed to calculate the mass transfer coefficient in MCD:

\[
\frac{1}{K_{oy}} = \frac{1}{\beta_{vg}} + \frac{1}{\beta_{lm}} + \frac{1}{\beta_{M}} + \frac{1}{\beta_{MD}},
\]  

where \(K_{oy}\) – coefficient of mass transfer in MCD (m/s); \(\beta_{vg}\) is the mass transfer coefficient in the core of the vapor-gas flow (m/s); \(\beta_{lm}\) is the coefficient of longitudinal mixing, taking into account the deviation from the ideal displacement model (m/s); \(\beta_{M}\) is the mass transfer coefficient, which takes into account the transfer of water from the membrane surface into the vapor-gas flow in the laminar boundary layer (m/s); \(\beta_{MD}\) is the coefficient of mass transfer, taking into account the diffusion of water molecules in the body of the membrane (m/s).

To determine the values of \(\beta_{vg}\) and \(\beta_{lm}\), the criterion equations for calculating the resistance to mass transfer in the granular layer were used:

\[
\beta_{vg} = \frac{D_{vg} \cdot Nu}{d_{eq}},
\]  

\[
\beta_{lm} = 0.0567 \cdot \frac{w}{1 - \varepsilon} \cdot Re^{0.22},
\]  

where \(D_{vg}\) is the diffusion coefficient in the vapor-gas mixture (m²/s); \(Nu\) - Nusselt criterion; \(d_{eq}\) – equivalent diameter (m); \(\varepsilon\) – porosity, \(w\) – vapor-gas flow velocity through the catalyst bed, (m/s); \(Re\) is the Reynolds criterion for the flow of the vapor-gas mixture in the catalyst bed in the MCD.

To calculate the coefficients of mass transfer in the laminar boundary layer of the membrane (\(\beta_{M}\)) and in the body of the membrane (\(\beta_{MD}\), empirical equations were obtained:

\[
\beta_{M} = 0.619 \cdot \frac{D_{vg}}{l_{M}} \cdot Re_{s}^{0.5385} \cdot Sc^{0.2065},
\]
\[
\beta_{MD} = \frac{D_M}{\delta} \left( \frac{\mu_l}{\mu_v} \right),
\]

(11)

where \(Sc\) is the Schmidt criterion; \(Re\) – Reynolds criterion in the boundary layer of the membrane; \(l_m\) is the sum of diameters of membranes in all MCD; \(D_v\) — diffusion coefficient in the vapor-gas mixture (m²/s); \(D_m\) — coefficient of diffusion of water in the membrane (m²/s); \(\delta\) – thickness of the working membrane (m); \(\left( \frac{\mu_l}{\mu_v} \right)\) — coefficient introduced for the transition from diffusion in liquid to diffusion in vapor, taken equal to the ratio of the dynamic viscosity of liquid water and vapor under normal conditions.

To calculate the diffusion coefficient in the membrane \((D_m)\), the following relationship was used:

\[
D_M = \frac{k \cdot T}{6 \cdot \pi \cdot r \cdot \left( \frac{W}{W_0} \right)},
\]

(12)

where \(k\) is the Boltzmann constant \((J/K)\); \(T\) is the temperature \((K)\); \(\mu\) – dynamic viscosity of the solvent \((Pa\cdot s)\); \(r\) – radius of a spherical molecule of a solute \((m)\); \(\left( \frac{W}{W_0} \right)\) – the relative permeability of the membrane, which is a coefficient that takes into account the state of the membrane and is numerically equal to the ratio of the experimentally determined value of the membrane permeability of thickness \(\delta\) to the permeability of a hypothetical membrane with \(\delta = 0\) at a given temperature.

Table 1 shows the results of calculating the mass transfer coefficients for some experiments in the study of ChIE in MCD with an MF-4SK membrane: a surface area of 42 cm² and a catalyst volume of 10 cm³ under various values of hydrogen flow \((G_H)\) and states of the membrane.

**Table 1. Calculated values of the coefficients of mass transfer of the ChIE process in MCD with an MF-4SK membrane in the H-form, catalyst RCTU-3SM**

| Parameter | \(\beta_v \cdot 10^3\) m/s | \(\beta_m \cdot 10^3\) m/s | \(\beta_m \cdot 10^3\) m/s | \(\beta_{MD} \cdot 10^3\) m/s | \(K_{oy \text{calc}} \cdot 10^3\) m/s | \(K_{oy \text{exp}} \cdot 10^3\) m/s |
|-----------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|
| MF-4SK industrial, \(\delta=250\ \mu m\), \(P=0.1\ MPa, T=333\ K\) | 123.46 | 11.82 | 8.25 | 8.77 | 3.04 | 3.08 |
| \(G_H=40\ \text{Ndm/h}\) | 171.00 | 27.54 | 11.98 | 8.77 | 3.16 | 4.27 |
| \(G_H=80\ \text{Ndm/h}\) | 206.90 | 45.16 | 12.90 | 8.77 | 4.78 | 4.74 |

| MF-4SK after the "modification-regeneration" cycle, \(\delta=200\ \mu m\), \(P=0.1\ MPa, T=333K\) | \(G_H=40\ \text{Ndm/h}\) | 133.46 | 14.47 | 3.02 | 21.94 | 4.27 | 4.30 |
| \(G_H=80\ \text{Ndm/h}\) | 184.86 | 33.71 | 13.10 | 21.93 | 6.32 | 6.29 |
| \(G_H=100\ \text{Ndm/h}\) | 205.30 | 44.26 | 14.77 | 21.93 | 7.05 | 7.10 |

It can be seen from the presented data that the proposed algorithm adequately describes the experimental data, and the differences between the experimental and calculated \(K_{oy}\) values do not exceed 10%.

Figure 2 shows a graphical interpretation of similar calculations performed for the MCD-TM contact device with tubular diaphragms. The experimental contact device had an outer diameter of a casing of 12 mm, where 10 TF-4SK membranes, each 170 mm long, were placed. Granules of the hydrophobic catalyst RCTU-3SM were evenly distributed between membranes. The volume of catalyst was 9 cm³. The experiments were carried out at atmospheric pressure and a temperature of 333 K. It should also be noted that at hydrogen flows from 40 to 100 Ndm/h, the speed of the vapor-hydrogen flow in the MCD was from 1 to 2.6 m/s.
Figure 2. Dependence of the mass transfer coefficients in the MCD-TM on the hydrogen flow at $P = 0.1$ MPa, $T = 333$ K.

The presented data show that the proposed model for calculating mass transfer characteristics adequately describes the process in a contact device with tubular membranes, and the maximum difference between the calculated and experimental $K_{oy}$ values does not exceed 10%.

The validation of the model was also carried out in a multistage countercurrent separation plant with MCD. Figure 1(c) shows a view of the assembly of a countercurrent separation module with MCD as part of an experimental installation for water detritization with concentrating (6 MCD) and exhaustive (12 MCD) parts and an electrolyzer as the lower flow circulation unit. The column was fed with tritium-tagged water supplied to the middle part of the column, and water of natural isotopic composition was supplied to irrigate the exhaustive part. Table 2 shows the values of the degrees of separation ($K$), the number of transfer units ($N_\gamma$), the number of theoretical separation stages ($N$) and the mass transfer coefficient ($K_{oy}$) for typical experiments in which the maximum speed of the vapor-hydrogen flow in the catalyst bed reached 2.0 m/s.

| $G_{H2}$, Ndm³/h | Concentrating part | Exhaustive part | $K_{oy, exp}$, $10^3$ m/s | $K_{oy, calc}$, $10^3$ m/s |
|------------------|-------------------|-----------------|---------------------------|---------------------------|
| 60               | 1.51              | 24.10           | 4.03±0.26                 | 4.13                      |
| 100              | 1.25              | 13.05           | 5.13±0.35                 | 5.16                      |
| 150              | 1.05              | 7.95            | 6.01±0.32                 | 6.08                      |

Table 2. Dependence of the mass transfer characteristics of the ChIE in the column on the hydrogen flow: $P = 0.1$ MPa; $T = 333$ K; $\alpha_{H-T} = 5.22^a$; $\lambda' = 0.273^b$; $\lambda = 1$; $\lambda_{ex} = 4$.

From the presented data it can be seen that with an increase in the hydrogen flow by 2.5 times, the mass transfer coefficient in the column changes by approximately 1.5 times. On the other hand, an increase in the hydrogen flow leads to a decrease in the number of theoretical separation stages, as a result of which a decrease in the separation capacity of the column is observed. This is in good agreement with the data obtained earlier and is associated with the influence of diffusion processes in the boundary layer of the membrane, which are practically independent of turbulization of the vapor-gas flow. It
should be noted that the values of $K_{oy}^\text{calc}$ calculated by the proposed method are in good agreement with experimental ones.

The results of studying the effect of temperature on the efficiency of the process of detritization of light water at $P = 0.1 \text{ MPa}$ and a fixed hydrogen flow of $100 \text{ Ndm}^3/\text{h}$ are shown in Figure 3.

**Figure 3.** Dependence of the mass transfer coefficient in MCD on temperature

As can be seen from the presented data, with increasing temperature in the column, there is a sharp increase in the values of the mass transfer coefficient. However, it should be noted that, in this case, under conditions of a fixed pressure and a hydrogen flow, an increase in the vapor-gas flow occurs both due to thermal expansion and due to an increase in the proportion of water vapor (in the investigated temperature range, $\lambda'$ increased by almost 6 times). In addition, due to an increase in the moisture content of the vapor-gas mixture, the proportion of hydrogen in it decreases – the main reagent of the process of chemical isotopic exchange of hydrogen with water.

Thus, if we exclude the influence of the CIE stage on the efficiency of mass transfer in MCD, the obtained dependence is in good agreement with the assumption made within the framework of the developed model about the significant contribution of diffusion processes involving the membrane to the resistance to mass transfer. This assumption can also be confirmed by the value of the temperature coefficient $E_{act} \text{obs} = (26\pm3) \text{ kJ/(mol\cdot K)}$, calculated from the data in Figure 3.

4. Conclusion
The complex of studies carried out has made it possible to develop highly efficient contact devices of a new type (MCD), which make it possible to create compact separation units for separating hydrogen isotopes by the CHIE method in the water-hydrogen system. The obtained experimental database and the mathematical model of mass transfer in membrane contact devices of various types developed on their basis can be used to design separation plants.

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