SIMULTANEOUS AMMONIA AND WATER TRANSPORT THROUGH A PERCHLOROVINYL MEMBRANE

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Abstract. Simultaneous mass transfer of ammonia and water through a gas membrane supported by a flat depth polymer filter using temperature difference between the feed and stripping solutions was studied. The use of a perchlorovinyl layer as a hydrophobic support for the gas membrane at increased temperatures was evaluated.

Key words: membrane desorption-absorption, membrane distillation, gas membrane, ammonia removal, perchlorovinyl filter.

INTRODUCTION

Ammonia can be removed from weak aqueous solutions, including waste water, by using a gas (air) membrane immobilized within the pores of a hydrophobic porous filter separating the feed and stripping solutions. Both the desorption of ammonia from water and the absorption by sulphuric acid solution can be carried out in the same apparatus (a pertractor) simultaneously [1-3]. In our previous work [4], an above 99% ammonia removal was achieved and the possibility of producing above 10% ammonium sulphate solution was shown. The possibility of using a depth perchlorovinyl filter as a hydrophobic gas membrane material was demonstrated [5].

All the above-mentioned procedures were carried out at room temperature without any temperature difference between the feed and stripping solutions. As the partial pressure of ammonia is strongly dependent on temperature, the increase of the feed temperature, respectively the creating of a temperature difference between the feed and stripping solutions, accelerates the ammonia transport; however, at an increased temperature wetting of the membrane can occur. Therefore, the experimental determination of the maximum allowable temperature for any membrane material is necessary.

In the presence of a temperature difference the membrane desorption-absorption of ammonia is accompanied by the simultaneous distillation of water. The interrelated concurrent mass transfer processes require additional investigation.

The present study aims at:
(1) the investigation of simultaneous transport of ammonia and water through a gas membrane supported by a depth perchlorovinyl filter in the presence of a temperature difference;
(2) establishing the possibility of using the perchlorovinyl layer as a support for the gas membrane at an increased temperature.

EXPERIMENTAL

The experiments using a temperature difference between the feed and stripping solutions were carried out in a countercurrent flow unsteady-state laboratory pertractor. The scheme of the apparatus and the construction of the membrane cell used are shown in Fig. 1. The membrane cell consists of two elongated compartments (channels) ($300 \times 31 \times 3$ mm). The flat membrane which separates the compartments consisted of a slightly calendered double perchlorovinyl layer 20CA (Silmet), made of ultrathin fibres with an average diameter of 1.5×10^{-6} m and applied to a support of thicker (5.7×10^{-6} m) fibres. The area of the membrane was 9.7×10^{-3} m², void fraction 0.63, and the thickness 165×10^{-6} m. The feed and stripping solutions passed the cell countercurrently, entering at the bottom and flowing out from the top of the channels. The solutions were recirculated by means of peristaltic pumps. The change of volumes of both the feed and stripping solutions was compensated by expansion tanks. The crossflow velocity at both sides of the membrane was pulsed with an average velocity $u_F = 3.2$ cm/s. In [6], we showed that under these circumstances the mass transfer coefficient is independent of flow velocity. Keeping in view the relatively high longitudinal flow dispersion ($Pe = 6$—9) as well as the short mean residence time of the feed and stripping solutions in the cell per 1 cycle (14—18 s) as compared with the overall process time (2—3 h), the membrane cell used can be regarded as a complex of two ideally mixed batch systems.
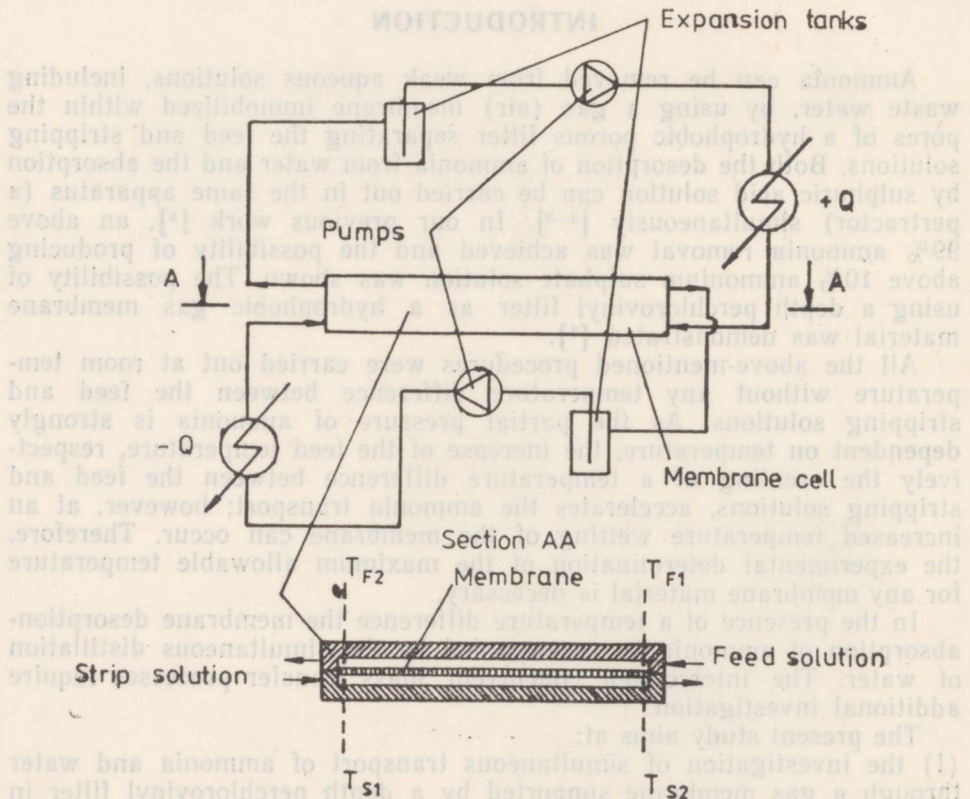

Fig. 1. Scheme of the experimental apparatus.

The inlet and outlet temperatures of both the feed and stripping solutions were measured using miniscale KMT-14 thermistors and a Wheatstone bridge. The temperature difference between the feed and stripping solutions was calculated as a logarithmic mean. The partial pressures of ammonia and water used in the calculations correspond to the mean feed and stripping phase temperatures.

As feed and stripping solutions, 0.36 M ammonia and 1 M sulphuric acid were used. The initial and final quantities of the solutions were weighed. The samples for analysis were taken from the feed and stripping solutions at fixed time intervals. The total ammonium concentration (the sum of free ammonia and ammonium ions) was determined colorimetrically with Nessler's reagent. From this the concentration of ammonia not dissociated was calculated using the value of temperature-dependent dissociation constant. The concentration of sulphuric acid was determined by titration with sodium hydroxide solution. All the reagents used were analytically pure.

RESULTS

Supposing a linear dependence of the partial pressures of ammonia and water on the length of the membrane pore, as well as a high mole fraction of water in the stripping solution ($x_{WS} > 0.98 \approx 1$) and a constant value of the activity coefficient of water in the sulphuric acid solution, $\gamma = 0.91$, we can obtain a differential equation for ammonia transport in an unsteady-state pertractor

$$d(G_F x_A) = \frac{k_A A}{P_i} x_A H \, dt, \tag{1}$$

where G_F is the molar quantity of the feed; x_A — the mole fraction of ammonia in the feed; A — membrane area, m²; H — Henry's constant, N/m²; k_A — mass transfer coefficient of ammonia, mol/m²s; and t — time, s. The mean partial pressure of an inert gas (air) can roughly be expressed as

$$P_i = P - \frac{P_{WF} + \gamma P_{WS} + x_A H}{2}, \tag{2}$$

where P is the total pressure, N/m²; P_{WF} and P_{WS} — the partial pressures of water in feed and stripping solutions, respectively.

In the case of a low temperature and no temperature difference between the feed and stripping solutions the mass transfer of water can be ignored, $G_F \approx$ const, and the integration of Eq. (1) gives

$$\ln(x_{A0}/x_A) = \frac{k_A A H}{P_i G_F} t. \tag{3}$$

For an unsteady-state process with the simultaneous ammonia and water transfer, i.e. in the case of a temperature difference between the feed and stripping solutions, as in our experiments, the following mass transfer equations were derived [6]:

for ammonia transport

$$\ln \frac{x_{A0}}{x_A} = \left(\frac{k_A H}{k_W (P_{WF} - \gamma P_{WS})} - 1 \right) \times$$

$$\times \ln \frac{G_{F0}}{G_{F0} - \frac{k_W A}{P_i} (P_{WF} - \gamma P_{WS}) t} \tag{4}$$

$$\frac{x_{A0}}{x_A} = \left(\frac{G_{F0}}{G_F}\right)^{\frac{k_A H}{k_W(P_{WF} - \gamma P_{WS})}} - 1 \tag{5}$$

where $P_{WF} - P_{WS} \neq 0$;

for water transport

$$\Delta G_S = G_S - G_{S0} = G_{F0} - G_F = \frac{k_W A}{P_i}(P_{WF} - \gamma P_{WS})t. \tag{6}$$

Here G_S and G_{S0} are the current and initial molar quantities of the stripping solution, G_{F0} — initial feed molar quantity and k_W — mass transfer coefficient of water, mol/m²s.

Ammonia desorption-absorption experiments using a temperature gradient and a perchlorovinyl layer as a support for the gas membrane

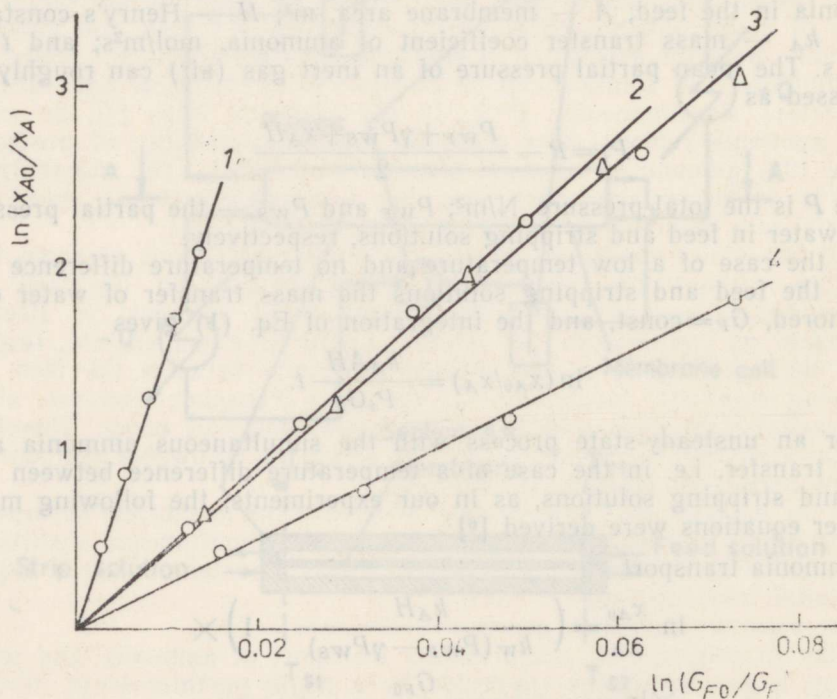| Exp. No.	Mean temperatures of solutions, °C			Molar quantity of feed, mol		Mass transfer coefficients, mol/m²s	
	T_F	T_S	ΔT	G_{F0}	ΔG	k_A	k_W
1	23.94	19.45	4.49	8.31	0.44	0.30	0.55
2	28.75	24.75	4.00	8.67	0.89	0.28	0.75
3	34.34	22.62	11.72	11.62	1.00	0.27	0.57
4	19.60	19.38	0.22	9.34	0.00	0.31	n. d.

n. d. — not determined.

Fig. 2. Dependence of the ammonia concentration ratio on the feed mole ratio. *1—4* numbers of experiments, see the Table.

The overall resistance to ammonia mass transfer, $1/k_A$, can be regarded as a sum of partial diffusion resistances in the feed and stripping solutions, $1/k_{AF}$ and $1/k_{AS}$, and in the membrane, $1/k_{AM}$, so

$$\frac{1}{k_A} = \frac{1}{k_{AF}} + \frac{1}{k_{AS}} + \frac{1}{k_{AM}}. \tag{7}$$

In our case, the mass transfer in the stripping solution is strongly accelerated by the fast chemical reaction, the stripping agent being in excess, so we may take $1/k_{AS} = 0$. The diffusion resistance of the feed aqueous boundary layer, $1/k_{AF}$ depends in general on the feed flow velocity. In the countercurrent-flow membrane cell the low pulsed flow velocity can guarantee a sufficient mixing of both the feed and stripping solutions, but not the absence of diffusion resistance of the laminar boundary layer in the feed. Nevertheless, it has been shown [6] that in this cell, at the flow velocity used in our experiments, the mass transfer coefficient k_A reaches a value practically independent of flow velocity, but the value obtained is somewhat smaller than in case of a well-mixed stirred-vessels cell [4].

The results of experiments are given in the Table. Fig. 2 displays the experimental data and the linear plots of $\ln(x_{A0}/x_A)$ vs. $\ln(G_{F0}/G_F)$ in the case of several temperature differences and feed molar quantities. The experimental points agree fairly well with Eqs. (4) and (5). The mean values of the mass transfer coefficients calculated from the slopes of linear plots were $k_W = 0.63$ mol/m²s for water and $k_A = 0.29$ mol/m²s for ammonia. This gives evidence of good mass transfer characteristics of the perchlorovinyl membrane.

The mass transfer rate of ammonia, being proportional to Henry's constant, is strongly accelerated by the increase of the feed temperature; however, in our experiments the wetting of the membrane occurred at the temperature above 35 °C.

CONCLUSIONS

In the presence of a temperature difference between the feed and stripping solutions, the desorption-absorption of ammonia through a gas membrane supported by a depth perchlorovinyl filter is accompanied by water distillation. The process is adequately described by an equation which takes into account the simultaneous mass transfer of both ammonia and water.

The rate of ammonia removal is accelerated by the temperature difference between the feed and stripping solutions, but the use of a perchlorovinyl layer as a support for the gas membrane is limited as at 35 °C the wetting of the membrane can occur.

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ÜHEAEGNE AMMONIAAGI JA VEE MASSIÜLEKANNE LÄBI PERKLOROVINÜÜLMEMBRAANI

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On uuritud üheaegselt kulgevat ammoniaagi ja vee ülekannet läbi hüdrofoobsel kiulisel lausperklorovinüülkangal paikneva gaasmembraani toite- ja vastuvõtulahuse erineva temperatuuri korral. On esitatud protsessi matemaatiline kirjeldus ja määratud massivahetuskoefitsientide arvväärtused. Temperatuuril üle 35 °C võib esineda perklorovinüülkanga märgumine.

ОДНОВРЕМЕННАЯ МАССОПЕРЕДАЧА АММИАКА И ВОДЫ ЧЕРЕЗ ПЕРХЛОРВИНИЛОВУЮ МЕМБРАНУ

Гуйдо РАЯЛО, Олег ТЕРЕПИНГ

Изучена одновременная передача аммиака и воды через газовую мембрану, иммобилизованную в порах фильтра из гидрофобной волокнистой перхлорвиниловой ткани, при наличии разницы температур питающего и принимающего растворов. Представлено математическое описание процесса, определены значения коэффициентов массопередачи. Установлено, что при температуре выше 35°C перхлорвиниловая ткань склонна к смачиванию.