REMOVAL OF VOLATILE COMPONENTS FROM WEAK AQUEOUS SOLUTIONS USING A GAS MEMBRANE

Guido RAJALO and Maya GLUSHKO

Eesti Teaduste Akadeemia Keemia Instituut (Institute of Chemistry, Estonian Academy of Sciences), Akadeemia tee 15, EE-0026 Tallinn, Eesti (Estonia)

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Abstract. The removal of volatile components (ammonia, phenol) from dilute aqueous solutions through a hydrophobic porous membrane is accelerated by the use of a temperature difference between the feed and stripping solutions; however, it is accompanied by pervaporation of water. Equations describing the concurrent unsteady-state mass transfer of the volatile component and water coincided well with the experimental results.

Key words: gas membrane, mass transfer, membrane desorption—absorption, membrane distillation.

Gas membranes immobilized within the pores of a hydrophobic microporous filter separating two aqueous solutions have been used to remove volatile solutes such as hydrogen sulphide, ammonia, free halogens, a.o. from water [1–3]. Both the desorption of the volatile component from water and the absorption by an aqueous stripping solution can be carried out in the same apparatus (a pertractor) simultaneously. Microporous polytetrafluoroethylene and polypropylene have been used as hydrophobic membrane materials. In our previous works [4, 5] diffusional characteristics of several microporous polymer materials were tested and the possibility of using the depth perchlorovinyl layer as a support for the gas membrane was demonstrated. In the transport of ammonia from a weak aqueous solution through a gas membrane ammonia removal of more than 99% was achieved and the possibility of producing simultaneously a solution of more than 10% ammonium sulphate was shown.

As the mass transfer in the stripping solution is strongly accelerated by the chemical reaction and the diffusion resistance of the laminar boundary layer in the feed at the stirring speed used has been shown to be negligible, the overall mass transfer coefficient equals the permeability of the
膜。因此，气态化合物在等温不稳定状态下的传质速率可以表示为：

\[
\ln \frac{x_{VF0}}{x_{VF}} = k_{V} \frac{A K_{VF}}{P_{i} G_{F}} t,
\]

(1)

其中，\(G_{F}\) 是进料的摩尔数量；\(x_{VF0}\) 和 \(x_{VF}\) 是进料的初始和当前气态化合物的摩尔分数；\(A\) 是膜面积，m²；\(K_{VF}\) 是气态化合物在进料中的相平衡常数，N·m⁻²；\(k_{V}\) 是气态化合物的整体传质系数，mol·m⁻²·s⁻¹；\(t\) 是时间，s。等温条件下，膜内气相的平均分压可以用以下公式表示。

\[
P_{i} = P_{T} - \frac{x_{VF0} K_{VF}}{2},
\]

(2)

其中，\(P_{T}\) 是总压，N·m⁻²。

实验结果表明，用氨溶液进行的实验结果与根据 Eq. (1) 所绘制的直线图相吻合。这使得能够确定几种微孔膜材料的传质特性，考虑到总压的变化率，按膜孔的平均分压可以用以下公式表示。

\[
k_{V} = \frac{c D_{VE}}{l} = \frac{c D_{V} \cdot \varphi}{l q (1 + K_{K})},
\]

(3)

其中，总摩尔浓度 \(c = P_{T}/(RT)\)，mol·m⁻³；Knudsen 比 \(K_{K} = D_{V}/D_{K}\)；\(D_{VE}\)、\(D_{V}\) 和 \(D_{K}\) 是有效、分子和 Knudsen 比的传质系数，m²·s⁻¹；\(R\) 是气体常数，J·mol⁻¹·K⁻¹；\(T\) 是温度，K；\(l\) 是膜厚度，m；\(\varphi\) 是膜的空隙率；和 \(q\) 是孔隙率。

上述所有提到的工作均在室温下进行，没有温度差。由于膜对气态化合物和相平衡常数的传质特性是温度敏感的，因此，进料温度的升高，特别是在酚的情况下，会大大增加传质速率，而传质速率的增加是由于温度差的影响，以及膜与进料的共同传质过程。因此，对传质过程的数学描述需要考虑膜和进料的两个成分的共同传质。
in general a system of partial differential equations, but in our case some simplifying assumptions can be made:

(1) at fixed temperatures of the feed and stripping solutions the rate of the mass transfer process is practically not affected by a simultaneous heat transfer, and

(2) as the concentration of the volatile component is low, its mass transfer does not influence the quantities of the feed and stripping solutions and the molar concentration of the water. On the contrary, the water transport affects strongly the quantities of the phases and hence, the concentration of the volatile component. So we regard water transfer as an independent process, but the transfer of the volatile component as connected with that of water.

The equations describing concurrent unsteady-state mass transfer in case of ammonia and water were derived in our previous work [6]. Basing on an equation describing the molecular diffusion of the water vapour through a stagnant air film immobilized in the membrane pores, and taking the water pressure profile as linear on the length of the membrane pore and the mole fraction of water (due to the low volatile component concentration) equal to 1, we obtain the equation describing the molar flux of water vapour in an unsteady-state pertractor, without any diffusion resistance of aqueous boundary layers, as

\[
\frac{dG_S}{dt} = \frac{k_W A}{P_i} (P_{WF} - \gamma_W P_{WS}),
\]

where \(G_S\) is the molar quantity of the stripping solution, mol; \(k_W\) is the overall mass transfer coefficient of water, mol·m⁻²·s⁻¹; \(P_{WF}\) and \(P_{WS}\) are vapour pressure of water in the feed and stripping solutions, respectively, N·m⁻²; \(\gamma_W\) is the activity coefficient of water in the stripping solution and

\[
P_i = P_T - \frac{P_{WF} + \gamma_W P_{WS} + x_{VF0} K_{VF}}{2}.
\]

At steady-state temperatures of the feed and stripping solutions, the mass transfer equation for water vapour can be obtained by integration of Eq. (4) as

\[
\Delta G_S = G_S - G_{S0} = \frac{k_W A}{P_i} (P_{WF} - \gamma_W P_{WS}) t,
\]

where \(G_{S0}\) is the initial molar quantity of the stripping solution. Equation (6) is a sufficiently good approximation for describing the mass transfer of water vapour.

In case of a fast chemical reaction in the stripping solution a differential equation for the transport of volatile component can be expressed as

\[-d (G_F x_{VF}) = -G_F \frac{dx_{VF}}{dt} - x_{VF} \frac{dG_F}{dt} = \frac{k_V A K_{VF}}{P_i} x_{VF},
\]
where \(-dG_F = dG_S, G_F = G_{F0} - G_S\), and \(G_{F0}\) is the initial molar quantity of the feed solution.

Substitution of \(G_F\) and \(dG_F/dt\) into Eq. (7) gives

\[
\frac{dx_{VF}}{x_{VF}} = \frac{A [k_v K_{VF} - k_w (P_{WF} - \gamma_w P_{WS})]}{P_i G_{F0} - k_w A (P_{WF} - \gamma_w P_{WS})} dt.
\]

(8)

Integration of Eq. (8) gives

\[
\ln \frac{x_{VF0}}{x_{VF}} = \left( \frac{k_v K_{VF}}{k_w (P_{WF} - \gamma_w P_{WS})} - 1 \right) \ln \frac{G_{F0}}{G_F} - \frac{k_w A}{P_i} (P_{WF} - \gamma_w P_{WS})
\]

(9)

or

\[
\frac{x_{VF0}}{x_{VF}} = \left( \frac{G_{F0}}{G_F} \right)^{k_v K_{VF}/k_w (P_{WF} - \gamma_w P_{WS}) - 1}
\]

(10)

where \(P_{WF} - P_{WS} \neq 0\) and \(K_{VF} \gg P_{WF} - \gamma_w P_{WS}\).

So, a relatively simple equation for calculating the concurrent mass transfer of volatile component and water is obtained. Equations (9) and (10) are universal, being valid for any kind of volatile components. In case of a soluted gas, such as ammonia, hydrogen sulphide, a.o., the phase equilibrium constant is equal to Henry's constant at the fixed feed temperature \(T_F\):

\[
K_{VF} = H_{TF}.
\]

(11)

In case of an evaporating component (phenol) the phase equilibrium constant equals fugitivity:

\[
K_{VF} = \gamma_V P_{VF},
\]

(12)

where \(P_{VF}\) and \(\gamma_V\) are the partial pressure and activity coefficient of the volatile component in the feed solution (at \(T_F\)).

Equation (9) gives an assemblage of linear plots, the slope depending on the physical properties of the components and mass transfer characteristics. In the Figure experimental data and linear plots of \(\ln(x_{VF0}/x_{VF})\) versus \(\ln(G_{F0}/G_F)\) are given for different volatile components (ammonia, phenol) and membranes (microporous polytetrafluoroethylene, depth perchlorovinyl layer). The experimental data in the Figure like those in our previous works [6–8] are in good agreement with Eqs. (9) and (10), thereby demonstrating the adequacy of the above mathematical description and confirming the simplifying presumptions used.
Dependence of the volatile component concentration ratio \((G_F/G_P)\) on the feed mole ratio \((x_{VF}/x_{VP})\).

1. ammonia; \(\Delta T=1.9\) K; tetrafluoroethylene membrane [6].
2. ammonia; \(\Delta T=4.5\) K; perchlorovinyl membrane [5].
3. phenol; \(\Delta T=4.7\) K; tetrafluoroethylene membrane [8].

REFERENCES

LENDUVA TE KOMPONENTIDIGE ERAALDAMINE LAHJADEST VESILAHIUJEST GAASTEMBRAANI ABIL

Guido RAJALO, Maia GLUSKO

Lenduvate komponentide (ammoniaagi, fenooli) eraldumine lahjadest vesilahustest läbi hüdrofoobse poorse membraani kiireneb toite- ja vastuvõtulahuse vahelise temperatuuridiferentsi olemasolul, kuid sellega kaasneb vee aurustumine. Tuletatud võrrandid lenduva komponendi ja vee üheaegse mittenäitikuga massiülekande kirjeldamiseks aproksimeerivad hästi katsetulemusi.

УДАЛЕНИЕ ЛЕТУЧИХ КОМПОНЕНТОВ ИЗ СЛАБЫХ ВОДНЫХ РАСТВОРОВ С ПРИМЕНЕНИЕМ ГАЗОВОЙ МЕМБРАНЫ

Гуайдо РАЯЛО, Майя ГЛУШКО

Выделение летучих компонентов (аммиака, фенола) из слабых водных растворов через гидрофобную микропористую мембрану ускоряется при разнице температур питания и принимающего растворов, но сопровождается испарением воды. Полученные уравнения для описания совместной нестационарной передачи летучего компонента и воды хорошо аппроксимируют экспериментальные данные.