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

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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 membrane. So the mass transfer rate of the volatile component in an isothermal unsteady-state batch pertractor can be expressed as follows:

$$\ln \frac{x_{\mathrm{VF0}}}{x_{\mathrm{VF}}} = k_{\mathrm{V}} \frac{AK_{\mathrm{VF}}}{P_{\mathrm{i}} G_{\mathrm{F}}} t, \tag{1}$$

where G_F is the molar quantity of the feed; x_{VF0} and x_{VF} are the initial and current mole fraction of the volatile component in the feed; A is the membrane area, m^2; K_{VF} is the phase equilibrium constant of volatile component in the feed, $N \cdot m^{-2}$; k_V is the overall mass transfer coefficient of the volatile component, $mol \cdot m^{-2} \cdot s^{-1}$; and t is time, s. The mean partial pressure of the stagnant gas in the membrane pores may be roughly expressed as

$$P_{\mathrm{i}} = P_{\mathrm{T}} - \frac{x_{\mathrm{VF0}} K_{\mathrm{VF}}}{2}, \tag{2}$$

were P_T is the total pressure, $N \cdot m^{-2}$.

The results of our experiments with ammonia solutions are in good agreement with the linear plots of x_{VF0}/x_{VF} versus time according to Eq. (1). This makes it possible to determine the mass transfer characteristics of several microporous membrane materials, keeping in view that

$$k_{\mathrm{V}} = \frac{cD_{\mathrm{VE}}}{l} = \frac{cD_{\mathrm{V}} \cdot \varphi}{lq\,(1 + K_{\mathrm{K}})}, \tag{3}$$

where the total molar concentration $c = P_T/(RT)$, $mol \cdot m^{-3}$; Knudsen's diffusion ratio $K_K = D_V/D_K$; D_{VE}, D_V, and D_K are the effective, molecular, and Knudsen's diffusion coefficients of the volatile component, respectively, $m^2 \cdot s^{-1}$; R is the gas constant, $J \cdot mol^{-1} \cdot K^{-1}$; T is temperature, K; l is the membrane thickness, m; φ is the void fraction of membrane; and q is the tortuosity of pores.

All the above-mentioned works were carried out at room temperature without any temperature difference between the feed and stripping solutions. As both the partial pressure of the volatile component and the phase equilibrium constant are strongly temperature-dependent, an increase in the feed temperature, accompanied by a rise of the temperature difference between the feed and stripping solutions may remarkably increase the mass transfer rate, particularly in case of phenol, but the transfer of the volatile component is accompanied by a simultaneous distillation of water. Thus the process will become similar to membrane distillation, although one of the components is absorbed chemically. So we have to deal with a two-component concurrent simultaneous mass transfer through a stagnant air layer, in which, due the unsteady-state conditions, the quantities of both solutions and the concentrations of their components are time-dependent. The mathematical description of such a process needs 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

$$\frac{\mathrm{d}G_{\mathrm{S}}}{\mathrm{d}t} = \frac{k_{\mathrm{W}}A}{P_{\mathrm{i}}}\left(P_{\mathrm{WF}} - \gamma_{\mathrm{W}}P_{\mathrm{WS}}\right), \tag{4}$$

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}; γ_{W} is the activity coefficient of water in the stripping solution and

$$P_{\mathrm{i}} = P_{\mathrm{T}} - \frac{P_{\mathrm{WF}} + \gamma_{\mathrm{W}}P_{\mathrm{WS}} + x_{\mathrm{VF0}}K_{\mathrm{VF}}}{2}. \tag{5}$$

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

$$\Delta G_{\mathrm{S}} = G_{\mathrm{S}} - G_{\mathrm{S0}} = \frac{k_{\mathrm{W}}A}{P_{\mathrm{i}}}\left(P_{\mathrm{WF}} - \gamma_{\mathrm{W}}P_{\mathrm{WS}}\right)t, \tag{6}$$

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

$$-\mathrm{d}\left(G_{\mathrm{F}}x_{\mathrm{VF}}\right) = -G_{\mathrm{F}}\frac{\mathrm{d}x_{\mathrm{VF}}}{\mathrm{d}t} - x_{\mathrm{VF}}\frac{\mathrm{d}G_{\mathrm{F}}}{\mathrm{d}t} = \frac{k_{\mathrm{V}}AK_{\mathrm{VF}}}{P_{\mathrm{i}}}x_{\mathrm{VF}}, \tag{7}$$

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

$$-\frac{dx_{VF}}{x_{VF}} = \frac{A\,[k_V K_{VF} - k_W\,(P_{WF} - \gamma_W P_{WS})\,]\,dt}{P_i G_{F0} - k_W A\,(P_{WF} - \gamma_W P_{WS})\,t}\,. \tag{8}$$

Integration of Eq. (8) gives

$$\ln\frac{x_{VF0}}{x_{VF}} = \left(\frac{k_V K_{VF}}{k_W\,(P_{WF} - \gamma_W P_{WS})} - 1\right)\ln\frac{G_{F0}}{G_{F0} - \dfrac{k_W A}{P_i}\,(P_{WF} - \gamma_W P_{WS})} \tag{9}$$

or

$$\frac{x_{VF0}}{x_{VF}} = \left(\frac{G_{F0}}{G_F}\right)^{k_V K_{VF}/k_W\,(P_{WF} - \gamma_W P_{WS}) - 1}\,, \tag{10}$$

where $P_{WF} - P_{WS} \neq 0$ and $K_{VF} >> P_{WF} - \gamma_W P_{WS}$.

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:

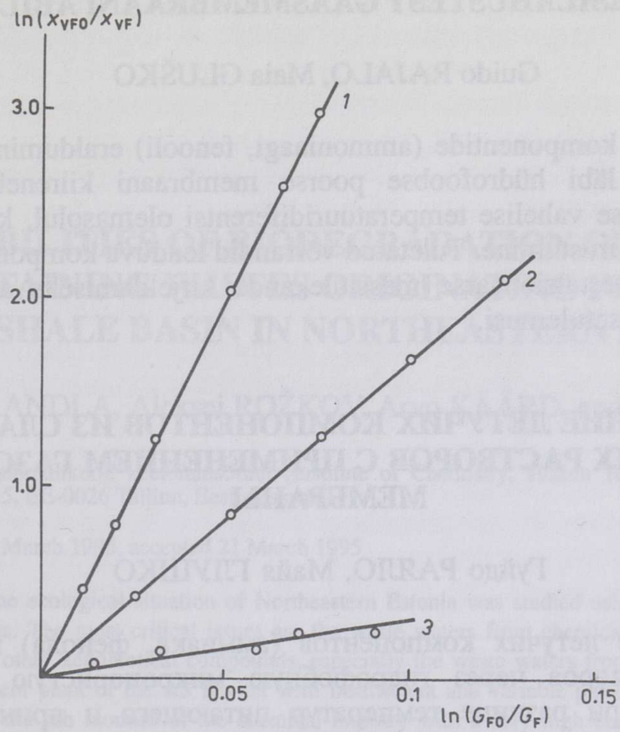
$$K_{VF} = H_{TF}\,. \tag{11}$$

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

$$K_{VF} = \gamma_V P_{VF}\,, \tag{12}$$

where P_{VF} and γ_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_{F0}/G_F) on the feed mole ratio (x_{VF0}/x_{VF}). *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].

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LENDUVATE KOMPONENTIDE ERALDAMINE LAHJADEST VESILAHUSTEST GAASMEMBRAANI ABIL

Guido RAJALO, Maia GLUŠKO

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 mittestatsionaarse massiülekande kirjeldamiseks aproksimeerivad hästi katsetulemusi.

УДАЛЕНИЕ ЛЕТУЧИХ КОМПОНЕНТОВ ИЗ СЛАБЫХ ВОДНЫХ РАСТВОРОВ С ПРИМЕНЕНИЕМ ГАЗОВОЙ МЕМБРАНЫ

Гуйдо РАЯЛО, Майя ГЛУШКО

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