Jun Xiang, Penggao Cheng, Wei Du, Songbo Wang, Qinxin Tang, Xuekui Wang, Na Tang
College of Chemical Engineering and Materials Science, Tianjin University of Science & Technology, Tianjin 300457, People's Republic of China.

Study on Membrane Absorption Performance of Bromine and Water Mixture Solution

Salt, Safety and the Environment

Key words: membrane absorption; bromine solution; orthogonal experiment

Abstract: As an important chemical raw material, bromine is widely applied in many fields, such as lithium bromide cryogens, bromine series fire retardants, photosensitive materials and pharmaceutical intermediates. Due to the different boiling points of bromine and water vapor, the bromine separation was achieved by heating the mixture of bromine and water under atmospheric pressure. In this paper, the membrane absorption performances of bromine solution were studied. And the regression orthogonal experiment was adopted to develop the optimal conditions. The effects of absorption time, temperature of mixture solution, concentration of drawing solution, and cross-flow velocity were evaluated during a membrane process. A hydrophobic polyvinylidene fluoride (PVDF) module was used, and different concentrations of NaOH were tested as drawing solutions. The results showed that the absorption rate of bromine increased with absorption time and higher temperature. The mass transfer coefficient was consistent with the Arrhenius relationship. When the concentration of drawing solution increased from 0.003 mol/L to 0.01 mol/L, the mass transfer coefficient increased from 4.75×10^{-4} cm/s to 6.02×10^{-4} cm/s, and the membrane absorption flux increased form 2.4×10^{-3} kg/(m^2·h) to 3×10^{-3} kg/(m^2·h). However, the effect of fluid dynamic conditions of the drawing solution was not obvious. The optimal operational conditions were summarized as follow: 0.01 mol/L NaOH was used as drawing solution,temperature of feed solution was 50°C, feed flow rate was 22.24 cm/s, and the concentration of bromine was 220 mg/L.

Bromine is an important chemical raw material. The industrialized bromine production methods are both distillation and air blowing, which are limited due to huge energy input, high bromine concentration in the brine, absorption tower flooding and back-mixing [1].

Cussler et al.[2-5] put forward the use of membrane absorption method to extract bromine for the first time in 1985. They used hollow fiber membranes to separate H_2S, SO_2 and NH_3 from aqueous solution, and derived mass transfer coefficient equations for various membrane absorption methods, such as gas membrane extraction. Since then, membrane absorption methods for aqueous bromine solutions attracted many researchers' interests. Later, some researchers [6,7] studied some key factors in the membrane absorption process of aqueous bromine solution.

In this study, membrane absorption performances of extracting bromine from aqueous bromine solution with polyvinylidene fluoride (PVDF) and hydrophobic hollow fiber membranes

tjtangna@tust.edu.cn (Na Tang); Tel: 0086+22+60602745

were studied, and factors which affected aqueous bromine solution membrane absorption performance were analyzed. Membrane absorption performance and transfer intensification of extracting bromine from brine with gas filled membranes were studied.

1. Materials and methods

1.1 Materials and instruments

Aqueous bromine solution, purchased from Tianjin Changlu Haijing Group, NaOH, $Na_2S_2O_3$ and KI purchased from Tianjin Yingda Xigui Reagent Factory. Crystal stirrer (BC-S211) brought from Shanghai Beikai Biological Chemical Equipment Co. Ltd.

1.2 Experimental device

The aqueous bromine solution of membrane absorption set up was shown in Fig. 1. The concentration of bromine in the feed solution was about 0.0001mol/L ~ 0.002 mol/L (pH≈3.5). After heating to a specific temperature by the constant temperature sink, the feed solution was pumped into the hollow fiber membrane module (tube pass), with NaOH solution pumped into the membrane module shell side simultaneously.

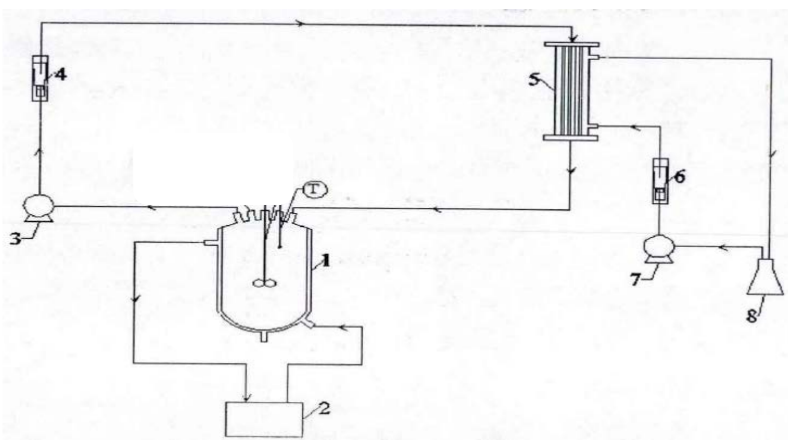

Fig. 1 Schematic diagram of aqueous bromine solution of membrane absorption set up

1. Circulating bottle of raw material liquid, 2. Constant temperature sink, 3. Peristaltic pump, 4. Flow meter, 5. PVDF hollow fiber membrane, 6. Flow meter, 7. Peristaltic pump, 8. Absorbent circulation bottle.

2. Result and discussion

2.1 Effect of absorption time on membrane absorption performance

As shown in Fig. 2, the absorption rate of bromine increased significantly with absorption time. In the early stage of membrane absorption reaction, the bromine absorption rate varied greatly. Because the concentration gradient and transmembrane driving force were larger at the beginning of the reaction. As the reaction time increased, both of the concentration gradient and the bromine absorption rate decreased. Theoretically, the bromine absorption rate can reach to 100% over time. Considering comprehensive factors, the membrane absorption time of this experiment was 20 min.

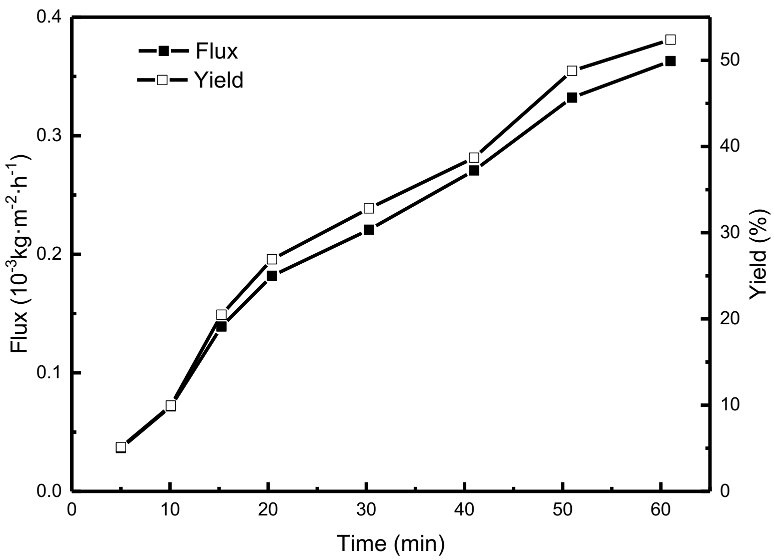

Fig. 2 The effect of membrane absorption time on flux and mass transfer coefficient of aqueous bromine solution for membrane absorption

As shown in Fig. 3, In (C_0/C_t) basically had a linear relation with membrane absorption time. Therefore, the membrane absorption process of aqueous bromine solution is in line with first order kinetics process in this study, which means the chemical reaction rate is proportional to initial concentration of reactants. This also explained why growth rates of flux and absorption time became slower with time: with the membrane absorption time increased, the initial concentration of bromine in feed solution and the reaction rate reduced, and then the concentration variation rate of bromine decreased.

Jun Xiang, Penggao Cheng, Wei Du, Songbo Wang, Qinxin Tang, Xuekui Wang, Na Tang
College of Chemical Engineering and Materials Science, Tianjin University of Science & Technology, Tianjin 300457, People's Republic of China.

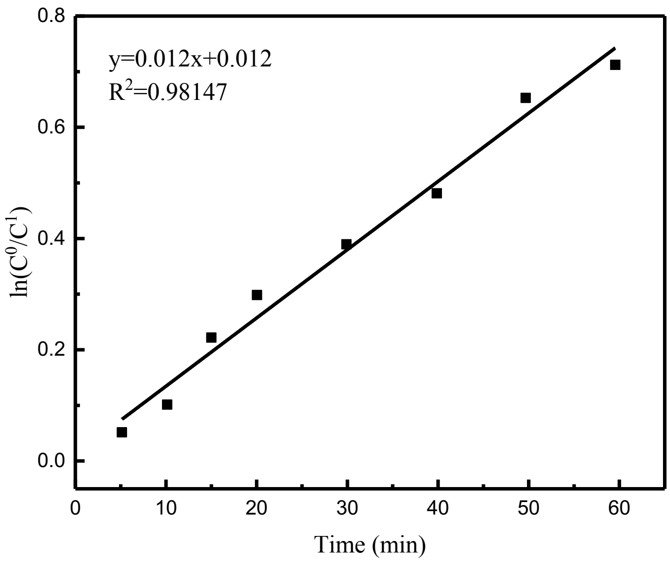

Fig. 3 Membrane absorption time vs. In (C^0/C^t)

2.2 Effect of bromine solution temperature on membrane absorption performance

Zhang et al. [16] indicated that there is an Arrhenius relationship between the mass transfer coefficient K and the feed temperature T. As shown in Fig. 4, the linear relationship between -lnk and 1/T is obvious, indicating that the relationship between the feed solution temperature and mass transfer coefficient of the aqueous bromine solution membrane absorption process is in line with the Arrhenius relationship.

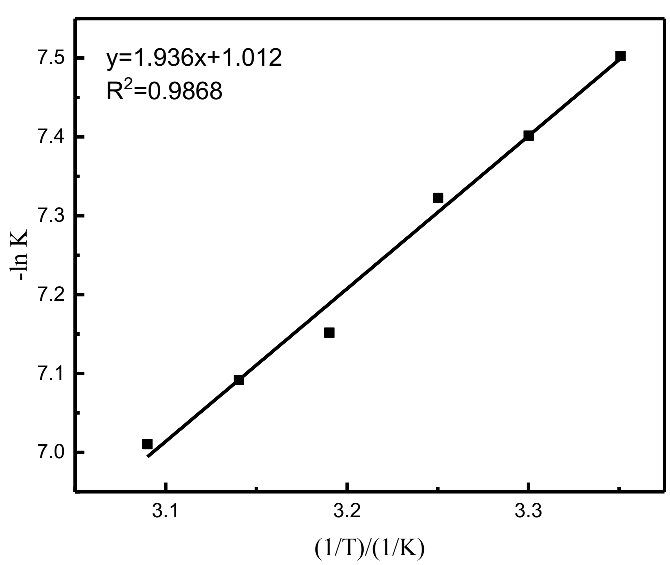

Fig. 4 Relationship between –lnK vs. 1/T

As presented in Fig. 5, the 2/3 index of ratio between temperature and viscosity has a good linear relationship with the mass transfer coefficient. The result is in accord with the results derived from Stokes - Einstein and Wilke - Change [8] equations, whose mathematical model describes the quantitative relationship between the temperature and the mass transfer coefficient well.

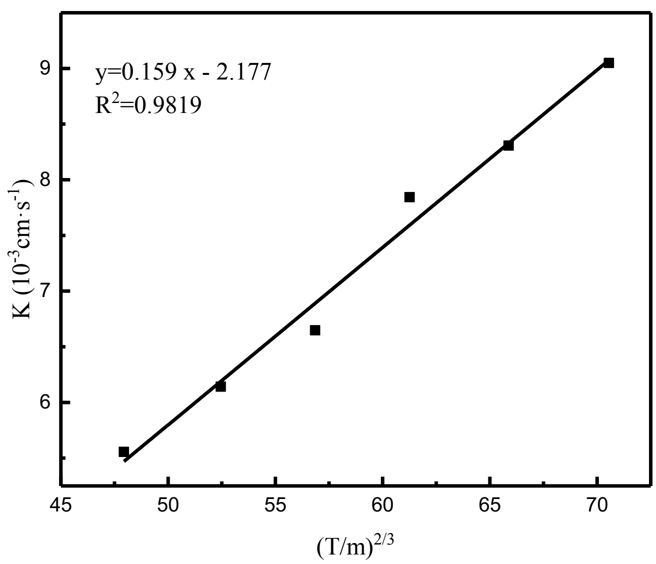

Fig. 5 Relationship between K vs. $(T/\mu)^{2/3}$

2.3 Effect of absorption solution concentration on membrane absorption performance

Absorbing solution (NaOH solution) reacted with bromine in feed solution. As the concentration of absorption increased, the absorption effect increased. As shown in Fig. 6, when the NaOH concentration increased from 0.003 mol/L to 0.01 mol/L, the mass transfer coefficient increased from 4.75×10^{-4} cm/s to 6.02×10^{-4} cm/s, and the corresponding membrane flux increased from 2.4×10^{-3} kg/(m^{2}h) to 3×10^{-3} kg/(m^2 h). When the concentration of NaOH solution continued to increase and kept in excess, the absorption performance of bromine remained stable.

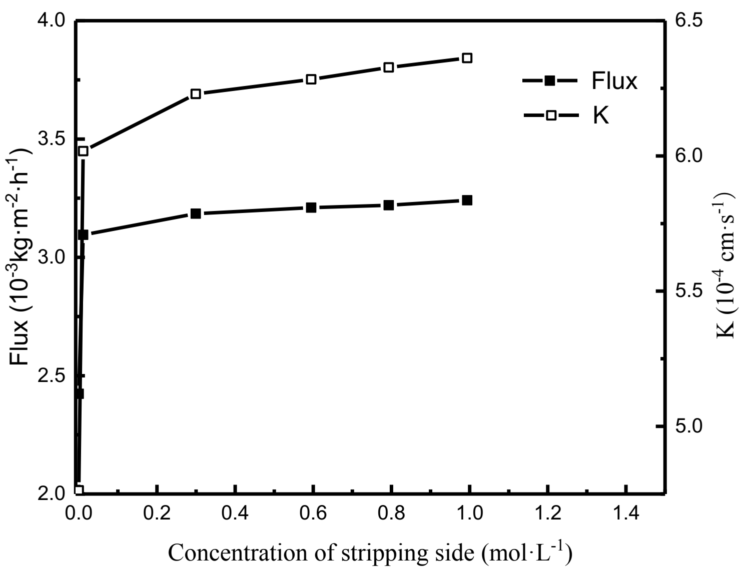

Fig. 6 The effect of concentration of stripping side (NaOH) on mass transfer coefficient and flux of aqueous bromine solution for membrane absorption

2.4 Effect of absorption solution flow rate on membrane absorption performance

Fig. 7 shows that the absorption solution flow rate has no significant effect on bromine absorption performance. This is because the bromine water membrane absorption process was controlled by main gas liquid, and the reaction rate in the absorption solution side was fast and irreversible. As the chemical reaction intensity is high, the fluid dynamics condition in the absorption solution side has little effect on aqueous bromine solution membrane absorption process.

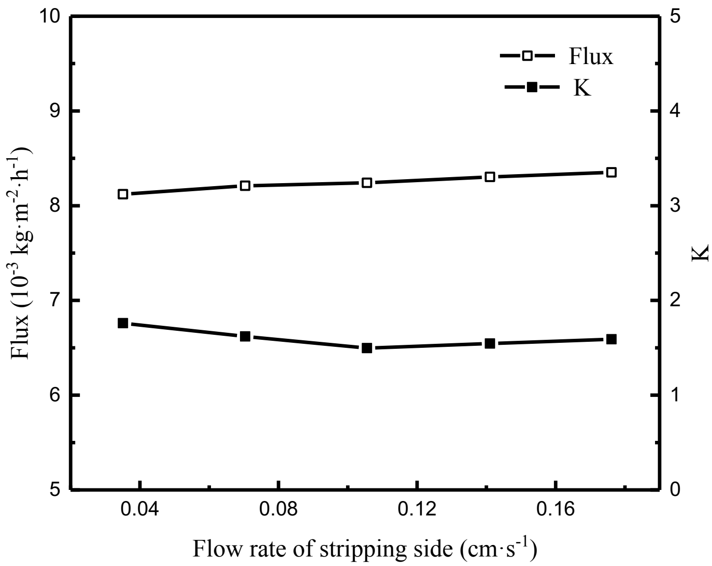

Fig. 7 The effect of flow rate of stripping side (NaOH) on mass transfer coefficient and flux of aqueous bromine solution for membrane absorption

3. Optimization of aqueous bromine solution membrane absorption process

The regression orthogonal test can obtain better test results with fewer test times, and the test results can be predicted and optimized by the established regression equation [9]. Test indexes were bromide absorption rate, mass transfer coefficient and membrane flux in membrane absorption process. In the orthogonal regression test, bromine content value range was [40, 220], feed solution flow velocity value range was [2.78, 22.24], and the feed solution temperature value range was [25, 50]. These three key factors were analyzed, and the factors and levels coding table of the bromine absorption process was shown in table 1.

Table 1. Factors and levels of coding table in the process of membrane absorption extracting bromine

Canonical variate z_j	Natural variable		
	Flow rate(cm/s)	Concentration of feed/(mg/L)	Temperature of feed/℃
Lower level (-1)	2.78	40	25
Uper level (1)	22.24	220	50
Zero level (0)	12.51	130	37.5
Changes interval Δ_j	9.73	90	

The optimized process for aqueous bromine solution membrane absorption process was obtained by the regression orthogonal experiment design: In the absorption solution side, the flux of NaOH solution was 2L/h and the concentration was 0.01mol/L; In the feed solution side, the temperature of the feed solution was 50℃, the flux was 22. 24 cm/s and feed solution concentration was 220 mg/L, with the membrane flux reaching to 6.17 × 10^{-3} kg / (m^2h).

Table 2 Simplified regression equations

Factor	Simplified regression equation
Absorption rate	$y=1.07*10^{-1}x_1+0.328$
Mass transfer coefficient	$y=7.94*10^{-4}x_3-5.8*10^{-4}$
Membrane flux	$y=1.142*10^{-5}x_1+2.407*10^{-5}x_2+1.71*10^{-5}x_3+2.078*10^{-7}x_1x_2-1.25*10^{-3}$

4. Conclusion

The membrane absorption method is one of the methods that cost low energy and have high extraction efficiency to purify bromine in bromide solution. With NaOH solution as absorbent, PVDF hollow fiber membrane as separation membrane, the effects of absorption time, aqueous bromine solution temperature, stripping solution concentration and flow rate and other operation conditions, membrane absorption process of aqueous bromine solution were studied.

The results showed that the relationship between the feed solution temperature and mass transfer coefficient of the aqueous bromine solution membrane absorption process is in line with the Arrhenius relationship. When the concentration of NaOH solution increased from 0.003 mol/L to 0.01 mol/L, the mass transfer coefficient increased from 4.75×10^{-4} cm/s to 6.02×10^{-4} cm/s, and the corresponding membrane flux increased from 2.4×10^{-3} kg/(m^2h) to 3×10^{-3} kg/(m^2h). The fluid dynamics conditions of the absorption solution had no significant influence on aqueous bromine solution membrane absorption. The optimum process of aqueous bromine solution membrane absorption was obtained by the regression orthogonal test: when feed temperature was 50°C, the feed flow rate was 22.24 cm/s, the feed concentration was 220 mg/L, the stripping flow rate was 2 L/h and the stripping concentration was 0.01 mol/L, an aqueous bromine solution membrane absorption flux 6.17×10^{-3} kg/(m^2h) was obtained. The fluid dynamics on the absorption side of the absorption fluid had no significant effect on the membrane absorption of aqueous bromide solution. The optimal process of membrane absorption process was obtained by regression orthogonal experiment: when feed temperature was 50°C, feed flow rate was 22.24 cm/s, feed concentration was 220 mg/L, stripping flow rate was 2 L/h and stripping concentration was 0.01 mol/L, the membrane absorption flux of aqueous bromine solution can reach to 6.17×10^{-3} kg/(m^2h).

References

[1] Zhang Linna, Liu Youzhi, Jiao Weizhou, et al. Development and research of bromine purification technology from brine[J]., Salt Lake Research. 2009; 17(1): 68-72. China.

[2] Zhang Qi, Cussler EL. Bromine recovery with hollow fiber gas membranes[J]. Journal of Membrane Science. 1985;24(1):43-57.

[3] Zhang Qi, Cussler EL. Hollow fiber gas membranes[J]. AIChE J. 1985;31(9):1548-1553.

[4] Yang Mingchen, Cussler EL. Designing hollow fiber contactors[J]. AIChE J. 1986;32(11):1910-1916.

[5] Zhang Qi, Cussler EL. Microporous Hollow fibers for gas absorption[J]. J Membr Sci. 1985;23:321-332.

[6]Wu Chunrui, Lv Xiaolong, Wang Guoqiang et al. Study on membrane extracting process of bromide[J]. Chem Ind Eng Prog. 2009;28(6):972-932. China.

[7] Wu Dan, Wu Chunrui, Zhao Heng et al. Study on the bromide absorption of the air - membrane absorption method [J].Water treatment technology. 2010;36(2):76-79. China.

[8] Sherwood TK, Pickford RL, Wilkie CR. Mass transfer theory[M]. Shi Jun, Li Pansheng translate. Beijing: Chemical Industry Press. 1988. China.

[9] Li Yunyan, Hu Chuanrong. Test design and data processing [M]. Beijing: Chemical Industry Press, 2005. China.

tjtangna@tust.edu.cn (Na Tang); Tel: 0086+22+60602745