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Study on the Separation of Bromine-Water by Membrane Pervaporation Technology

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1 Introduction

Bromine, an important industrial raw material, was widely applied in industry, agriculture and medicine. At present, many methods of producing bromine have been found. The air blowing method and steam distillation method is the two main technologies used in industry. In addition, there are also some novel methods, such as resin adsorption, gas membrane method, emulsion liquid membrane method and so on. Meanwhile, there are lots of disadvantages in the bromine industrial production, such as high-energy consumption, high cost and low production, etc. (Zhang et al. 1985).

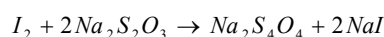
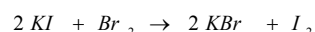
Pervaporation is a membrane separation as well as purification technique used for the separation of a desired component from liquid mixture through polymeric membranes. This process can be used for the dehydration of organic solvents, separation of organic-organic solvents, and removal of organics from aqueous solutions and recovery of aroma compounds in the food and cosmetic industries (Peter et al., 2008). Compared to some traditional separation techniques, such as distillation and rectification, the pervaporation technique has lots of advantages. For example, it has a high separation efficiency, low-energy consumption, sample device and low cost, etc. (Li et al., 2002; Jennifer et al., 2008). In consideration of the advantages of pervaporation, the increasing bromine demand and the disadvantages existing in industrial method of extracting bromine, the separation of bromine-water mixture by pervaporation technology was studied exploratively in this paper.

2 Experimental

PU was dissolved in THF by stirring for 4h~6h at

45°C. Two kinds of homogeneous solution of 10wt% and 15wt% by PU weight in solvent were obtained. In this way, twelve different blends, which were named as PU-I through PU-XII, were obtained. The polymeric solution was put in a dark environment for at 12h at room temperature to stand and defoam. Polymer films were prepared over suitable smooth glass plates by a hand casting knife. Membranes were formed by solvent evaporation at room temperature for 12h. The resulting dense membranes, which were dried in drying oven, were transparent with a thickness of 300µm, approximately.

Pervaporation tests were carried out using a lab scale apparatus which is schematically shown in Figure 1. The Br₂/H₂O mixture with different concentration of bromine were made up and calibrated by Na₂S₂O₃ (0.1000mol/l) standard solution, the principle is as below:



The mixture was poured into the feed reservoir with a capacity of 3000ml at room temperature. Feed was pumped through a peristaltic pump (Longer WT600-2J, China) to the membrane cell at the flow rate of 100ml/min. A round membrane with an effective area of 0.0045m² was used. Retentate stream was collected in a

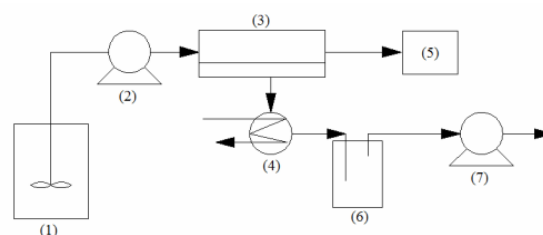


Fig. 1. Pervaporation apparatus: (1) feed reservoir, (2) peristaltic pump, (3) membrane cell, (4) condenser, (5) collection bottle of retentates, (6) collection bottle of penetrants, (7) vacuum pump.

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collection bottle. The permeated vapor went through the condenser which controlled the temperature at 5°C and was collected in other bottle under a vacuum of -0.1 MPa then calibrated by Na₂S₂O₃ standard solution.

3 Results and Discussions

3.1 Membranes

In our work, twelve different PU membranes that have been prepared present in Table 1.

Table 1 membranes prepared in experiment

The type of PU	The mass fraction of PU in membranes	The code of membranes
5180	10%	PU- I
	15%	PU- II
8180	10%	PU- III
	15%	PU- IV
8190	10%	PU- V
	15%	PU- VI
8195	10%	PU- VII
	15%	PU- VIII
6190x	10%	PU- IX
	15%	PU- X
6190y	10%	PU- XI
	15%	PU- XII

3.2 Swelling degree of membrane

In the swelling experiments, the membranes PU-I~PU-VIII were broken when put into bromine. The swelling results of membranes PU-IX~PU-XII are presented in Figure 2.

From these figures we can find that the DS of PU membranes increased very fast when they were just put in the bromine, and then it tended to a fixed value. It was obvious that there were large differences between the swelling degree in bromine and water of these four PU membranes. So it is possible for these four membranes to separate bromine-water system by pervaporation in theory. In addition, we can get that the swelling degree of PU-IX membrane in bromine is larger than others.

3.3 Pervaporation results

The obtained results from pervaporation tests are summarized in Figure 3. When the feed concentration was in 100 mg/L~400 mg/L, with the increasing of bromine concentration, the mass transfer impetus increased, which was beneficial to the dissolution and transmission of penetrants in membrane. So the permeation flux of these four membranes increased and this trend also became bigger with increasing feed concentration. Among these four membranes, the permeation flux of PU-IX was larger than others and the permeation flux of PU-XII was the smallest one. In consideration the fact that the swelling degree of PU-IX in bromine was also the biggest one among these four membranes in swelling experiments, so these results were consistent with each other. In theory, the increase of feed concentration will lead to the increase of permeation flux and which will further result in the

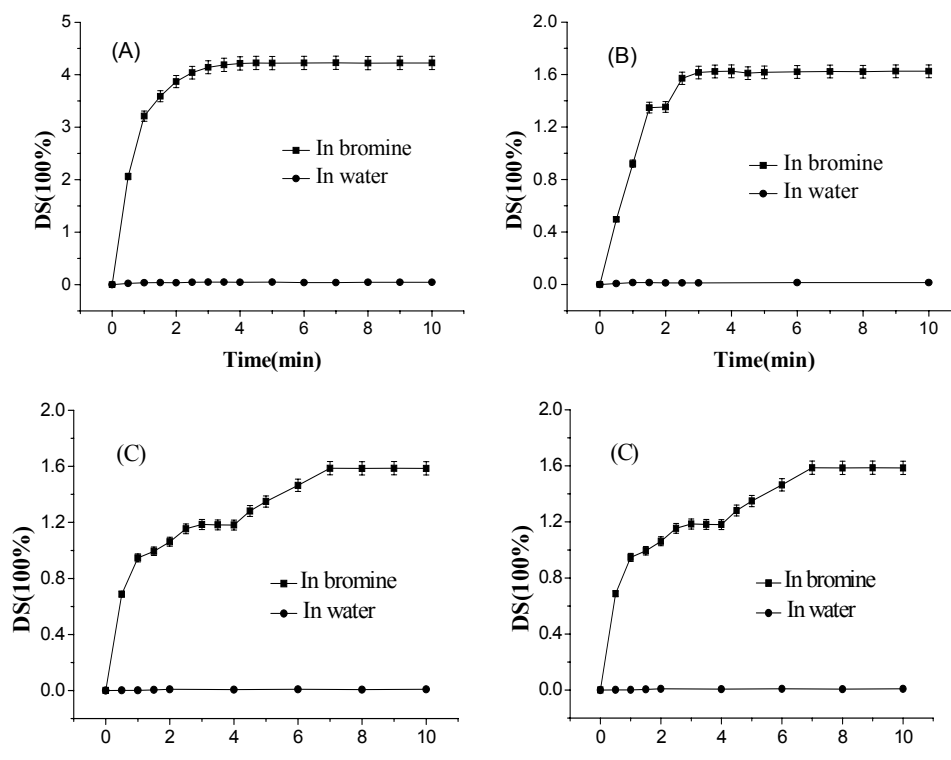


Fig. 2. The swelling degree curves of membranes. (A) PU-IX (B) PU-X (C) PU-XI (D) PU-XII.

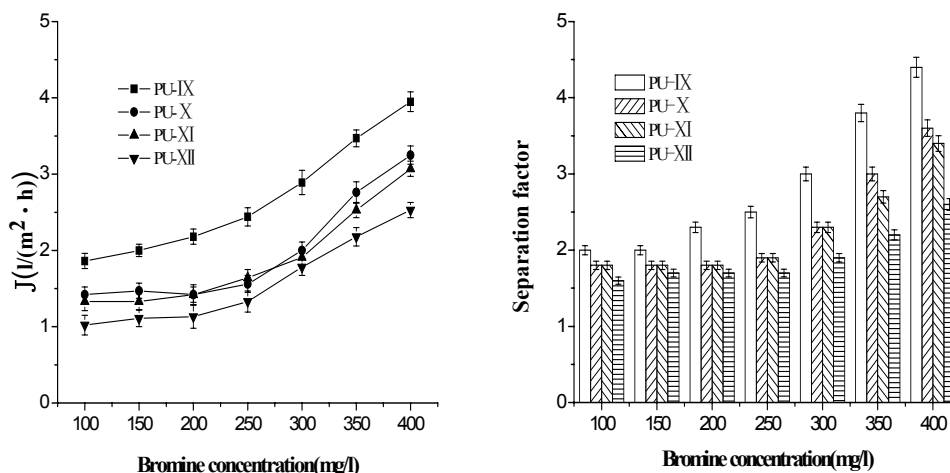


Fig. 3. Effects of bromine concentration on PV permeation flux and separation factor.

increase of membrane swelling degree; this will lead to the decrease of separation factor. But in our study, when the feed concentration was between 100 mg/L~400 mg/L, the increase of feed concentration was not enough to affect the separation factor of the membrane. On the contrary, the separation factor increased with increasing feed concentration. And in this process, the separation characteristics of PU-IX membrane were also the best one.

4 Conclusion

In this work, the polyurethane (PU) was employed as membrane material. Among the twelve different membranes we have prepared, the membrane PU-IX, PU-X, PU-XI and PU-XII have shown the possibility in the separation of bromine-water system by pervaporation. The separation performances of these four membranes have been studied in pervaporation experiments and the influence of bromine concentration on the permeation flux and separation factor of them have also been researched. When the feed concentration was in 100 mg/L~400 mg/L, the permeation flux of these four membranes increased and this trend also became bigger with increasing feed concentration, the separation factor also increased with increasing feed concentration.

Key words: pervaporation; polyurethane; bromine - water system.

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References

- Jennifer R. D., Amit C., and Feng X., 2008, Dehydration of ethylene glycol by pervaporation using poly(N,N-dimethylaminoethyl methacrylate)/polysulfone composite membranes. *Separation and Purification Technology*, 64: 63–70.
- Li J. D., Chen C. X., 2002, Laboratory and pilot-scale study on dehydration of benzene by pervaporation. *Journal of Membrane Science*, 203:127–136.
- Peter D., Teresa O., and Andrew G., 2008, Membranes for the dehydration of solvents by pervaporation. *Journal of Membrane Science*, 318: 5–37.
- Zhang Qi, Cussler E.L., 1985, Bromine recovery with hollow fiber gas membranes. *Journal of Membrane Science*. 24(1): 43–57.