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A Stable Supported Liquid Membrane Composed of Polypropylene Glycol and Tributyl Phosphate for Phenol Separation from Aqueous Solution

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Abstract : Tributyl phosphate (TBP), polypropylene glycol 4000 (PPG-4000), and the mixture of two compounds were examined as a liquid membrane in a supported liquid membrane (SLM) to separate phenol from aqueous solution. The feed concentration of phenol was varied in a broad range from 500 mg/L to 5,000 mg/L and different types of liquid membrane were prepared to elucidate their effects on separation of phenol. It was found that the modified PPG 4000 with TBP and toluene diisocyanate (TDI) might be used as a proper liquid membrane because the mass transfer rate examined with this membrane was higher than that through methyl isobutyl ketone (MIBK) which has been used as a conventional solvent in a solvent extraction process. The breakthrough pressure of the SLM is defined to be the pressure difference across the membrane at which the supported liquid membrane is not kept in the pores any more. It indicates how the SLM is stable. It was found that the breakthrough pressure of the modified PPG-4000 was much higher than those of typical organic solvents.

1. Introduction

Many organic substances, especially aromatic compounds such as phenol, are difficult to be removed or destroyed with current methods when the discharges are abnormal on their amounts and concentrations in wastewater. Several technologies for separation of phenol from aqueous solution have been investigated: adsorption by activated carbon [1,2], solvent extraction [3,4], and emulsion liquid membrane [5]. Separation of phenol from aqueous solution using a supported liquid membrane technology has been proposed and studied with various types of carrier such as trioctylamine (TOA) [6], dibenzo-18-crown-6 (DBC) [7], and so on [8,9].

The membrane technology shows some advantages in comparison with current competitive technologies, because of its relatively low energy consumption and low operating costs. It can be constructed in a small scale with the same capability of other processes.

The supported liquid membrane (SLM) is one type of the facilitated transports, which has higher selectivity than other membrane processes. The problem of the supported liquid membrane is known to be its instability of the system. The reasons of instability could be classified into several points which are illustrated in Fig. 1. One is the slow loss of the liquid membrane into water though it has low solubility in water. Another is the take off from pores where the liquid membranes are impregnated. The other point is the breakthrough pressure of the membrane due to the pressure difference.

The aims of this study are to find a proper

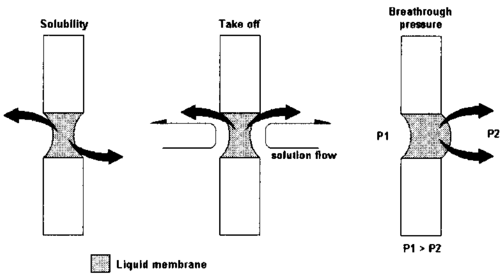

Fig. 1. The instability of SLM.

supported liquid membrane which might show the high separation ability as well as the high stability such as the modified PPG-4000 and TBP with a urethane reaction. To test the SLM, the overall mass transfer coefficients of phenol and the breakthrough pressures were explored as an indication of the separation ability of the SLM and the stability of the membrane, respectively.

2. Theory

If the transportation of phenol is occurred through a flat SLM, the differential mass balance can be expressed by equation (1).

$$-\frac{V_f}{A}\frac{dC_f}{dt} = K(C_f - C_s) \quad (1)$$

When the volume of strip side is V_s and the initial feed concentration is C_0, the overall mass balance is as follows:

$$V_f C_0 = V_f C_f + V_s C_s \quad (2)$$

If the volume of each side is equal, equation (2) can be simplified as

$$C_0 = C_f + C_s \quad (3)$$

Introducing equation (3) to equation (2) results in

$$\frac{dC_f}{(2C_f - C_0)} = \frac{A}{V_f}Kdt = -\frac{A}{V}Kdt \quad (4)$$

The integration of equation (4) with boundary conditions such that at t=0, $C_f=C_0$ and at t=t, $C_f=C_f$ results in equation (5):

$$\ln(2\frac{C_f}{C_0} - 1) = -\frac{KA}{V}t \quad (5)$$

If a sodium hydroxide aqueous solution is used as a strip solution, the concentration of phenol in the strip side is almost zero since sodium phenoxide is generated by the reaction between transported phenols and sodium ions. In this case, equation (1) is simplified as follows:

$$-\frac{V}{A}\frac{dC_f}{dt} = KC_f \quad (6)$$

The integration of equation (6) with same boundary conditions gives:

$$\ln(\frac{C_f}{C_0}) = -\frac{KA}{V}t \quad (7)$$

The overall mass transfer coefficient can be obtained from the slope of the plot of $\ln(C_f/C_0)$ versus time in equation (7).

3. Experimental

TBP from Junsei Chemical Co., PPG-4000 from Aldrich and their mixtures were used as the SLM solution which were filled in the pores of the PVDF membrane (Millipore, mean diameter=0.45 μm, thickness=120 μm). Toluene from Duksan Chemical Co. was used as a cosolvent to make mixture of TBP and PPG-4000. TDI (formular weight=174.15, density=1.225 g/cm^3) from Aldrich was used to link PPG-4000 molecules. Since both TDI and PPG are bifunctional chemicals, one mole TDI is required per mole of PPG to complete link all the PPG molecules. Basically, 4.36 g of TDI was used for 100 g of PPG-4000 (2.5×10^{-2} moles) for 100% molar ratio. To minimize the degree of polymerization during membrane preparation, the mixture was vigorously agitated for several minutes at the room temperature to prepare the modified PPG-4000 as soon as TDI was added to

PPG-4000. The mixture was immediately used to fill the pores of a membrane sheet. The excess mixture was wiped off from the membrane and then the membrane was heated in an oven at 60℃ for over 60 hours to complete the reaction. The Millipore membrane readily absorbed the mixture and it turned from opaque white to translucent when its pores were completely filled with the mixture. No catalyst was used in the reaction. The gel-like product formed after enough reaction time did not show a flow behavior.

The concentration of phenol in a sample was analyzed by HPLC (YL9500, YoungLin, Korea) with a reverse phase column (Nova-Pak C_{18}, Waters).

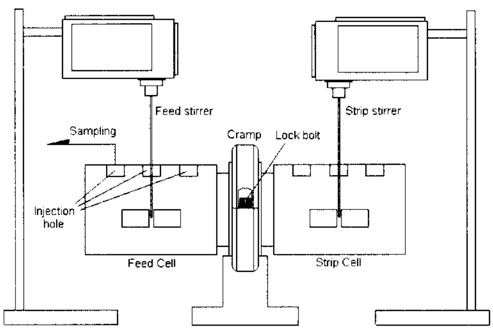

Fig. 2. A schematic diagram of separation apparatus.

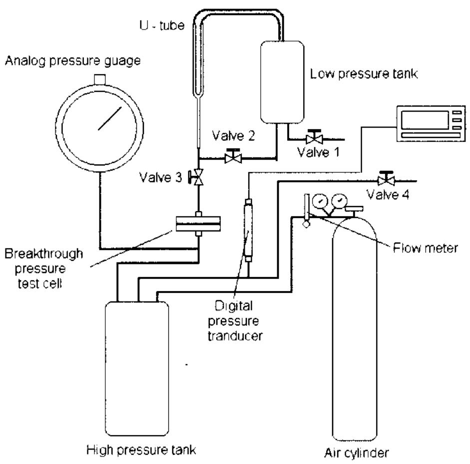

Fig. 3. A Schematic diagram of stability test equipment.

A schematic diagram of separation apparatus was illustrated in Fig. 2. The batch type separation apparatus was made of PTFE. The volume of both feed and strip side was 250 cm^3 and the effective transfer area was 11.34 cm^2.

The stability test equipment was illustrated in Fig. 3. It was composed of the accurate pressure gauge, the test cell, and the feed tank which was pressurized by the compressed air.

4. Results and Discussion

The overall mass transfer coefficients of three different liquid membranes are shown in Fig. 4. The overall mass transfer coefficient of TBP was found to be one order of magnitude higher than that of MIBK, which has been used as a conventional extractant and 5 times higher than that of PPG-4000. The overall mass transfer coefficient of PPG-4000 was comparably same as that of MIBK. It means that TBP and PPG-4000 can be utilized as a supported liquid membrane due to their separation abilities. TBP shows a higher dipole moment of phosphoryl group (P=O, μ=2.7) than that of MIBK (C=O, μ=2.4). It is thought that higher dipole moments of TBP might increase the mass transfer ability of phenol due to the higher possibility to interact phenol molecules. The higher mass transfer ability of PPG-4000 might be due to their hydrophobicity and unshared ether oxygens

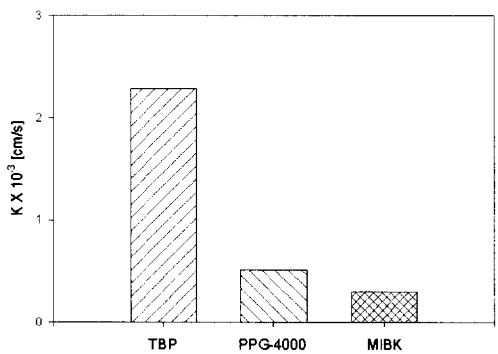

Fig. 4. Comparison of the overall mass transfer coefficients. (feed concentration of phenol= 500 mg/L)

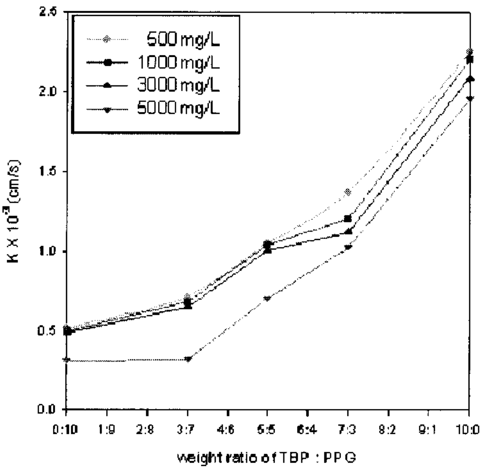

Fig. 5. The overall mass transfer coefficients of the membrane prepared from the simple mixtures.

since unshared ether oxygens in the main chain of PPG-4000 could form the hydrogen bonds with hydrogen atoms in phenol molecules.

The separation ability of SLM system could be improved if the mixture of TBP and PPG-4000 is used. In Fig. 5, the overall mass transfer coefficients of simple mixtures of TBP and PPG-4000 were plotted as a function of the weight ratio of TBP in the mixture. The overall mass transfer coefficient increases with the increase of the weight ratio of TBP to PPG-4000 as expected. This is maybe due to the higher reactivity of TBP with phenol than that of PPG-4000. There was no significant difference in the overall mass transfer coefficients with the initial concentration.

Breakthrough pressures of typical organic solvents, TBP, PPGs having various molecular weight and simple mixtures of TBP and PPG-4000 were listed in Table 1.

The breakthrough pressure of PPGs was initially expected to be high enough to be applied in a separation process. However, it turned out that the breakthrough pressure was not so high as expected and its magnitude was found to be comparable or even lower than those of the SLM of TBP and other typical solvents even if the breakthrough pressure increases as the molecular weight increases. The breakthrough pressures of the simple mixtures are between those of TBP and PPG-4000. To improve the stability of the SLM, PPG-4000 was modified by reacting with TDI. The overall mass transfer coefficient of the modified PPG-4000 was also measured.

The overall mass transfer coefficients of modified PPG-4000 were shown in Fig. 6 as a function of the weight ratio of TBP with PPG-4000 in the liquid membrane. The overall mass transfer coefficients were slightly lower than those of the simple mixtures. However, the difference in the magnitude was negligible. When the same compounds

Table 1. Breakthrough Pressures of Various Liquid Membranes

Liquid Membrane	Breakthrough Pressure (atm)	Liquid Membrane	Breakthrough Pressure (atm)
Toluene	1.22	PPG-725	>0.20
Heptane	1.11	PPG-1000	0.35
Kerosene	0.92	PPG-2000	0.51
Benzene	1.07	PPG-3000	0.55
Xylene	1.30	PPG-4000	0.63
TBP	0.51	7:3 TBP:PPG-4000	0.56
		5:5 TBP:PPG-4000	0.59
		3:7 TBP:PPG-4000	0.61

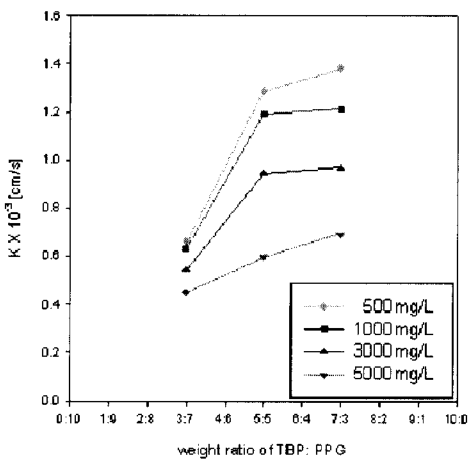

Fig. 6. The overall mass transfer coefficients of the membrane prepared from the modified PPG-4000.

Table 2. Breakthrough Pressures of the Membrane Prepared from the Modified PPG-4000

Liquid Membrane	Breakthrough Pressure (atm)
7:3 TBP:PPG-400 (100% TDI)	0.64
5:6 TBP:PPG-400 (100% TDI)	1.34
3:7 TBP:PPG-400 (100% TDI)	1.57

of the liquid membrane are used, the over mass transfer coefficients obtained with a low feed concentration are found to be slightly higher than those obtained with a high feed concentration. If the feed concentration is low, the most of the phenol molecules might react with the liquid membrane molecules at the feed side interface without any competition. However, as the concentration increases, a limited number of phenol molecules might react with the liquid membrane molecules and it results in a comparatively low mass transfer coefficient.

The breakthrough pressure of the modified PPG-4000 was shown in Table 2. The resulting breakthrough pressures were found to be higher than those of the simple mixtures. For example, the breakthrough pressure of the membrane by reacting the mixture of TBP/PPG-4000=3/7 with TDI was 1.57 atm. This value was about 2 times higher than those observed with other membranes prepared from simple mixtures.

5. Conclusions

The modified mixtures of TBP and PPG can be used as a proper liquid membrane because the overall mass transfer coefficient was observed to be higher than that of MIBK which has been used as a conventional extractant. The overall mass transfer coefficients were not changed with the initial feed concentration. Thus, the membrane fabricated from the modified PPG-4000 could be applied for separation of phenol from the aqueous solution regardless of feed concentrations. Their breakthrough pressures of the modified PPG-4000 were measured to be much higher than those of pure liquid membranes and the simple mixtures. Since the modified PPG-4000 shows a high permeability of phenol and a high stability, it could be used as a SLM. To increase the breakthrough pressure, it would be necessary to control the surface of the porous supports by a proper physicochemical treatment for preparation of functional group.

Acknowledgment

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