

일반강연 II-9

표면자유에너지 이론에 기초한 막오염 현상의 이해

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Understanding of Membrane Fouling in terms of Surface Free Energy Changes

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Introduction

One of the most dominating problems in a variety of industrial applications of membrane processes is membrane fouling that causes flux decline during membrane filtration, which is in a close association with economic feasibility of membrane systems. Membrane fouling can be primarily attributed to the interaction between membrane surfaces and fouling substances, e.g., the adsorption of organic matter, adhesion of colloidal particles, and deposition of inorganic precipitates. The extent of membrane fouling was found to be dependent on the membrane material used besides solution properties and operating conditions. In general, it is known that hydrophobic membranes are fouled relatively easily because of the hydrophobic interaction between membrane surfaces and organic matter present in solutions. However, some researchers have reported contradictory results that the hydrophobic membrane gave a less fouling tendency than the hydrophilic one. But little information is available yet to understand and explain both cases

clearly. The effect of membrane materials on fouling should be further evaluated in depth to give insight into fouling phenomena associated with the membrane-particle interactions. The purpose of this study was to investigate the fouling tendency in terms of surface free energy change caused by the interaction between membrane surfaces and particles.

Surface Free Energy Change

In relation to membrane fouling, the total free energy of the interaction between a fouling particle and a membrane surface can be expressed as a function of interfacial tensions:

$$\Delta G = A(\gamma_{SP} - \gamma_{PW} - \gamma_{WS}) \quad (1)$$

where A is the contacting area and the subscripts, s , p , and w indicate the phases, surface, particle, and water in the system, respectively. Based on the Fowkes' semiempirical interfacial tension theory, equation (1) can be transformed to:

$$\begin{aligned} \Delta G = & A(\gamma_s + \gamma_p - 2\sqrt{\gamma_s^d \gamma_p^d}) \\ & - A(\gamma_p + \gamma_w - 2\sqrt{\gamma_p^d \gamma_w^d}) \\ & - A(\gamma_w + \gamma_s - 2\sqrt{\gamma_w^d \gamma_s^d}) \end{aligned} \quad (2)$$

corresponding to

$$\Delta G = 2A(\sqrt{\gamma_p^d \gamma_w^d} - \gamma_w) + 2A(\sqrt{\gamma_w^d} - \sqrt{\gamma_p^d})\sqrt{\gamma_s^d} \quad (3)$$

Experimental

Biological broth with reasonably constant composition was applied for membrane filtration tests where microfiltration (MF) and ultrafiltration (UF) membranes used were made of different basic polymers with various nominal pore sizes (manufactured by Millipore or DDS).

Filtration of the biological broth was performed in a batch mode using a stirred cell (capacity 180 ml, effective membrane area 30.2 cm²) under the following conditions: temperature, 20±2°C; pressure, 1.0 bar; and stirring, 180 rpm. During filtration, the permeate mass was measured continuously using a balance (Satorius, B310S, Germany) to calculate the corresponding permeate flux. The contact angles of virgin membranes were measured for evaluation of hydrophobicity using a Goniometer (Rame Hart Inc., Model 100-00-115, USA) at room temperature.

Results and Discussion

In equation (3), membrane fouling is given as a function of γ_P^d and γ_S^d during filtration of aqueous solutions, which explains the interaction between the surface properties of membranes and particles in aqueous solution. If the dispersion component of the surface tension of particles is higher than that of water, the fouling increases as the dispersion component of the membrane surface tension increases and vice versa (Figure 1). It could be assumed that the dispersion force of macromolecules is higher than that of water molecules because normally the polarity of macromolecules are relatively low compared to that of water molecules. As a result, membrane fouling is expected to increase when the dispersion component of the surface tension of membranes increases in filtration of aqueous solutions.

To confirm the derived model based on the surface free energy change during fouling, experimental runs were performed with different material membranes. For the UF membranes with a MWCO of 20,000 dalton, no difference in fouling between membrane materials was observed, probably because of some dominant effects of pore plugging caused by small macromolecules rather than surface interactions. For the MF membranes, however, the fluoropolymer (PVDF) membrane gave the smallest fouling tendency, although most hydrophobic. The polysulfone membrane was the worst case in fouling and the cellulosic membrane that is most hydrophilic was only moderate. Apparently, these results

support the fact that the surface hydrophobicity itself is not enough to evaluate the extent of fouling caused by the interaction between membrane materials and fouling substances (particles) present in the feed solution. However, the fouling tendency was nearly in good agreement with the trend of the dispersion components of membrane surface tensions. It can thus be suggested that the smaller the dispersion component of the membrane surface tension, the less the membrane fouling occurs. This finding helps to find out the approximate tendency of membrane fouling caused by membrane-particle interactions and give guidelines for selection of appropriate membranes in the specific applications.

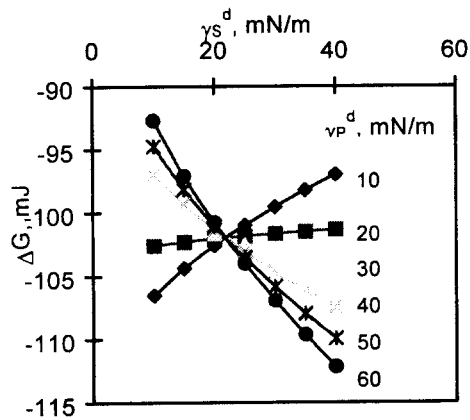


Figure 1. Surface free energy change as a function of the components of the surface tension of membranes and particles involved during membrane fouling.