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SEPARATION BEHAVIOR OF WATER-ALCOHOL SOLUTION BY PARTIALLY DITHIOCARBAMATED POLY(VINYL CHLORIDE) MEMBRANE

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ABSTRACT

Poly(vinyl chloride) was modified by reacting with sodium N-methyldithiocarbamate or N-methyl-N-carboxymethyldithiocarbamate to obtain crosslinked dithiocarbamated PVC(PMD,PSDC). In addition PSDC were substituted with metal ions of Na^+, Li^+ and Cs^+. PMD and PSDC were reacted with copper ions in alcohol or aqueous solution to produce chelate complexes of dithiocarbamated PVC, respectively(PMD-Cu^{2+}, PSDC-Cu^{2+}). PSDC was irradiated by ultra-violet light to enhance crosslinking(PSDC-UV).

Separation factor was found to be water-selective in the all pervaporation systems. Extremely high selectivity such as separation factor of more than 5000 was achieved for PSDC with the substitution degree of 12.3mol%, for chelate-complex PMD-Cu^{2+} and also for PSDC-Cu^{2+} in the low and/or high alcohol concentration region of alcohol-water mixture. However, the PSDC irradiated with utraviolet light did not exhibit higher selectivity.

INTRODUCTION

Pervaporation technology has well been introduced into the chemical processes for dehydration of oganic solvents since the middle of 1980. By using GFT composite membrane[1], dehydration system of organic solvents by pervaporation has now been commercialized also in Japan. However, it is said that the dehydration

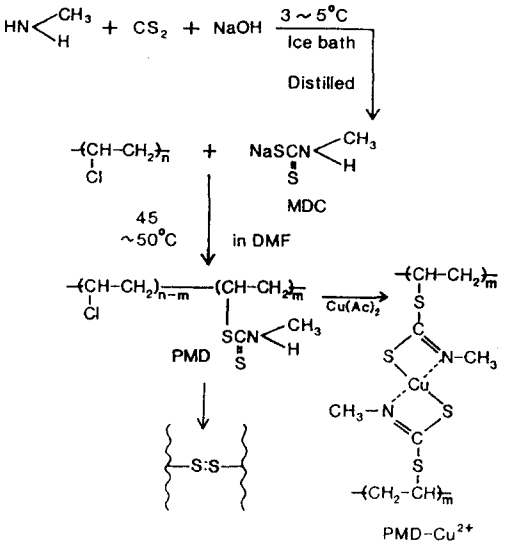
by pervaporation is still in the embryonic stage. A great number of water permeating membranes have so far been studied for dehydration, but most of them are basically water-soluble or ion-exchange membranes, which restrict the membrane application to only a little hydrated organic solvents.

In this study, making use of dithiocarbamation of poly(vinyl chloride), we attempted to obtain a high efficient pervaporation membrane for the purpose of separating aqueous alcohol solution, from the following viewpoints of study. Previously we reported that poly(vinyl chloride) can be easily modified by a dithiocarbamate compound and degree of substitution can be controlled by changing reaction condition[2]. Partially dithiocarbamated PVC was found to have properties of photosensitivity, chelate formation with metals, which looks promising for separation membrane, and excellent antiradiation. Because of equal affinity to both water and alcohol, it can be presumed that the membrane obtained has a advantage of being applicable to the whole region of feed concentration, viz.,low and high water content of organic solvents.

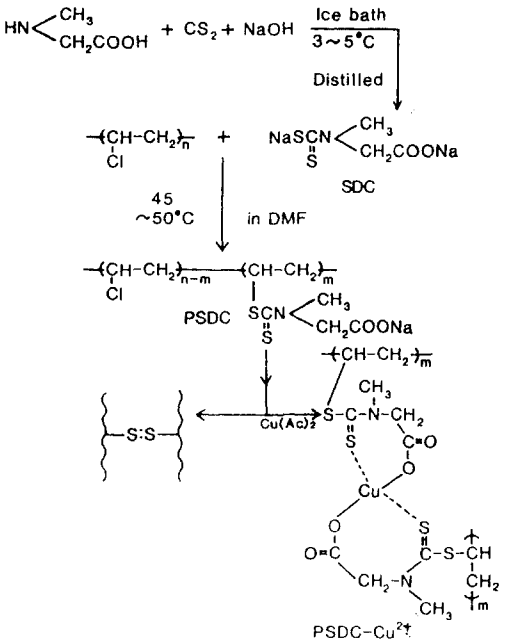
EXPERIMENTAL

Poly(vinyl chloride) and sodium N-methyldithiocarbamate or N-methyl-N-carboxymethyldithiocarbamate(SDC) were homogeneously reacted in DMF to produce partially dithiocarbamated PVC(PMD and PSDC) with degree of substitution of 3.8-18.0 mol%. Membrane of PMD and PSDC were prepared by a casting method. PSDC membrane were substituted with metal ions of Na^+, Li^+ and Cs^+ by immersing PSDC membrane in aqueous solution of the corresponging metal ion salt. PMD and PSDC were reacted with copper ions in alcohol or aqueous solution to obtain chelate complexes of dithiocarbamated PVC respectively(PMD-Cu^{2+}, PSDC-Cu^{2+}). Scheme 1 shows synthesis of PMD and PMD-Cu^{2+}, and Scheme 2 shows synthesis of PSDC and PSDC-Cu^{2+}. The both sides of PSDC membrane were alternately irradiated in air with a ultraviolet light lamp to enhance cross-linking(PSDC-UV).

Permeation and separation of water-alcohol solutions were



Scheme 1 Synthesis of PMD and PMD-Cu^{2+}.



Scheme 2 Synthesis of PSDC and PSDC-Cu^{2+}.

conducted with the separation membranes prepared from these polymer materials. Degree of swelling and alcohol concentration absorbed within the membranes immersed in water-alcohol solution were also measured.

RESULTS AND DISCUSSION

Degree of swelling for PSDC and PSDC-UV against water-alcohol solution showed that dithiocarbamated PVC has no distinct properties of hydrophilicity or hydrophobicity for aqueous alcohol solutions(Fig.1). The analysis revealed that more water was incorporated into the membrane by water-alcohol solution process. Permeation rate of PSDC with the substitution degree of less than 18.0mol% remained little changed all through the concentration region.

Permeation rates and separation factors have maxima in the SDC content region of 12.3mol%, in which a regular trade-off relationship dose not hold(Fig.2). Separation factor was found to be water-selective in the all pervaporation systems. Extremely high selectivity such as separation factor of 5000 was achieved

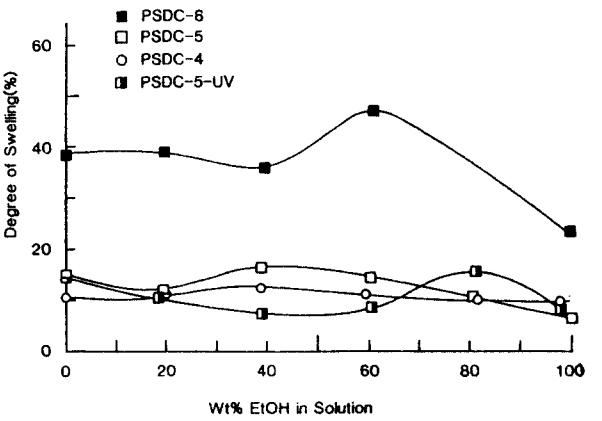


Fig.1 Effect of alcohol concentration on degree of swelling of PSDC and PSDC-UV.

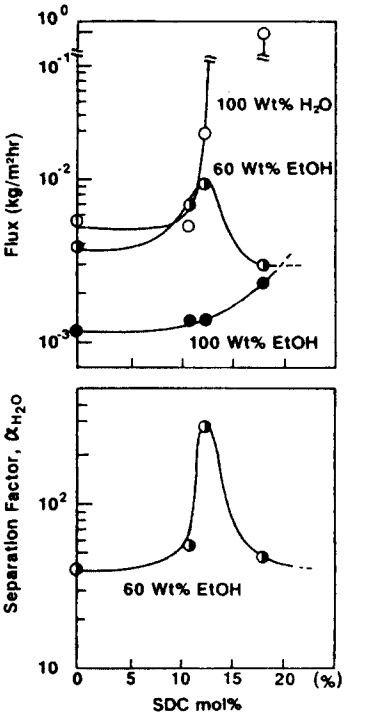


Fig.2 Dependence of flux and separation factor on SDC content for PSDC membranes at 25°C.

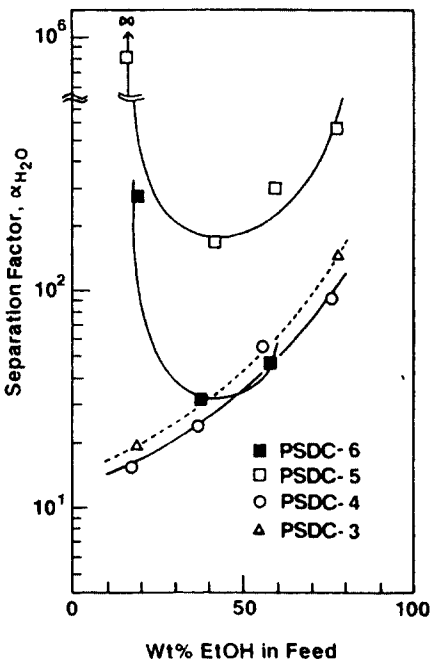


Fig. 3 Effect of feed composition on separation factor of water-ethanol mixture for PSDC.

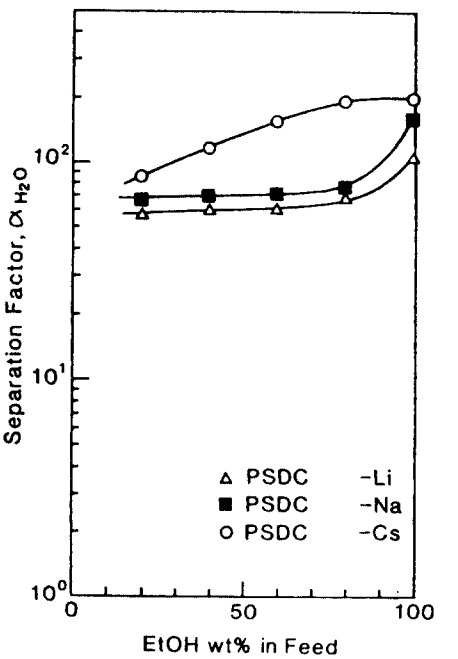


Fig.4 Effect of feed composition on separation factor of water-ethanol mixture for PSDC -Na, -Li and -Cs.

for PSDC with the substitution degree of 12.3mol% in the low alcohol concentration of water-ethanol solution(Fig.3). However, the PSDC irradiated with ultraviolet light did not exhibit higher selectivity.

In the whole region of concentration of ethanol-water mixture, separation factor decreased in the order of PSDC-Cs^+>PSDC-Na^+>PSDC-Li^+(Fig.4). This is also the order of aqua-ion radius of counter ion(Fig.5) and the order was quite in agreement with degree of swelling. Inversely separation factor decreased with an increase of radius of hydrated ion.

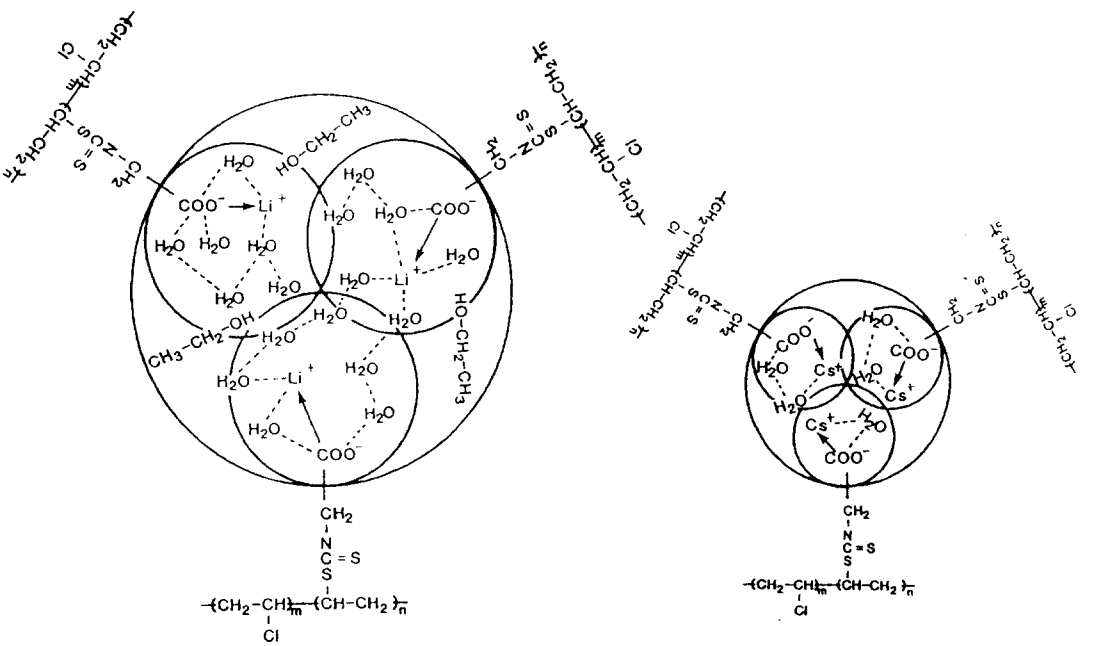


Fig.5 Effect of aquo-ion on separation of water-ethanol through metal substituted PSDC.

Separation factor was found to be water-selective in the all pervaporation systems. It was found that extremely high selectivity such as separation factor of over 5000 was achieved for chelate-complex PMD-Cu^{2+} in the low alcohol concentration region of ethanol-water mixture and the whole alcohol concentration region of 1-propanol-water mixture(Fig.6), and also for PSDC-Cu^{2+}

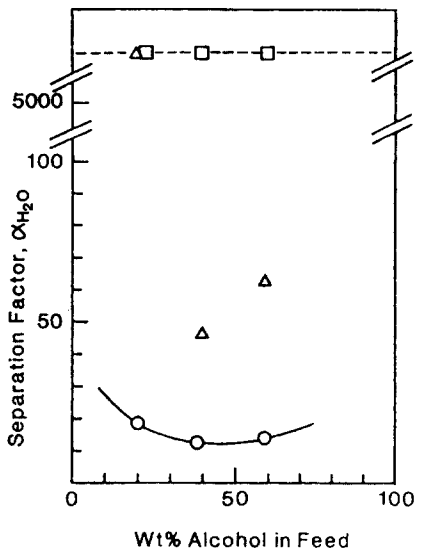


Fig.6 Effect of feed composition on separation factor for PMD-Cu^{2+} at 25°C.
Methanol:○, Ethanol:△, 1-Propanol:□

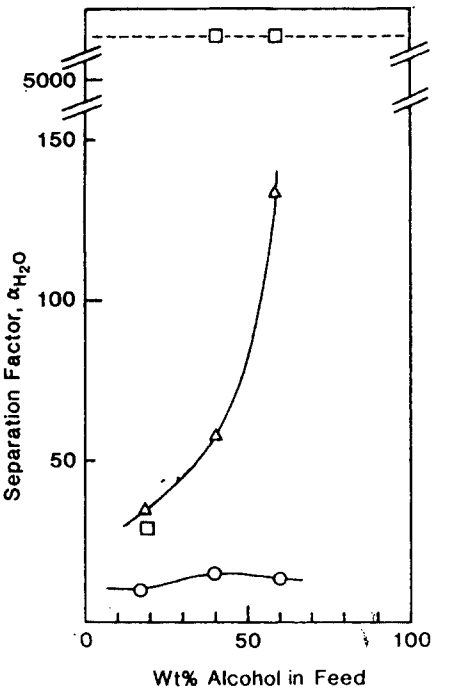


Fig.7 Effect of feed composition on separation factor for PSDC -Cu^{2+} at 25°C.
Methanol:○, Ethanol:△, 1-Propanol:□

in the high alcohol concentration of 1-propanol-water mixture(Fig.7).

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[2]T.Nakagawa,Y.Taniguchi and M.Okawara:Kogyo Kagaku Zasshi,70, 2382(1967);T.Nakagawa and M.Okawara:Kogyo Kagaku Zasshi,71, 2076(1968).