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Effect of additive on the formation of polyacrylonitrile membrane

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Abstract: The effect of additives $CaCl_2$ and $CaCl_2/H_2O$ on the properties of polyacrylonitrile(PAN) ultrafiltration(UF) membranes prepared by phase inversion process was studied. The dissolving capacity of the casting solution for $CaCl_2$ was enhanced by the addition of H_2O. The membranes are characterized in terms of the pure water flux and molecular weight cut-off(MWCO). The addition of $CaCl_2$ or $CaCl_2/H_2O$ to the casting solution increases the resulting membrane permeability.

Keywords: polyacrylonitrile; $CaCl_2$; H_2O; dissolving capacity; ultrafiltration membranes

Introduction

Polyacrylonitrile(PAN) is one of the versatile polymers that are widely used for making membranes due to its mechanical strength, thermostability, stability against chemicals and good solvent resistance. PAN has been used as a substrate for ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) (Kim, 2002; Schamag, 2001; Chandorikar, 1983). The structure of PAN membrane prepared by phase inversion process is asymmetric. The typical asymmetric structure (Lin, 1998) is composed of a thin and dense skin layer and a porous bulk that contains independent finger-like cavities enclosed in a porous solid matrix. The skin layer is responsible for the permeation or rejection of solutes whereas the porous bulk acts as a mechanical support. Koenhen *et al*. (Koenhen, 1977) suggested that the characteristic of the skin layer is influenced by the structure of the casting solution because of the rapid exchange of solvent and nonsolvent when a casting solution is immersed in a coagulation bath containing a nonsolvent.

The addition of a fourth organic or inorganic component to a polymer/solvent/nonsolvent system is a well-known technique to enhance the properties of membranes prepared by phase inversion process (Wang, 2000; Kim, 1996; Petrov, 1996; Tsai, 2000; Machado, 1999; Torrestiana-Sanchez, 1999; Aerts, 2000). Inorganic salt additives in casting solution are considered to change the solvent properties and/or the interaction between the macromolecule chains. In practice, the addition of inorganic salts to casting solutions was reported to be very effective to prepare membranes with higher performance (Lai, 1992; Botino, 1988). It is a common practice to add inorganic halide additives (most often LiCl, $ZnCl_2$) to polyacrylonitrile solution in order to fabricate membranes or filters with better performance (Kulkarni, 1996; Noboru, 1999). Cho *et al*. (Cho, 1994) found that addition of $ZnCl_2$ in the dope solution retards the coagulation rate in water; consequently, the spun fibers have a denser and finer structure. Shinde *et al*. (Shinde, 1999) examined the effect of various inorganic halides (LiCl, $ZnCl_2$ and $AlCl_3$) added to a casting solution of PAN in N, N-dimethyl formamide(DMF). They found that the addition of di- and trivalent salts resulted in membranes with a mode pore size similar to the membrane prepared without any additive, but significantly fewer number of large pores/defects and consequently higher rejection for *E. coli*. In this paper, the effect of $CaCl_2$ and $CaCl_2$ aqueous solution on the performance of PAN membrane was studied.

1 Experimental

1.1 Materials

Polyacrylonitrile (PAN) was purchased from Shanghai Jinshan Chemical Industry Factory and dimethylacetamide (DMAC) from Shanghai Organic Chemical Industry Factory. Calcium chloride($CaCl_2$) was obtained from Beijing Chemical Industry Factory. Lysozyme(14400 Dalton, Shanghai Lizhu), Pepsin(35000 Dalton, TBO, Tokyo), Albumin egg (45000 Dalton, Sigma) and Bovine Serum Albumin(BSA) (67000 Dalton, Beijing Shuangxuan) were used in the rejection test.

1.2 Viscosity determination

Viscosities of 12 wt. % PAN in DMAC containing various content of additives were determined with a falling Ball viscometer(Thermo Haake) at 20℃.

1.3 Preparation of membranes

In airtight glass bottle, calculated quantities of additives were mixed with a definite amount of DMAC. The solution was kept agitated for several hours for complete dissolution. A specified quantity of PAN was subsequently added and the solution was homogenized and kept for deairation.

The casting solution thus obtained was allowed to stand overnight before casting and then cast at room temperature on a smooth glass plate by a glass knife. The thickness of the membranes was controlled by the diameter of adhesive metal wires (0.195 mm) at the sides of the glass knife. No deliberate solvent evaporation period was allowed. The glass plate was immediately immersed in demineralized water at 20℃. Immediately phase inversion starts and after few minutes thin PAN membrane separated out from the glass. The membranes were rinsed with demineralized water repeatedly and wet stored until tested.

1.4 Flux and separation experiments

A common permeation test apparatus was used to measure pure water flux and protein separation of PAN membranes. The pure water flux and protein rejection were measured at 1 atm (Δp) and room temperature. The pure water flux is defined as,

$$\text{Pure water flux } (L/(m^2 \cdot h)) = Q/(A \times t). \quad (1)$$

Where, Q(L) is the volume of the permeation; A (m^2) is the area of the membrane and t (h) is the permeation time. The protein retention is defined as,

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$$R(\%) = (1 - C_p/C_b) \times 100. \quad (2)$$

Where, C_p is the concentration of protein in the permeation and C_b is the concentration of protein in the bulk solution.

The molecular weight cut-off (MWCO) was defined as the molecular weight of the "substance" which can be rejected with above 90% retention. And the MWCO profiles were constructed by measuring the retention values of four proteins: lysozyme, Pepsin, Albumin egg, and Bovine Serum Albumin(BSA). Protein rejection values were obtained using UV at 280 nm(Model UV-120-02, Shimadzu).

2 Results and discussion

2.1 Effect of $CaCl_2$

Table 1 shows the viscosities(η) of the solutions in both neat DMAC and DMAC containing various additives. The addition of $CaCl_2$ to PAN/DMAC solution causes a decrease in η, and the viscosity is lowest (651 mPa·s) when $CaCl_2$ concentration is 2 wt.%. This indicates that the $CaCl_2$ as additive would increase the diffusion rate between solvent and nonsolvent (Shinde, 1999). Reuvers (Reuvers, 1987) designated instantaneous and delayed demixing as a cause of porous and dense skin membranes, respectively. Instantaneous demixing should have a quick exchange rate of solvent and non-solvent, and delayed demixing have a slow rate. Some researchers have attempted to control the membrane morphology by adjusting the exchange rate of solvent and non-solvent(Cabasso,1976; 1977).

The effect of the concentration of $CaCl_2$ in the casting solution on the flux of the resulting membranes could clearly be observed with a series of PAN membranes prepared under identical conditions(Table 1). It is clear from the data shown in Table 1 that an increase in the concentration of $CaCl_2$ in the casting solution leads to an increase in membrane pure water flux and the pure water permeability rate increases almost linearly. When the concentration of $CaCl_2$ is 3 wt.%, the pure water flux of PAN membrane is 681 $L/(m^2 \cdot h)$ and, all of PAN membranes prepared from $CaCl_2$ have considerably higher flux than membranes prepared from neat DMAC.

Table 1 Effect of $CaCl_2$ on pure water permeability of PAN membranes without water

Membrane	Composition of casting solution, wt.%			Solution viscosity, mPa·s	Flux of the pure water, $L/(m^2 \cdot h)$	Retention of BSA, %
	P	S	A			
PAN1a	12	88	–	1399	248	93
PAN2a	12	87	1	963	450	93
PAN3a	12	86	2	651	540	92
PAN4a	12	85	3	708	681	92

Notes: P. polyacrylonitrile; S. DMAC; A. $CaCl_2$; coagulation bath-demineralized water at 20℃

The molecular weight cut off (MWCO) profiles are constructed for PAN membranes by measuring solute separation for four proteins of molecular weight ranging from 14400 to 67000 Dalton. For the various membranes prepared from $CaCl_2$ as additive, the molecular weight cut off(MWCO) profiles(Fig.1) are superposed at molecular weight of protein higher than 35000 Dalton and the molecular weight cut off is found to be around 60000 Dalton. The results indicated that $CaCl_2$ as additive can increase the pure water flux of PAN membrane and does not change the average pore size significantly compared with the PAN membrane prepared without any additive in the casting solution. Shinde *et al*. (Shinde, 1999) reached the same conclusion by examining the effect of various inorganic halides (LiCl, $ZnCl_2$ and $AlCl_3$) added to a casting solution of PAN in N, N-dimethyl formamide(DMF).

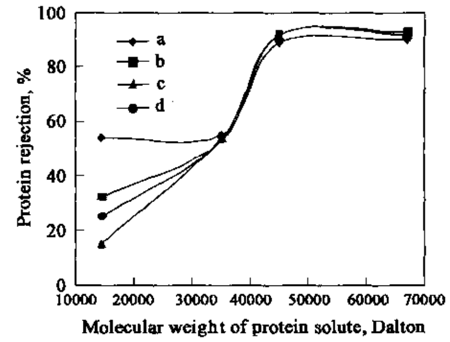

Fig. 1 MWCO profile of PAN membranes prepared from different concentrations of $CaCl_2$ (wt.%). $CaCl_2$ concentration: a = 0; b = 1; c = 2 and d = 3.

2.2 Effect of $CaCl_2$ aqueous solution

Inorganic salts additive as pore-forming regent can be used to increase the permeability of porous membrane, however, it is usually impossible to increase the concentration of a salt in the polymer solution beyond a certain value because of solubility limitations. Kraus *et al*. (Kraus, 1979) found that the salt concentration may be increased further by adding a different salt, preferably one having no common ion with the first salt. Here, the addition of H_2O can increase the solubility of solvent, and then increase the inorganic salt concentration. The effect of water on the PAN membrane performance was used as the second additive with $CaCl_2$ additive.

2.2.1 Properties of PAN/$CaCl_2$/H_2O/DMAC solution

The introduction of water as a non-solvent additive (NSA) into the polymer solution increases the polarity of solvent(DMAC) and the concentration of $CaCl_2$ in casting solution can be increased to 9 wt.%(Table 2). The η of casting solution increases with the addition of water, and the increase is directly proportional to water concentration(Table 3). Wang *et al*. (Wang, 2000a; 2000b) used water as additive and found that the viscosity increased too.

Table 2 Effect of $CaCl_2$ concentration on pure water permeability of PAN membranes with water

Membrane	Composition of casting solution, wt.%				Solution viscosity, mPa·s	Flux of the pure water, $L/(m^2 \cdot h)$	Retention of BSA, %
	P	S	$CaCl_2$	H_2O			
PAN1b	12	84	3	1	765	785	97
PAN2b	12	82	5	1	968	857	86
PAN3b	12	80	7	1	1205	906	86
PAN4b	12	78	9	1	1450	1050	70

Notes: P. polyacrylonitrile; S. DMAC; coagulation bath-demineralized water at 20℃

2.2.2 Effect of $CaCl_2$ concentration

The polymer dope with 12 wt.% PAN and 1 wt.% H_2O was used to study this effect. The concentration of $CaCl_2$ is increased from 3 wt.% to 9 wt.%. The permeability and protein retention of the PAN membranes is shown in Table 2. It can be seen that increase in $CaCl_2$ concentration gives PAN membranes with higher water permeation rates in all cases, but decreased protein retention.

2.2.3 Effect of H_2O concentration

The effect of H_2O concentration in the casting solution on membrane performance is studied by changing the amount of H_2O in casting solution, without changing the polymer and $CaCl_2$ concentration in the dope. Table 3 shows the pure water flux and protein retention of PAN membranes. The pure water flux increases with the increase of H_2O concentration in the dope, while the protein retention keeps unchanged. From Table 2 and 3, it can be seen that the pure water flux of PAN membrane is related to the amount of additive ($CaCl_2$ and H_2O) in the dope, and has no matter with the $CaCl_2$ and the H_2O concentration respectively. However, the protein retention of PAN membrane is controlled by the $CaCl_2$ concentration in the dope. It would be decreased by increasing the $CaCl_2$ concentration while the H_2O concentration was unchanged. The unchanged protein retention with higher concentration of H_2O can be gotten. Wang *et al*. (Wang, 1996) found that suitable small molecular non-solvent additives is useful in eliminating the large macrovoid formation. Fig. 2 shows that H_2O as non-solvent increases the protein retention of PAN membrane, which means the pore size of PAN membrane becomes small.

Table 3 Effect of H_2O concentration on pure water permeability of PAN membranes

Membrane	Composition of casting solution, wt.%				Solution viscosity, mPa·s	Flux of the pure water, $L/(m^2 \cdot h)$	Retention of BSA, %
	P	S	$CaCl_2$	H_2O			
PAN1c	12	84	3	1	765	785	97
PAN2c	12	81	3	4	964	1054	97
PAN3c	12	79	3	6	1156	988	95

Notes: P. polyacrylonitrile; S. DMAC; coagulation bath-demineralized water at 20℃

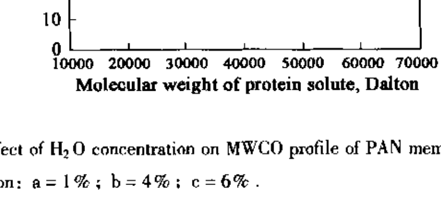

Fig. 2 Effect of H_2O concentration on MWCO profile of PAN membranes H_2O concentration: a = 1%; b = 4%; c = 6%.

3 Conclusions

Membranes with high permeation can be prepared from polyacrylonitrile polymer with $CaCl_2$ or $CaCl_2$ aqueous solution as additive, DMAC as solvent and water as the coagulation bath. The permeation of PAN membrane can be controlled by the amount of additives.

Changing concentration of $CaCl_2$ from 1 wt.% to 3 wt.% increases the membrane permeation and has little influence on the average pore radius.

The $CaCl_2$ concentration in the PAN/DMAC system can be increased to 9 wt.% as the addition of H_2O in casting solution.

The pure water flux of PAN membrane is controlled by the amount of additives. The more additives, the higher pure water fluxes.

The protein retention of PAN membrane is controlled by the content of $CaCl_2$ in the casting solution. The higher the $CaCl_2$ content, the lower the protein retention.

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