Poly(sodium vinylsulfonate)/chitosan membranes with sulfonate ionic cross-linking and free sulfate groups: preparation and application in alcohol dehydration

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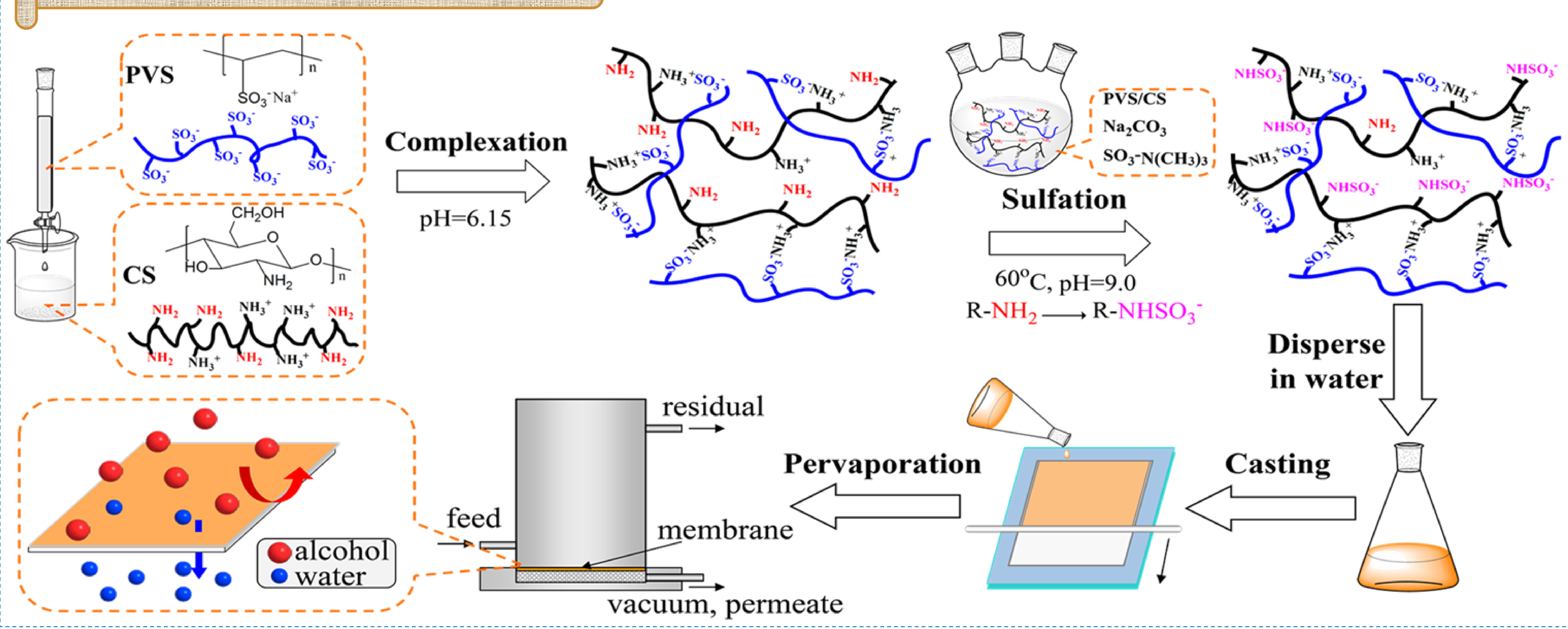
Introduction

Polyelectrolyte complexes (PECs) membranes present both high permeability and selectivity for solvent dehydration via pervaporation, but are less satisfactory in separating mixtures with strong interactions such as water/ethanol. Inspired by the fact that strong acid groups such as sulfonate and sulfate groups possess high hydrophilicity and the ability to form stable ion cross-linking structures, we expect that the introduction of strong acid groups will enhance the pervaporation dehydration performance. To this end we produce S-PVS/CS PECs with both sulfonate ionic cross-linking structures and free sulfate groups, which are fabricated from chitosan (CS) and poly(sodium vinylsulfonate, PVS) via the method of "complexation-sulfation". Unsurprisingly, S-PVS/CS membranes demonstrated significantly enhanced dehydrating performance.

Experimental



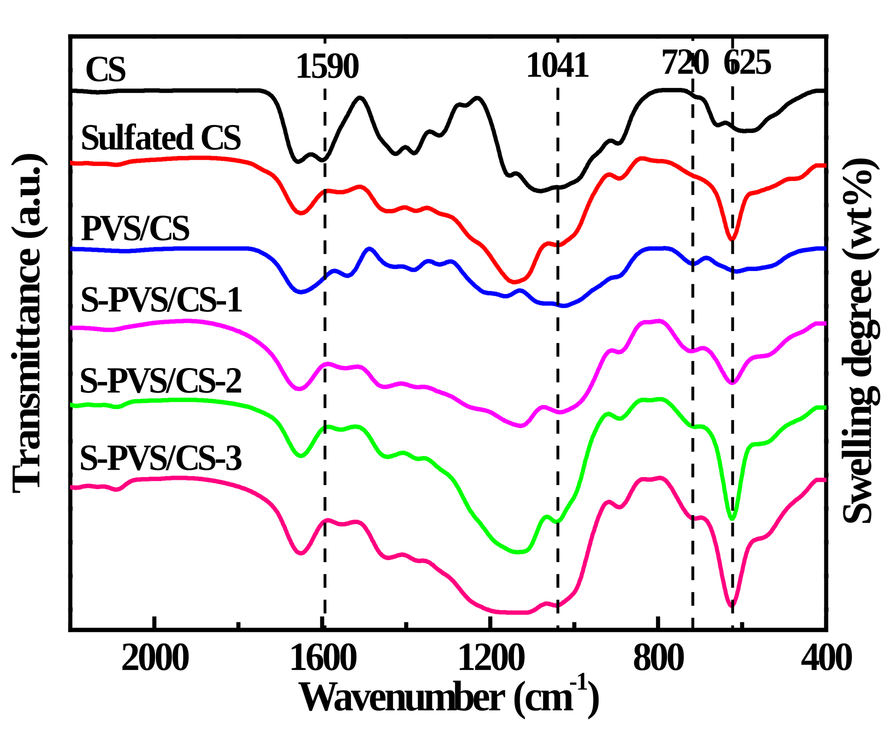
Results and discussion

I. Characterizations

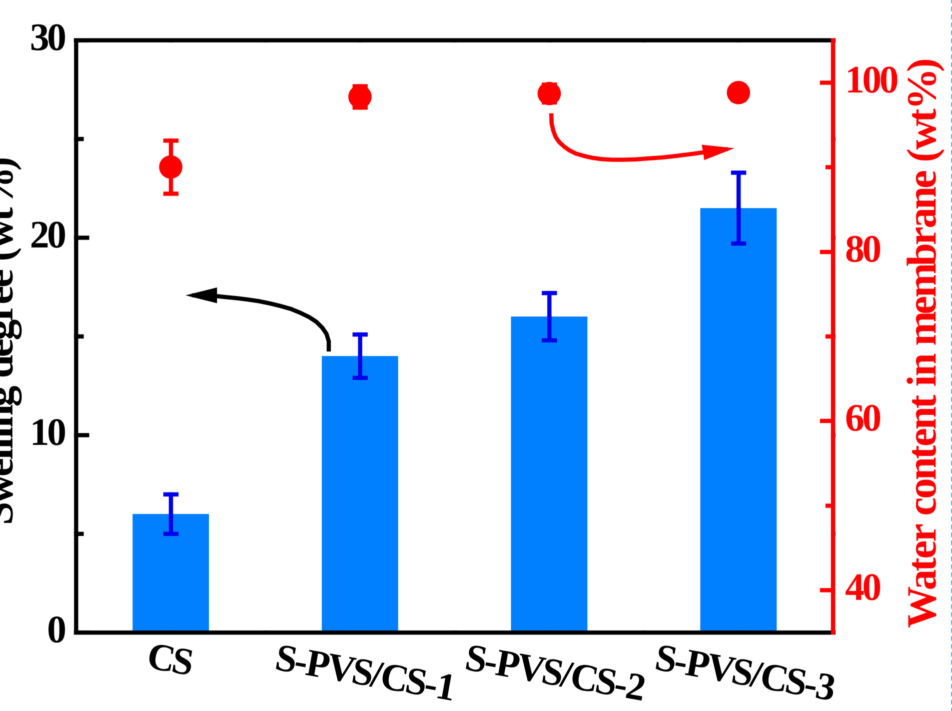
Table1. Compositions (determined by XPS), ζ potential and water contact angle of S-PVS/CS PECs, CS, and PVS membranes.

Samples	Molar ratio $(CH_3)_3N\bullet SO_3$:CS	S (At. %)	N (At. %)	S:N	DS[a]	ζ potential (mV)	WCA (°)
PVS/CS	-	1.43	3.52	0.406	-	-	47
S-PVS/CS-1	1	1.46	2.56	0.570	16.4%	-54.7 ± 1.8	38
S-PVS/CS-2	2	1.52	2.17	0.700	29.4%	-62.4 ± 2.2	33
S-PVS/CS-3	3	1.64	1.80	0.911	50.5%	-73.1 ± 3.0	21

[a] *Degree of sulfation. The ~10% undeacetylated units were taken into account as unreacted units*

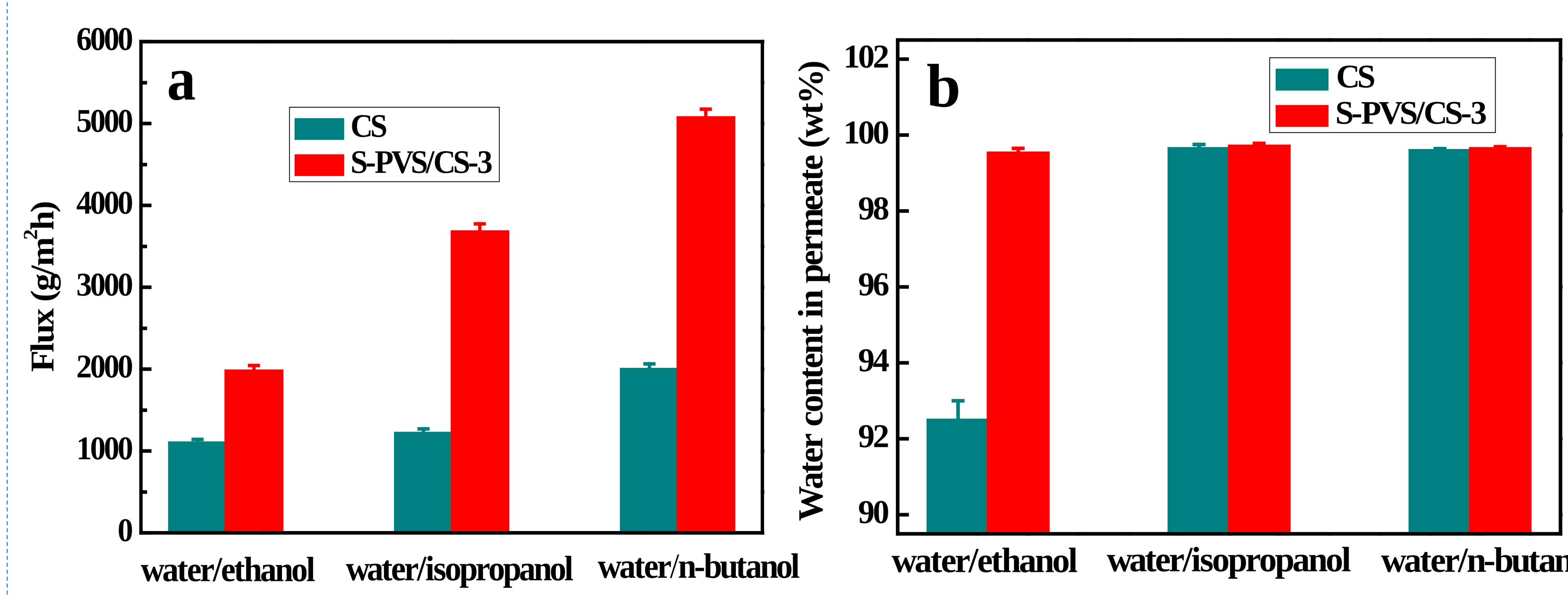


FT-IR spectra of CS, Sulfated CS, PVS/CS and S-PVS/CS.



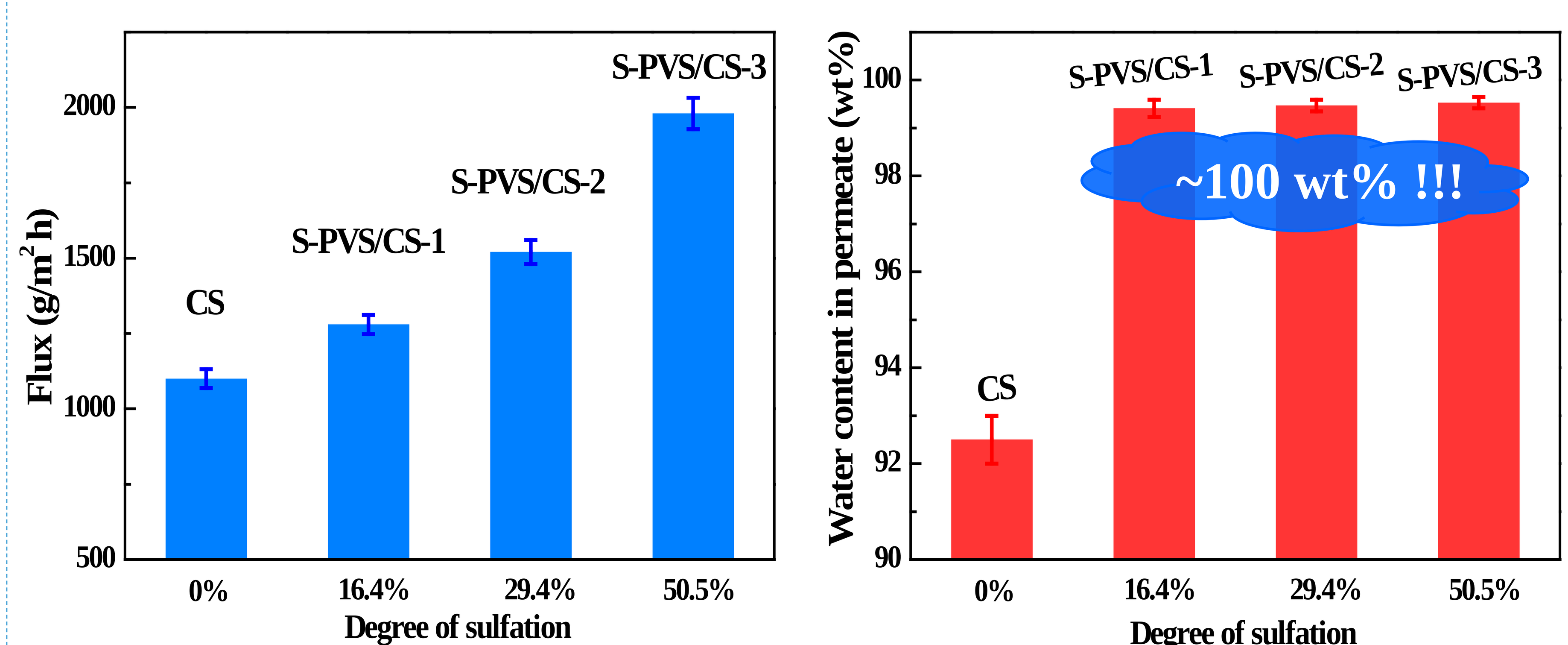
Swelling behavior of CS and S-PVS/CS PECMs immersed in 10 wt% water/ethanol mixture at 50 °C

II. Dehydrating different water-alcohol mixtures



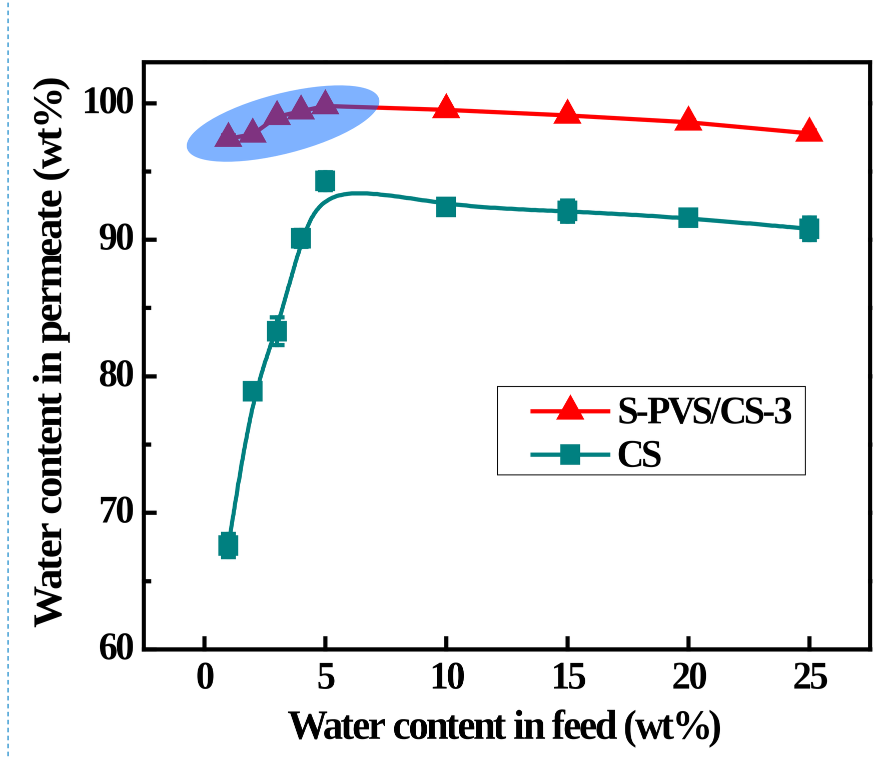
Permeate flux (a) and water content in permeate (b) of CS and S-PVS/CS-3 PECM in dehydrating 10 wt% water/ethanol, water/isopropanol and water/n-butanol mixtures, respectively, at 70oC.

III. Effect of Degree of sulfation on PV performance

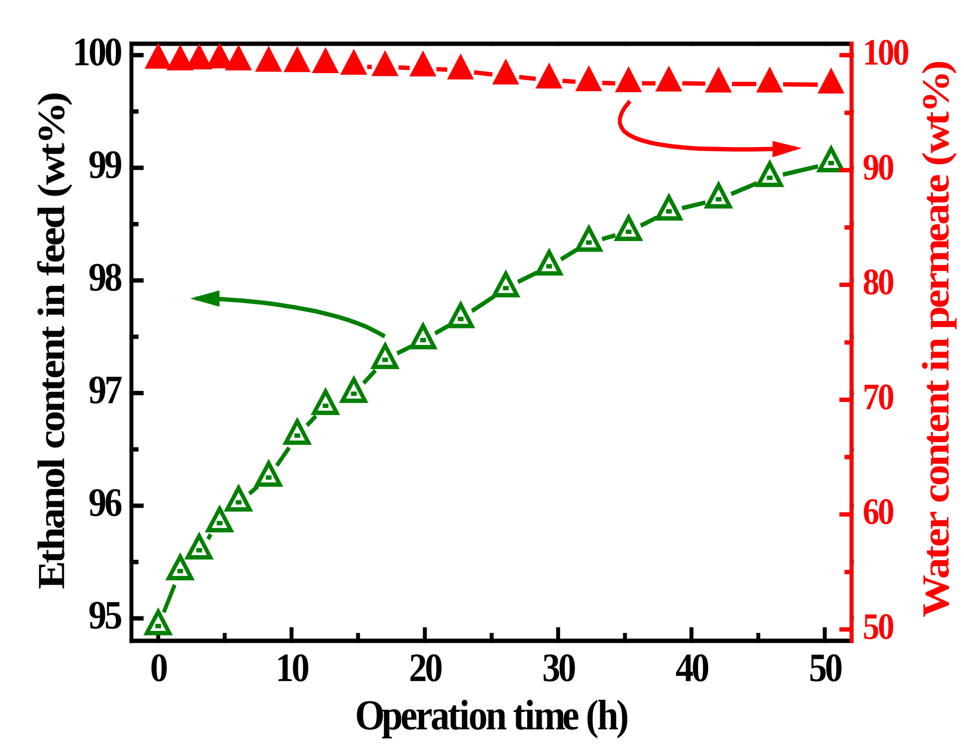


Effect of feed temperature on flux (a) and water in permeate (b) of CS membrane and S-PVS/CS PECMs in dehydrating 10 wt% water/ethanol mixture.

IV. PV performance at low feed water content



Water content in permeate for CS membrane and S-PVS/CS-3 PECM at 50 °C.



Continuous dehydrating an azeotropic water/ethanol mixture by S-PVA/CS-3 PECM. (18.09 cm^2, 500 g feed, 70°C)

Conclusions

- Water-soluble polyelectrolyte complexes with adjustable sulfonate ionic cross-linking and free sulfate groups were fabricated.
- Pervaporation performance was proportional to the amount of free sulfate groups.
- The flux and permeate water content in of S-PVS/CS-3 were 1980 g/m^2h and 99.55 wt% (70°C, 10 wt% water/ethanol), which outperform most previously reported membranes.
- PECMs were able to dehydrate an azeotropic water/ethanol mixture to fuel grade ethanol.