Supporting Information

Highly Stable Acid-Base Complex Membrane for Ethanol Dehydration by Pervaporation Separation

Council of Scientific & Industrial Research -Central Salt and Marine Chemicals Research Institute, G.B. Marg, Bhavnagar-364002 (Gujarat), India

Process of Ethanol dehydration of pervaporation:

Solution-diffusion mechanism takes place during the mass transfer through dense membrane in pervaporation separation. In a binary mixture permeating molecules interact with each other as well as with the polymeric considering to be a ternary system. The flux of the i^{th} component through the membrane is given by Fick's first law [1] as:

$$J_i = -\rho_m D_i \left(\frac{dW_{im}}{dl}\right) \tag{1}$$

The different parameters like temperature, concentration of the permeating components in the membrane and their coupling effect, affects diffusion coefficient. If we consider that the temperature is constant, then diffusion coefficient for components i and j can be described as [2]:

$$D_i = D_{io} \exp(A_{ii}W_{im} + A_{ij}W_{im})$$
⁽²⁾

and

$$D_j = D_{jo} \exp(A_{jj}W_{jm} + A_{ji}W_{jm})$$
(3)

where the constants A_{ii} , A_{ij} , A_{ji} , and A_{jj} , take into account the change in penetrant mobility in the swollen polymer and D_{i0} is the limiting diffusion coefficient at infinite dilution and A_{ij} is the 'plasticization' applied by the *j*th component on the diffusion of *i*th component.

By applying Eqs. (2) and (3) in Eq. (1) and integrating it over the thickness of the membrane with the assumption that the concentrations of the permeating components at the downstream are zero would yield the integrated flux for the i^{th} and j^{th} components:

$$J_{i} = \left(\frac{D_{io}\rho_{m}}{(A_{ii} - A_{ij})l}\right) \left[exp\left(A_{ii}W_{imf} + A_{ij}W_{jmf}\right) - exp\left(A_{ij}\right)\right]$$
(4)

$$J_{j} = \left(\frac{D_{jo}\rho_{m}}{(A_{jj} - A_{ji})l}\right) \left[exp(A_{jj}W_{jmf} + A_{ji}W_{jmf}) - exp(A_{ji})\right]$$
(5)

Plasticizing coefficient, A_{ii} , A_{jj} reflect the ability of a penetrant to increase self-diffusion; whereas, plasticizing coefficient, A_{ij} reflect the ability of less soluble penetrant (AN - j) to increase diffusion of more soluble water (*i*). It may be considered that permeability through self-diffusion is far more effective than coupled diffusion. Accordingly, one may assume, $A_{ii} \gg A_{ij}$ and $A_{jj} \gg A_{ji}$. Considering such assumptions we get equations:

$$J_{i} = \left(\frac{D_{io}\rho_{m}}{A_{ii}l}\right) \left[exp\left(A_{ii}W_{imf} + A_{ij}W_{jmf}\right) - 1\right]$$
(6)

and

$$J_{j} = \left(\frac{D_{jo}\rho_{m}}{A_{jj}l}\right) \left[exp\left(A_{jj}W_{jmf} + A_{ji}W_{jmf}\right) - 1\right]$$
(7)

 J_i and J_j are obtained from the permeation data, and from the sorption data W_{imf} and W_{jmf} can be calculated. From the Equations (6) and (7) the diffusion coefficient at different feed concentrations along with the plasticization coefficient can be determined.

- 1. Wijmans JG, Baker RW, Journal of Membrane Science 1995; 107: 1-21
- Mandal MK, Santc SB, Bhattacharya PK, Coll. Surf. A: Phys. Eng. Asp. 2011; 373: 11–21

Table S1: Elemental analysis of S-4 membrane before and after dipping 5 days in feed solution

| Elements | % Element presence membrane | | | |
|-------------------------------|-----------------------------|------|------|-------|
| - | С | Н | Ν | S |
| S-4 | 40.27 | 5.99 | 7.01 | 11.30 |
| S-4 membrane after 30 Days | 41.21 | 5.81 | 6.79 | 11.81 |



Figure S1:



Figure S2:



