

Multi-scales association modeling of membrane water resistance indexes

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Abstract In order to quantify and predict the water resistance of membrane, a multi-scales association model was built up based on the Fick's second law. Two water resistance indexes, balance time and seepage velocity, were put forward and calculated by the model for measuring the property of membrane water resistance. The association model linked macro-scale factors and micro-scale parameters together. The influence of macro-scale factors, environmental temperature and membrane thickness, and micro-scale parameters, water molecules diffusivity, membrane saturated water absorption rate and water escape concentration, were discussed. The properties of water resistances for two groups including 10 waterborne acrylate membranes samples were measured for validating the indexes calculated by the model. The well consistency between the results of calculations and experiments proved that the method of multi-scales association modeling for quantifying and predicting the membrane water resistance was feasible.

Keywords Multi-scale modeling · Membrane · Water resistance

1 Introduction

As the development of water-borne coatings, aqueous membrane materials were more and more used in many fields, such as electrical, biology and building. But because

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of hydrophilic properties, the membrane water resistance became an important factor for assessing the membrane materials performance. How to improve the service life of membrane in a moist environment became a key problem. An evaluation standard should be defined at first. But until now, there was not a theoretical rule had been built for quantitative describing the water resistance of membranes.

Recently, multi-scale problem had received increasing attention from many branches of science and fields [1]. SA Baeurle gave a survey about the multi-scale modeling by field-theoretic methodologies [2]. Multi-scale modeling and simulation of polymer nanocomposites were introduced by QH Zeng [3]. J Leon and M Manna constructed discrete systems of evolution equations by the method of multi-scale analysis [4]. The multi-scale model combined informatics-based optimal design was applied to the catalytic decomposition of ammonia [5]. One of multi-scale study methods was build up an association model from microscopic to macroscopic [6]. Molecule dynamic simulation [7], mathematical coupling [8,9] were used in solving the multi-scale problem.

In this study, a multi-scales association model, including the scales from microscopic to macroscopic, was set up based on the Fick's second law. Macro-scale factors like environmental temperature (T) and membrane height (H) and micro-scale parameters such as water molecules diffusivity (D), water absorption rate of membrane (C_{B0}) and water escape concentration (C_{B1}) were imported into the model. The model could give a quantitative description for the membrane water resistance characterization. As a part of membrane service life, the evaluation of water resistance could be used as a guide for choosing the suitable membrane for the specified condition.

2 Multi-scales association model designing

2.1 Definition, relationships and interactions

The meaning of water resistance should be defined at first. As the description of standard method, the water resistance was measured as how long time it would hold its properties when it was put in water. But it was different from the membrane materials. In this paper, the membrane water resistance was defined by two water resistance indexes which represented the time of protecting substrate away from the erosion of water. After that time, water would accumulate in the interfaces between the membrane and substrate and damage the substrate much faster than before it, although the film might not be spoil.

There were so many factors and parameters influenced the performance of membrane water resistance. Those uppermost were picked out. The relationships and interactions between them were cleared and showed by a diagram (see Fig. 1).

Contents in rectangles, monomer ration, temperature and membrane thickness, were macro-scale factors which were adjustable and could be controlled. Data in ellipse, water molecules diffusivity (D), saturated water absorption rate of membrane (C_{B0}) and water escape concentration (C_{B1}), were micro-scale parameters which were influenced by macro-scale factors. Membrane density was a special intermediate variable during the process of describing water resistance. It was changed by macro-scale

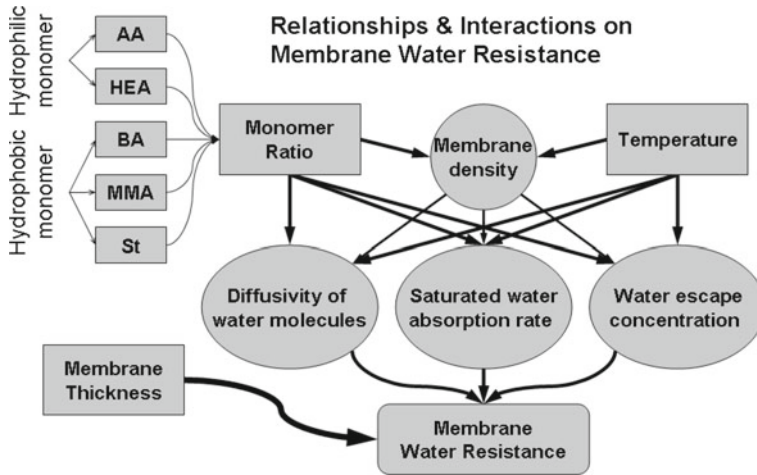


Fig. 1 Diagram of relationships and interactions in membrane water resistance study

factors (monomer ration and temperature) and affected other micro-scale parameters (D , C_{B0} and C_{B1}) in the same time.

D , C_{B0} and C_{B1} were all existed in both of the Fick's first law and second law. Fick's second law described a process of unsteady diffusion and the first law aimed at steady diffusion. Comparing the two laws, Fick's second law was more suitable for this study. A time dependent expression could obtain as an index for measuring the membrane water resistance.

2.2 Application of Fick's second law

Fick's second law (see Fig. 2) was used to describe a process of unsteady diffusion. It predicted how diffusion caused the concentration field to change with time. Fick's second law was defined as Eq. 1.

$$\frac{\partial \phi}{\partial t} = D \frac{\partial^2 \phi}{\partial x^2} \quad (1)$$

where ϕ was volume concentration of water (m^3/m^3), t was time (s), D was the diffusion coefficient (m^2/s), x was the position far away from the upper surface (m). By these equation, the water concentration at the position of h far away from the upper surface after t time ($C(h,t)$) could be calculated (see Fig. 2).

After substituted the macro-scale factors and micro-scale parameters into Fick's equation, the time related variable could be calculated. So a new membrane water resistance index, balance time (t_B), was put forward for measuring the time from initial state (t_0) to the moment that the water concentration at membrane lower surface reached the escape concentration (C_{B1}). The boundary conditions were defined as Eq. 2.

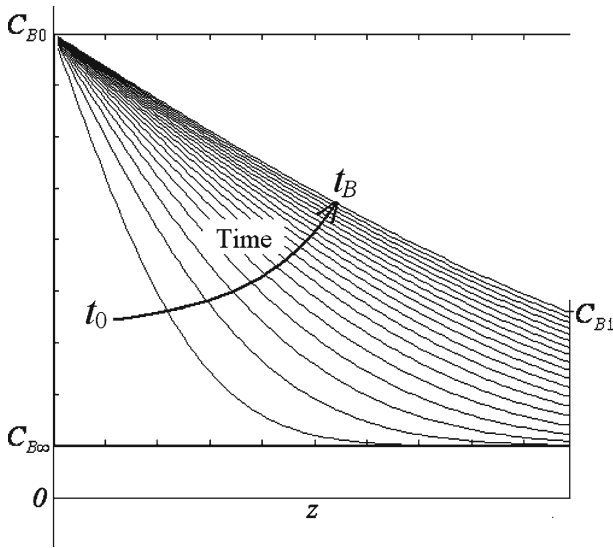


Fig. 2 The state of concentration field with time change (t_0 : initial time, t_B : balance time, z : thickness of membrane, C_{B0} : water concentration of membrane upper surface, C_{B1} : water concentration of membrane lower surface, $C_{B\infty}$: water concentration of environment)

$$\begin{cases} C(0, t_0) = C_{B0} \\ C(x, t_0) = C_{B\infty}, x \in (0, H] \\ C(0, t_B) = C_{B0} \\ C(H, t_B) = C_{B1} \end{cases} \quad (2)$$

where H was the thickness of membrane. Membranes with different thickness could be calculated by the model. And in experiments, the thickness could be controlled accurately by wet membranes coaters (Shanghai, China).

In order to simplify Eq. 1, a new variable ξ was defined as Eq. 3.

$$\xi \equiv \frac{H}{2\sqrt{D_Z \cdot t_B}} \quad (3)$$

where D_Z was the diffusivity of the water molecules along the thickness direction (Z -axis) in the membrane. t_B was the diffusion time of balance status. $2\sqrt{D_Z \cdot t_B}$, which called the diffusion length, provided a measurement of how far the diffusion of water molecules in the thickness direction at time t_B .

Both of Eqs. 2 and 3 substituted in Eq. 1 to found

$$C(H, t_B) = C_{B0} + (C_{B\infty} - C_{B0}) \cdot \text{erf}(\xi) \quad (4)$$

The function and parameters in Eq. 4 was described as follows:

$C(H, t_B)$ was the concentration at the membrane lower surface after t_B time of diffusion.

Function erf was called error function (or Gauss error function). It was a special function (non-elementary) of sigmoid shape which occurs in probability, statistics, materials science and partial differential equations. It is defined as Eq. 5:

$$\operatorname{erf}(\xi) \equiv \frac{2}{\sqrt{\pi}} \int_0^{\xi} e^{-\xi^2} d\xi \quad (5)$$

C_{B0} was the saturated water absorption rate of membrane, which was calculated as Eq. 6 [10].

$$C_{B0} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100\% \quad (6)$$

W_{dry} was the weight of dry membrane, W_{wet} was the weight of wet membrane which was immersed in deionized water until constant weight.

C_{B1} was the escape concentration of water molecule in the membrane lower surface. It means that if the water content at the lower surface increasing to C_{B1} , the membrane could be considered reached its balance status.

$C_{B\infty}$ was the balance water absorption rate of membrane. Because when the membrane placed in a real condition, water molecules would penetrate into the membrane slowly. After a long time, the seepage reached balance. The water absorption rate at that time was measured as $C_{B\infty}$.

Then a new group of nonlinear equations (Eq. 7) was found by substituted Eqs. 3, 4, 5 and the actual parameters.

$$\begin{cases} C(H, t_B) = C_{B0} + (C_{B\infty} - C_{B0}) \cdot \operatorname{erf}(\xi) \\ C_{B1} = C(H, t_B) \\ \operatorname{erf}(\xi) = 2/\sqrt{\pi} \cdot \int_0^{\xi} e^{-\xi^2} d\xi \\ \xi = H/2\sqrt{D_Z \cdot t_B} \end{cases} \quad (7)$$

Although the variables in Eq. 7 like thickness of membrane (H), diffusivity (D_Z), saturated water absorption rate (C_{B0}) and water escape concentration (C_{B1}) were known. But it was also a hard word for solving the balance time t_B , and it was figured out by an iterative method in this study.

Balance time (t_B) as one of membrane water resistance index could reflect the water resistance, but it was not an intuitive parameter which was comparable with the experiment results. So based on the balance time, a new variable seepage velocity (SV) was defined as another membrane water resistance index in Eq. 8. Seepage velocity stood for the degree of water molecules infiltration in the membrane at the status of unsteady diffusion.

$$SV = \frac{H \cdot \bar{C}}{t_B} = \frac{\int_{z=0}^{z=H} C(z, t_B) dz}{t_B} \quad (8)$$

2.3 Hypotheses

As the complex relationships and interactions, it was necessary making some simplifications to make the research more clear. Just the primary factors were discussed, and several hypotheses were proposed to ignore the effects caused by minor factors. First, there was an extremely thin layer on the membrane upper surface, which had reached saturated water absorption rate on the initial time. The layer provided the pressure difference between the two sides of the membrane. Second, the interior structure of the membrane was homogeneous and the water molecules diffusion was isotropic (described by diffusivity was $D_X = D_Y = D_Z$). So the diffusivity on Z-axis (D_Z) equaled to one third of D (namely $D_Z = D/3$). Third, membranes were fully dried. They were considered no water molecule exist, although there were some water molecules in them more or less in the real condition.

2.4 Diffusivity simulation

Diffusivity was an important parameter in this study. Water molecules diffusivity in membranes was calculated by Einstein relation as follows (see Eq. 9):

$$D = \frac{1}{6n} \lim_{t \rightarrow \infty} \frac{d}{dt} \sum_{i=1}^n [r_i(t) - r_i(0)]^2 \quad (9)$$

where n represented the number of water molecules. $r_i(0)$ was the original coordinates of i_{th} water molecule and $r_i(t)$ was the position of duration t . $[r_i(t) - r_i(0)]^2$, which was called mean squared displacements (MSD), stands for the displacement of water molecule during $0 \sim t$ time. This process was completed by molecular dynamics (MD) method [11] and the diffusivities were calculated by Eq. 10 [12].

$$D = \frac{\text{MSD}}{6 \cdot t} \quad (10)$$

2.5 Experimental validate method

In order to verify the correctness of seepage velocity calculated, a series of experiments have done. Primary monomers for synthesis included acrylic acid (AA), butyl acrylate (BA), hydroxyethyl acrylate (HEA), methyl methacrylate (MMA) and styrene (St). Membranes with different monomer ratio were made, which were listed in Table 1.

Base on the default monomer ratio (item 0, BA:MMA:St=18:10:5), two groups of films were made under the same condition. In group I, different contents of AA were added (item: 1~4). Both of AA and HEA were added in group II (item: 5~9). After drying, each membrane was covered to the top of tubular container which was

Table 1 Recipe for the membrane synthesis

Group	Item	AA	BA	HEA	MMA	St
	0	0	18	0	10	5
I	1	1	18	0	10	5
	2	2	18	0	10	5
	3	3	18	0	10	5
	4	4	18	0	10	5
II	5	1	18	1	10	5
	6	2	18	2	10	5
	7	3	18	3	10	5
	8	4	18	4	10	5
	9	5	18	5	10	5

filled with some water. The top area of tube was measured as S . The weight of system included the membrane, the container and water was weighted as W_0 . Put the system into a drying oven. After several hours (T), the system weight changed from W_0 to W_t because water molecule diffused out of the container. The volume fluxes (EVF, unit: m/h) on the unit area could be calculated as Eq. 11.

$$\text{EVF} = \frac{\Delta W}{\rho_{\text{H}_2\text{O}} \cdot S \cdot T} = \frac{W_0 - W_t}{\rho_{\text{H}_2\text{O}} \cdot S \cdot T} \quad (11)$$

3 Results and discussion

3.1 Effect of membrane thickness

Membrane thickness was the simplest factor of the water resistance. The thicker membrane had a better protect capability to the substrate because the longer balance time was needed. A longer balance time and lower seepage velocity were got for thicker membrane by the model, seeing Fig. 3.

Figure 3 showed the influence of membranes thickness on water resistance. As the thickness increased from 25 to 75 μm , which was three times thicker than 25 μm , the seepage velocity reduced from $2.76 \times 10^{-6} \text{m/s}$ to $1.10 \times 10^{-6} \text{m/s}$ which was nearly three times, too. But the balance time almost increased to 9 times longer than before. The results showed that the thicker membrane was, the better water resistance was, in a suitable thickness range.

3.2 Effect of diffusivity and saturated water absorption rate

The ratio of different monomer in polymer membrane was the decisive factor of influence micro-structure and water resistance. The change of monomer ratio would affect

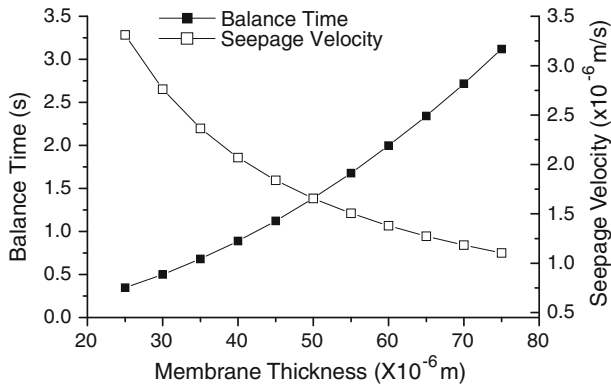


Fig. 3 Water resistance affected by the membrane thickness. ($T = 298\text{ K}$, $D = 10 \times 10^{-10}\text{ m}^2/\text{s}$, $H = 50\ \mu\text{m}$, $C_{B0} = 10\%$, $C_{B1} = 1\%$)

the diffusivity (D) and saturated water absorption rate (C_{B0}), and the influence rules on water resistance indexes were discussed.

Diffusivity was an important parameter in the equations of the Fick's diffusion laws. The diffuse behavior of water molecules in membrane were affected by the binding energies which caused by polymer around it. Binding energies between water molecules and homopolymers from five kind monomers (AA, BA, HEA, MMA, St) were compared. The result showed that the hydrophilic units, such as AA and HEA, had larger binding energies with water. The water molecules were bound closely, so the diffusivities were low. But the binding energies between the water molecules and hydrophobic units, for instance, BA, MMA and St, were much lower than the hydrophilic kind's. So the diffusivities of water molecules in them were higher.

Under the default condition, five fictitious membranes made up were compared. Their diffusivities and binding energy were calculated by molecules simulation. The balance time and seepage velocity were obtained by resolving Eq. 7.

From Fig. 4a, it was found the bigger binding energy was (absolute value), the smaller diffusivity was. As the results shown in Fig. 4b, the diffusivity of membranes made by hydrophilic monomers (AA, HEA) were smaller than that of hydrophobic membranes (BA, MMA, St). The minimum diffusivity D_{AA} was $4.365 \times 10^{-10}\text{ m}^2/\text{s}$, and the maximum value D_{St} was $15.881 \times 10^{-10}\text{ m}^2/\text{s}$. Figure 5 illuminated that the bigger diffusivity, the worse water resistance indexes were. The inverse relation between diffusivity and balance time and direct relation with seepage velocity could be found. All the results were consistent to the fact.

Saturated water absorption rate (C_{B0}) of membranes reflected the capability of containing the water, which was also a parameter related to monomer ratio. By adjusting the ratio of hydrophilic and hydrophobic monomers, the range of C_{B0} was obtained as 7.5% ~ 12.5%. Higher C_{B0} could provide a bigger concentration gradient which could decrease the balance time and increase the seepage velocity. Figure 6 showed the relationship between the balance time, seepage velocity and C_{B0} .

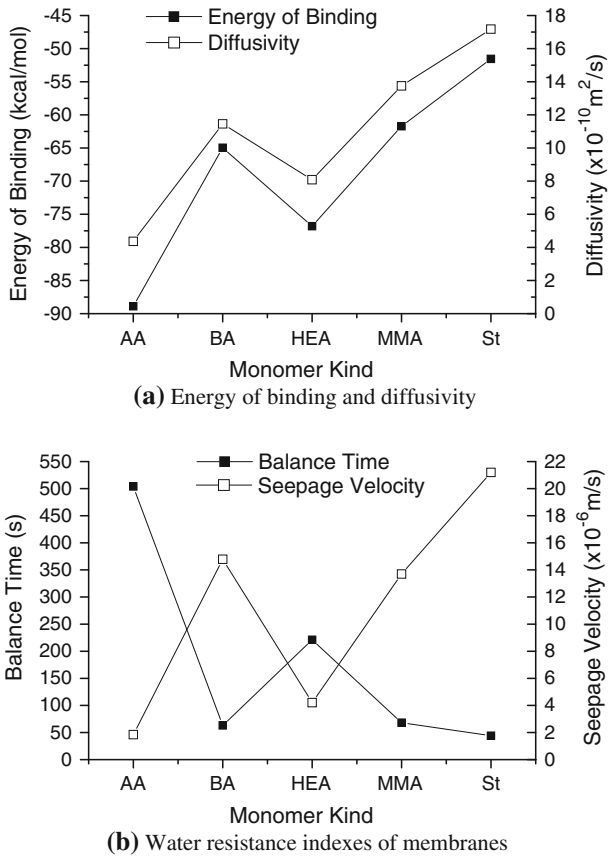


Fig. 4 Compared water resistance indexes of membrane by different monomer homopolymer. ($T = 298 \text{ K}$, $H = 50 \mu\text{m}$, $C_{B0} = 10\%$, $C_{B1} = 1\%$)

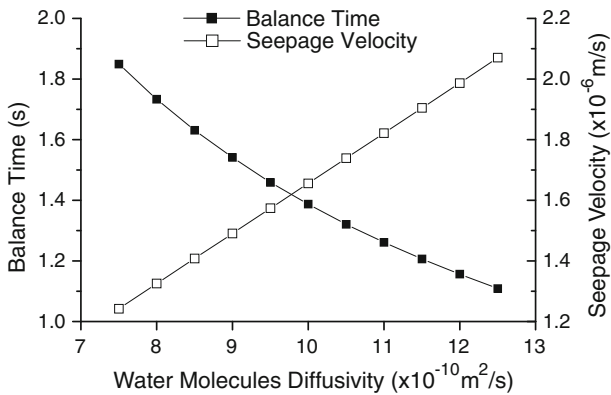


Fig. 5 Water resistance affected by water molecules diffusivity. ($T = 298 \text{ K}$, $H = 50 \mu\text{m}$, $C_{B0} = 10\%$, $C_{B1} = 1\%$)

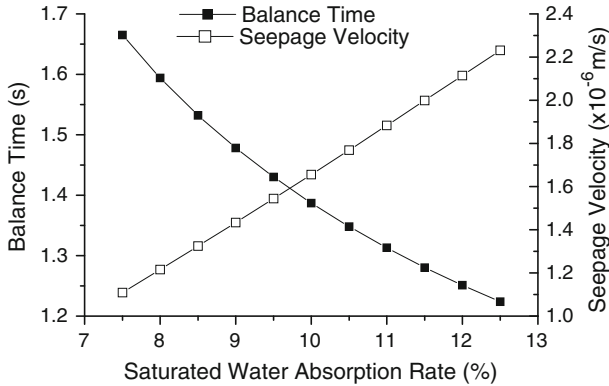


Fig. 6 Water resistance affected by membrane saturated water absorption rate. ($T = 298$ K, $D = 10 \times 10^{-10} \text{ m}^2/\text{s}$, $H = 50 \mu\text{m}$, $C_{B1} = 1\%$)

According to the depiction above, a new problem was noticed that in an acceptable range, the more AA in the membrane could decrease the diffusivities which were benefit to improve the water resistance. But at the same time, more AA would lead to a higher saturated water absorption rate which decreased the water resistance. The two contrary influences would be partly counteracted in the finally property of membrane. So the amount of AA used should be considered for the other properties, such as the mechanical strength, swelling effect and so on.

3.3 Effect of temperature

Although temperature parameter was not existed in the model of Fick's second law, water molecules diffusivity (D), membrane saturated water absorption rate (C_{B0}) and water escape concentration (C_{B1}) in the model were all affected by temperature.

Diffusivity (D) has a positive correlation with temperature. The relationship between them had been described by Nernst-Einstein Equation ($D = k_B \cdot T / 6 \cdot \pi \cdot \eta \cdot \alpha$) or Arrhenius Equation ($D = D_0 \cdot \exp(-E/RT)$) [13]. Membrane had a bigger saturated water uptake rate (C_{B0}) under a higher temperature. In the micro-scale, the interspaces between the monomers were enlarged under the higher temperature, so the water could permeate more easily. At the same time, water molecules in the membrane had higher kinetic energy which increased the average activity and decreased the escape concentration which was the lowest concentration of water molecules for pervasion. Another, density also affected by the temperature. Increase temperature could enlarge the molar volume and decreased the density which made the three mainly parameters change to the direction of getting bad water resistance. A group of water resistances under different temperatures were calculated by the model (see Fig. 7).

Figure 7 showed that the higher temperature decrease the balance time and increased the seepage velocity. The trend was consistent with the described above well.

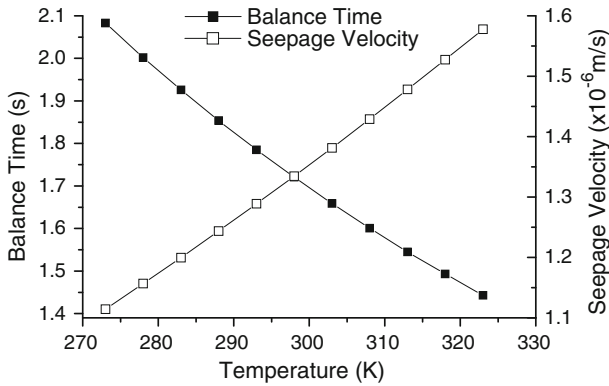


Fig. 7 Water resistance affected by the temperature. ($H = 50 \mu\text{m}$, $D^{298\text{K}} = 10 \times 10^{-10} \text{ m}^2/\text{s}$, $C_{B0}^{298\text{K}} = 10\%$, $C_{B1}^{298\text{K}} = 1\%$, $D^T = f(T, D)$, $C_{B0}^T = f(T, C_{B0}^{298\text{K}})$, $C_{B1}^T = f(T, C_{B1}^{298\text{K}})$)

Table 2 Calculated water resistance indexes compared with the experiment volume fluxes

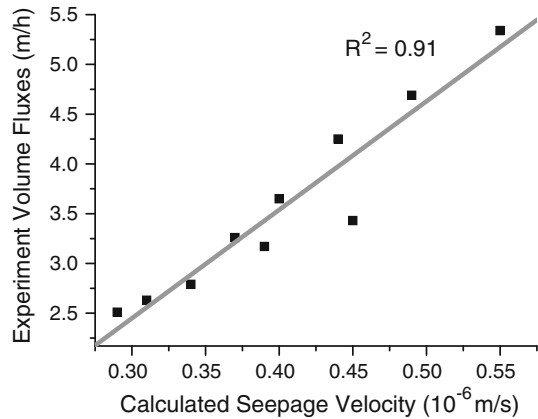
Group	Item	Experiment volume fluxes	Energy of combining	Diffusivity	Balance time	Calculated seepage velocities
I	0	5.34	-55.8709	12.85	6915	0.53
	1	4.69	-56.3424	11.96	7857	0.48
	2	4.25	-56.7643	11.24	8794	0.43
	3	3.65	-57.1441	10.64	9722	0.39
	4	3.26	-57.4877	10.14	10637	0.36
II	5	3.43	-56.4444	11.60	8560	0.44
	6	3.17	-56.9271	10.74	10100	0.38
	7	2.79	-57.3392	10.10	11529	0.33
	8	2.63	-57.6949	9.62	12848	0.30
	9	2.51	-58.0052	9.24	14063	0.28

3.4 Compared with the experiment result

According to the introduction of Sect. 2.4, experiments have done for validating the multi-scale association model of water resistance indexes. By the recipes listed in Table 1, the experiment volume fluxes (unit: m/s) and the calculated seepage velocities of the 10 membranes were compared in Table 2.

Because there were no functionality monomers in the default ratio membrane (item: 0), so the water molecules has a bigger diffusivities. The experimental seepage fluxes were much higher then the other groups. Both of the calculated indexes and experiment result proved it had bad water resistances. Results of group I showed the experiment volume fluxes were lower then the default, and the calculation results proved it. It could be explained from micro-scale that because of the bigger combining energy, the AA unit fettered water molecules and decelerated their diffusion. In the list of group

Fig. 8 The linear relationship between the calculation values and experiment values



II, AA and HEA were added at the same time. Experiment results showed the more functionality monomer there were, the better water resistances were. HEA played as a cross-linking agent, and made the membranes more difficult to seepage water.

The relationship between calculated seepage velocity and experiment volume fluxes from listed in Table 2 were shown in Fig. 8. The preferable linear regression coefficient proved the model was acceptable for quantitative describing water resistance indexes of membrane. It was useful for predicted the service life of membrane from the angle of water resistance.

It was reasonable to believe that, the model could be used to evaluate more systems in a wide range. Vinyl acetate membranes and fluorinated membranes were used for comparing their's water resistance indexes. Although there were lots of hydrophilic groups in vinyl acetate latexes, its water resistance indexes were low because of lower density and higher saturated water absorption rate. But for the fluorinated latexes, the higher densities and stronger hydrogen bonding effects decreased the diffusivities of water molecules in the membrane, which improved the water resistances of membranes.

4 Conclusion

A multi-scales association model for study on membrane water resistance were build up based on Fick's second law. Balance times and seepage velocities were calculated by the model as the water resistance indexes. The influence for the macro factors of membrane thickness, temperature and monomer ratio and micro-scale parameters of water molecules diffusivity (D), membrane saturated water absorption rate (C_{B0}) and water escape concentration (C_{B1}) were all discussed by the calculations of model. A preferable linear regression coefficient was obtained between the experiments and calculations. Above all, the model could give a quantitative description for the water resistance characterization of membrane. As a part of evaluation of membrane service life, the results would be used to guide the choosing and producing of membrane.

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References

1. J. Li, J. Zhang, W. Ge, X. Liu, *Chem. Eng. Sci.* **59**, 1687–1700 (2004)
2. S.A. Baeurle, *J. Math. Chem.* **46**, 363–426 (2009)
3. Q.H. Zeng, A.B. Yu, G.Q. Lu, *Prog. Polym. Sci.* **33**, 191–269 (2008)
4. J. Leon, M. Manna, *J. Phys. A: Math. Gen.* **32**, 2845–2869 (1999)
5. V. Prasad, D.G. Vlachos, *Ind. Eng. Chem. Res.* **47**, 6555–6567 (2008)
6. C.C. Han, D. Yan, J. Dong, *China Basic Sci.* (6), 25–29 (2003)
7. F.F. Abraham, J.Q. Broughton et al., *Europhys. Lett.* **44**(6), 783–787 (1998)
8. A. Ibrahimbegovic, D. Markovic, *Comput. Methods Appl. Mech. Eng.* **192**, 3089–3107 (2003)
9. R.E. Rudd, J.Q. Broughton, *Phys. Status Solidi (B)* **217**(1), 251–291 (2000)
10. L. Li, S. Zhang, Y. Chen et al., *Chem. Mater.* **17**, 839–845 (2005)
11. Y.C. Lin, X. Chen, *Chem. Phys. Lett.* **412**, 322–326 (2005)
12. H.T. Zhang, Y. Zhou, S.J. Dong et al., *Colloid Surf. A* **334**, 171–175 (2009)
13. Z. Chen, Q. Gu, H. Zou et al., *J. Polym. Sci. Polym. Phys.* **45**, 884–891 (2007)