

Theoretical Overview of Membrane Transport

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1. Introduction

Many researchers have discussed how membrane performance can be enhanced through an understanding of polymer science and engineering. The understandings of transport in porous membrane are used to achieve the isolation of certain components from mixtures. Particular emphasis is placed on the applicability of membrane separations for the isolation of macromolecules[1]. An awareness of membrane structure characteristics is required for the rational design of membranes for specific and/or new applications. This understanding rests on the knowledge of fields such as polymer thermodynamics[2], polymer adsorption [3, 4], diffusion in polymers[5, 6], reaction mechanism[7], and the dynamic behavior[8, 9] of polymer in porous membrane.

A membrane performs its function by allowing certain species to preferentially pass from one phase to the other. The permeation of macromolecule in porous membrane plays an important role in

various academic and industrial areas, such as food processing[10], biology[11], filtration process[12]. When polymer-to-pore size ratio is very small or large, the permeation of polymeric material becomes widely different. If this ratio is very small, the retention mechanism of polymer is dependent on its adsorption. However, if this ratio is bigger, the retention of polymer may be more complex due to hydrodynamical and steric effects. Such restriction of transport in polymeric membrane can be used to predict several transport coefficients from such fundamental information as the size, shape, and electrical charge of the polymeric material and pores. The properties of polymer in solution can be varied by environmental conditions. Ionic strength gives strongly influences on molecular adsorption and aggregation. The present study reviews various membrane permeation situations. This paper is to introduce the several theoretical points of views, showing that the various situations such as molecular size, interaction type have their own transport patterns and how they affect transport properties such

as diffusion coefficient, permeability, and equilibrium adsorption constant. Several membrane transport examples of polyelectrolytes are presented to show the applications of theoretical results in final section.

2. Theory

2. 1. Patterns of membrane transport

2. 1. 1. Macroscopic transport in membrane layers

The objective of this part is to investigate the dynamic interactions of convective diffusive transport of molecular species. The dynamic behaviors in membrane separation can be classified into two different types, direct and indirect interactions. The solution methodology is to apply operator-theoretic techniques [13] and inverse integral formulations [14] to analyze the dynamics of transport. A wide range of naturally occurring or synthetically constructed chemical, biological and biochemical phenomena can be studied within the framework of convective-diffusive transport. The operator-theoretic technique allows a full characterization of the dynamic behavior of systems without the complete numerical calculation of the governing differential models. This also allows for a coupling of different levels of information in a given system. Furthermore, the inverse integral formulation allows for a very efficient numerical strategy to solve the complete nonlinear differential model using information provided by the operator formulation. These solution can be also obtained by simulations on a supercomputer.

2. 1. 1. 1. Direct interaction

Direct interactions result from the diffusive or convective coupling through adjoining boundaries between macromolecules, a single domain composed by M -layered composite. The domain is considered in terms of sub-domains and the mathematical description accounts for the transport processes that occur inside these domains, as well as for those occurring between the domains through the environ-

mental media or phases. The interactions between the different membrane layers can be considered to be direct interactions since the layers are physically and geometrically in contact at their phase boundaries. A representative example is the transport of solutes in the layered membrane process. The diffusion coefficients, convective velocities and the phase distribution coefficients are allowed to vary from one layer to the next layer. Couplings between layers can be mathematically mediated through the equilibrium and flux boundary conditions[5].

2. 1. 1. 2. Indirect interaction

Indirect interaction can be considered by an interaction to mediate the interactions between two systems not physically adjacent. Indirect interactions can be mostly mediated in the membrane reactor by intervening fluid or gas regions. The indirect interactions mediated by the fluid medium [16] are able to display a broader class of collaborative behavior caused by the mutual interactions than those found showing only direct interactions. A mathematical analysis is performed to understand the solid phase in operator theory. The analysis has been pursued by using singularity theory and group-operator theory [17, 18]. This theoretical investigation can be performed using inverse integral formulation for the determination of regions of different behaviors in the parameter space and the identification of all steady states. The inverse integral formulation uses a non-linear integral operator of the Hammerstein-Voterra type[19] with a kernel given by the Green's function of the differential problem.

2. 1. 2. Molecular transport in membrane

The conformation behaviors of macromolecule have been investigated in the solution [20-22]. In this review paper, macromolecular transport in polymeric membrane or gel has been previously identified in the presence of electric field. Theoretical models can be extended by morphology and structure of gel media. Several regimes for

macromolecular separation in the polymeric membrane can be classified by pore size, molecular size and electric field.

2. 1. 2. 1. Ogston regime

In much smaller macromolecule than the pore size, the transport theory of macromolecule in the polymeric membrane is described by Ogston theory [23]. The Ogston model assumes that the migrating molecule behaves as an undeformable spherical particle. It does not take into account the fact that the migrating molecule can deform in order to squeeze through a pore. This model is assumed that the macromolecular chain is ideal; no excluded volume interaction exists and hydrodynamic interaction is negligible. The electrophoretic mobility (μ) macromolecular in the membrane is independent on chain length. It is equal to its free solution mobility(μ_0), multiplied by the probability that the molecule encounters a pore large enough to allow its passage, for example,

$$\mu = \mu_0 P \quad (1)$$

where P is the probability. The probability is that a given pore has a radius greater than or equal to the radius of the migrating particle. Macromolecular chain encounters around obstacle without serious change to chain shape and its conformation. The Ogston model of the pore size distribution predicts that, in a random network of linear polymers, the fraction of pores large enough to accommodate a spherical particle of radius of gyration, R_g , is

$$P = \exp[-\pi n L (r + R_g)^2] \quad (2)$$

where n is the average number of macromolecule strands per unit volume, L is the average fiber length, and r is the radius of the fiber. Therefore, combination of equation (1) and equation (2) gives the final expression describing the migration of a macromolecule through a polymeric network.

2. 1. 2. 2. Reptational regime

When the radius of gyration of macromolecule is

much greater than the radius of pore, large flexible chain molecules such as polyelectrolyte and DNA can migrate in a polymeric network. The pores are narrow and restrictive, and successful passage depends upon the limited number of conformations required for pore passage. This has been often explained by the reptation model. The macromolecules are spaced closely onto the pores, the chain may thread itself through consecutive pores. The chain behaves as if it is confined to a tube, the tube being formed by the consecutive series of pores. The dynamics of chains within a tube is described by the reptation mechanism presented by Doi and Edwards [24, 25], de Gennes [26] and Lerman and Frisch [27] for the electrophoretic of transport polyelectrolyte. The chain crawls through the tube much like a snake, to the direction of the tube being determined by the field-directed chain end. An important assumption of reptation theory is that the lateral fluctuations of the chain occur on a much shorter timescale than the forward motion by a sleeve surrounding the tube. The problem of reptational theory cannot predict the dynamic motion such as transient overshoot of the orientation because the length of tube is constant and the conformation of the tube is determined by the motion of the leading segment. In order to predict the fluctuations of the spring lengths between consecutive beads, only models with intratube or nonreptational degrees of freedom can explain these fluctuations such as transient overshoot. Hookean dumbbell model is an intratube model consisting of chains of "beads connected by rigid rods or spring. Theoretical models that include the main features of the macromolecule, i. e. extensibility, orientability, and flexibility, must be used. Figure 1 is a sketch of the cases for this approach by bead-spring chain. A very detailed description of the various mechanical models for kinetic theories can be found by Bird et al[28]. Rouse-Zimm model is another model for intratube model where the macromolecule is replaced by a bead-spring chain. Each bead has a charge q and is connected to its two neighbours by anharmonic

entropic springs. A hierarchy of models, beginning with a relatively simple framework and building to a more complete description, are considered in order to capture the essential features of the dynamics of the macromolecules inside the polymeric membrane.

The molecular models shown in Figure 1 have been in decreasing order of complexity. The Kirkwood-Riseman model[29] uses a freely rotating chain made up of "beads" joined together with massless "rods". The angles between successive rods are fixed. The Kramers model [30] is also composed of beads joined by rigid rods. However, the chain has universal joints at the beads. In the Rouse [31]-Zimm [32] chain also uses universal joints at the beads with the elastic dumbbell, which can be viewed in Figure 1 as a the Rouse-Zimm model. This simple model, although very useful for performing preliminary qualitative studies of the dynamics of the macromolecule, clearly has limitations. For example, it is incapable of mimicking the responses associated with the several degrees of freedom of the macromolecule. However, it has been a useful tool for developing a good understanding of the relationships between molecular motions and rheological properties. This model is the starting point for studying the behavior of the macromolecular chain under elongational flows. A more accurate description can be also obtained using the Kramers chain model [28]. The Kramers representation of the macromolecules is capable of capturing more degrees of freedom in comparison to the elastic dumbbell models although its solution would require more computational power. If one wants to investigate the behavior of the macromolecules under oscillatory fields (i. e either hydrodynamic or electric fields) one should be able to capture many of the internal molecular degrees of freedom. An excellent choice to study this case would be the Rouse-Zimm model, particularly if one desires to study effects at high frequencies. Finally, if one should want to have a very detailed description of the molecule, the model to use is the Kirkwood-Riseman chain since it has the capability of

describing chain orientation, small scale motion, finite extensibility, and chain stiffness.

This review paper simply introduces model equation using the elastic dumbbell model with a non-linear spring given by the velocity field under different electrical field conditions. The basic equation for the kinetic theory approach of macromolecules is set up. The elastic dumbbell model for the macromolecule is useful for developing a basic understanding of the macromolecular chain under different flow patterns and with different patterns of the electrical field. In this formulation, the interbead vector from bead to bead is denoted by \mathbf{R} . Assuming that $\Theta(\mathbf{R}, t)$ is the configurational probability density, if one wants to know the probability, $\Theta(\mathbf{R}, t) d\mathbf{R}$ that the dumbbell of n bead-springs in the cell which have conformation in the range $d\mathbf{R}$ about \mathbf{R} at time t one needs to solve the following equation of continuity (Bird[28]) in the configuration space:

$$\frac{\partial \Theta}{\partial T} = - \sum_i^N \left[\frac{\partial}{\partial R_i} \{ [\sigma \cdot \mathbf{R}] \Theta - \frac{\xi}{2kT} \sum_j^N T_{ij} \frac{\partial}{\partial R_j} \Theta - \frac{\xi}{2} F^{(c)} \Theta + \frac{\xi}{2} (F_2^{(e)} - F_1^{(e)}) \Theta \} \right] \quad (3)$$

The distribution of configuration $\Theta(\mathbf{R}, t)$ changes under an applied hydrodynamic fields as well as under an external (specified) electric field. Solutions to this equation provide very important insight into the behavior of the dumbbell in the polymeric membrane as a first approximation to the complete solution for the dynamics of the macromolecule inside the polymeric membrane structure. The segments of bead-spring fluctuate on timescales that closely resemble that of the chain's center-of-mass, the dynamics of the segments can be described by the diffusion of confined segments along the chain contour. The first term of right hand side of equation (3) is the hydrodynamic drag force, the second term is a Brownian force, the $F^{(c)}$ is the intermolecular force which includes mechanical forces between beads and electrostatic forces due to the changes in each bead. And $F^{(e)}$ represents the external force term like electric forces.

2. 2. Analysis of transport properties in porous membrane

2. 2. 1. Hydrodynamic effects in diffusion

The macromolecular transport in uncharged polymeric membrane by diffusion and electrophoretic convection is analyzed with two different kinds of models; one model accounts for the structure of the polymeric media and the other model does not account for the structure of the polymeric membrane.

2. 2. 1. 1. Non-structure geometrical model

Models for solute transport in porous media that do not account for the geometrical structure of the polymeric membrane begin by modifying the point species transport equation[33].

$$N_i = c_i v - D_e \nabla c_i - c_i u F \nabla \Psi \quad (4)$$

where N_i is the total molar flux of species i , D_e is the effective diffusion coefficient, v is the molar mean velocity, u is the electrophoretic mobility in solution, F is the faraday constant and Ψ is the electrostatic potential. Equation (4) includes diffusive, convective, and electrical transport terms. The effective coefficient is often expressed in terms of an overall tortuosity, τ' , as [34]

$$D_e = D_o \frac{K_{av}}{\tau'} \quad (5)$$

The overall tortuosity in equation (5) accounts for the combined effects of the increased path lengths for diffusion, constrictions in the cross-sectional areas available for diffusion, and hydrodynamic interactions between the solute and the pores. The available pore volume, K_{av} , given in equation (5) is the volume accessible for the solute of interest. The effects of constriction and increased path length are often separated to give

$$D_e = D_o \frac{\theta K_{av}}{\tau} \quad (6)$$

where θ gives the effects of constriction and τ gives the effects of increased path length [34]. These two empirical expressions have been widely used for an-

alyzing diffusion in porous media. Equation (6) is originally used for analyzing diffusion in porous heterogeneous polymeric particles. It implies that the effects of the media, through increased path length, i. e. tortuosity, are independent of the effects that depend upon both the solute size and the particle geometry. If the size of solute is less than the pore radius, it is reasonable to include in cases where the size of the solute is of similar magnitude as the pore space a hydrodynamic interaction term $f(\lambda)$ can be included to give[35, 36]

$$D_e = D_o \frac{\theta K_{av}}{\tau} \quad (7)$$

Equation (7) implies that the hydrodynamic effects are separable from the other solute and structure effects. This is not expected to be true in porous media that have a non-well-connected or "fractal" pore space[36]. In this type of media the hydrodynamic interactions, tortuosity, constriction, and size of the solute are not expected to be independent and they cannot be separated as implied in equation (6) [36]. In this case an overall tortuosity like equation (5), polymeric matrix and the hydrodynamic interactions as a function of the diffusing solute may be more useful [35]. When the driving force for diffusion in the pore is equal to the body force on the solute molecule[37], this body force is exactly balanced by the hydrodynamic force [38] if we neglect other body forces with the assumption of steady state motion in an isothermal fluid. The unperturbed fluid velocity for a long cylindrical pore has a parabolic velocity profile. The radial variations in concentration are of great importance. Rigorous calculations are presented for the effect of a constricting circular cylindrical boundary upon the translational Brownian motion of an isolated spherical particle suspended in a Poiseuille flow [39]. Their origins can be seen readily by considering steric restrictions on the possible positions of a rigid sphere within a cylinder. When a solute moving in streamline approaches at a distance of pore wall close to their radius of pores,

hydrodynamic interactions between the solute and pore wall occur along the axis of the pore throat. The hydrodynamic term of equation (7) has been elucidated earlier as arising from the restriction factor of convective transport. The hydrodynamic factor within cylindrical pore is introduced by several researchers [40–42]. The separation of molecules by size and shape takes place by steric hindrance at the entrance of the pores and by frictional resistance in the pores, both effects increasing with the ratio (λ) of the molecular diameter to the pore diameter. Therefore, the $f(\lambda)$ of equation(7) is expressed [43]by

$$f(\lambda) = 1 - 2.104\lambda + 2.089\lambda^3 - 0.948\lambda^5$$

2. 1. 1. 2. Structure geometrical model

Models that account for the geometrical structural features of the pore space assume some geometrical shape for the pores in the polymeric membrane. Hindered diffusion theory attempts to account for the hydrodynamic interactions between solute molecules and the pore surfaces [35]. This approach has been very successful for media of extremely well defined geometry such as etched membranes with precise parallel cylindrical pores. For polymeric membrane with much less well defined geometry hindered diffusion theory has recently been used in some theoretical models. Altenberger and Tirrell [44], using hindered diffusion theory, have obtained a relationship for the self diffusion coefficients of molecules in a network of random fibers, D_e . They found

$$\frac{D_e}{D_0} = K_{av}(1 - a_1\sqrt{T} - a_2T + \dots) \quad (8)$$

where a_1 and a_2 are constants as a function of the polymeric membrane and solute, and T is a concentration of polymer material. Self diffusion represents the Brownian, or thermal motion of a particular particle in a one component solution. Fick's law, or macroscopic diffusion coefficients, used in equation (4) represents transport due to concentration

gradients. In the limit of low solute concentration the self diffusion coefficient is equal to the Fickian diffusion coefficient. Another relatively new approach for analyzing transport in a porous media utilizes concepts from fractal analysis originally developed by Mandelbrot [45]. There are several kinds of fractals discussed by Mandelbrot, however the particular kind of fractal most applicable for characterization of porous media has to do with scaling laws, semi-similarity, and non-integral dimension. A fractal dimension is a geometrical property of irregular objects that have structural self-similarities over wide ranges of scales. For such highly irregular media a measured quantity such as surface area or volume is found not to be a fixed absolute value but to depend upon the yardstick used to measure the given quantity. For example, the pore volume V_p , measured in a membrane layer depends upon the size of the molecule ϕ , used for measuring the volume by

$$V_p \approx \phi^{3-\alpha}$$

where α is defined as the fractal dimension, or Hausdorff-Besciovitch dimension[45]. Fractal analysis has been used to study diffusion in porous media[46]. Diffusion in a porous membrane can be considered fractal for two distinct reasons. The motion itself, i. e. Brownian motion, is a special kind of fractal. The path of Brownian motion is a fractal with an integer dimensions. Brownian motion, a diffusional process often simulated by the statistical methods of random walks, has topological dimension of one since the motion traced out by the Brownian motion eventually twist and cross over itself until it has covered all points in space at least.

2. 2. 2. Diffusion of macromolecule

Though many macromolecules are flexible and take a random coil structure, there is a large class of macromolecules which are not flexible and often assume a rodlike structure. Rodlike macromolecules are much more easily oriented by an external field.

Theoretical treatment of rodlike macromolecules is much easier than for flexible macromolecules since rodlike macromolecules can have only two kinds of motion, i. e., translation and rotation. The rotational friction coefficient is obtained from the total torque due to the hydrodynamic friction. The total torque is given by the cross product of the angular velocity with the friction force acting on the segment. This torque force must be balanced with the external torque. Rotational diffusion coefficient can be derived from Stoke-Einstein equation [37]. The translational motion is considered as two different components. The rod moves along parallel and perpendicular direction to the velocity. Therefore, hydrodynamic drag has parallel and perpendicular components of the translational friction constant. The calculation of the parallel and perpendicular components of friction coefficient is based on the Kirkwood theory [28]. The translational diffusion coefficient can be calculated by substituting the velocity term into the continuity equation.

In a flexible polymer, we need to draw the primitive path [47], i. e., the shortest path connecting the two ends of the chain with the same topology as the chain itself relative to the obstacles. In the short time scale the motion of the polymer is regarded as wriggling around the primitive path. On a longer time scale, the conformation of the primitive path changes as the polymer moves, creating and destroying the ends of the primitive path. The motion of the primitive chain corresponds to the overall translation of the Rouse chain along the tube. The displacement of a primitive chain segment is calculated by a probabilistic description of the general time correlation function [24, 25, 48]. The contour length of the primitive chain fluctuates with time. The primitive chain is thus characterized by three parameters such as L of contour length, D of diffusion constant and " a " is called as the step length of the primitive chain, which must be expressed by the Rouse model parameters such as N is number of segment, " b " of bond length, ξ of friction constant.

The diffusion coefficient of the Rouse model for a flexible polymer can be identified as

$$D = \frac{kT}{N\xi}$$

k is the Boltzman constant and T is the Kelvin temperature. Note that L_a is equal to Nb^2 of the Rouse chain.

2. 2. 3. Permeability

Another important parameter in permeate membrane is the permeability of the solute. The hydraulic permeability is simply described by $K = (J/\mu)/\Delta P$ [49, 50]. The convective velocity inside membrane is given by

$$v = \frac{K}{A} \frac{\Delta P}{\mu} = f \frac{K p U^2}{A \mu}$$

The parameter λ is defined by $\lambda = (vA)/D = (KfpU^2)/(\mu D_e) = Re^2 Sc Kf / (A^2 \chi)$ [51], where J is the flux of fluid, f is the friction factor defined by the relationship $\Delta P = fpU^2$; U is the external flow velocity. μ is the viscosity and A is the surface area of permeate membrane, and $\chi = D_e/D_o$. Re and Sc are dimensionless numbers. The differential mass balance for the transport of the diffusing component can be described by considering a constant pressure gradient through the membrane. The zeroth and first absolute moment expressions are determined from the solution of differential mass balance. χ can be calculated by measuring moments [52]. The parameter, λ , is the same as Pelet number of dimensionless term, this parameter is useful when considering the quantitative effect of the intraparticle force convection. The effects of diffusion by convective velocity in the membrane is of current interest in a number of separation processes. Rodrigues [53, 54] and Dogu [55] have studied the effects of intraparticle convection inside membrane and gel particle systems. Particularly the dynamic behavior of solutes by convective velocity in the fluid phase is studied by Park [56]. The pressure drop of Darcy's law can be generally calculated by mass balance

equation inside the adsorbent particle [57] as defining molecular diffusion coefficient using pressure drop of inside particle. Another suggestion is that the pressure drop in the membrane can be solved by considering the indirect interaction problem between fluid and solid phases. Similar problems have been dealt by Ramkrishna and Arce [58, 59].

2. 2. 4. Concentration polarization effect

The concentration gradient near the membrane interface occurs due to the buildup of the retained solutes. This effect is called concentration polarization. It increases with increasing permeate flux, which reduces the driving force for permeation, resulting in a lower flux and a selective separation. Theoretical derivation can be achieved by the species continuity equation in the boundary layer as representing the back-diffusion of species *i* into the bulk liquid phase and the total convective flux of *i* toward the membrane. The mass balance equation with boundary conditions yields [49] as

$$\frac{C_{m,i} - C_{p,i}}{C_{b,i} - C_{p,i}} = \exp\left(\frac{J}{k}\right)$$

where C_m , concentration of *i* at the membrane interface, $C_{b,i}$ is that of *i* in the bulk phase, $C_{p,i}$ is that of *i* in the permeate. *J* is the total membrane flux, and *k* is mass transfer coefficient. The concentration of the retained solute at the membrane interface increases with respect to its concentration in the bulk phase if the ratio of the total flux and the mass transfer coefficient increases, thus reducing the concentration gradient across the membrane of the species *i* to be separated, and hence its flux. This unfavorable effects of concentration polarization can be reduced by increasing the mass transfer coefficient. High mass transfer coefficient can be achieved by maintaining a high flow rate of liquid phase along the membrane surface [7].

2. 2. 5. Effects of ionic strength on diffusion

Partitioning of molecules between small liquid-filled pores and bulk solution plays a large role in

membrane separation processes. The effects of molecular interactions between molecules and pore wall appear in expressions describing hindered diffusion and convection of solutes through small pores [60–62]. The observed reduction in the permeability of the membrane is consistent with monomer layer adsorption in the porous structure of the membrane. The effects of molecular adsorption on the permeability of the membrane reflect both blockage and constriction of the small pores of this membrane. The adsorption of solute in the porous wall of membrane can be expressed as a function of the surface diffusivity [63–67]. The theoretical or experimental derivations of this surface diffusivity aid the understandings of solute transport inside a membrane of high salt concentration. Theories of surface diffusion on porous solids of high surface area have been proposed for liquid-filled or gas-filled pores. For example, Higashi et al. [68] mention to be related the surface diffusivity to the effective bond energy between adsorbate molecules and the adsorbent surface. They assume that an adsorbed molecule hops instantaneously from one adsorption site until another vacant site is located. Gilland et al. [69] propose a different theory based upon writing a force balance for the adsorbed layer. Chen and Yang [70] study the concentration dependence of the observed surface diffusivity based on the kinetic approach of the random-walk and hopping mechanism and deduce an explicit formula for the surface diffusivity, which exhibits an increase or decrease with loading, depending upon the so-called blockage parameter. The hindered effects by ionic strength have been also researched in the porous polymeric media with gas and liquid substances by several researchers [66, 67]. The result obtained experimentally is that the tortuosity factor of equation (6) changes with an increase in the amount adsorbed. This is directly related to the time it takes to transverse a pore path. It increases with increasing ionic strength. Hence, the adsorption of macromolecule to the pore walls complicates the interpretation of restricted transport in a membrane. Expo-

sure of membrane to polyelectrolyte leads quickly to an irreversible decrease in pore radius. These interaction phenomena can be understood using the concepts of molecular engineering in the following section.

2. 2. 6. Long-range interactions in liquid-filled pores

Steric interaction and long-range intermolecular forces affect the radial distribution of solutes within pore, which influences the hydrodynamic interactions between the solute and pore wall. In analyzing such molecular interactions it is desirable to have a predictive theory to relate independently measurable properties of the molecules and the pore. The theoretical framework describes the effect of salt on both electrostatic and hydrophobic interaction[71]. At low ionic strength, the molecules are usually assumed to be a simple ion and their electrostatic free energy is calculated from the Debye-Huckel theory [72]. The molecules have been treated as dipoles following the theory of dipolar ions advanced by Kirkwood[73]. With increasing salt concentration, the average distance between the charge species becomes smaller and smaller. Consequently, more and more ionic binding to and clustering at the macromolecule are expected to occur, and at sufficiently high salt concentrations the concomitant ionic shielding makes the charged macromolecule effectively behave as a neutral dipole. Hence, Kirkwood model[73] may apply at high salt concentration. In this case the electrostatic free energy of molecules becomes proportional to the ionic strength and the dipole moment. As the salt concentration increases, the hydrophobic effects increase. This is thought to be attributed to the structure of water which is assumed to be altered in the vicinity of a nonpolar solute from the point of view of statistical thermodynamics.

Uhlig[74] and Eley[75] put forward a theory which relates the interactions of nonpolar substances to the surface tension of the solvent. This surface tension can be written as the free energy change for cavity formation given by Sinanoglu

[76]. The hydrophobic interaction is also reexamined by the surface tension through the thermodynamic nature of interfaces and of adhesion in the light of the Lifshitz theory[77] of the forces acting across condensed phases. The Lifshitz theory is developed by calculating the interaction between bodies in the fluctuating electromagnetic field created by the material. The theoretical results give expressions for the Hamaker coefficient. The expression for the surface tension is a function of the Hamaker coefficient describing liquid-liquid, long-range force interactions, the molecular weight, and the liquid density. Isralachvili[78] obtains the expression for the Hamaker constant based on the Lifshitz theory in order to calculate the van der Waals interaction between a molecule in the medium with surface.

The interaction energy in porous membrane can be considered as the result of attractive long-range forces between the solid and the liquid. The long-range intermolecular forces acting between two different phases can be represented by the potential energy of interaction. The Lennard-Jones potential [79] is commonly recommended for nonpolar molecules. The Sutherland potential[80] (so called, London potential) can be also obtained by replacing the repulsive contribution in Lennard-Jones potential. Recently method for calculating protein solubility is obtained by considering the protein molecules as hard sphere model [81]. Effective polymer-polymer interactions are taken to be volume-exclusion potentials derived using statistical mechanics. The excess chemical potential of the polymer due to the charges on all species is calculated using the mean spherical approximation for a mixture of charged hard spheres. The theoretical background is based on geometrical considerations put forward by Assakura and Oosawa [82]. Theoretical interaction in colloid is presented[83] for the electrostatic double-layer interaction between a colloid particle and a long cylindrical pore. The analysis of molecular interaction is employed by the Poisson-Boltzmann equation. Finally, the adsorption study of polymer by the mean-field theory can be theoretically pre-

dicted using quantum mechanical calculations. We will not treat this in this review. Interested readers can be referred to excellent references [2-4, 47].

3. Applications to membrane transport

3. 1. Electrodialysis

Electrodialysis [16] employs fixed-charge membranes to extract pure water from a salt solution. The system process is driven not by applied pressure (as in ultrafiltration and reverse osmosis) but by an electric field. The membranes are positioned at the top according to the ionic charge they allow to pass. The result is to separate pure water and salt solution by an electric field applied across a set of membranes. Convective-diffusion transport of electrolyte ions is selectively permeable to those ions bearing either a positive or a negative charge in each membrane. This electrodialysis is a good application using direct interaction of membrane separation process.

3. 2. Membrane transport in biotechnology

The diffusion, convection and reaction in each layer of the system of M-layers can be considered. The interplay of convective-diffusive transport with reaction yields a wide variety of steady state and dynamic behavior in biochemical and biological systems. Martine et al. [84] have formulated a multiple layer diffusion and convection model for the transport of auxin, a plant hormone, up the stem of a plant. Almirantis and Papageorgiou [85] have considered reaction boundary coupling between multiple layers in a one-dimensional system as a model of intercellular communication. Multiple linear and nonlinear reactions in convective-diffusion processes can be used in the cellular membranes as a basis for analyzing metabolic pathways. These analysis has been studied through lumping analysis [86], metabolic model [87], cybernetic model [88] such as glycolysis, the regulation of protein synthesis, and the energetic of active transport in cellular membrane [89].

3. 3. Membrane reactor

The biocatalyst [16] is physically trapped on one side of a suitable membrane in order for the resulting product to permeate through the membrane. The immobilization of the enzyme [90] by chemically or physically attaching them to solid surfaces is another application of membrane reactor. This research shows that indirect interactions are as important as the direct interactions in producing a wide variety of very interesting steady state and dynamic behavior in membrane bioreactor. Moreover, assemblies of packed particles in a bioreactor showing only interactions mediated by the fluid medium are able to display a broader class of collaborative phenomena (i. e. behaviors caused by the mutual interactions of the membranizing particles) than those found in assemblies showing only direct interaction. Examples of the phenomena found in assemblages of packed particles with only indirect interactions includes the fact that uniform steady states can show collaborative multiplicity and collaborative reversal of instability before breaking the symmetry [91, 92]. Another example can be shown in systems where particles of immobilized cells communicate through the bulk solution of well-mixed membrane reactor.

3. 4. Facilitated transport

Biological recognition and the relationships between structure and function are key areas that can be considered in facilitated membrane transport. Emulsion liquid membrane [93] and immobilized liquid membrane [94] are another examples of facilitated membrane transport. The quantitative description of these systems can be considered first from the thermodynamic approach [95-97] where binding equilibria are developed and second from the kinetic approach. Facilitated transport utilizes a carrier molecule (i. e. a molecule with a specific affinity for the species of interest) to selectively transport a specific solute across a barrier that would normally show limited solubility for the uncomplexed species of interest. The process con-

sists of three stages; 1) association with a carrier molecule on one side of the barrier, 2) transport of the permeant-carrier complex across the surface, and 3) dissociation of the permeant molecule on the other side of the membrane. This process can describe certain (non-active or nonmetabolic or energy dependent) biological transport. The driving force is still a concentration gradient, however the carrier serves to increase the selectivity of the transport and the rate of the transport.

3. 5. Active transport

An important application is in the transport of oxygen by hemoglobin and myoglobin [98]. The concept has been extended to industrial processes, and it is sometimes referred to as separations in liquid membranes [99]. Biological systems can accumulate or transport ions against a gradient of electrochemical potential (and chemical potential). Obviously energy must be expended in order to accomplish the mass transport. The energy use coupled to the transport is important in understanding how cells function. This kind of transport is called as an active transport. The active transport utilizes light, redox energy or ATP hydrolysis as an energy source.

3. 6. Electrofiltration of polyelectrolyte

A chainlike macromolecule undergoes motion in a polymeric membrane under the influence of an electric field. The electrophoretic mobility in the polymeric membrane is inversely proportional to the molecular length. It is again important to contrast this result with the free-solution case. As the electric field strength is increased, the random-walk coil becomes more elongated because of the induced orientation of the leading segment. This theoretical prediction can be applied to separate different sizes of polyelectrolyte in the membrane using electric field [100-103]. This is an application of reptational theory of polymer. Blood plasma processing using electrodialysis [104] has been interested in the removal of trace plasma components without altering

the functional or physicochemical properties. Electrofiltration [105] has been applied to dewatering colloidal dispersions. Ionophoresis [106] has been investigated with the aim of enhancing hydrophilic drug permeation through hydrophobic membranes. Ionophoretic techniques have been developed recently in the field of transdermal delivery systems.

4. Conclusion

This paper shows through many theoretical review papers how an understanding of polymer science and engineering can be used to enhance membrane performance. The effectiveness of a membrane strongly depends on its structure. The structure that develops during the membrane formation process can be understood through rigorous modeling efforts. Membranes have proved useful in the separation of biologically produced materials. An understanding of the interactions between the membrane surface and the materials being separated was also pursued. We have also reviewed many existing models that could be applicable to rigid and flexible polymers. The translational, rotational, and internal dynamics of macromolecules are very important properties to study membrane separation processes. These will be areas where innovative polymer scientist or engineer can make a significant contribution. Studies in biophysics will continue and will involve more complex and realistic situations.

Nomenclatures

A	: Surface area of pore
c_i	: Species molar concentration
D_e	: Diffusion coefficient
D_o	: Diffusion coefficient in free solution
f	: Friction coefficient
F	: Force term in equation(3)
l	: Average fiber length
K	: Permeability
K_{av}	: Pore volume
n	: Average number of polymer
N	: Total molar flux

P	: Pressure
P	: Probability in equation(1)
γ	: Fiber radius
R_g	: Radius of gyration
\mathbf{R}	: Interbead vector
T	: Polymer concentration
u, U	: Convective velocity in the fluid phase
v	: Convective velocity in the solid phase
V_p	: Pore volume

Greek letters

ϕ	: Molecular size
χ	: Relative ratio of effective diffusion coefficient to that in free solution
θ	: Constriction factor
τ	: Tortuosity
τ'	: Overall tortuosity
Ψ	: Electrical potential
λ	: Relative ratio of molecular size to pore size, Peclet number
μ	: Viscosity
Θ	: Probability density

Superscripts

e	: Electric field force
C	: Intermolecular force

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