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Multicomponent Diffusion in Highly Asymmetric Systems. An Extended Maxwell−Stefan Model for Starkly Different-Sized, Segment-Accessible Chain Molecules

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ABSTRACT: An extended version of the Maxwell−Stefan (EMS) equation is proposed to describe transport in multicomponent solutions of molecules that are starkly different in size and whose segments are all accessible for mutual frictional interactions. The proposed modification corrects the friction factor between the colliding molecules by replacing the molar species concentration by the molar segment concentration, or equivalently, by the volume fraction of the component. The new expression for the friction factor is consistent with the kinetic theory of Curtiss and Bird for polymer solutions in the limit of linear isotropic systems. When the classical generalized Maxwell−Stefan equation is applied to diffusion in a membrane-solvent system, the (unknown) molecular weight of the membrane must be specified. In EMS, however, such a specification is not required. Further, in contrast to a previous equation for polymer solutions proposed by Heintz and Stephan (*J. Membr. Sci.* **1994**, *89*, 153), EMS is consistent with restrictions given by the Gibbs−Duhem equation and by Onsager's reciprocity relations. The multicomponent diffusion equation proposed here is appropriate for modeling mass transfer in a variety of technologies, including membrane-separation operations, polymer drying and coating, and multicomponent transport in biological membranes, cells, and drug-delivery systems.

Introduction

Although the science of diffusion is not new, the rise in theoretical and experimental studies for multicomponent diffusion reflects a burgeoning interest from separation science, energy technology, nanotechnology, electrochemistry, and biology. In each of these (and other) areas, we encounter simultaneous transport of multiple chemical species.[2−5] Two different descriptions of multicomponent diffusion are normally employed: (a) the generalized Fick law,[5] where the material fluxes are written as a linear combination of driving forces (e.g., concentration gradients), and (b) the generalized Maxwell−Stefan (GMS) expression, where the driving forces are given as a linear combination of the material fluxes. Even though these formulations are formally equivalent, the Maxwell−Stefan description of diffusion is usually preferred and is adopted in this work. (GMS is independent of the choice of reference velocity. Also, GMS diffusivities are binary, symmetric coefficients with the clear physical meaning of inverse intermolecular friction; they have a weaker composition dependence than those in the generalized Fick's law.) The GMS equation for multicomponent material transport defines a quantity $\mathbf{d}_i$ according to[6−8]

$$c_{\mathrm{T}}RT\mathbf{d}_i \equiv c_i\nabla_{T,P}\mu_i + (\phi_i - \omega_i)\nabla p - \rho_i\mathbf{g}_i + \omega_i\sum_j \rho_j\mathbf{g}_j = RT\left[\sum_{j\neq i}\frac{c_ic_j}{c_{\mathrm{T}}\text{Đ}_{ij}}(\mathbf{v}_j - \mathbf{v}_i) + \sum_{j\neq i}\frac{c_ic_j}{c_{\mathrm{T}}\text{Đ}_{ij}}\left(\frac{D_j^{\mathrm{T}}}{\rho_j} - \frac{D_i^{\mathrm{T}}}{\rho_i}\right)\nabla(\ln T)\right] \tag{1}$$

where i is one of the diffusing species in the mixture; c_{T} is the total molar concentration; Đ_{ij} is the binary Maxwell−Stefan diffusivity; D_i^{T} is the thermal diffusion coefficient; ρ_i is a mass concentration; c_i is a molar concentration; ϕ_i is a volume fraction; ω_i is a mass fraction; μ_i is the chemical potential; $\mathbf{g}_i$ represents the external force per unit mass acting on species i; $\mathbf{v}_i$ is species velocity; and, finally, subscripts T,P in the gradient operator, ∇, indicate constant temperature and pressure.

The left side of eq 1 has dimensions of force per unit volume and represents the driving force for diffusion of species i, combining concentration diffusion, pressure diffusion, and external forced diffusion, respectively, as given by the first, the second, and the last two terms in the middle of eq 1. The term containing the temperature gradient represents thermal diffusion associated with the driving force for conductive heat transfer.

Equation 1 can be interpreted as a force balance.[3,9] The sum of driving forces acting on species i is opposed by the frictional resistance that species i encounters because of its relative motion with respect to species j in solution. This frictional resistance is given by the product of the difference in velocities ($\mathbf{v}_j - \mathbf{v}_i$) of the two colliding species, and a friction factor K_{ij}, proportional to the frequency of binary collision. For simple (i.e., small and nearly equal-size) molecules, the number of binary $i-j$ collisions per unit volume is proportional the product of the molar concentrations:[9]

$$K_{ij} = \frac{RT}{c_{\mathrm{T}}\text{Đ}_{ij}}c_ic_j \tag{2}$$

Therefore, the binary Maxwell−Stefan diffusivity Đ_{ij} has the physical meaning of the inverse of an intermolecular friction coefficient.[5] Maxwell−Stefan diffusivities are symmetric with respect to components i and j, obeying Onsager's reciprocity relations. For ideal sys-

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tems, they are independent of composition but, in general, they depend on composition.[2] Because only the difference of diffusive velocities ($\mathbf{v}_j - \mathbf{v}_i$) appears in eq 1, the Maxwell−Stefan formulation of multicomponent diffusion is independent of the choice of reference velocity.

Equation 1 has been successfully applied to describe multicomponent diffusion in simple fluid mixtures.[5] Recently, it has also been used to describe transport through polymeric membranes in a solution-diffusion framework.[1,10−26] However, application of eq 1 to a solvent-membrane system presents a problem: the molar concentration of the membrane is ill-defined because the molecular weight of a membrane is unknown. Hoch et al.[10] considered an isothermal and isobaric binary membrane/solvent system, and assumed that the membrane molar concentration, c_p, was negligible compared to that of the solvent, c_1. The final expression derived from eq 1 in the limit of $c_p \ll c_1$ contains the product of the diffusion coefficient and of the polymer molecular weight, $Đ_{1p}M_p$, as a fitting parameter, where subscripts 1 and p indicate solvent and polymer, respectively. From experimental mass-transfer data, $Đ_{1p}$ cannot be ascertained independently of M_p.

To circumvent this well-recognized deficiency, several suggestions have been made. Bausa and Marquardt,[11] and recently Paul,[12] converted mole fractions into weight fractions and defined a new effective Maxwell−Stefan diffusivity:

$$Đ'_{ij} = Đ_{ij}M_j\sum_k \frac{\omega_k}{M_k} \tag{3}$$

where M_j is the molecular weight of species j. Unfortunately, the new diffusivities $Đ'_{ij}$ are not symmetric (i.e., $Đ'_{ij} \neq Đ'_{ji}$). Further, they still contain the (unknown) molecular weight of the membrane.

In a similar manner, Heintz and Stephan[1] suggested that for a multicomponent, isothermal, isobaric system in the absence of external forces, the generalized Maxwell−Stefan equation be modified to

$$\frac{1}{RT}\nabla_{T,P}\mu_i = \sum_j \frac{\phi_j}{Đ_{ij}}(\mathbf{v}_j - \mathbf{v}_i) \tag{4}$$

where the diffusivities $Đ_{ij}$ are assumed to be symmetric.[18,19] The physical basis for eq 4 follows from the assumption that for molecules very different in size, the volume fraction, rather than the mole fraction, provides a more realistic measure of the friction of component j on the movement of component i. Several authors[17−20,22,24,27] adopted the modification proposed by Heintz and Stephan in a solution/diffusion framework. Unfortunately, eq 4 is inconsistent with the Gibbs−Duhem equation and with Onsager's reciprocity relations. Upon multiplying each side of eq 4 by c_i and summing over the index i, the left side must be zero because of the Gibbs−Duhem relationship. Unfortunately, the right side does not sum to zero when the $Đ_{ij}$ values are taken to be symmetric.

Recent work,[15,21,25,26,28−30] primarily that on drying and coating technology, uses a multicomponent diffusion equation derived from kinetic theory for monatomic liquids.[31,32] The final mathematical expression is identical to eq 1 with the GMS diffusivities replaced by Bearman and Kirkwood's friction factors ζ_{ij}[31,32] according to $Đ_{ij} = k_BT/c_TN_A\zeta_{ij}$, where k_B is Boltzmann's constant and N_A is Avogadro's number. Appropriate assumptions concerning the relationship between the various ζ_{ij}'s[30] allow calculation of the GMS diffusivities as a function of self-diffusion coefficients and allow elimination of the membrane molecular weight from the multicomponent diffusion equation. This approach is appealing because it reduces the number of diffusivities for an m-component system from $m(m - 1)/2$ to m and because the self-diffusion coefficients can be predicted using the free-volume theory of Vrentas and Duda.[33−37] Unfortunately, however, the invoked assumptions cannot be physically justified.

Other authors have proposed the concentration of arbitrarily defined segments as a measure of macromolecular concentration in GMS.[14,36−38] For example, Wesselingh and Bollen[38] adopted the chain repeat element of the polymeric species as the basic molecular unit to test the validity of their extension of free-volume theory for multicomponent Maxwell−Stefan diffusivities. However, Wesselingh and Bollen neither discuss nor derive any general formulation of the multicomponent diffusion equation for macromolecular solutions.

In the electrochemical literature, GMS is used to model multicomponent transport through membranes of fuel cells. A molecular weight for the membrane is arbitrarily chosen, most often equal to the so-called equivalent weight (the weight of the membrane per equivalent).[16,39,40] In other words, the sequence of macromolecular segments corresponds to the sequence of charged groups in the membrane. However, when the polymer chains have a low charge density, the segments are large compared to those of the other species in solution; for an uncharged membrane, the entire membrane reduces to a segment of large but unknown molecular weight.[41]

The goal of this work is to extend the generalized Maxwell−Stefan equation toward solutions of molecules with starkly different size and whose segments are all accessible for mutual frictional interactions (i.e., polymer solutions with negligible hydrodynamic interactions and steric hindrance, such as free-draining or concentrated macromolecular solutions, and membrane/solute/solvent systems). Our physical arguments for EMS are identical to those of Heintz and Stephan. However, in contrast to eq 4, our extension is consistent with the Gibbs−Duhem equation and with Onsager's reciprocity relations. When applied to membrane/solvent systems, EMS does not require knowledge of the membrane molecular weight. The macromolecular species is considered to be a component of the mixture, interacting with the other species not only by frictional forces, but also by conventional physicochemical forces. We do not here consider multicomponent transport in inert membranes and in porous media.[3,4,8,42−47]

Extended Maxwell−Stefan Theory

Derivation of EMS. Equation 2 is appropriate for simple fluid mixtures (all molecules are considered to be small spherical molecules of similar size, as shown in Figure 1a). However, the image in Figure 1a does not capture the physics of macromolecular solutions. Consider a binary solution of a large-molecular-weight solute, for example a polymer or a protein, in a small-molecular-weight solvent. Collisions between a solvent molecule and the solute involve only a small portion of

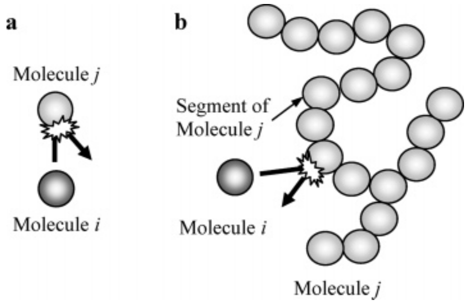

Figure 1. Collision between (a) equal-sized molecules and (b) molecules of starkly different sizes. In case b, only a small portion (=segment) of the large molecule *j* is affected by the collision with the small molecule *i*.

the large molecule, a portion whose size is roughly the same as that of the solvent molecule. We can model the large molecule as a collection of connected beads or segments.[48] It is convenient to define this segment as the portion of the polymer chain that is directly affected by a collision with a solvent molecule, as exemplified in Figure 1b. We assume that all segments in the large molecule have identical frictional properties.

Thus, by definition, a segment in the large molecule has roughly the size of a solvent molecule. Simple geometry indicates that, in a solution of an essentially linear polymer with negligible hydrodynamic interactions, all polymer segments are available for collision with solvent molecules, but for a globular polymer (e.g., protein) or a dendritic polymer, that may not be the case because of steric hindrance and/or significant hydrodynamic interactions.

When all segments are accessible for collision (i.e., in free-draining or concentrated polymer solutions, and in membrane/solute/solvent systems), the product of the segment molar concentrations describes the probability of collision for these two species (see Appendix A). Therefore, we define K_{ij} for segments

$$K_{ij} = RT\frac{c_i^0 c_j^0}{c_{\mathrm{T}}^0 \text{Đ}_{ij}^0} \tag{5}$$

where c_i^0 and c_j^0 are the segment molar concentrations of species *i* and *j*, c_{T}^0 is the total segment concentration, and Đ_{ij}^0 is the EMS diffusivity. Upon replacing eq 2 with eq 5, eq 1 becomes

$$c_{\mathrm{T}}^0 RT\mathbf{d}_i \equiv c_i\nabla_{T,P}\mu_i + (\phi_i - \omega_i)\nabla p - \rho_i\mathbf{g}_i + \omega_i\sum_j \rho_j\mathbf{g}_j = RT\left[\sum_{j\neq i}\frac{c_i^0c_j^0}{c_{\mathrm{T}}^0\text{Đ}_{ij}^0}(\mathbf{v}_j - \mathbf{v}_i) + \sum_{j\neq i}\frac{c_i^0c_j^0}{c_{\mathrm{T}}^0\text{Đ}_{ij}^0}\left(\frac{D_j^{\mathrm{T}}}{\rho_j} - \frac{D_i^{\mathrm{T}}}{\rho_i}\right)\nabla(\ln T)\right] \tag{6}$$

By definition, $\rho_i^0 = \rho_i$, $\phi_i^0 = \phi_i$, $\mathbf{v}_i^0 = \mathbf{v}_i$ and $c_i^0 = c_iN_i$ where the superscript 0 refers to segments, and N_i is the number of segments per molecule of species *i*.

EMS with Volume Fraction. For application, eq 6 is best rewritten in terms of measurable macroscopic quantities. We assume that there is no volume change upon mixing and convert the segment mole fraction into a species volume fraction according to

$$c_i^0 = \frac{\phi_i}{v_i^0} \tag{7}$$

where v_i^0 is the molar volume of an *i*-segment. Although choice of the segment unit (and therefore v_i^0) is arbitrary, it is reasonable, based on physical arguments, to assume equal size for all segments, independent of species *i*. With the assumption $v_i^0 = v$ for any species *i*, it can be shown that $c_{\mathrm{T}}^0 = 1/v$. Equation 6 then becomes

$$\frac{RT}{v}\mathbf{d}_i \equiv RT\left[\sum_{j\neq i}\frac{\phi_i\phi_j}{v\text{Đ}_{ij}^0}(\mathbf{v}_j - \mathbf{v}_i) + \sum_{j\neq i}\frac{\phi_i\phi_j}{v\text{Đ}_{ij}^0}\left(\frac{D_j^{\mathrm{T}}}{\rho_j} - \frac{D_i^{\mathrm{T}}}{\rho_i}\right)\nabla(\ln T)\right] = c_i\nabla_{T,P}\mu_i + (\phi_i - \omega_i)\nabla p - \rho_i\mathbf{g}_i + \omega_i\sum_j\rho_j\mathbf{g}_j \tag{8}$$

A convenient choice for v is the molar volume of the pure solvent or that of the component that has the smallest molecules. This choice of v is identical to the choice of the lattice size in Flory–Huggins polymer–solution theory[49] that is widely used to express the chemical potential of a species in a polymer solution or in a membrane as a function of the condensed-phase composition. When Flory–Huggins theory is used in conjunction with the Maxwell–Stefan equation, the v suggested here is a natural choice. For a mixture where all molecules are small with the same size v, $\phi_i = x_i$, $1/v = c_{\mathrm{T}}^0 = c_{\mathrm{T}}$. In this limiting case, the EMS equation, eq 8, reduces to the GMS equation, eq 1.

Discussion

The generalized Maxwell–Stefan equation is derived from the thermodynamics of irreversible processes.[5,8] Although irreversible thermodynamics provides information on the symmetry of friction factors K_{ij}, the mathematical form of K_{ij} given in eq 2 originates from molecular theories for dilute, monatomic gas mixtures[50] and for monatomic liquid mixtures.[31,32] Our extension of the generalized Maxwell–Stefan equation modifies only the mathematical form of the friction factor. Thus, EMS is consistent with irreversible thermodynamic principles. In particular, EMS obeys the Gibbs–Duhem equation. Also, the Đ_{ij}^0 in eq 5 are symmetric to preserve the K_{ij} symmetry as required by Onsager's reciprocity relations. Therefore, EMS corrects the deficiency in Heintz and Stefan's modification of GMS that does not simultaneously satisfy Onsager's reciprocity relations and the Gibbs–Duhem equation.

Moreover, the mathematical form of K_{ij} in eq 5 is consistent with a recent (approximate) kinetic theory for polymer solutions developed by Curtiss and Bird.[51–54] In this theory, a bead–spring model is adopted to represent a polymer chain. In the most recent paper[54] of Curtiss and Bird, the friction factor for an isotropic system is of the form:

$$\frac{\rho_i\rho_j}{m_i^0m_j^0}\frac{Z_{ij}}{k_{\mathrm{B}}T} \tag{9}$$

where m_i^0 is the molecular mass of a segment for species *i*, and Z_{ij} is a binary friction coefficient for the *i*–*j* pair. The ratio ρ_i/m_i^0 is the number concentration of beads for species *i*. Thus, the kinetic theory of Curtiss and Bird provides for Z_{ij} a segment-concentration dependence similar to ours. Z_{ij} is related to the EMS diffusivity $Đ_{ij}^{0}$ by

$$Z_{ij} = \frac{(k_{\mathrm{B}}T)^2}{c_{\mathrm{T}}^{0} N_{\mathrm{A}} Đ_{ij}^{0}} \tag{10}$$

However, in the Curtiss-Bird kinetic theory, the generalized driving force for diffusion, $c_{\mathrm{T}}RT\mathbf{d}_i$, differs somewhat from that given by irreversible thermodynamics as used in our development.[54]

A species molar concentration c_i remains in eq 8 as a multiplying factor of the chemical potential that is defined per mole of molecules, not per mole of segments. In practice, this molar concentration does not cause any difficulty when eq 8 is applied to transport through a membrane with unknown molecular weight because, in that event, only $(m - 1)$ equations (eq 8) are independent, where m is the number of components in the system (membrane included). Indeed, by summing over index i, both sides of eq 6 vanish: the middle because of the Gibbs−Duhem relation and the right side because of symmetry of indices i and j. Therefore, we do not need the equation for the membrane that is the only one where its unknown molecular weight appears.

Although a macromolecule is divided into segments to represent its friction with other species in the mixture, the chemical potential for a species i in EMS must account for the connectivity of chain segments. Therefore, the chemical potential must be derived from a polymer−solution theory; otherwise, there is no difference between a solution of segments and a solution of polymer molecules containing those segments. Because, for a given polymer molecule, the number of segments depends on the segment definition, neglecting chain connectivity results in thermodynamic descriptions that depend on the definition of the macromolecular segment for the friction factor.[39,41]

When all polymer segments are accessible for collision, (e.g., for dilute polymer solutions in the free-draining limit and for concentrated polymer solutions), we expect that EMS diffusivities, unlike GMS diffusivities, are independent of the molecular weight of the macromolecule, M_{w}, provided that M_{w} is sufficiently large (see Appendix A). It is well-known that the Fickian diffusion coefficient in concentrated polymer solution is insensitive to polymer M_{w}.[55,56] For a binary system, the relation between EMS diffusivity and Fickian diffusivity is derived in Appendix B (eq B6). This derivation is based on the assumption of no volume change upon mixing. The relation between the binary GMS diffusivity $Đ_{12}$ and the binary Fickian diffusivity D_{12} is

$$D_{12} = Đ_{12}\bar{v}_2 c_{\mathrm{T}}\left[\frac{1}{RT}\left(\frac{\partial \mu_1}{\partial(\ln c_1)}\right)_{T,P,n_2}\right] \tag{11}$$

where $\bar{v}_2$ is the partial molar volume of the polymer. (If $\bar{v}_2$ is negative, the derivative $(\partial\mu_1/\partial(\ln c_1))_{T,P,n_2}$, is also negative. Therefore, D_{12} is always positive.) Because the thermodynamic correction $[1/RT(\partial\mu_1/\partial(\ln c_1))_{T,P,n_2}]$ in eqs B6 and 11 is also independent of M_{w} for large polymer molecular weights, the EMS diffusivity is insensitive to M_{w}, whereas the GMS diffusivity must be molecular-weight dependent. Insensitivity to M_{w} of EMS diffusivities provides an important advantage when the multicomponent diffusion equation is applied to a polymer solution where the polymer's molecular weight is unknown or the polymer is polydisperse.

Table 1. Water Diffusivities in Soft-Contact-Lens Membranes for Three Different Diffusion Equations

soft contact lens[a]	$Đ_{1\mathrm{p}}M_{\mathrm{p}}$ [10^{-5} g cm^2/mol s][b]	$Đ_{1\mathrm{p}}^{0}$ [10^{-7} cm^2/s][b]	$D_{1\mathrm{p}}$ [10^{-7} cm^2/s][b]
HEMA	4.51	4.12	2.57
SofLens-98	5.26	6.26	3.78
SofLens-66	10.8	13.9	8.48

[a] For properties of these soft-contact-lens materials, see Hoch et al.[10] [b] $Đ_{1p}M_p$ is the product of a GMS diffusivity and an unknown membrane molecular weight, as calculated by Hoch et al.[10] $Đ_{1p}{}^{0}$ is the EMS diffusivity based on a segment molar volume equal to the molar volume of pure water. D_{1p} is the Fickian diffusivity.

Free-volume theory[33−37] shows that, for concentrated polymer solutions, the concentration dependence of Fickian diffusivity D_{12} is dominated by the large rise in free volume upon dilution, whereas it is much less affected by the concentration dependence of the thermodynamic correction. Equations B6 and 11 suggest that, if the thermodynamic correction decreases when the Fickian diffusivity increases with solvent concentration, $Đ_{12}^{0}$ and $Đ_{12}$ are stronger functions of composition than is the Fickian diffusivity. This behavior is in contrast with that of a binary mixture of small, nearly-equal size molecules, where the composition dependence of Fick's diffusion coefficient comes mainly from the thermodynamic factor and where the Maxwell−Stefan diffusivity is a weak function of composition.[5]

For interpretation of experimental diffusion data, the choice of the specific diffusion equation adopted determines the numerical value of the corresponding diffusivity. Table 1 shows EMS diffusivities, $Đ_{1\mathrm{p}}^{0}$, for water through soft-contact-lens materials obtained from steady-state water-flux data reported by Hoch et al.[10] In the calculation, we have used the EMS equation (eq B3) for an isothermal, isobaric, binary systems without external forces, and we have assumed a constant EMS diffusivity. Also, we have chosen a segment molar volume, v, equal to the molar volume of pure water and have adopted the same thermodynamic description of the water/soft-contact-lens systems used by Hoch et al.[10] Dimensional changes of the membrane are self-consistently accounted for by imposing conservation of the polymer mass.[10] For comparison, Table 1 lists Fickian diffusivities $D_{1\mathrm{p}}$ and the product $Đ_{1\mathrm{p}}M_{\mathrm{p}}$ used by Hoch et al.,[10] where M_{p} is the unknown membrane molecular weight and $Đ_{1\mathrm{p}}$ is GMS water diffusivity. (The Fickian diffusivities reported here differ from those given in Table 2 of Hoch et al.[10] The latter are obtained by converting $Đ_{1\mathrm{p}}M_{\mathrm{p}}$ into Fickian diffusivities at the average water content in the membrane (see eq 10 of Hoch et al.[10]), whereas ours are calculated directly from the experimental water fluxes.) In contrast to $Đ_{1\mathrm{p}}M_{\mathrm{p}}$, calculated EMS diffusivities have the same order of magnitude as the Fickian diffusion coefficients. This similarity is expected to hold for most polymer/solvent systems. Indeed, the ratio between Fickian and EMS diffusivities is equal to the thermodynamic correction factor $[1/RT(\partial\mu_1/\partial(\ln c_1))_{T,P,n_2}]$. We have evaluated this thermodynamic correction by using the Flory−Huggins equation for the chemical potential of a solvent (1) in a high-molecular-weight polymer (2). Figure 2 shows that the thermodynamic correction is of order 1 for a wide range of Flory interaction parameters χ, except at high polymer dilution. This feature of the EMS diffusivity is appealing for potential users who are accustomed to Fick's law.

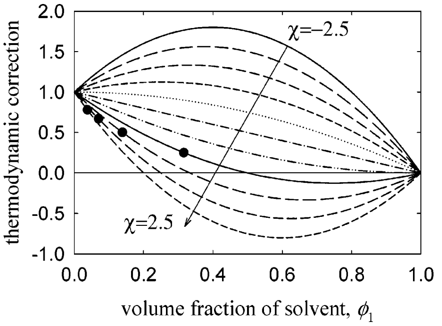

Figure 2. Thermodynamic correction $[1/RT(\partial\mu_1/\partial(\ln c_1))_{T,P,n_2}]$ calculated with Flory−Huggins theory for an infinite-molecular-weight polymer (2)/solvent (1) binary solution. Curves represent the thermodynamic correction with Flory parameter χ ranging from −2.5 to +2.5, at steps $\Delta\chi = 0.5$. Equation B7 in Appendix B shows that the ratio of diffusivities $D_{12}/Đ^0_{12}$ is equal to the thermodynamic correction when there is no volume change on mixing. In this case, the thermodynamic correction cannot be negative for a stable system. Moreover, for $\chi > 0.5$, the maximum solvent volume-fraction in the polymer (corresponding to equilibrium with a second phase of pure solvent) is indicated by the filled circles; therefore, for each curve with $\chi > 0.5$, only the portion to the left of the corresponding circle has physical meaning.

Conclusions

We have presented an extended Maxwell−Stefan equation (EMS) for solutions of molecules that are starkly different in size and whose segments are all accessible for mutual frictional interactions. Our derivation of the EMS equation (eq 6) is based on irreversible thermodynamics and on physically plausible assumptions about the molecular friction factor. The essential new ingredient of EMS is the expression for the friction factor K_{ij}, eq 5, where the probability of binary collisions is written in terms of segment molar concentrations rather than with molecule molar concentrations. The proposed form for K_{ij} is consistent with the kinetic theory of Curtiss and Bird for polymer solutions. In contrast to a previous re-formulation[1] of the multicomponent diffusion equation for polymer solutions, EMS is consistent with the Gibbs−Duhem equation and with Onsager's reciprocity relations.

EMS diffusivities are inverse friction coefficients between colliding segments; they are independent of polymer molecular weight for dilute polymer solutions in the free-draining limit and for concentrated polymer solutions, provided that the polymer molecular weight is large. In contrast to the original generalized Maxwell−Stefan equation (GMS), EMS is not affected by a membrane's unknown molecular weight (or molar concentration) when applied to transport of solutes through a polymer membrane in the solution-diffusion framework. For typical polymer/solvent binary systems, the EMS diffusivity has the same order of magnitude as that for the Fickian diffusivity over a wide solvent-concentration range.

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Appendix A: Scaling of Maxwell-Stefan Diffusivities with Molecular Weight

We present here a simple physical model to ascertain the polymer-molecular-weight dependence of EMS diffusivities for solutions of large-molecular-weight polymers. Consider a mixture of two species (i and j) of spheres, each of radius a. We calculate the frequency of collision between a sphere i and all spheres j. If sphere i moves for a time Δt with velocity $(\mathbf{v}_i - \mathbf{v}_j)$ relative to sphere j, the number of collisions, N_c, between sphere i and spheres j is equal to the concentration of spheres j (c^s_j) multiplied by the collision volume swept by the sphere i in its motion:

$$N_c = 4\pi a^2 c^s_j |\mathbf{v}_i - \mathbf{v}_j| \Delta t \tag{A1}$$

The frequency of collision f between all spheres i and all spheres j is therefore equal to the product of $N_c/\Delta t$ and the concentration of spheres i, c^s_i

$$f = 4\pi a^2 c^s_i c^s_j |\mathbf{v}_i - \mathbf{v}_j| \tag{A2}$$

Therefore, if we define ς_{ij} as the friction coefficient for the i−j pair, the frictional force $\mathbf{F}_{ij}$ experienced by spheres i and j is given by

$$\mathbf{F}_{ij} = 4\pi a^2 \varsigma_{ij} c^s_i c^s_j (\mathbf{v}_j - \mathbf{v}_i) \tag{A3}$$

Consider now a binary polymer/solvent system. Assume that a solvent molecule i consists of only one segment (one sphere), and that macromolecule j consists of n segments where each segment has the same size as that of segment i. Equation A3 represents the frictional resistance felt by the species i and j where c^s_j is the molar concentration of macromolecule segments participating in a collision, and where ς_{ij} is the average friction coefficient for an i−j pair of segments participating in a collision. For a given macromolecule, c^s_j depends on the accessible surface area for collision and, therefore, on its molecular conformation in solution. For large n and for a fixed concentration of segments in solution, we expect ς_{ij} to be independent of the number of segments present in a macromolecule, i.e., to be independent of polymer molecular weight. This independence follows because ς_{ij} is an average friction coefficient and because this average is taken only over those segments that participate in a collision.

The frictional resistances appearing in EMS (or GMS) have the same mathematical form as that in eq A3. Comparison of EMS (or GMS) with eq A3 enables us to draw some conclusions on the expected molecular-weight dependence of EMS (or GMS) diffusivities. Two limiting cases arise. In the first case, all segments of a macromolecule j can participate in collisions with molecules i. This situation corresponds to an infinite-dilute polymer solution in the free-draining limit,[57−59] or to a concentrated polymer solution, where hydrodynamic interactions are effectively screened. Here, the concentration of participating segments c^s_j is equal to the segment concentration c^0_j ($= nc_j$). Also, a macromolecule of n segments encounters a resistance that is n-times larger than that of its segments. Comparison of eqs A3 and 6 reveals that the EMS diffusivity $Đ^0_{ij}$ is inversely proportional to ς_{ij}. Thus, $Đ^0_{ij}$ has the meaning of the inverse friction factor between segments and is molecular-weight (M_w) independent when all polymer segments participate in collisions with solvent molecules, and n (or M_w) is large. Conversely, comparison of eq A3 with eq 1 shows that the GMS diffusivity is inversely proportional to $n\varsigma_{ij}$. Thus, a GMS diffusivity has the meaning of an inverse friction factor between molecules but they, regrettably, are molecular-weight dependent.

In the second case, a macromolecule in solution has a compact structure, and only a part of its segments participates in collisions with solvent molecules. This case represents, for example, the physics of a dendritic polymer solution or of an infinite-dilute solution of a linear polymer with strong hydrodynamic interactions. A polymer chain in a Θ-solvent has a compact structure, and its hydrodynamic behavior can be well represented by that of a large sphere of radius $R \propto n^{1/2}$.[59] Assume that a sphere of radius $R \gg a$ represents effectively a macromolecule. For each macromolecule, the total number of segments is n, and the segment density is n/V, where $V = 4\pi R^3/3$ is the volume of the macromolecule. The number of segments on the surface of a macromolecule is equal to the product of the segment density, $n/V \propto n^{-1/2}$, and the volume of a spherical shell of radius R and thickness a, $4\pi a R^2 \propto n$. Therefore, the number of segments on the surface is proportional to $n^{1/2}$, while the fraction of segments that lie on the surface of the macromolecule and, therefore, participate in a collision, is proportional to $n^{-1/2}$. Because $c_i^{\mathrm{s}} = c_i^0 = c_i$ and $c_j^{\mathrm{s}} \propto c_j^0 n^{-1/2} \propto c_j n^{1/2}$, eq A3 can be rewritten as

$$\mathbf{F}_{ij} \propto \frac{\varsigma_{ij}}{n^{1/2}} c_i^0 c_j^0 (\mathbf{v}_j - \mathbf{v}_i) \propto \varsigma_{ij} n^{1/2} c_i c_j (\mathbf{v}_j - \mathbf{v}_i) \qquad \text{(A4)}$$

Upon comparing eq A4 with EMS eq 6 and GMS eq 1, we find that, for an infinite-dilute polymer−solution in a Θ-solvent, the EMS diffusivity scales with macromolecule molecular weight M_{w} as $n^{1/2}$, whereas the GMS diffusivity scales with M_{w} as $n^{-1/2}$. Our simple physical model predicts that friction resistance encountered by an entire macromolecule is proportional to $n^{1/2}$, in agreement with the well-known result for an infinite-dilute polymer solution in a Θ-solvent.[57]

Appendix B: Relation between EMS and Fickian Diffusivities

Because most diffusion experiments are interpreted to yield binary Fickian diffusion coefficients, it is useful to obtain an expression that relates binary EMS diffusivities, Đ_{ij}^0, to the more familiar binary Fickian diffusivities D_{ij}. Consider an isobaric and isothermal binary system, without any applied external force: for example, a solvent (1) diffusing through a polymer film (2). According to Fick's law, the diffusive molar flux of solvent, $\boldsymbol{J}_1^{\square} = c_1(\mathbf{v}_1 - \mathbf{v}^{\square})$, with respect to the volume average velocity, $\mathbf{v}^{\square} = c_1\bar{v}_1\mathbf{v}_1 + c_2\bar{v}_2\mathbf{v}_2$, is

$$\boldsymbol{J}_1^{\square} = -D_{12}\nabla c_1 \qquad \text{(B1)}$$

where $\bar{v}_i$ is the partial molar volume of component i and D_{12} is the binary Fickian diffusivity. The fluxes $\mathbf{J}_i^{\square}$ are related by

$$\bar{v}_1\boldsymbol{J}_1^{\square} + \bar{v}_2\boldsymbol{J}_2^{\square} = 0 \qquad \text{(B2)}$$

If we assume that there is no volume change upon mixing, partial molar volumes, $\bar{v}_i$, can be replaced with the molar volume of the corresponding pure species, v_i. For an isobaric and isothermal binary system, the EMS equation for the solvent is

$$c_1\nabla_{T,P}\mu_1 = RT\frac{\phi_1\phi_2}{v\text{Đ}_{12}^0}(\mathbf{v}_2 - \mathbf{v}_1) \qquad \text{(B3)}$$

where we have also assumed $v_1^0 = v_2^0 = v$. By introducing the definition of volume fraction $\phi_i = c_i v_i$ and by replacing $(\mathbf{v}_2 - \mathbf{v}_1)$ with $(\boldsymbol{J}_2^{\square}/c_2 - \boldsymbol{J}_1^{\square}/c_1)$, eq B3 becomes

$$c_1\nabla_{T,P}\mu_1 = RT\frac{v_1 v_2}{v\text{Đ}_{12}^0}(c_1\mathbf{J}_2^{\square} - c_2\mathbf{J}_1^{\square}) \qquad \text{(B4)}$$

By using eq B2 and the identity $c_1v_1 + c_2v_2 = 1$, eq B4 can be rearranged to

$$\mathbf{J}_1^{\square} = -\text{Đ}_{12}^0\frac{v}{v_1}\left[\frac{1}{RT}\left(\frac{\partial\mu_1}{\partial(\ln c_1)}\right)_{T,P,n_2}\right]\nabla c_1 \qquad \text{(B5)}$$

Comparison of eq B1 with eq B5 gives the relation between EMS diffusivities Đ_{12}^0 and Fickian diffusivities D_{12}:

$$D_{12} = \text{Đ}_{12}^0\frac{v}{v_1}\left[\frac{1}{RT}\left(\frac{\partial\mu_1}{\partial(\ln c_1)}\right)_{T,P,n_2}\right] \qquad \text{(B6)}$$

If we choose $v = v_1$, i.e., a segment molar volume equal to that of the solvent, eq B6 reduces to

$$D_{12} = \text{Đ}_{12}^0\left[\frac{1}{RT}\left(\frac{\partial\mu_1}{\partial(\ln c_1)}\right)_{T,P,n_2}\right] \qquad \text{(B7)}$$

Because diffusivities represent the inverse of the binary friction between segments of two different species, they depend on the choice of the segment unit. However, EMS diffusivities Đ_{ij}^0 based on the segment size v are readily converted into EMS diffusivities $\text{Đ}_{ij}^{0\prime}$ based on some other segment size v', according to $\text{Đ}_{ij}^0 v = \text{Đ}_{ij}^{0\prime} v'$.

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