

ARTICLES

Flux–Force Formalism for Charge Transport Dynamics in Supramolecular Structures. 1. Activity Coefficient and Interaction Energy Considerations**R. Aldrin Denny and M. V. Sangaranarayanan****Department of Chemistry, Indian Institute of Technology, Madras-600 036, India**Received: June 2, 1997; In Final Form: September 24, 1997*

A comprehensive analysis starting from the formalism of irreversible thermodynamics, incorporating activity coefficients and interparticle interactions, is developed to derive expressions for mixed conductance, transport numbers, etc., for diffusive and electric field assisted electron hopping through polymer matrixes attached to electrode surfaces. The transport equation obtained is a combination of Dahms–Ruff diffusion and the Levich migration terms and includes short-range interparticle interactions under molecular field approximation as well as activity coefficient terms. The derived dynamical equation for electron flux follows a second-order law in species concentrations in contrast to the classical Nernst–Planck equation for ion migration. Applicable systems are thought to be organic π -conjugated electroactive polymers, electronically conducting polymers with covalently linked redox groups, i.e., metal ion redox site membranes, and ion-exchange polymers. The concept of self and tracer diffusion coefficients is brought into the formalism of charge transport in supramolecular structures. Some new insights regarding the identification of Onsager's coefficient in diffusion through supramolecular structures are also provided.

1. Introduction

The analysis of charge transport in supramolecular structures has been great interest for more than two decades.^{1–9} The charge propagation in these structures consists of several dynamical processes such as activation-controlled heterogenous electron transport at the metal/polymer film interface, segmental motion of the polymer films to provide proper orientation of redox active species, electric field assisted electron transport between spatially separated redox centers, and movement of counterions for maintaining electroneutrality. In addition to these, possible structural changes brought about by polymer morphologies also need to be considered. Amid such a scenario, it is therefore imperative to focus attention on different types of processes *in isolation* and presume their simultaneous nonoccurrence in any given experimental situation. While this strategy may be theoretically rewarding, the requisite data reduction of experimental parameters, which are invariably global and composite in nature, may invalidate methodologies that are isolated in objectives. Hence a general analysis, even if approximate, is likely to yield correct insights concerning the observed behavior. Consequently, we provide a first step in this direction by analyzing the combined effects of electron hopping between redox centers, counterion diffusion, ion pairing between redox sites and counterions, and influence of supporting electrolyte on the charge transport mechanism.

Theoretical studies carried out in this laboratory^{10–12} and elsewhere^{13–18} to study electron transport in chemically modified electrodes over the past decade indicate several interesting features concerning the nature of electron hopping (nearest neighbor vs long distance), estimation of redox capacity, influence of counterion movement, etc. The ability of these

electroactive polymer films to store electrical charge or to act as electrocatalysts depends on the rate of electron hopping in the polymeric region. The formulation of the dynamics of electron hopping via electron self-exchange constitutes the primary step in this analysis. The flux–force equation for this adjacent molecule-dependent bimolecular electron hopping is substantially different from the classical Nernst–Planck equation applicable for single-particle movement. The appropriate diffusion–migration equation governing the electron-transfer dynamics was provided by Savéant¹⁵ and Buck¹⁶ for systems without interaction and for interacting species by Chidsey and Murray.¹⁷

The formalism based on irreversible thermodynamics is particularly attractive in this context,¹⁹ because of the ease with which different coupled phenomena such as diffusion under thermal and electrical gradients, particle transport with chemical reactions/electron transfer, and hydrodynamic effects can easily be handled even for multicomponent situations. Furthermore, it is possible to analyze a hierarchy of different models which take into account additional sophisticated features encompassing interparticle interactions, distance dependence of electron transfer, system fluctuations, and the nature of stable steady states. However, a few difficulties (by no means unsurmountable) existing in such a pursuit need to be indicated, and these are (i) proper formulation of thermodynamic fluxes and forces for different diffusing species, (ii) identification of Onsager's phenomenological coefficients in terms of conventional diffusion parameters, and (iii) proper choice of reference frames needed for multicomponent analysis, etc.

There have been a few earlier attempts using an irreversible thermodynamics formalism to comprehend charge transport in

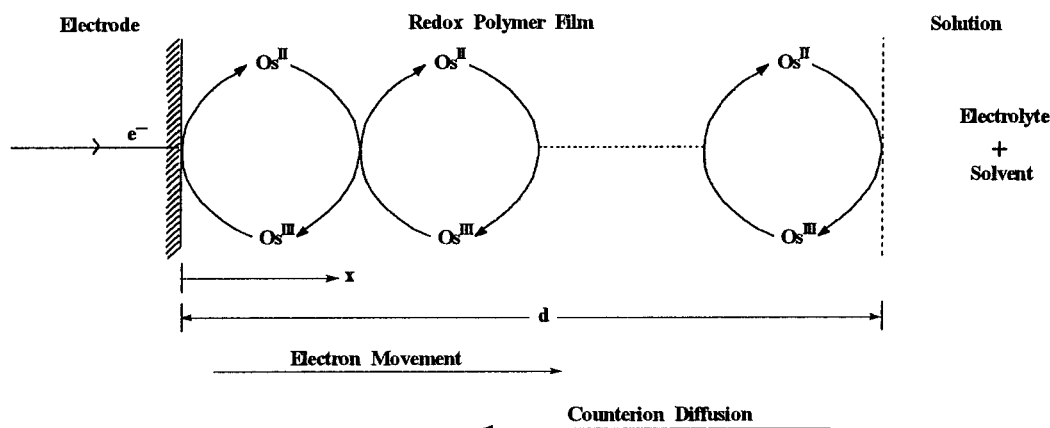
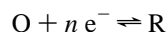


Figure 1. Schematic representation of charge conduction in a redox polymer film sandwiched between the electrode and the solution phase. The redox conduction occurs by electron self-exchange reactions between adjacent oxidized (acceptor) and reduced (donor) polymer sites. The figure depicts the processes at the negative (reductive) potential; however under oxidative potential, counterion diffusion occurs from the electrode to the solution phase, which is opposite the movement of electrons. d represents the thickness of the polymer film layer.

polymer films. Among them, mention may be made of Buck¹⁶ in the study of electron hopping in mixed conductors, so as to derive a second-order flux equation incorporating the correct Fermi level of electrons. A form of the Ricatti equation is shown to result from this analysis. Further, Chidsey and Murray¹⁷ have also indicated the usefulness of the approach based on irreversible thermodynamics by deriving appropriate conductance equations.

The purpose of this and the subsequent article (part 2) is (i) to provide a formalism based on nonequilibrium thermodynamics to describe the electron exchange between spatially separated redox centers, aided by an external electric field (the spatiotemporal diffusion—migration equation derived therefore has several novel features such as influence of activity coefficient of the redox species and interparticle interaction energy), (ii) to demonstrate the validity of identifying Onsager's phenomenological coefficients L_{ij} in terms of diffusion coefficients, well known in the transport of solutes in multicomponent liquid systems, (iii) to incorporate the influence of ion pairing and diffusivity of the redox active and electroinactive counterions on the conductivity and transport numbers, and (iv) to compare the predictions of the earlier simplified versions with the present unified model.

In this report, we consider a redox polymer that can exist in either an oxidized or reduced state involving an n electron transfer process,



Since these oxidation—reduction couples are connected to each other through the polymer backbone, their movement inside the matrix is restricted, and hence charge propagation is assumed to occur via site-to-site electron hopping. During the electron-hopping process, the oxidized and reduced electroactive ions get interconverted, and hence there exists an apparent motion of these molecules. When an electron from a reduced species hops to an adjacent oxidized species, an electroinactive counterion moves accordingly inside the polymer matrix in order to sustain electroneutrality. For example, during reduction of a film of poly[Os(bpy)₂(vby)₂](ClO₄)₃, when electrons propagate to the other end of the polymer chain via donor/acceptor electron self-exchange, counterions (ClO₄[−]) move opposite the direction of electron hopping and thereby the film maintains electroneutrality, thus additional ions will migrate out to the solution from the film, as shown in Figure 1. The movement of counterions is usually described by the classical Nernst—Planck equation²⁰

$$-J_c = D_c \left\{ \frac{\partial C_c}{\partial x} + \frac{z_c e}{k_B T} C_c \frac{\partial \phi}{\partial x} \right\}$$

It must be recognized that maintenance of electroneutrality implies inherently that electron hopping is coupled to the physical motion of electroinactive counterions. The dynamics of electron hopping thus depends on the nature of the electroactive ion and various association and dissociation processes that take place due to interaction of ionic species that affect electron transport. The incorporation of activity coefficients in modeling ion transport across membranes for symmetric cells is not new.²¹ For example, Eisenman and co-workers²² have analyzed different types such as fixed site, ionized mobile site, and liquid mobile site membranes with ion-pairing effects. However theoretical models in the context of electron transport through chemically modified electrodes have ignored activity coefficient variations under concentration gradient and electric field gradient conditions on the charge propagation dynamics assuming that interaction between particles and others remain the same when the ionic composition of the redox polymer is changed. As stated by Saveant,^{3g} such an assumption is unlikely to hold when ion concentrations involved are not negligible and ion aggregation occurs under these conditions. The role of activity on the equilibrium properties of electroactive polymer films has been first analyzed,^{2c,3c} and later its role in electrochemical responses has been considered.^{3e–g} It is therefore necessary to estimate the flux due to the apparent motion of oxidized and reduced species by means of electron self-exchange movement, which dictates the current during the electron transport process in terms of activity coefficient and interaction energy parameters.

2. Irreversible Thermodynamics Formalism

2.1. Flux Equations. The instantaneous state of reductant and oxidant may be characterized in terms of local concentrations (number density) ρ_R and ρ_O . In the conventional description, the transport of two components relative to the solvent is given by the molar flux densities J_i ,²³

$$J_i = \rho_i(v_i - v_0) \quad i = \text{R, O} \quad (1)$$

Here, v_0 and v_i are the velocities of the solvent and the i th solute constituent. The fluxes are driven by generalized forces X_i ,

$$X_i = -\text{grad}(\bar{\mu}_i) \quad (2)$$

where grad indicates $\partial/\partial x + \partial/\partial y + \partial/\partial z$ and $\bar{\mu}_i$ is the electrochemical potential of the i th constituent. The electrochemical potential term can be split into chemical and electrical parts, viz.,

$$\bar{\mu}_i = \mu_i^{\text{el}} + \mu_i^{\text{ch}} \quad (3)$$

To derive an expression for chemical potential, we consider an array of ρ equivalent sites in which ρ_{O} molecules of O and ρ_{R} molecules of R are distributed randomly. The partition function for an isolated molecule R on a site is q_{R} , and when two nearest-neighbor sites are both occupied by molecules, there is a potential energy of interaction ω between the molecules. Each molecule has Z closest neighbors, and there are in all $1/2 Z \rho$ pairs of these. Such pairs are of three kinds, namely, OO, RR, and OR, with the interaction energy $\rho_{\text{OO}}\omega_{\text{RR}}$, $\rho_{\text{RR}}\omega_{\text{RR}}$, and $\rho_{\text{OR}}\omega_{\text{OR}}$. This is a realistic model applicable for supramolecular structures if the forces between the sites are of sufficiently short range that only nearest-neighbor interactions need to be taken into account.

In the derivation of chemical potentials, we shall use a lattice model; that is, we assume that the motion of the molecules reduces merely to oscillations about some equilibrium positions. This assumption is valid for the present analysis due to the rigidity provided by the solid polymer support for electrochemically active redox molecules, thus giving the molecules some short-range order in the lattice. In this context, earlier impedance models of Mathis and Buck²⁴ and Armstrong et al.^{8,25} that deal with the nature of plasticizer and dielectric constant variation may be mentioned.

Summing all the neighbors of these ρ_{R} molecules, we have

$$Z\rho_{\text{R}} = 2\rho_{\text{RR}} + \rho_{\text{OR}} \quad (4)$$

and similarly

$$Z\rho_{\text{O}} = 2\rho_{\text{OO}} + \rho_{\text{OR}} \quad (5)$$

The canonical ensemble partition function for two particles in a solution can be written as²⁶

$$Q(\rho_{\text{R}}, \rho_{\text{O}}, T) = q_{\text{R}}^{\rho_{\text{R}}} q_{\text{O}}^{\rho_{\text{O}}} \sum_{\rho_{\text{OR}}} g(\rho_{\text{R}}, \rho_{\text{O}}, \rho_{\text{OR}}) e^{-W/k_{\text{B}}T} \quad (6)$$

where W in terms of number concentrations and intermolecular dispersion forces (ω) is

$$W = \rho_{\text{RR}}\omega_{\text{RR}} + \rho_{\text{OO}}\omega_{\text{OO}} + \rho_{\text{OR}}\omega_{\text{OR}} \quad (7)$$

and $g(\rho_{\text{R}}, \rho_{\text{O}}, \rho_{\text{OR}})$ is the number of arrangements of ρ_{R} molecules of reduced species R and ρ_{O} molecules of oxidized species O in ρ sites so that there are altogether ρ_{OR} pairs of nearest neighbors of oxidized and reduced molecules. Converting eq 7 using²⁷

$$\epsilon = \frac{Z}{2}(\omega_{\text{RR}} + \omega_{\text{OO}} - 2\omega_{\text{OR}}) \quad (8)$$

we obtain

$$Q(\rho_{\text{R}}, \rho_{\text{O}}, T) = (q_{\text{R}} e^{-Z\omega_{\text{RR}}/2k_{\text{B}}T})^{\rho_{\text{R}}} (q_{\text{O}} e^{-Z\omega_{\text{OO}}/2k_{\text{B}}T})^{\rho_{\text{O}}} \sum_{\rho_{\text{OR}}} g(\rho_{\text{R}}, \rho_{\text{O}}, \rho_{\text{OR}}) e^{\epsilon\rho_{\text{OR}}/Zk_{\text{B}}T} \quad (9)$$

At present, no rigorous mathematical treatment is available to evaluate $g(\rho_{\text{R}}, \rho_{\text{O}}, \rho_{\text{OR}})$ that is complete and exact. However

approximations that are fairly satisfactory for our purposes exist. According to the Bragg–Williams approximation, the simplest version in the hierarchy of interacting lattice gases, the configurational degeneracy and average nearest-neighbor interaction energy are both handled on the basis of random distribution of molecules among sites. Thus eq 9 becomes

$$Q(\rho_{\text{R}}, \rho_{\text{O}}, T) = (q_{\text{R}} e^{-Z\omega_{\text{RR}}/2k_{\text{B}}T})^{\rho_{\text{R}}} (q_{\text{O}} e^{-Z\omega_{\text{OO}}/2k_{\text{B}}T})^{\rho_{\text{O}}} \frac{(\rho_{\text{O}} + \rho_{\text{R}})! e^{\epsilon\rho_{\text{OR}}^*/Zk_{\text{B}}T}}{\rho_{\text{R}}! \rho_{\text{O}}!} \quad (10)$$

where

$$\sum_{\rho_{\text{OR}}} g(\rho_{\text{R}}, \rho_{\text{O}}, \rho_{\text{OR}}) = \frac{(\rho_{\text{R}} + \rho_{\text{O}})!}{\rho_{\text{R}}! \rho_{\text{O}}!}$$

and ρ_{OR}^* is the average value of ρ_{OR} .

$$\rho_{\text{OR}}^* = \frac{\sum_{\rho_{\text{OR}}} \rho_{\text{OR}} g(\rho_{\text{R}}, \rho_{\text{O}}, \rho_{\text{OR}})}{\sum_{\rho_{\text{OR}}} g(\rho_{\text{R}}, \rho_{\text{O}}, \rho_{\text{OR}})} = Z \frac{\rho_{\text{R}}\rho_{\text{O}}}{\rho_{\text{R}} + \rho_{\text{O}}} \quad (11)$$

Thus, the chemical potential of the reduced species can be written as

$$\frac{\mu_{\text{R}}^{\text{ch}}}{k_{\text{B}}T} = -\left(\frac{\partial \ln Q}{\partial \rho_{\text{R}}}\right) = \frac{\mu_{\text{R}}^{\circ}}{k_{\text{B}}T} + \ln \rho_{\text{R}} + \ln \gamma_{\text{R}} - \frac{\epsilon}{k_{\text{B}}T} \left(\frac{\rho_{\text{R}}}{\rho_{\text{O}} + \rho_{\text{R}}}\right)^2 \quad (12)$$

where

$$\frac{\mu_{\text{R}}^{\circ}}{k_{\text{B}}T} + \ln \gamma_{\text{R}} = -\ln(q_{\text{R}}(\rho_{\text{O}} + \rho_{\text{R}}) e^{-Z\omega_{\text{RR}}/2k_{\text{B}}T})$$

and ρ_{R}° denotes the standard chemical potential of reduced species, γ_{R} is the activity coefficient that arises due to the ion-pairing nature of the redox species, ϵ represents the “composite interaction energy” parameter consisting of the occupied site–occupied site interactions, and ω_{ij} is the absolute value of interaction energy between two nearest neighbors i and j . Using eqs 3 and 12, the electrochemical potential in general can be written as

$$\bar{\mu}_i = \mu_i^{\circ} + z_i e \Delta \phi + k_{\text{B}}T \ln \rho_i k_{\text{B}}T \ln \gamma_i - \epsilon \left(\frac{\rho_j}{\rho_i + \rho_j}\right)^2 \quad (13)$$

The above equation is valid only when the nearest-neighboring interactions are contributing to the total energy and needs modification if long-range forces such as Coulombic effects are also taken into consideration (note that $z_i e \Delta \phi$ represents the electrostatic interaction of ions with the external electric field and terms such as $z_i^2 e^2$, which reflect ion–ion interaction, are absent in eq 13).

If we impose the condition $\omega_{\text{OO}} \gg \omega_{\text{RO}}$ and/or $\omega_{\text{RR}} \gg \omega_{\text{RO}}$, it follows from eq 8 that ϵ is positive so that any molecule O prefers R as its nearest-neighboring partner than its own species. This leads to a perfectly alternate chain of redox active species when the oxidized and reduced species concentrations are equal and increases the electron-transfer rate. Alternatively, in the other limit, viz. $\omega_{\text{OO}} \ll \omega_{\text{RO}}$ and/or $\omega_{\text{RR}} \ll \omega_{\text{RO}}$, then $\epsilon < 0$, indicating that the species prefer to stay as pairs and

such interactions lead to phase separation and hence decrease the rate of electron hopping significantly. In this paper, we have assumed that the molecular interactions do not alter the arrangement of the redox active species attached to the polymer chain; that is this assumption is justified only when ϵ is small or comparable to the thermal energy $k_B T$.

According to the formalism of irreversible thermodynamics, phenomenological equations between forces and fluxes in terms of Onsager's coefficients (L_{ij}) are represented as

$$J_i = \sum_{j=R,O} L_{ij} X_j \quad i = R, O \quad (14)$$

By invoking Onsager's reciprocal relationship, viz., $L_{OO} + L_{OR} = 0$, the flux pertaining to the reduced species R can be written as

$$J_R = L_{RR} [\text{grad}(\overline{\mu_O} - \overline{\mu_R})] \quad (15)$$

Rearranging eq 5 using eq 3,

$$J_R = -L_{RR} \left\{ \frac{k_B T}{\rho_R \rho_O} \text{grad} \rho_R - ne \text{grad} \Delta\phi + 2\epsilon \text{grad} \rho_R + k_B T \text{grad} \left(\ln \frac{\gamma_R}{\gamma_O} \right) \right\} \quad (16)$$

where $n (=z_O - z_R)$, the number of electrons transferred, $\rho_R + \rho_O = 1$, and $\text{grad}(\rho_R) + \text{grad}(\rho_O) = 0$ have been employed to obtain the above equation. Here z_R and z_O are the charge of the reduced and oxidized species, respectively. Similarly, the activity coefficients for the reductant and oxidant are γ_R and γ_O .

It is tacitly presumed that when interactions between molecules are neglected, the activity coefficient becomes unity, implying that only one (either the interaction or activity coefficient term) is enough to describe the loss in activity. However our expression for the particle flux contains activity coefficients *as well as* interaction energy terms in view of the fact that the activity coefficient alone cannot account for all the interactions present in the system. The interaction energy terms incorporated in eq 16 essentially pertain to interactions between the electron-transfer active sites as assumed by Chidsey and Murray.¹⁷ The interactions present due to solvent, polymer, etc., can also increase or retard the electron-hopping process and thus influence the rate of charge transport. We may also recall that for electron self-exchange to take place, segmental motion of the polymer plays an important role in bringing the oxidant and reductant close to each other. Thus interaction energy becomes a function of solvent dynamics, which influences the segmental motion.^{21,24} However the activity coefficient considered in eq 16 accounts only for the loss in activity due to various ion aggregations that take place in the electroactive species. To reiterate, the *interaction term* accounts for the change in electron-transfer rate involving a *pair of sites*, and the *activity coefficient* considers the loss in activity due to various processes taking place at a *particular site*.

The conventional diffusion coefficients are related to Onsager phenomenological coefficients by^{28,29}

$$L_{ij} = \delta_{ij} \left(\frac{\rho_i}{k_B T} \right) D_i C_T + \left(\frac{\rho_i \rho_j}{k_B T} \right) D_{ij} C_T \quad (17)$$

where δ_{ij} is the Kronecker delta. It is important to reiterate the definition of the Onsager phenomenological coefficients (L_{RR}

and L_{RO}) that emerge from eq 17. L_{RO} is the flux of reductant due to unit thermodynamic force acting on the oxidant. In this way we can define L_{RR} as the distinct part of the flux of reduced species due to unit thermodynamic force acting on component R* multiplied by appropriate concentration factors, where R* differs from R only by a label that does not affect the interactions among the particles.²³

From eq 17 we write

$$L_{RO} = \left(\frac{\rho_R \rho_O}{k_B T} \right) D_{RO} C_T \quad (18)$$

Using Onsager's relations concerning direct and cross phenomenological coefficients, viz., $L_{RR} + L_{RO} = 0$, it follows that

$$L_{RR} = - \left(\frac{\rho_R \rho_O}{k_B T} \right) D_{RO} C_T \quad (19)$$

At this stage, we must emphasize the sign of L_{RR} vis à vis D_{RO} . On account of the laws of nonequilibrium thermodynamics concerning the dissipation function, Onsager's direct coefficients (in our case L_{RR} or L_{OO}) are always positive. In view of this, D_{RO} in eq 19 is negative. Substituting eq 19 in eq 16 and simplifying, we obtain

$$J_R = -D_{\text{hop}} C_T \left\{ \left[1 + \frac{2\epsilon}{k_B T} \rho_R \rho_O \right] \text{grad} \rho_R + \rho_R \rho_O \text{grad} \left[\ln \frac{\gamma_R}{\gamma_O} - \frac{ne}{k_B T} \Delta\phi \right] \right\} \quad (20)$$

where we have employed D_{hop} instead of $-D_{RO}$ so as to bring our equation into conformity with conventional Fick's second law of diffusion. Two limiting cases of eq 20 can easily be noticed; namely, (i) if $\gamma_R = \gamma_O$, i.e., when the electroneutrality coupling between the redox ion and the electroinactive counterion is assumed absent, eq 20 reduces to eq 25 of Chidsey and Murray¹⁷ and Denny and Sangaranarayanan,¹² and (ii) in addition, if $\epsilon = 0$, the above equation is identical to that of Saveant¹⁵ and Buck.¹⁶ And similarly,

$$J_O = -D_{\text{hop}} C_T \left\{ \left[1 + \frac{2\epsilon}{k_B T} \rho_R \rho_O \right] \text{grad} \rho_O + \rho_R \rho_O \text{grad} \left[\ln \frac{\gamma_O}{\gamma_R} + \frac{ne}{k_B T} \Delta\phi \right] \right\} \quad (21)$$

Although eq 17 above may be employed to write L_{RR} , we deliberately refrain from doing so here, since this would entail introducing the tracer diffusion coefficient (D_R) and the intradiffusion coefficient (D_{RR}).

2.2. Conductivity and Transport Number. To discuss the charge-transfer conductivity in a binary system undergoing electron hopping, it is once again convenient to use Onsager's nonequilibrium thermodynamics formalism. From eq 14,

$$J_R = L_{RR} X_R + L_{RO} X_O \quad (22)$$

$$J_O = L_{OR} X_R + L_{OO} X_O \quad (23)$$

In the study of electrical gradient experiments in modified electrodes, sandwich electrodes are recently being employed,^{2j} in which metal electrodes are coated with conducting polymers or with polymers containing redox centers over which a metal has been evaporated so as to cover the polymer. This evaporated metal is porous, permits only solvent and electrolyte molecules

to penetrate, and does not allow the polymer to diffuse out from the electrode surface. Conductance of the system can be measured by applying a potential difference across the porous and the metal electrode; under this condition, the concentration gradient is absent, and we have

$$J_R = -e(z_R L_{RR} + z_O L_{RO}) \left(\frac{\partial \psi}{\partial x} \right) \quad (24)$$

$$J_O = -e(z_R L_{OR} + z_O L_{OO}) \left(\frac{\partial \psi}{\partial x} \right) \quad (25)$$

where ψ is a small external potential difference applied between the two electrodes sandwiching a sample poised at an equilibrium potential E_{eq} . Thus the molar flux density for the reduced species can be written as

$$J_R = n e L_{RR} \left(\frac{\partial \psi}{\partial x} \right) \quad (26)$$

Similarly the molar flux density J_O across the solvent-fixed reference frame employed above is

$$J_O = -n e L_{OO} \left(\frac{\partial \psi}{\partial x} \right) \quad (27)$$

The dc current density j_e can be related to the flux density as

$$j_e = e \sum_i z_i J_i \quad i = O, R \quad (28)$$

Substituting eq 27 in eq 28

$$j_e = -n^2 e^2 L_{RR} \left(\frac{\partial \psi}{\partial x} \right) \quad (29)$$

where $L_{OO} = L_{RR}$. The relation between the dc current density j_e and electron conductivity κ_e is given by

$$j_e = -\kappa_e \left(\frac{\partial \psi}{\partial x} \right) \quad (30)$$

From eqs 19, 29, and 30

$$\kappa_e = \frac{n^2 e^2}{k_B T} D_{hop} \chi_O \chi_R C_T \quad (31)$$

Equation 31 was first provided by Levich³⁰ using kinetic arguments. In addition, the appropriate transport numbers relevant in this context are defined in the irreversible thermodynamics formalism as

$$t_i = \frac{z_i J_i}{\sum_i z_i J_i} \quad i = O, R \quad (32)$$

The transference number of oxidized (t_O) and reduced species (t_R) follows as

$$t_O = \frac{z_O}{n} \quad (33)$$

$$t_R = -\frac{z_R}{n} \quad (34)$$

The transport numbers given in eqs 33 and 34 account for the electron movement alone occurring in the polymer matrix.

Thus the electron transport number $t_e (=t_O + t_R)$ becomes unity. However this is only a special case, since under any normal conditions transport of charges due to counterions also needs to be considered, and this is carried out in part 2.

3. Discussion

Several interesting insights emerge from the above nonequilibrium thermodynamics formalism for electron transport in supramolecular structures. Firstly, we note the presence of an activity coefficient in the transport equations eqs 20 and 21 pertaining to charge transfer through chemically modified electrodes. This feature is distinctly different from other approaches customarily employed to derive flux equations invoking kinetic arguments either phenomenologically^{15,17,31} or using time-dependent microscopic formalisms such as kinetic Ising model versions.^{11,12} Even though the presence of the activity coefficient in eqs 20 and 21 arises naturally, its influence is difficult to quantify because of the complexities involved in solving these equations especially in non-steady-state experiments. Saveant¹⁸ has solved a simple version of eq 20 without interaction and activity coefficient terms for chronoamperometric techniques.

Secondly, the choice of reference frame needs some comments. In the conventional description of transport of ionic species in aqueous solutions, diverse reference frames are employed to analyze the movement of the charged species. Here we have resorted to the solvent-fixed reference frame due to the simplicity involved in deriving the transport equation, even though the volume-fixed reference frame has been observed to agree well with the experimental results.^{29,32} Although the use of other reference frames are not expected to alter the structure of the final transport equation, the dependence of D_{RO} on the intradiffusion coefficients is no longer valid. Incidentally, the derivation of equations such as 20 hitherto accomplished using other methods indicates that these have implicitly relied upon the solvent-fixed reference frame.¹⁶ This is not all. In the analysis of charge transport through redox polymer electrodes, the electric field dependence of the rate constant is invoked through Tafel-like laws, whereas here, this behavior is not explicitly presumed. Nevertheless, this dichotomy between thermodynamic formalism versus kinetic approaches can easily be unraveled at both phenomenological and microscopic levels. Furthermore, flux equations pertaining to transport in polyvalent redox complexes such as $^{33} RuL_3^+/RuL_3^0/RuL_3^-$, where L is 5,5'-dicarbo(3-acrylyl-1-propoxy)-2,2'-bipyridine, can be derived using identical prescription for L_{ij} given in eq 17 incorporating interaction terms as well under mean field approximation. The resulting equation is more general than eq 15 of Baldy et al^{33c} and shows the generality of the concepts based on irreversible thermodynamics.³⁴

A central issue in the nonequilibrium thermodynamic formalism concerns the composition of Onsager's phenomenological coefficients L_{ij} . The dependence of L_{ij} reported by Miller,²⁹ originally derived in the transport of ionic species in multicomponent solutions, is *valid even for diffusion under an electric field gradient*, as shown here. It is worth emphasizing that a hierarchy of transport equations can be formulated using this approach even for a given physical situation by employing different types of *ansatz* for the chemical potential of the species in place of eq 13. This would in turn lead to a better description of the systems especially in case of interacting redox species. In contrast to the above phenomenological description of transport phenomena, several microscopic approaches based on random walk models,³⁵ kinetic Ising models,³⁶ generalized

mobility³⁷ expressions, etc., can also be analyzed. In particular, the mapping of kinetic Ising model versions with phenomenological hopping equations with interparticle interaction has been carried out elsewhere.¹² Hence, the formalism of irreversible thermodynamics to derive a spatiotemporal migration expression indicates that a direct connection between Onsager's coefficient L_{ij} and microscopic transition probabilities may exist and is a direct consequence of charge transport models in supramolecular structures.

The diffusion coefficient arising from transport equations derived so far^{10,12,15, 17} is the apparent diffusion coefficient (D_E), which according to irreversible thermodynamics is the flow of the electrons in the absence of any other hindrance. An important aspect that deserves attention is the significance of D_{hop} in the particle flux equation (eq 20). The fact that the origin of D_{hop} has come from the concepts of irreversible thermodynamics implies that D_{hop} is the diffusion of the reductant in the presence of oxidized species. This diffusion occurs due to the apparent motion of the reduced species and hence is a measure of electron diffusion in the lattice consisting of oxidized species. Finally, the fact that D_{RR} and D_{R} denoting respectively the self and tracer diffusion coefficient can easily be brought into the study of charge transport in supramolecular structures indicates an important merit of this procedure.

4. Summary

The study of transport equations for electron hopping between redox centers in supramolecular structures pertaining to diverse experimental conditions is accomplished using the concepts of nonequilibrium thermodynamics. It is shown how irreversible thermodynamics provides a fundamental basis for deriving flux–force equations and thereby obtaining theoretical expressions for conductance and transport number as a function of system variables.

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Glossary

bpy	bipyridine
C	concentration (mol cm ⁻³)
D	diffusion coefficient (cm ² s ⁻¹)
e	quantity of charge on the electron (C)
g	statistical probability
j	current density (A cm ⁻²)
J	molar flux density (mol cm ⁻² s ⁻¹)
k_B	Boltzmann constant (J K ⁻¹)
L	Onsager's phenomenological coefficient (mol J ⁻¹ cm ⁻¹ s ⁻¹)
n	number of electrons transferred (mol ⁻¹)
q	particle partition function
Q	canonical ensemble partition function
t	transport number
T	temperature (K)
vby	vinyl bipyridine
X	generalized force (J cm ⁻¹)
z	charge of the species under consideration (mol ⁻¹)
Z	coordination number
γ	activity coefficient
δ_{ij}	Kronecker delta
ϵ	intermolecular interaction energy (J mol ⁻¹)
κ	conductivity (Ω^{-1} cm ⁻¹)

μ	chemical potential (J mol ⁻¹)
μ_1	electrochemical potential (J mol ⁻¹)
ρ	number concentration of species
v	velocity of the moving particle (cm s ⁻¹)
$\Delta\phi$	applied potential (V)
ψ	applied potential difference (V)
ω	intermolecular forces (J mol ⁻¹)

subscripts

e	electronic part
hop	electron hopping
o	solvent contribution
O	oxidized species
R	reduced species
T	total concentration

superscripts

ch	chemical part
el	electrical part
°	standard value
*	average value

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