

Diffusion of excess electrons in one- and two-component molecular solutions. A theoretical model

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A connection is made between the experimentally observed diffusion coefficient (D) of excess electrons in molecular fluids and the rate at which the excess electrons "jump" from one solvent molecule to another. A simple one-dimensional nearest-neighbor model is employed to develop a diffusion equation description of the microscopic excess-electron density function. Solution of this diffusion equation yields, in the one-component solution case, an expression for D in terms of the nearest-neighbor distance of the liquid, the solvent anion's diffusion coefficient, and the intermolecular electron hopping rate. The diffusion equation has also been solved in general for a binary solution as well as in two especially interesting limiting cases: when the rate of hopping from one kind of molecule (A) to the other (B) is much faster (slower) than the A-to-A or B-to-B hopping rates. In each case, it is demonstrated how the solution composition dependence of D can be used to extract the various electron hopping rates.

I. INTRODUCTION

In an earlier publication,¹ hereafter referred to as I, we showed how the rate of migration of excess electrons in one-component molecular liquids could be expressed in terms of solvent structure information (pair distribution functions and solvent diffusion coefficients) as well as electron tunneling and hopping rates. Consideration in I was restricted to those solvents in which the excess electron exists predominantly in localized states rather than solvents which permit the electron to be primarily in highly mobile delocalized quasifree states. For such cases, we were able to obtain a closed-form expression for $\langle r^2 \rangle_t$, the mean-square distance traveled by an electron within time t . The resultant equation is written in terms of the diffusion coefficient of a solvent anion D_s and the solvent's pair distribution function $\rho(R, 0)$ as follows:

$$\langle r^2 \rangle_t = 6D_s t + \int_0^\infty 4\pi R^4 \rho(R, 0) g(R, R, t) dR. \quad (1)$$

Here $g(R, R, t)$ contains all of the detailed information concerning electron tunneling and electron hopping dynamics, and is interpreted as the probability of finding an excess electron in a molecular orbital on a molecule at point R in the solution at time t , given that there was an electron at the origin at $t=0$. Equation (1) indicates that there are two parallel channels for the excess electron's migration. The first pathway involves the electron "riding" a solvent molecule; in the second, the electron jumps from one solvent molecule to another. Typical values for D_s are 10^{-5} cm²/sec, whereas the experimentally observed diffusion coefficients of excess electrons vary from 10^{-6} to 10^2 cm²/sec. Thus, it is quite possible for either of the two pathways to be dominant.

As was demonstrated in detail in I, the microscopic probability density $g(R, R, t)$ obeys an evolution equation of the following form:

$$\begin{aligned} \frac{d}{dt} g(\mathbf{R}, \mathbf{R}', t) = & i \int d\mathbf{S} \{ \rho(\mathbf{S}, \mathbf{R}) h(\mathbf{S}, \mathbf{R}) g(\mathbf{S}, \mathbf{R}', t) - \rho(\mathbf{R}', \mathbf{S}) \bar{h}(\mathbf{R}', \mathbf{S}) g(\mathbf{R}, \mathbf{S}, t) \} \\ & - \int d\mathbf{S} d\mathbf{S}' \{ \rho(\mathbf{S}, \mathbf{S}') \rho(\mathbf{S}', \mathbf{R}) F(\mathbf{S}, \mathbf{S}', \mathbf{S}', \mathbf{R}) g(\mathbf{S}, \mathbf{R}', t) + \rho(\mathbf{S}', \mathbf{S}) \rho(\mathbf{R}', \mathbf{S}') F(\mathbf{S}', \mathbf{S}, \mathbf{R}', \mathbf{S}') g(\mathbf{R}, \mathbf{S}, t) \\ & - \rho(\mathbf{R}', \mathbf{S}) \rho(\mathbf{S}', \mathbf{R}) F(\mathbf{R}', \mathbf{S}, \mathbf{S}', \mathbf{R}) g(\mathbf{S}', \mathbf{S}, t) - \rho(\mathbf{S}, \mathbf{R}) \rho(\mathbf{R}', \mathbf{S}') F(\mathbf{S}, \mathbf{R}, \mathbf{R}', \mathbf{S}') g(\mathbf{S}, \mathbf{S}', t) \}. \end{aligned} \quad (2)$$

The electron transfer integrals $\bar{h}(\mathbf{R}, \mathbf{R}')$ have been given in I in terms of the molecular orbitals $\phi(\mathbf{r}, \mathbf{R})$ and $\phi(\mathbf{r}, \mathbf{R}')$ centered at \mathbf{R} and \mathbf{R}' as

$$\bar{h}(\mathbf{R}, \mathbf{R}') = \langle \langle \phi(\mathbf{r}, \mathbf{R}) | h_e | \phi(\mathbf{r}, \mathbf{R}') \rangle \rangle, \quad (3)$$

where h_e is the electronic Hamiltonian including all N electron-molecule potential energy terms $u(\mathbf{r}, \mathbf{X}_i)$

$$h_e = -\frac{1}{2} \nabla_r^2 + \sum_{i=1}^N u(\mathbf{r}, \mathbf{X}_i). \quad (4)$$

The outer bracket in Eq. (3) refers to a thermal average over the translational, rotational, and vibrational degrees of freedom of the N solvent molecules. As discussed in detail in I, the tunneling contributions to the electron migration are contained in the $\bar{h}(\mathbf{R}, \mathbf{R}')$ terms which may be nonzero even at low temperatures.

For systems in which the excess electron is not localized on a given solvent molecule as a solvated anion (e.g., anthracene anion) but instead is localized via the formation of a small polaron,^{1(b),1(c)} the orbital $\phi(\mathbf{r}, \mathbf{R})$ represents a polaron orbital centered at \mathbf{R} . The development presented in I is sufficiently general to remain valid for this polaron case because the (strong) interac-

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tion between the excess electron and the solvent molecules was properly accounted for by carrying out a canonical transformation of the electron-solvent Hamiltonian. This transformation then permits one to speak of the migration of a "dressed" electron (polaron) in which the solvent molecules adjust their geometries as the excess electron moves throughout the solution. The essential point of relevance to the present paper is that the orbitals $\phi(\mathbf{r}, \mathbf{R})$, the transfer integrals $\bar{h}(\mathbf{R}, \mathbf{R}')$, and the fluctuations in these integrals (see below) apply equally well to cases in which the electron is bound to a solvent molecule as an anion and to cases involving small polaron formation. The reader is referred to I for more details on the derivations of the working equations.

The function $F(\mathbf{R}, \mathbf{R}', \mathbf{S}, \mathbf{S}')$ appearing in Eq. (2) is the equilibrium average (over solvent molecule degrees of freedom) of fluctuations in the electron transfer integrals $h(\mathbf{R}, \mathbf{R}') \equiv \langle \phi(\mathbf{r}, \mathbf{R}) | h_e | \phi(\mathbf{r}, \mathbf{R}') \rangle$

$$F(\mathbf{R}, \mathbf{R}', \mathbf{S}, \mathbf{S}') = \int_0^t \langle \delta h(\mathbf{R}, \mathbf{R}', t - \tau) \delta h(\mathbf{S}, \mathbf{S}', 0) \rangle dt, \quad (5)$$

where the fluctuation in h is defined as

$$\delta h(\mathbf{R}, \mathbf{R}', t) \equiv \langle \phi[\mathbf{r}, \mathbf{R}(t)] | -\frac{1}{2} \nabla_r^2 + \sum_{i=1}^N u[\mathbf{r}, \mathbf{X}_i(t)] \times | \phi[\mathbf{r}, \mathbf{R}'(t)] \rangle - \bar{h}(\mathbf{R}, \mathbf{R}'). \quad (6)$$

The time dependences $\mathbf{R}(t)$, $\mathbf{R}'(t)$, $\mathbf{X}_i(t)$ appearing in Eq. (6) reflect the time variation of the positions (\mathbf{R}) and vibrational-orientational coordinates (\mathbf{Q}_i, Ω_i) ($\mathbf{X}_i \equiv \mathbf{R}_i, \mathbf{Q}_i, \Omega_i$) of the solvent molecules. These fluctuation terms contain the electron hopping (via vibrational-rotational mode assistance) contribution to the electron migration. At low temperatures, fluctuations in the coordinates of the solvent molecules will be small and the \bar{h} terms will dominate. However, at temperatures for which significant deviations of the solvent molecules' coordinates are probable, the fluctuation terms F can become more important than the \bar{h} contributions. As Munn and Siebrand⁽⁴⁾ and Grover and Silbey⁽⁶⁾ have shown, the temperature at which the hopping (F) contributions begin to overcome the coherent (\bar{h}) contributions is (for exciton transport) of the order of the characteristic vibrational temperature of the lattice (solvent here) for those modes which are strongly coupled to the exciton (electron here). Even for optical phonons of frequency 1000 cm^{-1} , the coherent effects would be unimportant at temperatures⁽⁶⁾ above 100°K . For the remainder of the present work, we shall assume that the temperature is sufficiently so high that the hopping mechanism (via the F terms) will provide the dominant contribution to the excess electron's (or dressed electron's) migration. Hence, we shall, from now on, neglect the contributions from the tunneling integrals \bar{h} .

The results obtained in I which have been briefly outlined here can be extended in a straightforward fashion to the case of a two-component solution. For simplicity, the analysis of the present paper will be developed for a one-component system after which the two-component case will be presented.

Because the liquid solution is assumed to be spatially homogeneous (and, for the case of two-component solutions, entirely randomly mixed), the distribution function $\rho(\mathbf{R}, \mathbf{R}')$, the averaged electron transfer integral $\bar{h}(\mathbf{R}, \mathbf{R}')$, and the fluctuation function $F(\mathbf{R}, \mathbf{R}', \mathbf{S}, \mathbf{S}')$ are functions only of the distances between the (two through four) relevant solvent molecules; e. g.,

$$\rho(\mathbf{R}, \mathbf{R}') = \rho(|\mathbf{R} - \mathbf{R}'|). \quad (7)$$

By taking advantage of this fact and making several physically based but crude approximations to the three quantities mentioned above, we will demonstrate in Sec. II how Eq. (2) can be reduced to a diffusionlike equation for the case discussed earlier in which $F \gg \bar{h}$. This modification of Eq. (2) then permits us to identify the diffusion coefficient D of the excess electron and to give an explicit expression for D in terms of the fluctuation integrals. This identification provides us with a potentially useful relationship between experimentally measured electron diffusion coefficients and the interactions which exist between an excess electron and the solvent molecules (as contained in F). In Sec. II we also present analogous results for the diffusion of excess electrons in two-component solutions. Section III contains an analysis of the binary-mixture results under various relevant limiting situations. Section IV contains our concluding remarks.

II. THE DIFFUSION EQUATION

We now restrict Eq. (2) to the very special case of a one-dimensional² system in which the solvent molecules are evenly spaced by a distance a , and we assume that the electron transfer integrals $\langle \phi(\mathbf{r}, \mathbf{R}) | h_e | \phi(\mathbf{r}, \mathbf{R}') \rangle$ are nonzero only if $|\mathbf{R} - \mathbf{R}'| = a$ (i. e., if the molecules at \mathbf{R} and \mathbf{R}' are nearest neighbors). Moreover, only one molecular orbital is assumed to be thermally accessible to the excess electron at the temperatures of interest here. These assumptions allow us to write the unique nonzero electron transfer and fluctuation integrals as follows:

$$\bar{h}(I, J, t) = [\delta_{J, I+1} + \delta_{J, I-1}] \bar{h}, \quad (8)$$

$$F(I, J, K, L) = \delta_{I+1, J, K, L+1} \gamma_1 + \delta_{I+1, J, K, L-1} \gamma_2 + \delta_{I \pm 1, J} \delta_{K \pm 1, L} \gamma_3, \quad (9)$$

where $\delta_{A,B,C,D}$ simply means $\delta_{AB} \delta_{BC} \delta_{CD}$ and \bar{h} , γ_1 , γ_2 , and γ_3 are defined by Eqs. (8) and (9), e. g.,

$$\gamma_2 = F(I, I+1, I+1, I+2) = F(I, I-1, I-1, I-2), \quad (10)$$

and

$$\begin{aligned} \gamma_3 &= F(I, I+1, K, K+1) = F(I, I+1, K, K-1), \\ &= F(I, I-1, K, K+1) = F(I, I-1, K, K-1). \end{aligned} \quad (11)$$

Within the nearest-neighbor one-dimensional approximation, Eq. (2) reduces to the following equation involving the discrete indices I, J which label molecular positions:

$$\begin{aligned} \frac{d}{dt} g(I, J) = & i\hbar [g(I+1, J) + g(I-1, J) - g(I, J+1) - g(I, J-1)] \\ & - \left(4\gamma_1 g(I, J) + \gamma_2 [g(I+2, J) + g(I-2, J) + g(I, J+2) + g(I, J-2)] \right. \\ & - 2\gamma_3 (1 - \delta_{IJ}) [g(I+1, J+1) + g(I-1, J-1) + g(I+1, J-1) + g(I-1, J+1)] \\ & \left. - 2\delta_{IJ} \{ \gamma_1 [g(I+1, I+1) + g(I-1, I-1)] + \gamma_2 [g(I-1, I+1) + g(I+1, I-1)] \} \right). \end{aligned} \quad (12)$$

We now assume that the coherent (tunneling) contribution to g , which is contained in \bar{h} , is much smaller than the contributions made by the fluctuation terms contained in γ_1 , γ_2 , and γ_3 . Also, because $F(I, I+1, I+1, I+2)$ and $F(I, I+1, K, K+1)$ involve fluctuations in the geometrical configurations of three or four molecules, whereas $F(I, I+1, I+1, I)$ involves only two neighbor molecules, we assume, as Grover and Silbey^{1(e)} have done, that the latter terms will dominate and we therefore neglect γ_2 and γ_3 compared to γ_1 .

To recast Eq. (12) in differential form, we introduce the simplest finite-difference approximations³ to the spatial derivatives of $g(\mathbf{R}, \mathbf{R}', t)$. In particular, for a first derivative in the direction defined by the unit vector $\hat{\eta}$:

$$\frac{dg(\mathbf{R}, \mathbf{R}', t)}{d\mathbf{R}} \equiv \lim_{\epsilon \rightarrow 0} \frac{g(\mathbf{R} + \epsilon\hat{\eta}, \mathbf{R}', t) - g(\mathbf{R} - \epsilon\hat{\eta}, \mathbf{R}', t)}{2\epsilon} \cong \frac{1}{2a} [g(I+1, J, t) - g(I-1, J, t)], \quad (13)$$

where the positions \mathbf{R}, \mathbf{R}' correspond in the one-dimensional model employed here to I, J . Similarly, for the second derivative of $g(\mathbf{R}, \mathbf{R}', t)$

$$\frac{d^2 g(\mathbf{R}, \mathbf{R}', t)}{d\mathbf{R}^2} \cong \frac{1}{4a^2} [g(I+2, J, t) + g(I-2, J, t) - 2g(I, J, t)], \quad (14a)$$

or

$$\cong \frac{1}{a^2} [g(I+1, J, t) + g(I-1, J, t) - 2g(I, J, t)]. \quad (14b)$$

Each of the terms which appear on the right-hand side of Eq. (12) can, by employing the finite-difference approximations given in Eqs. (13) and (14), be expressed as spatial derivatives of $g(\mathbf{R}, \mathbf{R}', t)$. For example, the combination $[g(I+1, J+1, t) + g(I-1, J-1, t)] 2\delta_{IJ}$ can be approximated as follows:

$$\begin{aligned} & [g(I+1, I+1) + g(I-1, I-1)] \\ & \cong a^2 \frac{d^2 g(\mathbf{R}, \mathbf{R}, t)}{d\mathbf{R}^2} + 2g(I, I, t); \end{aligned} \quad (15)$$

analogously,

$$\begin{aligned} & g(I+1, J) + g(I-1, J) - g(I, J+1) - g(I, J-1) \\ & \cong a^2 \left[\frac{d^2 g(\mathbf{R}, \mathbf{R}', t)}{d\mathbf{R}^2} - \frac{d^2 g(\mathbf{R}, \mathbf{R}', t)}{d\mathbf{R}'^2} \right], \end{aligned} \quad (16)$$

where the time variable has been suppressed for convenience.⁴

After making finite difference approximations to all of the terms occurring in Eq. (12), one arrives at the following partial differential equation which contains time and spatial derivatives of $g(\mathbf{R}, \mathbf{R}', t)$:

$$\begin{aligned} \frac{d}{dt} g(\mathbf{R}, \mathbf{R}', t) = & -4g\gamma_1 [1 - \delta(\mathbf{R}, \mathbf{R}')] + 2\gamma_1 a^2 \delta(\mathbf{R} - \mathbf{R}') \\ & \times \frac{d^2}{d\mathbf{R}^2} g(\mathbf{R}, \mathbf{R}, t). \end{aligned} \quad (17)$$

In Eq. (17), the symbol $\delta(\mathbf{R} - \mathbf{R}')$ is to be interpreted⁵ as zero if $\mathbf{R} \neq \mathbf{R}'$, and unity if $\mathbf{R} = \mathbf{R}'$. The symbol g has

been used to represent $g(\mathbf{R}, \mathbf{R}', t)$, and the "diagonal" element $g(\mathbf{R}, \mathbf{R}, t)$ has been explicitly written out in Eq. (17) wherever it occurs. Recall that we have assumed that the coherent (tunneling) contribution to g , which is contained in \bar{h} , is much smaller than the contributions made by the fluctuation terms (see our earlier discussion), and that $\gamma_1 \gg \gamma_2, \gamma_3$. The desired equation which governs the time and spatial evolution of the excess electron's probability density is then obtained from Eq. (17) by setting $\mathbf{R} = \mathbf{R}'$. This step results in

$$\frac{dg}{dt}(\mathbf{R}, \mathbf{R}, t) = 2a^2 \gamma_1 \frac{d^2}{d\mathbf{R}^2} g(\mathbf{R}, \mathbf{R}, t). \quad (18)$$

The equation governing the off-diagonal elements of g is from Eq. (17):

$$\frac{d}{dt} g(\mathbf{R}, \mathbf{R}', t) = -4\gamma_1 g(\mathbf{R}, \mathbf{R}', t), \quad (19)$$

which shows that these off-diagonal elements decay in a time⁶ of the order of $(4\gamma_1)^{-1}$. The equation governing the diagonal elements is of the diffusion type ($dg/dt = D\nabla^2 g$) with a diffusion coefficient D given by

$$\begin{aligned} D = & 2a^2 \gamma_1, \\ = & 2a^2 F(I, I+1, I+1, I), \\ = & 2a^2 F. \end{aligned} \quad (20)$$

The excess electron diffusion coefficient is thus approximated⁷ in terms of the solvent anion's diffusion coefficient D_s and the result of Eq. (20) as $D = D_s + 2a^2 F$. Clearly the solvent molecule nearest-neighbor distance (a) and the fluctuations in the electron transfer integral (F) play essential roles in determining D . Recently Metiu, Kitahara, Silbey, and Ross⁸ have employed similar finite difference techniques to obtain a diffusion equation describing the migration of adsorbed atoms and molecules on surfaces.

For a binary mixture with components labeled by A and B, the generalization of Eq. (18) reads as follows (with the assumption that $\gamma_2 \ll \gamma_1$):

$$\frac{d}{dt} g_{AA} = 2X_A F_{AA} a^2 \frac{d^2}{dR^2} g_{AA} + X_B F_{AB} 2a^2 \frac{d^2}{dR^2} g_{BB}, \quad (21a)$$

$$\frac{d}{dt} g_{BB} = 2X_B F_{BB} a^2 \frac{d^2}{dR^2} g_{BB} + X_A F_{BA} 2a^2 \frac{d^2}{dR^2} g_{AA}, \quad (21b)$$

where g_{AA} and g_{BB} designate the excess electron probability density on the A and B type molecules, respectively. The mole fractions X_A and X_B entered Eqs. (21) via the assumption that the solvent molecules are randomly distributed which, for the one-dimensional nearest-neighbor model, implies that the pair distribution functions of nearest neighbors obey

$$\rho_{AA}(I, J) = X_A [\delta_{J, I+1} + \delta_{J, I-1}], \quad (22a)$$

$$\rho_{AB}(I, J) = X_A [\delta_{J, I+1} + \delta_{J, I-1}], \quad (22b)$$

$$\rho_{BB}(I, J) = X_B [\delta_{J, I+1} + \delta_{J, I-1}], \quad (22c)$$

and

$$\rho_{BA}(I, J) = X_B [\delta_{J, I+1} + \delta_{J, I-1}]. \quad (22d)$$

The fluctuation terms F_{AA} , F_{BB} , F_{AB} , and F_{BA} are equal to $F(I, I+1, I+1, I)$ with $I, I+1$ being AA, BB, AB, and BA, respectively.⁹

Solutions to Eqs. (21) for g_{AA} and g_{BB} can be accomplished by Fourier transforming the spatial dependence and then using standard techniques¹⁰ for solving coupled first-order linear (in time) differential equations. The result of carrying out such a treatment can be expressed as

$$g_{AA}(\mathbf{R}, \mathbf{R}, t) = (\pi\lambda_+ t)^{-3/2} \exp(-R^2/4\lambda_+ t) \alpha_+ + (\pi\lambda_- t)^{-3/2} \exp(-R^2/4\lambda_- t) \alpha_-, \quad (23a)$$

$$g_{BB} = \frac{1}{4} [C + X_B F_{BB} 2a^2 - X_A F_{AA} 2a^2] \times [C - X_B F_{BB} 2a^2 + X_A F_{AA} 2a^2] \times [C X_B 2a^2 F_{AB} F_{BA}]^{-1} [(\pi\lambda_+ t)^{-3/2} \exp(-R^2/4\lambda_+ t) - (\pi\lambda_- t)^{-3/2} \exp(-R^2/4\lambda_- t)], \quad (23b)$$

where the following definitions have been introduced for notational convenience:

$$\lambda_+ \equiv \frac{1}{2} (2X_A F_{AA} a^2 + 2X_B F_{BB} a^2 + C), \quad (24a)$$

$$\alpha_+ \equiv (-X_B F_{BB} 2a^2 + X_A F_{AA} 2a^2 + C)(2C)^{-1}, \quad (24b)$$

$$\alpha_- \equiv (C + X_B F_{BB} 2a^2 - X_A F_{AA} 2a^2)(2C)^{-1}, \quad (24c)$$

and

$$C = [(2a^2 X_A F_{AA} - 2a^2 X_B F_{BB})^2 + 16 a^4 F_{AB} F_{BA} X_A X_B]^{1/2}. \quad (24d)$$

In the special case where $X_A F_{AA} = X_B F_{BB}$, we find g_{AA} to be of the form shown in Eq. (23a) with

$$\alpha_+ = \frac{1}{2} = \alpha_-, \quad (25)$$

and

$$g_{BB} = \frac{1}{2} [(\pi\lambda_+ t)^{-3/2} \exp(-R^2/4\lambda_+ t) - (\pi\lambda_- t)^{-3/2} \exp(-R^2/4\lambda_- t)]. \quad (26)$$

The effective diffusion coefficient of an excess electron D can, for this mixture case, be defined by

$$6Dt = \langle r^2 \rangle_t, \quad (27)$$

which, in analogy to what was shown in I, can be expressed as

$$\langle r^2 \rangle_t = (6D_A P_A t + 6D_B P_B t) + \int_0^\infty 4\pi R^4 \rho_{AA}(R, 0) g_{AA} dR + \int_0^\infty 4\pi R^4 \rho_{BA}(R, 0) g_{BB} dR. \quad (28)$$

In writing Eq. (28) it was assumed that the excess electron was initially localized on an A-type molecule. Here P_A and P_B are the Boltzmann probabilities for finding an excess electron on A- and B-type solvent molecules, and D_A and D_B are the respective diffusion coefficients of these solvent anions in the mixture. Again assuming that the binary mixture is random, the pair distributions $\rho_{AA}(R, 0)$ and $\rho_{BA}(R, 0)$ can be expressed in terms of the probability $\rho(R, 0)$ of finding any solvent molecule at \mathbf{R} , given that there is an A-type solvent at the origin as

$$\rho_{AA}(R, 0) = X_A \rho(R, 0), \quad (29a)$$

$$\rho_{BA}(R, 0) = X_B \rho(R, 0). \quad (29b)$$

It is further assumed that $\rho(R, 0)$ approaches unity for values of R larger than a few nearest-neighbor distances. This implies that the dominant contributions to the integrals of Eq. (28), which for long time arise from the large- R properties of g_{AA} and g_{BB} , can be computed by setting $\rho(R, 0)$ equal to unity in these integrals. Having made the above two assumptions, Eq. (28) can be rewritten as follows

$$\langle r^2 \rangle_t = 6(D_A P_A + D_B P_B) t + 6X_A (\alpha_+ \lambda_+ + \alpha_- \lambda_-) t + X_B \beta [6\lambda_+ t - 6\lambda_- t], \quad (30)$$

where the factor appearing in Eq. (23b) has been defined as β for notational ease:

$$\beta \equiv \frac{1}{4} (C + X_B 2a^2 F_{BB} - X_A 2a^2 F_{AA}) \times (C - X_B 2a^2 F_{BB} + X_A 2a^2 F_{AA}) \times (X_B C 2a^2 F_{AB} F_{BA})^{-1}. \quad (31)$$

Comparing Eq. (30) with Eq. (27), we then conclude that the desired electron diffusion coefficient is given as

$$D = D_A P_A + D_B P_B + X_A [\alpha_+ \lambda_+ + \alpha_- \lambda_-] + X_B \beta [\lambda_+ - \lambda_-]. \quad (32)$$

The principal results which have been obtained thus far are Eqs. (19) and (20) for the one-component case and Eq. (24) and (32) for the binary mixture. These equations demonstrate how the long-time migration characteristics of excess electrons, as measured in the electron diffusion coefficient, can be used to probe the electron hopping rates (F_{AA} , F_{BB} , F_{AB} , and F_{BA}) if information is available about the solvent anion diffusion constants D_+ (or D_A , D_B) and the solvent's nearest neighbor distance¹¹ (a).

Having expressed D in terms of mole fractions, electron hopping integrals (F_{AA} , F_{BB} , F_{AB} , and F_{BA}) and the nearest-neighbor distance information (a), let us now analyze the binary mixture result for special types of liquid mixtures. This step can be carried out by considering the dependence of D upon the magnitudes of the four electron hopping rate coefficients F_{AA} , F_{BB} , F_{AB} , and F_{BA} .

III. ANALYSIS OF D FOR MIXTURES

A. Cases for which $\sqrt{X_A X_B F_{AB} F_{BA}} \ll (X_A F_{AA} - X_B F_{BB})$

If the probability (F_{AB}) of an excess electron hopping from the initial A-molecule site to a neighboring B site is negligible, it is rather straightforward to reduce Eqs. (24) and (31) to

$$\lambda_+ = 2a^2 F_{AA} X_A, \tag{33a}$$

$$\lambda_- = 2a^2 F_{BB} X_B, \tag{33b}$$

$$\alpha_+ = 1, \tag{33c}$$

$$\alpha_- = 0, \tag{33d}$$

$$\beta = 0, \tag{33e}$$

from which it follows that

$$D = D_A + X_A^2 2a^2 F_{AA}. \tag{34}$$

This result shows that the excess electron can migrate through the solution either by "riding" and (A-type) solvent molecule or by hopping from one A-type molecule to another. Clearly the factor of X_A^2 arises from the dilution of the system with B-type molecules. Such a situation would arise, for example, if the binding energy for an excess electron to an A-type molecule were considerably greater than that for a B-type molecule. Such would be the case in alcohol-alkane mixtures having a sufficiently high alcohol concentration to render probable the formation of deep electron traps involving the O-H groups of two or more alcohol molecules. In this case, a plot of D vs X_A^2 should yield a straight line whose slope is $2a^2 F_{AA}$.

In the event that the rate of hopping between A- and B-type molecules is small but not entirely negligible, i. e., if $\sqrt{X_A X_B F_{AB} F_{BA}} \ll (X_A F_{AA} - X_B F_{BB})$, then by expanding the square root appearing in Eq. (24d), one obtains

$$D = D_A P_A + D_B P_B + 2a^2 \{X_A^2 F_{AA} - X_A(1 - X_A) F_{AB} F_{BA} \times [X_A(F_{AA} + F_{BB}) - F_{BB}]^{-1}\} \tag{35}$$

It is clear that the part of D which depends upon solution composition (X_A) varies from zero to $2a^2 F_{AA}$ as X_A ranges from zero to unity. The function $X_A^2(1 - X_A) \times F_{AB} F_{BA} [X_A(F_{AA} + F_{BB}) - F_{BB}]^{-1}$ appearing in Eq. (35) goes through one minimum and one maximum as X_A varies. Therefore, D can possess a maximum and minimum if $F_{AB} F_{BA}$ is not a great deal smaller than F_{AA} . If $F_{AB} F_{BA}$ is negligible compared to F_{AA} , then the above term will be dominated by the $X_A^2 F_{AA}$ contribution, and D will not have a maximum or minimum except at $X_A = 0, 1$.

Note that if either F_{AB} or F_{BA} is very small, then the above result may arise. For example, if one is dealing with a mixture in which the A-type molecules are scavengers, then after a short induction time¹² the electrons will hop to the A molecules, and, now that F_{AB} is small, the electrons will "never" return to the B molecules. In such a case the diffusion of the electrons will be governed by the F_{AA} and D_A contributions.

B. Cases in which $\sqrt{X_A X_B F_{AB} F_{BA}} \gg (X_A F_{AA} - X_B F_{BB})$

If the relative concentrations of A- and B-type molecules are designed to make the rate of A-to-A hopping nearly the same as the rate of B-to-B hopping, then $X_A F_{AA} - X_B F_{BB} \cong 0$. If the electron hopping probability is much larger between different type molecules ($F_{AB}, F_{BA} \gg F_{AA}, F_{BB}$), then again $X_A F_{AA} - X_B F_{BB}$ can be ignored in comparison with $\sqrt{X_A X_B F_{AB} F_{BA}}$. In either case it follows that

$$C \cong 4a^2 \sqrt{X_A X_B F_{AB} F_{BA}}, \tag{36a}$$

$$\lambda_{\pm} = 2X_A a^2 F_{AA} \pm \frac{1}{2} C, \tag{36b}$$

$$\alpha_+ = \alpha_- = \frac{1}{2}, \tag{36c}$$

$$\beta = \frac{1}{2X_B} \sqrt{X_A X_B},$$

and hence

$$D = D_A P_A + D_B P_B + X_A^2 2a^2 F_{AA} + 2a^2 \sqrt{F_{AB} F_{BA}} X_A X_B. \tag{37}$$

As a function of composition¹³ (X_A) this form for D has a maximum at $X_A = \frac{1}{2} \sqrt{F_{AB} F_{BA}} (\sqrt{F_{AB} F_{BA}} - F_{AA})^{-1}$, which reduces to $X_A \cong \frac{1}{2}$, if $\sqrt{F_{AB} F_{BA}} \gg F_{AA}$. The value of D at the above maximum is given by

$$D = D_A P_A + D_B P_B + \frac{1}{2} a^2 F_{AB} F_{BA} (\sqrt{F_{AB} F_{BA}} - F_{AA})^{-1}, \tag{38}$$

which, if $\sqrt{F_{AB} F_{BA}} \gg F_{AA}$, reduces to

$$D \cong D_A P_A + D_B P_B + \frac{1}{2} a^2 \sqrt{F_{AB} F_{BA}},$$

As can be seen from Eq. (37), a plot of D vs X_A should be quadratic with a second-order coefficient equal to $2a^2 (\sqrt{F_{AB} F_{BA}} - F_{AA})$.

The physical meaning of the result given in Eq. (37) is clear. If the efficiency of hopping from A- to B-type molecules is higher than the A-to-A or B-to-B hopping rate ($\sqrt{F_{AB} F_{BA}} \gg F_{AA}, F_{BB}$), then the migration of an excess electron is determined by the A-to-B hopping rate. The electrons start on the A-types molecules and quickly hop to neighboring B molecules, after which they quickly return to an A rather than hopping to a neighboring B. This rate will pass through a maximum when one half of the molecules are A-type because it depends on a bimolecular encounter (nearest neighbor arrangement) of one A- and one B-type molecule whose probability is proportional to $X_A(1 - X_A)$. As the mole fraction of A-type molecules becomes so large that $X_A(1 - X_A) F_{AB} F_{BA}$ is no longer larger than $X_A^2 F_{AA}$, then the A-to-A hopping rate will become the dominant effect. This situation for which $\sqrt{F_{AB} F_{BA}} \gg F_{AA}, F_{BB}$ can be realized, for example, in solutions in which A and B constitute a reversible redox couple.

IV. CONCLUSION

In this paper we have demonstrated how one can relate experimentally measured diffusion coefficients of excess electrons in one- and two-component molecular solutions to the rate at which the excess electrons jump from one molecule to another. The result obtained depends upon the assumption that the temperature is sufficiently high for coherent effects to be neglected in comparison with fluctuation-induced hopping rates. By ap-

plying a simple one-dimensional nearest-neighbor model to our more general result of Ref. (1), we were able to obtain a closed-form expression for the electron diffusion coefficient; these primary results are expressed in Eqs. (20) and (32) for the one- and two-component solution, respectively.

For a binary solution, it was demonstrated how one could, through the solution composition dependence of the electron diffusion coefficient, extract information about the rates at which excess electrons jump among the two kinds of solvent molecules. Cases for which the hopping between like molecules is most probable as well as situations which are dominated by jumping from one type of molecule to a different type were analyzed in some detail.

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¹(a) J. McHale and J. Simons, *J. Chem. Phys.* **67**, 389 (1977). (b) T. Holstein, *Ann. Phys. (N.Y.)* **8**, 325, 343 (1959). (c) D. Emin, *Adv. Phys.* **22**, 57 (1973). (d) R. W. Munn and W. Siebrand, *J. Chem. Phys.* **52**, 47 (1970). (e) M. Grover and R. Silbey, *J. Chem. Phys.* **54**, 4843 (1971).

²One may question the potential of a one-dimensional model for describing the migration of an excess electron in a binary mixture. In particular, one worries about cases in which the electron cannot tunnel or hop past an especially high potential barrier; in the three-dimensional case, the electron could go "around" such barriers. However, as will be seen later, this problem will not arise in our treatment because of the probabilistic manner in which we treat the nearest neighbor distributions. Each molecule (of either A- or B-type) is assumed to have two neighbors whose interactions with this molecule are weighted averages of A-A, A-B, and B-B interactions, depending on the bulk mole fractions X_A and X_B . Because of this weighted average model, an electron will never find itself trapped between two very high potential barriers; it will always have some probability of "feeling"

the nonrepulsive molecules at each of its two neighbor sites.

³B. Carnahan, H. A. Luther, and J. O. Wilkes, *Applied Numerical Methods*, (Wiley and Sons, New York, 1969), p. 129.

⁴In carrying through this development properly, it is important to distinguish between terms such as those in Eq. (16) which involve derivatives of $g(\mathbf{R}, \mathbf{R}', t)$ with respect to either \mathbf{R} or \mathbf{R}' , and terms such as that shown in Eq. (15) which involve derivatives of the diagonal part of $g(\mathbf{R}, \mathbf{R}, t)$ with respect to \mathbf{R} . This distinction is essential because $[dg(\mathbf{R}, \mathbf{R}', t)/d\mathbf{R}]_{\mathbf{R}'=\mathbf{R}} \neq dg(\mathbf{R}, \mathbf{R}, t)/d\mathbf{R}$.

⁵This interpretation arises naturally from the $\delta_{I,J}$ terms appearing in Eq. (12).

⁶R. C. Tolman, *The Principles of Statistical Mechanics* (Oxford University, London, 1967).

⁷Grover and Silbey have, in Ref. 1(e), also obtained this kind of result for the one-dimensional nearest neighbor model.

⁸H. Metiu, K. Kitahara, R. Silbey, and J. Ross, *Chem. Phys. Lett.* **43**, 189 (1976).

⁹The convention used is that F_{AB} refers to hopping from an A molecule to a B molecule and vice versa for F_{BA} .

¹⁰S. W. Benson, *The Foundations of Chemical Kinetics* (McGraw-Hill, New York, 1960), p. 39-42.

¹¹The most logical connection is to choose a to be the first peak in the pair distribution function $\rho(R, 0)$ of the solvent.

¹²If the B-type molecules were scavengers, then within a very short time the excess electrons would migrate to the B molecules and Eq. (35) would hold if the indices A and B are interchanged.

¹³We assume that the composition dependence of $D_A P_A + D_B P_B$ is weaker than that of the electron hopping contributions to D . This is probably a reasonable approximation for those systems which attach the excess electrons to an empty molecular orbital of the solvent (e.g., anthracene in benzene). However, for binary mixtures in which the excess electrons are localized in traps which consist of two or more solvent molecules, it is more appropriate to replace $D_A P_A + D_B P_B$ by D_{trap} . Here D_{trap} represents the diffusion coefficient of the trap-plus-electron system, and is often expressed in approximate fashion as $D_{\text{trap}} = D_0 \exp [(-X_A E_A - X_B E_B)/kT]$ where E_A and E_B are the binding energies of an excess electron in the pure A and B solvents, respectively. Because the trap consists of both A and B molecules, it is natural that the activation energy for diffusion should depend upon the interaction energies of the excess electron with both species.