PHYSICAL REVIEW A VOLUME 18, NUMBER 4 OCTOBER 1978

Forced diffusion model for dark currents in low-conductivity fluids

P. Melman and A. Prock
Department of Chemistry, Boston University, Boston, Massachusetts 02215

(Received 17 November 1977)

An analysis of the potential and field profiles in low-dielectric constant liquids, where ions are thermally generated and recombine bimolecularly under applied voltage, is presented. The forced-diffusion model, which is described by a set of nonlinear differential equations, is solved numerically for a symmetrical case where the parameters of the positive and negative ions are equal. The solutions show a significant departure from the geometrical-potential distribution and the boundary conditions used lend themselves easily to generalization, which can include ion-injection and electron-transfer mechanisms.

I. INTRODUCTION

The phenomenon of extrinsic photoconductivity in low-dielectric-constant liquids is well known experimentally,[1] however, the different basic processes which govern the dynamics are incompletely understood. By the term extrinsic we mean a process which involves interaction between an excited state in the fluid and an electrode surface to produce a charge carrier. The means by which the excitation reaches the electrode is usually assumed to be through molecular diffusion, but there is some evidence that excitons may be involved.[2] Deexcitation near an electrode surface takes place through energy transfer[3] and electron transfer[4-6] mechanisms. Energy transfer processes were analyzed in detail[7] using classical electromagnetic theory treating the molecules as emitting multipoles near an interface. This theory appears to be applicable in extrinsic photoconductivity experiments because the energy transfer rate should depend only weakly on the local electric field through the Stark shift at the molecule. On the other hand, the excited electron transfer rate can depend on a number of mechanisms like thermal passage of the electron over a barrier, or tunneling through the barrier. These processes are all dependent on the local field strength and band structure of the electrode. For example, the experimental photocurrent always exhibts a voltage-dependent behavior which reflects the field dependence. There is no satisfactory theory of these complex processes and as a first step we will concentrate on the evaluation of the field strength. The field in these liquids can be due to changes other than those created by light. One always finds a dark current along with the photocurrent. By choosing the range of parameters (light intensity, applied voltage, and electrode spacing) we can arrange to have photocurrent small compared with this dark current. Therefore it is physically plausible to assume that in this case the local field is determined essentially by the dark current. This current is a result of generation and recombination processes and has its own mechanism of electron transfer at the electrodes. [The equilibrium problem for the case where there is a fixed number of positive and negative ions present was treated recently for an electrode spacing narrow compared with the diffuse double-layer thickness (as it is also in our case). In that work analytical solutions in terms of elliptic integrals were obtained where, again, the assumption of negligible adsorption was used.[16]] Once this model is analyzed by means of the theory of forced diffusion we can use the results to explore the mechanisms of photocurrent production in the same system. As will be discussed, even for very-low-conductivity liquids the potential profile can differ greatly from the geometric profile and can have a significant effect on the process of excited electron transfer.

II. DISCUSSION OF THE MODEL

Since the geometry of the electrode configuration in a photoconductivity experiment is usually one dimensional we will present the theory for this case only. The fluid between the electrodes is assumed to be highly resistive, which is the case in pure aromatic media, and therefore, the electrophoretic effect can be neglected. Furthermore, since for such media the solvent lacks a permanent dipole moment and the impurity level is very low, there is no significant orientation of solvent molecules at the electrode, and absorption may be assumed to be negligible. Therefore, in what follows we will assume there is no significant Helmholtz double layer. The current is produced at the electrodes by an electron transfer between the electrode and an adjacent ion (redox of impurity ions). Because this is a local mechanism it can be included in the boundary conditions of the differential equations which describe the forced diffusion of the ions in the bulk. Electron transfer to neutral molecules, which occurs at higher applied voltages (charge injection, i.e., redox of neutral molecules), can also be described by appropriate boundary conditions but will not be included at present and will be discussed in the next paper. It is useful to treat the problem in two parts. First by choosing the ion concentration at the electrode as an independent parameter it is possible to obtain a set of solutions independent of the current proucing mechanism. Then the particular mechanism is chosen so that it can be combined with the model-independent solutions to give for any applied voltage the potential and field profiles and the current density. The voltage dependence of the current, which is the only easily measurable quantity,[8] will serve then as a test for the particular assumed mechanism. For low light intensities, meaning when the photocurrent is small compared with the dark current, the field at the electrode will determine the electron transfer from the optically excited molecules and the field distribution will provide the driving force for the photocreated ions. The model that we have used in our analysis (namely, forced diffusion) was discussed by several authors. This work differs from those, first by retention of all terms in the set of differential equations and second by utilization of physically meaningful boundary conditions.

III. THEORETICAL ANALYSIS

The geometry is shown in Fig. 1. The liquid is contained between two infinite parallel plates under a total applied potential difference V. The ions in the fluid are generated (thermally) at a rate g/e, where e is the electron charge. They recombine through bimolecular collisions.

The process of forced diffusion is described by the following equation.

$$J_n = D_n e \frac{dn}{dx} - \mu_n e \frac{d\phi}{dx} n , \tag{1}$$

$$J_p = -D_p e \frac{dp}{dx} - \mu_p e \frac{d\phi}{dx} p . \tag{2}$$

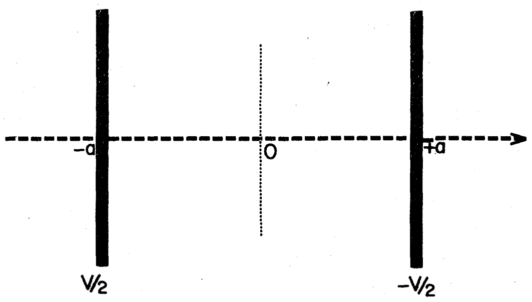

FIG. 1. Geometry of the electrodes. The electrode size is much greater than the separation distance $2a$.

The continuity equations in steady state are

$$\frac{dJ_n}{dx} + g_n - K_n np = 0 , \tag{3}$$

$$-\frac{dJ_p}{dx} + g_p - K_p np = 0 . \tag{4}$$

The potential satisfies the Poisson equation

$$\frac{d^2\phi}{dx^2} = -\frac{4\pi}{\epsilon}\rho = -\frac{4\pi e}{\epsilon}(p-n) . \tag{5}$$

Here n, p, J_n, J_p, μ_n, μ_p, D_n, D_p, K_n, K_p, g_n, and g_p are the concentrations of negative and positive ions and corresponding current densities, mobilities, diffusion coefficients, recombination constants and charge generation rates. ϕ is the electrostatic potential which includes the effect of the ions.

The boundary conditions for the potentials are

$$\phi(-a) = \tfrac{1}{2}V, \quad \phi(a) = -\tfrac{1}{2}V . \tag{6}$$

The boundary conditions on the charge densities are stated in terms of the current

$$J_p(-a) = 0, \quad J_n(a) = 0 , \tag{7}$$

$$J_p(a) = S_p p(a), \quad J_n(-a) = S_n n(a) . \tag{8}$$

It should be noticed that in Eqs. (1)–(5), $J(x)$ mathematically is only an auxiliary variable and the equations are in terms of n and p; but from the physical point of view it is impossible to impose meaningful boundary conditions on ion densities. Therefore conditions (7) and (8) are given in terms of currents so that charge exchange mechanisms can be incorporated in the rate constants S_p and S_n. These parameters appear also in solid-state theory where they are called surface recombination velocities. The set of equations (7) states that there is no charge injection (redox of neutral molecules) at the electrodes and it is only necessary to modify these conditions when injection is present.

It should be emphasized that even though the currents at the electrodes [Eq. (8)] are given as a product of ion density times a rate constant S_p or S_n this is not as restrictive as it appears. The way the differential equations can be treated allows one to include ion density dependence of the rates S_p and S_n. In Sec. IV we will treat the problem in which exchange currents are present. S_p and S_n in general will include the effects of the local field, electrode, and ion properties such as energy levels and densities of states.

In the treatment of this set of equations we will exploit certain symmetry properties which will lead to a tractable set of equations without sacrificing the physical reality of the problem. We will look at a problem where

$$\mu_n=\mu_p=\mu,\quad D_n=D_p=D,\quad g_n=g_p=g,\quad K_n=K_p=K,\quad S_n=S_p=S. \tag{9}$$

These assumptions allow us to reduce the set of five nonlinear equations to a set of three nonlinear, nonlocal equations. As is shown in Appendix A, the set (9) is a sufficient condition so that

$$J_p(x)=J_n(-x),\quad p(x)=n(-x). \tag{10}$$

The reduced equations are:

$$J_p=-De\,\frac{dp}{dx}-\mu e\,\frac{d\phi}{dx}\,p, \tag{11a}$$

$$-\frac{dJ_p}{dx}+g-Kp(x)p(-x)=0, \tag{11b}$$

$$\frac{d^2\phi}{dx^2}=-\frac{4\pi e}{\epsilon}\,[p(x)-p(-x)]. \tag{11c}$$

These contain in addition to ϕ only the single unknown p. We also make use of the Einstein relation that $\mu=De/kT$.

Equations (11) were solved numerically. For this purpose we transformed them by means of Green's functions into the following equations of the Fredholm type:

$$p(x)=e^{-\Phi(x)}\int_x^a\left((x'+a)g-K\int_{-a}^{x'}p(x'')p(-x'')\,dx''\right)e^{\Phi(x')}\,dx'+\frac{1}{S}\left(2ag-K\int_{-a}^{+a}p(x')p(-x')\,dx'\right)e^{\Phi(a)-\Phi(x)}, \tag{12}$$

$$\phi(x)=-\frac{Vx}{2a}+\frac{4\pi e}{\epsilon}\int_{-a}^{+a}\left(\frac{1}{2a}(a-x')(a+x)-(x-x')\theta(x-x')\right)[p(x')-p(-x')]\,dx', \tag{13}$$

where $\Phi=e\phi/kT$ and is dimensionless, θ is the usual step function, and $\Phi(a)=-eV/2kT$. From Eqs. (12) and (13) it can be seen that the solutions $p(x)$ and $\phi(x)$ [and therefore $J_p(x)$ through Eq. (11a)] are completely determined provided that S is known. It should be noticed that in Eq. (12) the coefficient of the exponent in the second term is simply the ion density at the electrode $p(a)$. This fact allows one to analyze the problem at first without the need to consider any model for S. Using $p(a)$ as an input parameter one obtains a family of solutions for any set of applied voltages. At this point one can construct a family of curves of $J_p(a)$ vs S for different values of applied voltage. The second step requires specific knowledge of S as a function of applied voltage for the particular system. This information, combined with the family of curves obtained in the first part will yield a prediction for current density versus applied voltage behavior. It is clear from this method that S is not restricted to any functional form and can even depend on $p(a)$. For example, when exchange current is considered then, as we will show for a simple model of this mechanism, S will have this dependence.

The field distribution is calculated from the following equation:

$$\phi'(x)=-\frac{V}{2a}+\frac{4\pi e}{\epsilon}\int_{-a}^{+a}\left(\frac{1}{2a}(a-x')+\theta(x-x')\right)\times[p(x')-p(-x')]\,dx'. \tag{14}$$

This form is especially useful to obtain accurate values when numerical methods are used.

IV. RESULTS AND DISCUSSION

Figure 2 presents the potential and field distribution calculated for a few cases which emphasize the characteristic behavior of this system under applied voltage. In each case the values of g and K are the same as used previously,[9] ($g/e=5\times10^{7}$ $\text{sec}^{-1}\,\text{cm}^{-3}$, $K/e=2\times10^{-13}$ $\text{sec}^{-1}\,\text{cm}^{3}$) and electrode spacing is 0.01 cm. In Figs. 2(a) and 2(b) the applied voltage is 0.1 V and the values of S are 5×10^{-4} and 10^{-6} C cm sec^{-1}, respectively. In Fig. 2(c) the applied voltage is 0.2 V and S is 6×10^{-6} C cm sec^{-1}.

It is clear from these results that the potential and field profiles differ from the geometrical ones, and the differences can be very large. Therefore any calculation which involves field strength has to take into account these differences, in particular when considering photoconductivity mechanisms, which are believed to be sensitive functions of electric field strength at the electrode. For a certain range of parameters the calculated field at the electrodes can be orders of magnitude larger than the geometrical even when current is flowing. This certainly cannot be ignored when considering charge motion in the electrode vicinity (e.g., charge transfer or escape of an ion from a modified image field).[10]

Figure 3 shows a family of curves of current density versus S for a range of applied voltages. As expected, for high values of S the current saturates, the reason being of course that it is impossible to draw more charges than are being produced. The curves appear to be of the same shape but shifted along the log$S$ axis. This is approxi-

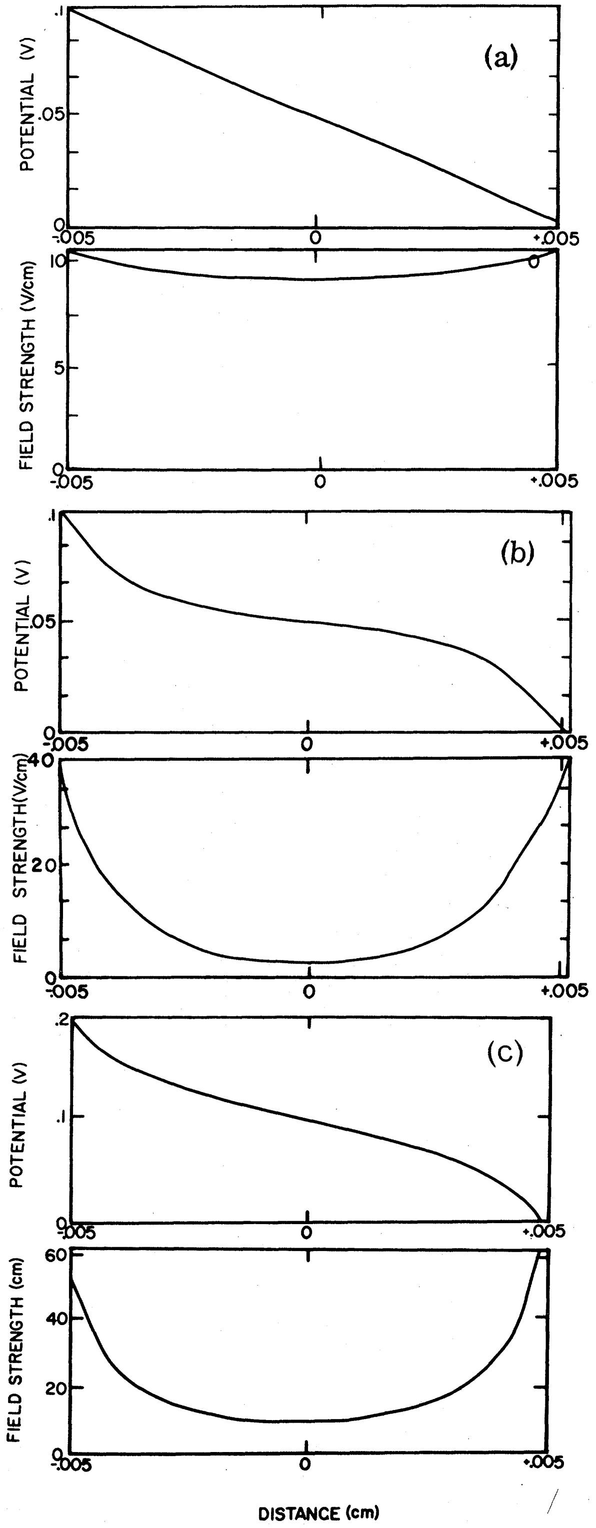

FIG. 2. Potential and field distribution in three characteristic cases. (a) Voltage applied is 0.1 V, S is 5 $\times 10^{-4}$ Coulomb cm sec^{-1}. (b) Voltage applied is 0.1 V, S is 6 $\times 10^{-6}$ Coulomb cm sec^{-1}. (c) Voltage applied is 0.2 V, S is 6 $\times 10^{-6}$ Coulomb cm sec^{-1}.

mately correct especially in the low-current range where the ion distribution approaches thermal equilibrium, and in the high-current range the saturation washes out the differences between the curves. Since we have not found in the literature a proof that in the presence of generation and recombination processes the current vanishes everywhere for zero-output current (this is the condition for the Einstein relation) we show this in Appendix B.

To illustrate the use of this method we will show the results of calculations of current voltage relationships in a case of exchange currents. The model we consider assumes that the measurable current arises from the difference between the zero voltage ion density at the electrode and the steady-state value. Mathematically it can be stated as

$$J = S_0[p(a) - p_0(a)]\,, \tag{15}$$

where $p_0(a)$ is the ion concentration at $V = 0$, which equals $\sqrt{g/K}$, and S_0 is a constant. The rate parameter S used in the theory is in this case

$$S = S_0[1 - p_0(a)/p(a)]\,. \tag{16}$$

Here S depends on $p(a)$ and the current vanishes at zero voltage as required. Figure 4 shows the three characteristic curves for values of $S_0 = 10^{-5}$, 10^{-6}, 10^{-7} C cm sec^{-1}. The current saturates as the voltage increases (as expected in the absence of injection). The saturation behavior has been known for a long time[11] but the detailed shape of these curves requires more careful investigation at low voltages.

V. COMPARISON WITH OTHER WORKS

Equations (11a)–(11c) describe the dynamics of ions, generated thermally and recombining bimolecularly. Their motion is governed by diffusion and electrostatic forces. The relative importance of these two processes can be determined on the basis of the full solution of these equations. In our numerical solutions, which included all terms, we found that not only is no term in Eq. 11(a) negligible, but they are even of the same order of magnitude. This is true even for small concentration gradients. In all cases where D and μ are related by the Einstein relation (which is true in a fluid) it is impossible to neglect diffusion by taking D to vanish. In other words, there is no way in which diffusion can be regarded as negligible in these liquids.[9,12] Discarding diffusion has another fundamental effect. Equations 11(a) and 11(b) give a second-order differential equation for concentration when combined. Therefore, two boundary conditions must be specified, and this is

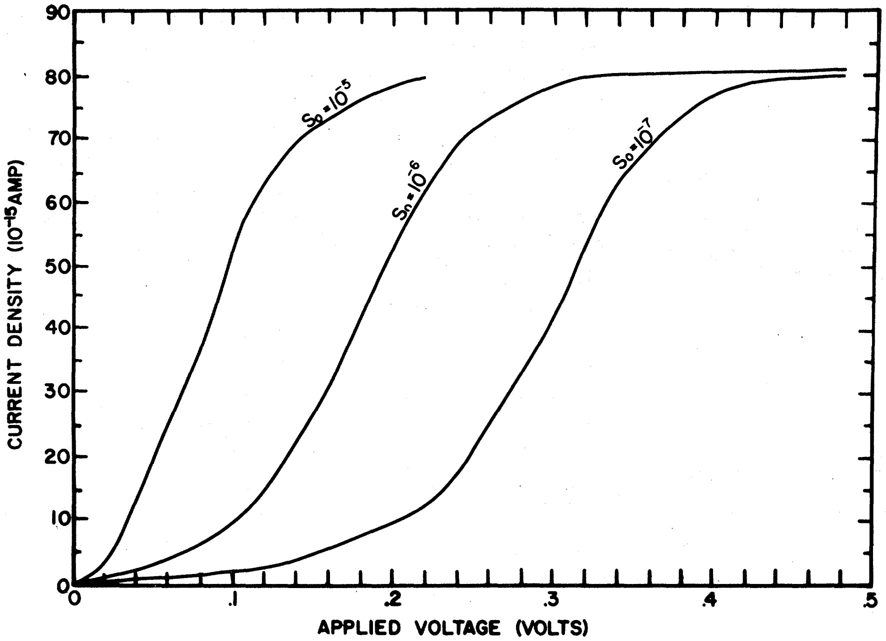

FIG. 3. Current density vs S for a range of applied voltages.

demanded on physical grounds because the processes at both electrodes determine the behavior. In every case the mathematics must reflect the physics of the problem. Discarding the diffusion term reduces the equations for p to first order, and it is hard to find a physical meaning for one boundary condition only.

In our calculations we found the ion concentrations at both electrodes to depend strongly on the rate transfer parameter S. Any attempt to fix the concentration at either electrode specifies a solution which, of course, is unphysical.[12] In addition, there is no further room to incorporate an electron transfer mechanism into the analysis.

In light of this discussion it appears that although this problem has been treated by a number of authors in the past our analysis seems to be the most consistent one. The structure of our treatment makes it clear how to generalize it so as to include unsymmetric systems, ion injection,[13,14] effects of

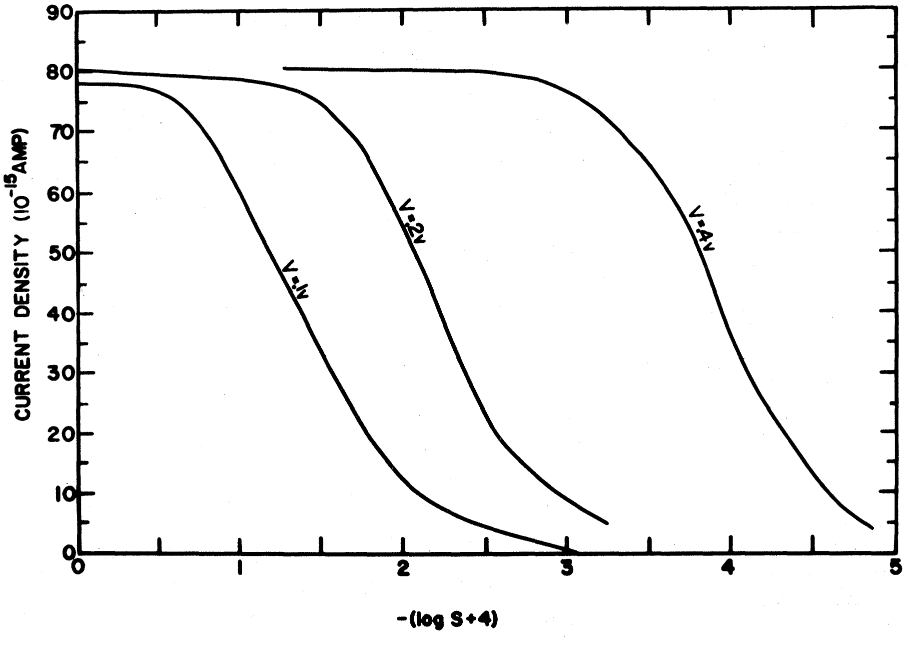

FIG. 4. Current density vs applied voltage for the exchange current model.

band structure[15] of the electrode material on the parameter S, and finally to use the information obtained to understand better the mechanisms of photoconductivity.

ACKNOWLEDGMENT

This work was supported in part by the National Science Foundation.

APPENDIX A: SYMMETRY PROPERTIES OF THE DIFFERENTIAL EQUATIONS

In order to show the symmetry of the differential equations we will reflect the coordinate system through the origin. For convenience we use the reflection operator R whose properties are

$$Ry(x)=y(-x), \quad [Ry(x)]'=-y'(-x),$$

$$Ry'(x)=-[Ry(x)]'=y'(-x),$$

$$R(y+z)=Ry+Rz, \quad R(yz)=RyRz\,.$$

Operating with R on the set of equations (1)–(5) and the boundary conditions (6)–(8) in the case when the parameters for positive and negative ions are the same, results in the following equations:

$$(RJ_n)=-De(Rn)'-\mu e\phi'(Rn)\,, \tag{A1}$$

$$(RJ_p)=De(Rp)'-\mu e\phi'(Rp)\,, \tag{A2}$$

$$-(RJ_n)'=-g+K(Rn)(Rp)\,, \tag{A3}$$

$$-(RJ_p)'=g-K(Rn)(Rp)\,, \tag{A4}$$

$$-R(\phi'')=\phi''=(4\pi e/\epsilon)[(Rp)-(Rn)]\,. \tag{A5}$$

The boundary conditions become

$$RJ_p(a)=0\,, \tag{A6}$$

$$RJ_n(-a)=0\,, \tag{A7}$$

$$RJ_p(a)=S[Rp(a)]\,, \tag{A8}$$

$$RJ_n(-a)=S[Rn(-a)]\,, \tag{A9}$$

$$\phi(a)=\tfrac{1}{2}V\,, \tag{A10}$$

$$\phi(-a)=-\tfrac{1}{2}V\,. \tag{A11}$$

A simple comparison of these equations to the original set shows that they are identical provided n and p are interchanged everywhere and the functions are evaluated at the reflected coordinates. This symmetry property makes the potential ϕ antisymmetric as was assumed.

APPENDIX B: THERMAL EQUILIBRIUM LIMIT OF THE DIFFERENTIAL EQUATIONS

Under conditions of thermal equilibrium it is, of course, expected that current at all points vanishes. However, this should be a property of the differential equations rather than an additional assumption. In the absence of generation and recombination processes it follows trivially for zero-output current from the continuity equation. It is, however, not immediately obvious that the current vanishes when these processes are present. The following considerations show that this is indeed the case. The proof is particularly simple for the symmetric case.

The sum of the two continuity equations (3) and (4) along with the condition of zero-output current gives

$$J_p(x)+J_n(x)=0\,. \tag{B1}$$

Using this condition and the result of Appendix A

$$p(x)=n(-x)$$

and the integrated form of the continuity equation [with b.c. $J_p(-a)=0$]

$$J_p(x)=g(x+a)-K\int_{-a}^{x} p(x')p(-x')\,dx'\,, \tag{B2}$$

one can get

$$J_p(x)=-J_p(-x), \quad J_n(x)=-J_n(-x)\,. \tag{B3}$$

From Eq. (B3) the currents have to be antisymmetric functions. However, an anitsymmetric function must vanish at the center where the potential is zero by symmetry. Consider an electrode placed at the center at zero potential. The half space created is again equivalent to the original problem with a zero-output current boundary conditions (of course, the voltage and spacing are changed but the local currents have to vanish at any voltage or spacing). Now the current is not an antisymmetric function of the distance unless it vanishes identically (to be rigorous there may be more than one halving process required to get rid of the antisymmetry of J).

---

[1] I. Adamczewski, *Ionization and Breakdown in Dielectric Liquids* (Taylor and Francis, London, 1969). This work quoted by many authors, describes extensive studies of dielectric liquids from a phenomenological viewpoint.

[2] C. J. Eckhardt and L. F.Nichols, Phys. Rev. Lett. 29, 1221 (1972).

[3] R. Chance, A. Prock, and R. Silbey, J. Chem. Phys. 62, 2245 (1975); 65, 2527 (1976); 63, 1589 (1975).

[4] H. Gerisher, Electroanal. Chem. Interfacial Electrochem. 58, 263 (1975).

[5] R. Memming and F. Möllers, Ber. Bunsenges. Phys.

Chem. 76, 475 (1972).

[6] R. Memming and G. Kürsten, Ber. Bunsenges. Phys. Chem. 76, 4 (1972).

[7] R. Chance, A. Prock, and R. Silbey, Adv. Chem. Phys. (to be published).

[8] The Kerr effect was used to measure the potential profile directly in the case of highly purified nitrobenzene. See the works of G. Brière, e.g., G. Brière, G. Cauquis, B. Rose, and D. Serve, J. Chim. Phys. 49, 66 (1969).

[9] M. Silver, J. Chem. Phys. 42, 1011 (1965).

[10] G. C. Hartmann and J. Noolandi, J. Chem. Phys. 66, 3498 (1977).

[11] N. Felici, B. Gosse, and J. P. Gosse, Radio General Electrique 85, 861 (1976).

[12] J. Malecki and P. Pieranski, Acta Phys. Polon. A 50, 581 (1976); 50, 597 (1976).

[13] *Conduction and Breakdown in Dielectric Liquids*, edited by J. M. Goldshchvartz (Delft University, Delft, 1975).

[14] M. Zahn, D. F. Tseng, and S. C. Pao, J. Appl. Phys. 45, 2432 (1974).

[15] R. Memming and F. Möllers, Ber. Bunsenges. Phys. Chem. 76, 475 (1972).

[16] C. J. Farina and K. B. Oldham, J. Electroanal. Chem. 81, 21 (1977).