

The Shape of the Current-Voltage Curve for a Flame Ionization Detector with Two Ionic Components

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Abstract

A theory of the shape of the current-voltage curve of the flame ionization detector when one positive ion, usually oxonium hydrate, is dominant has been extended to include a second positive ion, ammonium hydrate. The extension, though only to first order, accounts for the shape of some experimental curves.

1. Introduction

The work of Bolton and McWilliam (1971, referred to as Part 1) has shown how the shape of the current-voltage or i - V curve of the flame ionization detector (FID) can be understood in terms of the space charge in the region between flame and collector when there is one ionic component. Using I for the saturation current in the detector, the analysis showed that a plot of i/I against $V/I^{\frac{1}{2}}$ should be a universal curve and, for positive ion collection, there is much evidence for this; many organic additives to the flame have been examined. In Part 1, this universal curve, sigmoid in shape, was called a 'normalized' curve. Experimental work of Bolton *et al.* (1978, referred to as Part 2) on the mass-spectrometric and mobility analysis of flame ions showed that the single ionic component was the hydrated oxonium ion $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$. The number n must be an integer at any instant but will vary with time and the temporal average need not be an integer; low integer values were found in the mass spectra. Confirmation that n takes these values came from the work of Suck *et al.* (1981) who calculated theoretically the hydrate number n for oxonium hydrate ions found in the lower atmosphere. There were however some instances where the normalized curve for the FID was not reproduced and examples were given for positive ions in Fig. 1 of Part 2.

Fig. 1 in the present article shows some of the experimental curves together with a theoretically calculated curve and will be discussed in more detail in Section 3. It had been suspected that the departures from the normalized curve could be due to the presence of the hydrated ammonium ion $\text{NH}_4^+(\text{H}_2\text{O})_n$ in addition to the hydrated oxonium ion.

The mobilities of these two ions were measured in Part 2 and found to be $2.5 \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1}$ (ammonium) and $2.2 \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1}$ (oxonium), values which are significant in the discussion that follows.

In this article the basic theory of the FID current-voltage curves has been extended to include two ionic species of different mobilities. The description of the normalized curve can be condensed into the value of the $V/I^{\frac{1}{2}}$ for $i/I = 0.5$ and this is given

experimentally as $21 \times 10^4 \text{ V A}^{-\frac{1}{2}}$; we will call this point $(V/I^{\frac{1}{2}})_{\frac{1}{2}}$. Departures from the normalized curve were found to be such that the measured values of $(V/I^{\frac{1}{2}})_{\frac{1}{2}}$ were found to be less than $21 \times 10^4 \text{ V A}^{-\frac{1}{2}}$, or in other words the observed current-voltage curves lay above the normalized curve. Examples are given in Fig. 1 to which we will return after the mathematical analysis. In the present article we want to show that the curves lying above the normalized curve can indeed be explained by the presence of two ionic components, the oxonium hydrate and the ammonium hydrate.

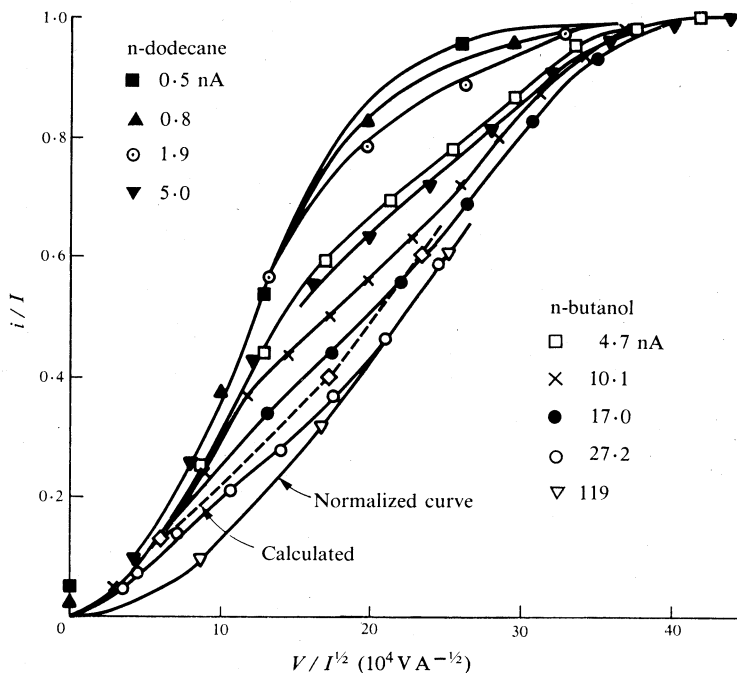


Fig. 1. Normalized curves plotted as the ratio of the current i to the saturation current I as a function of $V/I^{1/2}$ for the flame ionization detector for various saturation currents (in nA). The dashed curve is calculated for $I = 17 \text{ nA}$ in equation (66).

2. Planar Flame

In Part 1 it was pointed out that the geometry of the FID is cylindrical, but the one-dimensional analogue called a 'planar flame' was found to have a solution easier to follow. The equations of the planar flame are presented first leaving the experimental flame with its cylindrical symmetry to be treated in Section 3.

We expect the ionic carrier in a hot region to be the hydrated oxonium and, as the temperature decreases towards the collector, kinetic calculations by T. McAllister (personal communication 1982) have shown that the reaction with ammonia proceeds and the concentration of the ammonium ion increases. This action must be continuous across the region between flame and collector, but there seems to be no easy way of expressing this mathematically. Accordingly we have simplified the problem and have divided the region between flame and collector into

an initial hot region I and a second cool region II. The boundary between these two regions is $x = g$. The quantities needed are shown in Fig. 2. In region I, oxonium alone is present with number density $n'(x)$ and mobility k' . In region II, oxonium is present with number density $n(x)$ and mobility k and ammonium is present with number density $m(x)$ and mobility l .

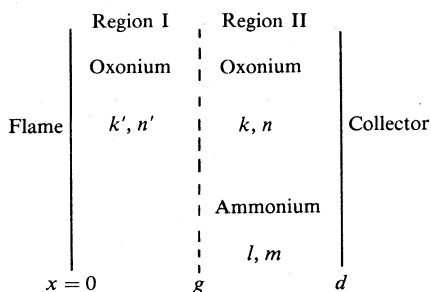


Fig. 2. Mobilities and number densities for ions in regions I and II for a planar flame.

The theory depends on Poisson's equation and the equation of continuity. We use $X(x)$ for the electric field at any point x between the flame and the collector. We will use the subscripts I and II where there may be doubt in the argument. We need to start with an expression for a single component current to make a comparison in the later discussion and we cannot just reproduce the result of Part 1 since we need to use the two values k' and k for the oxonium ion and the boundary $x = g$. The equations are as follows:

Region I: $0 \leq x \leq g$

$$X(x) = -dV(x)/dx, \quad (1)$$

$$\text{Current density: } i = en'k'X = \text{const.}, \quad (2)$$

$$\text{Poisson equation: } dX/dx = n'e/\epsilon_0. \quad (3)$$

where e is the electric charge and ϵ_0 the permittivity of free space. Thus, we have

$$dX^2/dx = 2i/\epsilon_0 k', \quad (4)$$

$$X^2(x) = (2i/\epsilon_0 k')(x + B'), \quad (5)$$

where B' is the constant of integration given by the physical conditions at the surface of the flame at $x = 0$. This constant follows directly from the argument in Part 1; we get

$$B' = (i/I)(k'/k)C'd, \quad (6)$$

where

$$C' = \epsilon_0 \alpha^0 k \delta / 2ek^0 d, \quad (7)$$

and where α^0 is the recombination coefficient of the positive and negative ions, and δ is the effective thickness of the ion formation region. In Part 1 the theory was expressed in terms of the single parameter C' . The opportunity has been taken in the present article to correct the denominator of C' . The numerical value of C' is about 0.3 though we do not use it here.

Region II: $g \leq x \leq d$

Equations (1)–(5) are needed with k replacing k' ; we get

$$X^2(x) = (2i/\epsilon_0 k)(x+B). \quad (8)$$

The new constant of integration B is given by the boundary condition at $x = g$, namely that the electric field is continuous:

$$X_I(g) = X_{II}(g). \quad (9)$$

Then B is given in terms of B' by

$$(2i/\epsilon_0 k')(g+B') = (2i/\epsilon_0 k)(g+B). \quad (10)$$

The current density i follows by integrating the field to give the modulus of the applied voltage V :

$$V = \int_0^g X_I(x) dx + \int_g^d X_{II}(x) dx, \quad (11)$$

which yields

$$V = (2i/\epsilon_0 k')^{\frac{1}{2}} \frac{2}{3} \{(g+B')^{3/2} - B'^{3/2}\} + (2i/\epsilon_0 k)^{\frac{1}{2}} \frac{2}{3} \{(d+B)^{3/2} - (g+B)^{3/2}\}. \quad (12)$$

We see that i/I is a function of $V/I^{\frac{1}{2}}$ which expresses the existence of the normalized curve. We need equation (12) to compare with the expression that will now be given when we incorporate two ions in region II.

Referring to Fig. 2 we see that the equations for region I are the same as equations (1)–(5). In region II the continuity of m is expressed through the equations

$$d(elXm)/dx = e\rho n, \quad (13)$$

$$d(ekXn)/dx = -e\rho n, \quad (14)$$

where $\rho = Ka_1$, with the concentration of ammonia a_1 assumed constant and with the rate constant K . We take ρ to be constant in region II and zero in region I, so that

$$\text{Poisson:} \quad dX/dx = e(n+m)/\epsilon_0, \quad (15)$$

$$\text{Current:} \quad i = eX(nk+ml). \quad (16)$$

To get the solution in region II we define

$$u(x) = m/n. \quad (17)$$

Taking the ratio of equation (15) to (16) we get

$$dX^2/dx = (2i/\epsilon_0 k)\{(1+u)/(1+ul/k)\}. \quad (18)$$

Next we find du/dx using dm/dx from (13) and dn/dx from (14); we get

$$X du/dx = \rho(u+k/l)/k. \quad (19)$$

The boundary conditions for equations (18) and (19) are (see equation 9)

$$u(g) = 0, \quad X_I(g) = X_{II}(g). \quad (20)$$

Before proceeding further, we can at this point pose a little more clearly the question needing an answer in this article: Do equations (18) and (19) yield a solution that gives a current-voltage curve deviating from the single-component normalized curve by an amount proportional to ρ ? In terms of equation (12) is there an extra term to be added to its right-hand side? If we restrict the argument to small values of ρ then the present article shows that the answer is yes, which removes some of the doubts in Part 2.

Equations (18) and (19) are coupled nonlinear equations and it seems difficult to solve them fully in analytic terms. An apparently straightforward perturbation technique is not the correct way to solve the equations. We can see this by dividing (18) by (19) to get

$$dX/du = (ik/\epsilon_0 \rho l) \{ (u+1)/(u+k/l)^2 \}. \quad (21)$$

This has the first order solution

$$X(x) - X(g) = (il/\epsilon_0 \rho k) u(x), \quad (22)$$

where $X(g)$ would have to be given by the boundary condition. The corresponding solution of (19) is

$$u(x) = \{ \rho / l X(g) \} (x-b),$$

and hence

$$X(x) - X(g) = \{ i/\epsilon_0 k X(g) \} (x-b). \quad (23)$$

This has lost the quantity ρ and in any case a linear expression for $X(x)$ is inappropriate for the whole of region II. We thus reject this perturbation technique and return to equations (18) and (19).

We know the values of k ($2.2 \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1}$ for oxonium hydrate) and l ($2.5 \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1}$ for ammonium hydrate) from Part II. The important thing to notice is that k and l are close in value. The reason for this is that both ions have similar masses and both have hydration shells with several water molecules so that the collision properties of the ions are very similar. We expand (18) to first order as

$$dX^2/dx = (2i/\epsilon_0 k)(1+uq), \quad (24)$$

where

$$q = 1 - l/k = -0.14, \quad (25)$$

and we seek a solution of (24) and (25) by successive approximations. The simplest approximation to (24) is given by dropping the term of order u and is the familiar function

$$X^2(x) = (2i/\epsilon_0 k)(x+B_0),$$

with B_0 to be determined by equation (9). This yields, similarly to (10),

$$(2i/\epsilon_0 k')(g+B') = (2i/\epsilon_0 k)(g+B_0), \quad (26)$$

and a comparison with (10) shows that $B_0 = B$. Next we solve (19) by dropping u in comparison with k/l to get

$$u(x) = (2\rho/l)(\epsilon_0 k/2i)^{\frac{1}{2}} L(x), \quad (27)$$

where

$$L(x) = (x+B)^{\frac{1}{2}} - (g+B)^{\frac{1}{2}}. \quad (28)$$

To get the next approximation to $X(x)$ we insert $u(x)$ from (27) into (24) to get

$$X^2(x) = (2i/\epsilon_0 k)(x+B_1) + (2i/\epsilon_0 k)^{\frac{1}{2}}(2q\rho/l)M(x), \quad (29)$$

where

$$M(x) = \int_g^x L(x) dx. \quad (30)$$

In (29) the constant of integration is B_1 which is found by the application of the boundary condition (9) and which yields $B_1 = B$, because $M(g) = 0$. The field $X(x)$ can be expressed to first order in ρ by

$$X^2(x) = (2i/\epsilon_0 k)(x+B) + (2i/\epsilon_0 k)^{\frac{1}{2}}(2q\rho/l)M(x). \quad (31)$$

Using the binomial theorem we get

$$X(x) = (2i/\epsilon_0 k)^{\frac{1}{2}}(x+B)^{\frac{1}{2}} + (q\rho/l)M(x)/(x+B)^{\frac{1}{2}}, \quad (32)$$

and the applied potential difference V follows from (11) as

$$V = (2i/\epsilon_0 k')^{\frac{1}{2}} \frac{2}{3} \{ (g+B')^{3/2} - B'^{3/2} \} + (2i/\epsilon_0 k)^{\frac{1}{2}} \frac{2}{3} \{ (d+B)^{3/2} - (g+B)^{3/2} \} \\ + (q\rho/l) \int_g^d dx M(x)/(x+B)^{\frac{1}{2}}. \quad (33)$$

The integral in (33) has a monotonically increasing integrand and consequently the integral has a positive value. We see that the first two terms in (33) are those that define the current-voltage curve for the two regions and one component, oxonium. We write (12) as $V/I^{\frac{1}{2}} = f(i/I)$ to describe the normalized curve. The third term in (33) is the correction arising from the presence of the second ionic component in the cool region II and it is dependent on i/I through the quantity B in (10) and (6); we have

$$B = g(k/k' - 1) + d(i/I)C'. \quad (34)$$

The sign of the correction to $f(i/I)$ is the same as that of q , which from (25) is negative. Qualitatively the experimental current-voltage curve for a planar flame would lie above the normalized curve. We will make the argument quantitative in the next section where we can turn with confidence to the actual cylindrical geometry of the FID. We should note from the $i^{\frac{1}{2}}$ in the denominator of the expression (27) for $u(x)$ that we cannot expect the solution to hold for low values of i but we should expect it to hold for $i/I \approx 0.5$. The same deduction is made for the cylindrical solution in the next section.

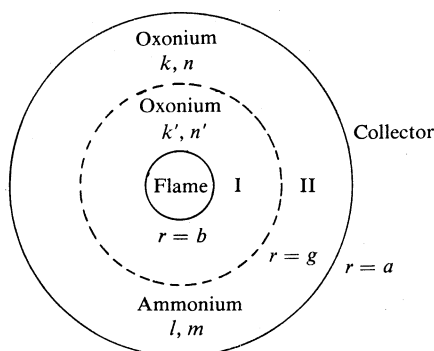


Fig. 3. Mobilities and number densities for ions in regions I and II for a cylindrical flame.

3. FID Flame: Cylindrical Symmetry

We now perform the analysis for the real experimental detector, which has cylindrical symmetry. We use the equation given in Part 1 and follow the pattern of steps in Section 2 of the present article. Fig. 3 shows the geometry of the detector. First we need to solve the equations with one ionic component and two regions:

Region I: $b \leq r \leq g$

$$R(r) = -dV(r)/dr, \quad (35)$$

$$\text{Current per unit length: } i = 2\pi r e R n' k', \quad (36)$$

$$\text{Poisson: } d(rR)/dr = en'/\epsilon_0. \quad (37)$$

Thus, we have

$$R^2(r) = (i/2\pi k' \epsilon_0)(1 + D'/r^2), \quad (38)$$

where D' is the constant of integration given by the physical conditions at the surface of the flame at $r = b$. Again, as for the planar flame, the expression for D' is given by

$$D' = b^2 \{ (k'/k)(i/I)C - 1 \}, \quad (39)$$

where

$$C = \alpha^0 k \delta \epsilon_0 / b e k'^{0.2}, \quad (40)$$

which is the single parameter used in the simple theory of Part 1. The opportunity has been taken to redefine C ; the denominator contains the square of k^0 , the mobility of the positive ion in the flame, and not the sum of the squares of the mobilities of the positive and negative ions in the flame. The estimated value of $C \approx 3$ fits very well the value measured in Part 1.

Region II: $g \leq r \leq a$

We have

$$R^2(r) = (i/2\pi k \epsilon_0)(1 + D/r^2). \quad (41)$$

The boundary condition is

$$R_I(g) = R_{II}(g), \quad (42)$$

and D is given in terms of D' by

$$(i/2\pi k' \epsilon_0)(1 + D'/g^2) = (i/2\pi k \epsilon_0)(1 + D/g^2). \quad (43)$$

The current per unit length i is determined by integrating the field to give the applied potential difference V :

$$V = \int_b^g R_I(r) dr + \int_g^a R_{II}(r) dr. \quad (44)$$

The two integrals are of the same kind and can be performed explicitly in terms of elementary functions as in Part 1, where it was pointed out that there is a useful simple approximation to the exact expression; it is used to give

$$V = (i/2\pi k'\epsilon_0)^{\frac{1}{2}}(g-b)(1+D'/gb)^{\frac{1}{2}} + (i/2\pi k\epsilon_0)^{\frac{1}{2}}(a-g)(1+D/ag)^{\frac{1}{2}}. \quad (45)$$

We note that D is a function of i/I and we see, as for the planar flame, that i/I is a function of $V/I^{\frac{1}{2}}$ expressing the existence of a normalized curve.

We now use the full data in Fig. 3 bringing in the ammonium ion through a finite value of ρ . Region I yields the same equations (35)–(38), whereas for region II

$$R(r) = -dV(r)/dr, \quad (46)$$

$$\text{Poisson:} \quad r^{-1}d(rR)/dr = e(n+m)/\epsilon_0, \quad (47)$$

$$\text{Continuity of } m: \quad r^{-1}d(rmlR)/dr = \rho n, \quad (48)$$

$$\text{Continuity of } n: \quad r^{-1}d(rnkR)/dr = -\rho n, \quad (49)$$

$$\text{Current per unit length:} \quad i = 2\pi reR(nk + ml). \quad (50)$$

As for the planar flame, we define $u = m/n$. Taking the ratio of equation (47) to (50) we get

$$Rd(rR)/dr = (i/2\pi k\epsilon_0)(1+u)/(1+ul/k). \quad (51)$$

Calculating du/dr and using (48) and (49) we get

$$Rdu/dr = \rho(u + k/l)/k. \quad (52)$$

The same argument as in Section 2 yields for small u

$$Rd(rR)/dr = (i/2\pi k\epsilon_0)(1+uq), \quad (53)$$

where, as before (equation 25), $q = 1 - l/k = -0.14$. To start the solution we drop the term of order u in (53) and get

$$R^2 = (i/2\pi k\epsilon_0)(1 + D_0/r^2), \quad (54)$$

with D_0 to be determined by the boundary condition (42), which yields

$$(i/2\pi k'\epsilon_0)(1 + D'/g^2) = (i/2\pi k\epsilon_0)(1 + D_0/g^2), \quad (55)$$

and from (43) we see that $D_0 = D$. Using this we solve (52) for a solution $u(r)$ proportional to ρ . The quantity k/l is of the order of unity and thus for $u \ll 1$ equation (52) can be simplified to

$$Rdu/dr = \rho/l, \quad (56)$$

which has the solution

$$u(r) = (\rho/l)(2\pi k\epsilon_0/i)^{\frac{1}{2}}P(r), \quad (57)$$

where

$$P(r) = (r^2 + D)^{\frac{1}{2}} - (g^2 + D)^{\frac{1}{2}}. \quad (58)$$

To get a better approximation to $R(r)$ we insert $u(r)$ from (57) into (53) to give

$$R^2(r) = (i/2\pi k\epsilon_0)(1 + D_1/r^2) + (i/2\pi k\epsilon_0)^{\frac{1}{2}}(q\rho/l)Q(r), \quad (59)$$

where

$$Q(r) = 2r^{-2} \int_g^r r P(r) dr. \quad (60)$$

In (59) the constant of integration is D_1 which is found by the application of the boundary condition (42), and because $Q(g) = 0$ this yields

$$(i/2\pi k'\epsilon_0)(1 + D'/g^2) = (i/2\pi k\epsilon_0)(1 + D_1/g^2), \quad (61)$$

and thus $D_1 = D$. The field $R(r)$ can be expressed to first order in ρ by

$$R^2(r) = (i/2\pi k\epsilon_0)(1 + D/r^2) + (i/2\pi k\epsilon_0)^{\frac{1}{2}}(q\rho/l)Q(r). \quad (62)$$

Using the binomial theorem, we get

$$R(r) = (i/2\pi k\epsilon_0)^{\frac{1}{2}}(1 + D/r^2)^{\frac{1}{2}} + (q\rho/2l)Q(r)/(1 + D/r^2)^{\frac{1}{2}}. \quad (63)$$

The applied potential is given by (44) as

$$V = (i/2\pi k'\epsilon_0)^{\frac{1}{2}}(g-b)(1 + D'/gb)^{\frac{1}{2}} \\ + (i/2\pi k\epsilon_0)^{\frac{1}{2}}(a-g)(1 + D/ag)^{\frac{1}{2}} + (q\rho/2l)J, \quad (64)$$

where

$$J = \int_g^a dr Q(r)/(1 + D/r^2)^{\frac{1}{2}}. \quad (65)$$

Again we are expanding V to first order in ρ . The integral J has a monotonically increasing integrand and therefore is positive. We see that the first two terms in (64) are those in (45) that define the normalized curve, namely the current-voltage curve for a single component (oxonium). The third term in (64) is the correction arising from the presence of the second ionic component in II, the cool region. Let us write the single component normalized curve as $V/I^{\frac{1}{2}} = f(i/I)$, then (64) can be rewritten as

$$V/I^{\frac{1}{2}} = f(i/I) + (q\rho/2l)J/I^{\frac{1}{2}}. \quad (66)$$

From (25), q is negative which means that the experimental current-voltage curve for the FID lies above the normalized curve as indeed is seen in Fig. 1. From (66) the shift away from the normalized curve is proportional to $I^{-\frac{1}{2}}$ and Fig. 4 confirms this using results taken from Fig. 1 at $i/I = 0.5$. Finally, the numerical value of the shift should depend on a_1 the concentration of ammonia. To get a number for

a_1 we need a value of the integral J , which can be performed in terms of elementary functions. We define $D = a^2 h^2$ and $s = g/a$, and then

$$\begin{aligned} J/a^2 = & \frac{1}{3}(1-s^2) + \frac{2}{3}h^2 \ln(1/s) + \{s^2(s^2+h^2)^{\frac{1}{2}} - \frac{2}{3}(s^2+h^2)^{3/2}\} \\ & \times h^{-1}(\ln[\tan\{\frac{1}{2}\arctan(1/h)\}] - \ln[\tan\{\frac{1}{2}\arctan(s/h)\}]) \\ & - (s^2+h^2)^{\frac{1}{2}}\{(1+h^2)^{\frac{1}{2}} - (s^2+h^2)^{\frac{1}{2}}\}. \end{aligned} \quad (67)$$

The geometric values are $a = 6.5$ mm and $b = 1$ mm. For the other quantities we make the following estimates: $g = 1.5$ mm, $k/k' = 2$ and the rate constant $K = 2.5 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ (Smith and Adams 1977). For $I = 17$ nA a value for the concentration of ammonia of $a_1 = 7 \times 10^{11} \text{ cm}^{-3}$ allowed equation (66) to be used for the three values $i/I = 0.2, 0.4$ and 0.6 , and the dashed curve in Fig. 1 is the result. It lies satisfactorily amongst the experimental curves.

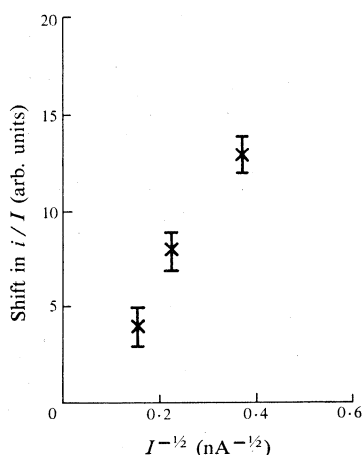


Fig. 4. Shift in i/I away from the normalized curve according to equation (66).

This value of the concentration a_1 , about 30 p.p.b., is somewhat higher than the published values for environmental ammonia (Tjepkema *et al.* 1981). It is expected that a certain amount of ammonia would be found in the FID so that we could expect a_1 to be higher than in other environments. We do not expect the present theory to hold for $i/I \rightarrow 0$ because equation (57) shows that the requirement of u small cannot be met for small i .

4. Discussion

There are some further questions that can be raised and partly answered. If we define the normalized curve to refer to a single positive ion carrier in the FID current, characterized by the point $(V/I^{\frac{1}{2}})_{\frac{1}{2}} = 21 \times 10^4 \text{ V A}^{-\frac{1}{2}}$, equation (66) shows that we could expect to find departures both above and below it if a second ion is allowed to be present. The special character of the positive ion current-voltage curves as given for instance in Fig. 1 arises from the feature that the two dominant positive ions are oxonium hydrate and ammonium hydrate which have very similar mobilities ($k = 2.2$ and $l = 2.5 \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1}$ respectively). Although the errors in these two measurements allow the ranges to overlap, the mobility results given in Fig. 6 of Part 2 are quite definite in saying that $l > k$.

Granted that there are large uncertainties in the parameters in the theory such as the radius g and the ratio of mobilities k/k' , the argument in the present article shows that departures from the normalized curve of the FID are due to the presence of more than one ionic species carrying the current.

The interpretation of the results for negative ion carriers is more uncertain. Measurements by McAllister *et al.* (1978) show that there are several negative carriers and their mobilities are not known.

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