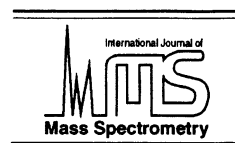




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# Schottky barrier governed injection of solvated ions through track membrane interfaced vacuum inlets

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## Abstract

Poly(ethylene terephthalate) track membranes (TM) were recently suggested for electrostatic injection of charged species into time-of-flight mass spectrometers (TOF-MS). A Schottky-type barrier reduction was investigated using a thermally activated extraction regime. A brief description of the physical processes involved is given. A wide range of the externally applied electrical potential,  $\Phi$ , was covered. Collector currents were found to exhibit an activation-like behavior,  $\sim \exp(-\Delta F/k_B T)$ , whereas the free energy difference,  $\Delta F$ , across the liquid-to-vacuum boundary is such that  $\Delta F = \Delta F_0 - \Delta F_\Phi$ . An externally controlled term,  $\Delta F_\Phi$ , was also sensitive to the salt concentration for the KCl/glycerol solutions used. A dramatic decrease of  $\Delta F(\Delta\Phi \rightarrow 0)$  was found for an increasing charge carrier concentration. In accordance with the thermionic emission mechanism of ion extraction, the Schottky effect has manifested itself in  $\Delta F_\Phi \sim \Phi^{1/2}$ . (Int J Mass Spectrom 198 (2000) 63–69) © 2000 Elsevier Science B.V.

*Keywords:* Time-of-flight; Membrane; Track-membrane; Extraction; Multichannel

## 1. Introduction

Numerous analytical applications utilize membrane based sampling techniques. Some of them are found, for instance, in kinetic studies of chemical and biological reactions, in analysis of environmental samples, in monitoring fermentation and electrochemical processes, etc. Most of the advances and significant approaches have been recently reviewed [1]. Amongst these is a high-field-mediated introduction of ions into mass spectrometers (MS). This research direction was pioneered by Simons, Colby, and Evans in the early 1970s [2]. It is frequently referred to as

the electrohydrodynamic ionization (EHDI) and does not employ membrane interfaces. Since then there have evolved various applications of electrospray and electrohydrodynamic processes in MS. Many relevant features of such analytical schemes have been evaluated and reviewed by Cook [3].

A direct introduction of cluster ions and their subsequent MS analysis, by means of the so-called track membrane (TM) inlets, was first reported by Yakovlev et al. [4]. The resulting electro-membrane ion-source (EMIS) technique offers both on-line sampling and mass spectrometric characterization of inorganic ions. Hence, this approach appears quite suitable for studying far larger organic entities such as biomolecules.

A typical EMIS utilizes a relatively dense channel

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network ( $10^7 \text{ cm}^{-2}$ ) of long (10–20 micrometer), yet narrow (submicrometer), channels [4,5] present in TM. Clearly, these geometrical constraints ought to determine and govern both the transport of charged species, as well as the local field structure.

An activation barrier limited charge extraction is expected to occur in EMIS. In this work we aim to experimentally substantiate such anticipation. An inherent feature of the Schottky effect is the increased thermionic emission due to the externally biased potential-energy barrier [6,7]. In this regard, our major objective was to investigate the possibility of Schottky-type reduction of the barrier. A thermally activated performance of such membranes was, hence, addressed.

Our first data was collected using glycerol. The latter is frequently employed in the TM-mediated charge-extraction applications. Then, a number of KCl/glycerol solutions were tested. For them, the extrinsic charge carrier concentration,  $\Delta C$ , is due to salt dissociation. Electroconductivity measurements were used to cross reference the values of  $\Delta C$  obtained. The carrier concentration range covered was taken up to 0.02 M.

For the sake of clarity, a special notation is used in the forthcoming presentation of our results. Let  $C$  be the total concentration of charge carriers in the liquid sample, so that  $C = C_G + \Delta C$ . The former figure corresponds to the pure solvent (glycerol). Our electroconductivity measurements suggest an intrinsic carrier concentration in glycerol (in the form of deprotonated molecules) of  $C_G \cong 5 \times 10^{-5} \text{ M}$  (or  $n \cong 2.5 \times 10^{22} \text{ m}^{-3}$ ). However, for the KCl/glycerol solutions  $C \cong \Delta C$ , because  $\Delta C \gg C_G$ . In what follows we make extensive use of a unitless quantity,  $X$ , defined as  $X \equiv C/C_G$ . Thus, for the pure solvent  $X = 1$ , it rises up to  $X \cong 400$  for  $\Delta C = 0.02 \text{ M}$ .

## 2. Theoretical considerations

In this section we briefly outline those physical grounds of EMIS operation that are relevant to our main theme. A recent interfacing of TOF-MS with EMIS suggests a working layout for  $m/z$  identification

of charged species [4]. However, any analytically reliable development in this field requires a full-scale consideration of the underlying physical processes involved in such ionic feedthroughs.

Similar to a more traditional, electrohydrodynamic ionization approach [3,8,9], high electrostatic field conditions are essential here too. In a submicrometer multichannel network, a feedback charging of the vacuum facing side of the TM is believed to be of prime importance in producing high local fields at the liquid/vacuum interface [10].

We note that in either of the EHDI or EMIS based approaches evaporation into vacuum occurs for those ions that are, *ab initio*, present in the liquid phase. Recall that in various EHDI applications [8] a strong electrostatic field is known to develop at the very edge of a fine metallic capillary. The liquid phase is in a highly unstable state there [9].

On contrary, only a minute disturbance of the liquid–vacuum interface is expected to occur for EMIS mediated vacuum inlets. Indeed, in accordance with the Rayleigh stability criterion, such ionic sources could sustain (given an appropriate choice of the polymer/liquid wetting angle) quite severe electrostatic fields, e.g. of the order of  $10^7 \text{ V/cm}$  [4,11].

There exists a quite complex interplay between the average (per channel) collector current,  $I$ , the local field strength,  $E$ , and the charge carrier concentration,  $X$ . Generally, the number of charged species (charge =  $q$ ) present at the liquid/vacuum interface,  $N$ , is also expected to depend on  $X$  and  $E$ . A steady-state regime of

$$I = qN\nu \quad (1)$$

was recently considered [12] for several mono- and di-valent ionic–salt/glycerol solutions. Within a single-particle approach, the probability of finding charged species at the vacuum side of the TM is proportional to  $1/\nu$ , where  $\nu$  is the effective escaping frequency, such that

$$\nu = \nu_0 T^2 \xi(E, X, T) \quad (2)$$

where  $\nu_0 \sim 10^{14} \text{ s}^{-1}$  and  $T$  is the absolute temperature. The  $T^2$  prefactor on the right-hand side of Eq. (2)

is well known [7] for thermionic emission processes; in our case, however, its variation is small and the term is considered to be constant. An activation-like function is then assumed [5,7] for  $\xi = \xi(E, X, T)$  of Eq. (2). This could be readily substantiated on the grounds of a steady-state charge extraction.

Indeed, any EMIS extracted charged specie is essentially composed of a charged entity (e.g. a negative ion or a deprotonated glycerol molecule) and a certain number of neutral solvent molecules attached to it [4,12]. Consider this cluster a subsystem of the total system that includes the entire droplet sample and the glycerol wetted TM. Then, for the system model for which, at fixed  $T$ , both the externally applied potential,  $\Delta\Phi$ , and  $X$  are kept constant, the straightforward thermodynamic considerations would hold.

The free energy of the system is assumed to be such that  $F = F_J(\Delta\Phi, X)$ . Here,  $J = L, R$  stands for the two possible configurations of the system—when the subsystem is found either to the left or to the right of the interface boundary provided by the TM (refer to Fig. 1). Clearly,  $F = F_L$  in the former and  $F = F_R$  in the latter case, respectively. The corresponding grand-partition functions are  $Z_L$  and  $Z_R$ . That is, with a usual notation involved,  $F_J = -k_B T \ln Z_J$ ,  $J = L, R$ , and  $Z = Z_L + Z_R$ .

The probability of finding the system with its subsystem in either one of the above mentioned states is then  $P_J = Z_J/Z$ ;  $J = L, R$ . Hence, for the conditional probability of a single charge extraction event,  $f \equiv P_R/P_L$ , and with  $\Delta F \equiv F_R - F_L$ , we arrive at

$$f = \exp(-\Delta F/k_B T) \quad (3)$$

Clearly, then,  $\Delta F$  would represent an activation barrier for such charge extraction processes. Recalling Eqs. (1) and (2), we observe that  $I \sim f$ . Hence, constructing  $I/I_0 = f(T)/f(T_0)$  and letting  $\Delta(1/k_B T) \equiv 1/k_B T_0 - 1/k_B T$ , one obtains

$$I/I_0 = \exp[\Delta F \Delta(1/k_B T)] \quad (4a)$$

or

$$\ln[I/I_0] = \Delta F \Delta(1/k_B T) \quad (4b)$$

We utilize Eq. (4b) in the forthcoming presentation of our experimental results. In polar liquids, both the polarization and the evaporation energy terms are expected to contribute to the activation energy,  $\Delta F = \Delta F_0 - \Delta F_\Phi$ , of Eq. (3). Here, the barrier depression term,  $\Delta F_\Phi$ , originates from the electrostatic field applied. For the Schottky barrier case this is [6,7]:

$$\Delta F_\Phi \sim q(qE)^{1/2} \quad (5)$$

Let us introduce another relation, which, in terms of Eq. (5), allows for the testing of the field dependence of  $\Delta F$ . For this purpose,  $\Delta\Phi$  and the local (nearby TM) electrical field,  $E$ , are interrelated by means of a “characteristic length” parameter,  $D$ , such that  $E = \Delta\Phi/D$ . In other words, with  $\Delta F = \Delta F_{0,X} - \Delta F_{\Phi,X}$ , we write (in SI units) the field dependent term:

$$\Delta F_{\Phi,X} \sim [q^3 \Delta\Phi / D 4\pi\epsilon_0\epsilon]^{1/2} = A_X [\Delta\Phi]^{1/2} \quad (6)$$

where  $\epsilon_0$  and  $\epsilon$  are the permittivity of vacuum and the static dielectric constant of glycerol ( $= 42$ ), respectively;  $A_X \equiv [q^3 / D 4\pi\epsilon_0\epsilon]^{1/2}$ . The subscript,  $X$ , is implicitly indicative of the carrier concentration dependent features of  $\Delta F$ .

Our last subject in this section is the carrier concentration dependence of  $\Delta F$ . Quite generally, both the concentration dependent entries of Eq. (6), namely,  $D$  and  $\epsilon$ , become smaller, the larger the electrical conductivity of ionic solution is. Therefore,  $\Delta F_{\Phi,X}$  is expected to increase as a function of increasing  $X$  (for  $\Delta\Phi \neq 0$ ). One would anticipate then, a smaller activation barrier,  $\Delta F$ . There exists no easy way of treating such a problem, hence, here we consider only the limiting case of  $\Delta\Phi \rightarrow 0$ . Clearly, then,  $\Delta F \rightarrow \Delta F_{0,X}$ . In this regime, the charge extraction is a diffusion limited evaporation process, for which case we may approximate

$$\Delta F_{0,X} \approx \Delta F_{0,1} - k_B T_0 \ln X \quad (7)$$

where  $\Delta F_{0,1}$  stands for  $X = 1$ , i.e. for the pure glycerol case. We used a simplifying assumption that the electrochemical potential of the extracted charged specie remains nearly the same irrespective of any atomic (or molecular) properties of the associated

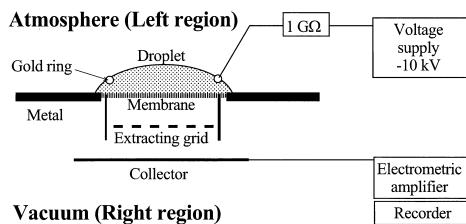


Fig. 1. Schematics of track membrane assembly for charge extraction from liquid-to-vacuum in thermally activated charge extraction processes.

charge carrying core involved (being either a deprotonated glycerol molecule or the monovalent ion).

### 3. Experimental

Our experimental setup is similar to the usual [12] EMIS facilities; its schematics are briefly shown in Fig. 1. Track membranes [4,5] of  $10^7$  channels per  $\text{cm}^{-2}$  were manufactured and characterized in Dubna (Russia) from a 20 micrometer thick poly(ethylene terephthalate) film. The mean channel diameter was 0.07 micrometer. Analytical purity glycerol (Fruarom, Israel) was used. After 12 h the liquid samples (droplets) were made afresh. The appropriate glycerol solutions (in a form of  $\sim 200 \mu\text{L}$  droplets) were applied to the ambient pressure side of the TM.

The dynamic vacuum conditions were produced using a STP-400 Turbo pump (Seiko-Seiki, Japan). The pump was positioned just beneath the TM inlet. TMs are used, therefore, to spatially separate these two regions as well as to allow for the high field charge extraction regime to be developed and maintained. This latter function was achieved in the following way.

Externally applied voltage drops,  $\Delta\Phi$ , were set by a stabilized high voltage power supply (Branderburg). The resulting negative bias was brought to the droplets by means of a metal electrode (gold ring). Thus, the negatively charged species were forced to move down the channel network towards the TOF-MS vacuum chamber held at various operational pressures ranging from  $10^{-2}$ – $10^{-7}$  mbar. The experimental

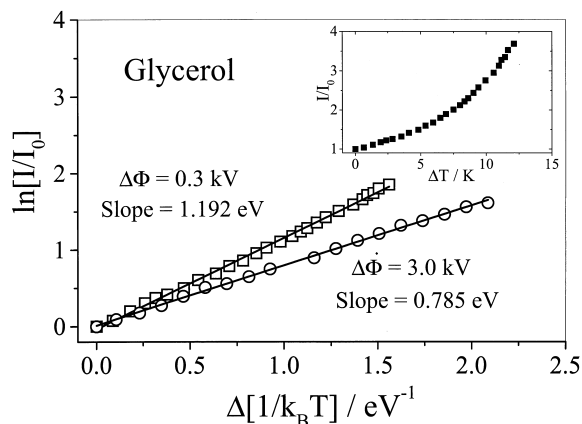


Fig. 2. Plot of  $\ln[I/I_0]$  vs.  $\Delta(1/k_B T)$ ; refer to Eq. (4b). The slopes provide the activation energy as a function of electrical field,  $\Delta F = \Delta F(\Delta\Phi)$ . Inset: a typical raw data for  $I/I_0$  vs.  $\Delta T = T - T_0$ ;  $T_0 = 291 \text{ K}$ .

readouts, in the form of the dc collector currents,  $I$ , were recorded by a nano-amperemeter (Yokogawa).

The temperature readings were obtained using a calibrated differential Cu–Co thermocouple referenced by a fixed point held at 273 K. The measuring joint of this thermocouple was directly immersed into the glycerol droplet (refer to Fig. 1). Precautions were undertaken to prevent any charge leakage through the thermocouple circuit. The uncertainties of the temperature readouts (due to the finite thermal conductivity and heat capacity of the thermocouple joint) have been estimated within 0.4–0.6 K. The temperature of the glycerol droplet increased at a rate of 1.2 K/min, from its ambient value,  $T_0$ , of about 291 K.

### 4. Results and discussion

A typical variation of the normalized TM current,  $I/I_0 = I(T, \Delta\Phi)/I(T_0, \Delta\Phi)$  as a function of temperature rise is illustrated in Fig. 2. A substantial increase of  $I/I_0$  for increasing  $T$  is exemplified in the inset. A thermally activated nature of the charge extraction is self-evident when the left side of Eq. (4b) is plotted versus  $\Delta(1/k_B T)$ . This is shown for two fixed values of the externally applied potential,  $\Delta\Phi$ . The positive slopes of the linear regression lines drawn through the data points provide our experimental entries for  $\Delta F$ .

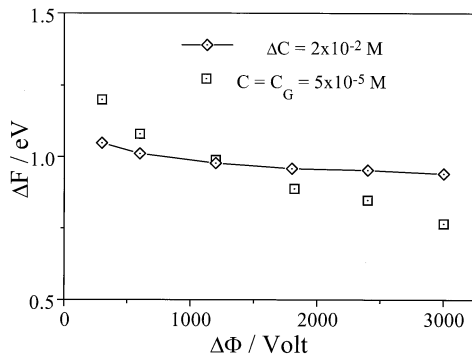


Fig. 3. Plot of  $\Delta F = \Delta F(\Delta\Phi)$  for the minimal,  $\Delta C = 0$  ( $X = 1$ ), and the maximal,  $\Delta C = 0.02$  M ( $X = 400$ ) KCl concentrations obtained in the usual operational range of EMIS ( $\Delta\Phi < 3$  kV).

Although at fixed  $T_0$  the current is known to increase with  $\Delta\Phi$ ; it appears that the higher the potential applied, the smaller the variation of  $I/I_0$ . The data in this figure also suggest that  $\Delta F$  depends on  $\Delta\Phi$ . Such behavior is illustrated in Fig. 3, where  $\Delta F$  obtained at several fixed values of  $\Delta\Phi$  (ranging from 0.3–3 kV), is shown for two limiting cases: a pure solvent and a 0.02 M KCl/glycerol solution.

The sensitivity of  $\Delta F$  to  $\Delta\Phi$  appears to level off with increasing  $X$ . For all the solution samples studied ( $X = 1$  inclusive),  $\Delta F$  was found to decrease with increasing  $\Delta\Phi$ . Although  $I_0$  tends to increase with  $X$ , the very response of  $I/I_0$  to  $\Delta\Phi$  appears to be smaller for higher ionic concentrations than for lower ones.

One also observes a dramatic decrease of  $\Delta F(\Delta\Phi \rightarrow 0)$  with an increasing charge carrier concentration. In this study the smallest  $\Delta\Phi$  for which a stable stationary charge extraction was still possible was 0.3 kV. Such data might be used to assess the limiting behavior of  $\Delta F(\Delta\Phi \rightarrow 0) = \Delta F_{0,X}$ .

In Fig. 4 we analyze such  $\Delta F(\Delta\Phi = 0.3$  kV) data for the entire range of  $X$  covered in this work. As is evident from the inset of this figure, the dependence is far from a linear one: for  $\Delta C \rightarrow 0$  (i.e.  $X \rightarrow 1$ ) the activation barrier is found to rise sharply to about 1.2 eV. However, when the data is plotted in terms of  $\ln(X)$  a fair linearity is found. In accordance with Eq. (7), there exists a reasonable agreement with the anticipated slope value of  $24$  meV  $\cong k_B T_0$ .

Observe also that  $\Delta C = 1$  M results in  $\ln(X) =$

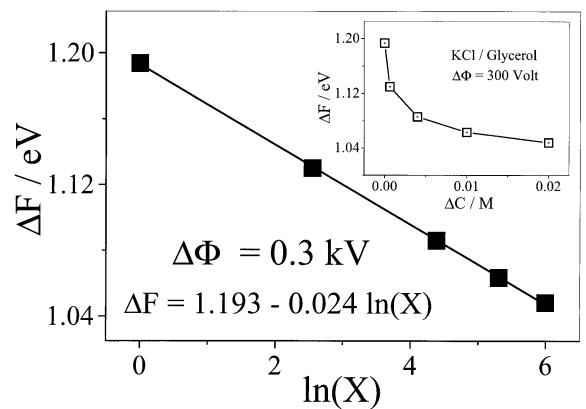


Fig. 4. In accordance with Eq. (7), the slope of the linear regression line through the data points is quite close to  $k_B T_0$ . Inset: the raw values of  $\Delta F$ , recorded for different  $\Delta C$  values, at the smallest  $\Delta\Phi$  ( $= 0.3$  kV) applied.

9.9. In turn, when the latter is substituted into the fit equation of the inset, one obtains  $\Delta F(\Delta\Phi \rightarrow 0, \Delta C \rightarrow 1$  M)  $\cong 0.96$  eV. Within our model it would correspond equally well to a hypothetical situation, where a “salt” of deprotonated glycerol molecules was added to a neutral glycerol solvent, so that the  $\Delta C \rightarrow 1$  M limit had been realized.

In such an instance, a very minute contribution to  $\Delta F$  would have been expected to come off the polarization effects. Hence, roughly speaking, the activation barrier would have been due solely to the enthalpy of evaporation, which for a single glycerol molecule is about 0.93 eV [13] and is reasonably close to the above estimated  $\Delta F(\Delta\Phi \rightarrow 0, C \rightarrow 1$  M) figure.

Our main experimental findings are related to Eqs. (5) and (6). Recall that a square-root type reduction of the activation energy as a function of the potential applied is anticipated for a Schottky barrier effect. Unfortunately, the data in Fig. 4 is inconclusive for such purposes. This is mainly due to experimental uncertainties inherent to EMISs.

To comply with our quest for the  $\Delta F_{\Phi,X} \sim [\Delta\Phi]^{1/2}$  behavior we had to extend our measurements far beyond the usual 2–3 kV operational range of EMIS. In this regard, we were successful in doing so for pure glycerol samples only. Any attempt at cov-

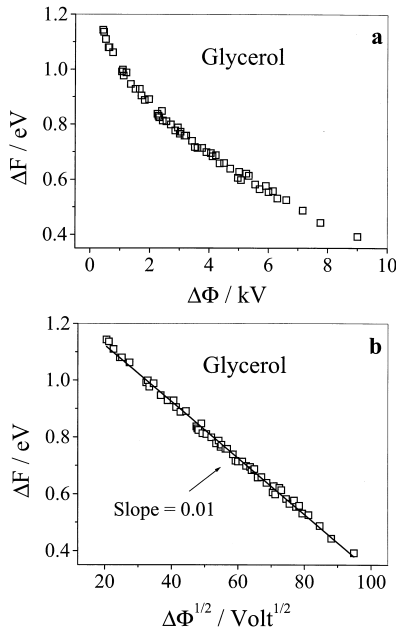


Fig. 5. (a) Full range  $\Delta F = \Delta F(\Delta\Phi)$  data for glycerol. (b) Plot of  $\Delta F$  vs.  $[\Delta\Phi]^{1/2}$ . Refer to Eqs. (5) and (6).

ering a wider range of  $\Delta\Phi$ s while keeping  $\Delta C \gg C_G$  has eventually resulted in a malfunctioning of EMIS.

In fact, the charge extraction was so intense that the liquid droplets, which were formed at the vacuum facing side of membrane, were short circuiting it, inevitably, to the grid. In a sense, with  $\Delta\Phi > 3$  kV, the EMIS was driven under such circumstances into a kind of “electrospray” operational mode.

In Fig. 5 we plot the full range glycerol data for  $\Delta F$ . To assess the possibility of a Schottky effect barrier reduction, the data is replotted as a function of  $[\Delta\Phi]^{1/2}$  in Fig. 5(b). The slope  $S \cong 0.01$  eV<sup>1/2</sup> and because  $S = A \equiv [q^3/D4\pi\epsilon_0\epsilon]^{1/2}$  we estimate  $D \cong 350$  nm. This figure is about 10 times smaller than the interchannel spacing (there are about  $10^7$  channels per cm<sup>2</sup>).

On the other hand, one might compare this figure with a characteristic length related to the extent of the local field region. This could be done using the so-called Debye length,  $L_D = (\epsilon\epsilon_0k_B T/2nq^2)^{1/2}$ . Because in our case  $n = 3 \times 10^{22}$  m<sup>-3</sup>, such  $D$  appears to be an order of magnitude larger than  $L_D$ . Note also that  $D$  is about five times larger than the

mean channel diameter ( $\cong 70$  nm), yet it is by far smaller than a typical channel length ( $\cong 10$   $\mu$ m).

Recall that a steady-state charge extraction process occurs according to the Rayleigh criterion of fluid stability:

$$\Delta p + E^2/8\pi - 2\gamma/r = 0 \quad (8)$$

for  $r > r_0$ , where  $r_0$  is the mean channel radius and  $\gamma$  is the surface tension of the liquid. Inserting  $r = D = 350$  nm,  $\Delta p = 10^6$  dyn/cm<sup>2</sup>, and  $\gamma \cong 50$  dyn/cm [13] we thus obtain a typical [12] field strength of  $E = 2.3 \times 10^6$  V/cm.

These estimates suggest that even though the characteristic length  $D$  found in our measurements does not appear to directly match any significant length scale of our TMs, its order of magnitude is self-consistent with the typical data for the local field strength values found at the liquid/vacuum interface.

## 5. Conclusions

Characterization of temperature effects upon operation of an electro-membrane ion source has been addressed. Theoretical considerations regarding the temperature dependence have been developed, suggesting a possible Schottky barrier limited behavior. Experimental data have been acquired for a wide range of potentials and concentrations.

The experimental results support the principal  $[\Delta\Phi]^{1/2}$  field dependence of a Schottky barrier limited charge extraction process in EMIS. One also observes a dramatic decrease of  $\Delta F(\Delta\Phi \rightarrow 0)$  with an increasing charge carrier concentration; it is in reasonable agreement with the model case considered.

No direct match, in terms of TM physical dimensions, was obtained for the characteristic length,  $D = 350$  nm. The latter is derivable from the Schottky-type barrier reduction effects. Nevertheless, a clear self-consistency of the data with the Rayleigh criterion of fluid stability encourages further investigative efforts.

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