

**Influence of the water content in mixed water-acetonitrile solvents upon
the kinetics and mechanisms of decomposition and stabilization
reactions at the illuminated n-GaAs/TMPD interface.**

S. Lingier and W.P. Gomes

Rijksuniversiteit Gent, Laboratorium voor Fysische Scheikunde

Krijgslaan 281, B-9000 Gent, Belgium.

Abstract.

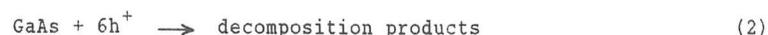
The competition between the anodic oxidation of the illuminated n-GaAs electrode and that of tetramethyl-p-phenylenediamine (TMPD) was studied by rotating ring-disk voltammetry as a function of the photocurrent density, the TMPD concentration, the pH and the solvent composition, i.e. the water to acetonitrile ratio. From the results, it is concluded that decreasing the water content of the water-acetonitrile mixture influences the kinetics in the sense of improving the stability of the photoelectrode, and that the subsequent electrochemical decomposition steps may involve either a free hole or a surface intermediate as the mobile surface species, depending on the composition of the electrolyte. These medium effects lead to a better insight into the structure of the decomposition intermediates of GaAs and into their chemical interactions with the solvent.

1. Introduction.

Gallium arsenide is an appropriate semiconductor material for photo-voltaic solar energy conversion because of its ideal energy band-gap (1.4 eV). The operation of an n-GaAs-based photoelectrochemical solar cell implies that the photogenerated positive holes oxidize a dissolved reducing agent Y at the semiconductor electrode:



whereas Z is reduced back to Y at the counterelectrode. The long-term operation of such a cell is hindered however by a competing anodic hole reaction in which the semiconductor decomposes⁽¹⁾:



In order to account for the presence of oxyanions among the decomposition products of reaction (2), Gerischer has suggested that water molecules participate to the reaction in acid medium⁽¹⁾. Consequently, the anodic decomposition process is expected to be efficiently suppressed by working in non-aqueous medium. Accordingly, the n-GaAs photoelectrode appears to be quite stable in water-free acetonitrile as the solvent, with 0.015 mol.dm⁻³ TMPD (N,N,N',N'-tetramethyl-p-phenylene diamine) added as the reducing agent Y. This conclusion was reached by Kohl and Bard⁽²⁾ from the fact that the GaAs electrode showed neither a change in weight nor in surface appearance after the passage of a considerable charge in this medium. In aqueous medium, which is more attractive for photoelectrochemical solar cells because water is cheap, non-hazardous and abundant, the prevention of the anodic photodecomposition of n-GaAs by a competing oxidation reaction of the type (1), denoted as the stabilization reaction, requires relatively high reducing agent concentrations (of the order of 1 mol.dm⁻³)^(3,4). It is therefore clear that, in view

of solar energy applications, the detailed knowledge of the role of water in the mechanism of the decomposition reaction (2) and in the kinetics of the competition between reactions (2) and (1) in aqueous medium is important.

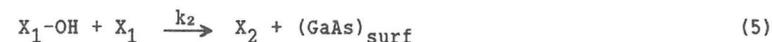
The competition between stabilization and decomposition can be quantitatively expressed by the stabilization ratio *s*, i.e. the fraction of the photocurrent corresponding to the anodic oxidation of TMPD. By using a rotating ring-disk (RRD) set-up in which the disk consists of n-GaAs and the ring allows to determine the oxidized form of TMPD quantitatively, the oxidation current of TMPD at the n-GaAs disk can be derived from the ring current, allowing the determination of the stabilization ratio. Recently, we have made an RRD voltammetric study on the competition between the photoanodic oxidation of TMPD and the photodissolution of n-GaAs in acid aqueous medium⁽⁵⁾. The stabilization ratio *s* was measured as a function of the analytical concentration *c* of TMPD, of the pH and of the total anodic photocurrent density. The results have been interpreted on the basis of the following mechanism. In the first electrochemical step of the six-equivalent oxidation reaction of GaAs, a mobile surface decomposition intermediate *X*₁ is assumed to be formed:



which can interact chemically with a water molecule to form an immobile intermediate *X*₁-OH according to the equilibrium reaction:



(*X*₁ is positively charged, whereas *X*₁-OH is neutral); the second decomposition step is assumed to involve the reaction between an immobile *X*₁-OH and a mobile *X*₁ species:



whereas the stabilization reaction is supposed to take place by electron transfer between TMPDH⁺ and *X*₂.

In the present study, it was our aim to further investigate the role of water in the reaction mechanism. Therefore, the influence of water on the kinetics of stabilization and photodecomposition was studied by performing stabilization measurements in TMPD-containing electrolytes in which water-free acetonitrile and acetonitrile-water mixtures of different composition were used as the solvent.

2. Experimental.

The measurements were performed on n-type GaAs single crystals purchased from Metallurgie Hoboken-Overpelt (Belgium). According to the specifications of the manufacturer, the density N_D of donors (Sn) ranged between 4.2×10^{16} and $5.5 \times 10^{16} \text{ cm}^{-3}$. Two samples (denoted by A and B) were used, the (111) face being exposed to the electrolyte. For details on the preparation of the ohmic contact and on the mounting of the sample into an RRD set-up, see ref. 6. The counter-electrode of the cell circuit was a Pt gauze and the reference electrode was an aqueous saturated sulphate electrode (SSE), except for the measurements in pure acetonitrile medium, in which case a Ag/Ag^+ electrode was used.

The indifferent electrolyte solution consisted of either acetonitrile or a acetonitrile-water mixture with 0.25 mol.dm^{-3} TBAP (tetrabutylammoniumperchlorate) and 0.25 mol.dm^{-3} LiClO_4 added respectively. The TBAP was dried under vacuum for four days. "As received" acetonitrile (Merck) contains 0.3 % (by weight) of water. By drying over molecular sieves (0.3 nm), the water content was decreased down to 0.003 %⁽⁷⁾. In order to prevent contamination by water and oxidation of TMPD by air during the measurements, a closed cell was used, and pure dry N_2 gas was bubbled through the solution.

The pH of the mixed water-acetonitrile solutions was determined by a glass electrode, which was calibrated by means of aqueous standard buffer solutions. It should be recalled that, in principle, proton activities determined in this way in solutions with different $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ ratios cannot be mutually compared.

The stabilizing agent used was TMPD. Dissolved TMPD may react with either one or two protons to form TMPDH^+ and TMPDH_2^{2+} , respectively. In what follows, TMPDH_2^{2+} , TMPDH^+ and TMPD will be denoted by Y_0 , Y_1 and Y_2 respectively. Only Y_1 ions and Y_2 molecules are expected to act as reducing agents^(8,9). The Y_0 , Y_1 and Y_2 equilibrium concentrations, y_0 , y_1 and y_2 respectively, were calculated from the concentration c of dissolved TMPD and from the acidity constants K_1 and K_2 of Y_0 and Y_1 respectively, which were determined for each solvent composition by titration of TMPD with HClO_4 .

Before the experiments, the GaAs electrode was etched chemically in $\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2:\text{H}_2\text{O}$ (3:1:1 by volume) and afterwards etched photoelectrochemically⁽⁶⁾. Illumination of the electrode was provided by a halogen incandescent lamp. The light intensity was varied by means of neutral density filters. All measurements were performed at room temperature (298 K).

3. Results.

3.1. Acetonitrile solution.

In neutral aqueous solution and in purely organic solution, the photoanodic decomposition products of GaAs are insoluble and form a passivating layer on the electrode surface, which causes a decrease in the photocurrent density. In these solutions, the decomposition of the n-GaAs

photoanode can be monitored by following the photocurrent density as a function of time at constant light intensity. In figure 1, the photocurrent density i at the n-GaAs/TMPD interface is shown as a function of time in "as received" acetonitrile and in dried acetonitrile. As can be seen, the photocurrent density at the n-GaAs electrode remains constant in dried acetonitrile during more than four hours ($s=1$), whereas in "as received" acetonitrile the photocurrent density decreases after two hours already ($s<1$). The slight amount of H_2O in acetonitrile (0.3 %) causes decomposition of the n-GaAs electrode. The formation of a passivating layer on the GaAs surface makes it however impossible to perform a kinetic study, e.g. measurements of s , i and c under steady-state conditions, at the n-GaAs/TMPD interface in acetonitrile. We have therefore added an acid ($HClO_4$) to the acetonitrile-water mixtures in order to dissolve the decomposition products and hence to prevent the formation of a passivating layer.

3.2. Mixed CH_3CN+H_2O solvent with 42 mol % (66 vol %) CH_3CN .

The relationship between s , i and c at constant electrode potential was measured in the mixed solvent with 42 mol% CH_3CN at different pH values in the range $1.5 \leq pH \leq 2.5$ (at $pH > 2.5$ the photocurrent decreases as a function of time because of the formation of an insoluble decomposition product layer on the semiconductor surface). It appears that s increases with increasing c , but decreases with increasing i and hence increasing light intensity. The results obtained on sample A are in good agreement with those for sample B. The data at a given pH were found to obey the kinetic law:

$$s^2/(1-s) = k \cdot (c^2/i) \quad (6)$$

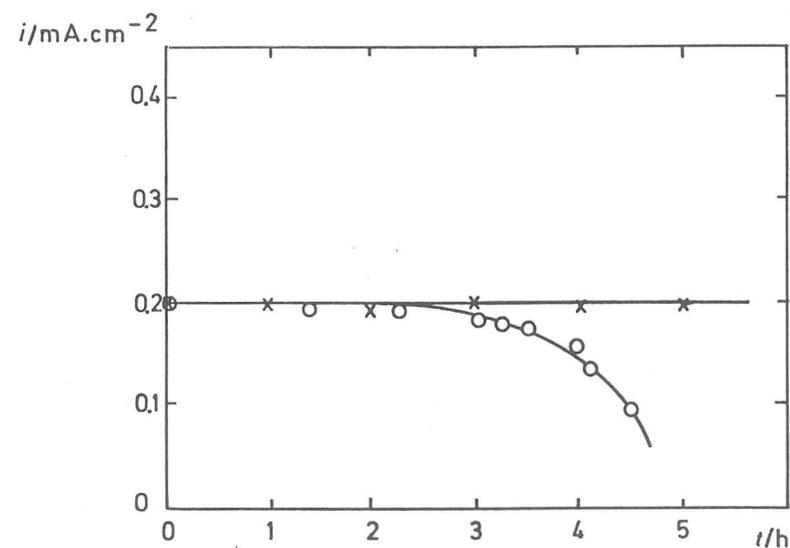


Fig. 1. Photocurrent density i as a function of time t .
GaAs sample A; $(\bar{1}\bar{1}\bar{1})$ face; $V = 0.0$ V vs. Ag^+/Ag .
Electrolyte composition: $0.25 \text{ mol} \cdot \text{dm}^{-3}$ TBAP + $0.1 \text{ mol} \cdot \text{dm}^{-3}$ TMPD
in "as received" acetonitrile (o) and in dried acetonitrile (x).

as can be seen in fig. 2, in which the data have been plotted as $\log [s^2/(1-s)]$ vs. $\log (c^2/i)$, yielding straight lines with slope unity. The kinetic law (6) has been observed previously, e.g. for the system n-GaAs/Fe²⁺(aq)⁽⁶⁾. The value of the proportionality factor k increases markedly with pH, as can be seen in table 1 (top row).

Table 1.			
Apparent rate constants for the system n-GaAs/TMPD in CH ₃ CN+H ₂ O (42 mol % CH ₃ CN).			
apparent rate constant	pH		
	1.5	2.0	2.5
$k / (\text{C.cm}^4.\text{mol}^{-2}.\text{s}^{-1})$	7.9	2.9×10^1	1.8×10^2
$k' = k.[\text{H}^+]^{-1} / (\text{C.cm}^7.\text{mol}^{-3}.\text{s}^{-1})$	2.5×10^5	2.9×10^6	5.8×10^7
$k''_{j=1} = k'.f_{j=1}(K_1, K_2, [\text{H}^+])^2 / (\text{C.cm}^7.\text{mol}^{-3}.\text{s}^{-1})$ (Y=TMPDH ⁺)	1.3×10^6	5.8×10^6	7.8×10^7
$k''_{j=2} = k'.f_{j=2}(K_1, K_2, [\text{H}^+])^2 / (\text{C.cm}^7.\text{mol}^{-3}.\text{s}^{-1})$ (Y=TPMD)	7.7×10^{15}	4.2×10^{15}	4.9×10^{15}

3.3. Mixed CH₃CN+H₂O solvent with 13 mol % CH₃CN.

The relationship between s, i and c was measured at pH 1.0, 1.5 and 2.0. Also in this case, s was found to increase with increasing c and

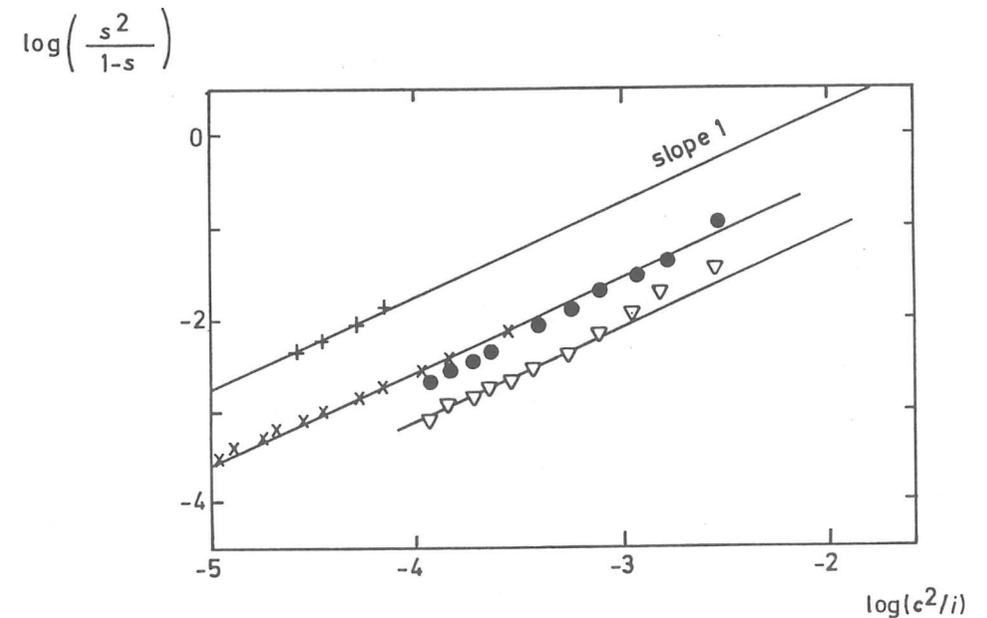


Fig. 2. $\log [s^2/(1-s)]$ vs. $\log (c^2/i)$.

GaAs sample A; (111) face; $V = -0.3$ V vs. SSE.

Electrolyte composition: $0.25 \text{ mol.dm}^{-3} \text{ LiClO}_4 + c \text{ mol.dm}^{-3} \text{ TMPD}$ in an CH₃CN + H₂O mixture with 42 mol % CH₃CN.

pH : 1.5 (∇) , 2.0 (x, \bullet) , 2.5 (+)

c : 0.074 (x, +) , 0.248 (\bullet , ∇)

with decreasing i , but importantly, s appeared to be a function of (c/i) instead of (c^2/i) . Specifically, the following kinetic law was found to hold at the three pH-values:

$$s^2/(1-s) + s/6 = m \cdot (c/i) \quad (7)$$

This is shown in fig. 3, in which the data have been plotted as $\log [s^2/(1-s) + s/6]$ vs. $\log (c/i)$, yielding straight lines with slope unity. The kinetic law (7) has been observed to hold previously for the system $n\text{-GaP}/\text{Fe}^{2+}(\text{aq})^{(10)}$. The value of the proportionality factor m again increases with pH, as can be seen in table 2 (top row).

Table 2.			
Apparent rate constants for the system $n\text{-GaAs}/\text{TMPD}$ in $\text{CH}_3\text{CN}+\text{H}_2\text{O}$ (13 mol % CH_3CN).			
apparent rate constant	pH		
	1.0	1.5	2.0
$m / (\text{C.cm.mol}^{-1}.\text{s}^{-1})$	5.5×10^1	1.5×10^2	2.1×10^3
$m'_{j=1} = m \cdot f_{j=1}(K_1, K_2, [\text{H}^+]) / (\text{C.cm.mol}^{-1}.\text{s}^{-1})$ (Y=TMPDH ⁺)	9.7×10^2	9.2×10^2	6.8×10^3
$m'_{j=2} = m \cdot f_{j=2}(K_1, K_2, [\text{H}^+]) / (\text{C.cm.mol}^{-1}.\text{s}^{-1})$ (Y=TMPD)	3.5×10^8	1.1×10^8	2.5×10^8

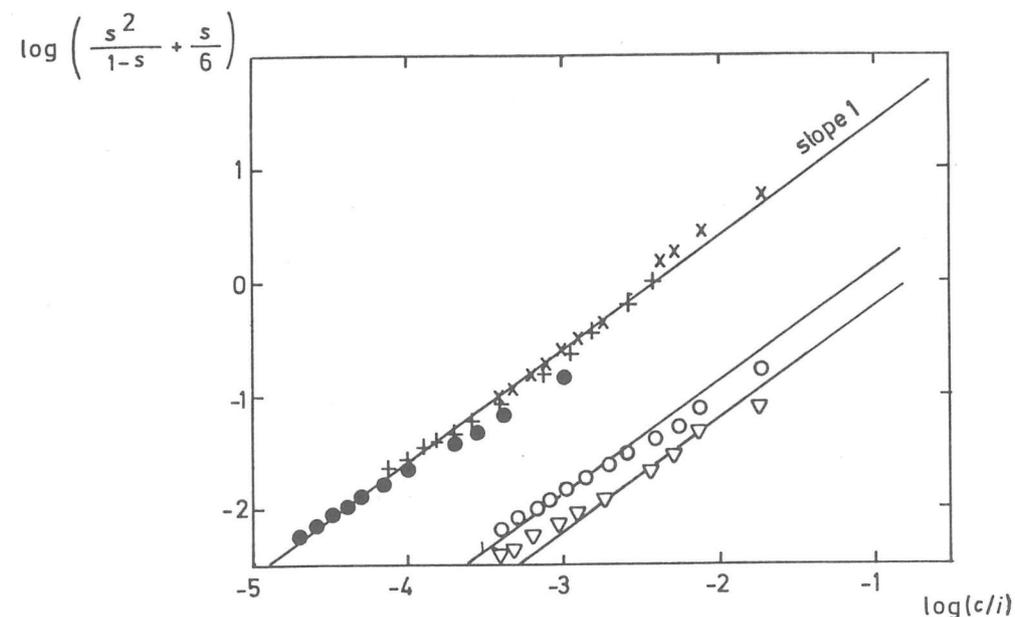


Fig. 3. $\log [s^2/(1-s) + s/6]$ vs. $\log (c/i)$.

GaAs sample A; $(\bar{1}\bar{1}\bar{1})$ face; $V = -0.3$ V vs. SSE.

Electrolyte composition: $0.25 \text{ mol.dm}^{-3} \text{ LiClO}_4 + c \text{ mol.dm}^{-3} \text{ TMPD}$ in an $\text{CH}_3\text{CN} + \text{H}_2\text{O}$ mixture with 13 mol % CH_3CN .

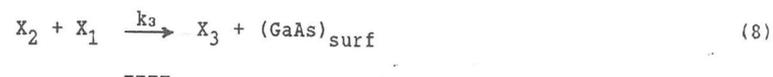
pH : 1.0 (∇) , 1.5 (o) , 2.0 ($\bullet, +, x$)

c : 0.011 (\bullet) , 0.041 (+) , 0.202 (x, ∇) , 0.216 (o)

4. Discussion.

The observation made by Kohl and Bard⁽²⁾ that the n-GaAs photoanode does not decompose in water-free acetonitrile, is confirmed by our results presented in section 3.1., from which it can be concluded that residual water in commercially available acetonitrile causes deterioration of the cell due to oxide formation on the semiconductor surface.

The kinetic law (eqn. (6)), which was found to describe the competition between the photoanodic oxidation of TMPD and that of GaAs in acetonitrile to which water was added to a mole ratio 42/58, can be interpreted on the basis of the following reaction mechanism. Reactions (3), (4) and (5) are supposed to be followed by four electrochemical steps in which a mobile intermediate X_1 participates, forming (immobile) intermediates of a higher degree of oxidation X_i ($i=3,4,5$), and eventually products which go into solution.



The oxidation of the dissolved stabilizing agent Y_j ($j=1$ or 2) is assumed to occur through reaction with X_1 :



(it is hereby assumed that only one type of reducing species reacts). That reaction mechanism (3)+(4)+(5)+(8)+... and (10) accounts for the observed kinetics can be shown as follows. From steady-state conditions it can be written:

$$dx_2/dt = k_2 \cdot x_1 \cdot x' - k_3 \cdot x_2 \cdot x_1 = 0 \quad (11)$$

and

$$dx'/dt = k_c \cdot x_1 \cdot [\text{H}_2\text{O}] - k_{-c} \cdot [\text{H}^+] \cdot x' - k_2 \cdot x_1 \cdot x' = 0 \quad (12)$$

where x_1 , x_2 , x' represent the surface concentrations of X_1 , X_2 and $X_1\text{-OH}$ respectively.

The decomposition current density is given by:

$$(1-s) \cdot i = 6e \cdot k_2 \cdot x_1 \cdot x' \quad (13)$$

where e is the elementary charge.

The current density associated with the oxidation of Y_j is then

$$s \cdot i = e \cdot k_{-1}^s \cdot x_1 \cdot Y_j \quad (14)$$

Eliminating x_1 , x' and x_2 from eqns. (11)-(14) and assuming quasi-equilibrium in eqn. (3) (i.e. $k_{-c} \cdot [\text{H}^+] \gg k_2 \cdot x_1$), one obtains:

$$s^2/(1-s) = \{e \cdot k_{-c} \cdot (k_{-1}^s)^2 \cdot [\text{H}^+] / 6 \cdot k_2 \cdot k_c \cdot [\text{H}_2\text{O}]\} \cdot (Y_j^2/i) \quad (15)$$

At a given pH, y_j is proportional to c , and hence eqn. (15) is in agreement with the experimental results presented in section 3.2. The experimental constant k is then interpreted as being equal to:

$$k = e \cdot k_{-c} \cdot (k_{-1}^s)^2 \cdot [\text{H}^+] / 6 \cdot k_2 \cdot k_c \cdot [\text{H}_2\text{O}] \quad (16)$$

In order to investigate whether our model can also explain the observed pH-dependence of k , the value of $k \cdot [\text{H}^+]^{-1}$, denoted by k' , was listed as a function of pH in table 1. As can be seen, k' is pH-dependent. Up to this point however, the pH-dependence of the concentration of the reducing agent y_j was not taken into account, i.e. we have considered the analytical concentration c instead of that of the actual reducing agent concentration y_j . The relationship between the concentration of one of the forms of TMPD and the analytical TMPD concentration c is given by:

$$y_j = c / f_j(K_1, K_2, [\text{H}^+]) \quad (17)$$

in which $f_j(K_1, K_2, [\text{H}^+])$ is a specific function for each form of dissolved TMPD. From eqns. (6), (15) and (17), the experimental constant k is then interpreted as being equal to:

$$k = \{e \cdot k_{-c} \cdot (k_{-1}^s)^2 \cdot [\text{H}^+] / 6 \cdot k_2 \cdot k_c \cdot [\text{H}_2\text{O}]\} \cdot \{f_j(K_1, K_2, [\text{H}^+])\}^{-2} \quad (18)$$

To check whether eqn. (18) accounts for the observed pH-dependence of k , the value of k' multiplied by $\{f_j(K_1, K_2, [H^+])\}^2$, namely k_j'' , is listed in table 1 as a function of pH for the two possible cases $j=1$ and $j=2$. As can be seen, k_j'' is pH-independent in the case where $Y=\text{TMPD}$. From the foregoing analysis it hence follows that the observed relationship between s , on one hand, and i , c and $[H^+]$ on the other hand, can be explained by a model involving the subsequent decomposition steps (3), (4), (5), (8) and the stabilization reaction (10), in which Y_j stands for TMPD. It follows from the expression (18) for k that as expected, decreasing the water content of the acetonitrile-water mixtures influences the kinetics in the sense of improving the stability of the photoelectrode (see also eqn. (6)). The relatively poor stability in this medium as compared to that in purely aqueous solutions is due to the fact that in the latter case, TMPDH^+ instead of TMPD acts as the electroactive species, and that in the given pH range, the TMPD to TMPDH^+ concentration ratio is small.

In acetonitrile-water mixtures containing 13 mol % CH_3CN only, the relationship between s , c and i is different as compared to the case mentioned above, and is given by eqn. (7). This equation can be interpreted on the basis of a decomposition mechanism in which a valence band hole instead of an X_1 intermediate acts as the mobile species in the electrochemical decomposition steps. When lowering the acetonitrile concentration from 42 to 13 mol %, apparently free holes take over the role of the mobile reactive surface species from the intermediates X_1 . This suggests that in the $\text{CH}_3\text{CN}+\text{H}_2\text{O}$ mixture with 13 mol % CH_3CN , the X_1 concentration is considerably decreased with respect to the 42 mol % CH_3CN case. A possible reason for this might be an increase in the equilibrium constant of reaction (4), due to a stabilization effect of the proton in the given medium⁽¹¹⁾. Although experimentally, the standard free enthalpy of the

proton curve as a function of composition in acetonitrile-water mixtures does indeed exhibit a minimum, the difference in value in the composition range considered is not pronounced. As in general however, a relatively large dispersion appears to exist in the literature values on the standard free enthalpies of proton transfer, it is our opinion that additional independent data would be needed in order to check the validity of the present hypothesis.

Two possible competition mechanisms will be presented here by which the experimental relationship between s , c , i and $[H^+]$ (eqn. (7)) can be interpreted.

The decomposition steps in the first mechanism are reactions (3) and (4) followed by:





whereas stabilization is assumed to occur through a reaction of the type (10). Expressing the decomposition current density by

$$(1-s) \cdot i = 6e \cdot k'_2 \cdot x_1 \cdot p_s \quad (22)$$

(p_s being the hole concentration at the surface) and the stabilization current density by eqn. (14), and considering the fact that steady-state conditions hold for x_1 and quasi-equilibrium conditions for reaction (4), the following kinetic expression is derived for this mechanism:

$$s^2/(1-s) + s/6 = (e \cdot k_{-1}^s \cdot k_1/6 \cdot k'_2) (y_j/i) \quad (23)$$

In the second mechanism, the chemical step (4) which follows reaction (3) is assumed to be irreversible:



The next electrochemical decomposition step is then supposed to be:



and to be followed by reactions (20)... to (21), whereas stabilization is assumed to take place through the second decomposition intermediate X_2 :



In this case, the decomposition and stabilization reactions compete for X_2 , so that the respective current densities are given by the following equations:

$$(1-s) \cdot i = 6 \cdot e \cdot k'_3 \cdot X_2 \cdot P_s \quad (27)$$

and

$$s \cdot i = e \cdot k^s_{-2} \cdot X_2 \cdot Y_j \quad (28)$$

Applying steady-state conditions to X_1 , $X_1\text{-OH}$ and X_2 then leads to

$$s^2/(1-s) + s/6 = (e \cdot k^s_{-2} \cdot k_1/6 \cdot k'_3) (Y_j/i) \quad (29)$$

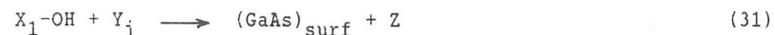
As at given pH, Y_j is proportional to c , both eqns. (23) and (29) are in agreement with the experimental kinetic expression (7). Hence, both mechanisms are kinetically indistinguishable. However, in view of the supposed low concentration of X_1 in the given medium, the first mechanism seems less probable.

In order to interpret the observed pH-dependence of m , the value of m was multiplied by $f_j(K_1, K_2, [H^+])$ for $j=1$ and $j=2$ (see eqn. (17)). From table 2, it appears that also here, TMPD is the electroactive species.

It should be remarked that a third mechanism of stabilization and decomposition at the n-GaAs photoanode in water-acetonitrile mixtures with 13 mol % CH_3CN can be proposed, leading to the same kinetic result as expressed in eqn. (7). In this mechanism, the immobile intermediate $X_1\text{-OH}$ either reacts with a valence band hole:



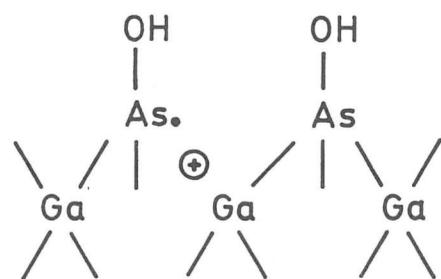
or captures an electron from Y_j :



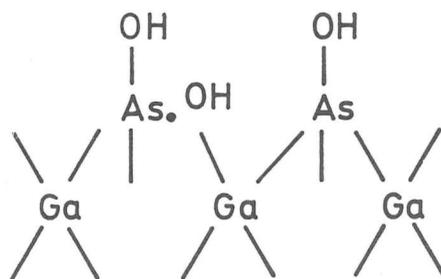
The latter reaction seems however to be structurally unlikely. Indeed, the first decomposition intermediate X_1 corresponds to a GaAs surface bond missing one electron. According to Gerischer⁽¹²⁾, this unpaired electron is situated on the more electronegative atom (As), leaving a positive charge on the Ga atom (see fig. 4(a)). Assuming that the attack takes place at a surface step, the positively charged Ga may be supposed to react with a water molecule, a process in which a proton is released and an immobile intermediate $X_1\text{-OH}$ formed (reaction (24)). The proposed structure of $X_1\text{-OH}$ is shown in fig. 4(b). An electron originating from a dissolved reducing agent cannot restore the broken bond between As and Ga in the case of $X_1\text{-OH}$, contrary to the case of X_1 . Therefore, reaction (31) and the corresponding mechanism seems to be unlikely. In fig. 4(c), a structure for the intermediate X_2 is proposed. As can be seen, the intermediate X_2 is, just like X_1 , likely to be able to capture an electron from the dissolved reducing agent, hence restoring the broken bond and forming $X_1\text{-OH}$ (see reaction (26)).

5. Conclusions.

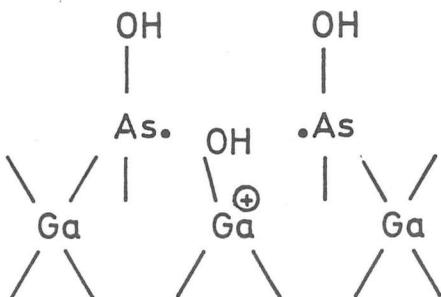
Two types of effects of the electrolyte composition, apart from the redox system, on the competing electrochemical kinetics at a n-GaAs photoanode have been observed. The first effect is the decreasing stability of the n-GaAs photoanode with increasing water content in water-acetonitrile mixtures going from purely acetonitrile to water-acetonitrile mixture with 42 mol % CH_3CN . The second one is the transition from one anodic decomposition mechanism of GaAs to another, when the acetonitrile content is decreased from 42 mol % down to 13 mol % in water-acetonitrile mixtures. These effects can be explained by assuming chemical reac-



(a)



(b)



(c)

Fig. 4. Proposed structures for the decomposition intermediates of GaAs:

X_1 (a) , $X_1\text{-OH}$ (b) and X_2 (c).

tion(s) occurring between decomposition intermediates and water molecules. This explanation leads to more insight into the chemical structure of the intermediates involved. However, techniques other than kinetic ones will be needed to obtain further information on the nature of all surface intermediates.

Acknowledgement.

The support of the I.I.K.W. (Interuniversitair Instituut voor Kernwetenschappen) to this work is gratefully acknowledged. One of the authors (S.L.) wishes to thank the I.W.O.N.L. (Instituut tot Aanmoediging van het Wetenschappelijk Onderzoek in Nijverheid en Landbouw) for a fellowship.

References.

- (1) H. Gerischer: Ber. Bunsenges. Phys. Chem. 69, 578 (1965).
- (2) P.A. Kohl and A.J. Bard: J. Electrochem. Soc. 126, 603 (1979).
- (3) K.C. Chang, A. Heller, B. Schwartz, S. Menezes and B. Miller: Science 196, 1097 (1977).
- (4) P. Allongue, H. Cachet, P. Cléchet, M. Froment, J.R. Martin and E. Verney: J. Electrochem. Soc. 134, 620 (1987).
- (5) S. Lingier, D. Vanmaekelbergh and W.P. Gomes: J. Electroanal. Chem. 228, 77 (1987).
- (6) D. Vanmaekelbergh, W.P. Gomes and F. Cardon: Ber. Bunsenges. Phys. Chem. 89, 987 (1985).
- (7) D.W. Breck: "Zeolithe Molecular Sieves", John Wiley & Sons, New York (1974).
- (8) U. Nickel and W. Jaenicke: Ber. Bunsenges. Phys. Chem. 86, 695 (1982).
- (9) U. Nickel, B. Mao Zhou and G. Gulden: Ber. Bunsenges. Phys. Chem. 89, 999 (1985).
- (10) D. Vanmaekelbergh, W.P. Gomes and F. Cardon: J. Electrochem. Soc. 129, 546 (1982).
- (11) K. Das, A.K. Das and K.K. Kundu: Electrochim. Acta 26, 471 (1981).
- (12) H. Gerischer: Surf. Sci. 13, 265 (1969).

(Received 3.May.1988)

Polarographic Studies On Mixed Ligand Complexes Of Cadmium-1-Methylimidazole-Oxalate System.

Gamal B. Mohamed* and A. M. Ahmed†

* Chemistry Department, Faculty of Education, Alexandria University, Alexandria, Egypt.

† Chemistry Department, Faculty of Science, Alexandria University, Alexandria, Egypt.

ABSTRACT:

The over-all formation constants of the mixed ligand complexes of 1-methylimidazole (1-MeIm) and oxalate (Oxal) with cadmium (II) have been studied polarographically at constant ionic strength, $\mu = 2.0$, (NaNO_3) and pH 8 at $25 \pm 0.1^\circ\text{C}$. The reduction of the complexes at a dropping mercury electrode, DME, is reversible and diffusion controlled. The constants for three mixed complexes of Cd(II) are $\log \beta_{11} = 4.0$ for $\text{Cd}(1\text{-MeIm})(\text{Oxal})$, $\log \beta_{12} = 4.4$ for $\text{Cd}(1\text{-MeIm})(\text{Oxal})_2$ and $\log \beta_{21} = 5.9$ for $\text{Cd}(1\text{-MeIm})_2(\text{Oxal})$. The tendency of a ligand to add to a complex and to substitute another ligand was compared.

* Author to whom correspondence should be addressed,