SPECTROSCOPICAL STUDY OF ANODIC MICRO-PLASMAS OBSERVED DURING ANODE EFFECT IN MOLTEN LiCl-KCl MIXTURES.

Jean-Paul Bardet, Jean-Claude Valognes, Pierre Mergault

Laboratoire de Physique des Liquides Ioniques.
Université Pierre et Marie Curie
Tour 15 - 4 Place Jussieu,
75252 Paris Cedex 05, France

ABSTRACT

The values of the main parameters of an anodic plasma obtained by electrolysis of a molten LiCl-KCl equimolecular mixture are stated, under a theoretical computation of the 4f4d4p-2p Li(I) lineshape, using Magnus frame for electronic perturbation and taking into account the effect of dynamic ion broadening: electric radial field intensity $|\mathbf{E}| = 160$ kV cm$^{-1}$, electronic density $N_e \approx 1.2 \times 10^{17}$ cm$^{-3}$, temperature between 5000 and 5500 K. For the chosen composition of the electrolytic bath, the runaway of electrons is inhibited by the fact that the micro-plasmas are both very thin (5 µm) and partially ionised, but for a pure LiCl electrolytic bath, there is runaway.

INTRODUCTION

In 1963, our laboratory began the spectroscopical study of the light emitted at the anode during anode effect (A.E.), in the purpose of obtaining data about the gaseous sheath surrounding the anode (1,2,3). As a matter of fact, in well-chosen electrolytic baths, electrodes, electrolytic cell feed voltages, the light emission is intense enough during a time long enough to permit a spectroscopic study. As is shown by using a high-speed cine-camera, there are only one or two electrical discharges on the anode surface at the same time (4), but they follow one another at random in

428
such a way that the whole surface seems to emit light with the same average brightness, provided the electrolytic voltage is great enough and has been applied between the electrodes after a lapse of an adequate period of time (a few seconds). Moreover, the short life created micro-plasmas locally vaporize the electrolytic bath and the heat they radiate is sufficient to maintain the gaseous sheath existence.

The life of the emission is only limited by the anode erosion, which depends on the electrolytic bath composition. Diagnostic methods of plasma spectroscopy are well suited to study the anodic plasma, because they do not modify the state of the sheath, neither in space, nor in time. Thus, theoretical spectroscopic line profiles are computed and compared with experimental data until they agree reasonably well.

EXPERIMENTAL RESULTS AND MAIN COMPUTATION HYPOTHESIS

The chosen method is better for very broad lines and, after several experiments (1,3,5,6), we have chosen to study the semi-degenerate 4f4d4p-2p Li(I) lines, using a molten equimolecular LiCl-KCl mixture as an electrolytic bath. A first computation of theoretical profiles in the frame of the impact approximation of the relaxation theory (7,8), considering an important self-absorption led (9) to a result close to experimental profiles (fig. 1). However, there were differences between experimental and theoretical profiles and we thought that a uniform electric field could be one reason for these differences; it was then necessary to modify the computation in order to account for this field (9,10).

The uniform electric field $E$ is polarized along the direction of observation (perpendicular to the anode axis); so, one observes only the $\sigma$ components of the lines. Furthermore, it is necessary to take the splitting of atomic energy levels into account in the theoretical computation, before the electronic and ionic microfields perturbations. At last, the electric field $E$ can produce an inhomogeneity of the micro-plasmas.
A thermodynamic study of the micro-plasmas (11,12) was carried out under the following assumptions:
- stationary micro-plasmas
- micro-plasmas submitted to the atomic pressure
- the validity of the Saha law
- a concentration of each element of the micro-plasma equal to the ionic concentration in the electrolytic bath.

A computation of temperature distributions was made by solving, for various values of \( \dot{E} \), the energy balancing equation. The anodic micro-plasmas were shown to be cold (electronic temperature \( T \approx 7000 \) K) and, from the values obtained for the correlation factor:

\[
\frac{r}{3} \frac{n_e}{e} \left( \frac{e^2}{4\pi \varepsilon_0 kT} \right) \]

\( (N_e : \text{electronic density} - e : \text{electronic charge}) \)

it became obvious that the hypothesis of a quasi-static ionic microfield was not suitable (12), whatever the value of \( \dot{E} \) may be.

The computation of theoretical electronic profiles based on the Griem-Baranger theory (7.8) and taking \( \dot{E} \) into account permitted us to evaluate \( |\dot{E}| \) to be of the order of 160 kV cm\(^{-1}\). For this value, the optical depth of the micro-plasmas is very weak and thus, self-absorption is negligible.

**THEORETICAL PROFILES COMPUTATION**

We computed again the theoretical profile of the 4f4d4p-2p Li(I) line by taking into account the effect of dynamic ion broadening. Then, the total profile is a sum of convolution products:

\[
\tilde{I}(\omega) = \sum \int \tilde{I}(\omega', a, a') \tilde{I}(\omega - \omega', a', a) \, \omega' \quad [1]
\]

\[
\tilde{I}(\omega; a, w) = \frac{4}{\pi} \Re \left[ \sum \int e^{-i \omega \xi} \tilde{P}(\xi_E, \xi_K) \tilde{c}(\xi) \times \right.
\]

\[
\left. x < a', \tilde{a}, \tilde{b}, \tilde{c} > \tilde{x} \quad \tilde{x} < a', \tilde{a}, \tilde{b}, \tilde{c} > \tilde{x} \right] \tilde{I}(\omega, a, a') \, dt \quad [2]
\]

430
\[
I(\omega, a', a) = \frac{1}{\hbar} \mathcal{R}_e \left[ e^{i\omega t} \int e^{i\omega t} \left( \sum \mathcal{U}(a) \right) \mathcal{A}_c \right] [3]
\]

(where \( \frac{1}{\hbar} \sum \mathcal{U}(a) \mathcal{A}_c \) is the thermal average of the evolution operators, the dipolar moment operator, \(|a>, |a'>, |c>\\))

Li(I) energy levels of main quantum number \( n = 4 \), perturbed by the field \( \mathcal{E} \). At last:

\[\mathcal{P}(t) = <\mathcal{P}(t) | a>\]

where \( \mathcal{P}(t) \) is the atomic density operator.

The partial ionic profiles \( I_\mathcal{P}(\omega; a, a') \) are computed by using the adiabatic solutions \( (13) \) of the equation:

\[\frac{i}{\hbar} \frac{\partial \mathcal{P}(t)}{\partial t} \left( \mathcal{A}_c + \sum \mathcal{U}_c(t) \right) \mathcal{P}(t) \]

In a first study, we computed the partial electronic profiles \( I_\mathcal{E}(\omega; a', a) \) in the frame of the impact approximation of the relaxation theory \( (7,8) \), just as in our former studies \( (9,10,12) \). So, we did the computations of \( I_\mathcal{P}(\omega; a, a') \), \( I_\mathcal{E}(\omega; a', a) \) and of \( I(\omega) \) for several values of \( \mathcal{E}, N_e \) and the corresponding values of \( \tau \) emerging from the thermodynamic study.

The theoretical profile showing the best agreement with the experimental one was so obtained for:

\( N_e = 1.2 \times 10^{17} \text{ cm}^{-3} (T_e = 5200 \text{ K}) \) and \( \mathcal{E}\mathcal{E} = 160 \text{ kVcm}^{-1} \)

A posteriori, the obtained value of \( \mathcal{E}\mathcal{E} \) justifies the use of the adiabatic solutions in the computation of the partial ionic profiles \( I_\mathcal{P}(\omega; a, a') \), since it sufficiently separates the forbidden line from the permitted one, even for the relatively great value of \( N_e \).

One can also notice that \( \mathcal{E}\mathcal{E} \) is twice greater than the critical electric field \( E_c \):

\[E_c = \frac{e}{8\eta N_e p_D^2}
\]

where \( p_D \) : Debye radius.\]
but one can reasonably suppose that the runaway phenomenon (14) is probably inhibited by the fact that the plasma is both very thin (5 μm) and partially ionised (neutral atoms are ten times as numerous as the electrons) (15).

However, the great value of $E$ sets the problem of the nature of the electrons-atom collisions, questioning again the computation of the partial electronic profiles.

It was then necessary to go through the study by using a better representation of the electronic perturbation, which permits:
- to introduce chronologic effect
- to take into account the strong electronic collisions, in another way than using a correcting term as in the previous studies (9, 10, 12, 15).

With this object, we chose to evaluate the electronic perturbation in the Magnus frame, which has the property to give for every term of the development a unit operator. As a matter of fact, writing the evolution operator $T(t)$ under the form:

$$T(t) = \exp \left( -i \frac{H_0 t}{\hbar} \right) U(t)$$

where:

$$U(t) = \exp \left[ -i \frac{\mathcal{J}(t)}{\hbar} \right],$$

Magnus showed (16) that the equation:

$$i \frac{\partial}{\partial t} \bar{U}(t) = \bar{V}(t) U(t)$$

where

$$\bar{V}(t) = \exp \left( i \frac{H_0 t}{\hbar} \right) V(t) \exp \left( -i \frac{H_0 t}{\hbar} \right)$$

(with, as $V(t)$, the electronic perturbator potential), is equivalent to the equation:

$$\frac{d\bar{A}(t)}{dt} = A(t) + \frac{1}{\hbar} \left[ A(t), \mathcal{J}(t) \right] + \sum_{n=1}^{\infty} \frac{(-1)^n}{2n!} B_n \left[ \ldots \left[ A(t), \mathcal{J}(t) \right], \mathcal{J}(t) \right] \ldots$$

where

$$A(t) = \frac{\bar{V}(t)}{\hbar},$$

($B_n$ : Bernoulli numbers).
One has, for \( J(t) \):

\[
J(t) = \frac{1}{2} \int_{0}^{t} A(t_1) \, dt_1
\]

(strong or weak collisions)

\[
J(t) = \frac{1}{2} \int_{0}^{t} \left[ A(t_2) \, A(t_1) \right] \, dt_2 \, dt_1
\]

(chronologic effect)

We did a systematic computation of the matrix elements of the operator \( J(t) \), for every alkali, for strong or weak electronic collisions.

Then, the impact approximation leads to the thermic average:

\[
J_e(t) = \frac{1}{2} \int_{0}^{t} \left[ A(t_2) \, A(t_1) \right] \, dt_2 \, dt_1
\]

(where we take for \( f(v) \) a maxwellian velocities distribution).

The width and the distance between peaks of the experimental profile lead, for the \( N_e \) values which are to be considered, to the impact limit:

At last, the total theoretical profile (computed by using the formula \( \text{[1]}, \text{[2]}, \text{[3]} \) giving the best agreement with the experimental profile is obtained for \( (17) \):

\[
|E| = 150 \, \text{kV cm}^{-1} \text{ and } N_e = 10^{17} \, \text{cm}^{-3}, \text{ values which are very near to those obtained by the latter study (15).}
\]

CONCLUSIONS

The Magnus profiles corrected with dynamic ion broadening have a greater width than the corrected Griem profiles (from 50 to 80%), but the widths of all the computed profiles are less important than the experimental widths. According to us, the main cause of this difference is the rapid evolution in time of the sheath geometry, which cer-
tainly produces during the life of each micro-plasma, a rapid evolution of $E$. Experimental profiles are the result of an integration, in space and time, of profiles which correspond to several numerical values of the parameters of A.E., when the computed profiles correspond to the average values of these parameters.

However, one can assert that the "anodic plasma" is cold ($T_e \approx 5200$ K), with a strong electronic density ($N_e \approx 10^{17}$ cm$^{-3}$), highly correlated, and perturbed by a polarized electric field of the order of 160 kV/cm.

Furthermore, one can note that the local thermodynamic equilibrium (L.T.E.) is bounded to the electrolytic bath composition. As a matter of fact, for an equimolecular mixture of LiCl and KCl, as here, since K is ten times as ionisable as Li, the electronic density is great enough to prevent the runaway of electrons (since the critical field is proportional to $N_e$, $E$ is only twice greater than $E_c$); but, if one uses a pure LiCl bath and the same voltage as before between the electrodes, $E$ will be twenty times as great as $E_c$, and the number of neutral atoms (practically the same as in the precedent case) will not be sufficient to prevent the electrons runaway; then, there will not be L.T.E. This is experimentally observed, since the anode is quickly vaporized when A.E. is obtained in an electrolytic bath of pure LiCl (18).
REFERENCES

1. P. Mergault and J. C. Valognes, Communication at the 16th meeting of the C.I.T.C.E., Budapest (1966).
2. D. Leteinturier, J. C. Valognes and P. Mergault, Electrochim. Acta 18, 905 (1973).
3. J. C. Valognes and P. Mergault, J. Phys. 34, 99 (1973).
4. C. Guilpin and J. Garbarz-Olivier, J. Chim. Phys. 75, 723 (1978).
5. P. Mergault, J. C. Valognes and C. Guilpin, C. R. Hebd. Seanc. Acad. Sci. Paris 273 C, 26 (1971).
6. P. Mergault, J. C. Valognes, J. Garbarz-Olivier and C. Guilpin, C. R. Hebd. Seanc. Acad. Sci. Paris 274 C, 241 (1972).
7. H. R. Griem, Plasma Spectroscopy, McGraw-Hill, New York (1964).
8. H. R. Griem, Spectral line broadening by Plasmas, Academic Press, New York (1974).
9. T. Biaz, J. C. Valognes and P. Mergault, J. Quant. Spect. Radiat. Transfer 14, 27 (1974).
10. J. C. Valognes and P. Mergault, J. Phys. 38, 905 (1977).
11. J. C. Valognes, J. Boukhicha, T. Biaz and P. Mergault, Rev. Int. Htes. Temp. Refract. 11, 73 (1973).
12. J. C. Valognes and P. Mergault, J. Quant. Spect. Radiat. Transfer 25, 471 (1981).
13. A. J. Barnard, J. Cooper and E. W. Smith, J. Quant. Spect. Radiat. Transfer 14, 1025 (1974).
14. J. P. Skarofsky, T. W. Johnston, M. P. Bachynski, The Particle Kinetics of Plasmas, Addison-Wesley, Reading Mass. (1966).
15. J. P. Bardet and J. C. Valognes, J. Phys. 44, 797 (1983).
16. W. Magnus, Comm. Pure Appl. Math. 7, 649 (1954).
17. J. P. Bardet and J. C. Valognes, J. Phys. 47, 1203 (1986).
18. J. C. Valognes, J. P. Bardet and P. Mergault, Spectrochim. Acta 42 B, 445 (1987).
Fig. 1—Experimental profile of the semi-degenerate 4f4d4p → 2p Li(I) line (no perturbed frequency: 4602.9 Å).

Fig. 2—Comparison between the typical experimental profile and the best theoretical profiles: 1 : Experimental profile; 2 : Corrected-Griem theoretical profile (\( \mathbf{E} = 160 \text{ kV/cm} \), \( N_e = 1.2 \times 10^{17} \text{ cm}^{-3} \)); 3 : Corrected-Magnus theoretical profile (\( \mathbf{E} = 150 \text{ kV/cm} \), \( N_e = 10^{17} \text{ cm}^{-3} \)).