The electrical charge of jet drops: a method of determining the mean sampling depth of bubbling

Bernard Dulieu *, Joan Aymami b, Gilbert Hamaide *

* Thermodynamique des milieux ioniques et biologiques, Laboratoire de Biorhéologie et Hydrodynamique physicochimique, LA CNRS n° 343, Université Paris-VII, Tour 33-43, E 2, 2, place Jussieu, 75251 Paris Cedex 05.

b Laboratoire de Physique des décharges, ER CNRS n° 114, École Supérieure d'Électricité, Plateau du Moulon, 91190 Gif-sur-Yvette.

Received 2/6/83, in revised form 26/10/83, accepted 10/11/83.

ABSTRACT

The electrical charge of jet drops ejected by bubbles bursting at the surface of aqueous dilute salt solutions is used to test Maclntyre’s microtome hypothesis. If Q is the charge ejected by bubbles of radius R bursting in solution of concentration C, then \( Q/(R^2 \sqrt{C}) \) must be a function of \( R \sqrt{C} \) alone. This function when plotted in a convenient form must give, for the case of uniform sampling, a straight line whose slope is the sampling depth. Data from Iribarne and Mason and from the present authors agree with this prediction. Collection of a well-defined set of drops constitutes the main experimental difficulty. The effect of diffusion of ions during collapse is estimated. The conclusion is reached that the microtome model is compatible with observations, the mean sampling depth being lower than \( 2 \times 10^{-3} \) times the bubble radius.


RÉSUMÉ

La charge électrique des gouttes de jet : un moyen pour déterminer l'épaisseur de la couche extraite par l'éclatement de bulles.

On utilise la charge électrique des gouttes de jet produites par l'éclatement de bulles à la surface de solutions aqueuses diluées de sel pour tester l'hypothèse du microtome de MacIntyre.

Si Q est la charge éjectée par des bulles de rayon R éclatant dans une solution de concentration C, le rapport \( Q/(R^2 \sqrt{C}) \) doit être une fonction de \( R \sqrt{C} \) seul. Cette fonction, sous une forme adéquate, doit, dans le cas d'un prélèvement d'épaisseur constante, être une droite dont la pente est la profondeur de prélèvement.

Les résultats d'Iribarne et Mason et ceux des présents auteurs confirment cette prédiction.

La collecte d'un ensemble bien défini de gouttes de jet constitue la principale difficulté expérimentale.

L'effet de la diffusion des ions pendant l'éclatement est estimé.

La conclusion est que le modèle du microtome est compatible avec les observations. La profondeur moyenne de prélèvement étant plus petite que \( 2 \times 10^{-3} \) fois le rayon de la bulle.


INTRODUCTION

Partly due to the overwhelming importance of bubbling as a source for sea-derived aerosol, the phenomenology of bubble bursting is now fairly well known (Blanchard, 1963; Blanchard, Syzdek, 1975). Nevertheless, certain aspects of the bursting of a single bubble at the air-water interface are still questionable. An example is the microtome effect described by MacIntyre (MacIntyre, 1968): the ability of jet-drops to skim a very thin layer of the bubble interior surface.
In 1967 Iribarne and Mason published a set of values for the electrical charge ejected by bubbles of definite radius bursting at the surface of diluted aqueous solutions of salts. In the same paper they showed that negative charges could be understood as the result of hydrodynamical skimming of the electrical diffuse layer which initially covers the bubble cavity. MacIntyre himself noticed that this was similar to his own model (MacIntyre, 1968; MacIntyre, 1972).

The present paper seeks to reexplore this path of investigation. We first give a short account of the method employed.

OUTLINE OF THE METHOD

The sampling depth

Figure 1 represents a schematic sketch of three successive stages of bubble collapse. Owing to the basic principles of hydrodynamic description, water which will ultimately form jet drops comes from a region lying between the original bubble surface and an unknown surface (Σ). The MacIntyre onion-like model supposes that for each jet drop, water comes from a concentric layer, which extends over the entire bubble interior. Let R be the bubble radius and an the sampling depth for n jet drops (n = 1 top jet drop, 2, ... 6). Then, combining volume conservation with the classical estimation that the jet drop radius is one tenth of the bubble radius, we obtain the estimation:

\[ a_n \sim 2 \cdot 10^{-3} R. \]  

Electrical charge of the sampled water

The relevant scale for charge variation with depth, near the gas-water interface, is the Debye length \( \delta_e \):

\[ \delta_e = \sqrt{\frac{\varepsilon k T}{2 e P_e}}, \]  

where \( \varepsilon, k, T, e, P_e \) are respectively: permittivity, Boltzmann constant, temperature, elementary charge and electrical volumic charge.

Let \( Q_n \) be the charge carried by the whole \( n \) first drops. It is shown in the Appendix that the plot of the natural logarithm of:

\[ K = \frac{32 \pi R^2 d_e \rho_e}{Q_n}, \]  

against:

\[ \frac{R}{d_e}, \]  

must give a straight line, whose slope \( \delta_e \) is just the non-dimensional value for \( a_n \), i.e.

\[ \delta_e = \frac{a_n}{R}. \]  

Experimental procedure

Basically the method outlined involves measurement of the sampling depth in term of Debye length. For this, small bubbles and large Debye length are required. Small bubbles of well-defined sizes were produced using the vibrating capillary method (MacIntyre, 1967).

Largest Debye lengths correspond to very low ionic concentrations. Solutions were prepared from twice distilled water which was degassed and stored under nitrogen pressure. This water then flows through an ion exchanging column (Millipore Milli Q ®), giving water whose nominal conductivity was 18 Megohms.cm at 20°C. Solutions were then prepared and immediately employed under nitrogen pressure.

The methods used to measure bubbles, to catch jet drops and to measure the charges are described in a previous paper (Aymami et al., 1982).

Since this paper was written, we have constructed a new apparatus which permits measurements at low temperature. We also modified the drop-catching system. In the new system, the metallic filter is positioned just above the bursting bubbles. Its elevation over the water surface can be changed (from 0 to about 10 cm) when the entire system is operating.

Collection of the aerosol is facilitated by the suction of nitrogen through the filter, and this suction can also be adjusted.

This permits observation of the charge carried by the different jet drops, or at least by the first two or three and the last three or four.

RESULTS

Room temperature

Jump heights of the various jet drops depend on the bubble size. To illustrate this precisely, Table 1 shows such heights which we measured for three sizes.

It is, in our opinion, quite impossible always to catch, for different bubble sizes, the same set of jet drops, even when rather large bubbles are involved.

Working with a given bubble size and varying the concentration thus probably constitutes the safest way of obtaining a significant set of results. Such a set was
obtained with values of R in a narrow range around 60 µ, the NaCl concentration varying from 6.2 \times 10^{-7} to 7.8 \times 10^{-5} mol/l. Corresponding points are plotted on Figure 2.

Examination of the charge values for different concentrations shows that for R/d_e values greater than about 1000, variances are very great (a value of Q is the mean of 25 successive measures, see Aymami et al., 1982 for details). This corresponds to measuring very little charges. It is equally well known that for great values of R/d_e, the charge becomes positive and the model needs not to be correct in that case. So, taking into account values of R/d_e lower than 1000, we obtain for best fit:

\[ \text{Ln}(K) = 4.47 \times 10^{-3} \frac{R}{d_e} + 3.387, \]  
\[ (6) \]

with a correlation coefficient of 0.9910.

This excellent value for the correlation coefficient proves that the concentration C plays a very small role, if any, apart from that which is explicitly taken into account.

The whole set of measurements by Iribarne and Mason (Iribarne, Mason, 1967) for NaCl at temperature 20-23°C gives for best linear fit:

\[ 4.25 \times 10^{-3} \frac{R}{d_e} + 3.530, \]  
\[ (7) \]

with a correlation coefficient of 0.9303.

This common value for the slope corresponds probably to the capture of four or five jet drops.

### Lower temperature

Results for 2-3°C, from Iribarne and Mason, for NaCl, are best fitted with:

\[ 2.67 \times 10^{-3} \frac{R}{d_e} + 3.35, \]  
\[ (8) \]

with the excellent coefficient 0.995. Such a great variation for the slope when temperature varies was somewhat surprising; to confirm this point, therefore, measurements were made at a temperature of 4-5°C. The results are plotted on Figure 3. The best fit, taking all these values into consideration, is:

\[ 2.73 \times 10^{-3} \frac{R}{d_e} + 3.78 \]  
\[ (9) \]

with coefficient (0.953).

### Table 1

<table>
<thead>
<tr>
<th>R (µm)</th>
<th>H_1 (mm)</th>
<th>H_2 (mm)</th>
<th>H_3 (mm)</th>
<th>H_4 (mm)</th>
<th>H_5 (mm)</th>
<th>H_6 (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>105</td>
<td>18</td>
<td>11</td>
<td>10</td>
<td>7</td>
<td>6</td>
<td>4</td>
</tr>
<tr>
<td>133</td>
<td>28</td>
<td>14</td>
<td>12</td>
<td>9</td>
<td>7</td>
<td>7</td>
</tr>
<tr>
<td>171</td>
<td>31</td>
<td>17</td>
<td>11</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

This is in close agreement with the Iribarne and Mason results. But it should be noted that this set of values was obtained with different radius. Selecting measures for constant R and same catching adjustment, only 5 points are kept, giving for the slope a higher value 3.66, and 0.996 for the correlation coefficient.

To determine the value of the charges carried by successive jet drops, filter height or suction, or both, were varied. But by this method it was not possible to obtain precise results. Nevertheless, we qualitatively observed that, at room temperature, all the drops are negative except perhaps the last ones, which can be slightly positive, the absolute charge being greater for the top drops. On the other hand, for a lower temperature around 3°C, the last drops carry an important positive charge, the whole being negative.

Taking all these facts into consideration, our opinion is that the slopes around 2.7 \times 10^{-3} at low temperature correspond both to the capture of less drops and to a real temperature effect.
IONS ARE NOT FROZEN

Collapse of a bubble in its first stage, up to jet formation, is slow compared with the jet emergence (see Fig. 1, MacIntyre, 1972). During this first stage, the area of a material slice of water at the free surface is reduced (this is the main source of energy for collapse).

The electrical diffuse layer is then not in equilibrium; the net ions flux tends to restore this equilibrium. For this, the net electrical charge must be reduced. In the Appendix, we provide an estimation for the duration \( t_e \) of this first stage.

Within this time, ions may move on a length \( l \) of order:

\[
l \sim \sqrt{D t_e},
\]

where \( D \) is a coefficient of diffusion for ions.

This length has to be compared with the "true" sampling depth \( \delta R \).

With \( D \sim 10^{-5} \text{ cm}^2/\text{sec.} \), we get for \( R = 60 \mu \text{m} \):

\[
l/R \sim 2.15 \times 10^{-3},
\]

i.e. a significative fraction of the observed slope. We also note that, as \( D \) is roughly proportional to the inverse of the viscosity of water, this figure is significantly lowered when the temperature is lowered from 20°C to 2-3°C, becoming of the order of \( 1.7 \times 10^{-3} \).

Then, one may suppose that the observed slope \( \delta_{ob} \) consists of the "true" sampling depth \( \delta_t \) plus a "diffusing depth" \( \delta_d \) which are then both of about the same magnitude.

To verify this point, we effected control measures using KCl and LiCl. This was done with \( R = 60 \mu \text{m} \) varying \( C \), with the same catching conditions as for NaCl.

Results are in Table 2.

Solving the equations:

\[
\delta_{ob}^{KCI} = \delta_t^{KCI} + \delta_{0}^{KCI},
\]

\[
\delta_{ob}^{LiCl} = \delta_t^{LiCl} + \delta_{0}^{LiCl},
\]

together with the additional relation suggested by (10):

\[
\frac{\delta_{0}^{KCI}}{\delta_{0}^{LiCl}} = \frac{D_{KCI}}{D_{LiCl}} = 1.21,
\]

one finds \( \delta_t = 1.8 \times 10^{-3}, \delta_{0}^{KCI} = 2.8 \times 10^{-3}, \delta_{0}^{LiCl} = 2.3 \times 10^{-3} \).

This value for \( \delta_t \) is close to the \( a \) priori estimation of \( a_0 \) given in a preceding section ("The sampling depth").

<table>
<thead>
<tr>
<th>Salt</th>
<th>Slope</th>
<th>Correlation coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>KCl</td>
<td>4.55 \times 10^{-3}</td>
<td>0.998</td>
</tr>
<tr>
<td>NaCl</td>
<td>4.47 \times 10^{-3}</td>
<td>0.991</td>
</tr>
<tr>
<td>LiCl</td>
<td>4.07 \times 10^{-3}</td>
<td>0.997</td>
</tr>
</tbody>
</table>

CONCLUSION

Quantitative analysis of the charge carried by jet drops, for given values of bubble radius and solution concentration, is compatible with the microtome hypothesis.

The main experimental difficulty resides in catching always the same set of jet drops. Ions are probably not to be considered as entirely frozen during the collapse time.

It may, nevertheless, be affirmed that the water contained in the jet drops comes from a surface layer whose depth is less than about \( 2 \times 10^{-3} \) times the bubble radius.

Acknowledgements

This work was partly supported by the CNRS (ATP Océanographie Chimique).

Our thanks are due to Mr. Cuesta, Mr. Lambert and J. F. Mourey for technical assistance.

The authors also wish to express their acknowledgements to Dr. R. Chesleet for his much appreciated encouragements.

Appendix

Bubble collapse on dimensional ground

Due to axial symmetry (\( \Sigma \); see Fig. 1) may be characterized through \( \theta \) and \( a(\theta) \). We shall only consider bubbles of radius less than 0.25 mm. For such small bubbles, collapse is mainly a transformation of surface free energy into kinetic energy. Then we expect the basic significant physical parameters to be the radius \( R \), the surface tension \( \sigma \) and the water density \( \rho \). Then, on dimensional ground, we write:

\[
t_e = \alpha \sqrt{\frac{\rho R^3}{\sigma}},
\]

\[
a(\theta) = \delta(\theta)R,
\]

\[
A = \gamma 4 \pi R^2,
\]

where \( t_e \) is the collapse duration, \( a \) the sampling depth and \( A \) the area initially covered by \( \Sigma \).

Within the experimental range considered for \( R \), we suppose that the unknown \( \delta \), \( \alpha \) and \( \gamma \) are pure numerical constants, except for \( \delta \), which may vary with \( \theta \).

To our knowledge, the only precise value for the collapse duration of a sufficiently small bubble is to be found in MacIntyre (1972).

The insertion of this value in (A 1) gives:

\[
\alpha \sim 0.3.
\]

Electrical charge

Following Iribarne and Mason, we use the Gouy-Chapman description for the electrical properties of the electrical diffuse layer.
Introducing the Debye length:
\[ d_e = \sqrt{\frac{\varepsilon k T}{2 \pi e \rho_\infty}} \tag{A 5} \]
and the adimensional potential
\[ y = \frac{e \psi}{k T} \tag{A 6} \]
where \( \psi \) is the electrical potential, we get for \( y \) the implicit expression:
\[ \tanh \left( \frac{y}{4} \right) = \tanh \left( \frac{y_0}{4} e^{-r/d_e} \right) \tag{A 7} \]
where \( r \) is the distance from the interface and
\[ y_0 = \lim_{r \to d_e} y \left( \frac{r}{d_e} \right) \tag{A 8} \]
Then the integration up to \( r = a \) gives for the net charge for a layer of unit area and depth \( a \), the expression:
\[ \sigma = 4 \rho_\infty d_e \sinh \left( \frac{a}{d_e} \right) \tag{A 9} \]
So, \( \sigma \) may depend on \( \theta \) through \( a/d_e \) and, integrating over the whole area \( A \), the water to be ejected contains initially a charge \( Q_0 \) which reads:
\[ Q_0 = R^2 \rho_\infty d_e f \left( \frac{R \delta}{d_e} \right) \tag{A 10} \]
During collapse, the electrical content of the ejected water may change and we may write:
\[ Q = \tau Q_0 \tag{A 11} \]
where \( Q \) is the measured charge.
Supposing further—as the simplest model to try—that the film thickness is uniform, \( i.e. \) that \( a \) is not \( \theta \) dependent, we get for \( Q \) the explicit form:
\[ Q = \tau \frac{16 \pi R^2 \gamma d_e \rho_\infty}{\sinh \left( R \delta/d_e + \alpha_0 \right)} \tag{A 12} \]
where:
\[ e^{-\alpha_0} = \left| \tanh \left( \frac{y_0}{4} \right) \right| \tag{A 13} \]
is an electrical parameter characteristic of the gas water interface.

Let \( K \) be given by:
\[ K = \frac{32 \pi R^2 \gamma d_e \rho_\infty}{Q} \tag{A 14} \]
Then it follows from (A 12) that:
\[ R \delta + \alpha_0 = \ln \left( K + \sqrt{K^2 + 4} \right) \tag{A 15} \]
and, as \( K \gg 4 \), this is mainly:
\[ \alpha_0 + \frac{R}{d_e} \delta = \ln \left( \frac{R}{d_e} K \right) \tag{A 16} \]
Choosing the elementary charge \( e \), the mole/litre, and the micrometre as unit for \( Q \), \( C \) and \( R \) respectively (A 16) for room temperature reads:
\[ \ln \left( 1.844 \times 10^7 \frac{R^2}{C} \right) = \delta \frac{3.28 \times 10^3 R \sqrt{C + \alpha_0} - \ln(yt)}{\ln(yt)} \tag{A 17} \]
So, if the above model is correct, plots of (A 17) must give a straight line whose slope is just \( \delta \) and whose ordinate for \( R/d_e = 0 \) is \( \alpha_0 - \ln(yt) \).
For instance, it is easy to show that if \( a \) varies with \( \theta \), then the graph must be concave.

REFERENCES