

APPLICATION OF POPULATION BALANCE MODELS TO THE STUDY OF NUCLEATION
AND GROWTH OF BUBBLES PRODUCED AT GAS EVOLVING ELECTRODES

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DECLARATION

I declare that this dissertation is my own, unaided work, except where specific acknowledgements are made. It is being submitted for the degree of Master of Science in Engineering in the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination in any other University.

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11 day of January, 1984.

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Abstract

The rate of mass transfer at gas evolving electrodes has been shown to be a strong function of the so-called bubble break off diameter of the gas bubbles leaving the electrode surface. This dissertation shows how the population balance can be applied to the formation of gas bubbles at gas evolving electrodes. This analysis provides a means of predicting the bubble break off diameter. Experiments were also performed to measure the bubble break off diameter as well as other parameters, such as the rate of bubble growth, used in the population balance models.

The effect of viscosity, electrolyte flowrate and current on the bubble break off diameter is also investigated. The flowrate and current have little effect on the bubble break off diameters, while the break off diameters show a decrease in size with increasing viscosity. The bubble break off diameters predicted by the population balance model and those measured were significantly larger than those reported in the literature.

Contents

	Page
Declaration	ii
Acknowledgements	iii
Abstract	iv
1. Introduction	1
1.1. Mass Transfer at Gas Evolving Electrodes	3
1.1.1. Mass Transfer Correlations of Stephan and Vogt (1979)	6
1.1.2. The Hydrodynamic Effect on Mass Transfer	8
1.2. Rate of Bubble Growth	11
1.2.1. The Rate Equation of Scriven (1959)	11
1.2.2. The Rate Equation of Darby and Haque (1973)	13
1.3. Predicting the Bubble Break Off Diameter	16
1.4. The Effect of Viscosity on the Bubble Break Off Diameter	18
1.5. Scope of this Research	19

	Page
2. Theory	20
3. Experimental	28
3.1. Description of the Apparatus	28
3.2. Measurement of $f(l)dl$ and N	30
3.3. Measurement of $g(l)dl$	32
3.4. Changing the Viscosity and Electrolyte Composition	32
4. Results	34
4.1. Typical Results	35
4.2. The Effect of using Glycerine or Magnesium Sulphate to Increase the Viscosity of the Electrolyte	39
4.3. Effect of Flowrate and Current	42
4.4. The Effect of Electroplating	44
4.5. The Number of Nucleation Sites per Unit Area	47
5. Analysis	48
6. Discussion and Conclusions	58
7. References	61

	Page
Appendix 1. Expressions for the Rate of Bubble Growth	66
1. Darby and Haque (1973)	66
2. Scriven (1959)	71
Appendix 2. Density Functions	79
Appendix 3. Measuring Bubble Diameters on the Electrode Surface	82
Appendix 4. Measuring Viscosity	96
1. The Ostwalds Viscometer	96
1.1. Calibration of the Ostwalds Viscometer	98
2. Measuring the Electrolyte Viscosity	99
Appendix 5. Results	101
Appendix 6. Measuring the Current Density	147
Appendix 7. Solving the Population Balance	149

1. Introduction

The rate at which an electrochemical reaction can occur will depend on the rate at which a reagent can reach the electrode or a product can be removed from it. If the rate at which a species A is brought to the electrode, is limiting, then the rate of production of this species A is given by

$$R_A = -D_A \frac{dC_A}{dx} \Big|_{x=0} \quad (1)$$

where R_A = rate of production of species A
 D_A = molecular diffusivity of species A
 C_A = concentration of species A at position x

By referring to figure 1, equation (1) can be written as

$$R_A = \frac{D_A}{\delta} (C_{A0} - C_{Ae}) \quad (2)$$

where C_{Ae} = concentration of species A at the electrode surface ($x = 0$)
 C_{A0} = bulk concentration of species A
 δ = thickness of the diffusion layer (see figure 1)

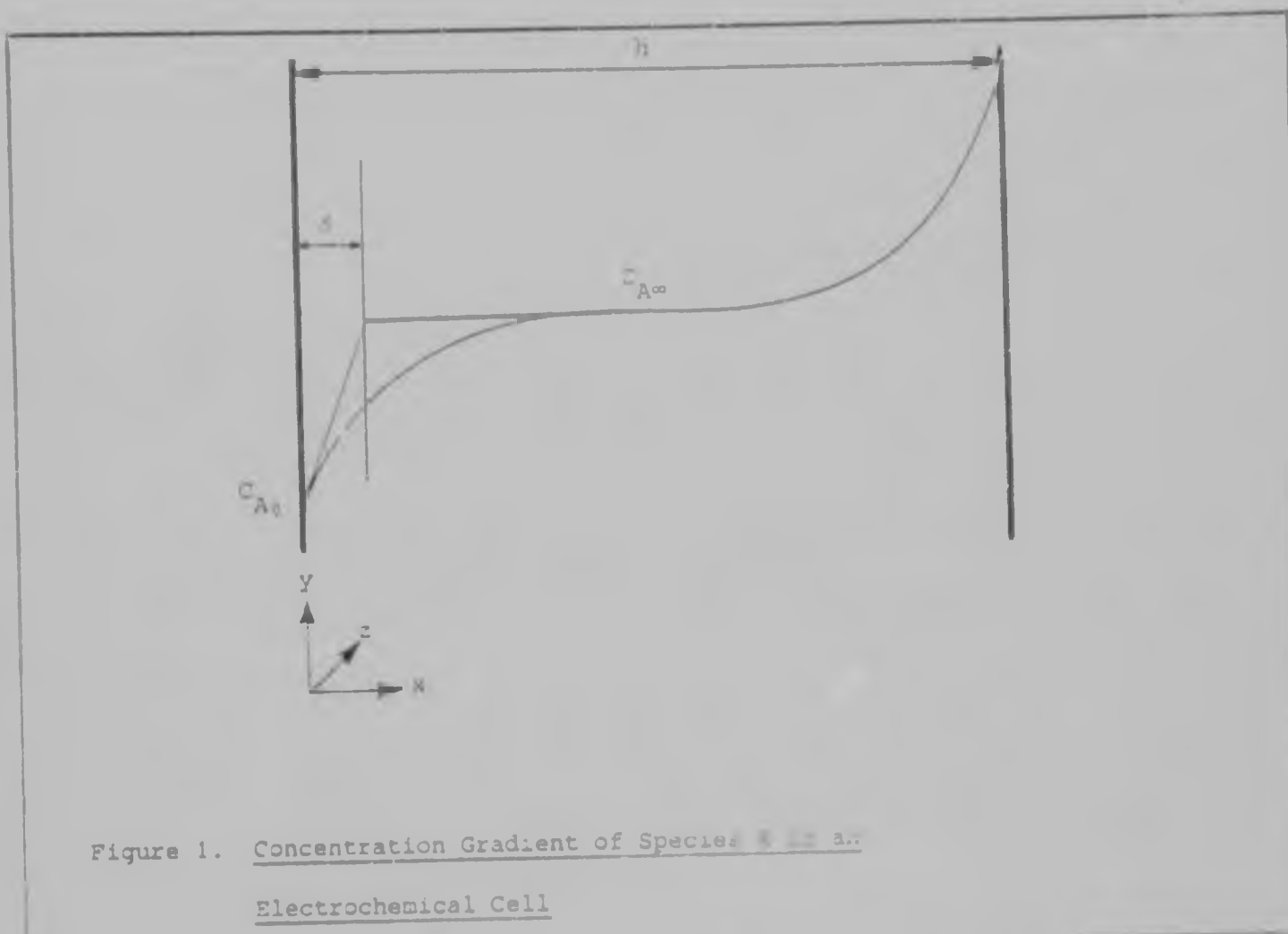


Figure 1. Concentration Gradient of Species A in an Electrochemical Cell

Defining the local mass transfer coefficient as

$$(k_L)_L = \frac{R_1}{C_{A1} - C_{A0}} \quad (3)$$

or $(k_L)_L = \frac{D_A}{L} \quad (4)$

The concentration gradient can be normalised by defining

$$C_A^* = \frac{C_A - C_{A0}}{C_{A\infty} - C_{A0}} \quad (5)$$

and $x^* = \frac{x}{h} \quad (6)$

$$\begin{aligned} \frac{dC_A^*}{dx^*} \Big|_{x^*=0} &= \frac{h}{C_{A\infty} - C_{A0}} \frac{dC_A}{dx} \Big|_{x=0} \\ &= \frac{h}{\delta} \quad (\text{by equations (1) and (2)}) \end{aligned}$$

from (4)

$$\frac{dC_A^*}{dx^*} \Big|_{x^*=0} = \frac{(k_L)_L h}{D_A} \quad (7)$$

The average mass transfer coefficient is thus

$$\bar{k}_L = \frac{1}{L} \int_0^L (k_L)_L dz \quad (8)$$

where L = length of the electrode in the z direction

The Sherwood Number is defined as

$$\text{Sh} = \frac{\bar{k}_L h}{D_A} \quad \text{and substituting for } \bar{k}_L \text{ gives}$$

$$\text{Sh} = \frac{1}{L} \int_0^L \frac{dC_A^*}{dx^*} \Big|_{x^*=0} dz \quad (9)$$

The Sherwood Number is the dimensionless surface concentration gradient over the mass transfer surface.

The rate of mass transfer is clearly effected by the size of δ . Movement of the electrolyte in the neighbourhood of the electrode can effect the size of δ . The movement of electrolyte can be brought

about in a number of ways:

- (1) Natural convection generated by density variations which may occur due to concentration or temperature changes.
- (2) Forced convection caused by pumping, mechanical agitation or air sparging.
- (3) Circulation of electrolyte caused by gases generated at the counter electrode.
- (4) Agitation of the layer of fluid near the surface of the electrode by the evolution of electrolytically produced gas.

This last means of effecting the mass transfer can considerably enhance the mass transfer because on detachment of the bubble, electrolyte will flow back into the region very rapidly, and in this way δ is reduced considerably.

In many electrochemical processes the production of gas at an electrode is important. Several examples are the electrolytic manufacture of gases such as chlorine, hydrogen and oxygen; electrowinning, refining and plating of metals which are associated with electrolytic hydrogen production. Vogt (1978) points out that mass transfer at gas evolving electrodes is governed by two phenomena acting simultaneously:

- (1) A macroconvective mass transfer caused by the liquid flow parallel to the electrode surface. This influences mass transfer by velocity distributions near the wall. This process is not directly related to the actual gas evolution.
- (2) A microconvective mass transfer caused by the liquid in the vicinity of a bubble attached to the electrode being pushed away by the bubble as it grows. This causes a disturbance in the diffusion layer and an increase in the mass transfer rate.

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The macroconvection only has an effect at very low current densities or in turbulent flow conditions. This means that under most operating conditions the microconvective work is dominant.

1.1 Mass Transfer at Gas Evolving Electrodes

Mass transfer processes at gas evolving electrodes are in many respects analogous to processes in nucleate boiling heat transfer. Bubbles grow from small nucleation sites which are tiny pits in the electrode surface. The gas bubbles increase in size due to mass transfer from the liquid phase either by evaporation (heat transfer) or by desorption of dissolved gas (mass transfer). When the bubbles become large enough for the buoyancy, pressure and inertia forces to overcome the adhesion forces, the bubble leaves the surface. While the bubbles are growing a convective flow is induced in the surrounding liquid. After the bubble detaches from the surface, liquid flows back to the former bubble centre.

The similarity between the heat and mass transfer processes has led researchers such as Vogt (1971) and Plesch et al. (1973) to develop correlations for mass transfer at gas evolving electrodes based on existing correlations for heat transfer in nucleate boiling. The fact that an electrolyte film is present on the electrode surface has led researchers such as Plesch et al. (1973) and Plesch et al. (1972, 1973) to modify the existing correlations to account for the presence of the electrolyte film.

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The similarity between the heat and mass transfer processes has led researchers such as Vogt (1978) and Stephan et al (1979) to develop correlations for mass transfer at gas evolving electrodes based on existing correlations for heat transfer (see section 1.1.1). The fact that an electrolyte flow is induced by ascending bubbles has led researchers such as Janssen et al (1970, 1979) and Fouad et al (1972, 1973) to develop hydrodynamic models based on experimental and

theoretical expressions. (see section 1.1.2)

1.1.1 Mass Transfer Correlations of Stephan and Vogt (1979)

Stephan et al (1979) made use of existing heat transfer correlations in order to establish a model for correlating mass transfer at gas evolving electrodes. The assumptions built into the model are:

- (1) The convection flow induced by the rapidly growing gas bubbles is decisive for mass transfer. The flow in the wake of the detached bubble is unimportant and has negligible effect on the mass transfer.
- (2) A certain small area may be attributed to each bubble. This microarea is part of the total surface, where a single bubble induces convection flow. The area exists from the time the bubble begins to grow till it detaches from the surface, and is regarded as constant in size. It is not influenced by other bubbles.
- (3) Due to the small distances and thin boundary layer, the flow along this microarea is assumed laminar.
- (4) The bubbles are assumed to be spherical or hemispherical.
- (5) The convection flow near the gas liquid interface is assumed to behave like plug flow, whereas the flow some distance away behaves like boundary layer flow.

The correlation finally put forward by Stephan et al (1979) is

$$Sh = 0.93 Re^{0.7} Sc^{1/3} \quad (10)$$

- where
- Sh = Sherwood number = $\frac{k_L d}{D}$
 - Re = Reynolds number = $\frac{Gd}{\mu}$
 - Sc = Schmidt number = $\frac{\mu}{D}$
 - k_L = mass transfer coefficient
 - D = molecular diffusivity
 - G = volumetric flow rate of the gas per unit area of electrode
 - d = bubble break off diameter
 - ρ = liquid density
 - μ = liquid viscosity

In order to test their correlation, Stephan et al (1979) applied equation (10) to a large volume of data presented in the literature. The errors incurred were fairly large, but no larger than errors incurred in using well established correlations for nucleate boiling which are successfully used in engineering design.

The data used by Stephan et al (1979) was obtained by using electrolytes of similar concentration. The concentrations ranged from 1 mole/l H₂SO₄ (with small amounts of salts present) to 2 mole/l N_aOH (with small amounts of salt). Hence the effects of electrolyte density and viscosity (see section 1.4) were not significantly tested.

1.1.2 The hydrodynamic effect on mass transfer

The evolution of gas bubbles at vertical gas evolving electrodes promotes mass transfer very well. At high rates of gas evolution, the rate of mass transfer is of the same order of magnitude as that obtained by intensive mechanical stirring (Fouad et al (1972)). The reason for this is the rising gas bubbles induce a flow of electrolyte near the electrode surface. This induced flow mixes the liquid in the bulk solution with the liquid in the Nernst diffusion layer, making the diffusion layer thinner. This means that the liquid in contact with the growing bubble has a higher concentration of dissolved gas than previously, and hence the mass transfer rate is higher. Janssen et al (1970) found that the thickness of the Nernst diffusion layer, δ , is dependent on the factors which determine the distance of the ascending bubbles from the surface, the number and size of the bubbles and their size distribution.

Fouad et al (1973) investigated the differences in the mass transfer coefficient obtained on vertical and horizontal electrodes. They observed that horizontal electrodes has higher mass transfer coefficients. This was ascribed to the build up of a hydrodynamic boundary layer and the Nernst diffusion layer whose thickness increases up the vertical electrode's height. This observation would support those of Fouad et al (1972) and Janssen et al (1970).

Janssen and Barendrecht (1979) developed a model for predicting i . This model is based on the correlation for mass transfer at an electrode:

$$Nu = \text{const} \cdot Sc^{1/2} \quad (11)$$

where $Nu = \text{Nusselt number} = \frac{k_L x}{D}$

$$Gr = \text{Grashof number} = g \frac{(c_L - c_G) x^3}{\nu^2}$$

$$Sc = \text{Schmidt number} = \frac{\nu}{D}$$

$k_L =$ mass transfer coefficient

$D =$ molecular diffusivity

$g =$ acceleration due to gravity

$c_L =$ liquid density

$c_G =$ gas density

$\nu =$ kinematic viscosity of the liquid = $\frac{\mu}{\rho_L}$

$\mu =$ dynamic viscosity of the liquid

$x =$ characteristic length

$$\text{where } Z = \frac{c_L}{k_L} = \frac{1}{\text{const}} \left(\frac{\rho_L \nu^2}{(c_L - c_G) g} \right)^{1/2} \quad (12)$$

For *free convection flow*, the buoyancy force per unit mass of the bubble resulting from the difference in densities of the gas and liquid is

$$\frac{(c_L - c_G) g}{c_L} = \frac{z c_L g}{(1 - z) c_L + c_G} \quad (13)$$

where $z =$ drag coefficient

$z =$ volumetric gas fraction on the bubble surface of the gas evolving electrode.

Also the volumetric flowrate per unit electrode area of eq. (3) is given by

$$Q = v_t \left\{ \frac{A}{1-\alpha} \right\} \tag{14}$$

where v_t = terminal velocity of a single bubble

$$\text{and } v_t = \frac{1}{12} g d^3 \frac{(\rho_l - \rho_g)}{\mu} \tag{15}$$

$$\eta = \frac{1}{4} \pi d^2 N z \tag{16}$$

where d = bubble break off diameter (diameter of the rising bubble)
 N = number of active sites per unit surface
 z = frequency of the bubble emission from an active site

Substituting (13), (14), (15) and (16) into (10) and assuming $C_g \ll C_l$

Janssen et al (1979) arrived at the equation

$$i = C \left(\frac{D}{2d N z} \right)^{2/3} \tag{17}$$

where C = constant evaluated from experiments.

Experiments showed that equation (17) described the mass transfer at gas evolving electrodes very well at low α where gas evolution was not significant.

1.2 Rate of Bubble Growth

Two rate equations for bubble growth are presented below. Both models are theoretically based and have been verified experimentally in the literature.

1.2.1 The rate equation of Scriven (1959)

Scriven (1959) arrived at an expression for the rate of bubble growth by writing a force, mass and energy balance to describe the situation, and then by making a number of simplifying assumptions to make it possible to arrive at a solution. Full details of his derivation are presented in Appendix 1. The solution he arrived at is

$$r = 2.8 \sqrt{Dt} \quad (18)$$

- where r = radius of the bubble
- D = mass diffusivity
- t = time
- ϵ = dimensionless growth constant

ϵ is defined by the equation

$$\frac{r}{L} = \frac{2.8 \sqrt{Dt}}{L} = 2.8 \sqrt{\frac{D}{L^2} t} = 2.8 \sqrt{\frac{D}{L^2} t} \exp(\beta^2 + \epsilon \beta^2) \int_0^{\infty} \exp(-x^2 - 2\epsilon \beta^2 x^2) dx$$

- where $\epsilon = 1 - \rho_g / \rho_l$
- ρ_g = density of the gas

$$\begin{aligned}
 \rho_L &= \text{density of the liquid} \\
 C_{\infty} &= \text{bulk concentration of the gas in the liquid} \\
 C_{\text{sat}} &= \text{concentration at saturation of the gas in the liquid} \\
 \text{or } r &= \sqrt{4Dx} \quad (19) \\
 \text{where } x &= \frac{4Dt}{\pi}
 \end{aligned}$$

In arriving at this solution, Scriven (1959) has assumed that the process is controlled by the mass transport of dissolved gas from the electrode surface to the bubble surface. In order to simplify his problem, Scriven (1959) made a number of assumptions which are valid for nucleate boiling, but whose validity needs to be verified under mass transfer control. An example of such assumptions is the neglecting of viscous, inertia and surface tension terms in the force balance, and the assumption that growing bubbles do not interfere with one another. (Full details of these assumptions are presented in Appendix II.)

Westerside et al (1961) and Glas et al (1964) measured bubble growth rates and confirmed the form of equation (19) to be correct. Westerside et al (1961) did however observe that two bubbles growing close together tended to compete for dissolved hydrogen, and hence their growth rates were smaller. Glas et al (1964) verified the assumption that the surface tension had negligible effect. They also found that the growth constant, K , was a function of current density, which is not entirely unexpected. They also observed an initial growth period before the bubbles grew according to Scriven's (1959) model. The reason Scriven (1959) does not predict this initial growth period is that one of his initial conditions in his solution was that at time

$t = 0$, the bubble radius was some small value r_0 . Glas et al (1964) observed that this initial growth was very rapid (about 2,000%) and varied from one electrode surface to another. The reason put forward is that, after polishing, the harder metals (such as nickel) produced smoother surfaces (fewer nucleation sites). This caused a high supersaturation of gas near the electrode, and so once the bubbles started to grow, their growth was rapid until the supersaturation was diminished.

1.2.2 The Rate Equation of Darby and Hague (1973)

Darby et al (1973) tried to elucidate the controlling rate process which limits the maximum rate at which bubbles are evolved at an electrode. They initially expected the rate of bubble growth to be analogous to that observed in nucleate boiling. If this were the case, the bubble radius would grow at a rate proportional to $t^{2/3}$. By observing the phase lag between the electrode current, which is proportional to gas generation, and the bubble growth rate, which corresponds to gas removal, they could deduce whether or not the mass transfer of hydrogen gas to the bubble is limiting (see Appendix 1).

Their experimental results showed that

This result was inconsistent with their initial expectations that the radius would be proportional to $t^{2/3}$. They also observed that

the mass transfer of hydrogen gas to the bubble was not the controlling rate process.

Applying Faraday's Law to the problem:

$$I(t) = zF \rho_m \frac{dV}{dt} \quad (21)$$

where V = volume of a bubble = $\frac{4}{3} \pi r^3$

t = time

ρ_m = molar density of the gas

F = Faraday's constant

$I(t)$ = instantaneous current which fluctuates with ϕ .

An average instantaneous current, \bar{I} , was used instead of $I(t)$ (see Appendix I), and integrating (21) gives

$$t = \left(\frac{z\bar{I}}{3zF\rho_m} \right)^{-1} \phi^{2/3} \quad (22)$$

which has the same form as (20). As confirmation to the validity of (22) the coefficients of (20) and (21) were equated, and \bar{I} was solved for. The value obtained for \bar{I} agreed with the measured value.

Darby et al (1971) then showed that the rate controlling step is a surface reaction: probably atomic hydrogen combining to form molecular hydrogen on the electrode surface.

The major difference between the two models presented in this section and section 1.2.1 is that the model of Darby et al (1971) holds for

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2.1. Investigating the Bubble Break Off Diameter

The bubble break off diameter, i.e. the diameter of the bubble when it leaves the surface, features very prominently in correlations for bubble break off diameter. In Janssen et al. (1979) the correlation of Stephan et al. (1979) is given as (10). The main transfer coefficient is proportional to the square root of the bubble break off diameter. Janssen et al. (1979), equation (11), shows that the main transfer coefficient is proportional to the square root of the bubble break off diameter. This is proportional to the square root of the bubble break off diameter.

It is noted that the correlation of Janssen et al. (1979) can be written as follows:

$$k = 0.01 \left(\frac{d_b}{\sqrt{g}} \right)^{0.5}$$

- d_b = bubble diameter
- ρ_l = liquid density
- ρ_g = gas density
- σ = surface tension
- g = acceleration due to gravity

Equation (11) is identical to the correlation of Janssen et al. (1979) approach to calculating bubble break off diameter. The correlation of Janssen et al. (1979) is based on the bubble break off diameter. Sides (1981) has shown that the electrical potential on an electrode surface varies significantly with position and time.

So when evaluating the mass transfer coefficient, the value of the bubble break off diameter used must either be obtained by experiment, or some average value obtained in the literature. Stephan et al (1979) recommend the values for the break off diameters of bubbles presented in table 1 to be used in calculations:

Table 1 Bubble Break Off Diameters recommended by Stephan et al (1979)

Gas	Electrolyte	Break off Diameter (μm)
Hydrogen	Alkaline	40
Oxygen	acidic	40
Oxygen	alkaline	50
Hydrogen	acidic	60
Others		30

1.4 The Effect of Viscosity on the Bubble Break Off Diameter

Ault et al (1975) investigated the operation of a zinc electrodeposition process. They found that by increasing the zinc sulphate to acid ratio in the electrolyte, the current efficiency increased until the zinc sulphate to acid ratio reached a certain value, and then the current efficiency decreased. They postulated that the drop in current efficiency was due to nodular growth and attendant short circuiting. The increase in nodular growth (dendritic growth) was believed to be due to the increased viscosity, and hence resistivity, of the electrolyte at a higher zinc sulphate to acid ratios. This postulate would seem to conflict with both equation (10) and equation (11), since both are independent of viscosity. In equation (11), the viscosity effect is cancelled since both the Reynolds and Schmidt numbers are raised to similar powers. The only way this conflict could be resolved is if the bubble break off diameters are affected by viscosity. Earlier work in the Department of Chemical Engineering at the University of the Witwatersrand by Herder et al (1981) has shown that the bubble break off diameter is affected by viscosity.

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1.5 Scope of this Research

When modelling the production of a particulate phase, such as in crystallisation, the growth and nucleation characteristics of a single particle can be incorporated into a population balance to produce an analysis and design procedure for large scale processes. The method of population balances is applied in this work to the electrolytic bubble growth on electrode surfaces and provides a means for predicting growth rates and nucleation rates of bubbles growing on the electrode surface.

To illustrate the above approach to the study of electrolytic gas evolution, the effect of viscosity on bubble break off diameter is investigated. Other parameters such as current density, electrolyte flowrate are also varied and their effect on the process is analysed.

2. Theory

In this section the population balance will be applied to electrolytic bubbles. To begin with, the following symbols must be defined:

- $f(l)dl$ = fraction of bubbles on the surface in the size range l to $l + dl$
 $g(l)dl$ = fraction of bubbles leaving the surface in the size range l to $l + dl$
 $u(l)$ = growth rate of bubble size l
 N = number of nucleation sites per unit area
 $\dot{\gamma}$ = number of bubbles nucleating per unit area per unit time.

It should be noted that at steady state the number of bubbles leaving the surface per unit area per unit time is also $\dot{\gamma}$. Also

$$\int_0^{\infty} f(l)dl = 1 \quad \text{and} \quad \int_0^{\infty} g(l)dl = 1$$

Now the population balance states:

$$\left[\text{Net rate of bubbles into size } l \text{ to } l + dl \text{ by convection} \right] = \left[\text{birth rate in size } l \text{ to } l + dl \right] - \left[\text{death rate in size } l \text{ to } l + dl \right] = 0$$

Expressing this mathematically:

$$\frac{-d(Nu(l)F(l))}{dl} + \gamma H(l - l_0) - \gamma g(l) = 0 \quad (1)$$

where
$$\int_0^\infty \gamma H(l' - l_0) dl' = \begin{cases} 0 & l < l_0 \\ \gamma(l_0) & l \geq l_0 \end{cases}$$

where l_0 = size of bubbles at nucleation.

There is a hidden assumption in this balance, and it is that the bubbles stop growing after they leave the surface.

Now the boundary condition in (1) is

$$f(l) = 0 \quad \text{when} \quad l = \infty \quad (2)$$

Hence (1) can be integrated from $l = \infty$ to $l = l$

$$Nu(l)f(l) = \gamma H(l - l_0) - \gamma \int_0^l g(l') dl'$$

or
$$f(l) = \frac{\gamma}{Nu(l)} H(l - l_0) - \frac{\gamma}{Nu(l)} \int_0^l g(l') dl' \quad \text{for } l \geq l_0$$

$$= \frac{\gamma}{Nu(l)} \left(1 - \int_0^l g(l') dl' \right) \quad \text{for } l > l_0$$

Now
$$\int_0^\infty g(l') dl' = 1 = \int_0^l g(l') dl' + \int_l^\infty g(l') dl'$$

$$\therefore f(l) = \frac{\gamma}{Nu(l)} \int_l^\infty g(l') dl' \quad l > l_0 \quad (3)$$

It is clear that if all the particles left the surface of the same size, l^* say, then

$$g(l) = \delta(l - l^*)$$

and
$$f(l) = \frac{1}{Nu(l)} \left[1 - H(l - l^*) \right]$$

Now let
$$G(l) = \int_0^l g(l') dl'$$

$$= 1 - \int_l^\infty g(l') dl'$$

Since $g(l) = 0$ at $l = \infty$

$$\frac{dG(l)}{dl} = -g(l) \quad (4)$$

The n^{th} moment of $g(l)$, is defined as

$$\bar{g}_n = \int_0^\infty l^n g(l) dl$$

From (4)
$$\bar{g}_n = - \int_0^\infty l^n \frac{dG(l)}{dl} dl \quad (5)$$

Integrating (5) by parts gives

$$\bar{g}_n = - \left[l^n G(l) \right]_0^\infty + \int_0^\infty n l^{n-1} G(l) dl \quad (6)$$

Now $\int_0^\infty l^n G(l) dl = \int_0^\infty l^n g(l) dl$

So $\int_0^\infty l^n G(l) dl = 0$ for all n

$$\int_0^\infty l^n G(l) dl = \begin{cases} 0 & \text{for } n \geq 1 \\ 1 & \text{for } n = 0 \end{cases}$$

But since only β_1, β_2, \dots are required, (8) becomes

$$\beta_n = \int_0^\infty l^{n-1} G(l) dl$$

Now from (3) $F(l) = \frac{r}{Nu(l)} g(l)$

$$\beta_n = \int_0^\infty l^{n-1} g(l) dl \quad (8)$$

Hence substituting β_n in (7) gives

$$\frac{d\beta_n}{dt} = \frac{rN}{q} \int_0^\infty l^{n-1} g(l) dl$$

At this point it is necessary to find a model for $g(l)$ the rate of bubble growth. The two models mentioned in section 1.2 and examined in detail in Appendix I will now be rearranged to a form suitable for substitution in equation (9)

Scriven (1959) shows:

$$\frac{dR}{dt} = \frac{1}{2} \frac{dR}{dt} \quad (10)$$

$$\text{ie } \frac{dl}{dt} = 2kt^{-2/3}$$

$$\therefore l = 4kt^{1/2} + \text{const} \quad (\text{at } t = 0 \quad l = l_0)$$

$$\therefore l - l_0 = 4kt^{1/2}$$

$$t^{-2/3} = \frac{3k}{l - l_0}$$

$$\therefore u(l) = \frac{dl}{dt} = \frac{3k^2}{l - l_0} \quad (10a)$$

$$\text{and } \frac{du(l)}{dl} = \frac{-3k^2}{(l - l_0)^2} \quad (10b)$$

On the other hand Darby et al (1971) show:

$$u = k't^{-2/3} = \frac{1}{3} \frac{dl}{dt} \quad (11)$$

$$\frac{dl}{dt} = 2k't^{-1/3}$$

$$l = 6k't^{2/3} + \text{const} \quad (\text{at } t = 0 \quad l = l_0)$$

$$\therefore l - l_0 = 6k't^{2/3}$$

$$\therefore t^{-2/3} = \frac{36 k'^2}{(l - l_0)^2}$$

$$\therefore u(l) = \frac{dl}{dt} = \frac{72 k'^3}{(l - l_0)^2} \quad (11a)$$

$$\therefore \frac{du(l)}{dl} = \frac{-144 k'^3}{(l - l_0)^3} \quad (11b)$$

In deriving (9) it was assumed that $l > l_0$. It is now assumed that the size of the bubble at nucleation, l_0 is negligible, ie $l_0 = 0$.

Hence if (10) is used in (9)

$$I_0 = \frac{e \cdot I_0 \cdot l_0}{4} \int_{-l_0/2}^{l_0/2} e^{-k|x|} dx \quad (12a)$$

and at $x = l_0/2$ (or $x = -l_0/2$)

$$I_0 = \frac{e \cdot I_0 \cdot l_0}{4} \int_{-l_0/2}^{l_0/2} e^{-k|x|} dx \quad (12b)$$

As I_0 can be measured, the integrals in (12a) and (12b) can be evaluated. This leaves the problem of evaluating the constants in terms of the integral. It can be measured fairly easily (see section 11) but it is a problem. By applying Faraday's law to the situation above constants can be produced.

Faraday's Law states -

- $n_g = \frac{It}{4e}$ n_g = no. of moles of gas produced in time t
- I = current flowing for t secs
- e = no. of electrons associated in producing 1 molecule of gas
- F = Faraday constant.

- $n_g = \frac{It}{4e}$ n_g = molar density of the gas produced
- V = volume of gas produced in t secs.

$$I = \frac{4en_g V}{t} \quad (13)$$

Now the volume of gas produced per unit area per unit time

$$= \int_{-l_0/2}^{l_0/2} e^{-k|x|} dx$$

1

1 1/2

1 1/2

1 1/2

1 1/2

Hence (12a) and (12b) become

$$q\beta_n = \frac{1}{\pi z F_0} \int_0^{\infty} \dots \quad (16)$$

$$q\beta_n = \frac{1}{\pi z F_0} \int_0^{\infty} \dots \quad (17)$$

Now the dipole moment p (section 3) can be found, and hence β_n can be obtained. In evaluating β from $g(\ell)$ a functional form for $g(\ell)$ is assumed (e.g. $g(\ell) = \dots$). Measured values for k and β are compared with values obtained from (16) and (17). The values of β obtained from (16) are compared with measured values in the literature.

$$\dots$$

The value of β calculated from (16) differs significantly from the value obtained from (17). The values of β obtained from (16) are compared with measured values in the literature.

3. Experimental

In section 1, it was shown that several parameters on the overall gas balance needed to be measured. The parameters that were measured were the fraction of bubbles on the surface in the size range l to $l + dl$, $f(l)dl$; the fraction of bubbles leaving the surface in the size range l to $l + dl$, $g(l)dl$; and the number of nucleation sites per unit area, N .

3.1 Description of the Apparatus

The bubbles were generated in a perspex cell 900 mm long, 150 mm high and 35 mm wide. The back wall of the cell was a copper plate which served as a cathode on which the bubbles grew. A 20 mm wide lead strip was embedded into the front wall of the cell just to the right of centre to act as the anode. The cathode and anode were connected to a power supply which could produce currents up to 20 A. The electrolyte was circulated through the cell. Flowrates of up to 500 ml/min could be achieved. In order to ensure that the flow across the electrode was laminar, the ends of the cell were packed with glass marbles and plastic drinking straws. This smoothed out any turbulence that may have arisen at the entrance and exit to the cell. Figure 3.1 is a diagram of the cell.

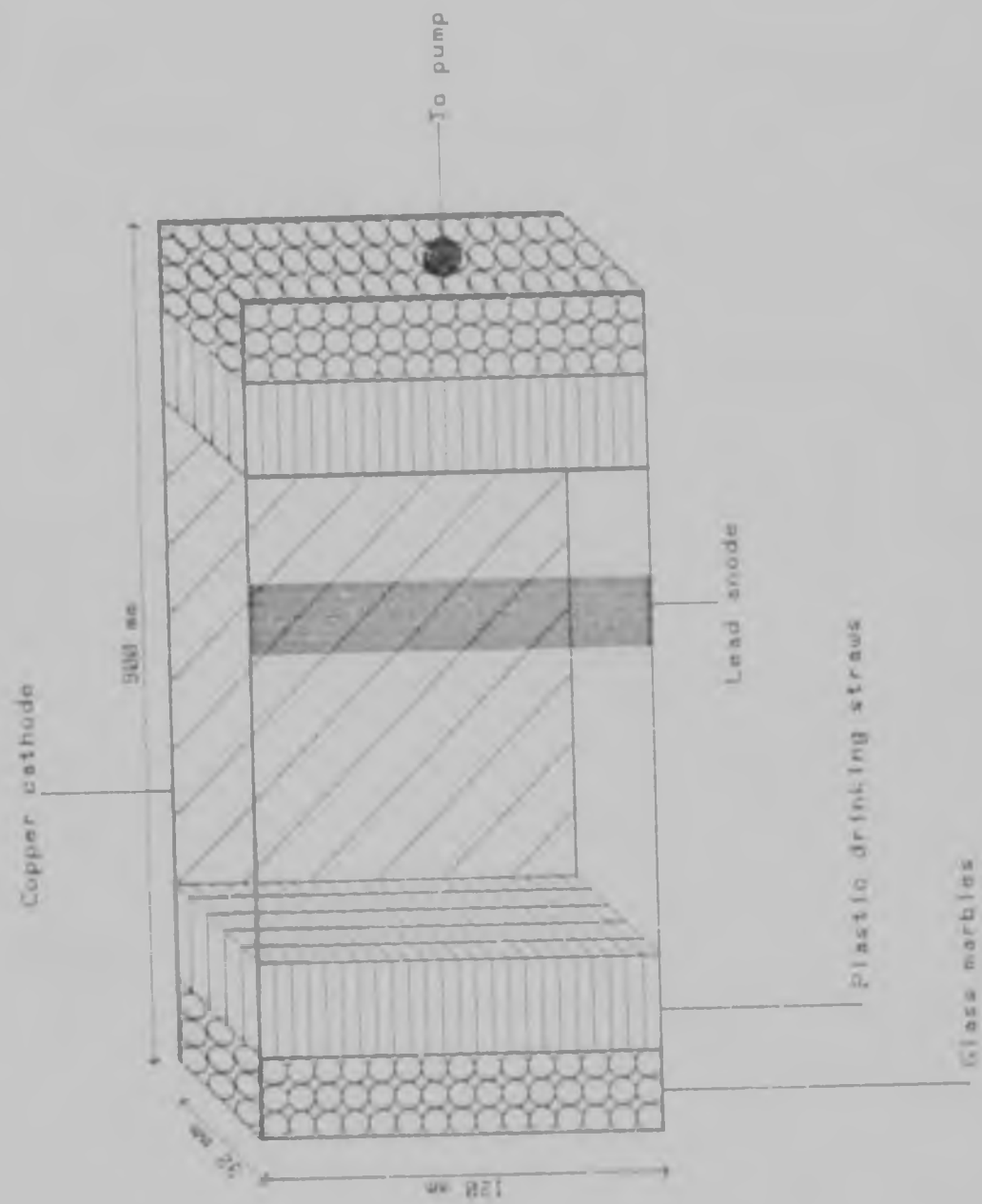


Figure 3.1 Diagram of the Cell

3.2 Measurement of $f(l)dl$ and N

Both the parameters $f(l)dl$ and N could be measured by analyzing the bubbles on the surface of the cathode. To do this a Wild M7 zoom stereomicroscope was mounted on the anode side of the cell and was focused on the cathode. A camera was attached to the microscope. A Braun F900 high speed flash was used to illuminate the cathode. The high speed flash "froze" any motion which may have caused blurring on the photographs. Photographs were taken of the bubbles on the cathode surface while the current and flowrate were set at some predetermined values. The photographs were developed and printed in the departmental dark room. The bubbles on the surface appeared as well defined spheres, while the bubbles not attached to the surface were out of focus due to the shallow depth of field caused by the high magnification of the microscope. See figure 3.1 for a typical photograph.

The diameters of the bubbles on the surface were measured with the aid of a micro computer and plotter. The photographs were placed on the plotter and with the aid of a digitizing sight, the computer could be told where the edges of each bubble were. A photograph of a ruler (taken under the same conditions as the bubbles) was used as a scale. This technique is fully described in Appendix 1. Having determined the size and number of bubbles on the surface of a known area, $f(l)dl$ and N could be determined.

N = number of bubbles measured / area over which measurements were made.

To find $f(l)dl$ the bubbles were sorted into size ranges and a normalised histogram of bubble sizes was drawn.

3.2 Measurement of $f(l)dl$ and N

Both the parameters $f(l)dl$ and N could be measured by studying the bubbles on the surface of the cathode. To do this a Wild M7 zoom stereomicroscope was mounted on the anode side of the cell and was focused on the cathode. A camera was attached to the microscope. A Braun F900 high speed flash was used to illuminate the cathode. The high speed flash "froze" any motion which may have caused blurring on the photographs. Photographs were taken of the bubbles on the cathode surface while the current and flowrate were set at some predetermined values. The photographs were developed and printed in the departmental dark room. The bubbles on the surface appeared as well defined spheres, while the bubbles not attached to the surface were out of focus due to the shallow depth of field caused by the high magnification of the microscope. See figure 3.2 for a typical photograph.

The diameters of the bubbles on the surface were measured with the aid of a micro computer and plotter. The photographs were placed on the plotter and with the aid of a digitizing sight, the computer could be told where the edges of each bubble were. A photograph of a ruler (taken under the same conditions as the bubbles) was used as a scale. This technique is fully described in Appendix 4. Having determined the size and number of bubbles on the surface of a known area, $f(l)dl$ and N could be determined.

$$N = \text{number of bubbles measured} / \text{area over which measurements were made.}$$

To find $f(l)dl$ the bubbles were sorted into size ranges and a normalised histogram of bubble sizes was drawn.

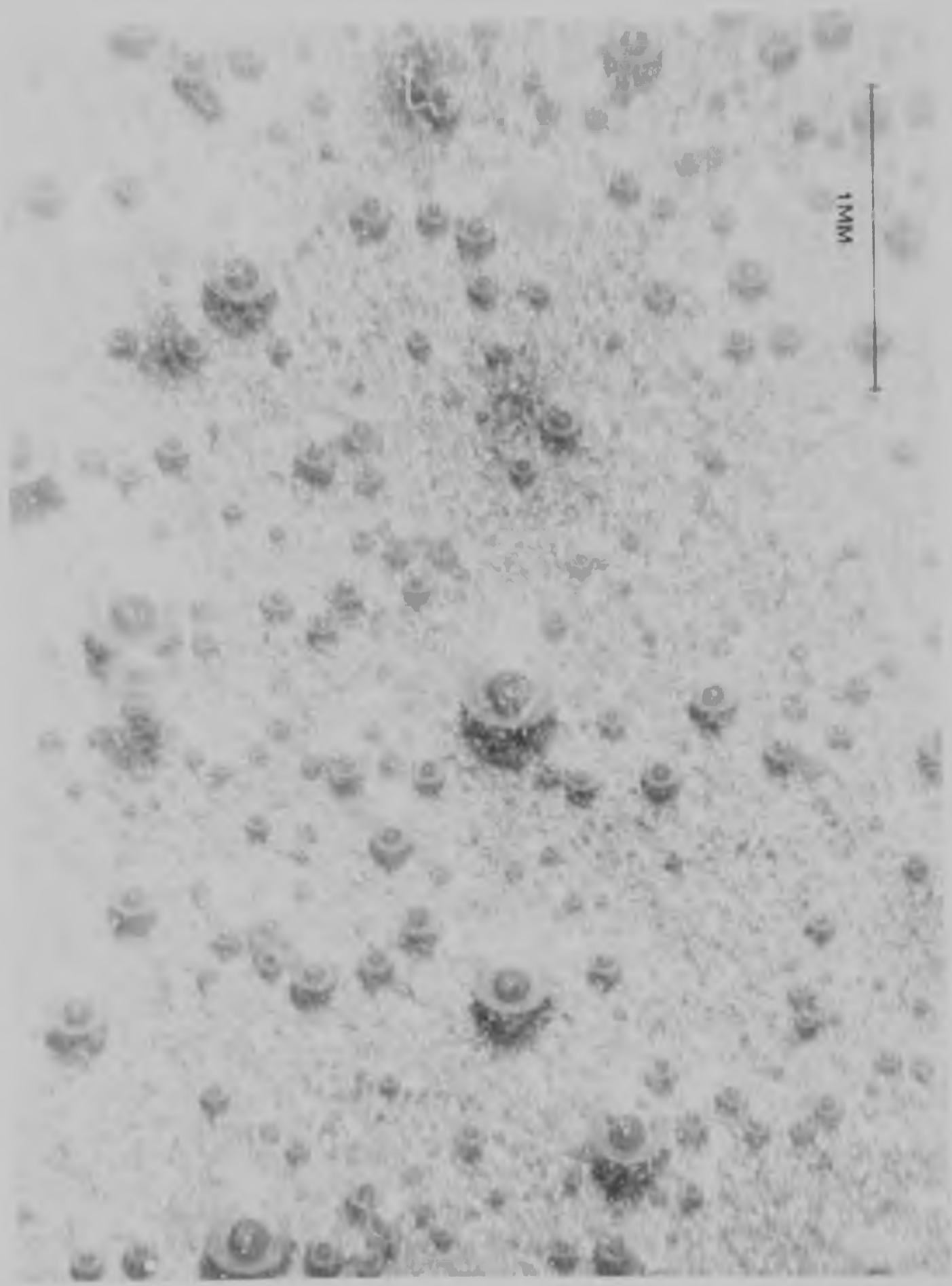


Figure 1.2 Photograph of nodules on the electrode surface

3.3 Measurement of $g(l)dl$

In order to measure $g(l)dl$ it was necessary to measure the size of the bubbles leaving the surface. Clearly the technique outlined in 3.2 would not serve this purpose because even if the depth of field was increased (by lowering the magnification) it would not be possible to differentiate between bubbles on the surface and bubbles off the surface. This problem was overcome by taking a cine of the bubbles on the surface. Because the bubbles grow at a high rate, it was necessary to use high speed photographic techniques. A Fastax 16 mm high speed camera was borrowed from the Mechanical Engineering Department and floodlights for illuminating the cell were borrowed from the Central Graphics Unit. From the cine it was clear which bubbles were attached to the surface and which were not, by virtue of the fact that the attached bubbles were stationary and the other bubbles were moving up. The film was projected onto a screen onto which a grid was drawn to enable the bubble diameters to be measured. The scale was again obtained by filming a ruler. The bubble diameters were sorted into size ranges and a histogram was drawn, which was in fact $g(l)dl$.

3.4 Changing the Viscosity and Electrolyte Composition

The cell could hold three litres of electrolyte solution. In each run 18 ml of sulphuric acid was used in the make up of the electrolyte solution (a concentration of 0.1 mol/l). The rest of the electrolyte consisted of an aqueous solution of either glycerine or magnesium

sulphate. The amounts of glycerine or magnesium sulphate used were varied so as to obtain the desired viscosity. The actual viscosity was measured using an Ostwalds Viscometer (see Appendix 4).

4. Results

During the experiments the viscosity of the electrolyte was varied using both glycerine and magnesium sulphate. The effect the glycerine and magnesium sulphate had on the results is shown in sections 4.1 and 4.2 below. The effect of current and flowrate on bubbles is shown in section 4.3 while the effect of viscosity is shown in section 4.4. A series of runs was performed using zinc sulphate as an electrolyte, and the effect electroplating had on the bubbles on the electrode surface was observed. These results appear in section 4.5.

Since a distribution of bubble sizes was observed, the average bubble size used to describe a particular run is chosen to be based on a volume distribution rather than on a number distribution. Hence the average bubble size d , is defined as

$$d = \frac{\int l^4 f(l) dl}{\int l^3 f(l) dl}$$

where $f(l)dl$ is the measured number distribution

So when presenting results, both the number mean bubble diameter and d are tabulated, while only d is used in the graphical presentations.

4.1 Typical Results

In this section samples of typical results obtained during the experiments are presented. The results are for runs using a pure water / sulphuric acid electrolyte (figure 4.1), water / glycerine / sulphuric acid electrolyte. (figure 4.2) and a water / magnesium sulphate / sulphuric acid electrolyte (figure 4.3). The results show a histogram of the bubble size distribution on the electrode surface and leaving the electrode surface. The size of the bubbles represented in these figures are the measured bubble diameters. Appendix 5 contains a full set of all results gathered over the period of this research.

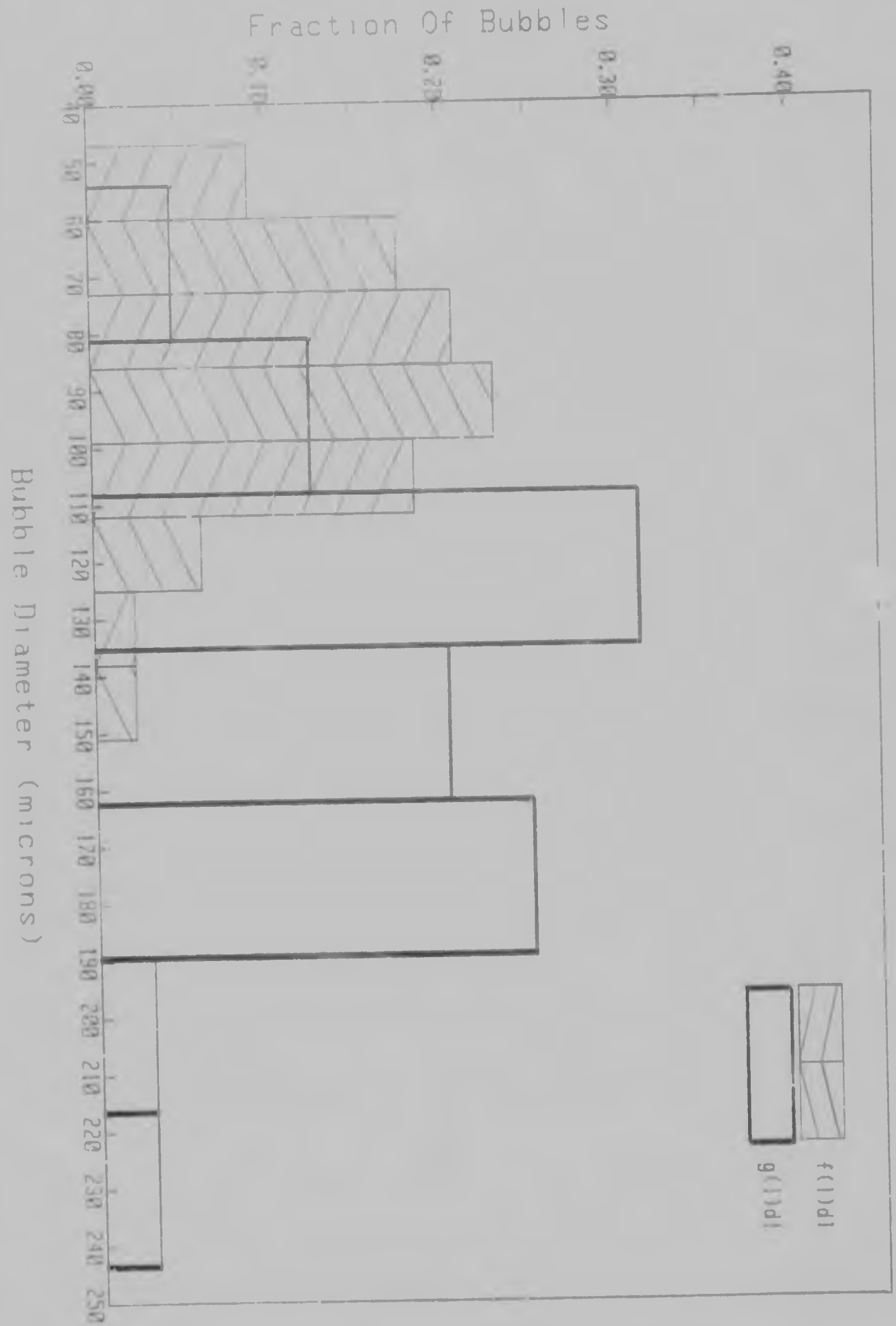
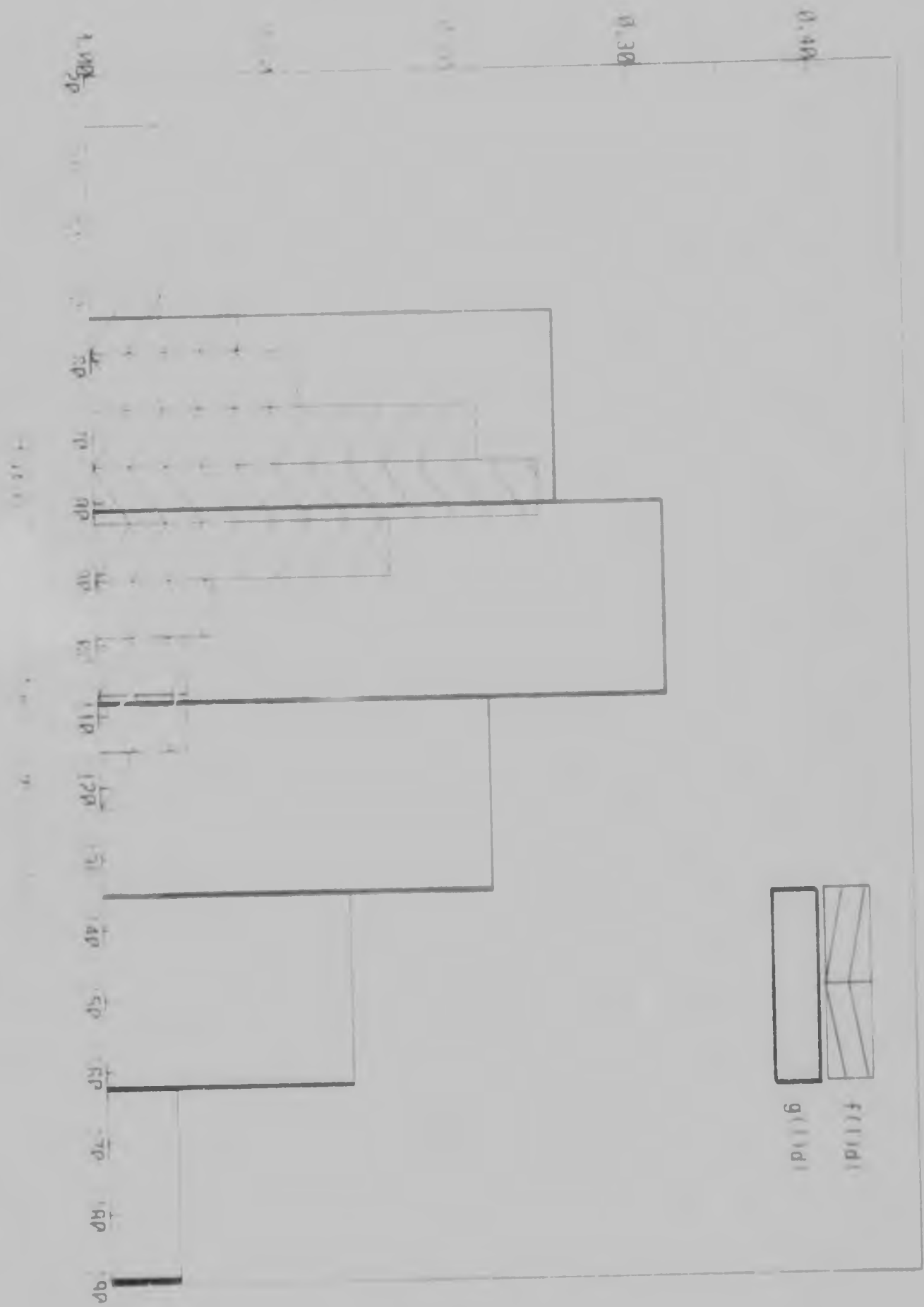


Figure 4.1 Typical Distribution - Water/H₂SO₄ Electrolyte

Distillation of bubbles



Distillation of 386 kg/m³ glycerine

July

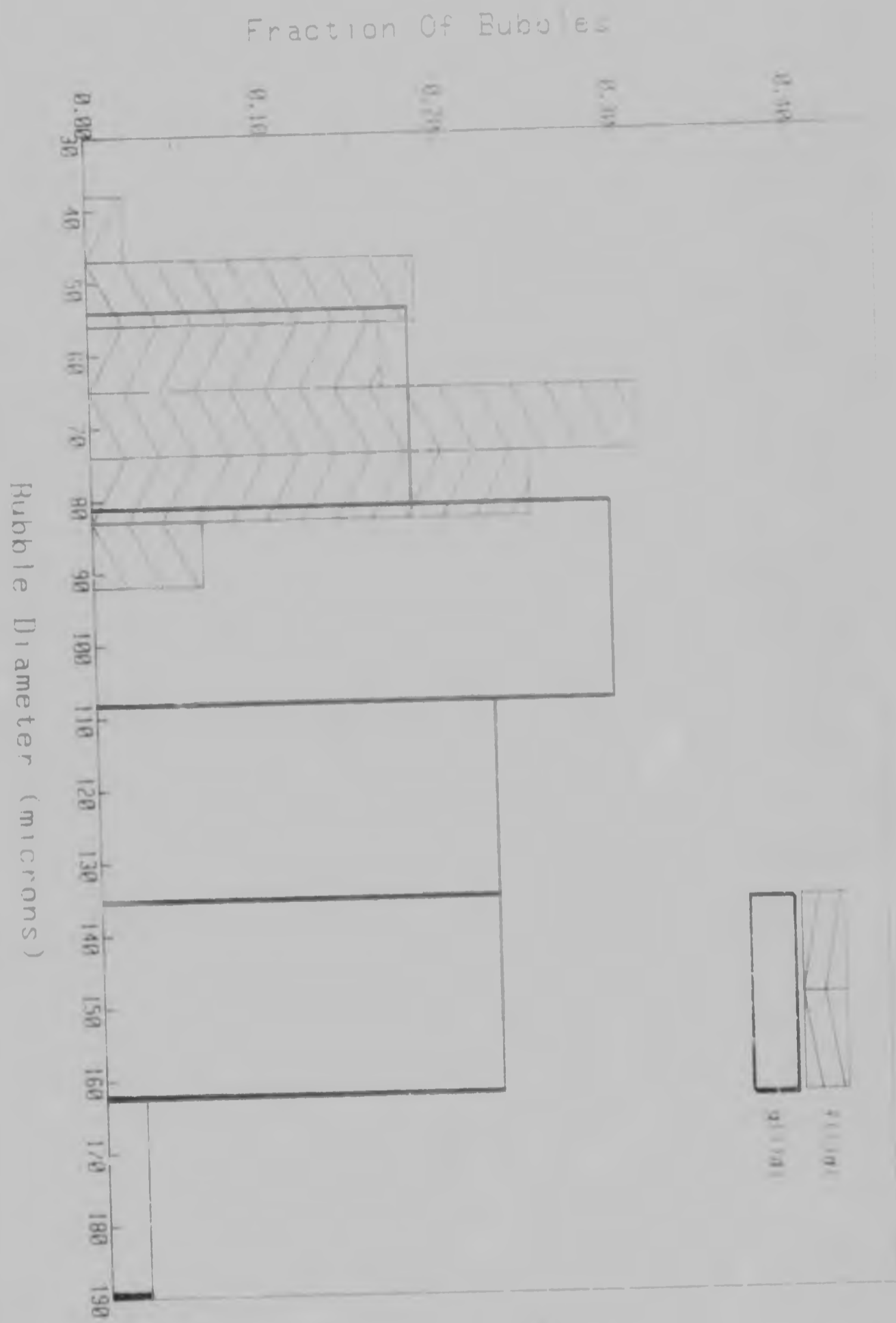


Figure 4. Bubble Diameter Distribution - 350 kg/m³ MgSO₄

4.2 The Effect of using Glycerine or Magnesium Sulphate to Increase the Viscosity of the Electrolyte

In this section the effect of using either glycerine or magnesium sulphate to alter the viscosity is shown. The results are given for the current fixed at 1 A and the flowrate set at 2.0 l/min. Table 4.1 shows the effect of glycerine concentration on the bubbles measured attached to and leaving the surface. The same effect is shown in table 4.2 for various magnesium sulphate concentrations. Figure 4.4 graphically illustrates these effects.

Clearly the mean bubble diameters, both on and leaving the surface, drop with increasing viscosity. The bubbles leaving the surface are larger than the bubbles on the surface, (as was evident from figures 4.1, 4.2 and 4.3). It is interesting to note that although the bubbles on the surface for the magnesium sulphate case are smaller than the bubbles on the surface for glycerine, the bubbles leaving the surface in the magnesium sulphate case are larger.

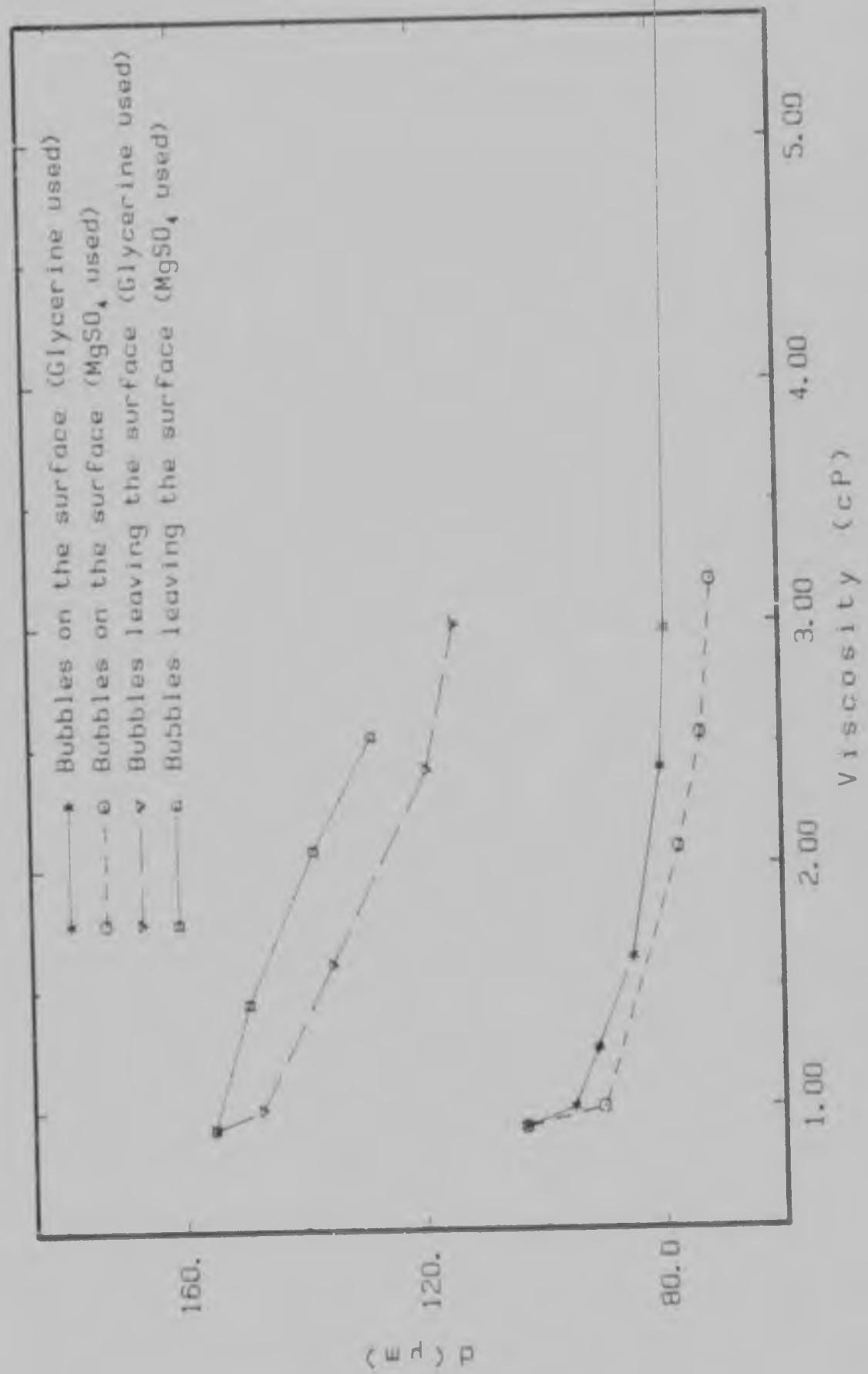
Table 4.1 Effect of Changing the Glycerine Concentration

Concentration of Glycerine (kg m ⁻³)	Viscosity (cP)	Mean bubble diameter on the surface (number distribution) (μ m)	Standard deviation of bubble diameters on the surface (number distribution) (μ m)	d ₅₀ on the surface (μ m)	Mean bubble diameter leaving the surface (number distribution) (μ m)	Standard deviation of bubble diameters leaving the surface (number distribution) (μ m)	d ₅₀ leaving the surface (μ m)
0,0	0,92	99	11	103	127	37	155
36,7	1,0	85	18	95	102	40	147
112,2	1,2	81	21	95	-	-	-
199,8	1,6	77	15	85	95	41	135
332,0	2,4	73	13	80	90	33	119
386,0	3,3	71	13	79	39	33	118
579,0	5,3	67	16	79	-	-	-

Table 4.2 Effect of Changing the MgSO₄ Concentration

Concentration of MgSO ₄ · 7H ₂ O (kg m ⁻³)	Viscosity (cP)	Mean bubble diameter on the surface (number distribution) (μ m)	Standard deviation of bubble diameters on the surface (number distribution) (μ m)	d ₅₀ on the surface (μ m)	Mean bubble diameter leaving the surface (number distribution) (μ m)	Standard deviation of bubble diameters leaving the surface (number distribution) (μ m)	d ₅₀ leaving the surface (μ m)
1,0	0,92	99	22	103	127	37	155
10,0	1,02	80	16	92	-	40	149
150,0	1,44	80	-	-	114	41	142
300,0	2,07	70	14	79	105	31	124
350,0	2,14	68	11	73	99	-	-
422,0	3,17	67	19	71	-	-	-

Figure 4.4 Effect of using Glycerine or $MgSO_4$ to alter the Viscosity



4.3 Effect of Flowrate and Current

Runs were performed to observe the effect the current and flowrate had on the bubble sizes at two different viscosities. The first was performed at the lowest viscosity (0,92 cP) where the electrolyte was a water / sulphuric acid solution. The second was performed at a high viscosity (5,8 cP) where the viscosity was raised by adding glycerine to the electrolyte. The results from these two runs are tabulated in tables 4.3 and 4.4 below.

Table 4.3 Effect of Current and Flowrate (Viscosity = 0,92 cP)

Flowrate (l/min)	d on the surface (μm)			
	Current (A)			
	1,0	3,0	5,0	10
2,00	103	108	108	-
3,75	97	97	91	-
4,60	104	96	77	79

Table 4.4 Effect of Current and Flowrate (Viscosity = 5,8 cP)

Flowrate (l/min)	d on the surface (μm)		
	Current (A)		
	0,5	1,0	1,5
1,18	83	84	87
2,00	87	79	84
2,90	85	82	87

From these results it is clear that the current had negligible effect on the bubble sizes on the surface, and did not effect the size distribution significantly (see Appendix 5 for size distribution results). At the low viscosity, the flowrate seemed to have a small effect on the bubble sizes on the surface. As the flowrate increases, the bubble size decreases.

Since the effect of flowrate and current was small on the size of the bubbles on the surface, it was assumed that this would be the case with the bubbles leaving the surface, and hence the bulk of the experiments were performed at a fixed current and flowrate - 1.0 A and 1.0 l/min.

4.4 The Effect of Electroplating

A series of runs were performed in which the viscosity of the electrolyte was varied using zinc sulphate rather than magnesium sulphate or glycerine. In these runs the zinc plated out on the cathode. The average bubble diameters observed on the electrode surface are tabulated below in table 4.5, and shown graphically in figure 4.5.

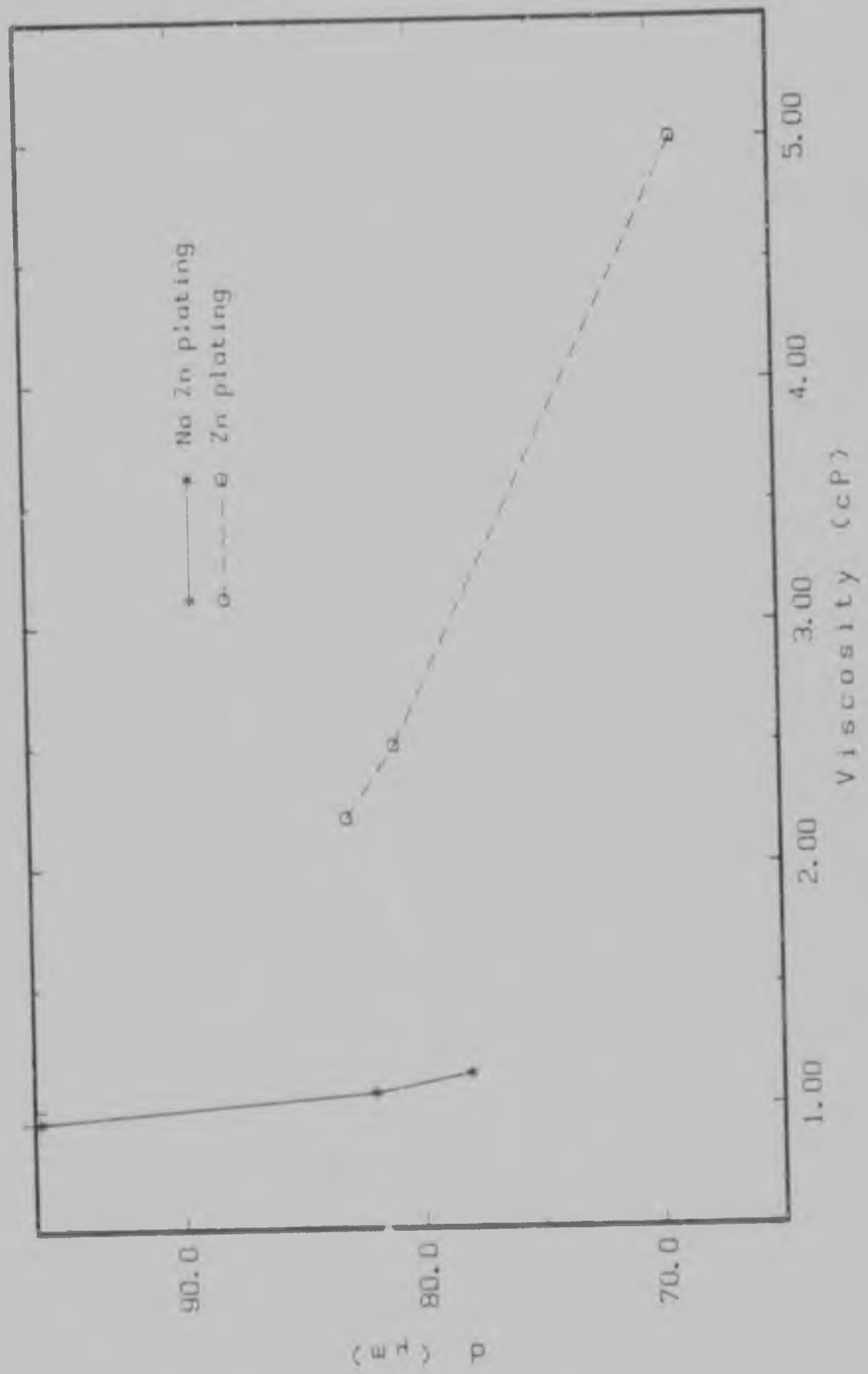
Table 4.5 Effect of Electroplating

Concentration of $ZnSO_4 \cdot 7H_2O$ (kg/m^3)	Viscosity (cP)	Mean bubble diameter on the surface (number dis- tribution) (μm)	Standard deviation of bubble diameters on the surface (number dis- tribution) (μm)	d on the surface (μm)
0,0	0,92	89	22	103
4,0	0,95	84	19	96
84,0	1,06	75	14	82
184,0	1,41	72	13	78
386,0	2,20	74	16	83
507,0	2,50	73	15	81
863,0	5,00	67	6	69

At the low viscosities (low zinc sulphate concentrations) the area of the cathode which was being plated could not be seen through the microscope. As the viscosity (zinc sulphate concentration) increased, the area being plated grew and could be observed. In the experiments, the runs performed at viscosities below 1,41 cP no coating was observed in the field of

measurement, while at the viscosities above 2,20 cP plating was observed. In both cases the bubble diameters decrease with viscosity. The overall trend seems to be much the same as for the cases where magnesium sulphate or glycerine were used.

Figure 4.5 The effect of electroplating



4.5 The number of Nucleation Sites per Unit Area

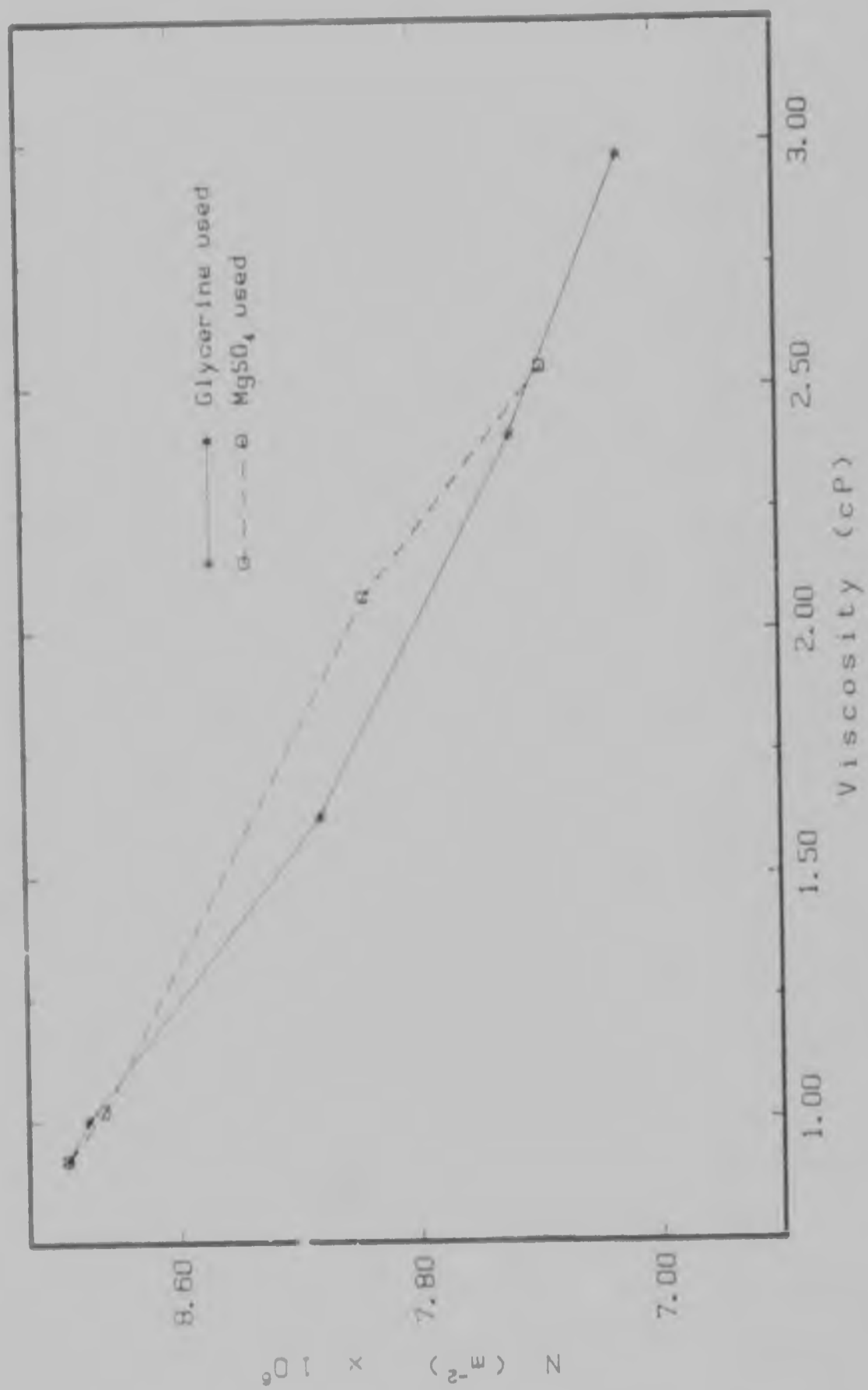
From the photographs of the bubbles on the surface, the number of nucleation sites per unit area of electrode surface, N , can be measured. This is done by simply counting the number of bubbles on a known area of the electrode. Since more than one photograph was taken during a run, an average was taken over each run. The values of N tabulated in table 4.6 are for runs at flowrates of 2,00 l/min and currents of 1,0 A. Figure 4.6 is a graphical representation of this.

Table 4.6 The number of Nucleation Sites per Unit Area

Electrolyte	Viscosity (cP)	N (m^{-2})
Water/ H_2SO_4	0,92	$8,966 \times 10^6$
Glycerine/ H_2SO_4	1,00	$8,898 \times 10^6$
Glycerine/ H_2SO_4	1,62	$8,120 \times 10^6$
Glycerine/ H_2SO_4	1,40	$7,480 \times 10^6$
Glycerine/ H_2SO_4	2,97	$7,114 \times 10^6$
$MgSO_4/H_2O/H_2SO_4$	1,02	$8,845 \times 10^6$
$MgSO_4/H_2O/H_2SO_4$	2,07	$7,697 \times 10^6$
$MgSO_4/H_2O/H_2SO_4$	2,54	$7,374 \times 10^6$

From the results it is clear that the effect of using either glycerine or magnesium sulphate in the electrolyte has a negligible effect on N .

Figure 4.6 The effect of Viscosity on N



Analysis

The following analysis is based on the assumption that the population is infinite and that the sample is drawn with replacement.

$$P(X = k) = \binom{n}{k} p^k (1-p)^{n-k} \quad (18)$$

$$P(X = k) = \frac{n!}{k!(n-k)!} p^k (1-p)^{n-k} \quad (19)$$

$$P(X = k) = \frac{n!}{k!(n-k)!} p^k (1-p)^{n-k} \quad (20)$$

(in respective)

The above analysis is based on the assumption that the population is infinite and that the sample is drawn with replacement. This is not always the case, and in such cases the binomial distribution is not applicable. The hypergeometric distribution is used when the population is finite and the sample is drawn without replacement. The probability mass function of the hypergeometric distribution is given by

$f(l)dl$ was measured (see section 3) and so the integral of the right hand side of equations (1a) and (1b) could be numerically evaluated. The current density was measured (see Appendix 6) and \bar{l} could be evaluated from the measured size distribution on the surface of the electrode. In this way the right hand sides of equations (1a) and (1b) could be evaluated.

From the distributions measured leaving the surface, β_n could be evaluated. To do this a functional form was given to $g(l)dl$, the fraction of bubbles leaving the surface in the size range l to $l + dl$. It was found that either a normal or a gamma density function fitted $g(l)dl$ quite well, the difference in using either one or the other was small. Hence having evaluated β_n , q could be evaluated by dividing the right hand side by β_n . An average value for q is taken over the first two moments. q is also evaluated from the expression

$$q = \frac{6i}{z_0 \pi r_m F \beta_n} \quad (3)$$

which was derived in section 2. In section 2 it was also shown that

$$Nk^2 = \frac{i}{72 z_0 \pi r_m F l} \quad (4a)$$

$$\text{or } Nk^{1/3} = \frac{i}{4 \pi z_0 \pi r_m F} \quad (4b)$$

Since N was measured (see sections 3 and 4) the values of k or $k^{1/3}$ (depending on which rate equation was used) could be evaluated.

A computer program was written to perform these calculations. This program is presented in Appendix 7 together with a description as to how the integrals in (1a) and (1b) were performed, and how β_n was evaluated.

The results obtained from this program are summarised in tables 5.1 and 5.2 below. The values of q calculated by equations (1a) and (1b) which are reported, are the mean values of q calculated over the first two moments.

Table 5.1 Calculated values for k and k'

Concentration of glycerine or $MgSO_4$	Viscosity (cP)	N (m^{-2})	k ($ms^{-1/3}$)	k' ($ms^{-1/3}$)
0	0,92	$8,966 \times 10^5$	$3,20 \times 10^{-5}$	$4,49 \times 10^{-5}$
36,7 kg/m ³ glycerine	1,00	$8,898 \times 10^5$	$3,29 \times 10^{-5}$	$4,50 \times 10^{-5}$
198,8 kg/m ³ glycerine	1,62	$8,120 \times 10^6$	$3,61 \times 10^{-5}$	$4,64 \times 10^{-5}$
332,0 kg/m ³ glycerine	2,40	$7,480 \times 10^6$	$3,85 \times 10^{-5}$	$4,77 \times 10^{-5}$
386,0 kg/m ³ glycerine	2,97	$7,114 \times 10^6$	$3,96 \times 10^{-5}$	$4,85 \times 10^{-5}$
10,0 kg/m ³ $MgSO_4 \cdot 7H_2O$	1,02	$8,845 \times 10^6$	$3,56 \times 10^{-5}$	$4,51 \times 10^{-5}$
280,0 kg/m ³ $MgSO_4 \cdot 7H_2O$	2,07	$7,697 \times 10^6$	$3,84 \times 10^{-5}$	$4,73 \times 10^{-5}$
350,0 kg/m ³ $MgSO_4 \cdot 7H_2O$	2,54	$7,374 \times 10^6$	$4,03 \times 10^{-5}$	$4,79 \times 10^{-5}$

Table 5.2 Calculated Values for q

Concentration of glycerine or MgSO ₄	Viscosity (cP)	Distribution assumed for $g(l)dl$	q from equation (3) (m ⁻² s ⁻¹)	q from equation (1a) (m ⁻² s ⁻¹)	q from equation (1b) (m ⁻² s ⁻¹)
0	0,92	Normal Gamma	3,874x10 ⁶ 3,796x10 ⁶	3,999x10 ⁶ 3,979x10 ⁶	4,353x10 ⁶ 4,332x10 ⁶
36,7 kg/m ³ glycerine	1,00	Normal Gamma	5,144x10 ⁶ 4,961x10 ⁶	3,477x10 ⁶ 3,457x10 ⁶	3,657x10 ⁶ 3,636x10 ⁶
198,8 kg/m ³ glycerine	1,62	Normal Gamma	7,535x10 ⁶ 7,107x10 ⁶	4,778x10 ⁶ 4,746x10 ⁶	5,096x10 ⁶ 5,063x10 ⁶
332,0 kg/m ³ glycerine	2,40	Normal Gamma	9,691x10 ⁶ 9,328x10 ⁶	4,890x10 ⁶ 4,861x10 ⁶	5,101x10 ⁶ 5,071x10 ⁶
386,0 kg/m ³ glycerine	2,97	Normal Gamma	1,008x10 ⁷ 9,682x10 ⁶	5,029x10 ⁶ 4,999x10 ⁶	5,300x10 ⁶ 5,268x10 ⁶
10,0 kg/m ³ MgSO ₄ · 7H ₂ O	1,02	Normal Gamma	4,916x10 ⁶ 4,729x10 ⁶	3,776x10 ⁶ 3,750x10 ⁶	4,062x10 ⁶ 4,034x10 ⁶
280,0 kg/m ³ MgSO ₄ · 7H ₂ O	2,07	Normal Gamma	5,809x10 ⁶ 5,543x10 ⁶	4,730x10 ⁶ 4,695x10 ⁶	4,978x10 ⁶ 4,942x10 ⁶
350,0 kg/m ³ MgSO ₄ · 7H ₂ O	2,54	Normal Gamma	7,916x10 ⁶ 7,600x10 ⁶	4,503x10 ⁶ 4,474x10 ⁶	4,713x10 ⁶ 4,682x10 ⁶

In Appendix 1 it is seen that k' must take on a value of $2,22 \times 10^{-3} \text{ I}^{1/3} \text{ ms}^{-1/2}$. Since the current used in all the runs tabulated in table 5.1 was 1 A, k' must equal $2,22 \times 10^{-3} \text{ ms}^{1/2}$ if the rate of bubble growth is described by equation (2b). Clearly the value of k' calculated is significantly smaller than this, and hence it is concluded that the bubbles do not grow according to equation (2b). Also in Appendix 1 a table of values for k obtained from the literature is presented. These values correspond to the measured values of k presented in table 5.1. This suggests that the bubbles are in fact growing according to equation (2a).

In figure 5.1, k is plotted against the viscosity of the two electrolytes used. Over the range of viscosity used, k does not change all that much - k increases by 24 per cent when glycerine is used in the electrolyte and increases by 26 per cent when magnesium sulphate is used in the electrolyte.

The values of q , the rate of bubble nucleation per unit area, calculated from equation (1b) (ie assuming a rate of bubble growth given by equation (2b)) can now be rejected since it has been established that the rate of bubble growth is well represented by equation (2a). It is clear from table 5.2 that the assumption of a normal or gamma distribution for the bubbles leaving the electrode surface has almost no effect on q . The values of q evaluated using equation (3) show more of an effect of viscosity than do the ones evaluated from equation (1a). This effect is shown in figure 5.2 where the values of q are calculated using the normal distribution assumption for $g(l)$.

Figure 5.1 The effect of Viscosity on k

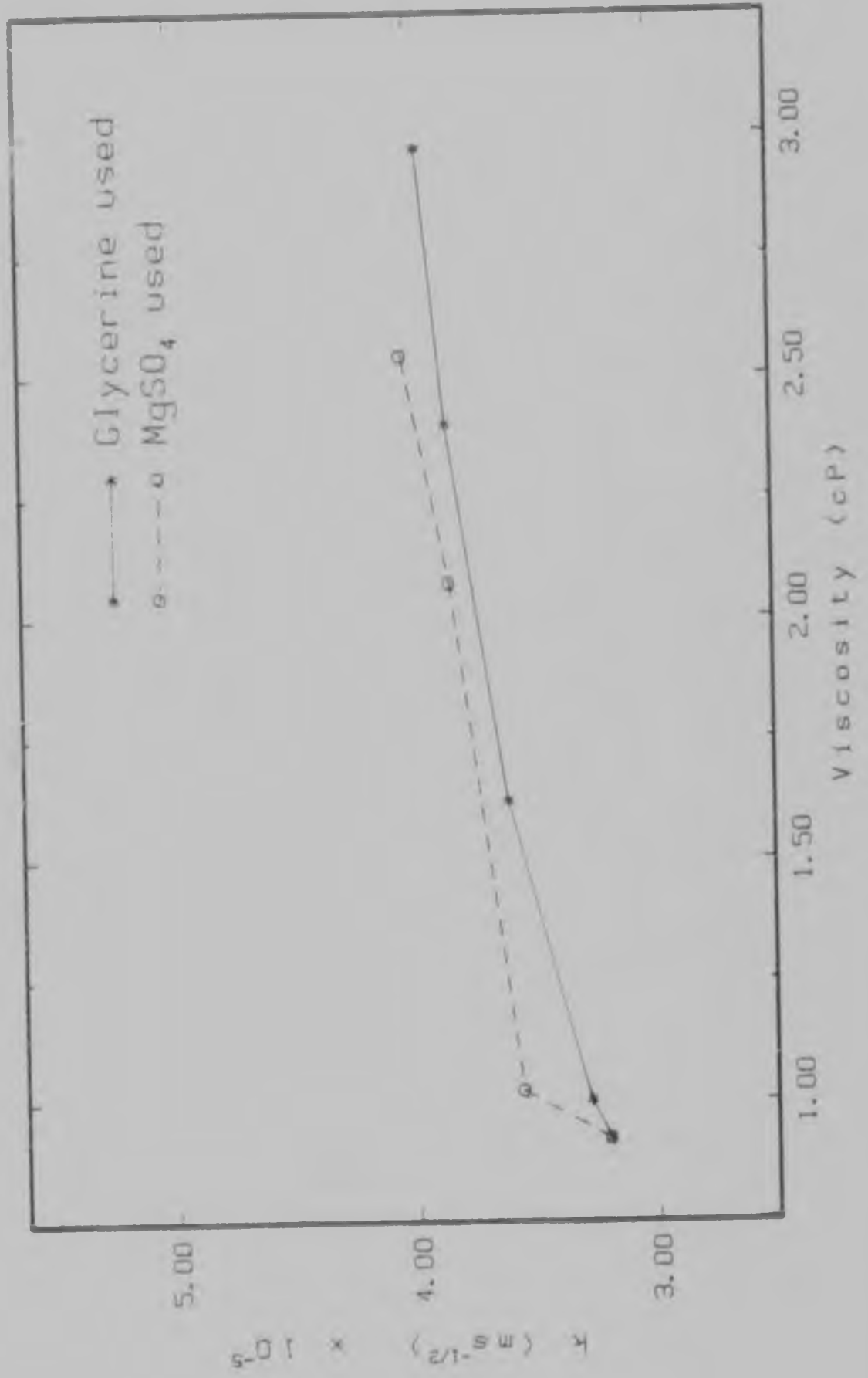
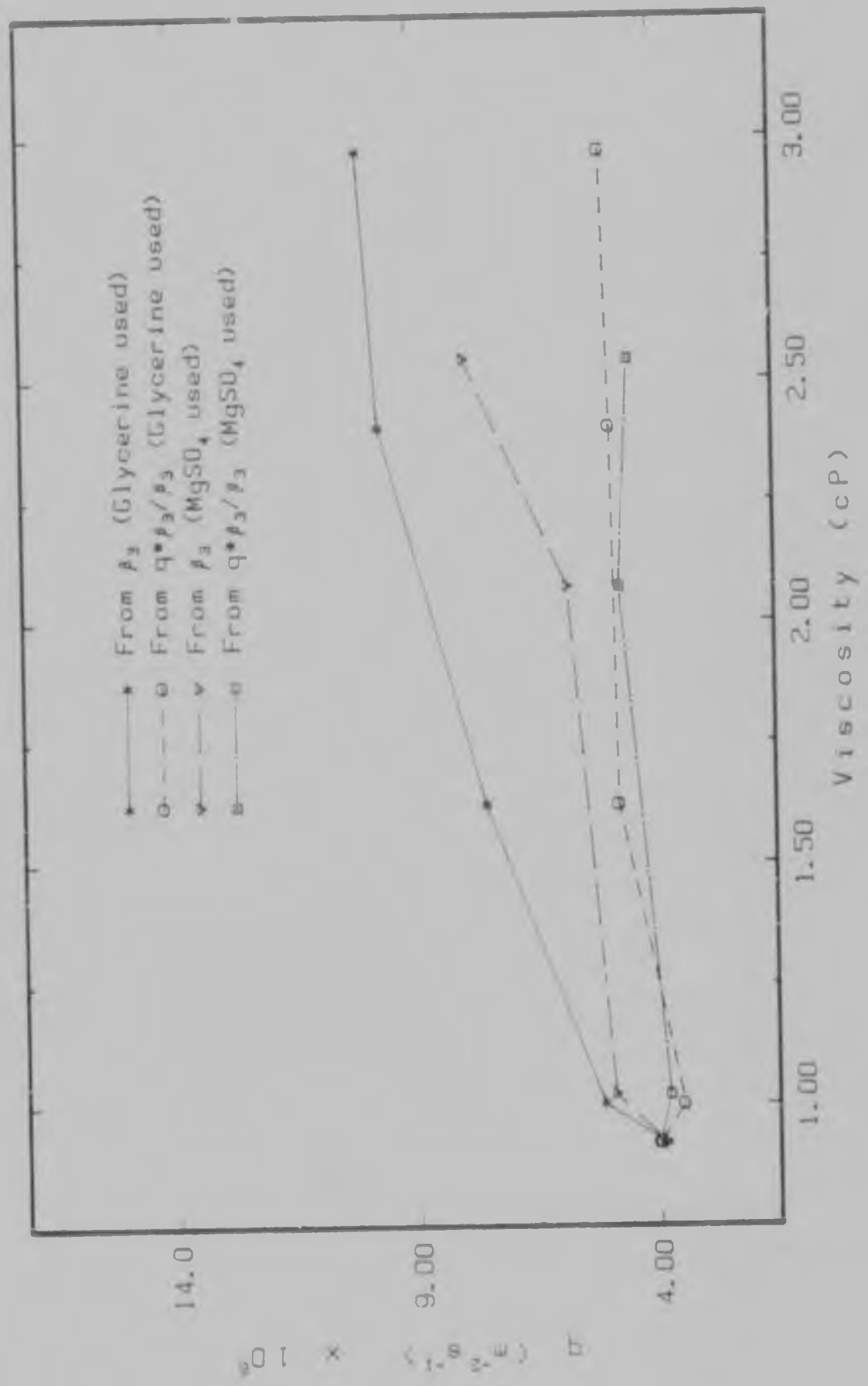


Figure 5.2 The effect of Viscosity on γ



The values of q obtained from equation (3) depend on the third moment of $g(l)$, i.e. β_3 . Since β_3 is very much smaller than β_1 and β_2 , numerical errors are expected to creep into this value of q . The values of q obtained from equation (1a) vary by about 15 per cent over the viscosity range used, and the use of glycerine or magnesium sulphate in the electrolyte has negligible effect.

To use the population balance as a means of predicting bubble break off diameters, k can be obtained from Glas et al (1964) for the current used. An experiment as described in section 3.2 needs to be done to establish N for the electrode and electrolyte used. As a result of this experiment the bubble size distribution on the electrode surface can also be obtained. This leaves three parameters to be solved for using the population balance: N ; the mean bubble diameter leaving the electrode surface, \bar{d} ; and the standard deviation of the bubble sizes leaving the surface, σ . Using equation (1a) the first three moments of the distribution of bubble sizes can be found:

$$\beta_1 = \frac{2i}{\pi^2 F_0 a l q} \int_0^\infty \frac{g(l)}{l} dl \quad (5)$$

$$\beta_2 = \frac{4i}{\pi^2 F_0 a l q} \quad (6)$$

$$\beta_3 = \frac{6i}{\pi^2 F_0 a l} \quad (7)$$

Now in Appendix 2 it is shown that

$$\beta_1 = \bar{d} \quad (8)$$

$$\beta_2 = \bar{d}^2 + \sigma^2 \quad (9)$$

$$\beta_3 = \bar{d}^3 + 3\bar{d}\sigma^2 \quad (10)$$

Substituting (8), (9) and (10) into (5), (6) and (7) gives three equations in the unknowns q , η and σ .

Having solved these three equations (which will require some sort of iterative numerical technique), the bubble break off diameter, d , can be calculated as

$$d = \frac{B_4}{B_1} = \frac{\eta^4 + 6\eta^2\sigma^2 + 3\sigma^4}{\eta^2 + 3\sigma^2}$$

Substituting (8), (9) and (10) into (5), (6) and (7) gives three equations in the unknowns q , η and σ .

Having solved these three equations (which will require some sort of iterative numerical technique), the bubble break off diameter, d , can be calculated as

$$d = \frac{34}{31} = \frac{n^4 + 6n^2a^2 + 3c^4}{n^2 + 3na^2}$$

6. Discussion and Conclusions

In situations where the production of a new phase results in the formation of particles such as gas bubbles, liquid droplets or solid crystals, the size of these particles is of considerable importance to the optimum performance of the process. At gas evolving electrodes the rate of mass transfer has been shown to be a strong function of the bubble break off diameter. For this reason a method of modelling the process would be useful. Population balance models, which incorporate growth and nucleation characteristics have been successfully applied to the analysis of crystallisation processes. In section 5 the population balance is applied to the production of bubbles at gas evolving electrodes. The population balance enables one to predict the bubble break off diameter after having determined three parameters. These parameters are the number of nucleation sites per unit area, the rate of nucleation per unit area and a rate constant associated with a model for the rate of bubble growth on the electrode surface.

In Appendix 1, two models for the rate of bubble growth on an electrode surface appearing in the literature have been reviewed. In section 4 it was found that the model of Scriven (1959) fitted the experimental data very well. The rate constant calculated from the experimental data compared favourably with that reported in the literature (see section 5). This rate constant showed negligible variation with electrolyte viscosity.

The number of nucleation sites per unit electrode area, N , is a function of the electrode type used. It was also found to be a function of the electrolyte viscosity. With increasing viscosity, N showed a drop of about 20 per cent over the viscosity range used. The increase in viscosity seemed to cause previously active sites to become inactive. A possible reason is that mass transfer of dissolved gas was reduced by the increased viscosity, and hence only certain sites near high local gas concentrations were able to receive gas for the bubbles.

The rate of bubble nucleation per unit area, q , was also measured. This quantity also remained constant with electrolyte viscosity. The type of electrolyte also made little difference to the results for N and q .

In order to apply the population balance, estimates for N , q and the rate constant, k , are needed. Glas et al (1964) shows how k varies with current. This variation of k with current is not unexpected after increase in the rate of bubble production was observed with increasing current. This observation could also suggest that q is a function of current, as seen in equation (15) in section 2. N , being a function of the electrode surface and viscosity needs to be measured specifically for the electrode and electrolyte used under given operating conditions. In order to avoid measuring q , an iterative method is proposed in section 5 whereby q , and the bubble break off diameter can simultaneously be calculated.

The value of the population balance method in analysing bubble growth at gas evolving electrodes is that only one fairly simple experiment needs to be done (see sections 3 and 5). Having established N , k can be obtained from Glas et al (1964) and then proceeding with the calculation outlined in section 5, a bubble break off diameter can be established. This bubble break

... in the ... applied in the calculation of mass transfer
... electrodes.

... three parameters were varied: the
... through the cell, the current passed between the
... and the viscosity of the electrolyte. The viscosity of the
... varied by adding either glycerine or magnesium sulphate.
These two substances were chosen because they are chemically very different
... would not react in any way at the electrode.

The effect of changing the current (at constant flowrate and viscosity)
did not have a significant effect on the size of the bubbles on the
electrode. An increase in the current did however increase the number of
bubbles produced, and hence the amount of gas produced. The increase in
gas production with increasing current is explained by Faradays Law, but
the fact that the bubble sizes remained approximately constant with changes
in current would suggest that the bubble break off diameter is not a
significant function of current over the range tested. Because the number
of bubbles produced increased rather rapidly with current, it was difficult
to photograph the cathode under high current conditions, as the bubbles
tended to make the solution murky. For this reason the range of currents
used was limited.

The flowrate had a small effect on the bubbles growing on the cathode. The
bubbles observed on the cathode at high flowrates were smaller than those
observed under low flowrate conditions. This effect is more marked in the
experiments performed using a low viscosity electrolyte because larger
flowrates could be achieved. The reason for the bubbles being smaller at

higher flowrates is that the higher flowrate causes a larger shear stress at the electrode surface. This shear stress then served to dislodge the bubbles off the electrode surface prematurely.

The use of glycerine or magnesium sulphate to increase the viscosity of the electrolyte did not appear to have a significant effect. As the viscosity increased over the range used, the mean bubble diameter on the surface (based on a volume distribution) decreased by between 25 per cent to 30 per cent, while the mean bubble diameter leaving the surface (the bubble break off diameter) decreased by between 20 per cent to 25 per cent. This decrease in bubble size with increasing viscosity was also observed during the runs in which zinc sulphate was added to the electrolyte to alter the viscosity. As the zinc concentration reached a certain value, the zinc began to plate out onto the cathode. At this point there was a sudden increase in the size of the bubbles produced but again as the viscosity increased beyond this point the bubble sizes again began to decrease. The reason proposed for this sudden jump in bubble size is that as the zinc began to plate out, the electrode surface changed, and so suddenly an essentially different electrode was being used.

The bubble break off diameters observed throughout these experiments were larger by more than a factor of two from those recommended by Stephan (1979). This is probably due to the fact that in this study the bubble break off diameters are based on volume distributions rather than on number distributions.

In conclusion, the population balance provides a means of modeling the electrolyte generation of gas. It also allows the bubble break off

diameter to be predicted for use in mass transfer calculations.

The population balance also predicts the distribution of bubble sizes leaving the electrode surface. In using the mean bubble break off diameter in the mass transfer calculations, one is assuming that the bubble size distribution has no effect on the mass transfer at gas evolving electrodes. It is possible, however, that the effect of the large bubbles is far more significant than the effect of the smaller bubbles (and vice versa), and hence the population balance provides a means of predicting the distribution and hence its effect on mass transfer.

The effect of viscosity on the bubble break off diameter was not as marked as was originally anticipated, and hence the conflict between Ault (1975) and Stephan (1979) as pointed out in section 1.4 is not resolved. It was, however, found that the bubble break off diameters measured in this study were larger than those presented by Stephan (1979) for the use in predicting mass transfer coefficients.

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Appendix 1. Expressions for the Rate of Bubble Growth

Two models for the rate of electrolyte bubble growth are described in detail in this appendix.

1. Darby and Haque (1973)

Darby et al (1973) set about trying to elucidate the controlling rate process which limits the maximum rate at which bubbles are evolved at an electrode. They set up an experiment in which hydrogen bubbles grew from a single nucleation site on the tip of a platinum wire. They initially expected the rate of bubble growth to be analogous to that observed in nucleate boiling, and postulated:

$$Sh = \text{constant} (Re Sc)^{0.5} \quad (1)$$

where $Sh = \frac{2k_L r}{D}$ = Sherwood number

$$Re = \frac{2r u_c}{\mu} = \text{Reynolds number}$$

$$Sc = \frac{r}{\rho_L D} = \text{Schmidt number}$$

$$k_L = \text{mass transfer coefficient for } H_2$$

$$r = \text{bubble radius}$$

$$D = \text{molecular diffusivity}$$

$$\rho_L = \text{liquid density}$$

μ = liquid viscosity
 and $u = \left(\frac{\sigma g (\rho_L - \rho_g)}{\rho_g} \right)^{0.25}$
 ρ_g = gas density
 σ = surface tension

Equation (1) predicts the bubble radius to grow in proportion to $t^{2/3}$, and assumes limiting hydrogen mass transfer.

Darby et al (1973) go on to show that the rate of gas generation at the electrode, r_g , is given by Faradays Law:

$$r_g = \frac{I}{nF} \quad (2)$$

where I = total instantaneous current
 n = number of electrons transferred per H_2 molecule
 F = Faradays constant.

The rate of mass transfer of dissolved gas from the solution to the bubble, r_c , is:

$$r_c = K_L A (C_{H_2} - \bar{C}_{H_2}) \quad (3)$$

where A = electrode area
 C_{H_2} = concentration of dissolved H_2 at the electrode
 \bar{C}_{H_2} = saturation concentration of H_2 in equilibrium with partial H_2 gas pressure

Finally, the rate of removal of gas from solution by the bubble, r_D is:

$$r_b = \rho_m \frac{\partial V}{\partial t}$$

ρ_m = molar density of hydrogen

V = bubble volume

t = time.

At steady state, $r_b = r_c$

A mass balance on the hydrogen gives:

$$V_L \frac{\partial C_{H_2}}{\partial t} = r_g - r_b = \frac{I}{nF} - \rho_m \frac{\partial V}{\partial t} \quad (5)$$

$$\text{or } V_L \frac{\partial C_{H_2}}{\partial t} = r_g - r_c = \frac{I}{nF} - k_L A (C_{H_2} - \bar{C}_{H_2}) \quad (6)$$

where V_L = volume of liquid

Now if mass transfer of hydrogen gas to the bubble is limiting (as in the case of the model discussed in section 2 of this appendix), k_L will be small and there will be a significant build up of dissolved gas in the liquid for a given current. Consequently there will be a lag between the electrode current, which is proportional to rate of gas generation, and the bubble growth rate, corresponding to gas removal. If mass transfer is not limiting (k_L large), the generated gas will be transported to the bubble essentially as fast as it is generated. In this case the electrode current and bubble growth rate should be in phase.

The results of Darby et al (1973) showed that:

$$r = 0,15t^{1/3} \quad (7)$$

This is inconsistent with the predictions of (1), and suggests that some mechanism other than hydrogen mass transfer is limiting. As further evidence of this, they noted that no phase lag between the electrode current and the bubble growth rate was evident.

Darby et al (1973) went on to apply Faradays Law:

$$I(t) = 2F \rho_m \frac{dV}{dt} \quad (8)$$

The current, $I(t)$, is the instantaneous total current passing through the electrode, and due to fluctuations with time it is written as a function of time. The average current, \bar{I} , was calculated in two ways:

$$\bar{I} = \frac{1}{t_1} \int_0^{t_1} I(t) dt \quad (9)$$

This integral was evaluated by integrating the $I(t)$ curve numerically.

$$\text{or } \bar{I} = \frac{2F \rho_m V_1}{t_1} \quad (\text{from Faradays Law}) \quad (10)$$

Here \bar{I} is calculated by measuring the volume of gas produced, V_1 , in a time t_1 .

The error between the two methods for calculating \bar{I} was found to be less than 10 per cent.

Now equation (8) can be integrated by replacing $I(t)$ with \bar{I} , and by writing $V = \frac{4}{3} \pi r^3$ to give:

$$r = \left\{ \frac{3\bar{I}}{8 \pi F \rho_m} \right\}^{1/3} t^{1/3} \quad (11)$$

Equation (11) is of the same form as the experimental result of equation (7).

By equating coefficients of equations (7) and (11) and solving for \bar{I} , Darby et al (1973) found that the calculated value of \bar{I} was equal to the average value obtained from (9) and (10).

Darby et al (1973) then go on to show that the rate controlling step is in fact a surface reaction (such as atomic hydrogen combining to form molecular hydrogen).

Now l = bubble diameter

$$l = 2r = 2 \left\{ \frac{3\bar{I}}{8\pi F \rho_m} \right\}^{2/3} t^{1/3}$$

$$\therefore u = \frac{dl}{dt} = \frac{2}{3} \left\{ \frac{3\bar{I}}{8\pi F \rho_m} \right\}^{2/3} t^{-2/3}$$

or $u = k't^{-2/3}$ (12)

where $k' = \frac{2}{3} \left\{ \frac{3\bar{I}}{8\pi F \rho_m} \right\}^{2/3}$

Assuming the gas behaves ideally:

$$\rho_m = \frac{P}{RT}$$

Hence at 25 C and 0,82 atm, $\rho_m = \frac{0,82 \cdot 1,01325 \times 10^5}{8,3143 (25+273)} = 33,5 \text{ mol/m}^3$

$$\begin{aligned} \therefore k' &= \frac{2}{3} \left\{ \frac{3\bar{I}}{8\pi \cdot 96500 \cdot 33,5} \right\}^{2/3} \\ &= 2,22 \times 10^{-3} \bar{I}^{2/3} \text{ mol}^{-2/3} \end{aligned} \quad (13)$$

2. Scriven (1959)

Scriven (1959) derived a model to describe the growth rate of spherical bubbles growing on an electrode surface in a quiescent liquid of infinite extent. The growth rate is a function of the difference between the pressure within the bubble and the ambient pressure, liquid inertia and viscosity, surface tension and the transport of energy and volatile material through the liquid to the bubble surface (i.e. heat and mass transfer). Scriven (1959) described the growth rate of the bubbles growing on an electrode surface by applying the fundamental equations of fluid dynamics (i.e. the equations of continuity, motion, energy and mass) and then solving simultaneously for the bubble radius as a function of time.

Equation of Continuity

The equation of continuity when written for spherical symmetry and an incompressible fluid can be integrated to give

$$uR^2 = f(t) \quad (14)$$

where u = radial velocity of the liquid being displaced by the growing bubble at a distance R from the bubble centre
 R = radial distance
 $f(t)$ = a function of time.

Since the term uR^2 is a function of time only, it can be evaluated at any radial position, say, at the bubble surface where $R = r$. The bubble surface moves with a velocity \dot{r} , while the liquid immediately adjacent moves with a velocity $u(r)$. The net velocity causes a mass flow of $4\pi r^2 \rho_L \{ \dot{r} - u(r) \}$ which must equal the rate of vaporization of volatile

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Since the term uR^2 is a function of time only, it can be evaluated at any radial position, say, at the bubble surface where $R = r$. The bubble is moving with a velocity \dot{r} , while the liquid immediately adjacent to the bubble surface has a velocity $u(r)$. The net velocity causes a mass flow of $4\pi r^2(u - \dot{r})\rho$ which must equal the rate of vaporization of volatile

material into the bubble:

$$\text{i.e. } 4 \pi r^2 \rho_L \{ \dot{r} - u(r) \} = \frac{d}{dt} \left(\frac{4}{3} \pi r^3 \rho_g \right)$$

where ρ_g = vapour density which is assumed constant.

Solving equation (15) for $u(r)$ gives:

$$u(r) = r \left| \frac{\rho_L \dot{r}}{\rho_L} \right| = \dot{r} r$$

Hence at the bubble surface (substituting equation (15) into equation (15))

$$uR = \dot{r} R^2$$

Equation of Motion

Writing the equation of motion in spherical coordinates for an incompressible Newtonian fluid, and assuming no external body forces:

$$\frac{\partial u}{\partial t} + u \frac{\partial u}{\partial R} = \frac{1}{\rho_L} \frac{\partial \tau}{\partial R} = \frac{\mu}{\rho_L} \frac{\partial^2 u}{\partial R^2}$$

where p = pressure in the moving fluid

ν = kinematic viscosity

Substituting for velocity from equation (17) and integrating over the radius from the bubble surface to infinity reduces equation (18) to:

$$\frac{r \dot{r} - p(r)}{\rho_L} = \frac{1}{2} \dot{r}^2 r^2 = \frac{\mu}{\rho_L} \frac{d^2}{dt^2} \left(\frac{4}{3} \pi r^3 \right)$$

where $\ddot{r} = \frac{d^2 r}{dt^2} = \frac{d \dot{r}}{dt}$

Now $p(\infty)$ is just the ambient pressure, p_a , while $p(r)$ is given by

$$p(r) = p_v + p_i - \frac{2\sigma}{r} \quad (20)$$

where p_v = partial pressure of the volatiles in the bubble
 p_i = partial pressure of inert gases in the bubble
 σ = surface tension

Now substituting (20) into (19) gives

$$\frac{p_v + p_i - p_a - 2\sigma/r}{\rho_L} = \frac{1}{3} \frac{d^2 r}{dt^2} + \frac{2}{3} \frac{dr}{dt} + \frac{4\sigma}{3\rho_L r} \quad (21)$$

The partial pressure of the volatile gas, p_v , is specified by assuming a thermodynamic equilibrium between vapour and liquid at the bubble surface. Hence it depends on temperature, which in turn depends on the rates of mass and energy transfer.

Equation of Energy

Writing the equation of energy for spherical symmetry, incompressible fluid, negligible viscous dissipation, no energy fluxes other than ordinary conduction, and constant thermal properties:

$$\frac{\partial T}{\partial t} + u \frac{\partial T}{\partial R} = \alpha \left[\frac{\partial^2 T}{\partial R^2} + \frac{2}{R} \frac{\partial T}{\partial R} \right] + \frac{Q}{\rho_L C_{pL}} \quad (22)$$

where T = temperature at a point R from the bubble centre
 α = thermal diffusivity
 Q = "heat generation" per unit volume
 C_{pL} = specific heat of the liquid.

Substituting (17) into (22) gives:

$$\frac{\partial T}{\partial t} = \alpha \left[\frac{\partial^2 T}{\partial R^2} + \frac{2}{R} \frac{\partial T}{\partial R} \right] - \frac{\epsilon r \dot{r}}{R^2} \frac{\partial T}{\partial R} + \frac{D}{\rho_L C_{pL}} \quad (23)$$

Equation of Mass

Writing the equation of mass for a two component system in which chemical reaction effects are absent; spherical symmetry, constant mass density, no mass fluxes other than ordinary diffusion, and constant mass diffusivity:

$$\frac{\partial C}{\partial t} = D \left[\frac{\partial^2 C}{\partial R^2} + \frac{2}{R} \frac{\partial C}{\partial R} \right] \quad (24)$$

where C = mass concentration of volatile species in solution

D = mass diffusivity

Substituting equation (17) into (24) gives

$$\frac{\partial C}{\partial t} = D \left[\frac{\partial^2 C}{\partial R^2} + \frac{2}{R} \frac{\partial C}{\partial R} \right] - \frac{\epsilon r \dot{r}}{R^2} \frac{\partial C}{\partial R} \quad (25)$$

At this point there are three equations (equations (21), (23) and (25)), in three unknowns (r , t , C and T). Hence, from this system of equations, r can be solved for in terms of t .

Initial Conditions

The initial conditions for equations (21), (23) and (25) are

$$\dot{r}(0) = 0 \quad (26)$$

i.e. the initial bubble growth velocity is zero.

$$T(R,0) = T_0 \quad (27)$$

$$C(R,0) = C_0 \quad (28)$$

i.e. the liquid is initially of uniform temperature and composition.

Scriven (1959) also assumes that initially the bubble radius is some size which is equal to the equilibrium radius at the initial conditions

$$\text{i.e. } r(0) = \frac{2\sigma}{p_{v0} + p_{i0} - p_a} \quad (29)$$

where p_{v0} = partial pressure of volatile gas at time $t = 0$
 p_{i0} = partial pressure of inert gas at time $t = 0$

Boundary Conditions at Infinity

If the "heat generated" term in equation (23) is independent of position at large distances then

$$T(\infty, t) = T_0 + \frac{1}{\rho_L c_{pL}} \int_0^t Q(\infty, t') dt' \quad (30)$$

The concentration of the dissolved gas at a large distance from the electrode is assumed constant at C_0 , hence

$$C(\infty, t) = C_0 \quad (31)$$

Boundary Conditions at the Bubble Surface

The boundary conditions at the bubble surface are obtained from mass and energy balances over the bubble surface. A mass balance, much like one used in equation (15), but now including a diffusion term gives:

$$m \rho_g \dot{r} = C(r,t) \{ \dot{r} - u(r) \} + D \left(\frac{\partial C}{\partial R} \right)_{R=r}$$

$$= C(r,t) (1 - \epsilon) \dot{r} + D \left(\frac{\partial C}{\partial R} \right)_{R=r}$$

where m = mass fraction of volatile gas in the bubble.

The energy balance after neglecting the kinetic energy terms, changes in vapour density, surface energy and internal energy, and heat of mixing reduces to:

$$\rho_g \dot{r} \left\{ \bar{L} + C_{p_g} (T(r,t) - T_0) \right\} = \rho_L C_{p_L} (T(r,t) - T_0) (1 - \epsilon) \dot{r} + k_t \left(\frac{\partial T}{\partial R} \right)_{R=r}$$

(33)

where \bar{L} = latent heat of vaporization

k_t = thermal conductivity

The partial pressure of the volatile gases is obtained assuming thermodynamic equilibrium between the liquid and gas phases.

At this point Scriven (1959) proceeds to make some simplifying assumptions to aid the solution:

(a) Viscous terms in equation (21) are neglected. This assumption is justified for liquids near their boiling point. During the early stages of growth this assumption is poor.

(b) Inertia and surface tension terms in equation (10) are neglected since they are only significant in the initial expansion.

(c) p_1 is neglected in equation (10) - i.e. no inert gases are assumed to be present.

(d) The "heat generated" terms in equations (23) and (30) are neglected.

Scriven (1959) then proceeds to solve the system of equations, and shows for bubble growth controlled by mass transfer (e.g., electrolytic bubble growth);

$$r = 2\beta \sqrt{Dt} \quad (34)$$

where β , the growth constant, is defined as

$$\frac{-L(C_0 - C_{sat})}{D(g^0 L - C_{sat})} = \beta(1, \epsilon) = 2\beta^2 \exp(\beta^2 + 2\epsilon\beta^2) \int_{\beta}^{\infty} x^{-2} \exp(-x^2 - 2\epsilon\beta^2 x^{-2}) dx$$

where C_{sat} = saturation concentration of volatile gas in solution.

The function β can be evaluated, and Scriven (1959) presents a table where by the value of β for a given ϵ and ϵ can be obtained.

Hence $r = \sqrt{kt}$
 or $l = 2r = \sqrt{4kt}$ (35)

k = rate constant for bubble growth

l = bubble diameter

and $\frac{dl}{dt} = \sqrt{k}$ (36)

Westerheide et al (1961) and Glas et al (1964) found the bubble radius, r , to be proportional to $t^{1/2}$ experimentally.

In his solution, Scriven (1959) assumed that the bubble was of a finite size at time $t = 0$ although $R = 0$ at $t = 0$. Because of this assumption, Scriven's model does not describe the rapid initial growth observed by both Westerheide et al (1961) and Glas et al (1964) before the asymptotic

growth predicted by the model.

Glas et al (1964) investigated this initial growth period, and found that its duration was of the order of 0,0006 seconds. They found that although the asymptotic growth was independent of the type of electrode used, the rapid initial growth was dependent on the type of metal. The reason proposed for this by Glas et al (1964) was that during this initial period surface tension forces were significant. The harder metal electrodes (such as nickel) produced smoother surfaces, and hence fewer nucleation sites. So the harder metals experienced a longer initial wait before bubbles started to form. This gives rise to large local supersaturation which in turn causes the very rapid early growth phase.

From (34) and (36) it is clear that $k = 8 \sqrt{D}$. Table A 1.1 below shows the values of k measured by Westerheide et al (1961) and Glas et al (1964).

Table A 1.1 Values of k Measured by Westerheide et al (1961) and Glas et al (1964)

Run	k (m s ^{-1/2})
H ₂ on Pt 0,083 A/cm ²	4,918 x 10 ⁻⁵
H ₂ on Pt 0,0392 A/cm ²	2,821 x 10 ⁻⁵
H ₂ on Ni 0,084 A/cm ²	5,303 x 10 ⁻⁵
H ₂ on Ni 0,034 A/cm ²	2,632 x 10 ⁻⁵
H ₂ on Ni 0,041 A/cm ²	3,154 x 10 ⁻⁵
H ₂ on Ni 0,076 A/cm ²	4,296 x 10 ⁻⁵
Westerheide et al (1961)	5,800 x 10 ⁻⁵
Westerheide et al (1961)	3,795 x 10 ⁻⁵

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Appendix 2. Density Functions

In section 5 it was mentioned that a functional form was given to the distribution of bubble sizes leaving the electrode surface, $q(l)$. From the shape of the measured distribution, it was felt that three possible density functions could describe the shape:

(1) Gamma density function:

$$g(l) = \frac{b^{a+1}}{\Gamma(a+1)} l^a e^{-bl}$$

where $a > 0$

$b > 0$

$l \geq 0$

and $\Gamma(a+1) = \text{gamma function} = \int_0^{\infty} y^a e^{-y} dy.$

(2) Beta density function:

$$g(l) = A \left(\frac{l}{l_m} \right)^b \left(1 - \frac{l}{l_m} \right)^c$$

where $0 \leq \frac{l}{l_m} \leq 1$

$$A = \frac{\Gamma(b+c+1)}{\Gamma(b+1) \Gamma(c+1)}$$

(3) Normal density function:

$$g(\ell) = \frac{1}{\sigma\sqrt{2\pi}} \exp \left\{ -\frac{(\ell - \eta)^2}{2\sigma^2} \right\}$$

where η = mean of the distribution
 σ = standard deviation of the distribution

It was found that the normal and gamma density functions best fitted the measured size distributions of the bubbles leaving the electrode surface.

The n^{th} moment of a density function is defined as

$$\beta_n = \int_{-\infty}^{\infty} \ell^n g(\ell) d\ell \quad (1)$$

for $n = 1, 2, 3, \dots$

Since $g(\ell)$ is a density function,

$$\int_{-\infty}^{\infty} g(\ell) d\ell = 1$$

Hence the moments of the gamma and normal density functions can be found by evaluating the integral in (1). In both cases the integral can be evaluated analytically.

For the gamma density function it is found that:

$$\beta_n = \frac{(a+n)(a+n-1) \dots (a+1)}{a^n} \quad (2)$$

For the normal density function it can be shown that

$$\begin{aligned}
 \beta_1 &= \eta \\
 \beta_2 &= \eta^2 + \sigma^2 \\
 \beta_3 &= \eta^3 + 3\eta\sigma^2 \\
 \beta_4 &= \eta^4 + 6\eta^2\sigma^2 + 3\sigma^4 \\
 &\vdots
 \end{aligned}
 \tag{3}$$

From the first two moments the parameters of the density function can be evaluated. The first moment of a density function is equal to the mean of the distribution, while the second moment is equal to the sum of the variance and the square of the mean of the distribution. This is evident from the first two moments of the normal distribution. For the gamma density function, β_1 and β_2 can be evaluated as described above. Equation (2) then gives

$$\beta_1 = \frac{a+1}{b} \tag{4a}$$

$$\beta_2 = \frac{(a+2)(a+1)}{b^2} \tag{4b}$$

Solving (4a) and (4b) simultaneously gives

$$a = \frac{2\beta_1^2 - \beta_2}{\beta_2 - \beta_1} \tag{5a}$$

$$b = \left(\frac{2\beta_1^2 - \beta_2}{\beta_2 - \beta_1} \right) \frac{1}{\beta_1} \tag{5b}$$

Using these values of a and b the n^{th} moment of the gamma density function can be evaluated.

Appendix 2: Measuring Bubble Diameters on the Electrode Surface

The method of taking photographs of the bubbles on the electrode surface is described. These photographs were taken through a microscope and then enlarged in the dark room. In order to establish the magnification achieved by the process, a ruler was placed up against the anode after each run and photographed under the same conditions as were used in the experiment (using the same magnification on the microscope and through the same electrolyte). This photograph of the ruler was then developed and printed under the same conditions as the photographs of the bubbles. In this way a means of scaling the bubble diameters measured from the photographs was obtained.

The actual measuring of the bubble diameters was done with the aid of a Hewlett Packard model 10 desktop computer and a Hewlett Packard HP 7470 A plotter. A digitizing sight was fitted into the plotter pen holder, and then by moving the sight from one edge of a bubble to the other, and digitizing the two positions, the bubble diameter could be measured in terms of plotter units. To convert the measurements from plotter units into microns, the two edges of the millimeter scale on the photograph of the ruler were digitized first, and hence the length of the one millimeter scale was known in plotter units, hence

$$\text{Bubble diameter in microns} = \frac{\text{bubble diameter in plotter units}}{\text{millimeter scale in plotter units}} \times 1000$$

The factor of 1000 converts the measurement from millimeters to microns.

The program presented at the end of this appendix allows the user to measure the millimeter scale as many times as required, and an average measurement was then taken (subroutine "Scale"). The user can then proceed to measure the bubble diameters on the photographs (subroutine "Measure"). Having completed the measurements the data is stored on disc for future reference. The mean and standard deviation of the bubble diameters is calculated in lines 1270 - 1360. The data is then sorted into size intervals and a histogram of the size distribution is drawn in subroutine "Plot" on line 2350. A normal distribution curve based on the measured mean and standard deviation is superimposed on the histogram (lines 2900 - 2950). The program also allows the user to read in the data at a later date (subroutine "Read" in order to reproduce the calculations and plot.

```

10 ! Program to measure bubble diameter 1 to sort them into six
20 ! intervals so that a histogram can be drawn.

30 OPTION BASE 1
40 DIM Bubblesize(200),Data(200),Dummy(200),Interval(200)
50 CONTROL 1,12;1 ! SWITCH OFF THE KEY LABELS
60 GRAPHICS OFF
70 OUTPUT 2 USING "0,K";"BK" ! CLEAR THE SCREEN
80 LINPUT "Has the data been previously stored ?",Y%
90 IF UPC$(Y$(1,1))="Y" THEN ! If yes, then skip the measuring routine
100 GOSUB Read
110 GOTO 1160
120 END IF !

130 ! INPUT THE VISCOSITY, CURRENT & FLOWRATE USED.

140 LINPUT "What was the viscosity (cP) ?",Viscosity%
150 LINPUT "What was the current (Amps) ?",Current%
160 LINPUT "What was the flowrate (l/min) ?",Flow% !

170 ! Set up measuring routine

180 PLOTTER IS 705,"HPGL"
190 PRINTER IS 1
200 Flag=0
210 Count=1
220 CONTROL 1,12;1
230 OUTPUT 2;"SCRATCH KEYBX" ! Clear the present keys
240 OUTPUT 2 USING "0,K";"BK" ! Clear the screen
250 OFF KEY
260 GRAPHICS OFF
270 ON KEY 5 LABEL "Measure" GOSUB Measure ! GOTO MEASURING ROUTINE
280 ON KEY 9 LABEL "Scale" GOSUB Scale ! GOTO ROUTINE TO MEASURE SCALE
290 CONTROL 1,12;1
300 GOTO 300 !

```

310 Finished: ! When finished 'EDITKEYS' are reloaded

320 MASS STORAGE IS ":HP9121,700,0"
330 LOAD KEY "EDITKEYS"
340 MASS STORAGE IS ":HP9121,700,1"
350 CONTROL 1,12;0 ! SWITCH ON KEY LABELS
360 GRAPHICS OFF
370 OUTPUT 2 USING "0,K";"BK" ! CLEAR THE SCREEN
380 STOP !

```

390 Scale: ! Scale routine which assumes the scale used is a measure of mm.
400       ! The scale can be measured any number of times. An average scale
410       ! is then calculated.

420 OFF KEY 9 ! DEACTIVATE KEY 9
430 I=1
440 Scale=0
450 PRINT TABXY(1,1), "Enter the scale as many times as you want."
460 PRINT "When finished press 'ENTER' on the plotter twice at the same point."
470 Start: DISP "Enter left hand point of mm scale."
480 Digitize(Xscale1, Yscale1) ! DIGITIZE THE ONE SIDE OF THE SCALE
490 DISP "Enter right hand side of mm scale."
500 Digitize(Xscaler, Yscaler) ! DIGITIZE THE OTHER SIDE OF THE SCALE
510 DISP ""
520 Xscale=ABS(Xscaler-Xscale1)
530 Yscale=ABS(Yscaler-Yscale1)
540 IF NOT Xscale AND NOT Yscale THEN Leap ! FINISHED MEASURING ?

550 ! Now find the distance moved by the plotter.

560 IF NOT Xscale THEN
570   Scale=Yscale+Scale
580   PRINT TABXY(1,10), "Scale = "; Yscale
590 ELSE
600   Scale=Xscale+Scale
610   PRINT TABXY(1,10), "Scale = "; Xscale
620 END IF
630 I=I+1
640 GOTO Start ! Measure the scale again.

650 Leap: I=I-1
660 Scale=Scale/I ! CALCULATE THE AVERAGE SCALE
670 Flag=1 ! Set Flag to show that scale has been entered
680 RETURN !

```

694 Measure: Routine to measure bubble diameter

```

700 IF NOT Flag THEN ! Check to see if scale has been set
710 BEEP 500,.8
720 DISP "ENTER SCALE FIRST"
730 WAIT 1.5
740 RETURN
750 END IF
760 OFF KEY 5 ! DEACTIVATE KEY 5
770 CONTROL 1,12;1 ! SWITCH OFF THE KEY LABELS
780 OUTPUT 2 USING "X","Y" ! CLEAR THE SCREEN

790 Next:PRINT TABXY(1,1),"When finished press 'ENTER' on the plotter twice at the same point."
800 DISP "POSITION PEN ON ONE SIDE OF THE BUBBLE & PRESS 'ENTER' ON THE PLOTTER"
810 Digitize(Xright,Yright) ! DIGITIZE ONE SIDE OF THE BUBBLE
820 DISP "POSITION PEN ON THE OTHER SIDE OF THE BUBBLE & PRESS 'ENTER' ON THE PLOTTER"
830 Digitize(Xleft,Yleft) ! DIGITIZE THE OTHER SIDE OF THE BUBBLE
840 X=ABS(Xright-Xleft)
850 Y=ABS(Yright-Yleft)
860 IF NOT X AND NOT Y THEN ! Check to see if user is finished measuring
870 N=Count-1
880 REDIM Bubsiz(-N)
890 GOSUB Store ! If finished then store the data
900 GOTO Stat ! and then proceed with the analysis.
910 END IF
920 IF NOT X THEN
930 Bubsiz(Count)=Y
940 GOTO 1040
950 END IF
960 IF NOT Y THEN
970 Bubsiz(Count)=X
980 GOTO 1040
990 ELSE ! Can only accept a measurement in the X or Y direction
1000 PRINT TABXY(1,10),"GOPS !!!!!!!!!!!!!!!!!!!!!!"
1010 BEEP 500,.8
1020 GOTO Next
1030 END IF
1040 Bubsiz(Count)=Bubsiz(Count)*1000/Scale ! Convert measurement to microns
1050 PRINT TABXY(1,10),"No. of bubbles measured = ",Count
1060 PRINT USING 1070;Bubsiz(Count)
1070 IMAGE "The last bubble size was ",DDDD.DD," microns"
1080 Count=Count+1
1090 GOTO Next ! Go to Next to measure next bubble

```

```

1100 Stat: ! Start of statistical analysis of bubble sizes

1110 INPUT "Do you wish to end now and not proceed with the calculations ?",Y$
1120 IF UPC$(Y$(1,1))="Y" THEN GOTO Finished !

1130 ! Initialising variables

1140 REDIM Data(N)
1150 MAT Data= Bobsize
1160 GCLEAR
1170 Flag=0
1180 Pltr=3 ! Defines plotter position
1190 Pl="INTERNAL" ! Defines plotter type
1200 Prntr=1 ! Defines printer position
1210 PRINTER IS Prntr
1220 PLOTTER IS Pltr,Ps
1230 GCLEAR
1240 GINIT
1250 OUTPUT 2 USING "0,K";"BK" ! CLEAR SCREEN
1260 CONTROL 1,12;1 ! SWITCH OFF KEY LABELS

1270 ! CALCULATE THE MEAN

1280 Mean=SUM(Data) ! Mean=mean bubble diameter
1290 Mean=Mean/N !

1300 ! CALCULATE THE STANDARD DEVIATION

1310 MAT Dummy= (Mean)-Data
1320 MAT Dummy= Dummy . Dummy
1330 Stddev=SUM(Dummy) ! Stddev=standard deviation of bubble diameters
1340 Stddev=SQR(Stddev/(N-1))
1350 PRINT USING 13a0,Mean,Stddev
1360 IMAGE "Mean = ",DDD.DDD," microns"; "Standard deviation = ",DDD.DDD," microns" !

1370 ! DIVIDE DATA INTO INTERVALS

1380 Smallest=MIN(Data(1)) ! Smallest=smallest bubble diameter
1390 Largest=MAX(Data(1)) ! Largest =largest bubble diameter
1400 PRINT USING 1410;Largest,Smallest
1410 IMAGE /,"The largest bubble is ",DDD.DD," microns",/,"The smallest bubble is ",DDD.DD," microns"
1420 Interval:INPUT "Enter the number of intervals you require",Divno
1430 IF Divno(1 OR FRACT(Divno))<>0 THEN ! MAKE SURE INPUT IS 10 AND AN INTEGER
1440 BEEP 500,1
1450 DISP "THAT IS NOT FUNNY"
1460 WAIT 2
1470 GOTO 1420
1480 END IF
1490 REDIM Interval(Divno) ! Interval()=number of bubbles in each interval
1500 MAT Interval= (0)
1510 Divlen=(Largest-Smallest)/Divno ! Divlen=length of each interval

1520 ! Loop to place each bubble in its correct interval

1530 FOR I=1 TO N
1540 FOR J=1 TO Divno
1550 IF Data(I)<=Smallest+J*Divlen AND Data(I)>Smallest+(J-1)*Divlen THEN
1560 Interval(J)=Interval(J)+1
1570 GOTO Skip
1580 END IF
1590 NEXT J
1600 BEEP 500,1
1610 DISP "ERROR IN Interval" ! A CHECK IN CASE NOT ALL BUBBLES ARE FOUND
1620 STOP
1630 Skip:NEXT I

```

```

1100 Start: Start of statistical analysis of bubble sizes

1110 INPUT "Do you wish to end now and not proceed with the calculations ?",Y$
1120 IF UPC$(Y$(1,1))="Y" THEN GOTO Finished '

1130 ! Initialising variables

1140 REDIM Data(N)
1150 MAT Data= Bobsize
1160 GCLEAR
1170 Flag=0
1180 Pltr=3 ! Defines plotter position
1190 Ps="INTERNAL" ! Defines plotter type
1200 Prntr=1 ! Defines printer position
1210 PRINTER IS Prntr
1220 PLOTTER IS Pltr,Ps
1230 GCLEAR
1240 GINIT
1250 OUTPUT 2 USING "0,K";"BK" ! CLEAR SCREEN
1260 CONTROL 1,12;1 ! SWITCH OFF KEY LABELS

1270 ! CALCULATE THE MEAN

1280 Mean=SUM(Data) ! Mean=mean bubble diameter
1290 Mean=Mean/N !

1300 ! CALCULATE THE STANDARD DEVIATION

1310 MAT Dummy= (Mean)-Data
1320 MAT Dummy= Dummy . Dummy
1330 Stdev=SUM(Dummy) ! Stdev=standard deviation of bubble diameters
1340 Stdev=SQR(Stdev/(N-1))
1350 PRINT USING 1360,Mean,Stdev
1360 IMAGE "Mean = ",DDD.DDD," microns",/, "Standard deviation = ",DDD.DDD," microns" !

1370 ! DIVIDE DATA INTO INTERVALS

1380 Smallest=MIN(Data(8)) ! Smallest=smallest bubble diameter
1390 Largest=MAX(Data(8)) ! Largest =largest bubble diameter
1400 PRINT USING 1410;Largest,Smallest
1410 IMAGE /,"The largest bubble is ",DDD.DD," microns",/, "The smallest bubble is ",DDD.DD," microns"
1420 Interval:INPUT "Enter the number of intervals you require",Divno
1430 IF Divno(1 OR FRACT(Divno))<>0 THEN ! MAKE SURE INPUT IS >0 AND AN INTEGER
1440 BEEP 500,1
1450 DISP "THAT IS NOT FUNNY"
1460 WAIT 2
1470 GOTO 1420
1480 END IF
1490 REDIM Interval(Divno) ! Interval()=number of bubbles in each interval
1500 MAT Interval= (0)
1510 Divlen=(Largest-Smallest)/Divno ! Divlen=length of each interval

1520 ! Loop to place each bubble in its correct interval

1530 FOR I=1 TO N
1540 FOR J=1 TO Divno
1550 IF Data(I)<=Smallest+J*Divlen AND Data(I)>Smallest+(J-1)*Divlen THEN
1560 Interval(J)=Interval(J)+1
1570 GOTO Skip
1580 END IF
1590 NEXT J
1600 BEEP 500,1
1610 DISP "ERROR IN Interval" ! A CHECK IN CASE NOT ALL BUBBLES ARE FOUND
1620 STOP
1630 Skip:NEXT I

```

```
1640 GOSUB Print ! Go to printing routine
1650 LINPUT "Do you wish to change the number of intervals ?",Y$
1660 IF UPC$(Y$(1,1))="Y" THEN 1420
1670 IF UPC$(Y$(1,1))("<"N" THEN
1680     BEEP 500,1
1690     DISP "BE SERIOUS"
1700     WAIT 1
1710     GOTO 1650
1720 ELSE
1730     LINPUT "Do you wish to print this result ?",Y$
1740     IF UPC$(Y$(1,1))("<"Y" THEN 1780
1750     Prnr=781
1760     GOSUB Print
1770     Prnr=1
1780     END IF
1790     PRINTER IS Prnr
1800     MAT Interval= (1/N)*Interval
1810     Top=MAX(Interval(X)) ! Top=size of the largest interval
1820     Top=(INT(Top*10)+1)/10
1830     GOSUB Plot ! Goto plotting routine
1840     GOTO Finished ! Go to Finished to end
1850     STOP !
```


1860 PRINT: Printing routine to output results

```

1870 PRINTER IS Prntr
1880 IF Prntr=1 THEN PRINT CHR$(12)
1890 PRINT USING 1900;Viscosity%,Current%,Flow%
1900 IMAGE "Solution viscosity is ",K," centipoise",/, "Current used was ",X," amps",/, "The flowrate is ",K," l/min",//
1910 PRINT "The number of points used is ";N
1920 PRINT USING 1930;Mean,Stddev
1930 IMAGE "Mean bubble diameter      = ",DDD.DDD," microns",/, "Standard deviation      = ",DDD.DDD," microns"
1940 PRINT USING 1950;Largest,Smallest
1950 IMAGE "Largest bubble diameter = ",DDD.DDD," microns",/, "Smallest bubble diameter = ",DDD.DDD," microns",///
1960 PRINT "INTERVAL NUMBER",TAB(21),"INTERVAL RANGE (microns)",TAB(60),"NUMBER OF BUBBLES"
1970 PRINT "-----",TAB(21),"-----",TAB(60),"-----"
1980 FOR I=1 TO Divno
1990   Y$(1,5)=VAL$(INT((Smallest+(I-1)*Divlen)*100)/100)
2000   Y$(6,8)=" - "
2010   Y$(9,13)=VAL$(INT((Smallest+I*Divlen)*100)/100)
2020   PRINT TAB(5),I,TAB(25),Y$,TAB(70),Interval(I)
2030 NEXT I
2040 RETURN

```

2050 Plot: Plotting routine

2060 ! This routine plots a histogram of the bubble diameters on the
 2070 ! surface of the electrode, and then draws a normal curve
 2080 ! calculated from the mean and standard deviation of the bubble
 2090 ! diameters through the histogram. The mean and the standard
 2100 ! deviation are also shown on the curve

2110 PLOTTER IS Pltr,P%
 2120 ALPHA OFF
 2130 GRAPHICS ON
 2140 IF Pltr=3 THEN GCLEAR ! If the plotter is the screen then clear
 2150 IF Pltr=3 THEN 2230 ! If the plotter is'nt the screen then pick up a pen
 2160 GRAPHICS OFF
 2170 OUTPUT 2 USING "G,K";"BK" ! Clear the ALPHA screen
 2180 DISP "Put a pen in the plotter and press 'CONT' when ready"
 2190 PAUSE
 2200 ALPHA OFF
 2210 GRAPHICS ON
 2220 OUTPUT 705,"SP1" ! Pick up a pen
 2230 DEG
 2240 LINE TYPE 1
 2250 LDIR 0
 2260 WINDOW Smallest-200Divlen,Largest+Divlen/2,Top,Top81.5 ! Plot scale
 2270 LORG 5
 2280 CSIZE 1,.5
 2290 CLIP Smallest,Largest,0,Top
 2300 AXES Divlen,.05,Smallest,0 ! Draw axes
 2310 CLIP OFF !

2320 ! Draw the histogram

2330 FOR I=1 TO Divno
 2340 IF Interval(I)=0 THEN 2370
 2350 CLIP Smallest+(I-1)*Divlen,Smallest+I*Divlen,0,Interval(I)
 2360 FRAME
 2370 NEXT I
 2380 CLIP OFF
 2390 CSIZE 3,.5
 2400 LORG 5 !

2410 ! Label the X axis

2420 FOR I=0 TO Divno
 2430 MOVE Smallest+I*Divlen,-Top/30
 2440 LABEL USING "DDD.DD",Smallest+I*Divlen
 2450 NEXT I
 2460 MOVE (Largest+Smallest)/2,-Top/10
 2470 CSIZE 5,.5
 2480 LABEL "Bubble diameter (microns)"
 2490 CSIZE 3,.5 !

2500 ! Label the Y axis

2510 FOR I=0 TO Top STEP .05
 2520 MOVE Smallest-Divlen/4,I
 2530 LABEL USING "Z.DD",I
 2540 NEXT I
 2550 CSIZE 4,.5
 2560 MOVE Smallest-Divlen,Top/2
 2570 LDIR 90
 2580 LORG 6

2590 LABEL "Fraction of bubbles" !

2600 ! Graph heading

2610 LORG 5

2620 LDIR 0

2630 CSIZE 8,1

2640 MOVE (Largest+Smallest)/2,Top*1.2

2650 FOR I=1 TO LEN(File\$)

2660 IF File\$(I,I)="_" THEN File\$(I,I)="." ! place "." in the file name
! with "."

2670 NEXT I

2690 LABEL File\$

2700 LINE TYPE 3,1

2710 LDIR 8

2720 LORG 5 !

2730 ! Label mean and standard deviation

2740 MOVE Mean,0

2750 IDRAW 0,Top

2760 IMOVE -Stddev,0

2770 LINE TYPE 1

2780 CSIZE 2,.5

2790 LABEL CHR\$(124)

2800 MOVE Mean-Stddev,Top

2810 IDRAW 2*Stddev,0

2820 LABEL CHR\$(124)

2830 MOVE Mean,Top

2840 LORG 4

2850 LABEL "M"

2860 MOVE Mean-Stddev/2,Top

2870 LABEL "-S"

2880 MOVE Mean+Stddev/2,Top

2890 LABEL "+S" !

2900 ! Fit a normal curve

2910 MOVE Smallest,0

2920 FOR I=Smallest TO Largest STEP Divlen/10

2930 Exponent=Divlen*EXP(-((I-Mean)/Stddev)²/2)/(Stddev*SQRT(2*PI))

2940 DRAW I,Exponent

2950 NEXT I

2960 IF Pltr=3 THEN 2980

2970 OUTPUT 705;"SP" ! Put pen down

2980 IF Flag=1 THEN 3140 ! If Flag is set then end

2990 GRAPHICS OFF

3000 LINPUT "Do you want a hard copy ?",Y\$

3010 IF UPC\$(Y\$(1,1))="Y" THEN ! If yes then output to plotter

3020 Flag=1

3030 Pltr=705

3040 P\$="HPGL"

3050 ALPHA OFF

3060 GRAPHICS ON

3070 GOTO Plot

3080 END IF

3090 GRAPHICS OFF

3100 LINPUT "Do you wish to make any changes ?",Y\$

3110 IF UPC\$(Y\$(1,1))="Y" THEN GOTO Interval

3120 IF UPC\$(Y\$(1,1))="N" THEN GOTO 3140

3130 GOTO 3100

3140 RETURN !

3150 Store Store data in disc

3160 MASS STORAGE IS 'HP9121,700,1'
3170 LINPUT 'What will the file be called?',Files
3180 CREATE BDAT Files,2,1792
3190 ASSIGN @File TO Files
3200 OUTPUT @File,1,N,Viscosity's Current's Flow's
3210 OUTPUT @File,2;Subsize(2)
3220 ASSIGN @File TO 2
3230 RETURN

3240 Read: ! Read data off disc

3250 MASS STORAGE IS ':4P9121,700,1'

3260 LIMPUT "Enter the name of the data file" Files

3270 ASSIGN @File TO Files

3280 ENTER @File,1;N,Viscosity\$,Current\$,Flow\$

3290 REDIM Data(N),Dummy(N)

3300 ENTER @File,2;Data(\$)

3310 ASSIGN @File TO \$

3320 RETURN

3330 STOP

3340 END !

3350 Digitize: | Subroutine to digitize points on the plotter

```
3360 SUB Digitize(X,Y)
3370 ASSIGN EP TO 765 | Assign an I/O path to the plotter
3380 OUTPUT EP USING "K";"DP" | Plotter is ready to digitize a point
3390 REPEAT | Loop until the 'ENTER' is pressed on the
3400 | plotter.
3410 OUTPUT EP USING "K";"OS" | Ask plotter if 'ENTER' has been pressed.
3420 ENTER EP;S | Receive plotter response.
3430 UNTIL BIT(S,2)() | Check if 'ENTER' has been pressed.
3440 OUTPUT EP USING "V";"OD" | Tells plotter to send its present position.
3450 ENTER EP;X,Y,P | Enter digitized point (plotter position).
3460 SUBEND !
```

Appendix 4 Measuring Viscosity

The viscosity of the electrolytes used was measured using an Ostwalds Viscometer. The method is outlined below.

1. The Ostwalds Viscometer

An Ostwalds Viscometer is essentially a "U" tube which has one limb a capillary (see figure A 4.1). There is a small bulb at the top of the capillary into which a volume of liquid is sucked from the bulb in the other limb. The liquid is then allowed to flow down through the capillary, and the length of time the volume of liquid takes to flow down the capillary is measured.

The flow of liquid through a capillary is described by the Poiseuille equation:

$$V = \frac{\pi Pr^3 t}{8\ell\mu} \quad (1)$$

where

- V = volume of liquid passing through the capillary
- r = radius of the capillary
- t = time taken for V to flow through the capillary
- ℓ = length of the capillary
- μ = viscosity of the liquid
- P = pressure difference due to the hydrostatic head between the two liquid levels.

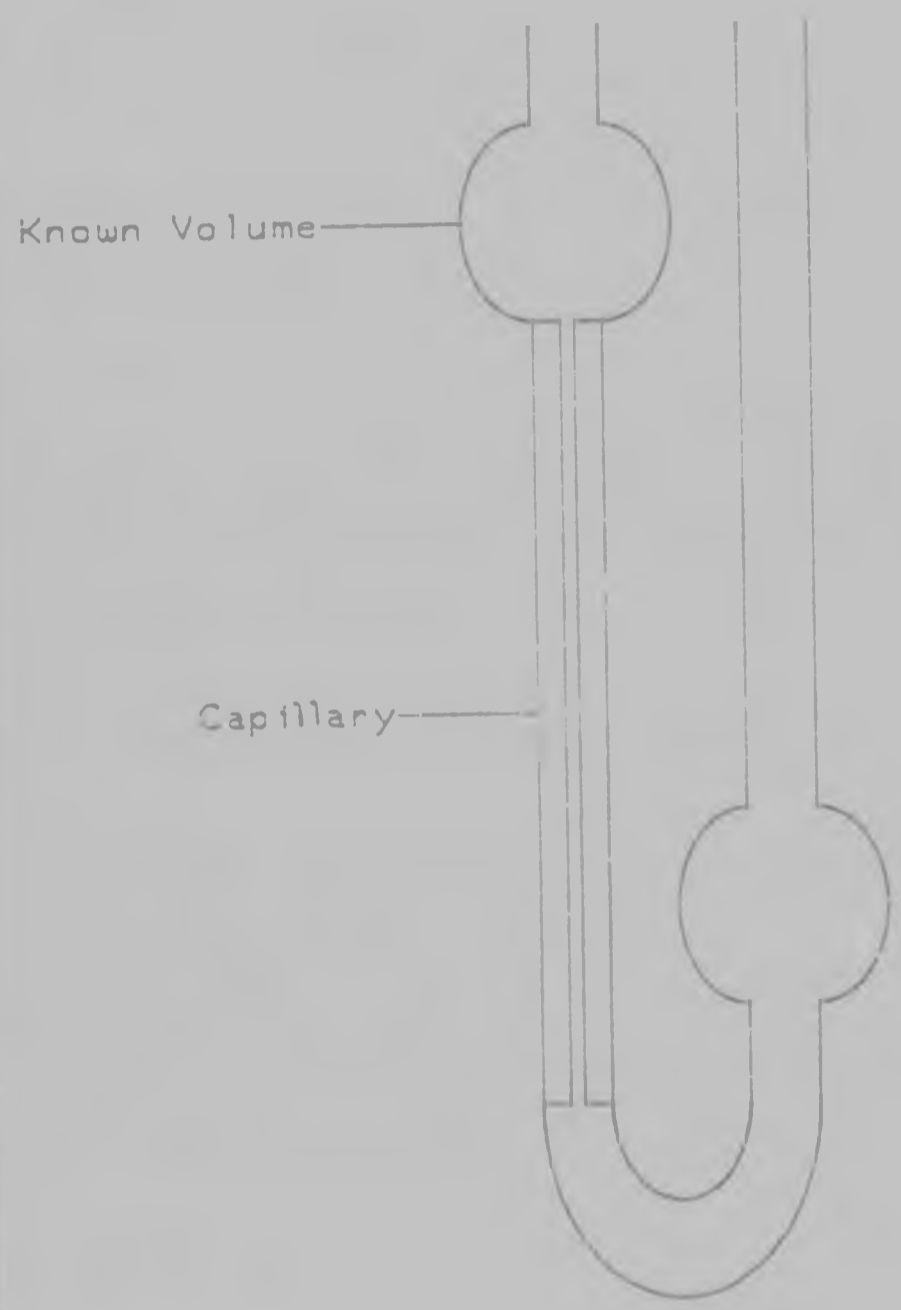


Figure A4.1 Ostwalds Viscometer

Now $P = \rho gh$ (2)

where $\rho =$ density of the liquid

$h =$ difference in height between the two liquid levels

Combining (1) and (2) and solving for μ

$$\mu = \frac{\pi \rho g h r^4}{8 l v} \quad (3)$$

For a given viscometer, the term $\frac{\pi g h r^4}{8 l v}$ is constant, and equal to k say.

Hence (3) becomes

$$\mu = k \rho t \quad (4)$$

In order to find k , the viscometer must be calibrated using a liquid of known density and viscosity. Having found k , the viscosity of a liquid whose density is known can easily be measured.

1.1 Calibration of the Ostwald Viscometer

Since density and viscosity are functions of temperature, k will also be a function of temperature. For this reason it is important to calibrate a viscometer at the temperature at which the viscosities are to be measured. The experiments were performed at approximately 25°C, and so the viscometer was calibrated at this temperature.

Pure water was used to calibrate the viscometer. Perry (1973) gives:

At 25° C $\mu = 8,904 \times 10^{-4}$ kg/ms

$\rho = 997,07$ kg/m³

The times for the water to flow through the capillary in nine series of runs are tabulated in table A 4.1 below

Table A 4.1 Calibration of Ostwalds Viscometer at 25° C

Run	Time (s)
1	106,8
2	107,0
3	107,1
4	107,2
5	106,9

The average time of 107,0 s was used. Hence

$$k = \frac{u}{\rho t} = \frac{8,904 \times 10^{-4}}{997,07 \times 107}$$

$$\therefore k = 8,346 \times 10^{-9} \text{ m}^2/\text{s}^2$$

2. Measuring the Electrolyte Viscosity

In order to ensure the temperature of the electrolyte remained constant during measurement, the viscometer was suspended in a constant temperature bath. The system was allowed to stand for a while until the electrolyte temperature reached the bath temperature. A temperature of 25° C was chosen because it was found that after the electrolyte had been under the spot lights during the experiment, its temperature was approximately 25° C.

In calculating the density of the solution the contribution from the sulphuric acid was ignored since it was in such a small quantity (18 ml in 3000 ml). The density of the glycerine/water mixture was calculated

by assuming no volume change on mixing, and hence it is simply the sum of the mass of water and glycerine divided by the sum of the volumes, i.e.

$$\rho = \frac{m_{\text{H}_2\text{O}} + m_{\text{glycerine}}}{V_{\text{H}_2\text{O}} + V_{\text{glycerine}}}$$

$$= \frac{V_{\text{H}_2\text{O}} \rho_{\text{H}_2\text{O}} + V_{\text{glycerine}} \rho_{\text{glycerine}}}{V_{\text{H}_2\text{O}} + V_{\text{glycerine}}}$$

The density of the magnesium sulphate/water solution was obtained from tables in the Handbook of Chemistry and Physics (1976).

The time t was measured several times, and an average was used in calculating the viscosity.

Appendix 5 Results

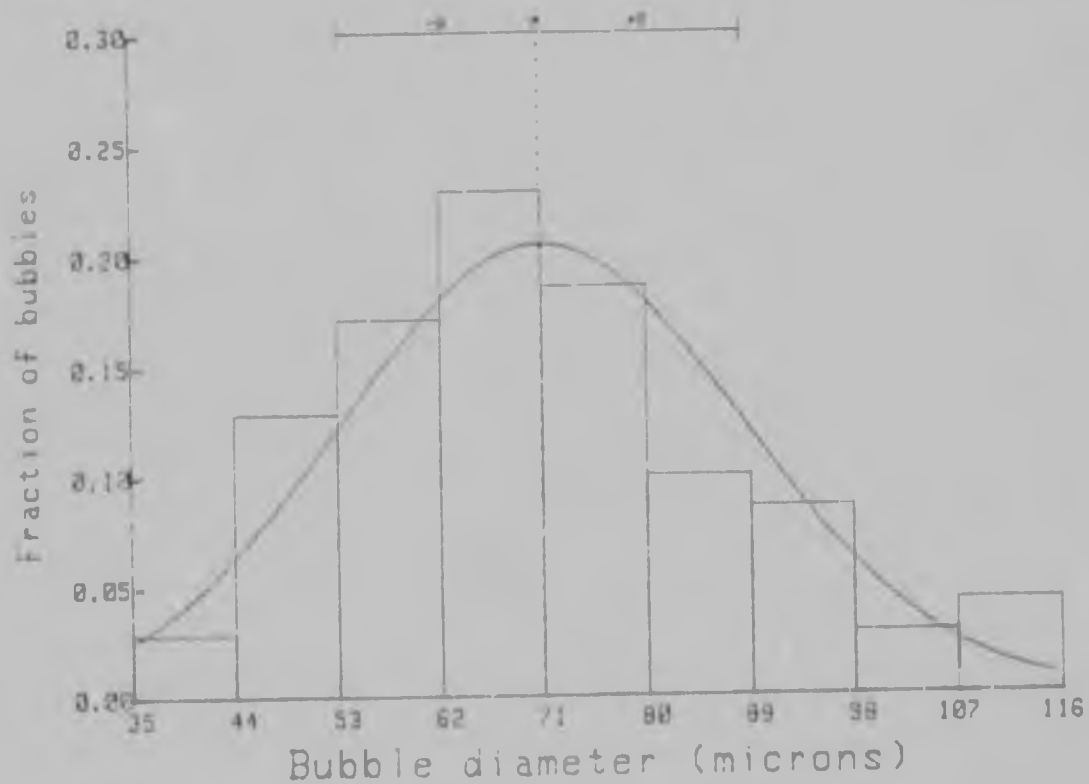
In this appendix a complete set of results is presented from all the experiments performed. The results obtained from the photographs of the bubbles on the electrode surface are presented first followed by the results obtained from the movies of the bubbles leaving the electrode surface. The results from the bubbles on the surface which are presented here take the form of a computer print out and histogram from the program presented in appendix 3. The print out gives the electrolyte viscosity, current and flowrate used during the run, as well as the mean and standard deviation of the bubble diameters measured as well as the size of the largest and smallest bubbles measured. The table below this information gives the fraction of bubbles in the size intervals into which the bubbles were sorted. The histogram is a graphical presentation of this table. A normal curve calculated from the mean and standard deviation of the measured distribution is drawn over the histogram. The vertical dotted line denotes the position of the mean bubble diameter, and the bar at the top of the figure denotes plus and minus the standard deviation from the mean. These results are presented in the following order: runs using water/sulphuric acid electrolyte, runs using glycerine in the electrolyte, runs using magnesium sulphate in the electrolyte, runs using zinc sulphate in the electrolyte.

Water / sulphuric acid electrolyte

Solution viscosity was 0.92 centipoise
 Current used was 1 amp
 The flowrate was 2.0 l/min

Mean bubble diameter = 71.079 microns
 Standard deviation = 17.59E microns
 Largest bubble diameter = 116.397 micron
 Smallest bubble diameter = 35.104 microns

INTERVAL NUMBER	INTERVAL RANGE (microns)	FRACTION OF BUBBLES
1	35.1 - 44.13	2.8571E-02
2	44.13 - 53.16	1.2857E-01
3	53.16 - 62.2	1.7143E-01
4	62.2 - 71.23	2.2857E-01
5	71.23 - 80.26	1.8571E-01
6	80.26 - 89.29	1.0000E-01
7	89.29 - 98.33	8.5714E-02
8	98.33 - 107.3	2.8571E-02
9	107.3 - 116.3	4.2857E-02

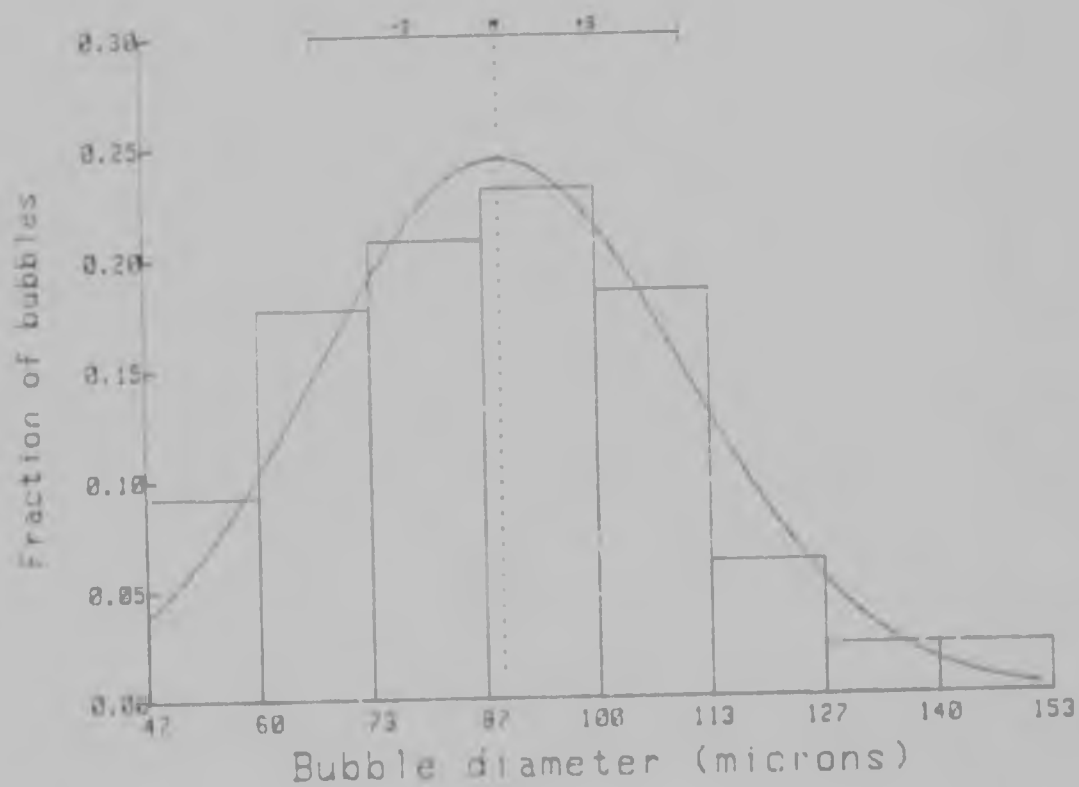


Water/sulphuric acid electrolyte

Solution viscosity was 0.9 centipoise
 Current used was 1 amp
 The flowrate was 2 l/min

Mean bubble diameter = 88.740 microns
 Standard deviation = 21.705 microns
 Largest bubble diameter = 153.201 microns
 Smallest bubble diameter = 46.899 microns

INTERVAL NUMBER	INTERVAL RANGE (microns)	FRACTION OF BUBBLES
1	46.89 - 60.18	9.2308E-02
2	60.18 - 73.47	1.7692E-01
3	73.47 - 86.76	2.0769E-01
4	86.76 - 100.0	2.3077E-01
5	100.0 - 113.3	1.8462E-01
6	113.3 - 126.6	6.1538E-02
7	126.6 - 139.9	2.3077E-02
8	139.9 - 153.2	2.3077E-02

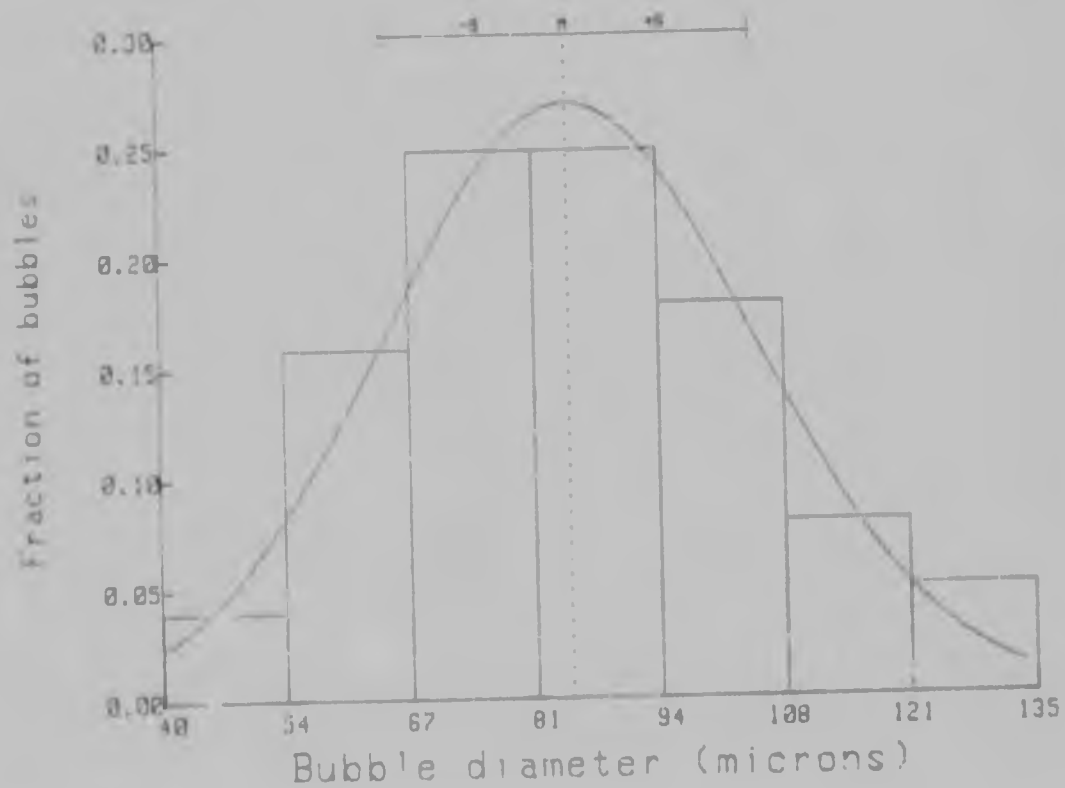


Water / sulphuric acid electrolyte

Solution viscosity was 0.92 centipoise
 Current used was 1 amp
 The flowrate was 3.75 l/min

Mean bubble diameter = 84.496 microns
 Standard deviation = 20.112 microns
 Largest bubble diameter = 134.975 microns
 Smallest bubble diameter = 39.991 microns

INTERVAL NUMBER	INTERVAL RANGE (microns)	FRACTION OF BUBBLES
1	39.99 - 53.56	3.9604E-02
2	53.56 - 67.12	1.5842E-01
3	67.12 - 80.69	2.4752E-01
4	80.69 - 94.26	2.4752E-01
5	94.26 - 107.8	1.7822E-01
6	107.8 - 121.4	7.9208E-02
7	121.4 - 134.9	4.9505E-02

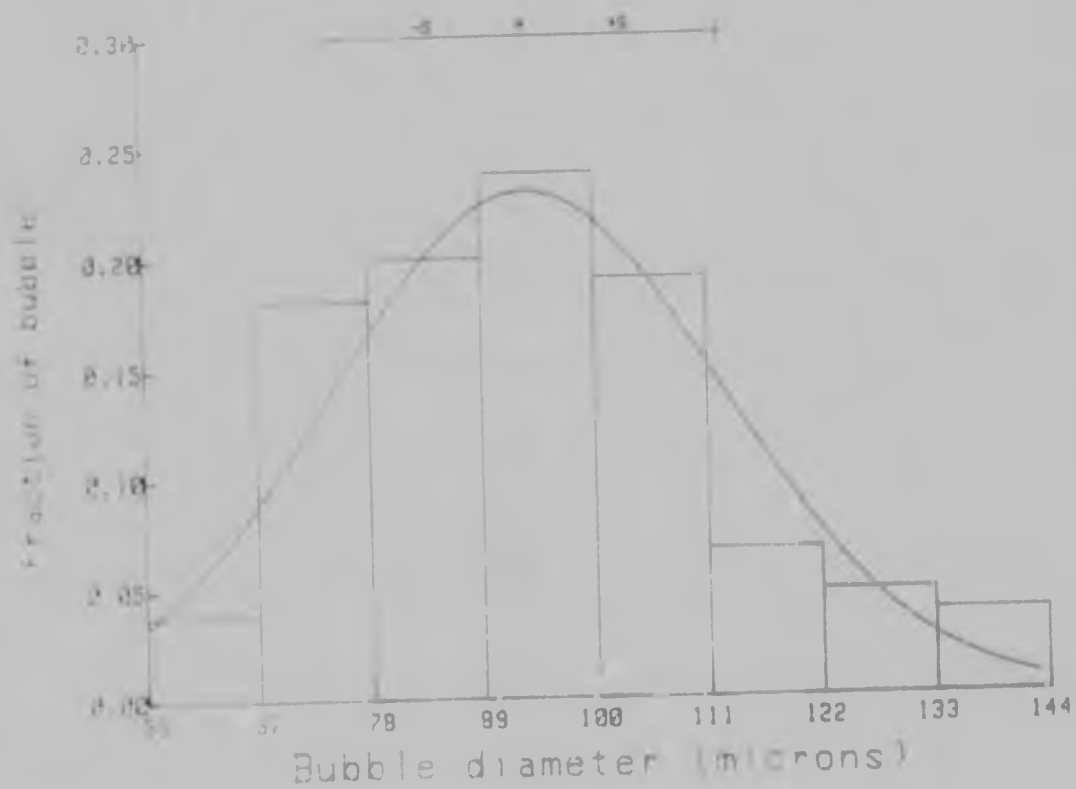


Water sulphuric acid electrolyte

Solution viscosity was 0.72 centipoise
 Current used was 1 amp
 The flow rate was 4 ml/min

Mean bubble diameter = 93.080 microns
 Standard deviation = 19.197 microns
 Largest bubble diameter = 143.931 microns
 Smallest bubble diameter = 55.497 microns

INTERVAL NUMBER	INTERVAL RANGE (microns)	FRACTION OF BUBBLES
1	55.49 - 66.55	3.8095E-02
2	66.55 - 77.6	1.8095E-01
3	77.6 - 88.65	2.0000E-01
4	88.65 - 99.71	2.3810E-01
5	99.71 - 110.7	1.9048E-01
6	110.7 - 121.8	6.6667E-02
7	121.8 - 132.8	4.7619E-02
8	132.8 - 143.9	3.8095E-02

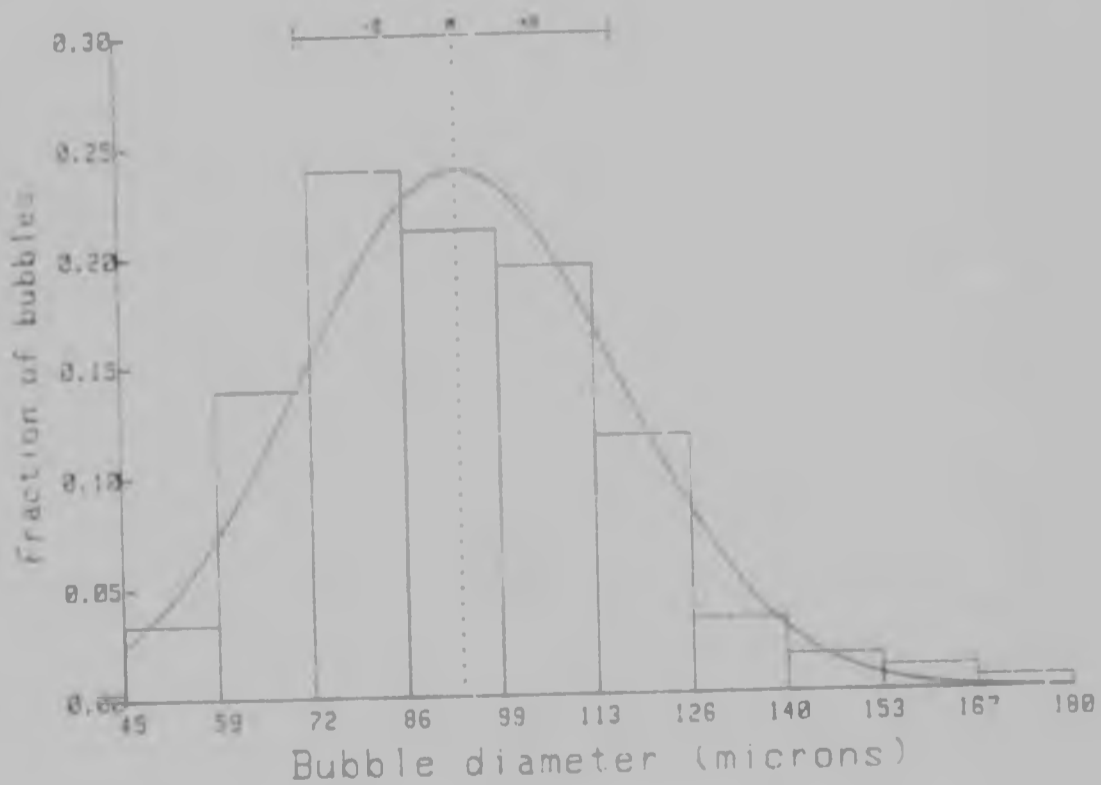


Water/Sulphuric acid electrolyte

Solution viscosity was 0.92 centipoise
 Current used was 3 amp
 The flowrate was 2 l/min

Mean bubble diameter = 73.423 microns
 Standard deviation = 22.565 microns
 Largest bubble diameter = 180.250 microns
 Smallest bubble diameter = 45.177 microns

INTERVAL NUMBER	INTERVAL RANGE (microns)	FRACTION OF BUBBLES
1	45.17 - 58.68	3.3333E-02
2	58.68 - 72.19	1.3889E-01
3	72.19 - 85.69	2.3889E-01
4	85.69 - 99.2	2.1111E-01
5	99.2 - 112.7	1.9444E-01
6	112.7 - 126.2	1.1667E-01
7	126.2 - 139.7	3.3333E-02
8	139.7 - 153.2	1.6667E-02
9	153.2 - 166.7	1.1111E-02
10	166.7 - 180.2	5.5556E-03

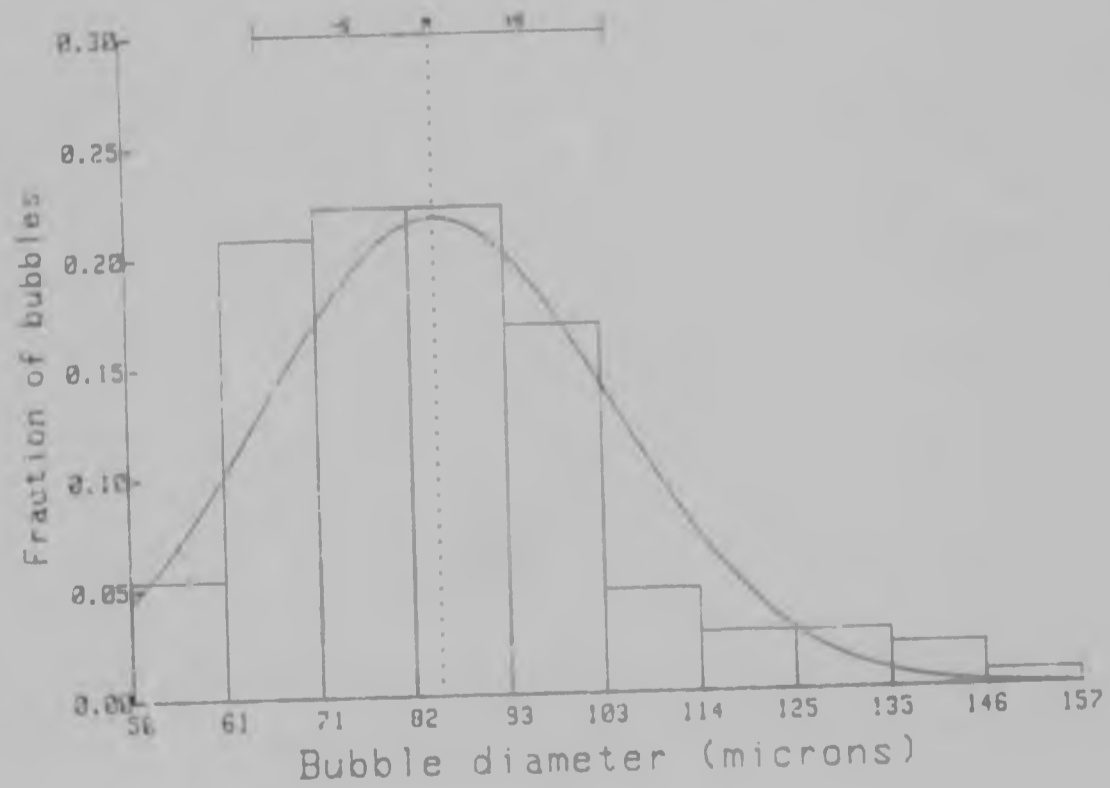


Water/sulphuric acid electrolyte

Solution viscosity was 0.92 centipoise
 Current used was 3 amp
 The flowrate was 3.75 l/min

Mean bubble diameter = 84.858 microns
 Standard deviation = 19.671 microns
 Largest bubble diameter = 156.807 microns
 Smallest bubble diameter = 49.873 microns

INTERVAL NUMBER	INTERVAL RANGE (microns)	FRACTION OF BUBBLES
1	49.87 - 60.56	5.3691E-02
2	60.56 - 71.25	2.0865E-01
3	71.25 - 81.95	2.2148E-01
4	81.95 - 92.64	2.2148E-01
5	92.64 - 103.3	1.6779E-01
6	103.3 - 114.0	4.6980E-02
7	114.0 - 124.7	2.6846E-02
8	124.7 - 135.4	2.6846E-02
9	135.4 - 146.1	2.0134E-02
10	146.1 - 156.8	6.7114E-03

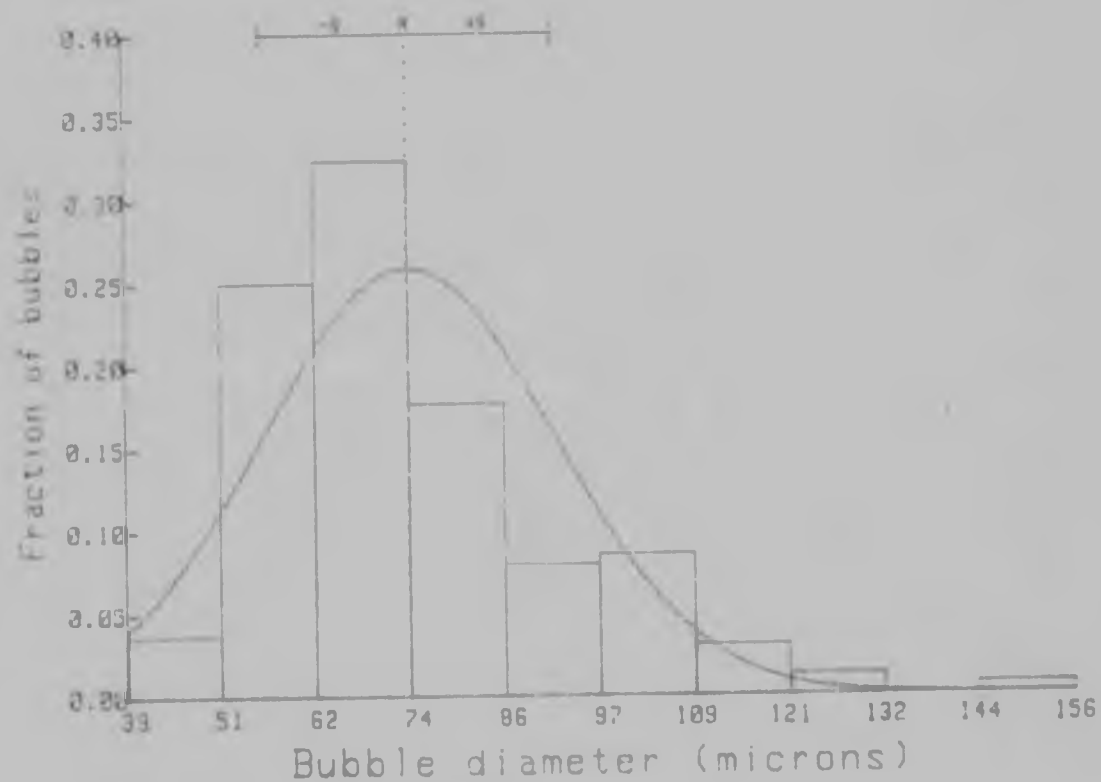


Water/sulphuric acid electrolyte

Solution viscosity was 0.92 centipoise
 Current used was 3 amp
 The flowrate was 4.60 l/min

Mean bubble diameter = 73.748 microns
 Standard deviation = 17.984 microns
 Largest bubble diameter = 155.535 microns
 Smallest bubble diameter = 38.884 microns

INTERVAL NUMBER	INTERVAL RANGE (microns)	FRACTION OF BUBBLES
1	38.88 - 50.54	3.5565E-02
2	50.54 - 62.21	2.5000E-01
3	62.21 - 73.87	3.2317E-01
4	73.87 - 85.54	1.7683E-01
5	85.54 - 97.2	7.9268E-02
6	97.2 - 108.8	8.5366E-02
7	108.8 - 120.5	3.0488E-02
8	120.5 - 132.2	1.2195E-02
9	132.2 - 143.8	0.0000E+00
10	143.8 - 155.5	6.0976E-03

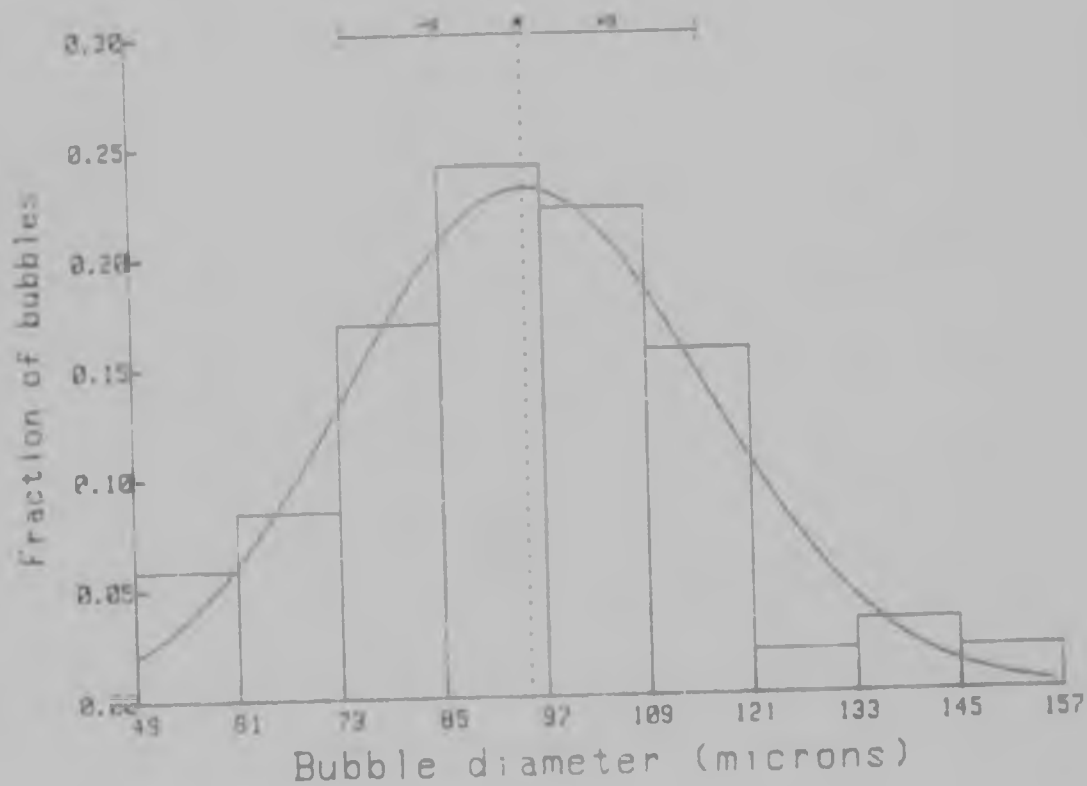


Water / sulphuric acid electrolyte

Solution viscosity was 0.92 centipoise
 Current used was 5 amp
 The flowrate was 2 l/min

Mean bubble diameter = 95.050 microns
 Standard deviation = 20.823 microns
 Largest bubble diameter = 157.174 microns
 Smallest bubble diameter = 49.064 microns

INTERVAL NUMBER	INTERVAL RANGE (microns)	FRACTION OF BUBBLES
1	49.06 - 61.07	5.8442E-02
2	61.07 - 73.08	8.4416E-02
3	73.08 - 85.1	1.6883E-01
4	85.1 - 97.11	2.4026E-01
5	97.11 - 109.1	2.2078E-01
6	109.1 - 121.1	1.5584E-01
7	121.1 - 133.1	1.9481E-02
8	133.1 - 145.1	3.2468E-02
9	145.1 - 157.1	1.9481E-02

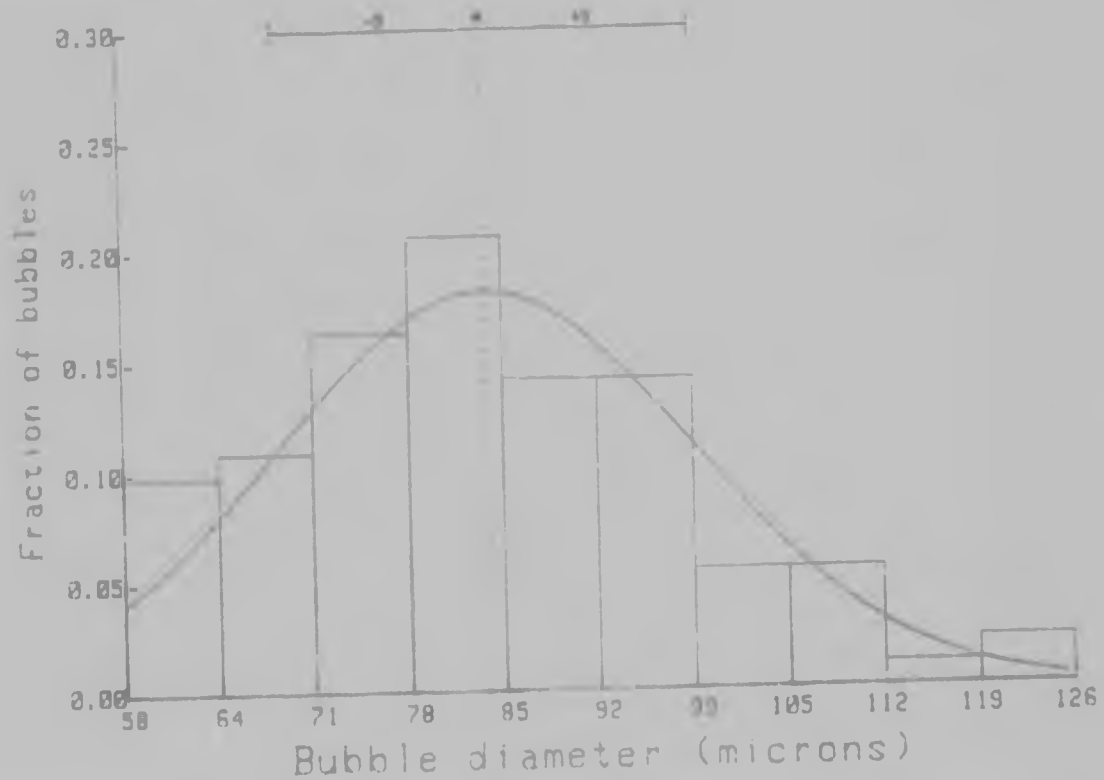


Water/Sulphuric acid electrolyte

Solution viscosity was 0.92 centipoise
 Current used was 5 amp
 The flowrate was 3.75 l/min

Mean bubble diameter = 83.670 microns
 Standard deviation = 11.990 microns
 Largest bubble diameter = 125.839 microns
 Smallest bubble diameter = 57.657 microns

INTERVAL NUMBER	INTERVAL RANGE (microns)	FRACTION OF BUBBLES
1	57.65 - 64.47	9.7826E-02
2	64.47 - 71.29	1.0870E-01
3	71.29 - 78.11	1.6304E-01
4	78.11 - 84.92	2.0652E-01
5	84.92 - 91.74	1.4130E-01
6	91.74 - 98.56	1.4130E-01
7	98.56 - 105.3	5.4348E-02
8	105.3 - 112.2	5.4348E-02
9	112.2 - 119.0	1.0870E-02
10	119.0 - 125.8	2.1739E-02

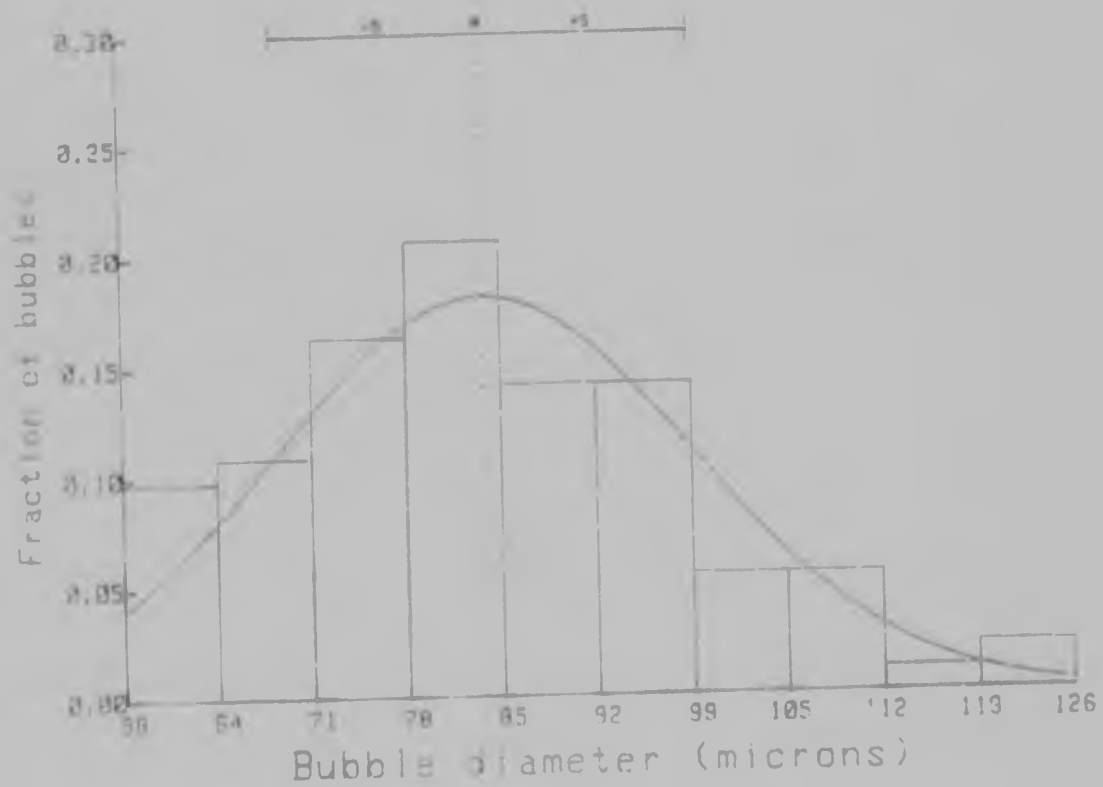


Water/sulphuric acid electrolyte

Solution viscosity was 0.92 centipoise
 Current used was 5 amp
 The flowrate was 3.75 l/min

Mean bubble diameter = 83.670 microns
 Standard deviation = 14.990 microns
 Largest bubble diameter = 125.839 microns
 Smallest bubble diameter = 57.657 microns

INTERVAL NUMBER	INTERVAL RANGE (microns)	FRACTION OF BUBBLES
1	57.65 - 64.47	9.7826E-02
2	64.47 - 71.29	1.0870E-01
3	71.29 - 78.11	1.6304E-01
4	78.11 - 84.92	2.0652E-01
5	84.92 - 91.74	1.4130E-01
6	91.74 - 98.56	1.4130E-01
7	98.56 - 105.3	5.4348E-02
8	105.3 - 112.2	5.4348E-02
9	112.2 - 119.0	1.0870E-02
10	119.0 - 125.8	2.1739E-02



Water / sulphuric acid electrolyte

Solution viscosity was 0.92 centipoise

Current used was 5 amp

The flowrate was 4.50 l/min

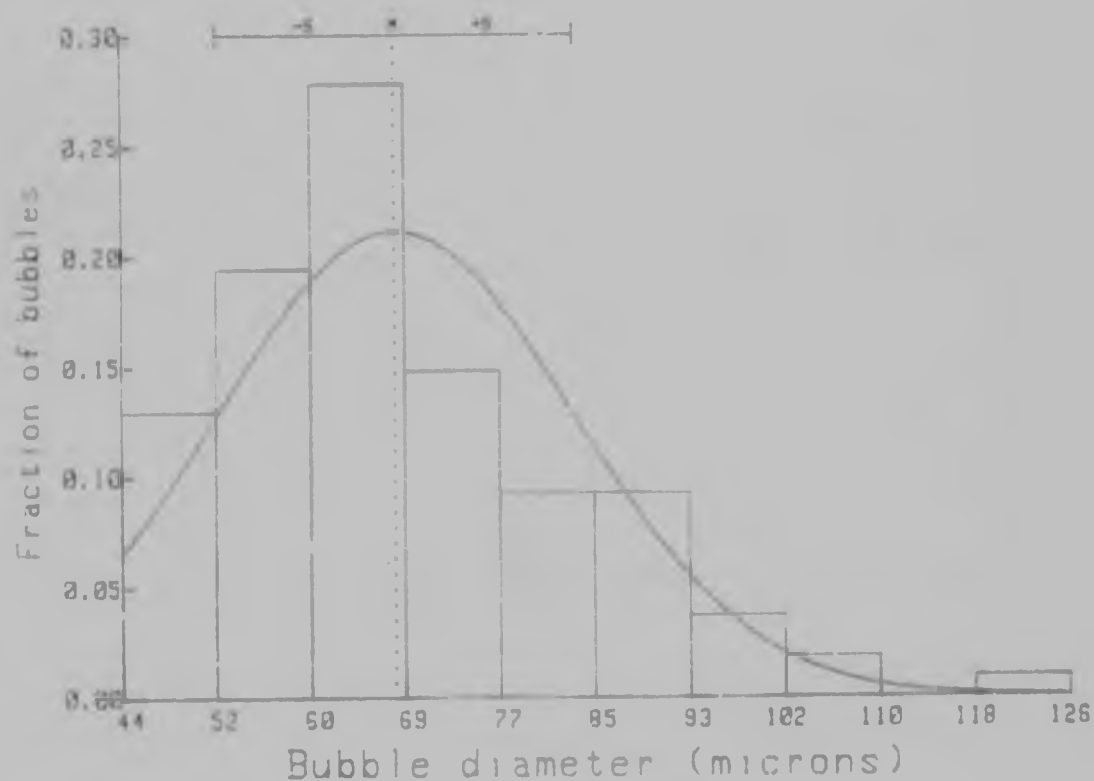
Mean bubble diameter = 67.709 microns

Standard deviation = 15.580 microns

Largest bubble diameter = 126.325 microns

Smallest bubble diameter = 43.799 microns

INTERVAL NUMBER	INTERVAL RANGE (microns)	FRACTION OF BUBBLES
1	43.79 - 52.05	1.2963E-01
2	52.05 - 60.3	1.9444E-01
3	60.3 - 68.55	2.7779E-01
4	68.55 - 76.8	1.4815E-01
5	76.8 - 85.06	9.2593E-02
6	85.06 - 93.31	9.2593E-02
7	93.31 - 101.5	3.7037E-02
8	101.5 - 109.8	1.8519E-02
9	109.8 - 118.0	0.0000E+00
10	118.0 - 126.3	9.2593E-03

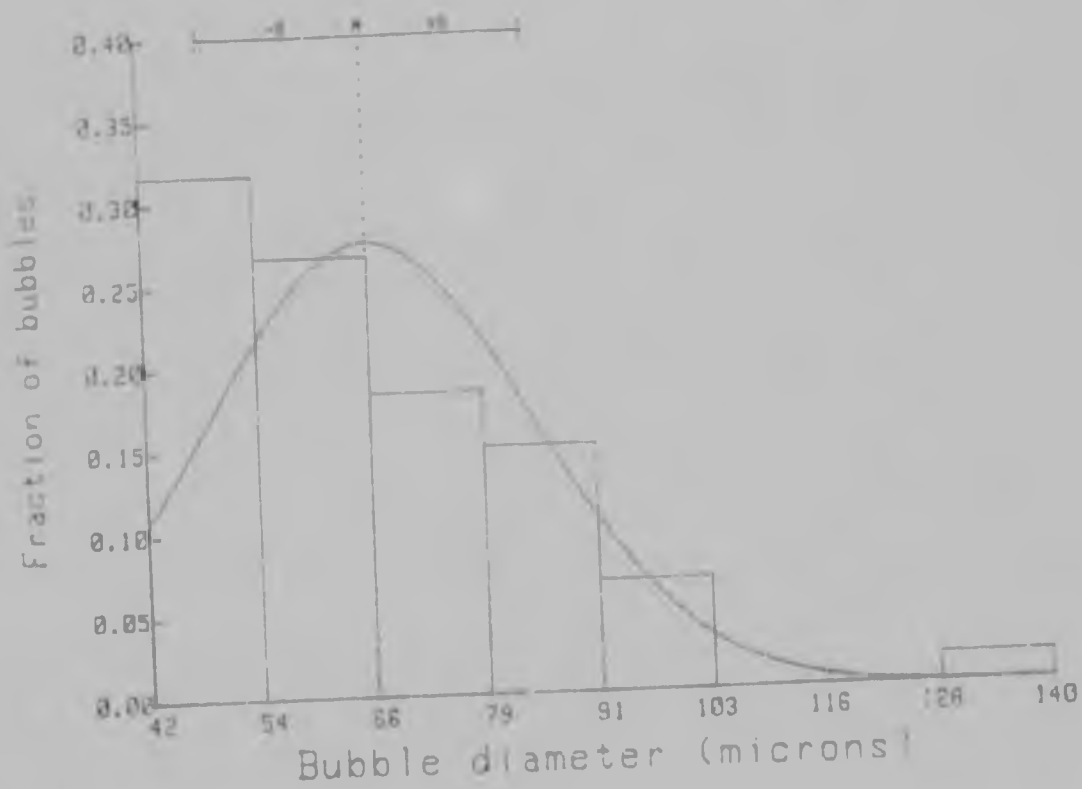


Water / sulphuric acid electrolyte

Solution viscosity was 0.92 centipoise
 Current used was 10 amp
 The flowrate was 4.60 l/min

Mean bubble diameter = 66.269 microns
 Standard deviation = 17.845 microns
 Largest bubble diameter = 140.270 microns
 Smallest bubble diameter = 41.714 microns

INTERVAL NUMBER	INTERVAL RANGE (microns)	FRACTION OF BUBBLES
1	41.71 - 54.03	3.1667E-01
2	54.03 - 66.35	2.6667E-01
3	66.35 - 78.67	1.8333E-01
4	78.67 - 90.99	1.5000E-01
5	90.99 - 103.3	6.6667E-02
6	103.3 - 115.6	0.0000E+00
7	115.6 - 127.9	0.0000E+00
8	127.9 - 140.2	1.6667E-02

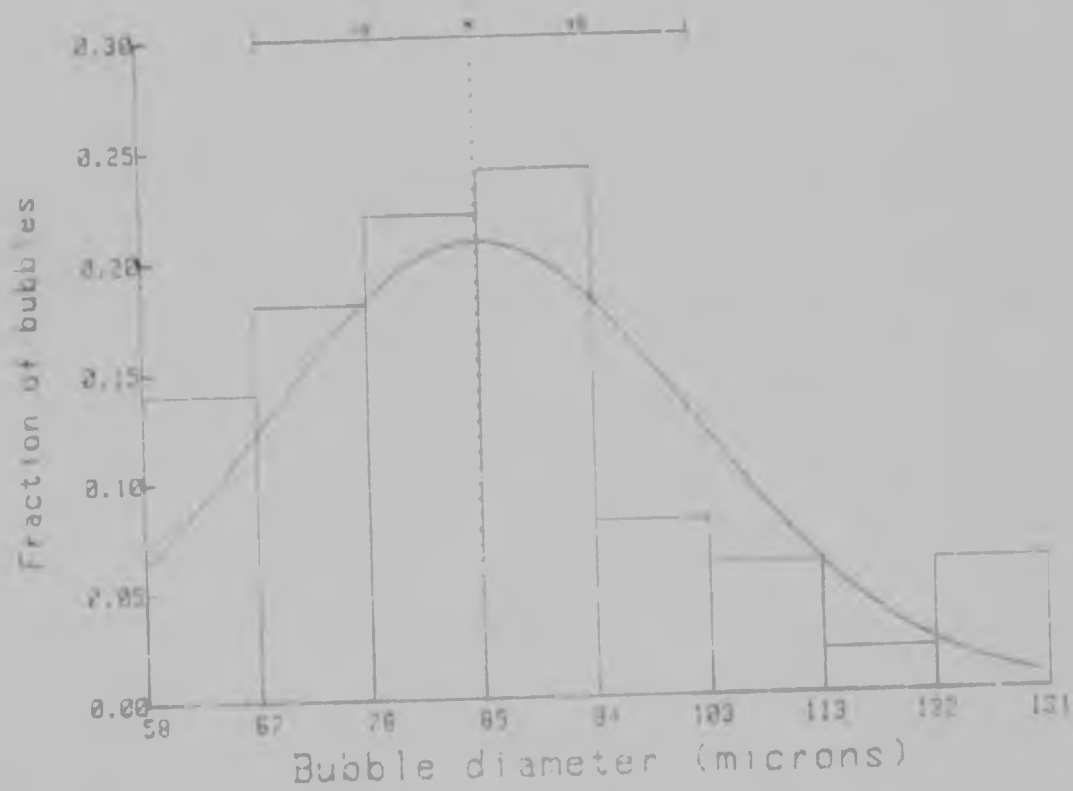


Conc. of glycerine = 36.7 kg/m³

Solution viscosity was 1.00 centipoise
 Current used was 1 amp
 The flowrate was 2.0 l/min

Mean bubble diameter = 84.935 microns
 Standard deviation = 17.525 microns
 Largest bubble diameter = 130.776 microns
 Smallest bubble diameter = 57.763 microns

INTERVAL NUMBER	INTERVAL RANGE (microns)	FRACTION OF BUBBLES
1	57.76 - 66.89	1.4000E-01
2	66.89 - 76.01	1.8000E-01
3	76.01 - 85.14	2.2000E-01
4	85.14 - 94.26	2.4000E-01
5	94.26 - 103.3	8.0000E-02
6	103.3 - 112.5	6.0000E-02
7	112.5 - 121.6	2.0000E-02
8	121.6 - 130.7	6.0000E-02

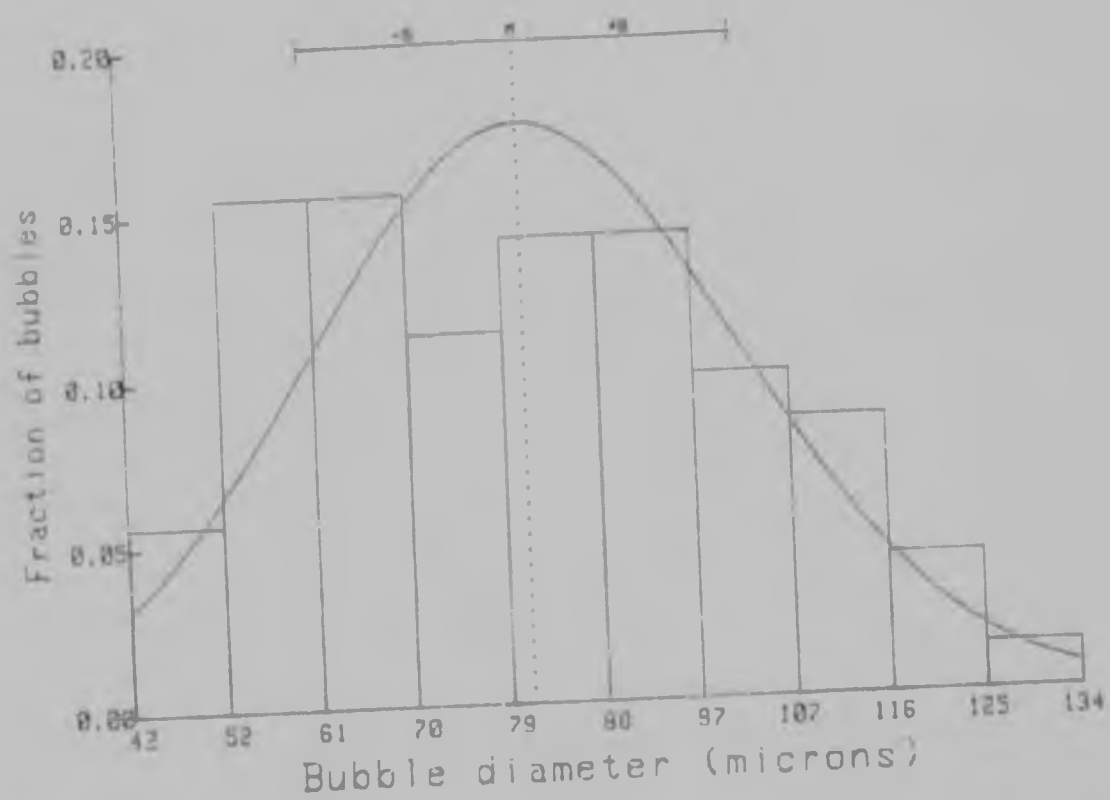


Conc. of glycerine = 1.12 kg/m³

Solution viscosity was 1.24 centipoise
 Current used was 1 amp
 The flowrate was 2.0 l/min

Mean bubble diameter = 81.075 microns
 Standard deviation = 20.865 microns
 Largest bubble diameter = 134.026 microns
 Smallest bubble diameter = 42.396 microns

INTERVAL NUMBER	INTERVAL RANGE (microns)	FRACTION OF BUBBLES
1	42.39 - 51.55	5.6338E-02
2	51.55 - 60.72	1.5493E-01
3	60.72 - 69.88	1.5493E-01
4	69.88 - 79.04	1.1268E-01
5	79.04 - 88.21	1.4085E-01
6	88.21 - 97.37	9.8592E-02
7	97.37 - 106.5	8.4507E-02
8	106.5 - 115.7	4.2254E-02
9	115.7 - 124.8	1.4085E-02
10	124.8 - 134.0	



Conc. of glycerine = 1.99 kg/m³

Solution viscosity was 1.62 centipoise

Current used was 1 amp

The flowrate was 2.0 l/min

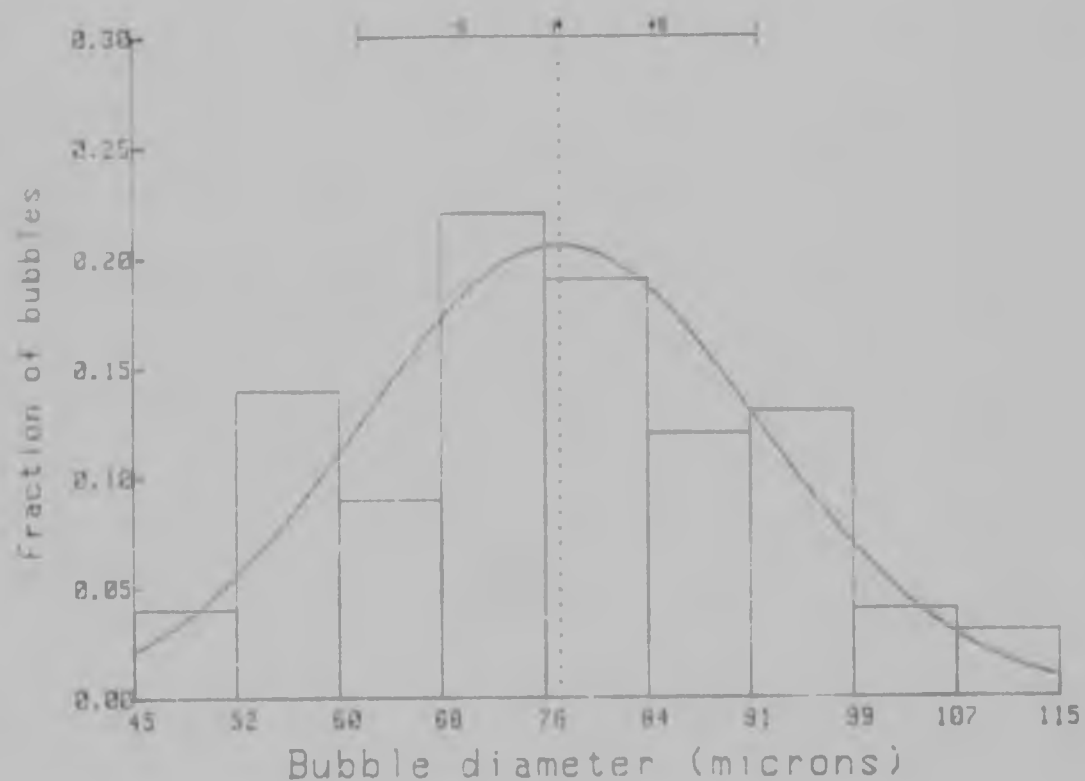
Mean bubble diameter = 76.908 microns

Standard deviation = 15.120 microns

Largest bubble diameter = 114.817 microns

Smallest bubble diameter = 44.651 microns

INTERVAL NUMBER	INTERVAL RANGE (microns)	FRACTION OF BUBBLES
1	44.65 - 52.44	4.0000E-02
2	52.44 - 60.24	1.4000E-01
3	60.24 - 68.03	9.0000E-02
4	68.03 - 75.83	2.2000E-01
5	75.83 - 83.63	1.9000E-01
6	83.63 - 91.42	1.2000E-01
7	91.42 - 99.22	1.3000E-01
8	99.22 - 107.0	4.0000E-02
9	107.0 - 114.8	3.0000E-02

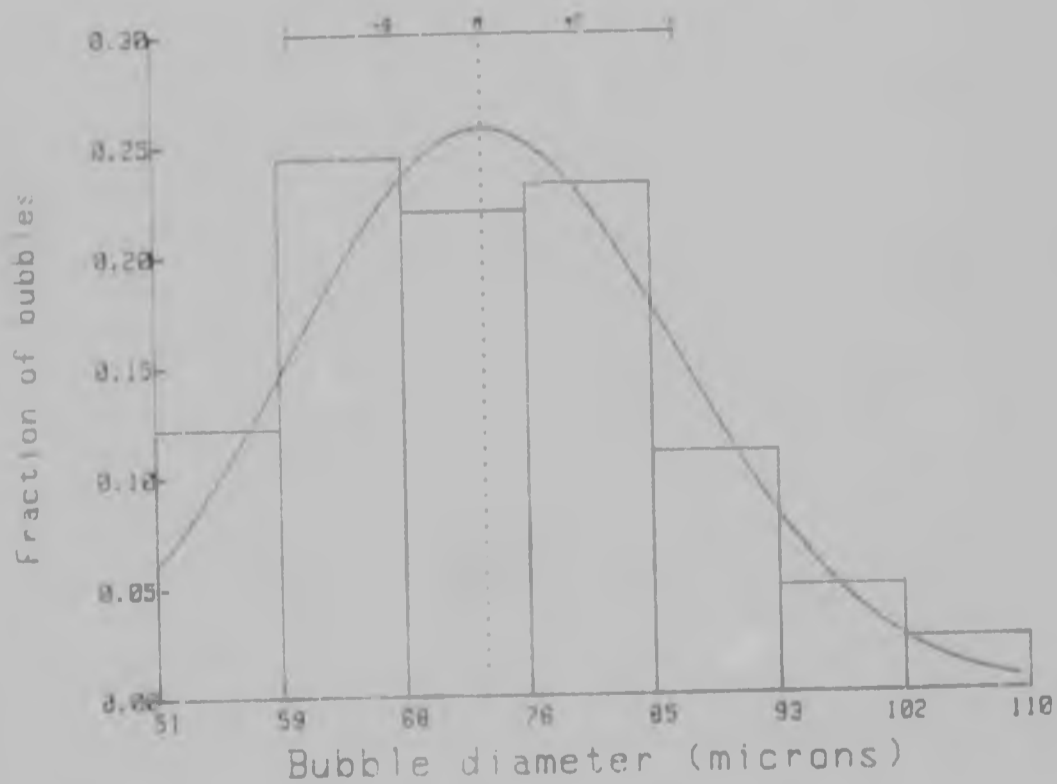


density of glycerol = 1.26 kg/m³

dynamic viscosity was 0.40 centipoise
 current used was 1 amp
 flow rate was 2.0 l/min

mean bubble diameter = 73.388 microns
 standard deviation = 13.205 microns
 largest bubble diameter = 110.399 microns
 smallest bubble diameter = 50.847 microns

INTERVAL NUMBER	INTERVAL RANGE (microns)	FRACTION OF BUBBLES
1	50.84 - 59.35	1.2195E-01
2	59.35 - 67.86	2.4390E-01
3	67.86 - 76.36	2.1951E-01
4	76.36 - 84.87	2.3171E-01
5	84.87 - 93.38	1.0976E-01
6	93.38 - 101.8	4.8780E-02
7	101.8 - 110.3	2.4390E-02



Conc. of glycerine = 33.6 kg/m³

Solution viscosity was 2.97 centipoise

Current used was 1 amp

The flowrate was 2.0 l/min

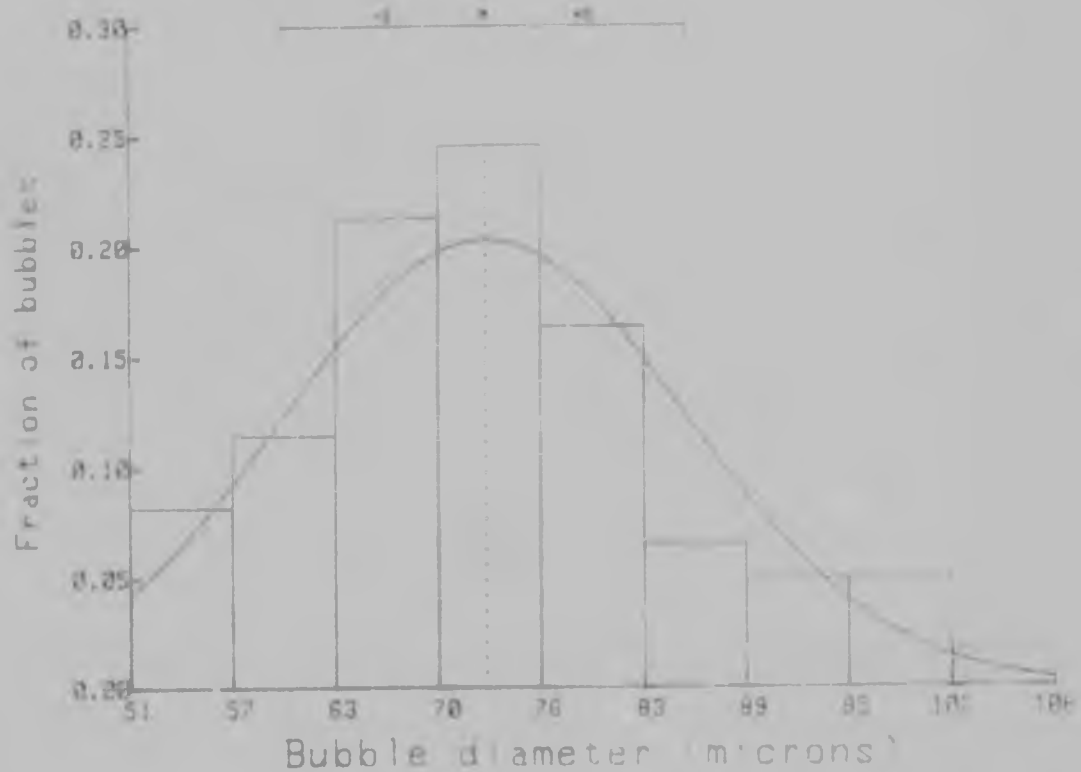
Mean bubble diameter = 72.742 microns

Standard deviation = 12.537 microns

Largest bubble diameter = 108.170 microns

Smallest bubble diameter = 50.633 microns

INTERVAL NUMBER	INTERVAL RANGE (microns)	FRACTION OF BUBBLE
1	50.63 - 57.02	0.1967E-02
2	57.02 - 63.41	0.1475E-01
3	63.41 - 69.81	0.2131E-01
4	69.81 - 76.2	0.2459E-01
5	76.2 - 82.59	0.2639E-01
6	82.59 - 88.99	0.2557E-02
7	88.99 - 95.38	0.1918E-02
8	95.38 - 101.7	0.1918E-02
9	101.7 - 108.1	0.1639E-02



Conc. of glycerine = 579 kg/m³

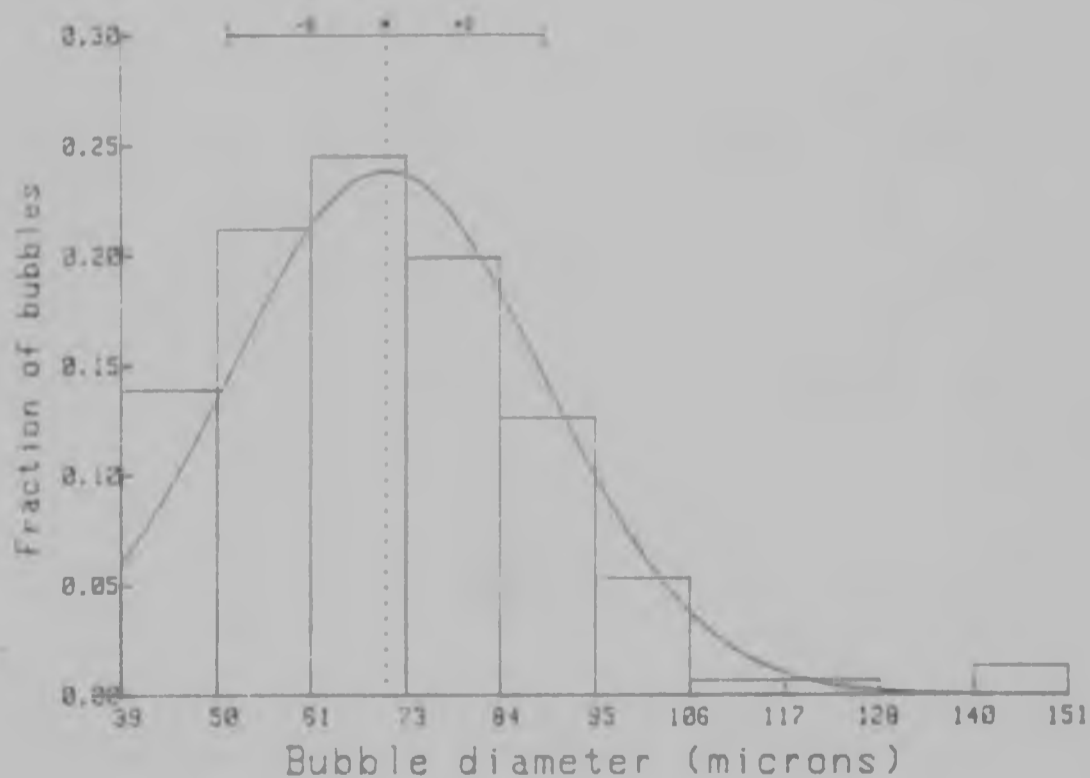
Solution viscosity was 5.8 centipoise

Current used was 0.5 amp

The flowrate was 1.18 l/min

Mean bubble diameter = 70.204 microns
 Standard deviation = 18.685 microns
 Largest bubble diameter = 150.726 microns
 Smallest bubble diameter = 39.079 microns

INTERVAL NUMBER	INTERVAL RANGE (microns)	FRACTION OF BUBBLES
1	39.07 - 50.24	1.3907E-01
2	50.24 - 61.4	2.1192E-01
3	61.4 - 72.57	2.4503E-01
4	72.57 - 83.73	1.9868E-01
5	83.73 - 94.9	1.2583E-01
6	94.9 - 106.0	5.2980E-02
7	106.0 - 117.2	6.6225E-03
8	117.2 - 128.3	6.6225E-03
9	128.3 - 139.5	0.0000E+00
10	139.5 - 150.7	1.3245E-02

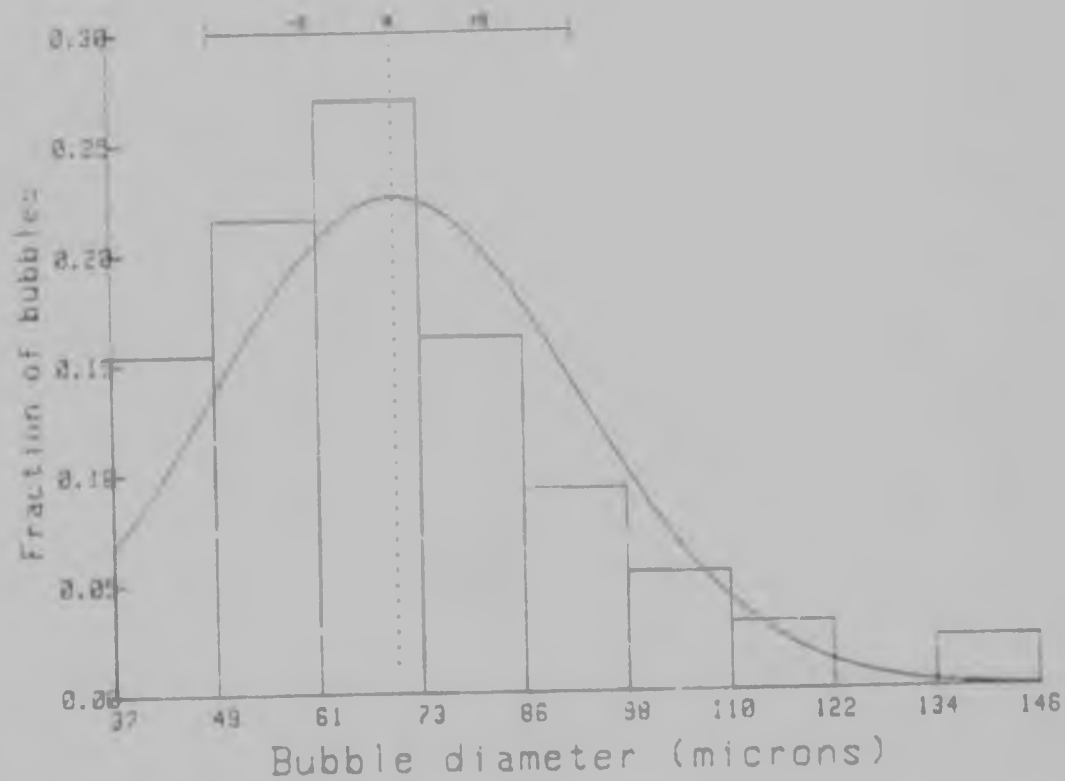


Conc. of glycerine = 529 kg/m³

Solution viscosity was 5.8 centipoise
 Current used was 0.5 amp
 The flowrate was 2.0 l/min

Mean bubble diameter = 70.550 microns
 Standard deviation = 21.278 microns
 Largest bubble diameter = 145.712 microns
 Smallest bubble diameter = 37.350 microns

INTERVAL NUMBER	INTERVAL RANGE (microns)	FRACTION OF BUBBLES
1	37.35 - 49.39	1.5385E-01
2	49.39 - 61.43	2.1538E-01
3	61.43 - 73.47	2.6923E-01
4	73.47 - 85.51	1.6154E-01
5	85.51 - 97.55	9.2209E-02
6	97.55 - 109.5	5.3246E-02
7	109.5 - 121.6	3.0769E-02
8	121.6 - 133.6	0.0000E+00
9	133.6 - 145.7	2.3077E-02

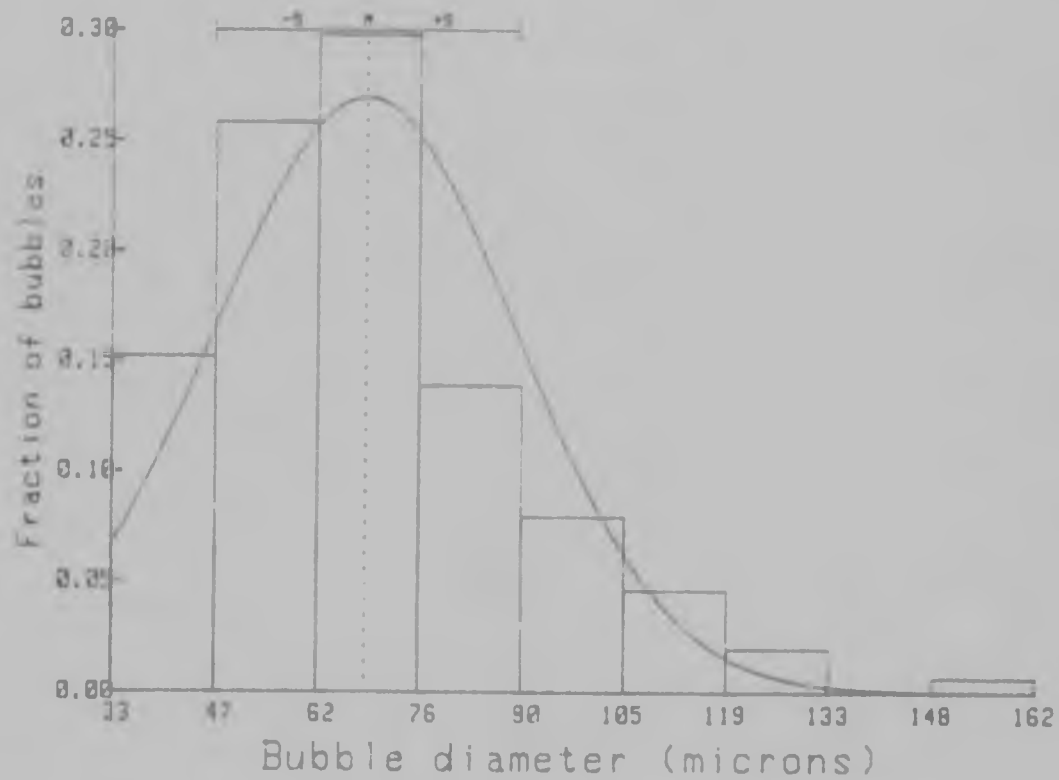


Conc. of glycerine = 529 kg/m³

Solution viscosity was 5.8 centipoise
 Current used was 0.5 amp
 The flowrate was 2.90 l/min

Mean bubble diameter = 68.398 microns
 Standard deviation = 21.149 microns
 Largest bubble diameter = 161.889 microns
 Smallest bubble diameter = 33.114 microns

INTERVAL NUMBER	INTERVAL RANGE (microns)	FRACTION OF BUBBLES
1	33.11 - 47.42	1.5232E-01
2	47.42 - 61.73	2.5823E-01
3	61.73 - 76.03	2.9801E-01
4	76.03 - 90.34	1.3907E-01
5	90.34 - 104.6	7.9470E-02
6	104.6 - 118.9	4.6358E-02
7	118.9 - 133.2	1.9868E-02
8	133.2 - 147.5	0.0000E+00
9	147.5 - 161.8	6.6225E-03

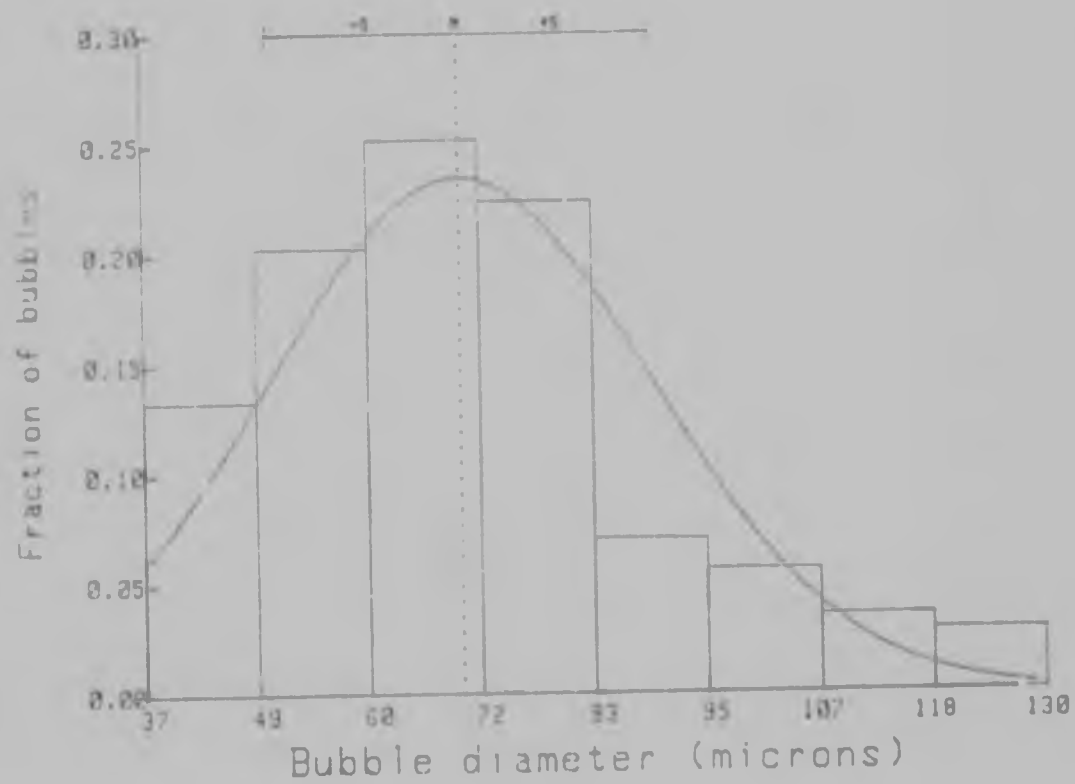


Conc. of glycerine = 579 kg/m³

Solution viscosity was 5.8 centipoise
 Current used was 1 amp
 The flowrate was 1.18 l/min

Mean bubble diameter = 69.778 microns
 Standard deviation = 19.652 microns
 Largest bubble diameter = 129.653 microns
 Smallest bubble diameter = 37.146 microns

INTERVAL NUMBER	INTERVAL RANGE (microns)	FRACTION OF BUBBLES
1	37.14 - 48.7	1.3287E-01
2	48.7 - 60.27	2.0280E-01
3	60.27 - 71.83	2.5175E-01
4	71.83 - 83.39	2.2378E-01
5	83.39 - 94.96	6.9930E-02
6	94.96 - 106.5	5.5944E-02
7	106.5 - 118.0	3.4965E-02
8	118.0 - 129.6	2.7972E-02

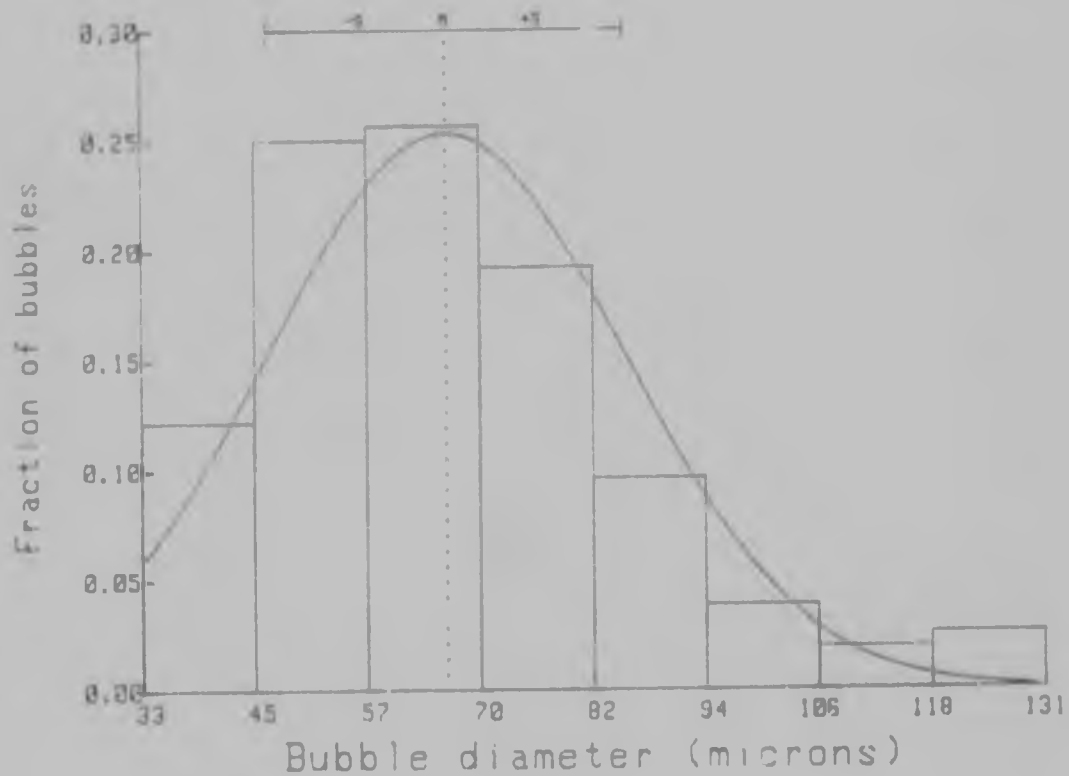


Conc. of glycerine = 579 kg/m³

Solution viscosity was 5.8 centipoise
 Current used was 1 amp
 The flowrate was 2.0 l/min

Mean bubble diameter = 65.879 microns
 Standard deviation = 19.215 microns
 Largest bubble diameter = 130.514 microns
 Smallest bubble diameter = 32.972 microns

INTERVAL NUMBER	INTERVAL RANGE (microns)	FRACTION OF BUBBLES
1	32.97 - 45.16	1.2179E-01
2	45.16 - 57.35	2.5000E-01
3	57.35 - 69.55	2.5641E-01
4	69.55 - 81.74	1.9231E-01
5	81.74 - 93.93	9.6154E-02
6	93.93 - 106.1	3.8462E-02
7	106.1 - 118.3	1.9231E-02
8	118.3 - 130.5	2.5641E-02

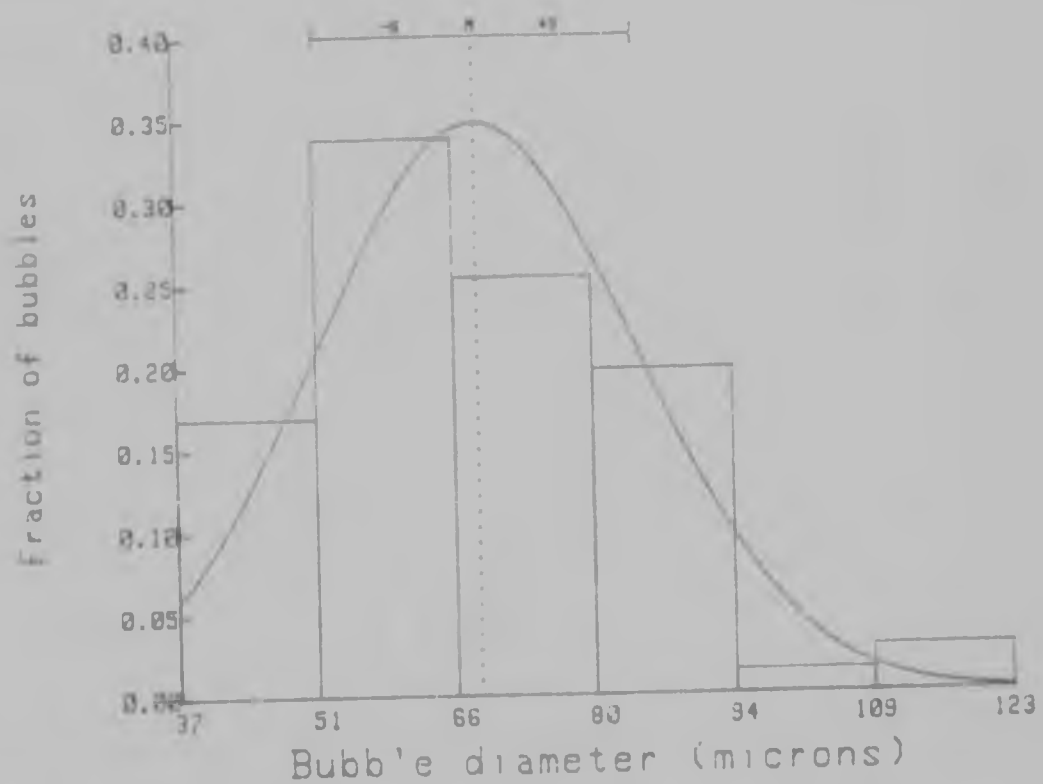


Conc. of glycerine = 529 kg/m³

Solution viscosity was 5.82 centipoise
 Current used was 1 amp
 The flowrate was 2.0 l/min

Mean bubble diameter = 68.060 microns
 Standard deviation = 16.452 microns
 Largest bubble diameter = 123.063 microns
 Smallest bubble diameter = 37.011 microns

INTERVAL NUMBER	INTERVAL RANGE (microns)	FRACTION OF BUBBLES
1	37.01 - 51.35	1.6901E-01
2	51.35 - 65.69	3.3803E-01
3	65.69 - 80.03	2.5352E-01
4	80.03 - 94.37	1.9718E-01
5	94.37 - 108.7	1.4085E-02
6	108.7 - 123.0	2.8169E-02

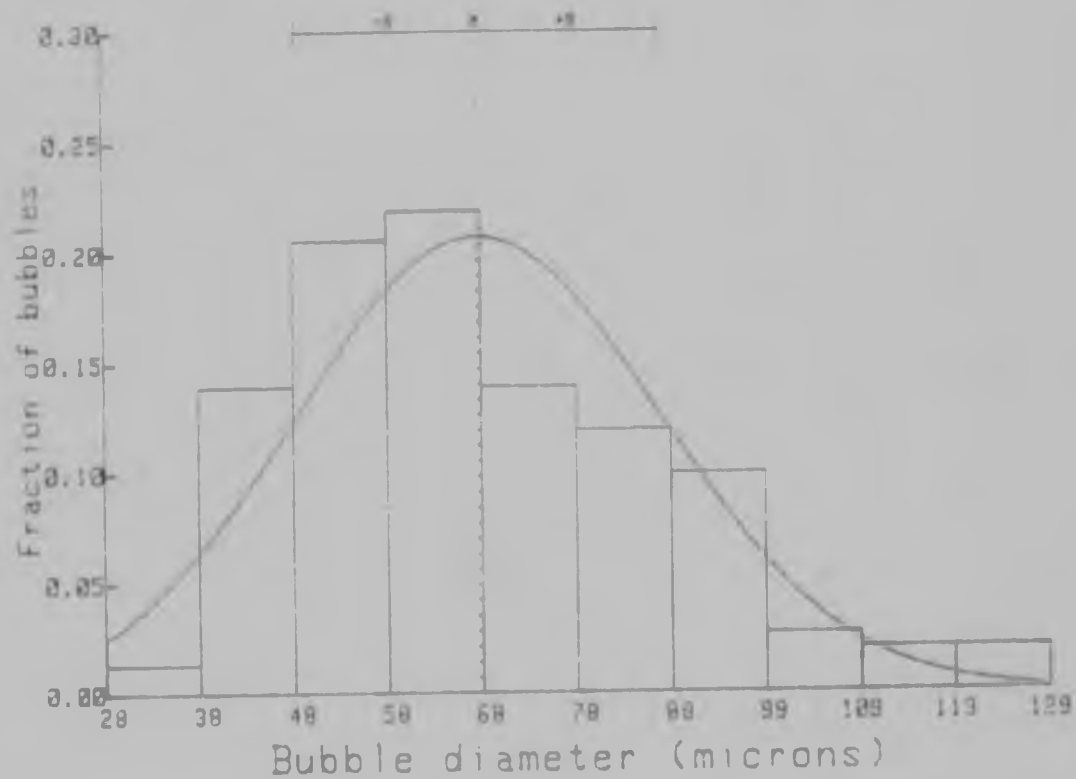


Cond. of glycerine = 579 kg/m³

Solution viscosity was 5.8 centipoise
 Current used was 1 amp
 The flowrate was 2.90 l/min

Mean bubble diameter = 67.867 microns
 Standard deviation = 17.487 microns
 Largest bubble diameter = 128.913 microns
 Smallest bubble diameter = 27.778 microns

INTERVAL NUMBER	INTERVAL RANGE (microns)	FRACTION OF BUBBLES
1	27.77 - 37.39	1.3245E-02
2	37.39 - 48	1.3907E-01
3	48 - 58.11	2.0530E-01
4	58.11 - 68.23	2.1854E-01
5	68.23 - 78.34	1.3907E-01
6	78.34 - 88.45	1.1921E-01
7	88.45 - 98.57	9.9338E-02
8	98.57 - 108.6	2.6490E-02
9	108.6 - 118.7	1.9868E-02
10	118.7 - 128.9	1.9868E-02

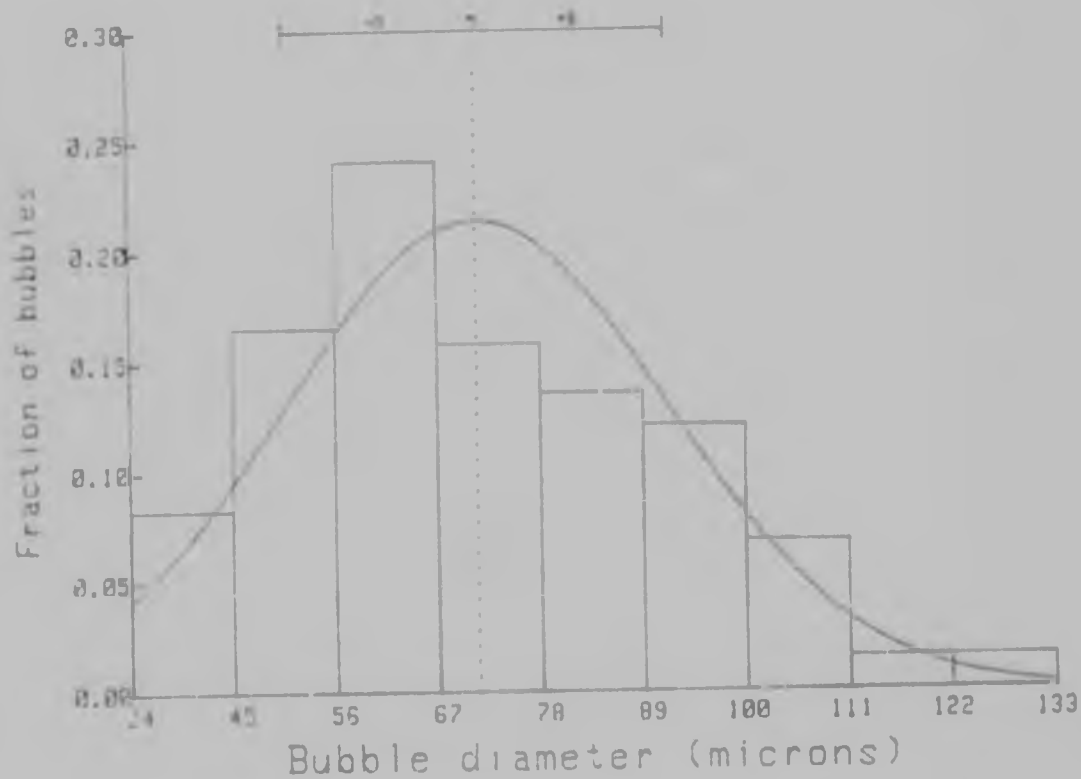


Conc. of glycerine = 579 kg/m³

Solution viscosity was 5.8 centipoise
 Current used was 1.5 amp
 The flowrate was 1.18 l/min

mean bubble diameter = 71.110 microns
 Standard deviation = 20.606 microns
 Largest bubble diameter = 133.272 microns
 Smallest bubble diameter = 33.775 microns

INTERVAL NUMBER	INTERVAL RANGE (microns)	FRACTION OF BUBBLES
1	33.77 - 44.82	8.2707E-02
2	44.82 - 55.88	1.6541E-01
3	55.88 - 66.94	2.4060E-01
4	66.94 - 77.99	1.5789E-01
5	77.99 - 89.05	1.3534E-01
6	89.05 - 100.1	1.2030E-01
7	100.1 - 111.1	6.7669E-02
8	111.1 - 122.2	1.5038E-02
9	122.2 - 133.2	1.5038E-02



Conc. of glycerine = 579 kg/m³

Solution viscosity was 5.8 centipoise

Current used was 1.5 amp

The flowrate was 2.0 l/min

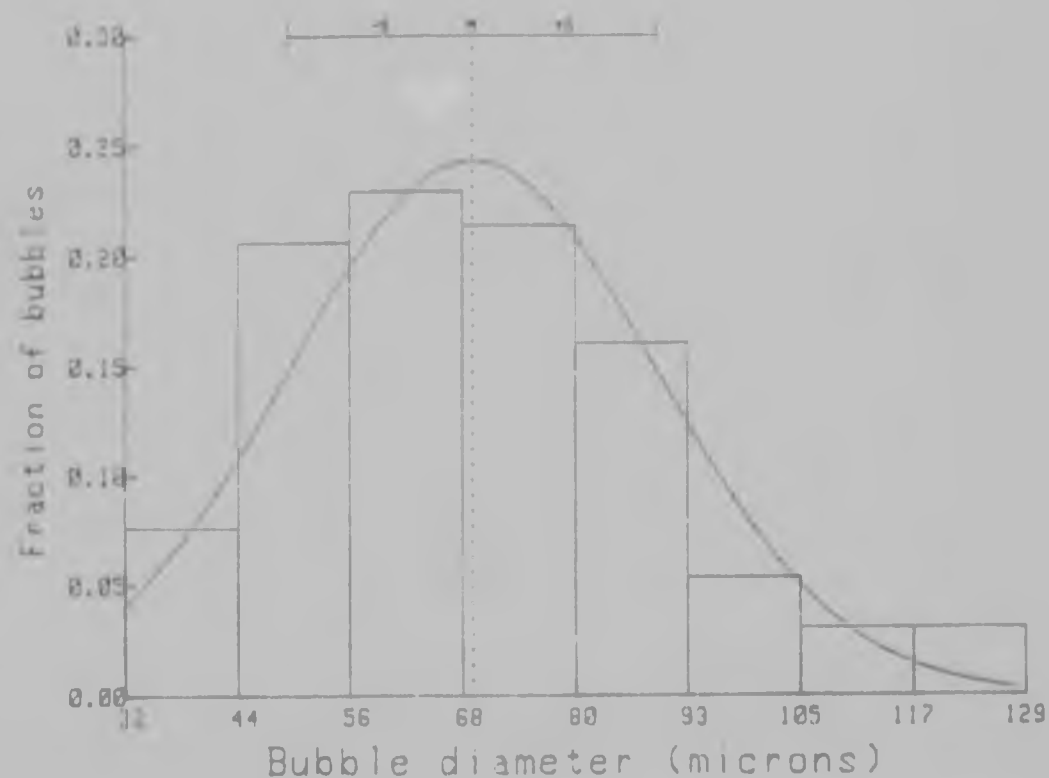
Mean bubble diameter = 69.374 microns

Standard deviation = 20.062 microns

Largest bubble diameter = 129.406 microns

Smallest bubble diameter = 31.574 microns

INTERVAL NUMBER	INTERVAL RANGE (microns)	FRACTION OF BUBBLES
1	31.57 - 43.8	7.6336E-02
2	43.8 - 56.03	2.0611E-01
3	56.03 - 68.26	2.2901E-01
4	68.26 - 80.49	2.1374E-01
5	80.49 - 92.71	1.6031E-01
6	92.71 - 104.9	5.3435E-02
7	104.9 - 117.1	3.0534E-02
8	117.1 - 129.4	3.0534E-02



Conc. of glycerine = 579 kg/m³

Solution viscosity was 5.8 centipoise

Current used was 1.5 amp

The flowrate was 2.90 l/min

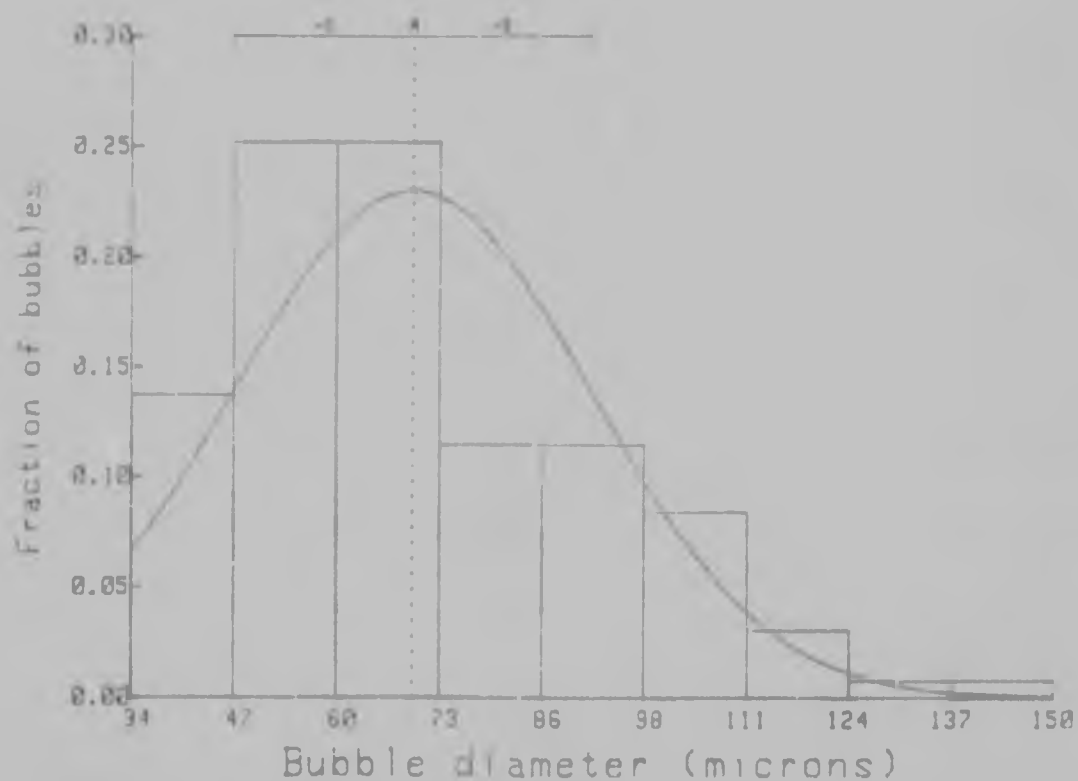
Mean bubble diameter = 69.234 microns

Standard deviation = 22.348 microns

Largest bubble diameter = 150.069 microns

Smallest bubble diameter = 33.961 microns

INTERVAL NUMBER	INTERVAL RANGE (microns)	FRACTION OF BUBBLES
1	33.96 - 46.86	1.3740E-01
2	46.86 - 59.76	2.5191E-01
3	59.76 - 72.66	2.5191E-01
4	72.66 - 85.56	1.1450E-01
5	85.56 - 98.46	1.1450E-01
6	98.46 - 111.3	3.3969E-02
7	111.3 - 124.2	3.0534E-02
8	124.2 - 137.1	7.6336E-03
9	137.1 - 150.0	7.6336E-03

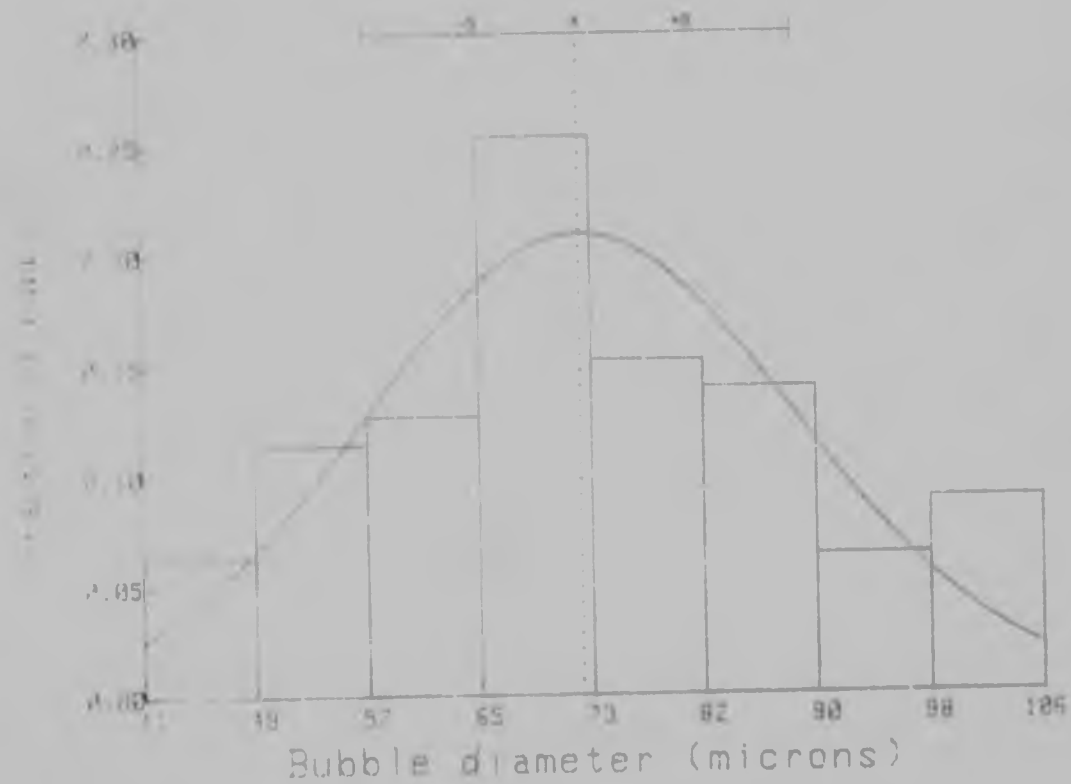


Concentration of Mg sulphate = 3.0 kg/m³

solution viscosity was 1.02 centipoise
 Current used was 1.0 amp
 The flowrate was 0.1/min

Mean bubble diameter = 72.627 microns
 Standard deviation = 15.636 microns
 Largest bubble diameter = 106.216 microns
 Smallest bubble diameter = 40.639 microns

INTERVAL NUMBER	INTERVAL RANGE (microns)	FRACTION OF BUBBLES
1	40.63 - 48.83	6.3291E-02
2	48.83 - 57.03	1.1372E-01
3	57.03 - 65.23	1.2658E-01
4	65.23 - 73.42	2.5316E-01
5	73.42 - 81.62	1.5190E-01
6	81.62 - 89.82	1.3924E-01
7	89.82 - 98.01	6.3291E-02
8	98.01 - 106.21	8.8608E-02



Conc. of Mg sulphate = 30 kg m⁻³

Solution viscosity was 2.07 centipoise

Current used was 1.0 amp

The flowrate was 2.0 l/min

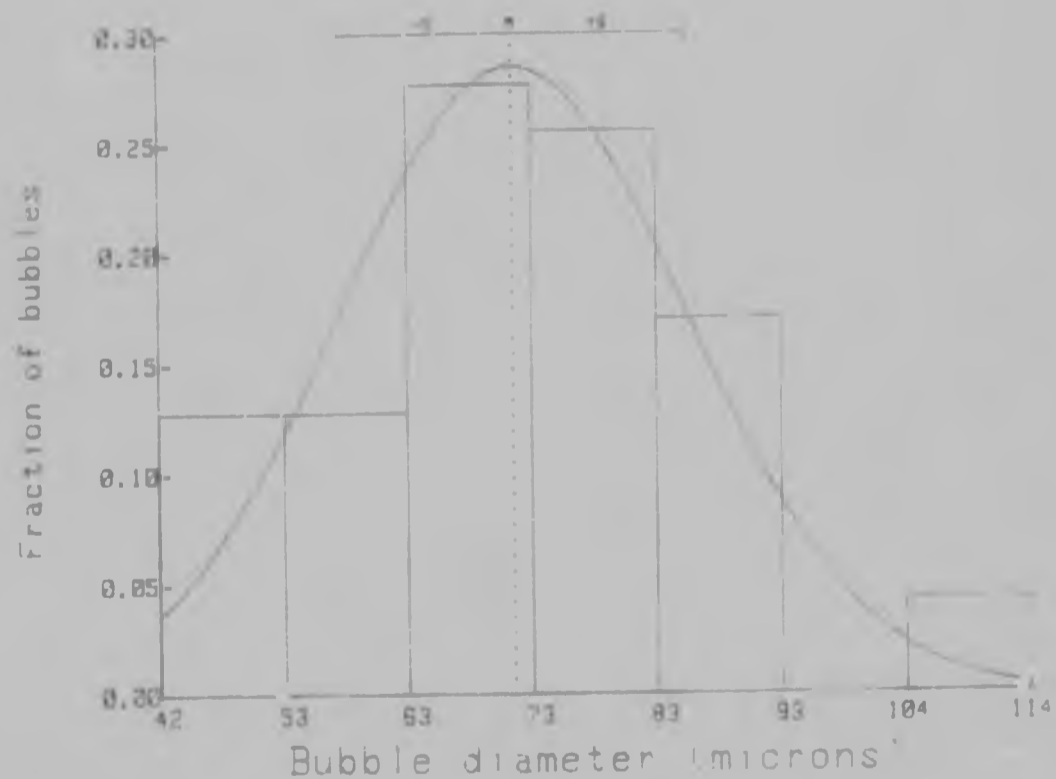
Mean bubble diameter = 71.507 microns

Standard deviation = 14.289 microns

Largest bubble diameter = 113.904 microns

Smallest bubble diameter = 42.426 microns

INTERVAL NUMBER	INTERVAL RANGE (microns)	FRACTION OF BUBBLES
1	42.42 - 52.63	1.2766E-01
2	52.63 - 62.84	1.2766E-01
3	62.84 - 73.05	2.7660E-01
4	73.05 - 83.27	1.5532E-01
5	83.27 - 93.48	1.7021E-01
6	93.48 - 103.6	3.0000E-01
7	103.6 - 113.9	4.2557E-02

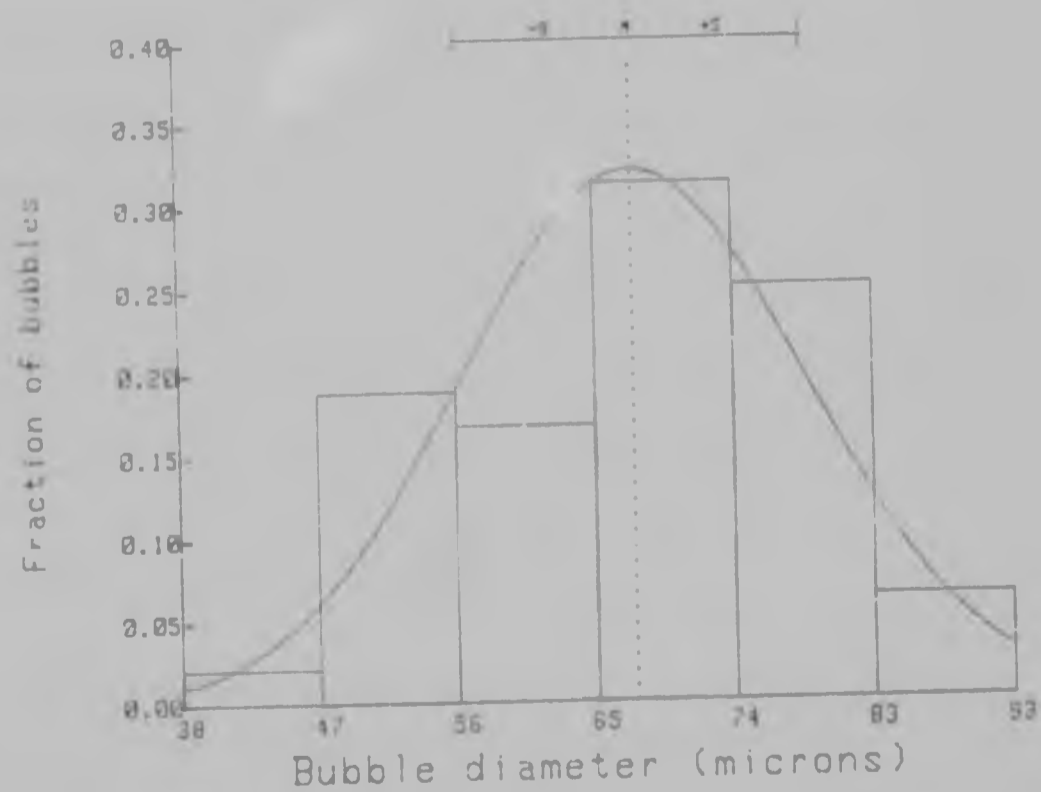


Conc. of Mg sulphate = 350 kg/m³

Solution viscosity was 2.54 centipoise
 Current used was 1.0 amp
 The flowrate was 2.0 l/min

Mean bubble diameter = 67.870 microns
 Standard deviation = 11.261 microns
 Largest bubble diameter = 92.552 microns
 Smallest bubble diameter = 38.218 microns

INTERVAL NUMBER	INTERVAL RANGE (microns)	FRACTION OF BUBBLES
1	38.21 - 47.27	2.0833E-02
2	47.27 - 56.32	1.8750E-01
3	56.32 - 65.38	1.6667E-01
4	65.38 - 74.44	3.1250E-01
5	74.44 - 83.49	2.5000E-01
6	83.49 - 92.55	6.2500E-02

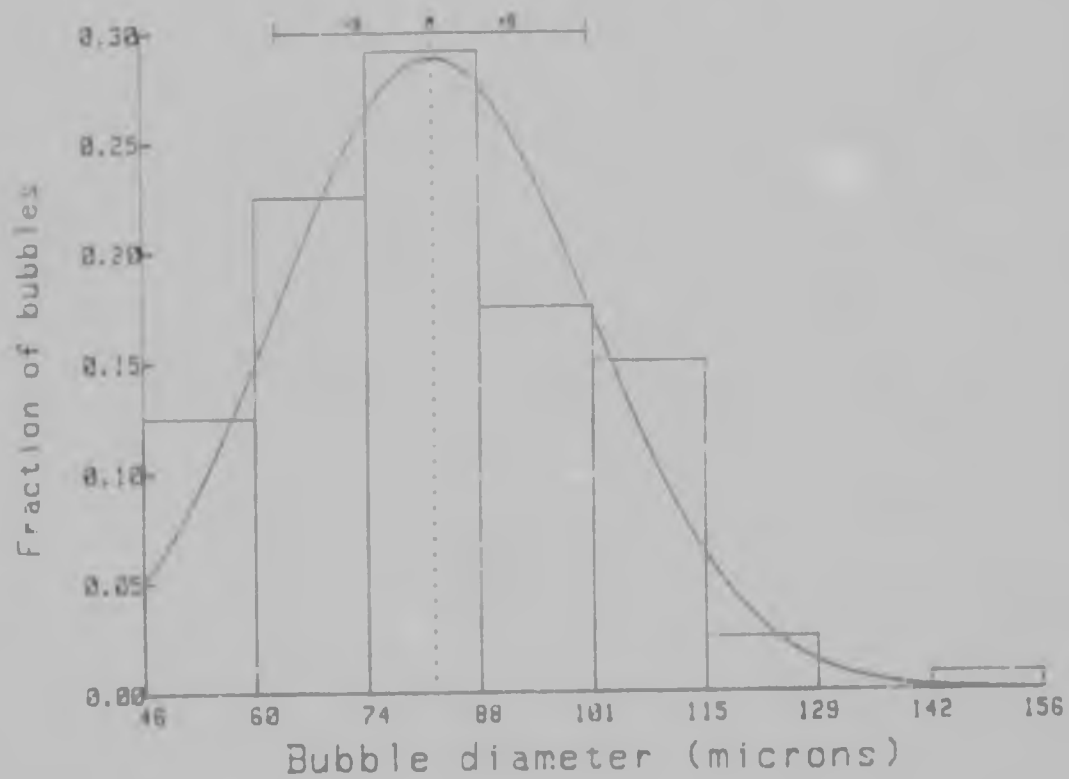


Concn. of Mg sulphate = 470 kg/m³

Solution viscosity was 3.17 centipoise
 Current used was 1.0 amp
 The flowrate was 2.00 l/min

Mean bubble diameter = 81.830 microns
 Standard deviation = 18.985 microns
 Largest bubble diameter = 156.168 microns
 Smallest bubble diameter = 46.306 microns

INTERVAL NUMBER	INTERVAL RANGE (microns)	FRACTION OF BUBBLES
1	46.3 - 60.03	1.2500E-01
2	60.03 - 73.77	2.2500E-01
3	73.77 - 87.5	2.9167E-01
4	87.5 - 101.2	1.7500E-01
5	101.2 - 114.9	1.5000E-01
6	114.9 - 128.7	2.5000E-02
7	128.7 - 142.4	0.0000E+00
8	142.4 - 156.1	3.3333E-03

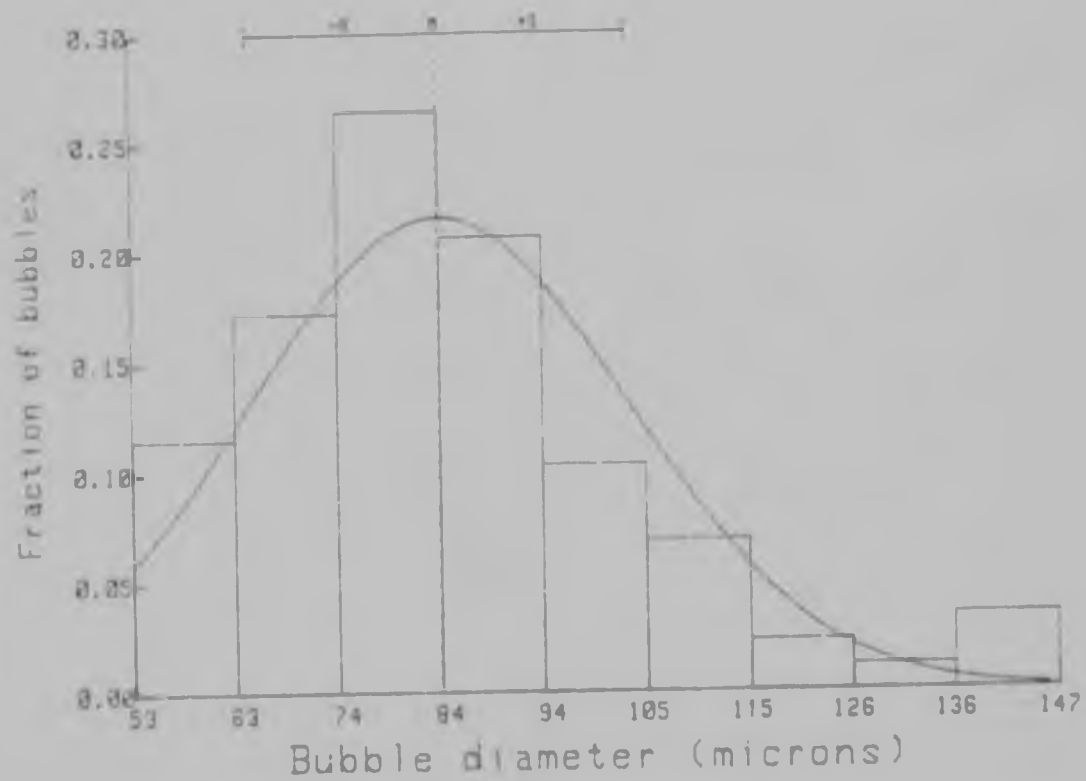


Conc. of zinc sulphate = 4.2 kg/m³

Solution viscosity was 0.95 centipoise
 Current used was 1.0 amp
 The flowrate was 2.00 l/min

Mean bubble diameter = 83.896 microns
 Standard deviation = 19.350 microns
 Largest bubble diameter = 146.850 microns
 Smallest bubble diameter = 52.576 microns

INTERVAL NUMBER	INTERVAL RANGE (microns)	FRACTION OF BUBBLES
1	52.57 - 63.05	1.1494E-01
2	63.05 - 73.52	1.7241E-01
3	73.52 - 84	2.7437E-01
4	84 - 94.47	2.0690E-01
5	94.47 - 104.9	1.0345E-01
6	104.9 - 115.4	6.8966E-02
7	115.4 - 125.9	2.2989E-02
8	125.9 - 136.3	1.1494E-02
9	136.3 - 146.8	3.4483E-02

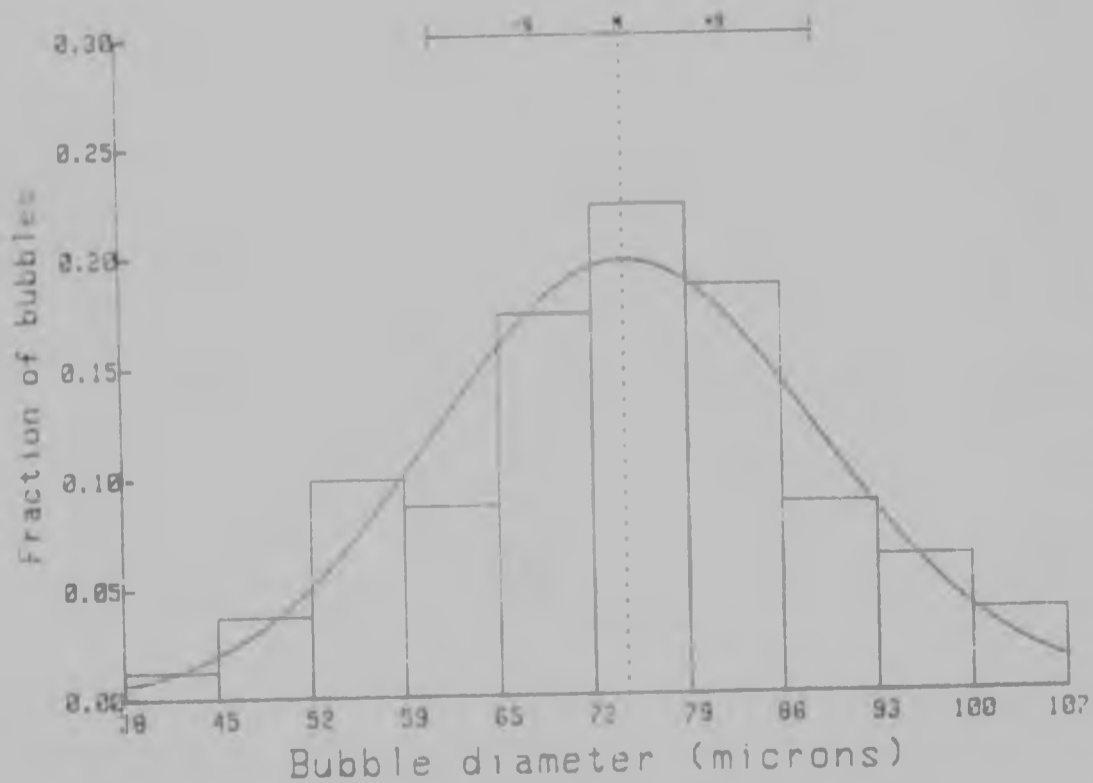


Conc. of zinc sulphate = 33.7 kg/m³

Solution viscosity was 1.06 centipoise
 Current used was 1.0 amp
 The flowrate was 2.00 l/min

Mean bubble diameter = 74.626 microns
 Standard deviation = 13.898 microns
 Largest bubble diameter = 106.594 microns
 Smallest bubble diameter = 37.940 microns

INTERVAL NUMBER	INTERVAL RANGE (microns)	FRACTION OF BUBBLES
1	37.94 - 44.8	1.2346E-02
2	44.8 - 51.67	3.7037E-02
3	51.67 - 58.53	9.8765E-02
4	58.53 - 65.4	8.6420E-02
5	65.4 - 72.26	1.7284E-01
6	72.26 - 79.13	2.2222E-01
7	79.13 - 85.99	1.8519E-01
8	85.99 - 92.86	8.6420E-02
9	92.86 - 99.72	6.1728E-02
10	99.72 - 106.5	3.7037E-02

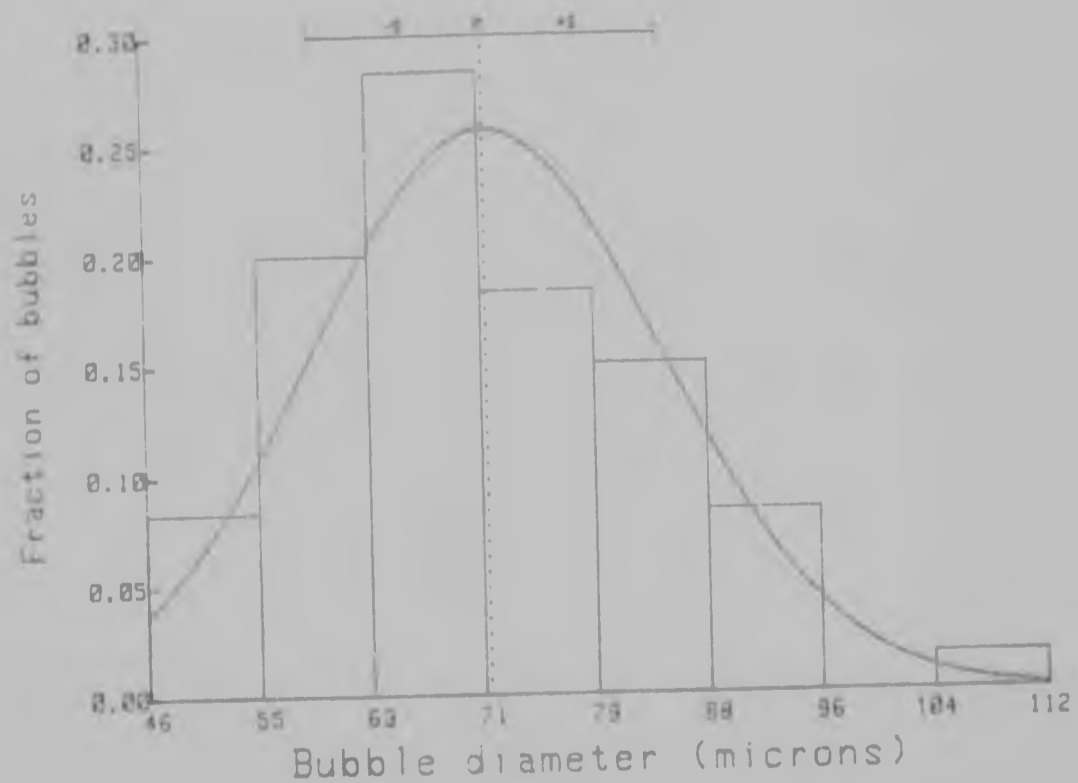


Conc. of zinc sulphate = 1.84 kg/m³

Solution viscosity was 1.14 centipoise
 Current used was 1.0 amp
 The flowrate was 2.00 l/min

Mean bubble diameter = 71.546 microns
 Standard deviation = 12.773 microns
 Largest bubble diameter = 112.314 microns
 Smallest bubble diameter = 46.459 microns

INTERVAL NUMBER	INTERVAL RANGE (microns)	FRACTION OF BUBBLES
1	46.45 - 54.69	8.3333E-02
2	54.69 - 62.92	2.0000E-01
3	62.92 - 71.15	2.8333E-01
4	71.15 - 79.38	1.8333E-01
5	79.38 - 87.61	1.5000E-01
6	87.61 - 95.85	8.3333E-02
7	95.85 - 104.0	0.0000E+00
8	104.0 - 112.3	1.6667E-02

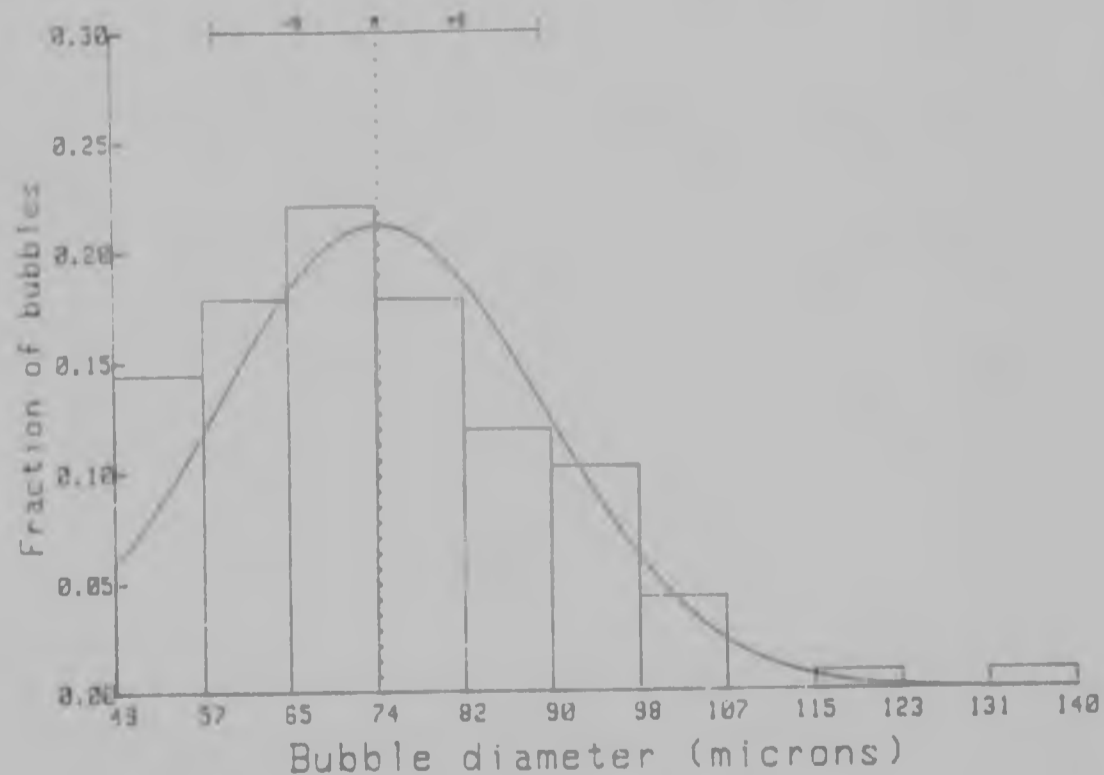


Conc. of zinc sulphate = 386 kg/m³

Solution viscosity was 2.2 centipoise
 Current used was 1.0 amp
 The flowrate was 2.00 l/min

Mean bubble diameter = 73.835 microns
 Standard deviation = 15.559 microns
 Largest bubble diameter = 139.69 microns
 Smallest bubble diameter = 48.748 microns

INTERVAL NUMBER	INTERVAL RANGE (microns)	FRACTION OF BUBBLES
1	48.74 - 57.01	1.4407E-01
2	57.01 - 65.28	1.7797E-01
3	65.28 - 73.55	2.2034E-01
4	73.55 - 81.81	1.7797E-01
5	81.81 - 90.08	1.1864E-01
6	90.08 - 98.35	1.0169E-01
7	98.35 - 106.6	4.2373E-02
8	106.6 - 114.8	0.0000E+00
9	114.8 - 123.1	8.4746E-03
10	123.1 - 131.4	0.0000E+00
11	131.4 - 139.6	8.4746E-03

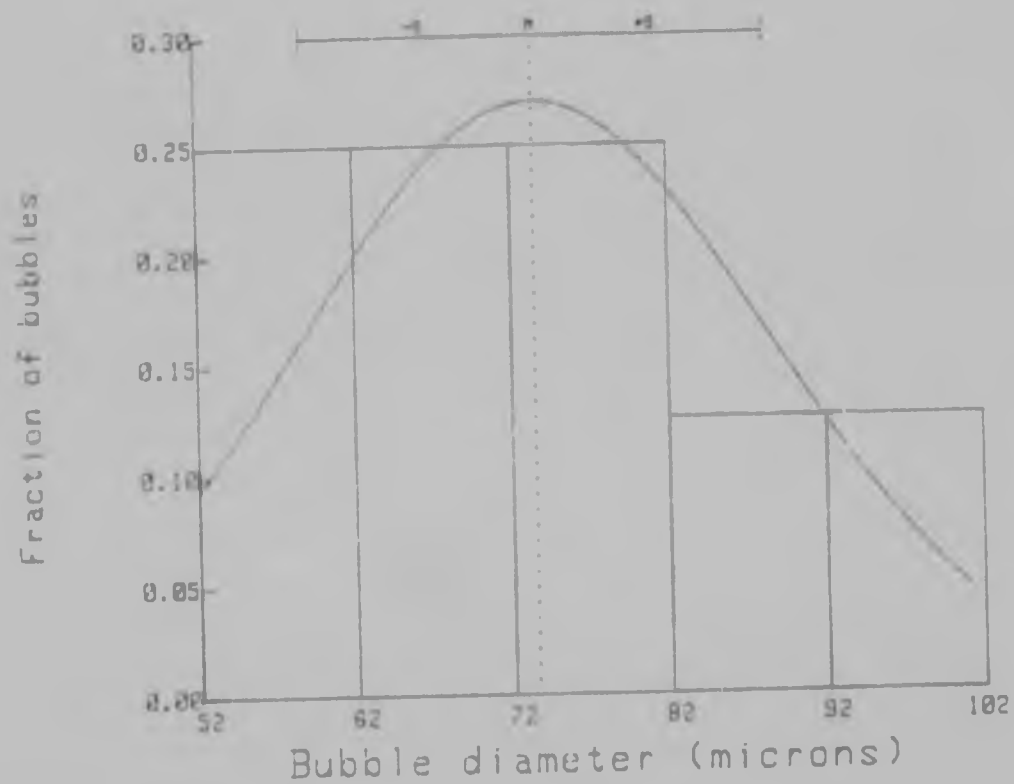


Conc. of zinc sulphate = 507 kg/m³

Solution viscosity was 2.5 centipoise
 Current used was 1.0 amp
 The flowrate was 2.00 l/min

Mean bubble diameter = 73.184 microns
 Standard deviation = 14.743 microns
 Largest bubble diameter = 101.664 microns
 Smallest bubble diameter = 51.732 microns

INTERVAL NUMBER	INTERVAL RANGE (microns)	FRACTION OF BUBBLES
1	51.73 - 61.71	2.5000E-01
2	61.71 - 71.7	2.5000E-01
3	71.7 - 81.69	2.5000E-01
4	81.69 - 91.67	1.2500E-01
5	91.67 - 101.6	1.2500E-01



The results obtained from measuring the bubbles leaving the electrode surface are tabulated in table A 5.1 below. These results were all obtained using a flowrate of 2,00 l/min and a current of 1,0 A.

Table A 5.1 Measurements of Bubble Sizes Leaving the Surface

Concentration of glycerine or MgSO ₄ (kg/m ³)	Viscosity (cP)	Mean Bubble Diameter (μm)	Standard Deviation of Bubble Diameters (μm)
-	0,92	127	37
36,7 kg/m ³ glycerine	1,00	112	40
36,7 kg/m ³ glycerine	1,50	95	41
332 kg/m ³ glycerine	2,40	90	33
386 kg/m ³ glycerine	3,00	89	33
150 kg/m ³ MgSO ₄	1,44	114	40
280 kg/m ³ MgSO ₄	2,07	105	41
350 kg/m ³ MgSO ₄	2,54	99	31

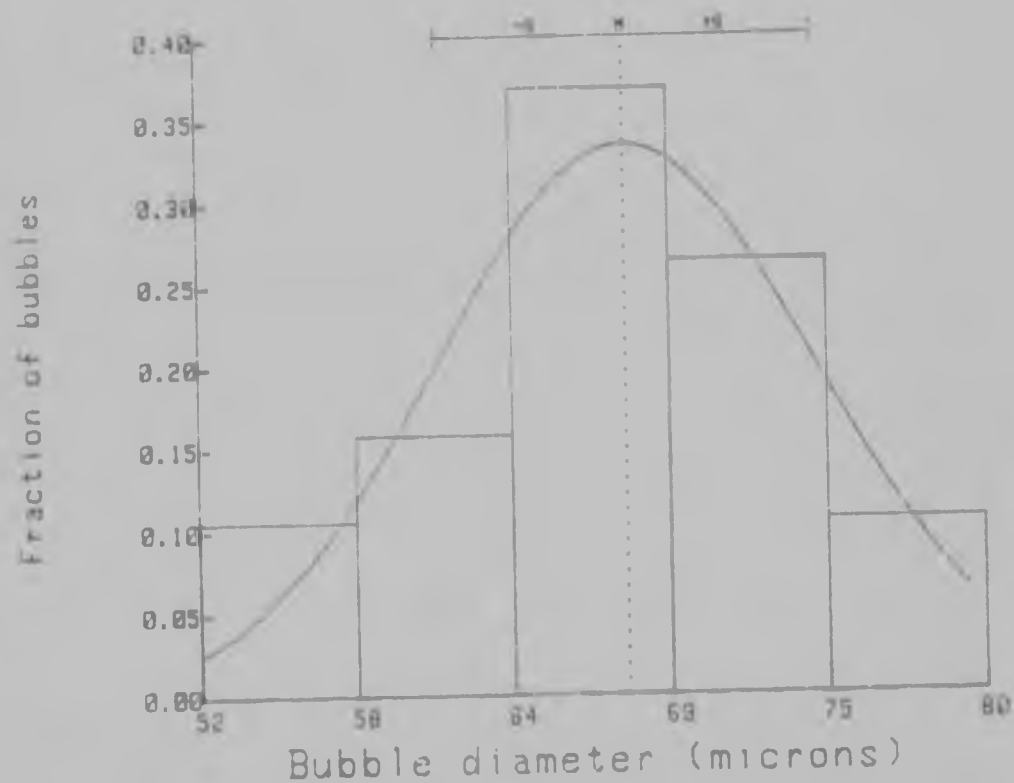
Histograms showing the distribution of the above runs are now presented. When results are available from the runs measuring bubble sizes on the electrode surface, the two distributions are superimposed on the same set of axes. The bold bars represent the bubbles leaving the surface while the hatched bars represent the bubbles on the surface.

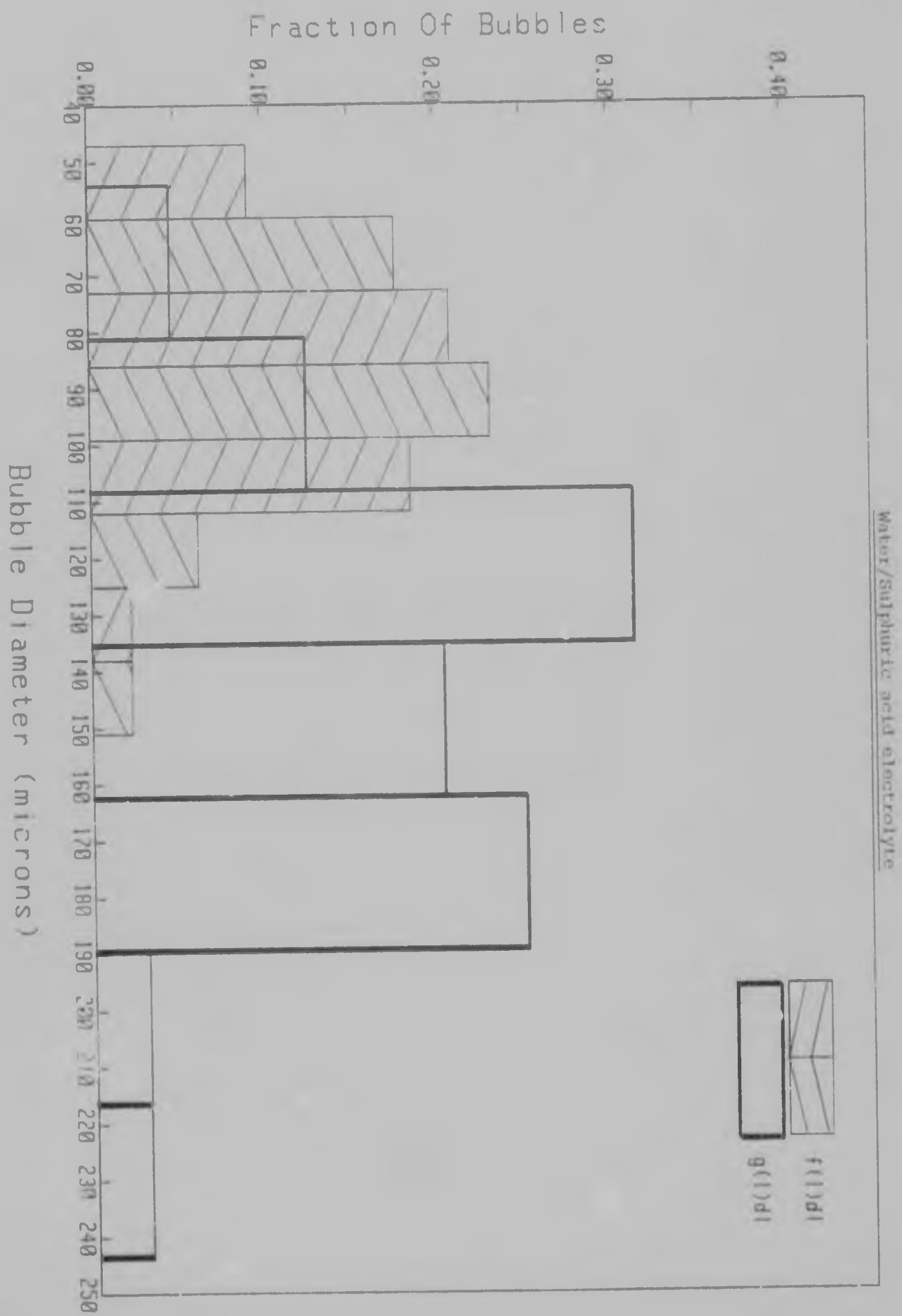
Concn. of zinc sulphate = 86.33 kg/m³

Solution viscosity was 5.0 centipoise
 Current used was 1.0 amp
 The flowrate was 2.00 l/min

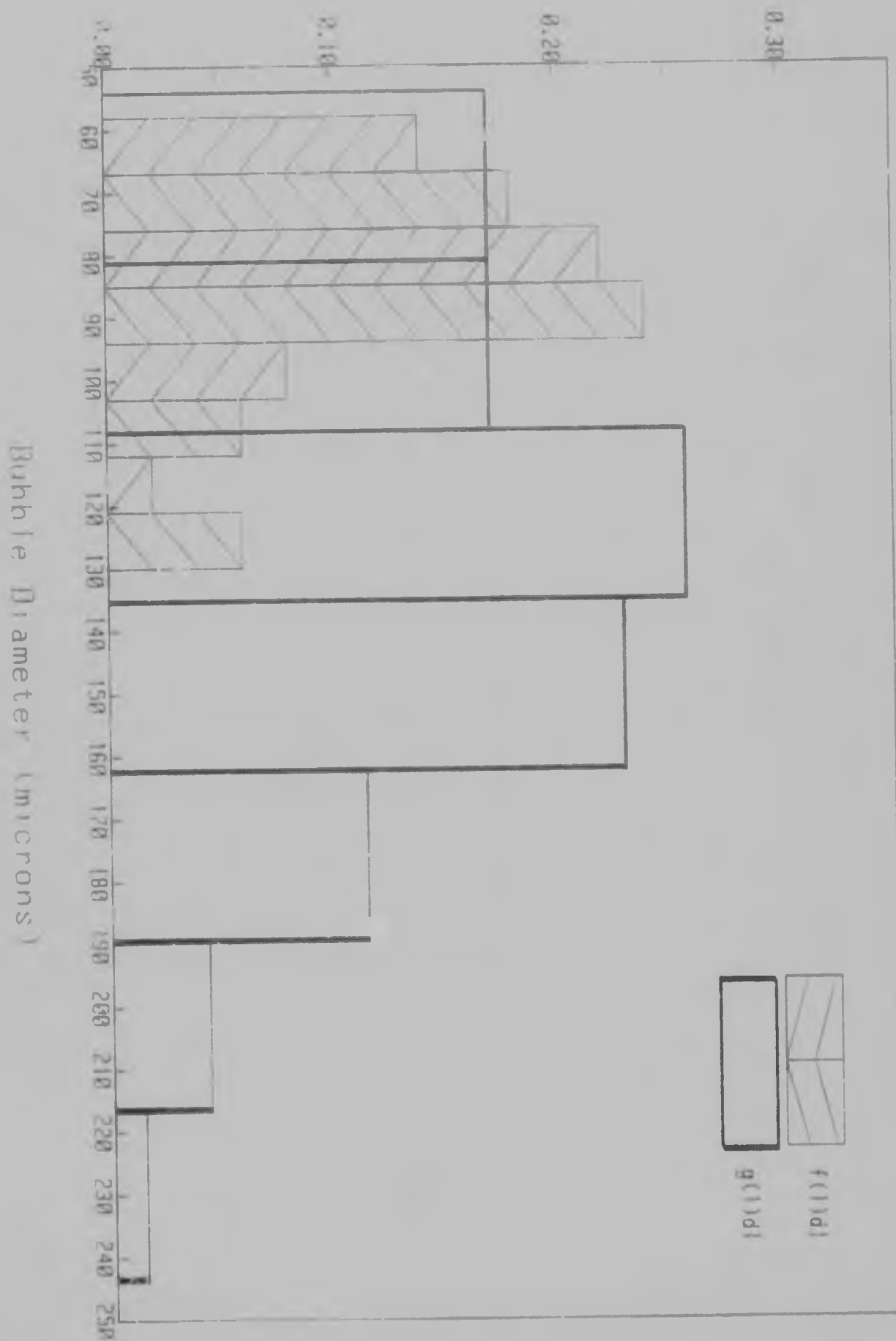
Mean bubble diameter = 67.498 microns
 Standard deviation = 6.629 microns
 Largest bubble diameter = 80.182 microns
 Smallest bubble diameter = 52.392 microns

INTERVAL NUMBER	INTERVAL RANGE (microns)	FRACTION OF BUBBLES
1	52.39 - 57.94	1.0526E-01
2	57.94 - 63.5	1.5789E-01
3	63.5 - 69.06	3.6842E-01
4	69.06 - 74.62	2.6316E-01
5	74.62 - 80.18	1.0526E-01

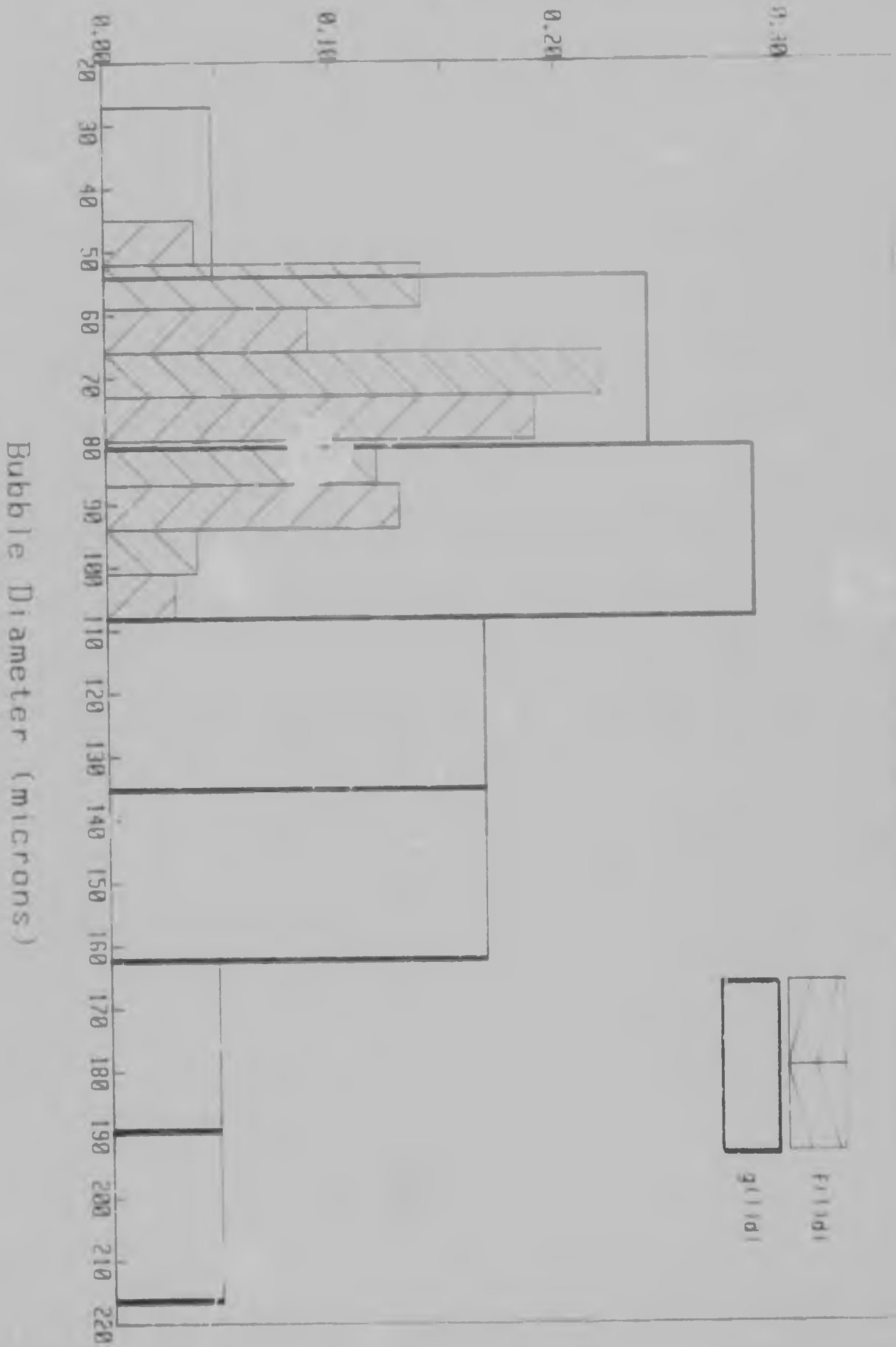




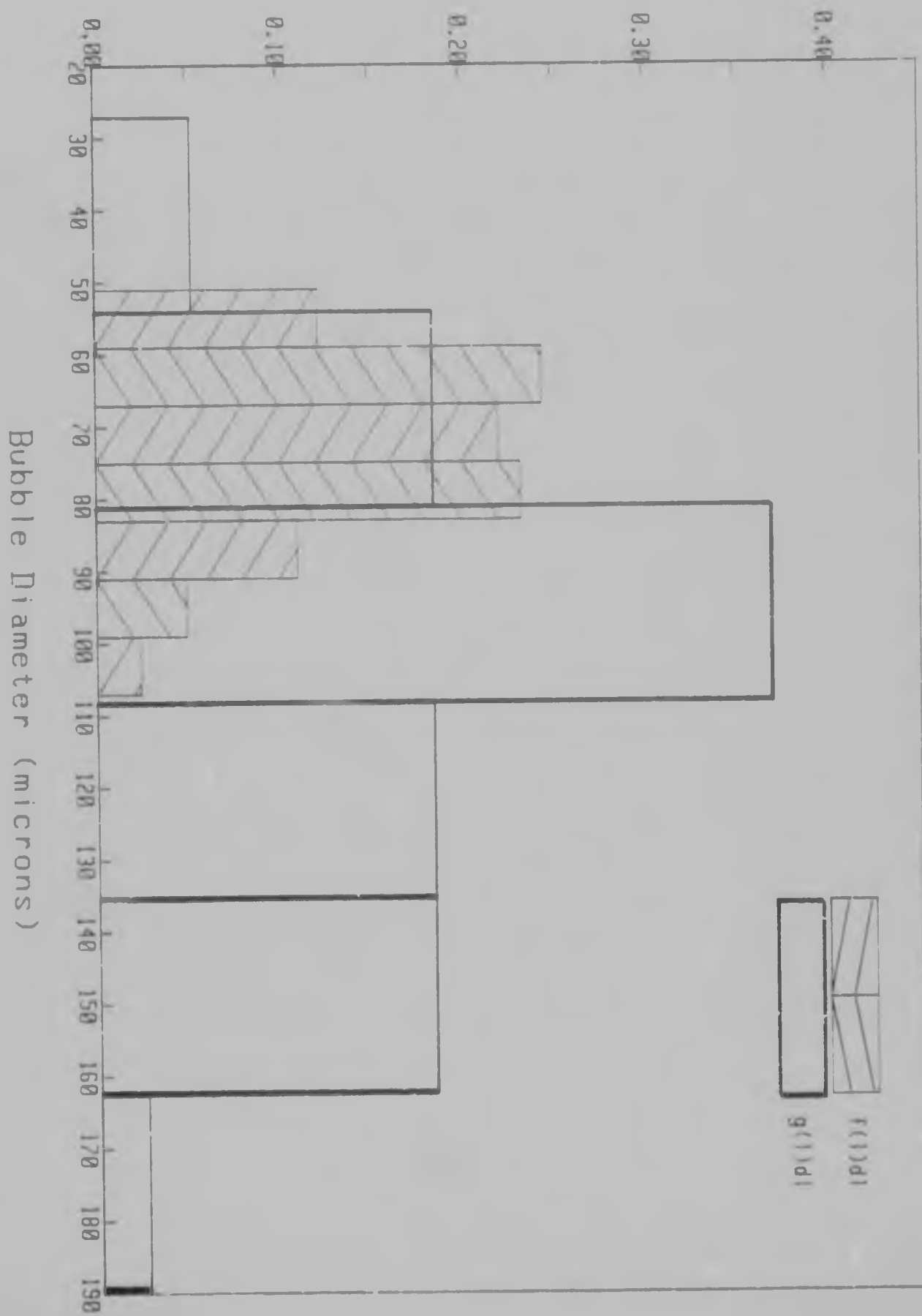
Fraction Of Bubbles



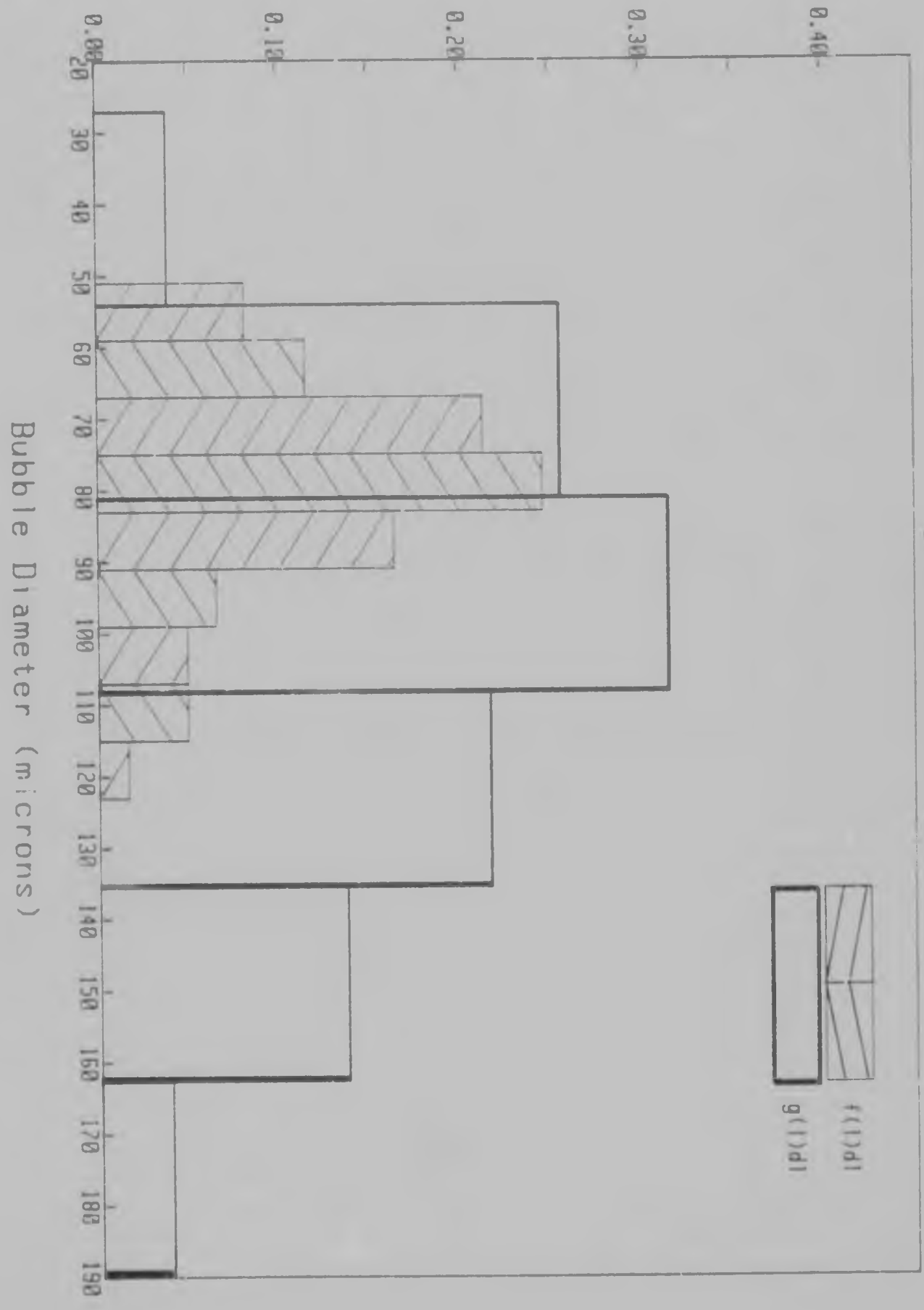
Fraction Of Bubbles



Fraction Of Bubbles

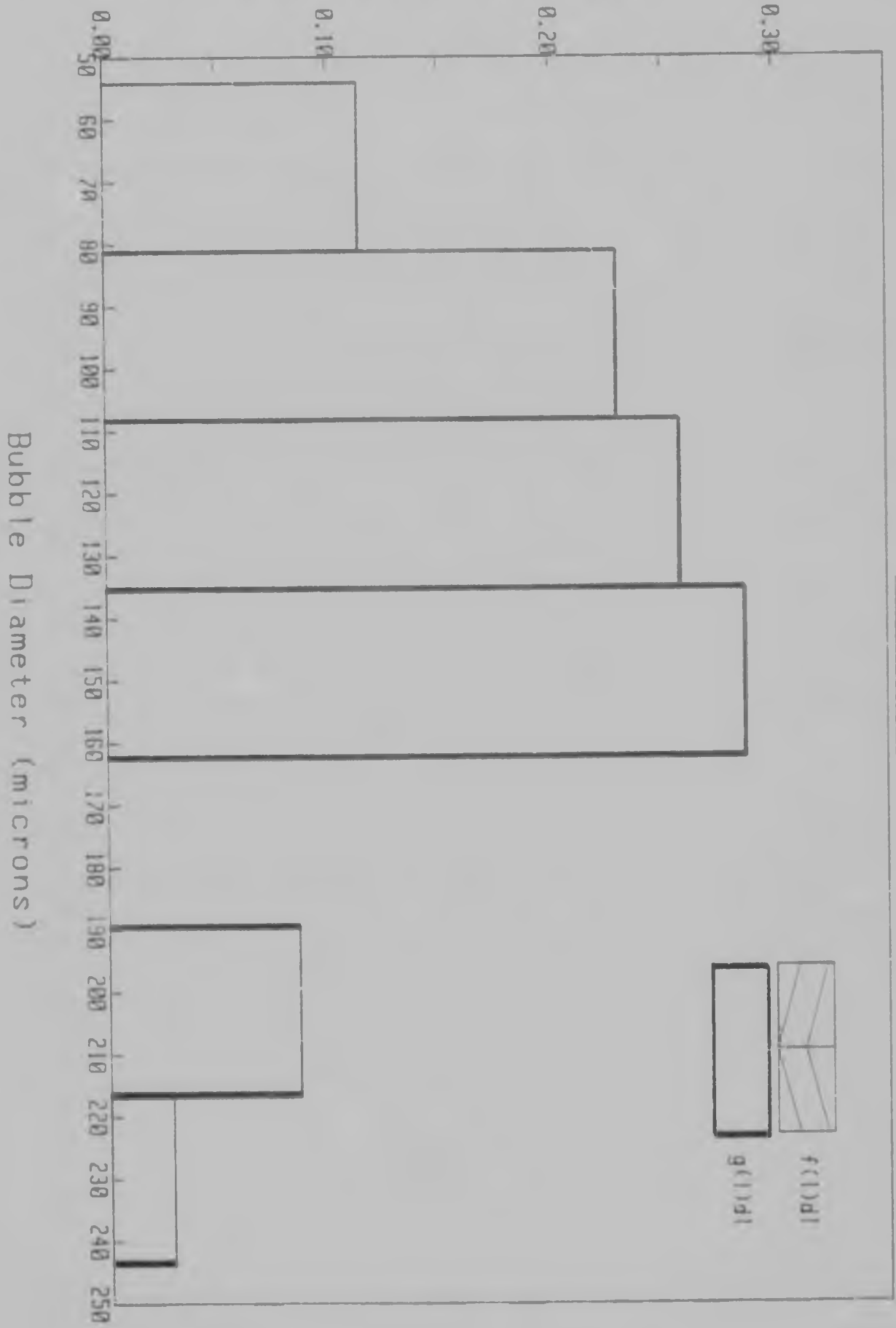


Fraction Of Bubbles

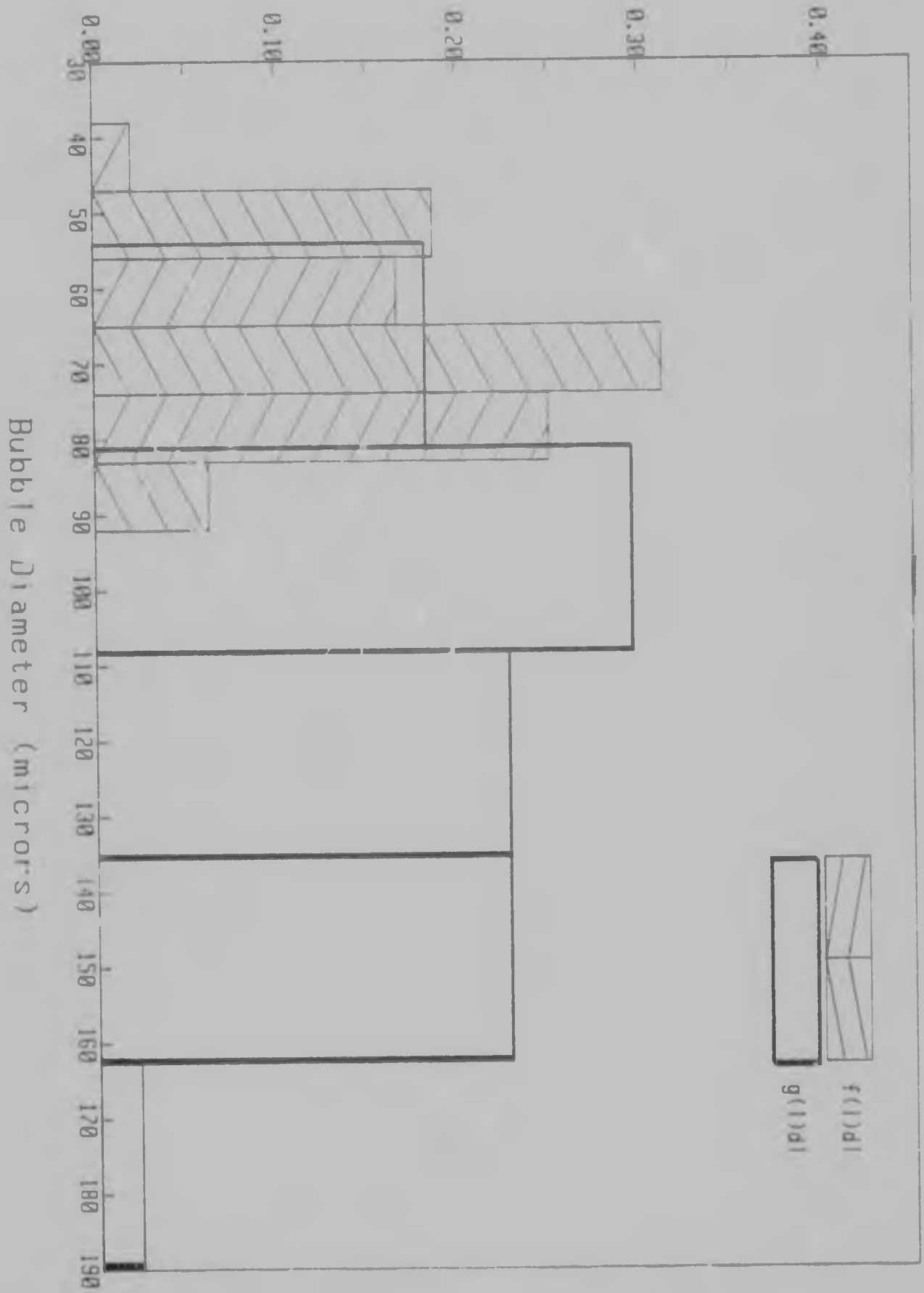


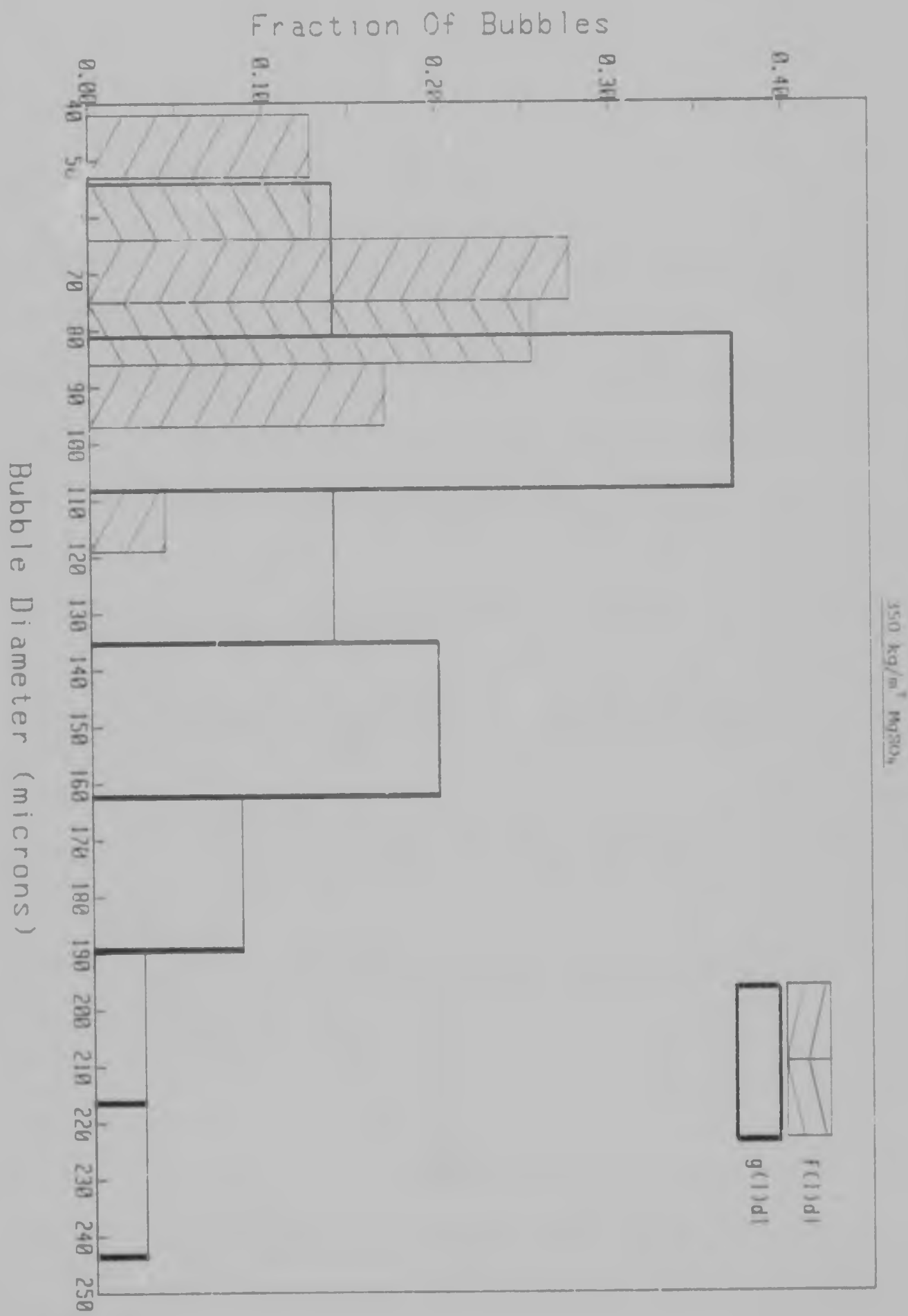
Fraction Of Bubbles

150 kg/m³ MgSO₄



Fraction Of Bubbles





Appendix 6 Measuring the Current Density

Kasper (1940) showed that the current distribution over a plane electrode, when the opposing electrode is a line electrode is:

$$i = \frac{a I_L}{r^2}$$

where i = the current density on the plane electrode, a distance r from the line electrode
 a = perpendicular distance between the line and plane electrodes
 I_L = current per unit length of the line electrode.

Figure A 6.1 is a pictorial representation of the system when viewed from above.

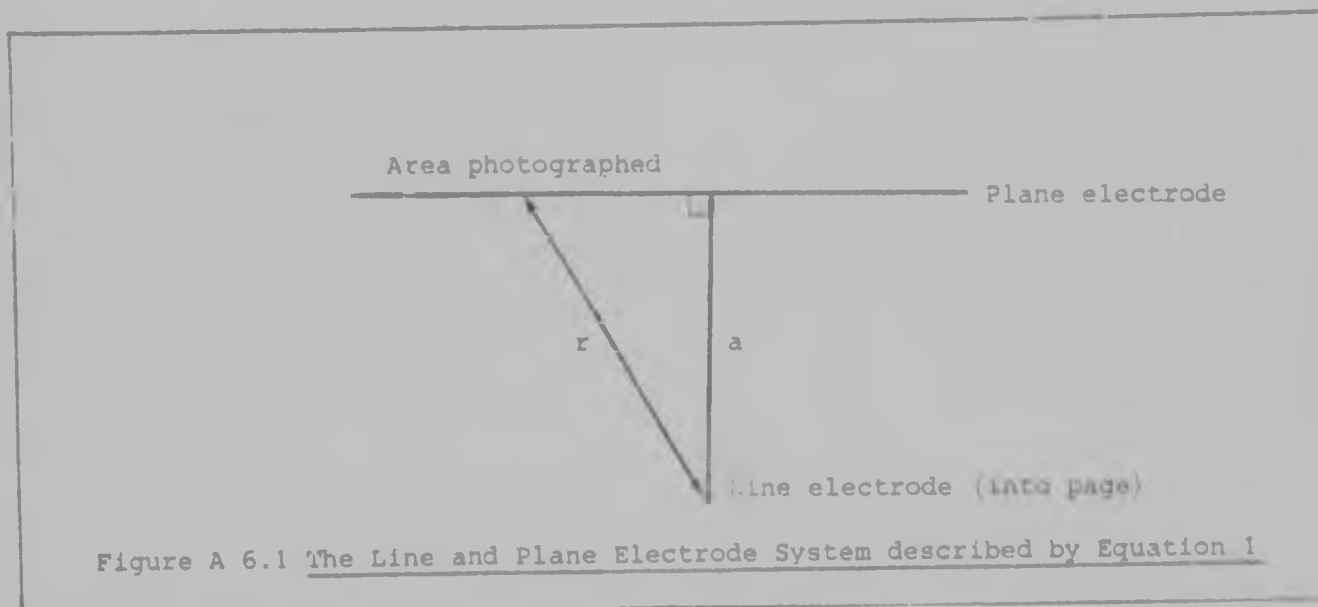


Figure A 6.1 The Line and Plane Electrode System described by Equation 1

Inherent in equation (1) is the assumption that the current density does not vary in the direction parallel to the line electrode.

For the system used in the experiments it was assumed that because the anode was so narrow compared to the cathode, the current densities could be calculated by equation (1). For the experiments:

$$a = 33 \text{ mm}$$

$$\text{length of the anode} = \text{length of line electrode} = 88 \text{ mm}$$

$$r = \text{position where photographs were taken, relative to the anode} = 60 \text{ mm}$$

$$\text{Hence } i = \frac{33 \times 10^{-3} I / 88 \times 10^{-3}}{\pi (60 \times 10^{-1})^2}$$

$$i = 33 I \text{ A/m}^2$$

$$\text{where } I = \text{measured current.}$$

Appendix 7 Solving the Population Balance

In the analysis section, section 5, it was shown that the population balance reduces to

$$q\beta_n = \frac{n2i}{\pi zF\rho_m \bar{l}} \int_0^{\infty} l^{n-2} f(l) dl \quad (1a)$$

or

$$q\beta_n = \frac{n2i}{\pi zF\rho_m} \int_1^{\infty} l^{n-3} f(l) dl \quad (1b)$$

Depending on whether the rate of bubble growth is taken to be

$$u(l) = \frac{3k^2}{l} \quad (1a)$$

or

$$u(l) = \frac{72 k^2 l}{l^2} \quad (2b) \text{ respectively.}$$

A computer program was written to perform these calculations.

The integrals on the right hand side of equations (1a) and (1b) were evaluated using a Simpsons rule integration. The bubble diameters measured on the electrode surface were sorted into an odd number of size intervals. The fraction of bubbles in each interval, $f(l)$, was then calculated by dividing the number of bubbles in each interval by the total number of bubbles measured (subroutine "Interval"). The value of the integrand could then be evaluated by multiplying $f(l)$ by l^{n-2} or l^{n-3} depending on whether equation (1a) or (1b) is being used, where l is the bubble diameter at the mid point of the respective interval, and

n is the order of the moment being considered (lines 1080 - 1110).

Hence:

$$\int_a^b p(l)dl = \frac{h}{3} \left[p_1 + 4p_2 + 2p_3 + 4p_4 + \dots + 4p_{m-3} + 2p_{m-2} + 4p_{m-1} + p_m \right]$$

Where $p(l)$ is the integrand of equation (1a) or (1b)

h = interval length

p_i = value of the integrand in the i^{th} interval

m = number of intervals (m must be an odd number)

Having evaluated the integral (subroutine "Integrate"), $q\beta_n$ can be evaluated from (1a) or (1b) (lines 1130 - 1140) since the constants in front of the integral are known quantities (\bar{l} is simply the mean of bubble sizes on the surface).

Having evaluated $q\beta_n$, an assumption about the distribution leaving the surface is made. Either a normal or a gamma distribution can be assumed. The parameters of the required distributions are then evaluated and the moments of this distribution can be calculated (lines 1290 - 1560) as outlined in appendix 2. The results are printed out in subroutine "Output". The results are presented in section 4. Sample print outs are presented after the program listing. These samples show the output of the program when first a normal and then a gamma distribution is assumed and either equation (2a) or (2b) is used to describe the rate of bubble growth. The results are all for the same run.

n is the order of the moment being considered (lines 1080 - 1110).

Hence:

$$\int_0^{\infty} p(\ell) d\ell = \frac{h}{3} \left[p_1 + 4p_2 + 2p_3 + 4p_4 + \dots + 4p_{m-3} + 2p_{m-2} + 4p_{m-1} + p_m \right]$$

Where $p(\ell)$ is the integrand of equation (1a) or (1b)

h = interval length

p_i = value of the integrand in the i^{th} interval

m = number of intervals (m must be an odd number)

Having evaluated the integral (subroutine "Integrate"), $q\beta_n$ can be evaluated from (1a) or (1b) (lines 1130 - 1140) since the constants in front of the integral are known quantities ($\bar{\ell}$ is simply the mean of bubble sizes on the surface).

Having evaluated $q\beta_n$, an assumption about the distribution leaving the surface is made. Either a normal or a gamma distribution can be assumed. The parameters of the required distributions are then evaluated and the moments of this distribution can be calculated (lines 1290 - 1560) as outlined in appendix 2. The results are printed out in subroutine "Output". The results are presented in section 4. Sample print outs are presented after the program listing. These samples show the output of the program when first a normal and then a gamma distribution is assumed and either equation (2a) or (2b) is used to describe the rate of bubble growth. The results are all for the same run.

10 ' Program to calculate the moments of the distributions of the
20 ' bubbles on and leaving the electrode surface.

30 ' The parameters k_a and N in the population balance are also
40 ' evaluated. Allowance is made for the assumption of a normal
50 ' or a gamma distribution of bubbles leaving the electrode
60 ' surface. The necessary changes in the program to allow for
70 ' these assumptions are shown in lines 1430-1560, 3620 & 3650-3660

```

80 OPTION BASE 1
90 CONTROL 1,12;1          Switch off keys.
100 GRAPHICS OFF
110 OUTPUT 2 USING "%X";"BK"  ' Clear the screen
120 GOSUB Read ' Read in the bubble diameters on the electrode surface
130 GCLEAR
140 Flag=0
150 Pltr=3                 Defines plotter position
160 Ps="INTERNAL"        Defines plotter type
170 Prntr=1               Defines printer position
180 PRINTER IS Prntr
190 PLOTTER IS Pltr Ps
200 GCLEAR
'0 GINIT
2.  ' OUTPUT 2 USING "%X";"BK" ' CLEAR SCREEN

230 ' CALCULATE THE MEAN BUBBLE DIAMETER ON THE ELECTRODE SURFACE

240 '          %a) ' Mean=mean bubble diameter
250 '          Mean/M

260 ' CALCULATE THE STANDARD DEVIATION OF THE BUBBLE DIAMETERS

270 %AT Dummy= (Mean)-Data
280 %AT Dummy= Dummy * Dummy
290 Stdev=SUM(Dummy) ' Stdev=standard deviation of bubble diameters
300 Stdev=SQR(Stdev/(M-1))
310 PRINT USING 320;Mean,Stdev
320 IMAGE "Mean = ,DDD.DDD, " microns",/, "Standard deviation = " DDD.DDD, " microns"
330 Smallest=MIN(Data(8)) ' Smallest=smallest bubble diameter
340 Largest=MAX(Data(8)) ' Largest =largest bubble diameter
350 PRINT USING 360,Largest,Smallest
360 IMAGE / "The largest bubble is ,DDD.DD, " microns" /, "The smallest bubble is ,DDD.DD, " microns"

370 ' GO TO SUBROUTINE 'Interval' TO SORT THE BUBBLE DIAMETERS INTO INTERVALS
380 Interval_call CALL Interval(M,Data(8) Interval(8),Divno,Divlen,Largest,Smallest) '
390 ' GO TO SUBROUTINE 'Print' TO DISPLAY THE INTERVALS ON THE SCREEN

400 Print_call:CALL Print(Viscosity$,Current$,Flow$,Prntr,M,Largest,Smallest,Divno,Divlen,Mean,Stdev,Interval(8))
410 IF Prntr=70; THEN Plot_call ' since the no. of intervals has been decided
420 Y$=""
430 INPUT "Do you wish to change the number of intervals?";Y$
440 IF UPC$(Y$(1,1))="Y" THEN
450 GOTO Interval_call ' and 'or' into a new no. of intervals
460 ELSE
470 M$=""
480 INPUT "Do you want to print the results?";M$
490 IF UPC$(M$(1,1))="Y" THEN
500 Prntr=701
510 GOTO Print_call ' and print results on the external printer

```



```
520 END IF
530 END IF !
```

```
540 ! SUBROUTINE 'Plot' DRAWS A HISTOGRAM OF THE BUBBLE DIAMETERS MEASURED
550 ! ON THE ELECTRODE SURFACE. THIS IS THE SAME ROUTINE AS SUBROUTINE
560 ! 'Plot' IN APPENDIX 2.
```

```
570 Plot_call:CALL Plot(Pltr,Ps,File$,Divno,Divlen,Largest,Smallest,Mean,Stdev,Interval,N)
580 OUTPUT 2 USING "*,X","BX" ! CLEAR SCREEN
590 IF Pltr=705 THEN Fit_prog
600 Y$=""
610 INPUT "Do you wish to make any changes?",Y$
620 IF UPC$(Y$(1,1))="I" THEN
630 GOTO Interval_call ! to change the number of intervals
640 ELSE
650 N$=""
660 INPUT "Do you want a hard copy?",N$
670 IF UPC$(N$(1,1))="Y" THEN
680 Pltr=705
690 Ps="HPGL"
700 GOTO Plot_call ! to plot the histogram on the plotter
710 END IF
720 END IF !
```

520 END IF
530 END IF !

152

540 ! SUBROUTINE 'Plot' DRAWS A HISTOGRAM OF THE BUBBLE DIAMETERS MEASURED
550 ! ON THE ELECTRODE SURFACE. THIS IS THE SAME ROUTINE AS SUBROUTINE
560 ! 'Plot' IN APPENDIX 2.

570 Plot_call:CALL Plot(Pltr,Ps,Files,Divno,Divlen,Largest,Smallest,Mean,Stddev,Interval(2),N)
580 OUTPUT 2 USING "0,K";"BK" ! CLEAR SCREEN
590 IF Pltr=705 THEN Fit_prog
600 Y\$=""
610 INPUT "Do you wish to make any changes?",Y\$
620 IF UPC\$(Y\$(1,1))="Y" THEN
630 GOTO Interval_call ! to change the number of intervals.
640 ELSE
650 N\$=""
660 INPUT "Do you want a hard copy?",N\$
670 IF UPC\$(N\$(1,1))="Y" THEN
680 Pltr=705
690 Ps="HPGL"
700 GOTO Plot_call ! to plot the histogram on the plotter.
710 END IF
720 END IF !

```

730 Fit_prog: ! Start of the moments calculation.

740 CONTROL 1,12;0
750 Prntr=1 ! This variable defines the printer location as the screen.
760 GRAPHICS OFF
770 OUTPUT 2 USING "0,K";"0X" ! Clears alpha screen.
780 Rate_flag=0 ! This variable will define which rate equation is used.

790 FOR I=0 TO 7 ! This loop will
800   ON KEY I GOSUB Dummy ! switch off the soft keys
810 NEXT I ! that are not needed.

820 ON KEY 8 LABEL "U=kt^-1/2" GOSUB U_half ! This key selects the rate
830 ! Equation U=kt^-1/2

840 ON KEY 9 LABEL "U=kt^-2/3" GOSUB U_2thirds ! This key selects the rate
850 ! equation U=kt^-2/3

860 PRINTER IS Prntr
870 PRINT "Use soft keys to select a rate equation"
880 ON CYCLE .3 GOTO Check ! and see if a rate equation has been selected
890 Hover:GOTO Hover ! until a rate equation has been chosen.

900 Carry_on:ON KEY 8 GOSUB Dummy ! This deactivates the
910 ON KEY 9 GOSUB Dummy ! soft keys after a rate
920 CONTROL 1,12;1 ! equation has been selected

930 OUTPUT 2 USING "0,K";"0X" ! Clear alpha screen
940 No_int=Divno ! Number of intervals

950 ALLOCATE F(1:No_int),L(1:No_int)
960 IF Rate_flag=2 THEN ! Check to see
970   Const=(28338VAL(Current$))/(PI82896484 6833.58Mean81.E-6) ! which rate
980 END IF ! const is
990 IF Rate_flag=3 THEN ! used & then
1000   Const=(28338VAL(Current$))/(PI82896484 6833 5) ! evaluate the
1010 END IF ! constant in
1020 ! front of the
1030 ! integral.

1040 IF Rate_flag<2 AND Rate_flag<3 THEN ! Make sure
1050   BEEP 150,1 ! Rate_flag
1060   DISP "OPPS !!!!!!!!!!!!!!!!!!!!!!!!!!!!!" ! has not
1070   STOP ! obtained
1080 END IF ! another
1090 ! value.

1100 FOR I=1 TO No_int ! Loop to find I
1110   L(I)=(Smallest+I8Divlen-Divlen/2)81 E-6 ! at the experimental
1120 NEXT I ! points.

1130 OUTPUT 2 USING "0,K";"0X" ! Clear the screen

1140 ! THIS LOOP CALCULATES THE MOMENTS
1150 No_of_moments=18 ! = the number of moments to be calculated.
1160 ALLOCATE w_beta(1:No_of_moments),Beta(1:No_of_moments),Q(1:No_of_moments)
1170 OUTPUT 2 USING "0,K";"0X" ! Clear the screen
1180 No_eval=13 ! No. of function evaluations to evaluate the moments of g(l).
1190 ALLOCATE Func(1:No_eval)
1200 FOR I=1 TO No_of_moments !

```

```

1210 FOR J=1 TO No_int           ! Loop to
1220   IF Rate_flag=2 THEN F(J)=1.E+6*Interval(J)*L(J)^(I-2) ! evaluate the
1230   IF Rate_flag=3 THEN F(J)=1.E+6*Interval(J)*L(J)^(I-3) ! integrand
1240 NEXT J                     ! at each l.

1250 CALL Integrate(F(I),No_int,Divlen*1.E-6,Integral) ! Evaluate the integral
1260 Integral=Integral*Const*I
1270 Q_beta(I)=Integral ! = q*beta(n)
1280 NEXT I

1290 Meta=Movie_mean*1.E-6      ! Mean (1E-6 CONVERTS TO m)
1300 Sigma=Movie_stddev*1.E-6  ! Standard deviation ( )
1310 H=6*Sigma/(No_eval+1)     ! Step length for integrating g(l).

1320 ! EVALUATE THE INTEGRAL I^n*g(l) ie THE n th MOMENT.

1330 FOR J=1 TO No_of_moments
1340   FOR I=1 TO No_eval
1350     Step_len=(Meta-3*Sigma)+(2*I-1)*H/2
1360     Func(I)=Step_len^J*EXP(-(Step_len-Meta)*(Step_len-Meta)/(2*Sigma*Sigma))/(Sigma*SQRT(2*PI))
1370   NEXT I
1380   CALL Integrate(Func(I),No_eval,H,Integral) ! Go to subroutine 'Integrate'
1390                                           ! to evaluate the moments.
1400   Beta(J)=Integral ! = beta(n)
1410   Q(J)=Q_beta(J)/Beta(J) ! = q calculated from beta(n).
1420 NEXT J !

1421 GOTO 1570
1430 !XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX

1440 ! If a gamma distribution is required lines 1290 to 1421 could be
1450 ! replaced by the following program lines:

1460 Gam_a=((Movie_mean/Movie_stddev)^2)-1 ! Evaluate a & b parameters in
1470 Gam_b=Movie_mean/(Movie_stddev^2)*1.E+6 ! gamma distribution.
1480 FOR N=1 TO No_of_moments
1490   Beta(N)=1
1500   FOR I=1 TO N           ! Loop to calculate
1510     Beta(N)=Beta(N)*(Gam_a+I) ! beta(n) from the
1520   NEXT I                ! parameters in the
1530   Beta(N)=Beta(N)/(Gam_b*N) ! gamma density function.
1540   Q(N)=Q_beta(N)/Beta(N) ! Calculate q from beta's.
1550 NEXT N
1560 !XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX

1570 ! CALCULATE q FROM beta(3).

1580 Q_calc=6.833*VAL(Current)/(28PI*96484.6833.5*Beta(3)) !

1590 ! NOW PRINT OUT THE RESULTS USING SUBROUTINE 'Output'.
1600 ! IF A GAMMA DISTRIBUTION WAS ASSUMED THEN REPLACE THE PARAMETERS
1610 ! 'Meta' AND 'Sigma' IN LINE 1620 WITH 'Gam_a' AND 'Gam_b'.

1620 CALL Output(File$,Viscosity$,Current$,Flow$,Rate_flag,Q(I),Meta,Sigma,Q_beta(I),No_of_moments,Beta(I),Movie_mean,Movie_stddev,Mean,Stddev,Q_calc,N_on)
1630 Y$=""
1640 INPUT "Do you want to change the number of intervals?",Y$
1650 DEALLOCATE F(I),L(I),Q_beta(I),Beta(I),Func(I),Q(I)
1660 IF UPC$(Y$(1,1))="Y" THEN Interval_call ! to change the no. of intervals
1670 Y$=""
1680 INPUT "Do you want to change the rate expression?",Y$
1690 IF UPC$(Y$(1,1))="Y" THEN Fit_prog ! to change the rate equation used.
1700 CONTROL 1,12;0 ! Switch off keys.
1710 PRINTER IS 1
1720 STOP !

```

```

1210 FOR J=1 TO No_int                ! Loop to
1220   IF Rate_flag=2 THEN F(J)=1.E+6*Interval(J)*L(J)^(I-2) ! evaluate the
1230   IF Rate_flag=3 THEN F(J)=1.E+6*Interval(J)*L(J)^(I-3) ! integrand
1240 NEXT J                            ! at each l.

1250 CALL Integrate(F(I),No_int,Divlen*1.E-6,Integral)! Evaluate the integral
1260 Integral=Integral*Const*I
1270 Q_beta(I)=Integral / = q*beta(n)
1280 NEXT I
1290 Meta=Movie_mean*1.E-6           ! Mean                ( 1E-6 CONVERTS TO m )
1300 Sigma=Movie_stddev*1.E-6       ! Standard deviation (
1310 H=6*Sigma/(No_eval+1)         ! Step length for integrating q(l).

1320 ! EVALUATE THE INTEGRAL  $\int_0^1 l^n q(l)$  ie THE n th MOMENT.

1330 FOR J=1 TO No_of_moments
1340   FOR I=1 TO No_eval
1350     Step_len=(Meta-3*Sigma)+(2*I-1)*H/2
1360     Func(I)=Step_len^J*EXP(-(Step_len-Meta)*(Step_len-Meta)/(2*Sigma*Sigma))/(Sigma*SQRT(2*PI))
1370   NEXT I
1380   CALL Integrate(Func(I),No_eval,H,Integral)! Go to subroutine 'Integrate'
1390                                     ! to evaluate the moments.
1400   Beta(J)=Integral / = beta(n)
1410   Q(J)=Q_beta(J)/Beta(J) ! = q calculated from beta(n).
1420 NEXT J

1421 GOTO 1570
1430 !XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX

1440 ! If a gamma distribution is required lines 1290 to 1421 could be
1450 ! replaced by the following program lines:

1460 Gam_a=((Movie_mean/Movie_stddev)^2)-1 ! Evaluate a & b parameters in
1470 Gam_b=Movie_mean/(Movie_stddev^2)*1.E+6 ! gamma distribution.
1480 FOR N=1 TO No_of_moments
1490   Beta(N)=1
1500   FOR I=1 TO N                ! Loop to calculate
1510     Beta(N)=Beta(N)*(Gam_a+I) ! beta(n) from the
1520   NEXT I                       ! parameters in the
1530   Beta(N)=Beta(N)/(Gam_b^N)    ! gamma density function.
1540   Q(N)=Q_beta(N)/Beta(N)      ! Calculate q from beta's.
1550 NEXT N
1560 !XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX

1570 ! CALCULATE q FROM beta(3).

1580 Q_calc=6*33*VAL(Current)/(2*PI*896484.6*33.5*Beta(3))

1590 ! NOW PRINT OUT THE RESULTS USING SUBROUTINE 'Output'.
1600 ! IF A GAMMA DISTRIBUTION WAS ASSUMED THEN REPLACE THE PARAMETERS
1610 ! 'Meta' AND 'Sigma' IN LINE 1620 WITH 'Gam_a' AND 'Gam_b'.

1620 CALL Output(File$,Viscosity$,Current$,Flow$,Rate_flag,Q,I,Meta,Sigma,Q_beta(I),No_of_moments,Beta(I),Movie_mean,Movie_stddev,Mean,Stddev,Q_calc,N_on)
1630 Y$=""
1640 INPUT "Do you want to change the number of intervals?",Y$
1650 DEALLOCATE F(I),L(I),Q_beta(I),Beta(I),Func(I),Q(I)
1660 IF UPC$(Y$(1,1))="Y" THEN Interval_call ! to change the no. of intervals
1670 Y$=""
1680 INPUT "Do you want to change the rate expression?",Y$
1690 IF UPC$(Y$(1,1))="Y" THEN Fit_prog ! to change the rate equation used.
1700 CONTROL 1,12;0 ! Switch off keys.
1710 PRINTER IS 1
1720 STOP !

```

```

1736 Dummy:RETURN      ! Dummy routine to deactivate the soft keys.

1740 U_half:Rate_flag=2      ! Defines the rate equation
1750 RETURN                ! as  $U=kt^{-1/2}$ .

1760 U_2thirds:Rate_flag=3  ! Defines the rate equation
1770 RETURN                ! as  $U=kt^{-2/3}$ .

1780 Read: ! Read data off the disc.
1790 MASS STORAGE IS * HP9121,700,.
1800 LINPUT "Enter the name of the data file",File$
1810 ASSIGN @File TO File$
1820 ENTER @File,1;N,Viscosity$,Current$,Flow$ ! Reads in the viscosity,
1830                                           ! current and flowrate used.
1840 ALLOCATE Data(N),Dummy(N),Interval(N)
1850 ENTER @File,2;Data(8)
1860 ASSIGN @File TO *
1870 INPUT "Enter the mean and standard deviation of bubble diameters leaving the surface",Movie_mean,Movie_stddev
1880 INPUT "Enter the value of N",N_on ! No. of nucleation sites per unit area
1890 RETURN !

1900 Check:IF Rate_flag=2 OR Rate_flag=3 THEN ! Checks to see if a rate equation
1910 OFF CYCLE                               ! has been chosen.
1920 GOTO Carry_on                           ! if so continue with calculations
1930 ELSE                                     ! otherwise wait
1940 GOTO Hover                               ! until one is entered
1950 END IF
1960 END !

```

```
1970 Integrate:SUB Integrate(F(X),No_int,H,Integral) ! Using Simpsons Rule.
1980   Integral=F(1)+F(No_int)           ! Start adding.
1990   FOR I=2 TO No_int-1 STEP 2
2000     Integral=Integral+4*F(I)       ! Add the 4* terms.
2010   NEXT I
2020   FOR I=3 TO No_int-2 STEP 2
2030     Integral=Integral+2*F(I)     ! Add the 2* terms.
2040   NEXT I
2050   Integral=Integral*H/3          ! Multiply by h/3.
2060 SUREND !
```

```

2070 Interval:SUB Interval(N>Data(8),Interval(8),Divno,Divlen,Largest,Smallest)
2080 OPTION BASE 1
2090 INPUT "Enter the number of intervals you require - make sure its an odd number",Divno
2100 IF Divno(1) OR FRACT(Divno)(>0) OR FRACT(Divno/2)=0 THEN
2110   BEEP 500,1
2120   DISP "THAT IS NOT FUNNY"
2130   WAIT 2
2140   GOTO 2090
2150 END IF
2160 REDIM Interval(Divno) ! Interval()=number of bubbles in each interval
2170 MAT Interval= (v)
2180 Divlen=(Largest-Smallest)/Divno! Divlen=length of each interval

2190 ! Loop to place each bubble in its correct interval

2200 FOR I=1 TO N
2210   FOR J=1 TO Divno
2220     IF Data(I)(=Smallest+J*Divlen AND Data(I))=Smallest+(J-1)*Divlen THEN
2230       Interval(J)=Interval(J)+1
2240       GOTO Skip
2250     END IF
2260   NEXT J
2270   BEEP 500,1
2280   DISP "ERROR IN 1810"
2290   STOP
2300 Skip:NEXT I
2310 MAT Interval= (1/N)*Interval
2320 SUBEND
2330 Print:SUB Print(Viscosity$,Current$,Flow$,Pntr,N,Largest,Smallest,Divno,Divlen,Mean,Stdev,Interval(8))
2340 PRINTER IS Pntr
2350 IF Pntr=1 THEN PRINT CHR$(12) ! CLEARS SCREEN
2360 PRINT USING 2370;Viscosity$,Current$,Flow$
2370 IMAGE "Solution viscosity is ",X," centipoise",/, "Current used was ",X," amps",/, "The flowrate is ",X," l/min",/
/
2380 PRINT "The number of points used is ";N
2390 PRINT USING 2400,Mean,Stdev
2400 IMAGE "Mean bubble diameter = ",DDD.DDD," microns",/, "Standard deviation = ",DDD.DDD," microns"
2410 PRINT USING 2420;Largest,Smallest
2420 IMAGE "Largest bubble diameter = ",DDD.DDD," microns",/, "Smallest bubble diameter = ",DDD.DDD," microns",//
2430 PRINT "INTERVAL NUMBER",TAB(21),"INTERVAL RANGE (microns)",TAB(60),"FRACTION OF BUBBLES"
2440 PRINT "-----",TAB(21),"-----",TAB(60),"-----"
2450 FOR I=1 TO Divno
2460   Y$(1,5)=VAL$(INT((Smallest+(I-1)*Divlen)*100)/100)
2470   Y$(6,8)=" - "
2480   Y$(9,13)=VAL$(INT((Smallest+I*Divlen)*100)/100)
2490   PRINT USING 2500;I,Y$,Interval(I)
2500   IMAGE 5X,DD,20X,K,25X,D.DDDD
2510 NEXT I
2520 SUBEND !

```



```

2530 SUB Plot(Pltr,P%,File$,Divno,Divlen,Largest,Smallest,Mean,Stdev,Interval(2),N)
2540 OPTIM BASE 1
2550 Plot!! Plotting routine

2560 Top=MAX(Interval(2)) ! Top = SIZE OF LARGEST INTERVAL
2570 Top=(INT(Top*10)+1)/10
2580 PLOTTER IS Pltr,P%
2590 ALPHA OFF
2600 GRAPHICS ON
2610 IF Pltr=3 THEN GCLEAR
2620 IF Pltr=3 THEN 2700! If the plotter isn't the screen then pick up a pen
2630 GRAPHICS OFF
2640 OUTPUT 2 USING "0,X";"0X"
2650 DISP "Put a pen in the plotter and press 'COHT' when ready"
2660 PAUSE
2670 ALPHA OFF
2680 GRAPHICS ON
2690 OUTPUT 705;"SP1"! Pick up a pen
2700 DEG
2710 LINE TYPE .
2720 LDIR 0
2730 WINDOW Smallest-2*Divlen,Largest+Divlen/2,-Top/5,Top*1.3! Plot scale
2740 LORG 5
2750 CSIZE 1,.5
2760 CLIP Smallest,Largest,0,Top
2770 AXES Divlen,.05,Smallest,0! Draw axes
2780 CLIP OFF !

2790 ! Draw histogram

2800 FOR I=1 TO Divno
2810 IF Interval(I)=0 THEN 2840
2820 CLIP Smallest+(I-1)*Divlen,Smallest+I*Divlen,0,Interval(I)
2830 FRAME
2840 NEXT I
2850 CLIP OFF
2860 CSIZE 3,.5
2870 LORG 5!

2880 ! Label X axis

2890 FOR I=0 TO Divno
2900 MOVE Smallest+I*Divlen,-Top/30
2910 LABEL USING "000.DD";Smallest+I*Divlen
2920 NEXT I
2930 MOVE (Largest+Smallest)/2,-Top/10
2940 CSIZE 5,.5
2950 LABEL "Bubble diameter (microns)"
2960 CSIZE 3,.5 !

2970 ! Label Y axis

2980 FOR I=0 TO Top STEP .05
2990 MOVE Smallest-Divlen/4,I
3000 LABEL USING "Z.DD";I
3010 NEXT I
3020 CSIZE 4,.5
3030 MOVE Smallest-Divlen,Top/2
3040 LDIR 90
3050 LORG 6
3060 LABEL "Fraction of bubbles" !

3070 ! Graph heading

```

```

3080 LORG 5
3090 LDIR 0
3100 CSIZE 8,1
3110 MOVE (Largest+Smallest)/2,Top&1.2
3120 FOR I=1 TO LEN(Files)
3130   IF Files(I,I)="_" THEN Files(I,I)="."
3140 NEXT I
3150 LABEL Files
3160 LINE TYPE 3,1
3170 LDIR 0
3180 LORG 5

3190 ! Label mean and standard deviation

3200 MOVE Mean,0
3210 IDRAW 0,Top
3220 IMOVE -Stddev,0
3230 LINE TYPE 1
3240 CSIZE 2,.5
3250 LABEL CHR$(124)
3260 MOVE Mean-Stddev,Top
3270 IDRAW 2*Stddev,0
3280 LABEL CHR$(124)
3290 MOVE Mean,Top
3300 LORG 4
3310 LABEL "M"
3320 MOVE Mean-Stddev/2,Top
3330 LABEL "-S"
3340 MOVE Mean+Stddev/2,Top
3350 LABEL "+S"

3360 ! Fit a normal curve

3370 MOVE Smallest,0
3380 FOR I=Smallest TO Largest STEP Divlen/10
3390   Exponent=Divlen*EXP(-((I-Mean)/Stddev)^2/2)/(Stddev*SQRT(2*PI))
3400   DRAW I,Exponent
3410 NEXT I
3420 IF Pltr=3 THEN 3440
3430 OUTPUT 705;"SP"! Put pen down
3440 GRAPHICS OFF
3450 SUREND !

```

```

3460 Output:SUB Output(Files,Viscosity$,Current$,Flow$,Rate_Flag,Q(X),Meta,Sigma,Q_beta(X),No_of_moments,Beta(X),Mean,Mean,
Mean,Movie_stddev,Mean,Stddev,Q_calc,Non)
3470 DIM A$(100)
3480 PRINTER IS 701;WIDTH (80)      ! Output to printer
3490 PRINT "%dD";File$;"%dA"
3500 PRINT
3510 PRINT USING 3520;Viscosity$,Current$,Flow$
3520 IMAGE "Solution viscosity = ",X," cP",/, "Total current = ",X," A",/, "Flowrate = ",X," l/min",/
3530 PRINT USING 3540;Mean$
3540 IMAGE /, "Average bubble diameter on the surface = ",D.DDD," microns"
3550 PRINT USING 3560;Stddev$
3560 IMAGE "Standard deviation of bubble diameters on the surface = ",D.DD.DD," microns",/
3570 PRINT USING 3580;Movie_mean$
3580 IMAGE "Average bubble diameter leaving the surface = ",D.DD.DD," microns"
3590 PRINT USING 3600;Movie_stddev$
3600 IMAGE "Standard deviation of bubble diameters leaving the surface = ",D.DD.DD," microns",/
3610 PRINT "Assuming a normal distribution of bubble diameters leaving the surface"
3620 ! If a gamma distribution was assumed then change line 3610 accordingly
3630 PRINT USING 3640;Meta,Sigma$
3640 IMAGE "Meta = ",X,MD.SDE," n",/, "Sigma = ",X,MD.SDE,X," n",/
3650 ! If a gamma distribution was assumed, line 3640 should read
3660 ! IMAGE "a = ",X,MD.SDE,/, "b = ",X,MD.SDE,X," 1/n",/
3670 PRINT USING 3680$
3680 IMAGE "%dD",17X,"-2 -1"
3690 PRINT USING 3700;Q_calc$
3700 IMAGE "q = ",D.DDDDE," n s      (calculated from the 3rd moment)",%dD"/
3710 K=338VAL(Current$)/(48P(896484.6833.58Non)) ! Calculate the rate
3720 IF Rate_Flag=2 THEN K=(K/(Mean$.E-6))^*.5 ! constant depending on which
3730 IF Rate_Flag=3 THEN K=K^(1/3) ! rate equation is used
3740 PRINT USING 3750$
3750 IMAGE "%dD",15X,"-2"
3760 PRINT USING 3770;Non$
3770 IMAGE "N = ",D.DDDE,X," n", "%dD", "(calculated from the measured N)"
3780 IF Rate_Flag=2 THEN
3790 PRINT "u(1) = 8(k^2)/1"
3800 PRINT USING 3810$
3810 IMAGE "%dD",22X,"1/2"
3820 PRINT USING 3830;K$
3830 IMAGE "where k = ",X,D.DDE,X," n/s", "%dD", "(calculated from the measured N)",/
3840 END IF
3850 IF Rate_Flag=3 THEN
3860 PRINT "u(1) = 144(k^3)/(1^2)"
3870 PRINT USING 3880$
3880 IMAGE "%dD",22X,"1/3"
3890 PRINT USING 3900;K$
3900 IMAGE "where k = ",X,D.DDE,X," n/s", "%dD"/
3910 END IF
3920 PRINT USING 3930$
3930 IMAGE "%dD",21X,"1 2",28X,"1",17X,"2"
3940 PRINT USING 3950$
3950 IMAGE "%dD 1 %dA",5X,"%dDq8B(calc) (n /n s)%dA",10X,"%dDR(predicted) (n )%dA",10X,"%dDq (1/n s)%dA"
3960 PRINT "%dD"
3970 FOR I=1 TO No_of_moments$
3980 PRINT USING 3990;I,Q_beta(I),Beta(I),Q(I)
3990 IMAGE DD,10X,D.SDE,18X,D.SDE,13X,D.SDE
4000 NEXT I
4010 PRINT "%dD" ! Go to the top of the next page
4020 PRINTER IS 16
4030 SUBEND !Z

```

Solution v. ...
 Total current = 1 A
 Flow rate = 2 l/min

Average bubble diameter on the surface = 88.740 microns
 Standard deviation of bubble diameters on the surface = 21.705 microns
 Average bubble diameter on the surface = 127.000 microns
 Standard deviation of bubble diameters on the surface = 36.000 microns

Assuming a normal distribution of bubble diameter leaving the surface

Mean = 27000E-04 m
 Sigma = 5.60000E-05 m

$\mu = 3.87445E+06 \text{ m}^{-2} \text{ s}^{-1}$ (calculated from the 3rd moment)

$N = 8.366E-11 \text{ m}^{-3}$

$\mu = 2.47E+11$
 $\sigma = 1.7E+11 \text{ m}^{-1/2}$

	$\mu \text{ (m}^{-2} \text{ s}^{-1})$	$\sigma \text{ (m}^{-1/2})$	$\mu \text{ (1/m}^2 \text{ s)}$
1	3.50E+02	1.26548E-01	3.59563E+06
2	6.22E-02	1.73186E-05	4.40143E+06
3	1.01779E-05	2.51636E-12	4.02879E+06
4	1.26399E-09	3.84322E-16	3.28898E+06
5	1.55165E-13	5.12532E-20	2.53317E+06
6	1.91227E-17	1.01304E-23	1.88755E+06
7	2.38659E-21	1.73061E-27	1.37904E+06
8	2.02816E-25	3.04214E-31	9.95404E+05
9	3.81226E-29	5.48455E-35	7.13323E+05
10	5.14799E-33	1.01122E-38	5.09786E+05

Solution viscosity = 0.92 cP
 Total current = 1 A
 Flowrate = 2 l/min

Average bubble diameter on the surface
 Standard deviation of bubble diameters on the surface

18.149 micron
 1.795 micron

Average bubble diameter on the surface
 Standard deviation of bubble diameters on the surface

117.000 micron

Assuming a normal distribution of bubble diameter leaving the surface

Mean = 1.27000E-04 m
 Sigma = 3.60000E-05 m

$q = 3.87445E+06 \text{ m}^{-2} \text{ s}^{-1}$ (calculated from the 3rd moment)

$N = 8.966E+06 \text{ m}^{-2}$

$u(1) = 144(k^3)/(1^2)$

where $k = 4.49E-05 \text{ m/s}^{1/3}$

<u>1</u>	<u>$q \times B_1(\text{calc}) \cdot \text{m}^1/\text{m}^2 \text{ s}$</u>	<u>$B_1(\text{predicted}) \cdot \text{m}$</u>	<u>$1/\text{m}^2 \text{ s}$</u>
1	5.11530E+02	1.26548E-04	1.04218E+02
2	8.07569E-02	1.73186E-08	1.66301E+02
3	1.01465E-05	2.51636E-12	1.03221E+02
4	1.19951E-09	3.84322E-16	3.12110E+01
5	1.40208E-13	6.12532E-20	1.28899E+01
6	1.65232E-17	1.01304E-23	1.63105E+00
7	1.97977E-21	1.73061E-27	1.14397E+00
8	2.42041E-25	3.04214E-31	7.95627E-01
9	3.02308E-29	5.48455E-35	5.51199E-01
10	3.85749E-33	1.01122E-38	3.81468E-01

Solution viscosity = 0.92 cP
 Total current = 1 A
 Flowrate = 2 l/min

Average bubble diameter on the surface = 88.740 microns
 Standard deviation of bubble diameters on the surface = 21.705 microns
 Average bubble diameter on the surface = 127.000 microns
 Standard deviation of bubble diameters on the surface = 36.000 microns

Assuming a gamma distribution of bubble diameters leaving the surface :

a = 1.14452E+01
 b = 9.79938E+04 1/m

q = 3.79563E+06 m⁻²s⁻¹ (calculated from the 3rd moment)

N = 8.966E+06 m⁻²

u(1) = B(k²)/1

where k = 3.20E-05 m/s^{1/2}

i	q × B _i (calc) (m ¹ /m ² s)	B _i (predicted) (m ¹)	q (1/m ² s)
1	4.55020E+02	1.27000E-04	3.58283E+06
2	7.62267E-02	1.74250E-08	4.37455E+06
3	1.01379E-05	2.56861E-12	3.94684E+06
4	1.26399E-09	4.04849E-16	3.12212E+06
5	1.55165E-13	6.79414E-20	2.28380E+06
6	1.91227E-17	1.20952E-23	1.58101E+06
7	2.38659E-21	2.27665E-27	1.04829E+06
8	3.02816E-25	4.51763E-31	6.70298E+05
9	3.91226E-29	9.42549E-35	4.15072E+05
10	5.14798E-33	2.06270E-38	2.49574E+05

Solution viscosity = 0.92 cP
 Total current = 1 A
 Flowrate = 2 l/min

Average bubble diameter on the surface = 88.740 microns
 Standard deviation of bubble diameters on the surface = 21.705 microns
 Average bubble diameter on the surface = 127.000 microns
 Standard deviation of bubble diameters on the surface = 36.000 microns

Assuming a gamma distribution of bubble diameters leaving the surface :

a = 1.14452E+01
 b = 9.79938E+04 1/m

q = 3.79563E+06 m⁻²s⁻¹ (calculated from the 3rd moment)

N = 8.966E+06 m⁻²

u(i) = 8(k²)/i

where k = 3.20E-05 m/s^{1/2}

i	q*Bi(calc) (m ¹ /m ² s)	Bi(predicted) (m ¹)	q (1/m ² s)
1	4.55020E+02	1.27000E-04	3.58283E+06
2	7.52267E-02	1.74250E-08	4.37455E+06
3	1.01379E-05	2.56861E-12	3.94684E+06
4	1.26399E-09	4.04849E-16	3.12212E+06
5	1.55165E-13	6.79414E-20	2.28380E+06
6	1.91227E-17	1.20952E-23	1.58101E+06
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Solution viscosity = 0.92 cP
 Total current = 1 A
 Flowrate = 2 l/min

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 Standard deviation of bubble diameters on the surface = 36.000 microns

Assuming a gamma distribution of bubble diameters leaving the surface :

$$a = 1.14452E+01$$

$$b = 9.79938E+04 \text{ 1/m}$$

$$q = 3.79563E+06 \text{ m}^{-2} \text{ s}^{-1} \quad (\text{calculated from the 3rd moment})$$

$$N = 8.966E+06 \text{ m}^{-2}$$

$$v(1) = 144(k^3)/(1^2)$$

$$\text{where } k = 4.49E-05 \text{ m/s}^{1/3}$$

<u>i</u>	<u>qxB_i(calc) (m²/m²s)</u>	<u>R_i (predicted) (m²)</u>	<u>q (1/m²s)</u>
1	5.11530E+02	1.27000E-04	4.02779E+06
2	8.07569E-02	1.74250E-08	4.63454E+06
3	1.01465E-05	2.56861E-12	3.95019E+06
4	1.19951E-09	4.04849E-16	2.96285E+06
5	1.40208E-13	6.79414E-20	2.06366E+06
6	1.65232E-17	1.20952E-23	1.36609E+06
7	1.97977E-21	2.27665E-27	8.69597E+05
8	2.42041E-25	4.51763E-31	5.35769E+05
9	3.02308E-29	9.42549E-35	3.20734E+05
10	3.85749E-33	2.06270E-38	1.87011E+05



Author Hoffman D L

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