JOURNAL OF APPLIED ELECTROCHEMISTRY **10** (1980) 223–228

On the conductivity and void fraction of gas dispersions in electrolyte solutions

L. SIGRIST, O. DOSSENBACH, N. IBL
Technisch-chemisches Laboratorium ETH, CH-8092 Zürich, Switzerland

Received 3 March 1979

A simple conductivity method for the measurement of void fractions in gas-electrolyte dispersions is described. The experimental correlation between the effective conductivity of the dispersion and the gas voidage is in very good agreement with the well-known Maxwell equation. The simplicity and versatility of the method are demonstrated in the experimental study of an electrolytic cell with simulated gas evolution. The measured gas void fraction has been correlated with the superficial gas and electrolyte velocities in accordance with a theoretical correlation given by Nicklin.

1. Introduction

Electrolytic cells with gas evolution occur widely in industrial practice. In the design of such cells attention has to be paid to the gas phase in many respects. The quantity of gas held in the inter-electrode gap is relevant to mass and heat transfer. Under certain conditions the stirring efficiency is a function of the volumetric gas fraction [1–3]. Furthermore, by reducing the mean density in the inter-electrode gap, the gas phase causes a fairly strong electrolyte circulation in the cell. This so-called gas lift can replace a mechanical pump if the cell is properly designed [4–6]. Finally, the dispersed gas leads to a diminution of the electrical conductivity of the mixture with respect to the gas-free solution which results in higher energy losses. Moreover, the current density distribution over the electrodes depends on the conductivity of the electrolyte [7]; for example, at vertical gas-evolving electrodes the ohmic resistance increases from bottom to top due to the increasing gas fraction thus causing a non-uniform current distribution [8–10]. The determination of the voidage in a partly gas-filled electrolyte solution is therefore of considerable practical interest.

In connection with a study of gas sparged systems we have used a simple method based on conductivity measurements for this purpose. In order to apply this method the correlation between the void fraction and the conductivity must be known. Theoretical equations have been derived by Maxwell [13] and Bruggemann [15] (see also [11]). They have been tested experimentally by different authors but mainly with suspensions of solid particles [12, 14]. We have therefore measured the correlation between voidage and conductivity for a partly gas filled electrolyte. In the following we will report the results obtained and show an application of the method in the study of an electrolytic model cell with simulated gas evolution.

2. The conductivity method

2.1. *Experimental*

Fig. 1 shows schematically the apparatus consisting of a polypropylene tube of 80 cm height and 7 cm inner diameter. An open gas separator was mounted on the top. The gas was dispersed in the electrolyte through a glass frit. The U-tube manometer was filled with isobutylbromide, above which there was gas-free electrolyte. The composition of the electrolyte solution was: 0·01 M $CuSO_4$, 0·1 M H_2SO_4, 0·1 M $NaNO_3$ and 1 vol% of ethanol. The addition of small quantities of alcohol yields smaller bubbles with a rather uniform size distribution (bubble diameter about 0·5 mm). Large bubbles lose their spherical shape and can give rise to an anisotropic situation inside the conductivity probe. To prevent errors in the

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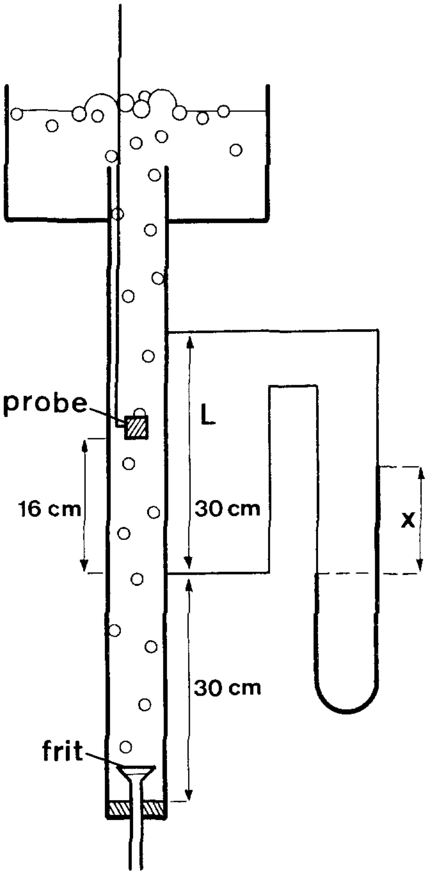

Fig. 1. Apparatus for testing the conductivity method (schematic).

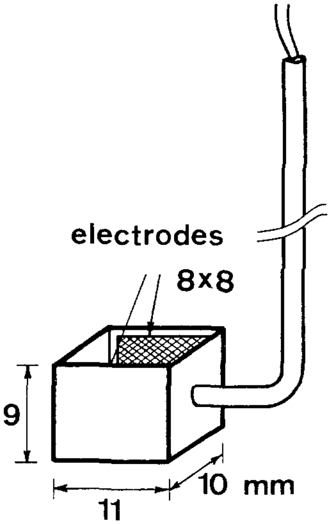

Fig. 2. Conductivity probe.

measurements the bubbles should be spherical and small with respect to the test volume. Cleaned dry air was used for the gas phase. All experiments were carried out at 25° C.

The conductivity probe (Fig. 2) was made of glass and mounted on a 50 cm long glass tube which contained the electric leads. The dimensions of the platinized platinum electrodes were 8 x 8 mm. The cell constant was measured to be $0.64\,\text{cm}^{-1}$.

The measurements were carried out with a commercial conductivity meter (Philips PW 9501/01). This instrument allows the direct measurement of the ratio K/K_0 with a precision of ± 0·5%, where K is the effective conductivity of the dispersion and K_0 that of the gas-free solution as the reference. The latter has been simulated by a resistor in the experiments. The ratio K/K_0 has been obtained by averaging the recorded oscillating signal. The measuring frequency was 2 kHz for all experiments.

The average gas voidage ϵ (also called void fraction, gas hold-up), defined as the ratio of gas volume to total volume†, was determined by measuring the hydrostatic pressure difference Δp over the height L (Fig. 1). Δp yields the average density:

$$\rho_{av} = \Delta p/(gL). \qquad (1)$$

If the distribution of the bubbles is uniform over L the average density ρ_{av} in the tube is linked with the densities of the liquid ρ_l and of the gas ρ_g through the gas void fraction ϵ:

$$\rho_{av} = (1-\epsilon)\rho_l + \epsilon\rho_g. \qquad (2)$$

By combining Equations 1 and 2 and neglecting the much smaller gas density compared to the liquid density, we obtain:

$$\epsilon = 1 - \Delta p/(gL\rho_l). \qquad (3)$$

2.2. *Results and discussion*

The experimental values of the conductivity ratio K/K_0 as a function of the gas voidage ϵ are pre-

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† The void fraction ϵ has to be distinguished from the volume flow fraction ϵ^* which in a two-phase flow system is defined as the ratio of the gas volume flow rate to the total volume flow rate (gas plus liquid). ϵ^* is equal to ϵ only in the somewhat hypothetical case of two-phase flow without slip, i.e. if the bubbles and the liquid had the same velocity.

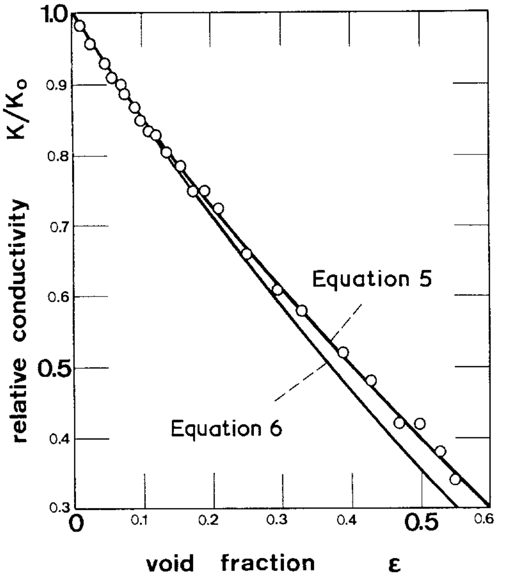

Fig. 3. Relative conductivity of the dispersion versus gas void fraction.

sented in Fig. 3 together with the theoretical correlation given by Maxwell who was the first to calculate the effective conductivity K of a two-phase dispersion. For a random suspension of spherical particles of uniform diameter d_p with the conductivity K_d in a continuous medium of conductivity K_0 he derived [13]:

$$\frac{K}{K_0} = \frac{K_d + 2K_0 - 2\epsilon(K_0 - K_d)}{K_d + 2K_0 + \epsilon(K_0 - K_d)}. \qquad (4)$$

In the case where K_d is very small compared to K_0 as for gas bubbles in an electrolyte, Equation 4 can be simplified:

$$\frac{K}{K_0} = \frac{1-\epsilon}{1+\epsilon/2}. \qquad (5)$$

In the derivation of Equation 4 Maxwell assumed that the average distance between the particles is large enough so that the electric field around the individual particles is not disturbed. According to an estimation of De la Rue and Tobias [14] this condition is fulfilled only for void fractions up to about 0·25. At this value the average distance between the spherical particles is about 30% of the particle diameter d_p, and the electric field around the spheres is markedly distorted. Equation 4 should therefore not be applicable above this limit. The lower curve in Fig. 3 represents the correlation given by Bruggemann [15] for the case of a non-conducting dispersed phase:

$$\frac{K}{K_0} = (1-\epsilon)^{3/2}. \qquad (6)$$

Bruggemann's treatment is based on Maxwell's Equation 4 but it implies the assumption of a large size-range of the particles. He further assumed that the field around a particle can be better represented if one uses for the conductivity of the surrounding medium the average value of the mixture rather than that for the continuous phase.

Experimental work on the conductivity of dispersions described in the literature is concerned mainly with solid particles rather than with gas bubbles. De la Rue and Tobias [14] have studied the conductivities of suspensions of solid particles (glass beads and sand) up to a voidage of 0·4. In the case of a large particle size-range their results were in rather good agreement with the Bruggemann equation, in accordance with the assumption underlying this model. For narrow size-ranges, however, the conductivity values tended to be somewhat higher and to lie between Bruggemann's and Maxwell's correlations. Turner [12] investigated dispersions of solid spherical particles in a large range of the ratio K_d/K_0. The author pointed out that, although the Maxwell equation should be valid only at low values of both ϵ and K_d/K_0, his results could be described very well by this relation up to $\epsilon = 0{\cdot}6$, provided that K_d/K_0 was not much larger than 1 (which is of course the case for non-conducting particles such as gas bubbles).

The results of the present study reveal, as can be seen in Fig. 3, that in the case of gas bubbles in an electrolyte solution Maxwell's relation seems to be superior to Bruggemann's and to be valid up to $\epsilon = 0{\cdot}6$. This can probably be explained by the fact that the size-range of bubbles in moderately concentrated electrolytes is rather narrow [1, 16]* and that therefore Maxwell's model is more appropriate in this case.

In practice the gas voidage will often not exceed values of about 0·1–0·15. In these cases a linearized form of Equations 5 or 6 can be used. By expanding Equation 5 in a Taylor series about

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* According to Marruci and Nicodemo [16] the bubble size distribution can be represented approximately by a Gaussian curve. As the electrolyte concentration increases the tendency to coalescence decreases, the distribution curves become sharper and are shifted toward smaller values of the bubble diameter.

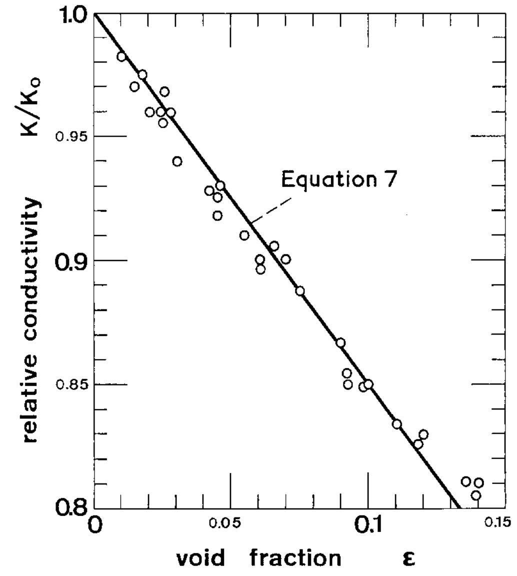

Fig. 4. Relative conductivity of the dispersion versus gas void fraction for small values of ϵ.

$\epsilon = 0$, or Equation 6 in a binomial series, and neglecting all but the first two terms, both correlations reduce to a simple form:

$$\frac{K}{K_0} = 1 - \tfrac{3}{2}\epsilon. \tag{7}$$

A plot of the experimental values in Fig. 4 shows that the data fit quite well this approximation and that for practical purposes Equation 7 can be used up to gas void fractions of about 0·12 without serious error.

The simplicity and versatility of the technique of measuring conductivities of dispersions as well as the good agreement of the experimental results with the theoretical correlation given by Maxwell suggest the use of conductivity measurements as a method for determining void fractions in gas–liquid dispersions.

3. Void fraction in an electrolytic cell with gas evolution

The conductivity method for measuring gas void fractions has been applied in a study of an electrochemical reactor with a gas evolving electrode (laboratory model cell). In a vertical parallel plate cell the influence of cell geometry, rate of gas evolution and of superimposed electrolyte flow on the fluid dynamics and on mass transfer has been investigated [1]. In particular the gas voidage ϵ at the top of the inter-electrode gap was measured as a function of the liquid flow velocity and of the rate of gas evolution by means of the conductivity method. The results of these measurements shall be presented in the following.† The gas evolving electrode was simulated by a porous plate (mean diameter of the pores about 5 μm) through which dry air was dispersed in the alkaline ferro/ferricyanide electrolyte. The gas volume flow rate per unit electrode area has been varied between 0·17 and 0·82 cm^3/cm^2 s and the superficial electrolyte flow velocity between 1·5 and 35·5 cm s^{-1}.

Fig. 5 shows some typical results of the gas void fraction ϵ as a function of the superficial gas velocity u_g (volume flow rate per unit cross-section of the inter-electrode gap) for different values of the liquid flow velocity u_l. As one can expect, the gas voidage increases with increasing gas flow rate and with decreasing superimposed electrolyte velocity. The data represented in Fig. 5 allow us to calculate the rising velocity u_b of the bubbles in the swarm since it is related to the superficial gas velocity u_g in a simple way:

$$u_b = u_g/\epsilon. \tag{8}$$

Many attempts have been made to get a reliable prediction of the voidage of two-phase dispersions from the operating variables [17, 18]. A simple equation was given by Nicklin [19] which correlates the rising velocity u_b of the bubbles in the swarm with the superficial velocities u_g and u_l and with the rising velocity u_0 of a characteristic single bubble in a stagnant liquid:

$$u_b = u_g + u_l + u_0 \tag{9}$$

In Fig. 6 the experimental values of u_b as calculated by means of Equation 8 are plotted versus the sum of the superficial velocities u_g and u_l for three different electrode distances d. As it is shown in the figure the data can be correlated by a straight line with unity slope. Extrapolation of these lines to $(u_g + u_l) = 0$ yields on the ordinate, according to Equation 9, the rising velocity u_0 of a single bubble. The so-derived value of u_0 is about 5 cm s^{-1}. According to the correlations given by Grassmann [20] this corresponds to a bubble

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† More experimental details can be found in [1]. The application of the conductivity method in connection with mass transfer at gas sparged electrodes is described elsewhere [2].

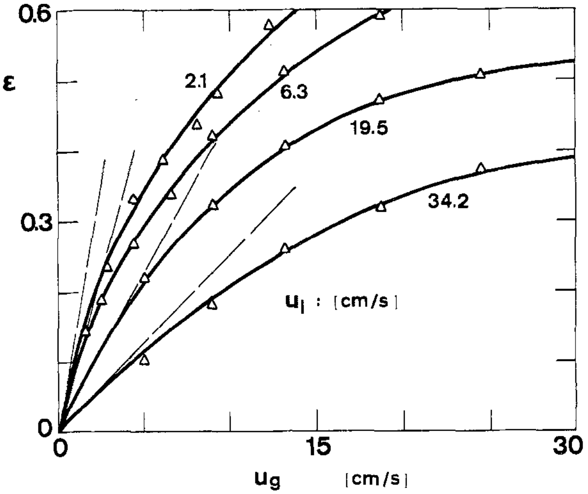

Fig. 5. Gas void fraction ϵ versus superficial gas velocity u_g for different electrolyte flow velocities u_l.

diameter of 0·43 mm. This is within the range of 0·4–0·45 mm obtained photographically. The photographic studies also showed that the tendency to coalescence was rather small and that the bubble size remained approximately constant over the whole operating range, as can be expected in moderately concentrated electrolyte solutions [16].

u_0 can also be obtained from the curves in Fig. 5. When u_g (and consequently ϵ) tends toward zero, Equation 9 reduces to:

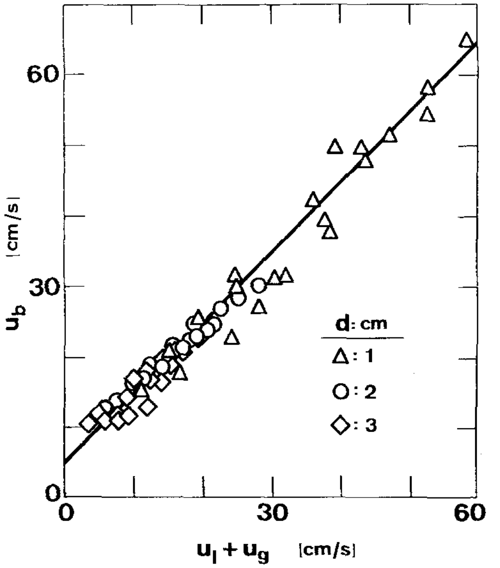

Fig. 6. Rising velocity u_b of the bubbles in the swarm versus sum of the superficial gas and liquid velocities for different inter-electrode distances d.

$$(u_b)_{u_g \to 0} = u_l + u_0. \tag{10}$$

On the other hand, by applying Hôpital's rule to Equation 8, we find:

$$(u_b)_{u_g \to 0} = \left(\frac{d\epsilon}{du_g}\right)^{-1}_{u_g=0}. \tag{11}$$

Hence by combining Equations 10 and 11

$$u_0 = \left(\frac{d\epsilon}{du_g}\right)_{u_g=0} - u_l. \tag{12}$$

Thus u_0 can be evaluated from the slopes at the origin of the ϵ/u_g-curves in Fig. 5. One calculates an average experimental value of about 4·5 cm s^{-1} which corresponds to a mean bubble diameter of 0·39 mm.

For some purposes the ratio of the gas volume to the liquid volume in the mixture may be of special interest as a characteristic quantity [2]. This ratio can be expressed as $\epsilon/(1-\epsilon)$. Combining and rearranging Equations 8 and 9, one gets:

$$\frac{\epsilon}{1-\epsilon} = \frac{u_g}{u_l + u_0}. \tag{13}$$

In Fig. 7 the experimental data are represented in this form with a value for u_0 of 4·7 cm s^{-1}. In this diagram the volumetric ratio gas-to-liquid at the top of the cell is a linear function of the superficial gas velocity, i.e. for a given electrode distance it is directly proportional to the current density. As the superimposed electrolyte flow velocity increases, this ratio, and consequently the void fraction, decreases. It also becomes smaller for larger bubbles (i.e. greater value of u_0).

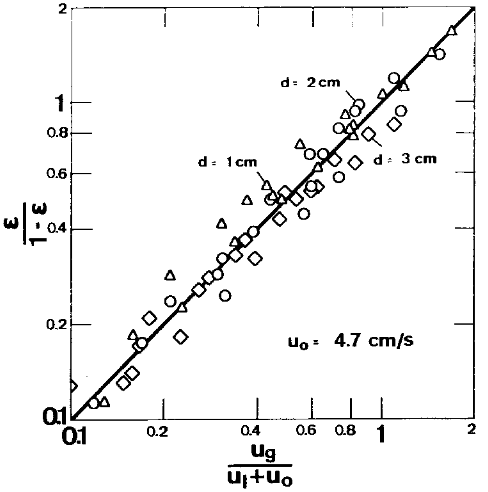

Fig. 7. Ratio of gas-to-liquid volume fractions $\epsilon/(1-\epsilon)$ as a function of u_g, u_l and u_0.

The size of the bubbles depends mainly on the physical properties of the system. Equation 13 is useful in practical situations for the calculation of the gas voidage as a function of u_g and u_l taking u_0 as a constant given by the mean diameter (which is a good approximation for moderately concentrated electrolytes). In cells without superimposed flow where the liquid circulates freely around the electrode plates due to the gas-lift effect of the bubbles the superficial velocities u_g and u_l are no longer independent of each other. However, Nicklin's correlation Equation 9 is still valid in these cases [1] and Equation 13 can therefore be used to determine the liquid circulation velocity from gas voidage measurements.

Acknowledgements

The authors are indebted to the Swiss Aluminium Funds for the financial support of this work.

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