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The voidage problem in gas–electrolyte dispersions

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Assessing the ohmic interelectrode resistance of electrochemical reactors with gas evolution requires data for the gas void fraction of gas–electrolyte dispersions. A voidage equation is derived taking account of the internal liquid flow in stationary electrolytes and at small liquid superficial velocities. The equation is a general form of available voidage equations.

Nomenclature

C	non-dimensional constant, Equation 8
n	exponent, Equation 5
S	cross-sectional area (m^2)
v_G	gas velocity ($m\,s^{-1}$)
v_L	liquid velocity ($m\,s^{-1}$)
v_s	rising velocity of a bubble swarm ($m\,s^{-1}$)
v_1	terminal rising velocity of a single bubble ($m\,s^{-1}$)
$\dot{V}_G$	volume flow rate of gas ($m^3\,s^{-1}$)
$\dot{V}_L$	volume flow rate of liquid ($m^3\,s^{-1}$)
α	fraction of cross-sectional area
ε	volume (void) fraction of gas
ε_m	geometric maximum of void fraction
ε_∞	maximum of void fraction in infinite gas flow

Indices

i	internal
t	total

1. Introduction

Interelectrode gaps of cells with one or more gas-evolving electrodes are filled with a dispersion of gas bubbles in the electrolyte. A quantitative assessment of the gas void fraction is of particular interest in electrochemical engineering since it is a basic quantity used in the determination of the local effective ohmic resistance and the resulting current distribution in the cell. The void fraction varies locally in directions both normal and parallel to the electrode surface and depends on numerous parameters, the most important being the flow rates of gas and liquid through a defined cross-sectional area. All attempts to assess the distribution of the void fraction in interelectrode gaps are based on simplified correlations involving these parameters. Although numerous investigations have been devoted to the problem of current distribution in cells with gas-evolving electrodes [1], a fully satisfactory answer to the problem is not yet available.

Particular difficulties arise from the lack of a reliable general correlation of the void fraction with the flow rates of gas and liquid, a fact which was recently pointed out with good reasons by Kreysa and Kuhn [2]. The authors studied the problem experimentally and confirmed the well-known fact that in electrochemical systems – but not only in these – the void fraction attains a maximum, the value of which is substantially smaller than unity; this behaviour is not represented by the available basic relationship discussed below. On the basis of a 'coalescence barrier' model the authors were able to improve the basic voidage equation. The present paper deals with the same problem in a different way. The objective is to eliminate properties of the voidage equation which are incompatible with reality.

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2. Basic relationship

Consider an interelectrode gap with a cross-sectional area, S, normal to the main flow direction and a flow of a gas–electrolyte dispersion with rates $\dot{V}_G$ and $\dot{V}_L$ across the area S. Owing to the density difference between the two phases, the rising velocity, v_G, of the bubble swarm is larger than the average velocity of the phases $(\dot{V}_G + \dot{V}_L)/S$

$$v_G = \frac{\dot{V}_G + \dot{V}_L}{S} + v_s \tag{1}$$

The velocity difference, v_s, can be experimentally obtained from the swarm velocity in a closed system where the average velocity is zero ($\dot{V}_G + \dot{V}_L = 0$), and is usually described in a form

$$v_s = v_1(1 - \varepsilon)^n \tag{2}$$

For small bubbles in electrochemical systems, v_1 can be calculated from Stokes' law, but as shown by Hine and Sugimoto [3], bubble coalescence can easily result in rising velocities exceeding the range of Stokes' law. According to Richardson and Zaki [4] the exponent, n, has a value of 4.65. On the basis of the equation of continuity and effective viscosity relationships, Zuber [5] obtained $n = 4.5$.

From Equations 1 and 2 one obtains an expression for the absolute gas velocity,

$$v_G = \frac{\dot{V}_G}{S} + \frac{\dot{V}_L}{S} + v_1(1 - \varepsilon)^n \tag{3}$$

Equation 3 makes clear that Equation 2 describes the gas velocity only in the case of zero average velocity of both phases, as essentially occurs (in the opposite direction) in settling tanks. In interelectrode gaps with gas evolution this condition is not given, not even if the electrolyte is stationary ($\dot{V}_L = 0$) as already stated by Behringer [6] and Nicklin [7].

Considering that the velocity, v_G, is interconnected with the gas flow rate by

$$v_G = \frac{\dot{V}_G}{S\varepsilon} \tag{4}$$

Equation 3 can be written

$$v_G = \frac{\dot{V}_L}{S(1 - \varepsilon)} + v_1(1 - \varepsilon)^{n-1} \tag{5}$$

In this or a similar form, Equation 5 has repeatedly been applied to electrochemical systems for the estimation of the effective ohmic resistance [8–11]. The classical treatise by Tobias [12] with the assumption of constant rising velocity of bubbles would correspond to $n = 1$.

Combining Equations 3 and 4 yields an implicit expression for the void fraction

$$\varepsilon = \left[1 + \frac{\dot{V}_L}{\dot{V}_G} + \frac{v_1(1 - \varepsilon)^n}{\dot{V}_G/S}\right]^{-1} \tag{6}$$

which is shown in Fig. 1 for $n = 4.5$. A comparison with experimental findings demonstrates two important objections to Equation 6.

(i) For $\dot{V}_L = 0$ the behaviour of Equation 6 is in strong disagreement with experimental results which unanimously show that under all conditions ε increases monotonically, approaching the limiting value, ε_∞, at large values of the gas flow rate [2, 4]. The structure of Equation 6 is also inconsistent with empirical voidage equations for bubble columns with stationary liquid. Rearranging Equation 6 for stationary electrolyte ($\dot{V}_L = 0$) in the form

$$\varepsilon(1 - \varepsilon)^{3.5} = \frac{\dot{V}_G/S}{v_1} \tag{7}$$

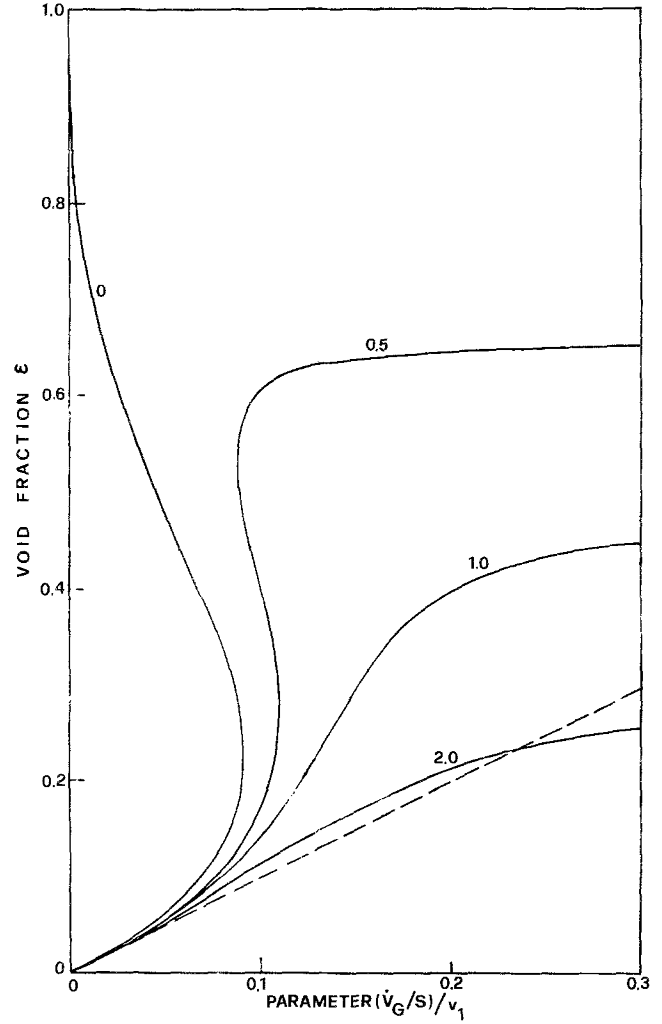

Fig. 1. Representation of Equation 6 for various values of the ratio $\dot{V}_L/\dot{V}_G$ and $n = 4.5$ (full line). Broken line for comparison: $n = 1$, $\dot{V}_L = 0$ (Tobias [12]).

demonstrates the fundamental difference to the empirically derived equation by Yoshida and Akita [14],

$$\varepsilon(1 - \varepsilon)^{-4} = C\dot{V}_G/S \tag{8}$$

where C is a complex of dimensionless groups containing the acceleration due to gravity and physical properties which jointly control v_1.

(ii) For $\dot{V}_L = 0$ all values of the void fraction are possible ($0 \leqq \varepsilon \leqq 1$). Obviously, the ability of Equation 6 to produce values of ε equal to or near unity is a striking insufficiency which results from the assumption of a gas continuum in Equation 4. In fact, no array of spherical particles in a surrounding continuum can result in a void fraction of unity. In real dispersions, the void fraction depends on bubble size distribution and on interfacial properties and, of course, on the random temporal arrangement of bubbles. In a cubic array spherical particles touching each other exhibit the loosest packing of $\varepsilon_m = \pi/6 = 0.5236$, whereas the closest packing corresponds to $\varepsilon_m = 0.7408$. In random packing neither the closest nor the loosest packing can be expected: a mean value of about $\varepsilon_m = 0.63$ is obtained. The value corresponds to the stochastic frequency maximum [15]. Of course, this value is not known to occur in gas–electrolyte dispersions, but there can be no doubt that the maximal void fraction is much lower than unity.

3. Modified voidage equation

To resolve both inconsistencies it must be realized that Equation 6 was derived for a situation where the dispersion flow is uniform over the total cross-sectional area. Experimental findings give rise to doubt that this condition exists in interelectrode gaps with low liquid flow rates and particularly in stationary electrolytes.

The term 'stationary electrolyte' means that there is no liquid flow across the boundaries of the interelectrode gap. This does not mean that the liquid is stagnant. Owing to momentum transfer from the rising bubbles, a certain amount of liquid is always transported together with the gas. In stationary liquid, the upward flow of bubble-enriched dispersion is balanced by downward flow of dispersion with low gas void fraction. Hine and Murakami [16] have described this internal flow pattern in a vertical interelectrode gap. It must be concluded that the liquid flow rate in Equation 6 must not be interpreted as the net liquid flow rate across the boundaries of the gap but as a complex value taking account of an internal liquid flow rate.

The ratio $\dot{V}_L/\dot{V}_G$ in Equation 6 will, therefore, be considered from now on as a ratio of total flow rates, $(\dot{V}_L/\dot{V}_G)_t$, which takes various forms under various conditions. In the limiting case of zero net liquid flow through the gap ($\dot{V}_L = 0$), it coincides with an internal flow ratio $(\dot{V}_L/\dot{V}_G)_i$:

$$(\dot{V}_L/\dot{V}_G)_t = (\dot{V}_L/\dot{V}_G)_i \qquad \text{for} \qquad \dot{V}_L = 0$$

As the net liquid flow increases, it increasingly superimposes on the internal flow the effect of which finally vanishes at large liquid net flow rates:

$$(\dot{V}_L/\dot{V}_G)_t = \dot{V}_L/\dot{V}_G \qquad \text{for} \qquad \dot{V}_L/\dot{V}_G \gg (\dot{V}_L/\dot{V}_G)_i$$

The simplest form to obey these conditions is

$$(\dot{V}_L/\dot{V}_G)_t = [(\dot{V}_L/\dot{V}_G)_i^2 + (\dot{V}_L/\dot{V}_G)^2]^{0.5} \tag{9}$$

With Equation 9 the voidage equation results in

$$\varepsilon = \left\{1 + \left[\left(\frac{\dot{V}_L}{\dot{V}_G}\right)_i^2 + \left(\frac{\dot{V}_L}{\dot{V}_G}\right)^2\right]^{0.5} + \frac{v_1(1-\varepsilon)^n}{\dot{V}_G/S}\right\}^{-1} \tag{10}$$

4. Discussion

Whereas the ratio $\dot{V}_L/\dot{V}_G$ represents operational values which are easy to assess, the quantity $(\dot{V}_L/\dot{V}_G)_i$ depends on the particular flow conditions and is generally unknown. However, it is possible to give an estimate of the value. Since the gas void fraction increases with increasing gas flow rate but does not exceed the upper bound $\varepsilon = \varepsilon_m$, one obtains from Equation 10 for $\dot{V}_G/S \to \infty$

$$(\dot{V}_L/\dot{V}_G)_i = \frac{1}{\varepsilon_m} - 1 \tag{11}$$

For $\varepsilon_m = 0.63$ one obtains a minimum value, $(\dot{V}_L/\dot{V}_G)_i = 0.59$.

Under real conditions the value ε_m is not attained. In large gas flow rates, the void fraction approaches a realistic maximum value, $\varepsilon_\infty < \varepsilon_m$. As observed in bubble columns with stationary electrolyte and with gas injection [17], as well as in gaps with gas evolved at an electrode at the bottom of the gap [3], an upward flow of dispersion forms in the central region of the cross-section. The corresponding downward flow of essentially bubble-free liquid is restricted to a region near the walls [18]. Assuming that the total dispersion upward flow is restricted to a partial cross-sectional area, αS, where Equation 10 applies, whereas the area $(1 - \alpha)S$ is free of bubbles, one obtains from

Equation 10

$$\frac{1}{\varepsilon'} = 1 + \left[\left(\frac{\dot V_\mathrm{L}}{\dot V_\mathrm{G}}\right)_\mathrm{i}^2 + \left(\frac{\dot V_\mathrm{L}}{\dot V_\mathrm{G}}\right)^2\right]^{0.5} + \frac{v_\mathrm{l}(1-\varepsilon')^n}{\dot V_\mathrm{G}/(\alpha S)} \tag{12}$$

With ε in each total cross-section equal to $\varepsilon'\alpha$, the internal flow ratio becomes

$$(\dot V_\mathrm{L}/\dot V_\mathrm{G})_\mathrm{i} = \left\{\left[\frac{\alpha}{\varepsilon} - 1 - \frac{v_\mathrm{l}(1-\varepsilon/\alpha)^n}{\dot V_\mathrm{G}/(\alpha S)}\right]^2 - \left(\frac{\dot V_\mathrm{L}}{\dot V_\mathrm{G}}\right)^2\right\}^{0.5} \tag{13}$$

For very large gas flow rates in stationary liquid with limiting conditions $\dot V_\mathrm{G}/S \to \infty$ and $\dot V_\mathrm{L} \to 0$, Equation 13 yields a realistic maximum value of the internal flow ratio

$$(\dot V_\mathrm{L}/\dot V_\mathrm{G})_\mathrm{i} = \frac{\alpha}{\varepsilon_\infty} - 1 \tag{14}$$

Since $\alpha \leqslant 1$,

$$(\dot V_\mathrm{L}/\dot V_\mathrm{G})_\mathrm{i} \leqslant \frac{1}{\varepsilon_\infty} - 1 \tag{15}$$

For a given gas–electrolyte dispersion with ε_∞, the internal flow ratio, given by Equation 15, cannot be exceeded. Inserting the maximum value of Equation 15 into Equation 10 yields a voidage equation

$$\frac{1}{\varepsilon} = 1 + \left[\left(\frac{1}{\varepsilon_\infty} - 1\right)^2 + \left(\frac{\dot V_\mathrm{L}}{\dot V_\mathrm{G}}\right)^2\right]^{0.5} + \frac{v_\mathrm{l}(1-\varepsilon)^n}{\dot V_\mathrm{G}/S} \tag{16}$$

At present ε_∞ cannot be predicted reliably and must be obtained from experiment for a particular gas–electrolyte system and particular operational conditions. Kreysa and Kuhn [2] found values of ε_∞ in the range of 0.11 to 0.46 for oxygen, hydrogen and chlorine evolved at electrodes.

The voidage equations used for the models to predict the interelectrode resistance of electrochemical reactors [8–11] coincide with Equation 16 for $\varepsilon_\infty = 1$ and, moreover $v_\mathrm{l}/(\dot V_\mathrm{G}/S) = 0$.

It must be pointed out that the term $(1/\varepsilon_\infty - 1)$ is valid at large gas flow rates only. The value is unknown at medium and low flow rates of gas, mainly since the bubble diameter depends markedly on the superficial gas velocity $\dot V_\mathrm{G}/S$ [3]. However, this point is of little importance since

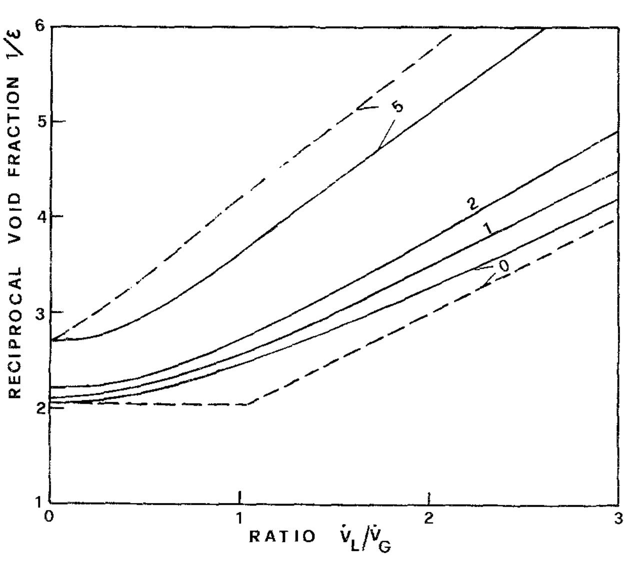

Fig. 2. Comparison of Equation 16 (full line) with Equation 17 (broken line) for $n = 4.5$ and $\varepsilon_\infty = 0.48$ (oxygen). Parameter, $v_\mathrm{l}S/\dot V_\mathrm{G}$.

the structure of Equation 16 is such that the effect of $(1/\varepsilon_\infty - 1)$ decreases as the ratio $\dot{V}_L/\dot{V}_G$ increases.

Equation 16 contains the same quantities as the voidage equation derived by Kreysa and Kuhn [2]:

$$\frac{1}{\varepsilon} = \frac{1}{\varepsilon_\infty} + \frac{v_1(1-\varepsilon)^n}{\dot{V}_G/S} + \frac{\dot{V}_L}{\dot{V}_G}\frac{1-\varepsilon/\varepsilon_\infty}{1-\varepsilon} \tag{17}$$

For stationary electrolyte ($\dot{V}_L = 0$), Equation 17 coincides with Equation 16:

$$\frac{1}{\varepsilon} = \frac{1}{\varepsilon_\infty} + \frac{v_1(1-\varepsilon)^n}{\dot{V}_G/S} \tag{18}$$

For finite liquid flow rates the two equations generally disagree. They are compared in Fig. 2.

5. Comparison with experimental data

The suitability of Equation 18 as a special form of Equations 16 or 17 for stationary electrolyte has already been examined by Kreysa and Kuhn in comparison with their experimental data [2]. However, the authors made use of the theoretical equation of Marrucci [19] which strongly disagrees with experimental data on the rising velocity of bubble swarms. The empirical Equation 2 with $n = 4.5$ which correlates experimental results reasonably well must be considered superior and will be used here.

From two sets of experimental data obtained by Kreysa and Kuhn [2] for stationary liquid (20% KOH) and gas fed through a porous plate (Fig. 12 of Ref. [2]), one reads $\varepsilon_\infty = 0.48$ for oxygen and $\varepsilon_\infty = 0.30$ for hydrogen. The terminal rising velocity of a single bubble, $v_1 = 0.05\,\mathrm{m\,s^{-1}}$, was directly taken from [2]. These data were used in Equation 18 which is shown in Fig. 3 together with the original data points.

It is seen that for hydrogen as well as for oxygen at low values of the void fraction, the calculated values are too small in comparison to Equation 18. The reason may at least partially be explained with reference to the experimental findings of Hine and Sugimoto [3]. They stated that the diameter of bubbles increases as the gas flow rate increases. The value $v_1 = 0.05\,\mathrm{m\,s^{-1}}$ used for Fig. 3 is probably too large at low values of the void fraction. Lower bubble diameter would result in lower values of the terminal rising velocity and thus would raise the void fraction.

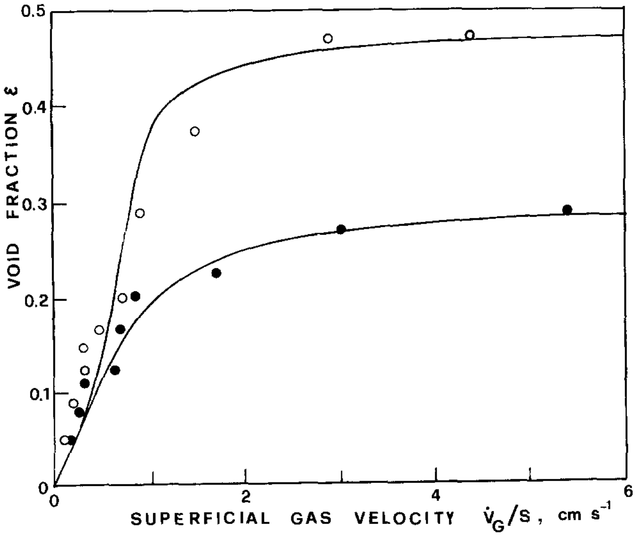

Fig. 3. Equation 16 compared with experimental data points of Kreysa and Kuhn [2]. Distribution of gas into 20% KOH solution, $\dot{V}_L = 0$, $v_1 = 5\,\mathrm{cm\,s^{-1}}$. ○, Oxygen; ●, hydrogen.

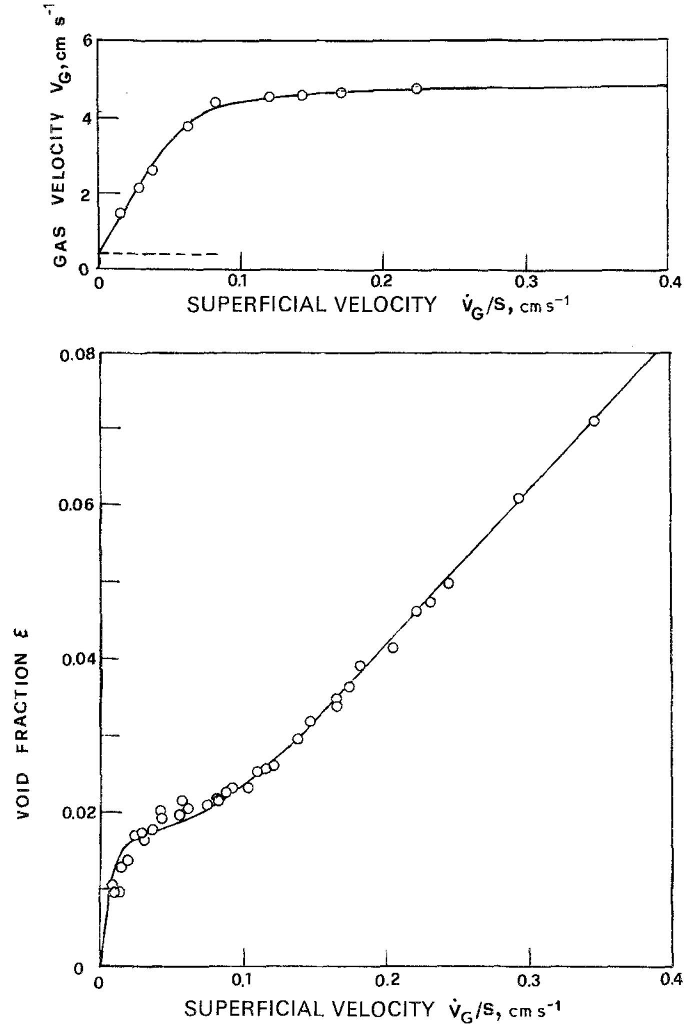

Fig. 4. (a) Void fraction versus absolute gas velocity. (b) Superficial gas velocity, $\dot V_G/S$, in comparison with Equation 4. Data points of Hine and Sugimoto [3], 5 M NaOH solution, 40° C, $\dot V_L = 0$, hydrogen evolved at electrodes.

Nonetheless, Fig. 3 shows that the correlation of experimental data under different conditions is satisfactory. It must be pointed out that the experiments refer to stationary liquid. The usefulness of Equation 16 for a moving electrolyte, $\dot V_L > 0$, is not yet supported by experiment, but can be supposed because the larger the liquid flow rate the more Equation 16 approaches Equation 6. However, there is not yet evidence for the hypothesis that the flow conditions in the experimental arrangements with gas injection or evolution at the bottom end of the channel agree with the conditions in interelectrode gaps of vertical electrodes with gas evolution over the total height.

A final remark on the strange behaviour of the void fraction at very small values, i.e. $\varepsilon < 0.03$ as observed by Hine and Sugimoto [3] (Fig. 4) may be given, The behaviour can easily be explained on the basis of values of v_G of bubbles as also given by the authors (Fig. 4). Inserting these data into Equation 4 gives excellent agreement with separately obtained void fraction data and highlights the distinct effect of variable bubble diameter on the void fraction.

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