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# *A quantitative assessment of bubble-curtain effects upon interelectrode resistance of a conductimetric cell*

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Adhesion of gas bubbles upon electrode surfaces of a conductimetric cell causes a reduction in the effective surface area of the electrodes and hence leads to false estimations of measured conductivities. By considering the random dispersal of bubbles on the electrode surfaces, the increase of interelectrode resistance due to bubble adhesion is determined as a function of the fractional surface area covered by the gas bubbles. An experimental study using an electrolytic tank with electrodes partially covered by spherical Styrofoam (insulating) spheres (which simulate the gas bubbles) is carried out. Computed results due to the present model and those of other existing models (based on Maxwell's and Bruggeman's formulations) are compared with the measured data.

## 1. Introduction

Interelectrode resistance of a conductimetric cell is significantly affected by the adhesion of gas/air bubbles upon the electrode surfaces [1]. The problem of bubble adhesion has been found to involve principally stationary adherent bubbles which appear from gas-evolving electrodes or from the gas/air dissolved in the solution. The bubbles formed on the electrodes partially insulate the surfaces so that the current density at the remaining portions of the electrodes is enhanced. Further, the reduced surface areas make the cell incompatible for measurement ranges of conductivity for which it was designed [1].

A quantitative assessment of the screening effect due to bubbles (more popularly known as the bubble-curtain effect) would enable proper design of electrodes in terms of geometrical area required and the required extent of increasing the surface area (or decreasing the current density) by coating the electrodes with spongy platinum-black. This is especially useful in industrial measurements involving on-line monitoring of conductivity of solutions with excessive dissolved gases.

Presently, a model is proposed to describe the variation of interelectrode resistance as a function of the fractional surface area covered by the adhering bubbles. This is done by considering the random nature of bubble dispersion on the electrode surfaces; and the cumulative growth of resistance with respect to the extent of bubble adhesion is characterized on the basis of statistical principles. Furthermore, an electrolytic tank experiment simulating the electrode system plus the bubbles is developed. Electrodes with bubble-adhesions are simulated by a pair of electrodes covered partially by randomly stuck Styrofoam (expanded polystyrene foam) spheres. The number of spheres determine the fractional coverage required; and the measured interelectrode conductivity of this simulated cell immersed in the electrolytic tank is correlated with the calculated results of the theoretical models.

## 2. Theoretical formulation

Recently Vogt [2] proposed a method of estimating the incremental ohmic resistance due to bubble adhesions at electrodes as a function of the fractional surface area masked by the bubbles. His relevant expressions are free from uncertain parameters such as the pinching factor [3] and his formulation is based on the determination of the effective conductivity of the mixture (of the

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bubbles and the solution) existing at the electrode surfaces via well-known relations due to Maxwell [4] and Bruggeman [5]; and hence the inter-electrode resistance is determined by appropriately including the estimated conductivities of the bubble-infested region in the relevant calculations. The models of Vogt [2] when compared with the earlier versions (due to Sides and Tobias [3]) have the merit of being free from empirical constants (such as the pinching factor) and the calculated values also fall in the range of results obtained by Sides and Tobias [3].

However, the analytical models of Vogt [2] have two major short-comings, namely, (a) there is no experimental evidence to support Vogt's models and (b) the formulation being based on Maxwell's or Bruggeman's principles is valid only for uniform dispersion of inclusions (bubbles) in the dispersed continuum; however, in practice, only a random dispersion of gas bubbles would exist at the electrodes; and therefore, it becomes necessary to seek an alternative method of calculating the effective conductivity of the bubble-included region by taking account of the chaotic nature of bubble dispersion. The relevant approach is given as follows.

The cell arrangement shown in Fig. 1 is considered for the purpose of the present analysis. In Fig. 1, two electrodes each with a surface area of $A$, are separated by a distance $L$. A monolayer of bubble adhesion is assumed to be on each electrode covering a fractional area $\theta_s$. The mean radius of adhering bubbles is taken as $R_M$. The electrolyte in the cell has a conductivity $\kappa_L$ so that the interelectrode resistance under a bubble-free condition is given by,

$$R = \frac{L}{\kappa_L A} \tag{1}$$

With the adhesion of bubbles on the electrode surfaces, the modified (enhanced) value of inter-electrode resistance may be written as,

$$R' = \frac{4R_M}{\kappa_e A} + \frac{L - 4R_M}{\kappa_L A} \tag{2}$$

where $\kappa_e$ represents the effective conductivity of the bubble-included region (Fig. 1b) resulting from the adhesion of a monolayer of bubbles covering a fractional area of $\theta_s$ upon the electrode surfaces. That is, the quantity $\kappa_e$ represents the effective conductivity of the mixture formed by the electrolytic solution and the dispersed bubbles which form a volume fraction $\phi$ in the region of adhered bubbles (Fig. 1b). Hence, the incremental resistance due to bubble adhesion is given by,

$$\Delta R = R' - R = \frac{4R_M}{A\kappa_L}\left(\frac{\kappa_L}{\kappa_e} - 1\right) \tag{3a}$$

or

$$\Delta R \frac{A\kappa_L}{4R_M} = \left[\frac{\kappa_L}{\kappa_e} - 1\right] \tag{3b}$$

The above expression (Equation 3) is the same* as the one suggested by Vogt [2] who expressed the ratio $(\kappa_L/\kappa_e)$ in terms of the volume fraction of bubbles, namely, $\phi$ on the basis of a mixture of the theories of Bruggeman [5] and Maxwell [4], appropriately applied to infinitely extended dispersing media (electrolytic solutions) with

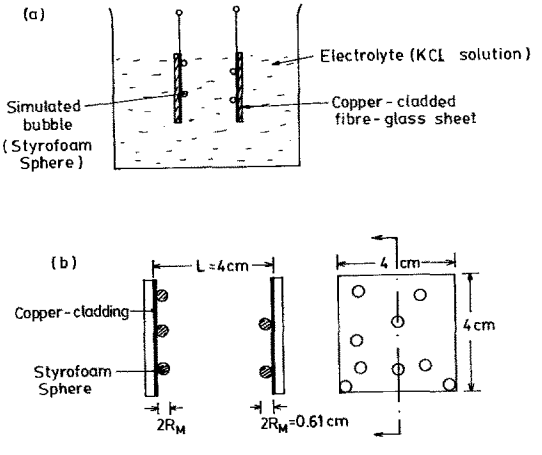


Fig. 1. (a) Test conductimetric cell with monolayer bubble-adhesion upon electrode surfaces; (b) test electrodes with simulated bubble adhesions.

* The quantity $4R_M$ in Equation 3 becomes $2R_M$ if bubble-adhesion is considered to be on a single electrode only [2]. Due to the symmetrical disposition of the electrodes and due to the possibility of bubble-adhesion on both electrodes, two layers ($4R_M$) of bubbles (one on each electrode, Fig. 1a) are considered here. Hence, the value of normalized incremental resistance remains unaltered, if adhesion on either one or both electrodes is considered.

uniformly dispersed inclusions (bubbles). Hence Vogt [2] proposed the following relations based on Bruggemen's [5] and Maxwell's [4] formulations, respectively:

$$\frac{\kappa_e}{\kappa_L} = (1-\phi)^{3/2} \tag{4a}$$

and

$$\frac{\kappa_e}{\kappa_L} = \left(1+\frac{3}{2}\frac{\phi}{1-\phi}\right)^{-1} \tag{4b}$$

Since the above relations (Equation 4) assume uniformly dispersed inclusions, their applicability to practical situations (in which the bubbles are rather randomly dispersed) becomes questionable if the chaotic disposition of the bubble inclusion in the electrolytic solution is considered. Hence, if the chaotic aspect of bubble dispersion is taken into account, it becomes necessary to formulate a stochastical model to depict the $\kappa_e/\kappa_L$ ratio and this model is described below.

### 3. Effective conductivity of a mixture formed by randomly included bubbles in a dispersing liquid

Considering a conducting liquid (such as an electrolytic solution), its effective conductivity would decrease when nonconducting (insulating) bubbles are included in it. In general, the included bubbles form a random volumetric dispersion in the dispersing liquid so that the whole medium can be regarded as a statistical mixture; and the effective conductivity ($\kappa_e$) of the medium becomes a random variable. Denoting the normalized resistivity as $x = \kappa_L/\kappa_e$ (the normalization constant $\kappa_L$ being the bubble-free electrolytic solution conductivity), the following characteristics can be attributed to the chaotic state of the bubble-included medium. Considering a fractional change in $\kappa_L/\kappa_e$, that is, $(dx/x)$, resulting from a volumetric change $(d\phi)$ due to bubble-inclusions, then $dx/x$ would be proportional to $d\phi$ as well as being functionally dependent on $x$ itself. Thus, the fractional value of $x$ will vary proportionally or logarithmically rather than linearly. That is,

$$\frac{dx}{x} = \alpha\, d\phi \log(\kappa_e/\kappa_L) \tag{5}$$

where $\alpha$ is a constant of proportionality. A possible solution of Equation 5 in the following form can be obtained:

$$x = \frac{\kappa_L}{\kappa_e} = \frac{1}{1-G(\phi)} \tag{6}$$

where $G(\phi)$ can be explicitly written as

$$G(\phi) = N_c\{\exp[-\exp(\alpha\phi)] + \beta\} \tag{7}$$

Here $\beta$ is a constant of integration and $N_c$ denotes the coordination number (that is, the number of contacts that a bubble makes with its neighbours). As the bubbles are spherical, the value of $N_C$ is 6. The constants $\alpha$ and $\beta$ in Equation 7 are not arbitrary. They can be determined by applying two limiting conditions pertaining to the extreme values of $\phi$, namely, 1 and 0, as follows.

From Equation 6, the normalized conductivity $\kappa_e/\kappa_L$ can be written as

$$\frac{\kappa_e}{\kappa_L} = 1-G(\phi) \tag{8}$$

and the limiting conditions applicable to Equation 8 are,

$$\frac{\kappa_e}{\kappa_L} = 1 \text{ or } G(\phi) = 0 \text{ at } \phi = 0 \tag{9a}$$

and

$$\frac{\kappa_e}{\kappa_L} = 0 \text{ or } G(\phi) = 1 \text{ at } \phi = 1 \tag{9b}$$

On applying these limiting values, $\alpha$ and $\beta$ in Equation 7 are determined to be

$$\alpha = \log_e \log_e \left[\frac{1}{(1/N_c)+(1/e)}\right] \tag{10a}$$

and

$$\beta = -\frac{1}{e} = -0.3679 \tag{10b}$$

where e is the exponential constant (2.7183). With $N_c = 6$, the value of $\alpha$ is $-0.4678$.

Furthermore, for a monolayer of bubbles with a thickness equal to the bubble diameter, the following relation is valid as indicated by Vogt [2]:

$$\phi = \frac{2}{3}\theta_s \tag{11}$$

Hence Equation 7 written in explicit form becomes,

$$\frac{\kappa_e}{\kappa_L} = 1 - 6\left\{\exp\left[-\exp\left(\frac{2}{3}\alpha\theta_s\right)\right] - \frac{1}{e}\right\} \quad (12)$$

Therefore, from Equation 3, the normalized value of incremental resistance is obtained as,

$$\Delta R\,\frac{A\kappa_L}{4R_M} = \frac{1}{1 - 6\left\{\exp\left[-\exp\frac{2}{3}\alpha\theta_s\right] - \frac{1}{e}\right\}} - 1 \quad (13)$$

The above relation (Equation 13) depicts the trend of macroscopic state of screening (or the curtain effect) being reached by virtue of the random arrangement of the bubbles. Or, in other words, Equation 13 formulates the nature of cumulative decay of the contiguous area between the electrolyte and the electrodes as a function of fractional masking by the random bubble inclusions. This process being statistical in nature, the relevant expressions given by Equations 12 and 13 intuitively measure the uncertainty or the entropy of the chaotic system constituted by the random bubble formations. Therefore the exponential (or logarithmic) nature of variation of the quantities involved is justified [7].

## 4. Experimental studies

As far as the authors know, there is no published experimental data available concerning the problem under discussion. The lack of experimental studies on this subject is due to the difficulty of obtaining a controlled amount of bubble formation upon the electrodes so that the measured electrolytic conductivity can be correlated quantitatively with the bubble coverage. However, a simulated experiment can be conducted as detailed below, which closely approximates the actual bubble curtain effect.

On the proposed simulation, an electrolytic tank (shown in Fig. 1) was built to hold a standard electrolyte (such as an aqueous solution of KCl of known conductivity). The electrodes used were copper-clad fibre glass sheets 4 cm × 4 cm in size. They were mounted in the tank so that the electrode surfaces were completely immersed in the solution. The interelectrode spacing was 4 cm. To simulate the bubbles, spheres made of Styrofoam (expanded polystyrene foam) and of mean diameter 0.61 cm were glued onto the electrode surfaces randomly. The number of spheres placed on the electrodes was determined on the basis of the required fractional area to be covered. Thus, considering the dimensions of the electrodes and the spheres, eight spheres were used to get an area coverage of about 15%; and multiples of eight were used to get increased percentage coverages up to 90%. Fig. 1b depicts a sample electrode plate covered randomly by a monolayer of the Styrofoam spheres. A pair of blank electrodes (without any spheres on their surfaces) was also used as a reference depicting the bubble-free situation.

The cell with a pair of test electrodes was excited by a constant current a.c. source at audio frequencies (Fig. 2) and the impedance across the cell was measured precisely. Each measurement pertaining to a pair of electrodes was done in a short time within which no formation of actual bubbles was observed. Measurements on the cell were performed at two close frequencies $f_1$ and $f_2$, so that from the respective values of measured impedances, namely, $Z_1$ and $Z_2$, the interelectrode resistance $R'$ was calculated from the following relation obtained by considering the equivalent circuit of the cell [7] illustrated in Fig. 2b. (The capacitive elements shown in Fig. 2b denote the polarization capacitance ($C_p$) and the interelectrode capacitance ($C_e$) associated with the cell):

$$\frac{f_2^2}{f_1^2} = \frac{Z_1^2 - R'^2}{Z_2^2 - R'^2} \quad (14)$$

Using the measured value of interelectrode resistance of the cell $R$ corresponding to the measurements with blank electrodes, the incremental resistance $\Delta R$ (that is, $\Delta R = R' - R$) was determined, and the normalization constant ($4R_M/\kappa_L A$) was calculated from the known values of $R_M$ (mean sphere radius equal to 0.305 cm), area of the electrode, $A$ (4 cm × 4 cm) and $\kappa_L$. (The value of solution conductivity $\kappa_L$ was determined by a conventional digital conductivity meter.)

For each pair of test electrodes, impedance was measured at various audio frequencies (400 Hz, 1000 Hz, 5000 Hz, 6000 Hz and 7000 Hz). The experiment was repeated with electrolytic solu-

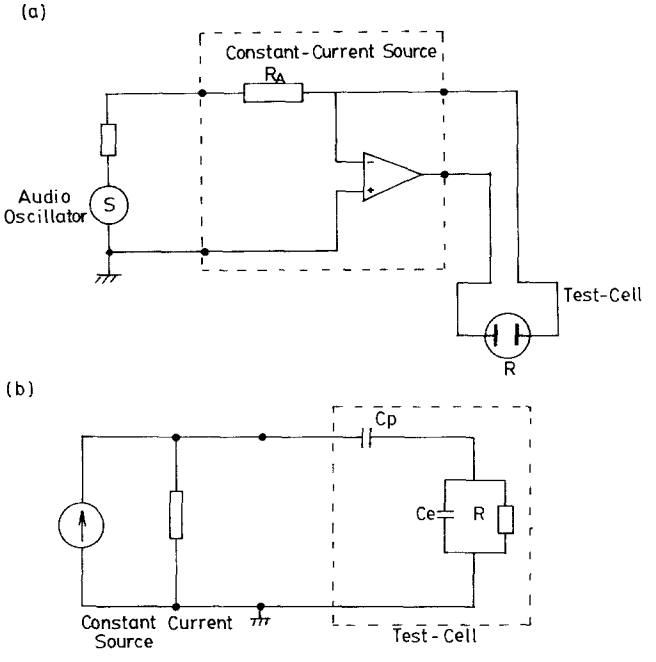


Fig. 2. (a) Cell-excitation by a constant current source; (b) equivalent circuit of the cell; R = interelectrode cell resistance under bubble-free condition; $R_p$ = polarization capacitance; $C_e$ = interelectrode capacitance.

tions of two different solute concentrations having conductivities ($\kappa_L$) equal to 30 and 34.5 mS cm$^{-1}$.

Mean values and the spread of the measured data on the incremental resistance (normalized) are indicated in Fig. 3 along with the theoretical results of the models due to Vogt [2]. Compared results in respect of the model developed in the present work are also shown in Fig. 3.

## 5. Discussion

The following inferences can be made on the basis of the results obtained in the present investigations:

(a) referring to Fig. 3, the experimental results closely agree with the theoretical model proposed indicating the validity of the analytical formulation

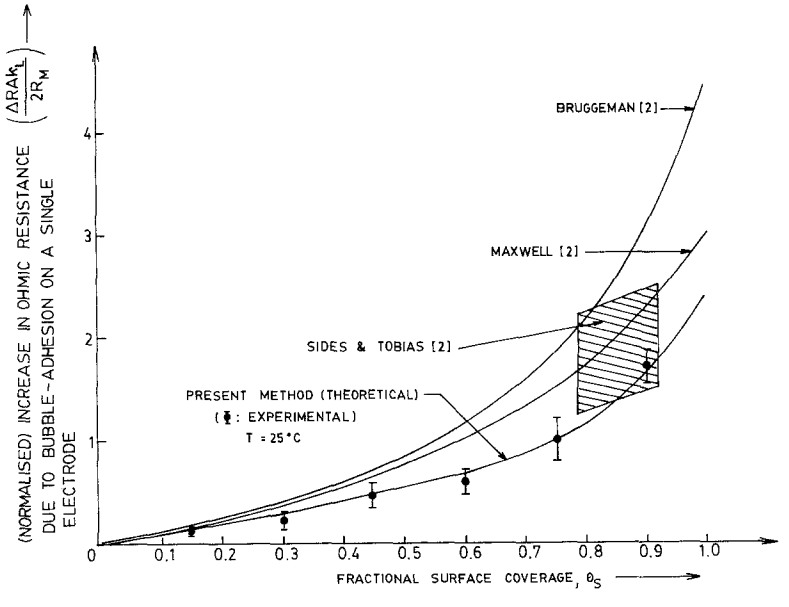


Fig. 3. Normalized incremental resistance of the cell due to bubble adhesion vs fractional surface covered by the bubbles: theoretical models of Maxwell, Bruggeman, Sides and Tobias and due to, the present method. Φ = experimental data from the simulated cell.

(b) the model presented here yields results which fall within the range of results given by Sides and Tobias [3] to an acceptable extent

(c) as experimentation with actual bubbles is not possible (due to the difficulty of getting bubble formations covering the electrode surfaces to a known extent), the present simulation technique offers solution for the measurement of the curtain effect. The measured results were consistent over different measurement frequencies and also for different electrolytic conductivities

(d) the analytical expressions of the present method are in closed form and are also free from any uncertain or empirical parameters such as the prinching factor [3]

(e) Bruggeman's [5] or Maxwells' [4] formulations are normally applicable to uniform arrangement or dispersion of inclusions in a continuum. For random dispersion of inclusions, these model would show deviations for high volume fractions ($\phi$); this could be inferred from relevant results on mixture permittivity formulae derived on the basis of Bruggeman's or Maxwells' method. Hence, the present method is more appropriate in view of the chaotic disorder involved in the dispersal of bubbles

(f) the results presented here indicate a logarithmic law of variation which is compatible with the random mixture law proposed by Lichtenecker and Rother [7]

(g) the present model is analogous to a cumulative growth of conductivity model developed by the authors in respect of powder solids [8]

(h) the method given here can also be extended to study the capacitive effects of bubble-curtains. Relevant time-domain studies on this aspect are in progress.

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