JOURNAL OF APPLIED ELECTROCHEMISTRY **17** (1987) 134–146

Pumping effect due to gas evolution in flow-through electrolysers

IVO ROUŠAR

Prague Institute of Chemical Technology, Department of Inorganic Technology, 166 28 Prague 6, Czechoslovakia

Received 19 August 1985; revised 21 February 1986

In electrolysers with recirculation where a gas is evolved, the pumping of electrolyte from a lower to a higher level can be effected by the air-lift effect due to the difference between the densities of the inlet electrolyte and the gaseous dispersion at the outlet. A balance equation for calculation of the rate of flow of the pumped liquid is derived. An equation for the calculation of the mean volume fraction of bubbles in the space between the electrodes is proposed and verified experimentally on a pilot electrolyser. The pumping efficiency of the air-lift effect is determined.

Nomenclature

a'_A, a'_C	constants of linearized Tafel Equation 7 (V)
b	electrode width (m)
b'_A, b'_C	constants of linearized Tafel Equation 7 ($V\,m^{-2}\,A^{-1}$)
c_{pE}	specific heat of electrolyte ($J\,kg^{-1}\,K^{-1}$)
d	interelectrode distance (m)
d_E	equivalent diameter of interelectrode space (m)
d_T	diameter of tubing (m)
E_A, E_C	potential of anode and cathode (V)
f	correction term, see Equation 11
F	Faraday's constant ($96\,484\,C\,mol^{-1}$)
g	acceleration of gravity ($9.81\,m\,s^{-2}$)
H	function defined by Equation 16
I_T	total current flowing through electrolyser (A)
j	local current density ($A\,m^{-2}$)
$\bar{j}$	mean current density ($A\,m^{-2}$)
j_ζ	reduced local current density
K_1, K_{2B}	criteria defined by Equations 12 and 13
K_3	criterion defined by Equation 9
Δl	pumping height equal to $l_E - l_T$ (m)
l_E	electrode height (m)
l_H	length of tubing above electrolyser (m)
l_T	level height in reservoir (m)
l_V, l_S	length of tubing, see Fig. 1 (m)
n_{O_2}, n_{H_2}	number of electrons transferred per molecule of O_2 or H_2
N_B, N_E	pumping power, pumping 'extra-power', Equations 28, 31 (W)
N_T	total power input for electrolysis (W)
Δp_M, Δp_p, Δp_z	pressure losses in the interelectrode space, in the inlet tubing and in elbows ($N\,m^{-2}$)
P	pressure at the upper edge of the electrode ($N\,m^{-2}$)
R	gas constant ($J\,K^{-1}\,mol^{-1}$)
Re, Re_M	Reynolds criterion for the electrolyte and for gas dispersion
S_A, S_C	thickness of anode and cathode (m)
T	temperature (K)
T_0, T_T	temperatures at the inlet and outlet (K)
ΔT	temperature difference, $T_T - T_0$ (K)
U	terminal voltage of electrolyser (V)
ΔU	increase of the mean voltage drop in the interelectrode space due to presence of bubbles (V)
v_E, v_M	velocities of electrolyte and of gas dispersion between electrodes ($m\,s^{-1}$)
v_p	velocity of electrolyte in inlet

0021-891X/87 $03.00 + .12

	channel ($\mathrm{m\,s^{-1}}$)
v_R	rising velocity of bubbles ($\mathrm{m\,s^{-1}}$)
$\dot{V}_E$	volume rate of flow of electrolyte ($\mathrm{m^3\,s^{-1}}$)
$\dot{V}_G(x)$	volume rate of flow of gas at height x ($\mathrm{m^3\,s^{-1}}$)
$\dot{V}_{GT}$	volume rate of flow of gas at upper electrode edge ($\mathrm{m^3\,s^{-1}}$)
x	distance from lower electrode edge (m)
$\alpha(x)$, $\bar{\alpha}$	volume fraction of bubbles at height x between electrodes, and its mean value (Equations 5a, 22a)
α_T	volume fractions of bubbles at upper electrode edge of electrolyte
α_∞	maximum volume fraction of bubbles
χ_A, χ_C, χ_E, χ_M	specific electric conductivity of anode, cathode, electrolyte and gas dispersion ($\Omega^{-1}\,\mathrm{m^{-1}}$)
ϱ_E, ϱ_M	density of electrolyte and gas dispersion ($\mathrm{kg\,m^{-3}}$)
μ_E, μ_M	dynamic viscosity of electrolyte and gas dispersion ($\mathrm{kg\,m^{-1}\,s^{-1}}$)
μ_0	dynamic viscosity of electrolyte at inlet temperature ($\mathrm{kg\,m^{-1}\,s^{-1}}$)
λ	friction coefficient of electrolyte in a tube
λ_M	friction coefficient of gas dispersion between electrodes
η_P	pump efficiency (%)
η_{O_2}, η_{H_2}	current efficiency for oxygen and hydrogen
ξ	reduced height coordinate, x/l_E
ΔE_{pot}	volume-specific potential energy difference of electrolyte ($\mathrm{J\,m^{-3}}$)
ΔE_{kin}	volume-specific kinetic energy difference of electrolyte ($\mathrm{J\,m^{-3}}$)
ΔE_{dis}	volume-specific dissipated energy of electrolyte ($\mathrm{J\,m^{-3}}$)

1. Introduction

In technical practice, circulation of electrolyte between a reservoir or reactor and the electrolyser proper is effected by means of a pump placed in the connecting tube. If a gas is evolved in the electrolyser it is possible to arrange that the gas dispersion (with a lower density) streams into the reservoir while the solution from the reservoir (without the gas bubbles) passes into the electrolyser. This principle is utilized in water electrolysis [1] and in electro-chemical production of chlorates [2], etc. If high rates of flow are not required, the principle is energetically acceptable and it operates reliably since there are no moving parts and no maintenance problems. For high rates of flow or large pumping height, pumping by the gas-lift effect is energetically too expensive.

2. Theoretical considerations

The calculation of the pumping rate is based on a pressure balance in the corresponding hydraulic circuit [3, 4] (Fig. 1). Bubbles are formed in the interelectrode space so that the mean relative content of the gas phase in a part of the circuit of height l_E is equal to $\bar{\alpha}$. In a part of the tubing at a height l_E above the electrolyser, the mean content of the gas phase is equal to α_T, which is higher than $\bar{\alpha}$. The electrolyte in the separator and in the connecting pipe of height l_T is without bubbles. Circulation of the electrolyte is caused by a difference between the density of the electrolyte at the inlet and that of the electrolyte in part of the electrolyser. The power consumed per unit volume of the flowing electrolyte ($\mathrm{W\,s\,m^{-3}}$ or $\mathrm{J\,m^{-3}}$) is changed irreversibly to heat by friction; any heat evolved in the system is conducted to the surroundings so that the system can be considered approximately isothermal.

Let us choose two levels, 1–1 and 2–2 (Fig. 1), at which the balance of the specific (volume) kinetic and potential energies are made. Then

$$\Delta E_{\mathrm{pot}} = g\varrho_E l_T - \varrho_E l_E(1-\bar{\alpha}) - g\varrho_E l_H(1-\alpha_T) \tag{1a}$$

$$\Delta E_{\mathrm{kin}} = \tfrac{1}{2}\varrho_E(\dot{V}_E/F_{11})^2 - \tfrac{1}{2}\varrho_E(1-\alpha_T)^{-1}(\dot{V}_E/F_{22})^2 \tag{1b}$$

$$\Delta E_{\mathrm{dis}} = \Delta p_M + \Delta p_p + \Delta p_z \tag{1c}$$

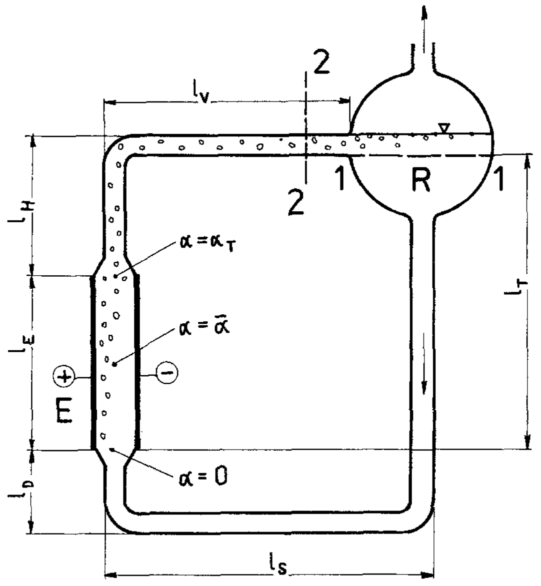

Fig. 1. Scheme of electrolyser with reservoir with electrolyte circulation caused by the formation of gas bubbles. l_E, Electrode height; l_H, vertical part of outlet tubing; l_D, vertical part of inlet tubing; l_v, l_s, length of connecting tubing at the outlet and inlet, respectively; l_T, height of inlet tubing (reactor) filled with electrolyte; E, electrolyser; R, separator. Direction of flow is denoted by arrows.

The second term in Equation 1a involves the mean volume fraction of bubbles, $\bar{\alpha}$, and the third term involves the volume fraction of bubbles at the top of the electrolyser, α_T. The cross-sectional areas of flow at the levels 1–1 and 2–2 are denoted as F_{11} and F_{22}. It should be noted that for closed systems the planes 1–1 and 2–2 should fuse to a single plane. For a closed system we usually presume that ΔE_{kin} in the separator is zero, i.e. is dissipated as heat.

The terms in Equation 1c correspond to losses due to friction in the section containing a mixture of the gas and electrolyte (Δp_M) or electrolyte only (Δp_p), and energy dissipated in places where the shape of the tube changes (Δp_z).

The above equations can be combined to give

$$g\varrho_E l_T - g\varrho_E l_E(1-\bar{\alpha}) - g\varrho_E l_H(1-\alpha_T) = \Delta p_M + \Delta p_p + \Delta p_z + \tfrac{1}{2}\varrho_E\left[\frac{(\dot{V}_E/F_{22})^2}{1-\alpha_T} - \left(\frac{\dot{V}_E}{F_{11}}\right)^2\right] \tag{1d}$$

The basic physical parameters for the gas dispersion with a bubble volume fraction, α, are given as

$$\varrho_M = \varrho_E(1-\alpha) \tag{2a}$$

$$\mu_M = \mu_E(1-\alpha)^{-2.5} \tag{2b}$$

$$v_E = \frac{\dot{V}_E}{wd}\left[\frac{1}{1-\alpha(x)}\right] \tag{2c}$$

$$v_G = \frac{\dot{V}_G(x)}{wd}\left[\frac{1}{\alpha(x)}\right] \tag{2d}$$

$$v_G = v_E + v_R[1-\alpha(x)]^{3.5} \tag{2e}$$

The expressions for the dynamic viscosity, μ_M, in Equation 2b and for the velocity of gas bubbles, v_G, in Equation 2e are discussed in [5]. In real dispersions containing spherical bubbles the volume fraction, $\alpha(x)$, cannot reach unity volume fraction. In a cubical arrangement the maximal volume gas fraction, α_∞, is 0.5236 and for the closest packing $\alpha_\infty = 0.7408$. For random packing a mean value of $\alpha_\infty = 0.63$ was predicted and corresponds to the stochastic frequency maximum [6]. Kreysa and Kuhn [7] slightly rearranged Equation 2e, introducing α_∞:

$$v_G = v_E + v_R[1 - \alpha(x)]^{4.5}\,[1 - \alpha(x)/\alpha_\infty]^{-1} \tag{2f}$$

The velocity of rising bubbles relative to the moving electrolyte, v_R, depends on the superficial gas velocity, $\dot{V}_{GT}/db$ [8], e.g. the bubble diameter is changed with the change of $\dot{V}_{GT}/bd$. The corresponding Reynolds number is given as

$$Re_M = \frac{\dot{V}_E d_E \varrho_E}{bd\mu_E}(1 - \alpha)^{2.5} = Re\,(1 - \alpha)^{2.5} \tag{3a}$$

where d_E is the equivalent channel diameter,

$$d_E = 2bd/(b + d) \tag{3b}$$

Here, b denotes electrode width and d denotes interelectrode distance. In practice, $b \gg d$.

The pressure losses in the interelectrode space can be calculated as

$$\Delta p_M = \lambda_M(l_E/2d_E)\varrho_E(\dot{V}_E/bd)^2\,(1 - \bar{\alpha})^{-1} \tag{4a}$$

where

$$\lambda_M = 96/Re_M \quad \text{for} \quad Re_M < 2300 \tag{4b}$$

$$\lambda_M = 0.314/Re_M^{0.25} \quad \text{for} \quad Re_M > 2300 \tag{4c}$$

Analogous equations apply for Δp_p. For Δp_z, the term l_E/d_E is set equal to the value found in tables [9]. For example, for a change in direction at a right angle, this term lies between 30 and 70.

The volume fraction of bubbles at a height x, can be expressed, using Equations 2c, 2d and 2f, as

$$\alpha(x) = \dot{V}_G(x)\alpha_\infty/\{\dot{V}_G(x) + [\dot{V}_G(x) + \dot{V}_E]\,[\alpha_\infty - \alpha(x)] + \alpha_\infty\, bdv_R\,[1 - \alpha(x)]^{5.5}\} \tag{5a}$$

where v_R represents the velocity of rising bubbles relative to the moving electrolyte due to buoyancy.

The volume fraction of bubbles at the top of the electrolyser can be expressed as

$$\alpha_T = \alpha_\infty \dot{V}_{GT}/[\dot{V}_{GT} + (\dot{V}_{GT} + \dot{V}_E)\,(\alpha_\infty - \alpha_T) + \alpha_\infty bdv_R(1 - \alpha_T)^{5.5}] \tag{5b}$$

The mean volume fraction of bubbles is given by

$$\bar{\alpha} = \int_0^1 \alpha(\xi)\,d\xi \tag{5c}$$

It was assumed [3] that $\bar{\alpha}/\alpha_T = 0.5$, corresponding to current densities being independent of x. It will be shown that this simplification is possible if $\alpha_T \to 0$, whereas in the general case of uneven current density distribution along the height of the electrolyser, $\bar{\alpha}/\alpha_T > 0.5$.

2.1. *Analytical calculation of $\bar{\alpha}/\alpha_T$ for a bipolar electrolyser neglecting the velocity of rising bubbles*

The equation for the voltage drop along a current line at height ξ in a bipolar electrolyser reads

$$U = a'_A + b'_A j(\xi) + a'_C + b'_C j(\xi) + j(\xi)\,[S_A\chi_A^{-1} + S_C\chi_C^{-1}] + j(\xi)\,d\chi_E^{-1}\left[1 + 1.5K_3 f\int_0^\xi \frac{j(\xi)}{\bar{j}}\,d\xi\right] \tag{6}$$

This gives the terminal voltage, U, of the electrolyser. The first four terms on the right-hand side correspond to the anode and cathode potentials.

$$E_A = a'_A + b'_A j(\xi) \tag{7a}$$

$$-E_C = a'_C + b'_C j(\xi) \tag{7b}$$

Equations 7a and 7b are justified only for small deviations of $j(\xi)$ about $\bar{j}$.

Then comes the voltage drop in the anode and cathode of thickness S_A and S_C and specific conductivity χ_A and χ_C, respectively. The last term represents the voltage drop in the space between the electrodes, where the specific resistivity of the gas dispersion is given by the Maxwell equation [3, 12], Equation 8a. There are also other equations for the calculation of χ_M [10, 11], but the Maxwell equation leads to an analytical solution. It is worth mentioning that the Maxwell equation slightly underestimates χ_M^{-1} so that a more uniform current density distribution is eventually obtained. Hence, for a flow-through system

$$\chi_M^{-1} = \chi_E^{-1}\left\{1 + 1.5\left[\frac{\dot{V}_G(x)}{\dot{V}_E}\right]\left[\frac{v_E(x)}{v_G(x)}\right]\right\} \tag{8a}$$

or

$$\chi_M^{-1} = \chi_E^{-1}\left[1 + 1.5K_3 f\int_0^{\xi}\frac{j(\xi)}{\bar{j}}\,d\xi\right] \tag{8b}$$

where

$$\frac{\dot{V}_G(x)}{\dot{V}_{GT}} = \int_0^{\xi}\frac{j(\xi)}{\bar{j}}\,d\xi \tag{9}$$

and

$$K_3 = \frac{\alpha_T}{1 - \alpha_T} \tag{10}$$

$$f = [\dot{V}_E + bdv_R(1 - \alpha_T)^{5.5}(1 - \alpha_T/\alpha_\infty)^{-1}]/[\dot{V}_E + bdv_R(1 - \alpha(x))^{5.5}(1 - \alpha(x)/\alpha_\infty)^{-1}] \tag{11}$$

Equation 8 is strictly valid only if $\alpha_T < 0.2$, whereas for higher values of α_T the specific electric resistivity of the dispersion is better expressed by the Bruggeman equation [10]

$$\chi_M^{-1} = \chi_E^{-1}\left[1 + K_3 f\int_0^{\xi}\frac{j(\xi)}{\bar{j}}\,d\xi\right]^{1.5} \tag{12}$$

Since we want to obtain an analytical solution, we use Equation 8 for $v_R = 0$ and for any values of α_T, taking into account that for higher values of α_T the calculated resistivity and the ratio of α/α_T will be smaller than with the use of Equation 12.

Introducing dimensionless criteria and simplexes

$$j_\xi = j(\xi)/\bar{j} \tag{13b}$$

$$K_1 = (U - a'_A - a'_C)/\bar{j}d\,\chi_E^{-1} \tag{13b}$$

$$K_{2B} = (b'_A + b'_C)/d\,\chi_E^{-1} + (S_A\chi_A^{-1} + S_C\chi_C^{-1})/d\,\chi_E^{-1} \tag{13c}$$

Equation 6, which is now valid only for $v_R = 0$, can be rearranged in the form

$$K_1 = K_{2B}j_\xi + j_\xi\left(1 + 1.5K_3\int_0^{\xi} j_\xi\,d\xi\right) \tag{14}$$

The value of K_1 (or U) is not known, but it can be calculated by using the equation for the current density balance

$$\int_0^1 j_\xi\,d\xi = 1 \tag{15}$$

Equation 14 can be transformed by substituting

$$\int_0^{\xi} j_\xi d\xi \;=\; H \tag{16}$$

into the form

$$K_1 \;=\; K_{2B}H' + (1 + 1.5K_3H)H' \tag{17}$$

The boundary conditions are $H(\xi = 0) = 0$, $H(\xi = 1) = 1$. Since the value of K_1 is not known, two boundary conditions are needed; the latter follows from Equation 15. The solution leads to

$$K_1 \;=\; 1 + K_{2B} + 0.75K_3 \tag{18}$$

$$H(\xi) \;=\; [(3K_1K_3\xi + (1 + K_{2B})^2)^{\frac{1}{2}} - 1 - K_{2B}]/1.5K_3 \tag{19}$$

$$H'(\xi) \;=\; j_\xi \;=\; K_1(3K_1K_3\xi + (1 + K_{2B})^2)^{-\frac{1}{2}} \tag{20}$$

The following equation is important for further calculations:

$$H(\xi) \;=\; \int_0^{\xi} j_\xi d\xi \;=\; \dot{V}_{\mathrm{G}}(\xi)/\dot{V}_{\mathrm{GT}} \tag{21}$$

Equation 5c can be rearranged by using Equations 5a and 21 for $v_{\mathrm{R}} = 0$ to the form

$$\bar{\alpha} \;=\; \int_0^1 \frac{\dot{V}_{\mathrm{G}}(\xi)d\xi}{\dot{V}_{\mathrm{E}} + \dot{V}_{\mathrm{G}}(\xi)} \;=\; \int_0^1 \frac{Hd\xi}{\dot{V}_{\mathrm{E}}/\dot{V}_{\mathrm{GT}} + H} \tag{22a}$$

From the definition of K_3, we then obtain

$$\frac{\bar{\alpha}}{\alpha_{\mathrm{T}}} \;=\; (1 + K_3)\int_0^1 \frac{Hd\xi}{1 + K_3H} \tag{22b}$$

By substituting Equation 19 for H in Equation 22b and integrating we obtain the resulting equation for the volume fraction of bubbles

$$\begin{aligned}\bar{\alpha}/\alpha_{\mathrm{T}} \;=\; & (1 + 1/K_3)\,\{1 - [(3K_1K_3 + (1 + K_{2B})^2)^{\frac{1}{2}} - 1 - K_{2B}]/K_1K_3 \\ & + (K_{2B} - 0.5)\ln[((3K_1K_3 + (1 + K_{2B})^2)^{\frac{1}{2}} - K_{2B} + 0.5)/1.5]\}\end{aligned} \tag{23}$$

This equation shows that the ratio of $\bar{\alpha}/\alpha_{\mathrm{T}}$ increases with the value of K_2 (K_2 increases with increasing b'_{A} and b'_{C} and decreasing $d\chi_{\mathrm{E}}^{-1}$) and approaches 0.5 for $K_3 \to 0$ (for low gas fractions).

In calculating the value of K_3 we must know the value of $\dot{V}_{\mathrm{GT}}$ corresponding to the total current, I_{T}, flowing through the system. For example, for diaphragm-less water electrolysis in alkaline medium (such as was used in our experiments) we have

$$\dot{V}_{\mathrm{GT}} \;=\; \frac{I_{\mathrm{T}}}{F}\left(\tfrac{1}{4}\eta_{\mathrm{O_2}} + \tfrac{1}{2}\eta_{\mathrm{H_2}}\right)\frac{RT_{\mathrm{T}}}{P} \tag{24}$$

where $\eta_{\mathrm{O_2}} \leqslant 1$, $\eta_{\mathrm{H_2}} \leqslant 1$ and RT/P is the molar volume of the (ideal) gas at a pressure P and temperature T_{T} at the upper edge of the electrolyser electrodes.

2.2. *Numerical calculation of $\bar{\alpha}$ for one cell of a bipolar electrolyser*

The voltage balance referring to a current line for a bipolar electrolyser using the Bruggeman equation 11 reads

$$U \;=\; a'_{\mathrm{A}} + b'_{\mathrm{A}}j_\xi + a'_{\mathrm{C}} + b'_{\mathrm{C}}j_\xi + j_\xi(S_{\mathrm{A}}\chi_{\mathrm{A}}^{-1} + S_{\mathrm{C}}\chi_{\mathrm{C}}^{-1}) + j_\xi\, d\chi_{\mathrm{E}}^{-1}\left(1 + K_3 f\int_0^{\xi}\frac{j_\xi}{\bar{j}}\,d\xi\right)^{1.5} \tag{25}$$

Equation 25 is valid for $j(\xi) \approx \bar{j}$; for other cases we can use $b_{\mathrm{A}}\ln[j(\xi)]$ and $b_{\mathrm{C}}\ln[j(\xi)]$ for the

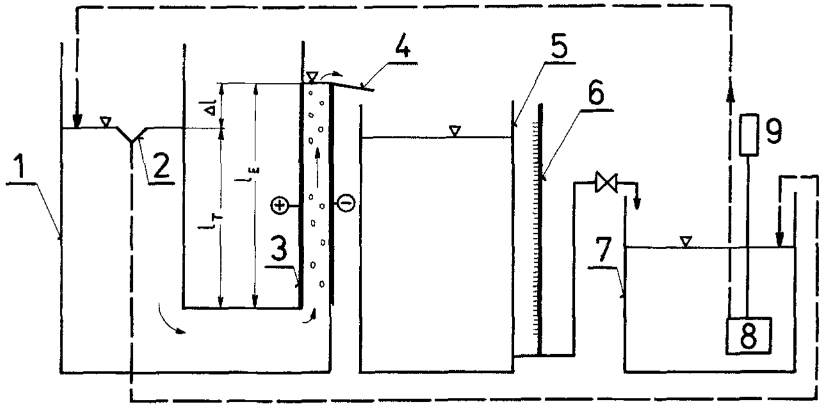

Fig. 2. Experimental set-up. 1, Reservoir with 200 litres 8.77% NaOH; 2, overflow to maintain the level; 3, one cell of bipolar electrolyser, 13 × 70 cm; 4, overflow to reservoir, 5, for measurement of the rate of flow; 6, water gauge for reservoir 5; 7, reservoir with soda lye; 8, pump with controllable speed of revolution of electric motor, 9. l_T, Level height in reservoir; l_E, electrode height; Δl, pumping height.

electrode polarization instead of b'_A and b'_C. Equation 25 can be rearranged using dimensionless numbers and simplexes into the form

$$K_1 = K_{2B} j_\xi + j_\xi \left(1 + K_3 f \int_0^\xi j_\xi \, d\xi\right)^{1.5} \tag{26}$$

Equation 15 is to be used for the calculation of K_1. The value of $\bar{\alpha}$ can be obtained by numerical integration of Equation 5c.

Using Equation 16 as the definition of H we have to solve Equation 27:

$$H' = \frac{K_1}{K_{2B} + (1 + K_3 f H)^{1.5}} \tag{27}$$

with boundary conditions $H(0) = 0$; $H(1) = 1$.

2.3. *Power loss due to pumping by the buoyancy effect of gas bubbles*

We shall consider the system shown in Fig. 2: the pumping power N_B and the pressure loss to be compensated are given as

$$N_B = \dot{V}_E \Delta p \tag{28}$$

$$\Delta p = \varrho_E g \Delta l \tag{29}$$

The bubble volume fraction at the upper edge of the electrodes, α_T, is a factor determining the mean voltage drop between the electrodes. Subtracting the mean voltage drop between the electrodes in the absence of bubbles from the aforementioned value, we obtain the voltage increment, ΔU, due to the presence of bubbles in the interelectrode gap.

$$\Delta U = \bar{j} d \chi_E^{-1} (K_1 - 1 - K_{2B}) \tag{30}$$

The extra power consumed due to the presence of the bubbles in the interelectrode gap, N_E, may be approximated by

$$N_E = I_T \Delta U \tag{31}$$

If the ratio of the power for pumping the fluid by the gas-lift effect to the extra power is defined as 'pumping efficiency' then this quantity is given by

$$\eta_P = \frac{N_B}{N_E} \times 100\ (\%) \tag{32}$$

The total power consumed in one cell of a bipolar electrolyser, N_T, is given by

$$N_T = jbl_E U \tag{33}$$

3. Experimental details and results

Equation 23 was verified on a pilot scale, undivided electrolyser for water decomposition. To a first approximation, the current efficiencies for H_2 and O_2 evolution, η_{O_2} and η_{H_2}, are set to 1. The electrolyte was 8.77% NaOH solution, the electrode width $b = 130\,\text{mm}$, electrode height $l_E = 703\,\text{mm}$ and interelectrode distance $d = 6\,\text{mm}$. The electrolyser was connected to a reservoir of 200 litres, whose outlet was connected to the lower part of the electrolyser. Current collectors were fastened at ten points on the rear faces of the electrodes so that the electrolyser could be considered as one cell of a bipolar electrolyser (Fig. 2). The electrolyte level in the reservoir could be changed from +70 to −320 mm with respect to the overflow located at the upper edge of the electrodes. The outflowing liquid passed into another reservoir which was provided with a water gauge to measure the flow rate of the electrolyte.

First, the local resistance and pressure losses in the space between the electrodes were measured at a chosen flow rate. The following expression for Δp_z was found:

$$\Delta p_z = 25.7\, \lambda \varrho_E v_E^2 \tag{34}$$

Afterwards, the liquid level in the reservoir was set at a chosen height, l_T, and the value of $\bar{\alpha}$ was calculated from the equation

$$g\varrho_E l_T - g\varrho_E l_E(1 - \bar{\alpha}) = \left(\lambda_M \frac{l_E}{d_E} + 51.4\, \lambda + 1\right) \frac{1}{2} \varrho_E \frac{v_E^2}{1 - \bar{\alpha}} \tag{35}$$

Here, the kinetic energy of the liquid at the inlet is neglected.

The system was not isothermal, since the temperature at the upper edge of the electrodes was always higher than at inlet ($T_T > T_0$). Therefore, the mean dynamic viscosity, μ, was calculated according to

$$\mu = \mu_0 \left[1 + \frac{1}{2\mu_0} \left(\frac{d\mu}{dT}\right)_{T_0} (T_T - T_0)\right] \tag{36}$$

and the gas volume at the upper edge of the electrodes as

$$\dot{V}_{GT} = \dot{V}_{GT,0} \left(1 + \frac{T_T - T_0}{293}\right) \tag{37}$$

In treating the data, the temperature difference between the outflowing and inlet electrolyte was calculated as

$$\Delta T = \left(U - \frac{\Delta H_{298}^0}{2F}\right) \frac{I_T}{\dot{V}_E \varrho_E c_{pE}} \tag{38}$$

The following physical constants were used: $\Delta H_{298}^0 = 241.8 \times 10^3\,\text{J}$ for water decomposition [13]; $c_{pE} = 3789\,\text{J}\,\text{kg}^{-1}\,\text{K}^{-1}$ [14]; $\mu_E = 0.00173\,\text{N}\,\text{s}\,\text{m}^{-2}$ [15]; $\varrho_E = 1095\,\text{kg}\,\text{m}^{-3}$ [16]; $\chi_E^{-1} = 0.03435\,\Omega\,\text{m}$ [17].

The substantial experimental data are presented in Figs 3, 4 and 5.

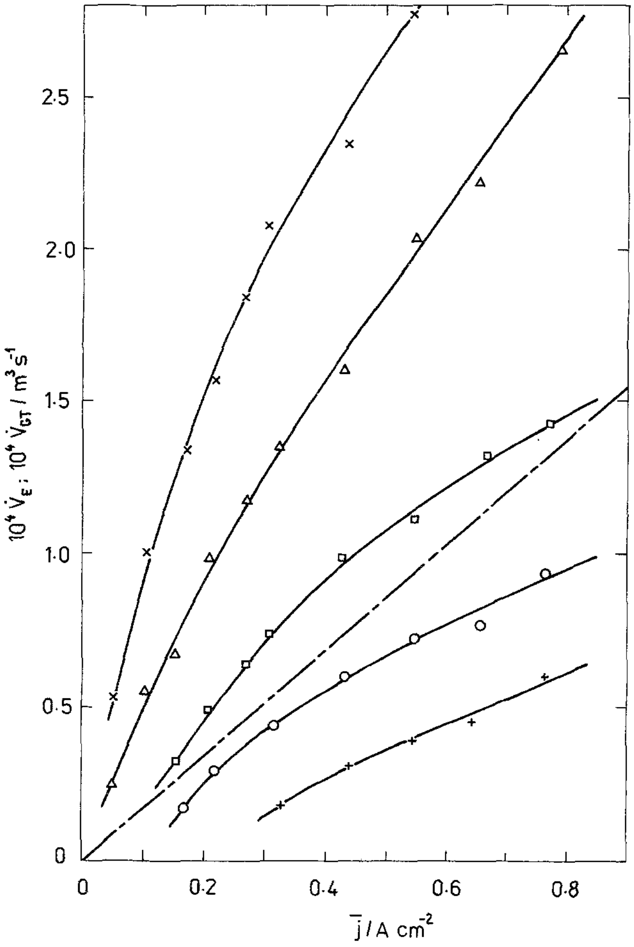

Fig. 3. Experimental values of electrolyte flow rate, $\dot{V}_E$ ($m^3 s^{-1}$), versus average current density, $\bar{j}$($A\,cm^{-2}$). The dashed line gives the $\dot{V}_{GT}$ values for different current densities. Values of Δl: ×, 40 mm; △, 80 mm; □, 160 mm; ○, 240 mm; +, 320 mm.

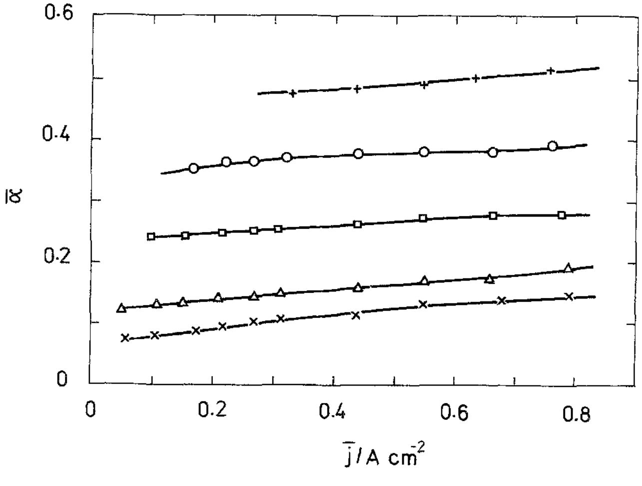

Fig. 4. Experimental values of $\bar{\alpha}$ as function of average current density, $\bar{j}$ ($A\,cm^{-2}$) for different pumping heights. Notation as for Fig. 3

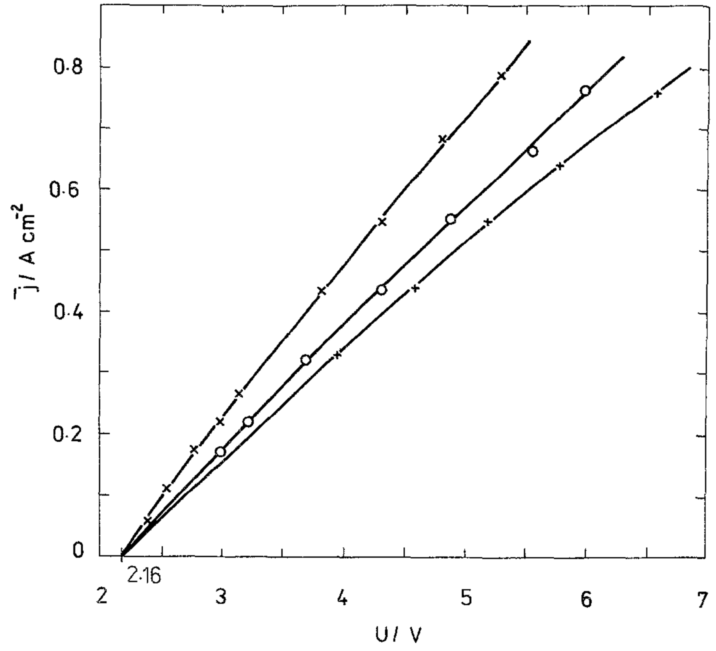

Fig. 5. Total voltage, U (V), on one cell of a bipolar electrolyser versus average current density, $\bar{j}$ (A cm^{-2}) for different pumping heights. Notation as for Fig. 3

4. Discussion

Based on experimental data and Equation 18, the values of $K_{2B} = 0.408$ and $(a'_A + a'_C) = 2.16$ V were calculated by the least squares method. The voltage drop of the electrodes and busbars is also included in the value of K_{2B}. The value 2.16 V for $(a'_A + a'_C)$ is higher than the thermodynamic value of 1.2 V due to linearization of the U–j relation in the range $\bar{j} \in \langle 0.005; 0.8 \rangle$ (A cm^{-2}). The values of $\bar{\alpha}$ were then calculated from Equation 23 (for $v_R = 0$) and the same quantities were calculated from the experimental data with the aid of Equation 35.

Numerical integration of Equations 5c and 27 for $v_R = 0$ resulted in values of $\bar{\alpha}$ higher (on average +12%) than those obtained by experiment. It was concluded that the bubbles have a certain rising velocity, v_R, resulting in a decrease of the value of α_T and hence $\bar{\alpha}$. For each experiment we used Equations 27, 5a and 5c to calculate such a value of v_R, for which the calculated and experimental values of $\bar{\alpha}$ were identical (see Fig. 6) for $\alpha_\infty = 0.63$. The v_R values were correlated with superficial gas velocity, $\dot{V}_{GT}/bd$,

$$v_R = v_R^0 + (0.752 \pm 0.125)\frac{\dot{V}_{GT}}{bd} \qquad (39)$$

where the upper and lower limits of the mean were calculated from the sample variance, s,

$$s^2 = \sum (x_i - \bar{x})^2/(n-1) \qquad (40)$$

using Student's statistic as $\pm t(n; 0.05)s/(n)^{\frac{1}{2}}$. The v_R^0 value was estimated as 0.5 cm s^{-1}. Equation 39 is valid for all experiments up to $\Delta l = 320$ mm. Equation 39 is only an approximation of a more complicated dependency as can be seen from Fig. 6. The average error of v_R is ±36%.

With the help of Equation 39 we recalculated the values of $\bar{\alpha}$, U, U_B, N_E and N_T for all experiments (Fig. 7). The calculated values of $\bar{\alpha}$ are distributed randomly about the experimental values of $\bar{\alpha}$ with an average error of ±4.1%. Some of the experimental and calculated data are given in Table 1. The values in Table 1 indicate that the best fit of K_{2B} using a least squares method for all data predicts lower cell voltage for $\Delta l = 40$ mm and higher cell voltage for $\Delta l = 320$ mm, compared to

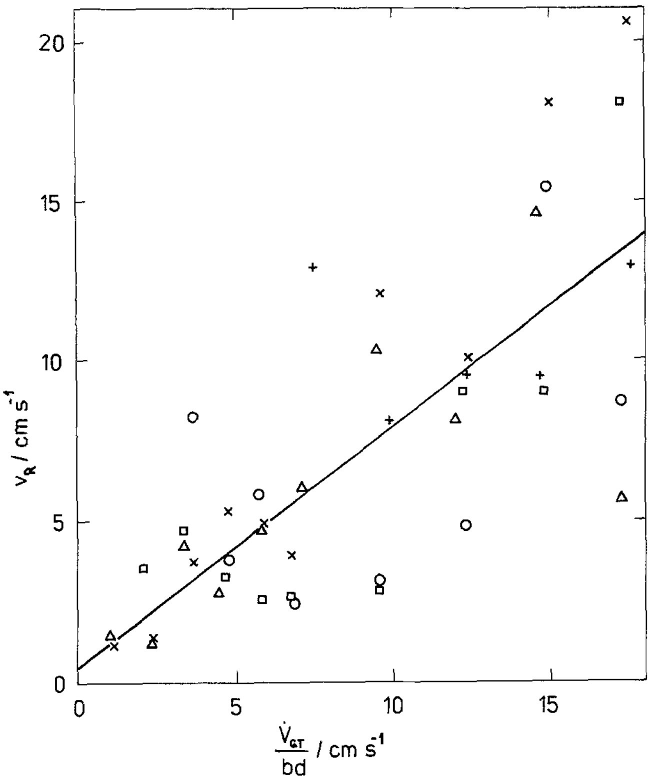

Fig. 6. Dependence of the calculated v_R (cm s^{-1}) values as function of the superficial gas velocity, $\dot{V}_{GT}/bd$ (cm s^{-1}), for the case where experimental $\bar{\alpha}$ is put equal to calculated $\bar{\alpha}$; (α_∞ = 0.63). Notation as for Fig. 3

experimental values. The greatest error in total cell voltage is +0.47 V for U = 3.95 V, but this system also results in a very high value of $\bar{\alpha}$ (Table 1).

The physical background of Equation 39 lies, according to Hine [8], in the dependency of v_R (or the bubble diameter) on the superficial gas velocity. Equation 2f can be used for the evaluation of experimental data for systems where 'channelling' of bubbles takes place. The rising velocity, v_R, calculated according to Stokes law is considerably smaller than the value calculated from Equation

Table 1. Experimental and calculated values for Δl = *40 mm and* Δl = *320 mm*

Δl *(mm)*	$\bar{j}$ *(A cm^{-2})*	U *(V)* *(experimental)*	U *(V)* *(theory)*	$\bar{\alpha}$ *(experimental)*	$\bar{\alpha}$ *(theory)*
40	0.055	2.40	2.33	0.0701	0.0695
40	0.109	2.56	2.50	0.0789	0.0754
40	0.172	2.80	2.71	0.0860	0.0872
40	0.219	2.98	2.86	0.0912	0.0941
40	0.268	3.15	3.03	0.0979	0.0979
40	0.312	3.25	3.17	0.1042	0.1005
40	0.438	3.80	3.62	0.1125	0.1213
40	0.547	4.30	4.01	0.1295	0.1299
40	0.648	4.80	4.52	0.1353	0.1465
40	0.793	5.30	4.94	0.1446	0.1566
320	0.328	3.95	4.42	0.4728	0.5179
320	0.438	4.60	4.91	0.4841	0.4854
320	0.547	5.20	5.64	0.4912	0.4905
320	0.640	5.80	6.23	0.4976	0.4910
320	0.766	6.60	6.90	0.5150	0.4800

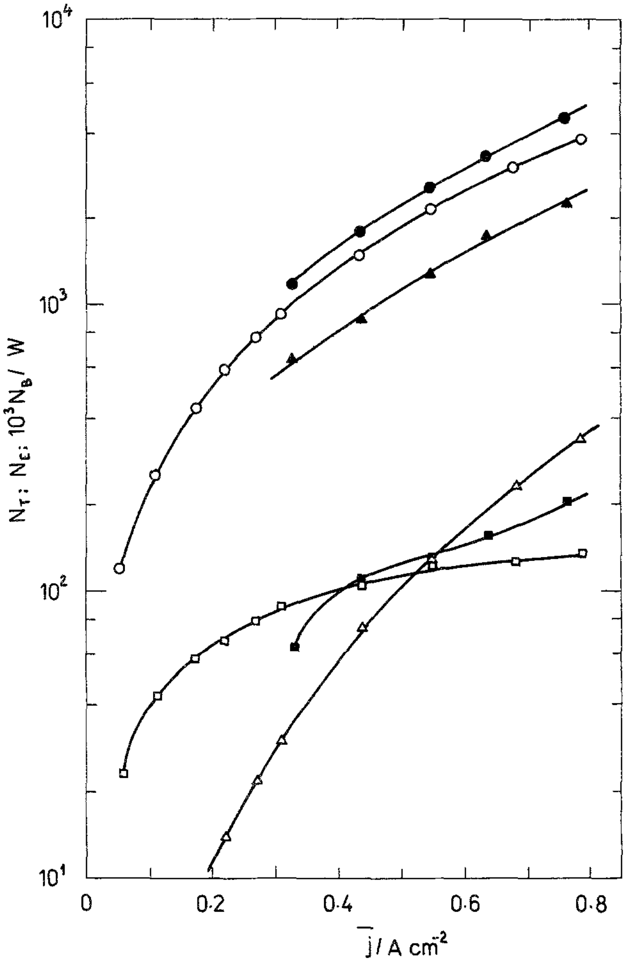

Fig. 7. Power consumed for electrolysis in one cell (N_T), 'extra-power' consumed due to the presence of gas bubbles in the electrolyte (N_E) and power required for pumping due to the gas-lift effect (N_B) as functions of the average current density, $\bar{j}$, for two pumping heights. Open symbols: Δl = 40 mm; solid symbols: Δl = 320 mm. N_T, ○ ●; N_E, △ ▲; N_B, □ ■.

39. This opinion supports the values published for a pilot plant electrolyser for chlorate production [18], with b = 148 mm, d = 9 mm and l_E = 700 mm. For evaluation of the data it was necessary to use unusually high rising velocities based on estimated bubble diameters (0.036–0.048 cm), because the experimental data indicated very low $\bar{\alpha}$ values. The experimentally measured bubble diameters were only 0.018–0.024 cm.

As a result, Equation 39 can be recommended for a system with $d \approx$ 6 mm and also for systems with recirculation of the electrolyte described in Fig. 1.

The 'pumping efficiency' was, in our system, in the range 0.01 to 3.5%. Nevertheless, the simplicity of pumping and the very low absolute values of power needed for pumping (N_E) compared to the total power input (N_T) make it feasible to use the bubbles for pumping (electrolyte circulation) in closed loops.

5. Conclusions

Equation 35, giving the volume fraction of bubbles, $\bar{\alpha}$, was verified experimentally on a pilot scale electrolyser. In the interelectrode gap the velocity of rising bubbles, v_R, is co-determined by the superficial gas velocity Equation 39 and by the flow of bubbles in 'channels' (in the swarm in the vicinity of the electrode) and therefore v_G can be approximated by Equation 2f. Equations 39 and 2f are also important in calculating the circulation rate or the pumping height for industrial electrolysers used in the production of hydrogen, oxygen or chlorates. Equation 39 represents a correction (4/20%) to be used in the calculation of $\bar{\alpha}$ or related quantities, e.g. χ_E/χ_M, in which the Stokes velocity of bubbles is put equal to zero ($v_R = 0$).

References

[1] A. Regner, 'Technická Elektrochemie I', Academia, Prague (1967) p. 360.
[2] A. T. Kuhn, 'Industrial Electrochemical Processes', Elsevier, Amsterdam (1971) p. 94.
[3] I. Roušar, *J. Electrochem. Soc.* **116** (1969) 676.
[4] I. Roušar, M. Provazník and P. Stuhl, *Coll. Czech. Chem. Comm.* **48** (1983) 2232.
[5] N. Zuber, *Chem. Eng. Sci.* **19** (1964) 897.
[6] D. P. Hanghey and G. S. G. Beveridge, *Chem. Eng. Sci.* **21** (1966) 905.
[7] G. Kreysa and M. Kuhn, *J. Appl. Electrochem.* **15** (1985) 517.
[8] F. Hine and T. Sugimoto, Paper 459 presented at the Electrochem. Soc. Meeting, Seattle (1978).
[9] V. Míka, 'Sbírka příkladů z chemického inženýrství', SNTL, Prague (1978) p. 123.
[10] D. A. G. Bruggeman, *Ann. Phys.* **24** (1935) 636.
[11] R. E. Meredith and Ch. Tobias, in 'Advances in Electrochemistry and Electrochemical Engineering', Vol. 2 (edited by P. Delahay and Ch. W. Tobias), Interscience, New York (1962) p. 15.
[12] J. C. Maxwell, 'A Treatise on Electricity and Magnetism', Vol. 1, Clarendon Press, Oxford (1881) p. 435.
[13] W. J. Moore, 'Physical Chemistry' (Czech translation), SNTL, Prague (1979) p. 91.
[14] J. W. Bertetti and W. L. McCabe, *Ind. Eng. Chem.* **28** (1936) 375.
[15] B. P. Nikolskij (ed.), 'Spravočnik Chimika', Vol. III, Khimiya, Moscow (1964) p. 718.
[16] *Ibid.*, p. 544.
[17] *Ibid.*, p. 666.
[18] I. Roušar, A. Regner and V. Cezner, *Coll. Czech. Chem. Comm.* **31** (1966) 4193.