JOURNAL OF APPLIED ELECTROCHEMISTRY **25** (1995) 273–278

Electrochemical mass transfer to regular packings in a bubble column

A. I. TASAT, O. N. CAVATORTA, U. BÖHM

Departamento de Industrias, Universidad de Buenos Aires, Ciudad Universitaria, 1428 Buenos Aires, Argentina

Received 11 April 1994; revised 6 September 1994

The behaviour of regular packings constructed from corrugated metal sheets was investigated since they constitute an attractive packing material for the electrochemical absorption of gases. Mass transfer coefficients for the regular packing contained in a circular electrolytical cell were determined by the electrochemical method with simulation of the absorption process by bubbling nitrogen through the column. Correlations for the mass transfer rate as a function of fluid dynamic parameters and fluid properties are presented.

List of symbols

A	electrode surface area (m^2)
c_0	bulk concentration ($mol\,m^{-3}$)
D	diffusivity ($m^2\,s^{-1}$)
E	gas hold-up = volume fraction of gas
F	Faraday constant ($A\,s\,mol^{-1}$)
Fr	Froude number = $Vs^2/g L$
g	gravitational acceleration ($m\,s^{-2}$)
Ga	Galileo number = $L^3\,g/\nu^2$
I	limiting current (A)
k	mass transfer coefficient ($m\,s^{-1}$)
L	characteristic length (m)
Re	Reynolds number = $V_s\,L/\nu$
Sc	Schmidt number = ν/D
Sh	Sherwood number = $k\,L/D$
St	Stanton number = k/V_s
V_s	superficial gas velocity ($m\,s^{-1}$)
z	valence change in electrochemical reaction
ν	kinematic viscosity ($m^2\,s^{-1}$)

1. Introduction

Treatment of industrial effluents is becoming an increasingly important problem in the chemical and related industries. In the 1980s and 1990s the demand for reliable and low cost processes for the purification of effluents started to grow.

Among modern gas purification processes is electrochemical absorption, allowing the removal of hazardous components from contaminated industrial gas streams. Thus, substances such as chlorine, nitrogen oxides and sulfur dioxide can be eliminated from waste gases by electrochemical reaction after dissolution in an electrolytic solution [1–4].

The electrochemical absorption can be performed in packed columns containing conductive particles. The packed bed acts as a traditional absorption column and simultaneously as an electrolytic cell with the packing material working as a three-dimensional electrode. Up-to-date graphite pellets [1] and Pb/PbO_2 spheres [4] have been used.

Among the commercial packings, regular packings constructed from corrugated metal sheets are an attractive option and are nowadays widely used in gas continuous packed columns, presenting several advantages in comparison with other packings: they provide large void fractions, a high degree of usable surface area and high mass transfer efficiency, yielding low equivalent heights of theoretical plate. Furthermore structured packings present low pressure drop per unit length and excellent radial mixing.

Usually, contaminating gases are only slightly soluble in aqueous solutions and the mass transfer rate is controlled by the liquid side resistance. Therefore a bubble column is more appropriate than a gas continuous packed column, in spite of the larger pressure drop for the gas. A larger residence time and higher turbulence intensity for the liquid phase can be achieved.

Due to the low solubility of the gases dilute solutions result, and if 'electrochemical' purification of gases is applied, the process is diffusion controlled. For an optimum space-time yield large electrode areas and high mass transfer rates are required. To obtain these objectives, the choice of regular packing, as electrodes in a bubble column, to work as an electrolytic cell is proposed. Problems such as difficult liquid feed distribution and liquid redistribution within the bed, common with irrigated packings, are avoided, since the liquid fills the whole column. The regular packing acts, not only as a three-dimensional electrode, but also as a static mixer and provides a large specific surface area. Turbulence generated by the gas bubbling also enhances the mass transfer rate to the electrodes [5].

The present work deals with the mass transfer to regular packing in a circular electrolytic cell with gas admission at the bottom. Fluid dynamics of the absorption process are simulated by bubbling

0021-891X

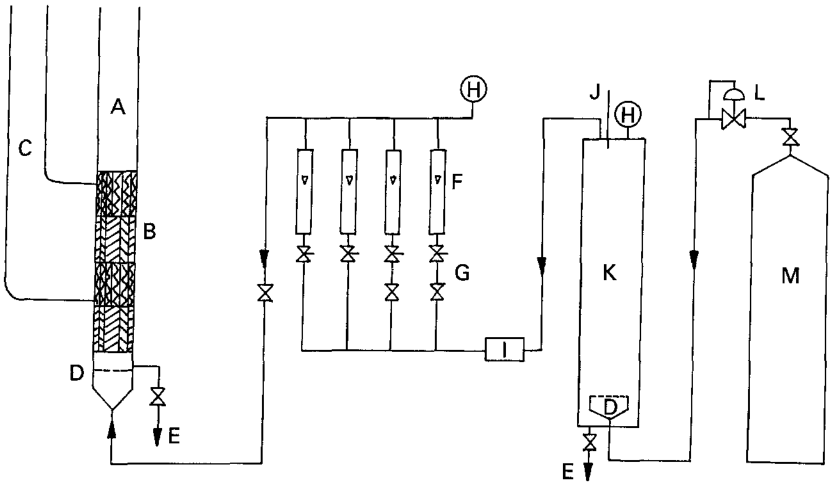

Fig. 1. Experimental setup: (A) bubble column, (B) regular packing, (C) open tube manometer, (D) distributors, (E) drain, (F) rotameters, (G) valves, (H) manometers, (J) thermometer, (K) gas saturator, (L) pressure regulator and (M) nitrogen tube.

nitrogen through the column, while mass transfer to the packing is studied by the electrochemical technique.

Since metallic structures have been introduced lately as catalyst supports in gas–liquid reactors, the results presented here will be useful, not only for the design of electrochemical absorption equipment, but also for gas–liquid catalytic reactors.

2. Experimental details

The experimental set-up is shown in Fig. 1. The test bubble column was constructed from Perspex tube, 5 cm in inner diameter and 60 cm high. Perforated plates of Lucite were used as gas distributors. They differed in hole diameter and number of orifices; Table 1 shows their geometric characteristics.

Figure 2 shows a schematic diagram of the regular packing. Four packs constructed of nickel sheets were stacked in the bubble column and rotated 90° from the adjacent element. Each packing element, 4.4 cm high, was composed of 11 corrugated sheets with an inclination angle of the triangular channels of 45°. The packing had a specific surface area of 568 m^{-1} and a void fraction of 0.88.

Mass transfer to this packing was studied by the limiting current method [6]. As indicated by Kreysa and Woebcken [2] in their investigation of gas/liquid mass transfer processes a suitable electrochemical system for the measurement of the electrochemical mass transfer rate is the reduction of ferricyanide ions in alkaline media, using an inert gas to obtain the hydrodynamic conditions of the process.

Table 1. Gas distributor characteristics

Distributor (code)	*Number of orifices*	*Hole diameter/mm*	*Layout*
D1/2–1	1	0.5	central orifice
D1/2–6	6	0.5	circle at 12.5 mm from centre
D1/2–18	18	0.5	circle at 12.5 mm from centre
D1–6	6	1.0	circle at 12.5 mm from centre

Equimolar solutions of potassium ferri- and ferrocyanide were used as electrolyte. Sodium hydroxide or a buffer of sodium carbonate and bicarbonate were chosen as supporting electrolyte and carboxymethyl cellulose sodium salt was added to the latter to vary the liquid physical properties. The dynamic viscosity varied from 1.14×10^{-4} Pa s to 11.5×10^{-4} Pa s and the diffusivity varied from $4.36 \times 10^{-10}\,m^2\,s^{-1}$ to $6.63 \times 10^{-10}\,m^2\,s^{-1}$. Although the diffusion coefficient of hexacyanoferrate ions is somewhat smaller than the diffusion coefficient of

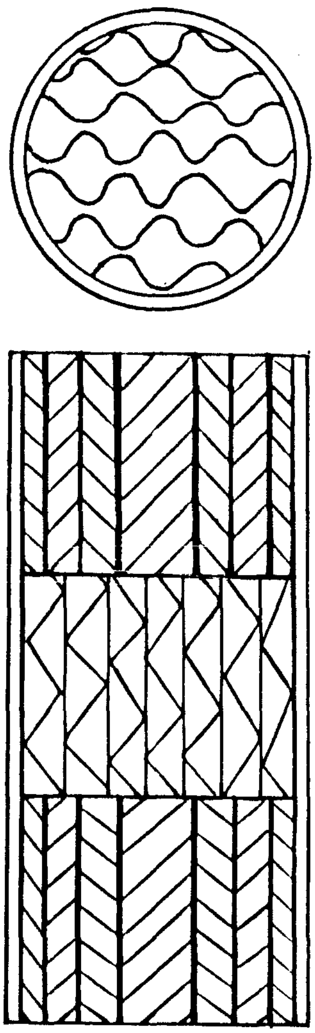

Fig. 2. Sketch of regular packing.

Table 2. Electrolytic solution characteristics

Solution (code)	$K_3Fe(CN)_6$ $K_4Fe(CN)_6$ $/kmol\,m^{-3}$	NaOH $/kmol\,m^{-3}$	Na_2CO_3 $NaHCO_3$ $/kmol\,m^{-3}$	CMC $/g\,dm^{-3}$	Sc
S1	0.001	0.5	–	–	1622
S2	0.001	–	0.4	–	2173
S3	0.01	0.5	–	–	1960
S4	0.01	–	0.4	3	9340
S5	0.01	–	0.4	6	24619

dissolved gases (for example $D_{Cl_2} = 12.5 \times 10^{-10}\,m^2\,s^{-1}$ approximately), the correlation of results in terms of dimensionless numbers describes the mass transfer phenomenon irrespective of the electrochemical system [6]. Table 2 shows the composition and Schmidt number of the solutions used. The mass transfer coefficients were obtained by applying the equation

$$k = \frac{I}{AzFc_0} \tag{1}$$

where A is the transfer surface area of the electroactive packing.

The first and second packing elements, from the bottom, were electrically insulated by epoxy-coating and acted as flow distributors. The third pack included three electrically active corrugated sheets (E_1, E_2, E_3) located at different distances from the packing centre. These acted as test electrodes (cathodes) and allowed the measurement of the mass transfer distribution in the pack. The last packing element was used as counterelectrode (anode) without any insulation. The large surface area of the anodic pack ensured that the observed limiting current was due to reaction at the cathode rather than at the anode.

Nitrogen was sparged in the column after humidification in a gas saturator. Superficial gas velocities, determined by the aid of a series of rotameters, were varied from 0.0007 to $0.12\,m\,s^{-1}$. Gas hold-up within the test section was determined by means of the manometric method using open tube manometers as indicated in Fig. 1.

All the experiments were performed at controlled room temperature and with no net liquid circulation.

3. Results and discussion

3.1. *Gas hold-up*

As stated in the literature [5, 7–9] the gas hold-up, that is the volume fraction of gas in the bubble column, plays an important role in the behaviour of electrolytic gas agitated systems and is a fundamental design parameter in such systems.

Initially, experiments were performed sparging nitrogen in water and determining the gas hold-up in the bubble column with the regular packing, testing different gas distributors. Figure 3 shows the effect of superficial gas velocity on the gas hold-up and, as can be seen, for the same gas velocity the gas hold-up does not depend on the gas distributor. Due to the excellent radial mixing, the structured packing acts as an effective flow distributor independently of the gas sparger at the column bottom. Therefore, the mass transfer experiments were performed with only one of the distributors, namely that with six 1 mm holes on a circle, 12.5 mm from the column axis.

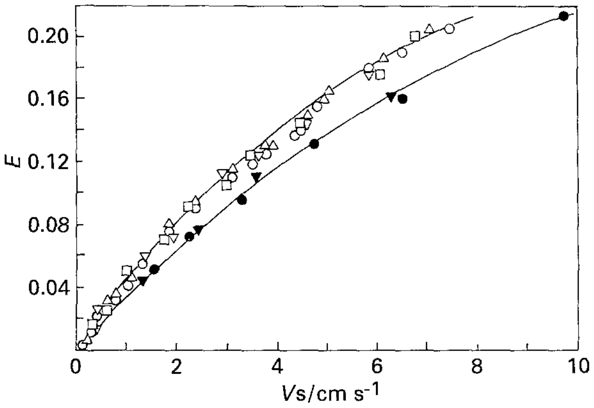

Fig. 3. Influence of gas distributor on gas hold-up in an empty column and in presence of regular packing. Empty column: (▼) D1/2-1, (●) D1-6. Regular packing: (▽) D1/2-1, (○) D1-6, (△) D1/2-6, (□) D1/2-18.

For comparison, results obtained with two of the spargers and without the packing are also shown (more details of the fluid dynamic behaviour of the empty column were given elsewhere [10]). From these results it is also clear that the presence of the packing enhances the gas void fraction in comparison to the empty column values. The same behaviour was found by Potthoff and Bohnet [11, 12], who studied the influence on gas hold-up of static mixers of the same type as the packing elements used in this work. In the intersections of the channels shear forces in the fluid streams produce deformation and subdivision of bubbles into smaller bubbles. The reduced rising velocity and the zigzag path of the gas through the different packs increase the residence time of the gas and, consequently, the gas hold-up.

Figure 4 shows the gas void fractions measured with all the solutions employed in the mass transfer experiments, together with data obtained with water. It can be inferred that the liquid properties have no

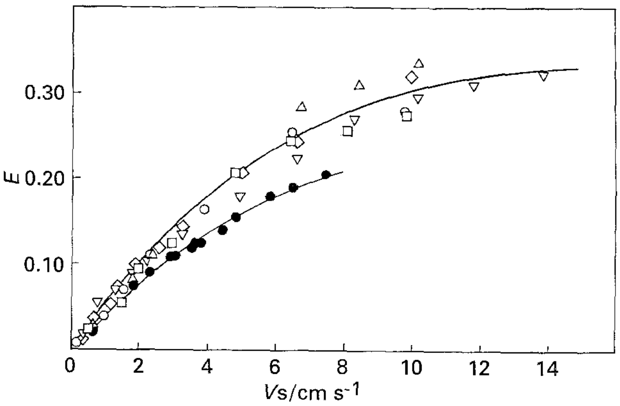

Fig. 4. Gas hold-up in the regular packing for all solutions tested: (□) S1, (△) S2, (○) S3, (▽) S4, (◇) S5; (●) comparison with data for water.

marked influence on the gas hold-up. For electrolytic solutions the values of gas hold-up are slightly higher than those for pure water owing to the presence of very small bubbles which are produced in electrolytes due to their coalescence-hindering properties [13–17].

In the range of the highest superficial velocities, the gas hold-up tends to a constant value, in accordance with the coalescense barrier model of Kreysa and Kuhn [17].

3.2. *Mass transfer*

As mentioned earlier, the effect of position within the packing on mass transfer was determined by measuring the limiting current on three corrugated active sheets in the pack. The electrode E_1 was the outer one, E_2 the third and E_3 the central corrugated sheet. Figure 5 shows the mass transfer coefficients obtained with these three electrodes indicating that there is no significant influence of the position of the electrode. Therefore the experimental values obtained with the three electrodes were averaged to yield mean mass transfer coefficients. These values were considered to describe the mass transfer behaviour of the packing and were used to obtain general correlations.

Figure 6 shows typical mass transfer data (k against V_s) for some solutions. Mass transfer rate increases with gas velocity over nearly the whole range investigated; for superficial velocities greater than 0.08 m s^{-1} a constant value is approached. However, Fig. 5 shows that, for the same experimental range, k increases continuously when the fluid dynamics are characterized by the gas hold-up. This fact agrees with the behaviour found by Cavatorta and Böhm for empty bubble columns [5, 7]. It was shown that the gas velocity affects the liquid to wall mass transfer coefficient and the gas void fraction in the same way. Since for high gas velocities the gas hold-up tends to a constant value (Fig. 4), the same occurs with the mass transfer coefficient.

Several theoretical and semitheoretical models have been proposed in the literature for describing liquid to wall heat or mass transfer, as reviewed elsewhere [7]. Two of these models were selected for interpretation of present data: one considering the motion of the bubble dispersion analogous with turbulent free convection [18] and the other based on the combination of the surface renewal theory with Kolmogoroff's theory of isotropic turbulence [19]. Thus, in order to correlate the mass transfer results with the fluid dynamic variables (gas hold-up or gas velocity) and with the liquid phase properties, two dimensionless functions, derived from the above mentioned models respectively, were employed.

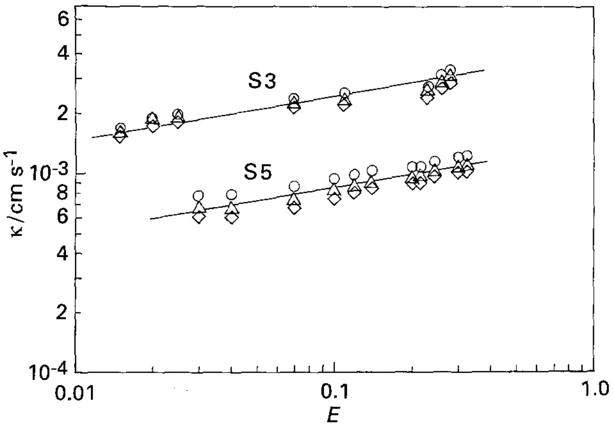

Fig. 5. Mass transfer coefficients as function of gas hold-up; influence of the position in the regular packing. Electrode: (○) E_1, (△) E_2 and (◇) E_3.

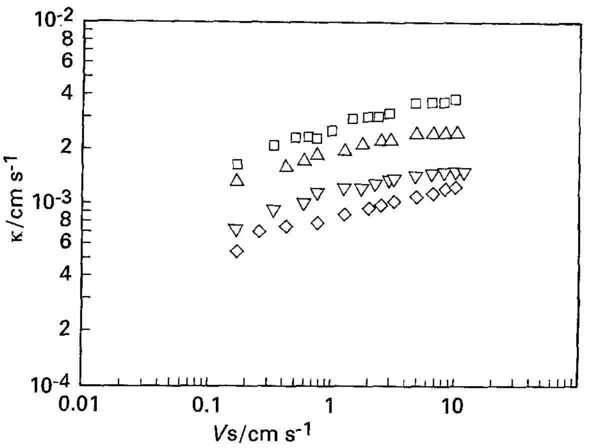

Fig. 6. Mass transfer coefficients as function of superficial gas velocity; effect of solution properties. Solution: (□) S_1, (△) S_2, (▽) S_4 and (◇) S_5.

Based on the first model the Sherwood number was correlated with the Schmidt number, the Galileo number and the gas void fraction to yield:

$$Sh = 0.246(Sc\,Ga)^{1/3}E^{0.19} \tag{2}$$

with a standard deviation of 3.1%.

According to the second theoretical model mentioned, however, the mass transfer coefficient, represented by the Stanton number was correlated with the Schmidt, Froude and Reynolds numbers to yield:

$$St = 0.074(Re\,Fr\,Sc^2)^{-0.28} \tag{3}$$

In this correlation the exponent 2 for the Schmidt number, proposed in investigations on heat transfer to solid surfaces in bubble columns [19, 20], was adopted. However, in mass transfer studies with gas sparged systems, the exponent 2.5 of the Schmidt number gave a better fit of data [5, 7, 9]. Therefore the functional relationship $St = f(Re\,Fr\,Sc^{2.5})$ was also tested, yielding:

$$St = 0.162(Re\,Fr\,Sc^{2.5})^{-0.26} \tag{4}$$

The standard deviations are 4.9% for Equation 3 and 2.3% for Equation 4, respectively. Both equations describe the mass transfer phenomenon with sufficient accuracy for practical purposes.

Figures 7 and 8 show the experimental data together with Equations 2 and 4, respectively. Some curves which fit the results obtained by other authors for electrolytic gas-agitated systems are also given on Figs 7 and 8 for comparison. As can be seen, for the

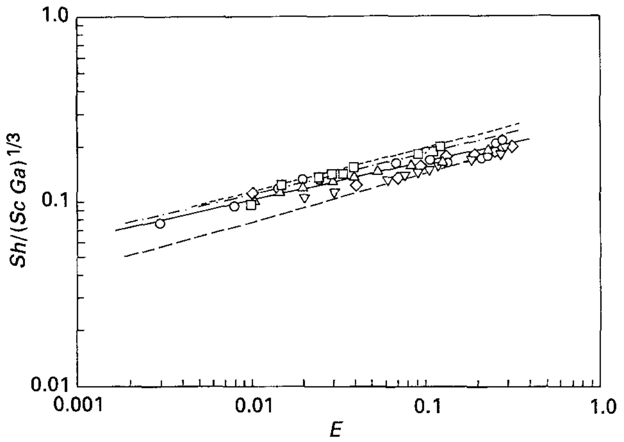

Fig. 7. General mass transfer correlation and comparison with other authors (fluid dynamic parameter: gas hold-up). Solution: (□) S_1, (△) S_2, (○) S_3, (▽) S_4 and (◇) S_5. (——) Regular packing (Equation 2); (- - - -) planar electrode [8]; (—· — · — ·) vertical cylinder [9]; (— — —) bubble column wall [5].

same gas hold-up or ($Re\,Fr\,Sc^{2.5}$), mass transfer rates are generally higher for objects (planar electrode [8], single screen [20] or cylinder [9]) placed on the column axis, while mass transfer coefficients for the wall of a circular [5] or rectangular [21] bubble column are smaller than those obtained with the regular packing. Again, this is due to the correspondence between gas void fraction and mass transfer coefficient. It is well known that in a bubble column without internals local gas hold-up is maximum at the column centre and decreases as the column wall is approached [22–24]. Due to their mixing properties regular packings produce more uniform gas hold-up over the column section. Potthoff [11], who measured gas velocity profiles and analyzed the radial variation of gas hold-up at the exit of a static mixer placed in a bubble column, found flat profiles for both parameters.

For a given overall gas void fraction, the value of the mass transfer coefficient depends on the place of measurement, that is, on the local gas hold-up. In a column with regular packing the gas void fraction over the whole section is greater than that near the wall of an empty bubble column and smaller than that in the centre. Mass transfer coefficients should vary in the same way. The data given in Figs 7 and 8 show the expected trend.

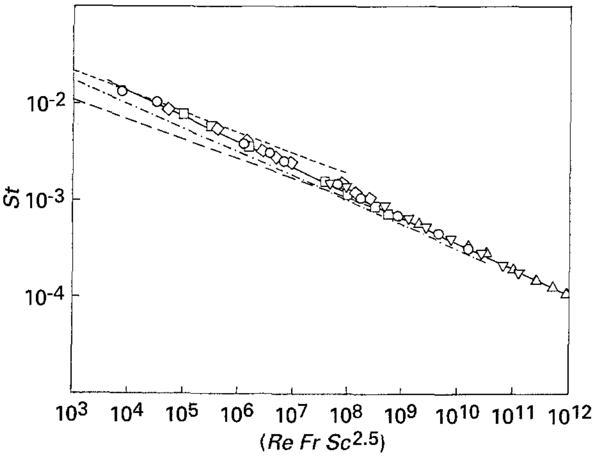

Fig. 8. General mass transfer correlation and comparison with other authors (fluid dynamic parameter: superficial gas velocity). Solution: (□) S_1, (△) S_2, (○) S_3, (▽) S_4 and (◇) S_5. (——) Regular packing (Equation 4); (- - - -) single screen [20]; (—· — · — ·) circular bubble column [7]; (— — —) rectangular bubble column [21].

As mentioned earlier, the mass transfer coefficients obtained in the present investigation do not vary with radial position within the packing element. This fact can also be explained by the existence of uniform gas hold-up over the column section.

4. Conclusion

Regular packings constructed from corrugated sheets of metal can be used as three dimensional electrodes, both in electrolytic cells with gas sparging and in devices for electrochemical absorption of gases. They provide a high surface area per unit volume of equipment and high mass transfer rates to the electrodes. Due to their excellent mixing properties the gas distributor and the position within the packing have no effect on the mass transfer rate.

Mass transfer to these packings can be described by correlations of the type used in other two-phase systems. Equation 2, relating the mass transfer rate to the gas hold-up, and Equations 3 or 4, relating k to the superficial gas velocity, can be used for design purposes.

Comparison with mass transfer results obtained in various electrolytic gas-sparged systems indicates that, under otherwise similar operating conditions, the mass transfer coefficients for regular packings are of the same order of magnitude as those observed with other geometries, being slightly smaller than the coefficients obtained with objects placed on the column axis. Nevertheless, the volumetric mass transfer coefficient which takes into account the effective area per unit volume of equipment, will be higher than the values that can be achieved with planar, cylindrical or wall electrodes.

References

[1] G. Kreysa and J. Külps, *Ger. Chem. Eng.* **6** (1983) 325.
[2] G. Kreysa and C. Woebcken, *Chem. Eng. Sci.* **40** (1985) 1221.
[3] C. Woebcken, Thesis, Universität Dortmund (1985).
[4] K. Jüttner, G. Kreysa, K. Kleifges and R. Rottman, *Chem. Ing. Tech.* **66** (1994) 82.
[5] O. N. Cavatorta and U. Böhm, *J. Appl. Electrochem.* **17** (1987) 340.
[6] J. Selman and C. Tobias, *Adv. Chem. Eng.* **10** (1978) 211.
[7] O. N. Cavatorta and U. Böhm, *Chem. Eng. Res. Dev.* **66** (1988) 265.
[8] S. Piovano, O. N. Cavatorta and U. Böhm, *J. Appl. Electrochem.* **18** (1988) 128.
[9] O. N. Cavatorta, U. Böhm and A. M. Chiappori de del Giorgio, *ibid.* **21** (1991) 40.
[10] O. N. Cavatorta and U. Böhm, *Lat. Am. J. Chem. Eng. Appl. Chem.* **15** (1985) 107.
[11] M. Potthoff, Thesis, Universität Braunschweig (1992).
[12] M. Potthoff and M. Bohnet, *Chem. Ing. Tech.* **65** (1993) 449.
[13] W. J. Braulick, J. R. Fair and B. J. Lerner, *AIChE J.* **11** (1965) 73.
[14] G. Marucci and L. Nicodemo, *Chem. Eng. Sci.* **22** (1967) 1257.
[15] R. R. Lessard and S. A. Zieminski, *Ind. Eng. Chem. Fundam.* **10** (1971) 260.

[16] H. Hikita, S. Asai, K. Tanigawa, K. Segawa and M. Kitao, *Chem. Eng. J.* **20** (1980) 59.

[17] G. Kreysa and M. Kuhn, *J. Appl. Electrochem.* **15** (1985) 517.

[18] L. Sigrist, O. Dossenbach and N. Ibl, *Int. J. Heat Mass Transfer* **8** (1979) 1393.

[19] W. D. Deckwer, *Chem. Eng. Sci.* **35** (1980) 1341.

[20] F. A. Katkout, A. A. Zatout, H. A. Farag and G. H. Sedahmed, *Can. J. Chem. Eng.* **66** (1988) 497.

[21] N. Ibl, R. Kind and E. Adam, *An. Quim.* **71** (1975) 1008.

[22] J. B. Joshi and M. M. Sharma, *Trans. I Chem. E* **57** (1979) 244.

[23] J. B. Joshi, *Trans. I Chem. E* **58** (1980) 155.

[24] T. W. Hilger and H. Hofmann, *Chem. Ing. Tech.* **58** (1986) 228.