ERRORS IN MEASUREMENT OF INTERFACIAL AREA AND MASS TRANSFER COEFFICIENT IN LIQUID IN APPARATUS WITH MOBILE PACKING

Zdeněk PALATÝ
Department of Chemical Engineering,
University of Chemical Technology, 532 10 Pardubice, The Czech Republic

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The paper deals with an analysis of errors of measurement of interfacial area and mass transfer coefficient in liquid in an absorber with mobile packing. The system of CO_2–NaOH has been used for the testing with recirculation of the absorption solution. The error of measurement of the absorption solution temperature, CO_2 concentration in the gas, the composition of absorption solution, the mass transfer coefficient in gas, and the volume of absorption solution at the beginning and at the end of the measurement have been investigated with regard to their effects upon the resulting values of specific interfacial area and mass transfer coefficient in liquid. From the simulation calculations it follows that the interfacial area is most strongly affected by the error of measurement of CO_2 concentration in gas, whereas the mass transfer coefficient in liquid is considerably affected by inaccuracies in measuring the volume of absorption solution at the beginning and at the end of experiment.

In an apparatus in which packing is essential for formation of gas–liquid interfacial area the latter is best measured by chemical methods. They are based on the theory of absorption with chemical reaction, and the interfacial area can be estimated from experimental absorption rate provided the kinetics of the respective reaction is known. A number of systems can be used for the measurements[1,2]. One of the most frequently used systems is that formed by CO_2 (mixed with air) and aqueous solution of NaOH. The chemical methods are time consuming and require simultaneous measurements of a number of primary quantities, out of which some are varying during the experiment – the temperatures of both phases, the concentration of absorbed component in gas, the composition of absorption solution, etc. As each of these values can be loaded with an error of measurement, it is important to know the effects of errors of measurements of primary quantities upon the final result. Such an analysis can identify the critical steps of the whole relatively complex procedure.

THEORETICAL

The absorbers with mobile packing have been constructed for treatment of gases and liquids at high flow rates of both the phases. Under such conditions, the time of contact of the two phases is short, the concentration change of the active component (i.e. NaOH) in the absorption solution after one passage through the apparatus is small, which makes a precise determination of absorption rate difficult. In order to achieve measurable concentration change of NaOH in these absorbers one can adopt the arrangement with recirculation of the absorption solution within a loop[3 - 7].

In ref.[7] a mathematical model was suggested enabling determination of interfacial area and derived with the presumption of negligible resistance to the mass transfer in gas phase and of the fast pseudo-first-order reaction. The nonsimplified model is represented by the following equation

$$V \frac{\mathrm{d}c_B}{\mathrm{d}\tau} - \frac{c_B}{\rho} \left(\dot{V}_S \rho_S + V \frac{\mathrm{d}\rho}{\mathrm{d}\tau}\right) =$$

$$= - \frac{z p_A H_A A}{H_A/k_G + [1/(D_A k_2 c_B + k_L^2)^{1/2}]} \left(1 + \frac{c_B M_A}{z \rho}\right) . \qquad (1)$$

If experimental data are available concerning the time dependence of NaOH concentration in the absorption solution then it is possible to use Eq. (*1*) for the determination of the interfacial area A and the mass transfer coefficient k_L in liquid. The procedure is based on the numerical integration of Eq. (*1*) followed by the optimization procedure.

EXPERIMENTAL

The principal part of experimental apparatus was a laboratory model of absorber with mobile packing, with the inner diameter of 58.5 . 10^{-3} m, with one plate of 65.5% free area. The height of absorption zone defined as the distance between the plate and the mist eliminator was 0.45 m. The mobile packing was formed by polystyrene spheres of 6 . 10^{-3} m diameter and the density of 1 000 kg m^{-3}. The gas phase was formed by a mixture of CO_2 (ca 1.5% v/v) and air. The absorption solution was aqueous NaOH of 0.5 kmol m^{-3} starting concentration, its inital volume being V_0 = 1.75 . 10^{-3} m^3. The solution circulated in a loop including a glass heat exchanger to ensure isothermal conditions. The temperature of measurements was 20 ± 0.5 °C. To avoid foaming, several drops of tricresyl phosphate were added to the absorption solution (final concentration ca 0.01% v/v). The apparatus used is described elsewhere[7].

The flow rates of both gas and liquid referred to the cross section of absorber were kept constant during one measurement, and at regular time intervals samples of the liquid for analysis were taken below the plate. The NaOH and Na_2CO_3 concentrations in the absorption solution were determined titrimetrically according to Winkler[8]. At the same time samples of inlet and outlet gases were taken and the temperatures of all the streams were measured. The content of CO_2 in both gaseous streams was determined by catharometry, the respective analyzer being calibrated before each measurement.

The experimental conditions are given in Table I.

TREATMENT OF RESULTS

When treating the results of measurements we presumed the reaction between CO_2 and NaOH to be of the pseudo first order. Moreover it was presumed that the interfacial area and mass transfer coefficient in liquid are constant within a measurement. The differential equation (*1*) was modified before the calculation proper of A and k_L, the modification concerning the H_A/k_G term. The values of mass transfer coefficient in gas for the conditions considered were taken from ref.[9]. As the present measurements give the $k_G a$ value for a different system (the system SO_2–NaOH was used in ref.[9]), the ratio H_A/k_G must be replaced by Eq. (*2*) with the application of film theory

$$\frac{H_A}{k_G} = \frac{H_A A}{k_G a\ S z_a} \frac{D_{SO_2}}{D_{CO_2}} . \qquad (2)$$

The procedure proper of determination of A and k_L can be summarized in the following steps:

1. The initial guess of interfacial area and mass transfer coefficient (the values used were 0.15 m^2 and $5 \cdot 10^{-4}$ m s^{-1}, respectively).

2. Numerical integration of Eq. (*1*) by the 4th order Runge–Kutta method with the integration step of 50 s, the initial condition $c_B = c_{B0}$ for $\tau = 0$. In this way we obtain the calculated values of concentration of active component in absorption solution at time intervals identical with those of the experimental values. With regard to the fact that the number of experimental values of NaOH concentration obtained from one experiment ($\bar{n} = 11$) was lower than the number of the calculated values with the integration step of 50 s, the time agreement between experimental and calculated values of NaOH concentration was determined by our own PC program. The value of the $d\rho/d\tau$ term was estimated from the second order polynomial approximating the time dependence of the density of absorption solution.

3. The calculation of the objective function defined by Eq. (*3*)

$$F(A, k_L) = \sum_{i=1}^{\bar{n}} q_i \left(c_{Bi,\,exp} - c_{Bi,\,calc}\right)^2 , \qquad (3)$$

where

$$q_i = 1/c^2_{Bi,\,exp} . \qquad (4)$$

4. The realization of one optimization step giving the corrected A and k_L values. The modified simplex method – the algorithm by Nelder and Mead[10] – was used for the optimization.

5. The procedure in steps *2* through *4* was repeated until reaching the minimum of the objective function (*3*).

The values of interfacial area corresponding to the minimum of the objective function (*3*) were recalculated to the specific interfacial area related to the volume of absorption zone in similar way as that given in ref.[7], and they are given in Table I together with the values of mass transfer coefficient.

The procedure given for determination of interfacial area and mass transfer coefficient in liquid presumes the knowledge of volume of absorption solution at a given time as well as the values of evaporation of solvent and further physical quantities such as D_A, k_2, H_A, and ρ. Their determination is described in detail elsewhere[7].

In the course of a measurement, the k_2 values were significantly affected by the chemical reaction taking place and by the evaporation of solvent, whereas the changes in D_A, H_A, and ρ were negligible (see Table II). All the changes mentioned were respected when integrating Eq. (*1*).

Furthermore, for the values found for the mass transfer coefficient in liquid and with application of data of Table III we also verified the presumptions[11] of the pseudo-first-order reaction between CO_2 and NaOH. The calculation showed that this condition is fulfilled both at the beginning and at the end of each measurement.

TABLE I
Measurement conditions

Measurement	u_G, m s^{-1}	u_L . 10^3, m s^{-1}	h_0 . 10^3, m	a, m^{-1}	k_L . 10^4, m s^{-1}
I	1.0	12.50	47	128	1.63
II	3.0	5.36	47	158	3.48

TABLE II
Intervals of values of physical quantities for measurements I and II

Quantity	I	II
D_A . 10^9, m^2 s^{-1}	1.61 – 1.58	1.60 – 1.54
k_2 . 10^{-3}, m^3 kmol^{-1} s^{-1}	8.00 – 5.77	7.33 – 5.34
H_A . 10^7, kmol m^{-3} Pa^{-1}	3.29 – 3.24	3.42 – 3.34
ρ . 10^{-3}, kg m^{-3}	1.016 – 1.022	1.017 – 1.024
μ, mPa s	1.12 – 1.14	1.12 – 1.15
$\dot{V}_S$. 10^8, m^3 s^{-1}	3.16	6.04

SIMULATION CALCULATION

The primary quantities which must be monitored in the measurement of interfacial area and mass transfer coefficient in liquid include the temperature of liquid, the concentration of absorbed component in gas, the concentrations of components of absorption solution, and the volume of absorption solution at the beginning and at the end of measurement. Although the differential equation (*1*) only contains the concentration of active component of absorption solution (i.e. NaOH), one must also know the concentration of reaction product (i.e. Na_2CO_3) because the physical quantities D_A, k_2, H_A, and ρ depend upon the concentrations of both the components. Beside the abovementioned primary quantities, Eq. (*1*) also contains the mass transfer coefficient in gas which is determined by an independent experiment. The estimate of error in a and k_L by means of the total differential is complicated by not only the calculation procedure proper, which is based on the numerical integration and optimization of parameters, but also by the comparatively complex relations used for calculation of the physical quantities D_A, k_2, H_A, ρ, and V_S. It is easier to follow the effect of errors in the primary quantities upon the final result by means of the simulation calculation.

In this procedure, the values of all primary quantities and of the a and k_L values estimated for them are considered to be reference values. Then for a selected relative error of measurement of a single primary quantity (the error with regard to the reference value) we adopt the calculation procedure based on numerical integration of Eq. (*1*) and subsequent optimization to determine the interfacial area and mass transfer coefficient in liquid. Thereafter these values are compared with the reference values of a and k_L, whereby one obtains the response (which is expressed by the relative error in a and k_L, respectively) to the simulated error of measurement of the primary quantity selected. In the two cases analyzed, the relative error in the primary quantities was varied within the limits from −10% to +10% in such a way that this interval might include the errors of measurement encountered in practice.

The results of simulation calculation are presented graphically in Fig. 1 and summarized in Table III.

DISCUSSION

Figure 1 gives the dependence of error of the interfacial area and mass transfer coefficient on the relative error of measurement of Na_2CO_3 concentration in the absorption solution within the limits from −10% to +10%. It can be seen that negative relative errors of measurement of Na_2CO_3 concentration result in lower a values and higher k_L values as compared with the respective reference values. At the relative error equal to −10% the interfacial area is ca 4.3 or 4.9% lower and the values of mass transfer coefficient are ca 5.7 or 9.8% higher in the two cases analyzed. The measurements loaded with an error of +10% give the values of a which are ca 4.0 or 4.6% higher and the k_L

values lower by ca 4.6 or 8.1%. The effect of error of measurement of other primary quantities (i.e. the temperature of absorption solution, CO_2 concentration in gas, NaOH concentration in absorption solution, the mass transfer coefficient in gas, and the volume of absorption solution at the beginning and at the end of experiment) upon the interfacial area and mass transfer coefficient in liquid can be seen in Table III.

TABLE III
Results of simulation calculation[a] for measurements I and II

δ_j[b]	$j = t$		$j = y$		$j = c_B$		$j = k_G$		$j = V_0$		$j = V_1$	
	δ_a	δ_{k_L}	δ_a	δ_{k_L}	δ_a	δ_{k_L}	δ_a	δ_{k_L}	δ_a	δ_{k_L}	δ_a	δ_{k_L}
						Measurement I						
-10.0	3.2	-8.7	11.4	-1.2	-2.3	-15.3	0.3	-1.3	-5.5	23.8	-4.9	-24.8
-5.0	1.6	-4.4	5.4	-0.6	-1.1	-7.6	0.1	-0.6	-2.7	11.8	-2.5	-11.8
5.0	-1.6	4.7	-4.9	0.5	1.1	7.5	-0.1	0.5	2.7	-11.6	2.4	10.6
10.0	-3.1	9.5	-9.3	1.0	2.0	15.0	-0.2	1.0	5.3	-23.3	4.8	20.5
						Measurement II						
-10.0	2.9	-8.2	11.3	-0.3	-1.6	-11.1	0.2	-0.3	-6.1	13.0	-4.3	-12.6
-5.0	1.4	-4.2	5.4	-0.1	-0.8	-5.6	0.1	-0.1	-3.0	6.3	-2.2	-6.1
5.0	-1.5	4.4	-4.8	0.1	0.7	5.6	-0.1	0.1	2.9	-5.9	2.1	5.8
10.0	-2.9	8.8	-9.2	0.2	1.3	11.1	-0.1	0.2	5.8	-11.6	4.1	11.5

[a] δ values in %; [b] j stands for the single primary quantity the relative error of which (δ_j) is pursued on δ_a and δ_{k_L}.

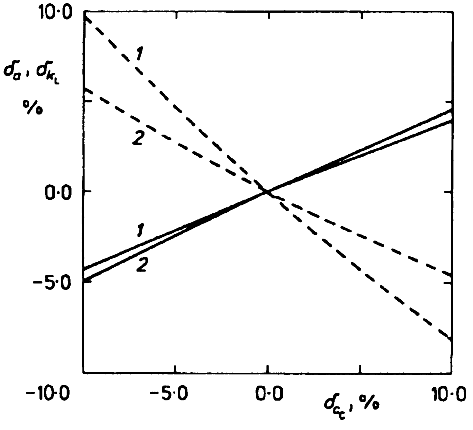

FIG. 1
Dependence of the error δ_a of interfacial area a (solid line) and the error δ_{k_L} of mass transfer coefficient in liquid k_L (dashed line) upon the relative error δ_{c_C} of sodium carbonate concentration c_C: *1* measurement I, *2* measurement II

From the table mentioned it is obvious that the experiments in which the temperature of absorption solution was masured with an error of −10% give the results for the interfacial area higher by ca 2.9 or 3.2% and those for the mass transfer coefficient lower by ca 8.2 or 8.7%. The relative errors of +10% lead to the *a* values lower by ca 2.9 or 3.1% and to the k_L values higher by ca 8.8 or 9.5%.

In the same sense as the error of measurement of temperature of absorption solution affects the interfacial area, the *a* value is also affected by the error of measurement of CO_2 concentration in gas. However, this error in CO_2 concentration has a much more profound effect than that in temperature above. The relative error of −10% results in an 11% increase in the interfacial area. Furthermore it is obvious that incorrectly measured CO_2 concentrations in gas have no significant effect upon the value of the mass transfer coefficient.

In the case of evaluation of the effect of error of measurement of NaOH concentration upon the interfacial area it can be seen that a 10% error in NaOH concentration causes at most 2.3% errors of interfacial area. However, the mass transfer coefficient in liquid is affected by inaccurate determination of NaOH content in absorption solution much more distinctly: the relative error of −10% results in lower k_L values (by 11.1 or 15.3%), whereas the relative error of +10% leads to higher k_L values (by 11.1 or 15.0%).

From the analysis of errors in Table III it follows that an error of measurement of some of the primary quantities significantly affects either the interfacial area or the mass transfer coefficient or both the quantities. An exception is the effect of error of measurement of mass transfer coefficient in gas upon *a* and k_L. In the two cases analyzed only small errors in the *a* and k_L values were found, viz. 0.3% and −1.3%, respectively (for the relative error of −10% in k_G). The low sensitivity of *a* and k_L to the changes in the mass transfer coefficient in gas is caused by the fact that the value of the term H_A/k_G in the denominator of the fraction at the right-hand side of the differential equation (*1*) is much smaller than the value of the other term.

The error of measurement of volume of absorption solution at the beginning and at the end of experiment affects significantly both the interfacial area and mass transfer coefficient in liquid. From Table III it is obvious that an error of 10% in these volume measurements can cause an error of as much as 6% in the resulting *a* value and an error of almost 25% in the resulting k_L value.

CONCLUSION

The interfacial area and mass transfer coefficient in liquid were measured in an absorber with mobile packing using the system CO_2–NaOH. The two quantities were estimated from the experimental time dependence of concentration of active component in absorption solution and from the mathematical model valid for the recirculation arrangement. The effects were followed of the error of measurement of temperature of absorption solution, CO_2 concentration in gas, the concentrations of components of absorption solution, the mass transfer coefficient in gas, and the volume of absorption solution at the beginning and at the end of experiment upon the interfacial area and mass transfer coefficient in liquid. From the analysis of the results of simulation calculations it follows that the interfacial area is most strongly affected by the inaccuracy in determining the concentration of absorbed component in gas, whereas the mass transfer coefficient in liquid is most strongly affected by the error of measurement of volume of absorption solution at the beginning and at the end of experiment. Hence for obtaining correct values for the interfacial area and mass transfer coefficient in liquid one needs a high-precision gas analyzer and precise estimation of volume of absorption solution.

SYMBOLS

A	interfacial area, m^2
a	specific interfacial area, m^{-1}
c	molar concentration, kmol m^{-3}
D	diffusivity, m^2 s^{-1}
H	Henry's law constant, kmol m^{-3} Pa^{-1}
h_0	static bed height, m
k_G	mass transfer coefficient in gas, kmol m^{-2} s^{-1} Pa^{-1}
k_L	mass transfer coefficient in liquid, m s^{-1}
k_2	second-order reaction rate constant, m^3 $kmol^{-1}$ s^{-1}
M	molar mass, kg $kmol^{-1}$
$\bar{n}$	number of experimental NaOH concentration values per one measurement
p	partial pressure, Pa
q	statistical weight, m^6 $kmol^{-2}$
S	cross section of column, m^2
t	temperature, °C
u	velocity, m s^{-1}
V	volume, m^3
$\dot{V}$	volume flow rate, m^3 s^{-1}
z	stoichiometric coefficient of NaOH
z_a	height of absorption zone, m
δ	relative error, %
μ	dynamic viscosity, m Pa s
ρ	density, kg m^{-3}
τ	time, s

Subscripts

A	related to component A (CO_2)
a	related to interfacial area
B	related to component B (NaOH)
C	related to component C (Na_2CO_3)
calc	calculated value
exp	experimental value

G	related to gas
k_G	related to mass transfer coefficient in gas
k_L	related to mass transfer coefficient in liquid
L	related to liquid
S	related to solvent (H_2O)
t	related to temperature
V	related to volume
y	related to CO_2 concentration in gas
0	initial
1	final

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