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On the mechanism and kinetics of the transport processes in system with intensive interphase mass transfer. 4. Effect of the interface concentration

B. Boyadjiev *, Chr. Boyadjiev

Institute of Chemical Engineering, Bulgarian Academy of Sciences, Acad G. Bontchev Str., Bl 103, 1113 Sofia, Bulgaria

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Abstract

A comparative analysis of the non-stationary absorption rate of pure (concentrated) gases in a stagnant liquids has been performed. The results obtained indicate that the rate depends on the equilibrium concentration at the interface. A theoretical relationship has been developed. The relationship confirms the experimental data and explains the differences between the absorption and desorption rates as well. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Absorption (desorption) mechanism; Mass transfer kinetics; Stability; Interface concentration effect

1. Introduction

In the previous papers [1–3], it was demonstrated that the mass transfer rate under a non-stationary absorption of pure (concentrated) gas by a stagnant liquid layer may be determined by the amount of substance Q (kg/m^2) absorbed per time t_0 (s):

$$Q = (1+\varepsilon)c^* \left[2\left(\frac{Dt_0}{\pi}\right)^{1/2} + \gamma\left(\frac{g}{\nu}\right)^{1/2} D^{3/4} t_0^{5/4} \right], \qquad (1)$$

where for low-soluble gases $\varepsilon \ll 1$ and c^* (kg/m^3) is the concentration at the liquid surface. In the case of a desorption process [3] from a saturated solution (a saturated aqueous solution of CO_2 contacting with gas phase containing N_2 for example) the value of $c^* = 0$ and the amount of the desorbed substance is

$$Q = c_0 \left[2\left(\frac{Dt_0}{\pi}\right)^{1/2} + \gamma\left(\frac{g}{\nu}\right)^{1/2} D^{3/4} t_0^{5/4} \right], \qquad (2)$$

where c_0 (kg/m^3) is the initial gas concentration in the solution.

In the relationships for Q the first term depends on the rate of the non-stationary diffusion in the stagnant liquid. The second terms of (1) and (2) occur due the loss of a stability of the process provoked by small perturbations of the concentration of absorbed gas at the liquid surface. These periodic perturbations with small amplitude grows continuously up to the establishing of a new stable state, i.e., self-organizing dissipative structure (process). The characteristic value of $c^*(c_0)$ is used in the relationships (1) and (2) in the case of absorption (desorption) to describe the concentration and its disturbances as well.

2. Analysis of the experimental data

There are a lot of experimental data published [4–6] concerning the non-stationary absorption of low-soluble gases. Some data are summarized in Table 1.

Figs. 1–7 show experimental data (the labels) concerning the system summarized in Table 1. They correlate well (Lines l) with the values of γ_{av} developed by the least squares method.

3. Theoretical analysis

Obviously the values of γ_{av} depend on the interphase concentration c^*. The suitable correlation developed is:

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[*] Corresponding author. Tel.: +359-2-704-154; fax: +359-2-734-936.

E-mail addresses: boby_@techno-link.com (B. Boyadjiev), chboyadj@bas.bg (Chr. Boyadjiev).

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Table 1
Systems considered as examples – basic data

No	Process	System	T (°C)	$D \times 10^9$ (m^2/s)	$\nu \times 10^6$ (m^2/s)	c^* (kg/m^3)	$\gamma \times 10^4$	$\gamma_{av} \times 10^4$
1	Absorption	100% CO_2–H_2O	23	1.88	0.97	1.60	3.70	4.20
2	Absorption	30% CO_2 (70% N_2)–H_2O	23	1.88	0.97	0.471	2.73	2.68
3	Absorption	7.1% CO_2 (92.9% N_2–H_2O	23	1.88	0.97	0.112	1.90	1.20
4	Absorption	100% Ar–H_2O	20	0.47	1.00	0.0599	1.63	1.79
5	Absorption	100% Ar–H_2O	10	0.35	1.30	0.0719	1.70	2.12
6	Absorption	100% Ar–C_2H_5OH	20	0.49	1.52	0.427	2.66	3.29
7	Desorption	(CO_2/H_2O)–N_2	20	1.88	0.97	0	0	−0.303

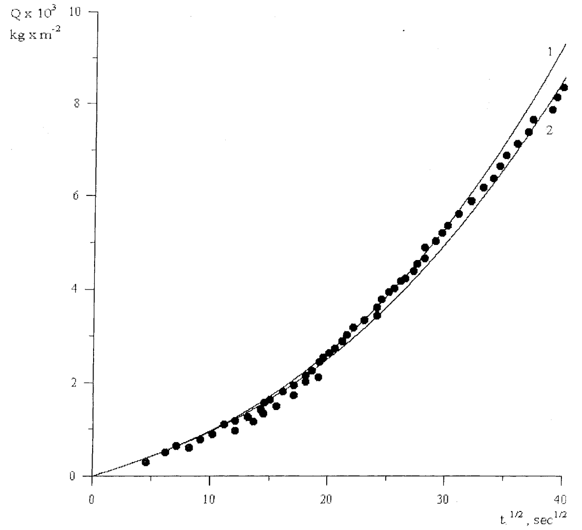

Fig. 1. Comparison of (1) for $\gamma = \gamma_{av}$ (Line 1) and (4) for $\gamma = 3.29 \times 10^{-4}\ c^{*1/4}$ (Line 2) with experimental data (labels) under absorption of 100% CO_2 in water ($c^* = 1.60$ kg/m^3) (see Table 1) at 23°C.

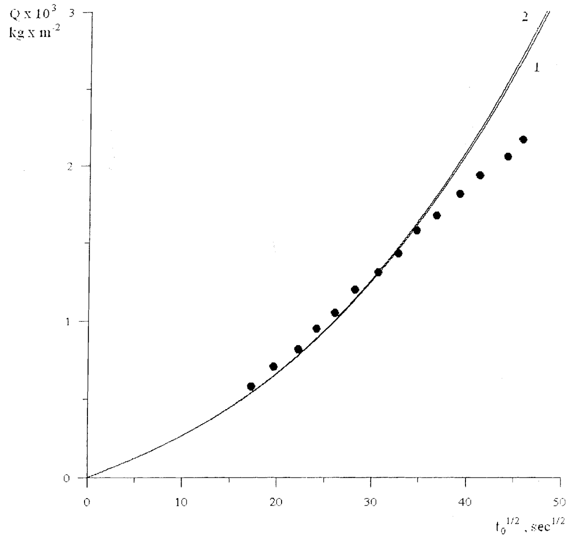

Fig. 2. Comparison of (1) for $\gamma = \gamma_{av}$ (Line 1) and (4) for $\gamma = 3.29 \times 10^{-4}\ c^{*1/4}$ (Line 2) with experimental data (labels) under absorption of 30% CO_2 (70% N_2) in water ($c^* = 0.471$ kg/m^3) (see Table 1) at 23°C.

$$\gamma = 3.29 \times 10^{-4}(c^*)^{1/4}. \qquad (3)$$

The substitution of (3) in (1) and (2) leads to a definitive relationship expressing the amount of the absorbed (desorbed) substance:

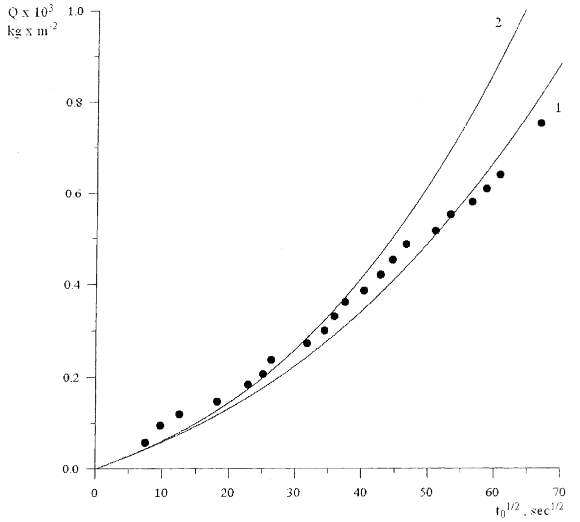

Fig. 3. Comparison of (1) for $\gamma = \gamma_{av}$ (Line 1) and (4) for $\gamma = 3.29 \times 10^{-4}\ c^{*1/4}$ (Line 2) with experimental data (labels) under absorption of 7.1% CO_2 (92.9% N_2) in water ($c^* = 0.112$ kg/m³) (see Table 1) at 23°C.

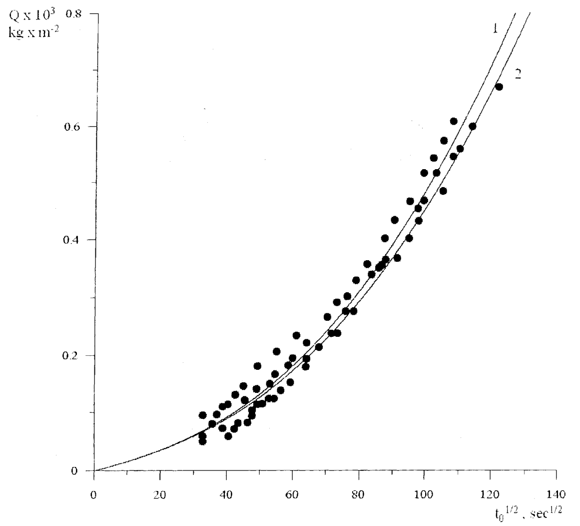

Fig. 4. Comparison of (1) for $\gamma = \gamma_{av}$ (Line 1) and (4) for $\gamma = 3.29 \times 10^{-4}\ c^{*1/4}$ (Line 2) with experimental data (labels) under absorption of 100% Ar in water ($c^* = 0.0599$ kg/m³) (see Table 1) at 20°C.

$$Q = 2c^*\left(\frac{Dt_0}{\pi}\right)^{1/2} + 3.29 \times 10^{-4} c^{*5/4}\left(\frac{g}{\nu}\right)^{1/2} D^{3/4} t_0^{5/4}, \tag{4}$$

$$Q = 2c_0\left(\frac{Dt_0}{\pi}\right)^{1/2}, \tag{5}$$

where under desorption $c^* = 0$.

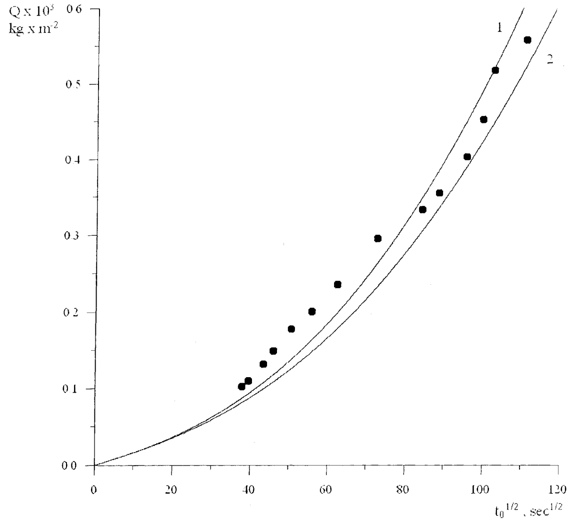

Fig. 5. Comparison of (1) for $\gamma = \gamma_{av}$ (Line 1) and (4) for $\gamma = 3.29 \times 10^{-4}\ c^{*1/4}$ (Line 2) with experimental data (labels) under absorption of 100% Ar in water ($c^* = 0.0719$ kg/m³) (see Table 1) at 10°C.

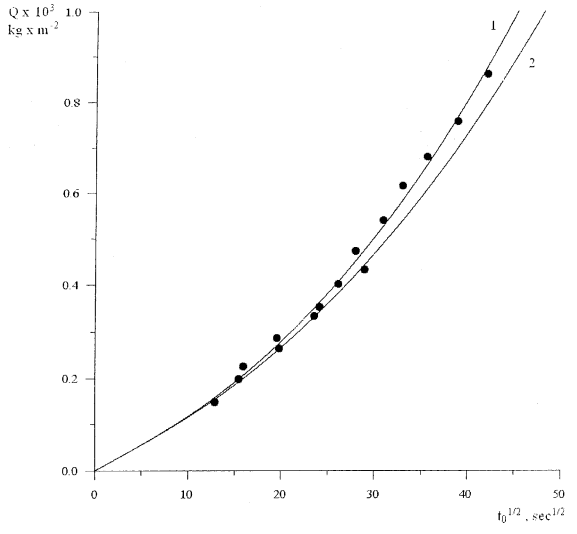

Fig. 6. Comparison of (1) for $\gamma = \gamma_{av}$ (Line 1) and (4) for $\gamma = 3.29\ 10^{-4} \times c^{*1/4}$ (Line 2) with experimental data (labels) under absorption of 100% Ar_2 in C_2H_5O ($c^* = 0.427$ kg/m³) (see Table 1) at 20°C.

Eqs. (4) and (5) are shown in Figs. 1–7 by Lines 2 together with the experimental data.

The results obtained and expressed by (4) cannot be explained by variations of the diffusivity or by the Henry constant. Such variations should lead to changes of D and c^* contributing to the first term of (4). The fact may be explained if different characteristic values of the

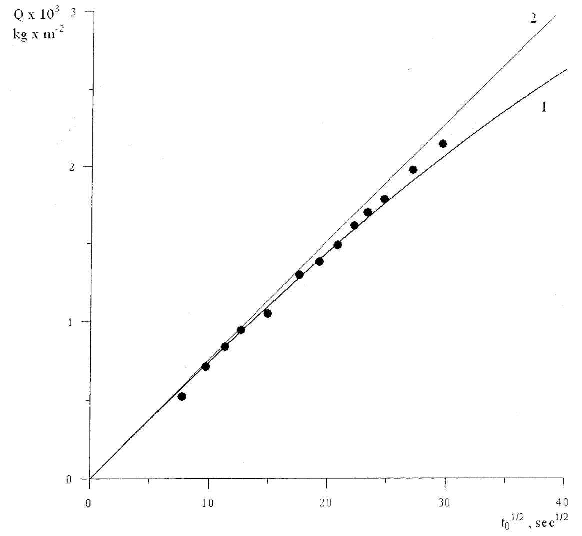

Fig. 7. Comparison of (2) for $\gamma = \gamma_{av}$ (Line 1) and (5) for $\gamma = 0$ (Line 2) with experimental data (labels) under desorption of CO_2 from a saturated water solution ($c^* = 0$) in N_2 (see Table 1) at 20°C.

concentration (c^*) and the disturbances of the concentration (c^*) should be introduced:

$$c_0^* = 3.29 \times 10^{-4} c^{*5/4}. \qquad (6)$$

In this sense c_0^* (kg/m^3) is the maximum concentration that may be reached by the disturbances of the surface concentration under the establishment of a stable periodic regime. The result expressed by (3) explains the differences exhibited by one and the same system under absorption and desorption, respectively. Under a desorption process the process is stable because $c^* = 0$ that leads to $\gamma = 0$, i.e., $c_0^* = 0$ (the disturbances attenuate).

Some differences between (4) and the experimental data (see for example Fig. 3) may be attributed to the low concentration of the gas (c^*) corresponding to the point of loss of stability by a different mechanism. This mechanism may be associated with concentration induced flows near the interface as a result of the insignificant concentration gradient. Under such a condition the occurrence of Benard instability is available [7,8]. Fig. 7 confirms this suggestion, because under desorption processes the Benard instability is impossible from a principle point of view. Moreover, under condition imposed by small times of the constant (t_0) the accuracy of the experimental data is not sufficient.

4. Conclusions

The theoretical analysis of the absorption kinetics complicated with a chemical reaction in the liquid phase done here continues the investigations performed in [1–3,9–11]. The main results show that, the deviations from the linear mass transfer theory cannot be explained by the Marangoni effect. The latter assumption is based on the fact that the thermal effect of the absorption is not sufficient to create a gradient of the liquid surface tension and a consequent loss of stability of the system.

The differences observed may be explained directly by the non-linear mass transfer effects. The large concentration gradients induce secondary flows oriented along the normal with respect the interphase boundary. The result of these secondary flows is the loss of stability of the system with respect to the small disturbances of concentration at the interface. The final result is that the disturbances grow up to the establishment of new stable (self-organizing) dissipative structure with a mass transfer rate significantly greater that predicted by the linear mass transfer theory.

The new intensive mass transfer process is characterized by the parameter (eigenvalue) γ , that depends on concentration at the interface. The reason of that is dissipative structure created as result of the non-linear mass transfer, i.e., the induced flow with a velocity depending on c^*.

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