

# Mass transfer with chemical reaction in conditions of spontaneous interfacial convection in processes of liquid extraction

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Received 11 January 1999; received in revised form 20 November 2000; accepted 20 November 2000

## Abstract

The paper investigates mass transfer with a chemical reaction in conditions of spontaneous interfacial convection (Marangoni effect). It is shown that a chemical reaction changes the ratio of phase resistance, with the result that the balance of forces at the surface is disturbed and interfacial instability is initiated. The effect of the concentration and the surface activity of a transferred reagent on the conditions of initiation of interfacial instability and the intensity of interfacial convection has been investigated. The determining parameters are the ratio of phase resistances, the surface activity and the concentration of a transferred reagent. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Mass transfer; Spontaneous interfacial convection; Marangoni effect; Phase resistance; Surface activity

## 1. Introduction

Spontaneous interfacial convection (SIC) initiated in liquid–liquid systems as a result of the interface hydrodynamic instability and caused by the dependence of the interfacial tension on the concentration of a transferred substance can essentially intensify mass transfer during extraction [1,2]. An increase in the mass transfer rate is achieved at the expense of a more intensive renovation of the interface and, correspondingly, an increase in the mass transfer coefficient.

In conditions of interfacial instability of the phase boundary associated with the interfacial tension (Marangoni effect) a chemical reaction evidently affects above all, the gradients of concentration and temperatures at the surface. They, in their turn, are responsible for the creation of gradients of interfacial tension and density, and thus determine the conditions of initiation of interfacial instability and the intensity of concomitant SIC.

Among the parameters that determine the balance of forces at the surface, the chemical reaction is directly related to the concentration and surface activity of the substances that participate in a joint reaction-mass-exchange process. The change of concentration in the course of a reaction results in the change of surface activity of transported sub-

stances and the driving force of mass transfer, which will also change depending on the reaction rate.

The paper studies the kinetic laws of mass transfer of carboxylic acids accompanied by a fast irreversible chemical reaction in conditions of interfacial instability. The mass transfer of acetic, propionic and butyric acids from an organic phase into a water solution of sodium hydroxide has been investigated for determining the effect of the concentration level of a transported substance and its surface activity on the mass transfer intensity and the conditions of SIC initiation.

## 2. Experiment work

Experiments were carried out in a thermostated Lewis cell with  $d = 0.04$  m and  $h = 0.11$  m. The volume of the contacting phase was  $V = 5 \times 10^{-5}$  m<sup>3</sup>. A thermostat was used to maintain the temperature constant,  $t = 20 \pm 0.1$  °C. The phases were agitated with a two-tier, two-paddle mixer; the paddles were situated at an angle less than 90° to the mixer axis. The agitation was accomplished by a synchronous engine of CA-54 model, reduction 1/1.37, with a mixture rotational speed  $n = 1.3$  rps. The schematic diagram of the set up is given in Fig. 1.

Before the beginning of an experiment the organic and the aqueous phase were mutually saturated for excluding the effect of mass exchange of solvents on the kinetic laws of mass transfer of the main transported substance. The transported

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**Nomenclature**

$C$	concentration (kmol/m <sup>3</sup> )
$d$	cell diameter (m)
$F$	specific interfacial area (m <sup>-1</sup> )
$h$	cell height (m)
$J$	flow of mass (kmol/m <sup>2</sup> s)
$K_D$	mass transfer coefficient in a “diffusion” regime (m/s)
$K_M$	mass transfer coefficient (m/s)
$K_{SIC}$	coefficient of mass transfer intensity (m <sup>4</sup> /kmol s)
$n$	stirring speed (rps)
$s$	coordinate along the surface (m)
$t$	temperature (°C)
$v$	pipette volume (m <sup>3</sup> )
$V$	phase volume (m <sup>3</sup> )

*Greek letters*

$\sigma$	interfacial tension (N/m)
$\tau$	time of contact (s)

substance was dissolved in the diving (organic) phase. The phases were thermostated before the beginning of an experiment for 30 min to exclude the effect of the temperature factor.

Experiments were carried out in the following order. The cell was filled with  $V = 5 \times 10^{-5} \text{ m}^3$  of the lower (heavy) phase, and then carefully, to exclude the formation of waves at the phase boundary (forced agitation during deposition),  $V = 5 \times 10^{-5} \text{ m}^3$  of the upper (light) phase was deposited

on the wall of the cell with the help of a pipette. During sub-coating the order of filling the cell changed. The count of the experiment time began at the moment of deposition. After the end of the deposition (subcoating) an agitating device was switched on. Sampling was performed with the help of a pipette  $v = 1 \times 10^{-7} \text{ m}^3$ ; the sample was collected in a flask and analyzed. During sampling the mixer was brought to a stop. A sample was taken from the middle of the given (organic) phase at certain intervals. The reproducibility of experimental data was evaluated by a triple duplication of experiments. The concentration of the transported substance (carboxylic acids) was established by potentiometric titration.

The concentration of sodium hydroxide was chosen from the condition of the process of a chemical reaction at the phase boundary. The limiting resistance to mass transfer in this case passes to the given (organic) phase [3].

The obtained experimental results are presented in the form of kinetic curves in the following coordinates: concentration of a transported substance ( $C_i$ ) versus time of the process ( $\tau_i$ ).

Next, mass transfer coefficients were found by the method of graphic differentiation of kinetic curves making use of the equation:

$$-\frac{dC_i}{d\tau_i} = K_{Mi} F \Delta C_i \quad (1)$$

where  $K_{Mi}$  is the mass transfer coefficient, (m/s);  $F$  is the specific interfacial area, m<sup>-1</sup>;  $C_i \approx C_i$  is the driving force of the process in mass transfer with a rapid chemical reaction

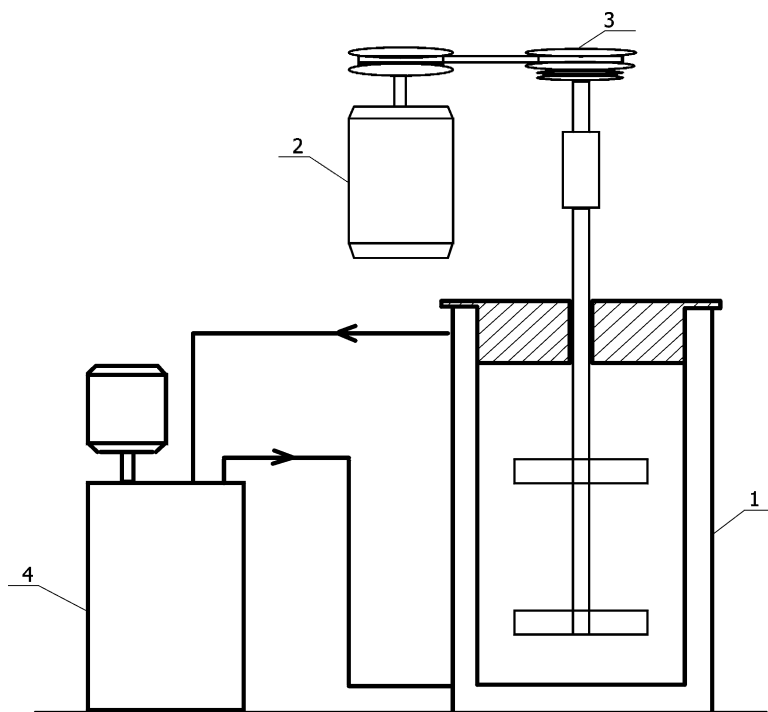


Fig. 1. Scheme of the experimental mounting: (1) Lewis cell; (2) engine; (3) reducer; (4) thermostat.

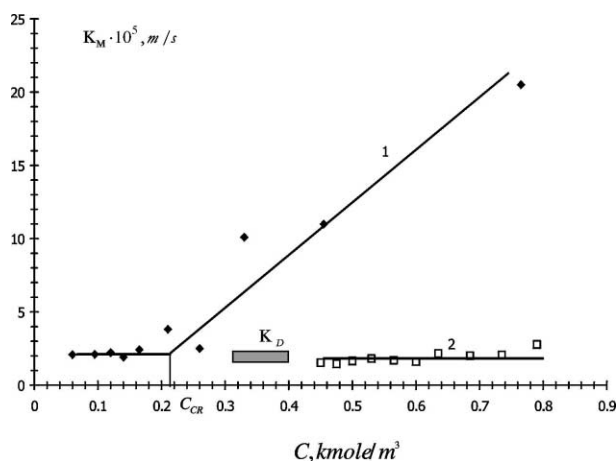


Fig. 2. Detection of interfacial instability. Mass transfer of butyric acid ( $C_0 = 1 \text{ kmol/m}^3$ ) from carbon tetrachloride into the water solution of sodium hydroxide ( $C_0 = 2 \text{ kmol/m}^3$ ): (1) without SAS; (2) with SAS (arcopol, 1.3 g/l).

equal to the concentration of a transported substance in the volume of the given phase,  $\text{kmol/m}^3$  [4].

The obtained data are presented in the form of dependencies of the mass transfer coefficient ( $K_{Mi}$ ) on the driving force of the process ( $c_i$ ).

Interfacial instability was revealed (Fig. 2) in the presence of strong surface-active substances (SAS). It is well known that some strong SAS (arcopol) can suppress interfacial convection, but does not impede the progress of mass transfer in a “diffusion” regime (diffusion–convective mechanism) [5].

### 3. Results

The intensity of interfacial convection and the conditions of SIC initiation were judged by the intensity coefficient ( $K_{SIC}$ ) and the critical concentration ( $C_{CR}$ ) the parameters of an empirical equation describing the process of mass transfer in SIC conditions [6]:

$$J = \begin{cases} [K_D + K_{SIC}(C - C_{CR})] \cdot C, & \text{at } C > C_{CR} \\ K_D \cdot C, & \text{at } C < C_{CR} \end{cases} \quad (2)$$

where  $K_D$  is the mass transfer coefficient in a “diffusion” regime (diffusion–convective mechanism), (m/s);  $K_{SIC}$  is the coefficient taking into account the mass transfer acceleration in an SIC regime,  $\text{m}^4/\text{kmol s}$ ;  $C_{CR}$  is the critical driving force (critical concentration),  $\text{kmol/m}^3$ ; and  $C$  is the concentration of a transported substance in the volume of the given (limiting) phase,  $\text{kmol/m}^3$ .

The conditions of initiation (cessation) of interfacial convection were evaluated by the critical driving force (concentration)  $C_{CR}$  (Figs. 2 and 3) corresponding to the transformation of the “diffusion” regime into the regime of SIC. The intensity of interfacial convection and mass transfer in the SIC regime was evaluated by the coefficient  $K_{SIC}$ .

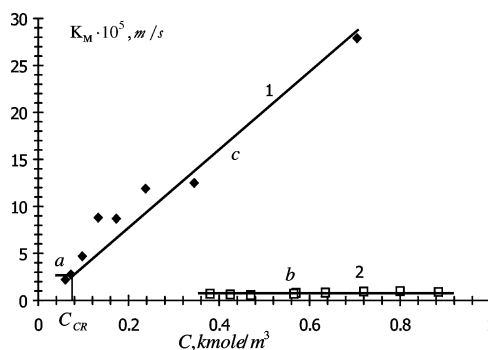


Fig. 3. Mass transfer of butyric acid ( $C_0 = 1 \text{ kmol/m}^3$ ) from dichloroethane: (1) into a water solution of sodium hydroxide ( $C_0 = 2 \text{ kmol/m}^3$ ); (2) into water.

Fig. 3 shows kinetic curves of mass transfer of butyric acid from dichloroethane into water (without a chemical reaction) and, in the same conditions, into an alkali aqueous solution. The mass transfer coefficient in a “diffusion” regime ( $K_D$ ) increases from  $0.8 \times 10^{-5}$  to  $2.3 \times 10^{-5} \text{ m/s}$  (in Fig. 3, curves a and b). Simultaneously, with the increase of mass transfer coefficient in a “diffusion” regime ( $K_D$ ) one can observe an increase of the mass transfer coefficient in an SIC regime (straight line c),  $K_M$  changes from  $2.3 \times 10^{-5}$  to  $28 \times 10^{-5} \text{ m/s}$ . The indicated kinetic relations were explained by the change of the values of concentration gradients at the interface and gradients of interfacial tension connected with them [7].

$$\frac{d\sigma}{ds} = \frac{\partial C}{\partial s} \times \frac{\partial \sigma}{\partial C} \quad (3)$$

where  $d\sigma/ds$  is the gradient of interfacial tension at the surface,  $\partial C/\partial s$  the gradient of concentration of a transported substance at the surface,  $\partial \sigma/\partial C$  the surface activity of a transported substance, and  $s$  the coordinate along the surface.

A change in the balance of surface and dissipative forces results in the initiation of interfacial instability. At a critical concentration of  $C_{CR} = 0.075 \text{ kmol/m}^3$  one can observe a transition from the SIC to the “diffusion” regime (Fig. 3).

An increase in the initial concentration of butyric acid (Fig. 4) leads to considerable changes in the conditions of SIC ( $C_{CR}$ ) initiation and the intensity of mass transfer in the SIC regime. The coefficient of mass transfer intensity  $K_{SIC}$  decreases from  $50 \times 10^{-5}$  to  $2.25 \times 10^{-5} \text{ m}^4/\text{kmol s}$ , the value of the critical driving force increases from 0.25 to  $1.1 \text{ kmol/m}^3$ . The obtained kinetic relations were explained by the decrease in the surface activity of a transported reagent (butyric acid) with increasing initial concentration.

It is common knowledge that in the series of carboxylic acids with increasing number of methylene groups, the surface activity increases. In this connection one would expect that in transportation of acetic, propionic and butyric acid a change in the conditions of SIC initiation and the mass transfer intensity. Mass transfer was studied in identical

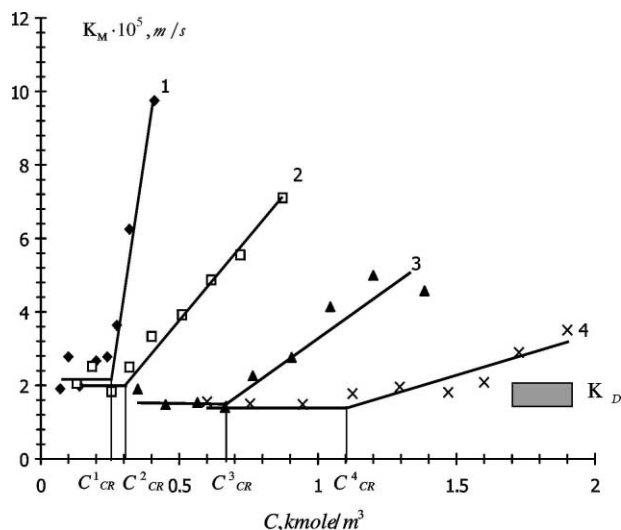


Fig. 4. Effect of the initial concentration of butyric acid in mass transfer from heptane into a water solution of sodium hydroxide ( $C_0 = 2 \text{ kmol/m}^3$ ) on the intensity of mass transfer in the SIC regime and the critical motive force ( $C_{CR}$ ). Experiments were carried out at a mixer rotational speed of  $n = 1.1 \text{ rps}$ . The butyric acid concentrations were: (1)  $C_0 = 0.47 \text{ kmol/m}^3$ ; (2)  $C_0 = 0.966 \text{ kmol/m}^3$ ; (3)  $C_0 = 1.48 \text{ kmol/m}^3$ ; (4)  $C_0 = 2.03 \text{ kmol/m}^3$ .

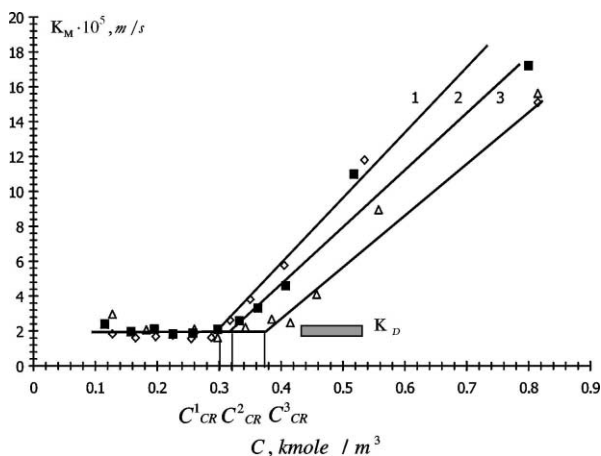


Fig. 5. Effect of surface activity of carboxylic acids on the intensity of mass transfer in the SIC regime. Mass transfer of acetic, propionic and butyric acid from benzene into a water solution of sodium hydroxide ( $C_0 = 2 \text{ kmol/m}^3$ ): (1) butyric acid ( $C_0 = 1.03 \text{ kmol/m}^3$ ); (2) propionic acid ( $C_0 = 1.03 \text{ kmol/m}^3$ ); (3) acetic acid ( $C_0 = 1 \text{ kmol/m}^3$ ).

conditions: the initial concentration of acids was equal to  $C = 1 \text{ kmol/m}^3$ , and the binding reagent was taken in excess of  $C = 2 \text{ kmol/m}^3$ . At these concentrations the reaction proceeds at the phase boundary, the mass transfer rate is limited by the given phase.

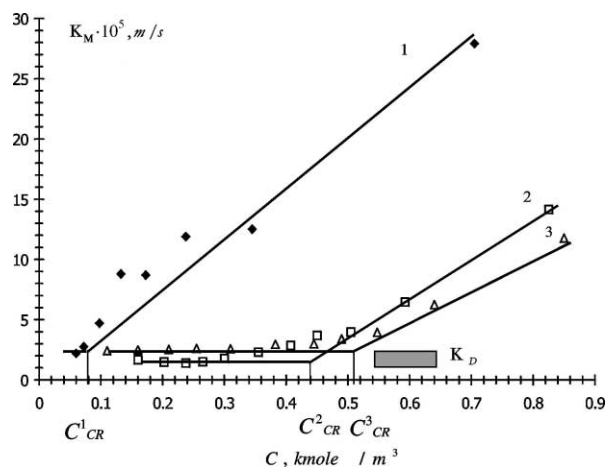


Fig. 6. Effect of surface activity of carboxylic acids on the intensity of mass transfer in the SIC regime. Mass transfer of acetic, propionic and butyric acid from dichloroethane into a water solution of sodium hydroxide ( $C_0 = 2 \text{ kmol/m}^3$ ): (1) butyric acid ( $C_0 = 1.03 \text{ kmol/m}^3$ ); (2) propionic acid ( $C_0 = 1.03 \text{ kmol/m}^3$ ); (3) acetic acid ( $C_0 = 1 \text{ kmol/m}^3$ ).

Figs. 5 and 6 give the results of mass transfer of acetic, propionic and butyric acids from organic solvents like benzene and dichloroethane into aqueous solution of sodium hydroxide.

With increasing surface activity of acids the mass transfer intensity increases from acetic to butyric acid, and the critical concentration decreases.

#### 4. Conclusion

Thus, a chemical reaction by changing the relation of phase resistances results in the change of boundary conditions at the interface and the initiation of interfacial instability. The determining parameters in this case are the ratio of phase resistances, the surface activity and the concentration of the transferring reagent.

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