

Modelling mass transfer coefficient for liquid-liquid extraction with the interface adsorption of hydroxyl ions

Javad Saien[†] and Shabnam Daliri

Department of Applied Chemistry, University of Bu-Ali Sina, Hamedan 65174, Iran

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Abstract—A combined model was used for prediction of overall mass transfer coefficient of drops in the liquid-liquid extraction process, prone to the deleterious effect of adsorbed hydroxyl ions onto the interface. The importance is due to the use of different pH waters as aqueous phase. The work is based on single drop experiments with a chemical system of toluene-acetone-water where the pH of the continuous aqueous phase was within the range 5.5-8, appropriate to most industrial waters, and can lead to rigid behavior of circulating drops. The combined model in conjunction with the correlation developed here for the ratio of interfacial velocity to drop terminal velocity that links the film mass transfer coefficients of both sides can be used satisfactorily for design purposes. This model gives a maximum relative deviation of less than $\pm 10\%$ for the mass transfer directions of dispersed to continuous phase and vice versa.

Key words: Adsorption, Combined Model, Liquid-liquid Extraction, Mass Transfer Coefficient, Hydroxyl Ion

INTRODUCTION

Mass transfer across liquid-liquid interfaces is subject to interference by adsorbed species including surface-active contaminants, electrolytes and ions. Generally, in many industrial processes, at least one of the phases in the liquid-liquid extraction systems is aqueous and in a number of so far recommended chemical systems for liquid-liquid extraction investigations, water has been introduced as the continuous phase [1,2]. It is while the source of water can be different, providing different level of pH. Even if no additional electrolytes were present in the system, the auto-dissociation of water supplies the ionic species [3]. The presence of different ions in liquid-liquid extraction can hardly be circumvented. This influence is investigated for different aspects in a number of publications [3-5].

In several studies, authors have reported that drops of an organic phase, in contact with water, carry an electrical charge which is usually negative [6,7]. It has been presumed that the origin of the negative charge at the organic-water interface is the adsorbed hydroxyl ions from the aqueous phase. With increasing pH, adsorption of hydroxyl ion increases, widening the surface charge layer around the drops [7-10]. The reduction of interfacial tension with pH can be attributed to this problem. Like contaminants, the hydroxyl ion may therefore act in several ways, such as by reducing interfacial tension and so changing any balance of drop formation leading to a change in average drop size and hence mass transfer coefficient by making the interface more structured. The hydroxyl ions can also exert an interfacial barrier layer due to their adsorption, leading to hydrodynamic revolutions in lowering interfacial mobilization [11,12].

For industrial column design circumstances, practical equations are required to incorporate the presence of contaminants or ions in a quantitative manner, at least for the common drop Reynolds num-

ber region of 100 to 600. The results can be used for mass transfer calculations based on discrete ranges of drop size [13,14].

Slater [15] developed a combined model, incorporating the effect of the adsorbed species and employed the parameter of ratio of drop surface interfacial velocity to terminal velocity, into the equation of overall diffusion coefficient as a coefficient for eddy diffusivity. Slater's purpose was to develop a combined model that is capable of including this retarding effect in the overall mass transfer coefficient through only one parameter with the advantage of its ease of application. On the other hand, due to some inconsistencies in the mathematical aspects of the combined model, several alternatives have been proposed for this model which are mainly based on experimental data [13,16-20].

The principal objective of this work is to apply the combined mass transfer model for the prediction of the rate of extraction with drops in aqueous phase where the increase of pH causes a significant reduction in the mass transfer. The model benefits the corrections for continuous and dispersed phase mass transfer coefficients, which includes the deleterious effect of adsorbing ions onto the interface.

THEORETICAL

Here the combined mass transfer model, which is based on the adsorption of compounds onto the interface between drops and the continuous phase, is employed to describe the mass transfer coefficient and its variation with different parameters.

1. Combined Mass Transfer Model

A list of the published correlations for the mass transfer coefficients for the circulating drops has been provided by Sanpui and Khanna [21]. Lochiel and Calderbank [22] developed a model describing the transfer of solutes, around a spherical drop when the Schmidt number is large, i.e., $Sc \gg 1$ (about 930 in this work),

$$Sh_c = \frac{2}{\sqrt{\pi}} \alpha^{0.5} Re^{0.5} Sc^{0.5} \quad (1)$$

[†]To whom correspondence should be addressed.
E-mail: saien@basu.ac.ir

where $\alpha = \bar{V}_i/V_t$ is the ratio of averaged tangential velocity component at the interface to the terminal velocity. A high value of α implies a high interfacial mobilization which favors the rate of mass transfer. The presence of adsorbing species at the interface leads to a reduction in α values. The continuous phase mass transfer coefficient, around the drops, is obtained from Eq. (1) by $k_c = Sh_c D_c/d$; where D_c is molecular diffusivity in the continuous phase.

The adsorption of present bulk surfactant ions onto the interface of a moving drop was considered by Lochiel [23], and a diffusion coefficient was considered for the adsorbed compound. The Gibbs adsorption theorem was applied for the relation between interfacial tension and the bulk concentration, and also the Langmuir adsorption isotherm for the relationship between the surface and bulk concentration of the adsorbing compounds. An equation was developed to calculate α , including a parameter (contamination factor) which is a complicated function of the diffusion coefficient of the adsorbed compound and physical parameters. This parameter should be determined from experimental data.

For mass transfer inside drops, the well-known "Newman equation" is frequently used. The Newman equation is based on the diffusion equation in the spherical drops and in spherical co-ordinates when the continuous phase resistance is absent,

$$k_d = \frac{-d}{6t} \ln \left[\frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp \left(-\frac{4\pi^2 n^2 D t}{d^2} \right) \right] \quad (2)$$

where t is contact time and D is molecular diffusivity inside the drops.

An overall effective diffusivity (D_{oe}) can be used for drop behavior envisaging both molecular and eddy diffusion in a sphere and using it in the Newman equation. The eddy diffusion contribution increases as drop size (and therefore its velocity) increases. Young and Korchinsky [24], Slater [15], Ghalehchian and Slater [13] and Saini and Barani [17] have proposed alternative effective diffusivity models. It has been attempted to describe the effect of adsorbing species in both phases with a single parameter. This has a significant industrial implication, especially when the resistance exists in both phases. In this regard and as the combined model, Slater and his co-workers have used in the combined model the contribution of effective diffusivity based on that used by Handlos and Baron [25]:

$$D_e = \frac{dV_t}{2048(1+\kappa)} \quad (3)$$

where $\kappa = \mu_d/\mu_c$ and the molecular diffusivity in the drops, to give overall effective diffusivity in the form:

$$D_{oe} = D + \alpha D_e \quad (4)$$

The term α , which represents the retardation effect of adsorbing species, is also applied to the drop side mass transfer coefficient, and this effect is linked to both film coefficients.

Whitman two-film theory is used to add the individual mass transfer resistance in continuous and dispersed phases and the overall mass transfer coefficient is calculated:

$$\frac{1}{K_{od}} = \frac{\phi}{k_c} + \frac{1}{k_d} \quad (5)$$

where ϕ is solute equilibrium distribution coefficient.

Because of inconsistency of the equation of α , developed by Lochiel [23], due to giving negative values when applied in accor-

dance to most circulating drops, several works [15,18,19] have attempted to obtain the values of α directly in accordance with experimental data and giving correlation for this parameter to be used in combined model, leading to a mathematical consistency and improving the combined model. Recently, Ashrafizadeh et al. [20] developed an empirical model for the contamination factor in the combined model for different types of adsorbed surfactants.

Here, the empirical equation given by Steiner [26] is used to verify whether drops reach the rigid behavior by the influence of adsorbing hydroxyl ions:

$$Sh_{cr} = 2.43 + 0.775 Re^{0.5} Sc^{0.33} + 0.0103 Re Sc^{0.33} \quad (6)$$

EXPERIMENTAL

The experimental work is as reported in our previous article [12]. The chemical system of toluene-acetone-water, a recommended system for liquid-liquid extraction studies [2], was chosen. The main specification of this system is its high interfacial tension. Toluene and acetone were Merck products with purities of more than 99% and 99.5%, respectively. Distilled water with an initial pH of 5.5 was produced from a special water source and was used. To adjust the pH, a 0.1 M solution of NaOH (supplied by Merck) was used to reach the desired pH in water as continuous phase.

The physical properties of the chemical system, including the range of the continuous phase viscosity and interfacial tension (with respect to variation in pH) at 20 °C (ambient temperature), are given in Table 1. The physical properties were measured with a self-adjustable temperature density-meter (Anton Parr DMA 4500) for measuring density and an Ostwald viscometer for measuring viscosity. Due to the variation of interfacial tension with pH [11], the corresponding values were considered for each solution having the appropriate pH value; meanwhile, the variation in viscosity was negligible since it was decreased only 3% within the ranges used. Organic and aqueous molecular diffusivities were applied from those reported by Baldauf and Knapp [27]. The values of equilibrium distribution of acetone between the phases at 20 °C under different pH values were examined and correlated by:

$$C_d^* = 0.839 C_c \quad (7)$$

where C_d^* and C_c are equilibrium dispersed phase (organic) and continuous phase (aqueous) concentrations of acetone (g/L), respectively ($\phi = 0.839$). As Fig. 1 shows, the change of pH in continuous phase, within the range used, would give no significant influence on the equilibrium distribution. The equilibrium data are in agreement with those reported by Brodkorb et al. [16], which includes

Table 1. Physical properties of chemical system: toluene - acetone - water at 20 °C. Density and molecular diffusivity of continuous phase are at neutral pH 7. Viscosity and interfacial tension ranges are within the range of pH: 5.5-8

Property	Dispersed phase	Continuous phase
ρ [kg/m ³]	866.15	998.15
μ [kg/m·s]	$10^{-3} \times 0.628$	$10^{-3} \times (0.990-1.025)$
D [m ² /s]	$10^{-9} \times 2.55$	$10^{-9} \times 1.09$
γ [mN/m]		29.98-32.79

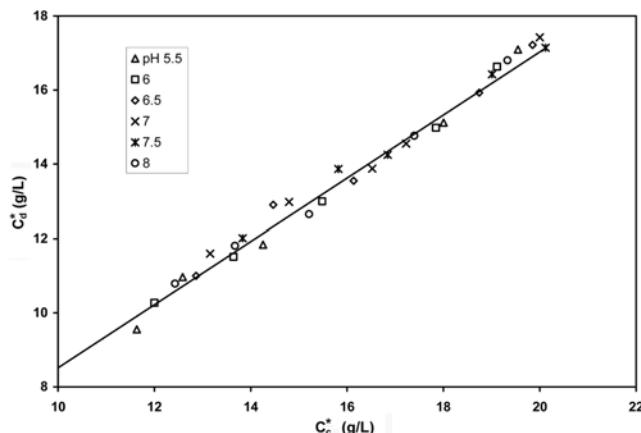


Fig. 1. Equilibrium distribution of acetone between phases under different values of aqueous phase pH at 20 °C.

data in either the presence or absence of phenol.

A Pyrex glass column (11.4 cm diameter and 51 cm height) was used as the contactor. Drop forming was provided, using a variety of glass nozzles located at the bottom of this column. The toluene phase was held in a glass syringe, conducted by an adjustable syringe pump (Phoenix M-CP) and flowed through a rigid tube to the glass nozzle. A small inverted glass funnel attached to a pipette and vacuum bulb was used to catch a sample of about 1 mL of dispersed phase at top of the column with 33 cm distance from initial point. Three samples were prepared for each concentration and were kept in closed sample tubes at a cold medium until GC analysis.

To omit the influence of unsteady mass transfer during the drop formation and its transient velocity, the initial drop concentration was considered for a location of moving drops at 6.5 cm above the tip of nozzles. Drop motion was observed to reach steady movement after about 40 mm travel. To determine the initial concentrations at this location, an empty small column equipped with the same nozzle was used. Drops were collected at the same distance of 6.5 cm and under the same phase conditions and drop sizes of the main column.

Knowing the flow-rate and the number of generated drops, during a particular period, the drop size was easily determined. Toluene drop diameters from 2.57 to 4.21 mm were generated. Table 2 lists the tip diameter of nozzles and the range of generated drop sizes for each direction of mass transfer. The size of each drop, formed at the tip of nozzles, is influenced by increasing in pH, mainly due to the decrease of interfacial tension [11].

The contact time of drops from the initial to the collection point was measured several times with a stopwatch and its average was considered. Terminal velocity of drops was obtained with respect

Table 2. Diameter of tip of nozzles and the range of drop diameters (mm), generated by nozzles at different pH values

Nozzle no.	Tip diameter (mm)	c → d	d → c
1	0.25	2.77-3.32	2.57-3.19
2	0.41	2.89-3.46	2.79-3.40
3	0.59	3.07-3.61	3.03-3.51
4	1.02	3.36-3.94	3.14-3.90
5	1.22	3.45-4.21	3.32-4.02

to the average times. Drops were spaced more than 60 mm apart, typically with a range of flow-rate between 20.54-120.23 mL/h.

Acetone concentration in the collected samples was measured with a GC (Shimadzu, 14B) with FID detector, calibrated with reference substances of toluene and acetone (Merck) for gas chromatography [12,21,28]. The concentration of acetone in the known samples was within the range of 1.5-44.7 g/L with 14 samples in calibration. All the equipment and glass-ware was cleaned with a Decon 90 solution, followed by several rinses with distilled water prior to experiments.

Experiments were conducted in both mass transfer directions of dispersed to continuous phase ($d \rightarrow c$) and vice versa ($c \rightarrow d$). Acetone was dissolved in the aqueous or the organic phase with initial concentrations of 43.3 g/L (5%) and 29.9 g/L (3%), for $d \rightarrow c$ and $c \rightarrow d$ directions, respectively. The pH of the aqueous phase was adjusted at 5.5, 6, 6.5, 7, 7.5 and 8 around its neutral value, the range of most natural and industrial waters. For each series of experimental data, initial and final concentrations, drop size and contact time were obtained. The experimental overall mass transfer coefficient values were calculated by using:

$$K_{od} = -\frac{d}{6t} \ln(1-E) \quad (8)$$

where d is the drop size, t is the contact time and E is the extraction fraction, defined by:

$$E = \frac{C_{df} - C_{di}}{C_d^* - C_{di}} \quad (9)$$

where C_{di} , C_{df} and C_d^* are the initial, final and equilibrium solute concentrations in drop phase, respectively. For $d \rightarrow c$ direction, C_d^* is zero, since the solute concentration in aqueous phase is zero for this case and introducing the drops through the column, even for a series of experiments with a nozzle under a specified pH, would not give a considerable solute concentration in the continuous phase. Meanwhile, the continuous phase was agitated very often with a stainless steel rod while the syringe pump was off.

RESULTS AND DISCUSSION

Fig. 2 shows the variation of overall mass transfer, obtained from

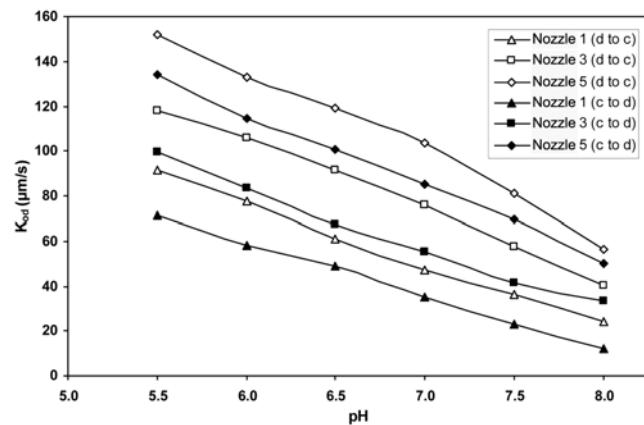


Fig. 2. Variation of overall mass transfer coefficient with pH for a number of nozzles in both directions.

Eqs. (8) and (9), with pH of aqueous phase. The overall mass transfer finds a significant reduction within 62.7-82.7% for the drops generated from a nozzle, as the pH increases. As was mentioned in the introduction, the reason can be attributed to the interfacial barrier layer due to the adsorption of hydroxyl ions and to the hydrodynamic revolutions in lowering interfacial mobilization, which in turn causes changes in the internal circulation of drops [6,8]. Of course, a part of the amount of reduction in K_{od} presented in Fig. 2 is due to the drop size reduction of about 17% on average, when pH increases within the applied range. The acidic pH in the aqueous phase provides a significantly higher rate of mass transfer for a specified drop size.

When the hydroxyl ions are adsorbed directly from the aqueous phase, the number of ions per unit area will depend on the hydroxyl ion concentration in the bulk of the aqueous phase, i.e., on the pH of this phase. As the pH increases, the surface becomes saturated with hydroxyl ions, and it would be expected that the thickness of the adsorbed layer is maintained almost constant. A relatively constant mass transfer coefficient could be expected under these conditions; however, it is not the case for the experiments in this work, since the aqueous phase pH was adjusted just around the neutral water pH.

To assess the role of hydroxyl ions as the main influencing parameter, the KOH reagent was used instead of NaOH to adjust the pH. No significant change of the overall mass transfer coefficient, within the range of used pH, was observed unless a minor shift to lower value (about 7.4% and 7.1% reduction in K_{od} at pH limit values of 5.5 and 8, respectively).

Fig. 3 shows that the mass transfer coefficient increases with drop size. Drops tend to higher internal circulating as the size increases, leading to enhancement in mass transfer. Meanwhile, large drops move faster with lower contact times. Fig. 4 shows the variation of maximum percentage of K_{od} reduction compared with the lowest pH of 5.5, for the five used nozzles. The important revealed observation is that small drops are more prone to this retarding effect. The higher contact times for small drops, which in turn provide higher adsorption of hydroxyl ions, can be a reason for this effect.

The range of drops used in this work is within the conditions of circulating drops, since the values of dimensionless group H defined in the model by Grace et al. [29] are in the range of 13.9-35.5 ($2 < H < 59.3$), corresponding to circulating drops:

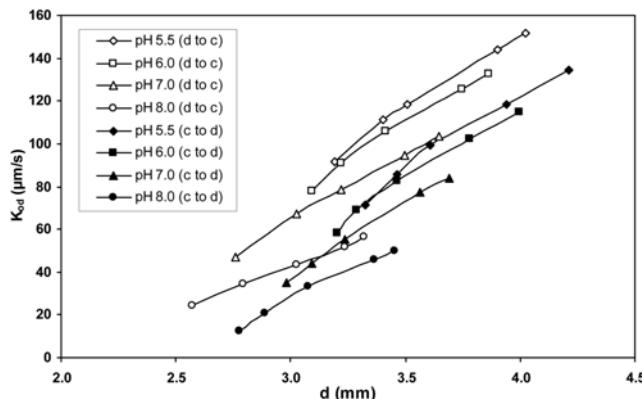


Fig. 3. Variation of overall mass transfer coefficient with drop size at different pH values in both directions.

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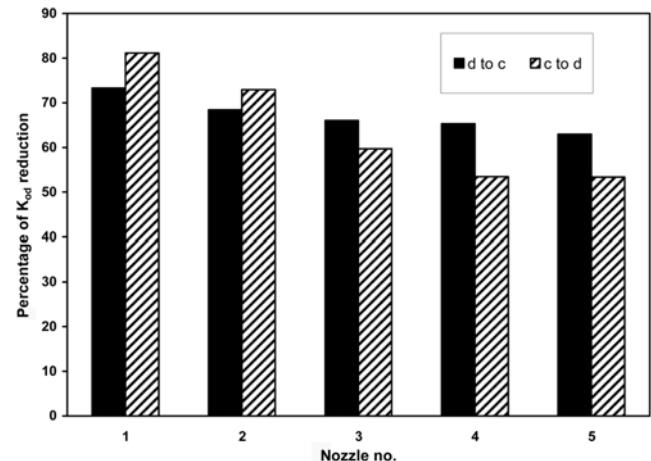


Fig. 4. Maximum percentage of K_{od} reduction due to pH, for drops of different nozzles in both directions.

$$H = \frac{4}{3} EöM^{-0.149} \left(\frac{\mu_c}{\mu_w} \right)^{-0.14} \quad (10)$$

where $Eö = gd^2 \Delta \rho / \gamma$ is the Eötvös number, $M = g \mu_c^4 \Delta \rho / \rho_c^2 \gamma^3$ is the Morton number, μ_c is the continuous phase viscosity, μ_w is the viscosity of water at 4 °C and γ is the interfacial tension. The value of 59.3 for H corresponds, approximately, to the transition between non-oscillating and oscillating drops. The range of drops Weber number is also within 0.4-2 (less than 3.58) and the range of ratio $Re / N_{PG}^{0.15}$ (N_{PG} is inverse of Morton number) is 4.93-14.28, i.e., less than 20 [30].

The mass transfer model, described in the theoretical section (Eqs. (1)-(5), (7)), was applied in accordance with the experimental conditions (obtained values of t , d , C_{di} , C_{df} with the appropriate physical properties). The appropriate α values were first obtained by adjusting its value with the iteration method, until the measured and the calculated overall mass transfer coefficients agreed while all other variables remaining fixed. The accuracy was set at a tolerance of $\pm 0.1 \mu\text{m/s}$ to give solutions correct to five/six decimal places. Higher α values are expected for higher K_{od} values (low pH and/or large drops).

The obtained values of α are within 0.134-0.933, for $d \rightarrow c$ and 0.089-0.856, for $c \rightarrow d$ directions. For one experiment in $d \rightarrow c$ direction and three experiments in $c \rightarrow d$ direction, small drops find reasonably rigid behavior (Table 3), i.e., Sh_c in combined model becomes lower than Sh_{cR} (Eq. (6)). Since the mass transfer coefficient is lower in the $c \rightarrow d$ direction, the number of estimated rigid drops is greater in this direction. On the other hand, for two experiments (large drops produced from nozzles 4 and 5) with the mass transfer direction of $d \rightarrow c$, the values of α exceed 1 (1.02 and 1.11). Therefore, the com-

Table 3. Drops with rigid behavior at the appropriate pH

Nozzle no.	d \rightarrow c		c \rightarrow d	
	d (mm)	pH	d (mm)	pH
1	2.57	8	2.87	7.5
1			2.77	8
2			2.89	8

combined model with the appropriate drop and continuous phase mass transfer coefficients predicts a lower overall mass transfer coefficient for them and α should be higher. Other parts of the model may have influence in this matter. For example Beitel and Heideger [31] have shown that the drop mass transfer coefficient can exceed that predicted by the Handlos and Baron equation even with surfactant present. For $c \rightarrow d$ direction, the values of α never reach 1 and the model

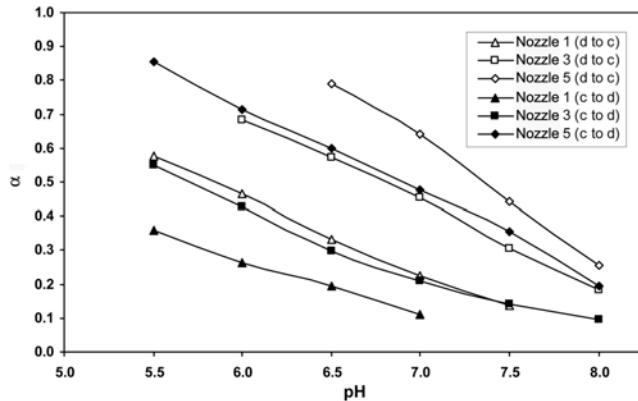


Fig. 5. Variation of α with pH for different nozzles in both directions.

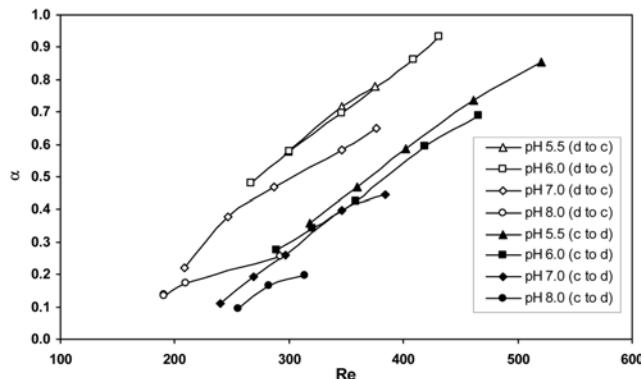


Fig. 6. Variation of α with drop Reynolds number at different pH values in both directions.

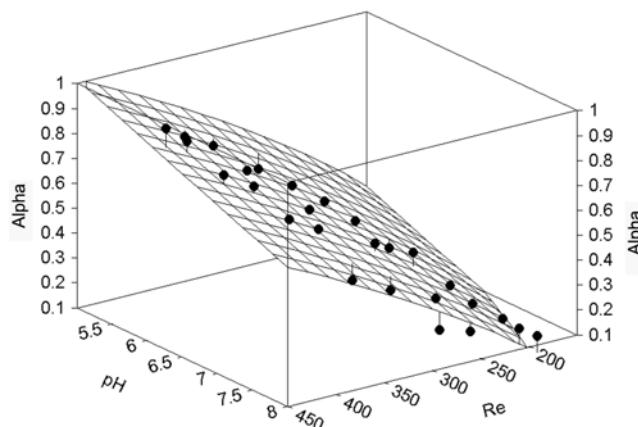


Fig. 7. The agreement of developed Eq. (11) (meshed lines) with experimental data for $d \rightarrow c$ direction.

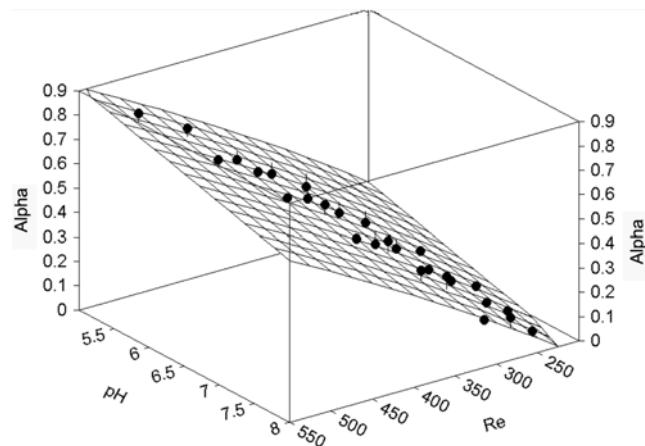


Fig. 8. The agreement of developed Eq. (11) (meshed lines) with experimental data for $c \rightarrow d$ direction.

Table 4. Parameters of Eq. (11)

Mass transfer direction	a_1	a_2	n_1	a_3	n_2	R^2
$d \rightarrow c$	7.05×10^{-4}	0.081	0.499	-0.162	0.894	0.97
$c \rightarrow d$	3.77×10^{-6}	0.140	0.729	-0.115	0.885	0.97

predicts higher values of overall mass transfer coefficient.

Figs. 5 and 6 show typically the variation of the parameter α , versus pH and Reynolds number. Dependence on drop size implies dependence on contact time, during which the surface adsorption of the hydroxyl ions is continued.

From variations presented in Figs. 7 and 8, it is obvious that the changes of α , under the conditions studied, are attributed by a nearly linear influence of pH and non-linear influence of drop Reynolds number. As a simplified correlation, applicable in the combined model, the data are nicely reproduced here with the correlation:

$$\alpha = a_1 + a_2 Re^{n_1} + a_3 pH^{n_2} \quad (11)$$

where a_1 , a_2 , a_3 , n_1 and n_2 are the parameters of the equation which were calculated in agreement with obtained α data. The values of these parameters, along with the regression coefficients, are listed in Table 4. The maximum relative deviation is $\pm 16.5\%$ for mass transfer direction of $d \rightarrow c$ and $\pm 19\%$ for $c \rightarrow d$. Figs. 7 and 8 show the goodness of fit in agreement with Eq. (11). This equation, which links the film mass transfer coefficients of both sides, is applicable for the circulating drops when moving in aqueous medium, containing the hydroxyl ions.

Applying the combined model, in conjunction with Eq. (11), provides K_{od} values with a maximum relative deviation of $\pm 9\%$ for mass transfer direction of $d \rightarrow c$ and $\pm 10\%$ for $c \rightarrow d$. This deviation is thought to be sufficient, considering an experimental error of approximately $\pm 5\%$ in K_{od} values. The combined model in its new form can therefore be used satisfactorily to predict the overall mass transfer coefficient.

CONCLUSIONS

The results show a significant reduction in the overall mass trans-

fer coefficient as the concentration of hydroxyl ions increases. The retarding effect of adsorbing ions can result in changing the circulating behavior until leading to the rigid behavior, according to the criterion given by Steiner [26,28] and within the important pH range of 5.5-8. This problem is more serious in the mass transfer direction of continuous to dispersed phase.

The combined mass transfer model, which incorporates the influence of adsorbing species onto the interface for mass transfer in both phases, and with the advantage of using one consistent parameter as the criterion of retarding adsorbed compounds, is satisfactory to describe the variation of the overall mass transfer coefficient. An empirical equation is required and was developed for the ratio of interfacial velocity to drop terminal velocity that is used to link the film mass transfer coefficients of both sides. The influence of physical properties, drop size and pH for the both mass transfer directions has to be taken into account in this equation.

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NOMENCLATURE

a_1, a_2, a_3 : constant and coefficients in Eq. (11)

C : solute concentration [g/L]

d : drop diameter [mm]

D : diffusivity [m^2/s]

E : extraction fraction defined by Eq. (9)

$E\ddot{o}$: Eötvös number, $E\ddot{o}=gd^2\Delta\rho/\gamma$

H : a dimensionless group defined in the Grace et al. [29] model.

k : phase mass transfer coefficient [$\mu\text{m}/\text{s}$]

K : overall mass transfer coefficient [$\mu\text{m}/\text{s}$]

n_1, n_2 : exponents in Eq. (11)

M : Morton number, $M=g\mu_c^4\Delta\rho/\rho_c^2\gamma^3$

N_{PG} : inverse of Morton number, $N_{PG}=\rho_c^2\gamma^3/g\mu_c^4\Delta\rho$

Re : drop Reynolds number, $Re=\rho_c V_d/\mu_c$

Sc : Schmidt number for continuous phase, $Sc=\mu_c/\rho_c D_c$

Sh_c : Sherwood number for continuous phase, $Sh_c=k_c d/D_c$

t : contact time [s]

\bar{V}_t : average tangential interfacial velocity [m/s]

V_t : terminal velocity of a drop [m/s]

We : drop Weber number, $We=\rho_c V_t^2 d/\gamma$

Greek Letters

α : ratio of drop surface interfacial velocity to terminal velocity

γ : interfacial tension [mN/m]

κ : viscosity ratio, $\kappa=\mu_d/\mu_c$

μ : viscosity [$\text{kg}/\text{m}\cdot\text{s}$]

ϕ : solute equilibrium distribution coefficient

ρ : density [kg/m^3]

Subscripts

c : continuous phase

d : dispersed phase

e : effective value

f : final value
 i : initial value
 o : overall value
 R : rigid condition

Superscript

$*$: equilibrium

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