

**MASS TRANSFER IN THE SYSTEM
WITH INSTANTANEOUS CHEMICAL REACTION
AND INTERFACIAL TURBULENCE
EXTRACTION OF ACETIC ACID FROM ISOBUTANOL
INTO AQUEOUS SOLUTION OF SODIUM HYDROXIDE**

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Extraction of acetic acid from isobutanol into aqueous solution of sodium hydroxide in the system with flat interface was studied. The effect of interfacial turbulence, induced by chemical reaction on the mass transfer rate of reacting components across the interface was determined independently from measurements of mass transfer rate of non-reacting solvents. The concept of enhancement factor was used for description of the phenomenon. The effect of interfacial turbulence on mass transfer rate was expressed by the additive term to the rate of energy dissipation on the interface.

Number of industrially important processes include extraction accompanied by a fast chemical reaction of the extracted compound. As an example it is possible to quote extraction of fatty acids accompanied by their reaction with hydroxides of alkaline metals. Attempts to describe the process in terms of the film or penetration theory for mass transfer and the idea of an instantaneous chemical reaction were not satisfactory. Discrepances between the theory and experimental data are explained by the changes in the hydrodynamic conditions on the interface due to interfacial turbulence which is induced by the chemical reaction.

Searle and Gordon¹ and Sherwood and Wei² have measured the mass transfer rate of fatty acids from organic solvents into aqueous solutions of bases. Sherwood and Wei photographed the vicinity of the interfacial area in these systems and found out that the reaction was accompanied by a spontaneous motion of the interface. Deviations of measured values of mass transfer coefficients from theoretical values calculated on the basis of the film or penetration theory have been about 100%. A theoretical description of extraction accompanied by both instantaneous chemical reaction and interfacial turbulence was proposed in the study³ in terms of the enhancement factor. The effect of interfacial turbulence on the mass transfer rate of reacting components was included only into the mass transfer coefficients of reacting components. This simplification enabled computation of enhancement factor from the relations formally identical with the film model. In this paper the proposed method was used for description of extraction of acetic acid from isobutanol by the aqueous solution of sodium hydroxide. This reaction has also been studied by the quoted authors^{1,2} and it is known to be accompanied by the interfacial turbulence.

The effect of the interfacial turbulence on the mass transfer rate of reacting components was determined independently from measurements of the mass transfer rate of solvents across the interface in the presence of chemical reaction and without any chemical reaction.

THEORETICAL

Calculation of the mass transfer coefficient was based on its dependence on the rate of energy dissipation at the interface in analogy to Bulička and Procházka⁴ and Hančil and coworkers⁵

$$k'_{ij} \sim D_{ij}^{0.5} (\epsilon'_j / \nu_j)^{0.25} . \quad (1)$$

The expression for the interfacial turbulence effect on the mass transfer coefficient has been derived on the basis of the following two assumptions. According to the first one, the total rate of energy dissipation in the diffusion layer at the interface is increased by the additive increment due to interfacial turbulence

$$\epsilon'_j = \epsilon_j + \epsilon_j^\sigma . \quad (2)$$

Moreover, it was necessary to make an assumption on distribution of the rate of energy dissipation ϵ^σ in the two phases. It was assumed that the ratio of the rates of energy dissipation caused by interfacial turbulence was equal to the ratio of the rates of energy dissipation in the hypothetical system with the zero interfacial turbulence

$$\epsilon_1^\sigma / \epsilon_2^\sigma = \epsilon_1 / \epsilon_2 . \quad (3)$$

By substitution of Eq. (2) into Eq. (1) the relation is obtained for the mass transfer coefficient in the form

$$k'_{ij} \sim D_{ij}^{0.5} (\epsilon_j / \nu_j)^{0.25} (1 + \epsilon_j^\sigma / \epsilon_j)^{0.25} . \quad (4)$$

For the rate of energy dissipation it is possible to substitute into Eq. (4) the corresponding mass transfer coefficients so that the relation is obtained

$$k'_{ij} = k_{ij} [1 + (k_{ij}^\sigma / k_{ij})^4]^{0.25} , \quad (5)$$

where the mass transfer coefficient k_{ij} is related to the mass transfer in the system with zero interfacial turbulence

$$k_{ij} \sim D_{ij}^{0.5} (\epsilon_j / \nu_j)^{0.25} \quad (6)$$

and the coefficient k_{ij}^σ is related to the rate of mass transfer due to interfacial turbulence

$$k_{ij}^\sigma \sim D_{ij}^{0.5} (\epsilon_j^\sigma / \nu_j)^{0.25} . \quad (7)$$

A combination of relations (3) and (7) yields the relation

$$k_{i1}^\sigma / k_{i1} = k_{i2}^\sigma / k_{i2} . \quad (8)$$

Mass transfer coefficients defined in this way can be used for description of extraction accompanied by the instantaneous chemical reaction of the extracted component and by the origin of interfacial turbulence. Let us assume that the component A is dissolved in the phase 1 and is transferred into the phase 2 where it reacts instantaneously and irreversibly with the component B. The reaction is accompanied by interfacial turbulence.

The mass flux of component A can be formalized by use of the enhancement factor by the relation

$$j_A = \Phi_{A2} k'_{A2} c_{A2}^* = k'_{A1} (c_{A1} - c_{A1}^* m_A) . \quad (9)$$

For calculation of the enhancement factor the approximate relation can be used

$$\Phi_{A2} = [1 + k'_{B2} c_{B2} / (k'_{A2} c_{A2}^*)] \cdot \chi . \quad (10)$$

The correction factor χ corrects the enhancement factor derived from the film model to a more realistic conception of the successive decay of turbulence at the interface. As it has been demonstrated in the study³ the correction factor is given by the ratio of diffusivities D_{B2}/D_{A2} and by the magnitude of the enhancement factor. Interfacial turbulence has practically no effect on the magnitude of the factor χ .

By a combination of relations (5) – (10), the mass flux of component A is obtained in the form

$$j_A = \Phi_{A2} k_{A2} [1 + (k_{A2}^\sigma / k_{A2})^4]^{0.25} c_{A2}^* = k_{A1} [1 + (k_{A2}^\sigma / k_{A2})^4]^{0.25} (c_{A1} - c_{A2}^* m_A) \quad (11)$$

and the enhancement factor takes the form

$$\Phi_{A2} = [1 + (D_{B2}^{0.5} c_{B2}) / (D_{A2}^{0.5} c_{A2}^*)] \cdot \chi \quad (12)$$

For computation of the mass flux of component A it is thus necessary to know, beside diffusivities and mass transfer coefficients without interfacial turbulence, a single parameter k_{B2}^σ .

By combination of Eqs (3), (6) and (7) the relation is obtained

$$k_{A2}^{\sigma}/k_{A2} = k_{12}^{\sigma}/k_{12} = k_{W1}^{\sigma}/k_{W1} \quad (13)$$

Relation (13) enables to use the measurement of mass transfer rate of the solvents as an independent indicator of the effect of interfacial turbulence on the magnitude of the mass transfer coefficient of the reacting component.

The mass transfer rate of non-reacting solvents can be described by relations

$$j_1 = k_{12}'(c_{12}^* - c_{12}) = k_{12}[1 + (k_{12}^{\sigma}/k_{12})^4]^{0.25} \cdot (c_{12}^* - c_{12}) \quad (14)$$

and

$$j_W = k_{W1}(c_{W1}^* - c_{W1}) = k_{W2}[1 + (k_{12}^{\sigma}/k_{12})^4]^{0.25} \cdot (c_{W1}^* - c_{W1}) \quad (15)$$

EXPERIMENTAL

The extraction of acetic acid from isobutanol into aqueous solution of sodium hydroxide was selected as the model system. The chemicals used for experiments were of *p.a.* grade. Isobutanol was redistilled. Distilled water was used. Concentration of acetic acid and of sodium hydroxide were determined by titration, concentration of isobutanol in the aqueous phase was determined chromatographically, concentration of water in the organic phase spectrophotometrically. Equilibrium mixtures were prepared in glass ampoules equipped by thermostated jacket and situated in the shaker. The experimental apparatus was a cell with a flat interface and vibrational mixing of both phases. The construction of the cell was described in the study³. The equipment was run continuously. The concentrations of isobutanol and water were determined in addition to the concentrations of reacting components in both the inlet and outlet streams. Before the experiment the inlet streams of the organic and aqueous phases were mutually partially pre-saturated with the aim to prevent the convective interphase flux which could origin due to the different mutual solubility of the solvents. The measurement was performed at 298 K, mean residence times 420 s and 1020 s, in the range of concentrations c_{B2} (0–0.75 kmol/m²), c_{A1} (0–1 kmol/m³), at two stirring rates $a = 3.2 \cdot 10^{-4}$ m, $f = 36$ s⁻¹; $a = 3.479 \cdot 10^{-4}$ m, $f = 66$ s⁻¹.

The combinations of concentrations c_{B2} and c_{A1} at which the reaction took place in the aqueous phase were selected in preliminary tests by adding into the system a small amount of an indicator that changed its colour during the reaction. All other experiments were performed exclusively with the selected concentrations. The volume of the cell was equal to $196 \cdot 10^{-6}$ m³, interfacial area to $1.962 \cdot 10^{-3}$ m². The phases were introduced into the cell and removed by dosing pumps. The holdups of phases were kept constant with the use of the overflow and control of the aqueous phase outlet by the solenoid valve provided with the conductivity sensor which controlled the position of interface. After the system came to steady state both the organic and aqueous phases were collected for 360 s. The average samples were taken from these amounts and analysed. Special attention has been paid to keeping the interface clean. The inlet streams passed through sintered glass, the total time of measurement (inclusive the time for steadying) was kept in all experiments at constant value so that possible contamination of the interface by impurities from both passing phases was in all experiments equal.

RESULTS

In application of the proposed theoretical description to the reaction of acetic acid with sodium hydroxide it is necessary to take into account that sodium hydroxide is in the aqueous phase practically completely dissociated. The diffusion rate of hydroxide ion in the film is affected by the presence of sodium ions and acetate ions evolved during the reaction. Thus, the mean effective diffusivity of hydroxyl ion \bar{D}_{B_2} was substituted for the diffusivity of reaction components \bar{D}_{B_2} into the relation (12). The relation was derived for calculation of the mean effective diffusivity from the assumption of validity of the Nernst equation⁶

$$\bar{D}_{B_2} = 2\mathcal{D}_{B_2}\{1 + [\mathcal{D}_{B_2}c_{B_2} + \mathcal{D}_{S_2}c_{S_2}]/(\mathcal{D}_{S_2}c_{B_2} + \mathcal{D}_{S_2}c_{S_2})\}^{0.5}. \quad (16)$$

The hypothetical diffusivity of ions alone was calculated from the relation

$$\mathcal{D}_i = \lambda_i RT / (z_i F^2). \quad (17)$$

Values taken from literature^{7,8} were substituted into Eq. (17)

$$\lambda_{B_2} = 20 \text{ m}^2/\Omega \text{ kg ekviv.}, \lambda_{S_2} = 4.1 \text{ m}^2/\Omega \text{ kg equiv.}, F = 0.65 \cdot 10^7 \text{ C/kg equiv.}, \\ R = 8.3143 \text{ J}^\circ\text{K mol}.$$

Diffusivity of acetic acid which is diffusing through the film practically nondissociated and diffusivity of isobutanol in water were found in literature^{1,2}

$$D_{A_2} = 1.23 \cdot 10^{-9} \text{ m}^2 \text{ s}^{-1}, \quad D_{I_2} = 0.7 \cdot 10^{-9} \text{ m}^2 \text{ s}^{-1}.$$

The assumption was made, that the ratio of mass transfer coefficients of acetic acid in the organic and aqueous phases was equal to the ratio of mass transfer coefficients of water into the organic phase and isobutanol into the aqueous phase

$$k_{A_1}/k_{A_2} = k_{W_1}/k_{I_2} = 0.95. \quad (18)$$

The value 0.95 was obtained from measurements of mass transfer of acetic acid from the organic phase formed by pure isobutanol into aqueous phase formed by the 0.1N solution of sodium acetate in water.

The distribution coefficients were expressed by the empirical relation in dependence on equilibrium concentrations of acetic acid and sodium acetate in the form

$$\ln(m_i e_2 / e_1) = B_i(1) + B_i(2)(M_A / e_2) c_{A_2}^* + B_i(3)(M_S / e_2) c_{S_2}^*. \quad (19)$$

Concentration of acetate ions at the interface is given by the relation⁶

$$c_{S2}^* = c_{S2} \{ (c_{B2}/c_{S2} + 1) \cdot [1 + (c_{B2} \mathcal{D}_{B2}) / (c_{S2} \mathcal{D}_{S2})] \}^{0.5}. \quad (20)$$

The parameters B were determined from experimental data by use of the Marquart method⁷:

$$\begin{aligned} B_A(1) &= 0.3199, & B_A(2) &= -1.272, & B_A(3) &= 0.729, & B_I(1) &= 2.323, \\ B_I(2) &= -2.425, & B_I(3) &= 3.564, & B_W(1) &= -1.633, & B_W(2) &= 5.81, \\ & & & & B_W(3) &= -3.75 \end{aligned}$$

(the mean quadratic deviation of measured and calculated data equals to 0.0701). The value of the distribution coefficient of sodium hydroxide was taken from literature¹ $m_B = 0.005$. Sodium acetate was considered to be insoluble in the organic phase. The fluxes of acetic acid and of isobutanol across the interface were calculated from the inlet and outlet concentrations of the reacting and nonreacting components. The values of the coefficient k'_{A2} were then calculated from Eq. (11) by use of Eqs (12), (16)–(20). The evaluation was performed numerically on the digital computer by the iterative procedure. The values of correction factors were read of the Fig. 1 published in our previous study³. The values of k'_{I2} were calculated for a certain value of the concentration of acetic acid at the interface from the experimental values of concentrations and fluxes of the nonreacting solvents by use of Eqs (13) to (15) and the component balances at the interface.

$$\sum_i M_i c_{i2}^* / \varrho_2 = 1 \quad (21)$$

$$\sum_i m_i M_i c_{i2}^* / \varrho_1 = 1. \quad (22)$$

The dependence of the coefficients k'_{A2} and k'_{I2} on concentration of sodium hydroxide in the aqueous phase are given in Fig. 1. These dependences were extrapolated to the condition of zero interphase turbulence, i.e. to the zero concentration of sodium hydroxide. The extrapolation for the mass transfer coefficients of acetic acid was performed by correlation of experimental data according to the relation

$$k' = \text{konst.}_1 + \text{konst.}_2 \ln(c_{B2} + \text{konst.}_3). \quad (23)$$

In this way the values

$$\begin{aligned} k_{A2} &= 3.476 \cdot 10^{-5} \text{ m s}^{-1} \quad (\text{for } a = 3.479 \cdot 10^{-4} \text{ m, } f = 66 \text{ s}^{-1}) \\ \text{and } k_{A2} &= 2.077 \cdot 10^{-5} \text{ m s}^{-1} \quad (\text{for } a = 3.2 \cdot 10^{-4} \text{ m, } f = 36 \text{ s}^{-1}) \end{aligned}$$

were determined.

The corresponding values $k_{12} = 2.622 \cdot 10^{-5} \text{ m s}^{-1}$ and $k_{12} = 1.567 \cdot 10^{-5} \text{ m s}^{-1}$ were computed from the values k_{A2} by use of Eq. (6). The values k_{A2} and k_{12} were calculated from the coefficients k'_{A2} and k'_{12} by use of relation (5). From Eq. (7) results the relation

$$k'_{A2}/D_{A2}^{0.5} = k'_{12}/D_{12}^{0.5} \quad (24)$$

The dependence of the quantities $k'_{A2}/D_{A2}^{0.5}$ and $k'_{12}/D_{12}^{0.5}$ on the concentration of sodium hydroxide in the aqueous phase is shown in Fig. 2 for both stirring rates.

DISCUSSION

In agreement with the conclusions of the studies^{1,2} it was found out that the concentration of sodium hydroxide in the aqueous phase had the greatest effect on the change in the mass transfer coefficient. From Fig. 1 it is obvious that the mass transfer coefficient increases with increasing concentration of sodium hydroxide up to the value about $c_{B1} = 1$, where it steadies at the constant value which is by about 70% larger than the value of coefficient at $c_{B2} = 0$. In comparison with the results of the study¹ the mass transfer coefficients determined from our experiments showed a smaller dependence on concentration of sodium hydroxide. In our opinion this

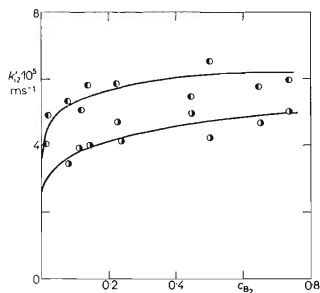


FIG. 1

Mass Transfer Coefficient k'_{12} in Dependence on Concentration of Sodium Hydroxide in Aqueous Phase for the Stirring Rate $a = 3.479 \cdot 10^{-4} \text{ m}$, $f = 66 \text{ s}^{-1}$

● k'_{A2} , ● k'_{12} .

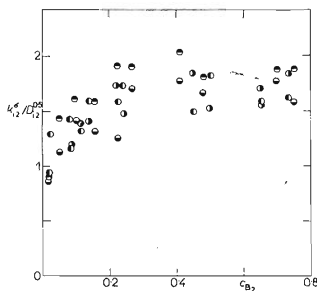


FIG. 2

Values of the Ratio $k'_{12}/D_{12}^{0.5}$ in Dependence on Concentration of Sodium Hydroxide in Aqueous Phase

○ $k'_{A2}/D_{A2}^{0.5}$, ● $k'_{12}/D_{12}^{0.5}$, $a = 3.479 \cdot 10^{-4} \text{ m}$, $f = 66 \text{ s}^{-1}$; ● $k'_{A2}/D_{A2}^{0.5}$, ● $k'_{12}/D_{12}^{0.5}$, $a = 3.2 \cdot 10^{-4} \text{ m}$, $f = 36 \text{ s}^{-1}$.

is due to the differing character of turbulence formed by the vibrating stirring and the turbulence formed by the turbine mixer used in the study¹. The experimental data are not sufficiently accurate to be used for a more precise physical interpretation of the effect of chemical reaction on the interfacial phenomena. The inaccuracy of description of the system is already manifested at evaluation of experimental data from physical mass transfer of components without chemical reaction. From measurements of physical mass transfer of pure solvents we have obtained the ratio of coefficients $k_{w1}k_{12} = 0.72$. Gordon and Sherwood⁹ have obtained, for mass transfer of pure solvents $k_{w1}/k_{12} = 0.706$. In measurements of physical mass transfer rates of solvents in presence of the third component (various fatty acids) the authors have obtained from the slope and intercept of the dependence $(1/K_{12})(D_{12}/D_{12})^{0.5}$ on $1/m_i$ the value of the ratio $k_{w1}/k_{12} = 1.146$. On basis of our measurements of the physical mass transfer rate of isobutanol and water between the organic phase formed by isobutanol and aqueous phase formed by 0.1N aqueous solution of sodium acetate we have obtained the value $k_{w1}/k_{12} = 0.95$. It is obvious that a number of assumptions made at evaluation of experimental data is not satisfied in the actual system. Even to the physical mass transfer of nonreacting components alone it would be necessary to apply the laws of multicomponent diffusion. It is not obvious that the assumption of equilibrium at the interface is justified. The conclusions, which can be made on basis of experimental data with chemical reaction are more or less qualitative and they only prove the plausibility of the formal description. The identical shape of the dependence $k_{ij}^0/D_{ij}^{0.5}$ on concentration c_{B2} for the reacting component as well as for the nonreacting solvent demonstrated in Fig. 2 proves that the proposed description by use of the enhancement factor and mass transfer coefficient, which in itself includes the effect of interfacial turbulence for all made simplifications, basically fits the mechanism of the process.

Finally it is possible to conclude that the experimental data have proved that the concept of the enhancement factor can be used also in the case of mass transfer with simultaneous chemical reaction accompanied by occurrence of interfacial turbulence. This factor can be calculated from the known physical mass transfer coefficients of reacting components. The effect of interfacial turbulence on the process rate can be expressed as the additive contribution to the rate of energy dissipation on the interface and included into the mass transfer coefficients of reacting components. The magnitude of this contribution depends first of all on the concentration of the reacting component in the reaction phase.

LIST OF SYMBOLS

- a amplitude of vibrations (m)
 B constants in Eq. (19)

c	concentration (kg mol/m ³)
D	diffusivity of component in the reacting film (m ² s ⁻¹)
\bar{D}	mean effective diffusivity of ions in the film m ² (s ⁻¹)
\mathcal{D}	hypothetic diffusivity of the ion alone (m ² s ⁻¹)
f	frequency of vibrations (s ⁻¹)
F	Faraday charge (C/kg ekv.)
j	mass flux (kg mol s ⁻¹ m ⁻²)
k	mass transfer coefficient (m s ⁻¹)
K	overall mass transfer coefficient (m s ⁻¹)
m	distribution coefficient
M	molecular weight
R	gas constant (J/°K mol)
T	temperature (°K)
v	velocity of fluctuations (m s ⁻¹)
z	valency
ϵ	rate of energy dissipation per unit of mass (m ² s ⁻³)
λ	ionic conductivity (m ² /kg equiv.)
γ	kinematic viscosity (m ² s ⁻¹)
ρ	density (kg/m ³)
ϕ	enhancement factor
χ	correction factor (Eq. (12))

Subscripts

A	reacting component in the organic phase (acetic acid)
B	reacting component in the aqueous phase (hydroxyl ion)
i	component
I	isobutanol
j	phase
S	acetate ion
W	water
1	organic phase
2	water phase

Superscripts

*	at interface
σ	due to interfacial turbulence
'	in the presence of interfacial turbulence

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