A SYSTEM FOR TESTING MASS-TRANSFER MODELS WITH A CHEMICAL REACTION IN LIQUID–DISPERSIONS: IODINE, n-HEPTANE/POTASSIUM IODIDE, POTASSIUM HEXACYANOFERRATE(II), WATER

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Mass transfer of iodine from n-heptane into the aqueous phase containing potassium iodide and potassium hexacyanoferrate(II) was investigated in a diffusion cell with vibrational agitation. The data obtained were employed to evaluate parameters of the model describing the transfer of iodine accompanied by the formation of triiodide and by oxidation of the hexacyanoferrate(II). The system described is suitable for testing mass-transfer models with a chemical reaction in the liquid–liquid dispersions, since, by a proper choice of concentrations of its reaction components, mass-transfer resistances in individual phases can be varied in a wide range and high sensitivity of parameters of the model can be achieved.

During many industrially important reactions or extraction processes in a liquid–liquid dispersion, the component passing across the interface from the depleted into the enriched phase reacts during this transfer with one of the components of the enriched phase. A chemical-engineering description of such a process, which is necessary for the design of the apparatus, is rather complicated and it requires data on the local density of the interface flux of the transferred component as well as data on the spatial distribution of phases, interface and concentrations of reacting components in the given equipment.

Even extremely simplified mass-transfer models with a chemical reaction in the dispersion contain many parameters, which cannot be determined for a given system only from data obtained by investigating the mass transfer in the dispersion. One way to solve this problem is to combine the information about the dependence of the density of interface flux on concentrations of reaction components obtained from kinetic experiments performed at a known magnitude of the interfacial surface and at well-defined hydrodynamic conditions, *e.g.*, in a diffusion cell with vibrational agitation[1], and data on mass-transfer coefficients in the dispersion obtained during investigations of the physical mass transfer in the dispersion in the given type of apparatus. On the assumption that the model describing the transfer with a chemical reaction is independent of changes in hydrodynamic conditions, *i.e.*, that such changes

in the mass-transfer coefficients, this model, after verification experiments in the diffusion cell, can be employed to express the local mass-transfer rate in the dispersion.

So far, no satisfactory verification of this method can be found in the literature. It is the aim of this work to select a system suitable for the experimental testing of this method to model reactions in liquid dispersions as well as to obtain a description of the mass-transfer rate of the reacting component across a flat interface in such a system.

SYSTEM

To obtain a sufficiently reliable description of the mass transfer of the reacting component in a model system it is desirable that the system selected satisfy the following requirements:

a) The component transferred reacts only in one phase and both the reaction mechanism and the formal description of its kinetics in the single-phase system are known.

b) The chemical reaction is sufficiently rapid, so that the equilibrium is reached effectively in the diffusion film, it possesses no significant thermal effects and it does not produce any interfacial instability.

c) The distribution of the mass-transfer resistance between the individual phases can be varied in a wide range by changing concentrations of the reaction components.

d) Concentrations of the reaction components can be easily analytically determined.

We selected iodine as the transferring component. It can be easily obtained in its pure form by sublimation, it is soluble in many solvents and it can be well determined by spectrophotometry. It possesses a high reactivity in the aqueous phase, so that we have at our disposal a considerable number of reactions satisfying the conditions required.
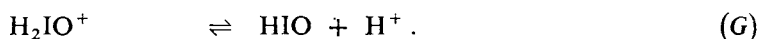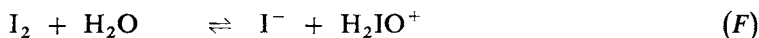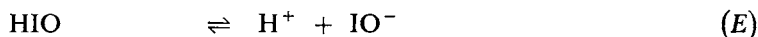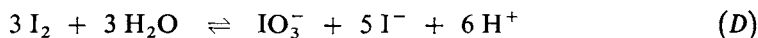
After some preliminary tests, we selected n-heptane as a solvent for iodine and potassium hexacyanoferrate(II) as a reaction counterpart of iodine in the aqueous phase, whose pH was stabilized by a phosphate buffer solution. In this system, the oxidation of the hexacyanoferrate proceeds in the diffusion film of the aqueous phase according to the stoichiometric equation

$$I_2 + 2\,Fe(CN)_6^{4-} \rightleftharpoons 2\,I^- + 2\,Fe(CN)_6^{3-} . \tag{A}$$
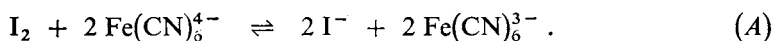
The arising iodide cations can further react with iodine molecules to yield triiodide cations

$$I_2 + I_- \rightleftharpoons I_3^- . \tag{B}$$

In the aqueous phase, iodine may exist still in other forms corresponding to the following equilibria:

$$I_2 + H_2O \quad \rightleftharpoons \quad I^- + HIO + H^+ \qquad (C)$$

$$3\,I_2 + 3\,H_2O \rightleftharpoons \quad IO_3^- + 5\,I^- + 6\,H^+ \qquad (D)$$

$$HIO \qquad \rightleftharpoons \quad H^+ + IO^- \qquad (E)$$

$$I_2 + H_2O \quad \rightleftharpoons \quad I^- + H_2IO^+ \qquad (F)$$

$$H_2IO^+ \qquad \rightleftharpoons \quad HIO + H^+. \qquad (G)$$

It has been shown by Reynolds[2] that hexacyanoferrate(II) is oxidized only by hydrated molecules of free iodine according to Eq. (A) and that none of the remaining iodine forms oxidizes the hexacyanoferrate with a significant rate.

Table I contains data on equilibrium constants of reactions $(B)–(G)$. It follows from these data that, at real iodine concentrations in a weakly acid or a neutral solution, only reactions (A) and (B) can affect significantly the concentration of I_2. In Table II we report forms of the rate equations and values of reaction constants of reactions $(A)–(C)$. It can be shown from these data that in a system, in which iodine passes into the hexacyanoferrate solution, only reactions (A) and (B) can affect the transfer rate, whereas during the transfer of iodine into the iodide solution, only reaction (B) need be considered.

Further it can be shown that in a wide concentration range, reaction (A) may be considered to be irreversible. So, e.g., during the contact of equal volumes of phases with initial concentrations $1 \cdot 5 \,.\, 10^{-3}$ kmol/m³ I_2 and $1 \cdot 0 \,.\, 10^{-2}$ kmol/m³ Fe(CN)$_6^{4-}$, the reversible reaction can be neglected up to a 99% conversion of iodine. Orientation tests, during which equal volumes of phases with concentrations $1 \cdot 0 \,.\, 10^{-3}$ kmol/m³ I_2 and $1 \cdot 0 \,.\, 10^{-2}$ kmol/m³ Fe(CN)$_6^{4-}$ were being contacted, have confirmed that the equilibrium organic phase does not contain iodine in an amount which could be determined either spectrophotometrically or by the titration by thiosulphate. Reaction (B) which is obviously at usual experimental conditions reversible, can be considered to be an equilibrium reaction with respect to values of its rate constants. This means that this reaction is in comparison with the diffusion of reaction components sufficiently rapid, so that it maintains concentrations of reaction components in the diffusion film in a mutual equilibrium.

Thus, the transfer of iodine into the aqueous phase in the system considered can be described as a transfer of a component accompanied by simultaneously proceeding rapid irreversible and equilibrium chemical reactions. A theoretical solution to the rate of such a transfer has been found earlier[3].

Although the fact, that two chemical reactions proceed simultaneously in the system selected, complicates its mathematical description, it brings on the other hand definite advantages, since, at a proper choice of concentrations of the reaction components, we can obtain data well determining all kinetics parameters of the model. Simultaneously, it offers a possibility to increase the reliability of the test of the model for an adequate description of the kinetic behaviour of the given system.

MODEL

If, for the sake of simplicity, we denote the individual reaction components by the symbols A for I_2, B for $K_4Fe(CN)_6^{4-}$, C for I^- and D for I_3^-, the reactions accompanying the transfer of the component A assume the form

$$A + 2B \rightarrow 2C \qquad\qquad (H)$$

TABLE I

Equilibrium constants of reactions $(B)-(G)$ at $298\cdot15°K$

Reaction	K	Lit.
(B)	$630-870$	$4-12$
(C)	$2\cdot6 . 10^{-13}-5\cdot4 . 10^{-13}$	$13-15$
(D)	$4\cdot0 . 10^{-48}$	16
(E)	$4\cdot5 . 10^{-13}$	17
(F)	$1\cdot2 . 10^{-11}-1\cdot0 . 10^{-8}$	$18-20$
(G)	$3\cdot0 . 10^{-2}$	19

TABLE II

Rate equations and constants of reactions $(A)-(C)$

Reaction	Reaction rate r	Constants	Lit.
(A)	$k_R . c_{I_2} . c_{Fe(CN)_6^{4-}} - k'_R c_{I^-} . c_{Fe(CN)_6^-}$	$k_R = 1\cdot3 . 10^3$ m^3/kmol/s $\quad k'_R = 4\cdot3 . 10^{-3}$ m^3/kmol/s	2
(B)	$k_R c_{I_2} . c_{I^-} - k'_R c_{I_3^-}$	$k_R = 4\cdot1 . 10^{10}$ m^3/kmol/s $\quad k'_R = 7\cdot6 . 10^7$ s^{-1}	21
(C)	$k_R c_{I_2} - k'_R c_{I^-} . c_{HIO} . c_{H^+}$	$k_R = 3\cdot0$ s^{-1} $\quad k'_R = 4\cdot4 . 10^{12}$ m^6/kmol^2/s	22

$$A + C \rightleftharpoons D. \tag{I}$$

By using relations derived[3] for the transfer of component A accompanied by reactions (II) and (I), the transfer velocity can be expressed by the relation

$$J_A = \{1/[1(p_A k_{A1}) + 1/(\phi k_{A2})]\}\,(c_{A1} - c_{A2}). \tag{1}$$

If the diffusivities of the reaction components in the aqueous phase are identical, the enhancement factor ϕ is expressed by the relations

$$\phi = \frac{\sqrt{Z^*}}{\mathrm{tgh}\,(\xi\sqrt{Z^*})}\,[1 + K c_{C2}^*/(1 + K c_{A2}^*)] \tag{2}$$

$$Z^* = (1 + 3K c_{A2}^*)\,(k_R D_A c_{B2}^{*2}/k_A^2)/[1 + K(c_{A2}^* + c_{C2}^*)] \tag{3}$$

$$\zeta = 1 - [K c_{A2}^*/(1 + K c_{A2}^*)]^2\,c_{C2}/[c_{A2}^*\sqrt{(\psi^2 - Z^*)}] \tag{4}$$

$$c_{A2}^* = (c_{A1} - J_A/k_{A1})/p \tag{5}$$

$$c_{B2}^* = c_{B2} - [(1 + K c_{A2}^*)\,c_{C2}^* - c_{C2}] \tag{6}$$

$$c_{C2}^* = [2(\phi - 1)\,c_{A2}^* + c_{C2}]/(1 + 3K c_{A2}^*). \tag{7}$$

If the iodine transfer into the iodide solution proceeds in the absence of the hexa-cyanoferrate, *i.e.*, $c_{B2} = 0$, the expression for the enhancement factor reduces to

$$\phi = 1 + K c_{C2}/(1 + K c_{A2}^*). \tag{8}$$

It follows from the foregoing that the transfer rate of iodine, J_A, is an implicit function of concentrations of the reaction components c_{A1}, c_{A2}, c_{C2}, which contains several parameters:

$$F(J_A, c_{A1}, c_{B2}, c_{C2}, p_A, K, k_R, D_{A2}, k_{A1}, k_{A2}) = 0. \tag{9}$$

Data obtained from measurements of the kinetics of the process in the diffusion cell do not alone yield the sufficient information for a reliable determination of all these parameters. Therefore it is desirable to determine some parameters from independently performed measurements, which yield data well defining the individual parameters. Then, the agreement between experimental kinetic data and the results calculated according to the model with parameters determined in this manner makes it possible to judge reliably on the adequacy of the proposed model.

For the verification of our model, we adopted the following procedure:

a) We determined the equilibrium distribution of iodine between the phases at variable concentrations of the iodide and from these data we found values of the distribution coefficient of iodine, p, the equilibrium constant of reaction (B), K.

b) Diffusivities of iodine in both phases, D_{A1} and D_{A2}, were determined from the response to the δ-injection into the laminar flow in the capillary.

c) Mass transfer coefficients of iodine in both phases, k_{A1} and k_{A2}, were evaluated from data obtained by measuring the kinetics of the iodine transfer into the aqueous phase with a variable concentration of the iodide. The relation $k_{A1}/k_{A2} = \sqrt{(D_{A1}/D_{A2})}$, whose validity for the description of the interfacial transfer on the diffusion cell has been confirmed earlier[1], was used as an inependent check of correctness of parameters evaluated.

d) Data on the transfer of iodine into aqueous solutions with a variable initial concentration of hexacyanoferrate(II) were used for determining the rate constant of reaction (A), k_R, and for testing the adequacy of the model.

EXPERIMENTAL

Substances employed. n-Heptane was refined by repeated shaking with concentrated sulphuric acid as long as it was coloured by reaction products, then it was washed with aqueous sodium carbonate and water, dried with sodium sulphate and finally purified by adsorption on active carbon. Iodine was purified by sublimation. The aqueous phase was prepared by weighing the calculated amount of AR grade potassium hexacyanoferrate(II) into a phosphate buffer solution. This buffer solution was obtained by mixing 8 volume parts of $1/15$M aqueous NaH_2PO_4 and 2 volume parts of $1/15$M aqueous Na_2HPO_4 prepared from AR grade chemicals.

Analytical methods. In the organic phase, iodine was determined spectrophotometrically at 554 nm which is the wavelength corresponding to the isobestic point. From calibration measurements, the molar absorptivity of iodine is 63 200 $m^2/kmol$. Samples of the aqueous phase were analysed by a iodometric titration with sodium thiosulphate. Concentration responses during measurements of the diffusivities were recorded refractometrically.

Measuring procedure. The equilibria were measured with the help of sealed ampuls to avoid losses of volatile components into the surroundings. Glass ampuls (25 ml) were filled from a pipette with 20 ml of the aqueous phase with the known iodide concentration varied in the range $0.0 - 9.0 \cdot 10^{-2}$ $kmol/m^3$ and with 2 ml of a hexane solution of iodine with the known concentration of $2.906 \cdot 10^{-3}$ $kmol/m^3$. The ampuls were then sealed and shaken for 6 h at $25°$C in a thermostated batch. After the separation of phases, the equilibrium concentration of iodine in the organic phase was determined spectrophotometrically.

Diffusivities of iodine were measured by the method of response to the δ-injection into the carrier phase flowing laminarily through the thermostated capillary as described in the literature[23]. The carrier phase was either n-heptane or the aqueous phase without iodine, the solution for the δ-injection was prepared by addition of iodine into the carrier phase.

The kinetics of the interfacial transfer of iodine was measured in a diffusion cell of the volume of 250 ml and provided with vibrational agitation[1]. Its scheme is in Fig. 1. All its parts con-

tacting the solutions were made of glass, teflon and titanium. The cell was thermostated to 25°C and it was filled with 100 ml of the aqueous phase of the known concentration of the iodide or the hexacyanoferrate(II). Then, the equal volume of the organic phase was added cautiously — not to disturb the flat interface — and the vibrational agitation was switched on. All experiments were performed at an identical agitation intensity. The agitator frequency was set to 30 Hz with an RC-generator, the amplitude setting of 1 mm was checked by a voltmeter. The voltmeter for this measurement was calibrated by the method described elsewhere[1]. After the agitation had been switched on, samples of the organic phase of the volume of 1 ml were withdrawn by a teflon capillary into a hypodermical syringe at regular intervals. The concentration of iodine in these samples was determined spectophotometrically. The initial concentration of iodine in the organic phase was varied in the range $1 \cdot 0 - 2 \cdot 0 \cdot 10^{-3}$ kmol/m^3. In the first series of experiments, the initial concentration of the iodide in the aqueous phase was varied in the range $8 \cdot 0 \cdot 10^{-4} - 1 \cdot 0 \cdot 10^{-2}$ kmol/m^2, in the second series, the initial concentration of the hexacyanoferrate(II) was varied within $5 \cdot 0 \cdot 10^{-3} - 2 \cdot 5 \cdot 10^{-1}$ kmol/m^3.

Data processing. From our measurements of the equilibria, we obtained data on equilibrium iodine concentrations in the organic phase, c_{A1}. At known initial concentrations of iodine in the organic phase, c_{A1}^0, and iodide in the aqueous phase, c_{C2}^0, it was possible, for the given ratio of the phases $\beta = V_1/V_2$, to express this concentration c_{A1} by solving mass balance equations of the components together with the equilibrium conditions

$$c_{A1} = p \, c_{A2} \tag{10}$$

$$K = c_{D2}/(c_{A2} \cdot c_{C2}) . \tag{11}$$

In this manner we obtained the relation

$$c_{A1} = p \, \frac{-b + \left[b^2 + 4K(1 + p\beta) \, \beta c_{A1}^0 \right]^{1/2}}{2K(1 + p\beta)} , \tag{12}$$

where

$$b = 1 + \left(c_{C2}^0 - \beta c_{A1}^0 \right) K + p\beta . \tag{13}$$

By minimizing the sum of squares of deviations between experimental concentrations of iodine in the organic phase and values calculated from Eq. (12), parameters p and K were determined.

During the processing of integral data from our kinetic measurements it was necessary to calculate time dependences of the iodide concentration in the organic phase by integrating the differential equation

$$V_1 \, dc_{A1}/dt = - J_A A \tag{14}$$

with the initial condition

$$t = 0 , \quad c_{A1} = c_{A1}^0$$

in which the density of flux of iodide across the boundary, J_A, is given by Eqs (1)—(7). Eq. (14) was integrated numerically and concentrations of components in the aqueous phase which were necessary for calculating the value of J_A, were determined from balance relations. These balance equations took into account the loss of the organic phase during the reaction due to the withdrawal of samples.

The right-hand side of Eq. (*1*) was calculated by an iterative solution of system (*1*)—(7), Eq. (*14*) was integrated by the Runge–Kutta–Merson method. Parameters of the model were determined by Marquardt's minimization of the sum of squared deviations between the experimental and calculated time dependence of the iodine concentration.

TABLE III

Equilibrium composition of phases, $c_{A1}^0 = 2.906 \ mol/m^3$, $V_2/V_1 = 5$

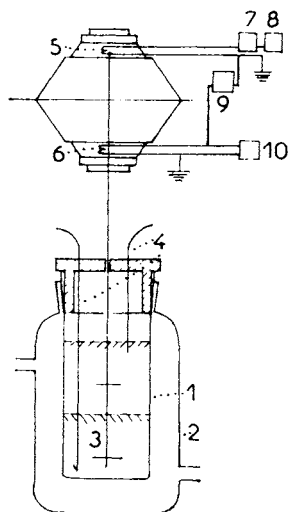| Total concentration of the iodide and triiodide in the aqueous phase mol/m³	Concentration of iodine in the organic phase mol/m³
0	2.375 ± 0.029
0.10	2.375 ± 0.051
0.50	2.257 ± 0.050
1.0	2.246 ± 0.025
5.0	1.691 ± 0.031
10.0	1.368 ± 0.016
50.0	0.505 ± 0.024
90.0	0.307 ± 0.005

FIG. 1

Cell with the vibrational agitation. 1 Vessel 250 ml, 2 thermostated jacket, 3 vibrational agitator with perforated disks, 4 capillaries for the withdrawal of samples, 5 driving electromagnetic coil, 6 measuring electromagnetic coil, 7 amplifier, 8 frequency generator, 9 voltmeter, 10 oscilloscope

Parameters k_{A1} and k_{A2} were determined from the first series of experiments with the iodine mass transfer into solutions of KI, the second series of experiments with the iodine mass transfer into solutions of $K_4Fe(CN)_6$ was used for evaluating the rate constant of the reaction, k_R.

RESULTS

Results of our equilibrium measurements are summarized in Table III which contains experimental equilibrium iodine concentrations in the organic phase at a variable total concentration of the iodide and triiodide in the aqueous phase given by the initial concentration of the iodide in this phase. The reported mean values and mean errors of the measurements were calculated from results of repeated experiments. By using Eq. (12), the distribution coefficient of iodine, $p = 25.8 \pm 0.3$, and the equilibrium constant of reaction B in the given system, $K = 495.7 \pm 1.2 \ m^3/kmol$, were calculated from these data.

Iodine diffusivities in the organic phase, $3.64 \cdot 10^{-9} \ m^2/s$, and in the aqueous phase, $1.26 \cdot 10^{-9} \ m^2/s$, were obtained by measuring the response to the injection of the sample enriched with iodine into the capillary[23].

Mass transfer coefficients of iodine in both phases were evaluated from results of measurements of the kinetics of mass transfer of iodine into the iodide solutions as $k_{A1} = 4.78 \cdot 10^{-5} \ m/s$ and $k_{A2} = 2.79 \cdot 10^{-5} \ m/s$. The agreement between the calculated course of the extraction of iodine and our experimental data is illustrated in Fig. 2.

From results of our measurements of the kinetics of the iodine mass transfer into hexacyanoferrate(II) solutions, the rate constant of reaction (A) was calculated
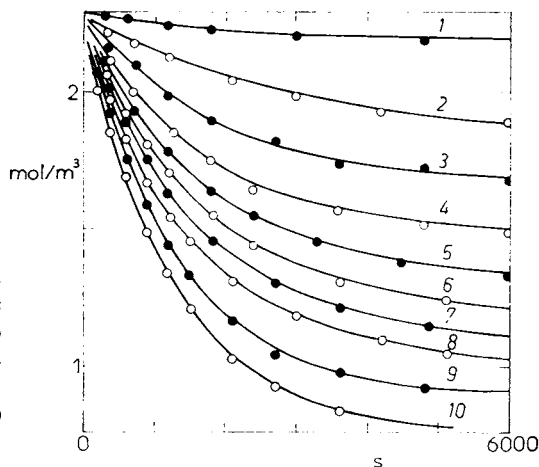

Fɪɢ. 2

Comparison of experimental and calculated concentrations of iodine in the organic phase during the transfer of iodine into solutions of the iodine of different concentrations 1 0·8, 2 8·0, 3 16·0, 4 24·0, 5 32·0, 6 40·0, 7 48·0, 8 58·0, 9 78·0, 10 97·0 mol/m³

at the given conditions as $k_R = 2 \cdot 19 \cdot 10^3 \, m^3/kmol$. The agreement between the calculated dependence of the concentration of iodine in the organic phase on the time of contact between both phases and our experimental data is depicted in Fig. 3.

DISCUSSION

The system selected satisfies requirements imposed on a testing system for the mass transfer with a chemical reaction. Here we tested a description of the transfer of a reaction component across a flat interface. Individual parameters of the model were evaluated from experimental data at conditions, where the objetive function is sufficiently sensitive to these parameters. During all evaluations of parameters, tests of good fit of the model were performed. They were always positive on a 95% significance level. The fact that the interfacial mass transfer of one reaction component is in the given system accompanied by two reactions, one of which is an equilibrium reaction, enables a reliable determination of transfer coefficients in both phases. The measurement of iodine diffusivities in both phases makes it possible to test independently the correctness of evaluated coefficients. The ratio of mass transfer coefficients evaluated from kinetic experiments, $k_{A1}/k_{A2} = 1 \cdot 71$, agrees excellently with the value $\sqrt{(D_{A1}/D_{A2})} = 1 \cdot 70$ as calculated from measured diffusivities. Our model of the kinetics of the interfacial mass transfer describes experimental data well in the whole range of concentrations with constants values of the transfer coefficients at conditions, where only reaction (A) proceeds and also at conditions, where reaction (B) is dominating.
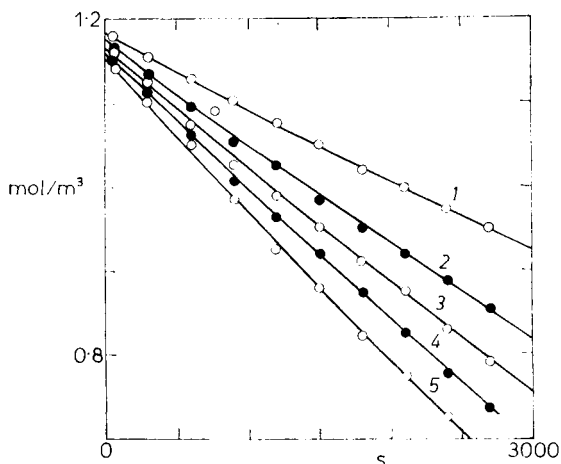

FIG. 3

Comparison of experimental and calculated concentrations of iodine in the organic phase during the transfer of iodine into solutions of potassium hexacyanoferrate(II) of different concentrations. *1* 10, *2* 27, *3* 62, *4* 100, *5* 250 mol/m³

Since the concentration of hydrogen ions in the given system was stabilized with a phosphate buffer solution and the parameters p, K and k_R are influenced by the presence of electrolytes in the aqueous phase, the parameters obtained are valid only for the given composition of the aqueous phase. From these reasons we can perform only an orientation comparison of our values with parameters from the literature extrapolated to zero concentrations of the components. The value of the constant $K = 495.7 \ m^3/kmol$, defined by concentrations according to Eq. *(11)* and evaluated at the given conditions, is somewhat lower than values of the thermo- dynamic equilibrium constant reported in Table I. In our experimental conditions, the value of the rate constant k_R of reaction *(A)* was higher $(2.19 \cdot 10^3 \ m^3/kmol/s)$ than in the literature[2] (Table II). It is well-known that the rate of ionic reactions can be strongly affected by the ionic association, which manifests itself especially if multi- valent ions are present in the solution, either as reacting components or as additional ions[24]. The increase in the oxidation rate of the hexacyanoferrate(II) with iodine in the presence of phosphate ions may be explained by the fact that these ions affect positively the activity coefficient of iodine in the aqueous phase and, subsequently, also the oxidation rate.

LIST OF SYMBOLS

A interfacial area
c concentration in the bulk phase
c^* concentration at the interface
D diffusivity
J interfacial flux
k mass transfer coefficient
k_R rate constant of the chemical reaction
K equilibrium constant of the reaction
p distribution coefficient of component A
t time
V volume of the phase
Z^* reaction module, Eq. *(3)*
ϕ enhancement factor
ξ relative thickness of the reaction zone, Eq. *(4)*

Subscripts

A   component A, I_2
B   component B, $Fe(CN)_6^{4-}$
C   component C, I^-
D   component D, I_3^-
1   organic phase
2   aqueous phase

Superscripts

o   initial value

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