MASS TRANSFER ACCOMPANIED BY CHEMICAL REACTION IN A LIQUID DISPERSION

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An experimental procedure has been worked out to measure mass transfer rates in the presence of a chemical reaction in a liquid dispersion in a batch mixed vessel by a dynamic method. Transfer rates have been observed of iodine between decalin and water phase containing potassium iodide. The transfer was described by the pseudohomogeneous model. Transport parameters of this model have been evaluated from the response of the system to a step concentration change in the continuous phase. The model of the experiment described distortion of the information in the sampling device for the continuous phase. Dependences have been measured of the iodine transfer coefficients in both phases on the intensity of mixing and volume hold-up of the dispersed liquid. By a suitable choice of the concentration in the continuous phase the ratio could be adjusted of the resistance against the transfer in both phases and the sensitivity could be affected of the objective function to the evaluated model parameters.

In view of the complexity of the phenomena taking place in a mixed liquid dispersion it is difficult to develop a mathematical description of the reactor with two liquid phases and to determine its structural parameters.

Simplifying assumptions must be adopted in the modelling. The simplest description of a reactor for two-phase reactions in a mixed vessel is the so-called pseudo-homogeneous model, where each phase is perfectly mixed without concentration gradients. The concentration changes of the components are here expressed in terms of the overall interfacial area of the dispersion and differential rate equations derived on the basis of the film theory of interfacial transfer.

While the equilibrium and kinetic parameters of the model, appearing in the rate equation, may be determined from independent experiments (by measuring the equilibrium and the kinetics in a cell with a defined interfacial surface), a sufficiently accurate determination of the transport parameters in the dispersion is difficult. For instance, in systems with a fast chemical reaction, where diffusional resistances play a significant role in the interfacial transfer, one has to know the transfer coefficients of individual components with considerable accuracy. Prediction of these coefficients from published correlations is not always for such purposes sufficiently accurate and their values must be determined experimentally for the given system in the model equipment. In order to investigate the concentration conditions in a mixed

dispersion it is sufficient to analyze the continuous phase which may be sampled from the vessel using a suitable frit impermeable for the drops of the dispersed phase. In batch experiments it is convenient to use the dynamic method of experiment, where, having reached the hydrodynamic equilibrium of the dispersion, a concentration change in the continuous phase is effected by injection of the reacting component, while detecting the response of the sampled phase by a suitable analyzer. If the reaction is fast the concentration changes in the reactor may be fast compared to the transfer characteristics of the measuring system and the processing of data must include also the distortion of the response due to the analyser and the transport delay of the sample.

The aim of this work has been to work out a method of measuring the mass transfer rates in a disperison, determine the mass transfer coefficients and judge the adequacy of the pseudohomogeneous model for description of a system with an instantaneous chemical reaction.

System

For the measurement of mass transfer with an instantaneous reversible reaction, we selected the system with extraction of iodine by decalin from the water phase containing iodide. A practically instantaneous reaction in the water takes place

$$I_2 + I^- \rightleftharpoons I_3^- . \tag{A}$$
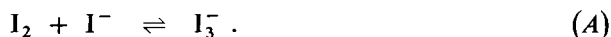
Undesirable side reactions may be suppressed by maintaining pH at a value above 5 by a suitable buffer. In view of the reversibility of the reaction one can affect, by addition of iodide and iodine into the water phase after reaching the equilibrium, the direction of interfacial transfer of iodine. The density of decalin is only slightly lower than that of water, which enables experiments at a low intensity of mixing and relatively large mean diameter of the droplets ($\sim 1 . 10^{-3}$ m) without allowing for any significant inhomogeneities to appear. Thus one can approximate conditions common in large size industrial reactors.

Rate Equation

If we use for the components of the reaction (A) the notation $A = I_2$, $C = I^-$, $D = I_3^-$, then the equilibrium constant of the reaction (A) may be defined as

$$K = c_{D2}/(c_{A2} . c_{C2}) \tag{1}$$

and the distribution coefficient of iodine as

$$p = c_{A1}/c_{A2} . \tag{2}$$

Eq. (2) holds at any instant at the interface and in case of equilibrium between both phases also for the volume concentrations.

An expression for the density of the flux of species A at the interface, according to the film theory and for the case of an instantaneous reversible chemical reaction of the type (A), was obtained by Olander[1] in the form

$$J_A^+ = k_{A2} E(c_{A2}^+ - c_{A2}). \tag{3}$$

The enhancement factor E the same author expressed as

$$E = 1 + q_A K c_2 / (q_D + K c_{A2}^+), \tag{4}$$

where $q_x = D_{C2}/D_{X2}$, $x = A, D$. The density of the flux J_A^+ may be written, using Eq. (2), as

$$J_A^+ = k_{A1}(c_{A1} - pc_{A2}^+). \tag{5}$$

By elimination of the unknown concentration c_{A2}^+ from Eqs (3), (4), and (5) a quadratic equation has been obtained for the density of the flux J_A^+. Physically meaningful is the root

$$J_A^+ = (b_1/2) - ((b_1/2)^2 - b_2)^{1/2}, \tag{6}$$

where b_1, b_2 are functions of the parameters p, K, k_{A1}, k_{A2}, the ratio of diffusivities q_x, and the mean volume concentrations of the reacting components in both phases

$$b_1 = k_{A1}(c_{A1} + pq_D/K) + k_{A1}k_{A2}(pq_A c_{A2} + c_{A1} - pc_{A2}),$$
$$b_2 = k_{A1}^2 k_{A2}(c_{A1} - pc_{A2})(c_{A1} + pq_A c_{C2} + pq_D/K)/(pk_{A1} + k_{A2}). \tag{7}$$

The density of the flux (6) describes, in accord with the film theory, the mass transfer between two phases with no concentration distribution.

EXPERIMENTAL

Chemicals used. Decalin was a mixture of *cis* and *trans* isomers. Fractions obtained from the raw material were rid of unsaturated and aromatic hydrocarbons by shaking with sulphuric acid, washing with a water solution of sodium carbonate and water. After redistillation a fraction from the boiling point temperature range between 188 and 194°C was taken. Purity of decalin was tested by spectrophotometry and chromatography. Decalin was stored in a sealed vessel in darkness. After use it was regenerated by shaking with a water solution of KI and $Na_2S_2O_3$ and redistilled. Iodine was purified before preparation of the solutions by sublimation. Potassium iodide of grade *p.a.* was used as such. Phosphate buffer of pH = 6·24 was prepared from chemicals of *p.a.* grade following the directions in ref.[2]. Potassium salt was substituted by natrium salt.

The densities of both phases were measured by pycnometry, viscosity by Ubbelohde visco-meter, interfacial tension by the method of weighted droplets and diffusivity of individual species by the method of measuring the concentration response to a Dirac impulse into the laminar flow in a capillary[3]. The diffusivity of the triiodide ion could not be measured for this ion exists only in equilibrium mixture with iodide and iodide ions. Mean values of the measured quantities are summarized in Table I. The variation of diffusivity over the entire concentration range used was less than 10% and for the remaining properties measured a negligible concentration change was found. All experiments were carried out at a temperature 25°C.

Analytical methods: Concentration of iodine in decalin was determined by spectrophotometry at the wave-length of the maximum absorption $\lambda = 522.5$ nm. The calibration experiments consisted of titration of iodide, extracted into a neutral water solution of KI, by $Na_2S_2O_3$. The titration was carried out up to complete decolouring of the solution. The calibration experiments served to evaluate molar absorptivity of iodine in decalin at the wavelength $\lambda = 522.5$ nm to obtain $\varepsilon = 1.017 \cdot 10^5$ kmol^{-1} m^2. The concentration of the iodine ions was determined by argento-metry. Concentration of iodine in water phase was measured by spectrophotometry in a flow--through cell of volume $7.0 \cdot 10^{-8}$ m^3 in the visible part of spectrum. Since in this part of spec-trum iodine and triiodide ions absorb, the method yielded the overall concentration of iodine $c_T = c_{A2} + c_{D2}$ at the wave-length of the isosbestic point $\lambda = 467$ nm, determined experimentally.

Experimental set-up: A cell with vibrating impellers, described earlier in ref.[4] was used to mea-sure the rate of interfacial mass transfer. The scheme of the set-up for the mass transfer measure-ments in the dispersion is shown in Fig. 1. The reactor is a cylindrical vessel 1 of radius $D_v = 0.105$ m, of height $H = 0.115$ m, equipped with four radial baffles 2, $D_v/10$ wide. The liquid was dispersed by an impeller 3 with four straight inclined blades (45°) of radius 0.45. D_v located $0.5 \cdot D_v$ above the bottom. The impeller was powered by a DC motor 4 with rpm control 5. The vessel consists of a lid 6, bottoms 7, 11 from stainless steel and of a glass cylinder 8. There are filling openings in the lid and a discharge opening and a phase separator, made of a fritted hydrophylized glass 10, mounted in the bottom of the vessel 11 by a screw 12. In the wall of the vessel there are two adjustable optical probes enabling measurements of the specific interfacial surface[5,6]. The probes were metal tubes, 0.01 m in diameter, provided inside with apertures to delimit the light beam and terminated in the vessel by planparallel glass windows. One probe 13 brings the parallel light to the measuring point while the other 14 diverts the light, that had passed through the suspension, toward a photodiode 15. The signal of the photodiode is lead to a data logger 16 to be amplified and recorded on a X—Y recorder, and punched into a paper tape. The continuous phase is sampled *via* a phase separator 9 and lead *via* a PTEE capillary 17

TABLE I

Properties of the system at 25°C

Property	Phase I	Phase 2
Density ϱ, kg m^{-3}	877·6	1 003·8
Viscosity v, m^2 s^{-1}	$2.597 \cdot 10^{-6}$	$9.494 \cdot 10^{-7}$
Diffusivity D_A, m^2 s^{-1}	$7.3 \cdot 10^{-10}$	$1.77 \cdot 10^{-9}$
Diffusivity D_C, m^2 s^{-1}	—	$2.20 \cdot 10^{-9}$
Interfacial tension σ, N m^{-1}	$5.08 \cdot 10^2$	

to a flow-through cell of a spectrophotometer **18**. The spectrophotometer allows for the continuous recording of the course of the detected concentration on both the recorder and the line printer with adjustable density of sampling. At the exit tube **19** from the cell there is a needle valve **20** for adjusting the flow rate of the sampled liquid. The tubing **19** is connected to a measuring vessel **21** for measuring the flow rate of the sampled phase.

The reactor was termostated with an accuracy of $0.2°C$ by water circulated through the labyrinth of the metal bottom. All parts coming in contact with the solution are made of glass, PTFE of stainless steel.

Measuring procedure: The equilibrium distribution of iodine: From the standard solutions of iodine in decalin and iodide in water of known concentration we prepared two-phase mixtures of volume $1 . 10^{-4}$ m^3 differing in initial composition and in the ratio of volumes of the two phases. The samples were shaken at $25°C$. After reaching equilibrium samples of the organic phase were taken and the equilibrium concentration of iodine in decalin was determined by spectrophotometry.

Transfer of iodine across the flat interface: The cell thermostated to $25°C$ was filled with $1 . 10^{-4}$ m^3 (100 ml) of water phase of known composition. The water phase was carefully layered with the same volume of the organic phase while care was taken to avoid any significant mixing of the phases. Together with the starting of the vibration of the mixer (amplitude 1 mm, frequency 30 Hz), the stopwatch was started. In known time intervals samples were taken of the
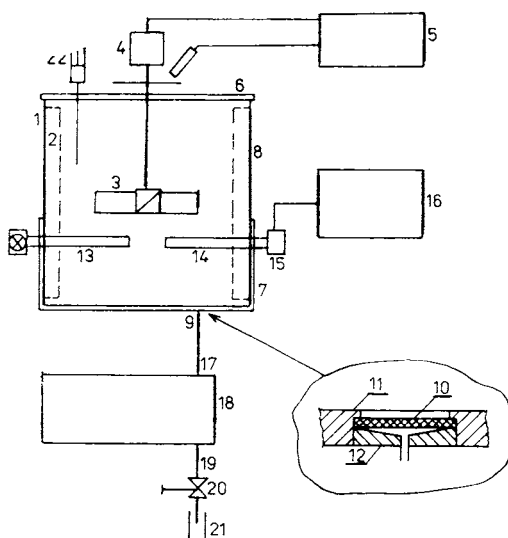

FIG. 1

Scheme of the set-up for mass transfer measurements in dispersion. **1** vessel of volume $1 . 10^{-3}$ . . m^3, **2** radial baffle, **3** impeller, **4** DC derivative motor, **5** frequency of revolution control, **6** lid of vessel, **7** metal wall of vessel, **8** glass cylinder, **9** phase separator, **10** glass frit, **11** bottom of vessel **12** thrust screw, **13** optical probe (source), **14** optical probe (receiver), **15** photodiode, **16** data logger, **17** PTFE tubing, **18** spectrophotometer UVIDEC 1, **19** PTFE tubing, **20** valve, **21** measuring vessel, **22** injection syringe

organic phase of volume $1 . 10^{-6}$ m^3 (1 ml) by a syringe with a PTFE capillary. pH of the water phase was measured in each experiment. The setting of the initial concentration of iodine and iodide and iodine in the water phase enabled us to determine the direction of iodine transfer between both phases. The experimental conditions during measurement of iodine transfer across the interface are summarized in Table II. A total of 14 experiments were carried out.

The measurement of the interfacial surface and iodine transfer in the dispersion: The measurements were realized using the set-up shown in Fig. 1. The mean specific interfacial surface was measured by the optical method[5,6], based on the absorbance of light in a dispersion of thickness L_0. This length of the optical path, L_0, *i.e.* the distance between the windows of the optical sonds **13** and **14**, was selected between 0·005 and 0·03 m in such a way as to provide optimum work of the amplifier of the voltage which is proportional to the intensity of light reaching the photodiode **15**. With the stilled mixer and separated phases we measured the intensity of the light I_0 passing through the layer of the water phase of thickness L_0 free of the droplets of the organic phase. After turning on the mixer the intensity I was measured of the light passing through the dispersion of the same thickness L_0. The measured voltages U_0 and U, corresponding to the intensities of the light I_0 and I, were recorded by the data logger **16** and punched on the paper tape.

The measurement of iodine transfer consisted of evaluation of the response of the absorbance to a step concentration change in the continuous phase recorded by the spectrophotometer. The reactor was filled with the water phase and the decalin phases of known compositions and volumes. The requested frequency of mixing was set and the dispersion was mixed during 1/2 up to 1 hour in order to reach the hydrodynamic equilibrium, which was monitored by measuring and recording the intensity of light passing through the dispersion. Simultaneously also the equilibrium composition distribution of iodine between both phases was being established. Having reached the hydrodynamic equilibrium the flow rate of the sampled water phase was set (6 to $14 . 10^{-8}$ m^3 s^{-1}) by the needle valve **20**. After flushing the separator of phases **9**, the tubing **17** and **19** and, the cell of the spectrophotometer by opening the valve **20**, a step change was effected in the continuous phase. Depending on the selected direction of the transfer a concentrated solution of potassium iodide (direction from the droplets), or an equimolar solution of iodine and potassium iodide (direction into the droplets) in the amount of $5 . 10^{-6}$ m^3 (5 ml) or exceptionally also $1·5 . 10^{-5}$ m^3 (15 ml) was injected into the space close to the mixer. Together with the injection of the sample the timer, controlling the printer of the spectrophotometer, providing for the recording of the absorbance of the flowing water phase at discrete time intervals, was actuated. The transient development of the absorbance was monitored on a connected line

TABLE II
Experimental conditions of iodine transfer across the flat interface

Flat direction of transfer	c_{A1}^{P} kmol m^{-3}	c_{T}^{P} kmol m^{-3}	c_{C2}^{P} kmol m^{-3}
From phase 1 into phase 2	$3·65 . 10^{-3}$ $1·73 . 10^{-3}$	0	0·1034 0·25 0·5
From phase 2 into phase 1	0	$5·7 . 10^{-3}$	$7·94 . 10^{-2}$

recorder. The volume flow rate of the sampled water phase was determined from the measurement of the time needed to fill a $5 . 10^{-6}$ m^3 (5 ml) measuring vessel. Reaching of the chemical equilibrium, signalled by a steady value of the absorbance, terminated the experiment. The sampling was stopped, the total volume of the sampled water phase was read off and the intensity of the light, I, was measured. After stopping the mixer and separation of the phases, the intensity of light, I_0, was measured. The content of the reactor was vacuumed out into a separation flask and the organic phase was regenerated. During cleaning, distilled water was forced into the reactor through a frit in order to prevent contact of the frit with the organic phase which might deteriorate the wettability of the frit. A total of 20 experiments of extraction of iodine into the water phase was performed under the conditions of comparable diffusion resistances at initial concentratons: $c_T^p = 0$ kmol m^{-3}, $c_{C2}^p = 0.074 - 0.1$ kmol m^{-3}, $c_{A1}^p = 0.6 - 2.0 . 10^{-2}$ kmol . . m^{-3}.

Under the conditions of dominating resistance in the continuous phase a total of 80 experiment was carried out. In one series of experiments the direction of transfer of iodine was induced from the dispersed phase into the continuous phase at the initial concentrations: $c_T^p = 0$ kmol m^{-3}, c_{C2}^p $0.2 - 2.5 . 10^{-2}$ kmol m^{-3}, $c_{A1}^p = 2.8 - 4.1 . 10^{-2}$ kmol m^{-3}, and in another series of experiments the direction of transfer was induced in the opposite direction: $c_T^p = 1.8 - 3.0$ . . 10^{-3} kmol m^{-3}, $c_{C2}^p = 3.0 - 5.0 . 10^{-3}$ kmol m^{-3}, $c_{A1}^p = 0$ kmol m^{-3}.

In individual series, the frequency of revolution of the impeller was varied $(4 - 6$ s$^{-1})$ as well as the volume hold-up of the dispersed phase $(0.055 - 0.33)$.

RESULTS

PROCESSING OF EXPERIMENTAL DATA

Equilibrium composition of iodine: During measurement of iodine distribution between both phases, equilibrium concentrations of iodine in the organic phase were obtained in dependence on the initial composition and the ratio of volumes of both phases. The values of the equilibrium constants, p, K, were determined by minimizing the sum of square deviations between the measured and calculated value of the equilibrium concentration of iodine in the organic phase. Equilibrium concentrations of iodine in the organic phase were computed from the balance on iodine by a method presented in ref.[2].

Transfer of iodine across the flat interface: The experiments on the transfer of iodine between both phases yielded discrete time dependence of concentration of iodine in the organic phase. A simultaneous processing of all experiments minimized the sum of square deviations between the measured and computed time profile of iodine concentration in the organic phase. Assuming that both phases, spare for the thin films on both sides of the interface, are perfectly mixed, the theoretical transient development of iodine concentration in the organic phase may be computed by integration of the following differential balance

$$dc_{A1}/dt = -J_A^+ A/V_1 \qquad (8)$$

with the initial condition $t = 0$, $c_{A1} = c_{A1}^p$.

The flux density J_A^+ in Eq. (8) was computed from Eq. (6) from the knowledge of the equilibrium constants, p, K, and the initial composition of both phases with the values $q_x = 1$. Minimization of the sum of square deviations of the measured and computed concentrations yielded values of the transfer coefficients for iodine in both phases.

Specific interfacial area in the dispersion: Since during the measurements of the intensity of the light by the photodiode the operating point was in the linear part of the characteristics of the photodiode, the specific interfacial surface α was determined from[5,6]

$$\alpha = 4 \ln \left(\overline{U}_0 / \overline{U} \right) / (X L_0) \tag{9}$$

using the mean values of the measured voltage of the photodiode.

Transfer of iodine in the dispersion: Under the given experimental configuration the continuous phase was sampled from the reactor at a constant volume flow rate, Q, where the concentration c_T was measured. Using the balance of iodine in the reactor with a uninterrupted withdrawal of the continuous phase, Eq. (8) was modified in such a manner that the transient development of the experimental concentration c_T was expressed in the form

$$dc_T/dt = \left(J_A^+ V_1 \alpha - Q c_T \right) / \left(V_2^p - Qt \right) \tag{10}$$

with the initial condition $t = 0$, $c_T = c_T^p$. The density flux J_A^+ was expressed from Eq. (6), with the ratios of diffusivities $q_x = 1$ and with the knowledge of the vector of initial concentrations c^p: c_{A1}^p, c_{C2}^p, c_T^p and the constants p, K. Eq. (10) was integrated numerically using the Runge–Kutta method. The result of integration was a time dependence of concentration $c_T(t, \Omega, \Theta)$, where Ω: $\{\alpha, Q, V_1, V_2^p, c^p\}$ was the vector of measured quantities and Θ: $\{k_{A1}, k_{A2}\}$ the vector of unknown structural parameters. In the configuration reactor-sampling device (separator + tubing)-analyzator, a significant distortion of the transferred information existed owing to the flow nonidealities. An impuls characteristic of the sampling device was modelled by a cascade on n ideal mixers of equal volume, V_M, with a plug flow cell of volume V_p in series as the probability density Γ − distribution in the form

$$g(t, Q, \Psi) = Q(Qt - V_p)^{n-1} \exp \left(-(Qt - V_p)/V_M \right) / (V_M^n \, \Gamma(n)), \tag{11}$$

where Ψ: $\{n, V_M, V_p\}$ is the vector of incidental parameters characteristic for the experimental arangement of the sampling device. The generalized impuls characteristic for the real sampling device has been carried out by changing from integer values of the parameter n to a real value while maintaining the functional relationship (11).

The time dependence of the computed concentration, c_{Tc}, at the measuring point was expressed by the following convolution integral

$$c_{Tc}(t, \mathbf{\Omega}, \mathbf{\Theta}, \mathbf{\Psi}) = \int_0^t c_T(\tau, \mathbf{\Omega}, \mathbf{\Theta}) \, g(t - \tau, Q, \mathbf{\Psi}) \, d\tau \qquad (12)$$

which was solved numerically.

Simultaneous evalutation of the incidental ($\mathbf{\Psi}$) and structural ($\mathbf{\Theta}$) parameters from a single experiment by means of Eq. (12) would lead to prohibitively large confidence intervals. Assuming the incidental parameters constant for the given arrangement of the sampling device, these parameters ($\mathbf{\Psi}$) were evaluated from independent experiments. In these experiments a step change was effected of the concentration c_T in the reactor without the organic phase. During evaluation of experimental results on mass transfer in the dispersion, the course of the concentration, c_T, in Eq. (12) was determined by solving the differential equation (10) and from known incidental parameters $\mathbf{\Psi}$. In both of these cases the vector of concentrations c_{Tc} was obtained by solving the convolution integral (12) for times t_i, corresponding to the instances of the automated sampling of the measured quantity, compared with the experimentally found vector of concentrations, c_{Tc}. Minimization of the sum of square deviations yielded optimum values of the unknown parameters.

MASS TRANSFER COEFFICIENTS

Processing of the equilibrium distribution data of iodine between the water and the organic phase in the investigated system provided the distribution coefficient of iodine, $p = 46.3$ and the equilibrium constant of the reaction (A), $K = 478.3 \, \mathrm{kmol}^{-1} \, \mathrm{m}^3$. The results of the kinetic measurements in the cell with flat interface yielded values of the iodine transfer coefficient in both phases, $k_{A1} = 1.17 \cdot 10^{-5} \, \mathrm{m \, s}^{-1}$ and $k_{A2} = 1.81 \cdot 10^{-5} \, \mathrm{m \, s}^{-1}$ under the assumption of $q_A = q_D = 1$. The agreement of the computed time dependence of iodine concentration with experimental data from extraction is illustrated in Fig. 2.

For the investigated range of the speed of revolution and hold-up of the dispersed phase in the reactor, the experimental specific interfacial surface ranged between 2 000 and 4 000 m^{-1}. Observed dependence on rpm was expressed as $\alpha \sim N^{1.8}$. The ratio of the specific interfacial surface for the same rpm at maximum and minimum hold-up was between 0.3 and 0.4.

The dependence of iodine transfer in the dispersion in the continuous phase on the hold-up was linear, while that on the rpm followed a power-law with an exponent over the rpm equalling 2.0. This result was expressed in the conventional form as

$$Sh = 9.2 \cdot 10^{-6}(1 + 2X) \, Re^2 \,. \qquad (13)$$

Fig. 3 illustrates a typical course of the measured response of the system to a step change of concentration in the reactor for both directions of iodine transfer, together with the computed response. The fit of the correlation (13) with the values computed from experiments is good. The largest deviation was less than 20% rel. The average relative error was 8·5% rel.

No significant dependence has been observed of iodine mass transfer coefficient in the dispersed phase on the rpm of the impeller or the hold-up of the organic phase. The mean value was evaluated of the coefficient of effective diffusivity in the recommended[7−10] expression for the calculation of the stationary value of the mass transfer coefficient in the droplets of dispersion as $\mathscr{K} = 3\cdot3 \pm 0\cdot6$. The adequancy of all models used for description of experimental data was in all cases statistically verified[11].

DISCUSSION

The equilibrium distribution of iodine between both phases was described by parameters p and K, their values being affected by composition of both phases. The value
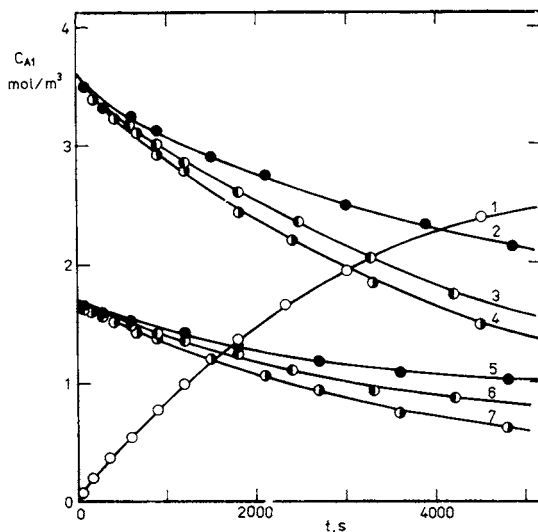
FIG. 2

Comparison of experimental and calculated iodine concentrations in the organic phase during transfer across the flat interface in both directions at various initial concentrations of potassium iodide in the water phase: $c_{C2}^{p} = 0\cdot0794$ kmol m^{-3}, ○, curve 1; $c_{C2}^{p} = 0\cdot1$ kmol m^{-3}, ●, curve 2 and 5; $c_{C2}^{p} = 0\cdot25$ kmol m^{-3}, ◑, curve 3 and 6; $c_{C2}^{p} = 0\cdot5$ kmol m^{-3}, ◐, curve 4 and 7

of K is slightly lower than that obtained for the water phase by Hudec[2] (495·7 kmol^{-1} . . m^3). The value of the distribution coefficient, p is a function of the used pair of liquids and for the decalin/water system no reference has been found in the literature.

The ratio of the mass transfer coefficients $k_{A1}/k_{A2} = 0·65$, evaluated from the kinetic experiments for the given ratios of diffusivities $q_A = q_D = 1$, is in good agreement with the values $\sqrt{(D_{A1}/D_{A2})} = 0·64$ calculated from experimental diffusivities. The kinetic experiments have confirmed the adequacy of the proposed functional form of the model of mass transfer across the flat interface with the values of the ratio of diffusivities $q_x = 1$ in the whole investigated concentration range with constant values of the mass transfer coefficient.

Numerical values of the specific interfacial surface were measured at various concentrations in both phases and hence the obtained results cannot be unambiguously correlated with N, and hold-up X. Even though the experimental data exhibit considerable scatter, the determined value of the approximate power-law dependence of α on N corresponds to the intensity of mixing, used in this work[11], in comparison with the value for the region of turbulent splitting of droplets[12].
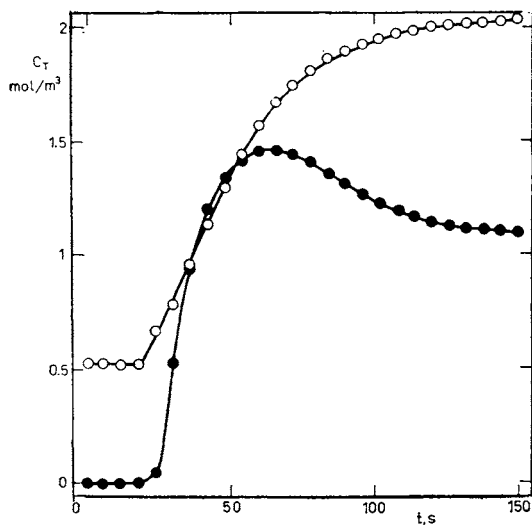

FIG. 3

Typical experimental and computed response of the system to a step concentration change in the dispersion with chemical reaction (plotted density of experimental points is half of the real density) ○ direction of transfer from the organic to water phase; ● direction of transfer from water to organic phase

With the aid of the proposed method[11], values have been obtained of the mass transfer coefficient in both phases in dependence on the speed of revolution of the impeller and the hold-up of the dispersed phase. It turned out that the mass transfer described by the pseudohomogeneous model with a simple expression for the enhancement factor, according to the film theory, appears satisfactory for the investigated system. The fit of the calculated and experimental data is illustrated in Fig. 3.

No significant trend has been observed in the investigated range of the speed of revolution of the impeller and the hold-up of the dispersed phase of the transfer coefficient k_{A1} and, accordingly, only a mean value of the coefficient of effective diffusivity has been evaluated. This value corresponds to the region of fully developed internal circulation within the droplet[8].

A comparison of evaluated transfer coefficients of iodine in the continuous phase with the values computed according to the expressions for the dissolution of solid particles[13−18] and for the transfer in the dispersion[19−23] showed a good agreement. The trend also observed in dependence on the speed of revolution of the impeller corresponds to that described in the literature[13~23]. The trend in the dependence on the hold-up was correlated in the form common for correlation[12] of the dependence of the specific interfacial surface on the hold-up. In the papers[20−21], the dependence of k_{A2} on the hold-up was expressed as a power expression of the type $k_{A2} \sim X^m$ with widely differing values of the exponent: $(m = 0.20 - 0.26)$ (ref.[20]) and $(m = -0.53)$ (ref.[21]). The correlation of our data in this manner yielded a value $m = 0.23$ in accord with ref.[20]. By analysis of the parametric sensitivity of the objective function, conditions have been found for a reliable evaluation of the mass transfer coefficient in both phases. In the given system the value of the overall resistance against the mass transfer is concentrated in the water phase and the objective function for the applicable concentration region is only little sensitive to the value of the transfer coefficient k_{A1}.

It may be concluded that the pseudohomogeneous model with the values of the parameters evaluated from experiments carried out following the proposed dynamic method sufficiently accurately describe the transfer of mass with an instantaneous reaction in the studied system.

LIST OF SYMBOLS

A	interfacial surface (m^2)
b_1	parameter $(kmol\ m^{-2}\ s^{-1})$
b_2	parameter $(kmol^2\ m^{-4}\ s^{-2})$
c	concentration $(kmol\ m^{-3})$
D	diffusivity $(m^2\ s^{-1})$
D_I	impeller diameter (m)
D_v	vessel diameter (m)
E	enhancement factor (l)

g	impuls characteristic (s^{-1})	
H	height of vessel (m)	
I, I_0	intensity of light $(W\,m^2)$	
J	flux density $(kmol\,m^{-2}\,s^{-1})$	
k	mass transfer coefficient $(m\,s^{-1})$	
K	equilibrium constant of chemical reaction (A) $(kmol^{-1}\,m^3)$	
L	length scale (m)	
L_0	length of optical path (m)	
m	exponent	
n	number of perfect mixers	
N	frequency of revolution of impeller (s^{-1})	
p	distribution coefficient (1)	
$q_x = D_{C2}/D_{x2}$	ratio of diffusivities, $x = A, D$ (l)	
Q	volume flow rate $(m^3\,s^{-1})$	
$Re = ND_1^2/\gamma$	Reynolds number in phase 2 (1)	
$Sh = kD_1/D$	Sherwood number in phase 2 (l)	
t	time (s)	
U, U_0	voltage (V)	
V	volume (m^3)	
X	volume hold-up (l)	
α	specific interfacial area A/V_1 (m^{-1})	
Γ	Gamma function (l)	
ε	molar absorptivity $(kmol^{-1}\,m^2)$	
$\boldsymbol{\Theta}$	vector of kinetic parameters	
$\mathcal{H}$	coefficient of effective diffusivity (l)	
ν	viscosity $(m^2\,s^{-1})$	
λ	wave-length (m)	
ϱ	density $(kg\,m^{-3})$	
σ	interfacial tension $(N\,m^{-1})$	
$\boldsymbol{\Psi}$	vector of parameters of sampling device	
$\boldsymbol{\Omega}$	vector of measured quantities	

Subscripts

A	iodine
C	iodide
D	triiodide
1	phase 1 organic
2	phase 2 water
T	total concentration in phase 2 of species A + D
e	experimental
c	calculated
P	plug flow section
M	ideally mixed section

Superscripts

+	related to interface
—	mean value
p	initial value

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