THE EFFECT OF INTERFACIAL CONVECTION ON MASS TRANSFER IN LIQUID–LIQUID SYSTEMS

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The effect of convective flows is examined on the interfacial mass transfer rate in the succinic acid–n-butanol–water system. The experiments were carried out in a mixed cell with flat interface under conditions of the succinic acid transfer being accompanied by the transfer of one of the solvents. The experiments have revealed a significant effect of transfer of another component on the rate of extraction of succinic acid. The mass transfer rate under these conditions can be well described by the model based on the theory of diffusion accounting for the interfacial convective flux.

In the calculations of extraction processes the mass transfer rate of the solute is commonly assumed to be proportional to the concentration difference between the bulk of the phase and the interface and the rate of transfer of other components is assumed to have no effect. If it is further assumed that the interface offers no resistance to mass transfer, the familar expression for the flux of the transferred component across the interface results

$$N_i = K_{xi}(x_i - y_i/m_i) = k_{xi}(x_i - x_i^+) = k_{yi}(y_i^+ - y_i). \qquad (1)$$

The over-all coefficient of mass transfer for constant coefficients k_{xi} and k_{yi} depends only on the distribution coefficient m_i

$$1/K_{xi} = 1/k_{xi} + 1/m_i k_{yi}. \qquad (2)$$

The simplifying assumptions used restrict the justification of the above simple expression only to cases when the mass fluxes of individual components across the interface are relatively small. In real extraction systems, however, the assumption of small interfacial fluxes is often not met. It is particularly so if the transport of the extracted solute in a certain part of the extraction column is accompanied by saturation of one of the phases by the other partly miscible solvent, or in case of extraction from concentrated solutions and multicomponent extractions usually in the

region around the feed of the reflux. Neglected convective flux across the interface may often bring about considerable errors of estimating the size of the equipment or the degree of separation.

The aim of this work is to experimentally verify the effect of the convective flux on the mass transfer rate of the extracted component between two liquid phases and to compare the results with the theoretical solution. The system chosen for measurement was that of succinic acid–n-butanol–water. Owing to high mutual solubility of the solvents one can achieve marked interfacial flux. In the batchwise experiments we observed the rate of transfer of succinic acid in both directions accompanied either co- or counter-currently with the transfer of one of the solvents.

THEORETICAL

In accord with the theory of diffusion the mass flux of the solute from the interface into the bulk of the phase x may be expressed by the following expression

$$N_{xi} = \bar{k}_{xi}(x_i^+ - x_i) + x_i^+ \sum_j N_{xj}, \quad i = 1, 2, \ldots, n; \ j = 1, 2, \ldots, n, \qquad (3)$$

where $\bar{k}_{xi}$ generally depends on the rate of mass transfer. This dependence is accounted for by a correction factor, Φ_x, as

$$\bar{k}_{xi} = \Phi_x k_{xi}, \qquad (4)$$

where k_{xi} is the mass transfer coefficient independent of the mass transfer rate.

Bird[1] presents relationships for the correction factor derived both on the basis of the film theory

$$\Phi_x = \left(\sum_j N_{xj}/k_{xj}\right) / \left(\exp\left(\sum_j N_{xj}/k_{xj}\right) - 1\right), \qquad (5a)$$

as well as the penetration theory

$$\Phi_x = \exp\left(-\left(\sum_j N_{xj}/k_{xj}\right)^2/\pi\right) / \left(1 + \mathrm{erf}\left(\left(\sum_j N_{xj}/k_{xj}\right)/\sqrt{\pi}\right)\right). \qquad (5b)$$

Similarly one can write for the mass flux of the solute from the interface into the bulk of the phase y the following relations

$$N_{yi} = \bar{k}_{yi}(y_i^+ - y_i) + y^+ \sum_j N_{yi}, \qquad (6)$$

$$\bar{k}_{yi} = \Phi_y k_{yi}, \qquad (7)$$

$$\Phi_y = \left(\sum_j N_{yj}/k_{yj}\right) / \left(\exp\left(\sum_j N_{yj}/k_{yj}\right) - 1\right), \qquad (8a)$$

or

$$\Phi_y = \exp\left(-\left(\sum_j N_{yj}/k_{yj}\right)^2/\pi\right)\Big/\left(1 + \operatorname{erf}\left(\left(\sum_j N_{yj}/k_{yj}\right)/\sqrt{\pi}\right)\right). \qquad (8b)$$

On taking the direction of the mass flux, N_i, from phase (x) into (y) as positive, *i.e.*

$$N_i = -N_{xi} = N_{yi}, \qquad (9)$$

one obtains from Eqs (3), (6) and (9) the following equations for the concentrations at the interface

$$x_i^+ = \left(k_{xi}x_i - N_i\right)\Big/\left(k_{xi} - \sum_j N_j\right), \quad y_i^+ = \left(k_{yi}y_i + N_i\right)\Big/\left(k_{yi} + \sum_j N_j\right). \quad (10), (11)$$

The assumption of equilibrium on the interface may be expressed as

$$y_i^+ = m_i x_i^+, \qquad (12)$$

where the distribution coefficient, m_i, is generally a function of $(n - 2)$ concentrations at the interface. On combining Eqs (10) through (12) one obtains

$$N_i = \frac{x_i - y_i/m_i + \left(x_i/k_{yi} + y_i/m_i k_{xi}\right)\sum_j N_j}{1/k_{xi} + 1/m_i k_{yi} + \left(1/k_{xi}k_{yi}\right)\left(m_i - 1\right)\sum_j N_j}. \qquad (13)$$

Comparing Eqs (1) and (13) the expression for the over-all mass transfer coefficient can be written as

$$K_{xi} = \frac{1 + \left[\left(x_i/k_{yi} + y_i/m_i k_{xi}\right)/\left(x_i - y_i/m_i\right)\right]\sum_j N_j}{1/k_{xi} + 1/m_i k_{yi} + \left(1/k_{xi}k_{yi}\right)\left(m_i - 1\right)\sum_j N_j}. \qquad (14)$$

The last expression changes into that given in Eq. (2) provided the fluxes of individual components are negligible $(N_j \to 0)$.

EXPERIMENTAL

Succinic acid used for experiments was of *p.a.* grade; *p.a.* butanol was redistilled. Distilled water was used. The composition of the binary mixture n-butanol–water was analyzed by refractometry; ternary mixtures were analyzed by titration on succinid acid, by chromatography on n-butanol and on water in the organic phase by Karl Fischer's method.

The measurement of the mass transfer rates was performed in a mixed cell with 40 cm^2 of flat interface in the arrangement due to Procházka and Bulička[2]. All experiments were carried out

at 20°C and identical rpm of the impeller in both phases equalling 250 ± 3 min^{-1}. The experiment was started by filling the cell with 430 ml of water and 430 ml of the organic phase and turning on the impellers. First sample from one or both phases was taken after 10 minutes. Additional samples were taken after 5, 10, 15, 25, 40, 90 and 120 minutes. In order to preserve constant hydrodynamic conditions during the experiment the volumes had to be maintained constant, particularly during experiments exhibiting large volume changes of the phases caused by interfacial transport of one of the solvents. This was achieved on the side of the phase increasing its volume by withdrawing appropriate amount of sample W_{xk}, or W_{yk} at a time t_k; on the side of the phase diminishing its volume by adding pure solvent F_{xk}, or F_{yk} at a time t_k to reach the original volume.

The samples taken in experiments with three-component system were analyzed on succinic acid; the content of solvent was determined only exceptionally.

A total of 9 series of tests were performed each consisting of 3 repeated experiments. In experimental runs designated A—C we observed the transfer rates in the binary system n-butanol–water, in D—F series the transfer of succinic acid from water to the organic phase, in G—J series the transfer of succinic acid from the organic to water phase.

In the majority of experiments the initial concentration of succinic acid in the water phase was made zero; in the other phase equal 2% by mass. Several experiments were carried out with the initial concentration of succinic acid 1% by mass in both phases. During the experiment (120 minutes) the system reached about 80—90% of the equilibrium values.

RESULTS

The data on the transient extraction were processed by an integral method evaluating the mass transfer coefficients as parameters of differential equations with the aim to match (the least sum of square deviations) the calculated and experimental transient development of the concentration. For this purpose it was necessary to describe the equilibrium of the succinic acid(1)–water(2)–n-butanol(3) system in terms of the distribution coefficients, m_i, defining by Eq. (12) the distribution of individual species between the organic (y) and the water (x) phase.

Using the published data[3,4] the equilibrium distribution of succinic acid within the concentration range $0-6\%$ mass was correlated by the following power expression

$$\log m_i = A_i + B_i x_1 + C_i x_1^2. \tag{15}$$

Numerical values of the parameters A_i, B_i, C_i are given in Table I. A comparison of the fitted equation with the published data is shown in Fig. 1, indicating a satisfactory agreement.

The mass transfer of the solute during batchwise extraction accounting for sampling and readjusting the volumes of the phases is described by the following differential equations

$$\frac{\mathrm{d}g_{ix}}{\mathrm{d}t} = -N_i A + \frac{\mathrm{d}}{\mathrm{d}t}\left(F_{xk}\,\delta(t_k)\,x_{Fi}\right) - \frac{\mathrm{d}}{\mathrm{d}t}\left(W_{xk}\,\delta(t_k)\,x_i\right), \tag{16}$$

$$\frac{dg_{iy}}{dt} = N_i A + \frac{d}{dt}\left(F_{yk}\,\delta(t_k)\,y_{Fi}\right) - \frac{d}{dt}\left(W_{yk}\delta(t_k)\,y_i\right). \tag{17}$$

where

$$x_i = g_{ix}/\sum_j g_{jx}\,, \quad y_i = g_{iy}/\sum_j g_{jy} \tag{18}, (19)$$

with the boundary conditions

$$t = 0\,, \quad g_{ix} = g_{ix}^0\,, \quad g_{iy} = g_{iy}^0\,. \tag{20}$$

In the numerical routine solving the differential Eqs (16) and (17), the mass fluxes of the components, N_i, were computed in two ways: a) A way incorporating the effect of the convective flow, $i.e.$ by solving the set of Eqs (4), $(5a)$, (7), $(8a)$, (10), (12),
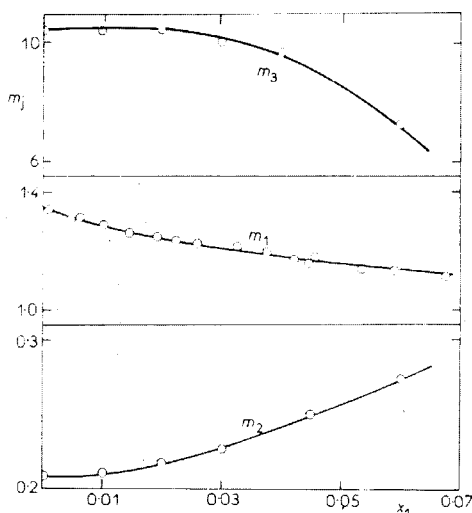

FIG. 1

A Plot of Distribution Coefficients *versus* Mass Fraction of Succinic Acid in Water Phase for Succinic Acid(1)–Water(2)–n-Butanol(3) System

——— Eq. (15), ○ experimental points[3,4].

TABLE I

Constants of Equilibrium Equation in System Succinic Acid(1)–Water(2)–n-Butanol(3) at $20°C$

Component	A_i	B_i	C_i
1	0·1271	1·752	9·18
2	−0·6815	0·438	25·62
3	1·0150	2·053	78·32

(13). Whether the correction factors Φ_x and Φ_y were computed from Eqs *(5a)* *(8a)*, derived from the film theory, or from Eqs *(5b)*, *(8b)*, derived from the penetration theory, turned out to be immaterial for the computed time course of the concentrations within the system. *b)* A way neglecting the effect of convection. *i.e.* from Eqs *(1)*, *(2)* and *(12)*.

TABLE II

Mass Transfer Coefficients for n-Butanol–Water System

Exp.	Initial conc. % by mass		Direction of transfer[a]	$k_{x3}^0 \cdot 10^3$ cm/s	$k_{y2}^0 \cdot 10^3$ cm/s
	y_2	x_3			
A	19·2	0	B* → W	3·44	—
				3·50	—
				3·56	—
B	0	7·8	B ← W*	—	2·30
				—	2·42
				—	2·33
C	9·0	0	B ⇄ W	3·40	2·35
				3·55	2·44
				3·43	2·40

[a] B organic phase, W water phase, W* Saturated phase.

The time course of the concentrations of all species was in both cases computed by the Runge–Kutta method using the known experimental conditions at the instant $t = 0$, *i.e.* g_{ix}^0, g_{iy}^0, the known amount and composition of the feed F_{xk}, F_{yk}, x_{Fk}, y_{Fk}, known volumes of withdrawn samples W_{xk}, W_{yk} at time t_k and for selected values of the coefficients k_{xi}^0, k_{yi}^0. The mass transfer coefficients k_{xi} and k_{yi} were evaluated from the relations $k_{xi} = k_{xi}^0 \varrho_x$, $k_{yi} = k_{yi}^0 \varrho_y$, where the density of the phases was computed as the weighted mean of the densities of pure components.

Iterative methods of calculation served to find the optimum values of the coefficients k_{xi}^0, k_{yi}^0 utilizing the method approximating the region about the minimum successively by a parabola[5].

The measurements with the binary system n-butanol–water were first processed by method *a)* to obtain the coefficients k_{x2}^0, k_{x3}^0, k_{y2}^0 and k_{y3}^0 on condition that in the given phase the coefficients of both components take on the same value $k_{x2}^0 = k_{x3}^0$ and $k_{y2}^0 = k_{y3}^0$. As it is apparent from the data in Table II the values of the coeffi-

cients obtained by the method accounting for the convective flux are practically independent of mutual initial saturation of the solvents. Using these results the values taken for the experiments with the transfer of succinic acid in the ternary system were: $k_{x2}^0 = k_{x3}^0 = 0.00347$ cm/s and $k_{y2}^0 = k_{y3}^0 = 0.00237$ cm/s.

The mass transfer coefficients for succinic acid were evaluated on assumption that the ratio of the coefficients in the water and the organic phase is for all components identical, *i.e.*: $k_{x1}^0/k_{y1}^0 = 0.00347/0.00237 = 1.46$. The values of the coefficient k_{x1}^0 by the method *a*) accounting for the effect of convection, and *b*) neglecting the convective flux are summarized in Table III. The C−E tests concern the transport of succinic acid from water to organic phase, F−H tests the transfer from organic to water phase. The last column of the table indicates the mean deviation of the mass transfer coefficient for multicomponent transport from the one-component one.

From Table III it is apparent that the method *a*) leads to values of the coefficient of mass transfer k_{x1} practically independent of the transfer of another component.

TABLE III

Mass Transfer Coefficient for Succinic Acid

Exp.	Direction of transfer	Initial conc. % by mass				$k_{x1} \cdot 10^3$ cm/s		Mean deviation	
		x_1	x_3	y_1	y_2	*a*	*b*	*a*	*b*
C	$x \xrightarrow{1} y$	2·0	7·7	0·0	19·2	2·82 2·85 2·80	2·85 2·88 2·83	—	—
D	$x \xrightrightarrows[2]{1} y$	2·0	7·7	0·0	0·0	2·85 2·81 2·94	3·33 3·31 3·45	+0·5	+18·7
E	$x \xleftrightarrows[3]{1} y$	2·0	0·0	0·0	19·2	2·70 2·84 2·86	2·45 2·58 2·59	−1·9	−10·2
F	$x \xleftarrow{1} y$	0·0	7·8	2·0	18·8	3·34 3·24 3·47	3·35 3·25 3·49	—	—
G	$x \xleftleftarrows[3]{1} y$	0·0	0·0	2·0	18·8	3·40 3·33 3·26	3·75 3·69 3·56	−2·0	+9·0
H	$x \xleftrightarrows[2]{1} y$	0·0	7·8	2·0	0·0	3·32 3·45 3·37	2·83 2·90 2·86	+1·0	−14·9

The values obtained by the method b), which incorporates the effect of convective flux, are in case of cocurrent transfer significantly higher, for counter-current transfer, on the contrary, significantly lower in comparison with the one-component transport. This applies both to the transfer from the water to the organic phase as well as for the opposite dirrection. The mean mass transfer coefficient obtained for the former case was $k_{x1} = 2.83 \cdot 10^{-3}$ cm/s, for the latter $3.35 \cdot 10^{-3}$ cm/s. The difference of these averages is probably caused by the dependence of the diffusivity of succinic acid on concentration. The fact that the mass transfer coefficient of the solute evaluated by the method a) is independent of the direction of the interfacial transfer demonstrates clearly the fact that the model used described correctly the effect of convection on the rate of extraction. The data in the last columns of Table III indicate that the deviation of the mass transfer rate obtained from the simplified model may reach under the given conditions as much as 20%. This deviation, of course, depends on the relative magnitude of the diffusional flux of the solute and total convective flux of all components. The effect will be thus most marked under situations when the concentration of the extracted solute is close to equilibrium. For instance, in the system considered and concentration of succinic acid 1% vol. in both phases under simultaneous transfer of one of the solvents the error of determining the mass flux due to neglected convection may reach up to 80%.

LIST OF SYMBOLS

A	interfacial area
F	feed
g	mass amount of component
k	mass transfer coefficient
k^0	mass transfer coefficient
m	distribution coefficient
n	number of components
N	mass flux
t	time
x	concentration of solute in water phase
x^+	concentration of solute in water phase on interface
y	concentration of solute in organic phase
y^+	concentration of solute in organic phase on interface
W	amount of sample
$\delta(t_k)$	Kronecker delta
Φ	correction factor on convective flux
ϱ	density

Subscripts

i, j	subscript for component
x, y	subscript for phase

REFERENCES

1. Bird R. P., Stewart W. E., Lighfoot E. N.: *Transport Phenomena*. Wiley, New York 1965.
2. Procházka J., Bulička J.: *Proceedings of International Solvent Extraction Conference*, Haag 1971.
3. Pavasovič V., Peruničič M., Míšek T.: Presented on the III-rd CHISA Congress, Prague, October 1972.
4. Hill A. E., Malisoff W. M.: J. Am. Chem. Soc. *48*, 918 (1926).
5. Dudnikov J.: *Postrojenie Matematičeskich Modelej Chimiko-Technologičeskich Objektov*. Chimija, Leningrad 1970.

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