INTERFACIAL INSTABILITY OF SOME HETEROGENEOUS LIQUID SYSTEMS

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Diffusion-induced interfacial instability has been examined for four ternary liquid–liquid systems. Quiescent systems have been studied by the schlieren technique. Under the forced turbulence of the phases the effect has been investigated of the instability on the mass transfer rate of the transported solute. The results of the observations in quiescent systems have been compared with the theoretical prediction following Sternling and Scriven. The results of the measurement of the mass transfer rates after all transients due to instability have died out have been confronted with the values computed according to the earlier published relations.

Heterogeneous systems of imperfectly miscible fluids may exhibit spontaneous motion of the interface induced either by diffusion (the so-called Marangoni effect) or by heat transfer. A comprehensive review on the Marangoni effect and the consequences of its existence has been published by Sawistowski[1]. From the papers quoted in this review those of major concern in the present study are: The theoretical paper of Sternling and Scriven[2] who proposed a two-dimensional mathematical model describing the flow induced by small perturbations in an originally quiescent system of two fluid phases with a linear concentration field of the solute. Various types of instabilities have been studied and criteria developed to predict the type of instability expected. Orell and Westwater[3], Linde and coworkers[4,5] and Sawistowski and coworkers[6,7] using the schlieren technique examined stability of a plane interface and of droplets experiencing diffusion in various systems. Linde and coworkers[8–10] and Sawistowski and coworkers[11] studied some aspects of the Marangoni effect affecting the rate of diffusion under the forced turbulence of phases. In our previous papers[12–14] theoretical model of the mass transfer was developed assuming a stable interface. Its validity was verified by measuring the rate of mutual dissolution in partially miscible binary systems in a stirred cell of new design. The resulting relation for partial mass transfer coefficient takes the form

$$\mathrm{Sh}_i = \varkappa\, \mathrm{Sc}_i^{1/2}\, \mathrm{Re}_i^{3/4}\, \Psi_{ij}\,, \tag{1}$$

where

$$\psi_{ij} = \left(\frac{1 + (n_j/n_i)^3\,(d_j/d_i)^2\,(\varrho_j/\varrho_i)\,(\nu_j/\nu_i)^{1/2}}{1 + (\varrho_j/\varrho_i)\,(\nu_j/\nu_i)^{3/2}}\right)^{1/4},$$

$\varkappa$ is an empirical constant depending on the geometry of the mixed cell; its value for the cell used is 0·06. This work is a continuation of the research of the kinetics of diffusion between two liquid phases under the forced turbulence.

The aim of this work is the study of interfacial instability of some ternary systems and its effect on the kinetics of diffusion in the stirred cell. Eq. (*1*) represents a reference relation for the calculation of the kinetics of a system with identical physical properties which does not display any interfacial instability.

EXPERIMENTAL

The liquid systems used. The folowing four systems were investigated: *1*) toluene–acetone–water, *2*) n-butanol–succinic acid–water, *3*) methyl isobutyl ketone(MIBK)–acetic acid–water, *4*) tetrachloromethane–acetone–water. The first three systems were chosen by the working party "Distillation, Absorption and Extraction" of the "European Federation of Chemical Engineers" as reference systems for studies of liquid–liquid extraction. Physical properties of the examined systems are shown in Table I. These values apply to mutually saturated systems and zero concentration of the solute.

All components of investigated systems were of *p.a.* purity grade. The solvents and water were twice distilled before use; water with addition of potassium permanganate, toluene from a mixture with methanole. The concentration of acetone in the water and the organic phases was determined by refractometry. The concentration of acids in the water phase was determined by titration using potassium hydroxide and phenolphthalein; in the organic phase by potentiometric titration using sodium methoxide in pyridine–methanol solution.

All measurements were taken at 20°C with the third component (solute) being transferred between mutually saturated solvents and the initial concentration of the transferred solute being zero or 5% in the phases. The instabilities at the interface between quiescent liquids were observed by the schlieren technique using a Zeiss Jena schlieren instrument with an 80 mm in diameter observation field. The experiments included observation of the behaviour of a droplet immersed

TABLE I

Physical Properties of the Systems Used at 20°C (mutually saturated phases in the absence of transferred component)[15,16,17,18]

System	Phase	ϱ g/cm^3	μ . 10^2 g/cm.s	D . 10^5 cm^2/s	σ dyn/cm	dσ/dc
Toluene–acetone–water	w	0·9982	0·963	1·15	36·0	−1·76
	o	0·8652	0·584	2·79		
n-Butanol–succinic	w	0·986	1·469	0·58	1·62	−0·17
acid–water	o	0·847	3·480	0·23		
MIBK–acetic	w	0·9961	1·088	1·07	10·7	−0·54
acid–water	o	0·8045	0·769	1·42		
Tetrachloromethane	w	0·9982	0·963	1·16	43	—
–acetone–water	o	1·594	0·965	1·86		

in the second phase as well as the phases separated by a plane interface. The droplet was always formed by the phase out of which the diffusion took place.

The rate of mass transfer under the forced turbulence was measured in a stirred cell described earlier[14]. It can be shown that under the batch operation and perfect mixing of the phases the time dependence of concentration of the diffusing solute can be described by:

$$\lg (c_w - \beta) = -\gamma K_w \tau + B\,, \tag{2}$$

where

$$\beta = \frac{G_0}{G_0 + mG_w}\left(\frac{mG_w}{G_0}\,c_w^0 + mc_0^0 + q\right),$$

$$\gamma = \frac{G_0 + mG_w}{G_0 G_w}\,A\varrho_w\,.$$

For a linear distribution and in the absence of the Marangoni effect the overall coefficient of mass transfer is independent of concentration and concentration driving force (assuming physical extraction). Eq. (*2*) then represents a straight line in semilog coordinates and the Marangoni effect should be detected as a deviation from the straight line because this effect intensifies with increasing driving force.

TABLE II

Behaviour of Interface for the Systems Studied

System	Direction of transfer	Existence of interfacial turbulence			
		Sternling and Sriven	droplet	flat interface	mixed cell
Toluene–acetone–water	w—o	yes	strong	strong	none
	o—w	no	weak	none	none
n-Butanol–succinic acid–water	w—o	no	none	none	none
	o—w	yes	weak-rapidly decaying	strong	none
MIBK–acetic acid–water	w—o	yes	weak	none	none
	o—w	no	strong	medium	exists
Tetrachloromethane–acetone–water	w—o	yes	strong	none	exists
	o—w	no	none	strong	exists

RESULTS

The qualitative results of this study are summarized in Table II. For comparison the table shows also predictions of the interfacial behaviour made according to Sternling and Scriven[2]. The corresponding schlieren pictures are shown in Figs 1–4*.

Fig. 5 shows a typical example of mass transfer transients in the mixed cell for systems 1–4 and both directions of the transfer. Qualitative assessment whether these dependences deviate from the straight course is indicated in the last column of Table II. The values of the overall mass transfer coefficients relating to the water phase, K_w, are summarized in Table III. In those cases where the dependence was not linear we *a*) determined the value $K_{w,\mathrm{lin}}$ related to the region free of the effect of interfacial activity and *b*) estimated the maximum value, $K_{W,\max}$, corresponding to the initial maximum concentration gradient. At least two measurements at different rpm's were carried out for each system and each direction of transfer keeping the ratio of rpm's, n_W/n_0, equal unity. The physical constants shown in Table I were used to compute the partial mass transfer coefficients, k_w and k_0, from Eq. (*1*) and these in turn served, with the aid of the linearized distribution curve:

$$c_W^* = mc_0^* + q \qquad (3)$$

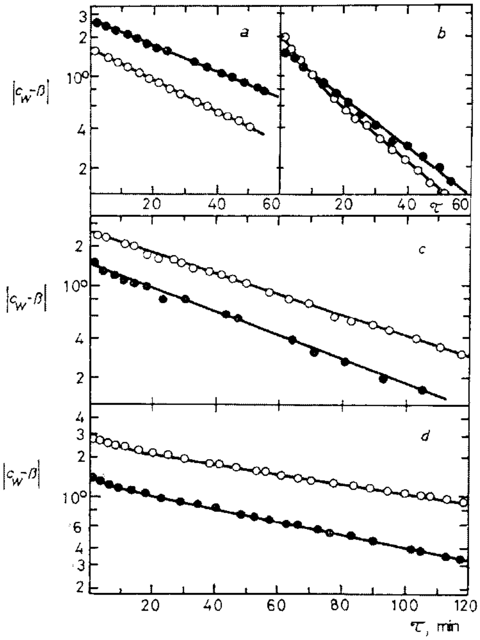

FIG. 5

Mass Transfer Rate in Mixed Cell

a System *2*, *b* system *3*, *c* system *1*, *d* system *4*, ● from water to organic phase, ○ from organic to water phase.

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* See insert facing p. 3186.

TABLE III

Results of Measurements in the Mixed Cell

System	n s^{-1}	$K_{w\,exp}$. 10^4 cm/s	$(K_{w\,exp}/n^{3/4})$. 10^4	k_w . 10^3 cm/s	k_0 . 10^3 cm/s	$K_{w\,theor.}$. 10^4	$\Delta c_{w\,krit.}$ g/100 g solv.
water to organic phase							
Toluene–acetone–water	3·23	4·92	2·04	3·44	5·35	17·2	
	4·31	6·70	2·23	4·26	6·64	21·3	
	5·93	8·70	2·31	5·41	8·43	27·0	
	8·08	12·20	2·55	6·83	10·64	34·1	
equilibrium: $c_w = 1·56\ c_0$							
organic phase to water							
	4·31	5·89	1·97	4·26	6·64	24·5	
	5·93	8·90	2·36	5·41	8·43	31·3	
	8·08	12·20	2·55	6·83	10·64	39·5	
equilibrium: $c_w = 1·1363\ c_0 + 0·6879$							
water to organic phase							
n-Butanol–succinic acid–water	4·31	10·6	3·53	2·20	1·38	9·7	
	5·93	13·7	3·62	2·80	1·75	12·3	
equilibrium: $c_w = 0·7984\ c_0 - 0·0040$							
organic phase to water							
	4·31	14·8	4·59	2·20	1·38	9·1	
	5·93	16·5	4·33	2·80	1·75	11·6	
equilibrium: $c_w = 0·8905\ c_0 - 1·2654$							
water to organic phase							
MIBK–acetic acid–water	4·31	16·2	5·40	3·90	4·50	15·8	
	5·93	17·5	4·59	4·95	5·71	20·0	
	8·08	25·0	5·20	6·25	7·21	25·3	
equilibrium: $c_w = 1·6954\ c_0$							
organic phase to water							
	4·31	16·7	5·60	3·90	4·50	17·9	0·95
	5·93	20·7	5·45	4·95	5·71	22·7	1·47
	8·08	27·3	5·67	6·25	7·21	28·6	1·02
equilibrium: $c_w = 1·3624\ c_0 + 0·7386$							
Tetrachloromethane–acetone–water	4·31	3·90	1·30	4·39	5·56	10·5	4·0
	5·93	5·20	1·37	5·57	7·06	13·3	3·5
	8·08	7·40	1·54	7·03	16·8	16·8	3·7
equilibrium: $c_w = 4·036\ c_0 + 0·030$							
organic phase to water							
	4·31	4·80	1·60	4·39	5·56	14·9	5·0
	5·93	5·60	1·47	5·57	7·06	18·9	5·2
	8·08	6·00	1·25	7·03	8·90	23·9	6·7
equilibrium: $c_w = 2·461\ c_0 + 2·000$							

to compute the theoretical value of the overall mass transfer coefficient:

$$K_{\mathrm{W,theor}} = \left(\frac{1}{k_{\mathrm{W}}} + \frac{m}{k_{\mathrm{O}}}\right)^{-1} . \tag{4}$$

Table III shows the values of k_{W}, k_{O}, $K_{\mathrm{W,theor}}$, the distribution constants m and q and the ratio $K_{\mathrm{W,exp}}/n^{3/4}$ expressing the dependence of the overall mass transfer coefficient on rpm.

DISCUSSION

Evaluating the intensity of interfacial activity from the schlieren pictures it must be considered that the intensity of the effect depends on the extent of the region affected by the induced convection, size of the turbulent elements (smaller size suggests higher intensity of turbulence) and, finally, the degree of deformation of the interface. Misleading may be evaluation on the basis of the contrast of the striae as it depends also on the magnitude of the gradients of the refractive index which are in turn proportional to the difference of the refractive indices of the solvent alone and that containing the maximum concentration of the solute. This phenomenon becomes effective in our cases for system 3 where the difference of the refractive indices for solute concentration 0 and 5% in the water phase equals 0·0032, in the organic phase 0·0004, *i.e.* by almost an order of magnitude less. This may explain why the structure of the striae near the droplet surface during the transfer from the water to the organic phase is so indistinct. The faintness of the structure in the organic phase near the plane interface may have the same reason.

The result of observations of interfacial instability in the originally quiescent phases may be summarized as follows: The behaviour of the interface on droplets essentially comports with the prediction following from the theoretical criteria of Sternling and Scriven. The only exception to this is the behaviour of the system MIBK–acetic acid–water. In this case, however, one has to consider the significantly weaker concentration dependence of the refractive index in the organic in comparison with the water phase as has been mentioned above.

The observation of the plane interface between two originally quiescent phases indicates that in all systems investigated the behaviour of the interface is strongly affected by mass-transfer-induced density gradient. Interfacial turbulence has been observed in all systems only in one direction of the transfer where gravitational convection due to the mass transfer appeared. While the theoretical model considers only small concentration differences, small impulses and neglects also the gravity induced density differences, our systems experience intensive interfacial concentration disturbances caused by concentration-difference-induced natural convection.

These disturbances then bring about intensive interfacial turbulence. In the opposite direction of the transfer, on the contrary, the intensity of transfer is damped by the gravity forces and the interfacial turbulence in none of the systems appears.

A rather surprising finding is the weak activity of the system 2. The explanation probably rests in the exceptionally low value of $d\sigma/dc$ as may be apparent from Table I. The relatively intensive turbulence on transfer from the organic to the water phase on the plane interface is apparently induced by gravitational instability.

Under the forced turbulence in the stirred cell the interfacial turbulence appeared only in system 3 on transfer from the organic to the water phase and in system 4 on transfer in both directions. In all these cases the estimated value $K_{W,max}$ exceeded K_W in the linear region free of the effect of interfacial turbulence by a factor of two to three. The measurements included the critical driving force at which the instability seems to disappear. These values, shown in Table III, indicate no effect of the frequency of revolution of the impeller.

In cases where on the originally quiescent interface the interfacial turbulence appeared but did not exist during measurement in the mixed cell, another schlieren observation was made with the used solvents from the cell experiment in order to detect eventual contamination of the substances in the cell. In no case, however, any deviations from the behaviour of the pure solvents were detected.

A comparison of the measured coefficients of overall mass transfer with the computed coefficients ($K_{W,theor}$) as these appear in Table III indicates deviations particularly in both systems with the transfer of acetone. Experimental values of K_w are always lower than the calculated ones which may be caused by a slow reaction of the transferred solute at the interface. At the same time it is apparent from Table I that both mentioned systems significantly differ from the rest in the higher value of σ which does not appear in the correlation (*1*).

LIST OF SYMBOLS

A	interfacial area
B	integration constant in Eq. (*2*)
c	concentration
c^0	initial concentration
d	diameter of impeller
D	diffusivity
e^2	v_w/v_0
G	mass of solvent
K	overall mass transfer coefficient
k	mass transfer coefficient
m	slope of linearized equilibrium curve
n	frequency of revolution of impeller (rpm)
q	abscissa of linearized equilibrium curve
$r^2 =$	D_w/D_0

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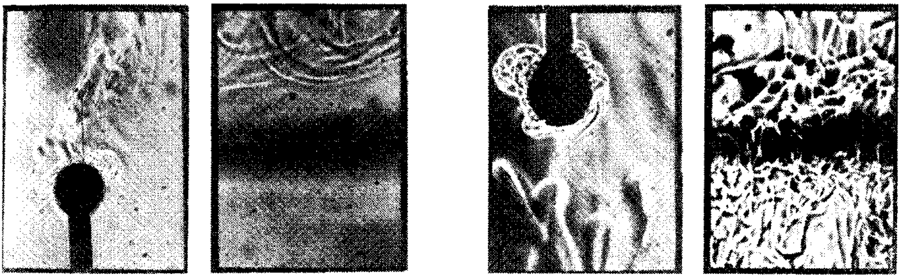

FIG. 1

Diffusion of Acetone

a From toluene to water, *b* from water to toluene.

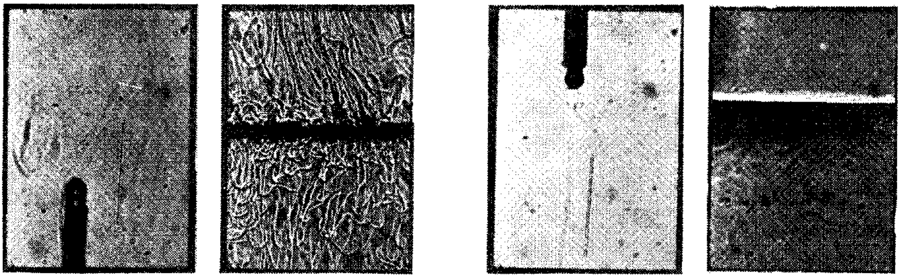

FIG. 2

Diffusion of Succinic Acid

a From n-butanol to water, *b* from water to n-butanol.

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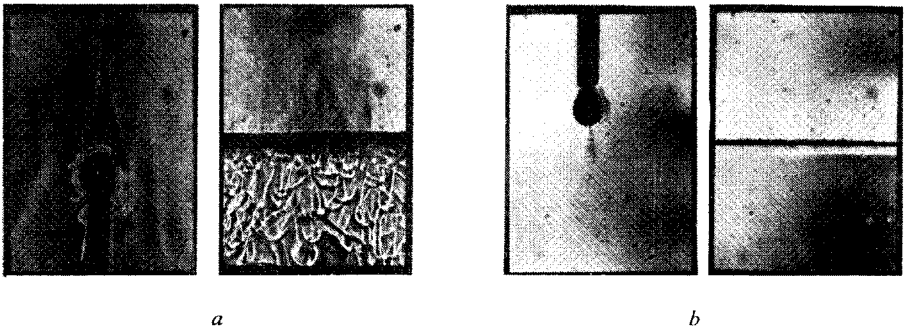

Fig. 3

Diffusion of Acetic Acid

a From MIBK to water, *b* from water to MIBK.

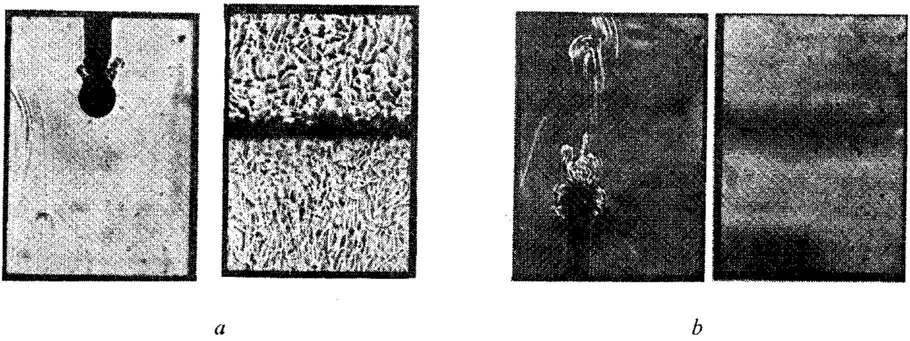

Fig. 4

Diffusion of Acetone

a From tetrachloromethane to water, *b* from water to tetrachloromethane.

$\mathrm{Re} = nd^2/\nu$	Reynolds number
$\mathrm{Sc} = \nu/D$	Schmidt number
$\mathrm{Sh} = kd/D$	Sherwood number
β	constant in Eq. (*2*)
γ	constant in Eq. (*2*)
$\varkappa$	constant in Eq. (*1*)
μ	dynamic viscocity
ν	kinematic viscosity
ϱ	density
σ	interfacial tension
τ	time
ψ	quantity defined in Eq. (*1*)

Subscripts

w	water phase
o	organic phase
i	phase i

REFERENCES

1. Sawistowski in the book: *Recent Advances in Liquid–Liquid Extraction* (C. Hanson, Ed.), p. 293. Pergamon Press, Oxford 1971.
2. Sternling O. V., Scriven L. E.: AICHE J. *5*, 514 (1959).
3. Orell A., Westwater J. W.: AICHE J. *8*, 350 (1962).
4. Linde H., Schwarz E.: Mber. dt. Akad. Wiss. Berl. *6*, 330 (1964).
5. Linde H., Sehrt B.: Mber. dt. Akad. Wiss. Berl. *7*, 341 (1965).
6. Sawistowski H., Goltz G. E.: Trans. Inst. Chem. Eng. *41*, 174 (1963).
7. Maroudas N. G., Sawsitowski H.: Chem. Eng. Sci. *19*, 919 (1964).
8. Linde H., Winkler K.: Z. Phys. Chem. (Leipzig) *225*, 223 (1964).
9. Linde H., Thiessen D.: Z. Phys. Chem. (Leipzig) *227*, 223 (1964).
10. Linde H., Winkler K.: Z. Phys. Chem. (Leipzig) *230*, 207 (1965).
11. Atagündüz G., Austin L. J., Sawitowski H.: Chem.-Ing.-Tech. *40*, 922 (1968).
12. Procházka J., Bulička J.: Proc. Int. Solvent Extraction Conference, p. 823, Hague 1971.
13. Bulička J.: *Thesis*. Institute of Chemical Process Fundamentals, Prague 1972.
14. Bulička J., Procházka J.: Chem. Eng. Sci., *31*, 137 (1976).
15. Pavasovich V. L., Perunichich M., Míšek T.: International Congress CH ISA 1972, Prague.
16. Alders L., Kos J., J. v. d. Leur: Recommended Systems for Liquid Extraction Studies EFCE.
17. Pavasovich V. L.: Recommended Systems for Liquid Extraction Studies EFCE.
18. Bulička J., Procházka J.: J. Chem. Eng. Data, in press.

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