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Use of image intensification for mass transfer studies in liquid–liquid systems*

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Abstract—An experimental method based on electro-optical image intensification of radiotracer compounds coupled with low-light-level photography was developed for concentration measurements of an organic solute in an aqueous phase. Experimental concentration profiles as a function of time were obtained in the aqueous phase of the water/ethyl acetate and water/isobutanol partially miscible systems. The results obtained for both liquid systems suggest the presence of interfacial activity and microconvection in the region close to the interface. In addition, the relationship between the solute concentration in the aqueous phase and the time elapsed since the contacting of the phases showed an oscillatory behavior with a period of 50–60 min.

INTRODUCTION

In the study of mass transfer between partially miscible liquids, temperature perturbations have been found to have an important effect in the generation of interfacial activity, which in turn is considered responsible for the enhancement of mass transfer rates. Austin *et al.* [1] and Ying and Sawistowski [2] did some work on partially miscible binary systems which was qualitative in nature. Using schlieren photography they looked at many systems and classified these into different groups depending on the intensity of interfacial movements. Their qualitative analysis and classification of systems has led to many more experimental and theoretical investigations on the subject. Bakker *et al.* [3] studied interfacial phenomena as related to mass transfer and made a quantitative classification of solutes according to their ability to impede or promote movement of a free interface. They divided the interfacial movements induced by differences in interfacial tension into two categories: large scale and microscale movement. In a later experimental work, Bakker *et al.* [4] looked at the influence of the microscale interfacial movement on the rate of mass transfer at a mobile interface, focusing mainly on extraction. They observed high mass transfer rates which were due to the microscale interfacial movements.

Nakaike *et al.* [5] used Mach–Zehnder interferometric methods to study qualitatively interfacial turbulence in order to find its relationship with mass transfer in liquid–liquid systems. Similar techniques were used by Davies and Thornton [6] in a study of mass transfer in the furfural/water system between a pendant droplet and the surrounding continuous phase. They observed high mass transfer rates in this system, which they suggested were partly due to the microconvection currents set up by the high heat of mixing of water and furfural-rich solutions. More recently, Thornton and Anderson [7] measured the frequency of disturbances at a predetermined position on the surface of a growing pendant droplet immersed in a second immiscible liquid phase. They noticed a series of violent and sporadic interfacial disturbances taking place in the drop when an undistributed solute was present in the continuous phase. These disturbances were possibly induced by Marangoni effects, which would also be responsible for increased mass transfer rates.

In an effort to acquire a better understanding of the phenomena of instability in liquid–liquid systems, both temperature and concentration profiles have been measured upon contacting two partially miscible liquids. This paper presents the method developed for concentration measurements of an organic solute in an aqueous phase as a function of time and position. This experimental method is based on electro-optical image intensification of radiotracer compounds coupled with low-light-level photography. In general, it consists of homogeneously distributing a ^{14}C radioactively tagged species in the top liquid phase, which upon diffusion into the bottom liquid phase interacts with a scintillating material. The interaction between beta particles and a scintillating material produces photons, which are then transmitted through an image intensification system and photographed. The intensity of the light transmitted is a measure of the concentration of the tagged species, which can be quantitatively determined by proper calibration of the system with a reference material. The basic principle of this experimental technique was earlier used by Hatters [8] for the measurement of liquid diffusion coefficients.

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NOMENCLATURE

a	constant used in equation (4) representing the concentration of organic solute at the interface [kgmol m^{-3}]
C	concentration of solute in aqueous phase [kgmol m^{-3}]
C_{EA}	concentration of ethyl acetate in aqueous phase [kgmol m^{-3}]
C_I	concentration of isobutanol in aqueous phase [kgmol m^{-3}]
D	diffusion coefficient of solute in aqueous phase [m^2 s^{-1}]
D_{GP}	horizontal distance in microdensitometer recording paper representing the position in the transfer cell [mm]
H_{GP}	vertical distance in microdensitometer recording paper representing the optical density or concentration [mm]
SA	specific activity [μCi μl^{-1}]
t	time [s]
z	position measured as distance from the interface [m].

EXPERIMENTAL SYSTEM

The contacting of the liquid phases is performed in a cylindrical Teflon transfer cell as shown in Fig. 1. The main objective of the transfer cell is to permit a smooth contact of two partially miscible liquids at a planar interface. The transfer cell is divided in two parts. The bottom section has one fluid well with a depth of 10 mm and a cross-section of 90 mm^2. This fluid well has a window on its side which consists of a fiber-optic faceplate. The purpose of this fiber-optic faceplate is to transmit the light generated by the interaction between the radiotracer and scintillating material to the input of the image intensifier tube. The shape selected for this faceplate was cylindrical with 25° bias cuts and plane surfaces on both ends, in order to measure concentrations as close as possible to the interface. The scintillating material used throughout this work was ZnS ; Cu, Al. A very thin and homogeneous layer of this material was deposited on a 3.56-μm-thick Mylar film. The coated Mylar film is placed on the inner surface of the fiber-optic faceplate, using a thin layer of silicon optical coupling gel to hold the film in place and minimize light losses. The procedure followed in the preparation of the scintillating material film is very important for the acquisition of reliable concentration data, and is described in detail by Aguirre [9].

The top section of the transfer cell has two fluid wells, one of which has the same cross-section as the one in the bottom section but with half its depth. This top fluid well has two openings in its top. A 1-ml hypodermic syringe is placed in one of them in order to introduce the lighter liquid which is radioactively tagged with ^{14}C; and the other is necessary for the displacement of air when this fluid well is being filled with liquid. The transfer cell is also instrumented with two chromel–alumel microthermocouples with a wire diameter of 25.4 μm. Its reference junction is placed in an ice bath to provide for a known constant reference temperature. One of the microthermocouples is placed in the bottom

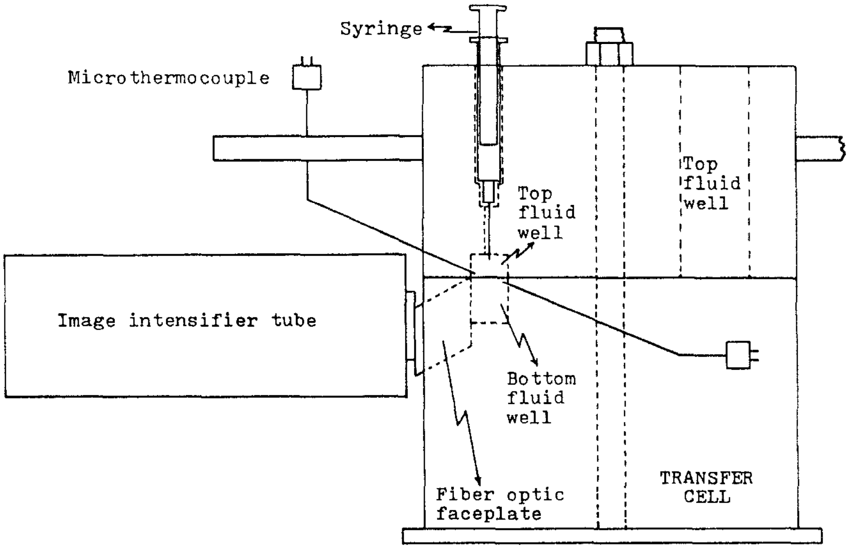


FIG. 1. Transfer cell for concentration measurements.

fluid well close to the interface, and the other one is placed in the small fluid well of the top section of the cell. The purpose of these microthermocouples is to make sure that both phases are at the same temperature before the contacting takes place.

Once the top and bottom fluid wells have been filled with the two partially miscible liquids, they can be contacted at a planar interface by slowly and smoothly rotating the upper section of the cell. Preliminary tests with a plexiglass cell showed that when the top fluid well was tightly covered eliminating all air spaces, this rotation procedure did not induce any external turbulence into the system.

The rotation of the upper section of the transfer cell must be done in complete darkness in order to be able to detect and photograph the light signal representing concentration levels in the bottom fluid well. Therefore, the transfer cell is also equipped with a mechanism to automatically stop the rotation of the upper section of the cell when the top and bottom fluid wells are perfectly aligned. Upon contact of the phases some of the radioactive species diffuses into the bottom phase, generating photons by interaction with the scintillating material. These photons are transmitted through the fiber-optic faceplate to the input of an image intensifier tube. The image intensifier tube used in this work was a RCA-4550 ruggedized, three-stage, cascaded, electrostatic-focus image intensifier having fiber-optic input and output faceplates. It requires a DC voltage of 2.65 V which was supplied by a Hewlett-Packard Harrison 6207B DC power supply. The luminance gain of the image intensifier tube is 50,000 at 295 K, which makes possible the detection of very low-intensity light signals.

The output signal from the image intensifier tube is recorded on photographic film at specified time intervals. A Pentax MX single lens reflex camera equipped with a 50-mm *f*/1.2 standard lens and a Samigon M/C close up lens No. 4 was used. The data were recorded on Kodak Tri-X Pan film, obtaining an ASA exposure index of up to 3200 when developed in Diafine developer. The use of this technique provides accurate concentration–position–time records of the radioactively tagged species in the bottom phase. Time exposures were required because the levels of light emitted at the output faceplate of the image intensifier tube were very low, and therefore photographic integration of the light signal was necessary.

The image developed on the photographic film was scanned using a microdensitometer to yield optical densities as a function of position at various times during the diffusional runs. Additional details concerning the experimental equipment and procedures are reported by Aguirre [9].

OPERATING PARAMETERS

Several operating parameters such as specific activity of the tracer material, exposure time, time interval between measurements and others had to be determined prior to the experimental runs. All of these parameters are interrelated, so various tests were performed to find their optimum combination.

The intensity of the light signal obtained is directly related to the specific activity per unit volume of the tagged compound present in the bottom phase at any given time. For the two systems studied, the tagged compound is the organic liquid which is only slightly soluble in the bottom or aqueous phase. This means that the specific activity of radioactive tracer in the bottom phase, which is where the concentration measurements are performed, is much lower than the specific activity in the top phase. As the specific activity of the solute increases, the exposure time required to record a given light signal on film decreases. The combination selected for these two variables was based on the volume requirement of tagged compounds. In order to optimize this combination the maximum aperture setting in the camera lens was used at all times, that is, an aperture of *f*/1.2. The specific activity selected for the pure organic compound in the top phase was of the order of 1 μCi μl^{-1}, which required an exposure time of 2 min in order to detect a wide range of concentrations in the bottom phase. This exposure time is short enough such that for a mass transfer process it can be considered an instantaneous measurement.

RESULTS

Concentration measurements were performed with the partially miscible systems water/ethyl acetate and water/isobutanol. In both cases the organic compound was tagged with ^{14}C, and its concentration in the aqueous phase was measured at various times. For most of the experimental runs the measurements consisted of a 2-min photograph for times of 10, 30, 60, 90 and 120 min after the contacting of the two pure liquids had taken place. Only one experimental run with the water/ethyl acetate system was different. In such case the measurements consisted of 1-min exposures for times of 10, 20, 30, 45, 60, 75, 90, 105 and 120 min after the contacting of the phases.

The light signal generated by the interaction between beta particles and the scintillating material was recorded as a black spot on the photographic film, and the optical density at different positions in this spot is related to a concentration profile. A typical sequence of light signals for the water/ethyl acetate system is presented in Fig. 2. In these photographs, the top boundary represents the edge of the fiber-optic faceplate which is observing concentrations at a distance of 0.7 mm from the interface. The scanning of the film is done from top to bottom in the vertical direction, obtaining a concentration profile from a position close to the interface to the bulk of the aqueous phase.

The intensity of the white signal in these photographs represents the concentration of ethyl acetate in the aqueous phase. It is interesting to note from Fig. 2 the growth of the boundary layer with time. For a time of

Table 1. Reproducibility of concentration measurements for water/ethyl acetate system

Time (min)	Standard deviation (kgmol m^{-3})	Variance (kgmol $m^{-3})^2$	Degrees of freedom
10	0.087	0.0075	68
30	0.256	0.066	64
60	0.210	0.044	52
90	0.273	0.074	68
120	0.330	0.109	60
All times	0.244	0.060	312

120 min, the light signal represents the region between 1 and 7 mm from the interface.

Reproducibility of experimental data

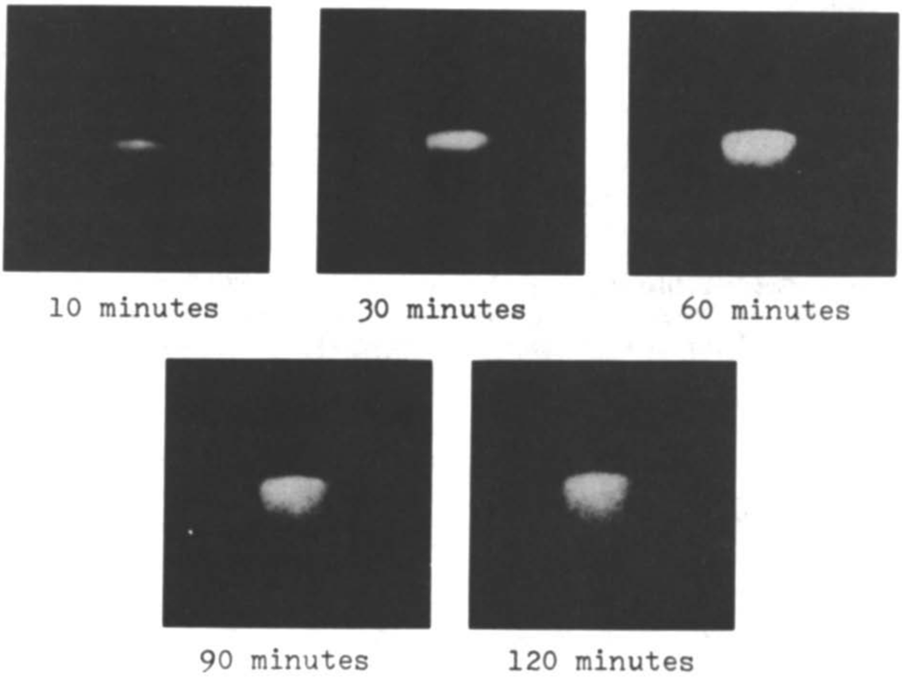
The reproducibility of the experimental data was determined from five experimental runs performed with the water/ethyl acetate system. The concentrations compared were those for an identical time and position in the transfer cell. The standard deviation for the concentration of organic compound in the aqueous phase was determined for each time and all the experimental data. These results are presented in Table 1. The average standard deviation for all the data with the water/ethyl acetate system is 0.244 kgmol m^{-3}, which is not as good as expected. However, there are certain characteristics of the data which are very well reproduced from one experimental run to the next, which will be discussed in the following section. The large value for the estimated standard deviation could be attributed to the convection which seems to be taking place in these systems, since a small perturbation at the initial stages of the run can be greatly magnified as time proceeds.

Calibration of systems

The light signal recorded on photographic film was analyzed with a microdensitometer. As a result, a curve of optical density as a function of position in the transfer cell was obtained. The coordinates of this resulting curve are measured as distances in millimeters, with the distance in the graph (D_{GP}) representing the position in the transfer cell and the height in the graph (H_{GP}) representing an optical density or concentration.

For the calibration of distances in the transfer cell, the procedure used consisted of taking photographs of a Mylar film coated with scintillating material. The width of this coated Mylar film was measured as accurately as possible, and it was exposed to room light prior to taking the photographs so that the sharp contrast in optical densities detected by the microdensitometer would represent the width of the Mylar film. This procedure was repeated several times, so the average was used to relate a distance on the inside surface of the fiber-optic faceplate with that obtained in the recording paper (D_{GP}). As a result, a value of D_{GP} of 1 mm represents 0.0484 mm inside the transfer cell.

The second type of calibration that had to be performed was that relating the specific activity per unit volume in the aqueous phase to the height obtained in the recording paper (H_{GP}). This calibration was done separately for both water/ethyl acetate and water/isobutanol systems. It consisted in preparing samples of aqueous solution at different and known specific activities and concentrations of organic compound. Several photographs were taken of the light



10 minutes 30 minutes 60 minutes

90 minutes 120 minutes

FIG. 2. Light signals representing concentration profiles at various times for water/ethyl acetate system.

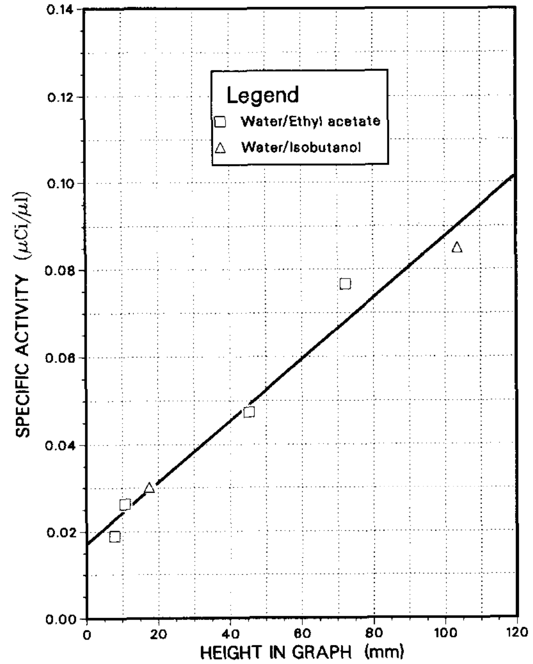


FIG. 3. Calibration of specific activity for systems studied.

signal produced by the interaction between these tagged solutions and the scintillating material. By analyzing these photographs with the microdensitometer, the height obtained in the recording paper was correlated to the specific activity in the aqueous solution. Both partially miscible systems show the same linear relationship between these two variables, as can be noted from Fig. 3. The straight line plotted in this figure was obtained by a least-squares fit of the calibration data, and it is represented by the following equation.

$$SA = 0.0172 + 0.000704\,H_{GP}. \tag{1}$$

The correlation coefficient of this fit is 0.969 and the standard deviation of the estimate with this expression is 0.0054 μCi μl^{-1}.

The relationship between the concentration of the organic species in the aqueous phase and the specific activity of such solution depends on the specific activity of the pure organic compound, its density and molecular weight. In the case of the two systems used throughout this work, such relationships are described by the following expressions.

Water/ethyl acetate system:

$$C_{EA} = 10.197\,SA. \tag{2}$$

Water/isobutanol system:

$$C_I = 11.50\,SA. \tag{3}$$

Based on these relationships, a value of 1 mm for the height in the recording paper (H_{GP}) represents a concentration difference of 0.0072 and 0.0081 kgmol m^{-3} for the water/ethyl acetate and water/isobutanol systems, respectively.

ANALYSIS AND DISCUSSION

The experimental data were compared to the theoretical concentration profiles obtained by solving a diffusion model for simultaneous mass and heat transfer in a stationary, partially miscible, binary liquid system. This diffusion model is described by a set of four partial differential equations which have been analytically solved by Perez de Ortiz and Sawistowski [10] by assuming a linear variation of the heat of solution with concentration. The solution for the concentration of organic solute in the bottom aqueous phase can be expressed as follows if the initial concentration is zero.

$$C = a\,\mathrm{erfc}\left(\frac{z}{\sqrt{4Dt}}\right). \tag{4}$$

The constant a depends on physical properties of the pure compounds and of the binary systems involved. It represents the concentration of organic solute at the interface, and has a value of 0.843 kgmol m^{-3} for the water/ethyl acetate system and a value of 1.064 kgmol m^{-3} for the water/isobutanol system. A plot of the average experimental data and theoretical concentration profiles for the water/ethyl acetate system is presented in Fig. 4. The solid lines represent the theoretical concentration profiles due to pure diffusion, and they correspond to the same times as the experimental data with time increasing from left to right in the graph.

This comparison shows that the experimental concentration profiles are consistently greater than those predicted by assuming pure diffusion. In addition,

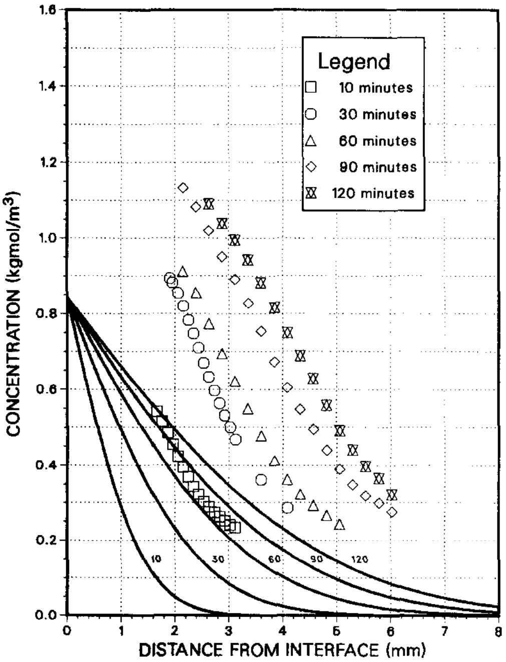


FIG. 4. Comparison of experimental and theoretical concentration profiles of ethyl acetate in aqueous phase.

it can be observed from Fig. 4 that at several positions the experimental concentrations of ethyl acetate in the aqueous phase are larger than the interfacial concentration or concentration at saturation conditions. This observation strongly suggests the presence of interfacial activity and convection which enhances the mass transfer rates, at least in the region close to the interface. Furthermore, the fact that some experimental concentrations are larger than the value at saturation conditions in the aqueous phase would lead to the conclusion that this interfacial activity is accompanied by bulk mixing with small droplets of the ethyl acetate-rich phase being transported to the aqueous phase. The presence of just a few small droplets of the ethyl acetate-rich phase in the aqueous phase would greatly increase the value of the measured concentrations, since the specific activity per unit volume of the pure ethyl acetate is 12 times greater than that of the saturated aqueous phase.

The same conclusions can be suggested for the water/isobutanol system as shown in Fig. 5. This figure shows a comparison between the experimental data and theoretical concentration profiles assuming pure diffusion for the water/isobutanol system.

There is an interesting characteristic of the experimental data which was noticed in all experimental runs. The experimental data for the water/ethyl acetate system showed an oscillatory behavior with time, having local maxima and minima with a period of the order of 50–60 min. Figure 6 presents this behavior for four different positions in the bottom fluid well, in which the concentration of ethyl acetate in the aqueous phase is plotted as a function of time. For any specific position in the bottom fluid well, the solute concentration should theoretically increase as time proceeds if the mass transfer process is controlled by pure diffusion. Therefore, the oscillatory behavior of ethyl acetate concentrations with a period of such magnitude suggests the existence of a very slow and intense convection process in the aqueous phase for up to 120 min after the contacting of the phases had taken place. This convection process is probably accompanied by very large and rapid perturbations of the interface. However, since the measurements were made by using exposure times of 2 min, the results obtained are an average of the concentrations and possible perturbations during that period of time. In order to be able to evaluate all types of convection patterns taking place in these systems it is necessary to make measurements with exposure times of just a few seconds, which can be achieved by increasing the specific activity of the radioactive tracers.

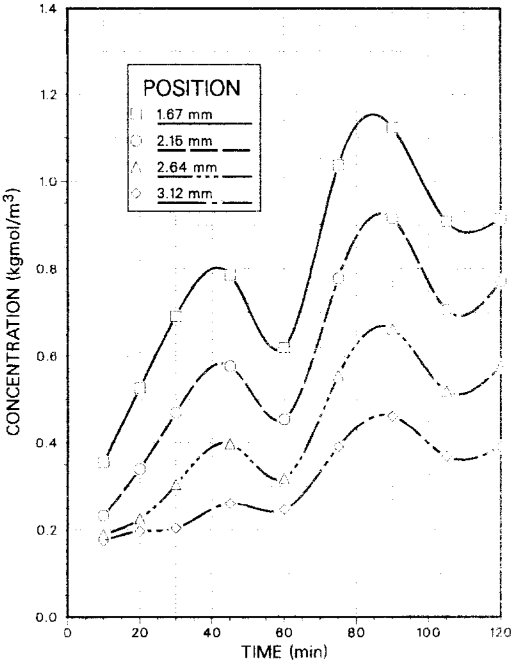


FIG. 6. Oscillatory behavior for the concentration of ethyl acetate as a function of time.

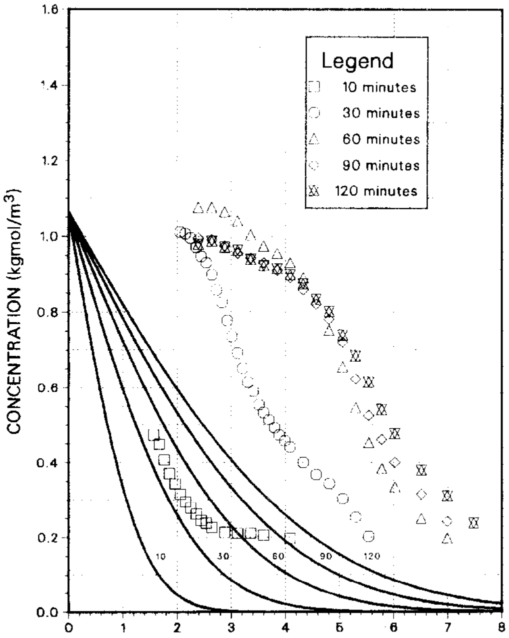


FIG. 5. Comparison of experimental and theoretical concentration profiles of isobutanol in aqueous phase.

Earlier work reported by Aguirre *et al.* [11] presents results on temperature measurements during mass transfer for various partially miscible liquid systems, including those used in the present work. Numerical simulation of temperature histories at various locations in the transfer cell have also been reported [12] when using a non-linear diffusion model.

CONCLUSIONS

The use of electro-optical image intensification of the light emitted by radioactive tracers, coupled with low-light-level photography, proved to be an adequate method to measure concentration profiles close to a liquid interface as a function of time. In reference to the experimental results obtained for the two partially miscible systems studied, it was noticed that the experimental concentration profiles were consistently greater than those predicted by assuming pure diffusion. This indicates that the experimental mass transfer rates are considerably greater than those due to diffusion alone, which is attributed to the presence of interfacial activity and convection. At several positions in the transfer cell the experimental concentrations of organic solute in the aqueous phase were larger than the concentration at saturation conditions. This indicates that the interfacial activity must be accompanied by mixing of the two bulk phases, which could be in the form of small droplets of organic phase penetrating the aqueous phase.

The experimental data for the water/ethyl acetate system showed an oscillatory behavior of concentrations with time having a period of 50–60 min. This oscillatory behavior suggests the presence of a slow and intense convection process in the aqueous phase. This convection process is probably accompanied by very large and rapid perturbations of the interface which could not be detected due to averaging of the concentration during a 2-min measurement.

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UTILISATION DE L'INTENSIFICATION D'IMAGE POUR LES ETUDES DE TRANSFERT DE MASSE DANS LES SYSTEMES LIQUIDE–LIQUIDE

Résumé—Une méthode basée sur une intensification d'image électro-optique de composés traceurs radioactifs couplée à une photographie à faible niveau de luminosité est développée pour des mesures de concentration d'un soluté organique dans une phase aqueuse. Des profils expérimentaux de concentration en fonction du temps sont obtenus dans la phase aqueuse d'acétate d'éthyle et d'isobutanol. Les résultats obtenus pour les deux systèmes liquides suggèrent la présence d'une activité interfaciale et d'une micro-convection dans la région proche de l'interface. De plus, la relation entre la concentration de soluté dans la phase aqueuse et le temps passé depuis le contact des phases montre un comportement oscillatoire avec une période de 50–60 min.

EINSATZ DER BILDVERSTÄRKUNG BEI STOFFÜBERGANGSUNTERSUCHUNGEN IN FLÜSSIG–FLÜSSIG-SYSTEMEN

Zusammenfassung—Ein experimentelles Verfahren, das auf der Grundlage der elektro-optischen Bildverstärkung und der Fotografie bei geringer Licht-Intensität aufbaut, wurde entwickelt, um in einer organischen wäßrigen Lösung Konzentrationsmessungen durchzuführen. Es ergeben sich zeitabhängige Konzentrationsprofile in der wäßrigen Phase der teilweise mischbaren Systeme Wasser/Äthylacetat und Wasser/Isobutanol. Die Ergebnisse für beide Flüssigkeitssysteme deuten auf das Vorhandensein von Grenzflächenaktivität und Mikrokonvektion im grenzflächennahen Bereich hin. Außerdem zeigte der Zusammenhang zwischen Lösungskonzentration in der wäßrigen Phase und der Zeit, die seit dem ersten Kontakt der Phasen vergangen ist, ein schwingendes Verhalten mit einer Periode von 50–60 Minuten.

ПРИМЕНЕНИЕ МЕТОДА УСИЛЕНИЯ ИЗОБРАЖЕНИЯ ДЛЯ ИЗУЧЕНИЯ МАССОПЕРЕНОСА В СИСТЕМАХ ЖИДКОСТЬ-ЖИДКОСТЬ

Аннотация—Экспериментальный метод, базирующийся на электрооптическом усилении изображения с радиоактивного индикатора в сочетании с низкоуровневым по освещенности фотографированием, развит для измерения концентраций органических растворов в жидкой фазе. Экспериментально получены профили концентрации для жидкой фазы частично смешанных систем вода-этилацетат и вода-изобутанол. Полученные для обеих жидких смесей результаты показывают наличие межфазной активности и микроконвекции в области, прилегающей к границе раздела фаз. Кроме того, обнаружена зависимость осциллирующего характера с периодом 50–60 минут между концентрацией раствора в жидкой фазе и интервалом времени, прошедшим с момента установления контакта между фазами.