Table 3. Ternary Diffusion Coefficients in Acetonitrile(1)-Benzene(2)-n Heptane(3) Mixtures at 25°C

$\overline{X}_1$	$\overline{X}_2$	$\overline{D}_{11}$*	$\overline{D}_{12}$	$\overline{D}_{21}$	$\overline{D}_{22}$
0.3906	0.3150	1.002 ± 0.051**	−0.462 ± 0.112	−0.232 ± 0.048	3.211 ± 0.089
0.0628	0.2048	3.121 ± 0.070	−0.291 ± 0.073	−0.863 ± 0.093	3.613 ± 0.108
0.0243	0.0693	4.257 ± 0.150	−0.200 ± 0.083	−0.421 ± 0.036	3.835 ± 0.030

* All the D_{ij} are in cm²/s (× 10⁵).
** Refers to standard deviation σ.

Ternary Diffusion Data

Ternary diffusion coefficients were computed from diaphragm cell measurements in the heptane rich region of the ternary diagram (Figure 1).

The ternary diffusion coefficients obtained at the three mean compositions are presented in Table 3. The first composition corresponds to a point in the neighborhood of the critical point.

DISCUSSION

The binary diffusion results confirm that the mutual diffusivity is a strong function of concentration. The linear correlation serves as a good approximation for a fitting function in the absence of any suitable theory to describe the diffusional behavior of partially miscible systems.

The ternary diffusion results indicate that coupling effects are fairly significant in that the cross diffusion coefficients are about 10 to 40% of the main diffusion coefficients. Further, it is found that the main diffusion coefficients are nearly equal except in the vicinity of the plait point. It seems that as the critical point is approached the magnitude of the cross terms remains on the order of normal cross terms in the unsaturated phase, but one of the main diffusion coefficients (corresponding to one of the partially miscible solvents) reduces in magnitude so as to produce the critical singularity.

CONCLUSIONS

The differential diffusion coefficients of acetonitrile in n-heptane at 25°C are measured between 0.09 and 0.21 molal concentration acetonitrile. The mutual diffusivity of the partially miscible binary system is a strong function of concentration. The concentration dependence is described by the relationship $\mathcal{D}(C) = 6.38 \times 10^{-5} - 0.148\ C$ with C expressed in mole/liter.

Ternary diffusion coefficient matrices are reported and the cross diffusion coefficients are about 10 to 40% of the main diffusion coefficients. The ternary data are reported at three mean concentrations in the heptane-rich region of the ternary space. The results indicate that as the critical point is approached, one of the main diffusion coefficients (corresponding to acetonitrile in this case) reduces in magnitude so that the determinant of the ternary diffusion matrix goes to zero.

The results of this study establish that the ternary diffusion coefficient matrices are significantly nondiagonal. The effect of this coupling on mass transfer in such a system is of obvious interest, and this is dealt with in Part II.

Part II. Mass Transfer and Interfacial Studies

The objective of this work is to experimentally examine mass transfer during liquid-liquid extraction in the system acetonitrile-benzene-n-heptane. The interfacial characteristics of the system are simultaneously investigated. (Part I deals with the diffusion properties of the system).

The mass transfer experiments are conducted in a stirred extraction cell of the Lewis type. The transfer between an unsaturated and nearly saturated phase is studied. The mass transfer coefficients for the partially miscible binary system, and for those ternary experiments in which the slope of the operating line was negative are found to be independent of the driving force. A photographic investigation, which employed the schlieren technique, indicates that Marangoni-type instabilities are absent in such experiments. However, in ternary experiments, in which the slope of the operating line is positive and above a certain critical value the mass transfer coefficients decreases as equilibrium approached. The schlieren results confirm the presence of interfacial turbulence for this case.

The driving-force dependence of the turbulent mass transfer coefficients is explained using a surface renewal model. The model provides a correlation for the results of ternary experiments in which interfacial turbulence is present.

Most correlations for design of mass transfer equipment have been obtained from experiments in which a solute transfers between two immiscible or mutually saturated solvents (Lewis, 1954b, McManamey et al., 1973; Mayers, 1961), or from studies on partially miscible binary systems (Lewis, 1954a; Austin and Sawistowski, 1967). In most practical situations, however, there are several components transferring across the interface, and interactions among the various fluxes and driving forces are expected. The effect of coupled flows on mass transfer in multicomponent liquid-liquid systems has received scant attention. Such information cannot be obtained directly from experiments in which a solute transferred between two immiscible or mutually saturated solvents since in this case there is in fact only one independent driving force in each phase.

Numerous investigations have been made on the stability of liquid-liquid interfaces and these have been reviewed recently (Sawistowski, 1971; Berg, 1972). Most studies (Bakker et al., 1967; Linde and Thiessen, 1964) tend to show a directional dependence of the mass transfer coefficient for a solute transferring between two immiscible or mutually saturated solvents. In multicomponent systems, however, with several components transferring in both directions, the theories developed could not be used to make predictions regarding the onset of interfacial turbulence.

The primary objective of the present work was the study of the mass transfer characteristics of a multicomponent liquid-liquid system. A ternary system was chosen for the investigation, and the goal was to establish mass transfer coefficients over a range of composition values. Mass transfer experiments were also conducted on the interfacially stable, partially miscible binary system, and the transfer coefficients obtained in this case served as reference values for the ternary experimental work. Although in this way interfacial turbulence could be detected in the ternary experiments, the presence of surface instabilities was confirmed by photographing the interface.

EXPERIMENT

Measurement of Mass Transfer Coefficients

The mass transfer studies were conducted in a stirred cell. The apparatus used was a modification of the Lewis cell. The glass and stainless steel cell is shown in Figure 3. The disk impellers were driven by variable speed d.c. motors. Vertical baffles were incorporated into the upper chamber to promote mixing. The total interfacial area was 25 cm^2. The experimental observations were made in an environmental room. The temperature of this room was controlled to remain at 25 ± 0.2°C.

The experiments were performed with the top phase stirred only. The bottom phase was recycled using a peristaltic pump. The flows in and out of the cell were adjusted such that the bottom phase remained homogeneous. In addition, the rates could be altered to ensure that the interface remained within the annular gap at all times.

At the beginning of each experiment, the bottom phase composition corresponded to near saturation with respect to the upper phase. In this manner the experiments were conducted with the conditions so contrived such that the composition driving forces in the top phase were much larger than those in the bottom phase. The observed behavior of the system could be thus related to the driving forces in the unsaturated (top) phase.

The initial experiments were directed towards the determination of the lower and upper speed limits of cell operation. The minimum speed at which bulk conditions were found to be uniform was 60 rev./min. The upper limit was fixed by the hydrodynamic stability of the interface and was as high as 150 rev./min. Based on these observations a reasonable speed for cell operation was chosen as 80 rev./min. All experiments were conducted at this one impeller speed.

Before each run the extraction cell was thoroughly cleaned with dilute chromic acid solution; if traces of grease appeared to be present, they were removed by washing with acetone. The actual experiment was started by first establishing a steady flow rate of the saturated phase through the bottom chamber of the cell. A piece of flexible tubing, which rested on the upper side of the center plate was used for gently introducing a thin layer of the top phase. The interface was cleaned by removing this layer by suction with a syringe. The top half of the cell was then filled, care being taken to ensure that the interface was not distrubed. Simultaneously, the flow rates were adjusted to maintain the level of the interface. Thereafter, stirring was commenced, and after allowing several minutes for the hydrodynamic conditions to become established, samples were taken from the two phases at about 5 to 10-min. intervals.

The concentrations were determined using gas-liquid chromatography. A Hewlett Packard F&M Model 5750 gas chromatograph equipped with a thermal conductivity detector was used for the purpose.

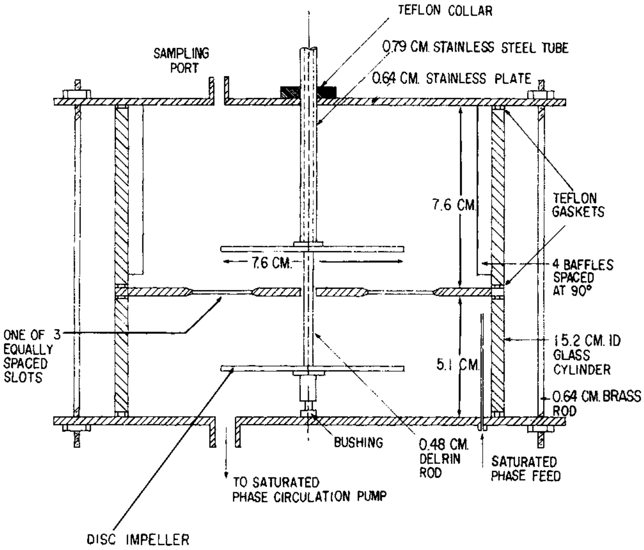

Fig. 3. Modified Lewis extraction cell.

TABLE 4. CLASSIFICATION OF SYSTEMS ACCORDING TO INTERFACIAL MASS TRANSFER PROCESS

System	Top x_1	Phase x_2	Composition x_3	m	Bottom x_1	Phase x_2	Composition x_3	Observation of transfer
I	0	0	1.0	—	0.962	0	0.038	Diffusional
II	0	0.05	0.95	−0.505	0.830	0.10	0.07	Diffusional
III	0	0.12	0.88	−0.209	0.83	0.1	0.07	Diffusional
IV	0	0.17	0.83	+0.128	0.83	0.1	0.07	Turbulent
V	0	0.21	0.79	+0.705	0.83	0.1	0.07	Turbulent
VI	0	0.25	0.75	+2.54	0.83	0.1		Turbulent

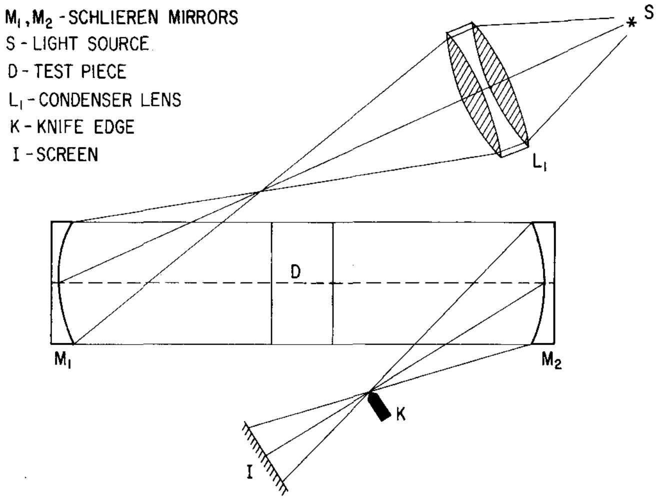

Fig. 4. Schematic view of the schlieren operating system.

Experimental Investigation of Interfacial Convection

The aim of the study was to explore the conditions under which interfacial activity occurred at the liquid-liquid interface. This involved photographing of the interface using a schlieren system. Both the partially miscible binary system and the ternary system were investigated for the presence of interfacial instabilities.

The schlieren apparatus consisted of a test cell, a schlieren optical system, and photographic equipment. The test piece used was made of fused pyrex of good optical quality. It had internal dimensions of 50 × 73 × 200 mm and was used with the long dimension vertical.

The schlieren system shown in Figure 4 employed two parabolic mirrors of 48-in. focal length. The light source used was a PEK 109 High Pressure Mercury Arc Lamp. The light source slit was a pinhole. The knife edge was a double edged razor blade. It was provided with micrometer adjustments. The knife edge and the slit could be moved along or perpendicular to the optical axis.

The light source S and the mirror M1 was placed so that the test section was illuminated by a parallel beam of light. Mirror M2 placed beyond the test section produced an image of the source in its focal plane (K) beyond which a camera was placed.

The experimental procedure consisted of filling the bottom third of the cell with the heavier phase. A plunger, made of fritted glass which fitted the inner walls quite strongly, was lowered until it was just above the liquid surface. The light phase was poured next on top of the diaphragm filling the cell about a third from the top. The plunger was then pulled straight up at an extremely slow rate to permit the formation of a calm, unperturbed interface. The cell was then sealed to prevent evaporation and the interface photographed at suitable intervals.

RESULTS

From each run in the cell, the concentration time curve for the top phase was produced. The bottom phase composition did not vary much during the run, but the change was recorded and accounted for in the calculation. For the experiment conducted on the binary system acetonitrile-*n*-heptane, the mole fraction-time curve is given in Figure 5.

In the ternary experiments, the rate of mass transfer was established by monitoring the mole fractions of any two components in both phases as a function of time. Several experiments were performed with the benzene/heptane ratio in the top phase varying. Simultaneously the saturated phase composition was also altered. Figure 6 shows the transfer paths obtained in the various runs plotted on a triangular diagram. All the composition trajectories were straight lines.

Calculation of Mass Transfer Coefficients

For a batch extraction of the type considered, the material balance equations for constituent and mixture moles in the two phases are

$$x_{it} N_{Tt} + x_{ib} N_{Tb} = N_i^0 = \text{constant} \quad (1)$$

$$N_{Tt} + N_{Tb} = N_T^0 = \text{constant} \quad (2)$$

where 0 denotes initial conditions and t, b denote the top and bottom phases, respectively. The phases are assumed to be well mixed. The material balance relations together with the equations

$$N_i = x_i N_T \quad (3)$$

and

$$N_T = \Sigma N_i \quad (4)$$

are used for the calculation of the amount of each phase N_T at each sampling time from the initial amount N_T^0 and the bulk phase composition x_i.

The mass transfer coefficients were defined on the basis of interfacial diffusive molar fluxes (J_{iI}) and the constituent driving forces ΔC_j. For the ternary system the equation expressing the relationship between the fluxes and forces can be written as

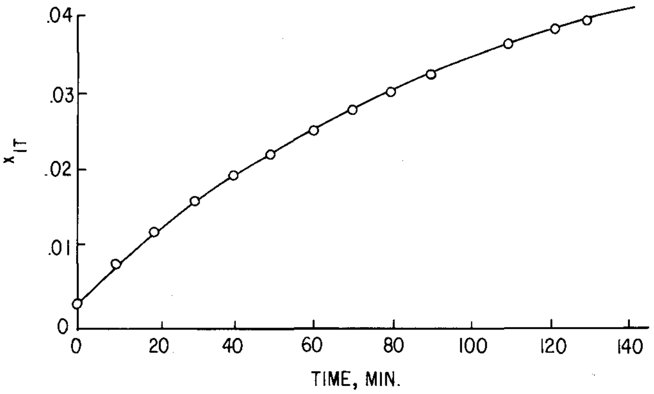

Fig. 5. Experimental mole fraction-time plot for binary extraction.

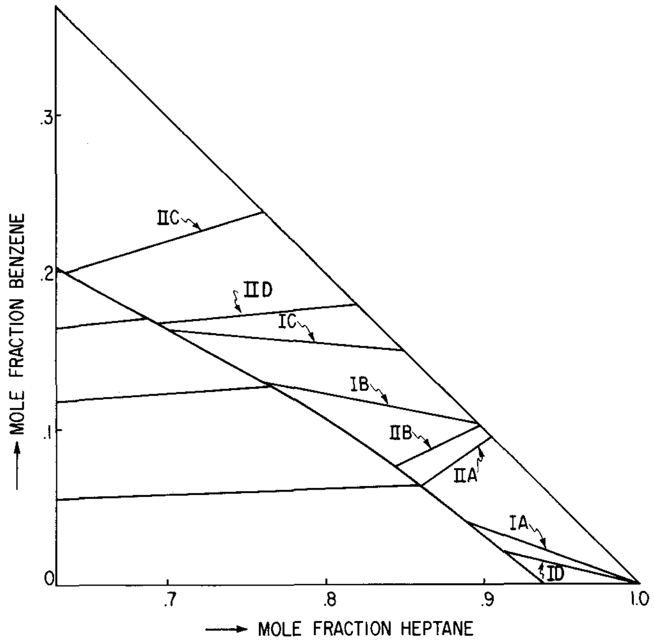

Fig. 6. Diffusion paths in ternary extraction runs.

$$J_{iI} = \sum_{j=1}^{2} k_{ij}\Delta C_j \tag{5}$$

The molar diffusion fluxes J_{iI} referred to the molar average velocity at the interface are defined as

$$J_{iI} = N_i^0 - N_T^0 x_i^* \tag{6}$$

where the quantities in the right-hand side of the equation refer to the top phase. Equation (6) can be rewritten as follows by using Equation (3)

$$J_{iI} = \frac{1}{A_I}\frac{d}{dt}\{N_T(x_i - x_i^*)\} \tag{7}$$

where A_I = interfacial area.

In the binary case, the problem reduced to estimation of the one independent, mass transfer coefficient k_B which was deduced from

$$k_B = \frac{\frac{1}{A_I}\frac{d}{dt}\{N_T(x_i - x_i^*)\}}{(C_i - C_i^*)} \tag{8}$$

The numerator of Equation (8) was calculated by differentiation after evaluating N_T from the material balance equations [Equations (1) and (2)]. A polynomial approximation whose coefficients were determined by a least squares fit was used to describe $N_T(x_i - x_i^*)$. Analytical differentiation of the polynomial expression was then used to resolve the derivatives at various times. The mass transfer coefficients so obtained for the binary system are presented in Figure 7. They clearly demonstrate that k_B did not vary appreciably during the course of a run.

In a ternary system the four transfer coefficients cannot be deduced from one experiment since only two independent flux measurements are available. However, if the transfer paths are straight lines, it can be shown (Appendix A) that this implies that the mass transfer coefficient matrix is diagonal. Therefore, Equation (5) can be rewritten as

$$J_{iI} = k_T(C_{it}^* - C_i) \tag{9}$$

The procedure used for evaluating k_T was similar to the one used for estimating k_B.

The ternary mass transfer coefficients for the experiments where the operating lines were of negative slope were approximately the same magnitude as k_B. The results plotted in Figure 8 show that the coefficients remained almost constant. In those ternary experiments in which the slope of the operating line was positive, the mass transfer coefficients generally decreased with time. These results are presented in Figure 9. The ternary extraction results clearly demonstrate that the mechanism of mass transfer is strongly dependent on the slope of the operating line. This was further investigated in the schlieren study.

Schlieren Investigation Results

In the schlieren study the liquid-liquid interface was photographed under a variety of experimental conditions. Since the objective was to make the observations under conditions similar to those prevailing during the mass transfer experiments, the bottom solution composition corresponded to saturation in all cases.

In the ternary system the effect of benzene driving force on interfacial behavior was examined by adjusting the composition of the top phase. Interfacial turbulence was observed in some of the cases only and the complete results are given in Table 4. In those situations, where surface instabilities occurred, the interface started teeming with activity the moment the phases were brought into contact. The interfacial turbulence patterns observed were disordered.

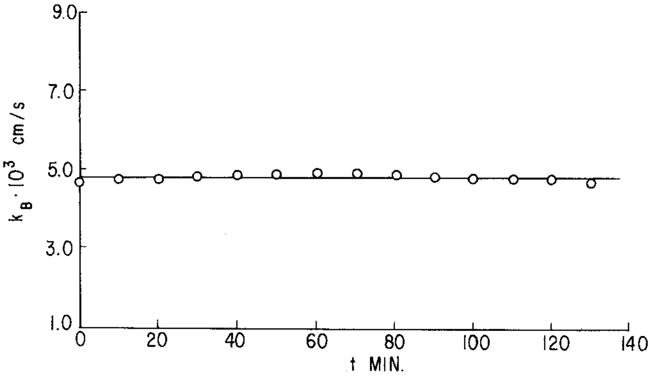

Fig. 7. Mass transfer coefficients plotted as a function of time for the system acetonitrile-heptane.

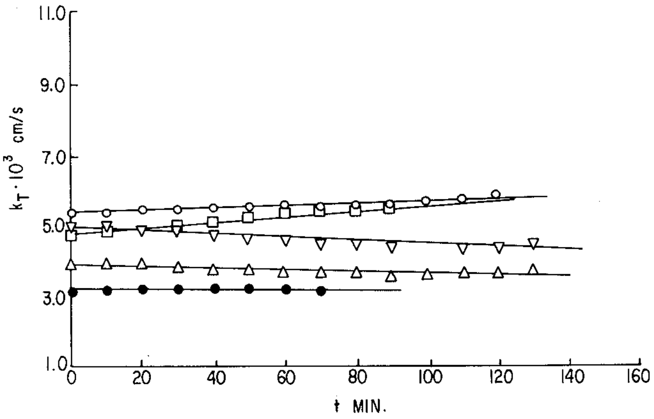

Fig. 8. Mass transfer coefficients plotted as a function of time for ternary experiments in which the slope of the operating line was negative.

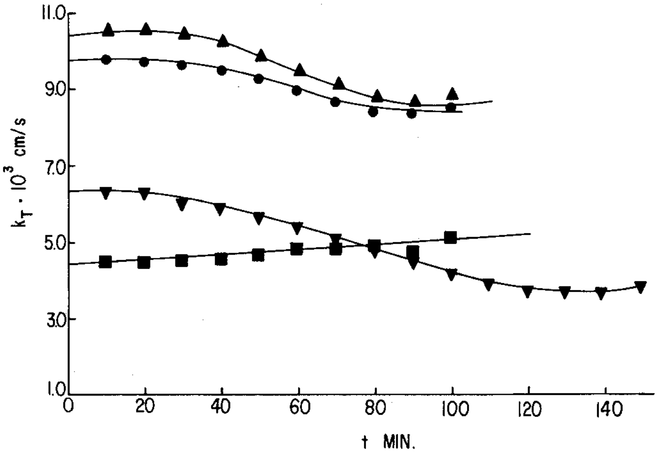

Fig. 9. Mass transfer coefficients plotted as a function of time for ternary experiments in which the slope of the operating line was positive.

DISCUSSION

Mass Transfer in the Partially Miscible Binary System

The binary diffusion results for the system acetonitrile-*n*-heptane (Part I) confirmed that the diffusion coefficient is a strong function of concentration. The mass transfer results indicate that k_B, the binary mass transfer coefficient did not vary appreciably during the course of a run (Figure 7) even though the bulk concentration was an exponentially increasing function of time (Figure 5). This anomaly was rationalized by calculating the interfacial fluxes from a simple model based on the penetration theory, taking into account the concentration dependence of the diffusion coefficient.

The binary mass transfer coefficient k_B can be written as

$$k_B = \frac{J_{iI}}{(C_i^* - C_{bi})} \tag{10}$$

where C_i^* and C_{bi} refer to the interfacial and bulk concentrations, respectively. The local value of the interfacial flux at a given instant of time can be written as

$$j_{iI} = -\mathcal{D}_I \frac{\partial c}{\partial y}\bigg|_{y=0} \tag{11}$$

where y is the coordinate normal to the interface. The diffusion is assumed to be unidirectional. J_{iI} in Equation (10) is the average value of the interfacial flux, which according to Higbie's penetration theory would be related to j_{iI} by

$$J_{iI} = \frac{1}{\theta}\int_0^\theta j_{iI}\,dt \tag{12}$$

where θ is the contact time. θ depends on the hydrodynamic conditions. In Equation (11) $\mathcal{D}_I$ is the diffusion coefficient corresponding to the interfacial composition. The binary diffusivity is a sharply decreasing function of concentration (Part I) and $\mathcal{D}_I$ is the minimum value of $\mathcal{D}$ over the composition range $c = 0$ to $c = c^*$.

In order to ascertain the exact functional dependence of k on $\mathcal{D}(c)$ a model based on the classical penetration theory was formulated. The method adopted is presented in Appendix B. The aim of the calculations was to arrive at an estimate of j_{iI} at a given instant of time. Figure 10 shows the solutions to the convective diffusion equation for $C_{bi} = 0.1\ C_i^*$ and $C_{bi} = 0.5\ C_i^*$. Each curve represents the composition profile at the interface corresponding to the bulk composition C_{bi}. The ordinate $\overline{C}$, a dimensionless concentration is equal to

$$\overline{C} = \frac{C_i(y,t) - C_{bi}}{C_i^* - C_{bi}} \tag{13}$$

The local value of the interfacial flux is calculated to be

$$j_{iI} = -\mathcal{D}_i \frac{(C_i^* - C_{bi})}{2(\mathcal{D}_0 t)^{1/2}} \frac{\partial \bar{c}}{\partial y}\bigg|_{y=0} \tag{14}$$

where

$$Y = \frac{y}{2(\mathcal{D}_0 t)^{1/2}} \tag{15}$$

The mass transfer coefficient calculated from Equations (10), (12), and (14) is thus

$$k_B = \frac{\mathcal{D}_I}{(\mathcal{D}_0\theta)^{1/2}} \frac{\partial \bar{c}}{\partial y}\bigg|_{y=0} \tag{16}$$

where θ the contact time is a function of the hydrodynamic conditions $\frac{\partial \bar{c}}{\partial y}\Big|_{y=0}$ corresponds to the slope of the concentration trajectories presented in Figure 10 at $y = 0$. It can be noted that even though the bulk composition increases from $0.1\ C_i^*$ to $0.5\ C_i^*$ the initial slope changes by less than 10%. Therefore, according to Equation (16), k_B should remain almost constant.

This analysis of the process demonstrates that even though the diffusion coefficient is strongly dependent on concentration the interfacial mass transfer rate, which is governed by the value of the diffusivity at the interface, remains almost constant. It therefore seems that the diffusion coefficient that should be used in correlating mass transfer data for partially miscible systems should correspond to the interfacial composition.

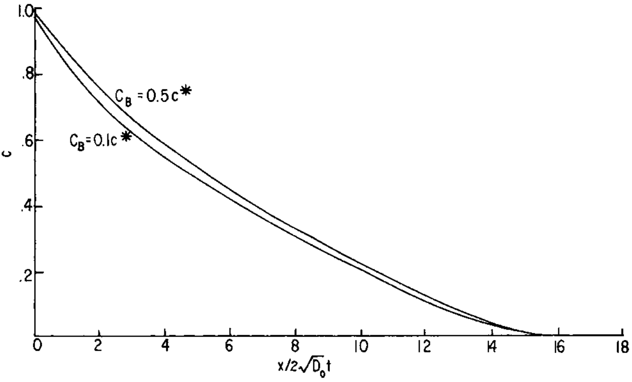

Fig. 10. Solutions of diffusion equation (Appendix B1) for concentration dependent diffusion coefficient given by $D(C) = 6.377 \times 10^{-5} - 14.76\ C \times 10^{-5}$.

Ternary Mass Transfer

The ternary diffusion results (Part I) indicate that coupling effects are fairly significant in that cross diffusion coefficients are generally about 10 to 40% of the main diffusion coefficients. Further, the main diffusion coefficients are found to be approximately equal except in the vicinity of the critical point.

The composition paths in all the extraction experiments were straight lines (Figure 6). As discussed in Appendix A, this implies that the mass transfer coefficient matrices are diagonal. In view of the fact that $\mathbf{D}$ is nondiagonal this can be explained by expressing the relation between $\mathbf{k}$ and $\mathbf{D}$ as

$$\mathbf{k} = \phi\,\mathbf{D}^n \tag{17}$$

where ϕ is a function of hydrodynamic conditions and n is an exponent between 0 and 1. The surface renewal theories predict n to be 0.5. It can be proved using Sylvester's theorem (Amundson, 1966) that for a given matrix $\mathbf{D}$, the off-diagonal elements of $\mathbf{D}^n$ would be halved if n is equal to 0.5. Therefore, the degree of coupling would be considerably reduced so that $\mathbf{k}$ would be almost a diagonal matrix.

The schlieren results (Table 1) confirm that interfacial turbulence was absent in the binary system and in those ternary experiments for which the slope of the operating line was negative. On the other hand, interfacial activity was found to be pronounced in the ternary system if m was positive. The decrease in the mass transfer coefficients with decreasing driving force for the ternary extraction runs in which m was positive (Figure 9) was therefore ascribed to the decay of interfacial turbulence. The dependence of k_T on the driving force was explained using a physical model.

In the following development, the mass transfer process in the stirred cell is assumed to be governed by the rate of surface renewal. If interfacial turbulence were absent, the average mass transfer coefficient can be approximated by an expression based on the penetration theory, that is,

$$k_0 = \left(\frac{4}{\pi}\right)^{1/2}\left(\frac{D_I}{\theta_0}\right)^{1/2} \tag{18}$$

where θ_0 is the time an element of liquid spends at the interface. θ_0^{-1} can be interpreted as a surface renewal rate, which would be expected to be a function of the stirring rate.

In the presence of interfacial turbulence spontaneous agitation at the interface can be seen, from one point of view, as increasing the rate of surface renewal. This effect can be expressed by

$$\frac{1}{\theta} = \frac{1}{\theta_0} + \frac{1}{\theta'} \tag{19}$$

where θ^{-1}, the surface renewal rate in the presence of interfacial turbulence and stirring is assumed to be the sum of characteristic renewal rates associated with stirring and interfacial turbulence respectively.

When interfacial instability occurs, the mass transfer is aided by the interfacial tension gradients. The interfacial stress S driving the flow is given by

$$S = \frac{\partial \sigma}{\partial z} \tag{20}$$

where z is the coordinate along the interface. σ, the interfacial tension, is expected to depend on the constituent compositions. For an n-component system therefore

$$\sigma = \sigma(C_1, C_2 \ldots . C_{n-1}) \tag{21}$$

Invoking the chain rule S can be rewritten as

$$S = \sum_{i=1}^{n-1} \sigma_{ci} \frac{\partial c_i}{\partial z} \tag{22}$$

where

$$\sigma_{ci} = \left(\frac{\partial \sigma}{\partial c_i}\right)_{cj} \tag{23}$$

Most experimental results tend to confirm that the concentration gradients along the interface are related to those normal to the interface. It is therefore postulated that

$$\frac{\partial c_i}{\partial z} \simeq \beta \frac{\partial c_i}{\partial y}\bigg|_{y=0} \tag{24}$$

where y is the coordinate normal to the interface. Now

$$J_{iI} = -\sum_j D_{ij} \frac{\partial c_j}{\partial y}\bigg|_{y=0} \tag{25}$$

or

$$\frac{\partial c_i}{\partial y}\bigg|_{y=0} = \sum_j d_{ij} J_j \tag{26}$$

where

$$\mathbf{d} = -\mathbf{D}^{-1} \tag{27}$$

From Equations (22) and (24) to (26), one obtains

$$S = \beta \sum_i \sigma_{ci} \sum_j d_{ij} J_j \tag{28}$$

Equation (28) can be rewritten as

$$S = \Sigma P_j J_j \tag{29}$$

where

$$P_j = \beta \sum_i d_{ij} \sigma_{ci} \tag{30}$$

For the 3-component case Equation (29) reduces to

$$S = P_2 J_2 + P_3 J_3 \tag{31}$$

Since

$$J_i = k_T C_T (\Delta x_i) \tag{32}$$

$$S = k_T C_T (P_2 \Delta x_2 + P_3 \Delta x_3) \tag{33}$$

In all the experiments

$$\frac{\Delta x_2}{\Delta x_3} = r = \text{constant} \tag{34}$$

so that, dividing Equation (33) by Δx_3, one gets

$$S = k_T C_T \Delta x_3 \, (P_2 r + P_3) \tag{35}$$

It is supposed that the instability is characterized by cells circulating at a particular velocity. The cells would be sustained if the interfacial stress S were counterbalanced by viscous forces such that

$$S = \eta \frac{\partial v}{\partial y} \tag{36}$$

The velocity gradient can be approximated by

$$\frac{\partial v}{\partial y} = \frac{y_0/\theta'}{y_0} = \theta'^{-1} \tag{37}$$

where y_0 is the characteristic dimension of each cell and θ' is related to the cell circulation time. From Equation (36), θ' is calculated to be

$$\theta' = \frac{\eta}{S} \tag{38}$$

Next, it is assumed that the mass transfer coefficient in the presence of interfacial turbulence can be expressed by a relationship similar to Equation (18) taking into account the reduced exposure time, θ, that is,

$$k_T = \left(\frac{4}{\pi}\right)^{1/2} \left(\frac{D_I}{\theta}\right)^{1/2} \tag{39}$$

From Equations (18), (19), (38), and (39) it can be shown that

$$k_T^2 = k_0^2 + \frac{4 D_I}{\pi} \, \frac{S}{\eta} \tag{40}$$

Substituting for S from Equation (35), Equation (40) simplifies to

$$k_T^2 = k_0^2 + \gamma \, k_T \Delta x_3 \tag{41}$$

with

$$\gamma = \frac{4\, D_I}{\pi} \, \frac{C_T}{\eta} \, (P_2 r + P_3) \tag{42}$$

Equation (41) can be rewritten as

$$k_T \left\{ 1 - \left(\frac{k_0}{k_T}\right)^2 \right\} = \gamma \, \Delta x_3 \tag{43}$$

From this one concludes that the variable on the left-hand side if plotted against Δx_3 should give a straight line passing through the origin for a given experiment. In order to verify this, one needs to know k_0.

Since k_0 was not directly obtainable from the results of experiments in which interfacial turbulence occurred, Equation (41) was employed. The plots of k_T^2 against $k_T \Delta x_3$ (Figure 11) were found to be linear, as expected, and the value of k_0 was obtained from the y-intercept. These values summarized below compare favorably with the mass transfer coefficients estimated for similar experiments in which interfacial turbulence was absent (Figure 8).

Run	k_0(cm/s) × 10^3
IIA	6.98
IIB	7.4
IIC	1.62

Finally, these values of k_0 were used to calculate the left-hand side of Equation (43). The resulting plots of

$k_T\{1 - (k_0/k_T)^2\}$ against Δx_3 are presented in Figure 12. In all cases, the correlation coefficients for the linear regression are about 0.99. Equation (43) therefore gives a means of expressing the mass transfer coefficient data for experiments in which interfacial turbulence is present.

In contrast to equation (41), the treatment of Davies (1972) suggests that k_T^2 should vary linearly with Δx_3. When plotted in this manner, the present data exhibit considerable nonlinearities.

The results demonstrate that mass transfer in interfacially unstable ternary systems, though understandably complex, can be explained in a simple way. Of course, in order to apply Equation (43) for predicting k_T, more data would be necessary. However, the results obtained certainly warrant further evaluation of the theory.

CONCLUSIONS

The following major conclusions are made based on the results of the investigation of mass transfer in the ternary liquid-liquid system acetonitrile-benzene-*n*-heptane.

1. The operating paths in the extraction experiments in which an unsaturated phase is treated with a nearly saturated phase are straight lines. From this it is concluded that the mass transfer matrices are diagonal.

2. It is possible to discern two distinct mechanisms of transfer from the results of the extraction experiments. In this regard it is established that in the ternary system, interfacial conditions, and thus the mechanism, can be altered by changing the slope of the operating line in the unsaturated phase.

3. In ternary experiments in which the slope of the operating line is negative, the results indicate that the mass transfer coefficients are independent of the driving force. Further, the coefficients are of the same magnitude as those obtained for the partially miscible binary system. In all such experiments the interface is stable as is confirmed from the results of the photographic investigation.

4. In those ternary experiments in which the slope of the operating line is positive and above a critical value the coefficients, in addition to being much higher than in the experiments described in the previous paragraph, decrease as equilibrium is approached. The schlieren results conclusively establish the presence of surface instabilities in all such experiments. The driving-force dependence of these coefficients obtained under conditions of interfacial turbulence can be described using a surface renewal model of the process.

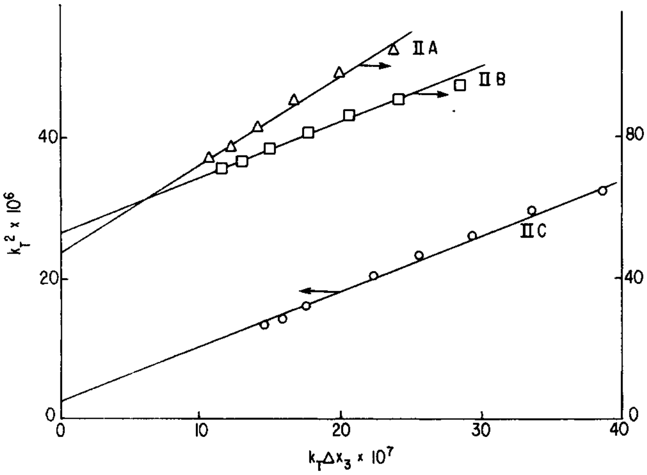

Fig. 11. Variation of k_T^2 with $k_T\Delta x_3$ for ternary extraction runs IIA, IIB, and IIC.

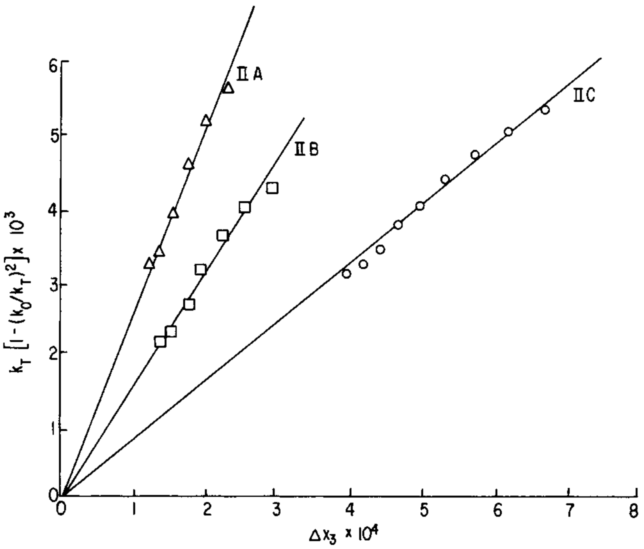

Fig. 12. Variation of $k_T\left[1 - \left(\frac{k_0}{k_T}\right)^2\right]$ with Δx_3 for ternary extraction runs IIA, IIB, and IIC.

NOTATION

a_1 = parameter defined by Equation (9a) in Part I
a_2 = parameter defined by Equation (9b) in Part I
A_I = interfacial area
c = molal concentration
C = molar concentration
$\mathcal{D}$ = binary mutual diffusion coefficient
D = characteristic ternary diffusivity
$\mathbf{D}$ = matrix of diffusion coefficients defined in a volume-fixed reference frame
D_{ij} = element of $\mathbf{D}$
D_1 = smaller eigenvalue of $\mathbf{D}$
J = molar flux
$\mathbf{k}$ = mass transfer coefficient matrix
k_{ij} = element of $\mathbf{k}$
$\mathbf{L}$ = matrix of phenomenological coefficients
L_{ij} = element of $\mathbf{L}$
m = slope of binodal curve
N = number of moles
$\mathbf{P}$ = modal matrix of $\mathbf{D}$
r = slope of operating line
S = interfacial stress
t = time
t^* = slope of tie-line
v = velocity
x = mole fraction
$\mathbf{X}$ = matrix defined by Equation (21) in Part I
y, z = distance coordinates

Greek Letters

α = slope of limiting tie-line at critical point
β = diaphragm cell calibration constant
γ = defined by Equation (42)
η = absolute viscosity
θ = contact time
$\boldsymbol{\mu}$ = matrix of composition derivatives of chemical potential
μ_{ij} = element of $\boldsymbol{\mu}$
σ = interfacial tension
τ = reduced run time

Subscripts

i, j = component
p = phase

b = bottom
t = top
B = binary
T = ternary
$*$ = equilibrium value
0 = initial value

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APPENDIX A

In the event the composition trajectories are linear, it follows that

$$\frac{dx_1}{dx_2} = \frac{x_1 - x_1^*}{x_2 - x_2^*} = r \tag{A1}$$

Since C_T, the total concentration, remained almost constant during the course of an experiment, Equation (5) could be rewritten as

$$J_{iI} = C_T \sum_j k_{ij}(\Delta x_j) \tag{A2}$$

Therefore

$$\frac{J_{1I}}{J_{2I}} = \frac{k_{11}(\Delta x_1) + k_{12}(\Delta x_2)}{k_{21}(\Delta x_1) + k_{22}(\Delta x_2)} \tag{A3}$$

where

$$\Delta x_j = (x_j - x_j^*) \tag{A4}$$

On substituting Equation (A1) into Equation (A3), we obtain

$$\frac{J_{1I}}{J_{2I}} = \frac{k_{11}\, r + k_{12}}{k_{21}\, r + k_{22}} = r \tag{A5}$$

Since Equation (A5) is valid for all values of m, it follows that

$$k_{12} = k_{21} = 0 \tag{A6a}$$

and

$$k_{11} = k_{22} = k_T \tag{A7}$$

Therefore

$$\mathbf{k} = k_T\,\mathbf{I} \tag{A8}$$

APPENDIX B

The interfacial flux was calculated by idealizing the process as follows: The mass transfer at the interface was assumed to be governed by the penetration type of mechanism. The entire volume of liquid was assumed to consist of discrete elements of liquid. It was supposed that each of the elements was exposed to the interface during which material was transferred to it. The problem was further simplified by postulating that the exposure times were small enough so that the bulk concentration C_{bi} could be considered to remain constant during the surface renewal.

The continuity describing the mass transfer can be written as

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial y}\, \mathcal{D}(c)\, \frac{\partial c}{\partial y} \tag{B1}$$

This was to be solved subject to the following initial and boundary conditions:

$$\begin{aligned} t = 0 \quad & c = c_{bi} \quad \text{for all } y \\ t > 0 \quad & c = c_i^* \quad y = 0 \\ & c = c_{bi} \quad y = \infty \end{aligned} \tag{B2}$$

The method of solution, which is based on an iterative technique, is discussed in detail by Crank (1957) for a diffusion coefficient-concentration relationship of the type

$$\mathcal{D} = \mathcal{D}_0\, f(c) \tag{B3}$$

For the system under consideration, acetonitrile-*n*-heptane from the diffusion results in Part I we obtain

$$\mathcal{D}_0 = 6.38 \times 10^{-5}$$

$$f(c) = 1 - \frac{0.148}{6.38 \times 10^{-5}}\, C$$

with c expressed in mole /liter.

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