putation facilities of University of Toronto were used for this investigation.

NOTATION

a, = delay time
a_{ij} = constants
$\mathbf{A}$ = coefficient matrix whose (i, j)th element is a_{ij}
$\mathbf{B}$ = constant matrix whose (i, j)th element is $a_{ij}\ \theta_{ij}$
c = reactant concentration
$\mathbf{C}$ = constant matrix whose (i, j)th element is $a_{ij}\ \theta_{ij}^2/2$
$\mathbf{G}$ = matrix defined by Equation (9)
$\mathbf{I}$ = identity matrix
K = proportional controller constant
p = expression given in Equation (21)
q = vapor stream flow rate
r = reaction rate; see Equation (30)
t = time
T = temperature
$x_i(t)$ = state variable
$\mathbf{x}(t)$ = state vector

Greek Letters

α = expression given in Equation (26)
β = expression given in Equation (27)
θ_{ij} = delay time

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Transport of Mass in Ternary Liquid-Liquid Systems

The diffusional behavior of the ternary partially miscible liquid system acetonitrile-benzene-*n*-heptane is investigated at 25°C using the diaphragm cell technique. The mutual diffusivity of the partially miscible binary system acetonitrile-*n*-heptane is found to be a strong function of concentration; the concentration dependence is described using a linear relationship. The diffusion coefficient matrix of the ternary system acetonitrile-benzene-*n*-heptane is determined at a number of points, and the ternary diffusion matrices are found to be significantly coupled with the off-diagonal elements of about 10 to 40% of the main diffusion coefficients.

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SCOPE

Most of the previous experimental work on interfacial mass transfer in ternary heterogeneous liquid systems has been restricted to mutually saturated bulk phases with only one transferring solute. However, practical mass transfer processes usually occur between unsaturated bulk phases and sometimes involve the simultaneous transfer of more than a single constituent. Furthermore, although some information has accumulated on the diffusion coefficients of ternary liquid systems, few parallel direct measurements of the corresponding mass transfer coefficients in such systems have been attempted. It is well known that the diffusive interactions in thermodynamically nonideal systems can be very pronounced; therefore, it is of interest to investigate the corresponding behavior of the mass transfer coefficients. In addition, mass transfer in liquid-liquid systems may be accompanied by interfacial instabilities. These alter the hydrodynamic conditions in the vicinity of the interface and thus affect the transfer rate. This means that conclusions cannot be drawn concerning the

effect of molecular diffusion on the transfer rates unless interfacial activity is either negligible or accounted for directly.

Therefore, this study is directed toward the simultaneous determinations of mass transfer rates, diffusion coefficients, and interfacial activity in the ternary liquid-liquid system: acetonitrile-benzene-*n*-heptane. The basic objective of this work is the direct comparison of mass transfer coefficients measured in a Lewis cell, with the diffusion coefficients obtained by the diaphragm cell technique, in order that the mechanism of the mass transfer process can be identified for such a partially miscible ternary system. In this way, the relative importance of both diffusive interactions and interfacial activity can be quantitatively assessed.

CONCLUSIONS AND SIGNIFICANCE

The diffusion coefficients of the partially miscible ternary liquid system: acetonitrile-benzene-*n*-heptane are strong functions of relative composition. The binary diffusivity of acetonitrile in *n*-heptane at 25°C varies by more than a factor of two over a mole percent range of only 2%. The ternary diffusion coefficient matrices contain interaction terms of about 10 to 40% of the main terms and the composition variation of the terms appears to become very strong near the critical point.

In contrast to the diffusion measurements, the mass transfer coefficients for this system, obtained in a modified Lewis cell, show no significant interaction effects. The mass transfer behavior of this system is characterized by the existence of interfacial instability which enhances the mass transfer rate. This interfacial activity is governed by the relative driving forces for the mass transfer process. It is established that, provided the ratio of the mole fraction driving forces exceeds a certain critical value, the mass transfer rates are enhanced because of the presence of interfacial instability. A model based upon the theory of surface renewal is developed to explain the results. The mass transfer coefficient data lend support to the theory which predicts the driving force dependence of the mass transfer coefficients.

Part I. Diffusion Studies

Most of the theoretical work related to diffusion in partially miscible systems has centered on studying diffusion at and near critical states. In particular, it is established that the mutual diffusion coefficient of a partially miscible binary system vanishes at a critical point (Levich, 1962). Furthermore, detailed requirements concerning the structure of multicomponent diffusion coefficient matrices at critical points can be established (Kirkaldy and Purdy, 1969).

A recent experimental study of mass transfer in the partially miscible ternary liquid system acetone-glycerol-water (Standart et al.) tends to confirm that the diffusion coefficient matrix becomes singular at the critical point. The experimental data were obtained in a modified Lewis cell. In the study of the transfer between unsaturated liquid phases, it was found that any diffusion path in the homogeneous ternary region which terminates at the critical point ultimately coincides with the limiting tie line and further becomes stationary in the region near the critical point. This indicates that interaction among the various flows can be very pronounced during mass transfer in multicomponent liquid-liquid systems.

Few general conclusions about the behavior of such systems can be made, however, because of the lack of diffusion data. The objective of the present work is to provide such information by experimentally investigating the binary and ternary diffusional behavior of the liquid-liquid system acetonitrile-benzene-*n*-heptane.

THEORY

The principles of the thermodynamic theory of critical phenomena were established by Gibbs (1906). The problem has been treated in great detail by Prigogine and Defay (1954) who enumerated the following conditions for stability in a ternary system.

$$\mu_{11} > 0 \quad \mu_{22} > 0 \quad \mu_{11}\mu_{22} - \mu_{12}^2 \geqq 0 \tag{1}$$

where

$$\mu_{ij} = \left(\frac{\partial \mu_i}{\partial x_j}\right)_{T,P} \tag{2}$$

The boundary separating the stable from the unstable states is given by

$$\mu_{11}\mu_{22} - \mu_{12}^2 = 0 \tag{3}$$

This relationship defines the spinodal curve which necessarily passes through the critical point. Any system whose representative point is located in the unstable region breaks up into two stable phases. The binodal curve is defined by the conditions of coexistence of the two phases, namely,

$$\mu_1' = \mu_1'' \quad \mu_2' = \mu_2'' \quad \mu_3' = \mu_3'' \tag{4}$$

The line joining the points representing two coexisting phases is called a *tie line*. It can be proved (Storonkin and Rusanov, 1960) that the equilibrium tie lines become parallel and converge at the critical point.

The thermodynamics of ternary systems in the vicinity of the critical point has been discussed by Storonkin and Rusanov (1960) and recently by Kirkaldy and Purdy (1969). Storonkin and Rusanov analyzed the relationships between the μ_{ij}, and it was shown that for any point on the binodal curve the following holds:

$$m = -\frac{\mu_{11} + t^*\mu_{12}}{\mu_{12} + t^*\mu_{22}} \tag{5}$$

where m = slope of the binodal curve at that point and t^* = slope of the tie line passing through the point.

At the critical point $m = t^*$ (= say α), and in addition Equation (3) applies so that

$$\alpha = -\frac{\mu_{12}}{\mu_{22}} \tag{6a}$$

and

$$\alpha^2 = \mu_{11}/\mu_{22} \tag{6b}$$

which are the spinodal relations of Kirkaldy and Purdy (1969).

Equation (5) can be combined with the expression for the matrix of diffusion coefficients to give a general equation for the diffusion coefficients valid at any point on the binodal curve. Thus, if the diffusion coefficient matrix is written (deGroot and Mazur, 1962) as

$$\mathbf{D} = \mathbf{L}\,\boldsymbol{\mu} \qquad (7)$$

then Equation (5) can be incorporated to give the following result for the diffusion coefficient matrix of a partially miscible ternary system at any point on the binodal curve:

$$\mathbf{D} = \mu_{11} \begin{bmatrix} L_{11} - \dfrac{L_{12}}{a_1} & -\dfrac{L_{11}}{a_1} + \dfrac{L_{12}}{a_2^2} \\ L_{12} - \dfrac{L_{22}}{a_1} & \dfrac{L_{22}}{a_2^2} - \dfrac{L_{12}}{a_1} \end{bmatrix} \qquad (8)$$

where

$$a_1 = \frac{t^* + m}{1 + \dfrac{mt^*}{a_2^2}} \qquad (9a)$$

and

$$a_2 = \sqrt{\frac{\mu_{11}}{\mu_{22}}} \qquad (9b)$$

At the critical point

$$m = t^* = \alpha \qquad (10)$$

so that from Equations (8) and (9)

$$|\mathbf{D}| = 0 \qquad (11)$$

The eigenvalues of $\mathbf{D}$, D_i, are defined by the characteristic equation for $\mathbf{D}$, which can be written as

$$(D_{12} - D)(D_{22} - D) - D_{12}D_{21} = 0 \qquad (12)$$

If Equation (11) applies, then

$$D_{11}D_{22} = D_{12}D_{21} \qquad (13)$$

Solving Equation (12) in this case, we found that the smaller eigenvalue of $\mathbf{D}$ vanishes at the critical point, that is,

$$D_1 = 0 \qquad (14)$$

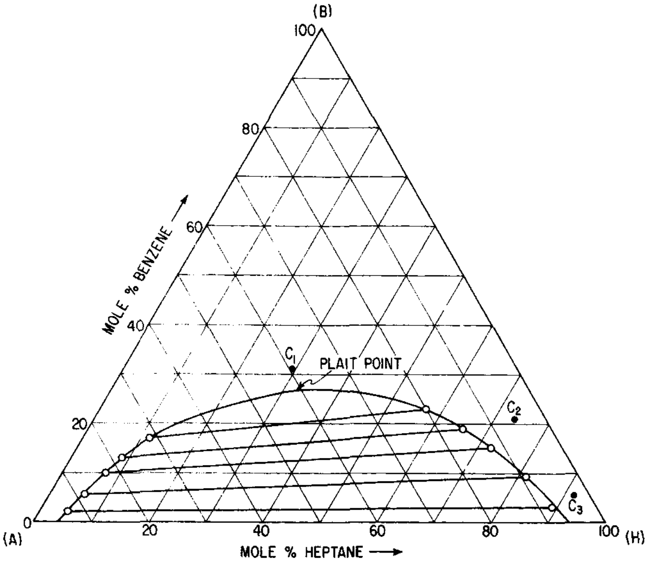

Fig. 1. Ternary liquid-liquid equilibria for the acetonitrile-benzene-*n*-heptane system at 25°C.

and the corresponding eigenvector at the critical coincides with the limiting tie line because

$$\frac{X_{21}}{X_{11}} = -\frac{D_{11} - D_1}{D_{12}} = \alpha \qquad (15)$$

From this one concludes that diffusive interaction effects become very significant near the critical point of a ternary system. It is our aim here to determine the change in the structure of the diffusion coefficient matrix as the critical point is approached. The diffusion measurements were made in the heptane-rich unsaturated phase.

EXPERIMENT

The system chosen for the investigation was acetonitrile(1)-benzene(2)-*n*-heptane(3). It is a type I system in which the liquid pairs 1-2 and 2-3 are miscible in all proportions at the prevailing temperature whereas 1 and 3 are partially miscible. The ternary liquid equilibria is typified by the isotherm shown in Figure 1. The tie line data were obtained by equilibrating

TABLE 1. LIQUID-LIQUID EQUILIBRIUM DATA FOR ACETONITRILE-BENZENE-*n*-HEPTANE AT 25°C

Mole fraction acetonitrile, X_1	Mole fraction benzene, X_2	Mole fraction heptane, X_3
[*] 0.0629	—	0.9371
0.9614	—	0.0381
0.0720	0.0384	0.8896
0.9348	0.0210	0.0442
0.0762	0.0631	0.8607
0.9127	0.0359	0.0514
0.1001	0.0989	0.8010
0.8809	0.0591	0.0600
0.1058	0.1273	0.7669
0.8602	0.0790	0.0608
0.1312	0.1560	0.7128
0.8265	0.1012	0.0723
0.1398	0.1705	0.6897
0.8150	0.1126	0.0724
0.1594	0.1941	0.6465
0.7814	0.1337	0.0849
0.1770	0.2170	0.6060
0.7462	0.1554	0.0984
0.2062	0.2319	0.5619
0.7191	0.1729	0.1080
0.2299	0.2467	0.5234
0.6857	0.1906	0.1238
0.3240	0.2695	0.4065
0.5800	0.2346	0.1855
[**] .459	0.26	0.281

In each case the first set of compositions corresponds to the heptane phase, the second set to the acetonitrile phase.

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[*] Binary equilibrium.

[**] Plait point composition; determined by extrapolation of the line data.

samples of mean composition in the immiscible region in a thermostatted shaker bath and is presented in Table 1. The three mean compositions at which the ternary diffusion coefficient measurements were made are denoted by C_1, C_2, and C_3 in Figure 1.

The diaphragm cell was utilized for the determination of diffusion data. The type of diaphragm cell and the experimental procedure employed were the same as those used in a previous work (Leffler and Cullinan, 1970). As before, an F & M Model 5750 gas chromatograph, coupled with a Hewlett Packard 3370A digital integrator, was used for the chemical analysis. The chemicals used in the cell experiments were all 99+ mol % quality reagent grade and were used as received.

The theory of the diaphragm cell has been reviewed elsewhere (Dunlop, 1972) for an $n + 1$ component system. The behavior of the diaphragm cell is governed by the following matrix equation

$$\frac{d\,\mathbf{\Delta C}}{dt} = -\beta\,\mathbf{D}\,\mathbf{\Delta C} \qquad (16)$$

and the following initial condition

$$\mathbf{\Delta C} = \mathbf{\Delta C}^0 \quad \text{at} \quad t = 0 \qquad (17)$$

β is a calibration parameter which depends on the volumes of the cell chambers and the diaphragm characteristics. Equation (16) can be integrated using Equation (17) to yield

$$\mathbf{\Delta C}^f = \exp\left(-\tau\,\mathbf{D}\right)\mathbf{\Delta C}^0 \qquad (18)$$

with

$$\tau = \beta t \qquad (19)$$

To determine all the elements of the $n \times n$ diffusion coefficient matrix $\mathbf{D}$ at least n independent cell runs must be performed at the same average concentration and at the same value of the reduced run time τ. If each vector of independent initial concentration difference $\mathbf{\Delta C}_i^0$ is arranged on a column of an $n \times n$ square matrix $\mathbf{C}^0$, then

$$\mathbf{C}^f = \exp\left(-\tau\,\mathbf{D}\right)\mathbf{C}^0 \qquad (20)$$

where $\mathbf{C}^f$ has columns which consist of the corresponding $\mathbf{\Delta C}_i^f$. Equation (20) can be solved to give

$$\exp\left(\tau\,\mathbf{D}\right) = \mathbf{C}^0\left(\mathbf{C}^f\right)^{-1} = \mathbf{X} \qquad (21)$$

The modal matrices of $\mathbf{D}$ and $\mathbf{X}$ are identical, and the eigenvalues of $\mathbf{D}$ and $\mathbf{X}$ are related by

$$D_i = \frac{1}{\tau}\ln X_i \qquad (22)$$

so that if $\mathbf{P}$ is the modal matrix of $\mathbf{X}$, $\mathbf{D}$ is directly obtained from the experimental data according to

$$\mathbf{D} = \mathbf{P}\begin{bmatrix} D_i & \\ & \diagdown \end{bmatrix}\mathbf{P}^{-1} \qquad (23)$$

The design of the experiments was based upon the analysis of Kosanovich and Cullinan (1971), which describes the optimum experimental conditions, C_i° and τ, for obtaining the best estimate of the diffusion coefficients in diaphragm cell experiments. The method was recently applied towards estimation of diffusion coefficients of a quaternary system (Rai and Cullinan, 1973). The procedure adopted by Rai and Cullinan (1973) was adapted to the ternary system in the present work.

RESULTS

Binary Diffusion Data

Binary diffusion coefficients for the system acetonitrile-*n*-heptane were measured at 25°C. All observations were made with acetonitrile dilute, and diffusion coefficients were obtained at several mean compositions.

The complete data for the binary system are presented in Table 2. The binary diffusivity-mean concentration data was found to be well correlated using linear regression as shown in Figure 2.

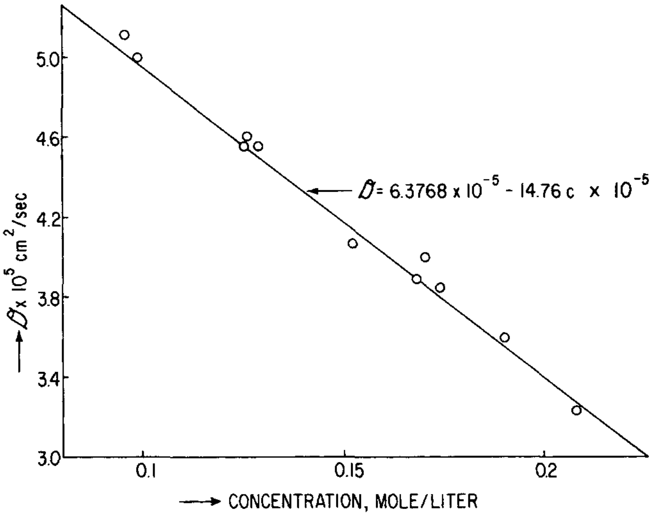

Fig. 2. The measured diffusion coefficient of acetonitrile in *n*-heptane at 25°C.

Table 2. Binary Diffusion Coefficients for the System Acetonitrile(1)-Heptane(3) at 25°C

Run	Cell	β*	C^0_{1T}**	C^0_{1B}**	C^f_{1T}**	C^f_{1B}**	t, mts	$\overline{C}_1$**	$\mathcal{D} \times 10^5$ cm^2/s
1	10	0.241238	0	0.24189	0.08399	0.17513	1483	0.12525	4.5470
2	30	0.193477	0	0.25852	0.07676	0.19190	1504	0.13179	4.6325
3	17	0.164080	0	0.29586	0.07167	0.24054	1399	0.15202	4.0715
4	10	0.241238	0	0.25151	0.07380	0.17688	1336	0.12555	4.6126
5	30	0.193477	0	0.25421	0.06851	0.19555	1381	0.12957	4.3268
6	17	0.164080	0	0.25446	0.06048	0.19865	1358	0.12795	4.5676
7	10	0.241238	0.09914	0.31646	0.16736	0.25069	2124	0.20841	3.1176
8	10	0.241238	0.04836	0.19193	0.11022	0.15373	1892	0.12606	4.3597
9	17	0.16535	0.04754	0.20337	0.10420	0.15478	2649	0.12747	4.2820
10	30	0.19482	0.08273	0.24970	0.14738	0.20365	2291	0.17087	4.0617
11	10	0.24124	0.08805	0.239195	0.15834	0.19987	2250	0.17136	3.9578
12	30	0.19482	0.04918	0.28999	0.11701	0.23891	1513	0.17377	3.8494
13	17	0.16535	0.04412	0.29521	0.09529	0.23742	1471	0.16801	3.8996
14	17	0.16917	0	0.19616	0.04877	0.13096	1577	0.09490	5.2879
15	17	0.16917	0	0.20464	0.04514	0.14320	1333	0.09825	5.0016

* Because the glass stirrers are actually in contact with the diaphragm and probably wear it by friction forces, there is a slight change in β with time. This necessitated recalibration of the cells every few weeks, and therefore the tabulated values of β for a particular cell are not constant.

** moles/liter.

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 cm^2/s (× 10^5).
** 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.