Ternary Mass Transfer in Liquid-Liquid Extraction

Isothermal mass transfer was studied in a stirred cell with movable baffles using a ternary system with partially miscible solvents (water-acetone-glycerol). The measurements were extended from the binary solvent pair to the vicinity of the critical point. It was found that the straight line composition paths in the homogeneous regions on extensions of the equilibrium tie lines characteristic of the critical region applied over the ternary diagram. The results could not be explained even qualitatively by assuming mass transfer without driving force interactions. The principles of irreversible thermodynamics were used to explain the observations and to evaluate the appropriate mass transfer coefficients.

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SCOPE

Practical mass transfer processes often occur between unsaturated bulk phases and frequently involve the simultaneous transfer of more than a single constituent. In contrast, most of the previous experimental work on interfacial mass transfer in ternary heterogeneous systems has been restricted to mutually saturated bulk phases with only one transferring solute.

Although some information has accumulated on the diffusion coefficients of ternary systems, no parallel direct measurements of the corresponding mass transfer coefficients in such systems have been attempted until now. Since it is well known that the diffusive interactions in thermodynamically nonideal systems can be very pronounced, it is of obvious interest to investigate the corresponding degree of coupling in the mass transfer coefficients.

The objective of this study was to measure directly the mass transfer coefficients for a ternary heterogeneous system in a situation in which simultaneous transfer occurred between unsaturated phases.

CONCLUSIONS AND SIGNIFICANCE

Mass transfer between unsaturated bulk phases of a ternary system with partially miscible solvents was studied in a modified Lewis cell. Measurements of the composition changes of corresponding phases in contact were carried out over the full range from the binary solvent pair to the region near the critical point. Qualitatively, the results indicated that, in general, the diffusive flux of each constituent depended not only on the composition driving force for that constituent, but also on the driving forces of the other diffusing species.

Given the necessity of adopting mass transfer relations which included terms to account for such interactions, experiments were performed in order to determine the mass transfer coefficients in each phase for a single set of compositions. The results show that the flux of a given constituent depends very strongly on the driving forces of the other diffusing species.

Most previous measurements of isothermal interfacial mass transfer in ternary heterogeneous systems have involved saturated or near saturated phases, particularly with nearly immisicible (and hence) mutually saturated carrier streams as in absorption and extraction where only one solute is transferred between the phases. Even if the carrier or solvent streams are partially miscible, if each remains saturated during the mass transfer, the constituent driving forces are severely constrained and there is in fact only one independent driving force in each phase (pseudo-binary behavior).

Therefore, it was considered of interest to investigate the case of such mass transfers, where the bulk phases could be unsaturated throughout the process, to establish the behavior of such true ternary constituent exchanges. A liquid-liquid extraction was chosen for simplicity of operation and also because the thermal effects accompanying the mass transfer are so small that the maintenance of isothermal conditions is easy. Such a process requires a system whose heterogeneous region occupies only part of the composition triangle (Figure 1) with substantial homogeneous regions in which the compositions of the bulk phases can shift during the mass transfer. We chose the system glycerol-water-acetone (Type 1) as a convenient one for our purposes. (Its only real disadvantages are the high viscosity and low volatility of glycerol which cause rapid changes in system properties in the glycerol rich region and difficulties in thermodynamic property evaluations respectively.) Schlieren studies indicate that Marangoni-type interfacial instabilities do not occur to any appreciable extent in this system.

The extraction was carried out in a modified batch Lewis extraction cell (Figure 2) with two turbine stirrers which can be either co- or counter-rotated. Vertical baffles aid the efficient mixing of the bulk phases and a horizontal

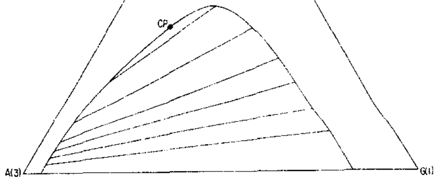

Fig. 1. Liquid-liquid equilibrium diagram for glycerol(1)-water(2)-acetone(3) system at 25°C.

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ring and disk baffle at the interface provide the calming action necessary to avoid rippling of the annular liquid-liquid interface. The ratio of the stirrer speeds can be varied and the stirrers were run at the maximum frequencies possible without agitating the interface. Because very large volume changes may occur during the extraction, the horizontal baffle system was made vertically movable over wide limits so that the interface could always be kept at the middle of the ring and disk baffles throughout the extraction process. Representative samples of the bulk phases were withdrawn through sampling tubes at suitable intervals during the equilibration. The whole extraction cell was thermostatted at 25°C and the stirrer drive provided by a regulated motor with the frequency checked by a timer-counter with a photocell pickup from a striped disk on a drive sheave.

The samples were analyzed by determining their density in Lipkin and capped bottle pyncnometers and their refractive indexes in a Zeiss dipping refractometer with a set of thermostatted prisms. By using a number of precautions especially with the refractometer measurements, standard deviations of $\sigma_d = 1.5 \cdot 10^{-4}$ and $\sigma_{ri} = 1.3 \cdot 10^{-5}$ were attained consistently. The compositions were represented by 5th order orthogonal polynomials of the density and refractive index in x_1, x_2 ($1 =$ glycerol, $2 =$ water, $3 =$ acetone). The resultant standard deviations of the composition determinations as found from analyses of mixtures of known compositions were $\sigma_{x_1} = 0.0015$, $\sigma_{x_2} = 0.004$, $\sigma_{x_3} = 0.004$.

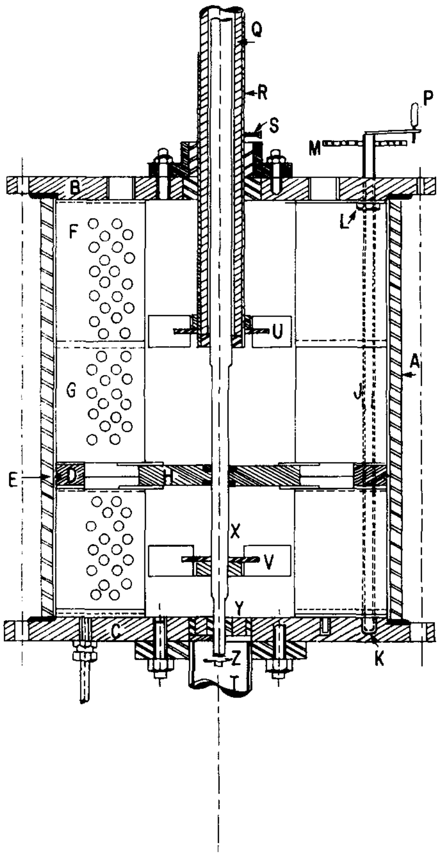

Fig. 2. Extraction cell. A: glass cylinder; B: top plate; C: bottom plate; D: movable interfacial ring; E: PTFE o-ring; F, G: vertical baffles; H: central baffle; J: threaded bolts; K: holes to seat bolts; L: nut; M: bicycle gear; N: bicycle chain; P: handle; Q: upper phase stirring shaft; R: stainless steel tube; S: locking screw; T: level compensator; U: upper phase propeller; V: lower phase propeller; X: lower phase stirring shaft; Y: teflon bushing; and Z: joining screw.

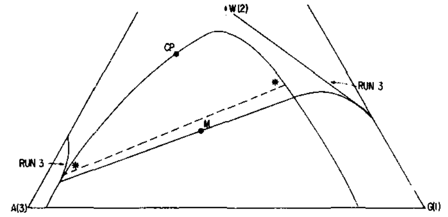

Fig. 3. Equilibrium paths in composition triangle.

After filling the cell with known amounts of the two unsaturated phases, the drive was started and the equilibration allowed to proceed. The bulk phase samples provided composition trajectories (x_1, x_2) in each phase and the known initial quantities gave the lever rule mixture point M (Figure 3) through which straight lines connecting corresponding composition points always passed. The equilibrium tie line through the mixture point gave the final equilibration points on the saturated binodal curves.

The material balances

$$N_{ta} + N_{tg} = N_{t0}$$
$$N_{ia} + N_{ig} = N_{i0} \qquad (1)$$

with the relations

$$N_i = x_i N_t, \quad N_t \equiv \sum_{i=1}^{3} N_i \qquad (2)$$

for the well mixed phases permitted calculation of the amount of each phase N_t at each sampling time from the initial amount N_{t0} and the bulk phase compositions x_i with redundancy. By differentiation, the interfacial total molar transfer rates

$$N_i \equiv \frac{dN_i}{dt} \quad N_t \equiv \frac{dN_t}{dt} \qquad (3)$$

could then be determined. The characterization of the mass transfer process is facilitated by the introduction of the constituent diffusive transfer rates, defined by (see Appendix A).

$$j_i \equiv \dot{N}_i - x_i \dot{N}_t \qquad (4)$$

Although these diffusive transfer rates can be found from this relation, it is more convenient as well as more accurate to employ Equations (2) and (3) to obtain the relation

$$j_i = N_t \frac{dx_i}{dt} \qquad (5)$$

for our batch process. In our ternary system there are only two independent driving forces and two independent mass transfer rates as is easily seen from Equation (5) for

$$\sum_{i=1}^{3} j_i = 0 \qquad (6)$$

Indeed if we take the ratio of Equation (5) for say glycerol and water ($i = 1, 2$), we find the useful expression

$$\frac{j_1}{j_2} = \frac{dx_1}{dx_2} \qquad (7)$$

The right-hand member is just the slope of the equilibration trajectory in mole fraction composition space for that phase. Note that the diffusive transfer rates in the two phases are not only not equal but are not simply related. It can be shown that there is also a linear dependence among the total constituent transfer rates and that a knowledge of the two independent diffusive transfer rates in each phase suffices to determine the complete system behavior during the equilibration process. The material balances already introduced furnish the additional relations required to make the situation well determined. This point is worth emphasizing for here we do not have the simple textbook cases of equimolar counterflow or negligible transfer of an immiscible carrier stream. Instead the total mixture transfer rate $\dot{N}_t$ can have either sign or even change sign during a given equilibration run as can any total or diffusive constituent transfer rate in this very general case.

The latter rates were evaluated by numerical differentiation of the composition data according to Equation (5). The results were smoothed within the limits of the composition determinations, and although the accuracies varied, typical standard deviations were 7 or 8% of the average values of the j_i. If desired, the total constituent transfer rates could then be found from Equation (4) and $\dot{N}_t$, also determined by graphical differentiation.

It is closely in keeping with convention to assume that the mass transfer driving forces are the differences between the interfacial (*) and the bulk phase constituent mole fractions

$$\Delta x_i \equiv x_i^* - x_i \tag{8}$$

and that, in general, we can write

$$N_i = \sum_{j=1}^{2} K_{ij} \Delta x_j \tag{9}$$

or

$$j_i = \sum_{j=1}^{2} k_{ij} \Delta x_j \tag{10}$$

It is easy to see that

$$k_{ij} = K_{ij} - x_i \sum_{k=1}^{3} K_{kj} \tag{11}$$

and as indicated above we shall usually consider only the diffusive transfer coefficients k_{ij}. Of course, these coefficients generally are functions of the composition of the given phase.

To evaluate the merits of these formulations it is appropriate to start with the simplest case first in which the diffusive coefficient matrix is assumed to be diagonal (that is, $k_{ij} = 0,\ i \neq j$) when it can easily be shown that the diagonal elements are equal ($k_{ii} = k$), except possibly in very dilute solutions (see Appendix B).

The simplifications introduced by this assumption suggest a test experiment in which one phase is initially saturated and the other lies on the straight line extension of the tie line from this saturated state. On combining Equations (7), (8), and (10) for this case we would have

$$\frac{dx_1}{dx_2} = \frac{x_1^e - x_1}{x_2^e - x_2} = m \quad [\text{diagonal } k] \tag{12}$$

where (x_1^e, x_2^e) are the interfacial concentrations in the unsaturated phase in equilibrium with the saturated phase. The trajectory thus has the same slope m as the ratio of the driving forces so one can only expect the former phase to equilibrate along the straight line joining x_i^e and x_i, for there is no driving force in either phase to cause a lateral displacement of the interfacial compositions along the binodal curves. (The mass transfers in the saturated phase are purely convective at constant composition under this assumption, as $\Delta x_i = 0$ and so $j_i = 0$ in that phase.) This result is valid regardless of how k varies with the composition of the phase because Equation (12) is a result valid for any diagonal formulations.

In this connection it must be remembered that the overall material balance lever rule requires that if the saturated phase shifts in composition along the binodal curve either way, the unsaturated phase must shift in the opposite direction away from the straight line path. No choice of interfacial states at phase equilibrium could give rise to such displacements assuming the validity of Equation (12). Equally, if the saturated phase has a fixed composition, the equilibration path must be straight by the lever rule [irrespective of the validity of Equation (12)], and further the saturated and interfacial states must be the same ($j_i = 0$ in the saturated phase and so $\Delta x_i = 0$ there).

Several test runs were made to test these arguments and it was found that the composition of the saturated phase (whether acetone or glycerol rich) did remain constant and the unsaturated path trajectory was a straight line within the limits of detectable experimental error, thus disposing of the argument that initially and hence subsequently the interfacial state might differ from the saturated tie line state.

We may now consider a general equilibration run with both phases unsaturated and laterally displaced on opposite sides of the final equilibrium tie line (Figure 3). Let us assume that initially the glycerol phase lies below (that is, water poorer) and the acetone phase, above (that is, water richer) the final equilibrium tie line.

Clearly, only if the diffusive coefficient matrix is diagonal and the interfacial compositions are constant (equal to the final equilibrium values) will the trajectory of the equilibrium path in either phase be a straight line. However, in all such runs with both phases unsaturated and laterally displaced on opposite sides of the equilibrium tie lines, nonlinear trajectories were observed in both phases.

The only explanation of such curvilinear paths in which the simplification of a diagonal diffusive mass transfer coefficient matrix might be retained must involve a deviation of the interfacial composition from the equilibrium state. To test this possibility, let us assume that initially the interfacial state tie line lies above (that is, water richer) this equilibrium tie line, as shown. According to Equation (12), the trajectory of the equilibration path should have a tangent which intersects the binodal curve at the interfacial state—in fact

$$x_1^* = m x_2^* + (x_1 - m x_2) \quad [\text{diagonal } k] \tag{12'}$$

is the equation of a straight line relating the interfacial state compositions in each phase. Thus the glycerol rich phase should have a trajectory concave to its binodal curve, while the acetone phase should have a trajectory convex to its binodal curve and could become saturated before equilibration. (If the interfacial tie line lay below the final equilibrium curve, the curvatures would be reversed.) The assumed position of the interfacial tie line would be explained if we assumed faster mass transfer in the acetone phase, tending to pull the interfacial state towards the acetone phase bulk state. On this assumption, if on the contrary the initial glycerol and acetone states lie above and below, respectively, the final equilibrium state, we would still expect a concave glycerol and a convex acetone trajectory. All experimental runs show this behavior (except where the acetone phase state reaches the final equilibrium state when the glycerol phase trajectory has bent so far that it follows the straight line path to final equilibrium).

We thus have a plausible qualitative explanation for our experimental results in conventional terms. It is next reasonable to employ Equation (12′) to find the interfacial state in each phase and thus to evaluate the (one) mass transfer coefficient in Equation (10) to complete the quantitative program.

We found, however, that in the majority of cases, that is, where we started with large lateral constituent driving force components parallel to the binodal curves together with large components parallel to the final equilibrium tie line, we obtained glycerol phase trajectories whose tangents completely missed the binodal curve during the early part of the run, and only during the last parts of the runs did the two interfacial states found from Equation (12′) approximate to mutual phase equilibrium *in any case.*

While one need not assume interfacial equilibrium, it is impossible to accept a mass transfer model which does not give *any* real interfacial state in even a single case. We are thus left with the necessity of abandoning the assumption of a diagonal mass transfer coefficient matrix and hence Equation (12).

The observed curvilinear paths, concave to the binodal curve in the glycerol phase (tending to approach coincidence with the extension of the equilibrium tie-line) and convex to the binodal curve in the acetone phase, are suggestive of mass transfer control in the more viscous glycerol phase. If the resistance to mass transfer is dominant in this phase, then the trajectory in this phase will approach a direction, as the transfer process proceeds, which corresponds with the eigenvector of the diffusive mass transfer coefficient matrix associated with the smaller eigenvalue. It is known that in the vicinity of the critical (plait) point the diffusion coefficient matrix becomes singular and the eigenvector corresponding to the vanishing eigenvalue coincides with the limiting tie-line (Kirkaldy and Purdy, 1969). The present observations indicate a possible generalization of this limiting behavior. In any case, if the glycerol phase trajectories are concave to the binodal curve, if there was approaching coincidence with the extension of the equilibrium tie-line, and if there was relatively little mass transfer resistance in the acetone phase, the trajectory in the acetone phase would be determined solely by material balance and would tend to be pulled in convex to the binodal curve and perhaps becoming tangent to it.

With the acceptance of the necessity of adopting the nondiagonal formulation of Equation (10) in order to explain our results, it is reasonable to attempt an evaluation of the (four) mass transfer coefficients for each phase at a single set of corresponding composition points in each phase. In this regard it is helpful to use information from the irreversible thermodynamics treatment which gives the result (Standart, 1967)

$$j_i = \sum_{j=1}^{2} {}_xk_{ij}\Delta X_j \qquad (13)$$

where $X_j = \ln a_j$.

In isothermal mass transfer the most suitable variable is the constituent chemical potential or equivalently the logarithm of its activity. In addition, if we assume the validity of the Onsager reciprocal relations for the ${}_xK_{ij}$ coefficients (Standart, 1967), it can be shown that the ${}_xk_{ij}$ coefficients are related by (Paybarah, 1973)

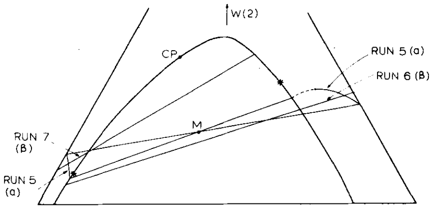

Fig. 4. Set of triple equilibrium runs in composition triangle.

$${}_xk_{11} - c_1\,{}_xk_{12} + c_2\,{}_xk_{21} - c_3\,{}_xk_{22} = 0 \qquad (14)$$

where

$$c_1 \equiv \frac{s_1 + 1 - (1 - x_2)\alpha_{t3}}{s_2 - x_2\alpha_{t3}} \qquad (15a)$$

$$c_2 \equiv \frac{s_2 + 1 - (1 - x_1)\alpha_{t3}}{s_2 - x_2\alpha_{t3}} \qquad (15b)$$

$$c_3 \equiv \frac{s_1 - x_1\alpha_{t3}}{s_2 - x_2\alpha_{t3}} \qquad (15c)$$

where

$$s_1 \equiv \frac{(x_1)_{\mathrm{av}}}{(x_3)_{\mathrm{av}}}, \quad s_2 \equiv \frac{(x_2)_{\mathrm{av}}}{(x_3)_{\mathrm{av}}} \quad \text{and} \quad \alpha_{t3} \equiv N_t/N_3 \qquad (16)$$

and finally $(x_i)_{\mathrm{av}}$ are the average constituent mole fractions in the integrated Gibbs Duhem equation between the bulk and interface states (Standart, 1968)

$$\sum_{i=1}^{3} (x_i)_{\mathrm{av}}\,\Delta \ln a_i = 0 \qquad (17)$$

These coefficients must also satisfy the second law inequality which here takes the form

$$\frac{(1 - \alpha_{3t})}{(1 - \alpha_{3t}x_3)}\,{}_x(k_{11}k_{22} - k_{12}k_{21}) > 0 \qquad (18)$$

In employing Equation (13), we thus have three independent coefficients and one independent interfacial concentration to determine but only two independent relations in each phase. In order to evaluate the unknowns, it is necessary to perform three carefully selected equilibration runs (Figure 4). One is a suitable curvilinear run with unsaturated bulk phases. Two straight line runs are also carried out, so chosen that the straight line trajectories (β) intersect the curvilinear runs (α) at points for the same instant. Thus in each phase if we assume the ${}_xk_{ij}$ are the same at the intersection point for the straight line and curvilinear runs with diffusive transfer rates $j_{i\beta}$ and $j_{i\alpha}$ and driving forces

$$\Delta X_i^e \equiv X_i^e - X_i \quad \text{and} \quad \Delta X_i^* \equiv X_i^* - X_i \qquad (19)$$

respectively, we can eliminate the transfer coefficients ${}_xk_{ij}$ to find a relation among the driving forces [compare Equation (12′)]

$$\Delta X_i^* + A_1\Delta X_2^* - A_2\Delta X_2^e - A_3\Delta X_3^e = 0 \qquad (20)$$

where

$$\begin{aligned} A_1 &\equiv (j_{1\beta} + c_2 j_{2\beta})/(c_1 j_{1\beta} + c_3 j_{2\beta}) \\ A_2 &\equiv (j_{1\alpha} + c_2 j_{2\alpha})/(c_1 j_{1\beta} + c_3 j_{2\beta}) \qquad (21) \\ A_3 &= (c_1 j_{1\alpha} + c_3 j_{2\alpha})/(c_1 j_{1\beta} + c_3 j_{2\beta}) \end{aligned}$$

As explained previously, even if we do not assume a simple diagonal mass transfer coefficient matrix as in Equation (12) and if the saturated phase remains fixed in composition during the run and hence the other phase equilibrates along a straight line, we know the interfacial state X_i^e. Thus Equation (20) is a straight line dependence between X_1^* and X_2^* for the curvilinear run, as we know X_i is for the bulk state as well. Once we know the interfacial state X_i^*, we can find the corresponding ${}_xk_{ij}$ from the relations

$$\begin{aligned} {}_xk_{11} &= (j_{1\alpha}\Delta X_2^e - j_{1\beta}\Delta X_2^*)/D \\ {}_xk_{12} &= (-j_{1\alpha}\Delta X_1^e + j_{1\beta}\Delta X_1^*)/D \\ {}_xk_{21} &= (j_{2\alpha}\Delta X_2^e - j_{2\beta}\Delta X_2^*)/D \\ {}_xk_{22} &= (-j_{2\alpha}\Delta X_1^* + j_{2\beta}\Delta X_1^*)/D \end{aligned}$$

with

$$D \equiv (\Delta X_2^e\Delta X_1^* - \Delta X_1^e\Delta X_2^*) \qquad (22)$$

and the Onsager reciprocal relations are satisfied.

Thus by performing this triple of runs and assuming the

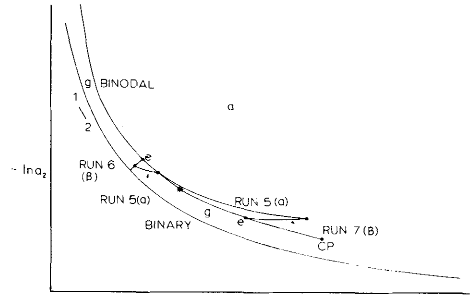

Fig. 5. Set of triple equilibration runs in ln activity space.

Onsager reciprocal relations in each phase, we can determine the interfacial state in each phase and thus check whether we have phase equilibrium at the interface. (If we were to assume phase equilibrium but not the Onsager relations in either phase, we would be one relation short.)

In order to employ these relations we require accurate values of the constituent activities. It is also instructive to plot the equilibration runs not only in mole fraction but also in activity and log activity spaces. There are available isothermal vapor-liquid equilibrium data at ambient conditions only for the water-acetone system (Beare et al., 1930) but by employing the liquid-liquid equilibrium tie line data determined during this program, the equality of the constituent activities in the saturated phases makes possible the determination of the numerical coefficients in suitable activity coefficient equations of state. The NRTL model was chosen and the coefficients determined by minimizing the sum

$$(a^*_{1a} - a^*_{1g})^2 + (a^*_{2a} - a_{2g}^*)^2 + (a_{3a}^* - a_{3g}^*)^2$$

for all the tie lines (Newsham and Vahdat, 1973). The system is, as may be anticipated, extremely nonideal.

Two sets of triple runs were performed. Satisfactory mutual intersections of both Equations (20) with the binodal curve were found for both sets of runs. In addition, these intersections (interfacial states) occurred for reasonable values of the saturated compositions when translated back into mole fraction concentrations. The mass transfer coefficients were calculated from Equations (22) and found to satisfy the Inequality (18). (See Table 1 and Figure 5) (Louizos, 1974).

It is believed that this is the first time a full double set of (partial) mass transfer coefficients have been determined for a ternary heterogeneous system together with the interfacial state without making any assumptions about relative mass transfer resistances under consistent hydrodynamic conditions.

Our future efforts will focus on parallel sets of triple runs in other parts of the phase diagram and the refinement of our evaluation methods for determining constituent diffusive transfer rates and activities to ensure that the conclusions are as general as possible. It will also be important to link these runs with runs in the glycerol-acetone binary and along the tangent to the critical state. (The latter runs have already been made.) It is clear, however, that these experiments promise to give a new insight into interfacial mass transfer.

It is important, however, to call attention to certain experimental and theoretical difficulties we encountered. First, it is desirable to carry out the straight line and curvilinear runs in each phase with the same bulk state and the same hydrodynamic conditions, that is, stirrer rev./min. The first triple runs did not satisfy this condition and were carefully repeated completely to eliminate a source of possible error involved in estimating the dependence of the diffusion fluxes on the stirrer rev./min.

Table 1. Diffusive Transfer Coefficients and Interfacial Compositions for the G-W-A System, Driving Force: ln Activity

SET 1

		Acetone phase		Glycerol phase	
		x_i	a_i	x_i	a_i
Bulk States	1	0.0150	0.1143	0.6910	0.6593
	2	0.1690	0.5320	0.2700	0.1807
	3	0.8160	0.8774	0.0390	0.3922
Interfacial states for straight line runs (2, 4)	1	0.0630	0.2164	0.5997	0.6214
	2	0.2590	0.5211	0.2395	0.1607
	3	0.6780	0.8622	0.1608	0.9389
Interfacial states for curvilinear runs (3)	1	0.0460	0.4290	0.4225	0.4096
	2	0.1070	0.3251	0.3990	0.3272
	3	0.8470	0.9092	0.1785	0.8721
Final equilibrium states for curvilinear runs (3)	1	0.0448	0.5031	0.5140	0.5172
	2	0.0824	0.2678	0.3190	0.2373
	3	0.8728	0.9209	0.1670	0.9032

Diffusive mass transfer coefficients*

	Acetone phase	Glycerol phase
X^k_{11}	+4.55	+12.04
X^k_{12}	+7.45	+0.405
X^k_{21}	+6.88	−2.51
X^k_{22}	+25.91	+3.76
RPMS	171	171

* $[X^{k'}_{ij}]$ = gmole/100 min

SET 2

		Acetone phase		Glycerol phase	
		x_i	a_i	x_i	a_i
Bulk States	1	0.0210	0.2169	0.6510	0.6061
	2	0.1200	0.4161	0.3200	0.2260
	3	0.8590	0.9024	0.0290	0.2969
Interfacial states for straight line paths (6, 7)	1	0.0433	0.3134	0.5550	0.5687
	2	0.1475	0.4140	0.2790	0.1976
	3	0.8092	0.8914	0.1660	0.9253
Interfacial states for curvilinear paths (5)	1	0.0445	0.4739	0.4680	0.4590
	2	0.0900	0.2877	0.3650	0.2860
	3	0.8655	0.9172	0.1670	0.8756
Final equilibrium states for curvilinear paths (5)	1	0.0445	0.5381	0.5170	0.5203
	2	0.0728	0.2427	0.3170	0.2351
	3	0.8827	0.9257	0.1660	0.9027

Diffusive mass transfer coefficients*

	Acetone phase	Glycerol phase
X^k_{11}	+3.68	+11.29
X^k_{12}	+4.25	+0.564
X^k_{21}	+3.32	−0.859
X^k_{22}	+11.56	+4.27
RPMS	81	162

* $[X^k_{ij}]$ = gmole/100 min

$$\sum_{i=1}^{3} (x_i)_{\text{av}}\Delta \ln a_i$$

(using Simpson's Rule)

	Straight line paths	Curvilinear paths
SET 1		
Acetone phase	0.00576	−0.00106
Glycerol phase	0.0114	0.0143
SET 2		
Acetone phase	0.000649	0.000369
Glycerol phase	0.0173	0.0191

Second, condition (17) should be exactly satisfied. Possibly due to errors in sampling and analyses but probably mainly due to errors in predicting the thermodynamic properties, the condition was not satisfied in the glycerol phase as well as we would wish (see Table 1), even using Simpson's three-point integration to find $(x_i)_{av}$. Not only were analyses more difficult to carry out in the glycerol phase, but we had no direct thermodynamic data there, unlike the acetone phase where vapor-liquid equilibria were available for the water acetone binary. In the glycerol-rich phase, we were thus entirely dependent on the liquid-liquid phase equilibria for activity data. Nevertheless, the intersections of the curvilinear interfacial state equation (20) in each phase occurred very close to the binodal curve as stated, providing a mutually consistent picture of interfacial equilibrium and satisfaction of the Onsager reciprocal relations well within the experimental errors. The calculated mass transfer coefficients are very sensitive to any such errors and are strongly concentration dependent as well. Their relation to conventional mass transfer coefficients will be explored in future papers.

We wish to thank Mr. C. Sgouris for careful checking of a number of the calculations.

NOTATION

a_i = activity of component i
A_i = parameters defined in Equation (21)
c_i = parameters defined in Equation (15)
D = parameter defined in Equation (22)
j_i = constituent diffusive transfer rate, Equation (4)
k_{ij} = constituent diffusive transfer coefficient, Eq. (10)
K_{ij} = constituent total transfer coefficient, Equation (9)
m = slope of composition trajectory, Equation (12)
Ni, N_t = constituent and mixture moles in phase
$\dot N_i$, $\dot N_t$ = constituent and mixture interfacial transfer rates, Equation (3)
s_1, s_2 = parameters defined in Equation (16)
t = time
x_i = constituent mole fraction
X_i = generalized constituent concentration
α_{ti} = ratio of transfer rates defined in Equation (16)
Δ = increment for concentration partial driving force
a = acetone rich phase
g = glycerol rich phase
i = ith constituent
0 = initial conditions
t = mixture
$*$ = interfacial value (curvilinear path)
e = interfacial value (straight line path)
α = curvilinear path
β = straight line path
$(\ )_{av}$ = average value in Equation (17)

LITERATURE CITED

Beare, W. G., G. A. McVicar, and J. B. Ferguson, "The Determination of Vapor and Liquid Compositions in Binary Systems II." *J. Phys. Chem.*, 34, 1310 (1930).

Kirkaldy, J. S., and G. R. Purdy, "Diffusion in Multicomponent Metallic Systems X. Diffusion at and Near Ternary Critical States," *Can. J. Phys.*, 47, 865 (1969).

Louizos, N., "Isothermal Mass Transfer in Liquid-Liquid Extraction," dissertation, Univ. Manchester, Inst. of Science and Technology (1974).

Newsham, D. M. T., and N. Vahdat, communication (1973).

Paybarah, A., "Isothermal Mass Transfer in Ternary Extraction," thesis, Univ. Manchester, Great Britain (1973).

Standart, G. L., "The Second Law of Thermodynamics for Heterogeneous Flow Systems—I. Basic Relations and the Curie Theorem," *Chem. Eng. Sci.*, **22**, 1417, 1627 (1967).

———., "The Second Law of Thermodynamics for Heterogeneous Flow Systems—III. Effect of the Conditions of Mechanical Equilibrium and Electroneutrality on Simultaneous Heat and Mass Transfer and the Prigogine Theorem," *ibid.*, **23**, 279 (1968).

APPENDIX A

It is preferable to express mass transfer formulations in terms of diffusive fluxes (defined in an appropriate frame of reference) rather than in terms of the total transfer fluxes. A logical reference velocity for the diffusive fluxes in the present case is the molar average velocity at the interface. The diffusive fluxes at the interface relative to this velocity are simply given by

$$j_i^* = \dot N_i - x_i^* \dot N_T \tag{A1}$$

In the present case the interfacial compositions are not known a priori so that the alternate diffusive fluxes, given by Equation (4) of the paper, are chosen

$$j_i = \dot N_i - x_i \dot N_T \tag{A2}$$

Combining Equations (A1) and (A2) it is seen that these diffusive fluxes are simply related by

$$j_i = j_i^* + \dot N_T \Delta x_i \tag{A3}$$

where Δx_i are the driving forces of Equation (8).

It is important to note that the diffusive transfer coefficients k_{ij} of Equation (10) are thus simply related to the diffusive transfer coefficients defined on the basis of interfacial fluxes defined relative to the molar average velocity at the interface. Thus if one writes

$$j_i^* = \sum_{j=1}^{2} k^*_{ij} \Delta x_j \tag{A4}$$

then combining Equations (A3) and (A4) with Equation (10) shows that

$$k_{ii} = k^*_{ii} + \dot N_T \quad i = 1, 2 \tag{A5}$$

$$k_{ij} = k^*_{ij} \qquad i, j = 1, 2 \quad i \neq j \tag{A6}$$

The coupling coefficients are the same in either formulation.

APPENDIX B

To investigate the consequences of a diagonal diffusive coefficient matrix, it is assumed that in Equation (10), $k_{ij} = 0$ if $i = j$. Then Equation (10) reduces to

$$j_i = k_{ii} \Delta x_i \tag{B1}$$

These fluxes obey Equation (6) so that

$$\sum_{i=1}^{3} k_{ii} \Delta x_i = 0 \tag{B2}$$

However, from Equation (8)

$$\sum_{i=1}^{3} \Delta x_i = 0 \tag{B3}$$

If Equation (B3) is used to eliminate the driving force of component 3 from Equation (B2), the result is

$$\sum_{i=1}^{2} (k_{ii} - k_{33}) \Delta x_i = 0 \tag{B4}$$

The driving forces in Equation (B4) are linearly independent so that Equation (B4) can only be satisfied if

$$k_{ii} = k_{33} = k \quad i = 1, 2 \tag{B5}$$

Thus the only consistent diagonal formulation must contain equal diagonal elements.

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