# Liquid Equilibria in the System Methyl Oleate–Methyl Palmitate–Acetonitrile–Hexane

## Significance in Craig Countercurrent Extraction

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**The system methyl oleate–methyl palmitate–acetonitrile–hexane was studied at 25° C. Although consisting of pure components, this system is typical of systems in which an attempt is made to separate lipids by countercurrent distribution. Equilibrium surfaces were determined by cloud point titrations. Tie lines were determined by a combination of weighing, gas chromatographic, and graphical techniques. A vector method was used to organize the data and to calculate tie-line segments and is applicable to any multicomponent heterogeneous system. The ratio of tie-line segments agreed with the ratio of experimentally determined phase masses within 2%. In a countercurrent distribution using this system, large deviations from ideality would occur. As solute was added to the system, solvent intersolubilities changed. Partition coefficients were shown to be a function of the total composition of the system and varied with ester concentration. The partition coefficient of a given methyl ester was influenced by the presence of the other methyl ester in the system. In addition, an isopycnic region, where the phases invert, was observed.**

COUNTERCURRENT distribution (CCD), as described by Craig, is widely used for the separation of lipids. Although there have been some studies of ternary liquid systems containing lipids (*1, 3, 5, 8, 10*), little work has been done on quaternary systems containing these compounds (*10*). One of the drawbacks to studying four-component phase equilibria is the difficulty of representing such systems geometrically. The use of vector notation and linear algebra (*7*) makes the organization of quaternary data easier and facilitates certain types of calculations. The vector method can be generalized to include systems of any number of components. In the present paper, this approach has been applied to the study of the system methyl oleate–methyl palmitate–acetonitrile-hexane at 25° C. The significance of these data in preparative scale CCD is discussed.

## EXPERIMENTAL

**Materials.** Methyl oleate and methyl palmitate were isolated from the methyl esters of common oils and shown to be $99^{+}\%$ pure by thin-layer and gas chromatographic analyses. Hexane and acetonitrile were reagent grade, distilled twice before use. Densities of the pure materials at 25° C. were: acetonitrile 0.777, hexane 0.664, methyl oleate 0.859, and methyl palmitate 0.847 gram per ml.

**Solubility Curves.** Ternary solubility data were obtained by cloud and clear point titrations. All experiments were performed in a thermostat at 25.0° ± 0.1° C. At least 1 hour was allowed for the attainment of thermal equilibrium. To determine solid-liquid equilibrium curves, a mixture containing solid phase was warmed slightly until homogeneous and kept at 25.0° ± 0.1° C. for at least 24 hours, during which precipitation occurred. The mixture was centrifuged, an aliquot removed, and its weight determined. Any solvent present was removed under a stream of nitrogen, and the weight of methyl esters was determined. Where the esters were mixed, their ratio was determined by gas chromatography. Using these data, the composition of solid-liquid equilibrium points could be calculated (Table I).

Gas chromatographic analyses were performed on an isothermal instrument designed at this laboratory. The two columns used were an 8-foot × 3/16-inch stainless steel tube packed with 25% ethylene glycol succinate polyester (EGS) on Chromosorb W (40- to 60-mesh, acid- and base-washed) and a 2-foot × 3/16-inch stainless steel tube packed with 15% nitrile silicone XE-60 on Chromosorb W (60- to 80-mesh). Helium was the carrier gas flowing at 32 ml. per minute for the EGS column and 71 ml. per minute for the XE-60 column. In both cases, the column temperature was 201° C., the injector block temperature was 246° C., and the detector (thermal conductivity cell) temperature was 209° C. An Infotronics CRS-11HSB digital integrator with automatic base line corrector was used to measure peak areas. To convert peak area to weight per cent, empirical correction factors for detector response and column conditions were determined by analyzing samples of known composition (*6*). Sample size was 0.08 $\mu$l. Correction factors for the XE-60 column agreed within ±0.8% and did not change appreciably with time. Correction factors for the EGS column agreed within ±1.1% and varied with time, necessitating frequent restandardization. Duplicate runs agreed within ±0.4% on the XE-60 column and within 1.0% on the EGS column. The XE-60 column had a much shorter time of analysis.

Quaternary equilibrium curves were determined using modifications of the methods of Branker, Hunter, and Nash (*2*). A mixture of methyl palmitate and methyl oleate was prepared, corresponding to a point on the line joining the two respective apices, such as point *M* in Figure 1. A known quantity of mixture *M* was then combined with a known quantity of a third component, and titrated with the fourth component to a cloud point. In this manner, curves such as *OP* and *QR* on plane *ADM* were obtained. Curves on two such planes were determined and plotted on equilateral triangles (Table II).

Figure 1 is a schematic representation of the quaternary diagram. Surface *PSOT* represents the composition of hexane-rich phases and surface *QURV* represents the composition of acetonitrile-rich phases. Surface *JKL* is the solid-liquid equilibrium surface. Constant solvent ratio

Table I. Ternary Solubility Data at 25° C.

(All data in terms of weight %)

| Me Palmitate | Me Oleate | Acetonitrile | Hexane |
|---|---|---|---|
| ... | ... | 85.5 | 14.5 |
| ... | 6.6 | 79.9 | 13.5 |
| ... | 11.3 | 80.1 | 8.6 |
| ... | 11.7 | 80.3 | 8.0 |
| ... | 17.8 | 77.0 | 5.2 |
| ... | 21.1 | 75.6 | 3.3 |
| ... | 28.3 | 70.4 | 1.3 |
| ... | 28.6 | ... | 71.4 |
| ... | ... | 4.2 | 95.8 |
| ... | 38.2 | 11.8 | 50.0 |
| ... | 48.1 | 15.2 | 36.7 |
| ... | 58.1 | 32.7 | 9.2 |
| ... | 55.8 | 44.2 | ... |
| 6.0 | ... | 83.9 | 10.1 |
| 9.9 | ... | 82.6 | 7.5 |
| 11.8 | ... | 82.2 | 6.0 |
| 18.1 | ... | 81.9 | ... |
| 34.8 | ... | 9.8 | 55.4 |
| 47.7 | ... | 14.7 | 37.6 |
| 62.2 | ... | 27.7 | 10.1 |
| 66.9 | ... | 33.1 | ... |
| 91.0[a] | ... | 9.0 | ... |
| 90.6[a] | ... | 6.9 | 2.5 |
| 90.7[a] | ... | 4.9 | 4.4 |
| 88.8[a] | ... | 1.5 | 9.7 |
| 87.8[a] | ... | ... | 12.2 |
| 5.9 | 21.1 | 73.0 | ... |
| 8.4 | 16.4 | 75.2 | ... |
| 9.8 | 14.6 | 75.6 | ... |
| 13.9 | 7.4 | 78.7 | ... |
| 10.2 | 47.6 | 42.2 | ... |
| 11.4 | 46.7 | 41.9 | ... |
| 24.2 | 35.6 | 40.2 | ... |
| 37.4 | 25.5 | 37.1 | ... |
| 38.0 | 25.8 | 36.2 | ... |
| 49.8 | 15.2 | 35.0 | ... |
| 86.8[a] | 7.6 | 5.6 | ... |
| 68.9[a] | 31.1 | ... | ... |
| 83.3[a] | 9.6 | ... | 7.1 |

[a] Solid-liquid equilibrium points.

Table II. Quaternary Solubility Data at 25° C.

(All data in terms of weight %)

| Me Palmitate | Me Oleate | Acetonitrile | Hexane |
|---|---|---|---|
| 1.8[a] | 3.4 | 82.1 | 12.7 |
| 3.5[a] | 6.4 | 80.2 | 9.9 |
| 6.0[a] | 11.3 | 78.4 | 4.3 |
| 9.7[a] | 18.0 | 7.8 | 64.5 |
| 16.5[a] | 30.7 | 13.9 | 38.9 |
| 20.8[a] | 38.8 | 25.5 | 14.9 |
| 2.9[b] | 1.5 | 84.0 | 11.6 |
| 6.5[b] | 3.6 | 81.7 | 8.2 |
| 10.3[b] | 5.6 | 80.1 | 4.0 |
| 13.4[b] | 7.3 | 6.0 | 73.3 |
| 20.7[b] | 11.3 | 8.6 | 59.4 |
| 30.6[b] | 16.6 | 14.1 | 38.7 |
| 38.9[b] | 21.2 | 24.9 | 15.0 |

[a] Starting solute mixture. 34.9% Me palmitate–65.1% Me oleate.
[b] Starting solute mixture. 64.8% Me palmitate–35.2% Me oleate.

planes were passed through *B, C,* and points on the *AD* axis from 75 to 5% hexane. When the intersections with surface *PSOT* were plotted, straight lines were obtained down to about 25% hexane, where a slight convex curvature was observed. Lines of intersection with *QURV* were irregularly curved.

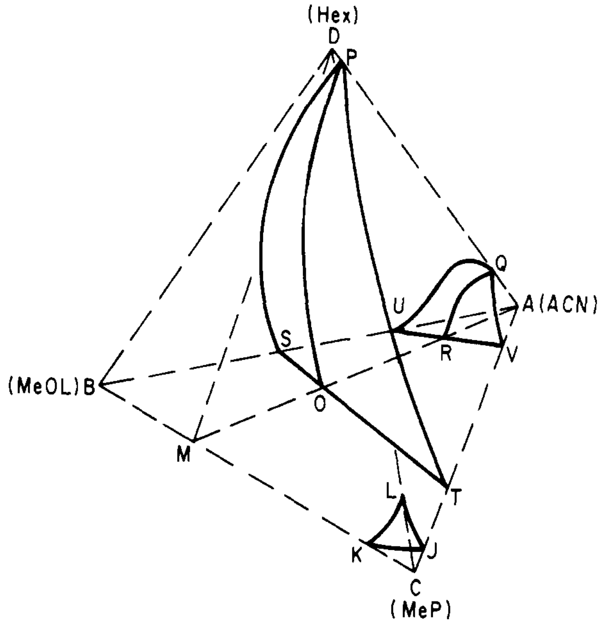

Figure 1. Schematic drawing of quaternary diagram at 25° C.

A. Acetonitrile C. Me palmitate
B. Me oleate D. Hexane

**Tie Lines.** Tie lines were determined as previously described (*1*). When methyl oleate and methyl palmitate were mixed, their ratio in each phase was determined by gas chromatography. For quaternary tie lines, a plane was passed through the hexane and acetonitrile apices and a point on the *BC* axis corresponding to the ratio of methyl esters in the hexane-rich phase. The intersection of this plane and the planes of constant solvent-rich ratios gave points which were plotted on an equilateral triangle. The point corresponding to the composition of the hexane-rich phase was located on the curve drawn through these points. An analogous procedure was performed to locate the point corresponding to the composition of the acetonitrile-rich phase. In this manner the weight per cent of each solvent in each phase was determined. Obviously the accuracy of this approach was limited by the accuracy with which the solubility curves were traced. These two points and the point representing the total composition of the system were plotted on the same triangle and connected by a straight line. This is equivalent to projecting the tie line onto an equilateral triangle (Table III).

Tie-line data can be used to calculate the partition coefficient, *K*, defined here as the molar concentration of solute in the hexane-rich phase divided by the molar concentration of solute in the acetonitrile-rich phase. Partition coefficients were determined in dilute solutions by adding small amounts of the solutes to a two-phase system of hexane and acetonitrile. Samples were equilibrated at 25° C. for at least 16 hours and analyzed as before. At least four determinations were made at each concentration. Standard error was within 3% of the mean value.

## RESULTS AND DISCUSSION

**Quaternary Diagram.** The four ternary faces are shown in Figure 2 (*a* to *d*). The systems represented by Figure 2 (*a* to *c*) are examples of Type II ternary liquid systems (*11*). The methyl oleate–methyl palmitate–hexane system is completely homogeneous, except at high concentrations of methyl palmitate where a solid phase appears. Curves at high methyl palmitate concentration (Figure 2, *b, c, d*) are solid-liquid equilibrium curves.

Tie-line data were checked by the lever rule. Line segment lengths were measured directly in ternary systems. For

### Table III. Tie Line Data at 25° C.

(In weight %)

| Tie Line | Hexane-Rich Phase: Methyl palmitate | Methyl oleate | Aceto-nitrile | Hexane | Density, g./ml. | Acetonitrile-Rich Phase: Methyl palmitate | Methyl oleate | Aceto-nitrile | Hexane | Density, g./ml. |
|---|---|---|---|---|---|---|---|---|---|---|
| 1-1 | . . . | 20.9 | 6.8 | 72.3 | 0.700 | . . . | 2.8 | 82.7 | 14.5 | 0.756 |
| 1-2 | . . . | 34.3 | 9.1 | 56.6 | 0.727 | . . . | 5.0 | 80.9 | 14.1 | 0.762 |
| 1-3 | . . . | 51.6 | 18.9 | 29.5 | 0.794 | . . . | 11.1 | 79.7 | 9.2 | 0.776 |
| 1-4 | . . . | 58.5 | 31.2 | 10.3 | 0.809 | . . . | 21.1 | 75.9 | 3.0 | 0.786 |
| 2-1 | 23.3 | . . . | 8.0 | 68.7 | 0.708 | 2.4 | . . . | 84.9 | 12.7 | 0.760 |
| 2-2 | 36.3 | . . . | 10.9 | 52.8 | 0.731 | 4.3 | . . . | 84.5 | 11.2 | 0.760 |
| 2-3 | 53.8 | . . . | 18.3 | 27.9 | 0.776 | 8.1 | . . . | 83.2 | 8.7 | 0.761 |
| 2-4 | 63.3 | . . . | 27.7 | 9.0 | 0.807 | 14.4 | . . . | 82.4 | 3.2 | 0.780 |
| 3-1 | 14.5 | 43.2 | 42.3 | . . . | 0.824 | 7.2 | 21.8 | 71.0 | . . . | 0.798 |
| 3-2 | 15.2 | 42.8 | 42.0 | . . . | 0.822 | 7.3 | 20.3 | 72.4 | . . . | 0.798 |
| 3-3 | 33.0 | 28.4 | 38.6 | . . . | 0.822 | 20.4 | 19.2 | 60.4 | . . . | 0.792 |
| 3-4 | 50.6 | 13.3 | 36.1 | . . . | 0.825 | 16.3 | 4.6 | 79.1 | . . . | 0.792 |
| 4-1 | 9.2 | 9.2 | 9.4 | 72.2 | 0.699 | 1.0 | 1.1 | 84.4 | 13.5 | 0.759 |
| 4-2 | 12.0 | 6.6 | 8.1 | 73.3 | 0.698 | 1.3 | 0.7 | 84.4 | 13.6 | 0.761 |
| 4-3 | 7.8 | 14.4 | 8.5 | 69.3 | 0.709 | 0.9 | 1.7 | 84.0 | 13.4 | 0.759 |
| 4-4 | 12.7 | 23.6 | 10.5 | 53.2 | 0.739 | 1.5 | 3.0 | 83.1 | 12.4 | 0.764 |
| 4-5 | 23.5 | 12.9 | 11.2 | 52.4 | 0.736 | 2.8 | 1.6 | 83.3 | 12.3 | 0.763 |
| 4-6 | 18.2 | 18.2 | 10.7 | 52.9 | 0.736 | 2.2 | 2.4 | 83.2 | 12.2 | 0.767 |
| 4-7 | 18.6 | 33.4 | 17.2 | 30.8 | 0.775 | 3.1 | 6.1 | 81.5 | 9.3 | 0.767 |
| 4-8 | 34.3 | 18.1 | 17.6 | 30.0 | 0.773 | 6.2 | 3.5 | 81.4 | 8.9 | 0.768 |
| 4-9 | 21.0 | 39.1 | 27.9 | 12.0 | 0.806 | 5.3 | 10.2 | 78.8 | 5.7 | 0.779 |
| 4-10 | 39.5 | 21.2 | 27.1 | 12.2 | 0.806 | 9.2 | 5.2 | 80.4 | 5.2 | 0.780 |

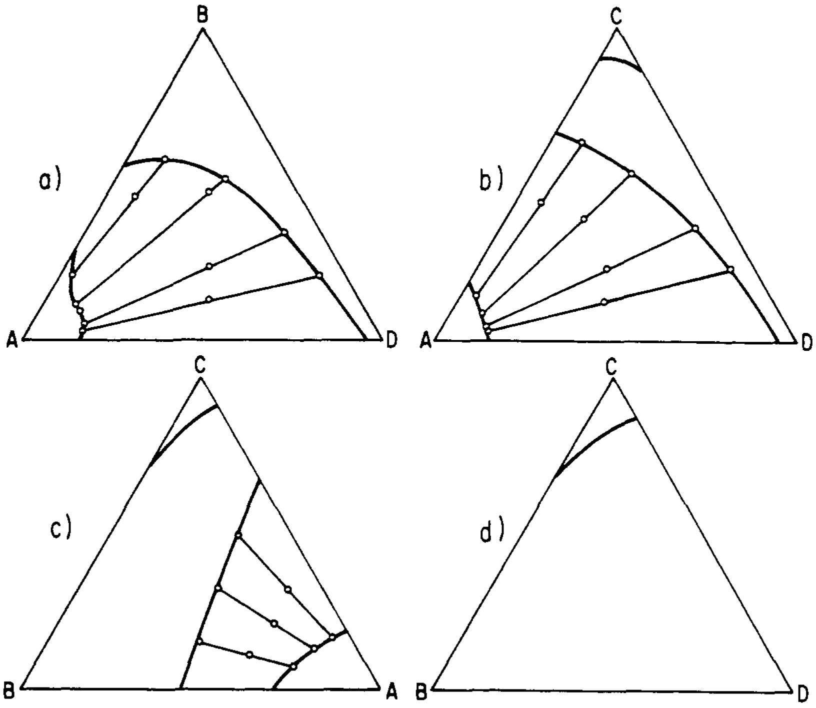

Figure 2. Faces of quaternary diagram

*a.* Acetonitrile
*b.* Me oleate
*c.* Me palmitate
*d.* Hexane

quaternary systems, the line-segment ratio was calculated using the generalized center-of-gravity rule for phase diagrams (7). Applying this treatment to a four-component, two-phase system one can write the mass balance equations

$$x_{i1}m_1 + x_{i2}m_2 = MX_i \qquad (i = 1, 2, 3, 4) \qquad (1)$$

where $x_{i1}$ and $x_{i2}$ are the weight fractions of the $i$th component in phases 1 and 2, $m_1$ and $m_2$ are the masses of the respective phases, $X_i$ is the weight fraction of the $i$th component in the system, and $M$ is the total mass of the system. If a four-dimensional vector space is defined with orthonormal basis vectors,

$$A_1 = [1, 0, 0, 0], A_2 = [0, 1, 0, 0], A_3 = [0, 0, 1, 0], A_4 = [0, 0, 0, 1]$$

the composition of each phase and of the total system may be represented vectorially. The resulting vectors can be combined in a matrix

$$\begin{bmatrix} x_{11}\,x_{12} & X_1 \\ x_{21}\,x_{22} & X_2 \\ x_{31}\,x_{32} & X_3 \\ x_{41}\,x_{42} & X_4 \end{bmatrix} \qquad (2)$$

where the first column represents the composition of phase 1, the second column represents the composition of phase 2, and the third column represents the over-all composition of the system.

Under the conditions that

$$X_1 + X_2 + X_3 + X_4 = 1, \qquad 0 \le X \le 1 \tag{3}$$

and

$$x_{1j} + x_{2j} + x_{3j} + x_{4j} = 1, \qquad 0 \le x_{ij} \le 1 \tag{4}$$

where

$$j = 1, 2, \text{ and } i = 1, 2, 3, 4$$

one may sum the system of Equations 1 to get

$$m_1 + m_2 = M \tag{5}$$

Equation 5 may now be substituted for any one of the four Equations 1 to give another consistent system of equations. With these equations one may state that

$$m_j = \frac{D'}{D'} M$$

where

$$D'_j = \begin{vmatrix} x_{i1} & X_1 \\ 1 & 1 \end{vmatrix} \qquad D' = \begin{vmatrix} x_{i1} & x_{i2} \\ 1 & 1 \end{vmatrix}$$

From linear algebra we know that the tie-line segment lengths can be represented by

$$L_1 = \frac{1}{(r-1)!} D'_1 \quad L_2 = \frac{1}{(r-1)!} D'_2 \tag{6}$$

where

$$D'_1 = \begin{vmatrix} x_{i1} & X_i \\ 1 & 1 \end{vmatrix} \qquad D'_2 = \begin{vmatrix} X_i & x_{i2} \\ 1 & 1 \end{vmatrix}$$

and $r$ corresponds to the number of phases. Evaluating the determinants $D'_1$ and $D'_2$ the lever rule becomes

$$\frac{m_2}{m_1} = \frac{L_1}{L_2} = \frac{x_{i1} - X_i}{X_i - x_{i2}} \tag{7}$$

Using data for all four components the expression on the right of Equation 7 was calculated four ways and averaged. Lever rule agreement is shown in Figure 3. Line-segment ratios and experimental mass ratios generally agreed within 2%.

**Significance in CCD.** The theoretical ideal treatment of Craig countercurrent extraction is based upon the binomial theorem (*4*) and makes certain assumptions which are approximated only in infinitely dilute solutions. The main assumptions are that the partition coefficient of a given solute is a constant and that there are no relative changes in phase volume with solute addition.

It is obvious from the tie-line data (Table III) that as the concentration of methyl esters increases in the system the relative solubilities of hexane in the acetonitrile-rich phase and of acetonitrile in the hexane-rich phase are changing. Relative-phase-volume changes in a countercurrent distribution have been discussed for ternary systems (*1*). Phase density data (Table III) show that as solute concentration increased, the density of the hexane-rich layer exceeded that of the acetonitrile-rich layer. Thus a phase inversion occurred between tie lines 1-2 and 1-3, and 2-2 and 2-3 in the ternary systems, and in a region between tie lines 4-4, 4-5, 4-6, and 4-7, 4-8 in the quaternary system. If this were to occur during a countercurrent distribution of these compounds the mobile phase would become the stationary phase and the stationary phase would become the mobile phase.

The partition coefficient is usually expressed as a function of solute concentration. This is incorrect, however, except at very low concentrations. Barford and coworkers (*1*) have pointed out that in ternary systems $K$ is a function of the concentration of two out of three components in the system.

From the definition of the partition coefficient stated earlier, $K$ for the $i$th component can be expressed as

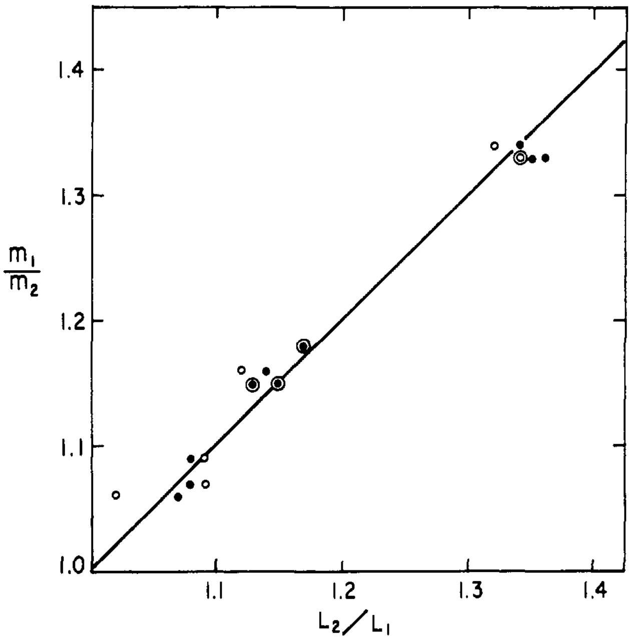

Figure 3. Tie-line correlation by lever rule

Concentric circles represent overlapping points

○ Measured line-segment ratio

● Segment ratio calculated from Equation 7

Line is plot of $m_1/m_2 = L_2/L_1$

$$K_i = \frac{x_{i1} m_1}{(MW)_i V_1} \bigg/ \frac{x_{i2} m_2}{(MW)_i V_2} \qquad (i = 1, 2, 3, 4) \tag{8}$$

where $(MW)_i$ is the molecular weight of component $i$, $V_1$ and $V_2$ are the volumes of phases 1 and 2, and the other terms have their usual significance. Assuming no volume changes on mixing

$$V_j = m_j \left( \frac{x_{1j}}{\rho_1} + \frac{x_{2j}}{\rho_2} + \frac{x_{3j}}{\rho_3} + \frac{x_{4j}}{\rho_4} \right) \quad (j = 1, 2) \tag{9}$$

where $\rho_i$'s are the densities of the pure components. Substituting Equation 9 into 8 and using Expression 4, one obtains

$$K_i = \frac{x_{i1}[\rho_1\rho_2\rho_3 + \rho_2\rho_3(\rho_4 - \rho_1)x_{12} + \rho_1\rho_3(\rho_4 - \rho_2)x_{22} + \rho_1\rho_2(\rho_4 - \rho_3)x_{32}]}{x_{i2}[\rho_1\rho_2\rho_3 + \rho_2\rho_3(\rho_4 - \rho_1)x_{11} + \rho_1\rho_3(\rho_4 - \rho_2)x_{21} + \rho_1\rho_2(\rho_4 - \rho_3)x_{31}]} \tag{10}$$

A similar expression can be derived for systems of any number of components. Equation 10 shows that $K_i = f(x_{ij})$. At constant temperature and pressure, a particular set of $X_i$ uniquely determines a set of $x_{ij}$. $K$ is not a function of solute concentration alone and, from Equation 3, three weight fractions must be stated to define $K$. If one has a method of analysis for every component in each phase, such a gas chromatographic procedure (*9*), $K$ may be calculated from Equation 10 without knowledge of exact sample size, phase masses, or phase volumes. Table IV compares $K$'s determined by the experimental methods previously described with those calculated from Equation 10. The values of $x_{i1}$ and $x_{i2}$ were known to at least two significant figures. Agreement is well within 2%.

Figure 4, *a*, is a plot of $K$ *vs.* log (weight % solute) at a fixed solvent ratio in two ternary systems. $K$ remains reasonably constant at low solute concentration but falls rapidly at high concentration. Figure 4, *b*, shows $K$ as a function of weight per cent solute at fixed solvent and fixed methyl ester ratios in the quaternary system.

Table IV. Partition Coefficients

| Tie Line | Methyl Palmitate $K_{obsd}$ | Methyl Palmitate $K_{Eq. 10}$ | Methyl Oleate $K_{obsd}$ | Methyl Oleate $K_{Eq. 10}$ |
|---|---|---|---|---|
| 4-1 | 8.58 | 8.67 | 7.66 | 7.65 |
| 4-2 | 8.64 | 8.71 | 8.05 | 8.11 |
| 4-3 | 8.64 | 8.53 | 7.72 | 7.69 |
| 4-4 | 7.51 | 7.57 | 8.02 | 8.14 |
| 4-5 | 8.01 | 8.07 | 7.66 | 7.76 |
| 4-6 | 7.85 | 7.95 | 7.22 | 7.29 |
| 4-7 | 6.11 | 6.01 | 5.53 | 5.45 |
| 4-8 | 5.57 | 5.53 | 5.22 | 5.17 |
| 4-9 | 4.11 | 4.08 | 3.97 | 3.95 |
| 4-10 | 4.45 | 4.42 | 4.20 | 4.20 |

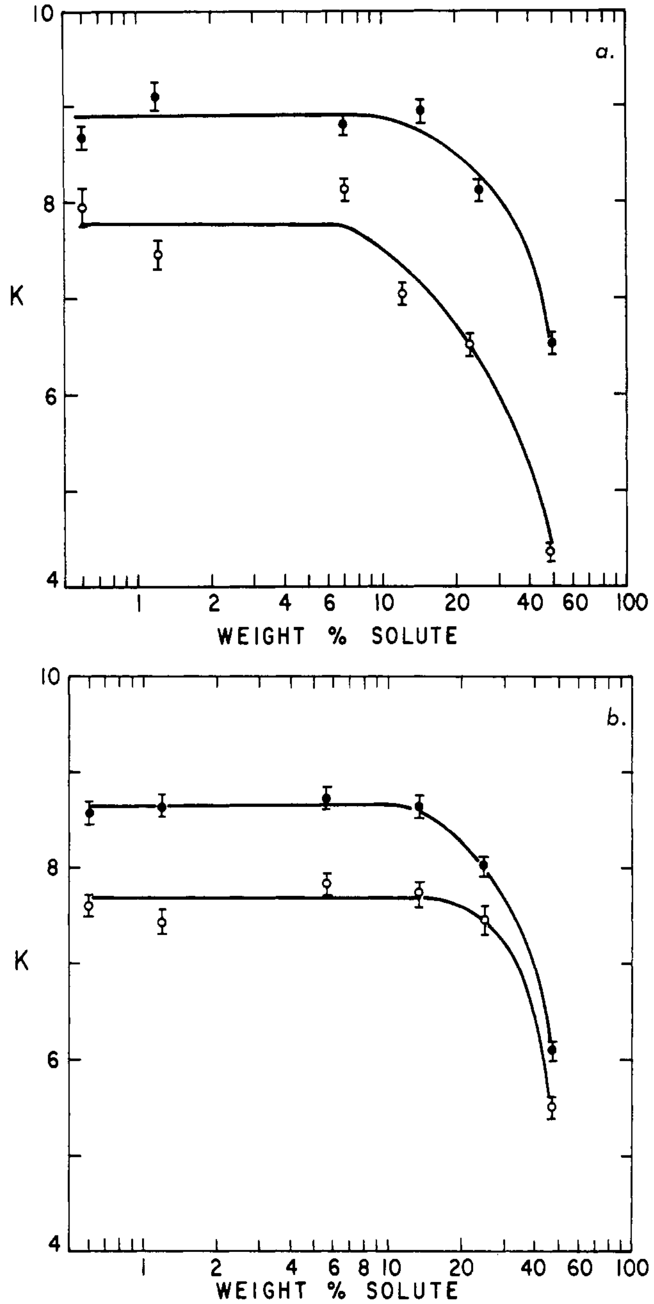

Figure 4. Partition coefficients of solutes

a. In ternary systems at hexane-acetonitrile ratio of 1.13

b. In quaternary system at hexane-acetonitrile ratio of 1.13 and methyl oleate–methyl palmitate ratio of 1.8

● Me palmitate

○ Me oleate

At low concentrations, $K$ for each ester was reasonably constant and did not differ appreciably from the ternary $K$'s. At higher concentrations, $K$ for methyl palmitate in the quaternary system was slightly lower than its $K$ in the ternary system. $K$ for methyl oleate, however, was much higher in the quaternary than in the ternary system—e.g., 24% higher at the 45% solute level. The net effect is that the $K$'s for the two esters in the quaternary system were much closer to one another at high concentrations than would be expected from the ternary data. Thus a poorer separation would be obtained in a countercurrent distribution than would be predicted using ternary $K$ data for this system.

These deviations from ideal countercurrent behavior become very important at high solution concentration. In order to predict the results of a preparative scale separation in this system adequately, quaternary data would have to be utilized.

## NOMENCLATURE

$x_{11}, x_{21}, x_{31}, x_{41}$ = weight fractions of components 1, 2, 3, and 4 in phase 1
$x_{12}, x_{22}, x_{32}, x_{42}$ = weight fractions of components 1, 2, 3, and 4 in phase 2
$X_1, X_2, X_3, X_4$ = weight fractions of components 1, 2, 3, and 4 in total system
$m_1, m_2$ = masses of phases 1 and 2, grams
$M$ = total mass of system, grams
$i$ = component designation, 1, 2, 3, or 4
$j$ = phase designation, 1 or 2
$r$ = number of phases
$K_i$ = partition coefficient of $i$th component
$(MW)_i$ = molecular weight of $i$th component
$V_1, V_2$ = volumes of phases 1 and 2, ml.
$L_1, L_2$ = lengths of line segments 1 and 2 of tie lines, mm.

### Greek Letters

$\rho_1, \rho_2, \rho_3, \rho_4$ = densities of pure components 1, 2, 3, and 4

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