Phase Equilibria and Countercurrent Distribution[1]

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Abstract

Ternary diagrams for methyl oleate/hexane/acetonitrile and methyl palmitate/hexane/acetonitrile systems were constructed from equilibria data obtained at 20.0 and 30.4C. The diagrams varied significantly with temperature; both systems showed expanded regions of immiscibility at the lower temperature. Both the partition coefficient of the methyl ester and the mutual solubility of hexane and acetonitrile, at each temperature, varied with ester concentration in the system. At high ester concentration, an inversion of the phases was observed. The countercurrent distribution of these compounds, as influenced by these effects, is discussed.

Introduction

ALTHOUGH EXTRACTION PROCESSES are commonly used in lipid separations, few phase-equilibria studies with these compounds are described in the literature. The studies of Chueh and Briggs (1) with unsaturated triglycerides in heptane/furfural and of Hixson and Bockelmann (2) with various ternary systems of acids, oils, and triglycerides with liquid propane are prominent in this area. The purpose of this report is to present the phase relationships of methyl oleate/hexane/acetonitrile and methyl palmitate/hexane/acetonitrile systems and to relate these observations to countercurrent distribution.

Experimental Section

Materials

The oleate and palmitate were isolated from the methyl esters of common oils by a combination of distillation, chromatographic, and crystallization techniques. Thin-layer and gas chromatographic analyses showed these esters to be better than 99% pure. Redistilled reagent grade hexane and acetonitrile were employed in these studies.

Solubility Data

Solubility data for the methyl oleate/hexane/MeCN and methyl palmitate/hexane/MeCN systems at 20.0 ± 0.1 and 30.4 ± 0.1C were obtained by titrating known mixtures with one of the solvents until the formation of a second phase was observed (cloud point) or until a two-phase system became homogeneous. The final compositions of the systems in wt % were calculated from the compositions of the starting mixtures and the volumes and densities of titrants used. A number of determinations were made at each temperature, but in the interest of brevity only binary solubility data are presented (Table I).

TABLE I

Solubility Data for Binary Systems

Temp. C	Solute wt %	MeCN wt %	Hexane wt %
30.4	......	5.0	95.0
30.4	......	86.5	13.5
30.4	49.4[b]	50.6	......
30.4	30.6[b]	69.4	......
20.0	......	88.6	11.4
20.0	......	4.6	95.4
20.0	6.7[b]	93.3	......
20.0	74.0[b-c]	......	26.0
20.0	65.5[a]	34.5	......
20.0	19.9[a]	80.1	......

[a] Methyl oleate.
[b] Methyl palmitate.
[c] Solid-liquid immiscible point.

Phase Equilibria

Known mixtures were prepared and equilibrated at constant temperature. After the volumes of phases were observed, weights of suitable aliquots as well as the weights of methyl ester in the aliquots were determined. From these data, the weights of each phase, the wt % of ester in each phase, and the partition coefficient (K_d) could be easily calculated. In this report K_d = molar conc. solute in hexane-rich phase/molar conc. solute in MeCN-rich phase.

Results and Discussion

Ternary diagrams (Fig. 1) for methyl oleate/hexane/MeCN and methyl palmitate/hexane/MeCN systems at 20.0 and 30.4C were constructed from the solubility data and the phase-equilibria studies described in the experimental section. Since only the percentages of solute could be conveniently determined in the two phases, the ends of the lines connecting phases in equilibrium with each other (tie lines) were placed where the solute percentage line crossed the solubility curves. By the lever rule (3), L/U = WU/WL where L = length of tie-line segment from the point giving the composition of the total system to the point denoting the MeCN-rich phase composition; U = a similar line segment for the hexane-rich phase; WU = wt hexane-rich phase; WL = wt of MeCN-rich phase. Table II shows these ratios to be in good agreement, thereby confirming the solubility curves as drawn from the titration data.

The oleate ternary at 30.4C was typical of a Type I system (3) with only one axis of immiscibility. The palmitate ternary at the same temperature showed two miscibility gaps, one along the MeCN-hexane axis and one on the MeCN-methyl palmitate axis. The appearance of the palmitate ternary suggests that two separate Type I curves had just merged at this temperature. In a separate experiment, palmitate was found to be completely miscible in MeCN at 31.7C, indicating that small temperature changes influenced this system significantly.

Indeed the ternary diagrams of both systems at 20.0 were greatly changed from those at 30.4C. The immiscible region of the oleate system had expanded considerably with this temperature decrease, and a miscibility gap was observed along the MeCN-oleate axis. A similar expansion of the liquid immiscible region occurred in the palmitate system. In addition, a solid-liquid immiscible region was found along the methyl palmitate-hexane axis at 20.0C, and, at high MeCN concentration, solid methyl palmitate existed

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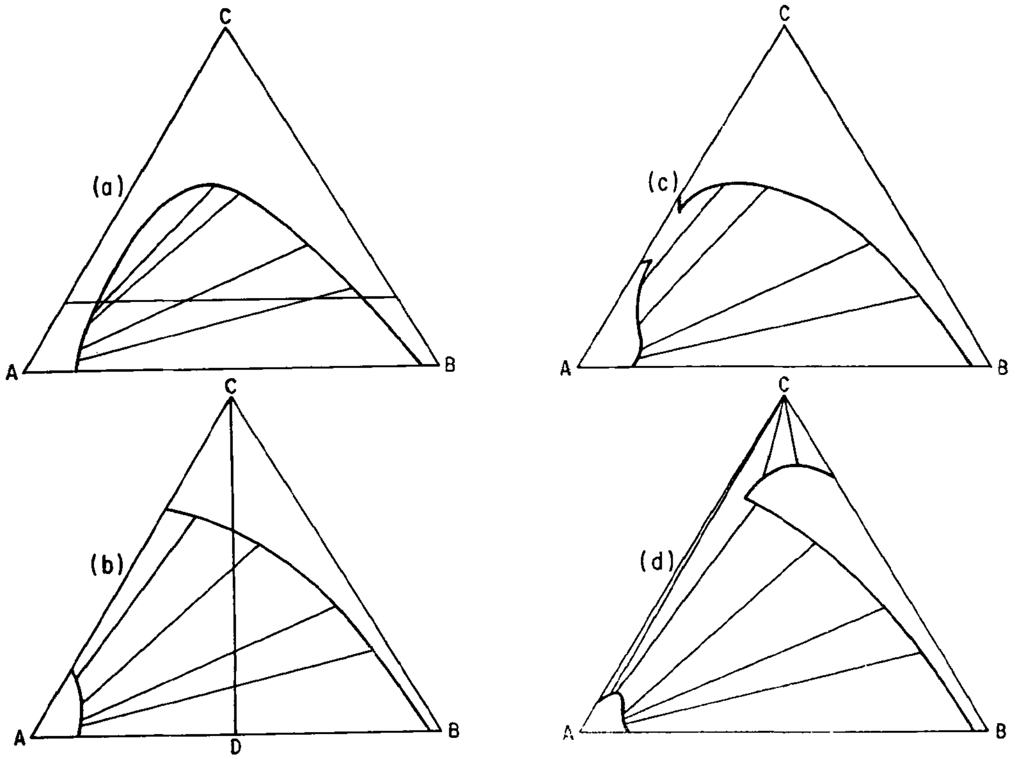

FIG. 1. Ternary diagrams: A = MeCN, B = Hexane, C = Solute. (a), Me oleate 30.4C; (b), Me oleate 20.0C; (c), Me palmitate 30.4C; (d), Me palmitate 20.0C.

in equilibrium with a homogeneous MeCN-rich phase.

The variation of these systems is also reflected in the variation of K_d with temperature (Fig. 2). The curves showed that K_d of both esters were significantly higher at 20.0C. Consider a countercurrent distribution of methyl oleate at the two temperatures. Assuming ideal distributions with constant K_d the peak maximum after 200 transfers would shift from Tube 162 at 20.0C to Tube 154 at 30.4C, as calculated from the binomial approximation (4). The volume ratio of the upper to the lower phase was 0.5.

It is apparent from Fig. 2 that the partition coefficients are also concentration-dependent. The partition coefficients were defined for a particular weight-fraction ratio of hexane to acetonitrile. The ternary diagrams show that a specific concentration of solute does not define a unique K_d. For example, as one moves along the 20% methyl oleate line in Figure 1a from solubility curve to solubility curve, an infinite number of tie lines are crossed, each one representing a different K_d. Thus curves such as those shown in Fig. 3 are required to treat adequately this variation in K_d.

Certain other relationships, common to all systems described herein, are important in CCD. As shown in Table II, as ester concentration increased, a point was reached where the density of the hexane-rich phase became higher than the density of the acetonitrile-rich phase and an inversion occurred. Thus there was a practical limit to the proportions of the components of these systems which could be employed in commonly used CCD apparatus, where the volume of the lower phase is fixed and only the upper phase is transferred. The ternary diagrams showed that the solute concentrations, where these inversions occurred, decreased

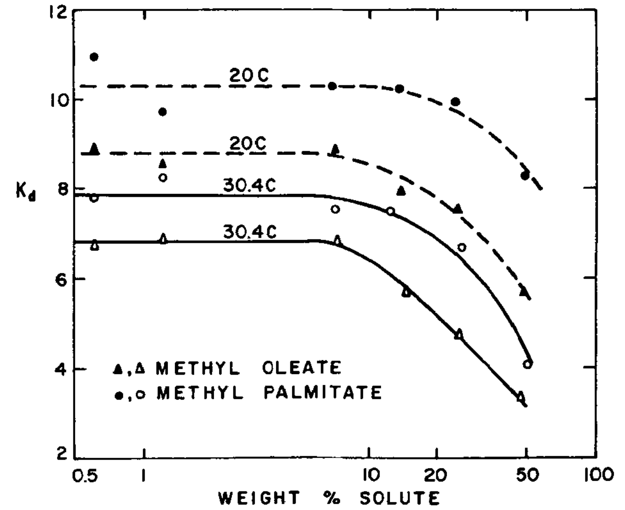

FIG. 2. Partition coefficients of methyl oleate (Δ) and methyl palmitate (O). Ratio of Hex-MeCN was 51/49 on wt % basis.

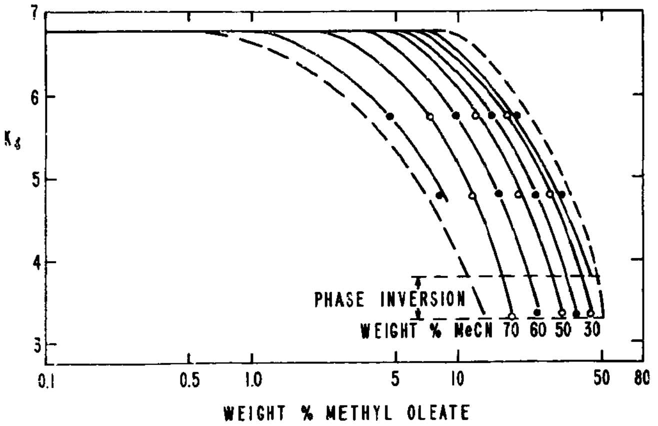

FIG. 3. Partition coefficient as a function of methyl oleate and MeCN conc at 30.4C.

TABLE II

Phase Equilibria

Hexane-rich phase				MeCN-rich phase				Ratio	
Sol.	MeCN	Hex.	Density	Sol.	MeCN	Hex.	Density	Wt	Segment
Wt %	Wt %	Wt %	g/ml	Wt %	Wt %	Wt %	g/ml		
22.8[a]	8.1	69.1	0.708	3.7	84.2	12.1	0.758	1.11	1.07
35.1[a]	12.0	52.9	0.730	7.1	81.4	11.5	0.756	1.28	1.33
50.3[a]	21.3	28.4	0.775	13.6	76.3	10.1		12.6	12.2
52.6[a]	27.1	20.3	0.784	15.4	74.9	9.7	0.770	1.04	1.08
23.5[b]	6.3	70.2	0.714	2.7	86.7	10.6	0.768	1.05	1.05
36.2[b]	8.8	55.0	0.737	4.6	85.6	9.8	0.768	1.31	1.33
54.7[b]	16.9	28.4	0.787	9.7	83.0	7.3	....	4.74	4.63
62.7[b]	26.8	10.5	0.819	16.7	80.8	2.5	0.787	1.52	1.47
21.0[c]	7.6	71.4	0.699	2.6	83.6	13.8	0.752	1.17	1.24
36.0[c]	11.7	52.3	0.728	5.2	81.7	13.1	0.756	1.39	1.32
52.3[c]	20.2	27.5	0.771	12.5	78.5	9.0	....	6.67	6.68
53.3[c]	38.0	8.7	0.796	24.4	72.5	3.1	0.770	2.89	2.78
23.2[d]	5.2	71.6	0.710	2.1	88.1	9.8	0.767	1.05	1.05
36.1[d]	7.8	56.1	0.736	3.5	87.5	9.0	0.767	1.41	1.35
55.5[d]	15.1	29.4	0.782	4.3	87.0	8.7	....	4.49	4.48
66.6[d]	24.3	9.1	0.816	11.2	85.4	3.4	0.783	1.48	1.48

[a] Methyl oleate—30.4C.
[b] Methyl oleate—20.0C.
[c] Methyl palmitate—30.4C.
[d] Methyl palmitate—20C.

as the hexane concentration decreased.

The phase-equilibria studies also demonstrated that phase volumes must change during a CCD run even though pre-equilibrated solvents were employed. As ester concentration is increased along line CD in Fig. 1b, a lengthening of the tie-line segments to the left of CD was observed. From the lever rule then, the weights of the MeCN-rich phases had decreased. Thus, at earlier stages of the distribution, the stationary phase would be washed out by the mobile phase. This phenomenon gives rise to a volume of upper phase retained in the CCD tubes since common equipment is constructed so that a constant lower-phase volume is required in order that all upper-phase can be transported. As the distribution progressed and ester concentration decreased, this dissolved stationary phase would be redistributed throughout the apparatus. Depletions of stationary phase in early tubes and an excess in the last tubes have been observed in CCD operations in our laboratory.

Analytical separations in CCD and chromatography are often idealized and treated as pseudo-binary systems. When preparative work is undertaken, nonideal situations occur. This means that all of these phenomena, as well as possible interactions between solutes (5), must be considered.

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