Phase Diagrams for Oil/Methanol/Ether Mixtures

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ABSTRACT: One-phase transmethylations of vegetable oils with methanol to form methyl esters occur considerably faster than conventional two-phase reactions. Addition of simple ethers is an efficient method for producing a single phase. Ternary phase diagrams have been determined at 23°C for oil/methanol/ether mixtures; these are useful when applying the one-phase method across a wide range of conditions. Soybean, canola, palm, and coconut oils were used in combination with five ethers, namely, tetrahydrofuran (THF), 1,4-dioxane (DO), diethyl ether (DE), diisopropyl ether (DI), and *tert*-butyl methyl ether (TBM). All five ethers can produce miscibility for all methanol/oil compositions. The ether/methanol volumetric ratios required for miscibility at a methanol/soybean or canola oil volumetric ratio of 0.20 (5.4 molar ratio) at 23°C are: THF, 1.15; DO, 1.60; DE, 1.38 DI, 1.57; and TBM, 1.57. For THF, this results in one-phase mixtures that contain 65 vol% oil. Soybean and canola oil form identical diagrams. Palm oil requires slightly less ether at the lower methanol concentrations, but coconut oil requires considerably less across the whole concentration range. Acid-catalyzed reactions, when performed at the boiling point of the most volatile component, require less ether than predicted from the diagrams.

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Diesel fuel, in the form of rapeseed methyl esters, is currently being manufactured and sold in many European countries. In the United States, extensive on- and off-road testing of soybean methyl esters, both in neat and blended forms (with petrodiesel), has occurred (1). Less attention has been given to the actual production of methyl esters. The base-catalyzed reaction between methanol and vegetable oils at ambient temperatures, although faster than the acid-catalyzed reaction, is still slow, hours rather than minutes being required for completion. Also, separation of the by-product, glycerol, is required. In 1984, it was determined that the methanol/oil molar ratio that is required to give methyl ester yields over 95% is approximately 6:1 (2). It was also concluded that 1.0 wt% sodium hydroxide, based on the oil, was the most efficient catalyst concentration. The equilibrium between hydroxide ion and methanol is used to provide the necessary methoxide ions because the use of sodium methoxide, which requires sodium metal in its production, is neither convenient nor inherently safe. The molar ratio of 6:1 and catalyst concentration of 1.0 wt% appear to be the values used in most industrial enterprises.

In 1986 (3), the acid- and base-catalyzed kinetics of both methanolysis and butanolysis (using butanol instead of methanol) of soybean oil were studied. For base-catalyzed reactions, the corresponding sodium alkoxides were used as catalysts. A major conclusion of the authors, regarding base-catalyzed reactions, was that butanolysis followed second-order kinetics, whereas methanolysis did not. In particular, for methanolysis, the intermediate mono- and diglycerides never reached the concentrations predicted by second-order kinetics. The other major conclusion for both methanolysis and butanolysis was that the rate constants for the removal of the second and third ester groups from the glycerides were considerably less than that for the removal of the first group. Two other important features of the kinetic data were not commented on by the authors The first was that methanolysis was 12–16 times slower than butanolysis, even though the former was carried out at 40°C and the latter at 30°C. There was also a lag time of about four minutes before significant methyl esters appeared, whereas butanolysis was 60% complete in 15–20 s, slowing dramatically thereafter. Recently, we explained these anomalies on the basis that the initial methanolysis mixture, even though it is stirred, consists of two phases, whereas the butanolysis mixture is a single phase (4,5). The initial concentration of oil in the methanol, where the catalyst is located, is also low, being 3.7 g · L^{-1} at 30°C with moderate agitation, and 5.7 g · L^{-1} after vigorous stirring for several minutes. This low rate of dissolving is consistent with the disparity in molar masses of the solvent and solute, and explains the lag time observed in methanolysis. The low solubility also explains the slow rate of reaction because the concentration of one of the reactants is low. The mass transfer limitations also explain why the mono- and diglycerides never build up to the expected levels. Once they are formed in the methanol phase, they preferentially react there, rather than move back to the oil phase.

Such an explanation suggested to us a method for considerably increasing the rate of methanolysis. We have recently described a group of ethers that will render the methanol/oil system one phase. For example, the addition of 1.25 vol of tetrahydrofuran (THF) per volume of methanol to the 6:1

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methanol/soybean oil mixture at ambient temperatures is sufficient to produce one phase and cause a dramatic increase in reaction rate (4). THF is particularly relevant because its boiling point is only 2°C different from that of methanol. Therefore, at the end of the reaction, the THF and excess methanol can be flashed together from the methyl esters and recycled. The molar volume of methanol is low compared to that of the oil, and therefore, the one-phase mixture has only a slightly larger volume than that for butanolysis. The oil accounts for 61% by volume of the mixture. The glycerol phase still separates, and surprisingly does so approximately four times faster than in the two-phase system.

The simple ethers, such as THF, 1,4-dioxane, diethyl ether, diisopropyl ether, and *tert*-butyl methyl ether, are particularly good cosolvents because they contain the balance of polar and nonpolar entities required to lower the interfacial surface tension between methanol and the oils. The nonpolar methyl group in methanol itself is too small to have the desired interaction with the oils. In comparison, the ethyl group in ethanol is sufficiently large to cause miscibility at 50°C for the usual 6:1 alcohol/oil molar ratio (6), and the butyl group in 1-butanol results in one phase at ambient temperatures.

Because of these findings, we believed there was a need for data on the miscibility of vegetable oil/methanol/ether mixtures in the complete range of methanol /oil molar ratios at ambient temperatures, and this paper addresses that requirement.

EXPERIMENTAL PROCEDURES

Four oils and five cosolvents were used for the study. The four oils were all food-grade products as follows: Soybean oil (Presidents Choice, Sunfresh Ltd., Toronto, Ontario, Canada), canola oil (100% Canadian canola oil; Sunora Foods Ltd., Calgary, Alberta, Canada), coconut oil (Kissan 100% coconut oil; Kissan International Inc., Scarborough, Ontario, Canada), palm oil (100% red palm oil from the Ivory Coast; Villgeoise Ltd., Abidjan, Ivory Coast). Food-grade products were chosen to remove some variability from the study. The results are still significant for cruder oils, in that absolute complete miscibility of the reactants is probably not required for the faster reactions. The use of food-grade products also allows for a better comparison of the four oils based on their known triglyceride compositions. The five ethers were obtained from Aldrich Chemical Company (Milwaukee, WI). The ethers and corresponding grades were as follows: THF, 99+%; 1,4-dioxane (DO), 99+%; *t*-butyl methyl ether (TBM), anhydrous 99.8%; diisopropyl ether (DI), anhydrous 99+%; and diethyl ether (DE), anhydrous 99.8%. Methanol (99+%) was obtained from Caledon Laboratories Ltd. (Toronto, Canada). The usual method for constructing ternary phase diagrams is to first measure the compositions of the various two phases that are in equilibrium in the two-phase region; the compositional pairs are then connected by tie lines to construct the phase diagram. Gas chromatography is most often used for determining compositions of the phases. Unfortunately, this ternary system consists of two volatile components and one high-molar mass component. It has been our experience that triglycerides, as found in vegetable oils, do not behave well or consistently in a gas chromatograph, when they are in high concentration in the sample to be analyzed. Specifically, contamination of the injector, after numerous injections, is common. We, therefore, chose the cloud point method, which works well for these mixtures. All measurements were performed at 23°C. This temperature was selected mainly because this was the laboratory temperature at which our initial measurements were made without temperature control. It is also a reasonable compromise to represent ambient summer temperatures in both Europe and the United States. For each oil, nine methanol/oil mixtures, containing normalized methanol volume ratios from 0.10 to 0.90, in 0.10 increments, were used. For each mixture, the ether was added from a burette to a stirred mixture of methanol and oil of known volumetric composition until the milkiness of the mixture just disappeared. The mixture was allowed to stand for two hours, and if the milkiness returned, more ether was carefully added to again achieve homogeneity. The volume of ether required to just achieve miscibility was noted. The compositions of the resulting mixtures obtained in this way for all original methanol/oil combinations were then plotted to form a phase diagram.

RESULTS

The results were all plotted in the form of ternary phase diagrams, with the 100% compositional points (normalized) for methanol, oil, and cosolvent being bottom left, bottom right, and the upper apex, respectively. Although twenty phase diagrams for the four oils and five ethers were constructed, careful superimposition of them revealed that some were virtually identical. Six different types of diagrams were identified, and these are numbered by type in the matrix shown in Table 2. Six diagrams, one representative of each type, are shown in Figures 1–6. They represent the combinations of methanol with soybean oil/THF (type 1), canola oil/DI (type 2), palm oil/THF (type 3), coconut oil/THF (type 4), palm oil/TBM (type 5), and coconut oil/DE (type 6).

The compositional scales on the diagrams are all in normalized volume units; knowledge of specific gravities and molar masses is required to convert them either to molar percentages or molar ratios. For convenience, Table 1 shows the approximate methanol/oil molar ratios equivalent to the normalized methanol volumetric contents in mixtures with soy-

TABLE 1
Approximate Methanol/Oil Molar Ratios, for Soybean, Canola, and Palm Oils[a]

NVC	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
MR1	2.4	5.4	9.2	14	21	32	50	86	193
MR2	1.7	3.9	6.7	10	16	23	37	63	141

[a] MR1 (middle row); for coconut oil, MR2, (bottom row); corresponding to the range of normalized volumetric methanol contents, NVC (upper row).

bean, canola, and palm oils (molar masses all assumed to be 870 Da), as well as with coconut oil (640 Da).

For soybean, canola, and palm oil, the usual 6:1 methanol/oil molar ratio employed in base-catalyzed transmethylation corresponds closely to 22% methanol by volume (i.e., 0.22 on the horizontal scale). Likewise, a molar ratio of 30:1, more appropriate for acid-catalyzed transmethylation, corresponds to 58 volume percentage methanol (or 0.58 on the horizontal scale). For coconut oil, these values are somewhat higher (0.28 and 0.66, respectively) due to the lower molar mass of this oil. If molar percentages had been used on the scales, the curves would have been compressed severely both to the left sides of the triangles and to the top apex as a result of the much smaller molar volumes of methanol and the ethers as compared to those of the oils. For example, for soybean, canola, and palm oils, the points, 0.22 and 0.58 on the lower scales, would become 0.86 and 0.97, respectively, if normalized on a molar basis.

In methyl ester formation, it is the methanol/oil ratio that is used to drive the reaction. Constant volume ratios, and, therefore, constant molar ratios, lie on the straight lines drawn from the appropriate points on the appropriate side to the opposite apex. The contribution of any component to any compositional point in a diagram is best illustrated by an example. The THF contribution for any point is found by drawing, through that point, a straight line parallel to the side joining the other two components (in this case, the base). The point, at which this line cuts the side having the scale that increases towards the THF apex (in this case on the left side), corresponds to the THF concentration. The contributions of the other two components are found in a similar way. In all diagrams, the regions under the curves formed by joining the data points correspond to the two-phase region, whereas the regions above the curves contain the compositions resulting in one phase. For clarity, we have not joined the data points.

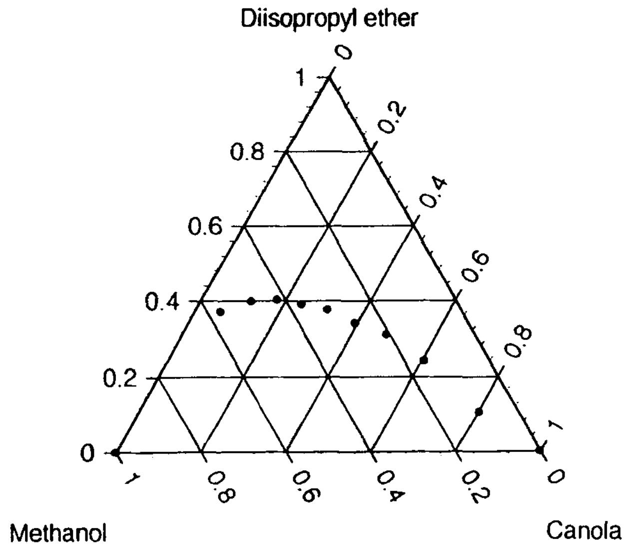

FIG. 2. Type 2 phase diagram: canola/methanol/diisopropyl ether.

DISCUSSION

Figures 1 to 6 show that all five ethers are good cosolvents for the methanol/oil mixtures. Miscibility can be achieved over the full range of methanol/oil compositions for all oils. For the twenty possible oil/methanol/ether combinations, only a maximum of approximately 40 vol% of an ether in the final mixture is ever required to achieve miscibility. This occurs for methanol contents of the original mixture in the range of 72–80% for the twelve samples in which either THF or coconut oil is not one of the components, as in Figures 2 and 4. Although soybean, canola, and palm oils behave similarly toward the ethers at the maximum in this regard, only soybean and canola oils behave completely the same over the

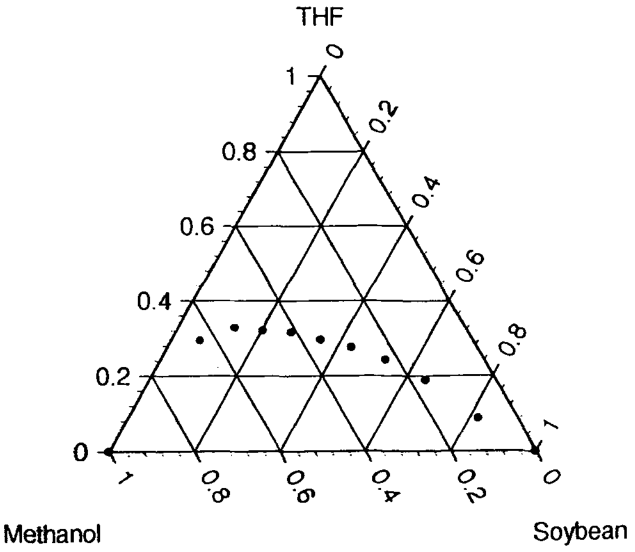

FIG. 1. Type 1 phase diagram: soybean/methanol/tetrahydrofuran (THF).

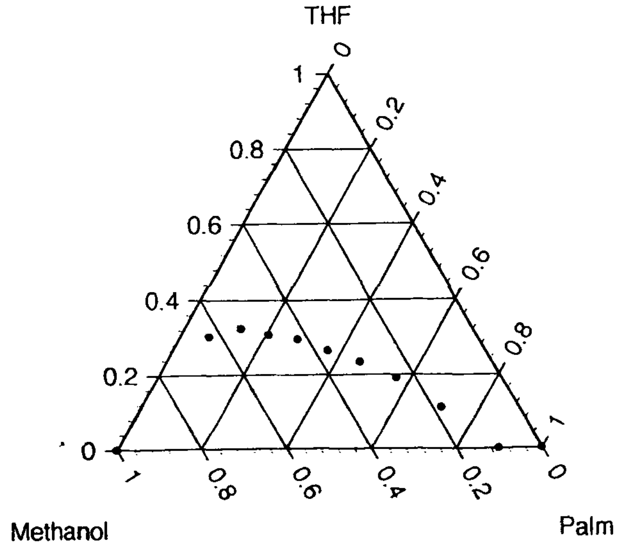

FIG. 3. Type 3 phase diagram: palm/methanol/THF. See Figure 1 for abbreviation.

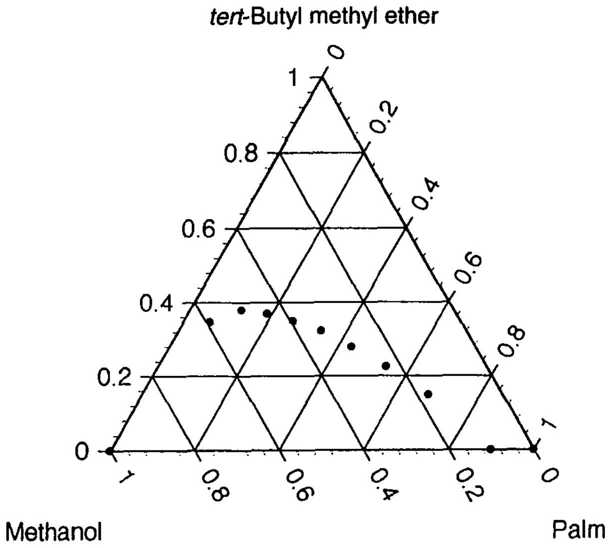

FIG. 4. Type 4 phase diagram: palm/methanol/*t*-butyl methyl ether.

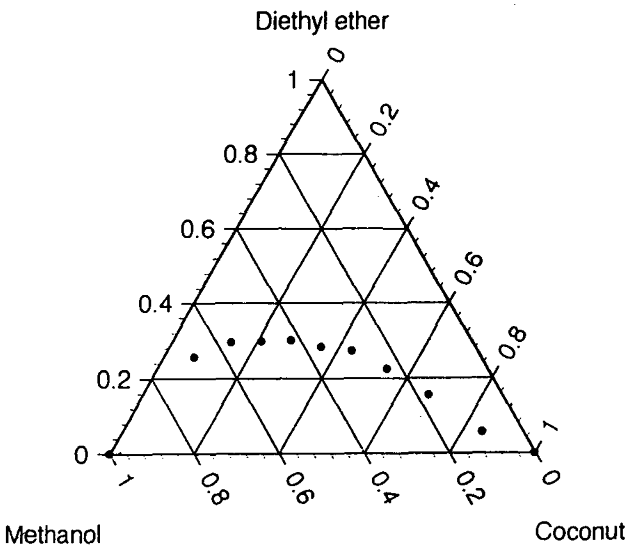

FIG. 6. Type 6 phase diagram: coconut/methanol/diethyl ether.

whole diagram. This reflects the unsaturated nature of these oils. Palm oil differs from them at the lower methanol concentrations, where slightly less of any of the ethers is required for miscibility. This can be seen by comparing Figures 2 and 4 as well as Figures 1 and 3. In addition, Table 2 shows that all ethers, except THF, have virtually the same effect on any oil. For all oils, THF is clearly the most efficient of the five ethers, which is the reason why column 1 in Table 2 differs from all others; the maximum amount ever required to achieve miscibility in the final mixture is approximately 33 vol%, again for original methanol contents in the 72–80% range. However, this range is considerably removed from the 6:1 methanol/oil molar ratio usually employed in base-catalyzed reactions, for which the methanol content is 22 vol% (i.e., 0.22 on the lower scale). However, it is closer to the 30:1 molar composition (0.58 on the lower scale) often employed in acid-catalyzed reactions. Such reactions are usually performed at the boiling point of methanol, in which case less cosolvent is required than shown in the diagrams. We have determined that the required THF/methanol ratio, required for miscibility at the 30:1 molar ratio, for soybean and canola oils is only 0.57 at 57°C, which leads to an oil concentration of 31 vol%.

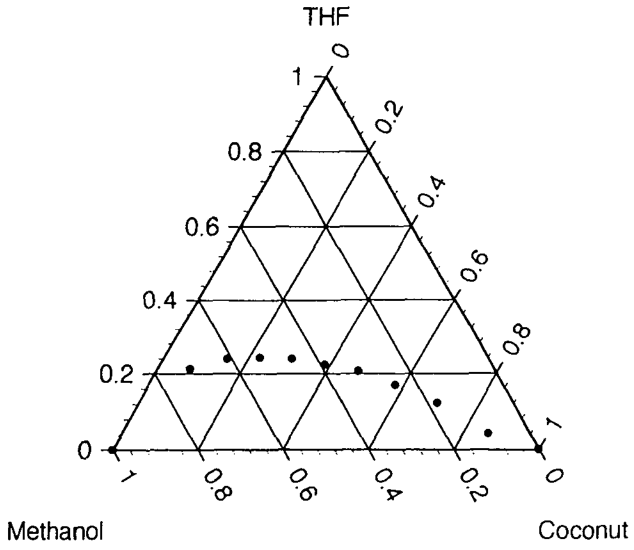

FIG. 5. Type 5 phase diagram: coconut/methanol/THF. See Figure 1 for abbreviation.

At the methanol/soybean oil ratio of 5.4 (0.2 volumetric ratio), the minimum ether/methanol volumetric ratios required for one phase are THF, 1.15; DO, 1.60; DE, 1.38; DI, 1.57; and TBM, 1.57.

For coconut oil, less of all ethers is required to achieve miscibility than for the other three oils. This shows that the relative contents of the nonpolar chains and the polar ester linkages in the oils are important. The maximum ether content required for miscibility with THF is 25 vol%, compared to 33 vol% for the other oils. For the other cosolvents, the value is 30–32 vol% for coconut oil, compared to 40 vol% for the other oils. The ratio of the two values in each mixture is virtually the same as the ratios of the molar masses of coconut

TABLE 2
Phase Diagram Type (by figure number) for Oil/Ether Combinations with Methanol

	Ether				
Oil	Tetrahydrofuran	Dioxane	Diethyl	Diisopropyl	*t*-Butyl Methyl
Soybean	1	2	2	2	2
Canola	1	2	2	2	2
Palm	3	4	4	4	4
Coconut	5	6	6	6	6

oil and the other oils. That is, the ratios of 25:33 and 31:40 (0.76 and 0.78) are close to the value of 640:870 (0.74).

THF is obviously the preferred cosolvent on the basis of volume required for miscibility, as well as boiling point considerations. However, the separation of the by-product, glycerol may be another important consideration, although solvent flashing usually precedes this step. We are currently measuring the degree of glycerol separation, as well as the separation rates for the five ethers. For THF, the bulk of the glycerol still separates at the bottom of the reaction mixture and does so more rapidly than in the two-phase reaction. However, we have achieved the production of 95 wt% methyl esters from soybean oil in 15 min by using 1.3 wt% sodium hydroxide as catalyst. When the reaction is this rapid, the glycerol could be separated by centrifugation.

We are continuing experiments that are designed to elucidate why base-catalyzed transmethylations slow down rapidly. The one-phase systems offer a more convenient method to accomplish this. Hydroxide depletion with the formation of soap may be one reason. The same phenomenon, noted in alkoxide-catalyzed reactions, may be caused by the presence of trace amounts of water. However, we have not ruled out other contributions, in particular, polarity effects (4).

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