Ternary Equilibrium Data for Production of Fish Protein Concentrate (FPC)

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Several ternary equilibrium diagrams were obtained for the purpose of evaluating the respective efficiencies of ethanol and isopropyl alcohol (IPA) for the commercial extraction of oil and water from raw fish to produce an edible protein concentrate called FPC (fish protein concentrate). Commercial extraction processes for the production of FPC were, in the past, generally developed empirically without the use of ternary diagrams and, consequently, there are inconsistencies in the literature concerning the relative merits of ethanol and IPA as extraction solvents and also concerning the effect of water on the extraction efficiency of these solvents. From the data presented, these inconsistencies can be clarified.

Raw fish, which may be unacceptable for human consumption for reasons of flavor or texture, can be transformed into a high-protein concentrate by means of a chemical solvent extraction process (*6*). This high-protein concentrate is generally referred to as FPC (fish protein concentrate) and can be added to such items as wheat flour to greatly enhance the nutritional quality of baked products. Three solvents have been reported as being satisfactory for the production of FPC: isopropyl alcohol (*1*, *2*, *4*), ethanol (*3*), and ethylene dichloride (*10*).

One of the first requirements for a solid-liquid extraction process is that there must be enough solvent present to dissolve the solute to be extracted. This information can be obtained from a mathematical treatment utilizing the data obtained from ternary equilibrium studies. In the production of FPC by alcohol extraction, water and fish oil are simultaneously extracted but the percentage of water greatly exceeds the percentage of fish oil. (Raw fish is approximately 65–78% water by weight.) There is a strict limit of 0.5% residual oil in the final FPC product (*5*) and, therefore, the primary purpose of the solvent extraction step is to remove oil from the raw fish. This amounts to reducing the oil content from a level sometimes as high as 40% on a dry solid basis to less than 0.5%. The presence of water affects the solubility of the fish oil in the solvent, but not always in a negative sense (*2*). A single determination of the solubility of pure fish oil in various pure solvents is of limited value only and consequently ternary diagrams may be necessary to present the overall picture. In additon, tie-line data are also needed for process design. Therefore, ternary equilibrium and tie-line data were obtained for several three-component systems at different temperatures to evaluate the respective solvent efficiencies of ethanol and IPA.

EXPERIMENTAL

Materials. Spectrograde isopropyl alcohol was used in the equilibrium studies, and absolute ethanol, as well as practical grade 2-methyl-3-butyn-2-ol, was also used without further purification. The fish oil used in these studies was extracted from a concentrated miscella obtained from the production of FPC (*7*) using methanol, chloroform, and hexane, respectively, as solvents. The solvents were then subsequently evaporated under a blanket of nitrogen at 50°C. An analysis by silicic acid column separation of the oil is presented in Table I.

Procedure. Several experimenters have tried such analytical methods as refractive index, surface tension, and density measurements without success to obtain ternary equilibria data (*8*, *9*, *12*, *14*), and there is also disagreement in the literature concerning the best method of visually determining the end point (*8*, *9*). An experimental method for conserving solute has been suggested by Othmer et al. (*15*), but it was unsatisfactory for this study. Solubility curves were determined by a modification of the cloud-point method described by Harris et al. (*9*).

About 50 ml of solvent were added to a 125-ml Erlenmeyer flask and weighed. A calculated amount of water was then added and, after reweighing, the flask was stoppered with an air-tight serum stopper. Each experimental point was planned in advance to prevent the duplication of points and to obtain equally spaced datum points. The stoppered flask was placed in a controlled temperature bath and brought up to the required temperature. The bath temperature was controlled at 1°C higher than the required temperature, and room temperature was always kept lower than the bath temperature. At this point it was important to reweigh the stoppered flask before adding the third component because of the buoyancy effect of the contained vapors. After reweighing, the fish oil was then added dropwise to the flask with a syringe to penetrate the self-sealing serum stopper. Titration was, therefore, carried out in an air-tight system to prevent the loss of vapors.

The cloud point was obtained by titrating from a clear solution to a cloudy solution at all times and, therefore, for certain portions of the curve the cloud point was obtained by adding water to weighted quantities of oil and alcohol. In the median range, as a check, water was also added to IPA and oil to produce the same point. Thus, if the solution was clear at the bath temperature and the maximum cloudiness developed within 10–20 sec after removing the flask from the bath, then the end point was considered to have been reached. The time required for the complete occurrence of the second phase was the calculated time required for the fluid temperature in the

Table I. Analysis of Fish Oil

Composition	Total compn, wt %
Hake oil	
Chloroform solubles	81.0
Chloroform–methanol (7:3 v/v) solubles	8.0
Methanol solubles	11.0
Menhaden oil	
Chloroform solubles	93.2
Chloroform–methanol (7:3 v/v) solubles	3.5
Methanol solubles	3.3

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sample bottle to drop 1°C. Although it was possible to get some cloudiness within 10–20 sec, without reaching the end point, the key to the titration was the requirement that maximum cloudiness developed within the time required, thereby indicating that two distinct phases were in equilibrium.

At high oil concentrations the end point was difficult to obtain visually and, consequently, equilibria data for the lower right-hand corner of the ternary diagrams were, in some instances, obtained by extrapolation.

To obtain tie-line data, about 80 grams of total sample weight were placed in a 125-ml Erlenmeyer flask. The flask was stoppered with a serum stopper, agitated, brought up to temperature, and allowed to reach equilibrium. Samples were then removed from the stoppered flask with a warm syringe and immediately analyzed for water (*11*) and oil (*16*). The elapsed time between withdrawal of the sample and analysis was critical and had to be kept to an absolute minimum.

Data are presented in Figures 1–4 at two different temperatures in the form of a continuous curve and a dotted curve. The continuous curves represent experimental data obtained at a higher temperature and the dotted curves represent data obtained at some lower temperature. The center of each dot on the dotted curves represents actual experimental points, and the continuous curves were drawn through actual data points in almost all cases. There was little scattering of data,

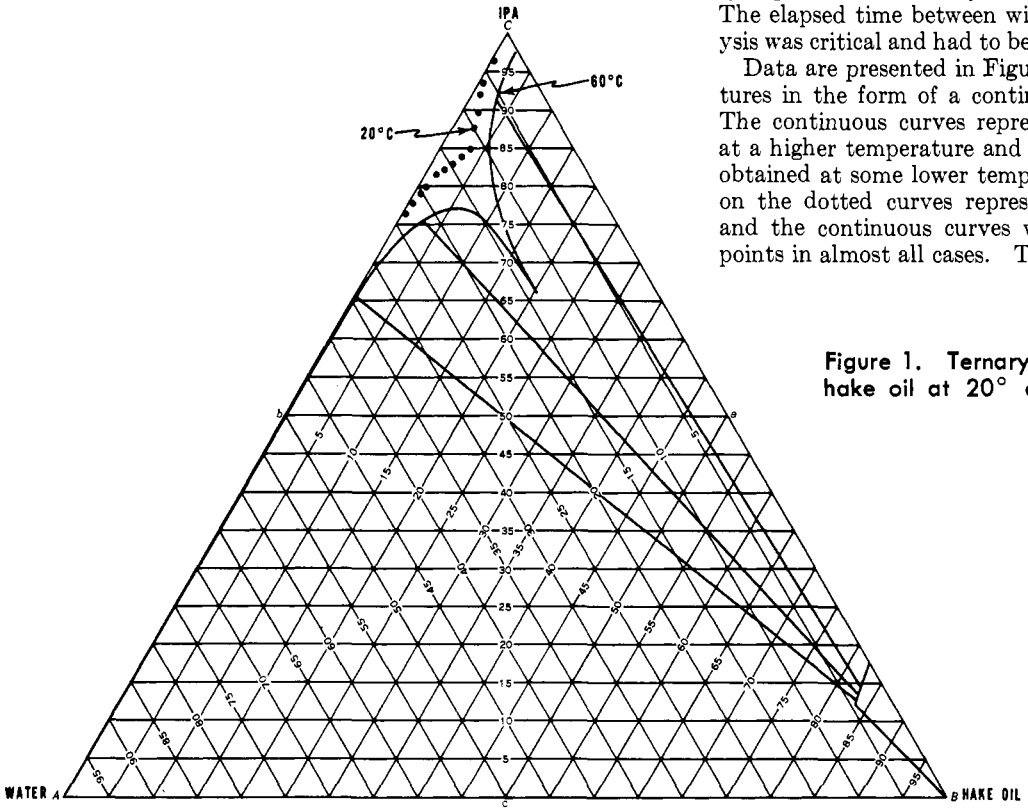

Figure 1. Ternary diagram for system water–IPA–hake oil at 20° and 60°C

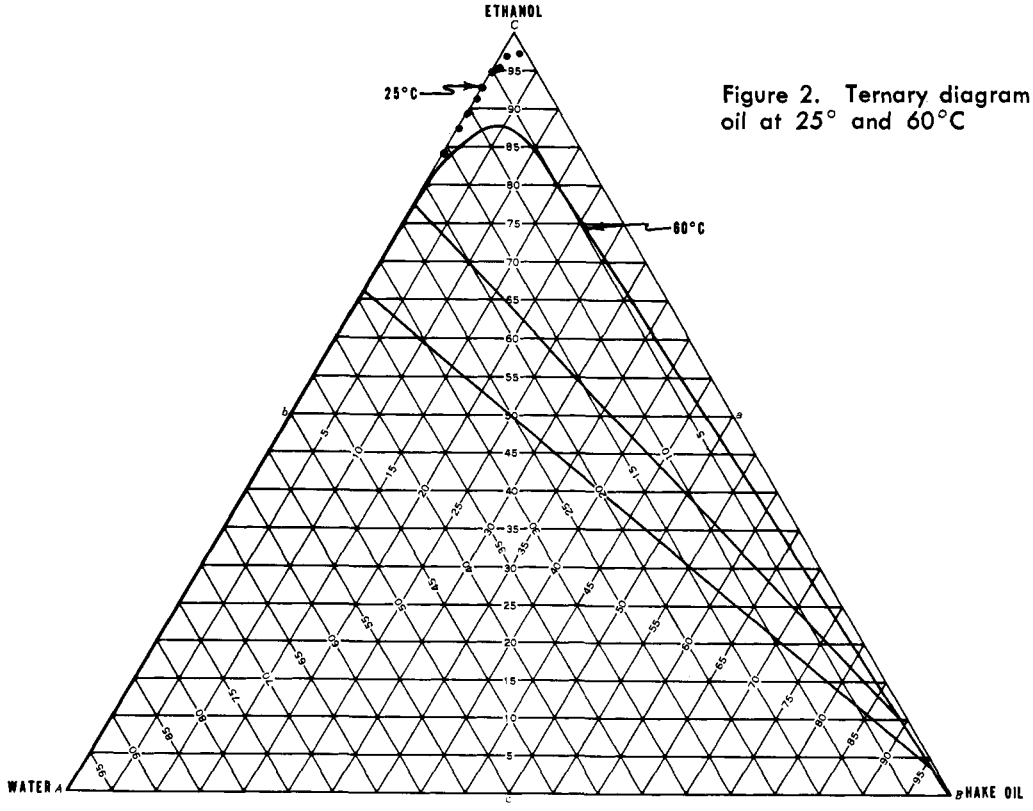

Figure 2. Ternary diagram for system water–ethanol–hake oil at 25° and 60°C

except at the lower temperatures (20–25–30°C), owing to the presence of a solid phase which made the end point difficult to determine. However, at the higher temperatures (40–50–60–70°C), the end point was so obvious that the data showed almost no scatter at all.

RESULTS

If all three components are liquids at the prevailing temperature, several types of ternary systems can be formed. Treybal (*17*) defines a Type 1 ternary system as being characterized by the formation of one pair of partially miscible liquids while a Type 2 ternary system is one which forms two pairs of partially miscible liquids. In addition, a Type 4 ternary system is characterized by the formation of solid phases.

Hake Oil. Figure 1 represents the ternary equilibria data for the system water–IPA–hake oil at 20° and 60°C. This system formed a Type 2 ternary system at all temperatures tested. Figure 2 represents the ternary equilibria data for the

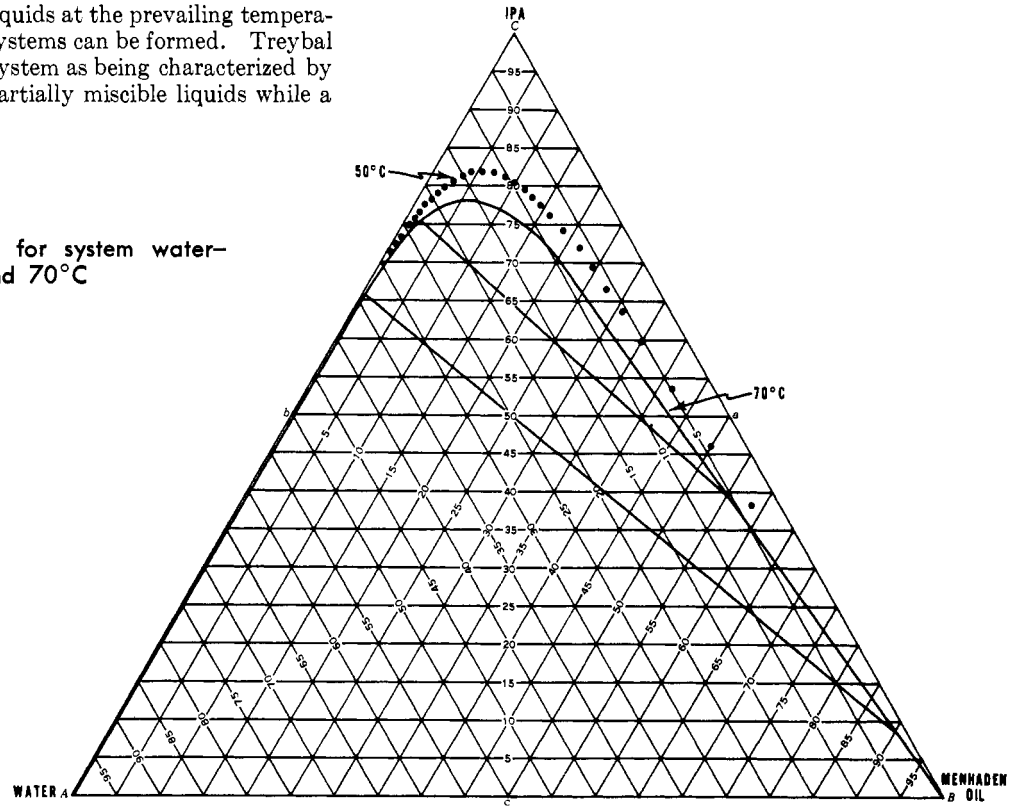

Figure 3. Ternary diagram for system water–IPA–menhaden oil at 50° and 70°C

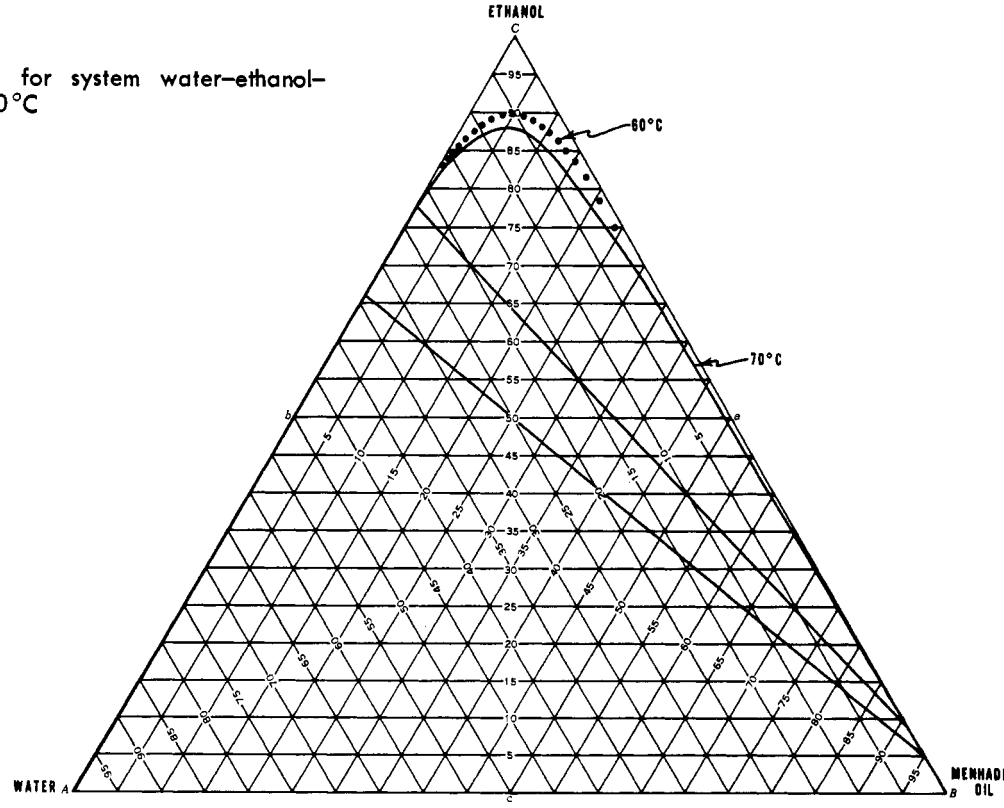

Figure 4. Ternary diagram for system water–ethanol–menhaden oil at 60° and 70°C

system water–ethanol–hake oil at 25° and 60°C. This mixture formed a Type 4 ternary system at 25°C and a Type 1 ternary system at 60°C. At the lower temperature, a small amount of wax-like components (saturated triglycerides, hydrocarbons, and sterols) settled out as a third phase. The higher experimental temperatures obviously exceeded the phase-transition temperature of these components. Ternary equilibria data were also obtained at other temperatures and the results indicated an increase in solubility with temperature as expected.

Menhaden Oil. Figure 3 represents the ternary equilibria data for the three-component system water-IPA-menhaden oil at 50° and 70°C. This system forms a Type 1 ternary system at temperatures of 40°, 50°, 60°, and 70°C. Figure 4 represents the ternary equilibria data for the system water–ethanol–menhaden oil at 60° and 70°C. Ternary equilibria data were also obtained at other temperatures, and the results obtained were as expected in most instances. It was noted that the solubility of menhaden oil in ethanol and in IPA was extremely low at 25°C.

DISCUSSION

Ternary equilibrium curves are presented for a number of systems and from the data presented it appears that IPA is a better overall solvent for the extraction from raw fish of either menhaden oil or hake oil if these oils have the characteristics listed in Table I. Since fish oil varies in composition depending on feed conditions, water temperatures, and maturation these variations could affect the solvency of the alcohols.

It was surprising to find that the system water-IPA-hake oil forms a Type 2 ternary system at 60°C, while the system water-ethanol–hake oil forms a Type 1 ternary system at the same temperature. Structurally, the only difference between IPA and ethanol is that IPA has one additional CH_3 group. Thus, a small change in solvent structure produced an unpredictably large change in the shape of the ternary equilibrium curve. This change in shape was unexpected as Harris et al. (*9*) obtained a Type 1 curve for both ternary systems consisting of water–ethanol–cottonseed oil and water–IPA–cottonseed oil. In addition, the fact that IPA forms a Type 1 ternary system with menhaden oil and water while it forms a Type 2 ternary system with hake oil and water could not be predicted. A satisfactory explanation for these results in terms of a reaction mechanism has not been reached.

The end point of the equilibrium curve for the upper right-hand portion of the system water–IPA–hake oil was difficult to obtain. This end point was an abrupt change from a single-phase solution to a two-phase solution and consequently the end point was easy to overshoot. However, the fact that a two-phase system did exist in this region of the curve is unquestionable.

A comparison of Figures 1 and 2 shows that 100% ethanol is a much better solvent than 100% IPA for pure, water-free hake oil at 60°C. However, this information alone could lead to a significant error in the choice of a solvent for the solvent extraction of raw hake. Close inspection of Figures 1 and 2 reveals that the presence of some water actually enhances the solubility of hake oil in IPA, whereas water in excess of 4% greatly reduces the solubility of hake oil in ethanol.

Dreosti (*3*) reported that ethyl alcohol was a better solvent than IPA for the extraction of hake fish meal. However, for lipid removal, IPA appears to be a better solvent than ethanol if the water content of the system is above 7%. Moorjani et al. (*13*) reported that isopropyl alcohol (IPA) was a slightly better solvent than ethyl alcohol in the preparation of FPC from whole or eviscerated fish. The statements by Dreosti and Moorjani can both be true as evidenced by the above ternary diagrams providing one knows the amount of water present in the fish, the type of fish being processed, and the water content of the solvent used.

In the production of FPC, a countercurrent extraction process is generally used and the liquid residue from the first-stage extractor can be decanted. When decanting this liquid residue, two equilibrium phases are formed, namely an oil-rich phase which can be subjected to further processing and a water-rich phase from which IPA can be recovered. Therefore, to obtain both qualitative and quantitative information for process design, tie-line data are required.

The work of Othmer and Tobias (*14*) shows that tie lines can be successfully correlated from a few experimental data points if the sum of the solute and minor nonconsolute component is regarded as obeying the Nernst law of distribution of a consolute in an immiscible pair of liquids. They found that a straight line resulted from a plot of log $(1 - a_1)/a_1$ vs. log $(1 - b_2)/b_2$ where a_1 is the fraction of solvent in the solvent phase and b_2 is the fraction of diluent in the other phase. To establish this straight line, only two experimental plots are necessary—i.e., two tie lines.

CONCLUSIONS

The equilibrium data indicate that IPA may be a better solvent than ethanol for the solvent extraction of lipids and water from raw hake and raw menhaden.

There is a minimum water content for the extraction of hake oil which will affect the efficiency of the solvent used. At 60°C, for a system containing less than 7% water, ethanol is a more efficient "solvent" than IPA for hake oil. However, for a system containing more than 7% water, at 60°C, IPA is a more efficient "solvent" than ethanol for hake oil.

The shape of the equilibrium curve for the system water–IPA–hake oil may be responsible for some of the controversy in the literature.

ACKNOWLEDGMENT

Appreciation is expressed to Bobby Willis for assistance in the analytical work.

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RECEIVED for review June 18, 1971. Accepted January 18, 1972.