and interpretation of X-ray diffraction patterns, to E. H. Melvin and B. L. Wilson for ultraviolet absorption spectra, and to C. H. Van Etten and C. E. McGrew for microanalyses.

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Acetone as a Selective Solvent for Vegetable Oils[1, 2]

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THE MODIFICATION of drying and semi-drying oils by extraction with a selective solvent has received considerable attention in recent years. A wide range of solvents has been investigated (9), but only furfural (2, 4) and liquid propane (1, 6) have warranted development to the point of commercial application. A third solvent which may find application in this field is acetone containing small proportions of water. Such a system was suggested by Jenkins (3) in a patent dealing with the use of "wet" furfural. It is a solvent which is readily available, is easily stripped from the oil, and requires no special equipment for handling. It has the added advantage that by varying the water content it may be "tailored" to the particular oil and separation involved.

Solubility and Selectivity

From the viewpoint of extraction efficiency the important properties of a solvent are a) solubility of the oil in it and b) selectivity, that is, the difference in iodine value between extract and raffinate on batch extraction. The effect of water content of acetone on these two properties is shown in Figures 1 and 2 for the batch extraction of a sample of soybean oil, I.V. 129.3, and a sample of linseed oil, I. V. 188.0. Solubility has been shown as the ratio of solvent to oil as this form is to be used later. Since a low solvent to oil ratio and high selectivity are desired, the variations of these properties with water content are conflicting. With reference to existing processes it appears however that a useful compromise can be obtained in the range of 3 to 7 parts water per 100 parts acetone by volume.

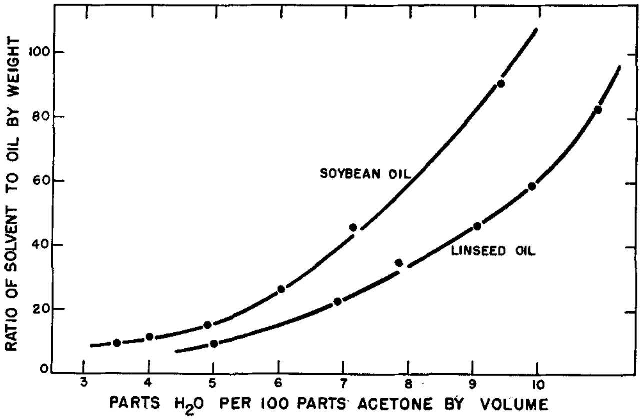

FIG. 1. Effect of water content of acetone on ratio of solvent to oil required at 25°C.

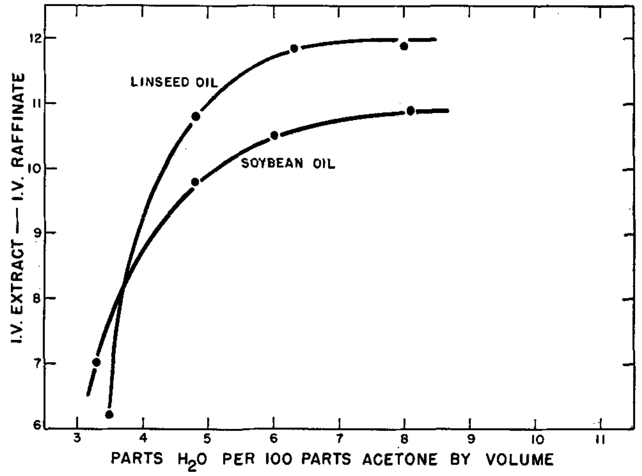

FIG. 2. Effect of water content of acetone on selectivity, *i.e.*, difference in iodine value between extract and raffinate oils.

Equilibrium Diagrams

The evaluation of the solvent for use in countercurrent column operation rather than in batch extraction is the important consideration. As in distillation the prediction and evaluation of extraction column operation is based on equilibrium data between phases over the concentration range involved. The particular type of equilibrium diagram used here is one adapted to extraction calculations by Maloney and Schubert (5) in which the ratio of solvent to solute is plotted against the concentration of components in the solute. As pointed out by Pratt (7) and illustrated by Rushton (8), in dealing with multi-component systems it is necessary to replace concentration by the value of some additive property of the system. The obvious choice of property in this system is iodine value. The required data are the solvent to oil ratios and iodine values of the oils in extract and raffinate phases over the range of iodine values likely to be encountered in fractionation. Ruthruff and Wilcock (9) in their

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[2] Issued as Paper No. 190 on the "Uses of Plant Products" and as N.R.C. No. 3627.

work on soybean oil and furfural covered a limited range of iodine values by varying the fraction of oil extracted. In the present work a wider range was covered by a stepwise batch extraction process in which the extract and raffinate oils from an initial extraction process were used as feed for second extractions and so on. It was found that nonglyceride materials present in the original oil rapidly built up in successive extract fractions and markedly affected solubilities and selectivities. Such material was therefore removed as completely as possible from the original oils by passing the oils in a hydrocarbon solvent through an alumina column. The linear relation between refractive index and iodine value for glycerides was used as a measure of the effectiveness of this treatment. This relation was checked after each successive extraction, and where necessary the alumina treatment was repeated. Samples obtained in this way were equilibrated with the solvent at a temperature of 25°C.

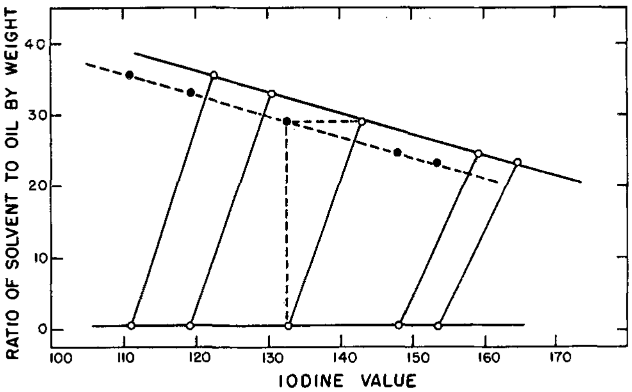

FIG. 3. Equilibrium diagram for soybean oil, using 6 parts water per 100 parts acetone as solvent.

Figure 3 shows the equilibrium diagram obtained for soybean oil, using 6 parts water per 100 parts acetone as solvent. Over the range covered the iodine values of the extract and raffinate phases varied linearly with solvent to oil ratio, and the selectivity remained constant. The conjugate line, located as shown by the broken lines from the ends of the tie lines, was plotted to facilitate interpolation between tie lines. A similar diagram, Figure 4, was obtained for soybean oil using 3.5 parts water per 100 parts acetone. Again the iodine values varied linearly with solvent to oil ratio, but the selectivity decreased at the higher iodine values. Since the extract lines were straight and nearly parallel for these two cases, the whole family of equilibrium curves over the useful range of water contents can be filled in from solubility and selectivity data. A similar diagram, Figure 5, was also obtained for linseed oil, using 5 parts water per 100 parts acetone as the solvent.

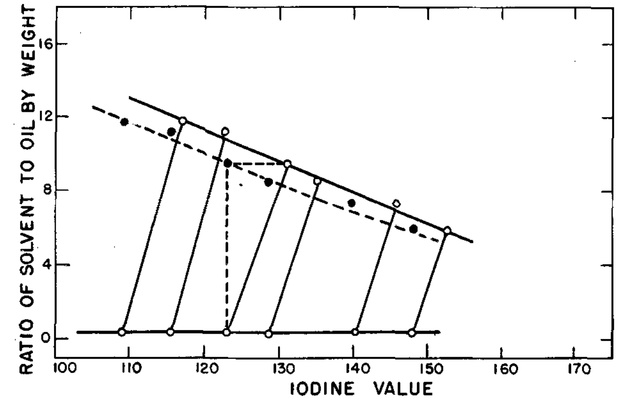

FIG. 4. Equilibrium diagram for soybean oil, using 35 parts water per 100 parts acetone as solvent.

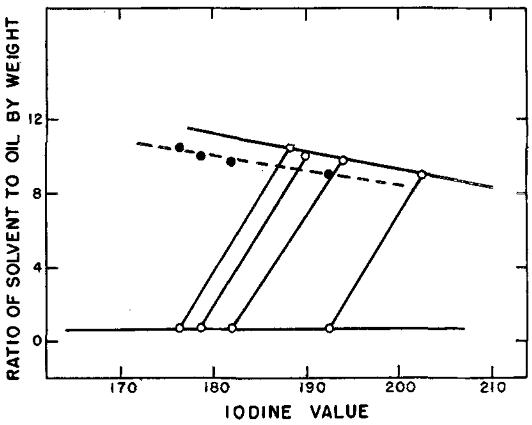

FIG. 5. Equilibrium diagram for linseed oil, using 5 parts water per 100 parts acetone as solvent.

Pilot Plant Operations

To evaluate the reliability of these diagrams for prediction of column operation and to estimate column efficiencies a number of runs were made in a packed column, 2 in. in diameter and 20 ft. high, and H.E.T.S. values were computed. Figure 6 is a schematic diagram of the column used. Oil was fed 11 ft. from the top of the column, and solvent was sprayed in at the bottom. The interface was maintained at the top of the column so that the oil-rich phase formed the continuous phase throughout the extraction zone. Extract overflowing from the top of the column passed to an evaporator where the solvent was stripped off and a portion of the extract oil was returned to the top of the column as reflux.

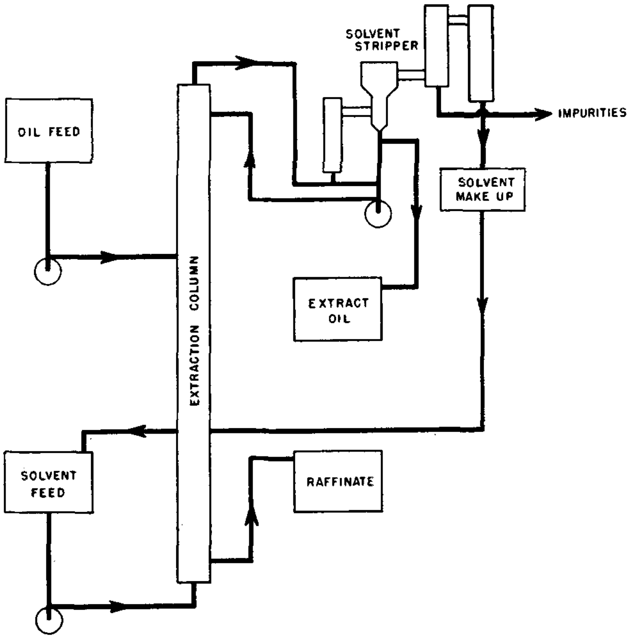

FIG. 6. Schematic diagram of pilot plant column.

TABLE I

Pilot Plant Data Obtained, Using a 20-ft. Packed Column with Soybean Oil I.V. 129.3 as Feed

Run No.	Packing	Parts H_2O per 100 parts acetone	Ratio of solvent to oil	Reflux ratio	Extract I.V.	Raffinate I.V.	Extract %	H.E.T.S.
1	¼" berl saddles	6.0	9.4	0.9	145.6	124.6	21.2	....
2	¼" berl saddles	6.0	21.4	2.8	151.0	118.7	33.1	2.9
3	¼" berl saddles	6.0	38.1	4.6	152.7	112.9	39.0	3.3
4	½" raschig rings	3.5	6.7	2.3	142.1	118.8	45.1	....
5	½" raschig rings	5.0	23.2	3.3	144.4	121.4	34.4	6.2
6	½" raschig rings	5.0	10.0	1.0	141.3	118.9	46.9	5.6

A small fraction of the solvent was withdrawn at the base of a short rectifying section to prevent impurities from building up on recycling. The remainder of the solvent was collected in a small holding tank, where it was checked for water content and returned to the main solvent storage. Samples of extract and raffinate were taken every hour, and the solvent to oil ratios and refractive indices of the oils were determined. When there was no change in these properties over a two-hour period, it was assumed that a steady state had been reached and samples were taken for iodine values. In all the runs the solvent to oil ratio of the extract from the column was below the extract line on the appropriate equilibrium diagram. This was attributed to a concentration of the non-glyceride components in the extract phase, particularly at the top of the column where extract oil was being returned as reflux.

The results of column operation are shown in Table I. The effect of increasing solvent to oil ratio and reflux ratio is much more marked in the first three runs than in the last three due to the larger number of stages with the smaller packing. H.E.T.S. values were computed by the graphical method outlined by Maloney and Schubert (5). This is illustrated for run number 3 in Figure 7. The points representing the feed, extract, and raffinate streams are located on the appropriate equilibrium diagram as F, E, and R, respectively. The operating point, M, for the section of the column above the feed is located on a vertical line through E and ME/EO, the reflux ratio, is 4.6. Since E is below the extract line, this reflux ratio is greater than would be predicted from the equilibrium data for the same operating point. The operating point, N, for the section of the column below the feed is located as the intersection of a vertical line through R and a line through M and F. Starting with the extract E leaving the top of the column, the raffinate in equilibrium with it, R_1, is determined from tie line data. The extract E_2 entering this stage from the stage below is found by joining R_1 to M. Returning to the extract line at E_2 is equivalent to assuming that the effect of non-glyceride constituents did not extend beyond the first stage. Although not strictly true, this appears to be a good working approximation. The raffinate for stage 2, R_2, is located from the tie line data, and this stepwise procedure is repeated until the iodine value of the feed is crossed. For the section below the feed operating point N is used in place of M, and the procedure is continued until the iodine value of the raffinate is reached. The total number of steps required is the number of theoretical stages involved, in this separation 6.0. Runs 1 and 4 were indeterminate in that the reflux ratio was so close to the minimum that a very small change in the reflux ratio resulted in a large change in the number of stages. These runs were consistent with the others however since an average H.E.T.S. value from the two following runs gave theoretical reflux ratios that were within experimental error of the measured values.

Since the H.E.T.S. values are consistent for a given packing and of the right order of magnitude for extraction work, it appears that this type of equilibrium diagram can be used to predict the variables involved in column operation. The net effect of applying these diagrams, which were necessarily determined on samples freed from non-glyceride components, to the fractionation of oils containing small amounts of such components is to predict a lower reflux ratio than is actually required without altering the solvent to oil feed ratio or number of stages involved.

Application of Equilibrium Diagrams

As an illustration of the application of these equilibrium diagrams suppose soybean oil, I.V. 130, is to be separated into two fractions having iodine values of 110 and 150. The variables to be determined are water content of the solvent, solvent to oil feed ratio, reflux ratio, and number of theoretical stages required. For a given water content there are limits between which actual operating conditions must be

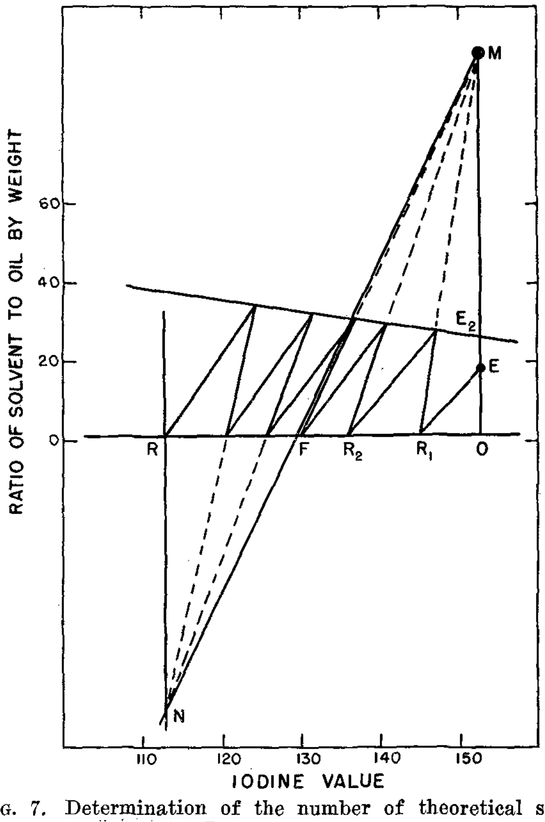

FIG. 7. Determination of the number of theoretical stages for run number 3, Table I.

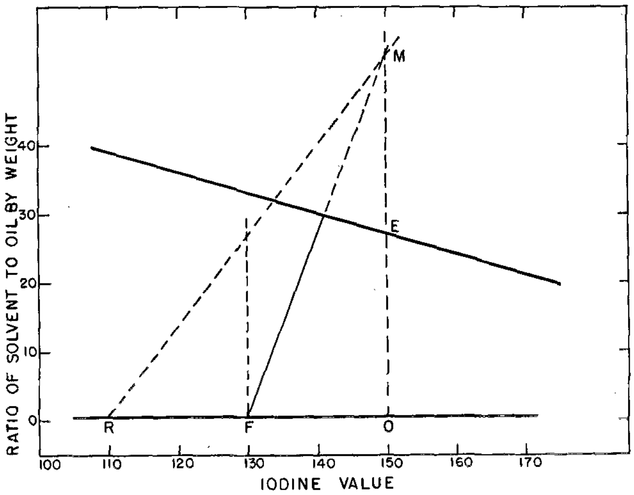

FIG. 8. Determination of minimum reflux ratio and solvent to oil ratio for hypothetical separation, using 6 parts H_2O per 100 parts acetone.

set: a) minimum reflux and solvent to oil ratio with an infinite number of stages and b) minimum number of stages with infinite reflux and solvent to oil ratio. The operating point, M, for minimum reflux, Figure 8, is located as the intersection of a vertical line through the iodine value of the extract and the tie line whose raffinate has the iodine value of the feed. The minimum reflux ratio, ME/EO, is 1.0. The minimum solvent to oil ratio, the solvent to oil ratio at which a line joining M to R crosses the iodine value of the feed, is 26:1. For the condition of minimum number of stages the operating points are at infinite distances from the iodine value axis so that lines joining raffinate points to the operating points are vertical.

TABLE II

Relation Between Water Content of Solvent and Minimum Limits for Extraction

Parts H_2O per 100 parts acetone	Min. reflux ratio	Min. solvent to oil ratio	Min. number of stages
6.0	1.0	26	3.7
5.5	1.1	21	3.8
5.0	1.2	17	4.0
4.5	1.6	14	4.2
3.5	3.2	13	6.2

Table II shows the minimum reflux ratio, solvent to oil ratio, and number of stages for various water contents of the solvent. There is a steady decrease in the minimum solvent to oil ratio required down to 4.5 parts water per 100 parts acetone with only a relatively small increase in the reflux ratio and number of stages. From 4.5 to 3.5 parts water however the small gain in decreased solvent requirement is more than offset by a sharp increase in the number of stages. The optimum water content appears therefore to be about 4.5 parts per 100 parts acetone. The effect of varying the reflux ratio on the number of stages and solvent to oil ratio required for this water content is shown in Table III. Optimum conditions here would depend on an economic balance between cost of capital equipment and cost of solvent recovery.

TABLE III

Effect of Reflux Ratio on Solvent to Oil Ratio and Number of Stages Required for 4.5 Parts Water per 100 Parts Acetone

Reflux ratio	Solvent to oil ratio	Number of stages
1.6	14	Infinite
2.0	15	9.4
3.0	20	7.0
4.0	25	5.0
Infinite	Infinite	4.2

Summary

It has been shown that useful fractionations of soyabean and linseed oils can be made, using a selective solvent consisting of 3 to 7 parts of water per 100 parts acetone. Equilibrium diagrams were determined for soybean oil, using 3.5 and 6 parts water per 100 parts acetone, and for linseed, using 5 parts water per 100 parts acetone. Operation of a packed column, 2-in. in diameter, 20 ft. high, showed that consistent H.E.T.S. values were obtained, using the above diagrams, and gave an average H.E.T.S. of 3.1 ft. for ¼-in. berl saddles and 5.9 ft. for ½-in. raschig rings.

The use of the equilibrium diagrams is illustrated by application to a hypothetical separation.

Acknowledgment

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Isomerization During Hydrogenation. I. Oleic Acid[1]

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IT HAS BEEN well established that partial hydrogenation of monounsaturated fatty acids is accompanied by the formation of several isomeric acids. Moore (9) isolated solid isomers from partially hydrogenated ethyl oleate and found that both geometrical isomerization and migration of double bonds to the 10 and 11 positions had occurred. Also Hilditch and Vidyarthi (7) found that partial hydrogenation of methyl oleate gave *trans* isomers as well as positional isomers with the double bond in the 8 and 10 posi-

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