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Boiling Point-Vapor Pressure-Composition Relations for Trichloroethylene-Cottonseed Oil Miscellas

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COLOR bodies are removed with the oil in the solvent extraction of cottonseed oil and must subsequently be removed from it in the production of an edible oil. If the miscella is heated to too high a temperature while removing the solvent, the color bodies may be "fixed" so that they cannot be removed by the usual refining and bleaching operations. It is desirable to have data on the boiling points of trichloroethylene-cottonseed oil miscellas at reduced pressures since in trichloroethylene extraction the solvent must be removed below atmospheric pressure to avoid overheating.

Harris (1) gives the distillation curves for separating and recovering solvents such as "Naphtha E" and ethylene dichloride from cottonseed oil. In the curves he compares the distillation ranges of mixtures containing 50% solvent and 50% cottonseed oil with the distillation ranges of the pure solvents at atmospheric pressure. Pollard, Vix, and Gastrock (3) reported the boiling point data at various concentrations of crude cottonseed oil and crude peanut oil over a range of pressures from 160 to 760 millimeters absolute in commercial hexane.

In the present investigation the boiling points of crude cottonseed oil-trichloroethylene miscellas of different compositions were determined. The trichloroethylene was of the commercial extraction grade having the following characteristics: boiling point at 760 mm., 188.4°F.; vapor pressure, 57.8 mm. Hg. at 68° F.; latent heat of vaporization (at boiling point), 103.0 B.t.u. per lb.; and specific gravity (liquid) at 68°/39°F. 1.464. The oil was a crude hydraulic oil.

Equipment and Procedure

A diagram of the apparatus used is shown in Figure 1. A 5-liter, 3-necked distilling flask equipped with a stainless steel stirrer operating at 250 r.p.m. served as a boiler. The shaft of the stirrer passed through a piece of glass tubing inserted in the cork stopper in the center neck of the flask. A short piece of tygon tubing was slipped over the upper end of the glass tubing with another piece of larger diameter tygon tubing over the upper end of the first piece. The space between the tygon tubing and the stirrer shaft was filled with silicone cock grease to act both as a lubricant for the shaft and as a vacuum seal. The mineral oil bath, 7, was heated by an electrical heating element inserted into the oil near the bottom. The bath was insulated with magnesia insulation. Vacuum was produced by an aspirator type of filter pump connected to the system through two ⅛-inch needle valves, 2, by means of which the pressure was controlled. A mercury manometer between flasks, 1 and 11, indicated the pressure in the system. Ice water was stored in a stainless steel container from which it was pumped to precooler, 5, and reflux condenser, 13, and then back to the container. Tygon and glass tubing were used to connect the various pieces of equipment.

In each run the composition of the miscella was kept constant while the pressure in the boiler was varied by adjusting the needle valve. Approximately 3 liters of miscella containing 10% oil by weight were fed into the boiler where it was heated from room temperature to boiling with the needle valve closed to give the lowest obtainable pressure. The miscella was stirred during heating below the boiling point. Stirring was stopped at the boiling point to prevent flooding into the condenser, 13. When the thermometer reading became constant, the temperature was recorded as the boiling temperature. During heating, ice water was circulated through the condensers to condense and return to the miscella any solvent which evaporated and thus keep the composition constant.

After the recording of the boiling point at the lowest pressure the needle valve was opened slightly to

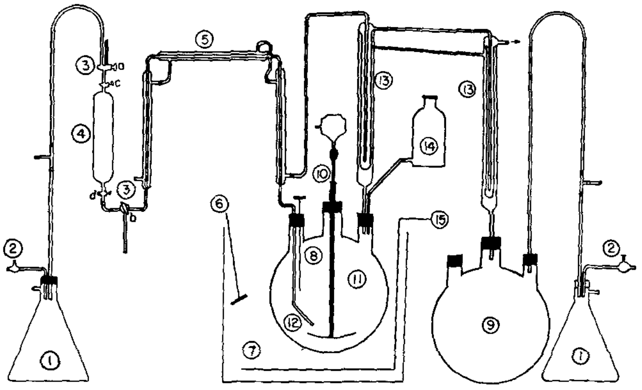

FIG. 1. Apparatus for determination of boiling point of oil-solvent mixture.

(1) 500-ml. flask; (2) ⅛-in. needle valve; (3) 3-way cock; (4) 200-ml. sampler; (5) precooler; (6) stirrer; (7) oil bath; (8) thermometer; (9) distillate receiver; (10) stirrer; (11) boiler; (12) sampling tube; (13) condenser; (14) feeding vessel; (15) heating element.

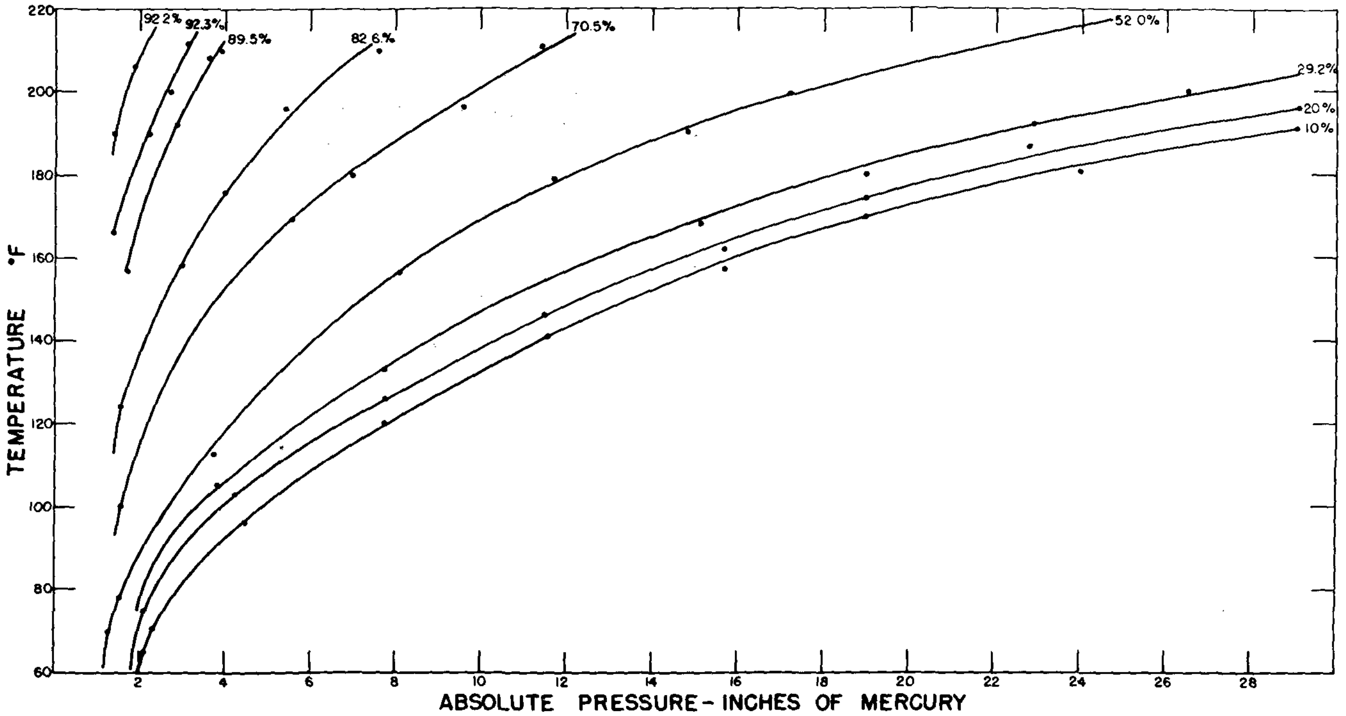

FIG. 2. Boiling point-vapor pressure curves for trichloroethylene-cottonseed oil miscellas of various constant oil compositions.

allow the pressure to rise. The boiling point corresponding to the new pressure was determined and recorded. Boiling points at a series of pressures were determined in this manner for the 10% miscella. The miscella was then allowed to cool and a sample was taken as a check on the composition. This was done by sucking it out through the sampling tube, 12, into the sampler, 4, from which it could be drained into a flask. The specific gravity of the sample was obtained by means of a Westphal balance, and the corresponding percentage of oil was determined from a specific gravity-composition curve constructed from data by Russell (4).

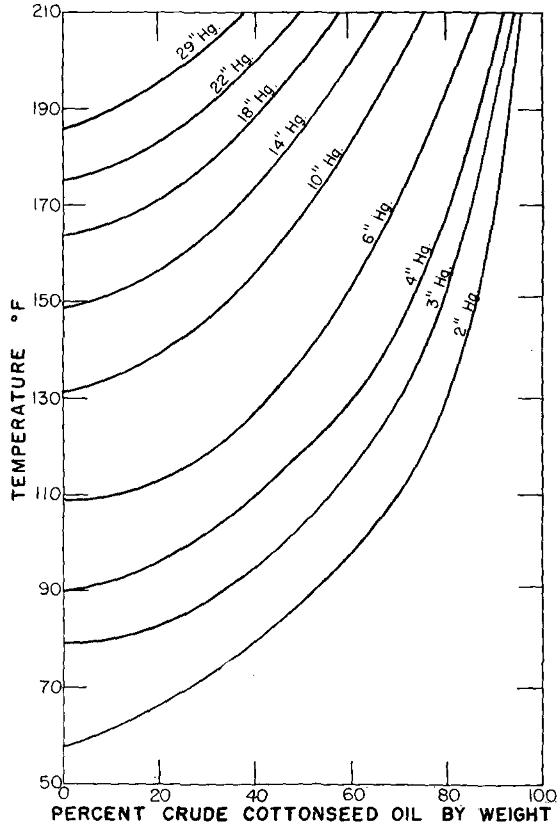

FIG. 3. Boiling point-composition curves for trichloroethylene-cottonseed oil miscellas at various constant pressures.

Sufficient oil was next added from bottle, 14, to increase the miscella oil concentration to the next desired point. The contents of the boiler were then stirred to give a uniform mixture, and a sample was withdrawn for an exact determination of the composition. The heat was then turned on and the procedure used with the 10% miscella was repeated to give the next of a series of boiling points. The oil content of the miscella was increased in this manner stepwise by the addition of oil to a concentration of 70%. Above this concentration the solvent was distilled off into flask, 9, to increase the percentage of oil without building up excessive amounts of miscella in the boiler. Since previous experience had indicated that oil from miscellas heated above 210°F. would probably be discolored, no data above this temperature were secured.

Discussion of Data

The data thus obtained for boiling points at various pressures for cottonseed oil-trichloroethylene mixtures at constant compositions are given in Figure 2. The data have been cross-plotted from Figure 2 to show the temperature-composition relation at constant pressures in Figure 3 and the pressure-composition relation at constant temperatures in Figure 4.

The data (Figure 2) indicate that as the oil content increases, the spread of boiling pressures decreases and reaches a minimum at 100% oil. Low absolute pressures are required to boil miscellas with an oil content from 90 to 100% if the temperature is kept below 210°F. At lower temperatures the spread of boiling pressures over the whole range of composition is small compared to the spread at the higher temperatures.

At a given pressure there is a small change in the boiling point for miscellas having the low oil content. However above 30% oil by weight there is a more pronounced temperature rise, and after 80% oil by weight there is a rapid rise in the boiling temperature at a given pressure for any increase in oil content. As the percentage of oil in the miscella is increased, the slope of the curves increases, gradually approaching a straight line for higher oil content miscella over the lower temperature portion. These relations are similar to those found previously in the laboratory for soybean oil-trichloroethylene miscellas (5).

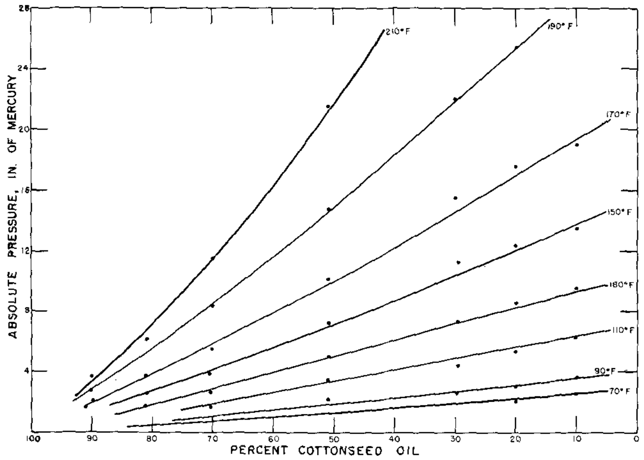

FIG. 4. Vapor pressure-composition curves for trichloroethylene-cottonseed oil miscellas at various constant temperatures.

The data obtained in this investigation were compared with values calculated from Raoult's law. No agreement between the observed and calculated values was found; the observed values in all cases were lower than the calculated values. According to Pollard, Vix, and Gastrock (3) the agreement between observed and calculated values of vapor pressure for hexane-cottonseed oil miscellas is good below approximately 50% oil. Above 50% there is appreciable deviation, which becomes increasingly great as the oil concentration approaches 100%. If we assume compound formation between the glycerides of the cottonseed oil and the trichloroethylene as postulated by Johnstone, Spoor, and Goss (2) for soybean oil and trichloroethylene, the reason for the low vapor pressure values of the cottonseed oil-trichloroethylene miscellas even below 50% oil is evident. This variation from the theoretical makes the experimental data desirable for the successful design and operation of solvent extraction plants.

Summary

The boiling points of crude cottonseed oil-trichloroethylene miscellas for pressures below atmospheric have been determined. The data indicate that the temperature-pressure relations for these miscellas differ from those of cottonseed oil-hexane miscellas in that, even below 50% oil concentrations, they are lower than those calculated by Raoult's law. Above 50% the deviation from the calculated values becomes greater.

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The Volatile Decomposition Products and the Organoleptic Characteristics of the Oxidative Polymers of Ethyl Linoleate[1]

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STUDIES (1, 2, 3) involving the volatile decomposition products formed by successive heat reversion and deodorization of soybean oil have led to the identification of a number of carbonyl compounds which have been suspected of contributing to the reversion flavor and odor. Similar results were obtained when soybean oil or methyl linolenate was autoxidized at room temperature (4, 5). In both cases acetaldehyde, propionaldehyde, and 2-pentenal were identified in the volatile decomposition products. However hexanal was found in the volatile decomposition products obtained from soybean oil but not methyl linolenate. Since hexanal was also found in the volatile decomposition products obtained from cottonseed oil which had been autoxidized at 70°C. (6), hexanal may be a degradation product of linoleic acid.

On the other hand, Sims (7) could find no correlation between flavor stability and polyunsaturation. Soybean oil hydrogenated so as to free it of linolenic and linoleic acid still reverted. Furthermore Mattil (8) chromatographed soybean oil and hydrogenated soybean oil and found no reduction in linolenic and linoleic acid content although the flavor stability of soybean oil was slightly improved and that of hydrogenated soybean oil was markedly improved. These

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[2] Portion of a thesis presented by S. S. Chang as partial fulfillment of the requirements for the degree of Doctor of Philosophy in Food Technology. Presented at the American Oil Chemists' Society meeting, Cincinnati, O., Oct. 21, 1952.