Thermal Conductivity of a Vegetable Oil-in-Water Emulsion

J. E. NOWREY[1] and E. E. WOODAMS[2]
Department of Dairy and Food Science, New York State College of Agriculture, Cornell University, Ithaca, N.Y.

KARLA LONGRÉE
New York State College of Home Economics, Cornell University, Ithaca, N.Y.

A parallel-plate type of apparatus for measuring thermal conductivities of liquids is described. The results of a study of the thermal conductivity of a vegetable oil-in-water emulsion are presented and compared with values predicted for such a system by several theoretical equations.

THERMAL CONDUCTIVITY values of fluid substances are needed for the intelligent design and operation of many types of processing equipment. These values cannot be obtained readily by experiment, because there is at present no commercially available "thermal conductivity meter" suitable for fluid materials. Although details of construction of thermal conductivity measuring apparatus can be found, the construction of such apparatus requires considerable shop time, careful workmanship, and precise electrical components if values with uncertainties of 5% or less are desired.

One can often find thermal conductivity values in handbooks or in published listings (*9*) for the elements, low molecular weight chemical compounds, and simple solution systems.

Semitheoretical and empirical methods for predicting thermal conductivity for relatively simple systems are also available (*2*).

For the more complex systems such as colloidal, biological, and food materials, few data are available and methods for predicting values for engineering purposes are still in a developmental state.

As part of an investigation in which thermal properties of fluid foodstuffs are required, a thermal conductivity measuring apparatus has been constructed. In addition to its use for specific materials, measurements on simplified model systems are being made in order to contribute to the establishment of generalized prediction methods.

EQUATIONS FOR CONDUCTIVITY OF TWO-PHASE MIXTURES

The thermal conductivity of two-phase mixtures has been the subject of many investigations. Although no generally satisfactory prediction method has been achieved, several methods have been developed which adequately characterize certain systems. The more rational are equations derived by postulating a geometric model and solving for the analogous electrical conductivity. Both circuit analysis and field theory have been used (*1, 4, 5, 7, 11, 12, 13*).

EXPERIMENTAL APPARATUS

Methods for measuring liquid thermal conductivities have been reviewed recently (*10*). The parallel plate apparatus was selected, since it appeared to offer the best balance between construction investment and utility for the anticipated studies.

A sketch of the chamber and cooling bath is presented as Figure 1. The sample chamber consisted of two copper disks separated by a Lucite ring. The disks were cut from ½-inch half-hard copper sheet, ASTM Specification B-152 Type ETP-Revere Alloy 100 (Ontario Metal Supply, Liverpool, N. Y.). Before cutting, a 0.003- to 0.005-inch thickness of nickel was plated to the surface at a local electroplating plant, to inhibit corrosion and to create a mirror finish on the disk surfaces in contact with the sample. Shoulders machined inside the Lucite ring held the copper disks apart. The disks and ring assemblage provided a sample chamber 0.265 inch thick and 3.750 inches in diameter.

A ⅛-inch hole was drilled through the Lucite ring and a short nipple of ⅛-inch i.d. plastic tube was cemented over it on the outer surface, to provide an overflow port to aid in filling the sample chamber. This was done by simply removing the top disk, which rested under its own weight on the shoulders machined in the Lucite ring. An excess of the fluid sample was charged and the top disk

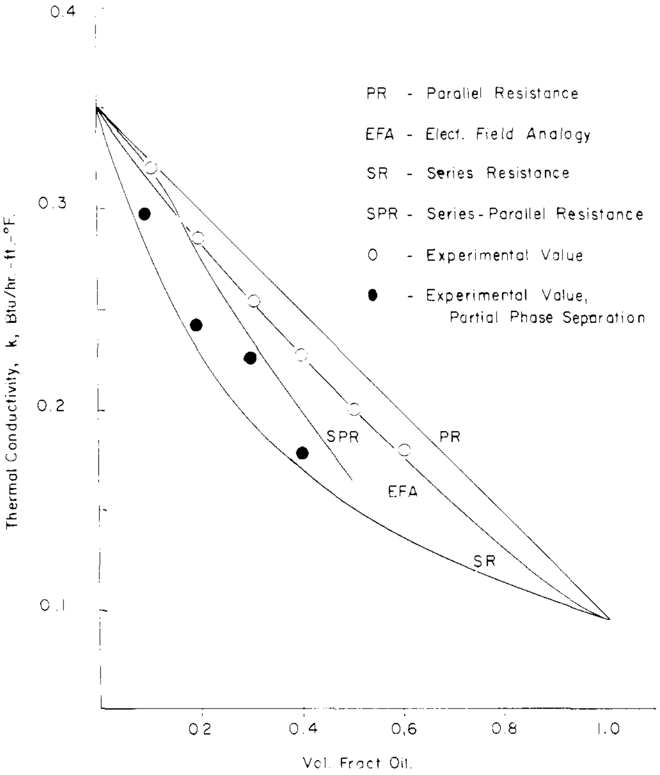

Figure 1. Sample chamber and water bath

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[1] Present address: Center for Naval Analyses, 1401 Wilson Blvd., Arlington, Va.

[2] Present address: New York State Agricultural Experiment Station, Geneva, N. Y.

pressed into place with due care to avoid air entrapment. Because of the very close clearance between the disk and ring, the excess fluid was forced through the overflow port. A short piece of flexible tubing attached to the overflow port nipple was used to prevent drainage from the chamber.

The bottom disk extended into a cold water bath constructed from ¼-inch Lucite sheet. Water was circulated through this bath from a 5-gallon refrigerated constant temperature bath. The bottom disk was secured to the bath and to the Lucite ring with epoxy cement.

A heating coil formed from a 6-foot length of 24-gage Chromel-Alumel thermocouple wire (Trinox TR-519, Pall Trinity Micro Corp., Cortland, N.Y.) was used to heat the top disk. This wire was encased in a ¼-inch 304 stainless sheath and fastened to the upper surface of the disk with plastic aluminum cement. The coil was connected in a simple series circuit to a 12-volt storage battery and variable resistors (two 1-ohm and one 200-ohm, 25-watt potentiometers). A d.c. voltmeter and a d.c. ammeter (both Weston Model No. 931) were appropriately connected in the circuit to measure energy input to the coil. The meters were calibrated using a Leeds & Northrup K-3 potentiometer.

This parallel plate apparatus was placed in the center of a volume of insulation with over-all dimensions of approximately 34 × 32 × 23 inches (Figure 2). For convenience in dismantling, the insulation was constructed in several rigid sections consisting of glass fiber or vermiculite encased within 1-inch sheets of expanded polystyrene.

Just above the heating coil the strata of insulating sections were interrupted by a ¼-inch thickness of Masonite. This supported a 1/32-inch aluminum sheet to which was attached an auxiliary heating coil, formed from a 30-foot length of type TWS-19 high temperature Thermwire (E. L. Wiegand Co., Pittsburgh, Pa.). This coil was used to provide an adiabatic shield to minimize vertical heat losses. It was connected to the 120-volt a.c. laboratory supply line through a variable transformer. A 3-ampere ammeter was used to indicate the power setting.

A total of 20 thermocouples were located in the apparatus and surrounding insulation (Figures 1 and 2). These were all 30-gage copper-constantan Leeds & Northrup type T with enamel, double glass wrap impregnated with a heat- and moisture-resistant compound. Beaded junctions were made by electric fusion in a carbon arc and then coated with General Electric Black Spirit varnish No. 271 for a distance of 6 inches from the junction. All thermocouples were calibrated against a standard thermocouple at 8°, 30°, 40°, and 80° C. using a Leeds & Northrup Model 8686 potentiometer. Quadratic temperature-voltage relations were developed for each.

Eight thermocouples (four on each copper disk) were used to measure the temperature gradient across the sample. These were extended through No. 52 holes drilled through the disks and secured to the inner faces with epoxy cement. Thermocouple locations were made by considering each disk to be divided into four equal areas, a central circle and three concentric annuli. One thermocouple was then located at the center of the circle and the other three were located at points midway between the inner and outer circumferences of each annulus.

The remaining 12 thermocouples were used for measuring temperatures needed in computations to account for various heat losses.

Thermocouple measurements were made with a Leeds & Northrup Millivolt potentiometer (Catalog No. 8686), using an ice-water reference junction, both phases from double-distilled water. Thermocouples and potentiometer were interconnected through a 24-point selector switch housed in an insulated box.

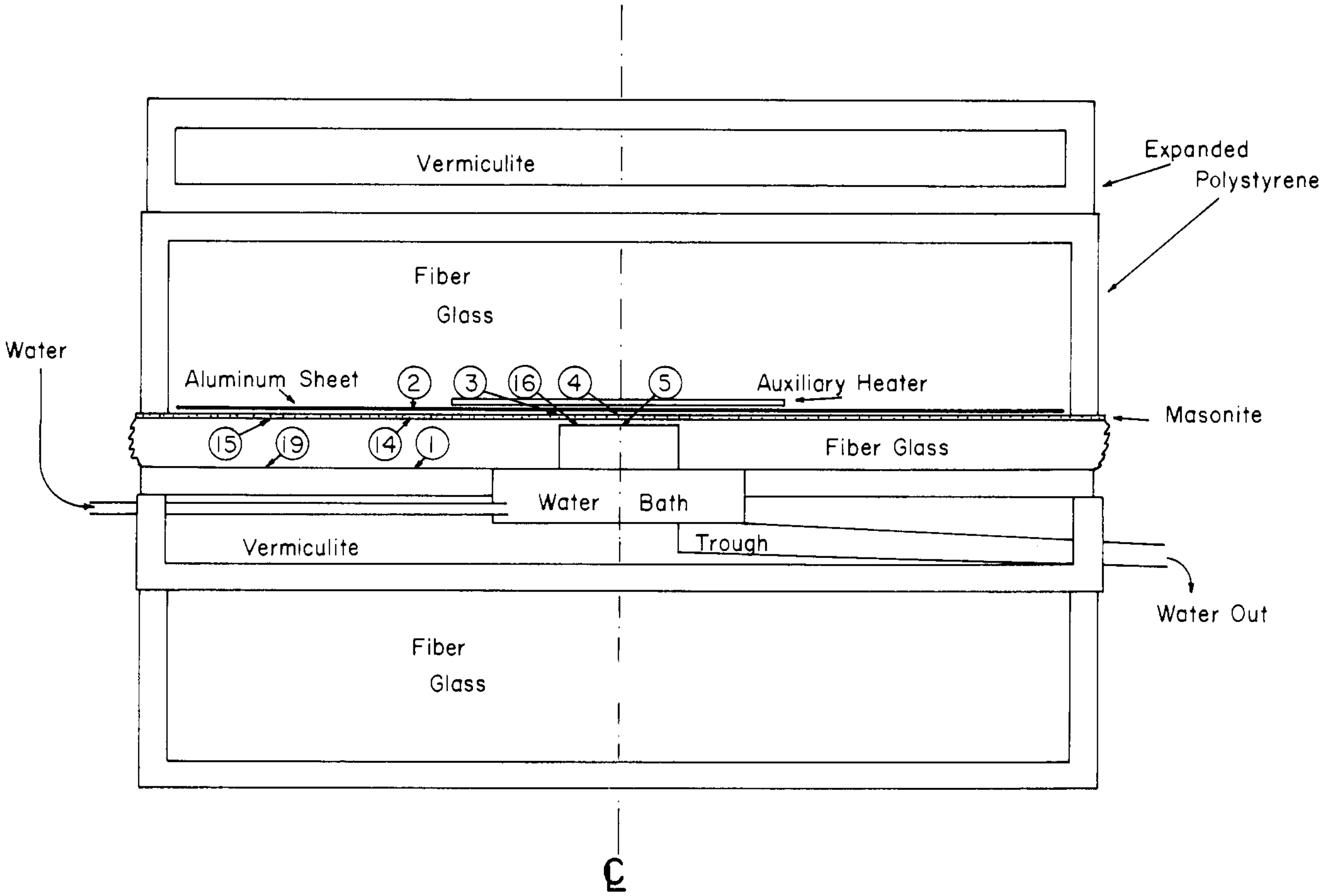

Figure 2. Insulation housing

INSTRUMENT CALIBRATION

Thermal conductivities were calculated from the steady-state equation for one-dimensional heat conduction,

$$Q/A = k\Delta t/L \tag{1}$$

Using the British system of units, Q was evaluated by

$$Q = 3.412\ EI \text{ B.t.u./hr.} \tag{1a}$$

Numerical values for A (0.0766 sq. foot) and L (0.0221 foot) were calculated from the sample chamber dimensions, and Δt was evaluated from the arithmetic average temperatures of upper and lower disk faces.

Corrections for the following losses were made:

Q_1. **External Resistance in Heating Coil Circuit.** This was evaluated by

$$Q_1 = 3.412\ I^2R \text{ B.t.u./hr.} \tag{2}$$

where R was the resistance of 80 inches of AWG No. 16 copper wire plus a 1¾-inch length of the heating coil projecting beyond the heating disk (a total of 0.244 ohm).

Q_2. **Radial Heat Loss from Sample Chamber.** The sample chamber was insulated radially with glass fiber. From the data of Kreith (*6*), an equation for thermal conductivity of packed glass insulation was derived by the method of least squares,

$$k_I = 0.0000722t + 0.0147 \text{ B.t.u./hr.-ft.-}^\circ\text{F.},\ 20 < t < 200^\circ \text{F.} \tag{3}$$

The radial heat loss was then estimated by calculating the heat flow perpendicular to the axis of two concentric cylinders from the inner radius, r_i, the distance of thermocouples 1 and 14 from the center line of the apparatus, to the outer radius, r_o, the corresponding distance of thermocouples 15 and 19. Thus, using Fourier's equation for cylinders,

$$Q_2 = \frac{2\ k_I L\Delta t}{\ln r_o/r_i} \text{ B.t.u./hr.} \tag{4}$$

using the arithmetic average of temperatures t_1, t_{14}, t_{15}, and t_{19} to evaluate k_I from Equation 3, the arithmetic average of $t_1 - t_{19}$ and $t_{14} - t_{15}$ for Δt, and for L, the height of the cylindrical volume, the measured thickness of the glass fiber blanket (1¼ inches).

Q_3. **Vertical Heat Exchange between Hot Disk and Auxiliary Heating Coil.** This can be either a loss or a gain. Equation 1 was used with k calculated for a series-composite of ¼-inch Masonite plus ¼-inch air gap (0.075 B.t.u./hr.-ft.-° F.), Δt an average established from thermocouple readings t_5, t_{16}, t_4, and t_3, and A as the upper surface area of the heating disk (0.0766 sq. foot).

Q_4. **Heat Loss by Conduction through Thermocouple Leads.** For the six thermocouples in or adjacent to the hot disk this was expressed as:

$$Q_4 = \frac{6\ (k_{\text{Cu}} + k_{\text{Con}})\ \Delta t A}{L} \text{ B.t.u./hr.} \tag{5}$$

with values for the thermal conductivity of copper (k_{Cu}) and constantan (k_{Con}) of 221 and 12.6 B.t.u./hr.-ft.-° F., respectively. The value of A, the cross-sectional area of the thermocouple wire, was computed to be 5.45×10^{-7} sq. foot, and the value of L, the length of each thermocouple, was 3 feet. The average temperature difference, Δt, was taken as the difference between room temperature and the arithmetic average values indicated by the six thermocouples.

Q_5. **Thermoelectric Heating in Heating Coil.** The heating coil was formed from a commercial thermocouple. This was simply a laboratory expedient; it was available and had suitable dimensions and electrical resistance. The fact that heat would be generated at the Chromel-Alumel junction was initially overlooked and hence a correction was applied for the thermoelectric effect.

$$Q_5 = 3.412\ IT\alpha \text{ B.t.u./hr.} \tag{6}$$

where T, the absolute temperature at the Chromel-Alumel junction, was approximated by $t_5 + 460^\circ$ R., and the thermoelectric power, α, was taken as 2.2×10^{-5} volt per ° R.

Q_6. **Heat Bypassing Sample through Lucite Ring.** This was calculated from Equation 1 using k – Lucite = 0.12 B.t.u./hr.-ft.-° F., the same Δt and L values as for the sample, and A based on the annular area of the ring at maximum thickness ($A = 0.0133$ sq. foot).

To facilitate the numerous potentiometer reading conversions and correction calculations, a Fortran computer program was prepared and the data were processed on a digital computer (*14*).

TEST SYSTEMS

Water, emulsifier (Calimulse DM, Pilot Chemical Co., Los Angeles, Calif.), and peanut oil (Penola Brand, F. Simonins Sons, Inc., Philadelphia, Pa.) were weighed into a Waring Blendor in the order given to ensure an oil-in-water emulsion. The emulsifying agent (a liquid concentrate of an amine-sulfonate) in all cases was 1% of the total mixture volume. In some cases thickening was required for increased emulsion stability. For these, a liquefied 4% agar solution was added to the water-emulsifier solution to give an agar concentration of 0.4 weight %. After a minute or so of mixing, depending on the degree of dispersion desired, the mixture was charged to a laboratory homogenizer (designed for National Dairy Producers Corp., 801 Waukegan Road, Glenview, Ill.). As with the commercial dairy homogenizer, particle size reduction was achieved by forcing the mixture through a narrow annular gap between a valve seat and a spring-loaded valve stem. Spring tension could be adjusted to give some control of particle size.

Before charging to the conductivity sample chamber, the emulsions were deaerated by holding under vacuum for 10 to 15 minutes.

Average drop diameters were measured from photomicrographs of samples taken before and after each thermal conductivity determination. A drop of diluted emulsion was suspended from a coverslip over the depression of a hanging drop microscope slide. After allowing at least 20 minutes for the drops to migrate to the coverslip surface, several fields were photographed and at least 400 drops were measured. A Polaroid Land camera was used and with type 37, ASA 3000 Polaroid film no blurring due to particle motion during exposure was observed. Magnification of 100× was used for all but the coarsest emulsions, for which 45× was more appropriate. Photomicrographs of a stage micrometer at the same magnification were used to convert magnified image diameters to actual dimensions.

DISCUSSION

Evaluation of Apparatus. The capabilities of the apparatus can be judged by consideration of the data presented in Table I. For sample temperatures (arithmetic average temperature of hot and cold disks) within a few degrees of room temperature and disk temperature differences of 5° F., steady state was attained within an hour; subsequent data sets at 30-minute intervals yielded values seldom varying more than one or two digits in the third place. Under such conditions the values were usually within 2% of accepted published values. At higher sample temperatures or temperature differences, attainment of steady-state conditions required several hours. The deviations between

Table I. Observed and Reported Thermal Conductivities

Fluid	Temp., ° F.	Δt, ° F.	*k*, B.t.u./Hr.-Ft.-° F. Obsd.	*k*, B.t.u./Hr.-Ft.-° F. Lit.	% Diff.	Ref.
Water	75.1	5.5	0.348	0.350	−0.6	(*8*)
	93.0	9.2	0.370	0.359	3.1	(*8*)
	101.1	1.2	0.349	0.362	−3.6	(*8*)
	102.9	4.5	0.363	0.363	0.0	(*8*)
	117.2	9.0	0.385	0.368	4.6	(*8*)
	144.1	8.4	0.403	0.378	6.5	(*8*)
99% aq. glyc.	106.5	8.4	0.159	0.167	−4.9	(*3*)
80% aq. glyc.	105.6	9.8	0.194	0.195	−0.5	(*9*)
Olive oil	101.5	20.1	0.097	0.096	1.0	(*15*)
	124.4	9.5	0.094	0.096	−2.1	(*15*)

Table II. Thermal Conductivity of Peanut Oil-in-Water Emulsions

Vol. % Oil	Temp., ° F.	Av. Drop Diam., Microns Init.	Av. Drop Diam., Microns Final	*k*, B.t.u./Hr.-Ft.-° F.
10.5	75.5	2.2	2.1	0.320
19.6	75.3	2.2	2.1	0.285
30.3	75.5	2.2	2.1	0.254
39.8	75.5	2.0	2.0	0.227
50.3	75.6	2.1	2.0	0.200
60.2	75.4	2.2	2.1	0.180
100.0	75.9	...	...	0.097

Table III. Thermal Conductivity of Emulsions with Partial Phase Separation (Creaming)

Vol. % Oil	Temp., ° F.	Av. Drop Diam., Microns Init.	Av. Drop Diam., Microns Final	*k*, B.t.u./Hr.-Ft.-° F.
9.3	75.2	2.3	2.2	0.297
19.1	75.8	2.5	2.5	0.242
29.0	75.7	2.3	2.4	0.226
38.9	76.2	2.4	2.3	0.178

observed and reported water conductivities at the two highest sample temperatures in Table I are believed to be due, partly at least, to not yet having reached steady state. Tests with temperature differences in the order of 1° F. or less gave values with increased uncertainty owing to the limitations of the electrical instruments used.

A modification in the design of the apparatus is recommended to ensure the absence of air pockets in tests with very viscous fluids, pastes, etc. These materials would not extrude through the overflow port when the upper disk was pressed into place and hence a sample volume exactly equivalent to the sample chamber volume was required. With the equipment design presented here this could be assured only by agreement of several replicate determinations.

Emulsion Conductivities. In Figure 3, the experimental points for both the stable emulsions (Table II) and those in which partial phase separation was observed (Table III) are superimposed on a grid showing values predicted by the various equations. The electric field analogy (*1*, *11*) gives values in excellent agreement with the experimental values for the stable emulsions. [The more rigorous forms of the electrical field analogy (*5*) give essentially the same value for this system.] The effect of partial phase separation is to shift the conductivity toward values predicted by the series resistance model (*13*), which one would expect to be the appropriate model for a system of separated phases.

As expressed by Jefferson and coworkers (*5*), the series-resistance, parallel-resistance, and electric field analogy equations work rather well for many systems in which the conductivities are of the same order of magnitude, but often do not when the conductivity ratio is in the range of 1000 to 1. Since their series-parallel resistance model was developed to give better agreement with values for high conductivity ratio mixtures, the fact that it is a poor model for this system in which the conductivity ratio is only 3.6 to 1 is perhaps not unexpected.

The results of the attempt to establish the effect of particle size were inconclusive. There was a suggestion of a trend to higher conductivities for the coarser dispersions. An argument can be made for the parallel-resistance model as being the limiting case for a mixture in which the dispersed phase consists of a few very large globules. On this basis one might expect increased conductivity for coarser emulsions. A test of this, however, must await a more refined experiment.

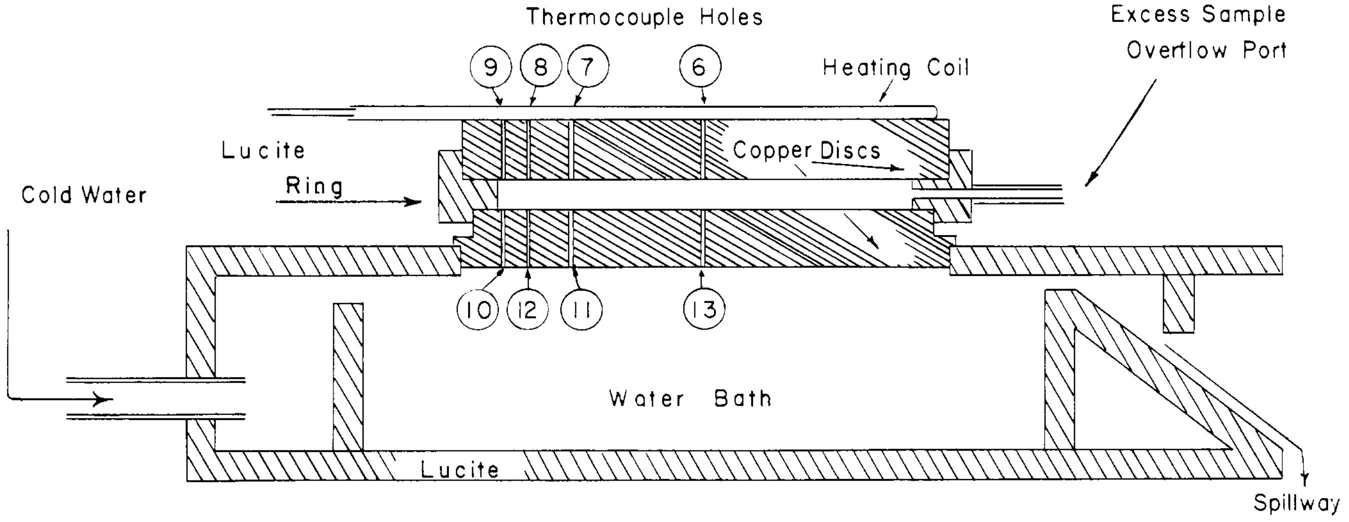

Figure 3. Experimental and calculated thermal conductivities for peanut oil-in-water emulsions

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NOMENCLATURE

A = area for heat transfer perpendicular to direction of heat flow, sq. ft.
E = voltage, volts
I = current, amperes
k = thermal conductivity, B.t.u./hr.-ft.-° F.
L = linear dimension, ft.
Q = heat flow rate, B.t.u./hr.
R = electrical resistance, ohms
r = radius, ft.
t = temperature, ° F.
T = absolute temperature, ° R.

Greek Letters

α = thermoelectric power, volts/° R.
Δ = increment or difference
Σ = summation

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Vapor-Liquid Equilibrium in the *n*-Octane–*p*-Cresol System

Z. L. TAYLOR, Jr., and R. E. WINGARD
Department of Chemical Engineering, Auburn University, Auburn, Ala. 36830

Isobaric vapor liquid equilibrium has been measured for the system *n*-octane–*p*-cresol at 760 mm. of Hg pressure. The measurements were made using a Jones type equilibrium still. Liquid phase activity coefficients are calculated, and the data are thermodynamically consistent.

THE possibility of using *p*-cresol as a selective solvent in separation of close boiling hydrocarbons has led to an investigation of vapor-liquid equilibrium of binary systems of *p*-cresol with several hydrocarbons (7). In the present work, isobaric vapor-liquid equilibrium has been measured for the system *n*-octane-*p*-cresol.

APPARATUS

The equilibrium still used to obtain the vapor-liquid equilibrium data was the same as that reported by Jones, Schoenborn, and Colburn (5) except that a small heating coil of three turns of 20-gage nichrome wire was wound around the condensate chamber to provide convective heating currents. This ensured adequate mixing of the condensing vapor and the condensate in the condensate chamber. The temperature was measured with a temperature potentiometer using a copper-constantan thermocouple. This temperature could be read within an accuracy of ±0.2° C. Barometric pressure was recorded for each determination. An absolute pressure of 760 ± 1.0 mm. of Hg was maintained by venting dry nitrogen through a Cartesian manostat and balancing the difference between atmospheric pressure and 760 mm. of Hg on the system.

A Bausch and Lomb Precision Refractometer was used to determine the refractive indices of the still samples. Sodium (589) D illumination was used. A constant temperature bath was used to maintain the refractometer prisms at 20° ± 0.1° C.

MATERIALS

A commercially available 99.9% *n*-octane was used. Chromatographic analysis of the *n*-octane was carried out on a 6-foot column of silicone 550 at 100° C. The analysis indicated three trace impurities of concentrations less than 0.005 mole %. No further purification of the *n*-octane was attempted. The physical properties of the *n*-octane are given in Table I.

The *p*-cresol was commercial practical grade, which was dried over calcium chloride and then distilled three times through a 36-inch Vigreaux fractionating column. After each distillation only the middle cut was retained. To ensure agitation in the boiling flask and prevent oxidation of the *p*-cresol, dry nitrogen was introduced through a capillary tube into the boiling liquid during each distillation. Freezing curves for the *p*-cresol gave a melting point range of 20°