3. Conductivities of boric acid solutions of *meso* and *levo* isomers have been measured, and the freezing points, boiling points, and liquid-vapor equilibrium data of aqueous solutions have been obtained.

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[CONTRIBUTION FROM SUN OIL COMPANY, EXPERIMENTAL DIVISION, NORWOOD, PA.]

Freezing Points and Polymorphism of the Eight C_9H_{12} Alkylbenzenes[1]

BY ALFRED E. HIRSCHLER AND W. B. M. FAULCONER

All of the eight isomeric C_9H_{12} alkylbenzenes have been prepared in this Laboratory; freezing points, purities, densities and refractive indices were determined in each case. Two freezing points were observed for four hydrocarbons, namely, pseudocumene, 1,2- and 1,3-methylethyl benzenes, and *n*-propylbenzene; while mesitylene was found to exhibit three, two of which were previously reported.[2]

In each case, the freezing point of the pure hydrocarbon was calculated. The values obtained agree well with those in a recent compilation by F. D. Rossini and associates at the National Bureau of Standards.[3]

Two additional freezing points have been calculated for hemimellitene, although they have not as yet been observed.

Experimental

Apparatus and Procedure.—The apparatus and procedure were in general similar to those described by Mair, Glasgow and Rossini.[4] For most of this work, the freezing cell was of such size that 27 ml. of hydrocarbon filled it to a depth of about 11 cm. In every case, that amount of hydrocarbon which would occupy 27 ml. at the freezing point was weighed into the cell. The temperature coefficients of density given by Lipkin and Kurtz[5] were used in calculating the desired weight of hydrocarbon. The stirrer consisted of a coil of nichrome wire.

In several cases (1,2- and 1,3-methylethylbenzenes) a larger freezing cell, containing 53 ml. at the freezing point, was also used. The freezing tube was a duplicate of that described by Glasgow, Streiff and Rossini.[6] The stirrer was the same as that described[6] except that the four $^1/_8''$ holes in each of the circular fins of the stirrer were absent.

Temperatures were measured by means of a 5-junction copper-constantan thermocouple which had been calibrated by the National Bureau of Standards to ±0.05°. The calibration was checked at the freezing point of mercury, and the sublimation temperature of carbon dioxide, and also by the determination of the freezing points of lots of *n*-heptane and 2,2,4-trimethylpentane whose freezing points were certified by the Bureau of Standards. A Leeds and Northrup Type K-2 Potentiometer was employed to measure the thermocouple e. m. f. The sensitivity was such that a 1-mm. scale deflection of the galvanometer corresponded to 0.003 to 0.006° over the range −40 to −100°. The cold junction was immersed in a stirred ice-bath; the ice used was prepared from distilled water.

The hydrocarbons were prepared in this Laboratory.[7] Densities were obtained by the use of Sun Oil Company Precision pycnometers,[8] and refractive indices by means of a Valentine Abbe refractometer.

Except in the case of mesitylene, the time–temperature freezing curves proved to be unsatisfactory for the determination of the freezing point and purity. Time–temperature melting curves were therefore employed. The procedure was as follows: The hydrocarbon was cooled by a bath of liquid nitrogen until enough of the sample was frozen so that the stirrer showed signs of laboring; whereupon the nitrogen was replaced with a constant-temperature warming bath such that the warming head of temperature was 25–50°. Crushed ice, a mush of carbon tetrachloride, or chloroform, or a mush of solid carbon dioxide in 50–50 carbon tetrachloride–chloroform provide suitable temperatures for this purpose. Frequent readings of time and temperature were taken until a temperature of about 10° above the freezing point was reached.

Due to the changing temperature head, the warming curve of the liquid is not a straight line. To find the slope of the warming curve at the melting point, the slope was measured at three or more points beginning somewhat above the point at which the last trace of solid disappears (indicated by an inflection in the warming curve). These time–temperature slopes were plotted against temperature and extrapolated to the melting point.

A complete time–temperature freezing curve was then obtained. The total time of freezing was calculated, correcting for change in temperature head and energy of stirring as described by Mair, Glasgow and Rossini.[4] The slope of the time–temperature cooling curve of the liquid at the freezing point was measured. The complete time of melting was calculated by multiplying the corrected time of freezing by the ratio of the slopes (absolute value) of the time–temperature cooling and the time–temperature melting curves. This value was used to estimate the fraction of solid phase at any point of the melting curve in a manner similar to that described by Mair, *et al.*,[4] for time–temperature freezing curves.

Test for Thermodynamic Equilibrium.—For the purpose of measurement of freezing points or purities, it is most important to know what portion of the time–temperature freezing or melting curve represents thermodynamic equilibrium between solid and liquid phases. Taylor and Rossini[9] have proposed a graphical method which indicates what portion of a given freezing or melting curve has the hyperbolic form which it should have if the liquid and solid phases are in thermodynamic equilibrium, and the rate of crystallization or melting is constant. According to

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[1] Paper presented before Philadelphia Section "Meeting in Miniature," June 13, 1945, and before the American Chemical Society Petroleum Division "Meeting in Print," Sept., 1945.

[2] Mair and Schicktanz, *J. Research Natl. Bur. Standards*, **11**, 665 (1933).

[3] Private communication with F. D. Rossini.

[4] Mair, Glasgow and Rossini, *ibid.*, **26**, 591 (1941).

[5] Lipkin and Kurtz, *Ind. Eng. Chem.*, *Anal. Ed.*, **13**, 291 (1941).

[6] Glasgow, Streiff and Rossini, *J. Research Natl. Bur. Standards*, **35**, in press (1945).

[7] Unpublished work of H. L. Johnson and R. A. Clark.

[8] Lipkin, Davison, Harvey and Kurtz, *Ind. Eng. Chem.*, *Anal. Ed.*, **16**, 55 (1944).

[9] Taylor and Rossini, *J. Research Natl. Bur. Standards*, **32**, 197 (1944).

this method of plotting, a straight line is obtained over that portion which represents equilibrium.

Extrapolation of the linear portion of a Taylor–Rossini plot to the initial time of freezing or the final time of melting provides an accurate means of extrapolating a time–temperature curve to obtain the freezing or melting point; the freezing points given in Table I were obtained by the use of this procedure.

A linear Taylor–Rossini plot does not necessarily indicate that equilibrium has been attained during a given experiment, since any portion of a time temperature curve which is hyperbolic in form will result in a straight line when plotted according to this method. (This, of course, was recognized by Taylor and Rossini.[9]) The possibility that a hyperbolic time–temperature curve will be the result of other factors than the existence of thermodynamic equilibrium must therefore be considered. That such a possibility is not a remote one, is indicated by the fact that we have encountered three instances (*i. e.*, isoöctane, 1-methyl-4-ethylbenzene and pseudocumene) in which the linear portion of a Taylor–Rossini plot was found not to represent thermodynamic equilibrium. In the case of isoöctane this was discovered because the sample was one of known purity (97%) whereas the calculated value was almost 98%. Both the freezing and melting curves for 1-methyl-4-ethylbenzene gave linear Taylor–Rossini plots; however, when the linear section of each plot was extrapolated to obtain respectively the freezing and melting points, it was found that the values obtained differed by 0.08°. This was taken as evidence that one of the curves, in this case the freezing curve, did not represent thermodynamic equilibrium.

The following very simple procedure has proved of value in the detection of cases of false or apparent equilibrium such as described above, and is recommended as a useful test for equilibrium. Three (or more, if desired) points are selected near the beginning, middle and end of that portion of the time–temperature curve which is thought to represent equilibrium; and the purity is calculated from the data at each point. If the several purity figures agree within their respective uncertainties, this fact provides additional (though not conclusive) evidence that substantial equilibrium was attained; on the other hand, should there be considerable disagreement, the time–temperature curve in question is unsuitable for the calculation of purity.

Any time–temperature curve which leads to the same calculated purity at a series of points chosen as above will result in a linear Taylor–Rossini plot over the same portion of the curve. The converse is not true, however; only those linear Taylor–Rossini plots which, when extrapolated, pass through the point $(Z - Zm)/(T - Tm) = 0$ (the terminology is that of Taylor and Rossini[9]) at the time corresponding to 100% crystallization will be found to result in the same calculated purity at all points of the curve.

As an example of the application of this method, over the portion of a time–temperature melting curve for pseudocumene which gave a linear Taylor–Rossini plot, the following series of percentage purity values was calculated: 97.6, 97.8, 98.07 and 98.12; the corresponding fractions crystallized were 0.16, 0.135, 0.116 and 0.10.

It should be noted that lack of agreement in the purities calculated at several different points on a time–temperature freezing or melting curve does not necessarily indicate the non-attainment of equilibrium. Other factors which may be responsible are: (1) formation of solid solutions, (2) substantial deviations from Raoult's law, or (3) the rate of crystallization or melting varying with time. If the sample for purity determination has been purified by a well considered procedure, impurities which could give rise to (1) or (2) will in most cases have been eliminated (at least in hydrocarbon systems of low molecular weight); proper selection of the experimental conditions will substantially eliminate (3). Regardless of the cause, however, a time–temperature curve is not suitable for the calculation of purity if there is a lack of agreement in purities calculated at several different points along that portion which is most likely to represent thermodynamic equilibrium.

It is possible that, in the absence of thermodynamic equilibrium, the proper combination of experimental conditions will result in a time–temperature curve which will give the same calculated purity at a series of different fractions crystallized. As a matter of routine, purities calculated from freezing experiments should be checked wherever possible by values obtained from melting experiments. Such a comparison is probably the surest method for the detection of a false equilibrium.

Experimental Results.—In Table I the observed freezing point, estimated purity and the freezing point calculated for the pure hydrocarbon are given for each hydrocarbon. For comparison, freezing point data taken from the literature are included. The various crystalline modifications are designated by Roman numerals in order of their freezing points, starting with the form of highest freezing point, which is the stable form (see discussion). Densities and refractive indices are given in Table II.

For the three trimethylbenzenes, the heats of fusion used for the calculation of purity were taken from Rossini[10]; in all other cases the heat of fusion was estimated from a freezing experiment as described by Mair, Glasgow and Rossini.[4] The uncertainty attached to these latter heat of fusion values is probably around ±15%.

The uncertainty in the heat of fusion introduces an equal percentage uncertainty into the cal-

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(10) Rossini, *J. Research Natl. Bur. Standards*, **11**, 553 (1933).

TABLE I

FREEZING POINTS AND PURITIES OF THE C_9H_{12} ALKYLBENZENES

Hydrocarbon	Cryst. form	F. p. obs., °C.	Purity, mole %	F. p. pure calcd., °C.	F. p. lit., °C.
n-Propylbenzene	I	−99.75	99 ± 0.3	−99.46	−100.1[11]
	II	−101.81		−101.51	......
Isopropylbenzene	I	−96.68	98.2 ± 0.3	−95.97	−96.1[12]
1-Methyl-2-ethylbenzene	I	−81.15	99 ± 0.3	−80.85	......
	II	−86.97[a]	98.4 ± 0.3	−86.50	−88.1[13]
1-Methyl-3-ethylbenzene	I	−95.81	99.2 ± 0.3	−95.63	......
	II	−97.27		−97.08	......
1-Methyl-4-ethylbenzene	I	−62.60	99 ± 0.3	−62.37	−63.7[13]
1,2,3-Trimethylbenzene (hemimellitene)	I	−25.75	99.4 ± 0.2	−25.40	−25.44[2]
1,2,4-Trimethylbenzene (pseudocumene)	I	−44.10	99.1 ± 0.3	−43.78	−44.05[2]
	II	−49.30		−48.97	......
1,3,5-Trimethylbenzene (mesitylene)	I	−44.84	99.7 ± 0.15	−44.73	−44.76[2]
	II	−49.93		−49.82	......
	III	−51.81		−51.68	−51.72[2]

[a] Data on modification II obtained on different preparation than used for modification I.

TABLE II

DENSITIES AND REFRACTIVE INDICES OF C_9H_{12} ALKYLBENZENES

Hydrocarbon	Density 20/4	Refractive index n^{20}_D
n-Propylbenzene	0.8621	1.4921
Isopropylbenzene	.8620	1.4914
1-Methyl-2-ethylbenzene	.8808	1.5043
1-Methyl-3-ethylbenzene	.8648	1.4965
1-Methyl-4-ethylbenzene	.8618	1.4950
1,2,3-Trimethylbenzene	.8944	1.5138
1,2,4-Trimethylbenzene	.8761	1.5047
1,3,5-Trimethylbenzene	.8653	1.4991

culated amount of liquid-soluble, solid-insoluble impurity. The calculation of the freezing point of the pure hydrocarbon is not affected by an error in the heat of fusion, but only by the accuracy with which the fraction frozen at any given time may be estimated from the freezing or melting experiments. It is estimated that the freezing points calculated for the pure hydrocarbon are correct to within 0.10 to 0.15°; while the observed freezing points are uncertain by 0.05° or less.

In one case, that of 1-methyl-2-ethylbenzene, the melting point of pure crystalline modification II was estimated from a different, and slightly less pure, preparation than that used for I. The refractive index and density in Table II were obtained on the best preparation.

Discussion of Results

In the case of four hydrocarbons, namely, *n*-propylbenzene, pseudocumene, 1,2- and 1,3-methylethylbenzenes, after recovery from undercooling on the freezing curves was begun, the temperature continued to rise slowly until the time at which it was necessary to stop stirring. The maximum temperature reached on freezing was in each case 0.2° or more below the temperature of melting. Each of these hydrocarbons was found to exhibit a rather high viscosity at the freezing point; that of 1-methyl-3-ethylbenzene was especially high. Apparently, attainment of thermodynamic equilibrium on freezing is difficult or impossible when the viscosity at the freezing point is rather high.

In the cases of isopropylbenzene and 1-methyl-4-ethylbenzene, while a considerable portion of the freezing curve was concave downward as it should be, extrapolation of the curves led to values of the freezing point about 0.1° lower than the melting point. Only for hemimellitene and mesitylene did the freezing points and melting points agree to 0.01°. It is significant that these two hydrocarbons are the ones most easily crystallizable of the C_9H_{12} aromatics.

The freezing point reported by Lien[12] for 1-methyl-2-ethylbenzene, −88.1°, indicates that he did not obtain the stable form, but was dealing with the metastable form II, for which we estimate −86.50° to be the freezing point.

It is interesting to note that small amounts of impurities appear to have a considerable effect upon the crystal form in which a given hydrocarbon tends to crystallize. One sample of pseudocumene of about 96% purity always crystallized in form II; several unsuccessful attempts were made to cause it to freeze in form I by means of seeding at temperatures just below the melting point of I. However, the transition from II to I occurred very readily in the solid phase; when the sample was solidified in form II, and then immediately re-melted, the melting point corresponding to form I was always observed. However, a second preparation of this hydrocarbon, 99% pure, and the one listed in Table I, crystallized most readily in form I, and when the liquid was seeded with a cold wire at

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(11) Doss, "Physical Constants of the Principle Hydrocarbons," 4th ed., The Texas Co., New York, N. Y., 1943.

(12) Smittenberg, Hoog and Henkes, THIS JOURNAL, **60**, 17 (1938).

(13) Lien, Dissertation, Ohio State University, 1941.

temperatures below the melting point of II, the stable form I appeared. By allowing the hydrocarbon to crystallize spontaneously below the melting point of II, it was possible to obtain a freezing curve corresponding to form II.

Three preparations of 1-methyl-3-ethylbenzene ranging in purity from about 97 to 99.2% have been examined. The first two always crystallized in form II; and it was not until the third was examined that it was discovered that a form of higher freezing point existed. Even in this case, in several experiments, the hydrocarbon always began to crystallize in form II despite constant seeding beginning at the freezing point of I. After about 25% of the sample was crystallized, transition to form I occurred in several experiments.

As cases of polymorphism, these systems must be either monotropic or enantiotropic. Consideration of the schematic pressure–temperature diagrams representing these relations[14] shows that in monotropy (if I is the higher melting form), $(\mathrm{d}p/\mathrm{d}T)_{\mathrm{I}} > (\mathrm{d}p/\mathrm{d}T)_{\mathrm{II}}$. Assuming ΔH_v of the liquid to be constant, this will be true when $(\Delta H_f)_{\mathrm{II}} < (\Delta H_f)_{\mathrm{I}}$. In monotropy no transition points are observed, though theoretically one exists above the melting point; and form I is stable at all temperatures. If $(\Delta H_f)_{\mathrm{II}} > (\Delta H_f)_{\mathrm{I}}$, the system is enantiotropic and there is a solid–solid transition temperature above which solid I is stable and below which II becomes the stable form. Here the freezing point of II can be calculated and is theoretically (if not actually) observable.

In systems 1, 3, 4, 7 and 8 (Table I) the duration and shape of the freezing and melting curves give evidence that the heats of fusion of the several crystalline forms are not greatly different. That of form I appears to be of the order of 5 to 10% greater than II. Consequently, in all of these cases, the systems should be monotropic; however the slopes of the vapor pressure curves of the several polymorphic forms are nearly equal.

In the case of hemimellitene, two solid–solid transitions below the freezing point have been reported[13] indicating the existence of three stable crystalline forms. This system is therefore enantiotropic. We have redetermined the transition temperatures; the heats of transition were also estimated. The values obtained are compared with those of Rossini[13] in Table III.

TABLE III

TRANSITION POINTS AND HEATS OF TRANSITION OF HEMIMELLITENE

Observer	Transition point, °C. I ⇄ II	Transition point, °C. II ⇄ III	Heats of transition, cal./mole II → I	Heats of transition, cal./mole III → II
Rossini	−46 ± 1	−58 ± 2	360 ± 40	280 ± 40
This work	−42.9 ± 0.2	−55.0 ± 0.2	200 ± 70	120 ± 60

The larger freezing cell, patterned after that of Glasgow, Streiff and Rossini,[6] was used for the measurements reported in Table III. The stirrer was placed at the bottom of the cell so that the thermocouple junction was surrounded by the cage-like stirrer. The annular fins of the stirrer served to reduce the temperature gradient between the center and the walls of the cell. It is believed that the existence of such a gradient in the apparatus used by Rossini is responsible for the low values for the transition points reported by him. Our values for the transition temperatures were checked using cooling as well as warming curves.

The metastable freezing points corresponding to hemimellitene II and III have been calculated, taking the heat of fusion of form I to be 2000 cal./mole[13] and employing our values for the transition temperatures. Using our values for the heats of transition, the freezing points corresponding to II and III are calculated to be −27.2 and −30.3°, respectively. Using the heats of transition given by Rossini[13] the corresponding temperatures are −28.2 and −33.5°. Hemimellitene should thus exhibit three freezing points within a range of not more than 10°. Only the stable one has so far been reported, which may be due in large part to the great ease with which this hydrocarbon crystallizes.

The existence of multiple freezing points for five C_9H_{12} alkylbenzenes, together with the calculated but so far unobserved occurrence in a sixth case, makes it appear probable that additional freezing points exist in this group of isomeric hydrocarbons. It may also be confidently predicted that a number of additional instances of this behavior will be found among other classes of hydrocarbons. This possibility should be kept constantly in mind whenever freezing points are measured and compared with data in the literature; or when purities are estimated from time–temperature freezing or melting curves.

Summary

For all of the eight isomeric C_9H_{12} alkylbenzenes, freezing points, purities, densities and refractive indices are reported. The freezing points of each hydrocarbon for zero impurity have been calculated.

Six of these hydrocarbons were found to exhibit polymorphism, five being monotropic and one enantiotropic. Several of these instances of polymorphism have not previously been reported.

The transition temperatures of hemimellitene have been redetermined, together with approximate values of the heats of transition. These data have been used to calculate approximate values for the metastable freezing points of hemimellitene II and III, which have not yet been observed experimentally.

A procedure is described which aids in the determination of what portion, if any, of a given time–temperature freezing or melting curve is suitable for calculation of purity.

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[14] Glasstone, "Textbook of Physical Chemistry," D. Van Nostrand Co., New York, N. Y., 1940, pp. 461–462.