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PHYSICAL CONSTANTS OF SOME LONG-CHAIN NORMAL PARAFFIN HYDROCARBONS

by

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CONTENTS

Introduction 1

Materials used
Synthesis 2

Purification 2

Standard of Purity 2

Experimental Procedure
Constant Temperature Bath 4

Bath Liquids 6

Density Determinations 8

Surface Tension Determinations 10

Viscosity Determinations 13

Results and General Discussion
Density Results 16

Temperature Coefficients of Density 20

Surface Tension Results 21

The Parachors 26

Viscosity Results 27

Nissan's Viscosity-Temperature Equations . . . 30

Viscosity-Surface Tension Relationships 32

Other Relationships 37

Summary 39

Bibliography 41

Appendix: Recommendations for Future Work 43

PHYSICAL CONSTANTS OF SOME LONG-CHAIN NORMAL PARAFFIN HYDROCARBONS.

INTRODUCTION

The object of this research was to investigate the density, surface tension, and viscosity of some long-chain n-paraffin hydrocarbons over as great a liquid range as possible; and to attempt to find relationships between the physical constants holding for large parts of the homologous series or just for individual members of the series.

To find relationships holding for parts of an homologous series, it is obviously desirable to measure the physical constants of as many of its members as possible. Time permitted the investigation of only three hydrocarbons, however, so the results found could only be compared to known relationships existing for the lower members of the series.

The three hydrocarbons investigated were Hexacosane ($C_{26}H_{54}$), Tetracosane ($C_{24}H_{50}$), and Octadecane ($C_{18}H_{38}$). Density and surface tension measurements were taken for all three, but viscosity measurements were taken for only the first and the last, because of an insufficient supply of pure tetracosane.

Apparatus for the measurements was set up; and various methods were tested and their limitations were determined. Work in this laboratory can thus proceed on these measurements for further members of the series with a minimum of experimentation.

MATERIALS USED

Synthesis:

Materials used were prepared and purified in this laboratory. Octadecane was synthesized by the Peterson electrolytic method[1] from Eastman Kodak Company capric acid. Tetracosane was synthesized by the Sorabji modification[2] of the Krafft method from Kodak lauryl alcohol. Hexacosane was synthesized by the Peterson electrolytic method from Kodak myristic acid.[3]

Purification:

Tetracosane and hexacosane were both treated with small quantities of concentrated sulphuric acid, following the method of Piper, et al.[4] All three were finally purified by repeated recrystallization from distilled acetic acid until the samples gave constant melting points.[3]

Standard of Purity:

Samples were considered of sufficient purity if their melting points and setting points were within 0.1° of the accepted values. Determinations were made by the standard method: a small sample being held in a fine capillary next to a thermometer bulb, and the two being immersed in concentrated sulphuric acid in a long-necked flask. Melting

points and setting points used were those observed by Seyer, et al,[5] whose results checked closely with those of Piper, et al,[4] and Hildebrand and Wachter.[6]

There was some doubt about the exact purity of the samples used, since they had all been stored in glass-stoppered bottles for at least three years since their purification. There may have been some change to isomers of similar melting points to those of the normal paraffins. This seems possible in that the densities determined near the melting points were all slightly higher than those that had been determined by Keays[3] when the samples had been freshly purified. Deansley and Carleton[7], in critically examining densities of the normal paraffins up to hexadecane, found that contaminants are in almost every case of higher density, and that lower densities are inherently more probable.

The values for the physical constants found may thus not be absolute values; but they will be close approximations to the absolute values. In any event, their temperature coefficients should be almost identical with the temperature coefficients of samples of the highest purity; and the various physical constants will be related to each other in a normal manner for the series.

EXPERIMENTAL PROCEDURE

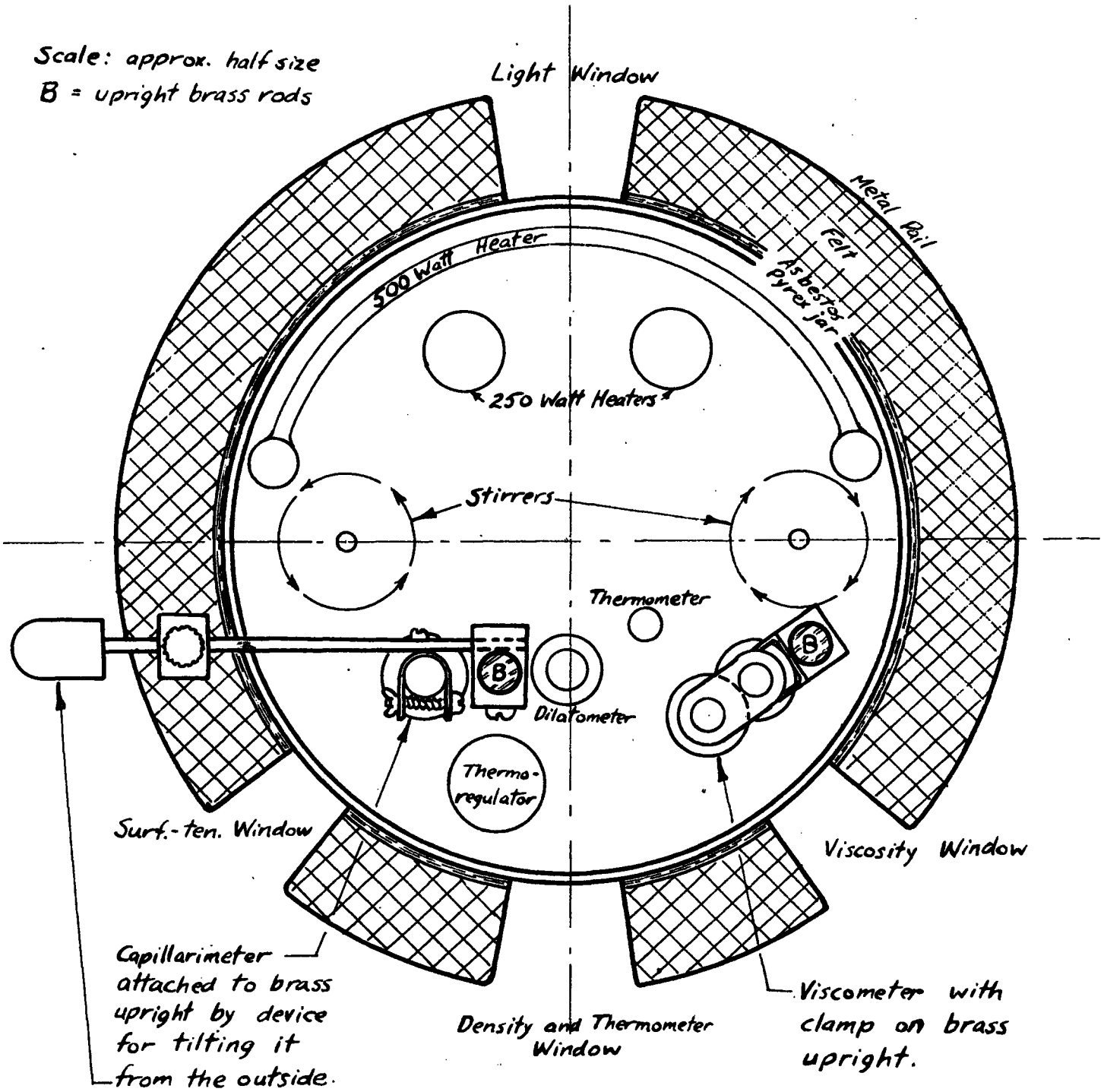
Constant Temperature Bath:

The equipment for measuring the density, surface tension, and viscosity was all immersed in the same constant temperature bath. Readings of all three were taken at the same temperature each time; and in one run the three constants were found over the complete range for a sample. Readings were taken exactly at each 10 degrees, instead of at odd temperatures, for ease of handling the results.

The bath was a cylindrical pyrex jar of 11 litres capacity. (20 cm diameter and 45 cm deep) (See Figures I, II, III, and IV). It was heavily lagged with asbestos and felt, and enclosed in a metal pail. The pail was fastened firmly to a bench; but, in order to cut vibration to a minimum, the jar was allowed to rest on a thick felt pad within it. The bath had a heavy wood-and-asbestos-board cover which fitted tightly, and from which all the apparatus within the bath, except the stirrers, was suspended. This, again, was an effort to reduce any external vibrations. Small windows were cut in the lagging to view the apparatus and to admit light. Care was taken to see that the glass was flawless at the windows.

The bath was heated by one 500-watt and two 250-watt Cenco immersion heaters distributed through the bath. The large heater was connected through several variable resistances to a single-tube Cenco-DeKhotinsky mercury thermo-

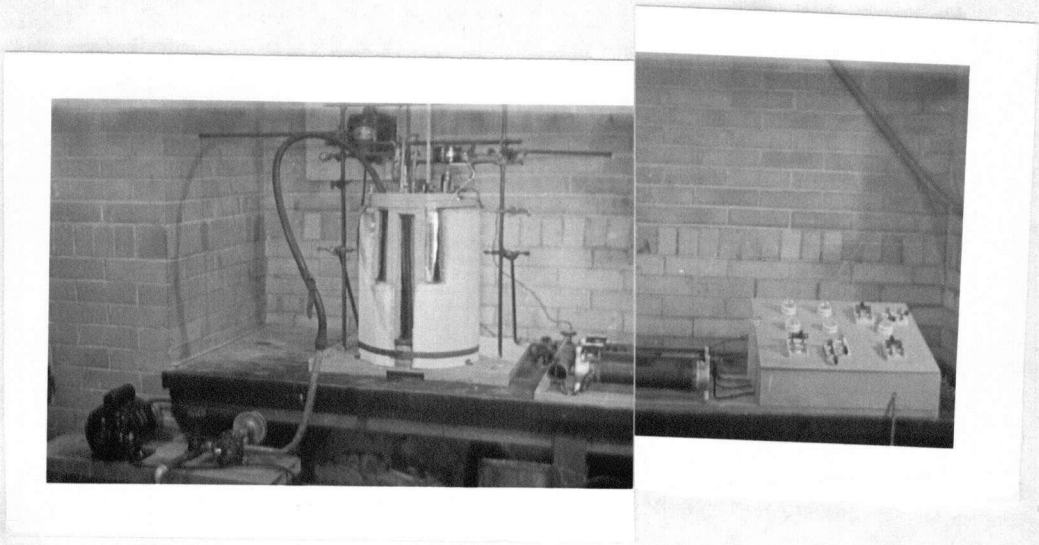
PLAN OF CONSTANT TEMPERATURE BATH



Heaters, thermometer, thermoregulator, and brass uprights held by asbestos-wood cover fitted on pyrex jar.

FIGURE I

Stirring
Motor



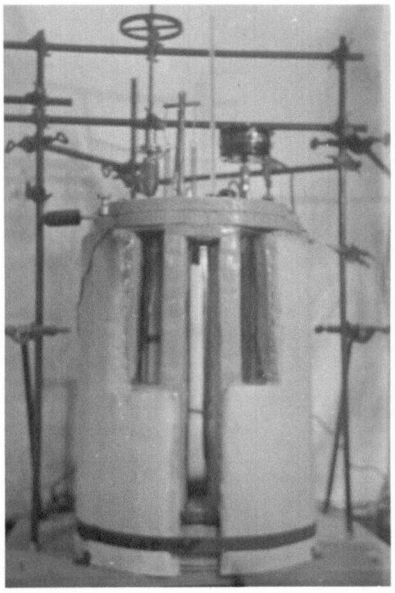
Switchboard

Bath
Liquid
Pump

Constant
Temperature
Bath

General View of Equipment

FIGURE II



Close-up view of Constant Temperature Bath

Close-up view of Bath Liquid Pump

FIGURE III

LAYOUT OF SWITCHBOARD

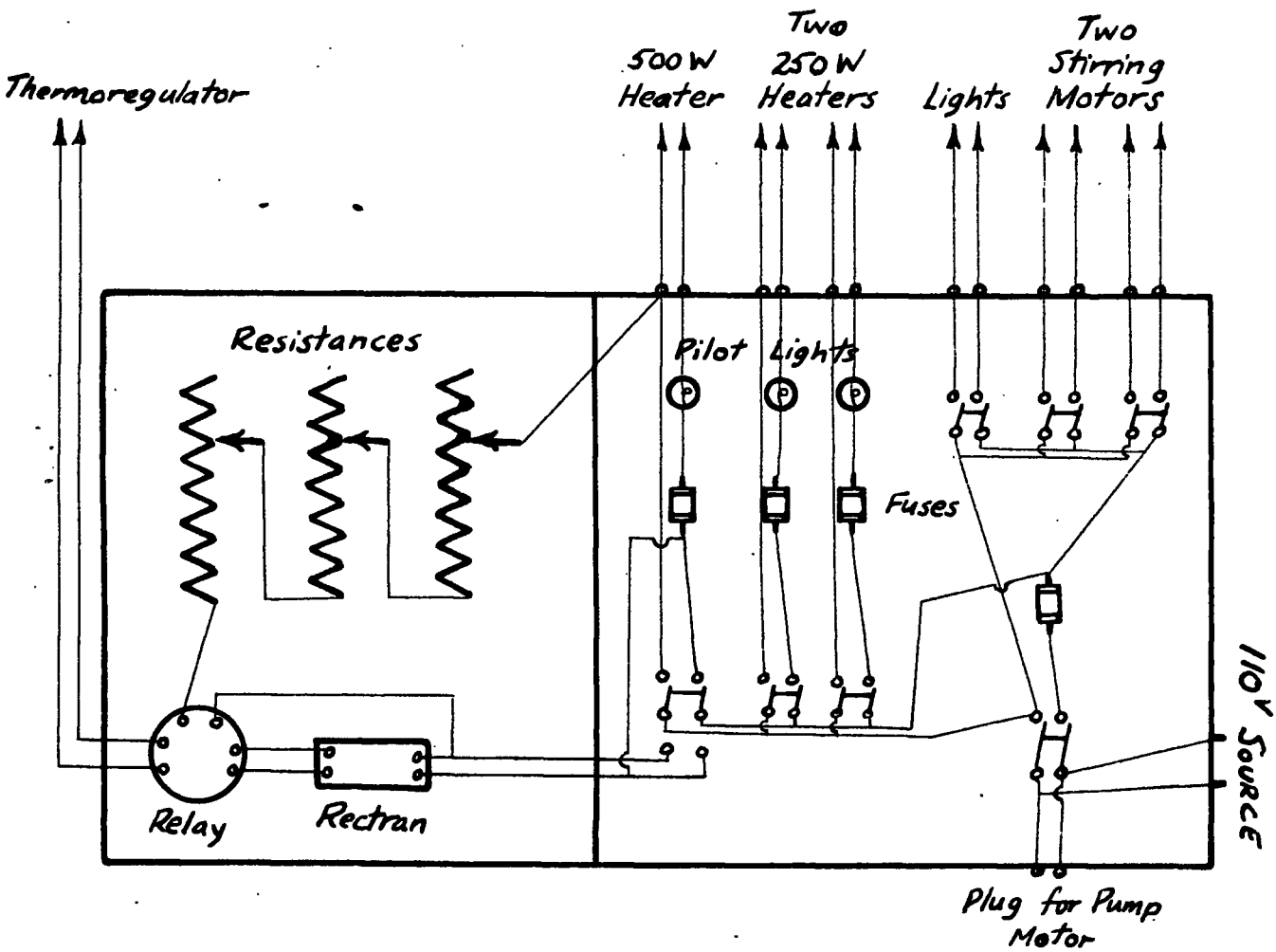


FIGURE IV

regulator with a precision control of 0.01 degrees from room temperature to approximately 150°C. It was found that above 150°C, thermoregulators did not function well, and manual control of the resistances was more satisfactory. The thermoregulator was used with an Aminco Supersensitive Mercury Relay. All electrical apparatus was controlled from a single switchboard well removed from the bath. (See Figure II).

The bath was equipped with two stirrers, each with three uplift propellers. For use on long runs, one stirrer was run by a ¼-hp motor fastened to a nearby wall. The other stirrer was operated by a small, smooth-running, laboratory motor, and was used for minimum vibration when taking readings.

The bath was lighted by long, low-wattage lights shining through a slot up its complete height. In this manner it was evenly lighted throughout with a minimum influence on the heat equilibrium within the bath.

Temperatures were measured by a series of mercury thermometers graduated in tenths of a degree. All thermometers were used completely immersed, and were previously calibrated against a Leeds and Northrup Platinum Resistance Thermometer tested by the Bureau of Standards. Temperatures were accurate to within 0.1 degree in the range from 20°C to 200°C, and were accurate to within approximately 0.2 degree from 200°C to 280°C.

The bath was tested for temperature strata or other temperature differences by means of a Beckmann

Differential Thermometer. At 50°C it did not vary more than ±0.01° at any point, and the regulator held the temperature to within ±0.05° over a period of time. At 100°C and 150°C it did not vary more than ±0.03° at any point, and the regulator held the temperature to within ±0.1°. This showed that the bath liquid, the stirring, and the temperature regulation were satisfactory.

A detailed sketch with photographs of the bath and ancillary apparatus is given in Figures I, II, III, and IV.

Bath Liquid:

The choice of a suitable bath liquid was difficult; and the characteristics of the various bath liquids proved to be the limiting factors determining the temperature range over which measurements could be accurately taken. The final choice was Stanolax (a medium petroleum oil made by Imperial Oil Company) for the range up to 60°C, and high-melting (128°-132°F) paraffin wax in the range 60°C to 280°C. Readings could not be taken above 280°C.

A more suitable choice in the range up to 90°C would have been water, since its thermal conductivity is 3½ times that of the petroleum oils, and its specific heat is at least twice that of oils or paraffin. Thus it would make accurate temperature control much easier in its range. It was not used, however, since it was found impossible to completely dry the bath when changing over from the lower range liquid to the paraffin wax; and it was found that the water

formed numerous small bubbles through the paraffin at the higher temperatures.

The disadvantages of paraffin wax as a high temperature bath liquid are that it rapidly chars and becomes opaque above 250°C, and that it flashes on hot spots, such as the immersion heaters or wires wound outside the glass, between 260°C and 280°C. To partially prevent the flashing, the bath was as tightly closed as possible at the top by means of asbestos plugged into all cracks, and the bath was very slowly heated in this range; but the flashing was impossible to prevent even in this way above 280°C.

Because the paraffin wax charred when exposed over long periods to high temperatures, it was necessary to change the liquid several times during a run. To facilitate the change, a small gear pump driven by a ¼-hp motor was used to draw the hot liquid quickly out of the bath through glass tubes and steel pipes. (See Figures III and IV). Fresh, preheated wax could then be poured in, and the previous temperature could be quickly attained once more.

Numerous organic bath liquids are mentioned in the literature, and several were tested, but all have the same drawbacks as paraffin wax, and none was found to be superior to it. Christensen and King[8] mention a mixture of ortho- and meta-phosphoric acid suitable up to 250°C. It was tried above 250°C, but was found to slowly turn to the meta state above 280°C. It has the advantage of high heat capacity and

no fire hazard; but it has the disadvantage that no metal or wooden fixtures can be used in it. Various molten salts were also tested as bath liquids, but all the salts tested were opaque around 300°C.

Stanolax and paraffin wax were thus chosen as the best compromises for bath liquids; and the temperature of operation was limited accordingly. To overcome their poor heat transfer and heat capacity qualities it was decided to use heavy insulation on the bath. Slow heat loss was also obtained by balancing the heat input and outflow fairly closely, and using a minimum of regulation.

Density Determinations:

Densities were determined by the dilatometric method. The dilatometers used consisted of 1-mm capillary about 35 cm long. A bulb about 1.5 cc in volume was blown onto one end. A larger bulb was then blown onto the top end to aid in filling. A small mark was etched near the lower end for reference. A sketch of the dilatometer used is given in Figure V. Three such dilatometers were required to cover the temperature range investigated.

All capillaries used were carefully selected pyrex tubing examined for constant cross-section throughout their length. They were examined by introducing a small column of mercury and measuring its length at centimeter intervals along the tube by means of a Cenco Measuring Microscope reading to 0.001 cm. A thermometer clamped to the tube was read at intervals to check on constant temperature.

DESIGN
OF
DILATOMETER

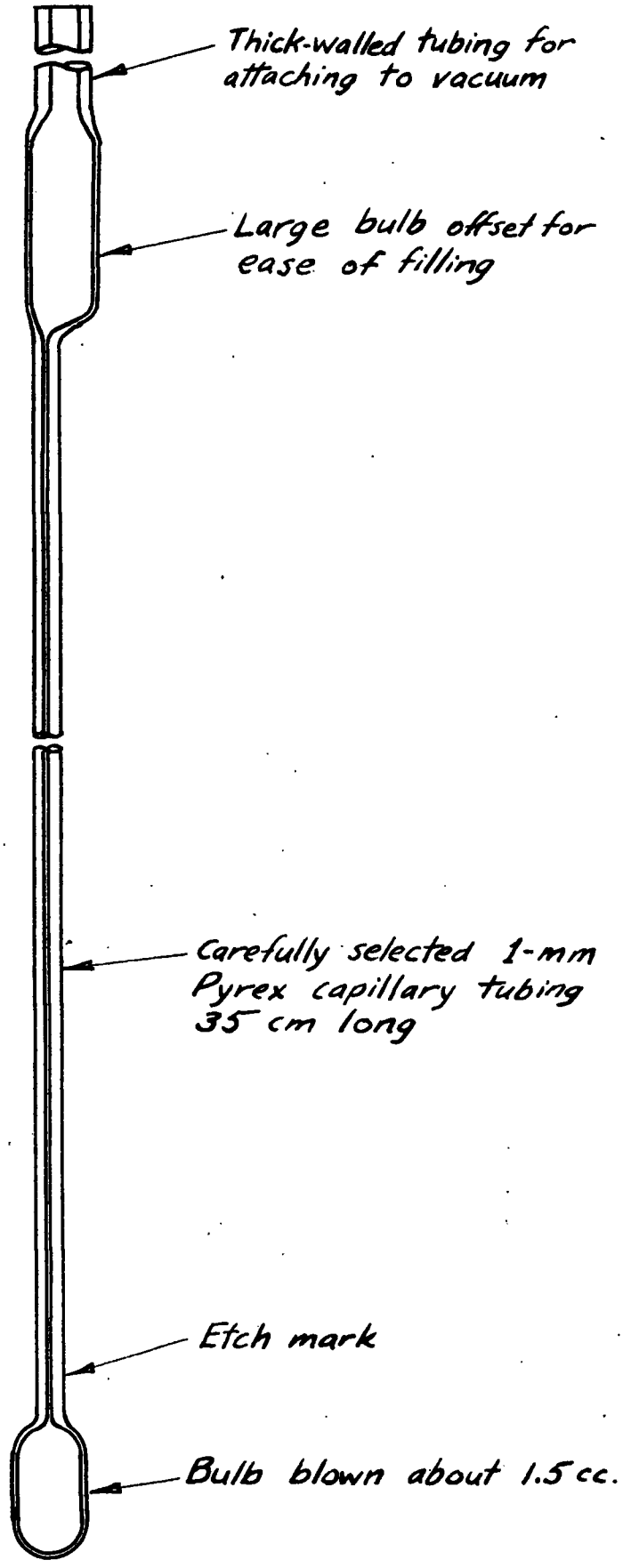


FIGURE V

The completed dilatometer was calibrated by distilling purified mercury into it under vacuum, weighing the mercury added, and measuring its position with regards to the etched reference mark. The position was measured for several different temperatures. It was then a simple matter to calculate the volume of the bulb and the cross-sectional area of the capillary, since the specific volume of mercury and its temperature coefficient of expansion are accurately known. Meniscus corrections and corrections for expansion of the glass were included in this and all subsequent calculations.

A dilatometer was filled with a paraffin sample by placing the sample in the upper bulb in the solid state. A high vacuum was then applied, and the sample was repeatedly melted and solidified until no dissolved gases remained. The whole dilatometer was then heated, and the sample was allowed to run down to the lower bulb. With practice, little adjustment of volume was then necessary. If there was an excess, however, it was removed by heating the dilatometer in a small bath (a very long-necked flask) to the highest temperature to be attained with that sample, then catching the excess in the upper bulb.

Any paraffin left in the capillary or upper bulb after the volume was adjusted was taken out by heating under vacuum and distilling it off.

The dilatometer was weighed before and after filling. It was attached to the vacuum system by rubber tubing in order not to affect the weight of the glass. Heating was done with an electric heater for the same reason. Weighing the long tube was fairly difficult, as it could only be laid flat across the scale pan. Weighing was done on a chainomatic balance with accurate weights calibrated to 0.0001 grams. Weighings were repeated until constant.

When full, the dilatometer was firmly clamped to an upright brass rod in the center of the bath. (See Figure I). Readings of meniscus height above the etched mark were taken with a Wm. Gaertner and Co. cathetometer reading to 0.005 cm.

Surface Tension Determinations:

Surface tensions were determined by the differential capillary rise method described by S. Sugden[9] and by Richards, et al[10].

The capillarimeter consisted of two different-sized capillaries joined at the bottom and open to the liquid at the bottom, all encased in a thin-walled tube just large enough to take the U-shaped capillaries. A sketch of the capillarimeter used is given in Figure VI.

DESIGN
OF
CAPILLARIMETER

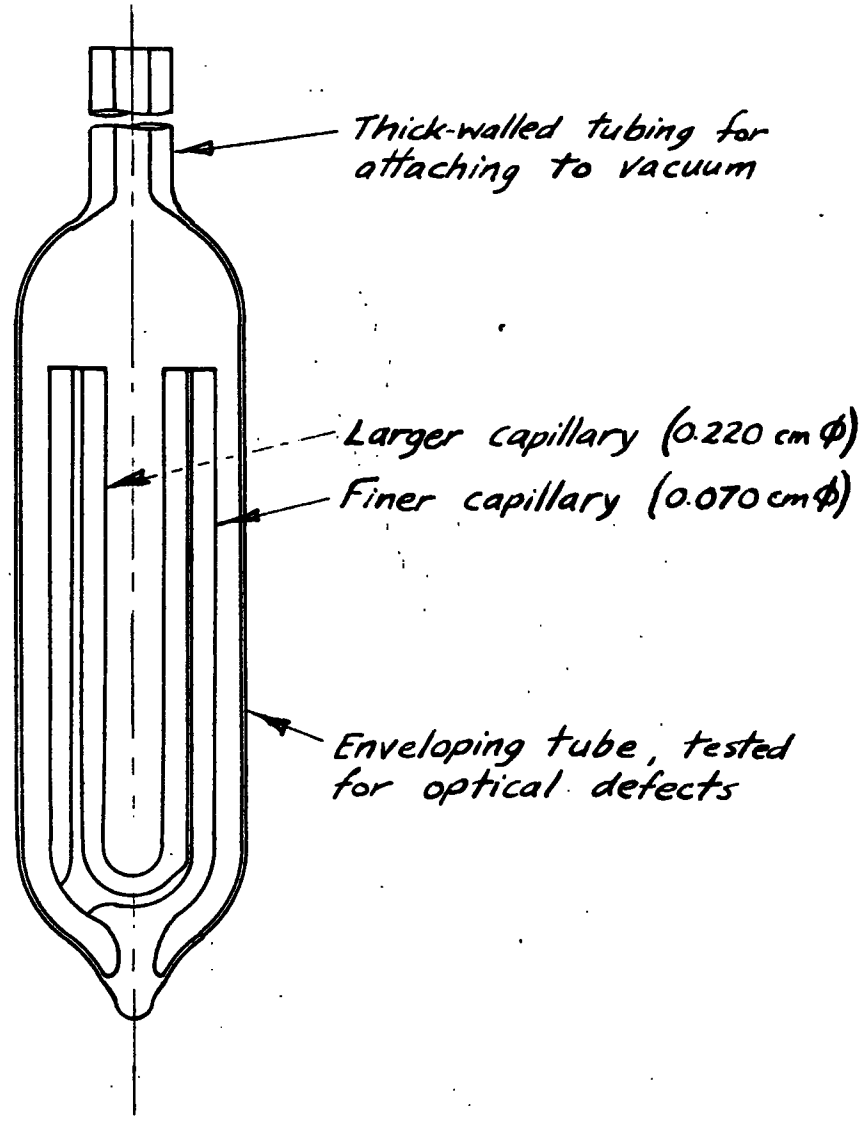
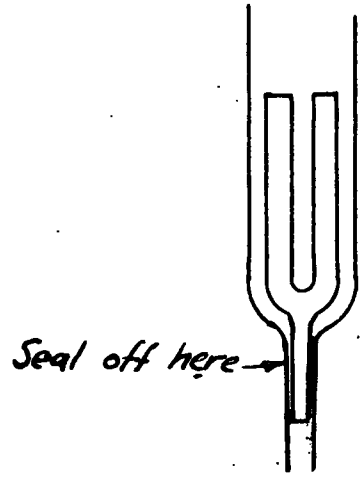


FIGURE VI



NOTE: Method of Sugden for holding capillaries in the tube was found to set up strains, and was difficult to clean; but it is the best way to join the capillaries to the enveloping tube, as shown.

The capillaries used had inside diameters of 0.220 cm and 0.070 cm at 20°C. Tubes with inside diameters of 0.152 cm and 0.020 cm were tested also. They gave larger differential readings; but the fine capillary was too fine to reach an equilibrium reasonably quickly because of extremely slow drainage.

The capillaries were carefully selected pyrex tubing examined in the same manner as that described for the dilatometer capillaries. The enveloping tube was 22-mm thin-wall pyrex, carefully examined for any optical defects by measuring an object inside it from different angles by means of a cathetometer.

The tubes were calibrated with pure benzene and with conductivity water. Before calibration, the tubes were carefully cleaned, washed at least 20 times with conductivity water, then dried under vacuum. Pure benzene was then distilled from sodium directly into the tube under vacuum, and the tube was sealed with the vacuum still on. In the case of the water, it was put in the tube after washing, then sealed under vacuum. The water did not stand in the tubes in the same region as the paraffins and the benzene did, but it gave a very nice check on the calibration and the uniformity of the capillaries.

The pure benzene was prepared in the following

manner: 500 cc of Baker's CP Analyzed Benzene (benzol-thiophene free) were crystallized in an ice bath until all but 50 cc were crystallized. This residue was discarded. After four such crystallizations a constant freezing point of 5.46°C was obtained, as measured by a Leeds and Northrup Platinum Resistance Thermometer. The benzene was then kept over sodium in a stoppered bottle, and used as soon as possible afterwards.

The conductivity water was prepared in the standard manner. Carefully distilled water was allowed to stand for a period with a little $KMnO_4$, after which it was again distilled in an all-glass, thoroughly-steamed, Pyrex apparatus with ground-glass joints. For calibration purposes a middle fraction was used immediately after distillation. The remaining water prepared in this way was used for washing apparatus.

Densities and surface tensions used for water and benzene were those given by Richards, et al[10]. The linear coefficient of expansion of pyrex glass, 0.32×10^{-5}, was applied to the calibration.

All samples of the paraffins were filtered for dust, and were loaded by means of long funnels. They were sealed in the capillarimeter under vacuum, hence the surface tensions measured were those under the substance's own vapour pressure.

Differential height measurements were taken by means of a Precision Tool and Instrument Co. cathetometer reading to 0.001 cm.

Viscosity Determinations:

Viscosities were determined by means of U-tube viscometers made according to the requirements of the British Standards Institute Standard No. 188-1937, "British standard method for the determination of viscosity of liquids in absolute (C.G.S.) units". Three sizes of these viscometers were used, with capillary bores 0.038 cm I.D. for the range 0.5 - 1.5 cs, 0.060 cm I.D. for the range 1.5 - 5.0 cs, and 0.115 cm I.D. for the range 5.0 - 7.0 cs.

The tubes were fitted with the specified brass clamps, and were firmly held in the bath by a clamp allowing adjustment for the vertical. Fittings were made for the tops of the viscometers to prevent contamination, yet to facilitate drawing the liquid into the higher reservoir and releasing it quickly. The suction was attached to an ordinary water suction pump to allow careful adjustment of the suction speed. For higher temperatures, the fitting was ground onto the viscometer. For lower temperatures it was found more convenient to use rubber connections, and take the excess weight from the top of the viscometer.

Bath temperature was controlled as specified in the above standard (see section on Constant Temperature Bath); and the calibrations and observations were carried out as

specified. The two finer tubes were calibrated with conductivity water, prepared as previously described. They later checked well against each other using the paraffins. The larger tube was calibrated against them using the paraffins. A.S.T.M. recommended viscosities for water were used in the calibration.

The British Standard viscometer is well designed and has been proved by Steiner[11] to give accurate results if carefully handled. Its check on the loading error is useful for work over large temperature ranges. At each temperature the fill was adjusted easily by means of a long fine tube with an eye-dropper bulb at one end. The viscometer was never moved during a run.

The only error that needed watching was the Kinetic Energy error. Cannon and Fenske[12], in discussing viscosity measurement errors, point out that the correction for the K.E. error should be kept below 0.2%, as it is only accurate to about 20%. The final error is then only 0.04%. Even within the specified ranges, however, the K.E. error in a British Standard viscometer may be as high as 0.5%, which may give a resultant error of 0.1%. This can be kept down only by changing sooner than recommended to a smaller-sized viscometer.

There was no error caused by the absorption of radiant heat in these determinations because paraffins were

being examined, and the bath liquid consisted of similarly-coloured paraffin wax. If other bath liquids were used, this error could become important at the higher temperatures.

The deciding error in these determinations was in the timing. The efflux time was measured by means of a Meylan stopwatch graduated in 1/5 seconds and checked against reliable timepieces. Steiner[11] has shown by careful work that stopwatches are, as a rule, not sufficiently precise for the precision measurement of viscosity. Above 100 seconds (the range used here) the error is probably within 0.2%. This error is directly reflected in the calculated viscosity, however, and since it is the largest single error in the determination it should be reduced in future. It can only be reduced by the use of some sort of electronic precision timer accurate to 0.01 seconds, such as described by Fry and Baldeschwieler[13], Penther and Pompeo[14], or Steiner[15].

With an electronic timer the limiting error is the optical reaction time of the observer, which Speakman[16] points out cannot be reduced by practice to less than 0.160 seconds. Since the same error is present in stopping and starting, however, there is compensation for total time elapsed; and since the instant of the passing of the meniscus is anticipated, it is reasonable to time to 0.01 seconds.

RESULTS AND GENERAL DISCUSSION

Density Results:

Results obtained in the density determinations are given in detail in Tables I, II, and III. The general equations for temperature coefficient of density were calculated in the ranges in which the samples were known not to have charred. The equations were calculated by the method of least squares, after assuming the first constant in each case for simplification. The number of terms necessary in the power series was determined by the method of finite differences, and was found in each case to be three terms (up to $c(t-t_0)^2$).

The accuracies of the readings were estimated to be as given for the equations. The coefficients of expansion are given are simply useful approximations in the lower temperature ranges.

Densities were determined for both rising temperature and lowering temperature and both checked closer than the accuracy given. There was no apparent hysteresis in any sample.

The density curves are shown in Figure VII. As would be expected, they are roughly parallel with slight curvature. Above 200°C the curves are not as regular as below. This is partly due to the fact that the samples charred slightly over a period of time above 200°C, and

TABLE I

Density of Octadecane ($C_{18}H_{38}$)

General equation calculated over range 30°C to 250°

$$d_t = 0.7833 - 0.674(10^{-3})(t-30) - 0.075(10^{-6})(t-30)^2 \pm 10^{-4}\Delta$$

where Δ = 5 in range m.p. - 200°
8 in range 200° - 250°
10 in range 250° - 280°

t°C	Spec Vol $V = 1/d$ (obs)	Density d (obs)	d (calc)	Diff ($\times 10^{-4}$)	d Krafft	d others
28.1			.7846			Dover 19
30	1.2765	.7834	.7833	-1	.7757	.7790(32°)
40	1.2877	.7766	.7766	0	.7688	
50	1.2990	.7698	.7698	0	.7618	.7756(42°)
60	1.3106	.7630	.7630	0	.7550	
70	1.3226	.7561	.7502	+1	.7482	
80	1.3346	.7493	.7494	+1	.7416	
90	1.3464	.7427	.7426	-1	.7349	
100	1.3589	.7359	.7357	-2	.7284	
110	1.3717	.7290	.7289	-1		
120	1.3850	.7220	.7220	0		
130	1.3982	.7152	.7152	0		
140	1.4120	.7082	.7083	+1		
150	1.4257	.7014	.7013	-1		
160	1.4397	.6946	.6944	-2		
170	1.4541	.6877	.6875	-2		
180	1.4686	.6809	.6805	-4		
190	1.4839	.6739	.6736	-3		
200	1.4997	.6668	.6665	-3		
210	1.5163	.6595	.6595	+1		
220	1.5335	.6521	.6525	+4		
230	1.5501	.6451	.6455	+4		
240	1.5669	.6382	.6385	+3		
250	1.5848	.6310	.6314	+4		
260	1.6028	.6239	.6243	+4		
270	1.6205	.6171	.6170	-1		
280	1.6391	.6101	.6101	0		

Coeff. of Expansion = approx. 0.0115 cc/deg/cc (range- m.p. to 100°)

TABLE II

Density of Tetracosane ($C_{24}H_{50}$)

General equation calculated over range 60°C to 250°C

$$d_t = 0.7749 - 0.646(10^{-3})(t - 60) - 0.10(10^{-6})(t - 60)^2 \pm 10^{-4}\Delta$$

where Δ = 5 in range m.p. - 200°
8 in range 200° - 250°
10 in range 250° - 280°

t°C	Spec Vol v = 1/d (obs)	Density d (obs)	d (calc)	Diff ($\times 10^{-4}$)	d Keays[3]	d others
50.7			.7809		.7772	Richter[20] .791(51°)
60	1.2906	.7748	.7749	+1	.7713	McKittrick[21] .7682(70°)
70	1.3012	.7685	.7684	-1	.7651	Van Hook[22] .764(76°)
80	1.3125	.7619	.7620	+1		Eggloff[23] .7628(76°)
90	1.3238	.7554	.7554	0		
100	1.3354	.7488	.7489	+1		
110	1.3471	.7423	.7424	+1		
120	1.3594	.7356	.7357	+1		
130	1.3717	.7290	.7292	+2		
140	1.3844	.7223	.7226	+3		
150	1.3970	.7158	.7160	+2		
160	1.4098	.7093	.7093	0		
170	1.4226	.7029	.7026	-3		
180	1.4363	.6962	.6960	-2		
190	1.4505	.6894	.6892	-2		
200	1.4649	.6826	.6825	-1		
210	1.4792	.6760	.6758	-2		
220	1.4940	.6693	.6689	-4		
230	1.5094	.6625	.6622	-3		
240	1.5250	.6557	.6554	-3		
250	1.5417	.6486	.6486	0		
260	1.5583	.6417	.6417	0		
270	1.5755	.6347	.6348	+1		
280	1.5936	.6275	.6276	+1		

Coeff. of Expansion = approx. 0.0112 cc/deg/cc (range - m.p. to 100°)

TABLE III

Density of Hexacosane ($C_{26}H_{54}$)

General equation calculated over range 60°C to 250°C

$$d_t = 0.7788 - 0.640(10^{-3})(t - 60) - 0.15(10^{-6})(t - 60)^2 \pm 10^{-4}\Delta$$

where Δ = 5 in range m.p. - 200°
10 in range 200° - 250°
15 in range 250° - 280°

t°C	Spec vol v = 1/d (obs)	Density d (obs)	d (calc)	Diff (x10⁻⁴)	d Keays[3]	d others
55.8			.7815		.7796	Schmidt[24]
60	1.2840	.7788	.7788	0	.7768	.7780(70°)
70	1.2947	.7724	.7724	0	.7707	.7691(89°)
80	1.3057	.7659	.7659	0	.7642	
90	1.3170	.7593	.7595	+2	.7565	Buckler[25]
100	1.3282	.7529	.7529	0		.7580(84°)
110	1.3399	.7463	.7464	+1		
120	1.3517	.7398	.7399	+1		
130	1.3639	.7332	.7333	+1		
140	1.3763	.7266	.7266	0		
150	1.3888	.7200	.7200	0		
160	1.4013	.7136	.7133	-3		
170	1.4144	.7070	.7066	-4		
180	1.4277	.7004	.6998	-6		
190	1.4411	.6939	.6931	-8		
200	1.4575	.6861	.6863	+2		
210	1.4718	.6794	.6796	+2		
220	1.4869	.6725	.6726	+1		
230	1.5030	.6653	.6657	+4		
240	1.5186	.6585	.6587	+2		
250	1.5356	.6512	.6518	+6		
260	1.5523	.6442	.6448	+6		
270	1.5698	.6370	.6378	+8		
280	1.5875	.6299	.6307	+8		

Coeff. of Expansion = approx. 0.0111 cc/deg/cc (range - m.p. to 100°)

Density - Temperature Curves
for
Hexacosane, Tetracosane, and Octadecane
in their liquid ranges.

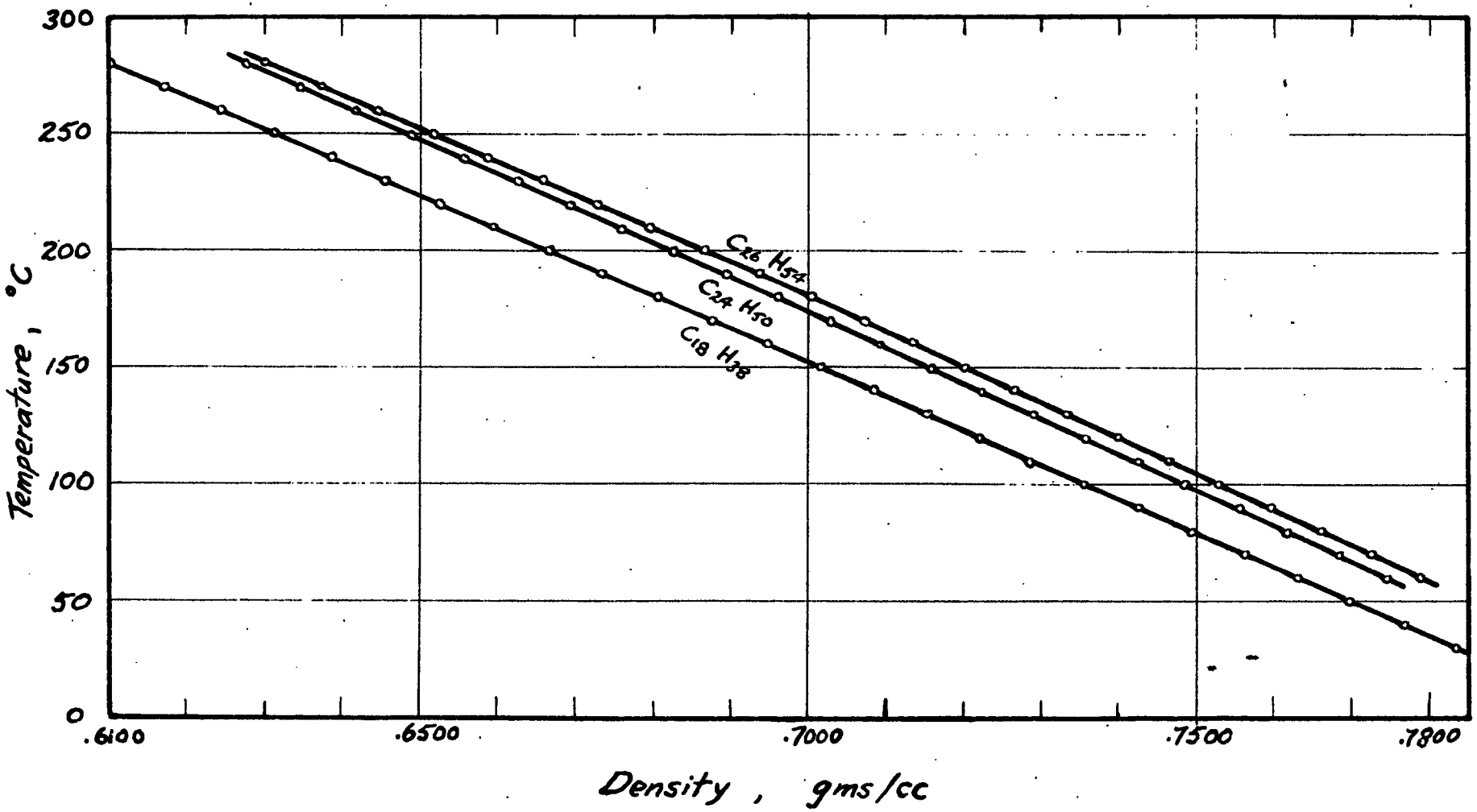


FIGURE VII

partly to the fact that in this range it is virtually impossible to prevent casual movements of the meniscus while taking readings.

At this point attention should again be drawn to the remarks in the section on Materials Used regarding the purity of the samples used and the accuracy of the densities determined.

Temperature Coefficients of Density:

Calingaert, et al[17], collected selected, smooth values of the temperature coefficients of density for the lower paraffin hydrocarbons to $C_{12}H_{26}$ and found the empirical relation:

$$d_t = d_{20} + a(t - 20) + (b/2)(t - 20)^2$$

where a = temp. coeff. of d = $-\dfrac{0.0298 + 0.00788N}{2.0162 + 14.0262N}$

b = temp. coeff. of a, and $\log(-b) = -5.3 - 0.1N$

They suggested this relation could be extrapolated at least as high as $C_{22}H_{46}$. If we extrapolate it, assuming it holds equally well for the relation:

$$d_t = d_s + a(t - t_s) + (b/2)(t - t_s)^2$$

where t_s is any reasonable temperature, as close to 20°C as possible, we can then compare it to the values found experimentally as follows in Table IV.

TABLE IV

	$C_{18}H_{38}$			$C_{24}H_{50}$		$C_{26}H_{54}$	
	$-a \times 10^3$	$-b \times 10^6$	d_{30}	$-a \times 10^3$	$-b \times 10^6$	$-a \times 10^3$	$-b \times 10^6$
observed	0.674	0.075	0.7833	0.646	0.10	0.640	0.15
Calingaert[17]	0.674	0.08	0.7764	0.646	0.02	0.640	0.013
Krafft[18]	0.7024	-0.395	0.7757				

Surface Tension Results:

Results obtained in the surface tension determinations are given in detail in Tables V, VI, and VII. A graph of the results is shown in Figure VIII.

Molar surface energy was taken as $\gamma(Mv)^{2/3}$ ergs per sq cm, and the Eotvos constant as $-\frac{d[\gamma(Mv)^{2/3}]}{dT}$.

A graph of the molar surface energy against temperature (See Figure IX) gives a reasonably straight line over the entire temperature range measured. It should be noted here that charring did not affect the surface tension results as much as it did the density and viscosity results at high temperatures because the liquids were sealed in the capillarimeter under high vacuum.

General equations are given for each paraffin in the form suggested by Ramsay and Shields:

$$\gamma(Mv)^{2/3} = k(t_c - t - \delta)$$

TABLE V

Surface Energy of Octadecane ($C_{18}H_{38}$)

General equation in the form of Ramsay and Shields :

$$\gamma(Mv)^{2/3} = 3.01\,(t_c - t - \delta)$$

where γ = Surface tension
M = Molecular weight = 254.48
t_c = Critical temperature = 490.5 (Wilson[26])
δ = 25 (obtained by graphical means)

t°C	v=1/d (obs)	γ dyn/cm (obs)	γ (other)	Molar surface energy $\gamma(Mv)^{2/3}$	Eotvos const.	Ramsay Shields const.	Parachor [P]
30	1.2765	28.71	Dover[19]	1357		3.11	754
40	1.2877	27.70	27.58	1317		3.09	751
50	1.2990	26.80	(32°)	1281	3.8	3.08	753
60	1.3106	25.86		1244		3.07	753
70	1.3226	25.04		1212		3.06	754
80	1.3346	24.17		1177		3.05	754
90	1.3464	23.38		1144		3.05	754
100	1.3589	22.60		1113	3.3	3.05	754
110	1.3717	21.84		1083		3.05	754
120	1.3850	21.06		1051		3.04	754
130	1.3982	20.31		1020		3.04	754
140	1.4120	19.70		996		3.05	754
150	1.4257	19.00		966	2.9	3.05	755
160	1.4397	18.18		931		3.04	758
170	1.4541	17.48		901		3.04	757
180	1.4686	16.70		866		3.03	755
190	1.4839	16.01		836		3.03	755
200	1.4997	15.45		814	2.9	3.06	758
210	1.5163	14.76		782		3.05	757
220	1.5335	14.26		762		3.09	757
230	1.5501	13.49		726		3.07	758
240	1.5669	12.75		690		3.05	758
250	1.5848	12.0		656	3.1	3.03	753
260	1.6028	11.4		627		3.04	753
270	1.6205	10.9		604		3.08	752
280	1.6391	10.3		575	2.6	3.09	750
				Averages –		3.06	755

Accuracy of γ - approx. ±0.05 (30°-100°) ±0.08 (100°- 240°)
±0.2 (240°-280°)

TABLE VI

Surface Energy of Tetracosane ($C_{24}H_{50}$)

General equation in the form of Ramsay and Shields:

$$\gamma(Mv)^{2/3} = 3.44(t_c - t - \Delta)$$

where γ = Surface tension
M = Molecular weight = 338.64
t_c = Critical temperature = 561.5 (Texas Co.)[27]
Δ = 25 (obtained by graphical means)

t^oC	v=1/d (obs)	γ # dyn/cm (obs)	Molar surface energy $\gamma(Mv)^{2/3}$	Eotvos const.	Ramsay Shields const.	Parachor [P]
60	1.2906	27.52	1585		3.33	1000
70	1.3012	26.85	1555		3.34	1003
80	1.3125	26.07	1518		3.33	1004
90	1.3238	25.45	1491		3.35	1006
100	1.3354	24.75	1458	3.2	3.34	1008
110	1.3471	23.90	1417		3.33	1008
120	1.3594	23.20	1383		3.33	1008
130	1.3717	22.38	1341		3.31	1007
140	1.3844	21.57	1301		3.29	1008
150	1.3970	20.83	1265	3.8	3.28	1008
160	1.4098	20.14	1230		3.27	1010
170	1.4226	19.42	1193		3.26	1012
180	1.4363	18.71	1157		3.25	1012
190	1.4505	17.87	1113		3.22	1011
200	1.4649	17.21	1078	3.8	3.24	1011
210	1.4792	16.76	1057		3.24	1013
220	1.4940	16.13	1024		3.24	1013
230	1.5094	15.45	988		3.23	1013
240	1.5250	14.85	956		3.23	1013
250	1.5417	14.18	919	3.4	3.21	1013
260	1.5583	13.5	882		3.20	1013
270	1.5755	13.0	855		3.21	1012
280	1.5936	12.4	822	3.0	3.21	1012
				Averages -	3.27	1009

No previous record of γ for $C_{24}H_{50}$ found in the literature.

Accuracy of γ - approx ± 0.05 (60°-100°) ± 0.08 (100°- 250°) ± 0.2 (250° - 280°)

TABLE VII

Surface Energy of Hexacosane ($C_{26}H_{54}$)

General equation in the form of Ramsay and Shields:

$$\gamma(Mv)^{2/3} = 3.49(t_c - t - \delta)$$

where γ = Surface tension
M = Molecular weight = 366.69
t_c = Critical temperature = 583.0 (Texas Co.[27])
δ = 25 (obtained by graphical means)

t^oC	v=1/d (obs)	γ dyn/cm (obs)	γ (others)	Molar surface energy $\gamma(Mv)^{2/3}$	Eotvos const.	Ramsay Shields const.	Parachor [P]
60	1.2840	27.8		1682		3.38	1081
70	1.2947	27.2		1650		3.39	1082
80	1.3057	26.4		1615		3.38	1084
90	1.3170	25.6		1576		3.37	1086
100	1.3282	24.9		1451	3.5	3.37	1087
110	1.3399	24.4	Schenck[28]	1517		3.38	1101
120	1.3517	23.6	24.79	1478		3.37	1092
130	1.3639	22.8	(115.4°)	1438		3.36	1089
140	1.3763	22.0		1395		3.34	1092
150	1.3888	21.3		1359	3.9	3.33	1093
160	1.4013	20.6		1322		3.33	1094
170	1.4144	20.1		1297		3.34	1097
180	1.4277	19.4		1260		3.34	1098
190	1.4411	18.8		1228		3.34	1098
200	1.4575	18.2		1199	3.1	3.34	1102
210	1.4718	17.6		1167		3.35	1104
220	1.4869	17.1		1139		3.37	1111
230	1.5030	16.5		1109		3.38	1109
240	1.5186	15.8		1069		3.36	1110
250	1.5365	15.2		1036	3.3	3.36	1111
260	1.5523	14.6		1002		3.36	1117
270	1.5698	14.0		966		3.36	1110
280	1.5875	13.5		937	3.3	3.37	1108
				Averages -		3.36	1094

Accuracy of γ - approx ±0.1 (60° - 100°) ±0.2 (100° - 200°) ±0.5 (200° - 280°)

Surface Tension - Temperature Curves
for
Hexacosane, Tetracosane, and Octadecane

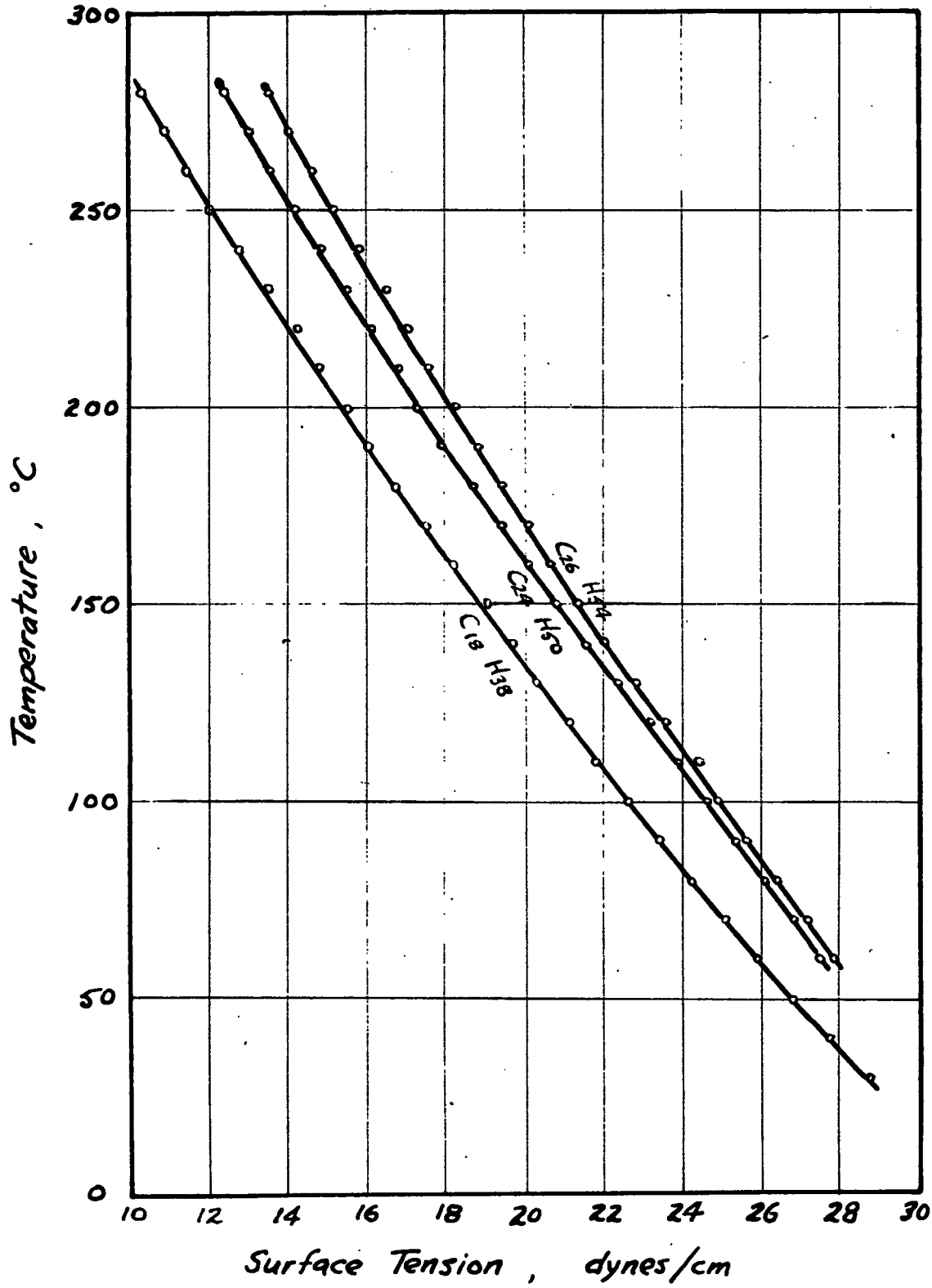


FIGURE VIII

Molar Surface Energy - Temperature Curves
for
Hexacosane, Tetracosane, and Octadecane

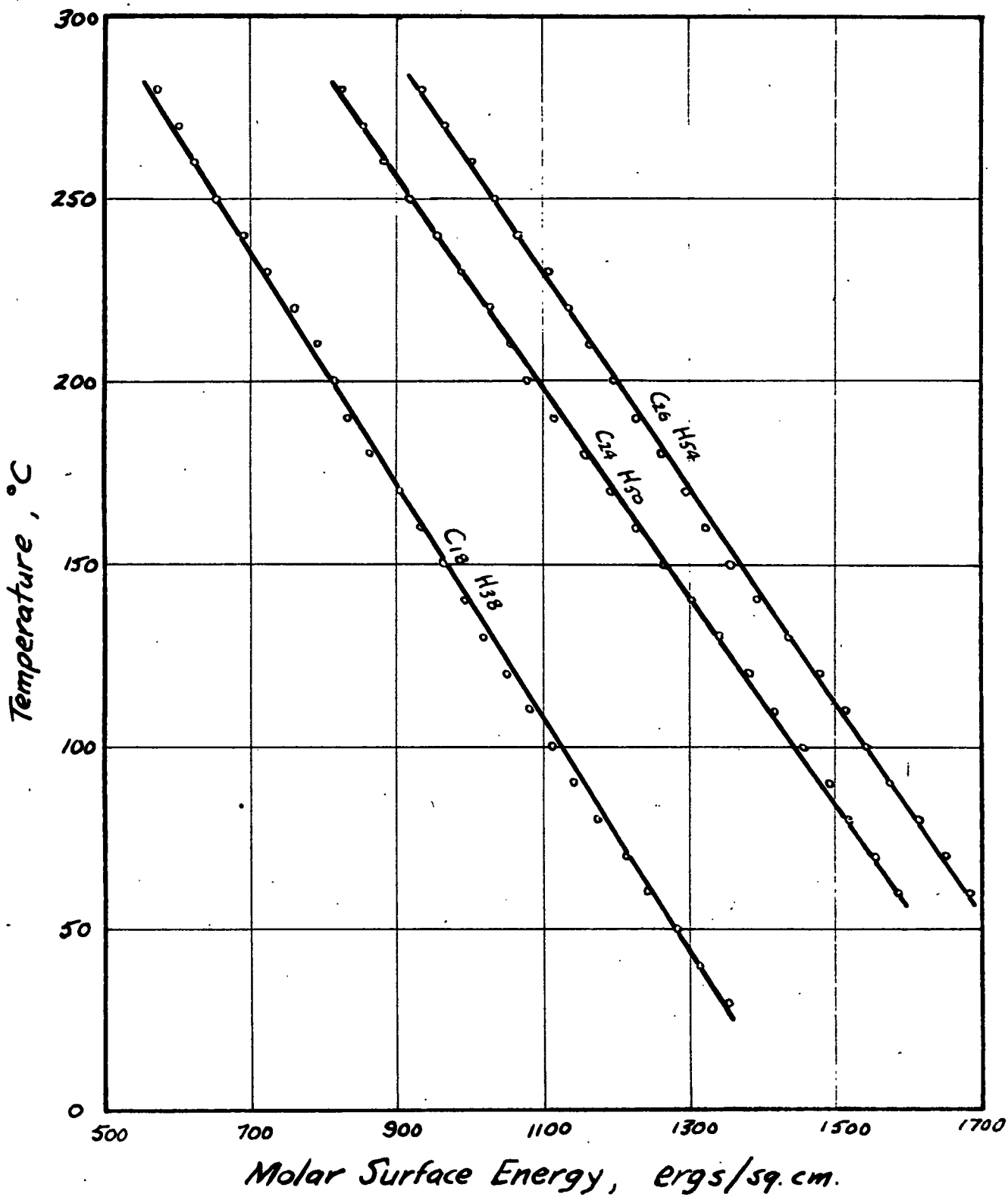


FIGURE IX

because it fits the results so well. The constant "ζ" was obtained by plotting the curve on large-scale graph paper and extrapolating to zero molar surface energy. In all cases it was found to be within a few degrees of 25 below the critical temperature. Since it is not a critical figure, and since it was difficult to determine exactly, it was taken as 25 in all three cases. This is not at all close to the figure of 6 found by Ramsay and Shields for many liquids, but it fits the cases well. The curve actually flattens out before it reaches this point, anyway, and becomes tangent to the temperature axis at the critical temperature.

The constant "k" was averaged from all readings. Walden discovered an empirical formula for k as follows:

$$k = 1.90 - 0.011 \Sigma n \sqrt{A}$$

where A is the atomic weight and n is the number of atoms of each element in the molecule. The k's calculated from this formula are compared in Table VIII to the observed values.

TABLE VIII

	$C_{18}H_{38}$	$C_{24}H_{50}$	$C_{26}H_{54}$
k (Walden's equation)	3.01	3.37	3.49
k (observed)	3.06	3.27	3.36

For finer results, $\gamma(Mv)^{2/3}$ should be replaced by $\gamma\left(\frac{M}{d - d'}\right)^{2/3}$ where d' is the density of the vapour. The vapour pressures for the paraffins have not been measured over all this range, however. Vapour densities could be calculated from the known vapour pressures up to 100°C, but they would be estimates, and since the correction is small it was not considered worth the time.

The Parachors:

The Parachor [P] is the constant in the equation:

$$[P] = \frac{M\gamma^{\frac{1}{4}}}{d-d'}$$

where the density of the vapour (d') may be neglected in comparison to that of the liquid.

S. Sugden proposed Parachor equivalents of C=4.8 and H=17.1 with a CH_2 increment of 39 in an homologous series. S. A. Mumford and J.W.C.Phillips proposed Parachor equivalents of C=9.2 and H=15.4 with a CH_2 increment of 40 in an homologous series. Table IX compares these calculated Parachors with the observed Parachors.

TABLE IX

	Calculated Sugden	Calculated M & P	Observed	Obs. by Schenck[28]
[P] $C_{18}H_{38}$	736.2	750.8	755	
[P] $C_{24}H_{50}$	970.2	990.8	1009	
[P] $C_{26}H_{54}$	1048.2	1070.8	1094	1082
CH_2 Increment	39	40	42	

Viscosity Results:

Results obtained in the viscosity determinations are given in detail in Tables X and XI. A graph of the results is shown in Figure X.

To find a straight-line relationship between the viscosity and temperature, a plot was first made of Andrade's simple equation: $\eta = Ae^{-b/T}$ (See Figure XI). As was to be expected, according to Evans[30], this gave a curve slightly convex to the 1/T axis. Since it straightened the curves considerably, however, it gave a good check on the validity of the readings. It was interesting to note that it markedly showed the effect of charring in the higher temperature range for Octadecane.

Modifications of various equations as described by Evans[30] were then plotted. The equation giving the best results in a reasonable form was that of Walther[31] as accepted by the A.S.T.M., and now called the A.S.T.M. Equation. This is an expected result, since the equation has proved very satisfactory for petroleum oils. The graph is shown in Figure XII.

General equations are therefore given for both the paraffins tested in the form of the A.S.T.M. Equation:

$$\log \log (\nu_T + \alpha) = A \log T + B$$

where ν_T is the kinematic viscosity

TABLE X

Viscosity of Octadecane ($C_{18}H_{38}$)

General equation in the A.S.T.M. form:

$$\log \log (\nu + 0.8) = -3.60 \log T - 0.437$$

where ν is the kinematic viscosity in centistokes
T is the absolute temperature
(Constants were obtained by method of selected points)

t°C	Density d	Kinematic visc. ν cs.	Dynamic visc. $\eta = \nu d$ cp.	η cp. (others)
30	0.7834	5.079	3.979	
40	0.7766	4.073	3.163	Ubbelohde[32]
50	0.7698	3.325	2.560	2.86 (40°)
60	0.7630	2.806	2.141	1.92 (60°)
70	0.7561	2.371	1.792	1.34 (80°)
80	0.7493	2.050	1.536	1.06 (100°)
90	0.7427	1.807	1.342	
100	0.7359	1.573	1.157	Dover[19]
				3.557 (32°)
110	0.7290	1.414	1.031	2.790 (42°)
120	0.7220	1.272	0.919	
130	0.7152	1.140	0.815	
140	0.7082	1.034	0.732	
150	0.7014	0.946	0.682	
160	0.6946	0.88	0.61	
170	0.6877	0.82	0.56	
180	0.6809	0.76	0.52	
190	0.6739	0.70	0.47	
200	0.6668	0.65	0.44	
210	0.6595	0.61	0.40	
220	0.6521	0.57	0.37	
230	0.6451	0.54	0.35	
240	0.6382	0.49#	0.32	
250	0.6310	0.45#	0.29#	
260	0.6239	0.41#	0.26#	
270	0.6171	0.38#	0.23#	
280	0.6101	0.34#	0.21#	

Accuracy - approx. ±0.005 in range 30°- 150°
±0.01 in range 150°- 250°

These figures are unreliable, as the sample could not be measured without charring.

TABLE XI

Viscosity of Hexacosane ($C_{26}H_{54}$)

General equation in the A.S.T.M. form:

$$\log \log (\nu + 0.8) = -3.24 \log T - 0.883$$

where ν is the kinematic viscosity in centistokes
T is the absolute temperature

(Constants were obtained by method of selected points)

t°C	Density d	Kinematic visc. ν cs.	Dynamic visc. $\eta = \nu d$ cp.	η cp. (others)
60	0.7788	6.383	4.971	
70	0.7724	5.277	4.076	Schmidt[25]
80	0.7659	4.370	3.346	5.109 (60°)
90	0.7593	3.695	2.843	1.790 (120°)
100	0.7529	3.197	2.407	
110	0.7463	2.745	2.048	
120	0.7398	2.388	1.767	
130	0.7332	2.134	1.564	
140	0.7266	1.907	1.385	
150	0.7200	1.699	1.224	
160	0.7136	1.53	1.09	
170	0.7070	1.41	0.99	
180	0.7004	1.28	0.90	
190	0.6939	1.19	0.82	
200	0.6861	1.10	0.76	
210	0.6794	1.02	0.69	
220	0.6725	0.95	0.64	
230	0.6653	0.87	0.58	
240	0.6585	0.82	0.54	
250	0.6512	0.77	0.50	
260	0.6442	0.72	0.47	
270	0.6370	0.70	0.44	
280	0.6299	0.68	0.43	

Accuracy - approx. ±0.005 in range 60°- 150°
±0.01 in range 150°- 250°
±0.02 in range 250°- 280°

Viscosity - temperature curves for Hexacosane and Octadecane

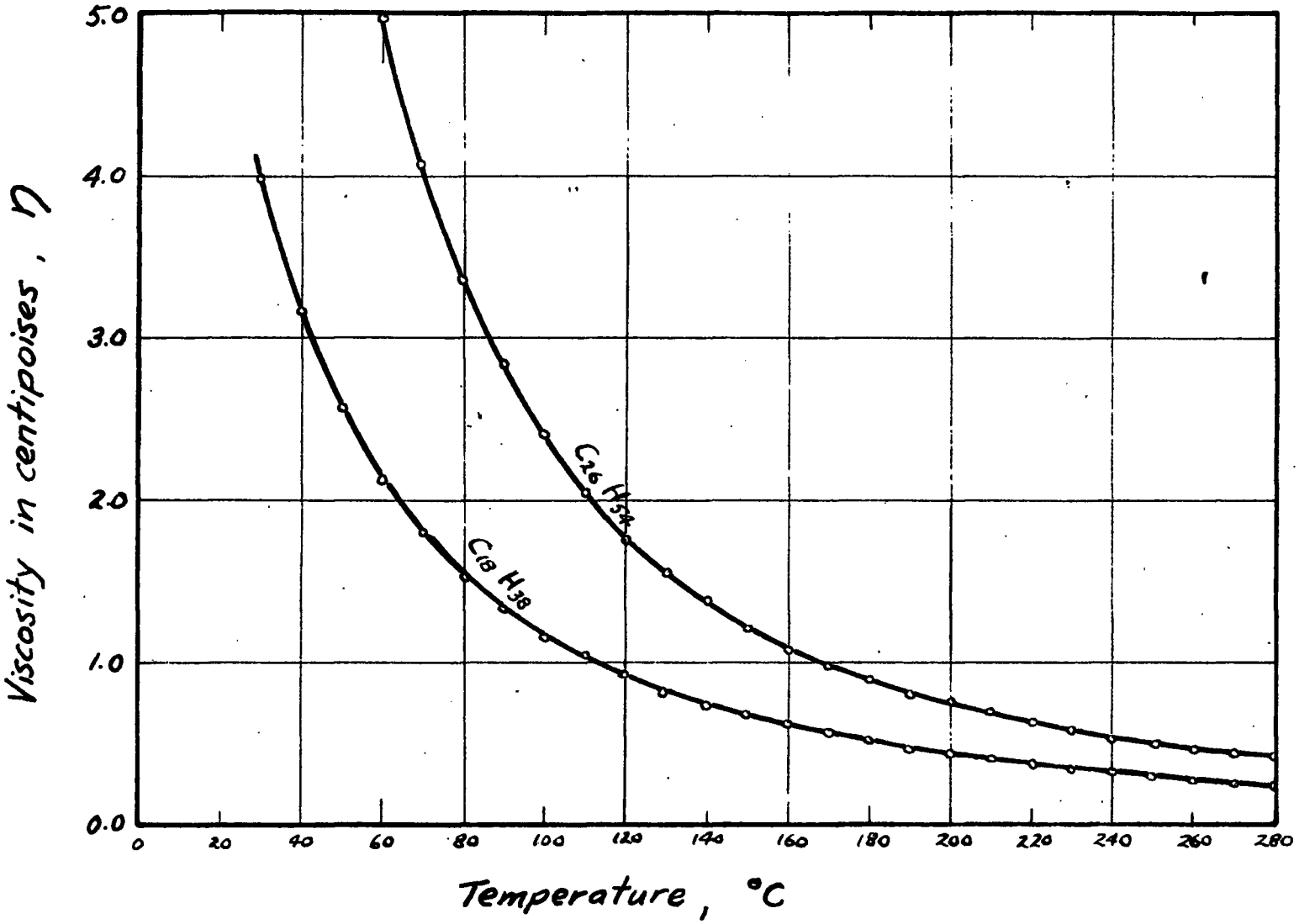


FIGURE X

Plot of $\eta = Ae^{-b/T}$ for Hexacosane and Octadecane

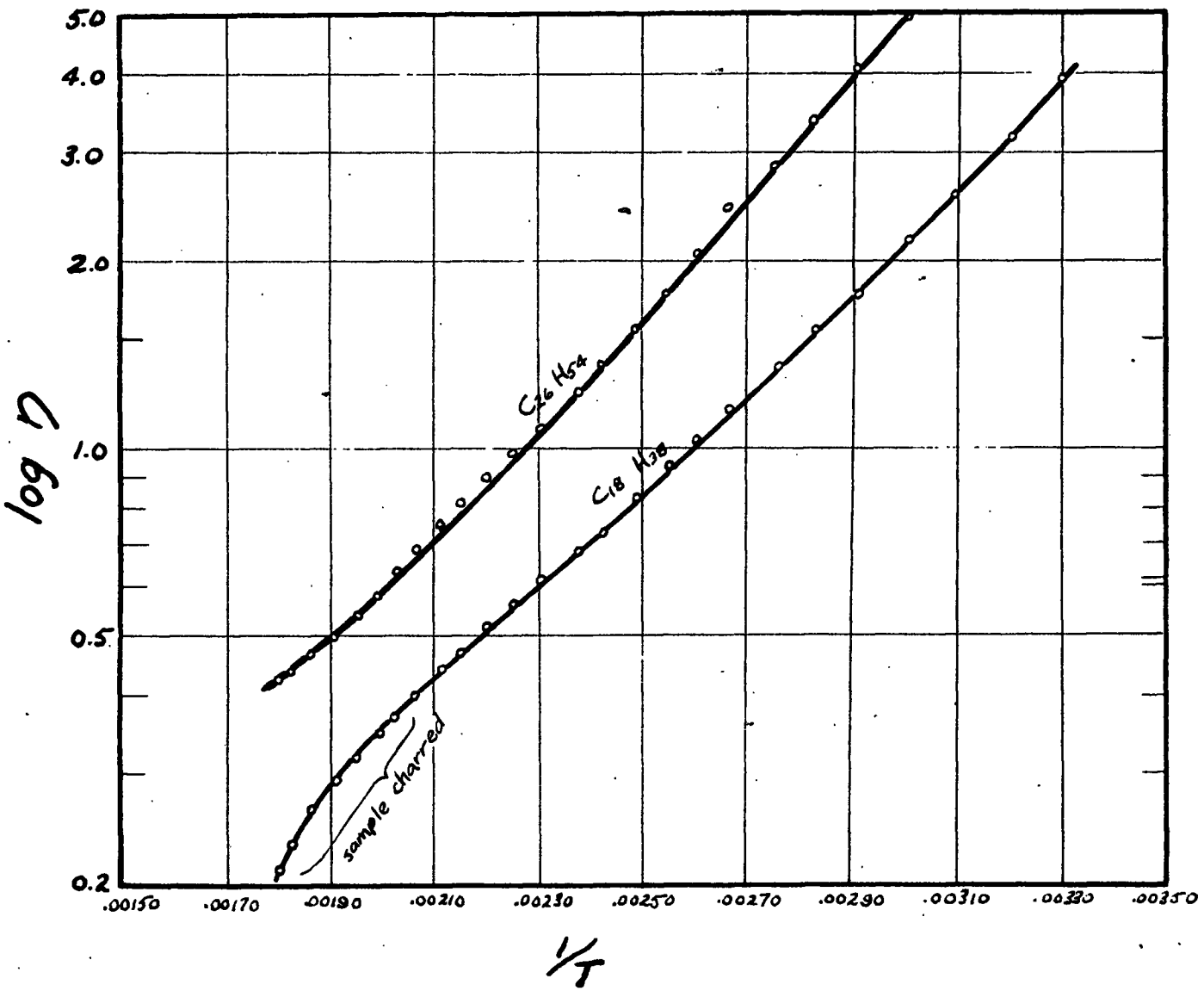


FIGURE XI

Plot of A.S.T.M. Equation
$\log \log (\nu_T + 0.8) = A \log T + B$
for Hexacosane and Octadecane

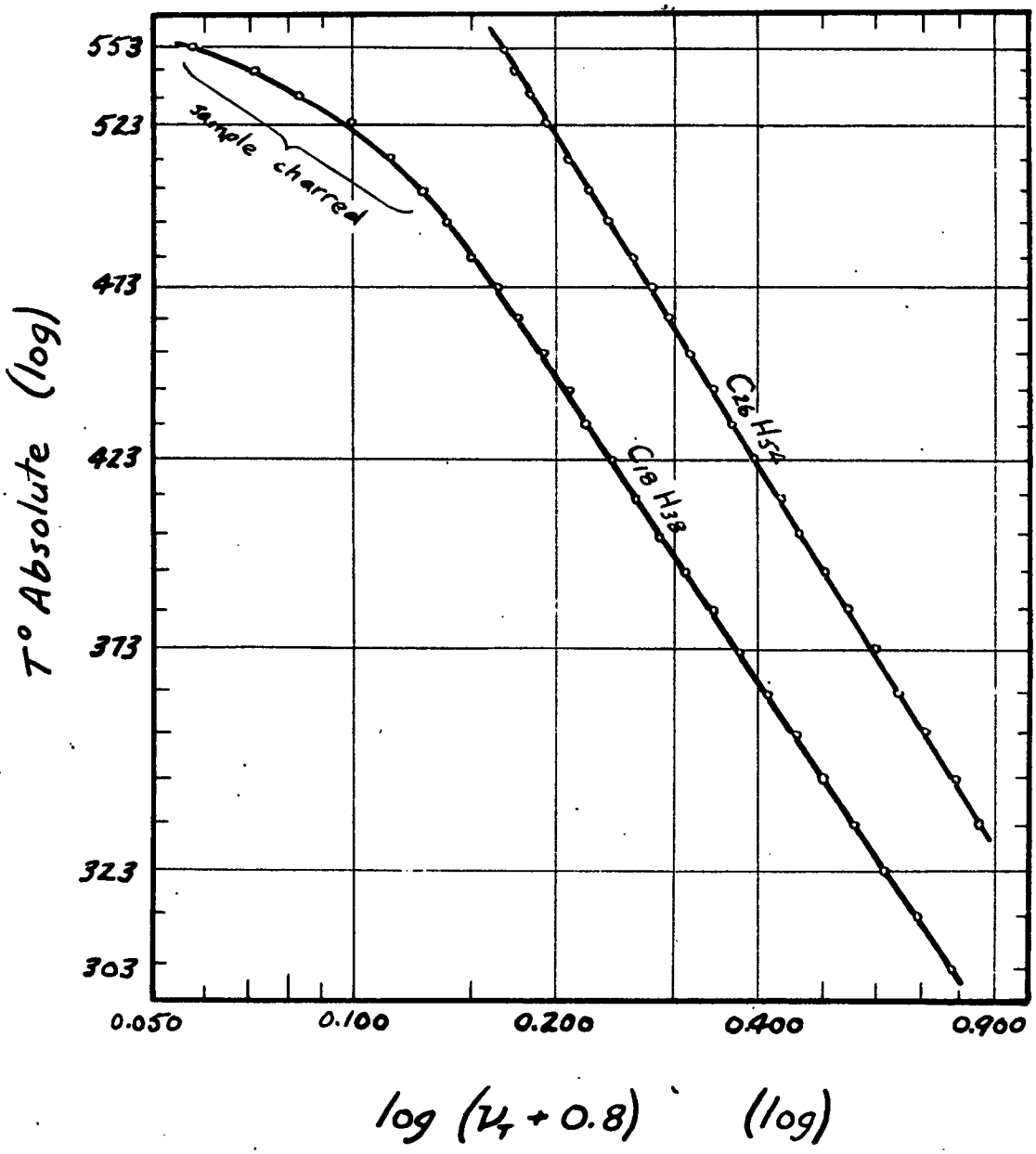


FIGURE XII

In the A.S.T.M. Equations the best "α" was found by experiment in both cases to be 0.8, which is the standard value for all petroleum oils. The constants A and B were determined by the method of selected points, and may be slightly different than if determined by least squares.

Nissan's Viscosity-Temperature Relationships:

Nissan[33] showed the relationship between the viscosities of all liquids, associated and unassociated, in a very comprehensive article. He points out that the graph of $\eta = A\ e^{-b/T}$ is not a straight line since "b" varies with temperature. He suggested that $T_{b.p.}/T$ (or T_B/T) is a fundamental function for considering dynamic properties, and that "b" in the above equation is the same function of T_B/T for all the normal paraffins. Thus plotting T_B/T against $\log\eta$ gives a "specific viscosity curve" for the homologous series.

He showed that all series of liquids or individual liquids would give similar curves which could be related in a simple equation to the "specific curve" of the paraffins. He proposed that for any liquid, for the same T_B/T:

$$\log(\eta_\ell) = C + D \log(\eta_p)$$

where η_ℓ = viscosity of liquid considered

η_p = viscosity of the paraffins.

Thus knowing any two experimental values of η_ℓ, the viscosity of any liquid can be calculated over a wide temperature range. He used the paraffins as the basis for

all the liquids since the values for η_p for each T_B/T are accurately known over a wide range.

Since he used the paraffins as a basis, but had data on no higher member in the series than $C_{18}H_{38}$, and that only to 100°C, it was thought to be of interest to see how these results over a wide temperature range compared with his specific curve. A plot was therefore made of T_B/T against log of viscosity in centipoises for the results for hexacosane and octadecane. (See Figure XIII). Then all the available data for the lower members of the series, taken from The Texas Company's "Physical Constants"[27], were surimposed on the same graph. The results were remarkably good, as can be seen.

No attempt was made to test Nissan's equations. The graph (Figure XIII) indicates good agreement, and a check on Nissan's values for η_p for T/T_B from 0.50 to 0.99 shows close agreement throughout. Since η_p has been determined very accurately for the lower paraffins, this work would not change the result, although it definitely strengthens them.

The boiling point of hexacosane at atmospheric pressure was obtained by applying Ramsay and Young's rule: $\frac{Ta}{T_B} = \frac{Ta'}{T_B'}$ for two substances chemically related.

The figures were again taken from The Texas Company's "Physical Constants"[27], and a correction was

Plot of log η against T_B/T for Hexacosane and Octadecane compared to other members of their homologous series.

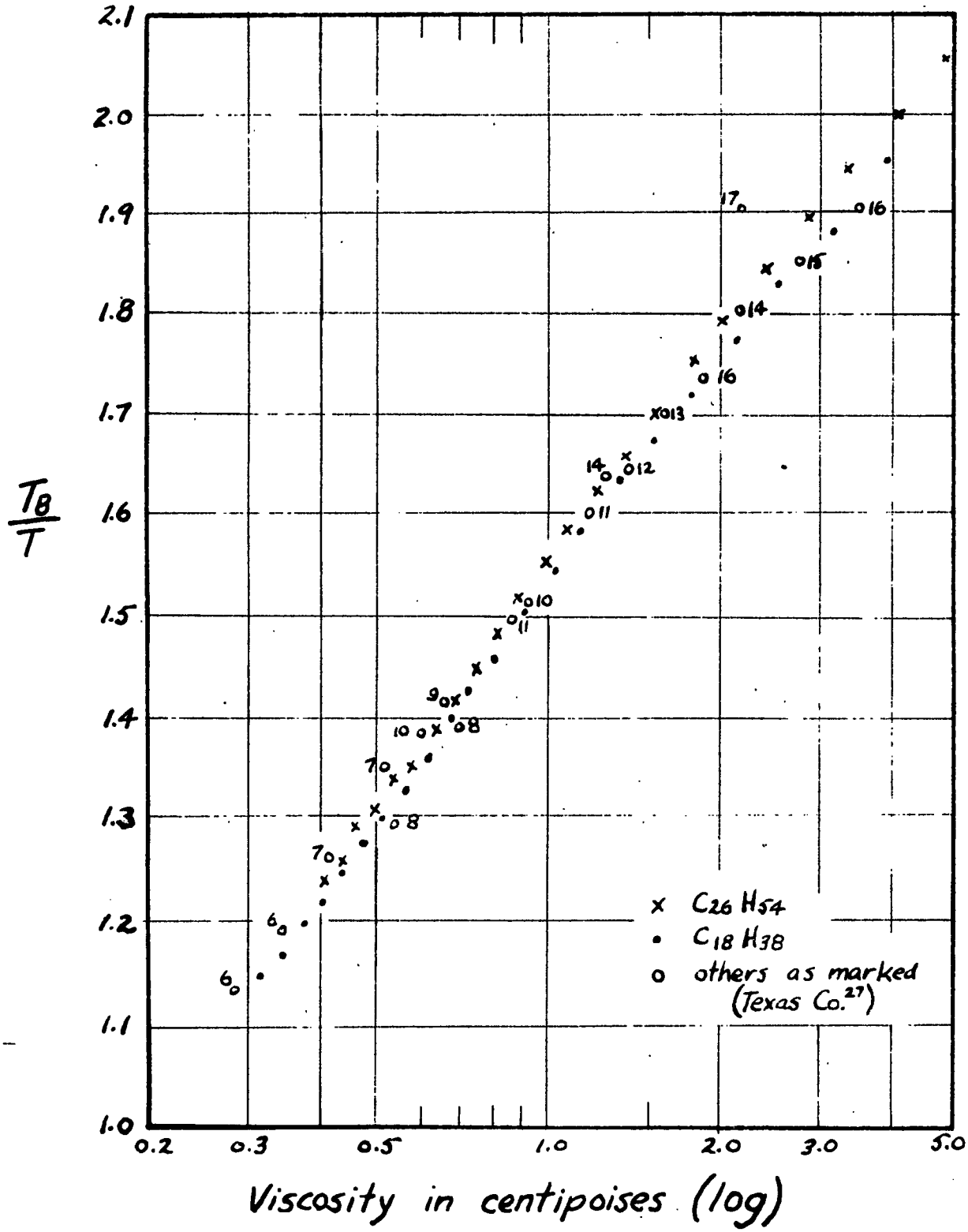


FIGURE XIII

applied, since it was found that in the normal paraffin series, as the members of the series become further removed from the desired member, the equation gives a higher and higher b.p. for that member. Since the rise in b.p. appeared to progress regularly, the equation was applied to several members than extrapolated to zero distance from hexacosane.

This method gave a boiling point of 413°C at atmospheric pressure for hexacosane. The results appear to have justified the method.

Viscosity-Surface Tension Relationships:

An attempt was made to find a straight-line relationship between the viscosity and the surface tension of the paraffins investigated.

The equation of Sharma[34], as reported in Chemical Abstracts:

$$\log \gamma = M \log \mu + C$$

did not hold for either kinematic viscosity (ν) or dynamic viscosity (η). Similarly, the equation of Silverman and Roseveare[35]:

$$\gamma^{-\frac{1}{4}} = (A/\eta) + B$$

did not give a straight line. The equation of Bueller[36]:

$$\log_{10}\log_{10}(\eta_{mp}) = 1.22\gamma^{\frac{1}{4}} - 2.9$$

or with adjustable constants as reported in the Chemical Abstracts as recommended by Tripathi[37]:

$$\log\log\eta = m\gamma^{\frac{1}{4}} + C$$

was then plotted. (Figure XV). It did not give a straight line over the whole range, but definitely showed possibilities. To investigate it further, it was first necessary to consider the validity of Souder's[38] viscosity-density relationships on which it was based.

Souder plotted the $\log_{10}\log_{10}$ of η in millipoises at constant pressure against the density in grams per cc of a great many liquids, and obtained a linear relationship over the intermediate ranges, with increasing curvature near the m.p. and b.p. In the straight-line regions, therefore:

$$\log\log(\eta_{mp}) = md + C$$

He found the two constants to be the same for most of the liquids, with "m" approximately 3.95 and C = -2.9 He then formed a "viscosity-constitutional index" I = m M (where M is the molecular weight), and found it could be treated in the same manner as the Parachor, and be built up with good accuracy from equivalents and increments.

His equations were tested, and found to hold well in ranges up to 100°C (Figure XIV); but the values obtained for "m" were in both cases larger than those expected. These values also increased markedly with

temperature, unlike the values for the lower homologs which Souder considered. Again, the comparison of the observed viscosity-constitutional index "I" with his calculated "I" was good only as long as we stay in the restricted range.

This agrees with his work in one sense; but it also agrees with Srinivasan and Prasad[41], who state that Souder's equation does not apply accurately even to unassociated organic liquids for the entire range for which measurements have been made. Since a comprehensive equation was desired to relate η and γ, it was decided to modify Souder's equation to give a linear relationship, and see what results could be obtained. The modification was not difficult, since the log of a log is a very powerful method of graphing, and a straight line can be forced in many different ways. Care must be taken, however, to see that the term that is logged twice be greater than 1.0 over all practical ranges, since if it is between 0 and 1.0 a complex number results.

The first attempt was to form an equation of the type:

$$\log \log (\eta_{mp} + \alpha) = md + B$$

Straight lines were obtained with

$\log \log (\eta_{mp} - 1.2) = 3.58\ d - 2.56$ for hexacosane, and $\log \log (\eta_{mp} - 0.2) = 3.54\ d - 2.57$ for octadecane.

This type of equation shows definite possibilities

because of the similarity of the two constants m and B; but it is awkward having a variation in "α", and millipoises are not the units used practically. Therefore centipoises were substituted, and straight lines were obtained with

$$\log \log (\eta_{cp} + 0.8) = 6.46\ d - 5.15 \text{ for hexacosane,}$$

and

$$\log \log (\eta_{cp} + 0.8) = 7.55\ d - 6.07 \text{ for octadecane.}$$

(See Figure XIV).

These showed more promise because of the constancy of "α", so Bueller's work was then investigated with this in mind.

Bueller[36] utilized the facts that the Parachor, $[P] = \frac{M\gamma^{\frac{1}{4}}}{d}$, is constant over a wide range, and that Souder's viscosity-constitutional index, $I = m\ M$ is also constant; and he combined them to form the equation:

$$\log_{10} \log_{10} \eta_{mp} = A\gamma^{\frac{1}{4}} + B$$

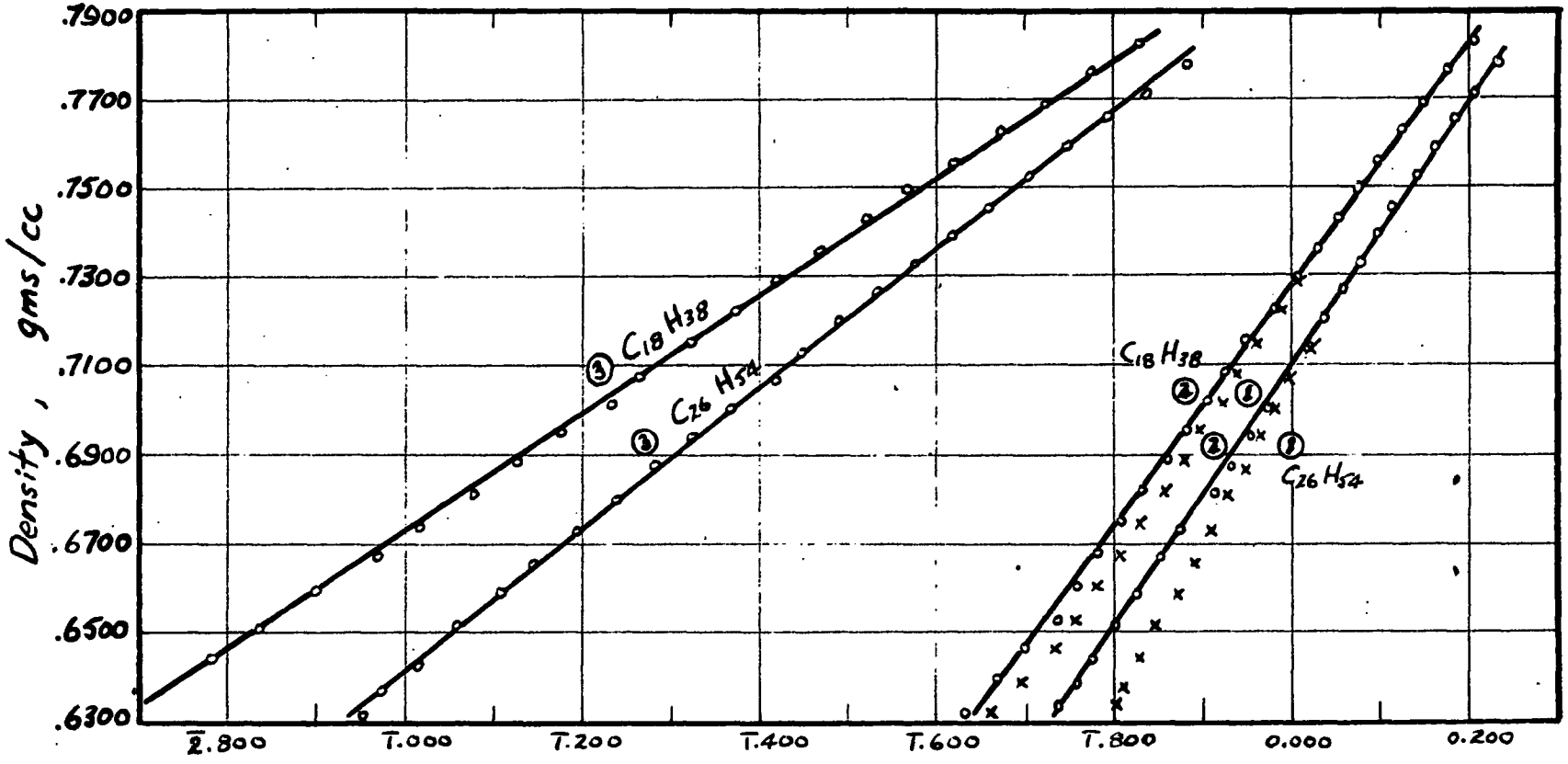
This equation naturally falls down where Souder's work falls down, and is hence only applicable to the lower homologs and to particular temperature ranges. For example, he found that I/P = 1.2, but suggested there was a tendency for I/P to increase as the carbon chain lengthens. In both cases observed, I/P was found to have a value of approximately 1.3, which is somewhat higher.

FIGURE XIV

Plot of Souder's Equation : $\log_{10}\log_{10}(\eta_{mp}) = md + A$ ①

with $\log_{10}{}^{\circ}\log_{10}(\eta_{mp} + \alpha) = md + B$ ②

and $\log_{10}\log_{10}(\eta_{cp} + \beta) = cd + D$ ③



$\log_{10}\log_{10}$ scale

For C_{18} — $\alpha = -0.2$
For C_{26} — $\alpha = -1.2$
For both — $\beta = +0.8$

Bueller's equation when plotted was found, as expected, to hold for only part of the region investigated. (See Figure XV). An adjustment was therefore made similar to the one made on Souder's equation, and straight line relationships were obtained as follows:

$$\log \log (\eta_{mp} - 1.2) = 1.41\gamma^{\frac{1}{4}} - 3.02$$ for hexacosane, and

$$\log \log (\eta_{mp} - 0.2) = 1.20\gamma^{\frac{1}{4}} - 2.59$$ for octadecane.

These were considered to be too awkward for any use, having three variable constants, so centipoises were again substituted, and the results were

$$\log \log (\eta_{cp} - 0.8) = 2.49\gamma^{\frac{1}{4}} - 5.86$$ for hexacosane, and

$$\log \log (\eta_{cp} - 0.8) = 2.55\gamma^{\frac{1}{4}} - 6.09$$ for octadecane. (See Figure XV). All constants were obtained by the method of selected points.

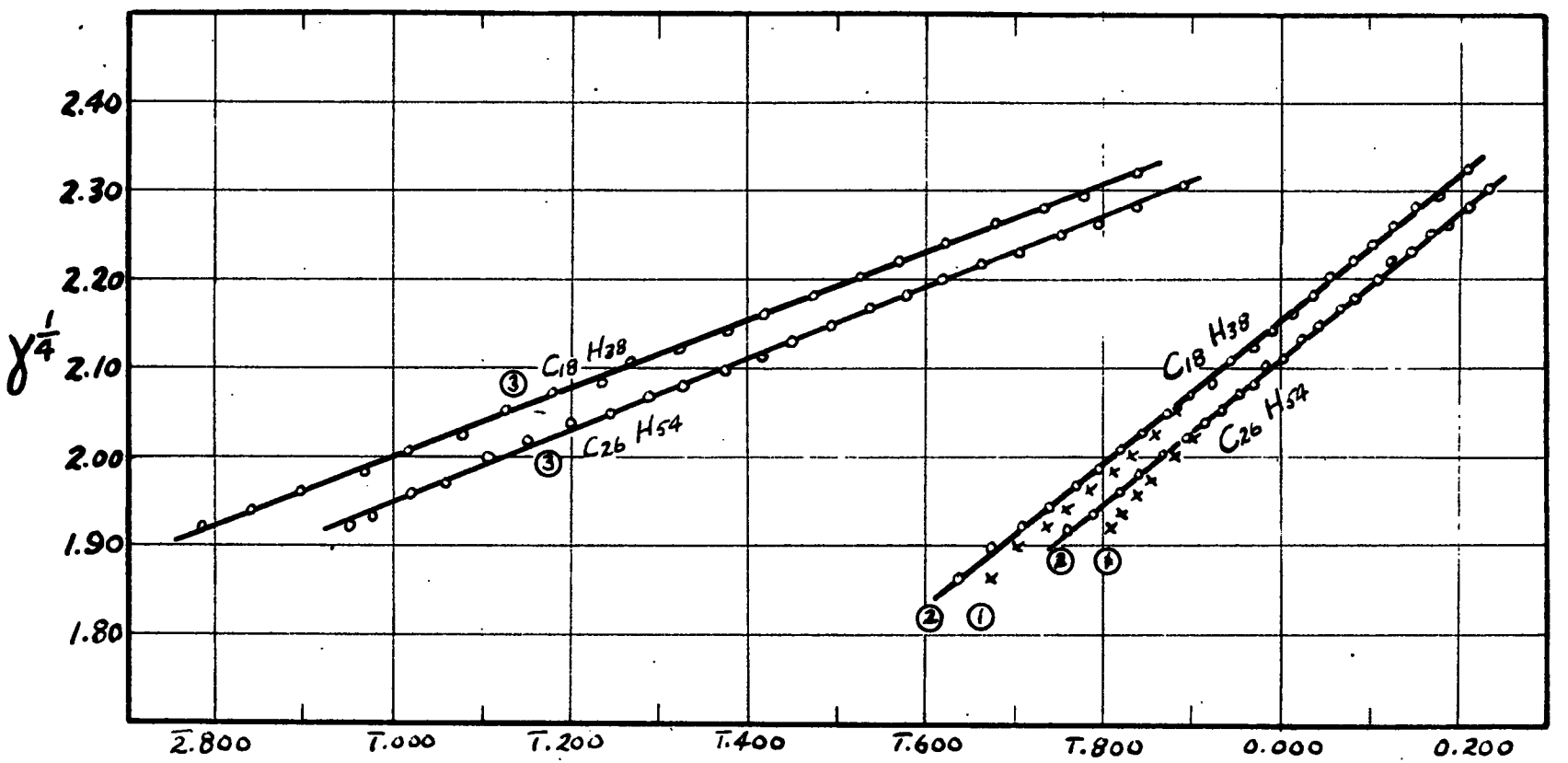
Three constant equations are ordinarily undesirable as too cumbersome for practical use; but the similarity of the constants in these two equations, and the fact that they hold over such a wide range of temperature for two normal unassociated liquids warrant their consideration.

FIGURE XV

Plot of Bueller's Equation : $\log_{10}\log_{10}(\eta_{mp}) = A\gamma^{\frac{1}{4}} + B$ ①

with $\log_{10}\log_{10}(\eta_{mp} + \alpha) = C\gamma^{\frac{1}{4}} + D$ ②

and $\log_{10}\log_{10}(\eta_{cp} + \beta) = E\gamma^{\frac{1}{4}} + F$ ③



$\log_{10}\log_{10}$ scale

For C_{18} — $\alpha = -0.2$
For C_{26} — $\alpha = -1.2$
For both — $\beta = +0.8$

The equation:

$$\log_{10} \log_{10} (\eta_{cp} + \alpha) = C\gamma^{\frac{1}{4}} + D$$

may well be the best existing equation relating viscosity and surface tension at equal temperatures.

Further investigation in the homologous series may indicate there is a simple relationship between the constants. The closeness of the slope of the two equations and the identical constants ($\alpha = 0.8$) cannot be chance. It also should be noted that Nissan's work, previously discussed, shows that the viscosity of all the normal paraffins at their b.p. at atmospheric pressure is 0.21 cp. Thus $\log_{10} \log_{10} (\eta + \alpha)$ will never be a complex value for the paraffins, since $\alpha = 0.8$, and $(\eta + \alpha)$ will always be greater than 1.0 for the entire ranges at atmospheric pressure. This may be of fundamental significance.

Other Relationships:

No attempt was made to relate viscosity and vapour pressure with the observed results. Since most of the existing relationships, such as those of Othmer[39] and Madge[40], depend on the Arrhenius equation:

$$(1/\eta) = A e^{B/RT}$$

and since in the plot of $\log \eta$ against $1/T$ as suggested by Andrade (Figure XI) the results were as to be expected (slight convexity to the $1/T$ axis), further investigation would probably only have substantiated the existing relationships without adding to them.

Higher homologs of a series usually follow two curves, one for the even and one for the odd; and there may be periodic discontinuities. Since only three even members of this series were investigated, little comparison can be made in this respect. Seyer, et al,[5] found $C_{29}H_{60}$ definitely in a different series than the evens with respect to behaviour near the melting point. Nissan's relationships, however, (See Figure XII and discussion), definitely show the lower odd members up to $C_{15}H_{32}$ to be in step with the evens. Whether the value given for $C_{17}H_{36}$ is in error, or whether it is the start of a new odd series through $C_{29}H_{60}$ is a question for further investigation.

Seyer, et al,[5] also found that $C_{24}H_{50}$ exhibited some anomalous characteristics, and possibly was the start of a discontinuity in the even series. It definitely appears to start a discontinuity in the behaviour of the even solids; but this investigation has not shown any break in liquid properties between the lower members of the series and $C_{26}H_{54}$. Again, further investigation is necessary.

SUMMARY

(1) The densities and surface tensions of C_{18}, C_{24}, and C_{26} and the viscosities of C_{18} and C_{26} were measured from their melting points to 280°C.

(2) The limit in taking such measurements was found to be 280°C, because of the characteristics of available bath liquids and because of the charring of the samples at this temperature.

(3) Equations were calculated for the temperature coefficients of the densities over the observed range.

(4) Equations in the form of Ramsay and Shields were calculated for the molar surface energies over the observed range.

(5) The values of the Parachors were found to be reasonably constant and to check closely with calculated values over the observed range.

(6) Equations in the A.S.T.M. form were calculated for the viscosities over the observed range, and were found to give good, straight-line relationships.

(7) Nissan's relationship of T_B/T to log η was tested over a much larger range than he previously had available to test. It checked very well.

(8) The boiling point of hexacosane was calculated to be 413°C at atmospheric pressure. This figure was checked by applying it in Nissan's relationships.

(9) Bueller's equation: $\log \log \eta_{mp} = C\gamma^{\frac{1}{4}} + D$ was modified to $\log_{10} \log_{10} (\eta_{cp} + 0.8) = A\gamma^{\frac{1}{4}} + B$, and was found to give such excellent results for C_{18} and C_{26} that its further investigation is recommended. This modification is the only known relationship between surface tension and viscosity to hold over complete liquid ranges from m.p. to b.p.

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APPENDIX

RECOMMENDATIONS FOR FUTURE WORK

(1) Investigators following this work should be warned of the danger of the paraffin bath in the region 250°C to 280°C. It flashes very easily in this temperature range, and sustained burning is difficult to prevent. The bath should be as completely enclosed at the top as possible, with holes only for stirring, adjusting the viscometer level, and tilting the capillarimeter. Fire extinguishing equipment, preferably of the foam type, should be at hand during a run. Externally-wound heating elements rather than immersion heating was attempted to eliminate hot spots, but it did not help at all. The wax flashes.

(2) In future, all paraffin samples investigated should be purified by recrystallization within a month before they are used. Only in this way can their absolute purity be guaranteed. Freezing and setting point determinations are not sufficiently accurate criteria, because of the formation of isomers that may behave similarly.

(3) A precision electronic timer is a definite necessity for accurate viscosity determinations, for reasons discussed in the body of this thesis. Steiner[15] gives the address of an English manufacturer of such timers. American manufacturers also make them. (See Fry and Baldeschweiler[13] and Penther and Pompeo[14]). It should be noted that a timer

is needed with a precision of only 1/100 of a second, but with a capacity to work to 2000 or 3000 seconds for general usefulness around the laboratory. Electronic timers are made with a great range of precision and of total-time capacity.

(4) The use of American types of viscometers should be investigated. Cannon and Fenske[12] report very low Kinetic Energy errors with their "master viscometers" and describe many useful types of viscometers in detail. In particular, their micro-viscometer, which requires as little as 0.25 cc of the substance for accurate work, is of interest, as the British viscometers require a considerable amount of the sample, and the high temperatures ruin it all. Viscosity measurements could not be taken on C_{24} because of the lack of pure material, yet there were at least 2 cc of it on hand.

(5) Water should be used as a bath liquid up to $90^{0}C$, and the bath dried as well as possible afterwards. Its advantages far outweigh its disadvantages. Possibly the wood block inside could be replaced by an all-metal block to facilitate drying the bath out.

(6) A small bath made of 70-mm pyrex tubing with 500-watt externally-wound heating wires and standard magnesia pipe insulation around it was tested for use at very high temperatures. It was found to be not big enough for the viscometer or capillarimeter, but held a dilatometer nicely. Temperatures inside can be controlled reasonably well by stirring and by varying the resistance in the heating circuit. It was particularly good for testing bath liquids at high temperatures.

(7) Nissan's[33] work appears to be very fundamental, and further viscosity determinations with the normal paraffins should be related to it.

(8) The modification as described of Bueller's equation relating viscosity and surface tension appears to have enough merit to warrant further investigation.