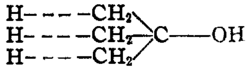
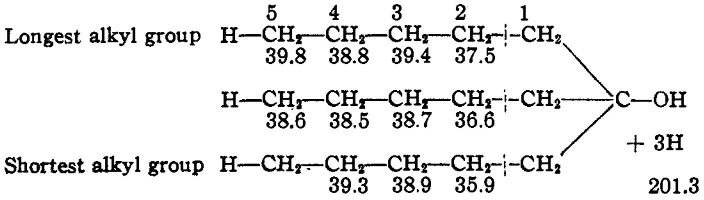


to be the determined value 201.3 of *t*-butyl alcohol, the parachor of any tertiary alcohol may be estimated by adding the CH_2 values for the various positions as given in Table II.

TABLE II

POSITION VALUES OF CH_2 IN PARACHORS OF TERTIARY ALCOHOLS



For example, the parachor for methylethyl butylcarbinol would be calculated by adding the values shown below.

t-butyl alcohol	201.3
butyl group	
1st CH_2 included in *t*-butyl linkage	——
2nd CH_2	37.5
3rd CH_2	39.4
4th CH_2	38.8
ethyl group	
1st CH_2 included in *t*-butyl linkage	——
2nd CH	36.6
methyl group included in *t*-butyl linkage	——
	353.6

Values for CH_2 units further removed from the —OH group than the amyl position may be considered constant at 40.0. It should be remembered in the use of this table that the actual value of the CH_2 is, in all cases, considered to be essentially a constant, 40.0. The values in the table to be added in calculation represent the sum of two factors; the increase of the added CH_2 minus the effect of increasing the carbon chain upon the $>$C——OH group. Also, each position value is only an average of values which (by the fundamental assumption of variation with different attached groups) would not be expected to be identical.

Summary

1. The refractive indices, densities, surface tensions, and parachors of nine additional tertiary alcohols have been reported for three temperatures.
2. The experimental values for the parachor have been shown to be in close agreement with the calculated values.
3. A table for the estimation of parachors for tertiary alcohols has been given.
4. Modifications in the bubbler for determining surface tension more accurately and rapidly have been described.

EMORY UNIVERSITY, GEORGIA

RECEIVED FEBRUARY 10, 1944

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF EMORY UNIVERSITY]

A Study of Organic Parachors. VII. A Series of Saturated Hydrocarbons[1]

BY OSBORNE R. QUAYLE, R. A. DAY AND GEORGE M. BROWN[2]

The parachor is one of the more useful constants in the correlation of the physical properties of organic compounds and their structures. The parachor, first considered an additive property, has been found to be susceptible to minor as well as to gross variations in structure. It is particularly so to any variations in the degree of unsaturation of the molecule. The parachor values in normal saturated hydrocarbons have been found to be almost unique in being additive in nature.[3] In calculating the values of other groups the alkyl residues are, therefore, considered to be of known value and are subtracted from the observed parachors determined for the whole compound. It is essential, therefore, that the validity of the accepted parachor value for the CH_2 increment in the saturated hydrocarbons be reëxamined from time to time as compounds of higher purity become available and as the techniques of measurement are improved.

Sugden,[4] the original worker in the field, upon examination of several series of various types obtained the values of 39.0 for CH_2, 17.1 for H, and 4.8 for C. Mumford and Phillips,[5] limiting their calculations to series of the same type, established the values: $CH_2 = 40.0$, $H = 15.4$, $C = 9.2$. Vogel,[6] studying esters and alkyl halides arrived at the values: $CH_2 = 40.3$, $H = 14.4$, and $C = 11.5$. Gibling[7] asserts that the CH_2 value seems to show progressively higher values throughout any homologous series due to decreasing "interference"

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(1) The authors wish to express their gratitude to Prof. E. Emmet Reid, research consultant to the department, for his continued interest and suggestions in connection with the problem; to the American Petroleum Institute for samples of hydrocarbons; and to the University Center in Georgia for a grant for the purchase of a constant temperature bath.

(2) New York Community Trust Fellow, Emory University 1942–43; present address Princeton University, Princeton, N. J.

(3) Even the values for the saturated chains are not considered to be strictly additive by some observers. However, they are at least essentially so. If variations exist they appear to be of a distinctly lower order of magnitude for chains of short or moderate length.

(4) Sugden, *J. Chem. Soc.*, **125**, 1177 (1924).

(5) Munford and Phillips, *ibid.*, 2113 (1929).

(6) Vogel, *ibid.*, 333 (1934).

(7) Gibling, *ibid.*, 299 (1941).

effects. His formula gives somewhat better agreement between observed and calculated values for high molecular weight compounds.

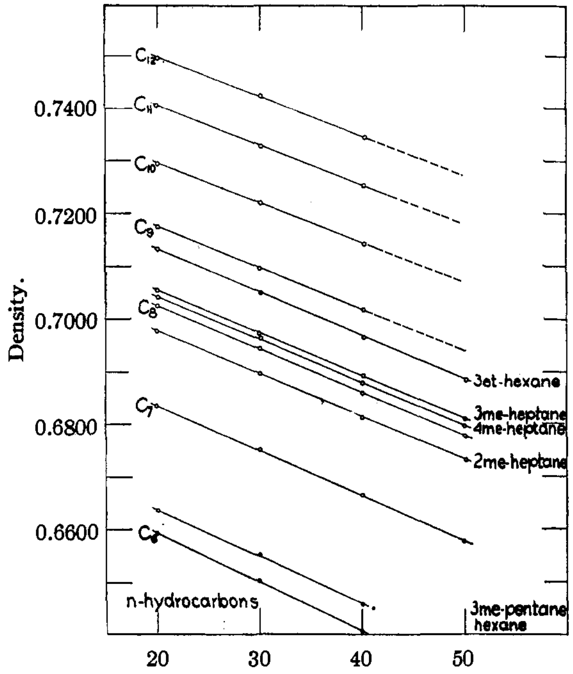

Fig. 1.—Densities of hydrocarbons.

The re-evaluation of the CH_2, C, and H values here reported is based upon the normal saturated hydrocarbons only, following the concept that variations in the apparent CH_2 value of other series are in fact variations in the values for the other non-hydrocarbon parts of the molecules. Branching the chain causes a decrease in the parachor which has been termed a strain constant. An average value of −3 for a single branching has been in general use. This does not appear to be a constant value. The hydrocarbons used in this work, with the exceptions of nonane, decane, undecane and duodecane, were prepared under the direction of Professor C. E. Boord of the Department of Chemistry of The Ohio State University as a part of the American Petroleum Institute Hydrocarbon Research Project in the Industrial Research Foundation of the University. The *n*-hexane, 2-methylpentane, 3-methylpentane and 3-ethylhexane were designated as "best liter" purity. The other A. P. I. hydrocarbons were designated as "pure." The nonane, decane, undecane, and duodecane were obtained from the Eastman Kodak Company and were refractionated. The boiling ranges of the latter samples were as follows: nonane, 148.6–148.7° at 738.0 mm.; decane, 97.8–98.4° at 69.0 mm.; undecane 108.7–109.0° at 50.5 mm.; duodecane, 66.0–66.1° at 2.3 mm.

The maximum bubble pressure method was used in the measurement of surface tension, the apparatus used being a modification[8] of that of Sugden. Surface tensions were checked by two observers. Each value reported represents a value calculated from a minimum of four observations. Where two or more values are recorded (Table I), these are entirely independent determinations made after intervening measurements, temperature changes, etc., in an endeavor to minimize any constant errors. All temperatures were maintained to within ±0.05°. The precision in the determination of surface tension was somewhat greater than one part in five hundred. The over-all precision in the determination of the parachor was in the order of one part in two thousand.

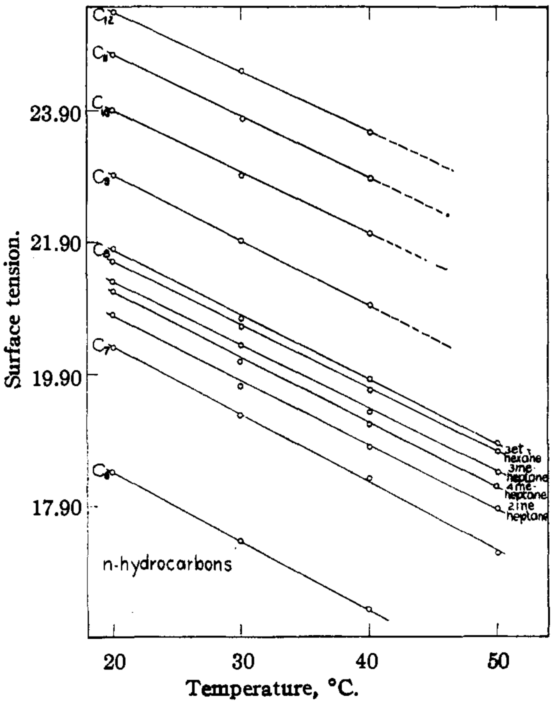

Fig. 2.—Surface tensions of hydrocarbons.

The densities and surface tensions determined are given in Table I. The parachor values were calculated by the equation $P = M\gamma^{1/4}/(D - d)$ where γ is the surface tension, M the molecular weight, D the density of the liquid, and d the density of the vapor at the same temperature. The calculated density of the vapor is relatively small and is included in the calculations only where its value is appreciable. The parachors of the normal saturated hydrocarbons and of the CH_2 increment are given in Table II. The parachors of the branched chain hydrocarbons and the values for the "strain constant" for branching are given in Table III.

The average CH_2 increment in the series of normal hydrocarbons is 40.0. There is no apparent change in this value as the chain increases within the limits here investigated. The change

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(8) O. R. Quayle and K. O. Smart, THIS JOURNAL, 66, 935 (1944).

TABLE I

DENSITIES AND SURFACE TENSIONS OF HYDROCARBONS

Alkane	Densities at 20°	30°	40°	50°	Surface tensions at 20°	30°	40°	50°
n-Pentane	0.6260				16.00			
					15.94			
					15.98			
n-Hexane	.6593	0.6502	0.6406			17.37	16.36	
						17.37	16.34	
n-Heptane	.6837	.6752	.6668	0.6580	20.31	19.26	18.33	17.24
					20.30	19.32	18.31	17.17
n-Octane	.7027	.6945	.6862	.6781	21.81	20.76	19.82	18.81
					21.78	20.74	19.85	18.83
n-Nonane	.7175	.7097	.7020		22.92	21.91	20.96	
					22.91	21.91	20.97	
						21.95		
n-Decane	.7295	.7221	.7145		23.92	22.91	22.05	
					23.92	22.92	22.04	
n-Undecane	.7406	.7330	.7256		24.72	23.80	22.88	
					24.70	23.77	22.88	
n-Duodecane	.7496	.7423	.7349		25.39	24.50	23.58	
					25.42	24.51	23.59	
					25.41			
2-Methylheptane	.6978	.6897	.6816	.6733	20.81	19.72	18.80	17.87
					20.81		18.80	17.88
3-Methylheptane	.7055	.6974	.6892	.6811	21.32	20.35	19.31	18.40
					21.30	20.33	19.38	18.46
4-Methylheptane	.7042	.6962	.6881	.6799	21.16	20.11	19.15	18.25
					21.14	20.07	19.13	18.21
3-Methylpentane	.6639	.6550	.6460		18.10	17.10	16.05	
					18.14	17.10	16.01	
						17.06		
						17.05		
						17.09		
3-Ethylhexane	.7134	.7051	.6969	.6887	21.62	20.61	19.67	18.73
					21.62	20.61	19.64	18.69

TABLE II

PARACHOR VALUES OF NORMAL HYDROCARBONS

Alkane	Parachor at 20°	30°	40°	50°	CH_2 at 20°	30°	40°	50°	CH_2, ave.
Pentane	231.0*4*								
Hexane	270.8*4*	270.7*0*	270.8*0*		39.8				39.8
Heptane	311.3*4*	311.2*1*	311.3*6*	310.5*8*	40.5*0*	40.5*1*	40.5*6*		40.5
Octane	351.1*3*	350.9*6*	351.2*8*	351.0*0*	39.7*9*	39.7*5*	39.9*2*	40.4*2*	39.8
Nonane	391.1*4*	391.0*9*	390.9*9*		40.1*0*	40.1*3*	39.7*1*		40.0
Decane	431.2*4*	431.1*4*	431.4*8*		40.1*0*	40.0*5*	40.4*9*		40.2
Undecane	470.5*6*	470.8*6*	471.0*8*		39.3*2*	39.7*2*	39.6*0*		39.5
Duodecane	510.1*4*	510.7*6*	510.8*6*		39.5*8*	39.9*0*	39.7*8*		39.8

Av. CH_2, 39.9 at 20°, 40.0 at 30°, 40.0 at 40°, over-all average 40.0

of parachor over the range of temperature studied is in no case over 0.15%. The maximum deviation from the average obtained for any calculated CH_2 increment is 1.7%; for any single compound 1.3%. It should be noted that while the value for CH_2 of 40.0 is identical with that reported by Mumford and Phillips,[5] (based on determinations of Hunten and Maass[9] primarily upon fatty acids) the value reported in the earlier work was obtained by averaging values which differed from each other by as much as 22%. Calculation from each determination of the present study gives an average atomic parachor value for H of 15.5; for C the value is 9.0.

The effect of branching the chain in the compounds studied is not uniform. The effect is increased as the branch is moved toward the center of the chain, and as the length of the branch chain is increased. Among the compounds here measured the effect is greatest in 3-ethylhexane, which has, obviously, the most symmetrical compact molecular structure. Since the parachor is a volume factor it might be expected that

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(9) Hunten and Maass, THIS JOURNAL, 51, 153 (1929).

Table III

Parachor Values of Branched Chain Hydrocarbons

Alkane	P, n-isomer	P, exp.	Strain per branch
2-Methylheptane	351.0	349.4	−1.6
3-Methylheptane	351.0	347.7	−3.3
4-Methylheptane	351.0	347.6	−3.4
3-Ethylhexane	351.0	345.0	−6.0
3-Methylpentane	271.0	267.9	−3.1
Calculated from previously recorded data			
3-Ethylpentane	311.0	304.2	−6.8
2-Methylhexane	311.0	309.1	−1.9
3-Methylhexane	311.0	307.3	−3.7
2,5-Dimethylhexane	351.0	347.2	−1.9
2,4-Dimethylhexane	351.0	344.9	−3.1
2,3-Dimethylhexane	351.0	344.1	−3.5
3,4-Dimethylhexane	351.0	342.6	−4.2
2,4-Dimethylpentane	311.0	307.5	−1.8
2,3-Dimethylpentane	311.0	304.3	−3.4
2,5-Dimethylheptane	391.0	384.9	−3.1
2,4-Dimethylheptane	391.0	381.1	−5.0
2,3-Dimethylheptane	391.0	373.1	−9.0
2,7-Dimethyloctane	431.0	426.4	−2.3
2,4-Dimethyloctane	431.0	422.9	−4.1

the most compact structure would have the lowest parachor. The same effect may be noted in parachor values calculated from previously recorded densities and surface tensions of hydrocarbons.[10] These values are also included in Table III. While certain regularities appear, sufficient data are not available to properly evaluate the variations in the effect of branching the chain.

Summary

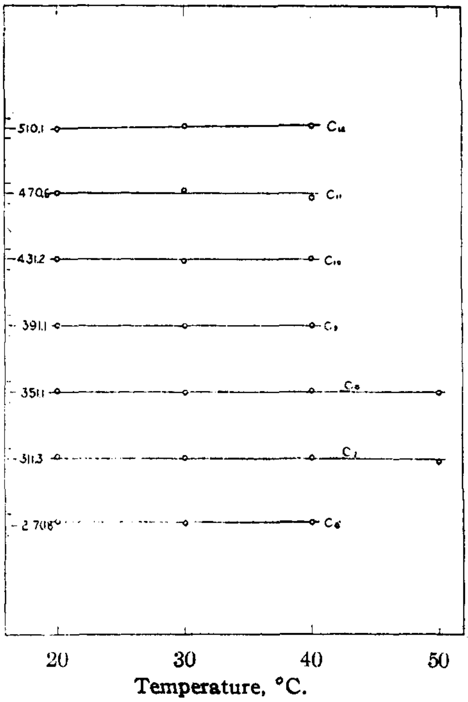

Fig. 3.—Parachors of normal hydrocarbons.

1. The densities, surface tensions, and parachors of a series of hydrocarbons of high purity have been reported.
2. The parachor value of the CH_2 group is reported as 40.0. The atomic parachor of H is reported as 15.5, that of C as 9.0.
3. There is no apparent change in the CH_2 increment as the chain is increased up to duodecane.
4. The effect of branching the chain is not constant in the saturated hydrocarbons

Emory University, Ga. Received February 10, 1944

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[10] M. P. Doss, "Physical Constants of Principal Hydrocarbons," Third Edition, Texas Corp., 1942.

[Contribution from the Charles E. Coates Chemical Laboratory, Louisiana State University]

A Spectrographic and Kinetic Study of the Alkaline Fading of Tetraiodophenolsulfonphthalein

By Edward S. Amis and Ralph Theodore Overman

The alkaline form of iodo phenol blue (tetraiodophenolsulfonphthalein) has a characteristic absorption curve the intensity of which is a function of the amount of the dye present in the blue form. If an excess of the alkaline hydroxide is added to a solution of the iodo phenol blue, the dye fades to a colorless condition. The rate of fading depends upon the concentration of hydroxide present. When the colorless solution is acidified, the characteristic yellow acid form of iodo phenol blue develops progressively with time. This regeneration reaction has been studied quantitatively in the case of the brom phenol blue.[1] It is possible to study the structure of the faded and unfaded form of the dyes both spectrographically and kinetically.

In this investigation a spectrographic study was made of both the unfaded and regenerated tetraiodophenolsulfonphthalein to determine whether the two were identical. A kinetic study of the fading process in the presence of iodide salt also was made. By these methods it was hoped that definite conclusions could be reached as to the validity of proposed mechanisms for the fading and regeneration processes.

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[1] Amis and Price *J. Phys. Chem.*, **47**, 338 (1943).