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Densities and Refractive Indices of Unsaturated Hydrocarbons

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This paper, dealing with densities (in g./cc.) and refractive indices (for the sodium D lines) of unsaturated aliphatic hydrocarbons in the liquid state at 20°, is an extension of previous work[1] on the liquid paraffins.

Most of the data have been taken from the tabulations by Ward and Kurtz,[2] Egloff[3] and Kravtzoff.[4] A few recent values by Brooks, Howard and Crafton[5] have also been considered. In order to conserve space, data from the first two of these references only are included in the figures and tables.

Density

It has been shown[1] that the molal volumes, V_s, of many saturated hydrocarbons are quite accurately given by the equation

$$V_s = V_n + K_v \qquad (1)$$

where

$$V_n = 26.9_6 + 16.4_9\, n + \frac{29._0}{n} \qquad (2)$$

and

$$\begin{aligned} K_v &= +1.1_5 \text{ for } C_m\, \underset{\displaystyle C}{C}\, C && (3a)\\ &= -0.7 \text{ for } C_m\, \underset{\displaystyle C}{C}\, C\, C && (3b)\\ &= +2.0 \text{ for } C_m\, \overset{\displaystyle C}{\underset{\displaystyle C}{C}}\, C && (3c) \end{aligned}$$

The type formulas here are obviously "skeleton formulas," hydrogen atoms not being shown. C_m represents an unbranched, saturated hydrocarbon chain containing m carbon atoms. The total number of carbon atoms in the molecule is n. Minor deviations from these relations are observed for compounds having too small values of m or n. Reliable values of K for other types of saturated hydrocarbons await the accumulation of more and better data.

In Figs. 1 and 2 are plotted, for various series of unsaturated hydrocarbons, differences between the experimental values of the molal volume (in cc.), V, and the values, V_s, computed by Equations 1, 2 and 3 for the corresponding saturated compound. Points are included for the lowest members of each series (for which there are data), even in cases for which the previous study shows Equation 3 to be inapplicable.

Similar data for other unsaturated compounds are collected in Table I.

Data designated by Ward and Kurtz as "questionable" or calculated from some temperature other than 20° are represented in the figures by *small* black circles and in the tables by numbers in parentheses. Averages of the data listed by Egloff for compounds for which he gives no "most reliable" values are represented in the figures by *small* open circles and in the tables by numbers in parentheses. In the few instances in which the Egloff values are identical with those from the Ward and Kurtz data, half-filled circles are used to represent both.

Some of the plotted and tabulated values are averages for two stereoisomers. The individual values for the isomeric compounds do not differ sufficiently to warrant consideration at this time of the effect of difference in orientation.

Since the values of $V_s - V$ for undecyne-1 and pentadecyne-1 differ so greatly from the values for other $C_m\, C{\equiv}C$ compounds, it seems very probable that their published densities are incorrect.

Practically within the consistency of the different experimental values for a given compound, the values of $V_s - V$ are seen to be constant for each series. The average values for each type agree reasonably well with the relation

$$V = V_s + K_v' \qquad (4)$$

where

$$\begin{aligned} -K_v' = {} & 6.0 \text{ for each terminal double bond}\\ & +6.5 \text{ for each non-terminal double bond}\\ & +2.0 \text{ additional for each double-bond carbon atom attached by single bonds also to two other carbon atoms}\\ & +2.5 \text{ additional for each pair of adjacent } (C{=}C{=}C) \text{ or conjugated } (C{=}C{-}C{=}C) \text{ double bonds}\\ & +15.0 \text{ for each terminal triple bond}\\ & +17.0 \text{ for each non-terminal triple bond}\\ & +1.0 \text{ additional for conjugation of a double bond and a triple bond.} \end{aligned} \qquad (5)$$

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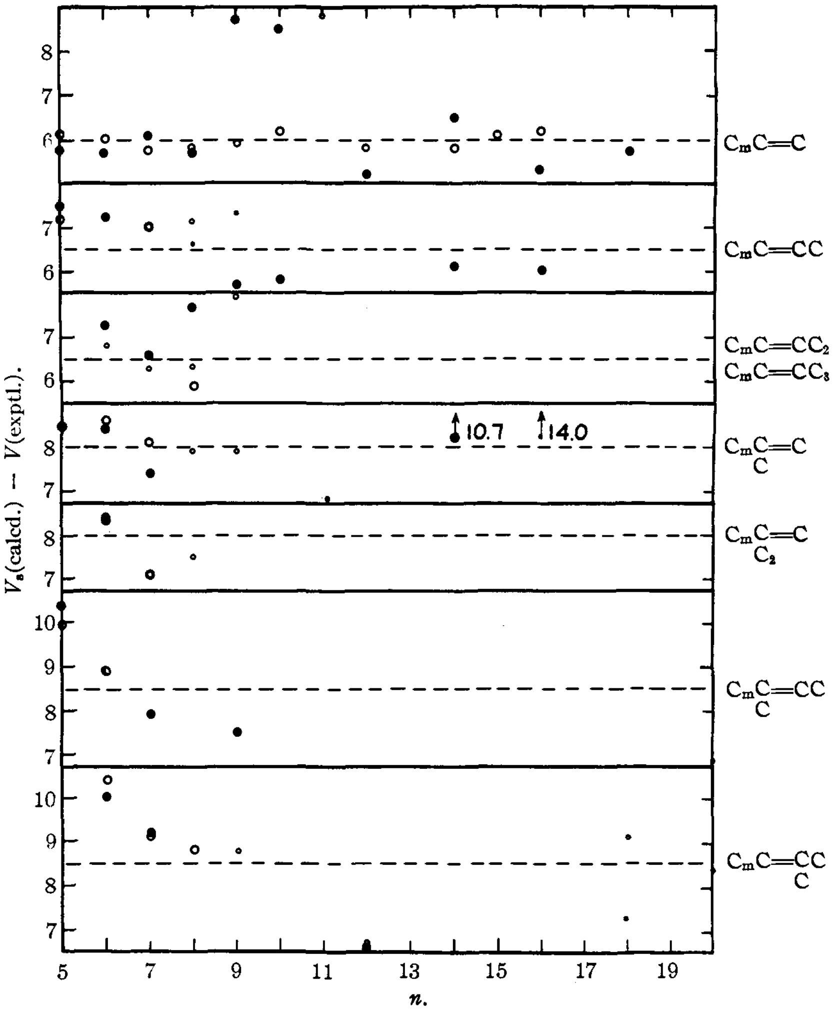
(1) M. L. Huggins, THIS JOURNAL, **63**, 116 (1941).

(2) A. L. Ward and S. S. Kurtz, Jr., *Ind. Eng. Chem., Anal. Ed.*, **10**, 559 (1938).

(3) G. Egloff, "Physical Constants of Hydrocarbons," Vol. I, Reinhold Pub. Corp., New York, N. Y., 1939.

(4) G. Kravtzoff, "Constantes Caractéristiques des Corps Organiques," Tables Annuelles de Constantes et Données Numériques, Vol. 13, No. 27, Hermann and Cie., Paris, 1939.

(5) D. B. Brooks, F. L. Howard and H. C. Crafton, *J. Research Natl. Bur. Standards*, **24**, 33 (1940).



○ ◐, Egloff; ● ◐, Ward and Kurtz.

Fig. 1.—Differences between experimental molal volumes of unsaturated hydrocarbons and those calculated for the corresponding saturated compound.

The magnitude of K'_v can also be computed by means of the equivalent equation

$$-K'_v = 2.75N_{=CH_2} + 3.25N_{=CHR} + 5.25N_{=CR_2} + 6.5N_{\equiv CH} + 8.5N_{\equiv CR} + 9.0N_{=C=} + 2.5N_{=C-C=} + 1.0N_{=C-C\equiv} \quad (6)$$

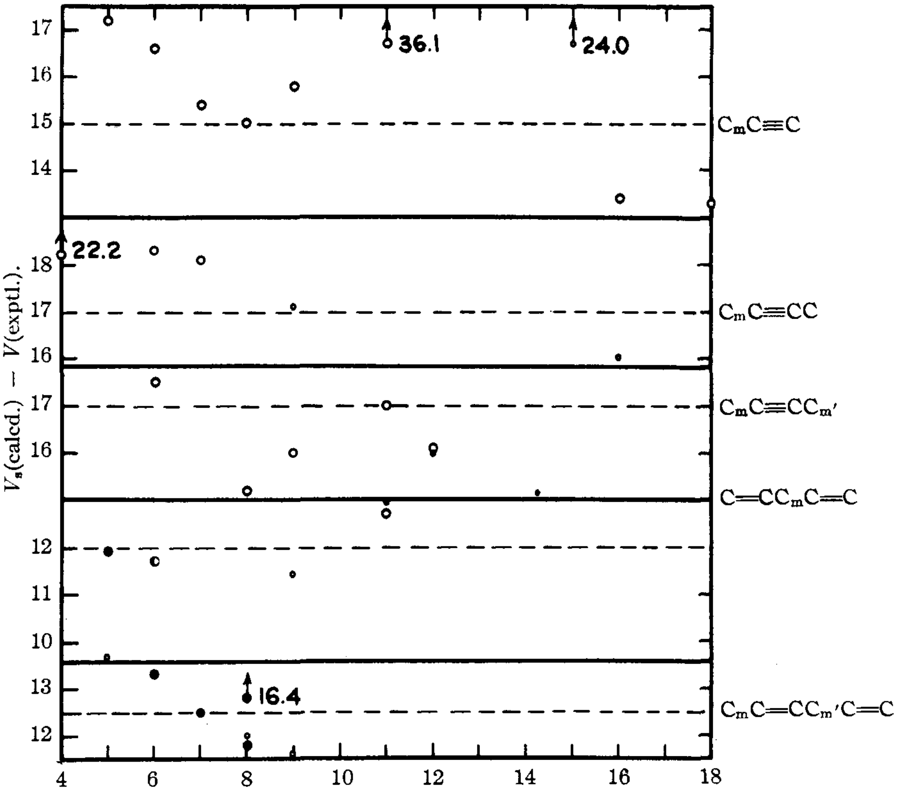
where the N's denote numbers of carbon atoms or conjugated systems of the types indicated. R here denotes any hydrocarbon radical, straight or branched.

The dotted lines in Figs. 1 and 2 and the figures in Column 4 of Table I show the magnitude of K'_v, computed according to Eq. 5 or Eq. 6.

It should be emphasized that great care must be used in applying these equations to compounds other than those in the particular classes tested. They would not be expected to be applicable, for example, to compounds of such types as $R_2C{=}CR_2$, $RCH{=}CR{-}CR{=}CH_2$ and $RCH{=}CR{-}CR{=}CHR$, in which two carbon atoms which are joined by a double bond or in the middle of a conjugated system are each bonded by single bonds to two R groups (not hydrogen).

The reliability of the equations and constants given above can also be judged from the average magnitudes of the differences between computed and observed densities. These are given in Table II for the series for which there are the most data.

In obtaining these averages, data represented in Figs. 1 and 2 by the smaller filled or open circles or in Table I by figures in parentheses have not been used. Values for undecyne-1 and octadiene-1,4 were also omitted, since the published densities are obviously much in error.



○ ◐, Egloff; ● ◐, Ward and Kurtz.

Fig. 2.—Differences between experimental molal volumes of unsaturated hydrocarbons and those calculated for the corresponding saturated compounds.

TABLE I

DIFFERENCES BETWEEN EXPERIMENTAL MOLAL VOLUMES AND REFRACTIONS OF VARIOUS UNSATURATED HYDROCARBONS AND THOSE CALCULATED FOR THE CORRESPONDING SATURATED COMPOUND

Skeleton formula	V_s (calcd.) − V (exptl.) Ward and Kurtz	V_s (calcd.) − V (exptl.) Egloff	$-K_V'$ Eq. 5	R_s (calcd.) − R (exptl.) Ward and Kurtz	R_s (calcd.) − R (exptl.) Egloff	$-K_r'$ Eq. 12
$C_4C{=}CC_4$		(3.4)	6.5		(−0.3)	0.4
$C_5C{=}CC_5$		(0.5)	6.5		(− .5)	.4
$C_6C{=}CC_6$		(5.8)	6.5		(.1)	.4
$C_8C{=}CC_8$		(8.5)	6.5		(.7)	.4
$C_{11}C{=}CC_8$	6.9	(7.1)	6.5			
$C_{11}C{=}CC_{10}$		(7.0)	6.5		(.1)	.4
$C_2C{=}CC_2C{=}CC$		(12.9)	13.0		(.7)	.8
$C_2C{=}C{=}C$		16.6	15.0		− .2	− .2
$C_4C{=}C{=}C$	14.9	14.7	15.0	−0.1		− .2
$CC{=}C{=}CC$	18.2	(18.2)	15.5			
$C_2C{=}C{=}CC$		(10.0)	15.5			
$CC{=}CC{=}C$	(15.3)	(15.5)	15.0	(−1.9)	(−1.7)	−2.1
$C_2C{=}CC{=}C$	15.9		15.0	−1.7		−2.1
$C_6C{=}CC{=}C$		(10.4)	15.0			
$CC{=}CC{=}CC$	15.5	(16.4)	15.5	−2.4	(−2.5)	−2.2
$C_2C{=}CC{=}CC$	15.5	(15.0)	15.5	−2.1	(−2.8)	−2.2
$CC\equiv CC{=}C$		(25.9)	24		(1.0)	1.1
$C_2C\equiv CC{=}C$		23.8	24			
$C_4C\equiv CC{=}C$		(24.3)	24		(1.2)	1.1
$C_7C\equiv CC{=}C$		(22.3)	24		(1.2)	1.1
$C\equiv CC_2C\equiv C$		31.5	30			
$C_5C\equiv CCC\equiv CC_5$		(33.0)	34			

TABLE II

AVERAGE DIFFERENCES BETWEEN OBSERVED AND CALCULATED DENSITIES (ρ) AND REFRACTIVE INDICES (n_D) FOR VARIOUS SERIES

Skeleton formula	Limitation for V additivity	$-K'_v$ (Eq. 5)	$-K'_r$ (Eq. 12)	ρ (obsd.) − ρ (calcd.) W. & K.	ρ (obsd.) − ρ (calcd.) Egloff	n_D (obsd.) − n_D (calcd.) Using obsd., ρ W. & K.	n_D (obsd.) − n_D (calcd.) Using obsd., ρ Egloff	n_D (obsd.) − n_D (calcd.) Using calcd., ρ W. & K.	n_D (obsd.) − n_D (calcd.) Using calcd., ρ Egloff
$C_mC=C$	m>2	6.0	0.5	0.0033(10)[a]	0.0007(10)[a]	0.0011(7)[a]	0.0008(8)[a]	0.0021(7)[a]	0.0008(8)[a]
$C_mC=CC_m'$	m>1; m'>0	6.5	.4	.0029(11)	.0042(1)	.0009(10)	.0025(1)	.0023(10)	.0049(1)
$C_m\underset{C}{C}=C$	m>1	8.0	.4	.0042(4)	.0023(3)	.0013(4)	.0003(2)	.0027(4)	.0010(2)
$C_m\underset{C}{C}=CC$	m>0	8.5	.3	.0025(4)	.0021(2)	.0013(4)	.0018(2)	.0012(4)	.0012(2)
$C_mC=\underset{C}{}C$	m>1	8.5	.3	.0060(3)	.0051(3)	.0019(3)	.0015(3)	.0049(3)	.0025(3)
$C_m\underset{C_2}{C}=C$	m>1	8.0	.3	.0031(2)	.0020(1)	.0008(2)	.0004(1)	.0026(2)	.0016(1)
$C_mC\equiv C$	m>2	15.0	3.3		.0057(7)		.0007(5)		.0033(5)
$C_m\equiv CC_m'$	m>1; m'>0	17.0	2.4		.0050(7)		.0011(6)		.0036(6)
$C=CC_mC=C$	m>0	12.0	1.0	.0010(2)	.0024(2)	.0009(2)	.0006(2)	.0015(2)	.0008(2)
$C_mC=CC_m'C=C$	m>0; m'>0	12.5	.9	.0027(3)		.0042(3)		.0046(3)	
$C_mC=CC=CC_m'$	m>0; m'>0	15.5	−2.2	.0001(2)		.0013(2)		.0013(2)	
All of above				.0031(41)	.0033(36)	.0014(37)	.0010(30)	.0025(37)	.0021(30)

[a] The numbers in parentheses are the numbers of compounds averaged.

In general, the differences average about three units in the third decimal place, *i. e.*, less than 0.5%. Similar computations for the other unsaturated hydrocarbons having published densities show about the same measure of agreement.

Refractive Index

As previously,[1] the molal refraction R will be defined by a Gladstone–Dale type of equation

$$R = V(n_D - 1) \qquad (7)$$

It has been shown that the molal refraction of a normal paraffin is given by the equation

$$R_n = 2.12 + 7.81_5 N \qquad (8)$$

and that the molal refraction of a saturated aliphatic hydrocarbon is related to that of the normal paraffin having the same number of carbon atoms by the equation

$$R_s = R_n + K_r \qquad (9)$$

where K_r depends on the numbers of methine groups, of quaternary carbon atoms (having no attached hydrogens), of bonds between methine carbon atoms, etc., according to Equation 10.

$$K_r = -0.40N_{CH} - 0.90N_C - 0.10N_{CH-CH} - 0.35N_{C-C} - 0.20N_{CH-C} + 0.20N_{CH-CH_3} + 0.30N_{C-CH_3} \qquad (10)$$

Figure 3 and Table I give differences between the experimental molal refractions of unsaturated hydrocarbons of various types and the molal refractions computed, according to Eqs. 9 and 10, for the corresponding saturated compound.

(A small circle, representing $R_s - R = 8.1$ for pentadecyne-1, was omitted from Fig. 3 because this value differs so much from those for other compounds in the same series.)

Satisfactory agreement is shown with the relation.

$$R = R_s + K_r' \qquad (11)$$

where

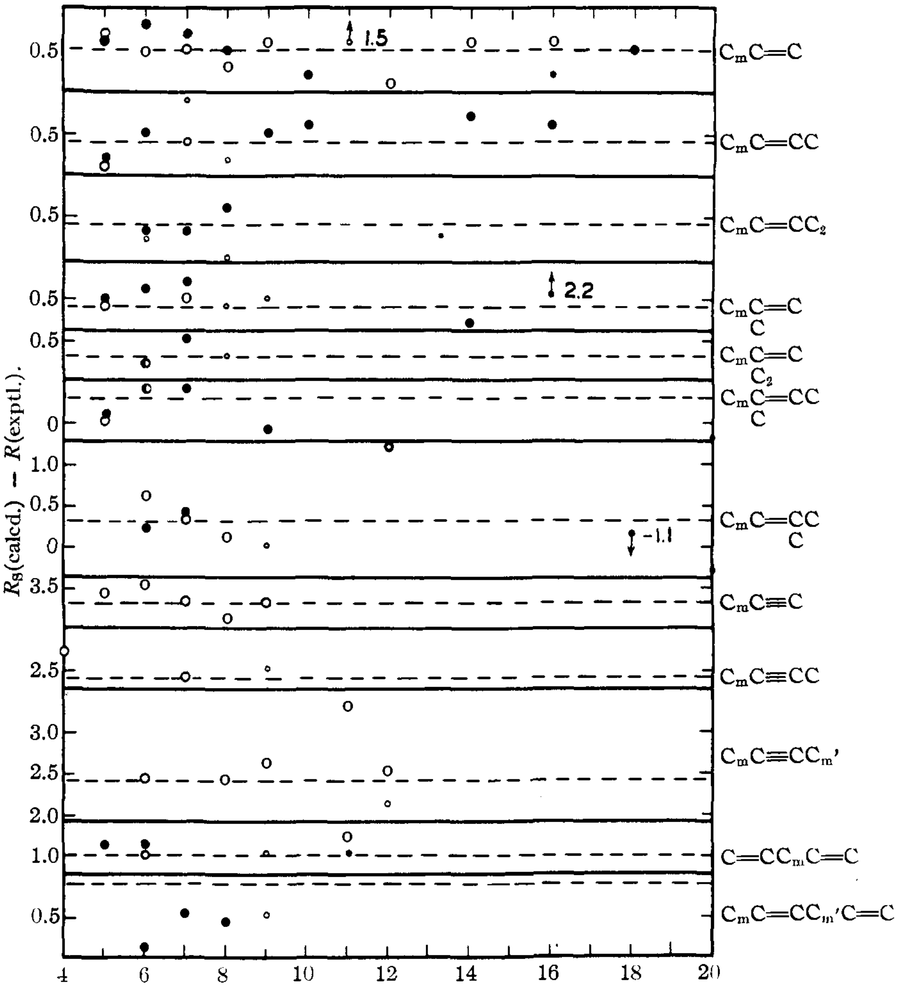
$-K_r'$ = (0.6 − 0.1 times the number of attached R groups) for each double bond
+(4.2 − 0.9 times the number of attached R groups) for each triple bond
−1.0 additional for two adjacent double bonds
−3.0 additional for two conjugated double bonds
−1.8 additional for a double bond and a triple bond conjugated together. (12)

K_r' can also be expressed by means of the following equivalent relation

$$-K_r' = 0.3N_{=CH_2} + 0.2N_{=CHR} + 0.1N_{=CR_2} + 2.1N_{\equiv CH} + 1.2N_{\equiv CR} - 1.0N_{=C=} - 3.0N_{=C-C=} - 1.8N_{=C-C\equiv} \qquad (13)$$

The values of K_r' for the series represented in Fig. 3 are indicated by the dotted lines.

The difference between the values of K_r' calculated according to Eq. 12 or 13 and the experimental figures (from Eq. 11) averages less than two-tenths of a unit—approximately the same as the average difference between the values published by Ward and Kurtz and those published by Egloff. Average differences between computed and observed refractive indices, both using the experimental densities and using molal volumes computed according to Equations 4 and 5 (or 6), are listed in Table II. (As with the densities, data represented by the smaller filled or open circles in the figures or by figures in parentheses in Table I were not included in the averages.) The general average is about 0.0012, *i. e.*, less than 0.1%, using observed densities, and 0.0023, *i. e.*, less than 0.2%, otherwise.



○ ◐, Egloff; ● ◐, Ward and Kurtz.

Fig. 3.—Differences between experimental molal refractions of unsaturated hydrocarbons and those calculated for the corresponding saturated compound.

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Summary

The figures in the tables in this and the preceding paper[1] show, *first*, that the previously used simple additivity relations for molal volume and molal refraction are not accurate within—or nearly within—the usual differences between different experimental measurements, and *second* that such accuracy can be achieved (for most of the compounds of interest) by the use of slightly more complicated equations. The constants in the refraction equations deduced agree with the assumption that each bond contributes a characteristic amount to the total molal refraction, depending, not only on the elements joined by the bond, but also on the numbers and kinds of other atoms attached to the two atoms joined by the bond in question. The effect of other atoms is of special importance if two unsaturated linkages are adjacent to $(C{=}C{=}C)$ or conjugated with $(C{=}C{-}C{=}C)$ each other.

The average agreement between calculated and observed values of both densities and refractive indices is not so good as was the case for the paraffins. This is, of course, to be expected, on account of the added complexities in the unsaturated compounds.

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