Densities and Optical Properties of Organic Compounds in the Liquid State. VI. The Refractive Indices of Paraffin Hydrocarbons and Some of Their Derivatives[*]

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Introduction

The purpose of this paper is to relate the refractive indices, n_D, of various liquid aliphatic organic compounds at 20°C to their composition. This relationship is best shown with the aid of molal refractions (R, R' or R''), defined by the equations

$$R=V(n_D-1), \tag{1}$$

$$R'=V(n_D^2-1), \tag{2}$$

and

$$R''=V\frac{n_D^2-1}{n_D^2+2}. \tag{3}$$

V is the molal volume. These molal refractions are approximately additively calculable from contributions of the atoms, atomic groups, or bonds composing the molecule.

Although Eq. (3) has the soundest theoretical basis for simple gaseous system, for condensed systems it seems necessary to choose between these relationships on a purely empirical basis[2]. Fairly extensive calculations by the writer, both for liquid organic compounds and for glasses[3] indicate that R, R', and R'' exhibit about the same degree of additivity. For the present purpose, we choose the simplest: R.

The molal volume is the molecular weight divided by the density. If experimental density values are not available or are insufficiently accurate, the molal volume can, in many cases, be computed by simple empirical relationships.[1,4,5,6,7].

A considerable amount of accurate density and refractive-index data for organic compounds is now conveniently available[8,9].

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This paper is a revision of parts of a previously published paper[1] and of an unpublished paper, entitled "Refractive Indices of Liquid Aliphatic Organic Compounds," presented October 3, 1940 at a meeting of the Optical Society of America in Rochester, New York, U. S. A.

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8) "Selected Values of Properties of Hydrocarbons," Circular of the National Bureua of standerds C461, U.S. Government Printing Office, Washington, D.C., (1947).

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These data form the basis for the results reported here.

Hydrocarbons

The additivity relationships may be described in terms of contributions from the different types of atoms (C, H), atomic groups (CH_3, CH_2, CH, C), or bonds (C-C, C-H). For example, for normal paraffins, C_nH_{2n+2}, the best data lead to

$$R_n=7.821n+2.064, \tag{4}$$

which is equivalent to

$$R_n=5.757N_C+1.032N_H \tag{5}$$

or

$$R_n=7.821N_{CH_2}+8.853N_{CH_3}. \tag{6}$$

No similar equation, involving a uniform contribution of each C-C bond and each C-H bond, fits the data, for either normal paraffins or those of other types. By differentiating between different types of C-C and C-H bonds, however, one can deduce satisfactory additivity equations and constants.

To do this, use is made of data for several other series of saturated aliphatic hydrocarbons. These data are well satisfied by equations of the form of Eq. (4), but with different values of the constant term. Putting

$$R=R_n+k=7.821n+2.064+k, \tag{7}$$

the following values of k have been found:

2-Methyl alkanes $k_1=+0.014$ (8)

3-Methyl alkanes and 4-methyl alkanes $k_2=-0.137$ (9)

2, 2-Dimethyl alkanes $k_3=+0.005$ (10)

3, 3-Dimethyl alkanes and 4, 4-dimethyl alkanes $k_4=-0.278$ (11)

As previously shown, these can be used to obtain relative bond refraction contributions, α_{ij}. The appropriate equations* are:

$$\alpha_{21}=(b-a)/2+2k_1-2k_2+k_3-k_4/2+5\delta$$
$$=3.325+5\delta \tag{12}$$

$$\alpha_{31}=\alpha_{22}=(b-a)/2+2k_1-2k_2+k_3-k_4/2$$
$$+4\delta=3.325+4\delta \tag{13}$$

$$\alpha_{41}=\alpha_{32}=(b-a)/2+k_1-k_2+k_3-k_4/2+3\delta$$
$$=3.174+3\delta \tag{14}$$

$$\alpha_{42}=\alpha_{33}=(b-a)/2+k_1-k_2+k_4/2+2\delta$$
$$=2.891+2\delta \tag{15}$$

$$\alpha_{43}=2.5+\delta \tag{16}$$

$$\alpha_{44}=2.0 \tag{17}$$

$$\alpha_{1H}=(b+a)/4-k_1/3+k_2/2-k_3/6$$
$$+k_4/12-\delta=2.397-\delta \tag{18}$$

$$\alpha_{2H}=(b+a)/4-k_1+k_2-k_3/2+k_4/4-2\delta$$
$$=2.248-2\delta \tag{19}$$

$$\alpha_{3H}=(b+a)/4-k_1+2k_2-3k_3/2+3k_4/4-3\delta$$
$$=1.967-3\delta. \tag{20}$$

The subscript 21 refers to a bond between a methylene carbon atom and a methyl carbon atom; the subscript 1H refers to a bond between a methyl carbon atom and a hydrogen atom; etc. The δ is an arbitrary constant, which need not be evaluated.

The molal refraction of saturated aliphatic hydrocarbons can also be represented by the equivalent relation

$$R_s=\sum_i N_i\alpha_i+\sum_{ij} N_{ij}\alpha'_{ij} \tag{21}$$

with the α_i and α'_{ij} values given in Table I.

Table I

Refraction contributions for substitution into eq. (21)

i	α_i	ij	α_{ij}
CH_3	8.853	CH–CH_3	+0.151
CH_2	7.821	C–CH_3	+ .283
CH	6.500	CH–CH	− .132
C	4.912	CH–C	− .088
		C–C	− .456

If either i or j is CH_2, the bond contribution α'_{ij} is zero. In other words, the α_i contributions given are those for i groups attached only to CH_2 groups.

Refractive indices computed with these relationships agree with the more precise experimental values to within a few units in the fourth decimal place. Since the results of extensive comparisons were summarized in Ref. 1, further comparisons need not be given here.

Derivatives

Molal refractions of a large number of α-substituted normal paraffin have been compared with those of the parent hydrocarbons. For each homologous series, the difference is found to be quite constant. Addition of $\alpha_{CH_3}-\alpha_{CH_2}$ to these differences gives the values (α_X) of the refraction contributions of the substituents (X), for compounds in which they are attached to CH_2. The same contribution can be used for derivatives of branched-chain paraffins, provided the attachment is to a methylene carbon. Application to derivatives in which the attachment is to a carbon bonded to only one hydrogen or to none has not been adequately tested.

The contributions of 12 X substituents are listed in Table II.

The normal nitriles (X=CN) have been very carefully studied and will serve to illustrate the measure of agreement with

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* The corresponding equations in Reference (1) were in error with regard to the coefficients of the k_1 and k_3 terms. Since these constants were then taken as zero, the relationships derived from these equations were not affected.

TABLE II
GROUP REFRACTION CONTRIBUTIONS FOR R–X AND R–Y–R′ COMPOUNDS

–X	α_X	–Y–	α_Y
–F	0.8	–O–	3.0
–Cl	9.6	–NH–	6.3
–Br	15.0	–S–	14.9
–I	24.6	–CO–	8.22
–OH	4.1	–CO–O–	10.6
–SH	15.1	–CO–O–CO–	19.8
–CN	8.88	–CO–NH–	14.4
–NH_2	7.2	–CH(CH_3)–	15.50
–CHO	9.7	–C(CH_3)$_2$–	23.18
–CO_2H	12.1		
–NO_2	11.2		
–ONO	11.7		

the assuption of constancy of the α contributions. (Table III)

TABLE III
REFRACTIONS OF n–ALKYL NITRILES, $C_mH_{2m+1}CN$

m	Ref.	d_4^{20}	R(exp)–R_m(calcd.)	n_D(expt.)	n_D(calcd.)
1	10	0.78212	8.176	1.34409	1.338
	11	.78204	8.167	1.34389	1.338
2	10	.78184	8.077	1.36600	1.363
	11	.78171	8.071	1.36585	1.363
	12	.78169	8.071	1.36585	1.363
3	10	.79090	8.031	1.38408	1.382
	11	.79085	8.027	1.38402	1.382
	12	.79085	8.010	1.38385	1.382
4	10	.79929	7.988	1.39745	1.3961
	11	.79919	7.960	1.39713	1.3960
	12	.79919	7.958	1.39711	1.3960
5	11, 12	.80531	7.925	1.40694	1.4063
6	11, 12	.80958	7.891	1.41419	1.4139
7	11	.81355	7.855	1.42018	1.42013
	12	.81362	7.850	1.42018	1.42016
	13	.81344	7.888	1.20344	1.42007
8	11	.81690	7.842	1.42522	1.42525
	12	.81684	7.847	1.42522	1.42522
9	11	.81967	7.846	1.42946	1.42947
	12	.81967	7.834	1.42940	1.42947
10	11, 12	.82180	7.838	1.43286	1.43290
11	11	.82390	7.844	1.43596	1.43597
	12	.82390	7.842	1.43595	1.43597
12	11	.82586	7.840	1.43867	1.43870
	12	.82574	7.845	1.43867	1.43864
13	12	.82792	7.848	1.44126	1.44126

The paraffin refractions R_m, were computed from Eq. (4), replacing n by m. For m greater than 5, these differ insignificantly from the best experimental values. (Cf. Ref. 1.) For m less than 5, experimental values are unobtainable. For $m=5$, the R-R_m values obtained using the *experimental* data for the paraffins from Refs. 8 and 10, are 7.912 and 7.897, respectively. For $m>6$, the average departure of the average R-R_m values from constancy is less than the average difference between the experimental values.

The reasons for the deviations from constancy of R-R_m, indicating deviations from additivity of the α-contributions, for the smaller values of m, will not be discussed at this time. It should be noted, however, that because of these deviation, in this and other series, refractive indices computed from the constants given here are much less accurate for the lower-molecular-weight compounds than for the higher members of the series.

The n_D (calc) values in Table III were from the experimental densities and an assumed constant value of $\alpha_{CN}=8.880$; hence R-$R_m=7.848$ and R_m is given by Eq. (4). For $m>6$, the calculated and experimental indices agree, on the average, within three units in the fifth decimal place.

Table II also lists α_Y-values, for compounds containing Y substituents bonded to two CH_2 groups. These contributions were obtained by substracting from the molal refraction of the compound R-Y-R′ that of the hydrocarbon RR′. For comparison and for future reference, the contributions of two hydrocarbon Y groups, computed from the equations of the preceding section, are included.

Summary and Conclusion

For the saturated hydrocarbons, the more accurate data, published since the first paper of this series[1)] was written, have been found to agree well with the previous additivity postulates. Revised values of the constants have been computed.

Refraction-contribution constants for various atoms and atomic groups, attached to CH_2 groups, have been deduced. Good additivity has been found, except for the compounds of lowest molecular weight in each series.

Pending further testing, caution should be observed in using the constants and additivity assumptions presented here in compounds containing $C=C$ and $C\equiv C$ bonds and in compounds in which the X and Y are attached to groups other than CH_2.

Discussion of the theoretical interpretation of the relative magnitudes of the group contributions will be postponed until a later time.

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