Refractive Indices and Densities of Normal Saturated Fatty Acids in the Liquid State

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Few systematic studies of the refractive indices of the saturated fatty acids are found in the literature; there is the classical work of Eijkman,[1] the investigation of Scheij[2] on the naturally occurring fatty acids, and the more modern work of Waterman and Bertram.[3] Determinations were made at arbitrary and scattered temperatures; only the work of Falk[4] on butyric acid embraces a large number of determinations over a wide range of temperature. We have measured the refractive indices of the normal saturated fatty acids in the liquid state, from caproic to stearic inclusive, at a sufficient number of temperatures between 20 and 80° to enable us to plot the variation of refractive index with temperature for each acid, as shown in Fig. 1. In addition, the densities of these acids were determined at 80° and these data were used to calculate the molar volume and the molar refractivity of each acid at that temperature. The refractive indices are listed in Table I and the densities in Table II. The values listed in Table I have not been corrected for the effect of temperature on the refractometer prism, since we feel that less confusion will arise among investigators using these figures if they are left uncorrected. Whenever we shall have occasion here to treat the refractive indices as functions of the homologous series, a correction given by

$$0.00006 \, (t - 20) \tag{1}$$

where t is the temperature at which the refractive index was determined, will be added. This is the correction for the refractometer prism only. A correction should also be applied for the effect of temperature on the compensating prisms in the refractometer, but since their temperature could be estimated only crudely, this correction will be omitted. Since the compensating prisms do not deviate the sodium D line, the correction is probably very small.

Experimental

The acids used were carefully purified; their preparation is described in another communica-

tion from this Laboratory.[5] Refractive indices were measured with an Abbe type refractometer, the temperature of whose prisms could be held constant to ±0.05. A calibrated thermometer was used. Densities were determined in a modified Ostwald pycnometer at 80 ± 0.05°. Weighings were corrected for the buoyancy of air.
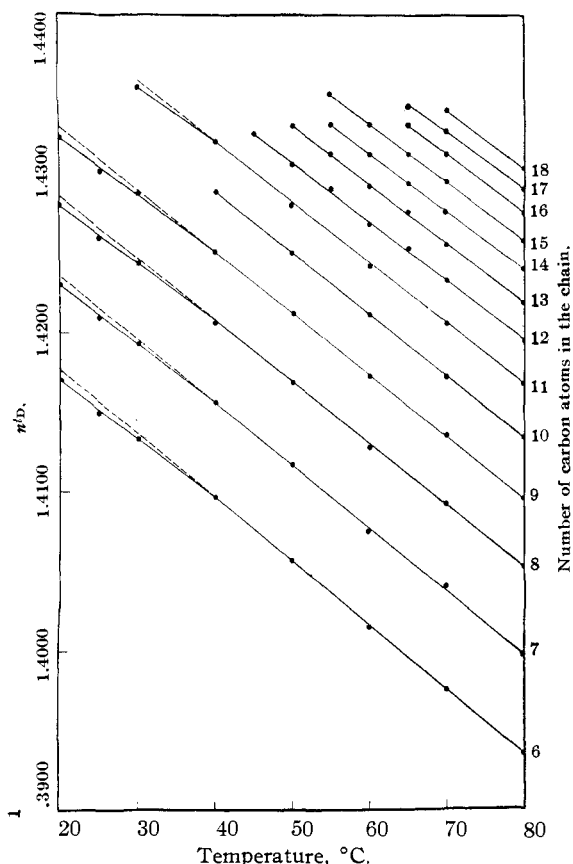

Fig. 1.—The variation of refractive index with temperature. Change of slope is shown by comparison with the extrapolation from the curve at higher temperatures. Extrapolation is represented by a dotted line.

Discussion

Molar Volumes.—The molar volumes at 80° of the acids from caproic through stearic were calculated from the densities determined in this work. By taking advantage of the fact that the densities of the straight chain saturated acids are linear functions of temperature, we were able to

(1) Eijkman, Rec. trav. chim., 12, 157 (1893).
(2) Scheij, ibid., 18, 182 (1899).
(3) Waterman and Bertram, ibid., 46, 699 (1927).
(4) Falk, THIS JOURNAL, 31, 96 (1909).
(5) Hoerr, Pool and Ralston, Oil and Soap, 19, 126 (1942).

TABLE I
REFRACTIVE INDICES (n^tD) OF NORMAL SATURATED FATTY ACIDS

Acid	20.0°	25.0°	30.0°	40.0°	45.0°	50.0°	55.0°	60.0°	65.0°	70.0°	80.0°
Caproic	1.4170	1.4150	1.4132	1.4095		1.4054		1.4012		1.3972	1.3931
Enanthic	1.4230	1.4209	1.4192	1.4155		1.4114		1.4073		1.4037	1.3993
Caprylic	1.4280	1.4260	1.4243	1.4205		1.4167		1.4125		1.4089	1.4049
Pelargonic	1.4322	1.4301	1.4287	1.4250		1.4210		1.4171		1.4132	1.4092
Capric				1.4288		1.4248		1.4210		1.4169	1.4130
Hendecanoic				1.4319		1.4279		1.4240		1.4202	1.4164
Lauric					1.4323	1.4304	1.4288	1.4267	1.4250	1.4230	1.4191
Tridecanoic						1.4328	1.4310	1.4290	1.4272	1.4252	1.4215
Myristic							1.4329	1.4310	1.4291	1.4273	1.4236
Pentadecanoic							1.4348	1.4329	1.4310	1.4292	1.4254
Palmitic									1.4328	1.4309	1.4272
Margaric									1.4340	1.4324	1.4287
Stearic										1.4337	1.4299

TABLE II
DENSITIES OF NORMAL SATURATED FATTY ACIDS AT 80°

Acid	$d^t{}_4$	Acid	$d^t{}_4$
Caproic	0.8751	Tridecanoic	0.8458
Enanthic	.8670	Myristic	.8439
Caprylic	.8615	Pentadecanoic	.8423
Pelargonic	.8570	Palmitic	.8414
Capric	.8531	Margaric	.8396
Hendecanoic	.8505	Stearic	.8390
Lauric	.8477		

TABLE III
MOLAR VOLUMES OF NORMAL SATURATED FATTY ACIDS

Acid	V_m at 20° Exptl.[a]	V_m at 20° Calcd.[b]	V_m at 80° Exptl.	V_m at 80° Calcd.[c]
Formic	37.71	40.51	....	....
Acetic	57.21	57.40	61.11[a]	63.38
Propionic	74.55	74.29	79.68[a]	80.63
Butyric	91.93	91.18	97.95[a]	97.88
Valeric	108.69	108.07	115.33[a]	115.13
Caproic	125.04	124.96	132.67[d]	132.38
Enanthic	141.89	141.85	150.07	149.63
Caprylic	158.57	158.74	167.30	166.88
Pelargonic	174.53	175.63	184.50	184.13
Capric			201.80	201.38
Hendecanoic			218.90	218.63
Lauric			236.29	235.88
Tridecanoic			253.27	253.13
Myristic			270.41	270.38
Pentadecanoic			287.61	287.63
Palmitic			304.56	304.88
Margaric			321.90	322.13
Stearic			338.85	339.38

[a] Calculated from densities obtained from references 2, 4, 6–11. [b] Calculated from equation (2). [c] Calculated from equation (3). [d] This figure and subsequent figures in this column were computed from densities in Table II.

convert data already in the literature[2,4,6-11] to the proper temperature and to extend this series of calculations at 80° down to acetic acid, and also to make a series of calculations from formic acid to pelargonic acid at 20° (see Table III). At 20° the molar volumes from acetic acid to pelargonic acid are adequately expressed by

$$V_m = 16.89n + 23.62 \qquad (2)$$

where n is the number of carbon atoms in the chain. At 80° the equation

$$V_m = 17.25n + 28.88 \qquad (3)$$

holds for butyric and higher acids. The deviation of the first three members of the series from linearity is quite sharp and the addition of a term of the form k/n does not extend the validity of the equation to include these three members. The molar volumes of the normal saturated acids, arranged serially, do not show as much deviation from a linear relation as noticed by Huggins[12] for the normal saturated hydrocarbons, nor does this deviation extend as far up the series for the acids as for the hydrocarbons.

(6) Timmermans and Hennaut-Roland, J. chim. phys., 27, 420, 422, 425 (1930); 29, 550 (1932).

(7) Merry and Turner, J. Chem. Soc., 105, 758 (1914).

(8) Eijkman, Chem. Zentr., 78, II, 1210 (1907).

(9) Dunstan, J. Chem. Soc., 107, 667 (1915).

(10) Deffet, Bull. soc. chim. Belg., 40, 385 (1931).

(11) Garner and Ryder, J. Chem. Soc., 127, 728 (1925).

(12) Huggins, THIS JOURNAL, 63, 116 (1941).

Refractivities.—In Fig. 1 we have plotted the refractive indices of the acids, corrected according to equation (1), against temperature. The refractive indices for each acid fall upon a straight line between 40 and 80°. Below this temperature a change of direction is observed. A plausible explanation of this phenomenon can be found in the theory of molecular refractivity and in current viewpoints on the structure of liquids consisting of polar molecules. To begin with, the molar refraction for visible light, calculated by the Lorentz–Lorenz equation, is equal to the electron polarization. A collection of molecules which are inherent dipoles, such as the molecules of a fatty acid, act on each other to cause more or less orien-

tation, even in the liquid state, and consequently produce an electric field within the body of the liquid. Onsager[13] has published a theoretical treatment of this effect on the determination of dipole moments of polar substances by means of an external electrical field. It is beyond the scope of this paper to attempt a quantitative treatment of the effect of the internal electric field on the bonding electrons in the relatively non-polar part of the fatty acid chain, and hence on the refractivity, but qualitatively we would expect the electron polarization of a substance such as a fatty acid to depend on the statistical orientation of the individual molecules within the body of the liquid. On the other hand, the thermal motions of these molecules will tend to produce disorder, and at some temperature they should be vigorous enough to completely overcome the restraints caused by dipole interaction. The molecules within the liquid will then exhibit a perfectly random configuration and the net field there will be zero. On these grounds we would expect to find a temperature for each acid above which the molar refractivity will be constant and below which it will depend on temperature. We have taken the data of Falk[4] for butyric acid and instead of smoothing out the values of the refractive index, we have calculated the molar refractivities from the data as they stand. This examination shows that the molar refractivity is practically constant above 42° and a linear function of the temperature below this point. This is the only fatty acid reported for which a sufficient number of molecular refractivities could be calculated from the original data over a wide temperature range.

To eliminate the possibility that the discontinuities in the plot of the refractive indices of the acids might be due to some systematic defect in the refractometer or in the calibration of the thermometer, the refractive index of n-heptane was determined between 20 and 50°. The data so obtained lie on a straight line and the data of Shepard, Henne and Midgley[14] also lie on this line in full agreement with ours.

If a plot of the molar refractivity of a normal fatty acid shows discontinuity with temperature, it can be shown that a plot of the refractive indices will also exhibit discontinuity. The densities of the fatty acids are continuous linear

functions of the temperature from zero to at least 80°. The density factor, then, will produce no discontinuity in the molar refractivity as calculated from the Lorentz–Lorenz formula

$$\frac{n^2 - 1}{n^2 + 2} \frac{M}{d}$$

but any discontinuity in the temperature variation of n will show up in the molar refractivity and vice versa, since it is impossible to eliminate n from the ratio $n^2 - 1/n^2 + 2$.

The molar refractivities of the normal saturated fatty acids, from caproic to stearic inclusive, can be expressed as a function of the number of carbon atoms in the chain by

$$R_m = 4.654n + 3.83 \qquad (4)$$

The observed values and those calculated from this formula are listed in Table IV.

TABLE IV

MOLAR REFRACTIVITIES OF NORMAL SATURATED FATTY ACIDS AT 80°

Acid	R_m (exptl.)[a]	R_m (calcd.)[b]
Caproic	31.70	31.75
Enanthic	36.34	36.40
Caprylic	41.08	41.06
Pelargonic	45.66	45.71
Capric	50.36	50.37
Hendecanoic	55.02	55.02
Lauric	59.73	59.68
Tridecanoic	64.35	64.33
Myristic	69.00	68.99
Pentadecanoic	73.65	73.64
Palmitic	78.30	78.30
Margaric	83.01	82.95
Stearic	87.59	87.61

[a] Computed from the formula $R_m = \dfrac{n^2 - 1}{n^2 + 2} \dfrac{M}{d}$, refractive indices corrected. [b] Calcd. from equation (4).

Summary

1. The refractive indices of the normal saturated fatty acids from caproic to stearic inclusive have been determined at a number of temperatures between 20 and 80°. For each acid the refractive indices are straight line functions of the temperature with an abrupt change of a slope at 40°.

2. An explanation of this change of slope has been presented.

3. The densities of these acids at 80° have also been determined. Molar volumes and molar refractivities for the homologous series have been computed and shown to be linear with respect to the number of carbon atoms in the chain.

(13) Onsager, THIS JOURNAL, 58, 1486 (1936).
(14) Shepard, Henne and Midgley, ibid., 53, 1948 (1931).

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