tion. Hydrogenolysis of actylated ricinoleic acid using copper-cadmium soaps for short periods caused dehydration; longer periods led to almost complete ester formation.

Conclusions

Over 90% hydrogenolysis of fatty acids to alcohols can thus be effected at 220–250C at pressures from 3500–4000 psi using as catalyst one per cent copper present as the fatty acid soap. Use of a catalyst consisting of 2% copper and one per cent cadmium will protect almost 90% of any monoethenoid unsaturation present. Ricinoleyl alcohol resulting from hydrogenolysis also contains 10% short-chain alcohols and 15% acid-alcohol esters.

Except that high pressures are necessary, the use of fatty acids as described has several advantages over esters. Pure acids are commercial products which can be used as such. Metal soap catalysts are easy to prepare. Against 5% copper chromite used to hydrogenolyse esters, the soap corresponding to 2% copper carbonate suffices for saturated acids. Hydrogenolysis of acids occurs very rapidly, and is easily judged by hydrogen absorption. An important further advantage is that unsaturation is preserved simply by having a cadmium soap also present.

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Physical Properties of Fatty Acid Methyl Esters. III. Dispersion

T. H. GOUW,[1] and J. C. VLUGTER, Department of Chemical Engineering, Technological University, Delft, The Netherlands

Abstract

The dispersion and the molar dispersions, according to Lorentz-Lorenz and to Gladstone-Dale, are presented at 20C and at 40C for the saturated fatty acid methyl esters from acetate to nonadecanoate and for methyl oleate, linoleate, linolenate, and erucate. Regression equations for these two additive properties have been computed for the saturated series. The limiting dispersion is computed for the Gladstone-Dale specific dispersion.

Introduction

FOR CONSTITUTIVE STUDIES the dispersion is an attractive property because it is closely related to the fine structure of the molecule. It has the advantage of being independent of errors in absolute units of calibration because the values are differential in origin. The temp dependence is small which obviates the need for critical temp adjustments during measurements.

The M dispersion, product of the dispersion and the M volume, may be expected to possess additive properties. According to Bruhl (1), however, this property is pre-eminently constitutive.

The failure of many earlier attempts to compute the M dispersion by summation of the contributing elements can be ascribed to this reason, as constitutive differences affect the dispersion much more than the refraction.

The majority of the papers on the application of the dispersion to structural problems is found in the field of hydrocarbon analysis (2,3,9,12). The scope and applicability has especially been expanded by the investigations of Grosse and Wackher (8) and Thorpe and Larsen (11). Applications are generally based on the constant value which the specific dispersion possesses for a class of compounds. This property can be deduced from the fact that mol wt are additive. Numerical values obtained from pure hydrocarbons proved to be consistent in synthetic mixtures, and this has substantiated the applicability of the specific dispersion to type analysis of hydrocarbons (10).

Dispersion and Molar Dispersion

In a previous communication (6,7) we have reported the refractive indices of the saturated fatty acid methyl esters from acetate to nonadecanoate, methyl oleate, linoleate, linolenate, and erucate, at 20C and 40C, for the H_α, H_β, Na_D, and the H_γ spectral lines. The dispersion, which is discussed in this paper, has been obtained as the difference between the refractive indices of the H_β and the H_α lines, although $n_\gamma - n_\alpha$ would have been more obvious. The gain in accuracy by using the larger values is, however, more than offset by the lower accuracy of the n_γ determinations.

Expressions most commonly used for the M dispersion are the Gladstone-Dale dispersion

$$D_{GD} = (n_\beta - n_\alpha) \cdot M/d = \sum_i c_i D_{i,GD} \qquad [1]$$

and the Lorentz-Lorenz expression

$$D_{LL} = R_\beta - R_\alpha = \sum_i c_i D_{i,LL} \qquad [2]$$

In these equations D_i is the increment of the contributing element i, c_i the number of these elements, R_m the Lorentz-Lorenz M refraction (7), and d the density.

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[1] Present address: California Research Corp., Richmond, Calif.

TABLE I

Dispersion and M Dispersion of Saturated Fatty Acid Methyl Esters

Compound	20C	40C	Lorentz-Lorenz		Gladstone-Dale	
	$n_\beta - n_\alpha$	$n_\beta - n_\alpha$	D_m^{20}	D_m^{40}	D_m^{20}	D_m^{40}
Acetate	0.00607	0.00589	0.265	0.266	0.482	0.481
Propionate	0.00631	0.00620	0.330	0.336	0.607	0.613
Butyrate	0.00664	0.00640	0.408	0.405	0.755	0.746
Valerate	0.00681	0.00663	0.476	0.477	0.889	0.885
Caproate	0.00700	0.00683	0.549	0.551	1.030	1.028
Oenanthate	0.00711	0.00697	0.618	0.623	1.165	1.166
Caprylate	0.00723	0.00708	0.690	0.694	1.305	1.304
Pelargonate	0.00732	0.00714	0.760	0.760	1.442	1.435
Caprate	0.00743	0.00725	0.834	0.834	1.587	1.578
Undecanoate	0.00751	0.00735	0.905	0.908	1.727	1.723
Laurate	0.00759	0.00738	0.979	0.975	1.871	1.854
Tridecanoate	0.00765	0.00745	1.051	1.048	2.012	1.996
Myristate	0.00768	0.00752	1.119	1.122	2.147	2.140
Pentadecanoate	0.00774	0.00757	1.192	1.194	2.291	2.281
Palmitate		0.00762		1.267		2.423
Heptadecanoate		0.00764		1.334		2.557
Stearate		0.00769		1.409		2.702
Nonadecanoate		0.00772		1.480		2.841

Assuming these two equations to be nearly equally satisfactory, the advantage of the Gladstone-Dale relation from the point of directness and simplicity is apparent. The Lorentz-Lorenz dispersion equation is, however, often applied in the literature because of the theoretical background. Both of these expressions will, therefore, be considered.

The dispersion and M dispersion of the saturated fatty acid methyl esters show in Table I.

Assuming the CH_2 increment, the difference in M dispersion between consecutive members, to be essentially constant for the higher members of the series the well-known linear correlation for a M additive property of a homologous series may also be applied to the M dispersion, i.e.,

$$D_m = A + n\,D_{CH_2} \qquad [3]$$

Taking only the values of methyl valerate and the higher members regression equations have been computed for equation 3. Numerical values show in Table II.

σ is the standard error of estimate. D_{CH_2} in Table II is at the same time the statistical average of the CH_2 increment.

Unsaturation

An estimate of the influence of unsaturation on the dispersion is obtained from the values of the unsaturated compounds investigated. These values show in Table III, and compared against data of methyl stearate at 20C and methyl behenate at 20C and 40C. The latter values have been obtained by extrapolation from the regression equations.

From the observed values the increment of the double bond has been estimated as 0.12 for the Lorentz-Lorenz expression, and 0.25 for the Gladstone-Dale equation. In both cases the influence of the temp is less than the possible errors due to other factors. Contrary to the M refraction, the observed increment for the double bond possesses a positive value. Another point of interest is the negligible influence of the *trans*-modification. This is demonstrated by the values related to methyl linolenate, where 27.5% of the double bonds are in the *trans*-configuration.

TABLE II

Regression Coefficients of M Dispersion

Molar dispersion	Temp	A	D_{CH_2}	σ
Lorentz-Lorenz	20C	0.118	0.0716	0.0014
	40C	0.120	0.0715	0.0019
Gladstone-Dale	20C	0.184	0.1403	0.0030
	40C	0.185	0.1396	0.0040

TABLE III

Dispersion and M Dispersion of Unsaturated Fatty Acid Methyl Esters

Compound	20C	40C	Lorentz-Lorenz		Gladstone-Dale	
	$n_\beta - n_\alpha$	$n_\beta - n_\alpha$	D_m^{20}	D_m^{40}	D_m^{20}	D_m^{40}
Stearate[b]			1.407	1.409	2.709	2.698
Oleate	0.00872	0.00849	1.525	1.517	2.958	2.928
Linoleate	0.00970	0.00951	1.649	1.649	3.222	3.211
Linolenate[a]	0.01071	0.01056	1.772	1.786	3.488	3.496
Behenate[b]			1.693	1.693	3.271	3.256
Erucate	0.00868	0.00854	1.807	1.817	3.515	3.515

[a] Contains 27.5% *trans* double bonds.

[b] Included as reference compound to facilitate comparison.

Specific Dispersion and Limiting Values

The relation between the specific dispersion, M dispersion, and the CH_2 increment is given by

$$D_{sp} = D_m/M = (A + n\,D_{CH_2})/(46.026 + 14.026\,n) \qquad [4]$$

The limiting specific dispersion is, therefore,

$$\lim_{n \to \infty} D_{sp} = D_{CH_2}/14.026 \qquad [5]$$

From our data the limiting specific dispersion can be computed as

	20C	40C
Lorentz-Lorenz	0.00511	0.00510
Gladstone-Dale	0.01001	0.00996

These values should be the same for all classes of compounds. For alkanes the limiting value is already closely approximated in the lower range mol wt. Generally speaking the specific dispersion of the alkanes can, therefore, be assumed to possess a constant value. To facilitate computation, a factor of 10^4 is usually included in the specific dispersions quoted in the literature. Due regard to this factor must, therefore, be given before comparing data. Thorpe and Larsen (11) assumed the Gladstone-Dale specific dispersion of the alkanes to possess a value of 98.4. The specific dispersion obtained from the data of Wibaut et al. (13) is 98.3, which is also the value obtained by von Fuchs and Anderson (5). Although there is some discrepancy between the values obtained from the alkanes in comparison to that obtained from the fatty acid methyl esters the difference is, however, much less than the possible error.

The limiting density has already been previously reported as 0.85407 at 20C and 0.84225 at 40C (6). Substitution of these values in the Gladstone-Dale version of equation 5 yields the limiting dispersion, $n_{\beta,\infty} - n_{\alpha,\infty}$, i.e., 0.00854 at 20C and 0.00838 at 40C. The limiting dispersion obtained from the limiting refractive indices (7) is 0.00876 at 20C and 0.00858 at 40C. Although these two sets of values obtained by two different methods are at variance with each other, the differences are smaller than the experimental error.

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