

LXXX.—*The Relation between Viscosity and Chemical Constitution. Part VIII. Some Homologous Series.*

By ALBERT ERNEST DUNSTAN, FERDINAND BERNARD THOLE, and
PERCY BENSON.

IN a recent paper (T., 1913, **103**, 127) it was shown that the curves connecting the logarithm of viscosity with molecular weights in an homologous series were linear. The data available for

demonstrating this conclusion were very limited, and consisted mainly of the relatively few members of the homologous series investigated by Thorpe and Rodger (*Phil. Trans.*, 1894, A, 185, 397).

Seeing that it had been found possible to make use of this additive behaviour of log. viscosity to calculate constants for some of the chief radicles, and therefrom to synthesise, with a fair degree of accuracy, molecular values, it appeared to be a matter of some interest to examine as many long homologous series as could conveniently be prepared, first to determine whether this additivity held good over a long range of molecular weight; secondly, whether the values for the homologous increment were reasonably close together; and, thirdly, to deduce, if possible, a series of atomic and group constants.

From what was found in the previous communication, it appeared that, within limits, there was a constant value for CH_2 in each series, but it is by no means certain yet whether it will be possible to combine these values into a constant for all series. In other words, compared with molecular magnetic rotation, it is not yet possible to assert that $\log. \eta = n \times \text{CH}_2 + C$, where n is the number of carbon atoms in the molecule and C is a series constant.

The data available in the cases of the alkyl iodides, fatty esters, ketones, ethers, and paraffins showed that the log. viscosity curves were parallel, and hence a constant CH_2 value is possible in these cases, but for hydroxylated compounds, and particularly for the fatty acids, this parallelism is departed from.

In the present paper we have again had the advantage of using material prepared by Dr. Pickard and Mr. Kenyon. Five series have been placed at our disposal, containing in the aggregate fifty-two esters of secondary alcohols. We desire to express our thanks for the loan of these substances, which are of unexceptionable purity.

Further, we have determined, with some exceptions, the viscosities of the methyl and ethyl esters of the fatty acids from the first to the eighteenth term, the fatty acids through the same range, and the primary alcohols from methyl to hexadecyl. In all cases measurements have been made at 25° , but in some at 50° , 70° , and 90° .

The apparatus used was of the horizontal capillary type described by one of us (Thole, T., 1913, 103, 22), and in the case of Dr. Pickard's specimens, where only 1 or 2 c.c. of liquid was available, use was made of a miniature viscometer holding 0.8 c.c. Other experimental details have been described in previous papers.

The acids and alcohols used were obtained from Schuchardt; the

784 DUNSTAN, THOLE, AND BENSON: THE RELATION BETWEEN

esters were made by the usual methods, and the material was carefully dried and purified before use.

Some of the earlier members of the series of fatty acids and their methyl and ethyl esters having been measured with extreme accuracy by Thorpe and Rodger (*loc. cit.*), a number of these have been re-examined in order to gain an idea of the accuracy of the viscosity results obtained by the authors' method and apparatus.

TABLE I.

Viscosities of some Lower Alcohols, Acids and Esters at 25°, compared with Thorpe and Rodger's Values.

	Our value.	Thorpe and Rodger.
Acetic acid	0.0113	0.0112
Propionic acid	0.0102	0.0102
<i>n</i> -Butyric acid	0.0146	0.0142
		[Gartenmeister, however, obtains a value about 0.0146]
Methyl alcohol	0.00546	0.00549
Ethyl alcohol	0.01084	0.01083
<i>n</i> -Propyl alcohol	0.0198	0.0199
Ethyl formate	0.00379	0.00380
Ethyl acetate	0.00418	0.00420
Ethyl propionate	0.00497	0.00497

These viscosities were determined in the instrument which was used for most of the viscosities of the higher members at 50°, 70°, and 90°. The times of flow of the above compounds at these higher temperatures would have been too small, and so Thorpe and Rodger's results have been used.

TABLE II.

Normal Primary Alcohols at 25°.

	Viscosity.	$\log. \eta \times 10^3$.	ΔCH_2 .
Methyl alcohol	†0.00553	2.7427	—
Ethyl alcohol	†0.01091	3.0378	—
Propyl alcohol	†0.02016	3.3045	—
Butyl alcohol	†0.02606	3.4160	0.1115
Hexyl alcohol	0.0437	3.6403	2×0.1126
Heptyl alcohol	0.0568	3.7542	0.1139
Octyl alcohol	0.07215	3.8582	0.1040

Average = 0.1107

Average read from smoothed curve = 0.109

† Thorpe and Rodger's data.

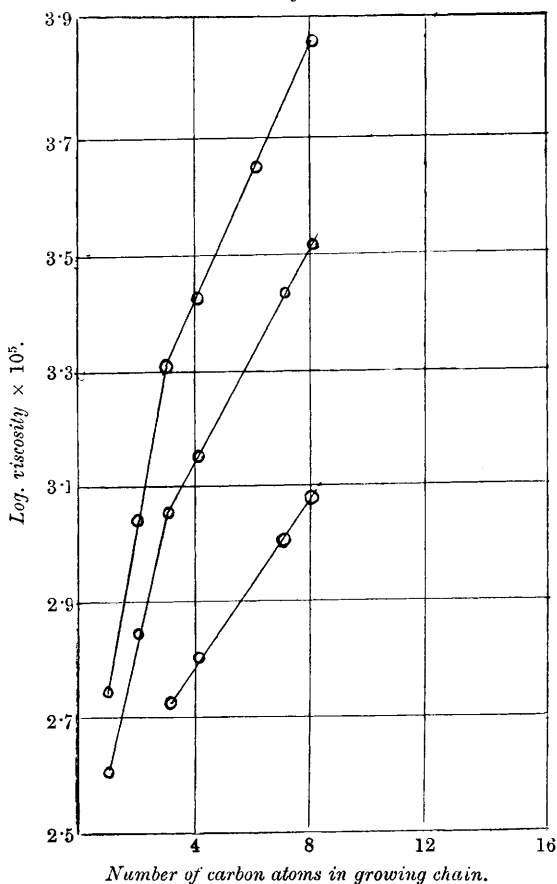
TABLE III. *Normal Primary Alcohols at 50°.*

	Viscosity.	$\log. \eta \times 10^5.$	ΔCH_2
Methyl alcohol	†0.00396	2.5977	—
Ethyl alcohol	†0.006975	2.8435	—
Propyl alcohol	†0.01128	3.0522	—
Butyl alcohol	†0.01409	3.1488	0.0966
Hexyl alcohol	0.0216	3.3341	2×0.0926
Heptyl alcohol	0.0268	3.4275	0.0934
Octyl alcohol	0.0322	3.5082	0.0807
Hexadecyl alcohol	0.146	4.1648	8×0.0821

Average = 0.0855

Average read from smoothed curve = 0.0881

† Thorpe and Rodger's data.

FIG. 1.
Primary alcohol.

Top curve : At 25°. Middle curve : At 50°.
Bottom curve : At 70°.

TABLE IV.

Normal Primary Alcohols at 90°.

	Viscosity.	$\log. \eta \times 10^5.$	$\Delta CH_2.$
Propyl alcohol	†0.00526	2.7210	—
Butyl alcohol	†0.006335	2.8017	0.0807
Heptyl alcohol	0.0100	2.9999	3×0.0661
Octyl alcohol	0.0121	3.0825	0.0826
Hexadecyl alcohol	0.0353	3.5479	—

Average read from smoothed curve = 0.0707

† Thorpe and Rodger's data.

TABLE V.

Normal Fatty Acids at 50°.

	Viscosity.	$\log. \eta \times 10^5.$	$\Delta CH_2.$
Formic acid	†0.010315	3.0134	—
Acetic acid	†0.00791	2.8982	—
Propionic acid	†0.00747	2.8733	—
Butyric acid	†0.009715	2.9874	0.1141
Valeric acid	0.0125	3.0974	0.1100
Hexoic acid	0.01687	3.2271	0.1297
Heptoic acid	0.0202	3.3058	0.0787
Octoic acid	0.0262	3.4178	0.1120
Nonoic acid	0.0347	3.5400	0.1222
Decoic acid	0.0434	3.6372	0.0972
Undecoic acid	0.07035	3.8473	2×0.1050

Average = 0.1086

† Thorpe and Rodger's data.

TABLE VI.

Normal Fatty Acids at 70°.

	Viscosity.	$\log. \eta \times 10^5.$	$\Delta CH_2.$
Formic acid	†0.00775	2.8893	—
Acetic acid	†0.00625	2.7896	—
Propionic acid	†0.006015	2.7975	—
Butyric acid	†0.00756	2.8785	0.0810
Valeric acid	0.00979	2.9794	0.1009
Hexoic acid	0.01186	3.0743	0.0949
Heptoic acid	0.0147	3.1685	0.0942
Octoic acid	0.01845	3.2669	0.0984
Nonoic acid	0.0231	3.3638	0.0969
Decoic acid	0.0288	3.4593	0.0955
Lauric acid	0.0408	3.6102	2×0.0754
Myristic acid	0.0676	3.8302	2×0.1101
Palmitic acid	0.0740	3.8692	—
Stearic acid	0.0939	3.9727	—

Average = 0.0941

† Thorpe and Rodger's data.

TABLE VII.
Normal Fatty Acids at 90°.

	Viscosity.	$\log. \eta \times 10^5$.	ΔCH_2 .
Formic acid	†0.00606	2.7825	—
Acetic acid	†0.00505	2.7003	—
Propionic acid	†0.00495	2.6946	—
Butyric acid	†0.006045	2.7813	0.0867
Hexoic acid.....	0.00881	2.9452	2×0.0820
Octoic acid	0.0130	3.1133	2×0.0840
Nonoic acid.....	0.0157	3.1957	0.0826
Myristic acid.....	0.0416	3.6188	5×0.0846
Stearic acid	0.0563	3.7505	—

Average = 0.0840

† Thorpe and Rodger's data.

FIG. 2.
n-Fatty acids.

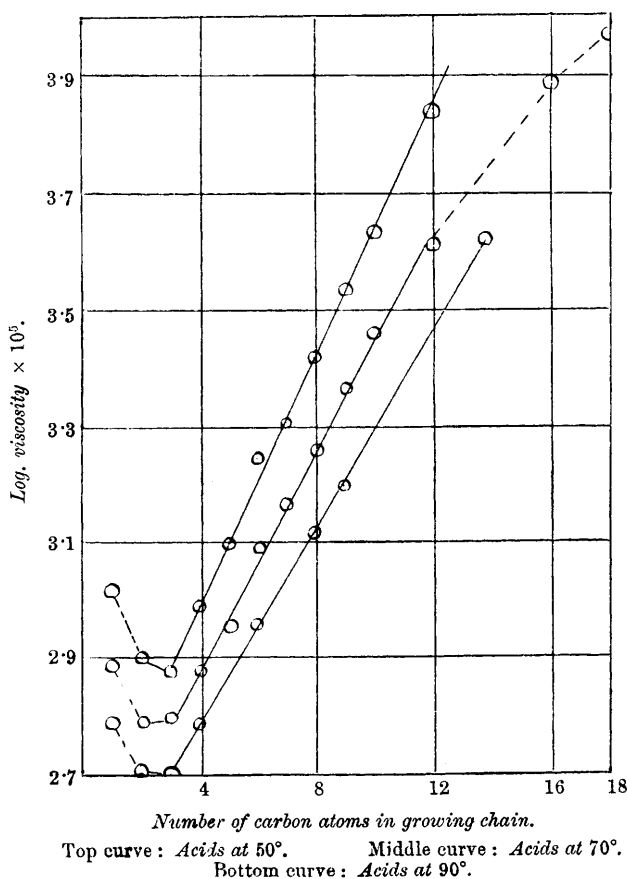


TABLE VIII.

Ethyl Esters of the Normal Fatty Acids at 25°.

	Viscosity.	$\log. \eta \times 10^5$.	ΔCH_2 .
Ethyl formate	†0.00382	2.5821	—
Ethyl acetate	†0.00425	2.6284	0.0463
Ethyl propionate	†0.00502	2.7007	0.0723
Ethyl butyrate	0.00635	2.8026	0.1019
Ethyl valerate	0.00759	2.8799	0.0773
Ethyl hexoate	0.00929	2.9680	0.0881
Ethyl heptoate	0.0111	3.0463	0.0783
Ethyl octoate	0.0138	3.1396	0.0933
Ethyl nonoate	0.01691	3.2281	0.0885
Ethyl laurate	0.0308	3.4883	—
Average, omitting first member = 0.0860			
Average read from smoothed curve = 0.0866			
Ethyl palmitate	0.0576	3.7604	4 × 0.0630

† Thorpe and Rodger's data.

TABLE IX.

Ethyl Esters of the Normal Fatty Acids at 50°.

	Viscosity.	$\log. \eta \times 10^5$.	ΔCH_2 .
Ethyl formate	†0.002995	2.4764	—
Ethyl acetate	†0.00326	2.5132	0.0368
Ethyl propionate	†0.003805	2.5803	0.0671
Ethyl butyrate	0.00458	2.6607	0.0804
Ethyl valerate	0.00536	2.7293	0.0686
Ethyl hexoate	0.00653	2.8153	0.0860
Ethyl octoate	0.00943	2.9645	—
Ethyl nonoate	0.0111	3.0466	0.0821
Ethyl laurate	0.174	3.2409	—
Average, omitting first member = 0.0728			
Average read from smoothed curve = 0.0756			
Ethyl palmitate	0.0314	3.4971	0.2562
Ethyl stearate	0.0375	3.5740	0.0769

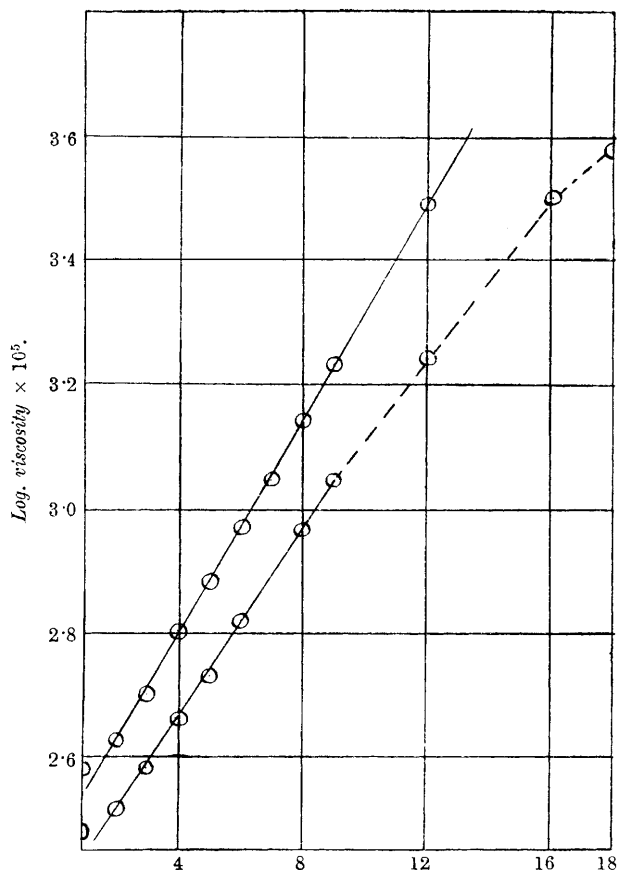
† Thorpe and Rodger's data.

TABLE X.

Esters of Undecan-β-ol at 25°.

	Viscosity.	$\log. \eta \times 10^5$.	ΔCH_2 .
Acetate	0.0281	3.4481	—
Propionate	0.0284	3.4534	0.0053
n-Butyrate	0.0362	3.5135	0.0601
n-Valerate	0.0374	3.5731	0.0596
n-Hexoate	0.0414	3.6167	0.0436
n-Heptoate	0.0491	3.6914	0.0747
n-Nonoate	0.0661	3.8203	—
n-Undecoate	0.0873	3.9409	—
Laurate	0.0966	3.9851	0.0442
Myristate	0.1233	4.0909	—
Average, omitting first member = 0.0579			
Average read from smoothed curve = 0.0588			

FIG. 3.
Ethyl esters of the n-fatty acids.



Top curve: At 25°. Bottom curve: At 50°.

TABLE XI.

Esters of Octan- β -ol at 25°.

	Viscosity.	$\log. \eta \times 10^3$.	ΔCH_2 .	
Acetate	0.0152	3.1809	—	
Propionate	0.0159	3.2004	0.0195	
n-Butyrate	0.0189	3.2772	0.0768	
n-Hexoate	0.0255	3.4070	0.1298	2×0.0649
n-Heptoate	0.0307	3.4872	0.0802	
n-Octoate	0.0364	3.5609	0.0737	
n-Nonoate	0.0422	3.6249	0.0640	
n-Undecoate	0.0582	3.7651	—	2×0.0701
Laurate	0.0687	3.8368	0.0717	
Myristate.....	0.0891	3.9498	—	2×0.565

Average, omitting first member = 0.0681

Average read from smoothed curve = 0.0706

3 F 2

TABLE XII.

Esters of Heptan- β -ol.

	Viscosity.	$\log. \eta \times 10^5$.	ΔCH_2 .
Acetate	0.0117	3.0686	—
Propionate	0.0125	3.0960	0.0274
<i>n</i> -Butyrate	0.0157	3.1957	0.0997
<i>n</i> -Valerate	0.0179	3.2538	0.0581
<i>n</i> -Hexoate	0.0219	3.3406	0.0868
<i>n</i> -Heptoate	0.02565	3.4091	0.0685
<i>n</i> -Octoate	0.0303	3.4816	0.0725
<i>n</i> -Nonoate	0.0369	3.5671	0.0855
<i>n</i> -Undecoate	0.05015	3.7002	—
Laurate	0.0590	3.7708	0.0706
Myristate.....	0.0775	3.8894	—

 2×0.0665 2×0.0593

Average, omitting first member = 0.0721

Average read from smoothed curve = 0.0715

TABLE XIII.

Esters of Hexan- β -ol at 25°.

	Viscosity.	$\log. \eta \times 10^5$.	ΔCH_2 .
Acetate	0.009445	2.9752	—
Propionate	0.0104	3.0182	0.0430
<i>n</i> -Butyrate	0.0133	3.1227	0.1045
<i>n</i> -Valerate	0.0156	3.1932	0.0705
<i>n</i> -Hexoate	0.0180	3.2552	0.0620
<i>n</i> -Heptoate	0.0215	3.3324	0.0772
<i>n</i> -Nonoate	0.0308	3.4883	—
<i>n</i> -Undecoate	0.0430	3.6338	—
Laurate	0.540	3.7323	0.0985
Myristate.....	0.673	3.8283	—

 2×0.0779 2×0.0727 2×0.0480

Average, omitting first member = 0.0700

Average read from smoothed curve = 0.0715

TABLE XIV.

Esters of Butan- β -ol at 25°.

	Viscosity.	$\log. \eta \times 10^5$.	ΔCH_2 .
Acetate	0.00601	2.7792	—
Propionate	0.00669	2.8252	0.0460
<i>n</i> -Butyrate	0.00839	2.9236	0.0984
<i>n</i> -Valerate	0.0101	3.0059	0.0823
<i>n</i> -Hexoate	0.0127	3.1032	0.0973
<i>n</i> -Heptoate	0.0152	3.1816	0.0784
<i>n</i> -Octoate	0.0182	3.2607	0.0791
<i>n</i> -Nonoate	0.0218	3.3386	0.0779
<i>n</i> -Undecoate	0.0325	3.5124	—
Laurate	0.0387	3.5881	0.0757
Myristate.....	0.0532	3.7256	—

 2×0.0869 2×0.0687

Average, omitting first member = 0.0818

Average read from smoothed curve = 0.0836

FIG. 4.
Esters of methylalkylcarbinols.

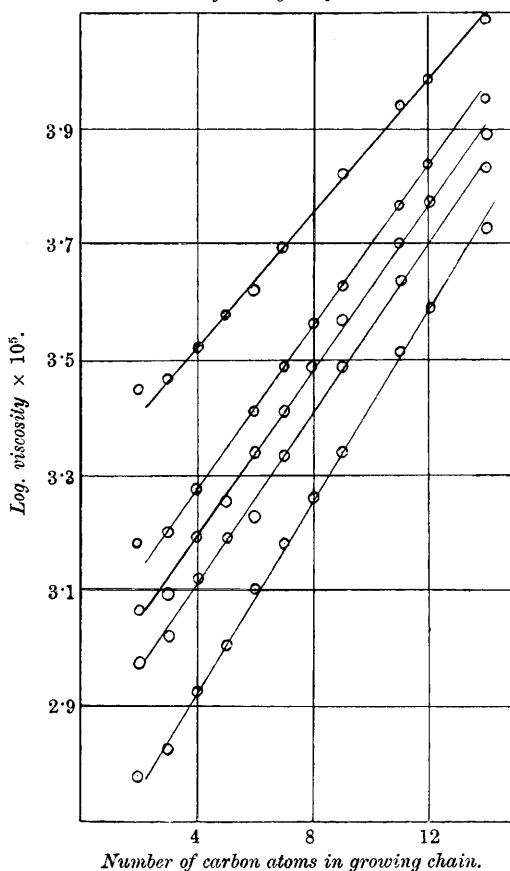


TABLE XV.

Methyl Esters of the Normal Fatty Acids at 25°.

	Viscosity.	$\log. \eta \times 10^5$.	ΔCH_2 .	
Methyl formate	†0.00332	2.5211	—	
Methyl acetate	†0.003625	2.5593	0.0382	
Methyl propionate	†0.00431	2.6345	0.0752	
Methyl butyrate.....	†0.005415	2.7336	0.0991	
Methyl octoate	0.0126	3.1006	—	4×0.0918
Methyl laurate	0.308	3.4891	—	4×0.0971

Average, omitting first member = 0.0930

Average read from smoothed curve = 0.0916

† Thorpe and Rodger's data.

TABLE XVI.

Methyl Esters of the Normal Fatty Acids at 50°.

	Viscosity.	$\log. \eta \times 10^5$.	ΔCH_2 .
Methyl acetate	†0.00284	2.4533	—
Methyl propionate	†0.00334	2.5237	0.0704
Methyl butyrate.....	0.00407	2.6096	0.0759
Methyl octoate	0.00846	2.9273	—
Methyl laurate	0.01852	3.2679	—

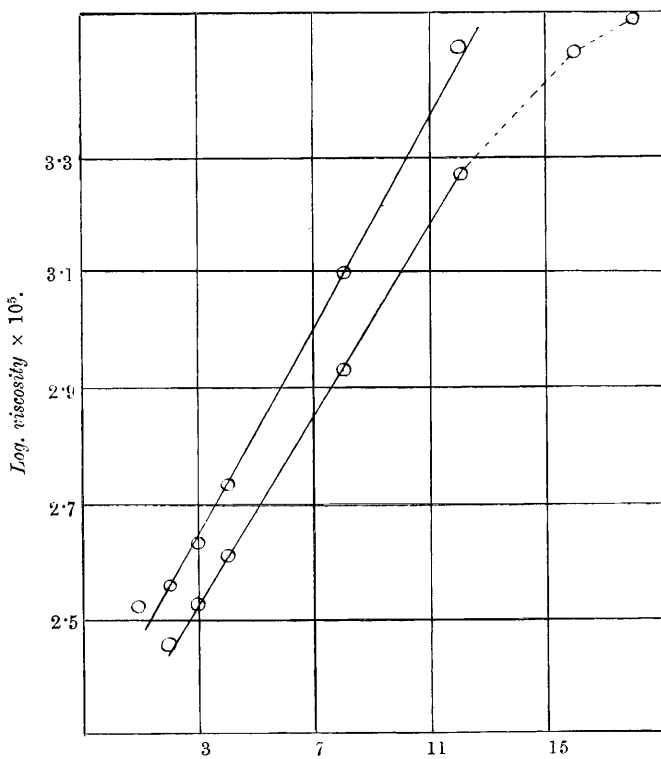
 4×0.0794 4×0.0851

Average = 0.0805

Average read from smoothed curve = 0.0829

† Thorpe and Rodger's data.

FIG. 5.

Methyl esters of the n-fatty acids*Number of carbon atoms in growing chain.*

Top curve : At 25°.

Bottom curve : At 50°.

TABLE XVII.

Average Values of the CH₂ Differences at 25°.

Series.	Number of members.	ΔCH_2 . Average.	ΔCH_2 . Average from smoothed curves.
Fatty methyl esters.....	6	0.0930	0.0916
Fatty ethyl esters	10	0.0860	0.0866
Esters of butan- β -ol	11	0.0818	0.0836
Esters of hexan- β -ol	10	0.0700	0.0715
Esters of heptan- β -ol	11	0.0721	0.0715
Esters of octan- β -ol	10	0.0681	0.0706
Esters of undecan- β -ol	10	0.0579	0.0588
Methylalkylcarbinols	8	0.0982	—
Primary alcohols	8	0.1107	0.109
Fatty acids	14	0.136	—

FIG. 6.

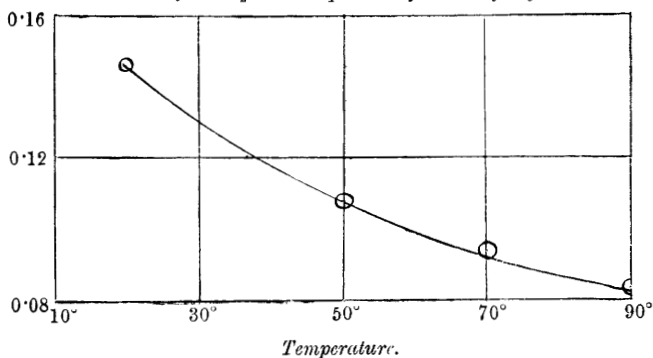
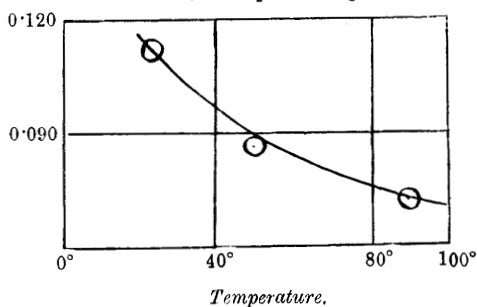
Variation of ΔCH_2 with temperature for the n-fatty acids.

FIG. 7.

Variation of ΔCH_2 with temperature.

Discussion of Results.

The esters of butan- β -ol, hexan- β -ol, heptan- β -ol, octan- β -ol, and undecan- β -ol may be conveniently considered first. The initial member is usually anomalous, giving a value of log. viscosity which is too high, whilst there is a tendency for the highest member to give a value which is too low. With these exceptions, the majority of the 52 esters lie on five straight lines, of which the middle three are parallel to one another, whilst the extremes converge. The value of the CH_2 differences for the esters of undecan- β -ol are the smallest we have hitherto encountered. To what extent the effect of high molecular weight modifies the homologous increment must remain at present an open question, but it is certainly remarkable that the greater the molecular weight of the group to which is attached the growing chain, the smaller is the effect of each CH_2 .

The tendency of the members of highest molecular weight to depart from linearity appears to be connected with this fact, and shows that not only must the gross effect of each CH_2 be considered, but also, perhaps, its percentage effect, which, of course, will become less as the molecular weight increases.

Turning to the results for the fatty acids, the most striking phenomenon is the behaviour of the first two members. The viscosities of formic and acetic acids are abnormally high. This may be ascribed to the high degree of association possessed by these two compounds, but even then the normal CH_2 difference for the series is exceptionally high as compared with, for example, the esters. It is hardly conceivable that the association factor should undergo so sudden a change at the third member and then remain content with each successive increment of CH_2 . Palmitic and stearic acids diverge considerably from the mean line, just as was the case with the highest member of the foregoing series.

The CH_2 differences diminish with rising temperature, and at 90° the value for the fatty acids approximates to that afforded by their ethyl esters at 25° . Whether this fact foreshadows another method for the attainment of a "corresponding temperature" remains to be settled by the accumulation of more data.

In the case of the primary alcohols, the abnormality of the first two members is again apparent, although in a direction opposite to what is generally the case, for these two substances have viscosities smaller than would be expected. No satisfactory reason can be adduced at present for this anomalous behaviour, since it is scarcely possible that the degree of association becomes greater as the homologous series is ascended.

From the propyl member onwards linearity is observed up to

the octyl term, but hexadecyl alcohol seems to illustrate the general behaviour of the members of high molecular weight in the other series.

General Conclusions.

When the CH_2 differences for all the series examined are compared, it will be noticed that the numerical values become less as the amount of residual affinity in the molecule decreases, namely, in the order: acids-primary alcohols-secondary alcohols-methyl esters-ethyl esters-esters of secondary alcohols.

Of the 93 compounds examined, the great majority fall on straight-line curves, with the exception of the initial and final members.

The higher the molecular weight of the nucleus to which the growing chain is attached, the lower is the value for the homologous increment. The CH_2 differences for any series at various temperatures lie on a smooth curve, from which can be interpolated the temperature of any desired CH_2 value, and hence a possible corresponding temperature.

It is our intention, having examined the above series containing associated compounds, to continue the investigation with a range of unassociated substances, such as the paraffins, ketones, alkyl haloids, in the expectation of meeting with more constant CH_2 differences.

We desire to thank the Research Committee of the Royal Society for a grant in aid of this work.

PHYSICAL CHEMISTRY LABORATORY,
EAST HAM TECHNICAL COLLEGE.
