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COMPARISON OF VISCOSITY AND MOLECULAR ARRANGEMENT IN TWENTY-TWO LIQUID OCTYL ALCOHOLS

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Abstract

A comparison is made between the x-ray diffraction halos of 22 octyl alcohols and their corresponding viscosities and an unmistakable correlation found. The assumptions are that the halos indicate periodicities, that the periodicities may be interpreted as structural in the "cybotactic" groups, and that the relative diffraction intensity of the halos computed by assuming crystal structure may be used to estimate roughly the perfection of the liquid groups. It thus is shown that there is a correlation between the coefficient of viscosity and the perfection of grouping in the direction of the length of the chain molecules. This corresponds with the reasonable view that the viscosity within the liquid groups is caused by longitudinal slippage. Moreover, since the groups at any instant occupy a large fraction of the volume of the liquid, this viscosity is an important part of that measured. This interpretation accounts for the negative temperature coefficient of the viscosity, since the size of the groups decrease with temperature. The experiments and conclusions are in accord with Andrade's theory of momentary "crystallization" and with Ornstein's theory of the formation of liquid crystal groups, yet it is to be noted that these theories deal with different aspects and not the entire phenomenon.

THE x-ray diffraction study by the author[1] of 22 octyl alcohols prepared in the laboratory of Professor E. Emmet Reid of Johns Hopkins University has made possible an interesting comparison of x-ray findings with the coefficient of viscosity of the same compounds. The comparsion as herewith presented, leads to the conclusion that this coefficient does have a dependence upon differences in the space arrangement (cybotaxis) of the molecules of liquid isomers as determined by x-ray data.

In the discussions in Nature[2] the differences in the origin of viscosity in liquids and gases is emphasized. The picture of the phenomenon in liquids as given by Andrade is that there is "a temporary union of molecules in contiguous layers, the duration of this union not exceeding the very brief time required for the molecules to acquire a common velocity of translation." This union takes place under the action of the molecular fields. "The general pic-

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[1] Stewart, Phys. Rev. **35**, 726 (1930).

[2] By E. N. da C. Andrade, J. Frenkel, D. H. Black ,E. W. Madge and Ambrose Fleming in issue of April 12, 1930, and by E. C. Sheppard, March 29, 1930.

ture is one of the liquid "crystallizing" in minute patches." It is evident that Andrade's view borders closely upon what the author has chosen to call the "cybotactic" condition of the liquid. The x-ray evidence by diffraction in liquids, both in this laboratory[3] and elsewhere,[4] has accumulatively stressed the correctness of the view that there are in a liquid minute groups[5] or bundles of molecules in each one of which there is sufficient periodicity to account for the diffraction halos obtained.

It is further evident that this periodicity is not caused merely by the effect of the volume of the molecules,[6] but also by all the forces arising in the molecular fields as well. The importance of the molecular fields may be obtained from a general comparison of the liquid and crystalline state, for example in density, compressibility and latent heat of evaporation. But as a specific illustration of the necessity of the introduction of these fields may be cited the difference in diffraction halos of 3-ethyl pentane[3] and diethyl carbinol.[3] Both molecules are admittedly of practically the same size and shape, yet with the former only one halo of importance appears, whereas with the latter there are two very prominent. The additional halo in the diethyl carbinol is caused by a periodicity in the direction of the molecular lengths, one which does not appear at all in the nonpolar compound. Moreoever, the periodicities indicated by the other diffraction maxima are not of the same magnitude. But it is the purpose of this article not to submit the large amount of evidence favoring the existence of minute well-ordered temporary regions or groups of molecules in a liquid, but rather to point out an interesting comparison of the coefficient of viscosity with the perfection of these molecular groups as shown by x-rays. The results have been hitherto unpublished, chiefly because they have appeared more suggestive than conclusive. But the discussion of liquid viscosity already mentioned and the current interest in obtaining the appropriate basis for a theory of that phenomenon would seem to require that the experimental evidence connecting the cybotactic view with the nature of viscosity be submitted. To this will be added a brief theoretical discussion of the cybotactic view.

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[3] See Stewart and collaborators, Morrow, Skinner, in a series of papers in Phys. Rev. from September 1927 to September 1931, and Spangler, Radiology **16,** 346 (1931).

[4] For reveiws of literature see, for example, Good, Physica Acta, p. 305, 1930.

[5] It must be emphasized that the word "group" when describing molecular structure in a liquid, refers not to a minute crystal, to a region having a defined boundary, or to a permanent condition of the molecules involved. It refers to a region or spot of effective (at that instant) regularity of structure in a liquid. This condition of regularity of space arrangement fades off continuously into much less regularity. Hence there is no sharp boundary. These regions are very numerous occupying a large fraction of the total volume of liquid. A group does not retain its identity as determined by its constituent molecules. It is not a fragment of material, but it is a condition of position and potential energy which varies throughout the liquid. The existence of any group is temporary, yet the orderliness of the structure in more than one direction demands that its existence has a time duration.

[6] Debye in J. of Mathematics and Physics **4,** 133 (1925) and in Phys. Zeits. **28,** 315 (1927) has shown that even spherical atoms when occupying as much as one-half of the total volume, will produce an x-ray halo. Also Zernike and Prins, Zeits. f. Physik **41,** 184 (1927) emphasize the space effect.

EXPERIMENTAL

In order to make the discussion intelligible, the relative diffraction intensity curves for the 22 octyl alcohols are shown in Figs. 1, 2, and 3.[7] The angle θ is that read on the spectrometer. The radiation is essentially that of Mo$K\alpha$, but is not strictly monochromatic. Nevertheless its lack of homogeneity does not here lead to incorrect interpretations. Especially it should be remarked that any misleading effect of the continuous radiation is avoided by having a low voltage on the tube and by using thicknesses of samples that are less than the optimum for Mo$K\alpha$ radiation. The original article may be consulted for the experimental details. It is assumed that these peaks indicate periodicity and that the most probable distance of separation of diffraction centers can be obtained by Bragg's law, $\lambda = 2d \sin \theta/2$. This assumption is warranted by the accepted view of crystal structure. The coherence in x-ray diffraction with crystals shows, by computation with Bragg's Law, the periodicities of the structure and in this interpretation both classical and quantum theories agree. Then for monochromatic radiation incident on a liquid, a band, instead of a line diffraction, may be interpreted as indicating not one periodicity but a number of them; as if one had powdered crystals with each set of planar separations varying over a small range in accord with a probability function. Some of the variation of periodicity, but much narrower in range,

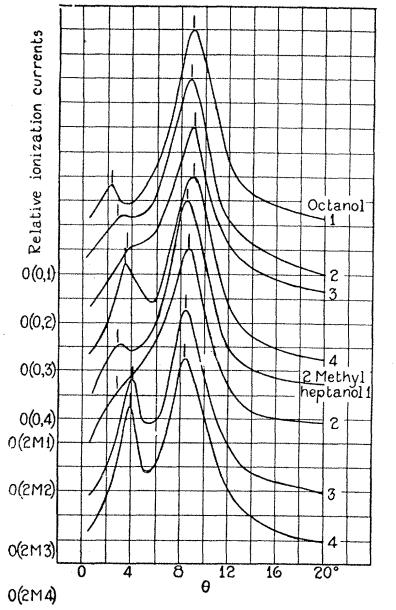

Fig. 1. X-ray diffraction; relative ionization currents of octyl alcohols.

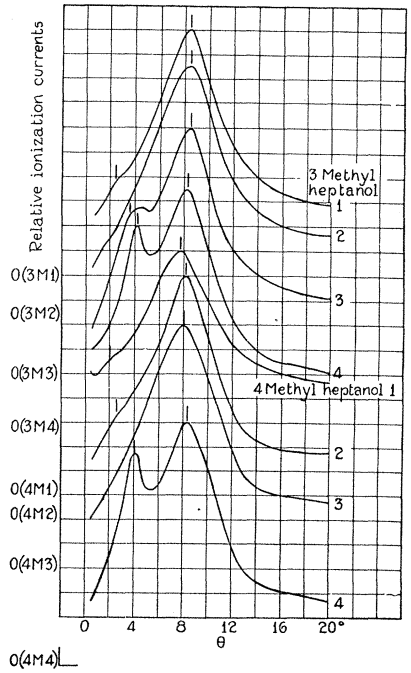

Fig. 2. X-ray diffraction; relative ionization currents of octyl alcohols

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[7] Stewart, Phys. Rev. **35**, 726–732 (1930).

may occur in the analogous single crystal also. The assumption of the correctness of Bragg's law for a liquid is thus based upon the straightforward conclusion that coherence indicates periodicity.

The periodicities obtained from the liquid are not sufficient to lead to a unique liquid structure. But it is in agreement with all the facts to assert that the molecules of n-alcohols, saturated normal fatty acids and n-paraffins[8] lie parallel in the so-called groups, with their long axes laterally equidistant and lying in two sets of parallel planes perpendicular to one another. This dimension is obtained from the major peak. On the other hand the position of the minor peak (not occurring with the paraffins) depends upon the length of the chain and is assumed to correspond to a periodicity having a direction or a component of a direction along the axes of the molecules. If the spacing of the molecules longitudinally is not orderly, permitting effective diffraction centers to lie in parallel planes cutting the molecular axes, the minor peak will not be in evidence. These statements are consistent with all the facts and are discussed fully in the articles cited.

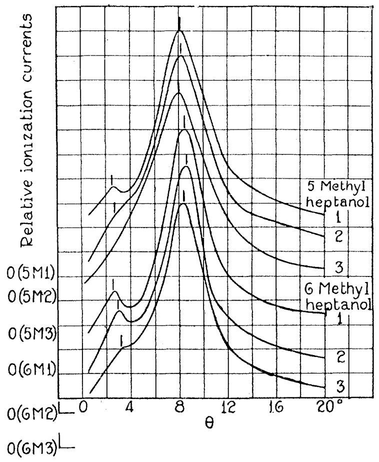

Fig. 3. X-ray diffraction; relative ionization currents of octyl alcohols.

If one now considers the structure factor, F, of the molecules just as in the case of a crystal, it is easily seen[9] that the x-ray intensity from the lateral periodicity of these molecules will always be large and comparable with each other, while from the longitudinal periodicity the coherent scattering will be less and the variation among the compounds greater.

But as noted in x-ray diffraction experiments, these longitudinal periodicities appear (in chain compounds) only with polar molecules. The molecular field of a nonpolar chain compound is not sufficient to produce the longitudinal periodicity. One might thus expect that the slippage in the liquid groups may occur parallel to the molecular lengths and that there is a varia-

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[8] Stewart and Morrow, Phys. Rev. **30,** 232 (1927); Morrow, Phys. Rev. **31,** 10 (1928); Stewart, Phys. Rev. **31,** 174 (1928).

[9] Spangler, Radiology **16,** 346 (1931).

tion in the intensities at the minor diffraction peaks not only because of structure factor but also because of the lack of perfection in the longitudinal periodicity.

One might thus anticipate that the viscosity would depend upon the perfection of the longitudinal periodicity, indeed, that the viscosity would increase with the perfection of grouping. This would be the case whether the groups occupied a large proportion of the volume or not. Clearly a comparison of the perfection of orderly longitudinal grouping with variation in viscosity would be advisable.

Degree of longitudinal periodicity in octyl alcohols compared with viscosity. The comparison just suggested must be of necessity crude, for one is not dealing with minute crystals wherein the structure factor of the molecules can be used with accuracy. Moreover, the structure of the liquid so-called groups is not definitely known. Reliance is placed merely upon a reasonable interpretation of diffraction curves.[9] The method of comparison is as follows.

TABLE I.

Compound	Heights of peaks	Computed relative heights	Col. 2–Col. 3 Ratio	Coefficient of viscosity
Octanol-1	11.0	24.9	0.433	0.204
Octanol-2	6.	12.4	.484	.218
Octanol-3	7.5	36.5	.206	.066
Octanol-4	27.2	69.0	.394	.154
2-methyl heptanol-1	11.0	49.5	.220	.083
2-methyl heptanol-2	6.0	40.0	.150	.091
2-methyl heptanol-3	28.0	104.	.270	.333
2-methyl heptanol-4	36.2	84.3	.430	.294
3-methyl heptanol-1	2.7	43.7	.062	.0361
3-methyl heptanol-2	0	29.1	0	.0311
3-methyl heptanol-3	16.5	140.	.118	.196
3-methyl heptanol-4	24.6	117.	.175	.042
4-methyl heptanol-1	1.0	53.2	.0188	.065
4-methyl heptanol-2	4.0	11.1	.364	.077
4-methyl heptanol-3	0.0	82.	0	.019
4-methyl heptanol-4	33.8	108.	.313	.322
5-methyl heptanol-1	6.0	13.6	.440	.137
5-methyl heptanol-2	4.0	4.46	.898	.047
5-methyl heptanol-3	0	84.5	0	.021
6-methyl heptanol-1	11.0	7.9	1.39	.227
6-methyl heptanol-2	17.8	3.92	4.54	.154
6-methyl heptanol-3	6.0	94.5	.0635	.026

In column two of Table I appear the relative heights of the secondary peaks as measured in Figs. 1, 2 and 3. In column 3 appear the relative heights these peaks should have if the diffraction occurred from powdered crystals having the structure mentioned. The computations for column 3 were made by Mr. Ross Spangler using the values of equivalent numbers of electrons as given by James and Brindley.[10] Column 3 then may be interpreted as indicating relative values of minor maxima in the diffraction curves which would occur if the groups were powdered crystals. Hence column 2 divided by column 3 would give a crude measure of the excellence or perfec-

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[10] James and Brindley, Phil. Mag. **12,** 87 (1931).

tion of longitudinal periodicity which actually exists. This quotient is placed in column 4. In column 5 are given the observed coefficients of viscosity of these octyl alcohols as determined by Professor E. C. Bingham. The comparison is now made between column 4 and column 5 in Figs. 4 and 5. The values are plotted with change in molecular structure. With OH stationary and CH^3 attached as a branch to the different C atoms, the comparison is made in Fig. 4. It is to be noted that the range of the variables is large and therefore the correlation is striking. Only three compounds of the 22 in column four do not show a correlation. Similar comments may be made concerning Fig. 5 in which the position of the OH group is made the variable in the molecular structure. Incidentally, it may be pointed out that the three compounds with which the comparison is not favorable are those in which the molecule has OH near one end and CH_3 in a branch near the other. This indicates similar reasons for the disagreement, and the nature of the assumptions leaves ample room for such reasons. Speculations upon these disagreements are omitted

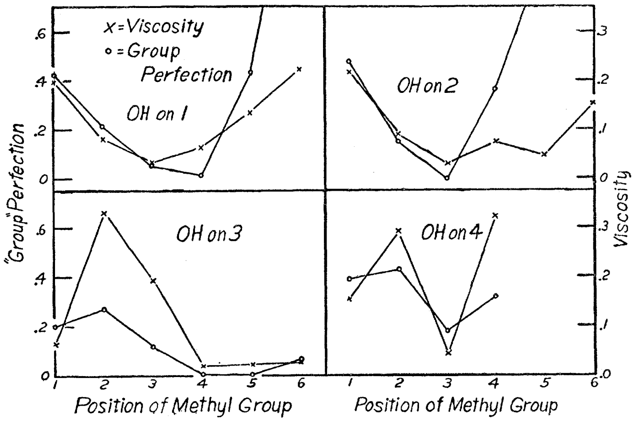

Fig. 4. Variation of "group" perfection and coefficient of viscosity.

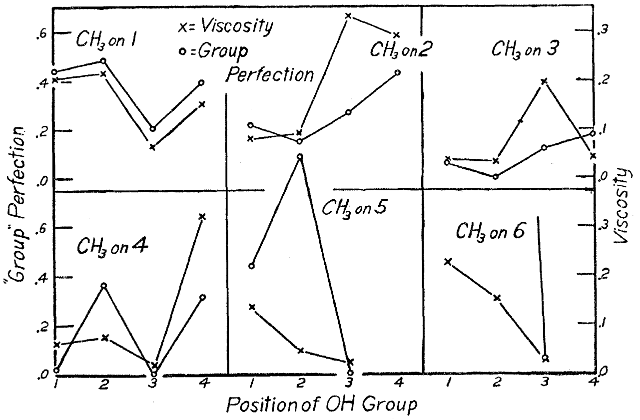

Fig. 5. Variation of "group" perfection and coefficient of viscosity.

as having no purpose in this paper. That the correlation in Fig. 4 is noticeably better than in Fig. 5 is in harmony with the fact that in the former the polar group for any curve pair is stationary in the molecule. It should be pointed out that our assumptions take no consideration of the viscosity of the less regularly arranged molecules, which may depend on "shape." This is because, as mentioned below, these molecules are relatively few in number. Consequently the longitudinal slippage within the molecular groups is the chief factor in viscosity. From the foregoing evidence it now appears that the conditions producing the cybotactic condition in a liquid should be used as a basis for the consideration of the nature of liquid viscosity. This procedure is justified chiefly because of the evidence for cybotactic groups accumulated through x-ray diffraction experiments, but yet in part also because of the corroborative experiments here described.

The cybotactic view can be embodied in mathematical expressions only by very crude approximations, for the nature of the molecular fields is not understood. One such may be by the assumption of Andrade[11] as to a temporary union of molecules of one layer with another. This may be regarded as recognizing the existence of non-rigid somewhat orderly regions or groups in which, for example, molecules having a long axis will slip by one another in the direction of this axis. Andrade's theory has not been published so that it is impracticable to comment further on its conformity with the concept of groups advocated by the author.

A different approach to a theoretical consideration may be borrowed from Ornstein's[12] theory of liquid crystals. If the molecule is unsymmetrical, having a long axis, it is assumed that a molecule exerts a couple upon a neighboring one, the potential energy being proportional to the cosine of the angle between their axes and to a function of the distance of separation of the centers of mass of the molecules. Boltzmann's principle is applied. The theory finally leads to an expression which shows that the volume of the well-ordered regions decreases with an increase in temperature. From the experiments with x-rays it has become evident that, since the coherent diffraction with liquids is of the same order of magnitude[13] as that of the same mass in the form of crystal powder, the volume of the molecular groups is a large fraction of the total volume. Thus, if within the groups or well ordered regions the viscosity were greater than in the ungrouped molecules, the volume of the groups would be important in determining the measured value of the viscosity. An increase in temperature, decreasing this volume, would decrease the viscosity, which is in accord with experiments. In order to compute the effect, one would need to develop a theory for the dependence of viscosity upon the volume of the groups present when that volume is a large fraction of the whole.

The two theories are not contradictory, but refer to different aspects each without any claim of completeness. Andrade's theory emphasizes the effect of momentary group formation, which interferes with slippage. Ornstein's

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[11] E. N. da C. Andrade, Nature, April 12, 1930.

[12] Ornstein, Zeits. f. Kristall. **79,** 90 (1931).

[13] Stewart, Phys. Rev. **37,** 9 (1931); See Fig. 1.

theory assumes a group which changes its size with temperature. In view of x-ray evidence concerning liquid diffraction it is reasonable to suppose that both conditions exist. It is significant that both causes lead to the correct sign of the change of viscosity with temperature and that both theories are in essential agreement with the cybotactic group view advocated by the author though as a matter of expediency they consider the conditions only in part.[14]

It is evident from the foregoing that a theory of viscosity which involves all the important aspects of the nature of a liquid is yet ahead, but that the theories of Andrade and of Ornstein are distinctly valuable. The cybotactic view would indicate the desirability of closer approximations in theory to the molecular fields existing in corresponding crystals. But until such fields are well understood the bases of theories proposed must of necessity be limited.

The reader is reminded that the correlation found between cybotactic group perfection and viscosity is presented because it seems opportune. The correlation is intrinsically not highly satisfactory. But the results do show an unmistakable relation, in spite of the various approximations that are of necessity made. This conclusion is however sufficient to emphasize the justification for the basis of viscosity theory similar to that given by Andrade. Not only does the temperature variation of viscosity point to an assumption of momentary union of molecules, but all x-ray diffraction experiments in liquids would urge the essential correctness of the assumption.

It is a pleasure to thank Professor E. Emmet Reid of Johns Hopkins University for the octyl alcohols used, Professor E. C. Bingham of Lafayette College for the viscosity data, and Dr. H. A. Zahl who, as a research assistant, took the x-ray data involved.

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[14] There has just come to the attention of the author the earlier suggestions of Raman (Nature **111**, 532 and 600 (1923). He assumed two states of aggregation in the liquid "solid" and "vapor," and that the viscosity was proportional to the relative numbers of molecules in the two states. Raman's assumptions, while not those of the author, are closely similar. Raman's expression for the viscosity of a liquid is the same as Andrade, $\eta = Ae(b/T)$, where η is the viscosity coefficient, A and b are constants and T is the temperature. This formula agrees remarkably well with observed temperature variations. See also Iyer (Ind. J. of Physics, V Pt. IV, 371 (1930) for a discussion of the significance of A and b in Raman's suggestion.