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THE CYBOTACTIC (MOLECULAR GROUP) CONDITION IN LIQUIDS; THE NATURE OF THE ASSOCIATION OF OCTYL ALCOHOL MOLECULES

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ABSTRACT

In resumè twelve experimental lines of evidence are cited in favor of the adoption of the molecular group theory of the nature of liquids. This theory is assumed in the interpretation of results with octyl alcohols.

The following twenty-two octyl alcohols were used: octanol −1, −2, −3, −4, 2-methyl heptanol −1, −2, −3, −4, 3-methyl heptanol −1, −2, −3, −4, 4-methyl heptanol −1, −2, −3, −4, 5-methyl heptanol −1, −2, −3, 6-methyl heptanol −1, −2, −3.

The value of the effective diameter of the primary normal alcohols is approximately 4.5 A. With these octyl alcohols the increase for OH and CH_3 in a branch is approximately 0.0 A and 0.24 to 0.75 A respectively. When attached to the same carbon atom the increase caused thereby is not noticeable. These results are in fair agreement with previous similar measurements of isomers with other primary alcohols.

Two types of association were found. When the OH group is attached to the end or next to the end of the alcohol molecule, two of these molecules are associated end to end, the lengths of the chains being in the same straight line. On the other hand when the OH group is attached to any other carbon atom, the molecules are associated side by side. This is shown by the planar distances in the direction of the molecule which indicate in the first case the length of two molecules and in the second case the length of a single molecule.

DURING the past four years evidence has been accumulating in favor of the view that in liquids in general there exist temporary, fairly orderly, not sharply defined molecular groups. A brief resumé of that evidence, as an introduction to the present experiments, is opportune. Skepticism concerning the correctness of this conception of molecular groups is natural, since it has formerly been accepted that the molecular motions in a liquid are somewhat independent. Moreover it is known that molecules of a gas, which are certainly not orderly, will give x-ray diffraction haloes.[1]

EVIDENCE FOR THE CYBOTACTIC CONDITION

It will be the purpose of this statement of evidence to present the material merely in outline. The reader can easily follow the argument by studying the experimental results mentioned in each case. For the sake of simplicity the references will be limited but the articles to which references are made contain the complete bibliography. It is believed that the evidence establishes the group theory as one worthy of confidence. The chief points will be now enumerated. All the experiments refer to x-ray diffraction.

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[1] Debye, Phys. Zeits. **30,** 524 (1929); **31,** 142 (1930).

1. Scattering centers at randon would produce a large scattering near 0°, for in the terms of a wave theory, the nearer the approach to 0° the more nearly the agreement in phase. But crystals and crystal powders would, if ideal, give zero diffraction near but not at 0°. With them, interference would produce zero intensity excepting at angles of regular reflection.[2] Now it is found that in liquids, in general, we find the diffraction near zero to be similar to that of crystal powders and not to amorphous substances. The author and his co-workers[3] habitually approach zero diffracting angle to the limit permitted by the resolving power of the instrument, 24′, and they find the intensity small and decreasing as 0° is approached.

2. With normal monobasic fatty acids,[4] one diffraction peak alters its angular position with the number of carbon atoms in the chain in such a manner that the corresponding lengths (computed by Bragg's diffraction law) vary linearly with the carbon content. This is precisely what has been found[5] with the same fatty acids in solid form and the distances and rate of change are approximately the same in the solids and liquids. Similar causes are presumably operating in the two cases. If the solid is crystalline, the liquid has molecular groups.

3. Comparisons between the solid and liquid diffraction curves show a clear similarity. Of course the diffraction peaks are diffuse as compared with the lines with crystals. But the prominent maxima are similarly located. Krishnamurti[6] has published comparisons of eight substances. There have also been published lauryl alcohol[7] and capric acid[8] diffraction curves. Triphenylmethane shows a like result. The chief maxima of intensity occur apparently at nearly the same angles of diffraction.

4. Binary solutions, where the components are miscible, show not the diffraction intensity maxima of both components, but a modification as of a single liquid. This is analogous to the case of a solid solution,[9] and can readily be explained by the molecules of the solute participating in the molecular groups of the solvent. This is a reasonable picture of the nature of a solution.

5. The area occupied by the cross-section of a molecule of normal monobasic acids in a surface film on water[10] is the area as computed by measurements within such a liquid assuming the group theory.[11] It is also the area computed from similar measurements on primary n-alcohols.[12] The grouping

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[2] Regular reflection occurring at a very small glancing angle less than the critical angle, need not be regarded here.

[3] See series of articles by Stewart, Stewart and Morrow, and Stewart and Skinner in Phys. Rev. 1927–29.

[4] Morrow, Phys. Rev. **31,** 10 (1928).

[5] See footnotes in Morrow, reference 4.

[6] Krishnamurti, Ind. Jour. Phys. III, II, 225 (1928).

[7] Stewart and Morrow, Phys. Rev. **30,** 232 (1927).

[8] Morrow, reference 4.

[9] Krishnamurti, Ind. Jour. Phys. III, III, 331 (1929); Hertlein, Zeits. f. Physik **54,** 341 (1929). Also unpublished results by A. W. Meyer of this laboratory.

[10] Adam, Proc. Roy. Soc. **99A,** 336 (1921); **101A,** 452, 456 (1922); **103A,** 676, 687 (1923).

[11] Morrow, reference 4.

[12] Stewart and Morrow, reference 7.

of the molecules in such a surface film is acknowledged. Similar dimensions obtained on the interior argues strongly for molecular groups.

6. The group theory leads to simultaneous measurements of two and occasionally three distances. These are in striking consistency and difficult of explanation otherwise. For example, the molecular "diameters" remain constant with increase in the length of the chain.[11,12] Again, di-n-propyl carbinol gives three distances,[13] of which two, 4.85 and 4.5 A.U., are consistent with the interpretation that the former is a measurement of the diameter in the direction of the branch and the latter the diameter of the chain perpendicular thereto, or the diameter of the primary n-alcohol.

7. Assuming the group theory, isomers of primary n-alcohols have been measured[12] and these have been found consistent with the usual chemical views as to structure.

8. The effect of temperature on the diffraction in liquids is, in general, similar to that in crystal powders, i.e., a shifting of the maxima to smaller angles, an increase in diffuseness and a decrease in intensity.[14]

9. There are two peaks with the primary n-alcohols[12] and only one with n-paraffins.[15] This is in harmony with the group theory. Each series has parallel chains, but the polar molecules produce a longitudinal orderly arrangement that makes possible the second spacing of diffraction centers as found by x-rays.

10. The relative magnitude of the two diffraction peaks in case of the n-alcohols and the saturated normal fatty acids indicate that the intensity obtained by the diffraction from the parallel planes containing the lengths of the chains is much greater than from the parallel planes passing across these chains. Consideration of the structure factor in these two cases shows that a relative magnitude of this order should be anticipated if the group interpretation is correct. The quantitative details of these considerations are not yet published.

11. Quantitatively the dimensions determined by some of the diffraction maxima are much too long to refer to parts of the same molecule and must refer to intermolecular spacing.

12. The integrated intensity in the region of the chief diffraction maximum for solid (powdered crystal) and liquid triphenylmethane (results unpublished), show approximately equal values. It is difficult to see how such coherence could be obtained from a liquid without groups.

These are the more conspicuous lines of argument. But even aside from the evidence, a moment's general consideration indicates the reasonableness of the cybotactic theory. For the molecular forces are evidenced in surface tension, where there is an orderly arrangement, and, with the closeness of approach of molecules in the liquid, these forces must everywhere be of importance. These force fields introduce potentials. From Boltzmann's statistical distribution law the largest number of molecules must be at the

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[13] Stewart and Skinner, Phys. Rev. **31,** 1 (1928).

[14] Vaidyanathan, Ind. Jour. Phys, III, III, 391 (1929); E. W. Skinner, not yet published.

[15] Stewart, Phys. Rev. **31,** 174 (1928).

least potential. It is then merely a question as to what the possible potentials are. Will the least potential be an orderly periodic arrangement or not? *A priori*, one cannot say, but such considerations would cause one to be ready to adopt the answer favored by experiments. From this view point the above twelve items of evidence seem to lead to the adoption of the cybotactic conception as the best description of the condition of least potential.

X-RAY DIFFRACTION IN OCTYL ALCOHOLS

The present contribution was made possible by Professor E. Emmet Reid of Johns Hopkins University who kindly lent samples of the twenty-two octyl alcohols made in his laboratory by Messrs. H. B. Glass and G. B. Malore. The following gives a statement of results and conclusions of x-ray diffraction measurements. The description of the apparatus and precautions may be found in one of the earlier articles.[16]

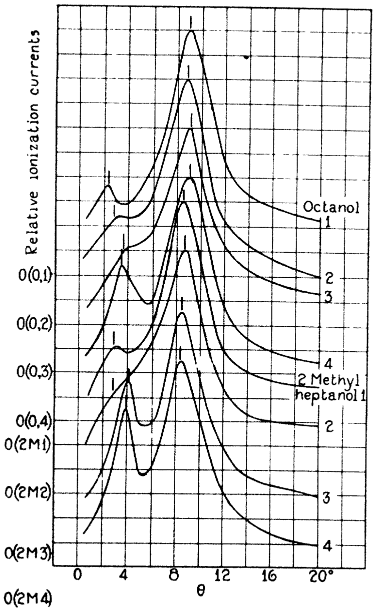

Fig. 1. X-ray diffraction; relative ionization currents of octyl alcohols.

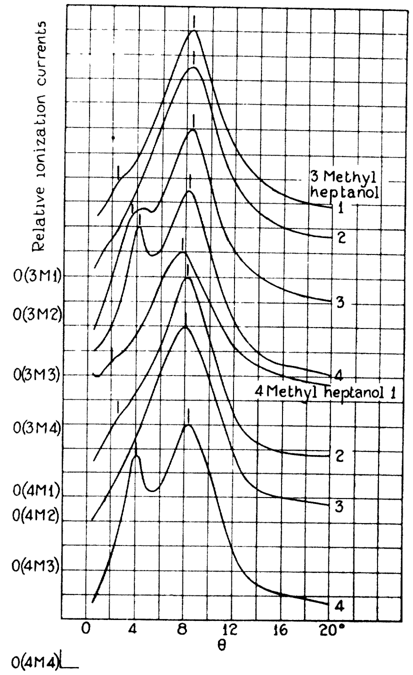

Fig. 2. X-ray diffraction; relative ionization currents of octyl alcohols.

In Figs. 1, 2 and 3 are presented the relative ionization currents obtained in a chamber placed at the varying angles of diffraction. In each figure the curves are displaced vertically and each major peak is given the same magnitude. In Fig. 4 are shown the diameters and lengths of the molecules. Bragg's law of crystal diffraction, $\lambda = 2d \sin \theta/2$, wherein λ is the wave-length, d, the separation of planes containing diffraction centers and θ, the angle of dif-

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[16] Stewart and Morrow, Phys. Rev. **30**, 232 (1927).

fraction, is used. The circle containing a cross is the length of the molecule estimated from the *n*-paraffin chain dimensions obtained in an earlier article.[17]

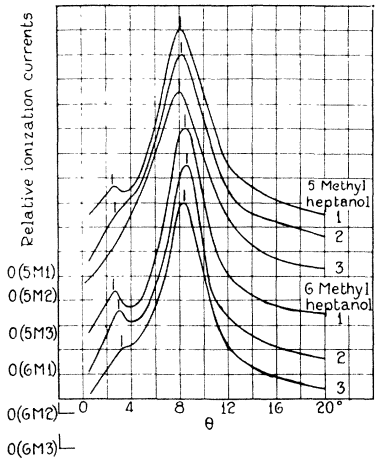

Fig. 3. X-ray diffraction; relative ionization currents of octyl alcohols.

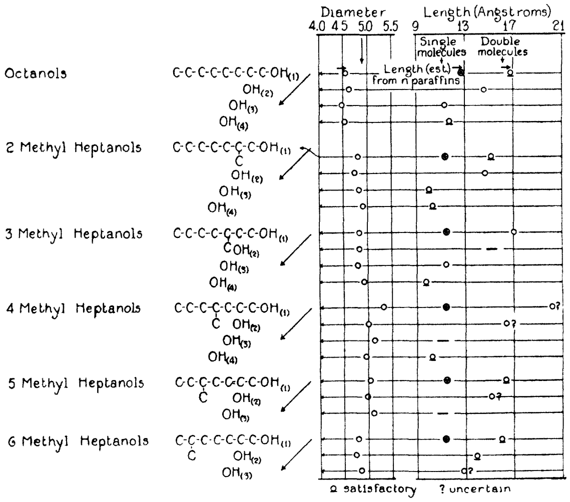

Fig. 4. Effective diameters and comparison of molecular **lengths** with separation of second set of diffraction planes.

CONCLUSIONS

1. *Molecular diameters.* The effective molecular diameter of octanol-1 is about 4.55×10^{-8} cm (or A.U., indicated merely by A, for the sake of brevity). This is more accurately the mean separation of planes containing parallel

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[17] Stewart, Phys. Rev. **32,** 153 (1928). The length of a normal paraffin molecule is $1.24n+2.70$ where n is the number of carbons and 2.70 is the length estimated for the two terminal hydrogen atoms. The formula is used for the alcohol molecules, save that n does not include the carbon atom in a branch.

molecules and, assuming a square array of the chains in a plane perpendicular thereto, this distance may be interpreted as the effective molecular diameter. It is to be noted that (1) with the group OH in a branch the diameter is not materially increased, (2) with CH_3 in a branch the diameter is increased by approximately 0.24A for 2-methyl-, 3 methyl- and 6 methyl-heptanol 1, (3) by 0.75A for 4-methyl-heptanol and (4) by 0.47A for 5-methyl heptanol. Items (1), (3) and (4) are closely in accord with previous findings on isomers of primary n-alcohols,[18] but the increases noted in (2) are approximately one-half as great. Also, as before, the effect on the diameter of the attachment of OH and CH_3 to the same C atom is not noticeable. The measurements are not in error by more than 0.05A, but there are other factors to consider. For example the compounds are doubtless not of the highest practicable purity. Also, we are interpreting the grouping in the simplest possible manner, and this picture of the grouping may be only approximately true. Again, the position of the peak in the curve is a statistical result and is not obtained with a *fixed* grouping of molecules.

2. *Association of molecules.* As shown in earlier articles[19] the distance computed from the position of the smaller peak depends upon the length of the molecule but cannot represent the molecular length or an integral value of it because the association produces effective diffraction centers that lie in planes not perpendicular to the molecular lengths. For the primary normal alcohols and the saturated normal fatty acids the distance between the planes was more than the length of the molecule and less than twice this distance. The interpretation was made that two polar groups were associated so that their molecules were placed end to end in the same line. Consequently the effective longitudinal diffraction centers occurred every two molecules. But the planes containing them were not perpendicular to the molecules. Thus the planar distance became less than twice the length of a molecule. In Fig. 4 of this contribution it is noticed that the determination of all the secondary peaks was not possible. But of those obtained, the computed planar distances represented in Fig. 4 convey an interesting result. All the molecules having OH at the end of the molecule or attached to the second C atom, show a distance between planes considerably greater than the computed molecular length and yet clearly less than twice this length. On the other hand when OH is attached elsewhere, the planar distance is approximately the computed molecular length. We hence have here *two different types of association. When the polar group OH is at 1 or 2, the association arranges the molecules end to end in the same line with two polar groups adjoining. When the OH is elsewhere, the associated molecules lie side by side.* This generalization is further verified by the cases of diethyl carbinol and di-n-propylcarbinol.[20] The computed molecular length of the former, using the same figures for distance occupied by atoms as described above, is 8.9A, and the latter 11.38A, whereas the distances between planes are 8.9A and 10.5A, respectively. Considering the

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[18] Stewart and Skinner, Phys. Rev. **31**, 1 (1928).

[19] Stewart and Morrow, reference 16 (for normal primary alcohols). Morrow, Phys. Rev. **31**, 10 (1928), (for saturated normal fatty acids).

[20] Stewart and Skinner, reference 18.

inaccuracy of the length computed from atomic dimensions in the molecule, this is clearly an agreement.

3. *Variation in magnitude of secondary peaks.* An interesting variation in relative heights of the secondary maxima can be seen in Figs. 1 to 3. This secondary diffraction peak is the most prominent in the cases of octanol-4, 2-methyl-heptanol-4, 3-methyl-heptanol-4, 4-methyl-heptanol-4; or, in other words, given the position of the methyl group, the secondary diffraction peak is always the greatest with the OH group on the fourth carbon atom. In fact, there is a variation in magnitude through any such set. These are significant facts but their interpretation is not altogether clear. In the first place one must expect the arrangement of atoms to affect the intensity of diffraction (through the much used structure factor, F). As to the major peak, the intensity of diffraction for all is sensibly the same. The experiments required the use of very thin cylindrical glass receptacles, one for each compound. Differences in these and in the sensitivity of the ionization chamber (which is refilled only once in several months), were not large and the results for the magnitude of the diffraction intensity at the major peaks, even including these unavoidable changes mentioned agreed for all the liquids with an average deviation of 17 percent and a maximum deviation from the mean of 30 percent. And this is what should be expected for the changes in structure of these molecules would result in but little change in the structure factor when the molecular length lies in the diffracting planes. Since, then, the magnitude of intensity of the major peaks is of the same order, comparison may be made of the secondary peaks as plotted in Figs. 1, 2, and 3, assuming the major peaks the same magnitude. The difference in secondary peaks is relatively very great. The structure factor for diffracting planes perpendicular to the molecular length, or at any considerable angle, would vary greatly also. Hence this may be in part the explanation of the experimental results. But the second possible explanation is that, although the molecules may lie with lengths parallel, and give well-marked diffraction planes containing these lengths, yet the molecules may not be so regularly arranged for the other set of planes mentioned. The space arrangement longitudinally may not be so perfect. One need not choose between these two factors, for both doubtless exist in important degrees. Computations are at present being made of the probable variation in structure factor, though of course there is much conjecture involved. As to the perfection of the grouping, there now appears some enlightenment through the study of the viscosity of these liquids. In fact, the viscosity is greatest where the secondary peak is greatest. This correlation is doubtless important and will be discussed in a future article by Dr. R. L. Edwards and the author. In the foregoing it must be understood that the cybotactic condition is not one in which the "groups" are definite, having constantly the same consituents, or the same dimensions or spacing. There must be groupings to give the diffraction effects at any instant, but the effect on the ionization chamber is a statistical one.

To Professor E. Emmet Reid for the use of the octyl alcohols and to Mr. H. A. Zahl, research assistant, who is responsible for the data described herein, I wish to express my thanks.