

The Structure of Aqueous Solutions of Perchloric Acid

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Perchloric acid is a member of the series of mineral acids which has not been previously studied by X-ray diffraction methods. Three different aqueous solutions have been examined. They contain 72, 65 and 58 g perchloric acid per 100 g solution, corresponding respectively to about 2, 3 and 4 molecules of water per molecule perchloric acid.

The theory for our investigations was republished recently¹. The average intensity functions, transformed to theoretical backgrounds, are illustrated by Fig. 1, and the corresponding $\sigma(r)$ -curves are given in Fig. 2. We have also verified the $\sigma(r)$ -curves by different modifications, which will be published later.

The oxygen atoms of a perchloric acid molecule are tetrahedrally arranged around the chlorine atom. Our $\sigma(r)$ -curves give values varying between 1.48 and 1.51 Å for the Cl—O distance, and the $\frac{\sigma(r)}{r}$ -curves² give 1.47 to 1.50 Å. 1.49 Å is in fair agreement with the available data³⁻⁵, and corresponds to a distance 2.43 Å between the oxygen atoms of the ClO_4^- -tetrahedron. Our $\sigma(r)$ -curves have maxima at about 2.4 Å. The maxima come out much smaller than one should expect according to the weight of this distance. This is probably due to the deep minimum found in the general form of the $\sigma(r)$ -curves around 2.4 Å.

Close packing of molecules and bonds between atoms of different molecules may both cause preferred distances that influence the distribution curves. The presence of hydrogen bonds is indicated by the shape of the curves at about 2.85 Å. An accurate determination of this distance from the $\sigma(r)$ -functions is impossible. Interference with other distances at both sides may take place, and the bond length may vary a little with the character of the oxygen atoms linked together. However, 2.85 Å is in good agreement with earlier results⁶⁻⁸.

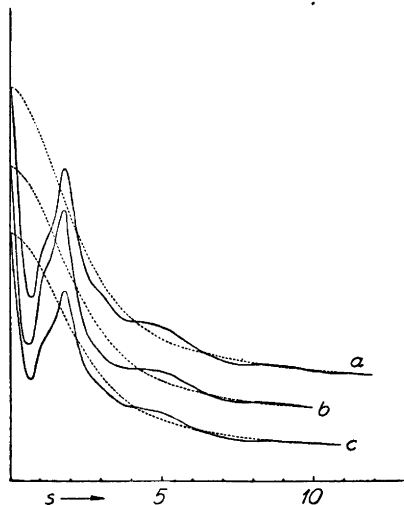


Fig. 1. Transformed intensity-curves (unbroken lines) and corresponding theoretical backgrounds (broken lines). a) 72% acid. b) 65% acid. c) 58% acid.

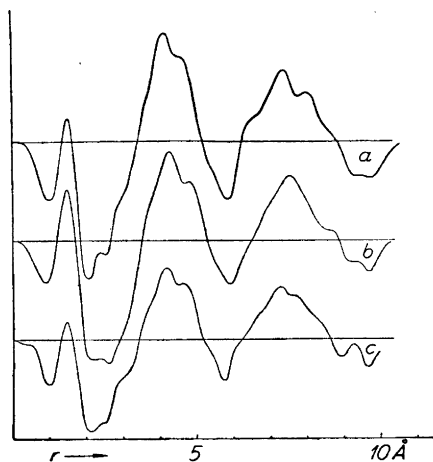


Fig. 2. $\sigma(r)$ -functions corresponding to Fig. 1.

The hydrogen bonds may connect two water molecules, two molecules perchloric acid or one of each sort. The first case leads to no new distances. For the other two we have tried different ways of placing the molecules relative to each other, and have found the structures of Figs. 3 and 4 to be the average arrangements agreeing best with the $\sigma(r)$ -curves. As one will see, the atoms

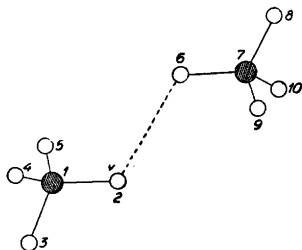


Fig. 3. One ClO_4^- -tetrahedron connected with another by a hydrogen bond. Numbers refer to Table 1. Open circles = oxygen atoms. Shaded circles = chlorine atoms.

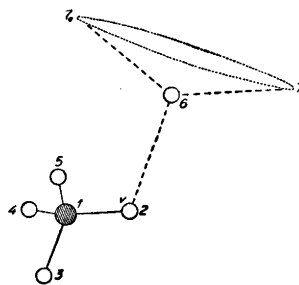


Fig. 4. A ClO_4^- -tetrahedron connected with the oxygen atom of a water molecule by a hydrogen bond. The broken circle refers to the possibilities of placing the next oxygen atom. Numbers refer to Table 2.

are placed in trans positions when possible. This is in agreement with the results of earlier investigations on sulphuric and phosphoric acids in aqueous solutions ^{7,8}, and is also assumed to be advantageous from energy considerations. For the angle ν of Fig. 3 we find the value 130° to agree best with the experimental results. This large value is probably caused by a repulsion between two ClO_4^- -tetrahedra. The angle ν of Fig. 4, however, is approximately 109.5° , the tetrahedral angle. The oxygen atom 7, lying somewhere on the circle shown in perspective in Fig. 4, may belong to a water molecule or a perchloric acid molecule. Anyway, the distance between the atoms 2 and 7 is approximately 4.65 Å. This is also a prominent distance occurring in the structure of liquid water ⁶. The structures of Figs. 3 and 4 give the distances in Tables 1 and 2, respectively.

Table 1. Distances between the atoms of Fig. 3.

Atoms	Distance in Å	Atoms	Distance in Å
1-2	1.49	4-7	5.65
2-3	2.43	4-9	5.86
2-6	2.85	5-9	6.34
1-6	3.98	3-7	6.40
4-6	4.27	4-8	6.60
3-6	5.24	3-8	7.65
1-7	5.28		

Table 2. Distances between the atoms of Fig. 4.

Atoms	Distance in Å	Atoms	Distance in Å
1-2	1.49	4-6	3.77
2-3	2.43	2-7	4.65
2-6	2.85	3-6	5.03
1-6	3.63		

As shown by Table 1, the Cl-Cl distance has no corresponding distinct maximum on the $\sigma(r)$ -curves. However, the minimum on the distribution curve for water in this range is considerably more pronounced than for perchloric acid. The following considerations concerning the close packing of molecules will also show that very few distances are found around 5.3 Å.

Of the three possibilities for close packing of two molecules, the packing of water molecules around a perchloric acid molecule will no doubt be most

important for the concentrations studied here. The resulting Cl—O distance may vary from 3.4 to 4.7 Å. Judging from the $\sigma(r)$ -curves, 4.2 Å is the preferred value. No definite values can be assumed for the resulting O—O distances, which may vary between 3.2 and 5.5 Å. A close packing of two perchloric acid molecules is unlikely, but packing of two water molecules may to some degree be responsible for the ascent of the curves at about 3.2 Å.

Next we want to investigate the distances between two molecules packed with a third one between them, or, as we shall call it, second order packing of molecules. Of the six possibilities for this second order packing, our concentrations eliminate three, leaving the following: water-perchloric acid-water, perchloric acid-water-perchloric acid and perchloric acid-water-water.

The first of these eventualities occurs most frequently. However, this packing can take place in numerous ways, leading to distances from 3.2 to 8.4 Å. Judging from this broad range and the fact that the weight of such a distance is small, the chance for any specific influence on the distribution curves is small.

The second of the above possibilities implies the distance between two molecules of perchloric acid. This distance has a considerable weight and explains the maximum between 7.3 and 7.4 Å on our $\sigma(r)$ -curves. This conclusion is supported by results obtained in investigations of liquids with spherical molecules^{1,9-11}. Calling the distance of the first order packing r_1 and that of the second order r_2 , both experimental and theoretical results show that the ratio $\frac{r_2}{r_1}$ has a value between 1.8 and 2.0, varying a little from liquid to liquid.

In the present case the situation is different. Even by using the approximation of spherically symmetrical molecules, the radii are not the same for the two sorts. Nevertheless, the value of the analogous ratio cannot be far from 1.8, and the value 1.75 obtained here is reasonable.

The third possibility for second-order packing is perchloric acid-water-water. From the above discussion of the water-water packing, it is not likely that the corresponding distances give a maximum on the distribution functions. However, they may to a certain degree account for the ascent of the $\sigma(r)$ -curves between 6 and 7 Å. This possibility is greatest for the most diluted of our solutions.

SUMMARY

The distance Cl—O in the ClO_4^- -tetrahedron has been found to be about 1.49 Å. Hydrogen bonds connect the molecules of the solutions, leading to the structures of Figs. 3 and 4. A close packing of molecules is also assumed and discussed in some detail.

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REFERENCES

1. Finbak, Chr. *Acta Chem. Scand.* **3** (1949) 1279, 1293.
2. Viervoll, H. *Acta Chem. Scand.* **1** (1947) 120.
3. Pauling, L. *The Nature of the Chemical Bond.* (1939) 222. Cornell University Press.
4. Stillwell, C. W. *Crystal Chemistry.* (1938) 417. New York and London, Mc Graw-Hill Book Company, Inc.
5. Wyckoff, R.W. G. *Crystal Structures.* (1951). New York, Interscience Publishers, Inc.
6. Finbak, Chr., and Viervoll, H. *Tids. Kjemi, Bergvesen, Met.* **5** (1943) 36.
7. Finbak, Chr., Rønning, O., and Viervoll, H. *Tids. Kjemi, Bergvesen, Met.* **4** (1944) 26.
8. Bastiansen, O., and Finbak, Chr. *Tids. Kjemi, Bergvesen, Met.* **5** (1944) 40.
9. Kirkwood, J. G. *J. Chem. Phys.* **7** (1939) 919.
10. Kirkwood, J. G. and Boggs, E. M. *J. Chem. Phys.* **10** (1942) 394.
11. Kirkwood, J. G., Lewinson, V. A. and Alder, B. J. *J. Chem. Phys.* **20** (1952) 929.

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