Physics. — *The orientation of watermolecules round charged particles.* By J. F. VAN ELTEREN. (Communicated by Prof. J. D. VAN DER WAALS Jr.)

The question is, how watermolecules are arranged round colloidal particles or, generally speaking, round charged particles. We must distinguish between positively and negatively charged particles. No question can arise about the orientation of the watermolecules round the positive particles, for the place of the points of charge in a watermolecule is known [1]. (Fig. 1.) With a positively charged particle the negative pole of the watermolecule will
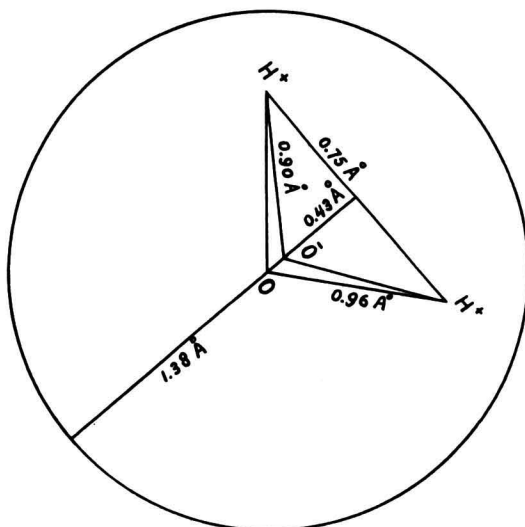

Fig. 1.

be directed to that particle; but both the positive charges are turned away. With negative particles the matter becomes more complicated. It is impossible to say at first sight, what the direction of the watermolecule will be. Two positions are possible, one symmetrical, the other non-symmetrical. In the non-symmetrical position one of the positive charges approaches as near as possible to the charged particle. We can, however, state at once, that in the non-symmetrical position the potential energy will decrease more quickly in proportion to the distance of the centre of the charged particle than in the symmetrical position. For, generally speaking, the potential energy of a dipole in its relation to a charged particle is inversely proportional to the square of the distance, whereas for a quadrupole it is inversely proportional to the cube of the distance. The forces operating between a dipole and a charged particle will cause a symmetrical orientation, but a non-symmetrical orientation in the case of a quadrupole. To show the working of this process, small rounds of blottingpaper, dipped in paraffin, on which little magnets had been placed, were brought on a surface of water. One of the poles of a magnet represented an ion,

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[1]   FOWLER–BERNAL, Trans. Far. Soc., **29**, 1049 (1933).

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the diameter of which was represented by test-tubes of various sizes. It appeared, (Fig. 2, 3, 4) that with a small ionic radius the non-symmetrical position was stable, and with a greater ionic radius the symmetrical position. Hence it was clear, that between water and single-charged ions both positions were possible.

Fig. 2.

negative ion
small ionic radius

Fig. 3.

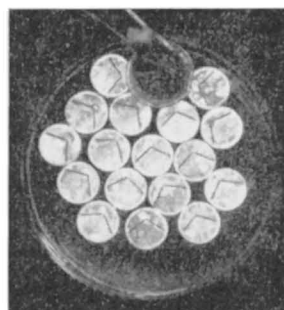negative ion
great ionic radius

Fig. 4.

positive ion

The potential energy of the watermolecule in relation to a charged particle was computed in dependence on the radius of the charged particle. The result of this computation is shown in the graph. (Fig. 5.) The ionic radii of F, Cl, Br and J, and of K, Na, Rb, Cs are shown on the absciss. From this graph some conclusions may be drawn.
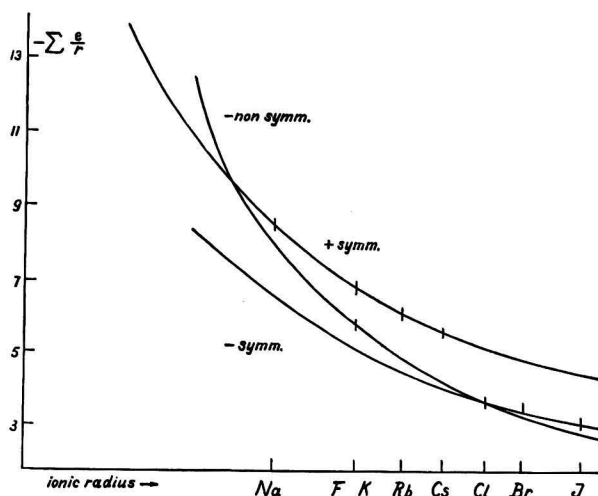

Fig. 5.

The F-ion takes up a peculiar place. In the first layer round the F-ion the watermolecule will take up a non-symmetrical position. In former computations of the hydration-energy this had never been taken into account. The lyotropic numbers are connected with this hydration-energy according to: $I/H = aL + b$. Here H and L are respectively the hydration-energy and the lyotropic number; a and b are constants. It often appears, that the F-ion does not correspond to the linear relation between this lyotropic number and the

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effect obtained [2]). The deviations can be explained by the particular position of the watermolecules.

We cannot conclude from this, how their position will be round colloïdal particles. We shall have to give an answer to the question, whether the charge of these colloïdal particles must be considered as points of charge which are found on the surface and each of which binds the watermolecules, or whether we are allowed to consider the charge as concentrated in the centre of the colloïdal particle.

From the graph it is clear, that in the case of positive particles — $\Sigma e/r$ is greater than in the case of negative ones. In the literature on this subject it is assumed, that with an equal ionic radius negative ions will have a greater hydration-energy than positive ones; for the positive pole of a water dipole is situated nearer to the periphery than the negative one [3]). Exactly the opposite, however, appears from our own computations, as the computed numbers are a measure of this hydration-energy; which is evident from the table. Here the relations to the hydration-energy are shown. Indications of this may also be found in the literature of the colloid-chemistry. E.g. SPEELMAN [4]) states, that in

	— $\Sigma e/r$	H	— $\Sigma e/r/H$
F	5.8	123	0.047
Cl	3.65	84	0.044
Br	3.4	73	0.047
J	3.0	64	0.047

flocculation-experiments with serumalbumen the alcohol number appears as non-symmetrical on both sides of the iso-electric point. With a low p_H, therefore with positively charged particles, the alcohol number is greater than with a high p_H. Which points to a stronger binding of the watermantle to positive particles.

Measurements of viscosity and other properties render a similar result.

SUMMARY.

1. F appears to deviate from Cl, Br and J. Experiments have borne this out.
2. In case of an equal ionic radius positive ions seem to bind the watermolecules more strongly than negative ones.
3. A possibility of computing hydration-energies is offered, in which, of course, the various correcting factors must be taken into account.

In a following article we hope to speak on this subject more at large. My thanks are due to Dr. E. H. BÜCHNER, who suggested the idea on which these considerations are based.

[2]) BÜCHNER, Recueil, **59**, 703 (1940).
  SARLUY, Thesis, Amsterdam (1940).
[3]) VAN ARKEL en DE BOER, Chemische Binding (1930).
[4]) SPEELMAN, Thesis, Amsterdam (1937).

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