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Chemistry. — *"The Doublerefractive Sol of Vanadium Pentoxide".*
By Prof. H. R. KRUYT. (Communicated by Prof. P. VAN ROMBURGH).

(Communicated in the meeting of March 25, 1916).

1. In the Jubilee Edition for ELSTER and GEITEL DIESSELHORST, FREUNDLICH and LEONARDT[1]) have made highly interesting communications as to the V_2O_5 sol. When dispersed colloidally in water, this substance gives a clear sol which, varying with the concentration, is from yellow to brown in transmitted light. If this sol is stirred, there are noticed in the liquid, particularly in the case of specimens that have been kept for some months, peculiar, twinkling diffusions, which might lead the observer to think that a finely divided crystalline sediment were stirred up from the bottom. Curiously enough, the turbidity does not disappear in the direction of the bottom of the vessel but it often ceases to be visible just after it has still been noticed in the middle of the cuvette. Moreover, a deposit is always absent.

If the sol is examined between crossed nicols, stirring seems to cause a clearer illumination of the field of vision; a continued investigation now taught that the sol when flowing in a definite direction behaves like a plate from a doublerefractive crystal.

In the cardioid ultra-microscope, the sol appeared to consist of elongated rod-shaped particles. The above-cited observers now arrived at the following explanatory hypothesis: by currency, the particles get in the position which causes only the slightest friction with other liquid layers namely with their longitudinal axis parallel to the direction of the current. This causes an orientation which brings about the doublerefraction.

They have made a series of experiments to state whether all phenomena were really in harmony with this surmise. Currency, magnetic field and galvanic current would presumably originate a ranging of the particles and indeed all the experiments which they carried out and in which they varied in all possible ways the vectors of the light-vibration and of the force applied to the system, seemed to lead to a light or dark field, just according to what was expected from the hypothesis.

In a second paper[2]), DIESSELHORST and FREUNDLICH could even

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1) DIESSELHORST, FREUNDLICH and LEONHARDT, Arbeiten aus den Gebieten der Physik, Mathematik, Chemie, JULIUS ELSTER und HANS GEITEL gewidmet, pg. 453—478, Braunschweig 1915.

2) DIESSELHORST and FREUNDLICH, Physikal. Zeitschr. **16**, 419—425 (1915). See also Zeitschr. f. Elektrochemie **22**, 27—33 (1916).

state that the analogy with a doublerefractive crystal goes so far that one notices the typical axial cross when the sol is examined in convergent polarised light, while the liquid moves in a direction coinciding with the microscope-axis.

A similar behaviour was exhibited by old Fe_2O_3 sols.

These experiences gave rise to interesting views as to the crystalline condition; they are principally of great importance for the theory of the liquid crystals; for the analogy with these substances is particularly striking.

2. In April 1915, I prepared a not very concentrated V_2O_5 sol. according to the method given by BILTZ[1]) It absolutely did not exhibit, on stirring, the dark diffusions, neither could I observe a light-phenomenon between crossed nicols either by simply placing them before a planeparallel cuvette or in the polarisation microscope. When in December I once again took the specimen in hand both phenomena were exhibited with manifest intensity. With this preparation the experiments now to be described have been made in January, February and March 1916.

The object of the research was to verify the above hypothesis with the ultramicroscope. It appeared to me that by means of the microscope it could be ascertained whether, indeed, the particles in the circumstances indicated range themselves in the way expected.

3. *Observation in the cardioid-ultramicroscope.* The specimen was strongly diluted to a faint yellow liquid; a drop of this was put into the instrument.

Source of light: WEULE arc-lamp. Objective: Special apochromatic (ZEISS). Compensation ocular 18.

The intenference images are highly peculiar: long pale blue streaks, certainly 20 times more in length than in width, are seen in quiet BROWNian movement, between these, small round discs in vivid motion. The apparent size of the rods is about 1 cm. They are elongated supple particles, which move about like little serpents, bend to and fro and take the form ∫ evidently under the influence of molecular thrusts in opposite direction near the termini. Further, V-shaped twin combinations are again moving more slowly, also some couplings of three and more rods to spiderlike complexes.

On the slide and covering glass larger complexes have deposited as little flakes; therein may be still observed plainly the single rods

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[1]) W. BILTZ, Nachr. Göttingen **1904**, 8.

sometimes straight, sometimes bent, so that they resemble bundles of sea-weed as found on the shore.

The preparation has a strong inclination to deposit such flakes; after a few hours all movement has ceased. This is not astonishing at all. If we assume that the breadth dimension of the particles lies just at the border of the ultramicroscopic visibility, this, according to ZSYGMONDI [1]), must (for metallic oxides) be judged at 30 $\mu\mu$, the length dimension will, therefore, lie in the order of 500 $\mu\mu$. If we consider that the distance between the two quartz glasses only amounts to 1 or 2 μ it will not cause any surprise that the particles do not keep on moving for a long time.

In connexion with what now follows it may be observed that the particles lie in the field of vision in completely arbitrary directions.

4. *Observations in the slit-ultramicroscope with a* BILTZ *cuvette.* Source of light as above. Objective Zeiss D*. Ocular HUYGENS 3 Now also we notice beside the round images which are in vivid motion elongated slowly moving particles. But a remarkable difference is shown: we only notice particles in a position perpendicular to the axis of the illuminating beam with deviation of at most 30°. Particles with their axes parallel to that of the illuminating beam are not to be seen, no more than those that exhibit deviations therefrom up to about 60°.

As it could not be supposed that in these circumstances the particles were already ranged, it became obvious that there should be an optical reason why *those* particles are invisible which are situated more or less parallel to the direction of the source of light (we shall in future call the position of these particles "sagittal" in contrast with that of the visible ones which lie "frontally"; for the ray of light arrives straight at the observer). This surmise was in agreement with the above-mentioned fact that with a cardioid condensor (which causes an all-round illumination of the preparation) the particles were seen in quite an arbitrary direction.

Subsequently, I have observed the preparation while it was passing slowly through the cuvette. A capillary exit tube which could be placed higher or lower by means of an elevator made it possible to regulate this velocity of currency at will. If indeed the particles are ranged by such a currency parallel to the direction of the current, the invisible sagittal particles should be rendered visible by the frontal flow. As a counting of the particles in a running liquid was very difficult, the clearing up of the field of vision was

[1]) Kolloidchemie, Leipzig 1912, blz. 11.

only watched with a sol that had been brought to a suitable dilution for this purpose. Indeed the field of vision becomes clearer when flowing takes place. But to the value of this result as a conclusive proof we may offer an objection because on account of the after images of the eye, the moving particles appear more elongated. More convincing would be a weakening of the light-cone by sagittal currency, but it is very difficult to realise a cuvette suitable for this purpose (See, however, the end of § 6.)

It should, however, be remarked that at these very small currency velocities the particles do not range themselves quite frontally.

5. SVEDBERG *Cuvette*.

Therefore we followed a course which gave more chance of a satisfactory result. We have verified whether under the influence of the electric cataphoresis, the particles range themselves parallel to the direction of the electric current. For this was constructed a cuvette[1]) as indicated in fig. 1.

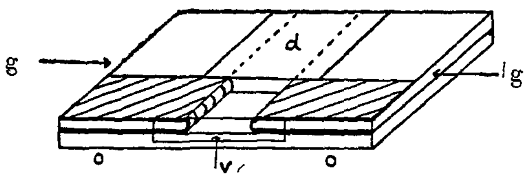

Fig. 1.

On a microscope slide two glass plates g were fastened; round these plates platinum foil was beaten (the striped part of the figure); a part of the channel formed between the glasses was filled with piceine, which was then covered with a covering glass d. Before the remaining part of the channel was a little pane v cut from a covering glass whilst, finally the little cuvette thus formed could be closed with a fitting glass lid. On the platinum foils the current of two accumulators (4 volts) could be brought by means of two copper springs, which are pushed up sideways and to which were soldered conducting wires.

The cuvette was pasted on a little table resting on the cardioid condenser and hence could be moved upwards and downwards by means of the accompanying screw (in these experiments the condenser itself was not used and therefore covered with a small copper cap to protect it from injury).

The beam of light now could enter through the pane *v*, the

[1]) Vgl. THE SVEDBERG, Nova Acta Reg. Soc. Sc. Upsaliensis [4] 2 No. 1, blz. 149 (Studien zur Lehre von den kolloiden Lösungen).

observation in the microscope took place through the covering glass placed over the channel (not drawn in Fig. 1).

When now the cuvette was filled with V_2O_5 sol in suitable dilution, I saw when closing the electric current, the particles move frontally through the field of vision towards the anode. The orientation of the rod-shaped particles was unmistakable, though not complete. The majority lies quite frontal, but a few move about, in a more slanting position with deviations of about 10°, more rarely of about 20°.

The orientation would, of course, be strengthened by bringing about a greater potential difference between the electrodes. The greater velocity of the motion and the rapid, complete cataphoretic accumulation of the particles at the anode then however, impeded the observation. Hence we proceeded to the alternating current which was furnished by a small RUMKORFF coil such as is used in the determination of the electric conductivity of electrolyte solutions. For COTTON and MOUTON [1]) have observed that a colloidally dispersed particle follows the impulses of the current and thus gets into vibration owing to an alternating current. Indeed, the little rods now orientated purely frontally and exhibited themselves as elongated rays of light in consequence of the after-images of the eye; these rays often reached from one side of the light-cone to the other. The field of view was much cleared up on closing the current, a phenomenon that may be valued in the same manner as indicated in § 4.

It should be noticed that sometimes, besides the vibration a one-sided cataphoretic motion occurred which caused a movement, sometimes from the left to the right, then again from the right to the left, occasionally even right across the field of vision. Particularly during the first moments after starting the inductor, such anomalies now and then occur. They correspond to the anomalies observed by DIESSELHORST, FREUNDLICH and LEONARDT in similar circumstances and are probably to be attributed to leakages in the circuit in connexion with the not yet stationary action of the RUMKORFF coil when just put in action.

6. *Modified cuvette.* Much more striking however, is the image when the cataphoresis is brought about parallel to the illuminating beam. For this was constructed a cuvette as shown in Fig. 2.

It differs from the first in so far that one of the platinum elec-

1) Journ. de Chim. phys. 4, 365 (1906).

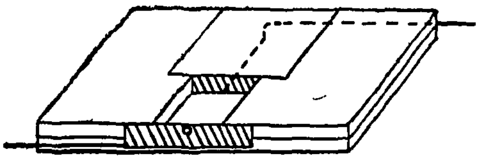

Fig. 2.

trodes is placed behind the front pane, the other before the piceine wall of the cuvette-space. The first electrode is perforated so that a small opening for the entering illuminating beam is at disposal.

If in this cuvette the current (either ordinary or alternating) was closed all elongated particles disappeared from the field of vision. If the current was again broken, the normal image reappeared.

About a minute after the circuit was closed the field of vision was so obscured that a sharp contour of the light-cone could no longer be distinguished. A few pointed images and a single flake still indicated the cataphoretic motion; after breaking off the current, the cone becomes again recognisable after about half a minute; after a minute a single elongated particle is again noticed; after two minutes the previous image has almost entirely returned.

This observation confirms the hypothesis of the German investigators as well as our assumption that the elongated particles would be invisible when situated with their longitudinal axis parallel to that of the illuminating beam. After these investigations had been closed there came to our knowledge a paper by SIEDENTOPF[1]), in which he discussed the same for particles which have microscopic dimensions in one direction and ultramicroscopic ones in the two other directions. Although the linear dimension of the V_2O_5 particles remains perhaps below the microscope demarcation and the theory of SIEDENTOPF may, therefore perhaps not be applied here without modification[2]), the cause of this remarkable phenomenon is pointed out in this paper all the same.

Incidentally, a remarkable observation has been made with this cuvette. Once, by mistake the first platinum electrode was connected with the *outer* wall of the front pane. On closing the current there still took place an obscuration of the field of vision; on closer examination the contact appeared to originate as follows: from that outer electrode, via the water immersion drop (which connects objective and covering glass), through a crevice between covering

1) SIEDENTOPF, Zeitschr. f. wiss. Mikroskopie **29**, 1 (1912). Also compare **25**, **424** (1908) and MAEY, **29**, 48 (1912).

2) See p. 38 of his first-mentioned treatise.

glass and front pane, through the sol to the posterior electrode. The motion now proved to have more the character of an electro-endosmotic process than that of cataphoresis; the narrow crevice between the two glass plates acted as a capillary opening. With a few flakes which are permanently luminous it could be ascertained that, on interrupting the current, the liquid flowed back. Hence, we have been able to incidentally make here an observation as to sagittally flowing liquid; the result corresponds with the expectation.

7. The fact of the disappearing of intenference images can also be observed without ultramicroscope. The fact stated can also be explained in this way that particles situated with their longitudinal axis parallel to the illumination direction do not disperse any, or but very little, light sideways. The TYNDALL phenomenon must, therefore, differ strongly with a V_2O_5 sol when this is submitted to cataphoresis, first with the electric field parallel, then with that field perpendicular to the luminous beam.

In a planeparallel vessel with square horizontal section was suspended on each wall a strip of tin foil. Two foils placed opposite each other were, at an equal height, provided with a small round opening, through which could pass a beam of light. As illuminating beam I used that of the slit-ultramicroscope after removing the back condenser, the objective AA (ZEISS). The tin foils were now connected with a commutator, which rendered it possible to let the current of a RUHMKORFF coil (of a somewhat larger type than the one discussed previously) pass at will between each pair of opposite tin electrodes. With this now a strong fading, or else a fierce flashing of the TYNDALL cone, appeared if this was observed by looking through the vessel from above.

By way of a "check", this experiment was repeated with distilled water, with a red gold sol and with a Fe_2O_3 sol (also with a sol three years old, respectively one that had been heated [1]) for 20 hours, at 100°); in those liquids, however, the phenomenon did not occur.

Utrecht, March 1916. VAN 'T HOFF-Laboratory.

[1]) See the article cited from the Jubilee-Edition ELSTER and GEITEL.