Chemistry. - "*Birefractive colloidal solutions*" by Prof. W. REINDERS. Communicated by Prof. J. BÖESEKEN.

(Communicated in the meeting of May 27, 1916).

H. FREUNDLICH, H. DIESSELHORST and W. LEONHARDT describe in the "Festschrift für ELSTER and GEITEL" [1]) a remarkable phenomenon observed with vanadium oxide sol. The reddish-brown, very permanent colloidal solution, which is quite clear with transmitted light exhibits with incident light, on stirring, silky schliers [2]) looking like a swarm of very minute crystals; at the same time it becomes birefractive. If the solution is allowed to flow through a tube with rectangular section placed between two crossed nicols, the field remains dark when the direction of the stream is parallel to the direction of extinction of one of the nicols; it however becomes strongly luminous so soon as the direction of the stream makes a certain angle therewith.

An elucidation of this phenomenon was given by the ultramicroscope which instead of luminous points showed very slender elongated needles, or pillars. When at rest these will occupy an arbitrary position so that the solution is then altogether isotropic. When the liquid is stirred, these needles will, however, arrange themselves with their axis in the direction of the movement. The particles are then directed and a column of liquid with all these particles similarly directed will be capable of behaving like an optic monaxial crystal whose optical axis coincides with the direction of the stream. A further investigation with convergent polarised light has completely confirmed this conception. It further appeared that, not only by mechanical stirring or by streaming, but also by introducing a magnetic field or by cataphoresis, the liquid becomes birefractive. H. R. KRUYT [3]) has been able to confirm by ultramicroscopic investigation that cataphoresis is really associated with a directing of the particles.

Whereas to the form of the particles and their being directed by external forces no further doubt need exist, this is by no means the case with the nature of the particles themselves. Are these anisotropic already, are they minute crystals, or may we suppose them to be isotropic and explain the double refraction by the unequal elasticity in different directions of the solution as an homogeneous whole?

[1]) Arbeiten aus den Gebieten der Physik, Mathematik und Chemie, Braunschweig 1915, 453.

[2]) Prof. G. A F. MOLENGRAAFF informed me, that the word *schlier* as a translation of the German word *Schliere* has been used by R. A. DALY in his book "Igneous rocks and their origin" 1914 p. 448.

[3]) These Proceedings Vol. XVIII. p. 1625.

A similar question arose in 1902 in regard to the *phenomenon of* MAJORANA [1]) based on the fact that a colloidal solution of $Fe(OH)_3$ becomes birefractive in a magnetic field and exhibits dichroism.

COTTON and MOUTON [2]), who have studied this phenomenon very accurately come, after full discussion of the different possibilities, to the conclusion that the explanation founded on the assumption of equally-directed, elongated but themselves isotropic particles is not satisfactory and that we must assume that the particles themselves are anisotropic. The idea that they consist already of small crystals seems to them a very likely one.

DIESSELHORST and FREUNDLICH do not express themselves positively on this question. At the discussion following a lecture of the last named at the meeting of the Bunsengesellschaft [3]) the question aroused great interest, without, however, an agreement being arrived at.

For our conception as to the amorphous condition and as to the nature of colloidal solutions it is of much importance. It also bears on the question what dimension the particles must have in order to exhibit crystalline properties and whether there is a continuity between free molecules and crystals.

In this respect F. and D. already pointed to the great similarity which this vanadium oxide sol exhibits with the liquid crystals. According to the structural-chemical investigations of VORLÄNDER [4]) the molecules of these anisotropic liquids must have an elongated form. Also LEHMANN [5]) points to this and BOSE [6]) explains the anisotropism of these liquids by assuming that the elongated molecules unite to clusters wherein they all have the same direction.

Finally, FREUNDLICH [7]) favours most the idea that the elongated particles of the V_2O_5 sol might be similar clusters of equally-directed molecules which, however, may not yet be called crystals, a link between amorphous and crystalline. It appears to me that such an assumption causes an unnecessary complication and that it is simpler to look upon these needles as being already crystals.

In this case there must be a continuity between these ultramicrones and the macro- or microscopically visible crystals.

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1) Rendiconti Acc. Lincei XI (1902)^1, 536; XI (1902)^2, 90.
2) Ann de chim. et de phys. (8) **11**, 145, 289 (1907).
3) Zeitschr. f' Electrochem. **22** 27 (1916).
4) Bes. d. Deutsch chem. Ges. **40**, 1970 (1907).
5) Die neue Welt der flüssigen Krystalle 1911, 187.
6) Phys. Zeitschr. **9**, 708.
7) Z. f. Elektrochem, **22**, 32.

I have endeavoured in two ways to demonstrate this continuity.

1. by allowing V_2O_5 particles to grow until they should have attained microscopic dimensions.

2. by so modifying the conditions of formation of the crystals of substances, which in ordinary circumstances form distinctly observable crystals, that they can only attain ultramicroscopic dimensions and by observing whether in this manner birefractive sols are formed also.

I. *The growth of V_2O_5 particles.*

It is a well known phenomenon that colloidal or very finely divided crystalline precipitates gradually become crystalline or more coarsely crystalline when they are left in contact with the liquid in which they originated.

A similar growth of the particles is also observable with the V_2O_5 sol. The freshly prepared sol is but little turbid with incident light and does not, on shaking, exhibit the silky diffusions, or only so with exceedingly strong illumination. The old sol is visibly more turbid and exhibits the silky schliers. Ultramicroscopically, FREUNDLICH and DIESSELHORST found the first to be hardly or not at all resolvable in ultramicrones, in the second they noticed very plainly the elongated particles. In the effect of the double refraction they found, however, no difference. No special attention, however, is devoted to this point.

As the recrystallisation proceeds as a rule much more rapidly at a higher temperature than at a lower one, I have watched the change of the V_2O_5 sol on heating on a water-bath.

The sol was prepared by triturating 6 grams of NH_4VO_3 in a morter with the equivalent quantity of 3 norm. HCl. After 10 minutes the liquid was filtered through a BUCHNER funnel. Washing was continued until the filtrate became darker and the filter got clogged. The deposit was then again washed twice by decantation and then brought into colloidal solution by briefly shaking with 150 cc. of water. The following day it was separated from a very gelatinous deposit and filtered. The clear dark brownish-red solution contained 12.4 grams of V_2O_5 per Litre.

A portion was preserved at the ordinary temperature (II*a*) and another portion heated on the water-bath in a Jena flask closed with a funnel (temp. 90°) the traces of waterevaporating thus being constantly replaced. After 1, $2^1/_2$, 5 and 9 hours a part of the liquid was pipetted off and rapidly cooled. These portions are called II*b*, II*c*, II*d* and II*e*.

With transmitted light they were all equally clear and of the same colour.

With powerful incident light II*a* was somewhat turbid but, on shaking, without a silky lustre; the others were always turbid in a steadily increasing degree and always exhibited an increasing silky lustre.

Placed in a 5 mm. wide cuvette between crossed nicols through which passed Na-light II*a* gave on stirring with a glass rod a very faint luminosity. With II*b* the luminosity was very bright and regular and quickly disappeared when stirring ceased. With II*c* a strong flashing took place, not regular however; dark and luminous schliers passed through the field, which again disappeared slowly; II*d* and II*c* exhibited this phenomeon still much stronger. Even without stirring the entire field was filled with dark and luminous schliers, which on stirring changed places. It made the impression as if a part was gelatinised. Also macroscopically the schliers in the cuvette were very plainly visible and when emptying the cuvette gelatinous, little lumps were present which, however, on dilution with water disappeared and dissolved evenly. The viscosity of the heated sols, particularly of II*e*, was plainly greater than that of the unheated sol. [1])

On examining under the ultramicroscope [2]) with cardioid-condenser II*a* exhibited many small strongly luminous ultramicrones with little or no difference in longitudinal or latitudinal dimension.

II*b* exhibited, beside these more circular and very luminous particles, very slender, faintly luminous long needles in the background.

With II*c* these slender bluish-luminous needles are more predominant, the whole field is filled with them and the bright luminous round particles have mostly disappeared.

II*d* also yielded many of these slender needles both very small and larger ones. Whereas, however, in the previous sols the particles

[1]) Two days after these experiments, the viscosity of these sols was determined with an OSTWALD viscosimeter The results were (temp. 20°).

	Flow in seconds	Relative viscosity as compared with water
water	93,0	1,00
II*a*	167,0	1,80
II*b*	194,2	2,09
II*c*	209,0	2,25
II*d*	248	2,64
II*e*	663	7,13.

[2]) ZEISS apochromatic V, compensation ocular 18.

freely moved about unrestrained, this was not the case here. Definite schliers of equally directed particles were very distinctly visible so that figures were formed which made one think of iron filings in a magnetic field or of hairs on a fur. A regularity in these figures is, however, wanting.

In II*e* this formation of schliers was still more stronger pronounced. The equally directed particles moved about in the schliers as in little water streams between more tranquil parts Occasionally in such a stream an obstacle was visible round about which the stream divided in two, then again to unite to one whole.

In a very convincing manner was thus brought here to light the inclination of the particles to arrange themselves all in the same direction in streaming water. The schliers macroscopically visible in polarised light will be no doubt formed in a similar manner by particles pointing in the same direction. In order to observe the influence of the dilution the quartz cuvette was cautiously opened and the sol present therein diluted with a drop of water when it was again examined under the microscope. The gelatinous mass had entirely disappeared; separate streams were no more to be seen and the whole field of vision was replete with the long needles in quite unrestrained motion such as was also the case with II*b* and II*c*.

The entire experiment thus shows

1. in the freshly prepared sol the ultramicrones do not exhibit a one-sided growth, the long needles are wanting.

2. on heating are formed needle-shaped ultramicrones of which the visible number and the size increases with the period of heating.

3. the phenomenon of double refraction is very trifling with the sol one day old, but gets stronger on heating.

4. The viscosity of the solution increases with the period of heating and finally there are formed quite transparent somewhat gelatinous lumps, which on dilution redissolve.

The sol used in this experiment was rather concentrated and even without heating it changed after some days to such an extent that on stirring it gave a decided double refraction. As it was not examined until one day after it had been prepared, the question whether entirely fresh sol was also birefractive remained unanswered.

Therefore, a new sol was prepared, the precipitate being obtained from a strong solution of NH_4VO_3 and hydrochloric acid.This precipitate was washed rapidly and brought into colloidal solution so that the sol was already filtered an hour after the precipitation and ready for investigation (D*a*). Per litre it contained 5.2 grams of V_2O_5. It also was very clear with incident light and gave no silky lustre

on stirring. The ultramicroscopic image showed clear round particles on a faint opalescent, optically non-resolvable back ground. On running through a tube with rectangular section (interior 8×2 mm.) at an angle of 45° placed between two crossed nicols in a ray of Na-light, *absolutely no flashing* could be noticed; the field remained quite dark.

A part of the solution was now heated for 4 hours on the water-bath (D*b*). It then, on stirring, exhibited the silky lustre. Ultramicroscopically very delicate needles were visible. When running through the tube placed at an angle of 45° between crossed nicols, the field became very strongly luminous; on placing it parallel to the direction of the polarization of one of the nicols the field, during the streaming remained dark.

The freshly prepared sol is therefore not birefractive. The phenomenon only sets in and increases in strength with the formation and the growth of the ultramicroscopic needles.

The solution D*b* was again heated for 12 hours on the water-bath. The particles were increased in dimension but not microscopically visible.

In a five months old fairly concentrated sol large ultramicroscopic needles were visible, which, however, were out of reach with the ordinary microscope.

Summarising it appears in a very convincing manner that a slow growth of the V_2O_5 ultramicrones is observable. This, however, is so trifling that we have hitherto not succeeded in obtaining particles of microscopically observable dimension.

II. *Birefractive sols of crystallisable substances.*

The peculiar silky lustre exhibited by old V_2O_5 sols on stirring is also noticed in the formation of different crystalline precipitates.

Some of these suspensions such as of $BaSO_4$, $BaSiF_6$, $SrSO_4$ mica, kaolin, soap, Hg_2Cl_2 and PbI_2 were now tested as to double refraction, of these the two last gave a positive result.

In order to succeed, the precipitate must, however, be very finely divided and not deposit so that the suspension has a colloidal character. It is obtained in that condition by allowing it to form in a very dilute solution and in the presence of a protective colloid.

PbI_2. a. 1 cc. of 0,1 n. Pb-acetate + 8 cc. of 0.05% gelatin + 1cc. of 0,1 n. KI were added together. There is formed an orange yellow suspension of a beautiful silky precipitate. This was too turbid to

be investigated in a cuvette of 5 mm. in polarised light. It was. therefore, diluted with an equal volume of water and now gave between two crossed nicols on stirring, very plainly an illumination of the field.

Microscopically were visible apparently round particles of about 1 μ section in a strong Brownian movement. With some which were a little larger it was plainly visible in these rotations that they were flat. Evidently we are dealing here with the small hexagonal mother of pearl-like glittering plates, which on crystallisation from warm gelatin-free solutions can be easily obtained in a larger dimension.

b. Pb-acetate and KI were mixed in the same proportion and the same dilution with this difference, however, that the gelatin solution was now 0.3 %. The solution was warmed a little, so that the originally yellow amorphous turbidity dissolved clear and colourless and the liquid was then cooled. After a quarter of an hour the solution was *greenish-yellow* opalescent with incident light, *brown* with transmitted light. After the lapse of 6 hours the turbidity had become somewhat stronger, but no deposit had formed yet; also none after 20 hours and on filtering the liquid passed unchanged through the filter. After 3 weeks a portion had subsided but the supernatant liquid had still the same appearance as the 6 hours old colloidal suspension.

At first the solution gave no silky lustre on stirring, but did so after half an hour. Between crossed nicols it gave on stirring a bright illumination of the field. When streaming through a tube with rectangular section, placed between the 2 crossed nicols the field became luminous when the direction of the stream made an angle of 45° with that of the direction of polarisation of the nicols. When it was parallel therewith the field remained dark.

Although the phenomenon was very much less strong than with V_2O_5-sol, the PbI_2-sol is still essentially of the same nature; the streaming column of liquid behaves like a birefractive crystal, of which the directions of extinction rest parallel and perpendicular to the direction of the stream.

Microscopically, nothing could be distinguished. The ultramicroscope exhibited very many small particles with a strong Brownian movement, yellow, brownish, red or of a more blue colour. Their light intensity varied very much, sometimes they suddenly dived in the field, and reappeared again. They made a strong impression of little discs toppling over their side.

As we now know that the PbI_2 crystals, on addition of increasing

quantities of gelatin, are obtained in steadily decreasing dimensions, we may assume that the ultramicrones in this gelatin-rich solution are again small PbI_2 crystals, hence, small plates of an optic monaaxial crystal of which the optic axis stands perpendicular to the plane of this plate.

On streaming, these plates will arrange themselves parallel to the direction of the stream.

The optic axis then stands perpendicular to the direction of the stream. It is evident that a column of these particles so directed will behave optically active and will extinguish parallel to or perpendicular to the direction of the stream.

HgCl. Solutions of NaCl and somewhat acidified $HgNO_3$ mixed in such proportion that the final solution contained 0.001 gram-molecule of HgCl per Litre, gave a nice silky suspension of HgCl needles of which the dimensions were about 0.5 at 10μ. These crystals belong to the tetragonal system and, according to GROTH [1]) are extraordinarely strongly birefractive.

By addition of some gelatin their dimension could be lessened. With 0.3% gelatin and 0,01 norm. HNO_3 a solution was obtained of yellowish-brown colour with transmitted light and milky bluish-white with incident light. It could be filtered without undergoing change and gave between crossed nicols a strong illumination of the field when being stirred. On running through a tube with rectangular section the field became luminous when the direction of the stream made an angle of 45° with the direction of polarisation of the nicols, but not if it ran parallel to one of them. The streaming column of liquid thus again behaves like a birefractive crystal of which the directions of extinction coincide with and stand perpendicular to the direction of the stream.

With the ultramicroscope elongated particles showing a peculiar flashing of light were very plainly visible; they dived suddenly in the field and reappeared and altogether made the impression of mall spillars tumbling over their top. The apparent dimension of these particles varied from $^1/_4 \times {}^1/_2$ to $^1/_4 \times 3\ \mu$.

The appearance of these particles altogether resembles that of the small HgCl crystals which could be obtained in a still microscopically visible dimension (up to $0.25 \times 1\mu$) by addition of somewhat less gelatin and which in a similar way displayed their Brownian movement.

As with the HgCl the size of the particles can be varied at will

[1]) GROTH, Chemische Krystallographie, (1906) I, 214.

and reduced to ultramicroscopic dimension and as the appearance of these particles remains quite the same, we may certainly assume that the ultramicrones also are small crystals.

The double refraction of the Hg sol must, therefore, be attributed to the presence of ultramicroscopic tetragonal needles which, when the liquid is streaming, arrange themselves parallel to each other.

Summarizing we thus may say that there exists continuity between the crystalline suspensions of PbI_2 and HgCl and the colloidal solutions of these substances which form in definite circumstances and become birefractive when in motion. The double refraction of these sols must be attributed to the crystalline structure of the ultra-microns.

In analogy herewith it is probable that also the ultramicrones of the V_2O_5-sol must be regarded as micro-crystals.

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Physics. — "*The field of a single centre in* EINSTEIN'S *theory of gravitation, and the motion of a particle in that field.*". By J. DROSTE. (Communicated by Prof. H. A. LORENTZ).

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In two communications [1]) I explained a way for the calculation of the field of one as well as of two centres at rest, with a degree of approximation that is required to account for all observable phenomena of motion in these fields. For this I took as a starting-point the equations communicated by EINSTEIN in 1913 [2]). EINSTEIN has now succeeded in forming equations which are covariant for all possible transformations [3]), and by which the motion of the perihelion of Mercury is entirely explained [4]). The calculation of the field should henceforth be made from the new equations; we will make a beginning by calculating the field of a single centre at rest. We intend to calculate the field completely and not, as before, only the terms of the first and second order. After this, we investigate the

[1]) Volume XVII p. 998 and vol. XVIII p. 760.

[2]) "Entwurf einer verallgemeinerten Relativitatstheorie und einer Theorie der Gravitation", TEUBNER. Or: Zeitschrift für Mathematik und Physik, vol. 62.

[3]) "Die Feldgleichungen der Gravitation" Sitzungsberichte der Kon. Preuss. Akad. der Wiss. 1915, p. 844.

[4]) "Erklarung der Perihelbewegung des Merkur aus der allgemeinen Relativitatstheorie" Sitzungsberichte der Kon. Preuss. Akad. der Wiss. 1915, p. 831.