LXII. Double refraction in colloids produced by electric endosmose

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LXII. *Double Refraction in Colloids produced by Electric Endosmose.* By H. W. MALCOLM, M.A., B.Sc., Ph.D., Carnegie Fellow of Aberdeen University*.

Introduction.

DOUBLE refraction in colloids has been the subject of numerous investigations; a summary is given by G. Quincke, *Ann. d. Phys.* x. p. 482 (1903), and *Ann. d. Phys.* xiv. p. 849 (1904). The latter paper deals with double refraction in gelatine produced by soaking and shrinking. It is shown that on cooling warm gelatine solution an optically isotropic jelly is obtained, built up of cells with walls of an oily nature, *i. e.*, showing surface-tension with the surrounding liquid. Prisms of this jelly when bent become doubly refracting, positively at places of dilatation, negatively at places of contraction, with optical axis parallel to the stress direction, as in the case of bent glass strips.

When an electric current flows through a jelly consisting of oily, water-poor liquid A with water-rich content B, one would expect, through the contact electricity at the places of contact of the heterogeneous substances, a transference of liquid along the cell-walls to take place, and simultaneously a displacement of the still-liquid, viscous cell-walls in the opposite direction, producing a state of strain and consequent double refraction.

Gelatine in Capillary Tubes.

A capillary tube 30 cms. long, outer diameter 1.2 mm., was filled with a 10 per cent. solution of gelatine and the lower end sealed off. Several such tubes were kept for a quarter of an hour in a long test-tube full of water at 100°, and slowly cooled, so that the gelatine solidified without strain and without double refraction; finally the upper end was sealed off too. As required, pieces 4.5 cms. in length were cut off and cemented to a glass slide. Over the ends of the tube were placed cover-glasses, supported by small empty pieces of the same tube. A drop of water was brought under each cover-glass, into which dipped platinum wires 0.5 mm. thick as electrodes; in this way disturbance due to gas-bubbles was avoided.

The slide was laid on the table of a microscope and could be examined between crossed nicols with different magnifying powers; between the prisms a wave-length selenite plate could be inserted, showing the red of the first order. The

* Communicated by the Author.

tube was so placed that a yellow colour corresponded to an expansion or positive dilatation, a blue colour to a contraction or negative dilatation, parallel to the axis of the tube. An eyepiece fitted with a Babinet's compensator could also be used, the upper nicol being slid to the side and a second, analysing prism put on top; the indications of the compensator were tested as to sign by means of a bent glass strip*. Current was obtained from the town mains or from a battery of cells.

When the circuit was closed there appeared, one or two millimetres from the positive end of the tube, a fine line, yellow with selenite plate, indicating a positive dilatation parallel to the axis of the tube. This line was to be seen the sooner the higher the voltage; its appearance varied—it was sharp or blurred, quiet or in rapid movement, according to the nature of the cell-walls that had been formed in the jelly. In general the line had a screw or wave-motion, in the direction of its length, and therefore perpendicular to its motion into the tube (fig. 1 c). This wave-motion was the more pronounced the higher the voltage and the more dried-up the gelatine.

Fig. 1.

Before the line, at the sides, were two blue spots indicating a negative dilatation parallel to the tube axis; these blue places came only after the yellow line had gone some distance into the tube, and not while its course was through soaked jelly; there the line was quiet without wave motion (fig. 1 a). This motion reappeared when the line had penetrated further into the tube. The line seemed sometimes the boundary of a parabolic surface (fig. 1 d†). Before the line a yellow colour spread slowly out; behind

* G. Quincke, *loc. cit.*

† G. Quincke, *Ann. d. Phys.* ix. p. 794 (1902).

came a blue spot and a varied and irregular mass of yellow and blue, simplest in the case of soaked tubes. The displacement of the line parallel to the tube axis and the transversal wave-motion both grew slower as the line got further into the tube; it spread out, lost its sharpness and grew blurred; the wave-motion gave way to an intermittent one. One could see the displacement of the central line in the compensator slowly rise to a maximum and suddenly fall to zero. Table I. gives the displacements over the yellow line

TABLE I.

Voltage applied.	Age of tube : days	Time : min. sec.		Displacement λ .	Current amp. $\times 10^{-6}$.
10.9	21	9	0	0.18	14
		11	45	0.16	12
		16	0	0.15	9
		20	15	0.16	8
		26	0	0.15	7
		43	0	0.14	4
12.0	16	18	0	0.20	14
		44	0	0.20	11
		78	0	0.21	10
24.5	15	10	0	0.22	28
		41	15	0.26	20
		103	0	0.27	12
50	10	18	0	0.10	30
		44	0	0.11	20
50	10	15	30	0.09	19
50	27	16	0	0.31	98
		44	0	0.30	64
		73	30	0.29	48
		100	0	0.29	30
100	23	5	45	0.18	60
		16	0	0.20	34
		34	0	0.20	22
		59	0	Max. 0.29	18
		81	0	" 0.22	16
200	22	1	0	0.14	240
		2	0	0.18	125
		3	30	0.20	98
		7	0	0.18	64
		14	0	0.12	45
		28	0	0.24	32
220	37	17	0	Max. 0.30	108
		38	0	" 0.27	16
220	14	12	30	0.18	126
		35	0	0.18	40

at different times after completing the circuit : the displacement is fairly constant in a given case, and is greater the higher the voltage and the longer the time that has elapsed before using the tube.

At the cathode a yellow colour (positive dilatation parallel to the tube axis) spread slowly out to meet the yellow line from the anode ; for small voltages the action was stationary before meeting had taken place. At meeting the line was often destroyed by a wave or mass of liquid running along the side of the tube. Afterwards movement and colour-change became irregular. The tubes kept their colours; the cell-walls had become solid through loss of water. An old used tube tried with higher voltage showed only small and slow changes. After the current had been passing some time, there appeared at the cathode shreds of gelatine and the water grew turbid ; with the microscope numerous hexagonal crystals were to be seen at this end of the tube. The speed with which the yellow line moved into the tube was measured by reading off its distance from the positive end of the tube on a glass scale placed beneath the microscope slide ; the figures in two cases are given in Table II. The

TABLE II.

228 volt ; $2r=1.4$ mm.				438 volt ; $2r=1.1$ mm.			
T.		s.	s^2/T .	T.		s.	s^2/T .
		mm.				mm.	
0	0	0		0	0	0	
	25	1	2.4		22	4	43.6
	40	2	6.0		42	6	51.6
	57	3	9.0	1	0	8	64.0
1	21	4	12.0		27	10	66.6
	47	5	14.3	2	0	12	72.0
2	20	6	15.4		43	14	71.3
	57	7	16.3		36	16	71.4
3	37	8	17.4	4	4	17	70.8
4	22	9	18.7		33	18	73.3
5	11	10	19.3	5	5	19	72.0
6	10	11	19.6		41	20	70.6
7	12	12	20.0	6	18	21	69.6
8	17	13	20.3	7	0	22	69.1
9	24	14	20.8		40	23	69.0
10	39	15	21.1	8	22	24	69.1
13	21	17	21.7	9	47	26	71.8
15	47	18	20.6	10	42	27	68.4
16	15	19	22.2	11	37	28	67.2
				12	32	29	67.3
$(s^2/T)=21.0$ $s^2r^2/TV=0.51$				$(s^2/T)=70.2$ $s^2r^2/TV=0.49$			

further the water has penetrated into the tube, the more it is dammed and the slower grows the motion; this may be caused by particles dragged along by the water blocking up the holes. Or the water may pass through holes in a series of transverse lamellæ; by hydrostatic pressure these lamellæ are pressed together and shut like a kind of valve. If the velocity is proportional to the voltage divided by the distance travelled, or $ds/dt = Au/s$, then $s^2 = Aut + \text{a constant}$, which is

Fig. 2.

to be put 0. In Table II. are given the values of s^2/T ; these increase till about one-fifth of the tube has been traversed; this increase is partly to be explained by the fact that the curves in fig. 2 do not begin from the origin. The values of s^2/T multiplied by the square of the radius and divided by the voltage are approximately equal.

If the cells are open and communicate with one another, water can be carried along the cell or tube walls; if they are shut, however, the water can only enlarge or diminish the cells by dissolving in the substance of the wall or in the contents of the cells, and thus produce a temporary dilatation positive or negative, with corresponding positive or negative double refraction. By the pressure of liquid into such stretched-out open cells, the observed temporary double refraction, positive perpendicular to the direction of transference of the water, would be expected; the later-appearing spot showing a negative dilatation is probably produced by reaction. At the sides of the glass tube the water is less moved than in the middle, on account of the transverse walls there; at the sides appears as a consequence a temporary positive dilatation perpendicular to the tube. Behind the first line appears a series of places with positive and negative double refraction, as in the case of shrinking of gelatine in short capillary tubes in air, alcohol, or glycerine*.

Gelatine in Shallow Dishes.

Shallow glass dishes, either square (5 cms. $\times$ 5 cms. $\times$ 1 cm.) or round ($2r=8$ cms.) were filled to a depth of 1 cm. with a 10 per cent. gelatine solution and examined at the end of 24 hours. The electrodes only touched the surface, otherwise the bubbles rising up had a disturbing influence.

At the anode came a furrow, at the cathode a swelling. The anode was surrounded by two hemispheres, the inner more distinct, and both sharp. The cathode was surrounded by a white hemisphere and by a second, outer one, difficult to see. The white colour came from countless, very small (0.003 to 0.01 mm.) crystals. Round the electrode the crystals were packed and stuck together. The crystals were of two kinds: (*a*) spherical, showing a black cross parallel to the long diagonals of crossed nicols, and (*b*) rhombohedral (CaCO_3 ?), growing dark and reappearing as the turn-table was rotated. This crystal formation may come (1) from loss of water, (2) from loss of gelatine, the presence of which may increase the solubility of the salt. If the cell-walls are covered with a layer containing salt, layer and cell-contents will be displaced in opposite directions, eddies will be formed and the salt layer loosened to crystallize out later. The furrow round the anode was about 1 mm. deep, and had smooth sides with sharp edges; the swelling round the

* G. Quincke, *Ann. d. Phys.* xiv. p. 849 (1904).

cathode was about 2 mms. high (see fig. 3 for the case of a cube of gelatine with electrodes touching the centres of

Fig. 3.

opposite faces). At the anode came a hole full of liquid ; round about the jelly had a deeper tint, as also at the outer boundary of the swelling at the cathode ; these places were harder than the surrounding jelly, and had suffered a loss of water or gain of gelatine. Sometimes the swelling at the cathode was radially striped or showed a network of fine cracks ; with the microscope could be seen drops of liquid oozing out at the crossing of two cracks. On standing these lines disappeared, and the rings round the anode lost their sharpness ; displaced water had been restored by diffusion.

The displacement of the central line in the compensator is shown in fig. 4. At the anode it increases, from the centre

Fig. 4.

out, to a maximum at the first hemisphere or inner edge of the furrow, then through zero to a maximum in the opposite direction at the second hemisphere or outer edge of the furrow ; at the inner edge the dilatation is negative, at the outer edge positive, parallel to the radius. At the cathode the displacement indicates a negative dilatation parallel to the radius

separated by a neutral zone from a positive outer zone. The figure was drawn after the current had been passing for an hour between electrodes at a potential-difference of 16 volts.

In Table III. is given the mean diameter of the furrow round the anode at various times, for the case of a cube of gelatine; also the square of the diameter divided by the time. The means of the values in the third column divided by the voltage give approximately the same number; thus the places of greatest double refraction form spherical surfaces, the square of the diameter of which is proportional to the time and to the voltage.

TABLE III.

T = Time from completion of electric circuit.
 $2r$ = Diameter in mm. of the ring round the anode.

5.6 Volts.				15 Volts.				24 Volts.				34 Volts.			
T.	$2r$.	$(2r)^2/T$.		T.	$2r$.	$(2r)^2/T$.		T.	$2r$.	$(2r)^2/T$.		T.	$2r$.	$(2r)^2/T$.	
0'	0''	0		0'	0''	0		0'	0''	0		0'	0''	0	
3	5	2.9	2.7	3	0	4.7	7.4	3	30	6.0	10.3	1	50	4.8	12.5
5	30	3.4	3.3	7	20	7.3	7.3	9	0	9.5	10.0	2	30	6.7	18.0
8	30	4.2	2.1	13	10	10.4	8.2	15	0	13.0	11.3	5	30	10.1	19.1
11	15	4.8	2.0	17	20	11.7	7.9	21	0	15.0	10.2	11	15	14.0	17.4
18	30	6.5	2.3	21	45	13.0	7.8	28	30	18.5	12.0	14	0	15.7	17.6
25	0	7.2	2.1	27	50	14.6	7.7	34	0	19.5	11.2	18	15	17.5	16.8
31	0	7.9	2.1	34	15	16.0	7.5	46	30	22.0	10.4	22	15	19.1	16.8
37	30	8.5	1.9	41	55	17.4	7.2					30	0	21.5	15.4
42	0	9.3	2.1												
48	0	10.7	2.3												
$((2r)^2/T)=2.3$ $(2r)^2/TV=0.41$				$((2r)^2/T)=7.6$ $(2r)^2/TV=0.51$				$((2r)^2/T)=10.8$ $(2r)^2/TV=0.45$				$((2r)^2/T)=17.2$ $(2r)^2/TV=0.51$			

Gelatine Solution.

One per cent. gelatine solution covered the bottom of a shallow glass dish to a depth of 1 mm. Two vertical platinum wires 5 cms. apart were connected to a battery of 40 volts. At the anode a white cloud spread outwards; behind the solution had jellied through loss of water or gain in gelatine; on its surface lines running perpendicular to the direction of the current were to be seen; these moved forward from time to time with a sudden, undulatory movement. If the solution through evaporation had grown thick crystals could be watched forming as before round the cathode; if the solution were still liquid, they were driven

away in all directions ; in course of time the crystals collected on the bottom of the dish.

Silicic Acid.

A thin film of colloidal silicic acid ($\sigma = 1.0189$, one month dialysed) was spread out on a glass slide. Liquid was driven away from the anode so that the surface of the slide dried up. Although the wires were clean the transference did not take place equally in all directions; radial furrows ran out from the electrode. At the cathode the acid was heaped up. As in the case of gelatine small (0.01 mm.) rhombohedral crystals were found round the cathode. With 440 volts feeble double refraction was to be seen in places round the anode giving a displacement of 0.04λ . With loss of water the acid fell into single pieces between cracks cutting everywhere at right angles. When a second slide was pressed on the top of the first after the acid had dried up, the distance apart was greater at the anode; only water had moved to the cathode.

Iron Hydrate.

Colloidal ferric hydrate was spread out on a glass slide. Liquid was driven away from the cathode; the jelly cracked and showed with the compensator a displacement of 0.29λ . Water collected at the anode; here crystals could be seen. The dried-up layer was thicker at the cathode than at the anode; water is moved to the anode and simultaneously colloid to the cathode, *i.e.*, in the opposite direction to gelatine, silicic acid and albumen.

Albumen.

Filtered albumen on a glass slide showed round the anode several concentric rings, the outer a zigzag or waved line. Before the cathode a crescent of small rhombohedral crystals could be seen. At the cathode the albumen was heaped up. Next day a second slide pressed on top was nearly the same distance apart at both ends. At the cathode the dry substance was folded up and loose from the slide.

Albumen coagulated in capillary tubes (prepared as above described) became transparent and liquid at the cathode; at the anode, on the other hand, it shrank and the water ran back along the sides of the tube.

My sincere thanks are due to Professor Quincke for ever-ready kindness and help during the course of the foregoing investigations.